Statistical Mechanics

- Lecture Notes -

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Preface

Here you find some lecture notes prepared for the course in Statistical Mechanics at SISSA. Many very nice books and lecture notes exist, and I do not pretend to add anything to what has been published: These are only my notes on the subject. The main references I will follow are the very nice Lecture Notes by Arovas [1], and the books by Peliti [2], Callen [3], Sethna [4], Pathria [5], and MacKay [6].

The notes are divided into two main parts: 1) Basic material and 2) Selected topics.

The basic material contains standard topics. Starting with a review of thermodynamics, the statistical ensembles are introduced, and standard applications (systems of free bosons and fermions) are illustrated. Next, after an interlude on transfer matrix and path-integral representation, the standard Weiss mean-field theory approach is presented, ending with a derivation of the Ginzburg-Landau action.

The selected topics include this year: the XY model in two-dimensions and the Kosterlitz-Thouless transition, and an introduction to (mostly) Ising lattice gauge theories.

Contents

1. Introduction to Entropy and Statistical Mechanics

I will illustrate here, through elementary examples, some useful concepts that hopefully will provide a small guided tour into some of the ideas of Statistical Mechanics.

During the tour, we will encounter some useful mathematics — large-N (saddle-point) techniques, Fourier/Laplace transforms, Legendre transforms — and some of the important actors in the game — entropy, energy, free-energy — together with the first bricks of the construction of the more general theory.

The discussion on Shannon's entropy follows quite closely the excellent book by MacKay [6].

1.1. The exponential dominance: Stirling

I start by illustrating an idea that keeps coming repeatedly when you discuss "entropy": the idea of *exponential dominance*, which can be simply understood with the following elementary considerations. Suppose you have a sum of the form

$$\Omega = \sum_i \mathrm{e}^{N\epsilon_i} \; .$$

where $\epsilon_i \geq 0$. Call $\epsilon_{\max}$ the largest of such ϵ_i. Then, for very large N you generally have:

$$\frac{1}{N} \log \Omega \simeq \epsilon_{\max} \; . \tag{1.1}$$

To understand the issue, suppose you have only one further term with $\epsilon_i = \epsilon_{\max} - \Delta$ in the sum. Then:

$$\frac{1}{N} \log \mathrm{e}^{N\epsilon_{\max}} \left(1 + \mathrm{e}^{-N\Delta}\right) = \epsilon_{\max} + \frac{1}{N} \log \left(1 + \mathrm{e}^{-N\Delta}\right) \to \epsilon_{\max} \; .$$

A bit more generally, suppose that a number $\sim N^{\alpha}$ of terms with $\epsilon_i < \epsilon_{\max}$ contribute to the sum. Then you can write:

$$\mathrm{e}^{N\epsilon_{\max}} < \Omega < N^{\alpha} \mathrm{e}^{N\epsilon_{\max}} \; .$$

Hence, taking the logarithms and dividing by N you get:

$$\epsilon_{\max} < \frac{1}{N} \log \Omega < \epsilon_{\max} + \alpha \frac{\log N}{N} \; ,$$

i.e., once again, Eq. (1.1) holds for large enough N.

An interesting application of the principle of exponential dominance is the *method of Laplace* for calculating integrals of functions of the form $\mathrm{e}^{N\phi(x)}$. Let us exemplify this with an application that leads to the famous Stirling approximation for the factorial $N!$:

$$\log(N!) = N \log N - N + \log \sqrt{2\pi N} + O(1/N) \; . \tag{1.2}$$

One possible way to derive the Stirling approximation starts from the integral representation

$$\Gamma(N+1) \overset{\text{def}}{=} \int_0^{\infty} \mathrm{d}x \; x^N \mathrm{e}^{-x} = N! \; ,$$

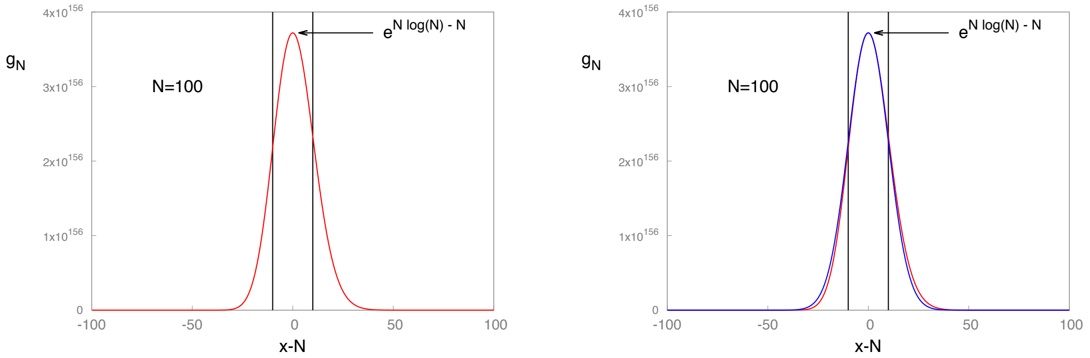

Figure 1.1.: On the left, the function $g_N(x) = \mathrm{e}^{N \log x - x}$, whose integral gives the factorial $N!$, for $N = 100$. On the right, in blue, the approximation by a Gaussian obtained by expanding the exponent near the maximum at $x_{\mathrm{max}} = N$.

which you can very easily prove by induction. This is the Euler's Γ-function at integer values of the argument. Next, we analyze the integrand $g_N(x) = \mathrm{e}^{N \log x - x} = \mathrm{e}^{N(\log x - x/N)}$, and discover that it has a maximum at $x_{\mathrm{max}} = N$ and two inflection points at $x_\pm = N \pm \sqrt{N}$. The value at the maximum is already very suggestive:

$$g_N(x = x_{\mathrm{max}} = N) = \mathrm{e}^{N \log N - N} \;.$$

To calculate the integral, let us start being brutal. We approximate it with the area of the rectangle of height equal to the maximum, $g_N(N)$, and basis equal to the distance between the two inflexion points, $2\sqrt{N}$. Our brutal estimate would than give:

$$I_{\mathrm{brutal}} = \sqrt{4N}\mathrm{e}^{N \log N - N} \;.$$

If you take the logarithm, you get the following estimate:

$$\log N! \approx N \log N - N + \log \sqrt{4N} \;.$$

Not that bad, for a rather swift calculation. Even more brutal is the approach of not even calculating the inflexion points, and approximate the area with a rectangle of basis $b = 1$, which would give only the first two terms of the Stirling formula, incidentally, the two terms that are more often used.

To get a much better result for the third term, $\log \sqrt{2\pi N}$, we resort to a gaussian approximation. Essentially, we expand the logarithm appearing in $g_N(x)$ close to its maximum at $x = N$ by retaining only the quadratic terms in the exponent. You get:

$$g_N(x) \approx g_N^{\mathrm{gau}} = \mathrm{e}^{N \log N - N} \mathrm{e}^{-\frac{(x-N)^2}{2N}} \;. \tag{1.3}$$

The integral, using the gaussian, is rather simple:

$$\int_0^\infty \mathrm{d}x \; \mathrm{e}^{N \log N - N} \; \mathrm{e}^{-\frac{(x-N)^2}{2N}} \approx \mathrm{e}^{N \log N - N} \int_{-\infty}^{\infty} \mathrm{d}y \; \mathrm{e}^{-\frac{y^2}{2N}} = \mathrm{e}^{N \log N - N} \sqrt{2\pi N} \;.$$

Taking the logarithm, you get the Stirling formula including the (third term) sub-leading logarithmic correction. Figure 1.1 shows the comparison between the exact g_N and the gaussian approximation g_N^{gau}.

1.2. Repeated flips of coins and frequency of letters

Flipping a coin is a standard starting point for probability. It is associated with a process, called the Bernoulli process, which can be formalised as follows:

$$X = \begin{pmatrix} 0 & 1 \\ p_0 & p_1 \end{pmatrix} , \tag{1.4}$$

where $p_0 + p_1 = 1$, and p_1 is the probability of getting Head (which we call "1"), while p_0 is that of getting Tail (which we call "0"). A more general process X, which Khinchin calls a "*finite scheme*" and MacKay an "*ensemble*", is build on a more general alphabet $\mathcal{A} = \{x_1, x_2, \cdots, x_{|\mathcal{A}|}\}$ of symbols/objects x_j, called "*outcomes*" of X, with $j = 1 \cdots |\mathcal{A}|$, where $|\mathcal{A}|$ denotes the number of possible outcomes in the set $\mathcal{A}$. For instance, $\mathcal{A}$ could be the English alphabet of 26 letters, including the space, as exemplified in Fig. 1.2 below.

i	a_i	p_i
1	a	0.0575
2	b	0.0128
3	c	0.0263
4	d	0.0285
5	e	0.0913
6	f	0.0173
7	g	0.0133
8	h	0.0313
9	i	0.0599
10	j	0.0006
11	k	0.0084
12	l	0.0335
13	m	0.0235
14	n	0.0596
15	o	0.0689
16	p	0.0192
17	q	0.0008
18	r	0.0508
19	s	0.0567
20	t	0.0706
21	u	0.0334
22	v	0.0069
23	w	0.0119
24	x	0.0073
25	y	0.0164
26	z	0.0007
27	–	0.1928

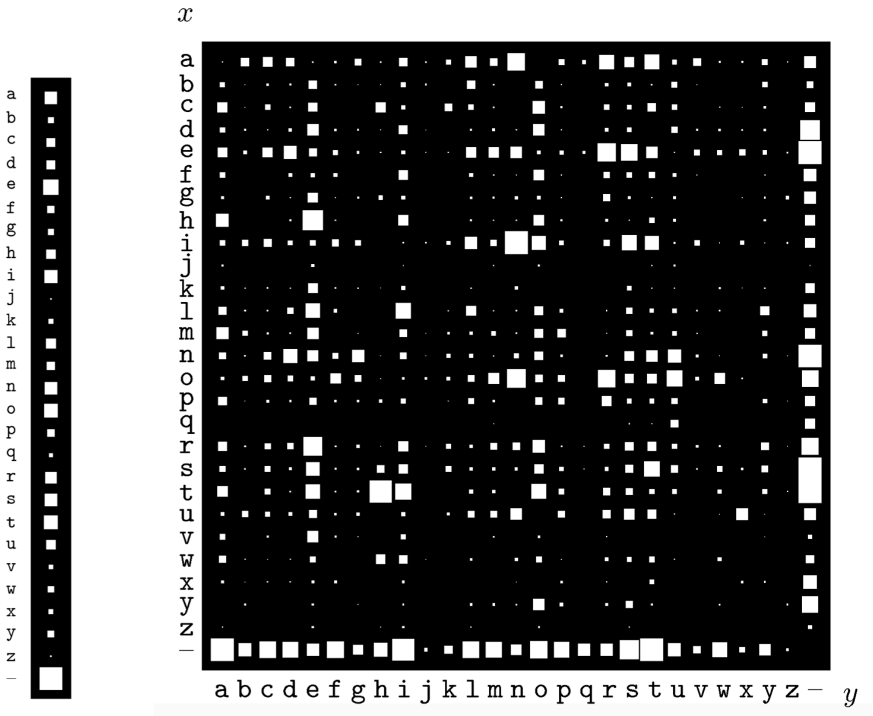

Figure 1.2.: (Left) The frequency of letters in English. (Right) The joint probability $P(x, y)$ of two consecutive letters x and y in a typical English text. Pictorially, larger probability is represented by a larger white square. Notice the presence of correlations, such that $P(x, y) \neq P(x)P(y)$. Figure taken from MacKey.

To fully specify X you have to assign the probability $P(x_j) = p_j$ of the occurrence of each outcome x_j, listing them for instance as:

$$X = \begin{pmatrix} x_1 & x_2 & \cdots & x_j & \cdots & x_{|\mathcal{A}|} \\ p_1 & p_2 & \cdots & p_j & \cdots & p_{|\mathcal{A}|} \end{pmatrix} , \tag{1.5}$$

Random variable. When the alphabet $\mathcal{A}$ is mapped into *real or integer numbers* (as in the Tail/Head case for the coin), X is often referred to as a *random variable*.

For a random variable X you can easily calculate the average and the variance of X with the usual definitions:

$$\begin{cases} \mathrm{E}[X] & = \displaystyle\sum_{j=1}^{|\mathcal{A}|} x_j P(x_j) \\ \mathrm{Var}[X] & = \mathrm{E}[X^2] - \mathrm{E}^2[X] = \displaystyle\sum_{j=1}^{|\mathcal{A}|} (x_j - \mathrm{E}[X])^2 P(x_j) \end{cases} , \tag{1.6}$$

where we have defined the ensemble X^2 to be given by:

$$X^2 = \begin{pmatrix} x_1^2 & x_2^2 & \cdots & x_j^2 & \cdots & x_{|\mathcal{A}|}^2 \\ p_1 & p_2 & \cdots & p_j & \cdots & p_{|\mathcal{A}|} \end{pmatrix} . \tag{1.7}$$

In the case of a Bernoulli process these are simple to calculate, $\mathrm{E}[X] = p_1$, $\mathrm{E}[X^2] = p_1$, hence $\mathrm{Var}[X] = p_1(1-p_1)$.

Now consider generating a sequence of N independent similar ensembles, which we denote by $X_{i=1\cdots N}$, with identical distribution of probability of the outcomes $P(x_j)$. Any outcome of this experiment is a *sequence* of N outcomes $\mathbf{x} = (x_1, \cdots, x_i, \cdots x_N)$. Notice that we have used here a "short notation", where x_i indicates the outcome of X_i, which is taken from the common alphabet $\mathcal{A}$. A more proper notation would be x_{j_i}, to denote the j-th outcome obtained at the i-th trial.

In the Bernoulli case an outcome-sequence would be $\mathbf{x} = (0,1,0,0,0,1,0,0,0,0)$, for instance, for $N = 10$. What is the probability of each individual sequence? Simple enough, since the repeated trials are all independent, hence the probabilities multiply:

$$P(\mathbf{x}) = p_0^{N_0} p_1^{N_1} , \tag{1.8}$$

where N_0 is the number of 0s, and N_1 the number of 1s, obviously with $N_0 + N_1 = N$. Suppose now that the coin is not "fair" (or the process generating the 0s and the 1s is not a coin, after all), and that $p_1 < p_0$, for instance $p_1 = 0.1$ and $p_0 = 0.9$. Then by far the *most probable* string is that with all 0s:

$$P(\mathbf{x} = (0,0,\cdots,0)) = p_0^N = (0.9)^N = 2^{-N\log_2(0.9)} \approx 2^{-15.2} ,$$

where the last estimate is for $N = 100$. [1] The *least probable* string is also obviously that with all 1s:

$$P(\mathbf{x} = (1,1,\cdots,1)) = p_1^N = (0.1)^N = 2^{-N\log_2(0.1)} \approx 2^{-332.2} .$$

But if you do the experiment, and $N = 100$, you know that you almost never get the most probably string with $N = 100$ 0s. How comes? You know very well that you *typically* obtain strings with $N_1 \approx p_1 N = 10$ and $N_0 \approx p_0 N = 90$. Indeed, as you know very well, the expected frequency $n_1 = N_1/N$ is given by

$$n_1 = \frac{N_1}{N} \approx p_1 .$$

Figure 1.3 shows the possible outcome of such an experiment. Notice that the probability of a "typical string" is:

$$P(\mathbf{x}_{\mathrm{typ}}) \approx p_0^{Np_0} p_1^{Np_1} = 2^{N(p_0\log_2 p_0 + p_1\log_2 p_1)} = 2^{-N(-p_0\log_2 p_0 - p_1\log_2 p_1)} \equiv 2^{-NH(X)} , \tag{1.9}$$

where we have defined the *Shannon entropy* of X as:

$$H(X) = -p_0\log_2 p_0 - p_1\log_2 p_1 = p_0\log_2\frac{1}{p_0} + p_1\log_2\frac{1}{p_1} . \tag{1.10}$$

The reason why we introduce the second way of writing will be clear in a while.

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[1] Beware of applying blindly the principle of exponential dominance. Recall that we have *exponentially many states* here, and entropy effects do play a crucial role in getting the typical strings.

$\mathbf{x}$	$\log_2(P(\mathbf{x}))$
`...1...................1.....1....1.1.......1........1...........1.....................1.......11...`	-50.1
`......................1.....1.....1.......1....1.........1.....................................1....`	-37.3
`........1....1..1...1....11..1.1.........11.........................1...1.1..1...1................1.`	-65.9
`1.1...1................1.......................11.1..1............................1.....1..1.11.....`	-56.4
`...11...........1...1.....1.1......1..........1....1...1.....1............1.........................`	-53.2
`..............1......1.........1.1.......1..........1............1...1......................1.......`	-43.7
`.....1........1.......1...1............1............1...........1......1..11........................`	-46.8
`.....1..1..1...............111...................1...............1.........1.1...1...1.............1`	-56.4
`.........1..........1.....1......1..........1....1..............................................1...`	-37.3
`......1........................1..............1.....1..1.1.1..1...................................1.`	-43.7
`1.......................1..........1...1...................1....1....1........1..11..1.1...1........`	-56.4
`...........11.1.........1................1......1.....................1.............................`	-37.3
`.1..........1...1.1.............1.......11...........1.1...1..............1.............11..........`	-56.4
`......1...1..1.....1..11.1.1.1...1.....................1............1.............1..1..............`	-59.5
`............11.1......1....1..1............................1.......1..............1.......1.........`	-46.8
`....................................................................................................`	-15.2
`1111111111111111111111111111111111111111111111111111111111111111111111111111111111111111111111111111`	-332.1

Figure 1.3.: Strings of bits generated by $N = 100$ independent Bernoulli trials with $p_1 = 0.1$.

> **Notation.** Here we adopt the standard notation $H(X)$ for Shannon's entropy associated with the random variable X. Later on, we will denote the Shannon entropy as $S^{\text{Shannon}}(\mathbf{P})$, where $\mathbf{P}$ denotes the probability distribution of the variable X.

There are a total of $\Omega_{\text{tot}} = 2^N = 2^{100} \approx 10^{30}$ strings $\mathbf{x}$ for $N = 100$. Can we estimate the number of "typical strings" we would get? The number of strings with a number of 1s *precisely* equal to N_1 is given by the binomial coefficient $\binom{N}{N_1}$, so the number Ω_{typ} of typical strings can be estimated as:

$$\begin{aligned} \log \Omega_{\text{typ}} \approx \log \binom{N}{Np_1} &= \log N! - \log(Np_1)! - \log(Np_0)! \\ &\approx N(-p_0 \log p_0 - p_1 \log p_1) = N \log(2)\, H(X) \; . \end{aligned} \tag{1.11}$$

Hence, $\log_2 \Omega_{\text{typ}} \approx NH(X)$, or:

$$\Omega_{\text{typ}} \approx 2^{NH(X)} \approx 2^{47} \approx 10^{14} \; , \tag{1.12}$$

where the last estimate applies to $N = 100$ and $H(X) \approx 0.47$ when $p_1 = 0.1$. I remark that

$$P(\mathbf{x}_{\text{typ}}) \times \Omega_{\text{typ}} \approx 2^{-NH(X)} 2^{NH(X)} \approx 1 \; . \tag{1.13}$$

So, in essence, the typical strings, whose number and probability was estimated above, seems to *exhaust* the whole probability! All the other *non-typical strings* — the vast majority, since $\Omega_{\text{typ}} \approx 2^{NH(X)} \ll \Omega_{\text{tot}} = 2^N$, including the most probable one $\mathbf{x} = (0, 0, \cdots, 0)$ — seems to count nothing in the total probability. We will soon "formalize" the previous argument through the use of a theorem, the *weak law of large numbers*.

Binomial distribution and strong law of large numbers. You know very well that the ingredients given above give rise to the Binomial distribution for the repeated Bernoulli trials. The probability of getting N_1 times a "1" in a sequence of N independent trials is:

$$\mathrm{Prob}(N_1, N) = \binom{N}{N_1} p_0^{N-N_1} \, p_1^{N_1} \; .$$

One can show, see App. A for more details and exercises, that the Binomial distribution approaches a Gaussian in the limit of a large number of trials N. This is one manifestation of the *strong law of large numbers.*

Before proceeding, let us generalise the previous concepts to a more general X. The expected number of times x_j is obtained in N trials is $p_j N$, hence we would estimate:

$$P(\mathbf{x}_{\mathrm{typ}}) \approx p_1^{Np_1} p_2^{Np_2} \cdots p_{|\mathcal{A}|}^{Np_{|\mathcal{A}|}} \equiv 2^{-NH(X)} \; , \tag{1.14}$$

where the Shannon entropy is now:

$$H(X) = -\sum_{j=1}^{|\mathcal{A}|} P(x_j) \log_2 P(x_j) = \sum_{j=1}^{|\mathcal{A}|} P(x_j) \log_2 \frac{1}{P(x_j)} \; . \tag{1.15}$$

Notice that, if for some reason you do not want to use the $\log_2$, for instance, if you plan to take derivatives where the standard natural log is much more comfortable to use, you can write Shannon's entropy as:

$$H(X) = -k_S \sum_{j=1}^{|\mathcal{A}|} P(x_j) \, \log P(x_j) = k_S \sum_{j=1}^{|\mathcal{A}|} P(x_j) \, \log \frac{1}{P(x_j)} \; , \tag{1.16}$$

where $k_S = 1/\log 2$. Next, the number of typical N-strings with the expected occurrence $N_j = p_j N$ is given by the multinomial coefficient:

$$\Omega_{\mathrm{typ}} = \frac{N!}{(p_1 N)! \cdots (p_{|\mathcal{A}|} N)!} \approx 2^{NH(X)} \; , \tag{1.17}$$

where we used once again the Stirling approximation for the factorials. Once again, observe that the typical strings essentially exhaust the total probability:

$$P(\mathbf{x}_{\mathrm{typ}}) \times \Omega_{\mathrm{typ}} \approx 2^{-NH(X)} 2^{NH(X)} \approx 1 \; . \tag{1.18}$$

Observe also that the total number of N-strings is

$$\Omega_{\mathrm{tot}} = |\mathcal{A}|^N = 2^{N \log_2 |\mathcal{A}|} \; . \tag{1.19}$$

Notice that if all events were equally probable, $p_j = 1/|\mathcal{A}|$, then

$$H(X) = \sum_{j=1}^{|\mathcal{A}|} P(x_j) \log_2 \frac{1}{P(x_j)} = \sum_{j=1}^{|\mathcal{A}|} \frac{1}{|\mathcal{A}|} \log_2 |\mathcal{A}| = \log_2 |\mathcal{A}|$$

hence $\Omega_{\mathrm{typ}} \approx \Omega_{\mathrm{tot}}$ is all events are equally probable. For a general distribution of $\{p_j\}$, however, you can show that:

$$H(X) = H(\{p_j\}) \leq \log_2 |\mathcal{A}| \; , \tag{1.20}$$

i.e., the Shannon entropy is *maximum* when $p_j = 1/|\mathcal{A}|$. There are several ways to prove this statement. [2]

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[2] One is based on the standard approach of Lagrange multipliers: maximising $H(X)$ in the domain $0 \leq p_j \leq 1$ with the constraint $\sum_j p_j = 1$. The actual proof that such extreme is a maximum is a bit more intricate and based upon induction.

A clean and instructive proof is based on Jensen's inequality for convex functions which we now quickly review. Consider a function $F(y)$ — with y possibly multi-dimensional, as long as the domain D of y is itself convex, i.e., $\lambda y_1 + (1-\lambda)y_2 \in D$ for all $\lambda \in [0,1]$ if $y_1, y_2 \in D$. We say that $F(y)$ is *convex* in its domain D — more clearly, $\smile$-convex — if:

$$F(\lambda y_1 + (1-\lambda)y_2) \leq \lambda F(y_1) + (1-\lambda)F(y_2) \; . \tag{1.21}$$

By induction, starting from the previous definition, you can easily prove that if $F(y)$ is $\smile$-convex then

$$F(\sum_j p_j y_j) \leq \sum_j p_j F(y_j) \qquad\qquad \text{if } \sum_j p_j = 1 \; . \tag{1.22}$$

which is a discrete form of the *Jensen's inequality.* [3] The proof that $H(X)$ is maximum when all $p_j = 1/|\mathcal{A}|$, applies Jensen's inequality to the $\smile$-convex function $F(y) = \log_2(1/y) = -\log_2(y)$. Take in the Jensen's inequality $y_j = 1/p_j$. Then

$$\sum_{j=1}^{|\mathcal{A}|} p_j y_j = \sum_{j=1}^{|\mathcal{A}|} p_j \frac{1}{p_j} = |\mathcal{A}| \; .$$

Moreover:

$$\sum_{j=1}^{|\mathcal{A}|} p_j F(y_j) = \sum_{j=1}^{|\mathcal{A}|} p_j \left(-\log_2 \frac{1}{p_j}\right) = -H(\{p_j\}) = -H(X) \; .$$

Then, by Jensen's inequality:

$$-\log_2|\mathcal{A}| = F(\sum_j p_j y_j) \leq \sum_j p_j F(y_j) = -H(X) \qquad\qquad \Longrightarrow H(X) \leq \log_2|\mathcal{A}| \; . \tag{1.23}$$

Summarising, when the p_j of the various outcomes x_j are *not equally likely*, then:

$$\frac{\Omega_{\text{typ}}}{\Omega_{\text{tot}}} \approx \frac{2^{NH(X)}}{2^{N\log_2|\mathcal{A}|}} = 2^{-N[\log_2|\mathcal{A}|-H(X)]} \overset{N\to\infty}{\longrightarrow} 0 \; . \tag{1.24}$$

A tiny fraction $2^{NH(X)}$ of the whole number of strings Ω_{tot} exhausts the probability!

1.3. Shannon's information content and entropy

Let us discuss the issue of the information content of the process X:

$$X = \begin{pmatrix} x_1 & x_2 & \cdots & x_j & \cdots & x_{|\mathcal{A}|} \\ P(x_1) & P(x_2) & \cdots & P(x_j) & \cdots & P(x_{|\mathcal{A}|}) \end{pmatrix} \; , \tag{1.25}$$

Consider the quantity:

$$h(x) \equiv \log_2 \frac{1}{P(x)} \tag{1.26}$$

This is a *random variable*, whose value depends on the outcome $x = x_j$ one gets. $h(x)$ is known as *Shannon's information content of the outcome* x. Below, we will try to justify why $h(x)$ is a meaningful way of quantifying the "information content" of an outcome x.

Property 1) Shannon's entropy as the average information. From the definitions given, Shannon's entropy $H(X)$ is the *average* of the information content $h(x)$ over all possible outcomes:

$$H(X) = \sum_{j=1}^{|\mathcal{A}|} P(x_j) \log_2 \frac{1}{P(x_j)} = \sum_{j=1}^{|\mathcal{A}|} P(x_j) h(x_j) \equiv \mathrm{E}[h] \; , \tag{1.27}$$

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[3] More generally, you could write it as:

$$F(\mathrm{E}[Y]) \leq \mathrm{E}[F(Y)] \; .$$

Property 2) The information of independent events. Consider another sequence Y *independent* from X:

$$Y = \begin{pmatrix} y_1 & y_2 & \cdots & y_j & \cdots & y_{|\mathcal{B}|} \\ P(y_1) & P(y_2) & \cdots & P(y_j) & \cdots & P(y_{|\mathcal{B}|}) \end{pmatrix} . \tag{1.28}$$

Then, you can define a sequence XY with alphabet $\mathcal{A} \otimes \mathcal{B}$ having $|\mathcal{A}||\mathcal{B}|$ elements as follows:

$$XY = \begin{pmatrix} x_1 y_1 & \cdots & x_{|\mathcal{A}|} y_1 & x_1 y_2 & \cdots & x_{|\mathcal{A}|} y_{|\mathcal{B}|} \\ P(x_1)P(y_1) & \cdots & P(x_{|\mathcal{A}|})P(y_1) & P(x_1)P(y_2) & \cdots & P(x_{|\mathcal{A}|})P(y_{|\mathcal{B}|}) \end{pmatrix} , \tag{1.29}$$

where we used the fact that the two processes are independent by writing $P(x_i, y_j) = P(x_i)P(y_j)$. If you want a simple case in which two events are *not independent*, let X be the first letter, and Y the second letter in a pair of letters in an English text: obviously, $P(x_i, y_j) \neq P(x_i)P(y_j)$, as subsequent letters in a text are somewhat *correlated*. But, if the two processes are independent, then the information content

$$h(x_i y_j) = \log_2 \frac{1}{P(x_i)P(y_j)} = h(x_i) + h(y_j) . \tag{1.30}$$

In words: the information content of the outcomes of two independent processes is simply the sum of the individual information content. By the way, you might easily show that Shannon's entropy of XY is also the sum of the two:

$$H(XY) = H(X) + H(Y) . \tag{1.31}$$

Hence, the actual importance of $h(x_j)$ is still not immediately evident: other objects based on the logarithm might do the job as well.

Property 3) Rare events give a large information. This property of $h(x_j)$, that will soon appear "very reasonable" through our game-examples, is the following: *The smaller is $P(x_j)$, the larger is its information content $h(x_j)$ of the outcome x_j.*

Why? Here is a simple example, based on the game that you have certainly played: *the hangman.* Suppose that I think of an Italian word with 9 letters, and you try the letter 'O'. You are lucky: the letter is in the word I had in mind. Here is the situation after your lucky try:

$$\_\ \underline{O}\ \_\ \_\ \_\ \_\ \_\ \_\ \underline{O}$$

The outcome of the letter 'O' has certainly increased your "information" on the word, but not in a very large way, as 'O' is quite common in Italian words. But suppose that, instead of 'O', you had boldly tried 'Q', and that your guess was right. I write:

$$\_\ \_\ \underline{Q}\ \underline{Q}\ \_\ \_\ \_\ \_\ \_ \ .$$

Your information on the word is enormously higher, as 'Q' is considerably less common than 'O': in the present case, the occurrence of two consecutive 'Q' immediately suggests that I was thinking of SOQQUADRO, the only italian word with a double-Q.

Let us play another game of guessing: you think of an integer number $n \in \{0, 1, 2, \cdots 63\}$. I can tell you the number you thought by asking you *exactly 6 questions*, each question being independent of the answer you give to the previous one. [4] Here are the 6 questions, with the corresponding answer

---

[4] This is a simplified version of the game of the 20 questions (recall: $Q1$ = is it alive?, $Q2$ = is it a human?, etc.), which allows to pin-down, with carefully chosen questions, an object that you might have thought. Recall that

$$2^{20} = 1,048,576$$

so that with 20 carefully chosen questions I should be able to discriminate into a "world" of more than a million possible "things".

you would give me if your number was $n = 17$:

$$\begin{array}{ll} Q1 : \text{Is } n \geq 32? & \text{NO} \\ Q2 : \text{Is } n \bmod 32 \geq 16? & \text{YES} \\ Q3 : \text{Is } n \bmod 16 \geq 8? & \text{NO} \\ Q4 : \text{Is } n \bmod 8 \geq 4? & \text{NO} \\ Q5 : \text{Is } n \bmod 4 \geq 2? & \text{NO} \\ Q6 : \text{Is } n \bmod 2 \geq 1? & \text{YES} \end{array} \tag{1.32}$$

Now I collect your answers, associating YES → 1, NO → 0:

$$0\;1\;0\;0\;0\;1 \rightarrow 2^4 + 2^0 = 17 \; ,$$

in other words the binary string with your answers univocally reconstructs the number $n = 17$. Observe that:

1) You can think of *any* n, hence the answer/digit to each question is equally likely: a 1 or a 0 with probability 1/2;

2) the answers to the questions $Q1 \cdots Q6$ are independent,

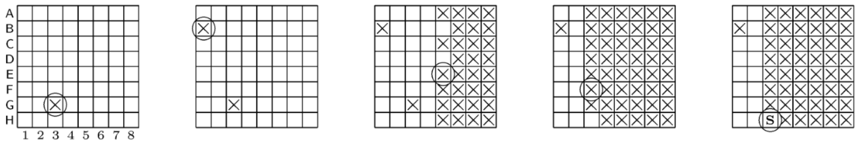
hence the information content you get is the *sum* of that for each answer. More formally, the elementary process of answering any question has two outcomes:

$$X = \begin{pmatrix} x_0 = 0 = \text{NO} & x_1 = 1 = \text{YES} \\ P(x_0) = \frac{1}{2} & P(x_1) = \frac{1}{2} \end{pmatrix} \; .$$

So, each question, independently of the answer, adds an information content $h(x_i) = \log_2 \left(\frac{1}{P(x_i)} \right) = \log_2 2 = 1$. The total information content after 6 questions, modelled by 6 independent but identical processes $X_1 \cdots X_6$, is:

$$h_1(x_{i_1}) + h_2(x_{i_2}) + \cdots + h_6(x_{i_6}) = 6 \text{ bits} \; . \tag{1.33}$$

Let us now play one more game, connected to the previous one but more sophisticated, because the different answers will no longer independent. It is a simplified version of the game of "*battleship*", played with a single "submarine" that you put in a 8×8 checkerboard, for instance in $H3$. Here the outcomes are always *two*: missed ≡ 0, and hit ≡ 1. In the first realisation you have a process:



move #	1	2	32	48	49
question	G3	B1	E5	F3	H3
outcome	$x = \mathtt{n}$	$x = \mathtt{n}$	$x = \mathtt{n}$	$x = \mathtt{n}$	$x = \mathtt{y}$
$P(x)$	$\frac{63}{64}$	$\frac{62}{63}$	$\frac{32}{33}$	$\frac{16}{17}$	$\frac{1}{16}$
$h(x)$	0.0227	0.0230	0.0443	0.0874	4.0
Total info.	0.0227	0.0458	1.0	2.0	6.0

Figure 1.4.: The game of "battleship" played with a single "submarine" in G3. In the illustration, the submarine is hit at move 49. Move 1 is G3, move 2 is B1, etc. Figure taken from the book by MacKey.

$$X_1 = \begin{pmatrix} 0 & 1 \\ P(0) = \frac{63}{64} & P(1) = \frac{1}{64} \end{pmatrix} \; .$$

If you are very lucky, and your first move is a "hit", H3, outcome $x_1 = 1$ of probability $P(1) = \frac{1}{64}$, then

$$h_1(x_1 = 1) = \log_2 \left(\frac{1}{P(1)} \right) = \log_2(64) = 6 \; .$$

You got 6 bits of information with the first lucky hit. Most likely your first move will be a "missed", for instance G3, outcome $x_1 = 0$ of probability $P(0) = 63/64$, then

$$h_1(x_1 = 0) = \log_2 \left(\frac{1}{P(0)} \right) = \log_2 \left(\frac{64}{63} \right) = 0.0027 \; .$$

You got very little information with the first unlucky hit. In such a case, you proceed with a second move, described by the following *conditional process*:

$$X_2\big|_{x_1=0} = \left(\begin{array}{cc} 0 & 1 \\ P(0) = \frac{62}{63} & P(1) = \frac{1}{63} \end{array} \right) .$$

Observe that now the probabilities that appear are *conditional probabilities*: $P(0) = P(x_2 = 0|x_1 = 0)$, and $P(1) = P(x_2 = 1|x_1 = 0)$. If you are lucky at your second move, $h_2(x_2 = 1|x_1 = 0) = \log_2(63)$ hence you have:

$$h_1(x_1 = 0) + h_2(x_2 = 1|x_1 = 0) = \log_2 \left(\frac{64}{63} \right) + \log_2(63) = \log_2 \left(\frac{64}{63} \cdot 63 \right) = \log_2(64) = 6 \; .$$

Again, upon hitting the submarine, you got 6 bit of information. More realistically, if you miss it, you get $h_2(x_2 = 0|x_1 = 0) = \log_2(\frac{63}{62}) = 0.0230$, hence a total information:

$$h_1(x_1 = 0) + h_2(x_2 = 0|x_1 = 0) = \log_2 \left(\frac{64}{63} \right) + \log_2 \left(\frac{63}{62} \right) = \log_2 \left(\frac{64 \cdot 63}{63 \cdot 62} \right) = \log_2 \left(\frac{64}{62} \right) = 0.0458 \; .$$

Let us proceed with the third move, represented by:

$$X_3\big|_{x_2=0,x_1=0} = \left(\begin{array}{cc} 0 & 1 \\ P(0) = \frac{61}{62} & P(1) = \frac{1}{62} \end{array} \right) ,$$

and suppose that you miss again, and you continue to miss up to move 32, represented by:

$$X_{32}\big|_{x_{31}=0\cdots x_1=0} = \left(\begin{array}{cc} 0 & 1 \\ P(0) = \frac{32}{33} & P(1) = \frac{1}{33} \end{array} \right) .$$

The total information you acquired with these 32 failures is:

$$\begin{aligned} h_{\mathrm{tot},32} &= h_1(x_1 = 0) + h_2(x_2 = 0|x_1 = 0) + \cdots + h_{32}(x_{32} = 0|x_{31} = 0 \cdots x_1 = 0) \\ &= \log_2 \left(\frac{64}{63} \right) + \log_2 \left(\frac{63}{62} \right) + \cdots + \log_2 \left(\frac{33}{32} \right) = \log_2 \left(\frac{64}{32} \right) = \log_2 2 = 1 \; . \end{aligned} \tag{1.34}$$

So, 32 unlucky moves give you 1 bit of information: a moment thought will tell you that you have eliminated *half* of the possibilities, exactly like after the first question Q1 in the game of guessing a number in $\{0 \cdots 63\}$. If you persist being unlucky all the way to move $48 = 32 + 16$, then your total information acquired will be:

$$\begin{aligned} h_{\mathrm{tot},48} &= h_1(x_1 = 0) + h_2(x_2 = 0|x_1 = 0) + \cdots + h_{48}(x_{48} = 0|x_{47} = 0 \cdots x_1 = 0) \\ &= \log_2 \left(\frac{64}{63} \right) + \log_2 \left(\frac{63}{62} \right) + \cdots + \log_2 \left(\frac{17}{16} \right) = \log_2 \left(\frac{64}{16} \right) = \log_2 4 = 2 \; . \end{aligned} \tag{1.35}$$

Two bits of information are acquired after 48 unlucky strikes because you eliminated another *half of the remaining half*, pretty much like after the second question Q2 in the game of guessing a number in $\{0 \cdots 63\}$. Now suppose that you move 49 is a hit. Since

$$X_{49}\big|_{x_{48}=0\cdots x_1=0} = \left(\begin{array}{cc} 0 & 1 \\ P(0) = \frac{15}{16} & P(1) = \frac{1}{16} \end{array} \right) ,$$

then

$$h_{49}(x_{49}=1|x_{48}=0\cdots x_1=0)=\log_2\left(\frac{1}{P(1)}\right)=\log_2(16)=4\ .$$

So, the hit at move 49 gives you the remaining 4 bits of information: you now know *precisely* the location of the submarine, which is totally equivalent to knowing a number in $\{0\cdots 63\}$, since there are 64 possible locations.

Notice that in this game I typically ask many more than 6 questions, but the total counting of Shannon's information content is, very reasonably, always 6 bits upon hitting the submarine.

1.4. Typicality and the (weak) law of large numbers.

Let X be, as before, a process

$$X=\left(\begin{array}{ccccccc} x_1 & x_2 & \cdots & x_j & \cdots & x_{|\mathcal{A}|} \\ P(x_1) & P(x_2) & \cdots & P(x_j) & \cdots & P(x_{|\mathcal{A}|}) \end{array}\right)\ , \tag{1.36}$$

with Shannon entropy $H(X)$. The information content $h(x_j)=\log_2(1/P(x_j))$ of outcome x_j will have a variance $\mathrm{Var}[h]$ in the elementary process X, which we can easily calculate:

$$\mathrm{Var}[h]=\mathrm{E}[h^2]-(\mathrm{E}[h])^2=\sum_{j=1}^{|\mathcal{A}|}P(x_j)h^2(x_j)-H^2(X)\ . \tag{1.37}$$

Suppose that you generate sequences $\mathbf{x}=(x_{j_1},\cdots,x_{j_N})\in\mathcal{A}_X^N$ by repeating N times the process X — i.e., constructing the joint process $X_1X_2\cdots X_N$ — assuming the various repetitions X_j are *independent* and identical to the elementary process X. You often read that the "N events are *independent and identically distributed*".

> **Typical strings.** To define a "typical" string, we stipulate that their probability $P(\mathbf{x})$ should be
>
> $$2^{-N(H+\epsilon)}\leq P(\mathbf{x})\leq 2^{-N(H-\epsilon)} \qquad\Longleftrightarrow\qquad \left|\frac{1}{N}\log_2\frac{1}{P(\mathbf{x})}-H\right|<\epsilon\ , \tag{1.38}$$
>
> with some arbitrarily small $\epsilon>0$. In words: typical strings are those whose "average information content" $\frac{1}{N}\log_2\frac{1}{P(\mathbf{x})}$ is "within ϵ" of the Shannon entropy H. More formally, we define:
>
> $$\mathrm{T}_{N,\epsilon}\equiv\left\{\mathbf{x}\in\mathcal{A}_X^N:\left|\frac{1}{N}\log_2\frac{1}{P(\mathbf{x})}-H\right|<\epsilon\right\} \tag{1.39}$$
>
> to be the *set of ϵ-typical sequences of N independent outcomes.* The goal of the remaining derivation is to show that
>
> $$\mathrm{Prob}\left(\mathbf{x}\in\mathrm{T}_{N,\epsilon}\right)\geq 1-\frac{\mathrm{Var}[h]}{\epsilon^2N} \tag{1.40}$$
>
> which tells us, in words, that the probability of a "typical" sequence goes to 1 when $N\to\infty$, for any value of $\epsilon>0$.

To proceed, we review here the *weak law of large numbers.* Let us start from a simple inequality, known as *Markov inequality.* Consider a *positive* random variable Y with probability (density) $P(y)$ and finite expectation $\mathrm{E}[Y]<\infty$. Take an arbitrary *positive* α and consider the probability $\mathbb{P}(y>\alpha)$.

Then you can show that: [5]

$$\textbf{Markov inequality:} \qquad \mathbb{P}(y > \alpha) \le \frac{\mathrm{E}[Y]}{\alpha} \; . \tag{1.41}$$

Consider now a random variable Z with a *finite variance*. Then you can show that:

$$\textbf{Chebyshev inequality:} \qquad \mathbb{P}(|z - \mathrm{E}[Z]| > \epsilon) \le \frac{\mathrm{Var}[Z]}{\epsilon^2} \; . \tag{1.42}$$

The proof is once again rather elementary: for instance, take $Y = |Z - \mathrm{E}[Z]|^2$, which is a positive random variable, with $\mathrm{E}[Y] = \mathrm{E}[(Z - \mathrm{E}[Z])^2] = \mathrm{Var}[Z] < \infty$, and apply to Y Markov's inequality taking $\alpha = \epsilon^2$. You get:

$$\mathbb{P}(|z - \mathrm{E}[Z]| > \epsilon) = \mathbb{P}(|z - \mathrm{E}[Z]|^2 > \epsilon^2) = \mathbb{P}(y > \alpha = \epsilon^2) \le \frac{\mathrm{E}[Y]}{\alpha} = \frac{\mathrm{Var}[Z]}{\epsilon^2} \; .$$

We are now ready to prove that weak law of large numbers. Consider the N repetitions $X_1 X_2 \cdots X_N$ of a process X with a finite variance, and the random variable

$$Z = \frac{1}{N} \sum_{i=1}^{N} X_i \; , \tag{1.43}$$

whose outcome are, in words, *the average of the N independent outcomes (measurements) of the X*. For instance, if X_i are Bernoulli trials with binary outcomes 0 and 1, then $Z = N_1/N$ represents the number of times a 1 occurs, normalised to N. In general:

$$\mathrm{E}[Z] = \frac{1}{N} \sum_{i=1}^{N} \mathrm{E}[X_i] = \mathrm{E}[X] \; , \tag{1.44}$$

since all $\mathrm{E}[X_i] = \mathrm{E}[X]$ are identical. The surprise is in the variance of Z. A simple calculation [6] shows that:

$$\mathrm{Var}[Z] = \frac{1}{N} \mathrm{Var}[X] \; , \tag{1.46}$$

a remarkable result which you know "well" by experience: the average of N measurements has a sharper distribution than the original quantity X, with a variance that scales to 0 as $1/N$: this is the reason why you accumulate statistics, after all!

---

[5] The proof is elementary:

$$\mathbb{P}(y > \alpha) = \int_{\alpha}^{\infty} \mathrm{d}t \; P(t) \le \int_{\alpha}^{\infty} \mathrm{d}t \; \left(\frac{t}{\alpha}\right) \; P(t) = \frac{1}{\alpha} \int_{\alpha}^{\infty} \mathrm{d}t \; t \; P(t) \le \frac{1}{\alpha} \int_{0}^{\infty} \mathrm{d}t \; t \; P(t) = \frac{\mathrm{E}[Y]}{\alpha} \; .$$

[6] By definition:

$$\begin{aligned}
\mathrm{Var}[Z] &= \frac{1}{N^2} \sum_{i,j} \mathrm{E}[X_i X_j] - (\mathrm{E}[Z])^2 = \frac{1}{N^2} \left(\sum_i \mathrm{E}[X_i^2] + \sum_{i \ne j} \mathrm{E}[X_i] \mathrm{E}[X_j] \right) - (\mathrm{E}[Z])^2 \\
&= \frac{1}{N^2} \left(\sum_i \mathrm{E}[X_i^2] + \sum_{i \ne j} \mathrm{E}[X_i] \mathrm{E}[X_j] + \overbrace{\sum_i \mathrm{E}[X_i] \mathrm{E}[X_i] - \sum_i (\mathrm{E}[X_i])^2}^{\text{add and subtract}} \right) - (\mathrm{E}[Z])^2 \\
&= \frac{1}{N^2} \left(\sum_i \mathrm{E}[X_i^2] - \sum_i (\mathrm{E}[X_i])^2 \right) + \cancel{\frac{1}{N^2} \left(\sum_{i,j} \mathrm{E}[X_i] \mathrm{E}[X_j] \right)} - \cancel{(\mathrm{E}[Z])^2} \\
&= \frac{1}{N} \left(\mathrm{E}[X^2] - (\mathrm{E}[X])^2 \right) = \frac{1}{N} \mathrm{Var}[X] \; .
\end{aligned} \tag{1.45}$$

The weak law of large numbers. The random variable

$$Z = \frac{1}{N}\sum_{i=1}^{N} X_i \; , \tag{1.47}$$

whose outcome are *the average of the N independent outcomes (measurements) of the X*, has a probability distribution such that, by Chebyshev's inequality:

$$\mathbb{P}(|z - \mathrm{E}[Z]| > \epsilon) \le \frac{\mathrm{Var}[Z]}{\epsilon^2} = \frac{\mathrm{Var}[X]}{N\epsilon^2} \; , \tag{1.48}$$

or, equivalently:

$$\mathbb{P}(|z - \mathrm{E}[Z]| < \epsilon) \ge 1 - \frac{\mathrm{Var}[X]}{N\epsilon^2} \; . \tag{1.49}$$

So, in words: the probability that an outcome for Z is "within ϵ" of its average $\mathrm{E}[Z]$ tends to 1 as $N \to \infty$.

Having established the weak law of large numbers, let us return to our typicality story. The probability $P(\mathbf{x})$ of a string $\mathbf{x} = (x_1, \cdots x_N) \in \mathcal{A}_X^N$, since the events are independent, is

$$P(\mathbf{x}) = P(x_1) \cdots P(x_j) \cdots P(x_N) \; ,$$

where we have condensed our notation by indicating simply as x_i the more proper but ugly x_{j_i}, for the outcome you get at the ith repetition. Hence, we have immediately that

$$\frac{1}{N}\log_2 \frac{1}{P(\mathbf{x})} = \frac{1}{N}\sum_{i=1}^{N} \log_2 \frac{1}{P(x_i)} = \frac{1}{N}\sum_{i=1}^{N} h(x_i)$$

If you recall that $H = \mathrm{E}[h]$, and you apply the weak law of large numbers to the random variable Z defined from the average (over repetitions) of the information content:

$$Z = \frac{1}{N}\sum_{i=1}^{N} h(x_i) \; , \tag{1.50}$$

observing also that $\mathrm{E}[Z] = \mathrm{E}[h] = H(X)$, we can immediately deduce that:

$$\mathrm{Prob}\,(\mathbf{x} \in \mathrm{T}_{N,\epsilon}) \equiv \mathrm{Prob}\left(\left| \frac{1}{N}\sum_{i=1}^{N} h(x_i) - \mathrm{E}[h] \right| < \epsilon \right) \ge 1 - \frac{\mathrm{Var}[h]}{\epsilon^2 N} \tag{1.51}$$

In the literature, the result expressed in Eq. (1.51) is known as *asymptotic equipartition principle.* [7] With the words of MacKay [6]:

> **Asymptotic equipartition principle**: For an ensemble of N identically distributed independent random processes $(X_1, X_2, \cdots X_N)$, with N sufficiently large, the outcome $\mathbf{x} = (x_1, x_2, \cdots, x_N)$ is almost certain to belong to a subset of $\mathcal{A}_X^N$ of only $2^{NH(X)}$ members, each having probability $P(\mathbf{x})$ "close to" $2^{-NH(X)}$.

In general, for $H(X) < \log_2|\mathcal{A}|$, the subset of typical sequences $\Omega_{\mathrm{typ}} \sim 2^{NH(X)}$ is a *negligible fraction* of the total number of sequences $\Omega_{\mathrm{tot}} = |\mathcal{A}|^N$:

$$\frac{\Omega_{\mathrm{typ}}}{\Omega_{\mathrm{tot}}} \sim \frac{2^{NH(X)}}{2^{N\log_2|\mathcal{A}|}} \sim 2^{-N(\log_2|\mathcal{A}|-H(X))} \xrightarrow{N\to\infty} 0 \; . \tag{1.52}$$

---

[7] Not to be confused with the "equipartition of energy" in the kinetic theory of gases and statistical mechanics.

1.5. Shannon's source coding theorem

What goes under the name of *Shannon's source coding theorem* is a result that builds on the asymptotic equipartition principle, but goes a bit forward. I will briefly mention this for completeness: more about data compression, both lossless and lossy, in the book of MacKay.

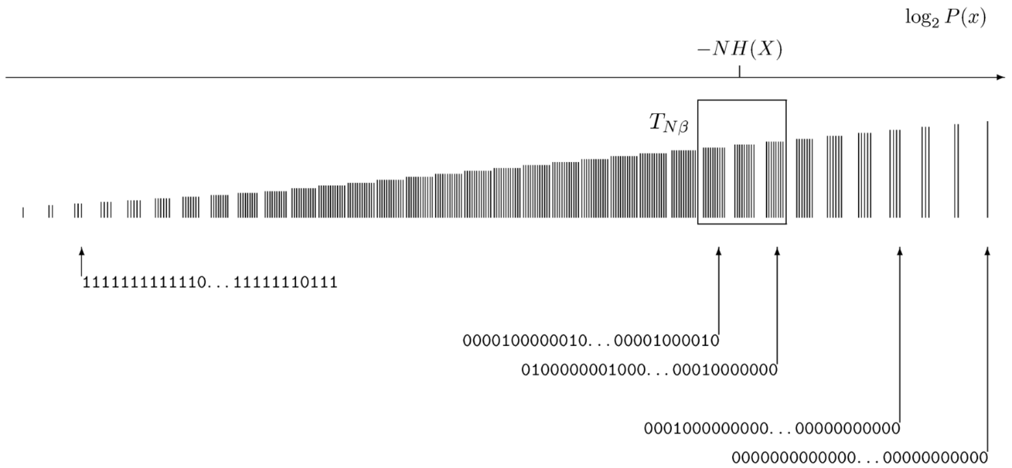


Figure 1.5.: Sketch of the probability of sequences of N bits in ascending order. The box highlight the typical set, with $\Omega_{\text{typ}} \sim 2^{NH(X)}$ members. To the far right the string with the highest probabilities are shown. When $N = 100$, since $H \approx 0.47$ for $p_0 = 0.9$ and $p_1 = 0.1$, you have 2^{-47} to be the probability of typical strings. On the contrary, the most and the least probable strings have probabilities $2^{-15.2}$ and $2^{-232.1}$, respectively. Figure taken from the book by MacKay.

But before we dive into some technical aspects of this story, try to do the following exercise.

Exercise 1.1. A horse race has 8 horses competing of different ability: their probability of winning a race is not uniform, but rather represented by the following process:

$$X = \begin{pmatrix} 0 & 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ p_0 = \frac{1}{2} & p_1 = \frac{1}{4} & p_2 = \frac{1}{8} & p_3 = \frac{1}{16} & p_4 = \frac{1}{64} & p_5 = \frac{1}{64} & p_6 = \frac{1}{64} & p_7 = \frac{1}{64} \end{pmatrix}$$

where we numbered the horses from 0 to 7.

(a) Calculate the Shannon entropy $H(X)$ of X. [Clearly, use base-2 logarithms.]

(b) Imagine now that you want to communicate the result of the winner of N identically repeated races. To do that, you use a telephone line where you can transmit bits, 0 or 1. You have to establish a unique code to indicate the horse which won each race. Clearly, a binary code $C_0 = 000, C_1 = 001, C_2 = 010, C_3 = 011, C_4 = 100, C_5 = 101, C_6 = 110, C_7 = 111$, would do: this is a very democratic code, which uses 3 bits for every race; the length of the string will need to be $3N$ bits if you want to transmit the result of N races. Consider now the following alternative code:

$$\begin{pmatrix} 0 & 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ p_0 = \frac{1}{2} & p_1 = \frac{1}{4} & p_2 = \frac{1}{8} & p_3 = \frac{1}{16} & p_4 = \frac{1}{64} & p_5 = \frac{1}{64} & p_6 = \frac{1}{64} & p_7 = \frac{1}{64} \\ C_0 = 0 & C_1 = 10 & C_2 = 110 & C_3 = 1110 & C_4 = 111100 & C_5 = 111101 & C_6 = 111110 & C_7 = 111111 \end{pmatrix}$$

Observe that we used codewords of increasing length to code horses that have a smaller probability of winning a race. In particular, we assigned the shortest possible codeword (1 bit), $C_0 = 0$, to the horse with the highest probability of victory. Would you be able to *uniquely decode* the following string?

$$00101100010$$

To how many races does it refer to? Which horse won the 4^{th} race? Which the 5^{th}?

(c) Suppose you want to communicate with a string of bits the result of a large number N of races: what is the average length L, in bits, of the string you would need?

(d) What is the relationship between the average length L of the string and the Shannon entropy $H(X)$?

(e) If all the horses where equally good, $p_0 = p_1 = \cdots = p_7 = \frac{1}{8}$, what would be the Shannon entropy $H(X)$? What would be the average length L for N races if you use the code proposed above? Would you use it? Or would you rather prefer the binary code instead?

The simple example contained in the previous exercise shows the basic idea of a *lossless variable-length encoding*: the best code you can invent to transmit a message will have an *average length related to the Shannon entropy of the process generating it.*

In the following, we will discuss *fixed length* encoding but with a probability of *loss of information*: we will, therefore, "count" how many strings you should try to "give a codeword to" if you renounce to some very improbable strings, which will have no codeword associated with it.

Returning for concreteness to our Bernoulli binary string example, suppose that you list all strings of N bits in order of increasing probability $\log_2 P(\mathbf{x})$, as sketched in Fig. 1.5. The strings can be divided into three classes:

1) the "*typical*" ones, with the usual assignment of ϵ to define typicality;

2) "*atypical*" strings but with *high probability* $P(\mathbf{x}) > 2^{-N(H(X)-\epsilon)}$;

3) "*atypical*" strings but with a *very small probability* $P(\mathbf{x}) < 2^{-N(H(X)+\epsilon)}$.

Let us now define a new set $\mathrm{S}_{N,\delta}$ as follows. Start from the string with highest probability $\mathbf{x}_{\mathrm{highest}}$, and include it in $\mathrm{S}_{N,\delta}$. Then continue down the list of sequences and keep adding them to $\mathrm{S}_{N,\delta}$ until

$$\mathrm{Prob}(\mathbf{x} \in \mathrm{S}_{N,\delta}) \geq 1 - \delta \;, \tag{1.53}$$

where δ is a small number of your choice. Notice that $\mathrm{S}_{N,\delta}$ contains, by construction, "atypical" sequences with large probability, class **2)** above, as well as "typical" sequences, class **1)**. A moment reflection should convince you that $\mathrm{S}_{N,\delta}$ can also be defined as being *the smallest subset of strings such that* $\mathrm{Prob}(\boldsymbol{x} \in \mathrm{S}_{N,\delta}) \geq 1 - \delta$. Define now the *essential bit content* of $\mathrm{S}_{N,\delta}$ from the number of its members $|\mathrm{S}_{N,\delta}|$, with the usual logarithm:

$$H_\delta(X^N) = \log_2 |\mathrm{S}_{N,\delta}| \;. \tag{1.54}$$

Obviously, if $\delta = 0$ you include *all sequences*, $\mathrm{S}_{N,0} \equiv \mathcal{A}_X^N$, hence $H_0(X^N) = N \log_2 |\mathcal{A}|$. You realise that $H_\delta(X^N)$ is the number of bits which you need to uniquely describe all elements of the set $\mathrm{S}_{N,\delta}$. Notice that if $\delta > 0$ some very improbable atypical strings are omitted from this set: if they occur, you would not be able to describe them. And now comes the statement of the theorem:

> **Shannon's source coding theorem**: Let X be a process with entropy $H(X)$. Consider the ensemble of N independent identically distributed random processes $(X_1, X_2, \cdots X_N)$. Then, for any arbitrarily small $\epsilon > 0$ and any δ, with $0 < \delta < 1$, there exists a sufficiently large N_0 such that for $N > N_0$:
>
> $$\left| \frac{1}{N} H_\delta(X^N) - H(X) \right| < \epsilon \tag{1.55}$$

Hence, in other words, if you allow for some losses, $\delta > 0$, you can describe with "essentially" $NH(X)$ bits all remaining strings. Concerning the proof: The fact that $H_\delta(X^N) < N(H(X) + \epsilon)$ is not difficult at all. Consider the typical set $\mathrm{T}_{N,\epsilon}$. We know that

$$\mathrm{Prob}(\mathbf{x} \in \mathrm{T}_{N,\epsilon}) \geq 1 - \frac{\mathrm{Var}[h]}{\epsilon^2 N} \geq 1 - \delta \ ,$$

by taking $N \geq N_0$ such that $\frac{\mathrm{Var}[h]}{\epsilon^2 N_0} \leq \delta$. But $\mathrm{S}_{N,\delta}$ is the *smallest subset that verifies that inequality*. Hence $|\mathrm{S}_{N,\delta}| \leq |\mathrm{T}_{N,\epsilon}|$. Let us put a bound on $|\mathrm{T}_{N,\epsilon}|$ by arguing as follows. The smallest probability that a typical string in $\mathrm{T}_{N,\epsilon}$ can have is $P(\mathbf{x}) = 2^{-N(H(X)+\epsilon)}$. Hence, the largest size that $\mathrm{T}_{N,\epsilon}$ can have can be bound by assuming that all strings have probability $2^{-N(H(X)+\epsilon)}$, which leads to:

$$2^{-N(H(X)+\epsilon)} |\mathrm{T}_{N,\epsilon}|_{\mathrm{largest}} \leq 1 \qquad \Longrightarrow \qquad |\mathrm{T}_{N,\epsilon}|_{\mathrm{largest}} \leq 2^{N(H(X)+\epsilon)} \ .$$

This immediately leads us to the conclusion:

$$H_\delta(X^N) = \log_2 |\mathrm{S}_{N,\delta}| \leq \log_2 |\mathrm{T}_{N,\epsilon}| \leq N(H(X)+\epsilon) \tag{1.56}$$

The fact that $H_\delta(X^N) > N(H(X)-\epsilon)$ is slightly more elaborate: see MacKay, Sec. 4.5 for details.

1.6. The ideal gas: Newton's approach

We now switchgear to physics, by considering one of the building problems of statistical mechanics: the ideal gas. I illustrate the concept of chaos by showing you some billiard animations, in particular the stadium billiard. The result is that it is quite reasonable to expect that the system visits in an essentially uniform way all the available phase space. The volume of the available phase space is hence the crucial quantity we need to consider. [8] More about these issues when we will discuss in more detail the ergodic hypothesis.

Consider N classical particles in three-dimensional space. The $6N$ dimensional phase space will be discretised by subdividing it into small cubes of volume h^{3N}, where h has the dimension of an action — indeed, we will see that the correct choice is just Planck's constant. The number of (discretised) states the system can visit when its energy is in the interval $[E-\Delta_E, E]$ is given by

$$\begin{aligned} \mathcal{N}_{\mathrm{states}}(E-\Delta_E, E) &= \frac{1}{N!} \int \frac{d^{3N}q d^{3N}p}{h^{3N}} \, \mathrm{I}_{[E-\Delta_E,E]}(H(\mathbf{q},\mathbf{p})) \\ &= \int_{E-\Delta_E}^{E} \mathrm{d}E' \, \underbrace{\frac{1}{N!} \int \frac{d^{3N}q d^{3N}p}{h^{3N}} \, \delta(E' - H(\mathbf{q},\mathbf{p}))}_{\Omega(E')} \ . \end{aligned} \tag{1.57}$$

Here

$$\mathrm{I}_{[a,b]}(x) = \theta(x-a)\,\theta(b-x) = \int_a^b \mathrm{d}x' \, \delta(x'-x) = \begin{cases} 1 & \text{for} \quad x \in [a,b] \\ 0 & \text{otherwise} \end{cases} \ ,$$

is the characteristic (or indicator) function of the interval $[a,b]$, while $\theta(\cdot)$ is the Heaviside θ-function, and the second form follows from the properties of the Dirac's delta function. Notice also the extra factor $1/N!$, which accounts for the so-called "correct Boltzmann counting" (introduced by Gibbs), which I ask you to accept with an act of faith for the time being. [9] Let us consider the quantity appearing inside the integral, which is a *density of states*:

$$\Omega(E) = \frac{1}{N!} \int \frac{\mathrm{d}^{3N}q \mathrm{d}^{3N}p}{h^{3N}} \, \delta(E - H(\mathbf{q},\mathbf{p})) \ . \tag{1.58}$$

---

[8] You are essentially maximising the entropy, by a limiting distribution that weights in a uniform way the available phase space.

[9] It was introduced to make the entropy properly extensive and is related to the indistinguishability of particles proper of a quantum approach. Both the $N!$ and the h^{3N} will appear when taking the appropriate classical limit of the quantum ideal gas.

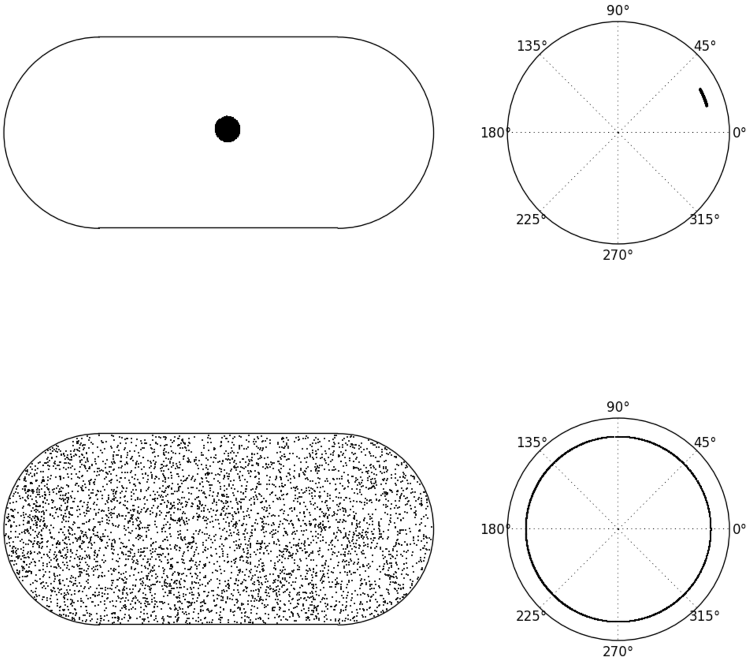


Figure 1.6.: The stadium mixing. (Top) The initial conditions, with configurations on the left and velocities on the right. (Bottom) A snapshot at a sufficiently large time. Figures due to Simone Ziraldo.

Since $\Omega(E)$ is usually a monotonic function of E we have that:

$$\mathcal{N}_{\text{states}}(E-\Delta_E,E) \;<\; \Delta_E\,\Omega(E) \;\leq\; E\,\Omega(E)\;. \tag{1.59}$$

We will soon argue that, in the limit of a large number of particles, these quantities are all *exponentially dominated* by what happens at E: they are completely insensitive to the value of Δ_E, and we can even take $\Delta_E = E$. More precisely we will see — with the explicit example of the ideal gas — that one expects: [10]

$$\lim_{N\to\infty}\frac{\log\mathcal{N}_{\text{states}}(E-\Delta_E,E)}{N} = \lim_{N\to\infty}\frac{\log\Delta_E\Omega(E)}{N} = \lim_{N\to\infty}\frac{\log E\Omega(E)}{N} = s(E)\;. \tag{1.60}$$

With a more relaxed notation, we will re-express the previous equality as:

$$\mathcal{N}_{\text{states}}(E-\Delta_E,E) \simeq \Delta_E\,\Omega(E) \simeq E\,\Omega(E) \simeq \mathrm{e}^{N\,s(E)} \stackrel{\text{def}}{=} \mathrm{e}^{\mathcal{S}(E)}\;, \tag{1.61}$$

where we have introduced the extensive entropy $\mathcal{S}(E) \stackrel{\text{def}}{=} N\,s(E)$. Here $\simeq$ means that we neglect, in the exponential, anything that is not extensive in N, for instance, terms proportional to $\log(N)$ or constants.

Let us proceed with the study of $\Omega(E)$. To cope with the Dirac's delta function, we use the standard trick of taking the Laplace transform:

$$Z(\beta) \stackrel{\text{def}}{=} \int_0^\infty \mathrm{d}E\;\Omega(E)\,\mathrm{e}^{-\beta E} = \frac{1}{N!}\int \frac{\mathrm{d}^{3N}q\,\mathrm{d}^{3N}p}{h^{3N}}\;\mathrm{e}^{-\beta H(\mathbf{q},\mathbf{p})} \stackrel{\text{def}}{=} \mathrm{e}^{-\mathcal{F}(\beta)}\;, \tag{1.62}$$

---

[10] It should be stressed that the limit $N\to\infty$ is always taken together with an infinite volume limit, by taking the ratio V/N (the volume per particle) or N/V (the density) *constant*. We omit to indicate the volume in all our formulas, for the time being.

where β is the Laplace variable and should be regarded as *complex*, in general, and with dimensions of inverse energy, while $\mathcal{F}$ is a useful dimensionless quantity which we have introduced by taking the logarithm of Z. [11] Notice that in general, all these quantities depend on V and N, a dependence that we omit for the time being. The information on $\Omega(E)$ will be retrieved, if I know how to calculate $Z(\beta)$, by performing an *inverse Laplace transform*: [12]

$$\Omega(E) = \int_{\beta_0-i\infty}^{\beta_0+i\infty} \frac{\mathrm{d}\beta}{2\pi i}\, \mathrm{e}^{\beta E} Z(\beta) = \int_{\beta_0-i\infty}^{\beta_0+i\infty} \frac{\mathrm{d}\beta}{2\pi i}\, \mathrm{e}^{\beta E - \mathcal{F}(\beta)} \;. \tag{1.63}$$

The path of integration in the complex-β plane which you need to calculate the inverse Laplace transform we are free to choose, as long as it stays to the right of any singularities of $Z(\beta)$: we assume that we start our path at some $\beta_0 - i\infty$ and end it at $\beta_0 + i\infty$, but the value of β_0 and the shape of the path is at our disposal. [13] Notice that, so far, we have not used the fact that our system is an ideal gas of non-interacting particles. If we assume that, the calculation of $Z(\beta)$ is simple: [14]

$$\begin{aligned} Z_{\mathrm{ideal}}(\beta) = \frac{1}{N!}\left[\frac{V}{h^3}\int \mathrm{d}^3p\, \mathrm{e}^{-\beta\frac{\mathbf{p}^2}{2m}}\right]^N &= \frac{1}{N!}\left[\frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}}\right]^N \\ &\approx \mathrm{e}^{N\log \frac{\mathrm{e}V}{N}\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}}} \;, \end{aligned} \tag{1.64}$$

wherein the last expression we have made use of the Stirling approximation, setting $N! \simeq (N/\mathrm{e})^N$. We can now proceed in two ways: we can calculate $\Omega_{\mathrm{ideal}}(E)$ either exactly, using the fact that $Z_{\mathrm{ideal}}(\beta)$ has a very simple dependence on β, a multiple pole $Z(\beta) \propto \beta^{-3N/2}$ when $3N$ is even and a simple branch cut when $3N$ is odd, [15] or rely on the second approximate form which suggests using a *saddle-point* technique in calculating the inverse Laplace transform.

We proceed with the saddle point technique because it illustrates a very general idea related to the equivalence of the so-called *statistical ensembles* in the thermodynamics limit: specifically, the micro-canonical ensemble, where $\Omega(E)$ is the actor, and the canonical (or Gibbs) ensemble, where one deals with $Z(\beta)$. We start by rewriting:

$$\Omega_{\mathrm{ideal}}(E) = \int_{\beta_0-i\infty}^{\beta_0+i\infty} \frac{\mathrm{d}\beta}{2\pi i}\, \mathrm{e}^{\beta E - \mathcal{F}_{\mathrm{ideal}}(\beta)} \;, \tag{1.67}$$

---

[11] Note that $Z(\beta)$ is dimensionless because $\Omega(E)$ has dimensions of inverse energy. If this is not your first statistical mechanics' course, you will recognize that $Z(\beta)$ is the canonical partition function, and $\mathcal{F} = \beta F$ where F is the free energy, while β will be related to temperature by $\beta = 1/(k_B T)$ where k_B is the Boltzmann constant.

[12] At variance with Fourier transforms, which are very symmetrical, the inverse Laplace transform involves an integral along a contour in the complex plane, known as Mellin's inverse formula or Bromwich integral (see Wikipedia).

[13] By the Cauchy residue theorem we can freely change the path of integration as long as you do not cross any singularity of the function.

[14] Simply use the Gaussian integral:

$$\int \frac{\mathrm{d}p}{\sqrt{2\pi}}\, \mathrm{e}^{-\beta\frac{p^2}{2m}} = \sqrt{\frac{m}{\beta}} \;.$$

[15] Proceeding exactly, we notice that if $3N$ is an even number, then $3N/2$ is an integer, and $Z(\beta)$ has a pole of order $3N/2$ in the origin $\beta = 0$: the residue of such a pole can be easily calculated by extracting the term $(\beta E)^{\frac{3N}{2}-1}/(\frac{3N}{2}-1)!$ coming from $\mathrm{e}^{\beta E}$, which leads to a simple pole $1/\beta$. This simple calculation gives: [16]

$$\Omega_{\mathrm{ideal}}(E) = \frac{1}{E\Gamma(\frac{3N}{2})N!}\left[\frac{V(2\pi m E)^{\frac{3}{2}}}{h^3}\right]^N \;. \tag{1.65}$$

When $3N$ is odd the integrand has a branch cut along the negative real axis: the calculation is nevertheless quite simple, and leads to the same result you see above when expressing everything in terms of the Euler $\Gamma(z)$ function, which now would be at half-integer arguments. By calculating $\log E\Omega(E)$ we can easily extract the extensive statistical entropy of the ideal gas as: [17]

$$\mathcal{S}_{\mathrm{ideal}}(E,V,N) = N\log\frac{\mathrm{e}V}{N}\left(\frac{4\pi m \mathrm{e} E}{3h^2 N}\right)^{\frac{3}{2}} \;. \tag{1.66}$$

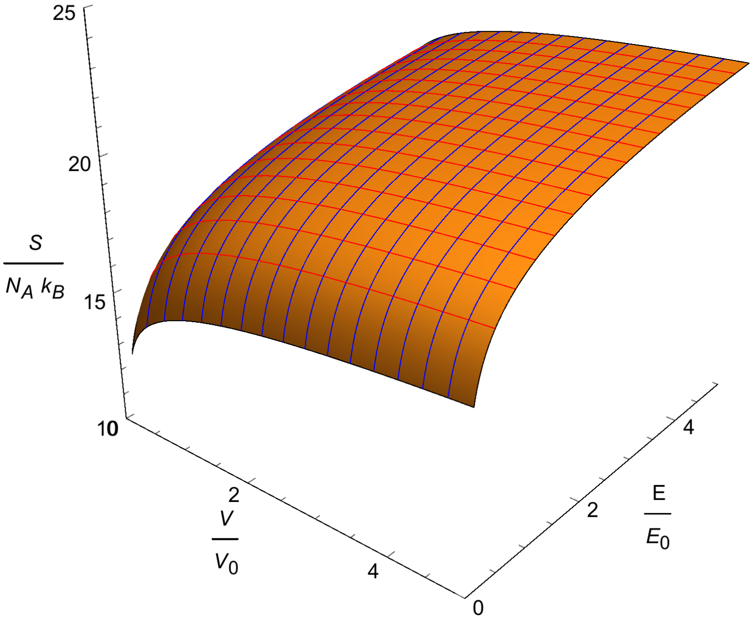


Figure 1.7.: The entropy of the ideal gas. Figure quite in scale: the point $(V/V_0 = 1, E/E_0 = 1)$ represents one mole of Argon, assumed to be an ideal gas, at $T_0 = 273.15$ K, $p_0 = 10^5$ Pa, $V_0 = 22.711$ dm^3. Notice concavity.

where

$$\mathcal{F}_{\text{ideal}}(\beta) \simeq -N \log \frac{\text{e}V}{N} \left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}} . \tag{1.68}$$

So far, β_0 is the (arbitrary) real part of the points where we start and finish our Mellin's contour in the complex plane. Now we calculate the stationary point of the quantity appearing in the exponential, $\beta E - \mathcal{F}_{\text{ideal}}(\beta)$. Hence, we calculate a value of β_0 by solving $\partial_\beta(\beta E - \mathcal{F}) = 0$:

$$E - \frac{\partial \mathcal{F}_{\text{ideal}}}{\partial \beta}\Big|_{\beta_0} = 0 \quad \Longrightarrow \quad E = \frac{3N}{2\beta_0} \quad \Longrightarrow \quad \beta_0 = \frac{3N}{2E} . \tag{1.69}$$

This result should ring a bell, if you remember the famous ideal gas law $E = \frac{3}{2}Nk_BT$, where T is the temperature and k_B the Boltzmann constant: essentially, the saddle point β_0 should be identified with $1/(k_BT)$.

For the time being, let us proceed as if we knew nothing about T and k_B. Notice, that we should in general think of β_0 as a function of the energy E we have set: $\beta_0(E)$. To expand $\beta E - \mathcal{F}_{\text{ideal}}$ around the stationary point β_0 we calculate the second derivative:

$$\frac{\partial^2(\beta E - \mathcal{F}_{\text{ideal}})}{\partial \beta^2}\Big|_{\beta_0} = \frac{3N}{2\beta_0^2} > 0 .$$

The third derivative gives:

$$\frac{\partial^3(\beta E - \mathcal{F}_{\text{ideal}})}{\partial \beta^3}\Big|_{\beta_0} = -\frac{3N}{\beta_0^3} .$$

Hence, around the stationary point we can write:

$$\beta E - \mathcal{F}_{\text{ideal}}(\beta) = \beta_0 E - \mathcal{F}_{\text{ideal}}(\beta_0) + \frac{3N}{4\beta_0^2}(\beta - \beta_0)^2 - \frac{N}{2\beta_0^3}(\beta - \beta_0)^3 \cdots$$

Notice that this immediately tells us that the stationary point of $\beta E - \mathcal{F}_{\rm ideal}(\beta)$ is a *minimum* along the real-β axis, but a *maximum* along the imaginary-β direction: it is a *saddle point*, as it should, because analytic functions cannot have maxima or minima in the complex plane. Now we set our Mellin's contour in the complex-β plane, parameterising it as

$$\beta(t) = \beta_0(1 + it) \ ,$$

with t going from $-\infty$ to $+\infty$. Since $\mathrm{d}\beta = i\beta_0 \mathrm{d}t$ we rewrite:

$$\Omega_{\rm ideal}(E) \approx \mathrm{e}^{\beta_0 E - \mathcal{F}_{\rm ideal}(\beta_0)} \, \beta_0 \int_{-\infty}^{+\infty} \frac{\mathrm{d}t}{2\pi} \, \mathrm{e}^{-\frac{3Nt^2}{4} + i\frac{Nt^3}{2} \cdots} \ , \tag{1.70}$$

One thing that should immediately catch your interest is that the correct extensive entropy is already reproduced by the mere saddle-point value:

$$\mathcal{S}_{\rm ideal}(E) = [\beta_0 E - \mathcal{F}_{\rm ideal}(\beta_0)] \, \big|_{\beta_0(E)} \ . \tag{1.71}$$

The contribution due to the saddle-point "Gaussian" integral, and even the factor β_0 appearing, give negligible power-law corrections in front of the leading exponential. We can ignore them altogether. [18]

Notice the very appealing extensive [19] form of this expression: it scales linearly with N with a logarithmic factor that depends only on the volume per particle $v = V/N$ (thanks to the Gibbs factor) and on the energy per particle $\varepsilon = E/N$, $\mathcal{S}(E,V,N) = N s\,(\varepsilon, v)$, where:

$$\mathcal{S}(E,V,N) = N s(\varepsilon, v) = N \log \mathrm{e}^{\frac{5}{2}} v \left(\frac{4\pi m \varepsilon}{3h^2}\right)^{\frac{3}{2}} \ . \tag{1.72}$$

Fig. 1.7 shows a plot of $\mathcal{S}_{\rm ideal}$ for fixed N, versus V and E.

This expression for the entropy, as written, will necessarily become *negative* — violating the third law of thermodynamics — when the phase space volume per particle becomes of the order of, or smaller than h^3: in this regime quantum effects will turn out crucial. Notice also that $\mathcal{S}$ expression is a *concave* function of its arguments, and a monotonic function of E. Hence you can invert it and express $E(\mathcal{S}, V, N)$. Explicitly, for the ideal gas you would have:

$$E_{\rm ideal}(\mathcal{S}, V, N) = N \left(\frac{3h^2}{4\pi m \mathrm{e}^{5/3}}\right) \mathrm{e}^{\frac{2\mathcal{S}}{3N}} \left(\frac{V}{N}\right)^{-\frac{2}{3}} \ .$$

Remark that $E(\mathcal{S}, V, N)$ is also extensive, monotonically increasing with $\mathcal{S}$, and *convex*. These properties of $\mathcal{S}(E,V,N)$ and of $E(\mathcal{S},V,N)$ — extensivity, monotonicity in the first variable (E or $\mathcal{S}$, respectively), and concavity (for $\mathcal{S}$) or convexity (for E) — will be quite crucial in the whole construction of thermodynamics. [20]

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[18] Try to do the quadratic Gaussian integral explicitly by rescaling variables to $y = \sqrt{N}t$, and you will see what happens: it give a power-law prefactor to the exponentially dominated entropy-related main term.

[19] To avoid misunderstandings, let us stress that "extensive" means that if you "double" your system, then $N \to 2N$, $V \to 2V$, $E \to 2E$, $\mathcal{S} \to 2\mathcal{S}$, i.e., every extensive property "doubles".

[20] We note here, in passing, that the derivatives of E do not contain the constant h and are ultra-simple:

$$\begin{aligned} \left.\frac{\partial E}{\partial \mathcal{S}}\right|_{V,N} &= \frac{2E}{3N} \qquad \equiv k_B T \\ \left.\frac{\partial E}{\partial V}\right|_{\mathcal{S},N} &= -\frac{2E}{3V} \qquad \equiv -p \end{aligned} \tag{1.73}$$

Here we have anticipated things a bit and introduced the general relationship that these derivatives have with two (intensive) variables well known to you: temperature T and pressure p. We will see how this comes about when studying thermodynamics. By putting the two expressions together we get the famous *equation of state of the ideal gas*:

$$pV = Nk_BT \ . \tag{1.74}$$

If you reconsider the previous saddle-point derivation, you will realise that it is much more general then for the ideal case: the crucial ingredient is that E, $\mathcal{S}$, $\mathcal{F}$ are all *extensive*, i.e., proportional to the number of particle N, and the integral is exponentially dominated by the saddle-point. So, we expect that in more general cases we will have:

$$\begin{aligned} \mathcal{S}(E) &= [\beta E - \mathcal{F}(\beta)] \big|_{\beta(E)} \\ E &= \frac{\partial \mathcal{F}}{\partial \beta}\Big|_{\beta(E)} . \end{aligned} \tag{1.75}$$

Notice also that

$$\frac{\partial \mathcal{S}}{\partial E} = \beta + \left(E - \frac{\partial \mathcal{F}}{\partial \beta} \right) \frac{\partial \beta}{\partial E} \equiv \beta(E) . \tag{1.76}$$

We will see soon that the physical interpretation of β is that $\beta = 1/(k_B T)$, where k_B Boltzmann's constant and T is the temperature, the parameter that controls the thermal equilibrium between bodies.

It is interesting that the relationships written above can be interpreted in a perfectly symmetric way. Invert $\beta(E)$ into $E(\beta)$, and write

$$\mathcal{F}(\beta) = [\beta E - \mathcal{S}(E)] \big|_{E(\beta)}$$

Alternatively:

$$\mathcal{F} + \mathcal{S} = \beta E ,$$

where, depending on the variable one wants to use, β or E, one should re-express everything appropriately.

We will see that this is nothing but a Legendre transform. More precisely, as written, it connects $\mathcal{S}$ and $\mathcal{F}$ as "Legendre pairs", and is very symmetrical. For historical reasons, in thermodynamics one tends to favour E rather than $\mathcal{S}$ — after all, it is simpler to "control" E, by insulating the system, than $\mathcal{S}$ —, and use T rather than β. Switching from the Entropy-scheme, in which the fundamental equation of thermodynamics would look something like $\mathcal{S}(E, V, N, \cdots)$ to the Energy-scheme, in which one deals with $E(\mathcal{S}, V, N, \cdots)$, — notice that only extensive variables appear in the arguments of both — the most natural definition of Legendre transform, which is commonly adopted in thermodynamics, is slightly less symmetric. We will adopt this way of looking at the Legendre transform, where E and the free-energy F are Legendre pairs, for instance.

Part I.

Basic material

2. Thermodynamics

Many very good books on thermodynamics are available. The presentation below is based on the book by Fermi, for Sec. 2.1, and on the books by Peliti [1] [2] and Callen [3], for the remaining part.

2.1. Carnot Thermodynamics

This section is meant as a brief recap of some of the traditional concepts explained in high-school and first-year courses on thermodynamics.

The 1st law of thermodynamics. You certainly recall that Joules (1840-1850) proved the equivalence of heat and work, which led to a clear formulation of the 1st law of thermodynamics, extending the concept of conservation of energy to the thermodynamical realm:

$$\Delta E = Q + W \ , \tag{2.1}$$

where ΔE denotes the change in the *internal energy* of the system, upon doing a transformation. Here I adopt the convention that $Q > 0$ when heat is given *to* the system, while $Q = -Q^{\text{rel}} < 0$ if some positive heat $Q^{\text{rel}} > 0$ is released to the environment. Less universal is the sign convention on the work W. Here $W > 0$ when work is performed *on* the system. Viceversa, $W = -W^{\text{ext}} < 0$ when a positive useful work $W^{\text{ext}} > 0$ is extracted *from* the system. [a]

[a] Engineers, for obvious reasons, tend to use W^{ext} in their formulas. Independently of the signs of these quantities, we will use sometimes $Q = -Q^{\text{rel}}$ and $W = -W^{\text{ext}}$ in our manipulations.

Thermal engines are thermodynamical systems going through operating cycles, which try to convert "heat" into useful "mechanical work". [2] These engines have a fundamental limitation set by physics: in trying to convert "heat" into "mechanical work", you *have to waste part of that heat*, **necessarily**. [3] This is essentially the content of Kelvin's formulation of the 2nd law of thermodynamics.

Refrigerators are like reversed thermal engines: they transfer heat from a cold body to a hot body/environment, but to do so you *must perform some work*, **necessarily**. [4] This is essentially the content of Clausius's formulation of the 2nd law of thermodynamics. [5] [6] You have seen already

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[1] Notice that Peliti adopts a different convention on the meaning of "convex" versus "concave" for a function, exactly opposite to ours (and to what you find in Wikipedia, for instance). So, if you extract only parts of arguments from that book, remember that when Peliti says "convex", you should translate into "concave" (i.e., $\frown$-convex for extra-clarity), and vice-versa.

[2] Generally, engines do cycles that transform "some form of energy" into mechanical work. In some engines, for instance, electrical motors, energy is transformed into mechanical work without fundamental limitations (apart from friction, which you can in principle reduce to smaller and smaller values by improving your technology). Thermal engines have a fundamental limitation set by the 2nd law of thermodynamics.

[3] The reverse is not true: I can totally transform work into heat; a bit of a waste, but that is essentially what you do with an electrical heater.

[4] Other possibilities are given in presence of two heat baths. In particular, the *thermal accelerator* is a system in which work is done on the system to accelerate the natural flow of heat from the hot source to the cold one.

[5] Once again, the reverse is not true: simply unplug your refrigerator and open up its door.

[6] Modern air conditioners, with "inverters", have two reversed directions built-in: they can work as refrigerators (during

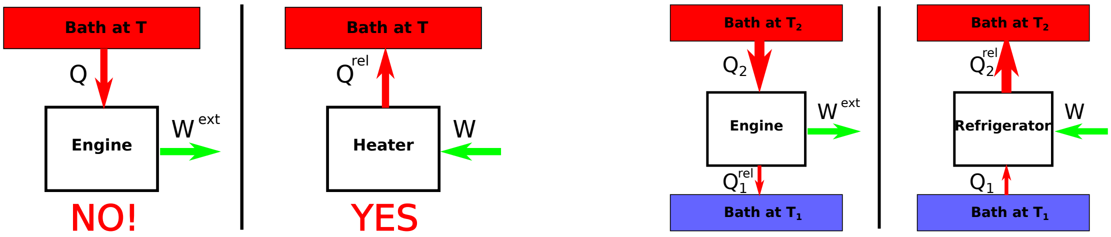

Figure 2.1.: Left: An impossible-to-build thermal engine, violating Kelvin's formulation of the 2nd law, and the (perfectly allowed) waste of work that you do with your electrical heater. Right: A thermal engine and a refrigerator.

the proof of the fact that the two formulations of the 2nd law are indeed equivalent: I will not repeat that proof here.

Briefly, thermal engines have to operate with *at least two* heat-reservoirs, at temperatures T_1 and $T_2 > T_1$. They take an amount of heat $Q_2 > 0$ from the T_2-reservoir, they perform some work $W^{\mathrm{ext}} > 0$, and they release some smaller quantity of (wasted) heat $Q_1^{\mathrm{rel}} > 0$ to the T_1-reservoir. They do that by performing cycles, i.e., returning to the initial state repeatedly. The first-law tells us that $\Delta E = 0$, hence $W^{\mathrm{ext}} = Q_2 - Q_1^{\mathrm{rel}}$.

Efficiency of thermal engines. The efficiency of the engine is by definition the ratio of the work performed W^{ext} over the heat absorbed Q_2. Hence

$$\eta = \frac{W^{\mathrm{ext}}}{Q_2} = \frac{Q_2 - Q_1^{\mathrm{rel}}}{Q_2} = 1 - \frac{Q_1^{\mathrm{rel}}}{Q_2} \,. \tag{2.2}$$

Notice that $0 \le \eta \le 1$. The 2nd law will force the second inequality to be strict: $\eta < 1$.

Carnot understood that the crucial ingredient to maximize the efficiency, for fixed T_1 and T_2, is the *reversibility* of the engine.

Reversibility. Reversibility needs some comments. In essence, reversibility requires a *quasi-static transformation*, in which the system very slowly evolves by infinitesimal steps which proceed through equilibrium states. But this is not enough. Reversibility requires that you can *macroscopically* "undo" the process, by an infinitesimal change in the control parameters, reversing the direction of the action performed. This requires, in particular, that all sources of friction be eliminated. For instance, a reversible isotherm is one in which the temperature of the reservoir is infinitesimally different from that of the system, in such a way that an infinitesimal quantity of heat flows in/out of the system, heat that the system uses to perform/absorb work. Such an action can be reversed, by adjusting the temperature of the reservoir, provided one neglects the friction between the piston and the chamber, which always opposes the motion. Joule's free expansion provides an example of an *irreversible* process: the system expands in vacuum while no heat is absorbed, nor work performed. Even if you think of this expansion as proceeding through infinitesimal small free-expansions (just imagine a long tube with a myriad of small faucets you can open one after the other), it is clear that you cannot macroscopically "undo" each infinitesimal step.

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summer) or as "heat pumps" (during winter). The latter, however, should not be regarded as a "thermal engine" because it uses (electrical) work rather then producing it. The inverter simply implements an exchange of the "role" of the two bodies in a refrigerator: a "heat pump" takes away heat from the (colder) outside environment to give it to your house.

A perfectly reversible engine can execute a reverse cycle, working as a refrigerator: absorb $Q_1 > 0$ from the low-temperature thermostat at T_1, absorb some work $W = -W^{\rm ext} > 0$ to release a large amount of heat $Q_2^{\rm rel} > 0$ to the T_2 (high-temperature) thermostat, with exactly the same "efficiency" [7] $\eta = \frac{W}{Q_2^{\rm rel}}$. We can prove the following:

Carnot theorem. Among all thermal engines working with two heat-reservoirs at T_1 and T_2:

(a) No engine can have an efficiency larger than that of a reversible engine.

(b) Reversible engines must have the same efficiency, independently of the working substance of the engine.

(c) A reversible engine has (maximal) efficiency given by:

$$\eta_{\rm rev} = 1 - \frac{T_1}{T_2} \ . \tag{2.3}$$

Proof. Statement (a) is proved by contradiction. Imagine there is some wonder engine with the efficiency

$$\eta_{\rm wonder} = \frac{W^{\rm ext}}{Q_2} > \eta_{\rm rev} = \frac{W^{\rm ext}_{\rm rev}}{Q_{2,\rm rev}} = \frac{W_{\rm rev}}{Q^{\rm rel}_{2,\rm rev}} \ ,$$

where in the last equality we have reversed the cycle of the reversible engine. Now construct a combined engine that uses the wonder-engine to produce $W^{\rm ext}$ and a (reversible) Carnot refrigerator absorbing *exactly* that work $W_{\rm rev} = W^{\rm ext}$ produced by the wonder-engine. The supposed inequality

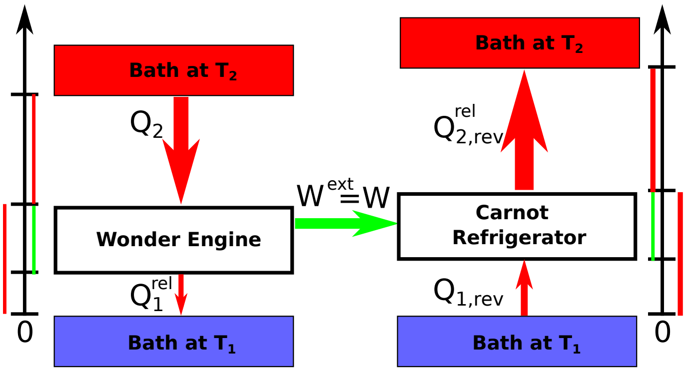

Figure 2.2.: The set-up to prove Carnot's theorem. The width of the arrows indicates the amount of heat. The green and red segments on the left and right axis correspond to the work and heat. The efficiency is the ratio of "green to red segments": the lower is the position of the rectangle denoting the system, the larger is the efficiency. The supposed larger efficiency for the wonder engine implies less released heat (smaller arrow, lower system box) as compared to the heat absorbed by the Carnot refrigerator, using the same work extracted from the wonder engine. The net result is heat transferred from T_1 to T_2, against Clausius' formulation of the 2nd law.

$$\frac{W^{\rm ext}}{Q_2} > \frac{W_{\rm rev}}{Q^{\rm rel}_{2,\rm rev}} \equiv \frac{W^{\rm ext}}{Q^{\rm rel}_{2,\rm rev}} \qquad \Longrightarrow \qquad Q_2 < Q^{\rm rel}_{2,\rm rev} \ ,$$

hence $Q^{\rm rel}_{2,\rm rev} - Q_2 > 0$ is the overall heat released *to* the T_2-reservoir. Energy balance (1st principle) requires that

$$W^{\rm ext} = Q_2 - Q_1^{\rm rel} = Q^{\rm rel}_{2,\rm rev} - Q_{1,\rm rev} = W_{\rm rev} \qquad \Longrightarrow \qquad Q^{\rm rel}_{2,\rm rev} - Q_2 = Q_{1,\rm rev} - Q_1^{\rm rel} > 0 \ ,$$

---

[7] Notice that usually the performance of a refrigerator is defined in a slightly different way, through a *coefficient of refrigeration* $\kappa = Q_1/W$.

hence $Q_{1,\mathrm{rev}} - Q_1^{\mathrm{rel}} > 0$ is the heat absorbed *from* the T_1-reservoir. The combined effect of the wonder-engine-plus-Carnot-refrigerator is therefore to transfer a certain amount of heat $Q_{1,\mathrm{rev}} - Q_1^{\mathrm{rel}} > 0$ from a cold reservoir to a hot reservoir, without other effects. This violates the 2nd law of thermodynamics in the formulation by Clausius. Statement (b) is now very simple: we did not use any particular property of the "wonder engine": imagine it is a second reversible engine working with a newly invented substance: we proved that its efficiency cannot be larger than the first reversible engine. But, exchanging the roles of the two, it cannot also be smaller! Hence *all reversible engines must have the same (maximal) efficiency.* Statement (c) follows from the fact that the maximal efficiency is independent of the substance. Hence you can calculate it using an *ideal gas* as a working substance. A prototypical reversible cycle working between T_1 and T_2 is the *Carnot cycle*, made by two reversible isotherms, and two reversible adiabatics. [8] A standard calculation, typically performed in high school, shows that the efficiency of the reversible Carnot cycle is indeed [9]

$$\eta_{\mathrm{rev}} = 1 - \frac{Q_1^{\mathrm{rel}}}{Q_2} = 1 - \frac{T_1}{T_2} \; .$$

Efficiency vs maximum power. One important observation is that maximum efficiency does not mean that a Carnot engine is particularly useful. Indeed, reversibility requires a very slow operation: ideally, you should produce work in a cycle that lasts an infinitely long time. This implies that the *power* produced, which is the work per unit time, goes to zero. It is interesting to ask how to design a *maximum power* engine. The endo-reversible engine described by Curzon & Alhborn [3] does that.

Carnot inequality. Carnot's theorem implies that for any engine working between T_1 and T_2 we have:

$$\eta = 1 - \frac{Q_1^{\mathrm{rel}}}{Q_2} \le \eta_{\mathrm{rev}} = 1 - \frac{T_1}{T_2} \qquad \Longrightarrow \qquad \frac{Q_2}{T_2} - \frac{Q_1^{\mathrm{rel}}}{T_1} = \frac{Q_2}{T_2} + \frac{Q_1}{T_1} \le 0 \; . \tag{2.4}$$

In the last step, we have replaced $-Q_1^{\mathrm{rel}} = Q_1 < 0$. We will refer to Eq. (2.4) as the *Carnot inequality.* From now on we will write all heat exchanges as Q_i, in such a way that heat has an arbitrary sign: positive if heat is absorbed, negative if released.

---

[8] Alternative cycles, like the Stirling cycle which substitutes the two adiabatics with two isochores, can also be made reversible, and therefore with maximal efficiency. Nevertheless, while a reversible adiabatic needs just that you isolate your system from the reservoirs and you perform/absorb work by a quasi-static expansion/compression, reversible isochores require that you continuously adjust the temperatures of the reservoirs giving/absorbing heat in such a way that they are infinitesimally close to that of the system, while the system increases/decreases its temperature from T_1 to T_2 or vice-versa. Hence, the Carnot cycle is in a sense the most "economical" one in terms of heat-reservoirs. For a discussion of the efficiency of several well-known cycles, see Arovas.

[9] The fact that η_{rev} is a universal function of the two reservoirs temperatures, together with the fact that an ideal gas Carnot cycle leads to $Q_1^{\mathrm{rel}}/Q_2 = T_1^e/T_2^e$, where $T_{1,2}^e$ denotes the *empirical temperatures* measured by, for instance, gas thermometers, led Kelvin to introduce an absolute temperature scale by simply *defining* the ratio of the absolute temperatures of two systems as the efficiency of the Carnot cycle operating between two reservoirs held in thermal equilibrium with the two systems:

$$\frac{T_1}{T_2} \equiv 1 - \eta_{\mathrm{rev}} \; .$$

This definition is universal, because the efficiency of a reversible engine is universal, and can be in principle made into an actual "graduated" scale as explained in the book by Huang. Quite nicely, it coincides with the empirical gas thermometer scale in the regions where gas thermometers can operate, provided you fix a common reference point, which is taken to be the temperature of the triple point of water: $T_0 = 273.16$ K°.

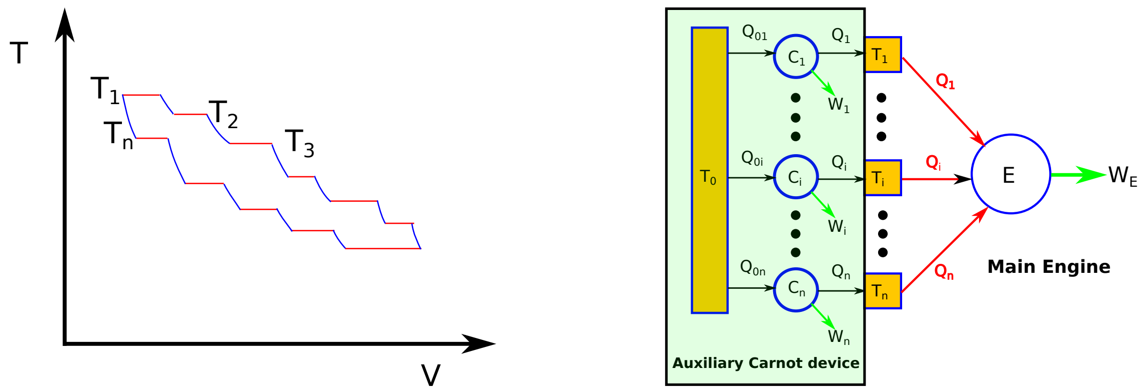

Figure 2.3.: Left: A cycle in the $T - V$ plane working with n reservoirs at temperatures T_i. Red horizontal lines are isotherms (with an exchange of heat Q_i), blue lines are adiabatics (just a sketch) during which no heat is exchanged. Right: An arbitrary engine E exchanging heat Q_i during isotherms with reservoirs at temperatures T_i, producing a work $W_{\mathrm{E}}^{\mathrm{ext}}$. The left part sketches the auxiliary system made by n Carnot reversible engines so devised that they "give back" (if $Q_i > 0$) or "take" (if $Q_i < 0$) exactly an amount of heat Q_i from each T_i-reservoir, while their second reservoir is a common one at temperature T_0.

Clausius inequality. Consider now the arbitrary cycle represented in a $T - V$ diagram of Fig. 2.3. The system goes through a series of isotherms at different temperatures T_i $(i = 1, \cdots, n)$; the isotherms are connected by adiabatics (where heat is not exchanged). Call Q_i the heat exchanged during the isotherm at T_i, where $Q_i > 0$ for expansions, $Q_i < 0$ for compressions. What Clausius proved in 1865 is a generalisation of Carnot's inequality, i.e.:

$$\sum_{i=1}^{n} \frac{Q_i}{T_i} \leq 0 \,, \tag{2.5}$$

the equal sign applying only if the cycle is *reversible*.

A proof of this statement proceeds as follows. Imagine that we supplement our engine with a series of n reversible Carnot cycles working between a common reservoir at temperature T_0 and the various T_i-reservoirs. This auxiliary Carnot system is devised in such a way as to "give back" (if $Q_i > 0$) or "take" (if $Q_i < 0$) exactly an amount of heat Q_i from each T_i-reservoir, in such a way that each T_i-reservoir is left in its initial state at the end of each cycle of the combined system. Correspondingly, each Carnot cycle takes/gives back a quantity of heat Q_{0i} from the T_0 reservoir, performing a work W_i^{ext} (which can be positive, or negative if the Carnot engine works like a refrigerator). The Carnot relationships imply that [10]

$$\frac{-Q_i}{T_i} + \frac{Q_{0i}}{T_0} = 0 \qquad \Longrightarrow \qquad Q_{0i} = T_0 \frac{Q_i}{T_i} \,.$$

The total heat Q_0 exchanged by the Carnot cycles with the T_0-reservoir is therefore

$$Q_0 = \sum_{i=1}^{n} Q_{0i} = T_0 \sum_{i=1}^{n} \frac{Q_i}{T_i} \,.$$

Let $W_{\mathrm{E}}^{\mathrm{ext}}$ be the work performed by the main engine E. The total work performed during the cycle is

$$W^{\mathrm{ext}} = W_{\mathrm{E}}^{\mathrm{ext}} + \sum_{i=1}^{n} W_i^{\mathrm{ext}} \,.$$

But the combined effect of the main engine plus Carnot auxiliary system is to perform a cycle during which heat Q_0 is exchanged with a *single reservoir*, producing a work $W^{\mathrm{ext}} = Q_0$. Hence, by Kelvin's formulation

---

[10] Notice that if $Q_i > 0$ the Carnot system has to give back that heat, meaning that it *releases* heat to the T_i-reservoir, hence the $-Q_i < 0$ term below.

of the 2nd law we must have:

$$W^{\text{ext}} = Q_0 = T_0 \sum_{i=1}^{n} \frac{Q_i}{T_i} \leq 0 \;, \tag{2.6}$$

the equal sign applying only if the engine E is *reversible*.

Quite clearly, you can make the cycle in Fig. 2.3 as close as you wish to an arbitrary cycle in $T-V$ space: you just need to take $n \to \infty$, exchanging infinitesimal amounts of heat δQ_i with each reservoir at a dense mesh of temperatures T_i. In that limit, the Clausius inequality can be written in terms of an integral:

$$\oint \frac{\delta Q}{T} \leq 0 \;. \tag{2.7}$$

The equal sign applies only to *reversible cycles*, for which δQ can be identified with an (inexact) differential form $\text{đ}Q$, for which we write: [11]

$$\oint \frac{\text{đ}Q}{T}\bigg|_{\text{rev}} = 0 \;. \tag{2.8}$$

The fact that a cyclic reversible transformation has zero integral of $\text{đ}Q/T$ implies that, while $\text{đ}Q$ is an inexact differential form, $\text{đ}Q/T$ is an *exact differential*.[12]

The entropy function. The integral

$$\int_{\gamma^{\text{rev}}_{\text{i}\to\text{f}}} \frac{\text{đ}Q}{T} = S(\mathbf{X}_{\text{f}}) - S(\mathbf{X}_{\text{i}}) \;, \tag{2.9}$$

is independent of the (reversible) transformation γ^{rev} one might consider, and depends only on the final and initial points $\mathbf{X}_{\text{f/i}}$. S is a state function, the entropy, whose exact differential is given by:

$$\mathrm{d}S = \frac{\text{đ}Q}{T} \;. \tag{2.10}$$

More about the meaning of the thermodynamical variables $\mathbf{X}$ in the following sections.

Ideal gas example. Let us apply this idea to calculate the entropy difference for an *ideal gas*, for which $pV = Nk_BT$ and $E(T) = \frac{3}{2}Nk_BT$. The reversible path $\gamma^{\text{rev}}_{\text{i}\to\text{f}}$ is made by an isotherm at T_{i}, which changes the volume from $V_{\text{i}} \to V_{\text{f}}$, followed by a reversible isochor at V_{f}, which changes the temperature from $T_{\text{i}} \to T_{\text{f}}$. During the isotherm the heat and the work are equal (recall that $E(T)$ does not depend on the volume), hence the entropy change during the (reversible) isotherm is

$$\Delta S_{\text{rev.isotherm}} = \frac{Q_{\text{rev}}}{T_{\text{i}}} = \frac{W^{\text{ext}}_{\text{rev}}}{T_{\text{i}}} = Nk_B \log \frac{V_{\text{f}}}{V_{\text{i}}} \;.$$

Then we do a reversible isochor at V_{f}. Since the constant volume heat capacity of the monoatomic ideal gas is $C_v = \frac{3}{2}Nk_B$ we get an entropy change: [13]

$$\Delta S_{\text{rev.isochor}} = \int_{T_{\text{i}}}^{T_{\text{f}}} \mathrm{d}T\, \frac{C_v}{T} = \frac{3}{2} Nk_B \log \frac{T_{\text{f}}}{T_{\text{i}}} \;.$$

---

[11] We restrict the use of $\text{đ}Q$ to infinitesimal *reversible* transformations, while δQ indicates a generic infinitesimal quantity of heat exchanged.

[12] One often says that $1/T$ is the integrating factor for the inexact differential $\text{đ}Q$.

[13] More generally, if we use the 3rd law of thermodynamics, which states that S vanishes at $T = 0$ (this law is inherently quantum in nature), then you can, for instance, obtain the entropy at any finite T by integration of the specific heat at constant volume $C_v(T, V)$:

$$S(T,V) = \int_0^T \mathrm{d}T'\, \frac{C_v(T',V)}{T'} \;.$$

More about this later on.

The total entropy change is, therefore:

$$\Delta S = N k_B \log \frac{V_\mathrm{f}}{V_\mathrm{i}} + \frac{3}{2} N k_B \log \frac{T_\mathrm{f}}{T_\mathrm{i}} = N k_B \log \frac{V_\mathrm{f}}{V_\mathrm{i}} \left(\frac{T_\mathrm{f}}{T_\mathrm{i}} \right)^{\frac{3}{2}} \;, \tag{2.11}$$

which gives precisely the same result as our statistical mechanics calculation in Eq. (1.72). [14]

Let us explore a few consequences of Clausius' inequality. Consider a general transformation $\gamma_{\mathrm{i}\to\mathrm{f}}$ followed by a reversible transformation $\gamma^{\mathrm{rev}}_{\mathrm{f}\to\mathrm{i}}$. We get:

$$\int_{\gamma_{\mathrm{i}\to\mathrm{f}}} \frac{\delta Q}{T} + \int_{\gamma^{\mathrm{rev}}_{\mathrm{f}\to\mathrm{i}}} \frac{{\mathchar'26\mkern-12mu d}Q}{T} \le 0 \quad \Longrightarrow \quad \int_{\gamma_{\mathrm{i}\to\mathrm{f}}} \frac{\delta Q}{T} \le S(\mathbf{X}_\mathrm{f}) - S(\mathbf{X}_\mathrm{i}) = \Delta S \;. \tag{2.13}$$

If the transformation $\gamma_{\mathrm{i}\to\mathrm{f}}$ occurs in an *isolated system* — one usually calls such a transformation an *adiabatic* —, it must imply no exchange of heat, $\delta Q = 0$. Hence:

> **2nd law in terms of entropy.** For an arbitrary transformation in *isolated systems* the entropy cannot decrease:
>
> $$\Delta S = S(\mathbf{X}_\mathrm{f}) - S(\mathbf{X}_\mathrm{i}) \ge 0 \;. \tag{2.14}$$
>
> *Reversible* transformations of *isolated* systems (reversible adiabatics) have $\Delta S = 0$. They are also called *isoentropic* transformations. More generally, if you consider the system plus its environment, which is by definition isolated, you necessarily have that for any transformation the total entropy cannot decrease:
>
> $$\Delta S^{\mathrm{tot}} = \Delta S^{\mathrm{S}} + \Delta S^{\mathrm{E}} \ge 0 \;.$$

Consider now isothermal transformations, where the system is maintained in contact with a thermal reservoir at temperature T. Clausius' inequality, as encoded in Eq. (2.13), now implies that

$$\int_{\gamma_{\mathrm{i}\to\mathrm{f}}} \frac{\delta Q}{T} = \frac{Q_T}{T} \le S(\mathbf{X}_\mathrm{f}) - S(\mathbf{X}_\mathrm{i}) = \Delta S \qquad \Longrightarrow \qquad Q_T \le T\Delta S \;, \tag{2.15}$$

where Q_T is the heat exchanged with the thermostat. If you call W_T the work done on the system during the transformation, and you use the 1st law $\Delta E = Q_T + W_T$ then you conclude that

$$\Delta E = E(\mathbf{X}_\mathrm{f}) - E(\mathbf{X}_\mathrm{i}) = Q_T + W_T \le T\Delta S + W_T \;. \tag{2.16}$$

Helmholtz free-energy and isothermal work. We will see later on that the quantity $F = E - TS$ is an important thermodynamical potential, relevant when you can *control the temperature* T. It is known as *Helmholtz free-energy*. For isothermal transformations $\Delta F = \Delta E - T\Delta S$, hence we deduce that the Clausius' inequality directly leads, through Eq. (2.16), to the following *isothermal work inequality*:

$$\Delta F = F(\mathbf{X}_\mathrm{f}) - F(\mathbf{X}_\mathrm{i}) \le W_T \;. \tag{2.17}$$

The equal sign applies to *reversible isotherms*, which shows that the free-energy acts as a sort of "*bank account balance*" for work: the change in free energy is equal to the amount of *reversible work* performed on the system. For a general isothermal transformation, some work is inevitably *dissipated*, i.e., it does not increment the free-energy of the system:

$$W_{\mathrm{diss}} = W_T - \Delta F \ge 0 \;. \tag{2.18}$$

More about these facts when we will discuss stochastic thermodynamics inequalities.

---

[14] Recall that Eq. (1.72), after introducing the Boltzmann constant, leads to:

$$S(E,V,N) = N k_B \log \mathrm{e}^{\frac{5}{2}} v \left(\frac{4\pi m \varepsilon}{3h^2} \right)^{\frac{3}{2}} \;, \tag{2.12}$$

where $\varepsilon = E/N$ and $v = V/N$. Using the fact that $\varepsilon = E/N = \frac{3}{2} k_B T$ for an ideal gas, you see that the two calculations agree.

2.2. Entropy and the fundamental principle

The elementary considerations of the previous section are unsatisfactory for at least two reasons:

1) How should I select the variables $\mathbf{X}$ which supposedly govern the behaviour of the entropy function S or of the other thermodynamical potentials? What are such $\mathbf{X}$ and how many variables should I use?

2) The 2nd law appears encoded by Clausius' inequality. We have seen specific implications for *adiabatics* and for *isotherms*, but the scheme does not seem general and flexible enough.

We will now see how it is possible to give a new mathematical dress to the 2nd law of thermodynamics, building the whole theory starting from some specific requirements given to the *entropy function*.

So, let us assume that there is a set of extensive variables describing your system, like E (the total energy) V (the volume), N (the total number of particles), for a simple homogeneous fluid. This is called the *fundamental hypothesis of thermodynamics* which states that it should be possible to fully characterise the thermodynamical state of a system by specifying an appropriate (small) set of *extensive variables.* [15] More generally we denote these extensive variables by:

$$\mathbf{X} = (X_0 = E, \underbrace{X_1, \cdots, X_r}_{=\underline{\mathrm{X}}}) = (E, \underline{\mathrm{X}}) \; . \tag{2.19}$$

The extensive variables $\underline{\mathrm{X}} = X_1, \cdots, X_r$ can be thought as "*generalised displacements*" giving rise to a *reversible work* (inexact) differential form [16] [17]

$$đW = -p\,\mathrm{d}V + \mu\,\mathrm{d}N + \cdots = \sum_{i=1}^{r} f_i\,\mathrm{d}X_i = \underline{\mathrm{f}} \cdot \mathrm{d}\underline{\mathrm{X}} \; . \tag{2.20}$$

The associated *generalised forces* $\underline{\mathrm{f}} = (f_1, \cdots, f_r)$ are *intensive variables,* [18] for instance $f_1 = -p$, $f_2 = \mu$, etc. The generalised forces should be regarded, themselves, as functions of the relevant thermodynamical variables $(E, \underline{\mathrm{X}})$, for the time being, or, when we switch to the energy-scheme (see below), $(S, \underline{\mathrm{X}})$.

We will give now a new dress to the 2nd law of thermodynamics, by formulating it in more mathematical terms. We will see how useful this reformulation is. Let us assume that you are given an entropy function $S(E, V, N)$ — or more generally $S(E, \underline{\mathrm{X}}) = S(\mathbf{X})$ — which is a *continuous* function [19] of the set of extensive variables describing your system with the following properties:

Additivity. If a system is made of two parts, described by $S_1(\mathbf{X}^{(1)})$ and $S_2(\mathbf{X}^{(2)})$, then the combined system $1 \cup 2$ has entropy

$$S_{1\cup 2}(\mathbf{X}^{(1)}, \mathbf{X}^{(2)}) = S_1(\mathbf{X}^{(1)}) + S_2(\mathbf{X}^{(2)}) \; . \tag{2.21}$$

---

[15] In more complex systems you might have to include the number of several different chemical species, $N_1, \cdots, N_k$, or the total magnetisation $\mathbf{M}$ of your system, or the area of some surface which is relevant in describing the contact between several systems, etc. All of these should be included in the list of the extensive variables.

[16] $đW$ is the infinitesimal work associated with a **reversible** transformation in which the $\underline{\mathrm{X}}$ change infinitesimally. Reversibility is important, as evident from a quasi-static infinitesimal Joule expansion in vacuum, where no work is performed although V changes to $V + \mathrm{d}V$.

[17] In homogeneous crystalline solids, the usual isotropic term $p\mathrm{d}V$ appearing in the work should be supplemented by stress-strain terms of the form $V\sum_{ij}\sigma_{ij}\mathrm{d}\epsilon_{ij}$ where σ_{ij} is the stress tensor and ϵ_{ij} the strain tensor appearing in the theory of elasticity.

[18] Intensive variables, like p or μ, should not be confused with "densities", like E/N, V/N, or N/V. We will comment on this distinction later on.

[19] In most cases this continuous function is also continuously differentiable, except at phase transitions, where the derivatives can have discontinuities. More about this later on.

Monotonicity in E. S is an increasing function of E: [20]

$$\left.\frac{\partial S}{\partial E}\right|_{\underline{\mathrm{X}}} = \beta(E, \underline{\mathrm{X}}) > 0 \,. \tag{2.22}$$

Concavity. S is a concave function of all its arguments.

These requirements, together with the fundamental "principle of maximum entropy", which I am going to illustrate and then formulate, encode essentially the 2nd law of thermodynamics.

Before doing that, let us observe that additivity implies that if I join together two identical copies of my system, then I must have $S(2E, 2\underline{\mathrm{X}}) = S(E, \underline{\mathrm{X}}) + S(E, \underline{\mathrm{X}}) = 2S(E, \underline{\mathrm{X}})$. More generally, by playing with different integers and fractions of the system, I expect that additivity implies *extensivity* of the entropy, which can be more generally expressed as:

$$S(\lambda \mathbf{X}) = \lambda S(\mathbf{X}) \qquad \forall \lambda > 0 \,. \tag{2.23}$$

Mathematically, this can be rephrased by saying the S is a *homogeneous function* of degree 1, for which we could apply Euler's theorem (see Wikipedia), [21] as we will do in a short while. Next, we observe that since S is concave, then it must be a concave function of E alone: If I plot $S(E, \underline{\mathrm{X}})$ versus E at fixed $\underline{\mathrm{X}}$ the derivative $\beta(E, \underline{\mathrm{X}})$ will decrease as E increases. Hence we understand that if we define instead:

$$\left.\frac{\partial S}{\partial E}\right|_{\underline{\mathrm{X}}} = \beta \overset{\mathrm{def}}{=} \frac{1}{T^S} > 0 \,, \tag{2.25}$$

then $T^S(E, \underline{\mathrm{X}})$ will be an *increasing* function of E. We will soon see that T^S can be identified with the absolute temperature of a system in equilibrium, but for the moment we add a label "S" to it.

Let us now consider a system made of two parts that, although in contact, are initially isolated from each other, as well as from the external world, through a thermally insulated wall. System 1 and 2 are initially in equilibrium, characterised by extensive variables $(E_1^{\mathrm{in}}, \underline{\mathrm{X}}_1)$ and $(E_2^{\mathrm{in}}, \underline{\mathrm{X}}_2)$, respectively, and have entropy $S_1(E_1^{\mathrm{in}}, \underline{\mathrm{X}}_1)$ and $S_2(E_2^{\mathrm{in}}, \underline{\mathrm{X}}_1)$. Because of additivity, the total entropy is

$$S_{1\cup 2}(E_1^{\mathrm{in}}, E_2^{\mathrm{in}}, \underline{\mathrm{X}}_1, \underline{\mathrm{X}}_2) = S_1(E_1^{\mathrm{in}}, \underline{\mathrm{X}}_1) + S_2(E_2^{\mathrm{in}}, \underline{\mathrm{X}}_1) \,.$$

Now we remove the insulation in the wall separating 1 from 2 so that the two systems can exchange energy and reach a final equilibrium state. The total energy $E = E_1 + E_2 = E_1^{\mathrm{in}} + E_2^{\mathrm{in}}$ is conserved, but the share of energy that the two systems will make will be different. How? The principle of maximum entropy will tell us that among all possible choices of E_1 and E_2, the final equilibrium is realised when the entropy of the combined system is *maximum*, i.e.,

$$\mathrm{Max}_{E_1+E_2=E}\; S_{1\cup 2}(E_1, E_2, \underline{\mathrm{X}}_1, \underline{\mathrm{X}}_2) \qquad \Longrightarrow \qquad (E_1^{\mathrm{eq}}, E_2^{\mathrm{eq}}) \,. \tag{2.26}$$

In other words, by maximising the total entropy under the given constraint of fixed total energy one obtains the actual equilibrium sharing of energy that the system will get to. Before we proceed with this simple calculation, let us stress the "among the possible choices of E_1 and E_2" means that I am

---

[20] I use the standard "thermodynamical" notation of explicitly expressing the variables that are kept fixed, which might appear redundant, because a partial derivative always requires that. The advantage of this notation is that I have immediately under control the full set of variables that the function and the derivative I am calculating will be dependent upon: above, for instance, I might omit the variables in $\beta(E, \underline{\mathrm{X}})$ and simply write β. Having control of the variables is vital in a field in which changing variables, with the associated partial derivative gymnastic, can become quite a nightmare.

[21] A function $f(\mathbf{x})$ is (positively) homogeneous of degree k if for every $\lambda > 0$ you have that $f(\lambda \mathbf{x}) = \lambda^k f(\mathbf{x})$. If $f(\mathbf{x})$ is continuously differentiable, then Euler theorem states that:

$$\mathbf{x} \cdot \boldsymbol{\nabla} f(\mathbf{x}) = k f(\mathbf{x}) \,. \tag{2.24}$$

assuming that I consider the entropy of a *virtual state*, characterised by $(E_1, E_2, \underline{X}_1, \underline{X}_2)$, which is *not an equilibrium state*, unless I introduce appropriate constraints that force it (for instance, preparing the two initial systems with the given values of E_1 and E_2 and maintaining the constraint of thermal insulation). Callen calls such virtual states *constrained equilibrium states.* We will see later further uses of this concept of accessing "virtual states" and minimising/maximising functions in a similar way. To calculate the constrained maximum, we introduce a Lagrange multiplier and search for the extremum, for fixed $\underline{X}_1, \underline{X}_2$, of the function

$$\widetilde{S}(E_1, E_2, \lambda) = S_1(E_1, \underline{X}_1) + S_2(E_2, \underline{X}_1) - \lambda(E_1 + E_2 - E) \ .$$

The two derivatives with respect to E_1 and E_2 give:

$$\begin{cases} \dfrac{\partial S_1}{\partial E_1}\Big|_{\underline{X}_1} = \lambda \\ \\ \dfrac{\partial S_2}{\partial E_2}\Big|_{\underline{X}_2} = \lambda \end{cases} \quad \Longrightarrow \quad \frac{\partial S_1}{\partial E_1}\bigg|_{\underline{X}_1} = \frac{\partial S_2}{\partial E_2}\bigg|_{\underline{X}_2} \ . \tag{2.27}$$

Hence, equilibrium is realised when the two energy-derivatives of the entropies match, i.e.:

$$\frac{\partial S_1}{\partial E_1}\bigg|_{\underline{X}_1} = \frac{1}{T_1^S(E_1^{\rm eq}, \underline{X}_1)} \equiv \frac{1}{T_2^S(E_2^{\rm eq}, \underline{X}_2)} = \frac{\partial S_2}{\partial E_2}\bigg|_{\underline{X}_2} \ .$$

But we can say even more. Since the entropy is maximised (more comments about why we must have obtained a maximum, and not simply an extremum, below), we can say that:

$$S_1(E_1^{\rm eq}, \underline{X}_1) + S_2(E_2^{\rm eq}, \underline{X}_2) \geq S_1(E_1^{\rm in}, \underline{X}_1) + S_2(E_2^{\rm in}, \underline{X}_2) \ . \tag{2.28}$$

But each $S_i(E_i, \underline{X}_i)$ is a concave function of its energy E_i. And one of the characteristics of concave functions is that *they stay below their tangent at any point.* Hence, for instance:

$$S_1(E_1^{\rm eq}, \underline{X}_1) - S_1(E_1^{\rm in}, \underline{X}_1) \leq \frac{\partial S_1(E_1^{\rm in})}{\partial E_1}\bigg|_{\underline{X}_1} (E_1^{\rm eq} - E_1^{\rm in}) = \frac{1}{T_1^{\rm in}}(E_1^{\rm eq} - E_1^{\rm in}) \ ,$$

where $T_1^{\rm in}$ denotes the *initial* "temperature" (we have omitted the "S" label) of system 1. A similar equation holds for system 2, initially at "temperature" $T_2^{\rm in}$. Rearranging the terms in Eq. (2.28) we, therefore, deduce that:

$$\begin{aligned} 0 \quad &\leq \quad \left[S_1(E_1^{\rm eq}, \underline{X}_1) - S_1(E_1^{\rm in}, \underline{X}_1)\right] + \left[S_2(E_2^{\rm eq}, \underline{X}_2) - S_2(E_2^{\rm in}, \underline{X}_2)\right] \\ &\leq \quad \frac{1}{T_1^{\rm in}}(E_1^{\rm eq} - E_1^{\rm in}) + \frac{1}{T_2^{\rm in}}(E_2^{\rm eq} - E_2^{\rm in}) = \left(\frac{1}{T_1^{\rm in}} - \frac{1}{T_2^{\rm in}}\right)(E_1^{\rm eq} - E_1^{\rm in}) \ , \end{aligned} \tag{2.29}$$

where we used that $Q_2 = E_2^{\rm eq} - E_2^{\rm in}$, the "heat absorbed-or-released" by 2, is the opposite of $Q_1 = E_1^{\rm eq} - E_1^{\rm in}$. So you see that $Q_1 > 0$ goes with $T_1^{\rm in} < T_2^{\rm in}$ and vice-versa. Hence, the principle of maximum entropy and the concavity of S has led us to Clausius' formulation of the 2nd law: Heat flows spontaneously (and irreversibly) from "hot" to "cold" bodies.

This suggests that $T^S(E)$ is indeed a "measure" of temperature: it signals thermal equilibrium and the direction of heat flow. In general, if T^S is a generic *monotonic function* of the absolute temperature T, it would do its job correctly. But we can show that T^S must be a *linear function* of the absolute temperature T: hence, if you measure it in the appropriate scale, you can simply identify T^S with the absolute temperature T.

To show this, imagine that we construct a thermal engine with two usual "heat reservoirs", one at a high temperature T_2 and one at a lower temperature $T_1 < T_2$. This time, however, we imagine that the whole system is enclosed in a perfectly insulating enclosure so that the only exchange of energy with the external world is through the mechanical work W that the engine produces. Let us re-examine in more detail what we mean by *heat-reservoir*. Before the engine cycle starts, the T_2-reservoir has energy $E_2^{\rm in}$, while at the end of the cycle, it has energy $E_2^{\rm fin}$ and has given to the system a certain amount of heat $Q_2 = E_2^{\rm in} - E_2^{\rm fin} > 0$. Consider now the entropy of the T_2-reservoir as a function of its energy E_2, $S_2(E_2, \underline{X}_2)$. Since its energy has decreased, $E_2^{\rm fin} = E_2^{\rm in} - Q_2 < E_2^{\rm in}$, you would imagine that not only the entropy of the reservoir has decreased but also is temperature should be slightly decreased (remember that S_2 is a concave function of E_2, which implies that $T_2^S(E_2)$ is a monotonically increasing function of energy). Nevertheless, since the initial energy of the reservoir is *immensely larger* than the heat Q_2 it gives up in a cycle — $E_2 \gg Q_2$ — you can reasonably approximate $S_2(E_2, \underline{X}_2)$ with its linear-term Taylor expansion. With the shorthand $T_2^S(E_2^{\rm in}) = T_2^S$ we can therefore write:

$$S_2(E_2) \approx S_2(E_2^{\rm in}) + \frac{1}{T_2^S}(E_2 - E_2^{\rm in}) \;.$$

A similar hypothesis, and formula, holds for the T_1-reservoir, but remember that the engine gives heat $\mathcal{Q}_1 = E_1^{\rm fin} - E_1^{\rm in} > 0$ to the reservoir. At the end of the cycle, the engine has produced a work W returning to its initial state (hence $\Delta E = 0$ and $\Delta S = 0$ for the engine alone). The work $W^{\rm ext}$ produced, by the 1st law of thermodynamics, is equal to

$$W^{\rm ext} = Q_2 - Q_1^{\rm rel} = \Big[E_2^{\rm in} - E_2^{\rm fin}\Big] - \Big[E_1^{\rm fin} - E_1^{\rm in}\Big] \;.$$

On the other hand, the total entropy change of the two reservoirs should be non-negative, hence: [22]

$$\Delta S_{\rm tot} = \underbrace{\Big[S_2(E_2^{\rm fin}) - S_2(E_2^{\rm in})\Big]}_{\frac{-Q_2}{T_2^S}} + \underbrace{\Big[S_1(E_1^{\rm fin}) - S_1(E_1^{\rm in})\Big]}_{\frac{Q_1^{\rm rel}}{T_1^S}} = -\frac{Q_2}{T_2^S} + \frac{Q_1^{\rm rel}}{T_1^S} \ge 0 \;.$$

By using this inequality, which implies $Q_1^{\rm rel} \ge Q_2 \frac{T_1^S}{T_2^S}$, we can derive that

$$W^{\rm ext} \le Q_2 \left(1 - \frac{T_1^S}{T_2^S}\right) \;.$$

But from Carnot's theorem and Kelvin's definition of the absolute temperature scale, we know that

$$W^{\rm ext} \le Q_2 \left(1 - \frac{T_1}{T_2}\right) \;.$$

Hence, we conclude that:

$$\frac{T_1}{T_2} = \frac{T_1^S}{T_2^S} \;, \tag{2.30}$$

i.e., we can identify T^S with the absolute temperature T (provided we fix the same reference point T_0, the triple point of water).

One thing that you might ask is: you imposed that the entropy has an *extremum*, through the method of Lagrange multipliers, but who guarantees that this is indeed a maximum? Concavity is once again the crucial ingredient. Let us see why. Consider the total entropy of a composite system as a function of all the extensive variables of each of the subsystems. Additivity tells us that

$$S_{\rm tot}(\mathbf{X}_1, \mathbf{X}_2, \cdots) = \sum_j S_j(\mathbf{X}_j) \;.$$

Each of the S_j is a concave functions of its variables, hence $S_{\rm tot}$ is also a concave functions of the whole collection of extensive variables $(\mathbf{X}_1, \mathbf{X}_2, \cdots)$. The constraints are that some of these variables are kept fixed, — in the previous example, all the variables except E_1 and E_2 — while some of the variables can change (I "relax" some "walls", for instance allowing the flow of heat) but with an overall constraint still in place — in the previous case $E_1 + E_2 = E$. Overall, the constraints make up a "*hyper-plane*" in the whole space $(\mathbf{X}_1, \mathbf{X}_2, \cdots)$. The restriction of the total entropy $S_{\rm tot}$ to such a hyper-plane is what I am trying to "extremize", and, as I will now show, indeed "maximise"

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[22] Notice that we are using here the Clausius inequality. This is a bit unsatisfactory, as we would like to derive everything from the maximum entropy principle. I think that this can be done, but we have no pretence of being axiomatic here. So we take this shortcut at this point.

(automatically, no need to check). Indeed, the restriction of a concave function to a hyperplane is still a concave function. [23] Contrary to each individual $S_j(\mathbf{X}_j)$ — which, I remind you, is the entropy of a subsystem in equilibrium for a value of the extensive parameters $\mathbf{X}_j$ — which are concave but have generally no extremal point (think of the ideal gas entropy), the concave total-entropy function S_{tot} restricted to the hyper-plane set by the constraints *can have an extremum* (this is what the Lagrange method gave us).

> **The importance of concavity.** *The extremum of a concave function, if it exists, must be a maximum.* In one dimension, the result is trivial to picture and show. More generally, the key ingredient is that a concave function lies always *below its tangent plane*: at an extremal point, where the gradient vanishes, this implies that the function is always *below the extremal value*, which is, therefore, a maximum.

Let's return to our simple example of two subsystems, but we now consider the slightly more complex case in which the wall between system 1 and 2 is *movable*, so that the two systems can redistribute also their volumes, under the new constraint that $V_1 + V_2 = V$ is fixed. The principle of maximum entropy for the combined system tells us that the re-distribution of energies and volumes will lead to a maximum of:

$$\mathrm{Max}_{\mathrm{Constraints}}\, S_{1\cup 2}(E_1, E_2, V_1, V_2, \underline{X}_1, \underline{X}_2) \quad \Longrightarrow \quad (E_1^{\mathrm{eq}}, E_2^{\mathrm{eq}}, V_1^{\mathrm{eq}}, V_2^{\mathrm{eq}}) \;, \tag{2.31}$$

where $\underline{X}_1$ and $\underline{X}_2$ denote the other (fixed) variables of system 1 and 2. The maximum is obtained from the Lagrange multiplier function

$$\widetilde{S}(E_1, E_2, V_1, V_2, \lambda_1, \lambda_2) = S_1(E_1, V_1, \underline{X}_1) + S_2(E_2, V_2, \underline{X}_1) - \lambda_1(E_1 + E_2 - E) - \lambda_2(V_1 + V_2 - V) \;.$$

The derivatives with respect to E_1 and E_2 imply, as before, equal temperatures:

$$\left.\frac{\partial S_1}{\partial E_1}\right|_{V_1, \underline{X}_1} = \frac{1}{T_1} \equiv \frac{1}{T_2} = \left.\frac{\partial S_2}{\partial E_2}\right|_{V_2, \underline{X}_2} \;.$$

The derivatives with respect to V_1 and V_2 imply the new condition:

$$\begin{cases} \left.\dfrac{\partial S_1}{\partial V_1}\right|_{E_1, \underline{X}_1} = \lambda_2 \\[2ex] \left.\dfrac{\partial S_2}{\partial V_2}\right|_{E_2, \underline{X}_2} = \lambda_2 \end{cases} \quad \Longrightarrow \quad \left.\frac{\partial S_1}{\partial V_1}\right|_{E_1, \underline{X}_1} = \left.\frac{\partial S_2}{\partial V_2}\right|_{E_2, \underline{X}_2} \;. \tag{2.32}$$

Hence we understand that equilibrium is now regulated also by the volume derivative of the entropy:

$$\left.\frac{\partial S}{\partial V}\right|_{E, \underline{X}} \stackrel{\mathrm{def}}{=} \frac{p}{T} \;. \tag{2.33}$$

Here p is a quantity that we will soon discover to be related to the *pressure*. For the time being, let us take it as a definition of the volume derivative of S. Hence, in presence of a movable wall that allows the exchange of energy, the maximum entropy principle predicts that equilibrium is obtained by imposing that $T_1 = T_2$ and $p_1 = p_2$. Again, since $S_i(E_i, V_i, \underline{X}_i)$ is a concave function of its energy E_i and volume V_i, it must *stay below its tangent plane at any point*. Hence, for instance:

$$S_1(E_1^{\mathrm{eq}}, V_1^{\mathrm{eq}}, \underline{X}_1) - S_1(E_1^{\mathrm{in}}, V_1^{\mathrm{in}}, \underline{X}_1) \le \frac{1}{T_1^{\mathrm{in}}}(E_1^{\mathrm{eq}} - E_1^{\mathrm{in}}) + \frac{p_1^{\mathrm{in}}}{T_1^{\mathrm{in}}}(V_1^{\mathrm{eq}} - V_1^{\mathrm{in}}) \;,$$

---

[23] More generally, you can easily show that the restriction of a concave function to any domain that is *convex* — i.e., it contains all the points $\lambda x_2 + (1-\lambda)x_1$ with $\lambda \in [0,1]$ if it contains x_1 and x_2 — is still concave.

where $T_1^{\rm in}$, and $p_1^{\rm in}$ denotes the *initial* temperature and "pressure" of system 1. A similar equation holds for system 2, initially at temperature $T_2^{\rm in}$, with "pressure" $p_2^{\rm in}$. Maximisation of the total entropy implies, once again, that:

$$\begin{aligned} 0 &\le \left[S_1(E_1^{\rm eq},V_1^{\rm eq},\underline{\rm X}_1) - S_1(E_1^{\rm in},V_1^{\rm in},\underline{\rm X}_1)\right] + \left[S_2(E_2^{\rm eq},V_2^{\rm eq},\underline{\rm X}_2) - S_2(E_2^{\rm in},V_2^{\rm in},\underline{\rm X}_2)\right] \\ &\le \left(\frac{1}{T_1^{\rm in}} - \frac{1}{T_2^{\rm in}}\right)(E_1^{\rm eq}-E_1^{\rm in}) + \left(\frac{p_1^{\rm in}}{T_1^{\rm in}} - \frac{p_2^{\rm in}}{T_2^{\rm in}}\right)(V_1^{\rm eq}-V_1^{\rm in}) \;. \end{aligned} \tag{2.34}$$

In particular, if the initial state was such that energy was in equilibrium, and the common temperature of the two systems is T, then the first term vanishes and the inequality implies

$$0 \le \frac{1}{T}\,(p_1^{\rm in} - p_2^{\rm in})\,(V_1^{\rm eq} - V_1^{\rm in}) \;.$$

Hence $p_1^{\rm in} > p_2^{\rm in}$ implies that $V_1^{\rm eq} > V_1^{\rm in}$ for a spontaneous process, as you expect from the interpretation of p as pressure. Quite nicely, the new dress for the 2nd law produces a consequence that appears to *extend* Clausius' formulation to other variables, like p here.

The final simple application of the law of maximum entropy is the derivation of equilibrium when the wall is *semi-permeable* to a given chemical species denoted by k, such that $N_{k,1}+N_{k,2}=N_k$: such k-particles can move across the wall (leading automatically to energy exchange). A similar calculation will bring now to the equality, at equilibrium, of the derivatives with respect to N_k of the two entropies. [24] Here the crucial quantity is

$$\left.\frac{\partial S}{\partial N_k}\right|_{E,\underline{\rm X}} \stackrel{\rm def}{=} -\frac{\mu_k}{T} \;, \tag{2.35}$$

where $\underline{\rm X}$ denotes all extensive quantities except E and N_k. One can show that μ_k is indeed the chemical potential of the chemical species k. We will also see the reason for the minus sign. More on the derivatives of the entropy function in the next section.

With these examples in mind, it will be easier to understand the general principle of maximum entropy:

> **Principle of maximum entropy.** For a composite system made by different subsystems initially isolated from each other by wall-type constraints, and at fixed total energy E, the final equilibrium state after some of these constraints are released is the one that maximises the total entropy as a function of the free-variables (virtual states).

Exercise 2.1. The following exercise, taken from Callen, shows how to use the principle of maximum entropy, in a slightly more complex situation, to derive the condition for mechanical equilibrium. Consider the system in Fig. 2.4, where you assume that the system has no external pressure acting on it, it is overall thermally isolated from the external world (total $E = E_1 + E_2 + E_3$ is conserved), but heat can flow from one container to the other through the table on which the containers rest (which makes otherwise no other contribution in this problem). Express the constraints between the volumes of the three containers due to the rigid bar shown in the figure as *two* linear equations relating V_1, V_2, and V_3. Maximise the total entropy (you need 3 Lagrange multipliers) to find a relationship between the equilibrium pressures of the three containers, as well as the three final temperatures. (Assume, as we will soon show, that what enters in the volume derivative of the entropy is indeed the pressure p.)

---

[24] Callen nicely summarises these three examples by arguing that, as T is the (generalised) "potential that governs heat flow", and p is the "potential that governs volume changes", in the same spirit, μ is the "potential that governs matter flux". "Potential" here should be understood in the sense that, for instance, *differences in chemical potential* provide a "generalised force" to matter flow, from regions of high μ to regions of low μ. When different chemical species can react together, the final chemical equilibrium is indeed regulated by the chemical potentials of the different species. μ is, therefore, a crucial concept in thermochemistry. More about this, maybe, later on.

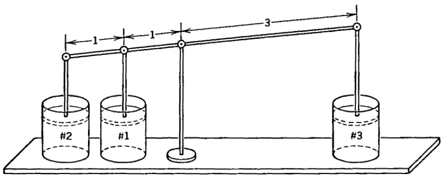

Figure 2.4.: A system of three containers with gases inside, in thermal equilibrium through the common thermally conducting table, and in absence of any external pressure.

2.3. The energy-scheme and the principle of minimum energy

The 2nd law of thermodynamics was reformulated in terms of the properties of the entropy function, which depends on E and on the other extensive quantities. Let us now reformulate it by inverting the relationship between S and E to express $E(S, \underline{X})$. This is in principle easy: since $S(E, \underline{X})$ is a monotonic function of E, we can always invert it. It is simple to show that $E(S, \underline{X})$ shares the properties we have seen for $S(E, \underline{X})$:

Additivity. If a system is made of two parts, described by $E_1(\mathbf{X}^{(1)})$ and $E_2(\mathbf{X}^{(2)})$, then the combined system $1 \cup 2$ has energy [25]

$$E_{1\cup 2}(\mathbf{X}^{(1)}, \mathbf{X}^{(2)}) = E_1(\mathbf{X}^{(1)}) + E_2(\mathbf{X}^{(2)}) \ . \tag{2.36}$$

Monotonicity in S. E is an increasing function of S, and by the chain rule you get: [26]

$$\left.\frac{\partial E}{\partial S}\right|_{\underline{X}} = T(S, \underline{X}) > 0 \ . \tag{2.37}$$

Convexity. E is a convex function of all its arguments.

The fact that E is a convex function follows from the fact that S is concave and monotonic in E. You can prove it using the definition of convex/concave functions (see Peliti's book on page 26), or, more simply, by observing that if the tangent plane to $S(E, \underline{X})$ is *above* the entropy function at any point, then when you consider $E(S, \underline{X})$, the same plane will appear *below* the energy function. Additivity, once again, implies that E is a homogenous function of degree one, for which Euler's theorem applies (more about this in a short while):

$$E(\lambda \mathbf{X}) = \lambda E(\mathbf{X}) \qquad \forall \lambda > 0 \ , \tag{2.38}$$

where now $\mathbf{X} = (X_0 = S, \underline{X})$.

If you want to practice on your ability to recognise if a given putative fundamental equation, $S(E, \underline{X})$ or $E(S, \underline{X})$, satisfies or not the essential requisites of thermodynamics (additivity, monotonicity, concavity/convexity), consider Problem 1.10-1 and 1.10-2 in Callen's book.

Let us now consider the other derivatives of $E(S, \underline{X})$ at constant S. To do that, consider infinitesimal reversible iso-entropic transformations: they must involve no heat exchange, hence the change in energy must be due to work only, by the 1st law:

$$\mathrm{d}E|_S = \text{đ}W = \sum_{i=1}^{r} f_i \, \mathrm{d}X_i \ .$$

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[25] Additivity here requires, clearly, that we neglect non-extensive terms that originate from the boundary of the two systems. Clearly, what we need to assume is that the interactions are reasonably short-ranged. Long-range interactions lead to a failure of the additivity property.

[26] Strictly speaking, I should denote the derivative as $\widetilde{T}(S, \underline{X}) = T(E(S, \underline{X}), \underline{X})$ because it is not the same function as the $T(E, \underline{X})$ appearing in the previous section. We simplify our notation, since the indication of the variables, or even simply knowing what are the variables of the function, automatically suggests the correct dependence.

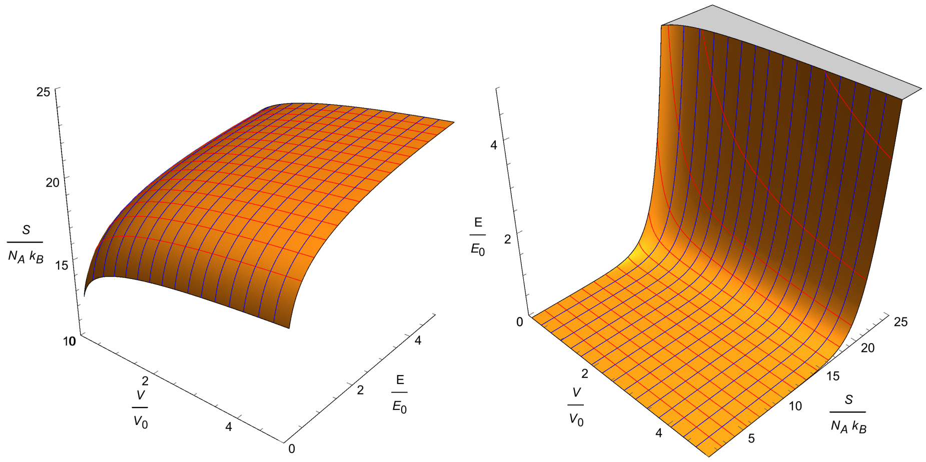

Figure 2.5.: (Left) The entropy function of the ideal gas, versus E, V. (Right) The energy function of the ideal gas, versus S, V.

Therefore, the derivatives of E at fixed S give us directly the generalised forces f_i:

$$\left(\frac{\partial E}{\partial X_i}\right)_S = f_i(S, \underline{X}) \ . \tag{2.39}$$

This expression, together with Eq. (2.37), allows us to write the full differential of the function E as:

$$\mathrm{d}E = \overbrace{T\,\mathrm{d}S}^{\text{đ}Q} + \overbrace{\sum_{i=1\cdots r} f_i\,\mathrm{d}X_i}^{\text{đ}W} \ , \tag{2.40}$$

where we have underlined the heat and work contributions, according to the 1st law. In the concrete example of a homogeneous fluid we would write, for instance:

$$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N \ , \tag{2.41}$$

which immediately encodes all the remaining first derivatives of E:

$$\begin{cases} \left.\dfrac{\partial E}{\partial V}\right|_{S,N} = -p(S,V,N) \\ \\ \left.\dfrac{\partial E}{\partial N}\right|_{S,V} = \mu(S,V,N) \end{cases} \tag{2.42}$$

We are now ready to explore the consequence of the homogeneity condition (2.38), which follows from Euler's theorem on homogeneous functions. Taking a derivative with respect to λ, and setting $\lambda = 1$, we easily derive from Eq. (2.38) (see Eq. (2.24)) that:

$$E(S, \underline{X}) = T\,S + \sum_{i=1}^{r} f_i\,X_i \ . \tag{2.43}$$

For a simple homogeneous fluid this condition reads:

$$E(S,V,N) = T\,S - p\,V + \mu\,N \ . \tag{2.44}$$

Notice the non-trivial nature of such an equality: it implies in particular that all derivatives of E — like T, p, μ, etc. — must be homogeneous functions of degree 0, i.e., *intensive* variables.

Let us now return to the derivatives of $S(E, \underline{X})$ we have already encountered in our applications of the maximum entropy principle. We promised to show that they are indeed related to pressure and chemical potential. Let us see why. A first fast route to show this consists in simply taking the expression for the differential $\mathrm{d}E$, and inverting it to find the differential $\mathrm{d}S$:

$$\mathrm{d}S = \frac{1}{T}\,\mathrm{d}E - \sum_{i=1}^{r} \frac{f_i}{T}\,\mathrm{d}X_i \;. \tag{2.45}$$

For a homogenous fluid:

$$\mathrm{d}S = \frac{1}{T}\,\mathrm{d}E + \frac{p}{T}\,\mathrm{d}V - \frac{\mu}{T}\,\mathrm{d}N \;. \tag{2.46}$$

The expression for $\mathrm{d}S$ immediately encodes all the first derivatives and shows the promised result. If you are not satisfied by this rather swift derivation, then use more formally the properties of composite and inverse functions. We do this explicitly to illustrate some useful tricks which consist in applications of the chain rule of differentiation. Similar things appear repeatedly in thermodynamics. [27] Since S and E are inverse functions, you can clearly write:

$$\mathbb{S}(\mathbb{E}(S,\underline{\mathrm{X}}),\underline{\mathrm{X}}) = S \;,$$

where we have momentarily denoted by $\mathbb{S}$ the *function* and by S the variable (and will similarly do for $\mathbb{E}$ and E). If you take a derivative of the previous expression with respect to S, keeping all the $\underline{\mathrm{X}}$ fixed, applying the chain rule you get:

$$\left(\frac{\partial \mathbb{S}}{\partial E}\right)_{\underline{\mathrm{X}}} \left(\frac{\partial \mathbb{E}}{\partial S}\right)_{\underline{\mathrm{X}}} = 1 \quad\Longrightarrow\quad \left(\frac{\partial \mathbb{S}}{\partial E}\right)_{\underline{\mathrm{X}}} = \left(\frac{\partial \mathbb{E}}{\partial S}\right)_{\underline{\mathrm{X}}}^{-1} \;, \tag{2.47}$$

which leads to the result for the temperature T we have already seen. But if you take the derivative with respect to a different variable X_i included in $\underline{\mathrm{X}}$, which appears in $\mathbb{S}$ both directly and through the dependence of $\mathbb{E}$ on X_i, then you get: [28]

$$\frac{\partial \mathbb{S}}{\partial E}\frac{\partial \mathbb{E}}{\partial X_i} + \frac{\partial \mathbb{S}}{\partial X_i} = 0 \quad\Longrightarrow\quad \frac{\partial \mathbb{S}}{\partial X_i} = -\left(\frac{\partial \mathbb{E}}{\partial S}\right)^{-1}\frac{\partial \mathbb{E}}{\partial X_i} = -\frac{f_i}{T} \;, \tag{2.48}$$

which shows the promised relationship between derivatives of E and derivatives of S.

It is worth taking a small break to illustrate, by manipulating a bit the previous expressions, an important non-trivial identity of thermodynamics, the so-called *triple product identity*. We rewrite the first expression appearing in Eq. (2.48) by stressing (some of) the variables kept constant in taking the partial derivatives:

$$\left(\frac{\partial \mathbb{S}}{\partial E}\right)_{X_i} \left(\frac{\partial \mathbb{E}}{\partial X_i}\right)_{S} = -\left(\frac{\partial \mathbb{S}}{\partial X_i}\right)_{E} \;. \tag{2.49}$$

Consider now the function $\mathbb{X}_i(E,S,\widehat{\underline{\mathrm{X}}})$, where $\widehat{\underline{\mathrm{X}}}$ denotes all variables $\underline{\mathrm{X}}$ except X_i, obtained by (locally) inverting $\mathbb{S}(E,\underline{\mathrm{X}})$. The derivatives at fixed E (and $\widehat{\underline{\mathrm{X}}}$, which we omit indicating) are related by:

$$\left(\frac{\partial \mathbb{S}}{\partial X_i}\right)_{E} = \left(\frac{\partial \mathbb{X}_i}{\partial S}\right)_{E}^{-1} \;. \tag{2.50}$$

Substituting in Eq. (2.49) we can finally write:

$$\left(\frac{\partial \mathbb{S}}{\partial E}\right)_{X_i} \left(\frac{\partial \mathbb{E}}{\partial X_i}\right)_{S} \left(\frac{\partial \mathbb{X}_i}{\partial S}\right)_{E} = -1 \;. \tag{2.51}$$

Observe how a naif application of the chain rule of partial derivatives would predict the wrong result that the product of these three derivatives would give $+1$, while the correct result is -1. So, beware of

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[27] One of the aspects of thermodynamics, which can easily generate confusion, is that functions of state can become variables and vice-versa. For instance, the entropy is a function that becomes a variable when you invert it in favour of E.

[28] We did not want to make the notation too clumsy, but you should notice that $f_i(S,\underline{\mathrm{X}})$ and $T(S,\underline{\mathrm{X}})$ should be interpreted as $f_i(\mathbb{S}(E,\underline{\mathrm{X}}),\underline{\mathrm{X}})$ and $T(\mathbb{S}(E,\underline{\mathrm{X}}),\underline{\mathrm{X}})$ when you use them in the expression below.

such swift calculations. If you want to become an athlete in the thermodynamics gymnastic of partial derivatives, go to Appendix B.4.

We are now ready to consider how the principle of maximum entropy translates in the new scheme in which energy is the fundamental function.

> **Principle of minimum energy.** For a composite system made by different subsystems initially isolated from each other by wall-type constraints, and at *fixed total entropy* S, the final equilibrium state after some of these constraints are released is the one that minimises the total energy as a function of the free-variables (*alias* virtual states, or constrained equilibrium states).

This result is quite easy to derive, a bit more difficult to visualise in general. Fig. 2.6 tries to visualise, for the case of thermal equilibrium of two ideal gases, how is it that the maximum entropy principle implies a minimum energy principle and vice-versa (see also Callen's Figs. 5.1 and 5.2). Let us start with a formal proof, followed by some discussion that we find in Callen's book. Let $\underline{X}$ denote the collection of *all the extensive variables*, beside the *total energy* E, which appear in any of the subsystems making up the composite system we are considering. Notice that $\underline{X}$ includes here the energies of the different subsystems (except one whose energy is obtained from the constraint of total energy E), as well as their volumes, particle numbers, etc. Some of these variables are fixed by wall-type constraints, some are free (virtual states) because we might remove some constraints, and we know that their values $\underline{X}^{\mathrm{eq}}$ are such that the entropy is maximum, for the given total energy E. Hence, if $\Delta\underline{X}$ denotes a variation of the free parameters, and $\underline{X}^{\mathrm{eq}} + \Delta\underline{X}$ any virtual state away from equilibrium, we know that:

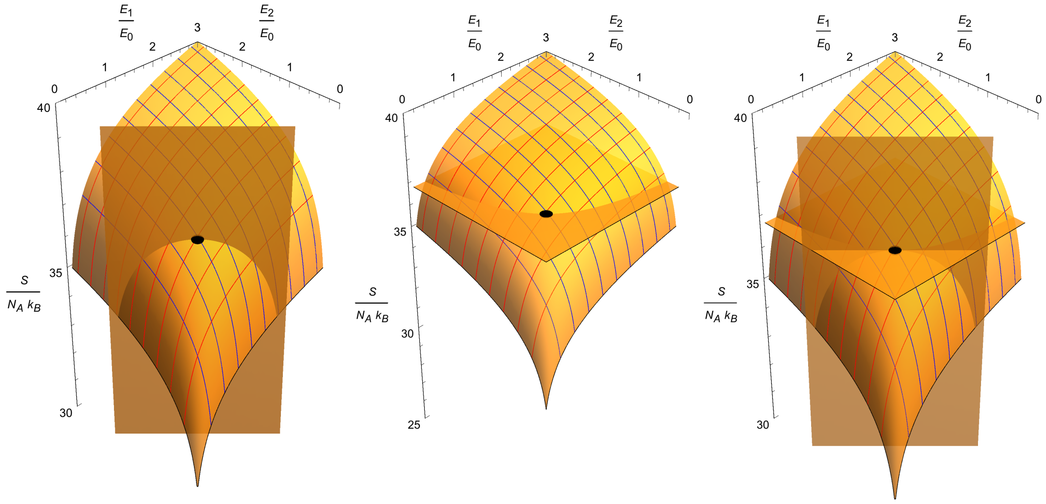

Figure 2.6.: (Left) The total entropy of two ideal gases, each with one mole of particles at the same volume V_0, versus the energies of the two gases, together with the plane of $E = E_1 + E_2$. The black sphere is the maximum entropy equilibrium state. (Center) The same equilibrium state (black sphere), seen as a minimum total energy state at constant S. **Notice the unusual direction of increasing E_1 and E_2 in the two energy axes.** Notice also that, starting from the *same* initial point, the two processes lead to generally different final equilibrium points. (Right) Both the plane of total S and that of total E, shown together.

$$\Delta S = S(E, \underline{X}^{\mathrm{eq}} + \Delta\underline{X}) - S(E, \underline{X}^{\mathrm{eq}}) \leq 0 \,.$$

Since S is a monotonically increasing function of E, there must exist some $E' \geq E$ such that

$$S(E', \underline{X}^{\mathrm{eq}} + \Delta\underline{X}) = S(E, \underline{X}^{\mathrm{eq}}) \,.$$

Since $E' > E$, when you invert the relationship between S and E you will write the previous equation, equivalently, by:

$$E(S, \underline{\mathrm{X}}^{\mathrm{eq}} + \Delta\underline{\mathrm{X}}) \geq E(S, \underline{\mathrm{X}}^{\mathrm{eq}}) \ , \tag{2.52}$$

which shows that the total energy is minimum at the equilibrium, for fixed total entropy S. [29]

Callen gives also the following physical argument to justify the result. Suppose that the equilibrium state is not associated with minimal energy at constant S. You could then subtract energy from the system, keeping S constant, by performing some reversible work W in adiabatic conditions. Subsequently, you can give back that work in the form of heat Q transferred to the system. The internal energy of the system would return to its original value, but the total entropy would now increase due to the heat transfer. Hence, the initial state would not be associated with maximum entropy.

Callen discusses also the analogy between this problem and the iso-perimetric problem in geometry: you know that the circle can be equally well characterised as the figure of *maximal area for a given perimeter*, or as the figure of *minimum perimeter for given area.* Nevertheless, the two strategies suggest two different routes to obtaining the "circle", which lead to different final "states". If you start from a square of area $A = L^2$ and perimeter $P = 4L$, and you deform the shape by keeping the perimeter fixed, you will find that the maximum-area figure is a circle of radius $R = 2L/\pi$. Viceversa, by deforming the square while keeping the area fixed, you find that the minimum-perimeter figure is a circle of radius $R = L/\sqrt{\pi}$. In any case, once a given "extremal" circle is obtained, that figure satisfies both extremal conditions for its final values of area and perimeter. These two routes towards the final equilibrium are also present in the thermodynamical case. Suppose you have a thermally insulated cylinder with a piston inside (assumed to be thermally conducting), which divides the system into two subsystems 1 and 2. You now remove the constraint on the position of the piston and allow the two subsystems to change their volumes and reach equilibrium at fixed total energy E. They do so by maximising the entropy, which implies equal pressures for the two subsystems at equilibrium. Alternatively, you can reach an equal-pressure equilibrium state keeping the entropy constant, by doing reversible work with the piston, which you imagine attached to some external shaft pushing on a spring and compressing it. If this process is done very slowly (reversibly), entropy is kept constant, while the internal energy of the system is *decreased* — because we do work and get no heat — until it reaches a minimum in the equilibrium equal-pressure state [30]. Notice that the two final equilibrium states are *different*, like in the iso-perimetric problem, but they share the property that they are both minimum-energy and maximum-entropy with respect to variations of free parameters.

Exercise 2.2. Make detailed calculations of these two different strategies for reaching an equal-pressure final equilibrium for the case of an ideal gas occupying the two portions 1 and 2.

Exercise 2.3. Re-derive our conditions for thermal and mechanical equilibrium by using the minimum energy principle, instead of maximum entropy.

---

[29] A proof based on evaluating the first and second derivatives of $E(S, \underline{\mathrm{X}})$ with respect to a free parameter X in terms of the corresponding ones for $S(E, \underline{\mathrm{X}})$ is given in Callen's book, on page 134. The crucial minus sign in the second derivative that transforms a maximum into a minimum is essentially related to the minus sign appearing in Eq. (2.48). Indeed you can show (see Callen's Eq. 5.7) that at an extremal point:

$$\left.\frac{\partial^2 E}{\partial X^2}\right|_S = -T \left.\frac{\partial^2 S}{\partial X^2}\right|_E .$$

[30] Lorenzo Fant observes that the shaft system implies a slight imbalance in the two final pressures since there is a force contribution due to the spring. Make estimates assuming that the spring constant is very small, and discuss more carefully

2.4. Equations of state

The equations of states are just the expressions of the various intensive parameters (generalised forces) in terms of the extensive ones. An explicit example by using an ideal gas will clarify the matter. Consider the fundamental equation $S(E, V, N)$, which I recall here:

$$S(E, V, N) = Nk_B \log \frac{\mathrm{e}V}{N} \left(\frac{4\pi meE}{3h^2N} \right)^{\frac{3}{2}} . \tag{2.53}$$

You can write T, p, and μ as a function of (E, V, N) by taking derivatives of S:

$$\begin{cases} \frac{1}{T} = \frac{\partial S}{\partial E} = \frac{3}{2} \frac{k_B N}{E} \\ \\ \frac{p}{T} = \frac{\partial S}{\partial V} = \frac{k_B N}{V} \\ \\ \frac{\mu}{T} = -\frac{\partial S}{\partial N} = +\frac{5}{2} k_B - \frac{S}{N} \end{cases} . \tag{2.54}$$

We will later show that, quite generally, μ can be always re-expressed as a function of the other two intensive parameters T and p. [31] Let us ignore it for a while. Notice that the first equations of state simply tells us that $E = \frac{3}{2} Nk_BT$. The second is the well known ideal gas equation of state $pV = Nk_BT$. But, properly speaking, the equation of state $pV = Nk_BT$, alone, is insufficient to reconstruct the whole fundamental equation $S(E, V, N)$: you need the equation for T to be able to reconstruct S.

Exercise 2.4. Assume that you are given a fundamental equation of the form:

$$S_{\mathrm{vdW}}(E, V, N) = Nk_B \log \left[A(v - b) \left(\varepsilon + \frac{a}{v} \right)^c \right] \tag{2.55}$$

where, as usual, $v = V/N$ and $\varepsilon = E/N$. Here b and a are constants with appropriate dimensions (the van der Waals constants that we will meet later on, experimentally available for many gases), while $c = 3/2$, or $5/2$ or anything you want. A is a constant with dimensions $[\text{Length}]^{-3}[\text{Energy}]^{-c}$. Derive the two equations of state for T and p, and observe that they lead to the famous van der Waals isoterms:

$$p = \frac{k_BT}{v - b} - \frac{a}{v^2} . \tag{2.56}$$

In a completely identical way, you can deduce the equations of state for the intensive parameters, in the energy scheme, from $E(S, V, N)$: obviously, the resulting T, p, μ will now be functions of S, V, N. In full generality, if $E(S, \underline{\mathrm{X}})$ is the energy function expressed in terms of the extensive variables, where $\underline{\mathrm{X}} = (X_1 \cdots X_r)$, then you know that:

$$\begin{cases} T(S, \underline{\mathrm{X}}) = \dfrac{\partial E}{\partial S} \\ \\ f_i(S, \underline{\mathrm{X}}) = \dfrac{\partial E}{\partial X_i} \end{cases} . \tag{2.57}$$

These $r + 1$ equations, expressing T and the generalized forces f_i — all of them being intensive quantities — as a function of the extensive variables are known as *equations of state*. We will show later on that only r intensive variables are capable of independent variation, as there is a relationship between the $r + 1$ derivatives of E, known as Gibbs-Duhem relation. See Sec. 2.7.3 on the Gibbs potential for more details.

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[31] For the ideal gas, for instance:

$$\mu = \frac{5}{2} k_BT - k_BT \log \frac{\mathrm{e}k_BT}{p} \left(\frac{2\pi mek_BT}{h^2} \right)^{\frac{3}{2}} .$$

2.5. Concavity of S and thermodynamic stability

We have stressed that S is a concave function of its extensive parameters, while E is convex. This, essentially, encodes the 2nd law in a mathematical framework. Let us see the consequence of concavity in the context of thermodynamic stability. Suppose you had two identical systems described by $S(E,V,N)$, isolated from each other and the external world by adiabatic walls. The total entropy of the composite system is $2S(E,V,N)$. Imagine now that the wall separating the two systems is made thermally conducting, and that you propose an exchange of energy (heat) between them, such that system 1 gets $E_1 = E - \Delta E$, while system 2 has $E_2 = E + \Delta E$. The total entropy for this (virtual) configuration is $S(E - \Delta E, V, N) + S(E + \Delta E, V, N)$. Suppose that $S(E,V,N)$ was monotonic in E but not concave, like the example shown in Fig. 2.7(left). Then you immediately deduce that:

$$2S(E,V,N) < S(E-\Delta E,V,N) + S(E+\Delta E,V,N) \;, \tag{2.58}$$

which would imply that the system would spontaneously try to maximise its total entropy by making the energy different between the two systems: the initial equilibrium configuration with equal energies (and temperatures) would then be *unstable*. Stability would on the contrary require:

$$2S(E,V,N) \geq S(E-\Delta E,V,N) + S(E+\Delta E,V,N) \;, \tag{2.59}$$

By taking the limit $\Delta E \to 0$ you realize that stability requires, locally, $\frac{\partial^2 S}{\partial E^2} \leq 0$. Similarly, you can write a condition for stability against redistributions of volumes (assuming you make the wall separating the two systems mobile), which locally implies $\frac{\partial^2 S}{\partial V^2} \leq 0$. Similarly, for any other extensive variable X you would require $\frac{\partial^2 S}{\partial X^2} \leq 0$. But these local conditions are not enough to guarantee concavity and stability. For instance, if you observe Fig. 2.7(right), you will see that there are regions — like BC and EF — where $\frac{\partial^2 S}{\partial X^2} \leq 0$: nevertheless, the system is unstable there. Indeed, if the initial value of X is exactly in the middle of the BF region, $X^{\mathrm{in}} = \frac{1}{2}(X(B) + X(F))$, then the entropy would increase by a redistribution of $\Delta X = \frac{1}{2}(X(F) - X(B))$, leading to a final entropy $S(X(B)) + S(X(F)) > 2S(X^{\mathrm{in}})$. The only way in which the given $S(E, \underline{X})$ can be made *stable* is by constructing the *concave envelope of its tangents*, as shown in Fig. 2.7(right) by the straight line segment BHF.

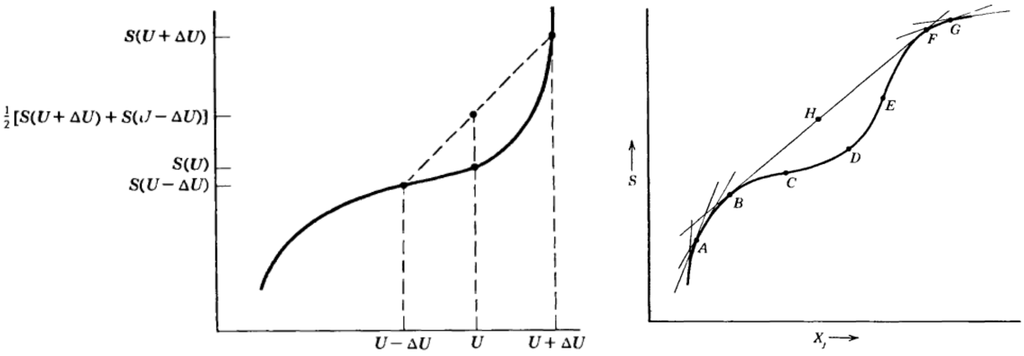

Figure 2.7.: (Left) A non concave but monotonic $S(E,V,N)$ versus E. Notice that $S(E,V,N) < \frac{1}{2}(S(E - \Delta E, V, N) + S(E + \Delta E, V, N))$ because the curve is above its tangent in the point E. Instability follows. (Right) A general non-concave $S(E, \underline{X})$ versus one of its extensive variables X. Notice that the system is unstable even in regions in which the second derivative is negative, like BC and EF. Figures taken from Callen's book [3]. Notation: U, in Callen's book, denotes the internal energy E.

As anticipated before, having negative second derivatives is not enough to guarantee concavity. What you would need is a negative semi-definite *Hessian*. In the simple case of a homogenous fluid with $S(E,V,N)$, denoting $\mathbf{X}=(E,V,N)$ and $\Delta\mathbf{X}=(\Delta E,\Delta V,\Delta N)$, you see that:

$$\Delta S = S(\mathbf{X}+\Delta\mathbf{X})+S(\mathbf{X}-\Delta\mathbf{X})-2S(\mathbf{X}) = \underbrace{(\Delta E,\Delta V,\Delta N)\left(\begin{array}{ccc} \frac{\partial^2 S}{\partial E^2} & \frac{\partial^2 S}{\partial E\partial V} & \frac{\partial^2 S}{\partial E\partial N} \\ \frac{\partial^2 S}{\partial V\partial E} & \frac{\partial^2 S}{\partial V^2} & \frac{\partial^2 S}{\partial V\partial N} \\ \frac{\partial^2 S}{\partial N\partial E} & \frac{\partial^2 S}{\partial N\partial V} & \frac{\partial^2 S}{\partial N^2} \end{array}\right)\left(\begin{array}{c} \Delta E \\ \Delta V \\ \Delta N \end{array}\right)}_{\sum_{ij}\mathbb{H}^S_{ij}\Delta X_i\Delta X_j\le 0 \text{ for stability}} + \cdots$$

The condition for a negative semi-definite Hessian $\mathbb{H}^S$, which is a real symmetric matrix because the mixed second derivatives are identical upon exchange of variables — a condition that will lead to the so-called *Maxwell relations* between different apparently unrelated derivatives of intensive variables —, is that all the eigenvalues λ_i of the Hessian are non-positive $\lambda_i \le 0$. Clearly, the extensivity of the entropy function demands exact linearity if you move along the direction $\mathbf{X}$: $S(\lambda\mathbf{X}) = \lambda S(\mathbf{X})$. This leads to the conclusion that one of the eigenvalues must vanish: more precisely the one associated with the eigenvector $(E,V,N)^T$ (or $\mathbf{X}$ in the general case). If you restrict the ΔX to variations of E and V at *fixed* N — i.e., take $\Delta N \equiv 0$ — you can reduce your Hessian to the 2×2 sub-matrix

$$\mathbb{H}^S = \left(\begin{array}{cc} \frac{\partial^2 S}{\partial E^2} & \frac{\partial^2 S}{\partial E\partial V} \\ \frac{\partial^2 S}{\partial V\partial E} & \frac{\partial^2 S}{\partial V^2} \end{array}\right)$$

which must be negative semi-definite, implying: [32]

$$\left\{\begin{array}{l} \frac{\partial^2 S}{\partial E^2} \le 0 \\ \frac{\partial^2 S}{\partial V^2} \le 0 \\ \frac{\partial^2 S}{\partial E^2}\frac{\partial^2 S}{\partial V^2} - \left(\frac{\partial^2 S}{\partial E\partial V}\right)^2 \ge 0 \end{array}\right. . \tag{2.60}$$

The first two conditions are quite clear. The third condition comes from the fact that the determinant of a matrix with two negative eigenvalues must be positive!

The physics behind these stability conditions is easier to extract by working in the energy scheme, where the fundamental equation $E(S,V,N)$ must now be *convex* for stability, otherwise, you would violate the minimum energy principle. Identical arguments, including that on extensivity, lead then to the conclusion that the reduced 2×2 Hessian of the energy function

$$\mathbb{H}^E = \left(\begin{array}{cc} \frac{\partial^2 E}{\partial S^2} & \frac{\partial^2 E}{\partial S\partial V} \\ \frac{\partial^2 E}{\partial V\partial S} & \frac{\partial^2 E}{\partial V^2} \end{array}\right)$$

must be positive semi-definite, implying:

$$\left\{\begin{array}{lll} \frac{\partial^2 E}{\partial S^2} = \left(\frac{\partial T}{\partial S}\right)_V & = \frac{T}{C_v} \ge 0 & \\ \frac{\partial^2 E}{\partial V^2} = -\left(\frac{\partial p}{\partial V}\right)_S & = \frac{1}{V\kappa_S} \ge 0 & \\ \frac{\partial^2 E}{\partial S^2}\frac{\partial^2 E}{\partial V^2} - \left(\frac{\partial^2 E}{\partial S\partial V}\right)^2 & = \frac{T}{V\kappa_S C_v} - \left(\frac{\partial T}{\partial V}\right)_S^2 = \frac{T}{V\kappa_S C_v} - \left(\frac{1}{V\alpha_S}\right)^2 \ge 0 & \end{array}\right. . \tag{2.61}$$

A physical interpretation now urges. We have already indicated the main physical quantities involved in these stability conditions. Let us start from the top, which expresses the fact that the temperature is a monotonically increasing function of S at constant V. Although everything would be more clear by working with a thermodynamic potential in which T is the relevant variable (the Helmholtz free-energy F, see below), it is quite clear that

$$T\left(\frac{\partial S}{\partial T}\right)_V \stackrel{\text{def}}{=} C_v \ge 0 \,, \tag{2.62}$$

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[32] See Arovas, Eqs.(2.259)-(2.263) for an explicit proof in this 2×2 case. More generally, you realize that a quadratic form that is negative (semi)-definite must have necessarily non-positive elements in the diagonal. There is a simple reason for that: do you see why? Next, the determinant is a product of the eigenvalues. Here I have two negative eigenvalues, hence the determinant must be positive.

must be the *specific heat at constant volume*, because $T\mathrm{d}S = đQ$ is the heat necessary to lead to an increase of T by $\mathrm{d}T$ at constant V. The second stability condition has to do with the fact that the pressure p is a monotonically *decreasing* function of V at constant S, which requires the *isoentropic compressibility* to be non-negative:

$$-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S \stackrel{\text{def}}{=} \kappa_S \geq 0 \;, \tag{2.63}$$

The third condition guarantees that a concerted variation of E and V does not lead to a reduction of the total energy at constant S. [33] As previously mentioned, the equality of the mixed derivatives tells us that:

$$\frac{\partial^2 E}{\partial S \partial V} = \frac{\partial^2 E}{\partial V \partial S} \quad \Longrightarrow \quad -\left(\frac{\partial p}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S \;, \tag{2.64}$$

one of the many Maxwell relations that you can write from the equality of the mixed second derivative of any state function. [34] We have used this fact in writing the third inequality, which you can see involves also the *iso-entropic thermal expansivity*

$$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S \stackrel{\text{def}}{=} \alpha_S \;. \tag{2.65}$$

Notice that this is certainly not the most common thermal expansivity you encounter in an experiment. Much more accessible, experimentally, would be the *constant pressure thermal expansivity*

$$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \stackrel{\text{def}}{=} \alpha_p \;. \tag{2.66}$$

Exercise 2.5. Calculate κ_S, α_S, and α_p for a monoatomic ideal gas, using the fact that isoentropic transformations have $VT^{\frac{3}{2}} = \text{const}$ and that the equation of state $pV = Nk_BT$ is satisfied. The calculation of $C_v = \frac{3}{2}Nk_B$ is easier by working with the free-energy $F(T,V,N)$, but you can easily perform it by expressing the entropy S of the ideal gas in terms of the temperature T. Observe that α_S is negative, but this is not a problem. Verify that all the stability conditions are satisfied.

2.6. The Legendre transform

I will present here the Legendre transform, that you have likely seen in Hamiltonian mechanics, through two different points of view: one related to mechanical equilibrium in presence of an external force, the second related to line geometry.

Suppose you have a classical particle in a potential $\mathrm{U}(\mathrm{x})$. We assume that $\mathrm{U}(\mathrm{x})$ is (strictly) convex, i.e., it stays always above its tangent and has no straight-line pieces, as sketched in Fig. 2.8. [35]

---

[33] It is simple to show that an Hessian of the type:

$$\begin{pmatrix} 1 & 2 \\ 2 & 1 \end{pmatrix}$$

is associated to a quadratic form which is not positive definite.

[34] One should not underestimate the fact that this equality while being mathematically trivial, is experimentally highly non-trivial: if you didn't know that there must be a state function $E(S,V,N)$ governing the thermodynamics of your system, you would be highly surprised by measuring the equality of two apparently unrelated quantities. Since we are working with extensive variables, this Maxwell relation is not that easy to measure experimentally. It will be much easier to interpret similar relations when we will switch to thermodynamic potentials which involve intensive variables, like the Gibbs potential $G(T,p,N)$.

[35] In the figure $\mathrm{U}(\mathrm{x})$ has a minimum at some point x_0 but this is not necessary. All you need is that $\mathrm{U}''(\mathrm{x}) > 0$. In higher dimension, you would need to require that the Hessian is positive definite. More precisely, what we have required is often called a *strictly convex* function. Notice that strictly convex functions, like x^4 can have a vanishing second derivative somewhere: so, the condition on a positive definite Hessian is only sufficient to have strict convexity. Simple convexity might allow $\mathrm{U}''(\mathrm{x}) \geq 0$, or a positive semi-definite Hessian in the multi-dimensional case. We will write our equations in such a way that they apply to the multi-dimensional case.

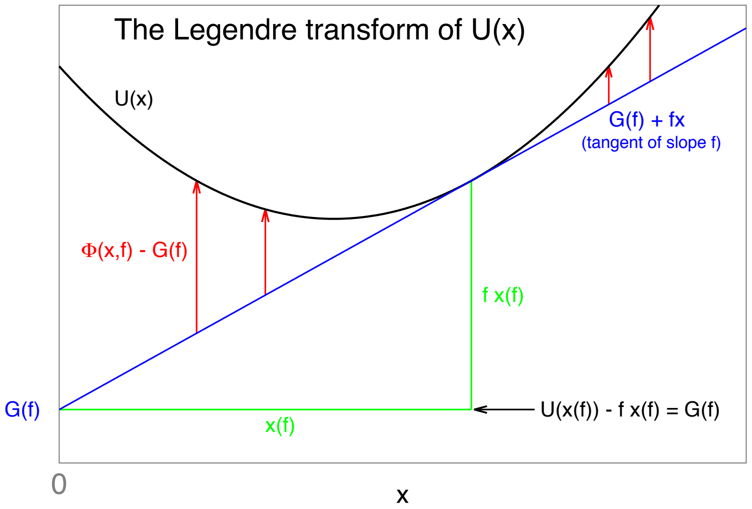

Figure 2.8: Geometrical construction behind the Legendre transform of U(x), for the problem of mechanical equilibrium in the potential U(x) in presence of an extra force f. The meaning of the various quantities is explained in the text.

New potential: Consider now the equilibrium problem for a particle in that potential *under the action of an extra constant force* f. The new potential in presence of f has an extra term $-\mathrm{f}\cdot\mathrm{x}$:

$$\Phi(\mathrm{x},\mathrm{f}) = \mathrm{U}(\mathrm{x}) - \mathrm{f}\cdot\mathrm{x}\,. \tag{2.67}$$

New equilibrium: The new equilibrium point x(f) is obtained by imposing

$$\partial_{\mathrm{x}}\Phi(\mathrm{x},\mathrm{f})|_{\mathrm{x(f)}} = 0 \quad\Longrightarrow\quad \partial_{\mathrm{x}}\mathrm{U}|_{\mathrm{x(f)}} = \mathrm{f}\,.$$

The condition $\partial_{\mathrm{x}}\mathrm{U}(\mathrm{x}) = \mathrm{f}$ univocally [36] defines an equilibrium point x(f) because the derivative $\partial_{\mathrm{x}}\mathrm{U}(\mathrm{x})$ is *monotonically increasing*, since U(x) is convex. The **geometrical interpretation** is the following: Because the derivative $\partial_{\mathrm{x}}\mathrm{U}(\mathrm{x})$ is monotonically increasing, if you try to "approach" the curve with a straight-line of given slope f you will "touch" it at a uniquely defined point x(f). [37]

The tangent: Let us construct the tangent t(x) of U(x) at the new equilibrium point x(f):

$$\mathrm{t}(\mathrm{x}) = \mathrm{U}(\mathrm{x}(\mathrm{f})) + \mathrm{f}\cdot(\mathrm{x}-\mathrm{x}(\mathrm{f})) = \mathrm{G}(\mathrm{f}) + \mathrm{f}\cdot\mathrm{x}\,,$$

where we defined G(f) to be the intercept with the y-axis of the tangent:

$$\mathrm{G}(\mathrm{f}) \stackrel{\mathrm{def}}{=} \mathrm{U}(\mathrm{x}(\mathrm{f})) - \mathrm{f}\cdot\mathrm{x}(\mathrm{f}) \equiv \Phi(\mathrm{x}(\mathrm{f}),\mathrm{f})\,. \tag{2.68}$$

The last equality stresses the fact that such a quantity *coincides* with the value of the new potential *at* the equilibrium point, $\Phi(\mathrm{x}(\mathrm{f}),\mathrm{f})$. The G(f) so defined is the *Legendre transform* of U(x). See Fig. 2.8 for a graphical representation of all the quantities introduced so far.

The knowledge of G(f) encodes all the information you need to reconstruct U(x): you know all the tangents for all possible slopes. In a line-geometry framework, you might reconstruct the full curve for U(x) from the *envelop* of the various tangents, [38] as illustrated in Fig. 2.9.

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[36] Equivalently, $-\partial_{\mathrm{x}}\mathrm{U}(\mathrm{x}) + \mathrm{f} = 0$, as the total force vanishes. Notice that this might happen even if the potential U(x) has no minimum in absence of the extra force.

[37] Notice that if you allow convexity with the milder requirement $\mathrm{U}''(\mathrm{x}) \geq 0$, there might be straight-line pieces in the graph of U(x): when f "matches" the slope of the straight-line pieces, the corresponding x(f) is not uniquely defined,

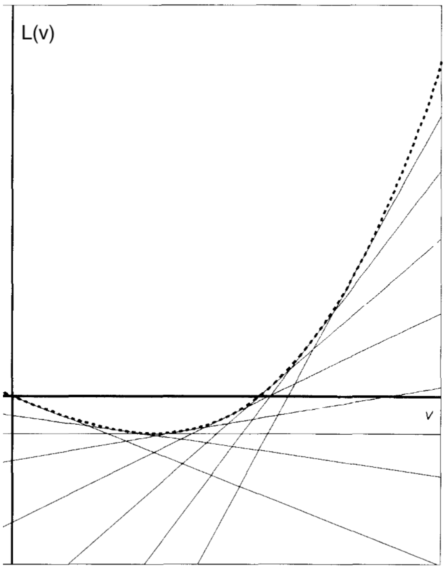

Figure 2.9: Reconstructing a convex function, here denoted by $L(v)$, from the envelop of its tangents. Figure adapted from Fig. 5.2 on pag. 214 of the book by José & Saletan on Classical Mechanics.

A variational bound: One important fact concerning the tangent $t(x)$ is that, since $U(x)$ is convex, it stays always *above* its tangents, in particular that at $x(f)$. Hence:

$$U(x) \geq t(x) = G(f) + f \cdot x \quad \Longrightarrow \quad \Phi(x,f) = U(x) - f \cdot x \geq G(f) \equiv \Phi(x(f),f) \; .$$

We have therefore transformed the equilibrium problem in the presence of an extra force f into a *variational problem.* The new potential $\Phi(x,f)$, being itself convex, has indeed the nice properties that: [39]

$$\begin{cases} \partial_x \Phi(x,f)|_{x(f)} = 0 & \Phi \text{ is stationary at } x(f) \\ \Phi(x,f) \geq \Phi(x(f),f) \equiv G(f) & \Phi \text{ is minimum at } x(f) \end{cases} \; . \tag{2.69}$$

First derivative of $G(f)$: If you calculate $\partial_f G(f)$ you easily [40] establish that: [41]

$$\partial_f G(f) = -x(f) \; . \tag{2.70}$$

---

and the Legendre transform shows a discontinuity in the derivative at that f: we will see that this happens at first-order transition points, where you have phase coexistence.

[38] Callen gives a nice discussion of the reason why $U(x(f))$ alone, seen as a function of f, loses information contained in $U(x)$. Essentially, if you know $U(x(f)) = \widetilde{U}(f)$ as a function of f, you know the value of the function when the slope is f but you lost information about the precise point $x(f)$ *where* this occurs. To retain that information, you have to know the intercept of the tangent at $x(f)$ for each given f: this will uniquely give you both $x(f)$ and $U(x(f))$ for given f.

[39] The variational principle can be cast in the form:

$$G(f) = \min_x \Phi(x,f) = \min_x (U(x) - f \cdot x) \; .$$

[40] Using the chain rule:

$$\partial_f G(f) = \cancel{\partial_x U(x(f)) \cdot \partial_f x(f)} - \cancel{f \cdot \partial_f x(f)} - x(f) \equiv -x(f) \; .$$

[41] You see below the starting point of the inverse Legendre transform, with a conspicuos minus sign — recall that in the direct transformation we had $\partial_x U(x) = f$ — due to our definition. A mathematician would write $G(f) = f\,x(f) - U(x(f))$ in such a way that $\partial_f G(f) = x(f)$, and this is, by the way, what you usually do in Hamiltonian mechanics as well, when you switch from the Lagrangean to the Hamiltonian, hence the change of sign in the potential energy that you get there. Stiking to our thermodynamics definition of Legendre-transform, you can equivalently regard our relationships as

$$U(x) = G(f(x)) + xf(x) \; ,$$

which shows that $U(x)$ is the inverse Legendre transform of G.

Hence, the derivative of the Legendre transform $\mathrm{G}(\mathrm{f})$ immediately gives you the equilibrium point $\mathrm{x}(\mathrm{f})$. You should appreciate that the whole process of solving the implicit equation $\partial_{\mathrm{x}}\mathrm{U}(\mathrm{x}) = \mathrm{f}$ to get $\mathrm{x}(\mathrm{f})$ was indeed instrumental to construct $\mathrm{G}(\mathrm{f})$, but if someone gives you $\mathrm{G}(\mathrm{f})$, then you find the equilibrium point $\mathrm{x}(\mathrm{f})$ by just taking a derivative.

Concavity of $\mathrm{G}(\mathrm{f})$: Take now a further derivative of $\partial_{\mathrm{f}}\mathrm{G}(\mathrm{f})$:

$$\partial^2_{\mathrm{ff}}\mathrm{G}(\mathrm{f}) = \partial_{\mathrm{f}}(\partial_{\mathrm{f}}\mathrm{G}(\mathrm{f})) = -\partial_{\mathrm{f}}\mathrm{x}(\mathrm{f}) \; .$$

On the other hand, by taking the derivative of $\partial_{\mathrm{x}}\mathrm{U}(\mathrm{x}(\mathrm{f})) = \mathrm{f}$ with respect to f, it is simple to deduce that:

$$\mathrm{f} = \partial_{\mathrm{x}}\mathrm{U}(\mathrm{x}(\mathrm{f})) \quad \Longrightarrow \quad 1 = \partial_{\mathrm{f}}\partial_{\mathrm{x}}\mathrm{U}(\mathrm{x}(\mathrm{f})) = \partial_{\mathrm{f}}\mathrm{x}(\mathrm{f}) \cdot \partial^2_{\mathrm{xx}}\mathrm{U}(\mathrm{x}(\mathrm{f})) = -\partial^2_{\mathrm{ff}}\mathrm{G}(\mathrm{f}) \cdot \partial^2_{\mathrm{xx}}\mathrm{U}(\mathrm{x}(\mathrm{f})) \; .$$

Therefore, we conclude that:

$$\partial^2_{\mathrm{ff}}\mathrm{G}(\mathrm{f}) = -[\partial^2_{\mathrm{xx}}\mathrm{U}]^{-1}|_{\mathrm{x}(\mathrm{f})} \; . \qquad (2.71)$$

Hence, $\mathrm{G}(\mathrm{f})$ is *concave* if $\mathrm{U}(\mathrm{x})$ is convex, and viceversa.

Exercise 2.6. If you want to practice a bit, try to apply the previous construction to $\mathrm{U}(\mathrm{x}) = \mathrm{a}e^{\alpha\mathrm{x}}$, and to $\mathrm{U}(\mathrm{x}) = \mathrm{a}\mathrm{x}^4$. The peculiar behaviour of the derivative of the Legendre transform when the function has straight line pieces is appreciated if you study the following case: $\mathrm{U}(\mathrm{x}) = \mathrm{a}(\mathrm{x}-1)^2$ for $\mathrm{x} > 1$, $\mathrm{U}(\mathrm{x}) = 0$ in $\mathrm{x} \in [-1, 1]$ and $\mathrm{U}(\mathrm{x}) = \mathrm{a}(\mathrm{x}+1)^2$ for $\mathrm{x} < -1$.

The previous equations might be carried over, with essentially no modification, to the multi-dimensional case where $\mathrm{x} \in \mathbb{R}^n$: this is the reason why we wrote $\mathrm{f}\cdot\mathrm{x}$ in a kind of "scalar product" form. What we still miss to do thermodynamics is what happens when you Legendre-transform a function $\mathrm{U}(\mathrm{x},\mathrm{y})$ with respect to *some* of its arguments (x), leaving the other arguments (y) untouched. The modifications are simple, but we need to mention a few things about convexity which will turn out to be important in the study of thermodynamics.

So, let us consider a convex function $\mathrm{U}(\mathbf{x},\mathbf{y})$ of its $n+m$ arguments and repeat the previous steps by Legendre-transforming only the n-dimensional variable $\mathbf{x}$. See App. B for a few useful info about convexity. We now explicitly switch to a multi-dimensional notation. So, for every $\mathbf{y}$ we define a modified potential $\Phi(\mathbf{x},\mathbf{f},\mathbf{y}) = \mathrm{U}(\mathbf{x},\mathbf{y}) - \mathbf{f}\cdot\mathbf{x}$, where $\mathbf{f}$ is n-dimensional, which has the properties that:

$$\begin{cases} \partial_{\mathbf{x}}\Phi(\mathbf{x},\mathbf{f},\mathbf{y})|_{\mathbf{x}(\mathbf{f},\mathbf{y})} = \mathbf{0} & \Phi \text{ stationary at } \mathbf{x}(\mathbf{f},\mathbf{y}) \\ \Phi(\mathbf{x},\mathbf{f},\mathbf{y}) \geq \mathrm{U}(\mathbf{x}(\mathbf{f},\mathbf{y}),\mathbf{y}) - \mathbf{f}\cdot\mathbf{x}(\mathbf{f},\mathbf{y}) \equiv \mathrm{G}(\mathbf{f},\mathbf{y}) & \Phi \text{ minimum at } \mathbf{x}(\mathbf{f},\mathbf{y}) \end{cases} . \qquad (2.72)$$

As before, $\mathbf{x}(\mathbf{f},\mathbf{y})$ is the solution of implicit equation

$$\partial_{\mathbf{x}}\mathrm{U}(\mathbf{x},\mathbf{y})|_{\mathbf{x}(\mathbf{f},\mathbf{y})} = \mathbf{f} \; , \qquad (2.73)$$

and it is quite simple to show that:

$$\partial_{\mathbf{f}}\mathrm{G}(\mathbf{f},\mathbf{y}) = -\mathbf{x}(\mathbf{f},\mathbf{y}) \; . \qquad (2.74)$$

The derivative with respect to the untransformed variables $\mathbf{y}$ are identical to those of U, as you can immediately verify: [42]

$$\partial_{\mathbf{y}}\mathrm{G}(\mathbf{f},\mathbf{y}) = \partial_{\mathbf{y}}\mathrm{U}(\mathbf{x},\mathbf{y})|_{\mathbf{x}(\mathbf{f},\mathbf{y})} \; . \qquad (2.75)$$

---

[42] Indeed:

$$\partial_{\mathbf{y}}\mathrm{G}(\mathbf{f},\mathbf{y}) = \cancel{\partial_{\mathbf{x}}\mathrm{U}(\mathbf{x}(\mathbf{f},\mathbf{y}),\mathbf{y}) \cdot \partial_{\mathbf{y}}\mathbf{x}(\mathbf{f},\mathbf{y})} - \cancel{\mathbf{f}\cdot\partial_{\mathbf{y}}\mathbf{x}(\mathbf{f},\mathbf{y})} + \partial_{\mathbf{y}}\mathrm{U}(\mathbf{x}(\mathbf{f},\mathbf{y}),\mathbf{y})$$

What is more boring, but useful for thermodynamics, is to derive the convexity properties of $G(\mathbf{f},\mathbf{y})$. To do that, let us start from $\partial_{\mathbf{x}}\mathrm{U}(\mathbf{x}(\mathbf{f},\mathbf{y}),\mathbf{y}) = \mathbf{f}$, which we write in components as:

$$\mathrm{f_a} = \partial_{\mathrm{x_a}}\mathrm{U}(\mathbf{x}(\mathbf{f},\mathbf{y}),\mathbf{y}) \ ,$$

and take a derivative with respect to f_b. Using the chain rule we get:

$$\delta_{\mathrm{ab}} = \partial_{\mathrm{f_b}}\mathrm{f_a} = \partial_{\mathrm{f_b}}\mathrm{x_c}(\mathbf{f},\mathbf{y})\ \partial^2_{\mathrm{x_c x_a}}\mathrm{U}(\mathbf{x}(\mathbf{f},\mathbf{y}),\mathbf{y}) = -\partial^2_{\mathrm{f_b f_c}}\mathrm{G}(\mathbf{f},\mathbf{y})\ \partial^2_{\mathrm{x_c x_a}}\mathrm{U}(\mathbf{x}(\mathbf{f},\mathbf{y}),\mathbf{y}) \ .$$

So, if you define the partial $n\times n$ Hessian of U to be:

$$[\mathbb{H}^{\mathrm{U}}(\mathbf{f},\mathbf{y})]_{\mathrm{ab}} \overset{\mathrm{def}}{=} \partial^2_{\mathrm{x_a x_b}}\mathrm{U}(\mathbf{x}(\mathbf{f},\mathbf{y}),\mathbf{y}) \quad\Longrightarrow\quad [\mathbb{H}^{\mathrm{G}}(\mathbf{f},\mathbf{y})]_{\mathrm{ab}} \overset{\mathrm{def}}{=} \partial^2_{\mathrm{f_a f_b}}\mathrm{G}(\mathbf{f},\mathbf{y}) = -[[\mathbb{H}^{\mathrm{U}}(\mathbf{f},\mathbf{y})]^{-1}]_{\mathrm{ab}} \ . \qquad (2.76)$$

If U is convex, then its restriction to the variables $\mathbf{x}$ is convex, hence the partial Hessian $[\mathbb{H}^{\mathrm{U}}]_{\mathrm{ab}}$ is positive definite. [43] Hence you conclude that $\mathrm{G}(\mathbf{f},\mathbf{y})$ is **f**-concave if U is convex.

The proof that $\mathrm{G}(\mathbf{f},\mathbf{y})$ is **y**-convex, as the original $\mathrm{U}(\mathbf{x},\mathbf{y})$ it came from, is a bit more complex (in particular in the multidimensional case, see [1]). Give it a try.

2.7. The thermodynamic potentials

We would like to move from the fundamental equation written in the energy scheme, $E(S,\underline{X})$ or $E(S,V,N)$ for a simple system, to a new potential that uses some of the intensive variables which come from the derivatives of E. In this section, we will keep N fixed and Legendre-transform only S and/or V. Later on, when considering the grand-canonical ensemble, in which some calculations are extremely easy and convenient, we will Legendre-transform E with respect to S and N.

2.7.1. The Helmholtz free-energy: from S to T

The simplest example of Legendre transform of E is one in which, in the notation of the previous section $\mathrm{U}(\mathrm{x},\mathrm{y}) = E(S,\underline{X})$ where $\mathrm{x} = S$ and $\mathrm{y} = \underline{X} = (V,N)$ (in the simplest case). Hence, the corresponding f would be the temperature:

$$\frac{\partial \mathrm{U}}{\partial \mathrm{x}} = \mathrm{f} \quad\Longrightarrow\quad \frac{\partial E}{\partial S} = T \ .$$

By inverting $T(S,\underline{X})$ you can re-express $S(T,\underline{X})$ — the new equilibrium point $\mathrm{x}(\mathrm{f})$ for given slope $\mathrm{f} = T$ — and the correct potential that keeps all the information we had in $E(S,\underline{X})$ is the so-called Helmholtz free-energy: [44]

$$F(T,\underline{X}) = E(S(T,\underline{X}),\underline{X}) - TS(T,\underline{X}) \ . \qquad (2.77)$$

The corresponding derivatives are

$$\begin{cases} \dfrac{\partial F}{\partial T} = -S(T,\underline{X}) \\[2ex] \dfrac{\partial F}{\partial \underline{X}} = \dfrac{\partial E}{\partial \underline{X}} \end{cases} , \qquad (2.78)$$

where all quantities should be regarded as functions of $(T,\underline{X})$. So, for the simple $E(S,V,N)$ we get:

$$\mathrm{d}F = -S(T,V,N)\,\mathrm{d}T - p(T,V,N)\,\mathrm{d}V + \mu(T,V,N)\,\mathrm{d}N \ .$$

---

[43] Alternatively, $[\mathbb{H}^{\mathrm{U}}]_{\mathrm{ab}}$ being the partial Hessian of a bigger positive definite Hessian must be itself positive definite: just evaluate it on vectors which are restricted to the variables of interest and you get your result.

[44] Callen would write this as $E[T]$ — really $U[T]$ since U is the internal energy in Callen — meaning that we Legendre-transform the variable S in E into its intensive generalised force T. Notice also that, in the literature, the Helmholtz free-energy is sometimes denoted by A, from the German *Arbeit* (Work).

A bit of physical understanding is in order. Suppose you have an empty box of volume V, completely isolated from the surrounding world, except for thermal contact with a reservoir kept at temperature T. I ask: how much *work* should I do to assemble a system of N interacting particles inside that box, while heat can be exchanged with the reservoir? In the beginning, I have no particles, hence I start from $E = 0$ and $S = 0$. In the end, the total energy is $E(T, V, N)$. The 1st law tells me that

$$E(T, V, N) = Q + W ,$$

where Q is the heat exchanged with the reservoir, and W is the work I have done to assemble the system. [45] But we can imagine that the construction is very slow, and the heat exchange is reversible so that you can write that:

$$Q = T\Delta S = TS(T, V, N) ,$$

where I have used that also the initial entropy was 0.

Free-energy as a work investment. Hence the work done *on* the system to build it is:

$$W = E(T, V, N) - TS(T, V, N) \equiv F(T, V, N) . \tag{2.79}$$

You see from this argument that F is like an "investment" of work done to build the system: notice that this work is *less* than the total energy E because the building of the system was helped by some *positive heat* Q entering the system from the reservoir.

If F is seen as a "bank account" of work, when you make a "withdrawal of work", the balance of the account should decrease and vice-versa. This is precisely what happens, at least for reversible transformations at constant T. Recall that from the 1st principle

$$\Delta E = Q + W ,$$

expressing conservation of energy *independently* of the nature of the transformation, reversible or not. If the transformation is *reversible* and occurring at fixed temperature T, then $Q_T^{\rm rev} = T\Delta S$. Hence, from the 1st law you conclude that:

$$\Delta F = \Delta E - T\Delta S = W_T^{\rm rev} .$$

If some positive work is done on the system, $W_T^{\rm rev} > 0$, then F increases by the same amount and vice-versa. If the transformation starts and ends at the same fixed T but is otherwise *irreversible*, then $Q_T \leq T\Delta S$, by Clausius inequality. From that, you can easily derive that in general:

$$\Delta F = \Delta E - T\Delta S \leq W_T . \tag{2.80}$$

Example Joules' free expansion.

A famous example of irreversible process is Joule's free expansion of a rarefied (ideal) gas in vacuum, by removal of a wall separating the gas from an empty container. [a] The system is completely isolated, hence $\Delta Q = 0$. We do no work, hence $\Delta W = 0$. Nevertheless, the entropy increases $\Delta S > 0$ and the free-energy decreases $\Delta F < 0$. Since $\Delta F < 0$ the system has effectively diminished its "potential" to do useful work. Incidentally, while the total energy must be conserved, because of the 1st law, the fact that the temperature does not change is due to the ideal nature of the gas, and to the temperature equation of state $E = \frac{3}{2} N k_B T$.

[a] The process occurs at fixed temperature T, for an ideal gas.

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[45] Notice the positive sign in front of W because it is the work done *on* the system.

Exercise 2.7. After inverting the ideal gas entropy $S(E,V,N)$ to express $E(S,V,N)$, calculate the ideal gas free-energy $F(T,V,N)$. Observe that F is T-concave while being convex in the other two variables. Calculate the work done during a reversible isothermal expansion at temperature T by using $F(T,V,N)$. Confirm that you obtain the same result by using the standard integration of $p\mathrm{d}V$ together with the ideal gas equation of state $pV = Nk_BT$.

Returning to the fundamental principle, one can show that the maximum entropy/minimum energy principle leads to a minimum free-energy principle. More precisely, from $E(S,\underline{X})$ for a composite system, for which you know that $E(S,\underline{X}^{\rm eq})$ is minimum, you can Legendre transform the energy obtaining $F(T,\underline{X}) = E(S(T,\underline{X}),\underline{X}) - TS(T,\underline{X})$. Let $F(T,\underline{X}^{\rm eq})$ be the free-energy in equilibrium. You can show that:

Principle of minimum Helmholtz free-energy. For a composite system made by different subsystems kept at *fixed temperature* T, the final equilibrium state after some of these constraints are released is the one that minimizes the total Helmholtz free-energy as a function of the free-variables (virtual states).

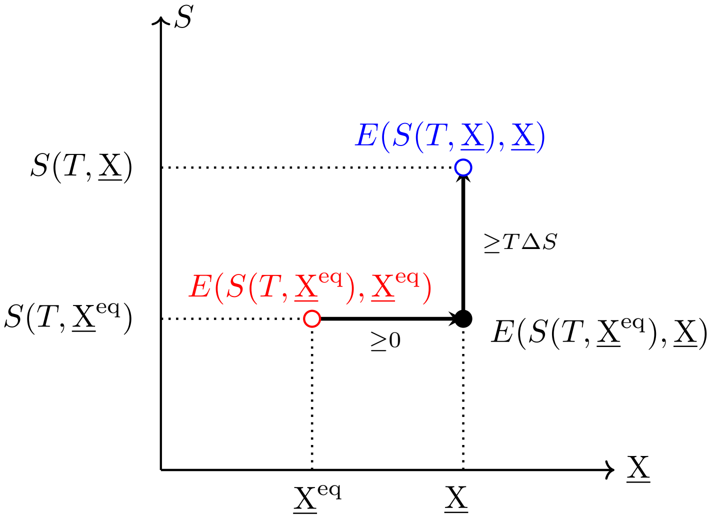

Figure 2.10: The $S - \underline{X}$ "plane" with a few "energy points" used in the proof of the minimum free-energy principle. See text for details.

A proof of this principle proceeds as follows. We want to show that

$$\Delta F = F(T,\underline{X}) - F(T,\underline{X}^{\rm eq}) \geq 0 \;.$$

Writing the terms explicitly, and adding and subtracting a term $E(S(T,\underline{X}^{\rm eq}),\underline{X})$, see Fig. 2.10 for a schematic representation of the $S,\underline{X}$ domain, we indeed get:

$$\begin{aligned}\Delta F &= \underbrace{\left[E(S(T,\underline{X}),\underline{X}) - E(S(T,\underline{X}^{\rm eq}),\underline{X})\right]}_{\geq T\Delta S \text{ by convexity of } E} - T\underbrace{\left[S(T,\underline{X}) - S(T,\underline{X}^{\rm eq})\right]}_{=\Delta S} \\ &+ \underbrace{\left[E(S(T,\underline{X}^{\rm eq}),\underline{X}) - E(S(T,\underline{X}^{\rm eq}),\underline{X}^{\rm eq})\right]}_{\geq 0 \text{ by minimum } E \text{ principle}} \geq 0 \;. \end{aligned} \tag{2.81}$$

Notice that we have essentially used only the minimum energy principle (in the last term, where the total entropy is the same), and the convexity of E (in the first term). Similar proofs can be written down for all the minimum potential principles that you can write for the various Legendre transforms of the energy $E(S,\underline{X})$.

Info: We stress that the Helmholtz free-energy is very important in statistical mechanics because it is directly calculated in the *canonical ensemble*.

2.7.2. The Enthalpy: from V to p

Suppose that $E(S,V,\underline{\mathrm{X}})$, where here and in the following $\underline{\mathrm{X}} = X_2 \cdots X_r$ denotes the collection of the other extensive variables. Take now $\mathrm{x} = V$ and $\mathrm{y} = (S, \underline{\mathrm{X}})$. Hence, the corresponding f would be $(-p)$:

$$\frac{\partial \mathrm{U}}{\partial \mathrm{x}} = \mathrm{f} \quad \Longrightarrow \quad \frac{\partial E}{\partial V} = -p \; .$$

By inverting $p(S,V,\underline{\mathrm{X}})$ you can re-express $V(S,p,\underline{\mathrm{X}})$ and the correct potential that keeps all the information we had in $E(S,V,\underline{\mathrm{X}})$ is the so-called Enthalpy:

$$H(S,p,\underline{\mathrm{X}}) = E(S, V(S,p,\underline{\mathrm{X}}), \underline{\mathrm{X}}) + pV(S,p,\underline{\mathrm{X}}) \; . \tag{2.82}$$

The relevant derivatives are

$$\begin{cases} \dfrac{\partial H}{\partial S} = \dfrac{\partial E}{\partial S} = T \\ \\ \dfrac{\partial H}{\partial p} = V(S,p,\underline{\mathrm{X}}) \\ \\ \dfrac{\partial H}{\partial X} = \dfrac{\partial E}{\partial X} \end{cases} , \tag{2.83}$$

where all quantities should be regarded as functions of $(S,p,\underline{\mathrm{X}})$. So, for the simple $E(S,V,N)$ we get:

$$\mathrm{d}H = T(S,p,N)\,\mathrm{d}S + V(S,p,N)\,\mathrm{d}p + \mu(S,p,N)\,\mathrm{d}N \; .$$

As before, one can prove a *minimum enthalpy principle* for transformation occurring at constant S and p. Moreover, one can show that the enthalpy is the "potential for Heat", as F was the "potential for Work". H is loved by chemists because chemical reactions involve the release/absorption of heat that can be measured by calorimetric techniques. We will have not much to deal with it.

2.7.3. The Gibbs potential: from (S,V) to (T,p)

Suppose that we want to Legendre-transform $E(S,V,\underline{\mathrm{X}})$ with respect to both S and V. Hence $\mathrm{x} = (S,V)$ and $\mathrm{y} = (\underline{\mathrm{X}})$. The corresponding f would be $(T,-p)$, and the derivatives are exactly as seen before. We now invert to obtain $S(T,p,\underline{\mathrm{X}})$ and $V(T,p,\underline{\mathrm{X}})$, and write the *Gibbs potential*:

$$G(T,p,\underline{\mathrm{X}}) = E(S(T,p,\underline{\mathrm{X}}), V(T,p,\underline{\mathrm{X}}), \underline{\mathrm{X}}) - TS(T,p,\underline{\mathrm{X}}) + pV(T,p,\underline{\mathrm{X}}) \; . \tag{2.84}$$

The relevant derivatives are

$$\begin{cases} \dfrac{\partial G}{\partial T} = -S(T,p,\underline{\mathrm{X}}) \\ \\ \dfrac{\partial G}{\partial p} = V(T,p,\underline{\mathrm{X}}) \\ \\ \dfrac{\partial G}{\partial X} = \dfrac{\partial E}{\partial X} \end{cases} , \tag{2.85}$$

where all quantities should be regarded as functions of $(T,p,\underline{\mathrm{X}})$. So, for the simple $E(S,V,N)$ we get:

$$\mathrm{d}G = -S(T,p,N)\,\mathrm{d}T + V(T,p,N)\,\mathrm{d}p + \mu(T,p)\,\mathrm{d}N \; .$$

Notice that we have written $\mu(T,p)$ because μ, being intensive (i.e., a homogenous function of degree 0 in Euler's terminology) cannot depend on N. Indeed, extensivity implies that for a simple system described by (S,V,N) we have the Euler relation, see Eq. (2.44):

$$E = T\,S - p\,V + \mu\,N \; , \tag{2.86}$$

which indeed holds for whatever variables you decide to work with! So, in the (T, p, N) scheme appropriate to G we have that:

$$G(T, p, N) \equiv E - T\,S + p\,V \equiv \mu(T, p)\,N\ . \tag{2.87}$$

Hence, G is exactly linear in N, and the Gibbs potential "per particle" is precisely $\mu(T, p)$. Extensivity suggests that we could use the volume and entropy per particle as well: [46]

$$s(T, p) = \frac{S(T, p, N)}{N} \qquad\qquad v(T, p) = \frac{V(T, p, N)}{N}\ . \tag{2.88}$$

It is easy to show, from the form of $\mathrm{d}G$, that we can write the differential of μ as follows:

$$\mathrm{d}\mu = \left(\frac{\partial \mu}{\partial T}\right)\mathrm{d}T + \left(\frac{\partial \mu}{\partial p}\right)\mathrm{d}p = -s(T, p)\,\mathrm{d}T + v(T, p)\,\mathrm{d}p\ . \tag{2.89}$$

This is a particular case of the so-called *Gibbs-Duhem* relation, which relates the differential of the intensive variables among each other. Physically, it tells that only *two* of them are independent: if you fix T and p, then μ is a function of (T, p).

More generally, the extensivity of $E(S, \underline{X})$ implies the Euler relationship

$$E(S, \underline{X}) = T\,S + \sum_{i=1}^{r} f_i\,X_i = \mathbf{f}(\mathbf{X}) \cdot \mathbf{X}\ , \tag{2.90}$$

where we have extended our notation setting $\mathbf{f} = (f_0 = T, f_1, \cdots, f_r)$ and $\mathbf{X} = (X_0 = S, X_1, \cdots, X_r)$. Notice that:

$$\frac{\partial E}{\partial \mathbf{X}} = \mathbf{f}\ .$$

Hence, the Legendre transform of $E(\mathbf{X})$ with respect to *all the extensive variables* must vanish:

$$\Phi(\mathbf{f}) = E(\mathbf{X}(\mathbf{f})) - \mathbf{f} \cdot \mathbf{X}(\mathbf{f}) = 0\ .$$

The vanishing of this function of the intensive variables implies a relationship among them. Since $\Phi = 0$ implies that $\mathrm{d}\Phi = 0$, but on the other hand

$$\mathrm{d}\Phi = \frac{\partial \Phi}{\partial \mathbf{f}} \cdot \mathrm{d}\mathbf{f} = -\mathbf{X}(\mathbf{f}) \cdot \mathrm{d}\mathbf{f}\ ,$$

then we conclude that the following general *Gibbs-Duhem relation* must hold:

$$\mathbf{X}(\mathbf{f}) \cdot \mathrm{d}\mathbf{f} = 0\ . \tag{2.91}$$

Written for a simple system this reads:

$$S\mathrm{d}T - V\mathrm{d}p + N\mathrm{d}\mu = 0 \quad\Longrightarrow\quad \mathrm{d}\mu = -s(T, p)\,\mathrm{d}T + v(T, p)\,\mathrm{d}p\ ,$$

as indeed found previously.

Quite generally, one defines the number of *thermodynamical degrees of freedom* to be the number of *intensive variables capable of independent variation*. If we have $r + 1$ extensive variables, the number of thermodynamical degrees of freedom is r. For a simple system, $r = 2$.

---

[46] Note that while $S(E, V, N)$ is in general *not linear* in N, we have that $S(T, p, N)$ must be exactly linear in N.

2.8. Stability conditions from the Gibbs potential

Let us return to a simple system described, in the Gibbs potential framework, by $G(T,p,N) = \mu(T,p)N$. If we write the 2×2 Hessian of G with respect to (T,p), or equivalently, by dividing by N, that of μ we get:

$$[\mathrm{d}^2\mu] = \left[\begin{array}{cc} \frac{\partial^2\mu}{\partial T^2} & \frac{\partial^2\mu}{\partial T \partial p} \\ \frac{\partial^2\mu}{\partial p \partial T} & \frac{\partial^2\mu}{\partial p^2} \end{array} \right] . \tag{2.92}$$

Stability requires this Hessian to be negative (semi)-definite. But physically:

$$\frac{\partial^2\mu}{\partial T^2} = -\frac{\partial s}{\partial T} = -\frac{c_p}{T} \leq 0 ,$$

where we defined the *specific heat at constant pressure*:

$$C_p(T,p,N) = T \left(\frac{\partial S}{\partial T} \right)_p = N c_p(T,p) . \tag{2.93}$$

So, local stability with respect to T (redistributions of energy) requires $c_p \geq 0$. Similarly:

$$\frac{\partial^2\mu}{\partial p^2} = \frac{\partial v}{\partial p} = -v\kappa_T \leq 0 ,$$

where we defined the *isothermal compressibility*:

$$\kappa_T(T,p) = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T . \tag{2.94}$$

So, local stability with respect to p (redistributions of volume) requires $\kappa_T \geq 0$. But stability requires also that $\det[\mathrm{d}^2\mu] \geq 0$ (the product of two non-positive eigenvalues is non-negative). Looking at the off-diagonal elements we first observe that the equality of the mixed derivatives implies the following *Maxwell relation*:

$$\frac{\partial^2\mu}{\partial p \partial T} = \frac{\partial^2\mu}{\partial T \partial p} \quad \Longrightarrow \quad \left(\frac{\partial s}{\partial p} \right)_T = \left(\frac{\partial v}{\partial T} \right)_p \equiv v\alpha_p , \tag{2.95}$$

where we have introduced the *volume expansivity at constant* p, also known as *coefficient of thermal expansion*:

$$\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p . \tag{2.96}$$

Notice the non-trivial experimental fact implied by this trivial mathematical consequence of the existence of a state function $\mu(T,p)$. Notice also that, while α_p is often positive, it can also be *negative*, like for water close to freezing (remember your last beer forgotten in the ice compartment?) Stability requires only that:

$$c_p \kappa_T \geq T v \alpha_p^2 , \tag{2.97}$$

and, as you notice, only α_p^2 enters: the sign of α_p is not important.

Exercise 2.8. Calculate the Gibbs potential $G(T,p,N)$ for the monoatomic ideal gas. Calculate then the specific heat c_p, the isothermal compressibility κ_T and the coefficient of thermal expansion α_p. Verify the stability conditions.

2.9. Reconstructing S, V and μ from thermodynamic integration

An large body of information is available on the behaviour of $c_p(T,p)$ and $\kappa_T(T,p)$ for many substances at various T and p. What can we do with those measurements? We can reconstruct

$s(T,p)$, $v(T,p)$ and $\mu(T,p)$. To see this, observe that that the definition of $c_p(T,p)$ implies that:

$$s(T,p) - s(T_0,p) = \int_{T_0}^{T} \mathrm{d}T' \, \frac{c_p(T',p)}{T'} \; .$$

Using the 3rd law, $S(0,p) = 0$, we could even calculate the absolute entropy of our system as:

$$s(T,p) = \int_{0}^{T} \mathrm{d}T' \, \frac{c_p(T',p)}{T'} \; . \tag{2.98}$$

A similar strategy allows to reconstruct $S(T,V,N)$ from data for the specific heat at constant volume $C_v(T,V,N)$.

Concerning $v(T,p)$ the situation is also quite simple. If you have measured $\kappa_T(T,p)$, then

$$\log \frac{v(T,p)}{v(T,p_0)} = -\int_{p_0}^{p} \mathrm{d}p' \; \kappa_T(T,p') \; ,$$

or, more explicitly:

$$v(T,p) = v(T,p_0) \; \mathrm{e}^{-\int_{p_0}^{p} \mathrm{d}p' \kappa_T(T,p')} \; . \tag{2.99}$$

Once you have $s(T,p)$ and $v(T,p)$, the integration of the Gibbs-Duhem form in Eq. (2.89) gives directly the desired $\mu(T,p)$. For instance, you can select an integration path (any path is equivalent, since we are dealing with an exact differential form) made by two straight lines connecting the intial point (T_0,p_0) to the desired final point (T,p), one at constant p_0 with increasing T (γ_T) and the second at constant T with increasing p_0 (γ_p).

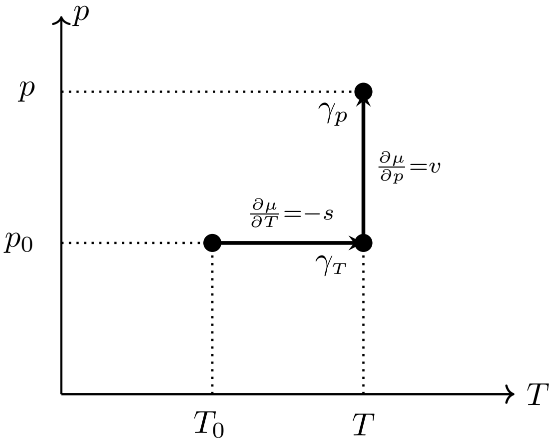

Figure 2.11: The $p-T$ plane with the paths used to reconstruct the chemical potential. See text for details.

The result is:

$$\mu(T,p) - \mu(T_0,p_0) = \int_{\gamma_T+\gamma_p} \mathrm{d}\mu = -\int_{T_0}^{T} \mathrm{d}T' \; s(T',p_0) + \int_{p_0}^{p} \mathrm{d}p' \; v(T,p') \; . \tag{2.100}$$

Notice that unlike entropy – for which the 3rd law fixes an absolute reference value at $T = 0$ —, μ, like any other “energy-related” quantity, is given only with respect to some arbitrary reference point: only differences are meaningful.

2.10. The meaning of imposing convexity: the example of latent heat.

Suppose that a certain energy fundamental equation $E(S,V,N)$ has the form given in Fig. 2.12 (top/left). You will notice that the curve is convex, as it should, but it has a straight line BC. What is it? Observe also the two pieces of dashed curves, which appear as the natural continuation of AB, and CD. These dashed curves have been eliminated by the construction of an envelope of tangents, leading to the straight line BC. Physically, the tangent to E is the temperature T: hence that straight line means that there is a *fixed temperature* T^* that the system shows, while the entropy increase by some amount ΔS. This is a signal of a 1st order transition occurring at T^*: indeed, a familiar experience from the boiling of a pot of water. The system increases its energy by a certain amount, the latent heat $\Delta Q = T^* \Delta S$, while the temperature does not change at all, hence the use of the word "latent", as you well know. The temperature $T(S)$ is plot right below the $E(S)$ curve. You see that the two dashed lines would represent a "metastable (overheated) liquid" (close to B) and a "metastable (overcooled) vapour" (close to C). These metastable states might be obtained under some conditions; generally, it takes even the slightest perturbation to reveal their intrinsic instability, eventually leading to the stable state represented by the straight line BC. Physically, the line BC is a *mixture* (coexistence) of the two phases in B and C, represented by a convex combination:

$$\mathbf{X} = \lambda \mathbf{X}_C + (1-\lambda)\mathbf{X}_B \ ,$$

with $\lambda \in [0,1]$. The straight-line BC means that

$$E(\mathbf{X}) = E(\lambda \mathbf{X}_C + (1-\lambda)\mathbf{X}_B) = \lambda E(\mathbf{X}_C) + (1-\lambda) E(\mathbf{X}_B) \ ,$$

i.e., in words, the energy of the mixture is the convex combination of the energies of the pure states.

So far, we have discussed the two left plots, which refer to the energy scheme. Whenever such situations occur, a better description is obtained by switching to a scheme in which the intensive variable T becomes the control variable, e.g., the Gibbs potential $G(T,p,N)$. [47] In the right plots, you see that, if S is considered not a variable, but rather a function of T, then it has a *jump* at the transition: this jump is reflected in a slope discontinuity of $G(T)$ at T^*.

The same phenomenology would occur if you plot, for instance, $F(T,V,N)$ for this system: you would see a straight-line piece which signals that the pressure p does not change as V increases, and again a slope discontinuity would be observed in $G(T,p)$. So, straight-line pieces signal *phase coexistence* (e.g., a liquid coexisting with a vapour) and the correct variables to use in such cases are the intensive variables T, p, while the extensive variables (S and V) show jumps.

A very nice problem regarding these aspects, and making sense of the Maxwell construction in the pV isotherms of a van der Waals fluid is suggested in the final problems.

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[47] The Helmholtz free-energy $F(T,V,N)$ would be equally good for the purpose, but you will see that at the transition also the volume of the two phases is discontinuous, and the pressure p is the other natural intensive control variable.

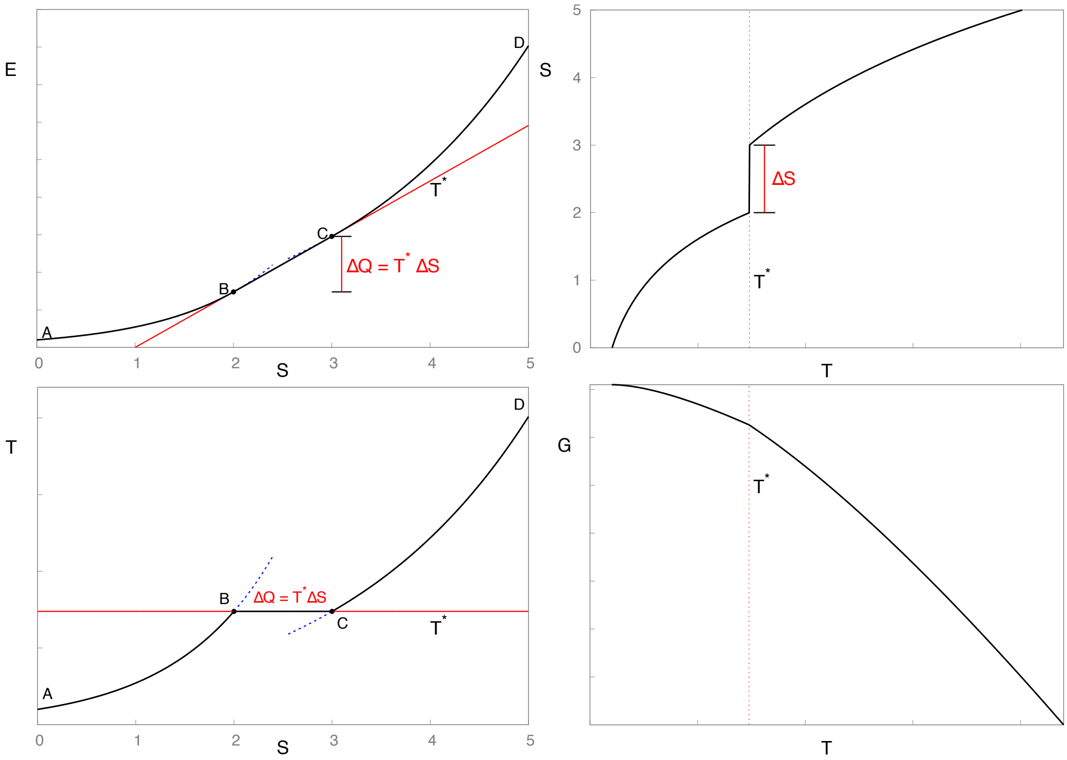

Figure 2.12.: A system showing a 1st order phase transition at a temperature T^*, with associated latent heat.

3. Statistical mechanics ensembles

The goal of the present chapter is to give a flavour of how a statistical description can be given for the measurement of physical observables, which bypasses the extremely complex dynamical problem posed by the classical (Newton or Hamilton) or quantum (Schrödinger) dynamics of a system with many degrees of freedom.

We will see that two important aspects of this journey towards a statistical description of observables touch upon the concepts of ergodicity [7–10] and mixing [8, 9], which have been quite well studied in the classical world, much less in the quantum case. The first, ergodicity, is a fundamental hypothesis introduced by Boltzmann and Maxwell while laying the foundations of classical statistical mechanics; remarkably, is still a widely studied problem in the mathematical and physics community. The concept of mixing concerns the way a classical out-of-equilibrium state reaches thermal equilibrium and is deeply connected to irreversibility, probably one of the most intriguing concepts of thermodynamics.

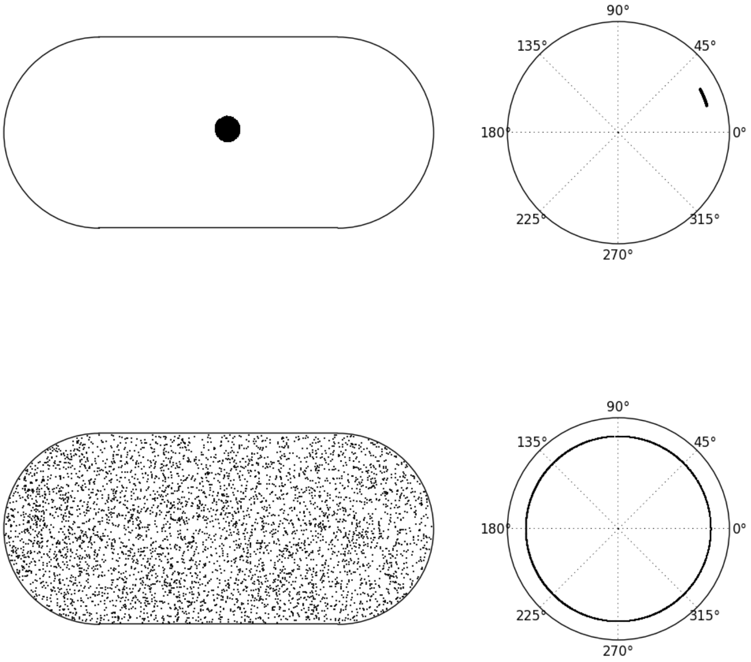

Figure 3.1.: The stadium mixing. Figures due to Simone Ziraldo.

In some way, the billiard animations shown in the introductory lectures, of which we reproduce here two snapshots, should give a flavour of the idea behind the statistical description of a many-body dynamical system, at least in the classical case. Another possible clue to the micro-canonical description of a system emerges from our analysis of Shannon's entropy, and might be phrased by saying that "events that are exponentially more probable will typically occur". Finally, the guided problem presented in App. C should make you appreciate how a micro-canonical description emerges from the time-reversal invariant dynamics described, after a phase-space coarse-graining, by a classical master equation.

3.1. The ergodic problem and the classical micro-canonical ensemble

The first goal of our discussion is to justify the big conceptual steps in going from *mechanics* (classical or quantum) — where we have the deterministic equation of motion of a large number N of particles —, to a *statistical description* of the relevant measurement of some *physical observable*. We will give here some heuristic arguments in favour of the *fundamental postulate* linking the thermodynamic entropy to the phase space volume. The arguments are much developed in the classical case — classical chaos in dynamical systems is a very mature field —, less so in the quantum case, but have enjoyed a certain popularity in the last 30 years, when physicists became again interested in the foundations of quantum statistical mechanics.

3.1.1. Hamilton and Liouville

We begin with a brief recap of classical Hamiltonian dynamics, which has no pretence of rigour or completeness: we refer the reader to the book by Arnold, or Ref. [11], for details and rigour. The classical dynamics description of a system of N particles is based on Hamilton's equations:

$$\begin{cases} \dot{\mathbf{q}} & = +\frac{\partial H}{\partial \mathbf{p}}(\mathbf{q}(t),\mathbf{p}(t)) \\ \dot{\mathbf{p}} & = -\frac{\partial H}{\partial \mathbf{q}}(\mathbf{q}(t),\mathbf{p}(t)) \end{cases} \qquad \Longrightarrow \qquad \dot{\mathbf{x}} = \mathbf{V}(\mathbf{x}(t)) \;, \tag{3.1}$$

where $\mathbf{q} = (\mathbf{q}_1, \cdots, \mathbf{q}_N) \in \mathbb{R}^{3N}$ denote positions, $\mathbf{p} = (\mathbf{p}_1, \cdots, \mathbf{p}_N) \in \mathbb{R}^{3N}$ the momenta, and $\mathbf{x} = (\mathbf{q}, \mathbf{p}) \in \mathbb{R}^{6N}$ a variable which lives in the so-called *phase space* of the system. Here $\mathbf{V}(\mathbf{x})$ is a vector function in phase space determining the *velocity field* for the Hamiltonian flow, which you can directly read from Hamilton's equations. These equations determine in a unique deterministic way the motion of all particles once a suitable initial condition $\mathbf{q}(0)$ and $\mathbf{p}(0)$, hence $\mathbf{x}(0) = \mathbf{x}_0$, is given. Notice that the Hamiltonian velocity field $\mathbf{V}(\mathbf{x})$ has *zero divergence*:

$$\boldsymbol{\nabla}_{\mathbf{x}} \cdot \mathbf{V} = \sum_{i=1}^{N} \left[\frac{\partial}{\partial \mathbf{q}_i} \left(\frac{\partial H}{\partial \mathbf{p}_i} \right) + \frac{\partial}{\partial \mathbf{p}_i} \left(-\frac{\partial H}{\partial \mathbf{q}_i} \right) \right] = 0 \;, \tag{3.2}$$

by Schwartz's theorem on the equality of the mixed second derivatives for sufficiently regular functions $H(\mathbf{q}, \mathbf{p})$.

Time averages and phase-space distributions. Consider now a *single trajectory* in phase space $\mathbf{x}(t)$, originating from the initial condition $\mathbf{x}_0 = \mathbf{x}(t = 0)$ and the corresponding infinite-time average of a given quantity $A(\mathbf{x})$:

$$\overline{A} = \lim_{\mathrm{T}\to\infty} \frac{1}{\mathrm{T}} \int_0^{\mathrm{T}} \mathrm{d}t\, A(\mathbf{x}(t)) = \lim_{\mathrm{T}\to\infty} \frac{1}{\mathrm{T}} \int_0^{\mathrm{T}} \mathrm{d}t \int \mathrm{d}\mathbf{x}\, A(\mathbf{x})\, \rho(\mathbf{x}, t) \tag{3.3}$$

where $\rho(\mathbf{x}, t) = \delta(\mathbf{x} - \mathbf{x}(t))$ is a Dirac's delta function centred at the moving particle position $\mathbf{x}(t)$, with $\rho(\mathbf{x}, 0) = \delta(\mathbf{x} - \mathbf{x}_0)$. More generally, we can consider an *ensemble of trajectories* originating from different initial points $\mathbf{x}_0^{(j)}$, each weighted with a weight factor $p_j \in [0, 1]$ such that $\sum_j p_j = 1$, and evolving into $\mathbf{x}^{(j)}(t)$ according to Hamilton's equations. The corresponding *distribution* $\rho(\mathbf{x}, t)$ in phase space is given by:

$$\rho(\mathbf{x}, 0) = \sum_j p_j \delta(\mathbf{x} - \mathbf{x}_0^{(j)}) \qquad \Longrightarrow \qquad \rho(\mathbf{x}, t) = \sum_j p_j \delta(\mathbf{x} - \mathbf{x}^{(j)}(t)) \;. \tag{3.4}$$

By the usual trick of coarse-graining, we can also adopt a continuous description, where $\rho(\mathbf{x},0)$ is the distribution *density* in phase space, and $\rho(\mathbf{x},t)$ the corresponding evolution according to the Hamiltonian flow. The density distribution $\rho(\mathbf{x},t)$ is such that

$$\int \mathrm{d}\mathbf{x}\,\rho(\mathbf{x},t) = 1 \qquad \forall t \geq 0\;. \tag{3.5}$$

The corresponding *ensemble average* of the time-averages $\overline{A}$ is given by:

$$[\overline{A}]_{\mathrm{ens}} = \lim_{\mathrm{T}\to\infty} \frac{1}{\mathrm{T}} \int_0^{\mathrm{T}} \mathrm{d}t \int \mathrm{d}\mathbf{x}\, A(\mathbf{x})\,\rho(\mathbf{x},t) = \lim_{\mathrm{T}\to\infty} \frac{1}{\mathrm{T}} \int_0^{\mathrm{T}} \mathrm{d}t\,\langle A\rangle_t\;, \tag{3.6}$$

where the last equality defines the ensemble average of $A(\mathbf{x})$ at time t:

$$\langle A\rangle_t = \int \mathrm{d}\mathbf{x}\; A(\mathbf{x})\rho(\mathbf{x},t)\;. \tag{3.7}$$

Observe now that $\rho(\mathbf{x},t)$, like all distribution functions expressing the motion of "conserved objects", must obey a *continuity equation*, where the associated *current* is nothing but $\mathbf{J}(\mathbf{x},t) = \rho(\mathbf{x},t)\mathbf{V}(\mathbf{x})$, in perfect analogy with electromagnetism. The continuity equation will read:

$$\frac{\partial}{\partial t}\rho = -\boldsymbol{\nabla}_{\mathbf{x}} \cdot \mathbf{J}(\mathbf{x},t) = -\boldsymbol{\nabla}_{\mathbf{x}} \cdot (\rho\mathbf{V})\;. \tag{3.8}$$

By using the fact that $\mathbf{V}(\mathbf{x})$ has zero divergence, we can write

$$\boldsymbol{\nabla}_{\mathbf{x}} \cdot (\rho\mathbf{V}) = (\boldsymbol{\nabla}_{\mathbf{x}}\rho)\cdot\mathbf{V} + \rho\cancel{\boldsymbol{\nabla}_{\mathbf{x}}\cdot\mathbf{V}} = \mathbf{V}\cdot(\boldsymbol{\nabla}_{\mathbf{x}}\rho)\;.$$

There are two equivalent ways of writing out the consequences of such divergence-less nature of the Hamiltonian flow. The first is to write a differential equation obeyed by $\rho(\mathbf{x},t)$, which is known as *Liouville equation*:

$$\frac{\partial}{\partial t}\rho = -\mathbf{V}\cdot\boldsymbol{\nabla}_{\mathbf{x}}\rho = \sum_{i=1}^{N} \left(\frac{\partial H}{\partial \mathbf{q}_i}\frac{\partial \rho}{\partial \mathbf{p}_i} - \frac{\partial H}{\partial \mathbf{p}_i}\frac{\partial \rho}{\partial \mathbf{q}_i} \right) \overset{\mathrm{def}}{=} \{H,\rho\}_{\mathrm{PB}} \tag{3.9}$$

where in the last equality we recognise the *Poisson brackets* of H and ρ. [1] The second is that the *total derivative* of $\rho(\mathbf{x}(t),t)$ vanishes:

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho(\mathbf{x}(t),t) = \frac{\partial}{\partial t}\rho + \dot{\mathbf{x}}\cdot\boldsymbol{\nabla}_{\mathbf{x}}\rho = \left(\frac{\partial}{\partial t} + \mathbf{V}\cdot\boldsymbol{\nabla}_{\mathbf{x}}\right)\rho = 0\;. \tag{3.11}$$

This in turn means that $\rho(\mathbf{x}(t),t) = \rho(\mathbf{x}_0,0)$, which says that $\rho(\mathbf{x}(t),t)$ is *constant along Hamiltonian trajectories.*

Liouville theorem. Consider now a region $R_0 \subset \Omega(E)$ in the phase space available to the system at fixed total energy E (E is a conserved quantity in Hamiltonian flow). You can associate to it a characteristic (or indicator) function $\mathrm{I}_{R_0}(\mathbf{x})$ such that:

$$\mathrm{I}_{R_0}(\mathbf{x}) = \left\{ \begin{array}{ll} 1 & \text{if } \mathbf{x}\in R_0 \\ 0 & \text{if } \mathbf{x}\notin R_0 \end{array} \right. \;. \tag{3.12}$$

---

[1] Notice the similarity with the quantum mechanical von Neumann's equation obeyed by the density matrix $\hat{\rho}$. More precisely, if $\hat{\rho}(0) = |\psi(0)\rangle\langle\psi(0)|$ is the initial density matrix, then $\hat{\rho}(t) = |\psi(t)\rangle\langle\psi(t)| = \hat{U}(t)\hat{\rho}(0)\hat{U}^{\dagger}(t)$ obeys the von Neumann equation:

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho}(t) = \frac{1}{i\hbar}[\hat{H},\hat{\rho}]\;. \tag{3.10}$$

In particular, observe that the Liouville equation is *linear*, and the whole evolution of $\rho(\mathbf{x},t)$ might be also regarded as a linear problem in phase space.

You can measure the *volume* of R_0 by the corresponding integral: [2]

$$\mathrm{vol}(R_0) = \int \mathrm{d}\mathbf{x} \, \mathrm{I}_{R_0}(\mathbf{x}) \; . \tag{3.13}$$

Next, take the classical time-evolution operator $U_t(\mathbf{x}_0) = \mathbf{x}(t)$, with $\mathbf{x}(0) = \mathbf{x}_0$, which we might also denote by $\mathbf{x}(t, \mathbf{x}_0)$. You can consider the image under U_t of the region R_0, defined by:

$$R_t \equiv U_t(R_0) = \{\mathbf{x} \,|\, \exists \mathbf{x}_0 \;\text{ such that }\; \mathbf{x} = U_t(\mathbf{x}_0)\} \; . \tag{3.14}$$

Let us take as initial distribution

$$\rho(\mathbf{x}, 0) = \frac{\mathrm{I}_{R_0}(\mathbf{x})}{\mathrm{vol}(R_0)} \qquad \Longrightarrow \qquad \int \mathrm{d}\mathbf{x} \; \rho(\mathbf{x}, 0) = 1 \; .$$

Under evolution, since $\rho(\mathbf{x}(t), t) = \rho(\mathbf{x}_0, 0)$, it is easy to realise that:

$$\rho(\mathbf{x}, t) = \frac{\mathrm{I}_{R_t}(\mathbf{x})}{\mathrm{vol}(R_0)} \; .$$

But the total integral of $\rho(\mathbf{x}, t)$ must be 1, hence:

$$1 = \int \mathrm{d}\mathbf{x} \; \rho(\mathbf{x}, t) = \frac{\int \mathrm{d}\mathbf{x} \, \mathrm{I}_{R_t}(\mathbf{x})}{\mathrm{vol}(R_0)} = \frac{\mathrm{vol}(R_t)}{\mathrm{vol}(R_0)} \qquad \Longrightarrow \qquad \mathrm{vol}(R_t) \equiv \mathrm{vol}(R_0) \; . \tag{3.15}$$

The last equality says that the Hamiltonian flow *conserves the phase space volume* [3] of any region R_0: this is one of the ways of expressing the *Liouville theorem* of Hamiltonian mechanics. However, you should refrain from thinking that since $\mathrm{vol}(R_t) = \mathrm{vol}(R_0)$ the “shape” of R_t is somewhat related, perhaps weakly deformed, to that of R_0: we will return to this issue again when discussing the Poincaré recurrence theorem and the concept of “mixing”.

Constants of motion. To proceed, we need to discuss the concept of *constant of motion.* Let us see what happens, in general, to a quantity $A(\mathbf{x})$ defined in phase space under time evolution. It is immediate to show that once again the Poisson's brackets govern the motion: [4]

$$\frac{\mathrm{d}}{\mathrm{d}t} A(\mathbf{x}(t)) = \dot{\mathbf{x}} \cdot \boldsymbol{\nabla}_{\mathbf{x}} A(\mathbf{x}) = \mathbf{V} \cdot \boldsymbol{\nabla}_{\mathbf{x}} \mathbf{A}(\mathbf{x}) = \{A, H\}_{\mathrm{PB}} \; . \tag{3.17}$$

By definition, a *conserved quantity* or *integral of motion* of the Hamiltonian flow is a function $I_\alpha(\mathbf{x})$ defined in phase space such that

$$I_\alpha(\mathbf{x}(t)) = I_\alpha(\mathbf{x}_0) \; , \tag{3.18}$$

which in turn can be expressed equivalently as:

$$\frac{\mathrm{d}}{\mathrm{d}t} I_\alpha(\mathbf{x}(t)) = \dot{\mathbf{x}} \cdot \boldsymbol{\nabla}_{\mathbf{x}} I_\alpha = \mathbf{V} \cdot \boldsymbol{\nabla}_{\mathbf{x}} I_\alpha = \{I_\alpha, H\}_{\mathrm{PB}} = 0 \; . \tag{3.19}$$

$I_1(\mathbf{x}) = H$, the Hamiltonian itself, is always a constant of motion, provided H does not depend explicitly on t. What other constants of motion would a system have? It depends. In general, the phase space has dimension $2n$, where $n = 3N$ is the configuration space dimension for particles in three dimensions. A system is said to be *completely integrable* in the Liouville sense if a set of n (hence, as you see an extensive number) independent integral of motion exists $\{I_1 = H, I_2, \cdots, I_n\}$ such that $\{I_\alpha, I_{\alpha'}\}_{\mathrm{PB}} = 0$. Without entering in the details of this wonderful construction, which you can find

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[2] In general, a Lebesgue integral, if the region is not very regular.

[3] In hydrodynamical terms, you can think of the distribution $\rho(\mathbf{x}, t)$ as representing an *incompressible fluid* moving under the action of a zero-divergence stationary dissipation-less velocity flow $\mathbf{V}(\mathbf{x})$.

[4] Again, notice the analogy with the Heisenberg's equations of quantum mechanics:

$$\frac{\mathrm{d}}{\mathrm{d}t} \hat{A}_{\mathrm{H}}(t) = \frac{1}{i\hbar} [\hat{A}_{\mathrm{H}}(t), \hat{H}] \; . \tag{3.16}$$

discussed in all details in the book by Arnold, let me exemplify this definition with some examples. For a single particle in one-dimension, $n = 1$ hence $\{I_1 = H\}$ is enough to guarantee integrability. [5] The motion of a particle in a central potential is also integrable, as $\{H, L^2, L_z\}$ are integral of motions. [6] An assembly of harmonic oscillators would also be integrable, as you can easily realise. What is less trivial is that there are many-body one-dimensional non-linear interacting problems, for instance, those generically known as *Calogero-Moser-Sutherland* models, which are integrable. One of its variants reads:

$$H = \frac{1}{2}\sum_{j=1}^{N}(p_j^2 + \omega^2 q_j^2) + g^2 \sum_{j\neq j'}^{N} \frac{1}{(q_j - q_{j'})^2} \,. \tag{3.20}$$

But complete integrability, and even the presence of constants of motions beyond the Hamiltonian itself, is more the exception than the rule. [7] Generic systems tend to have only the Hamiltonian H as a constant of motion.

Physical observables. Not all functions $A(\mathbf{x})$ defined in phase space are physically meaningful, or in any case, we cannot hope to be able to describe them all by statistical techniques. We need to distinguish thermodynamically relevant *physical observables* as those *extensive* quantities which vary very little when only a few degrees of freedoms are changed. For a physical observable, we would expect a behaviour such as the one sketched in Fig. 3.2. Let me give you some elementary examples. The total kinetic energy of the system:

$$K = \sum_{j=1}^{N} \frac{\mathbf{p}_j^2}{2m} \,, \tag{3.22}$$

certainly qualifies as an observable: it is extensive, and if you change the momenta of a few particles, the fractional change of K is of order $O(1/N)$. The same considerations apply to the total one-body potential and the total interaction potential:

$$U_{1-\text{body}} = \sum_{j=1}^{N} V_{1-\text{body}}(\mathbf{q}_j) \qquad\qquad U_{\text{int}} = \frac{1}{2}\sum_{j\neq j'}^{N} V_{\text{int}}(|\mathbf{q}_j - \mathbf{q}_{j'}|) \,. \tag{3.23}$$

Notice that the previous quantities, while being physical observables, are not constant of motion: only their sum, the total energy, is a constant of motion. An obvious constant of motion is the total number of particles N, which you can view as the integral of the local density of particles [8]

$$n(\mathbf{r}) = \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{q}_j) \qquad \Longrightarrow \qquad N = \int_V \mathrm{d}\mathbf{r}\; n(\mathbf{r}) \,. \tag{3.24}$$

You can easily write down quantities which are *not observables*. For instance:

$$\prod_{j=1}^{N} \theta(r_0^2 - |\mathbf{q}_j|^2) \tag{3.25}$$

---

[5] Indeed, energy conservation allows to define a one-dimensional manifold in the (q,p) two-dimensional phase space over which the trajectory lives. One can then reduce the problem to integration, as you know very well from elementary mechanics.

[6] The conservation of $\mathbf{L}$ implies two of the three Kepler laws, but you should notice that $\{L_x, L_y\}_{\text{PB}} = L_z$, hence you can extract only two integral of motions, L^2 and L_z, as you probably know from the quantum mechanical solution to the problem.

[7] A very famous exception is the Fermi-Pasta-Ulam-Tsingou model:

$$H = \frac{1}{2}\sum_{j=0}^{N}(p_j^2 + (q_{j+1} - q_j)^2) + \frac{\alpha}{3}\sum_{j=0}^{N}(q_{j+1} - q_j)^3 \,, \tag{3.21}$$

where $q_j = x_j - ja$ denote the displacement from the equilibrium positions ja of a system of non-linear oscillators with fixed boundary conditions $q_0 = q_{N+1} = 0$. This model gave the birth to a lot of studies in non-linear physics, chaos, integrability, etc.

[8] Technically, the density itself, being not an extensive observable, falls outside of the realm of the observables that you would consider in thermodynamics. However, this quantity has certainly the status of an observable in a statistical mechanics context.

is a quantity which is equal to 1 is *all* particles are contained in a sphere of radius r_0 around the origin, but it is enough to have one particle leaving that sphere for the quantity to abruptly jump to 0.

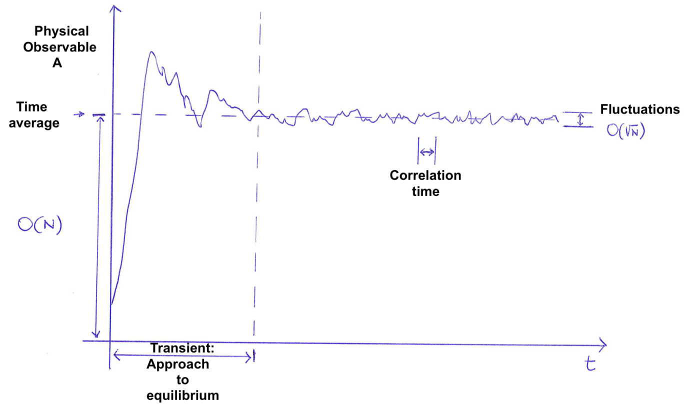

Figure 3.2: A sketch of the behaviour in time of a physical observable, for one particular realization of the dynamics. While the initial point can change, the final steady-state value, with fluctuations around a well-defined time average, is usually independent of the initial conditions. The goal of statistical mechanics is to provide a theory to calculate those time averages in terms of a handful of macroscopic parameters.

3.1.2. Ergodicity and the long-time average of observables

Let us now consider again the issue of the time average of $A(\mathbf{x})$, but we now assume that $A(\mathbf{x})$ is a physical observable. First of all: why do we consider time averages in the first place? At the end of the nineteenth century, Boltzmann argued that the *measurement of a physical quantity necessarily requires a finite amount of time.* Hence, the result of a measurement provides us with an average over a certain finite time interval. The measurement time interval is usually much larger than any characteristic time-scale of the corresponding microscopic dynamics. Hence, to all practical purposes, it is legitimate to assume that a measurement of $A(\mathbf{x})$ will be essentially given by the *infinite time average* of $A(\mathbf{x}(t))$. Theoretically, you could start your "molecular dynamics" simulations from different initial points, and the results of the infinite time average should be identical for all different simulations. Hence, it should make no difference in the calculation of the averages if we also include an "ensemble average":

$$\left[\overline{A}\right]_{\mathrm{ens}} = \lim_{\mathrm{T}\to\infty} \frac{1}{\mathrm{T}} \int_0^{\mathrm{T}} \mathrm{d}t \int \mathrm{d}\mathbf{x}\, A(\mathbf{x})\, \rho(\mathbf{x},t) = \lim_{\mathrm{T}\to\infty} \frac{1}{\mathrm{T}} \int_0^{\mathrm{T}} \mathrm{d}t\, \langle A \rangle_t \; . \tag{3.26}$$

Suppose [9] that the distribution itself "converges" to a stationary distribution for $t \to \infty$:

$$\lim_{t\to\infty} \rho(\mathbf{x},t) \longrightarrow \rho_{\mathrm{st}}(\mathbf{x}) \; . \tag{3.28}$$

If such a $\rho_{\mathrm{st}}(\mathbf{x})$ exists, since the dynamics of $\rho(\mathbf{x},t)$ is given by:

$$\frac{\partial}{\partial t}\rho(\mathbf{x},t) = \sum_{i=1}^{N} \left(\frac{\partial H}{\partial \mathbf{q}_i} \frac{\partial \rho}{\partial \mathbf{p}_i} - \frac{\partial H}{\partial \mathbf{p}_i} \frac{\partial \rho}{\partial \mathbf{q}_i} \right) = \{H, \rho\}_{\mathrm{PB}} \tag{3.29}$$

the limiting stationary distribution should satisfy $\{H, \rho_{\mathrm{st}}\}_{\mathrm{PB}} = 0$. Now, suppose that the system admits k independent constants of motions $\{I_1 = H, I_2, \cdots, I_k\}$. Then, the limiting stationary distribution must be a *function* of the integral of motions:

$$\rho_{\mathrm{st}}(\mathbf{x}) = F(I_1(\mathbf{x}), I_2(\mathbf{x}), \cdots, I_k(\mathbf{x})) \; . \tag{3.30}$$

---

[9] Please regard this as a swift "physicist" approach to the subject. A more careful approach would be to postulate that the limit exist in a weaker sense, i.e., under an average with all physical observables:

$$\lim_{t\to\infty} \int \mathrm{d}\mathbf{x}\; A(\mathbf{x})\; \rho(\mathbf{x},t) \longrightarrow \int \mathrm{d}\mathbf{x}\; A(\mathbf{x})\; \rho_{\mathrm{st}}(\mathbf{x}) \; . \tag{3.27}$$

If the limit exists, then you can easily show that it dominates the infinite-time integral: $\left[\overline{A}\right]_{\mathrm{ens}} = \int \mathrm{d}\mathbf{x}\; A(\mathbf{x})\; \rho_{\mathrm{st}}(\mathbf{x})$. But the infinite time-average of A might exist even if $\langle A \rangle_t = \int \mathrm{d}\mathbf{x}\; A(\mathbf{x})\, \rho(\mathbf{x},t)$ has bounded fluctuations around some average value.

Indeed, it is simple to show [10] that since $\{H, I_j\}_{\rm PB} = 0$, then automatically $\{H, \rho_{\rm st}\}_{\rm PB} = 0$.

By far the most common case — for a system that is non-integrable and with appropriate conditions (confined in a box) which kill all the trivial constants of motions such as total momentum or total angular momentum — is that the only relevant constant of motion is the Hamiltonian itself, hence $\rho_{\rm st}(\mathbf{x}) = F(H(\mathbf{x}))$. Hence, if the $\rho(\mathbf{x}, 0)$ was chosen such that it lies entirely in the manifold with $H(\mathbf{x}) = E$, then

$$\rho_{\rm st}(\mathbf{x}) = \rho_{\mu{\rm CE}}(\mathbf{x}) \equiv \frac{\delta(E - H(\mathbf{x}))}{\Omega(E)} , \tag{3.32}$$

where $\Omega(E)$ is an appropriate normalisation factor (see below). This, essentially, defines the *micro-canonical ensemble* distribution $\rho^{\mu{\rm CE}}(\mathbf{x})$ in terms of which we now formulate the *ergodic hypotesis*:

$$\overline{[A]}_{\rm ens} \equiv \langle A \rangle_{\mu{\rm CE}} = \int {\rm d}\mu \; A(\mathbf{x}) \; \rho_{\mu{\rm CE}}(\mathbf{x}) \tag{3.33}$$

where ${\rm d}\mu$ denotes the integration measure in phase space, which we are free to rescale by an appropriate dimensional constant h^{3N}, end even with a Gibbs counting factor [11] $1/N!$:

$${\rm d}\mu = \frac{{\rm d}\mathbf{x}}{N! h^{3N}} = \frac{1}{N!} \prod_{i=1}^{N} \frac{{\rm d}\mathbf{q}_i {\rm d}\mathbf{p}_i}{h^3} , \tag{3.34}$$

as long as the total volume $\Omega(E)$ appearing as a normalisation factor in $\rho_{\mu{\rm CE}}(\mathbf{x})$ is accordingly calculated as:

$$\Omega(E) = \int {\rm d}\mu \; \delta(E - H(\mathbf{x})) \quad \Longrightarrow \quad \int {\rm d}\mu \; \rho_{\mu{\rm CE}}(\mathbf{x}) = 1 . \tag{3.35}$$

Notice that, although our argument went through the assumption that the distribution $\rho(\mathbf{x}, t)$ "converged" to a stationary micro-canonical distribution, the ergodic hypothesis requires less: it only requires that the "infinite time average" of the distribution approaches the micro-canonical one: [12]

$$\lim_{{\rm T}\to\infty} \frac{1}{\rm T} \int_0^{\rm T} {\rm d}t \; \rho(\mathbf{x}, t) \longrightarrow \rho_{\mu{\rm CE}}(\mathbf{x}) . \tag{3.36}$$

More about the distinction between ergodicity — which is the less stringent requirement in Eq. (3.33) — and mixing — which is the more stringent requirement in Eq. (3.27) — below.

A slight relaxation of the strict restriction to the manifold with $H(\mathbf{x}) = E$ is possible and indeed advisable since one might object that it is impossible to control with infinite precision the initial energy of all the initial points described by $\rho(\mathbf{x}, 0)$. Indeed, let us assume that $\rho(\mathbf{x}, 0)$, when analysed in its energy content, occupies an interval of energies $[E - \Delta_E, E]$, say with a flat histogram. Then, if you denote by ${\rm I}_{\mu{\rm CE}}(\cdot)$ the so-called indicator (or characteristic) function of the energy interval $[E - \Delta_E, E]$:

$${\rm I}_{\mu{\rm CE}}(x) = \begin{cases} 1 & \text{if } x \in [E - \Delta_E, E] \\ 0 & \text{otherwise} \end{cases} \tag{3.37}$$

---

[10] Simply use the chain rule for derivatives with the function $F(y_1, \cdots, y_k)$:

$$\begin{aligned} \{H, \rho_{\rm st}\}_{\rm PB} = \{H, F(I_1 \cdots I_k)\}_{\rm PB} &= \sum_{i=1}^{N} \left(\frac{\partial H}{\partial \mathbf{q}_i} \frac{\partial F}{\partial \mathbf{p}_i} - \frac{\partial H}{\partial \mathbf{p}_i} \frac{\partial F}{\partial \mathbf{q}_i} \right) \\ &= \sum_{j=1}^{k} \frac{\partial F}{\partial y_j} \sum_{i=1}^{N} \left(\frac{\partial H}{\partial \mathbf{q}_i} \frac{\partial I_j}{\partial \mathbf{p}_i} - \frac{\partial H}{\partial \mathbf{p}_i} \frac{\partial I_j}{\partial \mathbf{q}_i} \right) = \sum_{j=1}^{k} \frac{\partial F}{\partial y_j} \{H, I_j\}_{\rm PB} = 0 . \end{aligned} \tag{3.31}$$

[11] As you remember from the first lectures, the Gibbs counting factor is crucial to get a properly extensive entropy at the classical level. It comes naturally from the classical limit of the quantum ideal gas calculation, together with the appropriate factors of h^{3N}, as we shall see later on.

[12] Again, we should better intend the limit in the weak sense: under average with all possible physical observables, which is what Eq. (3.33) actually states.

the limiting micro-canonical distribution would be given by

$$\rho_{\mu\mathrm{CE}}(\mathbf{x}) \equiv \frac{\mathrm{I}_{\mu\mathrm{CE}}(H(\mathbf{x}))}{\mathcal{N}_{\mu\mathrm{CE}}(E)} \tag{3.38}$$

with the normalisation factor given by:

$$\mathcal{N}_{\mu\mathrm{CE}}(E) = \int \mathrm{d}\mu \, \mathrm{I}_{\mu\mathrm{CE}}(H(\mathbf{x})) = \int_{E-\Delta_E}^{E} \mathrm{d}E' \, \Omega(E') \, . \tag{3.39}$$

Once again, the ergodic hypothesis stipulates that long-time averages should be reproduced by the micro-canonical averages calculated with $\rho_{\mu\mathrm{CE}}(\mathbf{x})$. [13]

The ergodic condition [14] can be "pictured" in many ways: an interesting geometrical "picture" is that a system is ergodic when the trajectory $\mathbf{x}(t)$ passes close to nearly all the states compatible with the conservation of energy, see Figure 3.3, for almost all possible initial conditions.

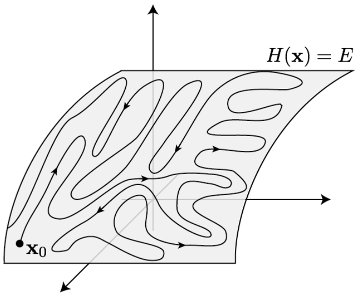

Figure 3.3: A sketch of an ergodic trajectory in phase space Γ. The grey surface is the set of configurations with energy E, the micro-canonical energy shell, where E is the energy of the initial state $\mathbf{x}_0$. An ergodic trajectory $\mathbf{x}(t)$ passes close to nearly all the states with energy E as t approaches ∞.

Ergodicity has been mathematically proven for a small set of systems, mainly billiards with hardcore spheres [12, 13]. A lack of ergodicity could come from many factors: integrability, on one extreme, and glassiness, on the other. A classical system is integrable when there is a complete set of constants of motion which restricts the dynamics to essentially one-dimensional degrees of freedom. In this case, ergodicity can be in some sense "recovered" by restricting the micro-canonical average to the appropriate surface in which all the constants of motion are fixed. More interesting is the case of systems that are "close to integrability": when the Hamiltonian is slightly perturbed from an integrable one, the trajectories remain "trapped" in surfaces, called invariant tori, and they are unable to fill the available phase space. A numerical example of this effect was discovered by Fermi, Pasta, and Ulam [14]; the mathematics of it is contained in the famous Kolmogorov-Arnold-Moser (KAM) theorem [11, 15–17]. Glasses, at the other extreme, are a well-known class of systems where ergodicity fails. In these systems, the configuration is dynamically trapped in a subset of the phase space and the system is not able to fill the allowed micro-canonical energy shell in any reasonable time scale. Glassy dynamics has been shown even in simple systems, e.g., lattice Hamiltonians with density constraints, for instance when a particle on a lattice cannot have more than a given number of occupied neighbouring sites [18]. Glassiness, and ergodicity breaking, is also present in disordered systems, like spin glasses [19], i.e., disordered magnets with frustrated interactions. Besides these

---

[13] Notice that when Δ_E is small, you can approximate:

$$\mathcal{N}_{\mu\mathrm{CE}}(E) \simeq \Delta_E \Omega(E) \, ,$$

and therefore:

$$\rho_{\mu\mathrm{CE}}(\mathbf{x}) \simeq \frac{\mathrm{I}_{\mu\mathrm{CE}}(H(\mathbf{x}))}{\Delta_E \Omega(E)} \xrightarrow{\Delta_E \to 0} \frac{\delta(E - H(\mathbf{x}))}{\Omega(E)} \, .$$

[14] Notice that ergodicity and chaos [11] are not synonyms: in ergodicity, we analyse the filling of the phase space while in chaos we study the behaviour of the trajectories starting from similar initial conditions. This means that if a system is ergodic it is not necessarily chaotic, and the opposite (for instance, N-bodies in gravitational interaction is chaotic but not ergodic). At the same time, chaos gives to the ergodic hypothesis even more importance: if a system is chaotic, even if we know the initial state $\mathbf{x}_0$ we will not be able to follow its dynamics because any small error, even infinitesimal, generates divergent trajectories.

well-studied cases, it is commonly believed that in most of the non-trivial classical Hamiltonians with many degrees of freedom ergodicity is fulfilled [9].

3.1.3. Ergodicity versus mixing and the Poincaré recurrence theorem

Question: if we start from an out-of-equilibrium state, will the observables approach their equilibrium (micro-canonical) value as time proceeds? The answer to this important question is deeply rooted in the concept of mixing.

Recall the definition we have already given before. A system is said *mixing* if for any initial ensemble $\rho(\mathbf{x}, 0)$ and any observable $A(\mathbf{x})$ we have:

$$\lim_{t\to\infty} \int \mathrm{d}\mu \; A(\mathbf{x}) \; \rho(\mathbf{x}, t) \overset{\text{relaxes to eq.}}{\longrightarrow} \int \mathrm{d}\mu \; A(\mathbf{x}) \; \rho_{\mu\mathrm{CE}}(\mathbf{x}) \; . \tag{3.40}$$

In other words, this means that, in a mixing system, the mean value at time t of $A(\mathbf{x})$ approaches, for large times, the micro-canonical average. To illustrate the concept of mixing, we sketch in Fig. 3.4 possible different types of flow in phase space starting from an initial ensemble which is concentrated in a finite volume of phase space (the deformed rectangles). During the time evolution the volume occupied by the initial ensemble moves and deforms, building a flow inside the phase space. From Liouville's theorem, the volume is conserved by the flow, but the shape can evolve and be deformed in many ways. The simplest case is illustrated in panel (a) of Fig. 3.4, in which the initial volume moves without distortion, returning to the initial position in phase space after a certain time: in this case, the flow sweeps a finite fraction of the available phase space. This flow is neither ergodic nor mixing. An example of ergodic flow is shown in panel (b) of Fig. 3.4, where the initial shape is only slightly altered, but it never returns to its initial location and visits essentially every region of available phase space. Finally, panel (c) of Fig. 3.4 illustrates a mixing flow: here the shape of the initial distribution is highly distorted as time increases and evolves into an octopus with contorted arms which grow into extremely fine filaments that spread out uniformly over the whole phase space. An example of a mixing flow is shown in Fig. 3.5. Essentially, in a mixing flow, starting from an initial out-of-equilibrium ensemble the distribution $\rho(\mathbf{x}, t)$ evolves towards the equilibrium one, i.e., the micro-canonical ensemble in the case of an isolated system. As one might guess by looking at the sketches of Fig. 3.4, mixing is a stronger condition than ergodicity: it implies ergodicity but is not implied by it. Like for ergodicity, mixing has been mathematically proven only for a few simple

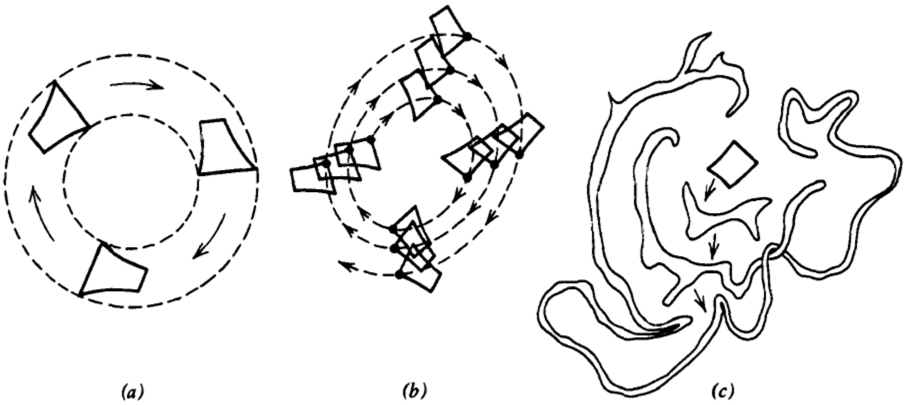

Figure 3.4.: Sketch of three types of flow in phase space. (a) non-ergodic: the initial sample moves without distortion, returning to the initial condition after a finite time; (b) ergodic: the shape of the initial sample is only slightly altered by time evolution but it never returns to the initial condition and it sweeps out the allowed portion of phase space; (c) mixing: the shape is distorted by time evolution and after an infinite time it spreads out over the whole allowed phase space. Figure taken from Ref. [9].

systems. The most known result is due to Sinai who proved, in 1962, that the hard-sphere gas is ergodic and mixing [12]. It has also been proved rigorously [20] that mixing is strongly connected to the instability of trajectories associated with chaotic dynamics in phase space, and is deeply related to the issue of irreversibility [8].

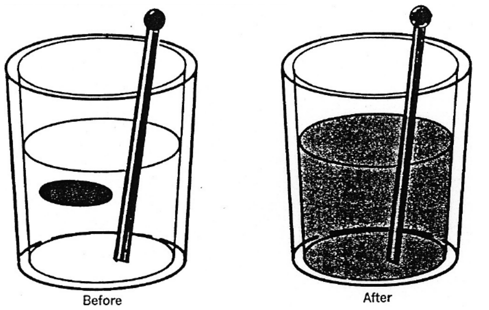

Figure 3.5: An example of a mixing flow: 20% of rum and 80% of cola produce, after mixing, a "Cuba libre". The figure is taken from Ref. [8]. If the initial drop is substituted by oil, then a vigorous shaking will only produce an ergodic motion of oil drops, which will never mix with the surrounding medium.

The following simple example shows the difference between ergodicity and mixing. Consider the simple evolution defined on the two-dimensional torus $\{(q,p)\,|\,\text{with } q \mod (1),\ p \mod (1)\}$:

$$\begin{cases} \dot{q} = 1 & \Rightarrow\ q = q_0 + t \qquad \mod (1) \\ \dot{p} = \alpha & \Rightarrow\ p = p_0 + \alpha t \qquad \mod (1) \end{cases} \tag{3.41}$$

with $\alpha = \tan(\theta)$ irrational. [15] Consider now an "observable" $A(q,p)$. On the torus, it will be a periodic function of (q,p), which we can expand in Fourier series:

$$A(q,p) = \sum_{n,m} \hat{A}_{n,m} \mathrm{e}^{2\pi i(mq+np)} \ .$$

Hence we have that:

$$A(q(t),p(t)) = \sum_{n,m} \hat{A}_{n,m} \mathrm{e}^{2\pi i(m(q_0+t)+n(p_0+\alpha t))} \ .$$

The infinite-time average is simple to calculate:

$$\begin{aligned} \overline{A} = \lim_{T\to\infty} \frac{1}{T}\int_0^T \mathrm{d}t\, A(q(t),p(t)) &= \hat{A}_{0,0} + \sum_{n,m}^{\neq(0,0)} \hat{A}_{n,m} \mathrm{e}^{2\pi i(mq_0+np_0)} \lim_{T\to\infty} \frac{1}{T} \frac{\mathrm{e}^{(m+n\alpha)2\pi i T} - 1}{2\pi i(m+n\alpha)} \\ &= \hat{A}_{0,0} \ . \end{aligned} \tag{3.42}$$

This system is evidently ergodic, as the time-average is reproduced by the totally flat distribution $\rho_{\mathrm{st}}(q,p) = 1$:

$$\langle A \rangle_{\mathrm{st}} = \int_0^1 \mathrm{d}q \int_0^1 \mathrm{d}p\, A(q,p)\rho_{\mathrm{st}}(q,p) = \hat{A}_{0,0} \ .$$

But the flow is far from mixing: if you take a small ball R_0 as initial $\rho(q,p,t=0)$ the shape of this ball is essentially undistorted by the flow: the ball simply moves at an angle θ, bouncing with periodic boundary conditions at the border of the torus. Hence $\rho(q,p,t)$ *does not converge* to the flat distribution $\rho_{\mathrm{st}}(q,p) = 1$, but rather comes infinitely close, and infinitely many times, to any point in phase space.

An early paradox that puzzled the fathers of statistical mechanics is given by the Poincaré recurrence theorem. The theorem is simple to state and prove. A few definitions will clarify the notation. Let $U_t(\mathbf{x}_0)$ denote the (Hamiltonian) evolution operator (or flow) for the initial point $\mathbf{x}_0$ at time t:

$$\mathbf{x}(t,\mathbf{x}_0) = U_t(\mathbf{x}_0) \ .$$

Correspondingly $U_t(R)$ denotes the image under U_t of all points in a region R:

$$U_t(R) = \{\mathbf{x}' \,\big|\, \exists \mathbf{x} \in R \text{ such that } \mathbf{x}' = U_t(\mathbf{x})\} \ .$$

---

[15] Notice that α is irrational for "almost all" values of the angle θ.

Let now R_0 be a small neighborhood of some point $\mathbf{x}_0$ in phase space:

$$R_0 = \{\mathbf{x} \big| |\mathbf{x} - \mathbf{x}_0| < \delta\} \ .$$

Fix now an arbitrary fixed time τ and consider the stroboscopic images of an initial region R_0 of phase space: $U_\tau(R_0)$, $U_\tau^2(R_0) = U_\tau(U_\tau(R_0))$, etc. Figure 3.6 illustrates the content of the theorem. The theorem states:

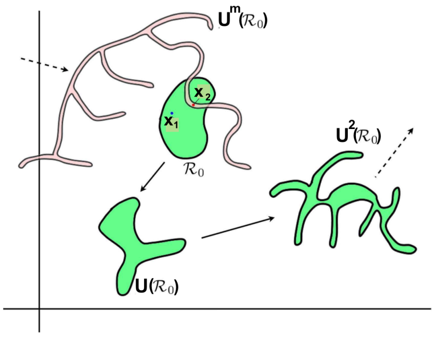

Figure 3.6: Illustration of the Poincaré recurrence theorem. Figure adapted from Arovas.

> **Poincaré recurrence theorem.** If the phase space volume is *finite*, and the evolution operator is *invertible* and *volume-preserving*, then in any finite region R_0, there exists a point $\mathbf{x}_1 \in R_0$ such that $\mathbf{x}_2 = U_\tau^m(\mathbf{x}_1) \in R_0$ for some finite value of m.

Proof: The proof proceeds by contradiction. If the thesis is assume false, then all $U_\tau^k(R_0)$ will have to be *disjoint sets*, for all values $k \in \mathbb{N}$. Hence:

$$\mathrm{vol}\left(\bigcup_{k=0}^{\infty} U_\tau^k(R_0)\right) = \sum_{k=0}^{\infty} \mathrm{vol}\left(U_\tau^k(R_0)\right) = \mathrm{vol}\,(R_0) \sum_{k=0}^{\infty} 1 = \infty \ ,$$

which contradicts the hypothesis that the phase space volume is finite. Here we have used the fact that the flow is volume-preserving. If the different $U_\tau^k(R_0)$ cannot be all disjoint, there must exist two integers $k < l$ such that

$$U_\tau^k(R_0) \cap U_\tau^l(R_0) \neq \emptyset \ .$$

But the invertibility of U_t will allow us to apply U_τ^{-k} to the previous set, hence:

$$R_0 \cap U_\tau^{l-k}(R_0) \neq \emptyset \ .$$

Let us now call $m = l - k > 0$. Take an element $\mathbf{x}_2 \in R_0 \cap U_\tau^m(R_0)$, and define $\mathbf{x}_1 = U_\tau^{-m}(\mathbf{x}_2)$. Then we have found an $\mathbf{x}_1 \in R_0$ such that $\mathbf{x}_2 = U_\tau^m(\mathbf{x}_1) \in R_0$, which is what we wanted to prove. The puzzling aspect of the recurrence theorem is illustrated in Fig. 3.7: a bottle containing vapours of a perfume is opened in a room empty of molecules (left); after a very short time (centre) all molecules have uniformly occupied the room; in a sufficiently long time (right), a recurrence should be expected, and all molecules should be back in the bottle. A few comments are in order. The bottle can be imagined to be arbitrarily small so that the configuration space neighbourhood of the initial point $\mathbf{x}_0$ can be imagined to be very small. Moreover, given the initial velocities of all the perfume molecules, you can consider a region R_0 around $\mathbf{x}_0$ which is indeed arbitrarily small. Two aspects of the theorem should make you confident that no real violation of irreversibility is practically implied by the recurrence theorem. First, the theorem guarantees that a suitable $\mathbf{x}_1 \in R_0$ can be found such that $U_\tau^m(\mathbf{x}_1) = \mathbf{x}_2 \in R_0$: this implies that in general you have to *fine tune* the initial condition inside the small region R_0 to obtain recurrence. Second, the effective time $m\tau$ for recurrence might be extremely large, indeed even larger than the age of the universe. Finally, such a rare occurrence would not, in any event, modify the time average of a physical observable; indeed you might argue that, during the measurement time, the molecules would return to the "typical" situations predicted by statistical mechanics.

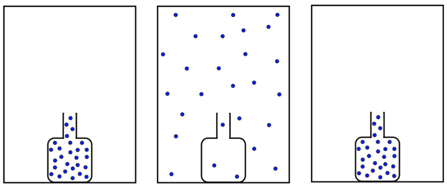

Figure 3.7: Illustration of the Poincaré recurrence theorem. Figure adapted from Arovas.

Returning to the concept of *mixing*, here is an equivalent formulation, mathematically more convenient, which proceeds through the "measure" of regions in phase space. Let us denote by

$$\mu(R_0) = \mathrm{vol}(R_0) = \int \mathrm{d}\mu \; \mathrm{I}(R_0) \; ,$$

the volume of a region R_0 in phase space, where $\mathrm{I}(R_0)$ is the indicator function of R_0, and Ω is the full phase space of finite volume. Recall that $U^n_\tau(R_0)$ has the same volume as R_0, by Liouville theorem: $\mu(U^n_\tau(R_0)) = \mu(R_0)$. Then mixing requires that for any measurable region B you have:

$$\lim_{n\to\infty} \frac{\mu(U^n_\tau(R_0)\cap B)}{\mu(B)} = \frac{\mu(R_0)}{\mu(\Omega)} \qquad \forall B \;\text{ with }\; \mu(B) > 0 \; . \tag{3.43}$$

In words, for very long time, the fraction of $U^n_\tau(R_0)$ in *any* region B approaches the absolute volume fraction of R_0 in the full phase space Ω.

To summarise, the various types of behaviour we have discussed can be classified in a hierarchy as shown in Fig. 3.8.

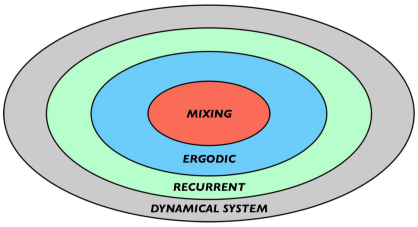

Figure 3.8: The hierarchy of behaviours for Hamiltonian systems. Figure taken from Arovas.

3.2. Ensembles in quantum statistical mechanics

In this section, we briefly overview the statistical approach to *closed* quantum systems. A closed quantum system is described by a Hamiltonian $\widehat{H}$, which is a Hermitian operator [21]. A state of the system is described by a wave-function $|\Psi\rangle$ and the "phase space" [16] is given by the associated Hilbert space [21]. The dynamics is governed by the Schrödinger equation, which is a linear first-order in time partial differential equation:

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} |\Psi(t)\rangle = \widehat{H}\, |\Psi(t)\rangle \; , \tag{3.44}$$

where $|\Psi(t)\rangle$ is the wave-function at time t. We will denote by $|\Psi_0\rangle \equiv |\Psi(0)\rangle$ the initial state.

---

[16] Notice the immensely different degree of complexity that quantum mechanics poses. To represent N classical particles in $3d$ we need to specify $6N$ real numbers, hence a number which scales linearly with N. On the contrary, even a single quantum particle in $1d$ requires specifying a *wave-function*, hence an infinite-dimensional space is required. Even upon truncating the single-particle Hilbert space to a finite number N_{states}, the quantum problems associated with N particles will require dealing with a Hilbert space of dimension $(N_{\text{states}})^N$, hence exponentially large in the number of particles.

We start with some observations. Given any orthonormal basis set $\{|\alpha\rangle\}$ of the Hilbert space, the initial wave-function $|\Psi_0\rangle$ can be expressed as

$$|\Psi_0\rangle = \sum_\alpha c_\alpha |\alpha\rangle \ , \tag{3.45}$$

where $c_\alpha \equiv \langle\alpha|\Psi_0\rangle$. An exact description of the initial state requires the knowledge of all the c_α's, whose number grows as the Hilbert space dimension, i.e., *exponentially* with the system size. Therefore, like in classical physics, a statistical approach is essential when you want to deal with macroscopic systems. The second remark has to do with the linearity of the Schrödinger equation, as opposed to the generally non-linear Hamiltonian dynamics of classical physics. Due to linearity, if the basis chosen is given by the eigenstates $|\alpha\rangle = |\phi_\alpha\rangle$ of the Hamiltonian $\widehat{H}$, with eigenvalues E_α, the solution of Eq. (3.44) is:

$$|\Psi(t)\rangle = \sum_\alpha c_\alpha \mathrm{e}^{-i\frac{E_\alpha t}{\hbar}} |\phi_\alpha\rangle \ . \tag{3.46}$$

If we regard this time evolution as a trajectory in "phase space", quantum dynamics seems far from being ergodic. Indeed, the square modulus of $\langle\phi_\alpha|\Psi(t)\rangle = c_\alpha \mathrm{e}^{-iE_\alpha t/\hbar}$, proportional to the probability of getting E_α in a measurement of energy, *does not change* in time during the evolution:

$$|\langle\phi_\alpha|\Psi(t)\rangle|^2 = |c_\alpha|^2 \ .$$

As the time advances, only the phase of $\langle\phi_\alpha|\Psi(t)\rangle$ "rotates" in the complex plane. Let us denote by

$$E_0 \equiv \langle\Psi_0|\hat{H}|\Psi_0\rangle = \sum_\alpha E_\alpha |c_\alpha|^2 \quad \overset{\text{conserved}}{\Longrightarrow} \quad \langle\Psi(t)|\hat{H}|\Psi(t)\rangle = E_0 \ , \tag{3.47}$$

the average energy of the initial state, which is a conserved quantity. We will further assume that $|\Psi_0\rangle$ is a reasonable physical state, prepared as an eigenstate of some other many-body Hamiltonian $\widehat{H}_0$, in a setting that is often referred to as *quantum quench*. We will then assume that, while E_0 is extensive $E_0 \propto N$, the energy spread ΔE_0 of the state $|\Psi_0\rangle$ is sub-extensive, for instance

$$\Delta E_0 = \sqrt{\sum_\alpha (E_\alpha - E_0)^2 |c_\alpha|^2} \propto \sqrt{N} \ . \tag{3.48}$$

In the Hilbert space, the "hyper-surface" of constant energy E_0 is given by all the normalized states $|\Phi\rangle = \sum_\alpha b_\alpha |\phi_\alpha\rangle$ which satisfy the "hyper-ellipsoid" equation $E_0 = \langle\Phi|\hat{H}|\Phi\rangle = \sum_\alpha E_\alpha |b_\alpha|^2$. The states touched by $|\Psi(t)\rangle$ during the quantum dynamics are evidently just a small subset of such "hyper-ellipsoid", since the $|c_\alpha|^2$ are fixed: therefore, whatever is the Hamiltonian and the initial state, there is a huge set of normalised states $|\Phi\rangle$ with energy E_0 which is neither touched nor close to the trajectory of $|\Psi(t)\rangle$. In summary, the conservation of the quantity $|\langle\phi_\alpha|\Psi(t)\rangle|^2 = |c_\alpha|^2$, directly implied by the linearity of the Schrödinger equation, seems to prevent any kind of ergodicity, at least in the classical sense: *the time evolution of a quantum system does not uniformly sample all vectors in Hilbert space with given energy.* This fact was underlined by von Neumann [22, 23] in his seminal work on the quantum mechanical counterpart of the ergodic theorem.

A further element that makes the quantum evolution very different, at least superficially, from the classical one is the fact that the Schrödinger equation is *linear*, while Hamilton's equations are in general non-linear. [17] Non-linearities, typically, bring a chaotic behaviour of trajectories, which tend

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[17] As a disclaimer to the discussion which is about to follow, consider the following paragraph, taken from a Wikipedia footnote on ETH. "As an intuitive explanation for why quantum chaos must be handled differently from classical chaos, some authors contrast the linearity of the Schrödinger equation to the non-linear nature of the equations of motion for classically chaotic systems, emphasizing in particular that the inner product between vectors in Hilbert space is preserved in contrast to the exponential separation between classical points in phase space. This is misleading, however, as the Schrödinger equation is equivalent to the von Neumann equation specialized to the case of a pure state, and the von Neumann equation is directly analogous to the classical Liouville equations — $\partial_t\rho(\mathbf{x},t) = \{H,\rho\}_{\mathrm{PB}}$ — which is also linear. In other words, this apparent difference between quantum and classical mechanics is only an artefact of comparing different representations of the dynamical equations; once classical mechanics and quantum mechanics are put on equal footing, their dynamical equations are both linear, so that linearity per se cannot be responsible for the different tools necessary to study quantum versus classical chaos."

to depart exponentially fast from each other, even if they start from very close by initial points. On the contrary, the overlap between two "nearby states" will stay perfectly constant in quantum mechanics, as you can immediately verify:

$$\langle\psi_2(t)|\psi_1(t)\rangle = \langle\psi_2(0)|\hat{U}^\dagger(t,0)\hat{U}(t,0)|\psi_1(0)\rangle = \langle\psi_2(0)|\psi_1(0)\rangle \; . \tag{3.49}$$

You might be thinking that there is no hope for "ergodicity" in quantum mechanics, given all these observations. But this is too fast a conclusion: nature is, after all, quantum.

To better appreciate the crucial role played by non-linearity in the potential entering in the quantum Hamiltonian [24], consider the quantum dynamics of a system governed by the non-relativistic Hamiltonian:

$$\widehat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{x}}) \; . \tag{3.50}$$

Quite clearly, you might easily adapt the arguments that follow to a system made of many interacting particles. Given an arbitrary Hermitean operator $\hat{A}$, the expectation value on the state $|\psi(t)\rangle = \mathrm{e}^{-i\widehat{H}t/\hbar}|\psi(0)\rangle$ is

$$\langle\psi(t)|\hat{A}|\psi(t)\rangle = \langle\psi(0)|\mathrm{e}^{i\widehat{H}t/\hbar}\hat{A}\mathrm{e}^{-i\widehat{H}t/\hbar}|\psi(0)\rangle \; . \tag{3.51}$$

The expression on the right-hand side defines the Heisenberg representation of the operator $\hat{A}$, as you know very well:

$$\hat{A}_{\mathrm{H}}(t) \overset{\mathrm{def}}{=} \mathrm{e}^{i\widehat{H}t/\hbar}\hat{A}\mathrm{e}^{-i\widehat{H}t/\hbar} \; , \tag{3.52}$$

in terms of which we have:

$$\langle\psi(t)|\hat{A}|\psi(t)\rangle = \langle\psi(0)|\hat{A}_{\mathrm{H}}(t)|\psi(0)\rangle \; . \tag{3.53}$$

As you know, one can write a differential equation satisfied by $\hat{A}_{\mathrm{H}}(t)$ by simply taking the derivative with respect to time. It is simple to show that:

$$i\hbar\frac{d}{dt}\hat{A}_{\mathrm{H}}(t) = \mathrm{e}^{i\widehat{H}t/\hbar}[\hat{A},\widehat{H}]\mathrm{e}^{-i\widehat{H}t/\hbar} = [\hat{A}_{\mathrm{H}}(t),\widehat{H}] \; , \tag{3.54}$$

an equation known as *Heisenberg equation of motion* for the operator $\hat{A}_{\mathrm{H}}(t)$. Incidentally, if the operator $\hat{A}$ commutes with $\widehat{H}$, then $\hat{A}_{\mathrm{H}}(t) \equiv \hat{A}$ and, as a consequence:

$$\langle\psi(t)|\hat{A}|\psi(t)\rangle = \langle\psi(0)|\hat{A}|\psi(0)\rangle \; . \tag{3.55}$$

Hence, in words, $\langle\psi(t)|\hat{A}|\psi(t)\rangle$ is a *constant of motion.*

Let us now use Heisenberg's equations of motions for $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$ to calculate how the average position and momentum evolve in time. Recall that the operators $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$ have canonical commutation relations and that they verify:

$$[\hat{x}_j, f(\hat{\mathbf{p}})] = i\hbar\nabla_j f(\hat{\mathbf{p}}) \qquad \text{and} \qquad [\hat{p}_j, V(\hat{\mathbf{x}})] = -i\hbar\nabla_j V(\hat{\mathbf{x}}) \; , \tag{3.56}$$

provided the functions $f(\mathbf{p})$ and $V(\mathbf{x})$ can be Taylor expanded. Using these results, it takes very little to show that the Heisenberg's equations of motions for $\hat{\mathbf{x}}_{\mathrm{H}}(t)$ and $\hat{\mathbf{p}}_{\mathrm{H}}(t)$ read as follows:

$$\begin{cases} \dfrac{\mathrm{d}\hat{x}_{j,\mathrm{H}}}{\mathrm{d}t} &= \dfrac{\hat{p}_{j,\mathrm{H}}}{m} \\[2ex] \dfrac{\mathrm{d}\hat{p}_{j,\mathrm{H}}}{\mathrm{d}t} &= -\nabla_j V(\hat{\mathbf{x}}_{\mathrm{H}}) \end{cases} \; . \tag{3.57}$$

Consider now the expectation values of position and momentum which we briefly denote by $\langle\hat{\mathbf{x}}\rangle_t \overset{\mathrm{def}}{=} \langle\psi(t)|\hat{\mathbf{x}}|\psi(t)\rangle$ and $\langle\hat{\mathbf{p}}\rangle_t \overset{\mathrm{def}}{=} \langle\psi(t)|\hat{\mathbf{p}}|\psi(t)\rangle$. Using Heisenberg's equations you immediately conclude that:

$$\begin{cases} \dfrac{\mathrm{d}}{\mathrm{d}t}\langle\hat{\mathbf{x}}\rangle_t &= \dfrac{\langle\hat{\mathbf{p}}\rangle_t}{m} \\[2ex] \dfrac{\mathrm{d}}{\mathrm{d}t}\langle\hat{\mathbf{p}}\rangle_t &= -\langle\psi(t)|\boldsymbol{\nabla}V(\hat{\mathbf{x}})|\psi(t)\rangle \end{cases} \; . \tag{3.58}$$

Notice that the last equation is non-classical, because in general

$$\langle\psi(t)|\boldsymbol{\nabla}V(\hat{\mathbf{x}})|\psi(t)\rangle \neq \boldsymbol{\nabla}V(\langle\hat{\mathbf{x}}\rangle_t) \ .$$

And from this equation, you appreciate immediately the role of the non-linearities appearing in $V(\mathbf{x})$. Indeed, if $V(\mathbf{x})$ is quadratic, then the expectation values of $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$ satisfy precisely the classical equations of motions of a system of harmonic oscillators. However, if non-linear terms appear in $V(\mathbf{x})$, then $\boldsymbol{\nabla}V(\hat{\mathbf{x}})$ involves higher powers of $\hat{\mathbf{x}}$, and you if try to generate their Heisenberg's equations, you keep generating other operators, in a never-ending system of coupled differential equations.

3.2.1. Diagonal ensemble and Eigenstate Thermalisation Hypothesis (ETH)

Ergodicity in quantum mechanics is a far from trivial concept, and von Neumann's work has stimulated a large body of literature in the last thirty years, aimed at understanding how a statistical description emerges from a fully coherent (unitary) Schrödinger dynamics. [18] Qualitatively, we might say that quantum mechanics provides a natural coarse-graining of "phase space", due to the uncertainty principle. Any initial wave-function has a finite width in position and momentum; because of "mixing", it gets spread all over the energy shell and the asymptotic expectation value of the observables coincides with the average on the micro-canonical ensemble [25]. To make these considerations more precise, in analogy with the analysis of classical trajectories in phase space sketched above, let us consider in more detail the dynamics of states in the Hilbert space and the average of observables. Consider some operator $\hat{A}$ and calculate its average on the time-evolved state $|\Psi(t)\rangle$:

$$\langle\hat{A}\rangle_t \equiv \langle\Psi(t)|\hat{A}|\Psi(t)\rangle = \sum_{\alpha,\alpha'} \mathrm{e}^{-i(E_{\alpha'}-E_\alpha)t/\hbar}\, c^*_\alpha\, c_{\alpha'}\, \underbrace{\langle\phi_\alpha|\hat{A}|\phi_{\alpha'}\rangle}_{[A]_{\alpha\alpha'}} \ .$$

Take now the integral over a large time T, as we did in the classical case:

$$\overline{\langle\hat{A}\rangle_t} \equiv \lim_{\mathrm{T}\to\infty}\frac{1}{\mathrm{T}}\int_0^{\mathrm{T}} \mathrm{d}t\, \langle\hat{A}\rangle_t = \lim_{\mathrm{T}\to\infty}\frac{1}{\mathrm{T}}\int_0^{\mathrm{T}} \mathrm{d}t\, \sum_{\alpha,\alpha'} \mathrm{e}^{-i(E_{\alpha'}-E_\alpha)t/\hbar}\, c^*_\alpha\, c_{\alpha'}\, [A]_{\alpha\alpha'} \ . \tag{3.59}$$

If you assume that the system is finite (so that the spectrum is discrete) and that $\widehat{H}$ is the only "constant of motion" (i.e., there are no other "symmetries" in the problem or any other operators that we might diagonalise simultaneously with $\widehat{H}$, getting a "crossing" of eigenvalues), then the eigenvalues will typically "*repel each other*" so that the gap between two different states is non-vanishing, i.e,

$$E_{\alpha'} - E_\alpha \neq 0 \qquad \text{if} \qquad \alpha \neq \alpha' \ . \tag{3.60}$$

Assuming such a *non-degenerate spectrum*, the time-integral reproduces a delta-function: [19]

$$\lim_{\mathrm{T}\to\infty}\frac{1}{\mathrm{T}}\int_0^{\mathrm{T}} \mathrm{d}t\, \mathrm{e}^{-i(E_{\alpha'}-E_\alpha)t/\hbar} = \delta_{E_\alpha,E_{\alpha'}} = \delta_{\alpha,\alpha'} \ .$$

Here, the infinite-time-average of $\hat{A}$ becomes:

$$\begin{array}{rcl} \overline{\langle\hat{A}\rangle_t} & = & \displaystyle\sum_\alpha |c_\alpha|^2 [A]_{\alpha\alpha} = \mathrm{Tr}\left[\hat{\rho}_{\mathrm{diag}}\hat{A}\right] \equiv \langle\hat{A}\rangle_{\mathrm{diag}} \\ & \text{where} & \\ \hat{\rho}_{\mathrm{diag}} & \equiv & \displaystyle\sum_\alpha |c_\alpha|^2 |\phi_\alpha\rangle\langle\phi_\alpha| \end{array} \ . \tag{3.61}$$

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[18] For this section I am particularly in debt with Angelo Russomanno and Silvia Pappalardi.

[19] For a many-body system, energy eigenvalues are extensive, i.e., proportional to the number of particles N, while the number of eigenstates in the spectrum increases *exponentially* with N: hence, the typical energy splitting δ_E is *exponentially small* in N. Technically, the time T you would need to distinguish two such eigenstates differing by δ_E should be fantastically large, larger than the so-called *Heisenberg time*:

$$\mathrm{T} \gg \mathrm{T}_{\mathrm{Heis}} \sim \frac{2\pi\hbar}{\delta_E} \sim \mathrm{e}^N \ .$$

The object we have introduced is a density matrix constructed out of the coefficients $|c_\alpha|^2$, and is usually called the *diagonal ensemble* density matrix. You can regard it as a time-average of the original pure-state density matrix $\hat{\rho}(t) = |\Psi(t)\rangle\langle\Psi(t)|$:

$$\overline{|\Psi(t)\rangle\,\langle\Psi(t)|} = \lim_{\mathrm{T}\to\infty} \frac{1}{\mathrm{T}} \int_0^{\mathrm{T}} \mathrm{d}t \sum_{\alpha,\alpha'} \mathrm{e}^{-i(E_{\alpha'}-E_\alpha)t/\hbar}\, c_\alpha^*\, c_{\alpha'}\, |\phi_{\alpha'}\rangle\langle\phi_\alpha| = \sum_\alpha |c_\alpha|^2\, |\phi_\alpha\rangle\,\langle\phi_\alpha| \equiv \hat{\rho}_{\mathrm{diag}}\;. \tag{3.62}$$

So far, there is no hint of ergodicity in the Hilbert space, and the diagonal ensemble *cannot* be regarded as a statistical description of our system, as its construction depends explicitly on the very large number of constants of motion $|c_\alpha|^2$ which are determined by the *initial state* $|\Psi_0\rangle$.

What we would aim at, is that the result of the average can be equivalently expressed by what we might call the *micro-canonical density matrix*

$$\hat{\rho}_{\mu\mathrm{CE}}(E) = \frac{1}{\mathcal{N}_{\mu\mathrm{CE}}(E)} \sum_\alpha \mathrm{I}_{\mu\mathrm{CE}}(E_\alpha)\, |\phi_\alpha\rangle\,\langle\phi_\alpha|\;, \tag{3.63}$$

where $\mathrm{I}_{\mu\mathrm{CE}}(\cdot)$ is the indicator function of the micro-canonical energy shell interval [20] $[E-\frac{\Delta_E}{2}, E+\frac{\Delta_E}{2}]$, and the normalisation, $\mathrm{Tr}[\hat{\rho}_{\mu\mathrm{CE}}] = 1$, requires:

$$\mathcal{N}_{\mu\mathrm{CE}}(E) = \sum_\alpha \mathrm{I}_{\mu\mathrm{CE}}(E_\alpha) = \text{ Number of energy eigenvalues in } [E-\tfrac{\Delta_E}{2}, E+\tfrac{\Delta_E}{2}] \equiv \mathrm{Shell}(E)\;. \tag{3.64}$$

Here, as in the classical case, the *Boltzmann's fundamental hypothesis* would be to assume that the number of states in the micro-canonical shell is essentially the exponential of the thermodynamic entropy

$$\mathcal{N}_{\mu\mathrm{CE}}(E) = \sum_\alpha \mathrm{I}_{\mu\mathrm{CE}}(E_\alpha) \;\simeq\; \mathrm{e}^{S(E,\underline{\mathrm{X}})/k_B}\;, \tag{3.65}$$

$\underline{\mathrm{X}}$ being the remaining extensive conserved quantities present in the Hamiltonian (for instance V and N for a simple fluid). Let us stress here that, in a many-body system, the total number of eigenstates is exponentially large in N, while the energies are extensive: hence, you can allow yourself a micro-canonical width Δ_E with a rather large freedom, for instance sub-extensive: $\Delta_E \propto N^\alpha$ with $\frac{1}{2} < \alpha < 1$.

Such a micro-canonical description is expected to hold for all those initial states $|\Psi_0\rangle$ whose $c_\alpha \neq 0$ only for $E_\alpha \in \mathrm{Shell}(E_0)$. If you recall that the energy fluctuations ΔE_0 are assumed to be sub-extensive, $\Delta E_0 \propto \sqrt{N}$, then it is enough to take a shell width $\Delta_E \propto N^\alpha$ with $\alpha > \frac{1}{2}$ to guarantee that *essentially all* energy eigenstates contributing to $|\Psi_0\rangle$ fall inside the micro-canonical shell $\mathrm{Shell}(E_0)$, for large N. But still, the micro-canonical density matrix corresponds to having *constant* $|c_\alpha|^2 = 1/\mathcal{N}_{\mu\mathrm{CE}}$ over the whole energy shell $\mathrm{Shell}(E_0)$, while the c_α of the initial state are definitely not constant.

We seem to have reached a paradox: on the one hand, if the observables relax to some steady-state value, the latter has to be given by the average over the diagonal ensemble in Eq. (3.62); on the other hand, if there is thermalisation, any detailed information on the *initial state* must be forgotten, and such a steady-state value should coincide with the micro-canonical average:

$$\langle\hat{A}\rangle_{\mu\mathrm{CE}}(E_0) \equiv \mathrm{Tr}\left[\hat{A}\,\hat{\rho}_{\mu\mathrm{CE}}(E_0)\right]\;, \tag{3.66}$$

associated to the density matrix in Eq. (3.63) for the energy shell $\mathrm{Shell}(E_0)$.

Borrowing a paragraph from Wikipedia:

> In principle it is thus an open question as to whether an isolated quantum mechanical system, prepared in an arbitrary initial state, will approach a state which resembles thermal equilibrium,

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[20] We take here a more symmetric energy shell, centred at the energy E with width Δ_E.

> in which a handful of observables are adequate to make successful predictions about the system. However, a variety of experiments in cold atomic gases have indeed observed thermal relaxation in systems which are, to a very good approximation, completely isolated from their environment, and for a wide class of initial states [26,27]. The task of explaining this experimentally observed applicability of equilibrium statistical mechanics to isolated quantum systems is the primary goal of the Eigenstate Thermalisation Hypothesis (ETH). [....] The principal philosophy underlying the ETH is that instead of explaining the ergodicity of a thermodynamic system through the mechanism of dynamical chaos, as is done in classical mechanics, one should instead examine the properties of matrix elements of observable quantities in individual energy eigenstates of the system.

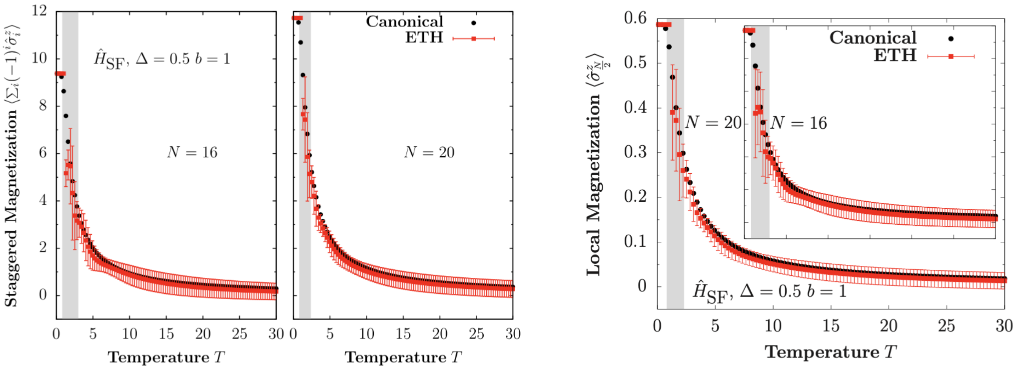

Figure 3.9.: Test of ETH on the Heisenberg chain model with a staggered field, to break integrability. Notice decrease of the variance of the various diagonal matrix elements (denoted by ETH) for increasing N. Notice also the grey shaded low-temperature region, where the low-energy part of the spectrum shows the most prominent deviations from ETH. Figure taken from Ref. [28].

To solve this apparent paradox, and understand the mechanism behind thermalisation, one has to look at the properties of the observables and their matrix elements. To make the following discussion less abstract, let us write down a concrete non-integrable model for which we expect thermalisation to occur. Take a spin chain composed of N spin-1/2, in a perturbed variant of the so-called XXZ Heisenberg chain:

$$\widehat{H} = \underbrace{J \sum_{j=1}^{N-1} \left(\hat{\sigma}_j^x \hat{\sigma}_{j+1}^x + \hat{\sigma}_j^y \hat{\sigma}_{j+1}^y + \Delta\, \hat{\sigma}_j^z \hat{\sigma}_{j+1}^z \right)}_{\text{Heisenberg XXZ}} + b \sum_{j \text{ even}} \hat{\sigma}_j^z \ . \tag{3.67}$$

For $b = 0$ we have a Heisenberg chain model, which is Bethe Ansatz integrable when periodic boundary conditions (PBC) are used. The phase diagram of this model has three phases as a function of the anisotropy Δ: a Néel antiferromagnetic phase, for $\Delta > 1$, a ferromagnetic phase for $\Delta < -1$, and a Luttinger liquid phase for $-1 < \Delta < 1$. For $\Delta > 0$ the nearest-neighbour correlations between spins are antiferromagnetic, but a proper antiferromagnetic long-range order (LRO) is possible only in the Néel phase for $\Delta > 1$. The role of b is to *break integrability.*

What has been found is that, in many cases, thermalisation of *local observables* — both extensive but also fully local (see below) — occurs at the level of their expectation values on *each single eigenstate*: given any energy eigenstate $|\phi_\alpha\rangle$ with energy E_α, the matrix element of the observable $\hat{A}$ on $|\phi_\alpha\rangle$ "equals" the micro-canonical average: [21]

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[21] A more general version of ETH can be given for all the matrix elements, in the form:

$$[A]_{\alpha\alpha'} \equiv \langle \phi_\alpha | \hat{A} | \phi_{\alpha'} \rangle \simeq \delta_{\alpha,\alpha'} A_{\mu\rm CE}(E_\alpha) + \mathrm{e}^{-S(\bar{E})/2k_B} f_{\hat{A}}(\bar{E},\omega)\, \xi_{\alpha,\alpha'} \ , \tag{3.68}$$

where $\bar{E} = (E_\alpha + E_{\alpha'})/2$ and $\hbar\omega = E_{\alpha'} - E_\alpha$.

$$[A]_{\alpha\alpha} \equiv \langle\phi_\alpha|\,\hat{A}\,|\phi_\alpha\rangle \simeq A_{\mu\mathrm{CE}}(E_\alpha) + \mathrm{e}^{-S(E_\alpha)/2k_B} f_{\hat{A}}(E_\alpha)\,\xi_\alpha \;. \tag{3.69}$$

where $A_{\mu\mathrm{CE}}(E) = \langle\hat{A}\rangle_{\mu\mathrm{CE}}(E)$ is a short-hand notation for micro-canonical average. This assumption is called *Eigenstate Thermalisation Hypothesis* (ETH). Here "equals" means "*up to an exponentially small fluctuating term*" (notice the entropy factor), where $f_{\hat{A}}(E)$ is a smooth function and ξ_α a random number with 0 mean and unit variance. To exemplify the concept of *local observable* consider, in the spin-chain example given above, $\hat{A} = \hat{\sigma}^z_j$, the spin at a given site j; but also

$$\hat{A} = \sum_j^{\text{region}} (-1)^j \hat{\sigma}^z_j \;, \tag{3.70}$$

the staggered magnetization calculated for all spins in a certain (extensive) region of the system.

ETH implies that, by taking an initial state $|\Psi_0\rangle$ with overlaps c_α restricted to the micro-canonical energy shell Shell(E_0), the time-average of the observable equals its micro-canonical average: [22]

$$\overline{\langle\hat{A}\rangle_t} \equiv \overline{\langle\Psi(t)|\,\hat{A}\,|\Psi(t)\rangle} = \sum_\alpha |c_\alpha|^2\;[A]_{\alpha\alpha} \simeq \langle\hat{A}\rangle_{\mu\mathrm{CE}}(E_0)\;. \tag{3.71}$$

Figure 3.9, taken from Ref. [28], illustrates the validity of ETH for the non-integrable variant of the Heisenberg spin chain model presented above, with $\Delta = 0.5$ and $b/J = 1$. Notice the comparison of the various diagonal matrix elements (denoted by ETH) with the Gibbs ensemble calculation (rather than the micro-canonical average) as a function of T, calculated from the derivative of the total entropy with respect to E.

Moreover, one can give arguments showing that $\langle\Psi(t)|\,\hat{A}\,|\Psi(t)\rangle$ will stay "for most of the time" close to the micro-canonical average, with small time-fluctuations whose importance vanishes in the thermodynamic limit. [23]

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[22] The algebra is simple. Neglecting the exponentiallly small entropy-related correction, we need to consider $A_{\mu\mathrm{CE}}(E_\alpha)$ which can be Taylor expanded up to second-order around $E_0 = N\varepsilon_0$ as follows:

$$A_{\mu\mathrm{CE}}(E_\alpha) = A_{\mu\mathrm{CE}}(E_0) + \frac{(E_\alpha - E_0)}{N} A'_{\mu\mathrm{CE}}(\varepsilon_0) + \frac{(E_\alpha - E_0)^2}{2N^2} A''_{\mu\mathrm{CE}}(\varepsilon_0) + \cdots$$

The first-order correction vanishes by definition, while the second-order term is proportional to $\Delta E_0^2/N^2$, and hence gives $O(1/N)$ corrections by the assumed sub-extensivity of ΔE_0.

[23] Time fluctuations of the expectation around the thermal average originate from the off-diagonal terms $[A]_{\alpha\alpha'}$

$$(\delta A_{\mathrm{time}})^2 = \overline{\Big[\langle\Psi(t)|\,\hat{A} - \overline{\langle\hat{A}\rangle_t}\,|\Psi(t)\rangle^2\Big]} = \sum_{\alpha\neq\alpha'} |c_\alpha|^2\,|[A]_{\alpha\alpha'}|^2\,|c_{\alpha'}|^2\;. \tag{3.72}$$

If we assume that the off-diagonal matrix elements $[A]_{\alpha\alpha'}$ fluctuate little with α and α' around their typical value $[A]^{\mathrm{typ}}_{\alpha\alpha'}$, we can use the ETH to show that they are very small. This can be easily done by considering, for each eigenstate $|\phi_\alpha\rangle$, the expectation value of the quantum fluctuation operator $(\hat{A} - [A]_{\alpha\alpha})^2$. Such expectation, because of ETH, has to be equal to its micro-canonical value; it can be argued to be of order 1 if $\hat{A}$ is a local operator [29] or, at most, order N if $\hat{A}$ is an extensive operator, the sum of local operators. Hence, at worst we find

$$N \sim \langle\phi_\alpha|\,(\hat{A} - [A]_{\alpha\alpha})^2\,|\phi_\alpha\rangle = \sum_{\alpha'}^{\neq\alpha} |[A]_{\alpha\alpha'}|^2 \simeq \mathrm{e}^{S(E)/k_B}\left|[A]^{\mathrm{typ}}_{\alpha\alpha'}\right|^2 \tag{3.73}$$

where $S(E) = k_B \log \mathcal{N}_{\mu\mathrm{CE}}(E)$ is the entropy on the energy shell, which is extensive in N. Therefore, substituting $|[A]^{\mathrm{typ}}_{\alpha\alpha'}|^2 \sim N\mathrm{e}^{-S(E)/k_B}$ in place of $|[A]_{\alpha\alpha'}|^2$ in Eq. (3.72), we can estimate the time fluctuations of $\hat{A}$ as

$$(\delta A_{\mathrm{time}})^2 \sim N\mathrm{e}^{-S(E)/k_B}\;.$$

In many-body systems, since the entropy is extensive, this quantity is exponentially small in N. Therefore, ETH implies the relaxation of the expectations of the observables to the thermal average.

Time fluctuations should not be confused with quantum fluctuations which, for each t, give an uncertainty

$$\delta A_t^2 = \langle\Psi(t)|(\hat{A} - \langle\hat{A}\rangle_t)^2|\Psi(t)\rangle\;.$$

3.3. From the micro-canonical to the canonical ensemble

Summarising what we discussed in the previous sections, for a closed quantum system obeying the ETH we can calculate averages of observables through the micro-canonical ensemble. The prescriptions are the following:

$$\textbf{Quantum } \mu\text{CE} \quad \left\{ \begin{array}{rcll} \langle \hat{A} \rangle_{\mu\text{CE}} & \equiv & \mathrm{Tr}\left[\hat{A}\,\hat{\rho}_{\mu\text{CE}}\right] & \\ \hat{\rho}_{\mu\text{CE}} & = & \dfrac{1}{\mathcal{N}_{\mu\text{CE}}} \displaystyle\sum_{\alpha} \mathrm{I}_{\mu\text{CE}}(E_\alpha)\; |\phi_\alpha\rangle \, \langle\phi_\alpha| & \\ \mathcal{N}_{\mu\text{CE}}(E) & = & \displaystyle\sum_{\alpha} \mathrm{I}_{\mu\text{CE}}(E_\alpha) \quad \overset{\text{Boltzmann}}{\simeq} & \mathrm{e}^{S(E,\underline{X})/k_B} \end{array} \right. . \tag{3.74}$$

An essentially identical prescription holds in the classical ergodic case, where the difference is essentially only in the way we calculate the number of states:

$$\textbf{Classical } \mu\text{CE} \quad \left\{ \begin{array}{rcll} \langle A \rangle_{\mu\text{CE}} & \equiv & \int \mathrm{d}\mu \; A(\mathbf{x})\, \rho_{\mu\text{CE}}(\mathbf{x}) & \\ \rho_{\mu\text{CE}}(\mathbf{x}) & = & \dfrac{1}{\mathcal{N}_{\mu\text{CE}}} \, \mathrm{I}_{\mu\text{CE}}(H(\mathbf{x})) & \\ \mathcal{N}_{\mu\text{CE}}(E) & = & \displaystyle\int \mathrm{d}\mu \; \mathrm{I}_{\mu\text{CE}}(H(\mathbf{x})) \quad \overset{\text{Boltzmann}}{\simeq} & \mathrm{e}^{S(E,\underline{X})/k_B} \end{array} \right. . \tag{3.75}$$

The whole of thermodynamics follows from the knowledge of $S(E,\underline{X})$. But the calculation of the available number of states in the micro-canonical energy shell is non-trivial for all except a few highly idealised situations.

As discussed in the introductory lectures, a Laplace transform, *alias* switching to the canonical ensemble, where the temperature T is the control parameter and $F(T,\underline{X})$ is the fundamental quantity, would simplify the calculations enormously. The entropy $S(E,\underline{X})$ and the Helmholtz free-energy $F(T,\underline{X})$ contain the same information, and, provided the system under consideration is *thermodynamically large* and forces are *short ranged*, one can use the micro-canonical ensemble or the canonical one, and it should make no difference: this concept is usually called *equivalence of the ensembles*, and you can find rigorous approaches where these matters are clarified (see for instance the books by Ruelle or Gallavotti).

Here I want to show that there is a different route by which the canonical ensemble can be "derived" (under the appropriate hypothesis of infinitesimally small coupling to a large bath), a route that does not require that the system under consideration is thermodynamically large: you can do statistical mechanics of a *small system* (a single spin, or a single atom), as long as this system is in contact with a *bath* which is thermodynamically large.

Let us see how to "derive" the quantum canonical ensemble starting from $\hat{\rho}_{\mu\text{CE}}$, by using the device of regarding the system we are interested in as a *subsystem* of a much larger system $S \cup B$ with Hilbert space $\mathcal{H}_S \otimes \mathcal{H}_B$, comprising the system (S, with Hilbert space $\mathcal{H}_S$) and a large reservoir "bath" (B, with Hilbert space $\mathcal{H}_B$).

What we have still to verify is that fluctuations around the micro-canonical average coincide with thermal fluctuations. General statistical mechanics arguments predict fluctuations scaling like $1/\sqrt{N}$ with respect to the thermal average. The exponentially small time-fluctuations are indeed not enough: we need to consider also the contribution of quantum fluctuations $\langle\Psi(t)|(\hat{A} - \langle\hat{A}\rangle_t)^2|\Psi(t)\rangle$ which, analytically in the general semiclassical chaotic case [30] and through numerical experiments on an ergodic hard-core bosons model [26], have been shown to behave as expected.

Infinitesimal coupling assumption. We will assume that the Hamiltonian of the combined system is:

$$\widehat{H} = \widehat{H}_S + \widehat{H}_B + \epsilon \widehat{H}_{SB} \ , \tag{3.76}$$

where $\widehat{H}_{S/B}$ is the Hamiltonian of the System/Bath, while $\widehat{H}_{SB}$ is the System-Bath interaction, which we assume to be present — to allow energy exchange between S and B — but *infinitesimally small*. The factor ϵ in Eq. (3.76) reminds us of that assumption. Due to this assumption, the energy eigenstates of $\widehat{H}$ are given by *products* of eigenstates $|\phi_\alpha\rangle$ of $\widehat{H}_S$, with energy E_α, and eigenstates $|\Phi_b\rangle$ of $\widehat{H}_B$, with energy E_b. I will denote them by $|\phi_\alpha, \Phi_b\rangle = |\phi_\alpha\rangle \otimes |\Phi_b\rangle$, with a corresponding energy is $E^{\mathrm{tot}}_{\alpha,b} = E_\alpha + E_b$.

Consider now an operator $\hat{A}_S$ which acts *only on the system Hilbert space* $\mathcal{H}_S$, and calculate the full micro-canonical average according to the prescriptions given above:

$$\langle \hat{A}_S \rangle_{\mu\mathrm{CE}} = \mathrm{Tr}_{S\cup B} \Big[\hat{A}_S \, \hat{\rho}_{\mu\mathrm{CE}} \Big] = \mathrm{Tr}_S \Big[\hat{A}_S \, \underbrace{\mathrm{Tr}_B \, \hat{\rho}_{\mu\mathrm{CE}}}_{\hat{\rho}_S} \Big] = \mathrm{Tr}_S \Big[\hat{A}_S \, \hat{\rho}_S \Big] \ ,$$

where:

$$\hat{\rho}_{\mu\mathrm{CE}} = \frac{1}{\mathcal{N}_{\mu\mathrm{CE}}} \sum_{\alpha,b} \mathrm{I}_{\mu\mathrm{CE}}(E_\alpha + E_b) \, |\phi_\alpha, \Phi_b\rangle \, \langle \phi_\alpha, \Phi_b| \ . \tag{3.77}$$

Our goal is to show that, if the bath B is a very large system, then the reduced density matrix $\hat{\rho}_S$ acting on the system, S is the *canonical Gibbs ensemble* density matrix

$$\hat{\rho}_S = \hat{\rho}_{\mathrm{CE}} = \frac{\mathrm{e}^{-\beta \widehat{H}_S}}{\mathrm{Tr}_S \, \mathrm{e}^{-\beta \widehat{H}_S}} \qquad \text{with} \qquad \beta = \frac{1}{k_B T} = \frac{1}{k_B} \frac{\partial S_B}{\partial E} \ , \tag{3.78}$$

where T is the temperature set by the bath through the usual thermodynamic relationship in terms of the entropy of the bath $S_B(E, \underline{\mathrm{X}})$.

To show this, let us start observing that

$$\begin{aligned}
\hat{\rho}_S = \mathrm{Tr}_B \, \hat{\rho}_{\mu\mathrm{CE}} &= \sum_{b'} \langle \Phi_{b'} | \sum_{\alpha,b} \frac{\mathrm{I}_{\mu\mathrm{CE}}(E_\alpha + E_b)}{\mathcal{N}_{\mu\mathrm{CE}}(E)} \, |\phi_\alpha, \Phi_b\rangle \, \langle \phi_\alpha, \Phi_b| \, |\Phi_{b'}\rangle \\
&= \sum_{\alpha,b} \frac{\mathrm{I}_{\mu\mathrm{CE}}(E_\alpha + E_b)}{\mathcal{N}_{\mu\mathrm{CE}}(E)} \, |\phi_\alpha\rangle \, \langle \phi_\alpha| \\
&= \sum_{\alpha} \frac{\mathcal{N}^B_{\mu\mathrm{CE}}(E - E_\alpha)}{\mathcal{N}_{\mu\mathrm{CE}}(E)} \, |\phi_\alpha\rangle \, \langle \phi_\alpha| = \sum_\alpha P_\alpha \, |\phi_\alpha\rangle \, \langle \phi_\alpha| \ .
\end{aligned} \tag{3.79}$$

In this derivation, I have used the fact that:

$$\sum_b \mathrm{I}_{\mu\mathrm{CE}}(E_\alpha + E_b) = \mathcal{N}^B_{\mu\mathrm{CE}}(E - E_\alpha) \ ,$$

in terms of the number of bath states in the micro-canonical shell at $E - E_\alpha$. Moreover, we can re-express the full $\mathcal{N}_{\mu\mathrm{CE}}(E)$ as a convolution, as follows:

$$\begin{aligned}
\mathcal{N}_{\mu\mathrm{CE}}(E) &= \sum_{\alpha,b} \mathrm{I}_{\mu\mathrm{CE}}(E_\alpha + E_b) = \sum_\alpha \mathcal{N}^B_{\mu\mathrm{CE}}(E - E_\alpha) \\
&= \int_0^\infty \mathrm{d}E_s \, \sum_{\alpha,b} \delta(E_s - E_\alpha) \, \mathrm{I}_{\mu\mathrm{CE}}(E_s + E_b) \\
&= \int_0^\infty \mathrm{d}E_s \, \underbrace{\sum_\alpha \delta(E_s - E_\alpha)}_{\Omega_S(E_s)} \, \underbrace{\sum_b \mathrm{I}_{\mu\mathrm{CE}}(E_s + E_b)}_{\mathcal{N}^B_{\mu\mathrm{CE}}(E - E_s)} \\
&= \int_0^\infty \mathrm{d}E_s \, \Omega_S(E_s) \, \mathcal{N}^B_{\mu\mathrm{CE}}(E - E_s) \ ,
\end{aligned} \tag{3.80}$$

where I have introduced the *many-body density of states* for the system eigenvalues: [24]

$$\Omega_S(E_s) = \sum_\alpha \delta(E_s - E_\alpha) \; . \tag{3.81}$$

Observe that the weights P_α appearing in the mixed state $\hat{\rho}_S$ are correctly normalised:

$$\sum_\alpha P_\alpha = \sum_\alpha \frac{\mathcal{N}^B_{\mu\mathrm{CE}}(E-E_\alpha)}{\mathcal{N}_{\mu\mathrm{CE}}(E)} = 1 \; . \tag{3.82}$$

So far, no approximation was made.

Now the crucial assumption is made that the bath is *large*, hence $\mathcal{N}^B_{\mu\mathrm{CE}}(E-E_s) \simeq \mathrm{e}^{S_B(E-E_s)/k_B}$ is exponentially large, and the integral appearing in Eq. (3.80) will be dominated by the *maximum* of the integrand $\mathrm{e}^{\log\Omega_S(E_s)+S_B(E-E_s)/k_B}$ — recall the Laplace method discussed in the introductory lectures —, which occurs at an energy E_* such that:

$$\frac{\partial}{\partial E_s}\log\Omega_S(E_s)\bigg|_{E_*} = \frac{1}{k_B}\frac{\partial}{\partial E}S_B(E-E_*) \; . \tag{3.83}$$

The energy E_* represents the *average* “energy share” that the system gets from the contact with the large bath, as we have seen in thermodynamics, when discussing equilibrium in presence of a thermal conduction wall. This exponential dominance implies that the bath entropy can be safely expanded close to $E_s = E_*$ and the expansion can be stopped at the *linear order* into the deviation $E_s - E_*$:

$$S_B(E-E_s) = S_B(E-E_*) + \frac{1}{T}(E_* - E_s) + \cdots \tag{3.84}$$

because $|E_* - E_s|$ — which will span in the end the spectrum of the system S — is very small on the scale of the energies of the bath (and of the total energy E). Hence, we can re-express, with the usual shorthand $\beta = 1/(k_B T)$:

$$\mathcal{N}^B_{\mu\mathrm{CE}}(E-E_s) \simeq \mathrm{e}^{S_B(E-E_s)/k_B} \approx \mathrm{e}^{S_B(E-E_*)/k_B}\,\mathrm{e}^{\beta(E_*-E_s)} \; .$$

Using this approximation we can easily see that:

$$\begin{aligned}\mathcal{N}_{\mu\mathrm{CE}}(E) \approx \int_0^\infty \mathrm{d}E_s\, \Omega_S(E_s)\,\mathrm{e}^{S_B(E-E_*)/k_B}\mathrm{e}^{\beta(E_*-E_s)} &= \underbrace{\int_0^\infty \mathrm{d}E_s\, \Omega_S(E_s)\,\mathrm{e}^{-\beta E_s}}_{Z_S(\beta)}\; \mathrm{e}^{S_B(E-E_*)/k_B}\mathrm{e}^{\beta E_*} \\ &= Z_S(\beta)\; \mathrm{e}^{S_B(E-E_*)/k_B}\mathrm{e}^{\beta E_*} \; . \end{aligned} \tag{3.85}$$

Hence the weights P_α appearing in Eq. (3.79) for $\hat{\rho}_S$ are simply given by: [25]

$$P_\alpha = \frac{\mathcal{N}^B_{\mu\mathrm{CE}}(E-E_\alpha)}{\mathcal{N}_{\mu\mathrm{CE}}(E)} \approx \frac{\mathrm{e}^{-\beta E_\alpha}}{Z_S(\beta)} \; ,$$

where

$$Z_S(\beta) = \int_0^\infty \mathrm{d}E_s\, \Omega_S(E_s)\,\mathrm{e}^{-\beta E_s} = \sum_\alpha \mathrm{e}^{-\beta E_\alpha} = \mathrm{Tr}_S\, \mathrm{e}^{-\beta \widehat{H}_S} \; , \tag{3.86}$$

is the canonical partition function.

Summarising, the quantum canonical ensemble is defined, given the Hamiltonian $\widehat{H}$ of the system (we omit here the subscript S) as follows:

---

[24] In any finite quantum system with a discrete spectrum, this quantity would be a sum of very many (indeed exponentially many) Dirac's delta in any finite energy interval. It is simple to define an appropriate average of it in each finite energy interval Δ_E, which involves the (micro-canonical) entropy.

[25] Notice that the average reference energy E_* and the bath entropy $S_B(E-E_*)$ both cancel from the final result!

$$\textbf{Quantum CE}\quad \left\{ \begin{array}{lcl} \langle \hat{A} \rangle_{\mathrm{CE}}(T,\underline{X}) & \equiv & \mathrm{Tr}\left[\hat{A}\,\hat{\rho}_{\mathrm{CE}}\right] \\ \hat{\rho}_{\mathrm{CE}} & = & \dfrac{1}{Z_{\mathrm{CE}}} \displaystyle\sum_{\alpha} \mathrm{e}^{-\beta E_\alpha}\, |\phi_\alpha\rangle\,\langle\phi_\alpha| = \dfrac{\mathrm{e}^{-\beta\widehat{H}}}{Z_{\mathrm{CE}}} \\ Z_{\mathrm{CE}} & = & \displaystyle\sum_{\alpha} \mathrm{e}^{-\beta E_\alpha} = \mathrm{Tr}\,\mathrm{e}^{-\beta\widehat{H}} \quad \overset{\text{Thermodynamics}}{\equiv} \quad \mathrm{e}^{-\beta F(T,\underline{X})} \end{array} \right. . \tag{3.87}$$

To verify that indeed thermodynamics requires that $Z_{\mathrm{CE}} = \mathrm{e}^{-\beta F}$, let us consider the average energy $E(T,\underline{X}) = \langle\widehat{H}\rangle_{\mathrm{CE}}$, where $\underline{X}$ denotes as usual the extensive variables, such as $(N, V, \cdots)$, which are held fixed. On one hand, the canonical ensemble prescription gives:

$$E = \langle\widehat{H}\rangle_{\mathrm{CE}} = \sum_{\alpha} E_\alpha \frac{\mathrm{e}^{-\beta E_\alpha}}{Z_{\mathrm{CE}}} = -\frac{\partial}{\partial\beta} \log Z_{\mathrm{CE}} \; . \tag{3.88}$$

On the other hand, thermodynamics requires that

$$E = F + TS = F - T\frac{\partial F}{\partial T} = F + \beta\frac{\partial F}{\partial\beta} = \frac{\partial}{\partial\beta}(\beta F) \; . \tag{3.89}$$

This shows [26] that indeed $\log Z_{\mathrm{CE}} = -\beta F$ is the correct thermodynamical identification.

The previous derivation can be repeated almost precisely in the classical case, where the prescriptions for the canonical ensemble read:

$$\textbf{Classical CE}\quad \left\{ \begin{array}{lcl} \langle A \rangle_{\mathrm{CE}}(T,\underline{X}) & \equiv & \int \mathrm{d}\mu\; A(\mathbf{x})\,\rho_{\mathrm{CE}}(\mathbf{x}) \\ \rho_{\mathrm{CE}}(\mathbf{x}) & = & \dfrac{\mathrm{e}^{-\beta H(\mathbf{x})}}{Z_{\mathrm{CE}}} \\ Z_{\mathrm{CE}} & = & \displaystyle\int \mathrm{d}\mu\; \mathrm{e}^{-\beta H(\mathbf{x})} \quad \overset{\text{Thermodynamics}}{\equiv} \quad \mathrm{e}^{-\beta F(T,\underline{X})} \end{array} \right. . \tag{3.90}$$

It is simple [27] to show that the entropy in the canonical ensemble can be given an explicit expression in terms of $\hat{\rho}_{\mathrm{CE}}$ as follows:

$$S(T,\underline{X}) = -k_B\langle\log\hat{\rho}_{\mathrm{CE}}\rangle_{\mathrm{CE}} \equiv -k_B\,\mathrm{Tr}\left[\hat{\rho}_{\mathrm{CE}}\log\hat{\rho}_{\mathrm{CE}}\right] = -k_B\sum_{\alpha} P_\alpha \log P_\alpha \; , \tag{3.91}$$

where $P_\alpha = \mathrm{e}^{-\beta E_\alpha}/Z_{\mathrm{CE}}$ is the Gibbs canonical probability of each *single eigenstate* of $\widehat{H}$. This shows a clear relationship between the thermodynamical entropy and the Shannon (or von Neumann) entropy.

The previous considerations should remind you of our discussion about Shannon entropy in the introductory lectures. [28] If we take

$$S[\{P_\alpha\}] = -k_B\sum_{\alpha} P_\alpha \log P_\alpha \; , \tag{3.92}$$

---

[26] A student was observing that this only fixes the two quantities, up to a temperature-independent function of the extensive variables $\underline{X}$.

[27] Use that

$$\hat{\rho}_{\mathrm{CE}} = \frac{\mathrm{e}^{-\beta\widehat{H}}}{Z_{\mathrm{CE}}} \quad \Longrightarrow \quad \log\hat{\rho}_{\mathrm{CE}} = -\beta\widehat{H} - \log Z_{\mathrm{CE}} \; ,$$

which immediately gives the correct thermodynamic relation $F = E - TS$ using $\langle\widehat{H}\rangle_{\mathrm{CE}} = E$ and $\log Z_{\mathrm{CE}} = -\beta F$.

[28] Recall that there we denoted the Shannon entropy as

$$H[\{P_\alpha\}] = -\sum_{\alpha} P_\alpha \log_2 P_\alpha = -k_S\sum_{\alpha} P_\alpha \log P_\alpha \qquad \text{with} \qquad k_S = \frac{1}{\log 2} \; .$$

to be the expression for the Gibbs-Shannon entropy of the "probability distribution" P_α, then maximising it in the presence of the normalisation constraint $\sum_\alpha P_\alpha = 1$ leads immediately to the micro-canonical distribution:

$$\mu\text{CE} \quad \begin{cases} P_\alpha &= \dfrac{\mathrm{I}_{\mu\text{CE}}(E_\alpha)}{\mathcal{N}_{\mu\text{CE}}} \\[2ex] \mathcal{N}_{\mu\text{CE}}(E) &= \displaystyle\sum_\alpha \mathrm{I}_{\mu\text{CE}}(E_\alpha) \\[2ex] S(E,\underline{\mathrm{X}}) &= k_B \log \mathcal{N}_{\mu\text{CE}}(E)\;. \end{cases} \quad . \tag{3.93}$$

In the canonical ensemble, the Gibbs-Shannon entropy distribution is maximised with the additional constraint that the average energy is fixed to be:

$$E = \sum_\alpha E_\alpha\, P_\alpha \;. \tag{3.94}$$

A simple calculation with the help of the Lagrange multiplier technique [29] show that the corresponding maximum for the total entropy now gives the canonical ensemble distribution:

$$\text{CE} \quad \begin{cases} P_\alpha &= \dfrac{\mathrm{e}^{-\beta E_\alpha}}{Z_{\text{CE}}} \\[2ex] Z_{\text{CE}} &= \displaystyle\sum_\alpha \mathrm{e}^{-\beta E_\alpha} \\[2ex] S(T,\underline{\mathrm{X}}) &= -k_B \displaystyle\sum_\alpha P_\alpha \log P_\alpha\;. \end{cases} \quad . \tag{3.97}$$

3.4. Probability distributions of observables in the canonical ensemble

The fact that you can calculate the expected values, and even the probability distributions, of observables that are beyond the realm of thermodynamics is one of the great advantages of the statistical approach.

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[29] We introduce two Lagrange multipliers, λ and β, and calculate the maximum of

$$\mathbb{S}[\{P_\alpha\},\lambda,\beta] = S[\{P_\alpha\}]/k_B - \lambda\left(\sum_\alpha P_\alpha - 1\right) - \beta\left(\sum_\alpha P_\alpha E_\alpha - E\right) \;.$$

The derivatives with respect to the multipliers, when set to 0, impose the constraints, as usual. The derivative with respect to P_α leads to:

$$-\log P_\alpha - 1 = \lambda + \beta E_\alpha \quad\Longrightarrow\quad P_\alpha = \frac{\mathrm{e}^{-\beta E_\alpha}}{\mathrm{e}^{1+\lambda}} \;.$$

Normalisation requires that

$$\mathrm{e}^{1+\lambda} = \sum_\alpha \mathrm{e}^{-\beta E_\alpha} \stackrel{\text{def}}{=} Z(\beta) \;. \tag{3.95}$$

Finally, a simple calculation shows that the constraint on E simply reads:

$$E = \sum_\alpha P_\alpha E_\alpha = \frac{1}{Z}\sum_\alpha E_\alpha \mathrm{e}^{-\beta E_\alpha} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \log Z}{\partial \beta} \;. \tag{3.96}$$

Beware of misunderstanding the Boltzmann weights. One common misunderstanding is to believe that $P_\alpha = \mathrm{e}^{-\beta E_\alpha}/Z_{\mathrm{CE}}$ represents the probability of observing an energy $E_s \approx E_\alpha$, while the correct interpretation is that P_α is the probability of observing the *single eigenstate* $|\phi_\alpha\rangle$ of energy E_α. In the classical framework, this would be similar to thinking that the probability of energy E_s is $\mathrm{e}^{-\beta E_s}/Z_{\mathrm{CE}}$, while you know that the latter is simply the probability density $\rho_{\mathrm{CE}}(\mathbf{x}) = \mathrm{e}^{-\beta H(\mathbf{x})}/Z_{\mathrm{CE}}$ in phase space, and a huge volume of phase space, which we should account for, shares the "same microcanonical" energy $E_s = H(\mathbf{x})$. In the Bernoulli trials with random strings of bits discussed in the introductory lectures, it would be similar to misunderstanding the probability of a single string, with the probability of strings having a certain number of 0s and 1s, which include large combinatorial — entropy related — factors.

Classically, you would indeed say that:

$$\begin{aligned}\mathrm{Prob}_H(E_s) &= \int \mathrm{d}\mu\, \delta(H(\mathbf{x})-E_s)\, \rho_{\mathrm{CE}}(\mathbf{x}) = \int \mathrm{d}\mu\, \delta(H(\mathbf{x})-E_s)\, \frac{\mathrm{e}^{-\beta H(\mathbf{x})}}{Z_{\mathrm{CE}}} \\ &= \int \mathrm{d}\mu\, \delta(H(\mathbf{x})-E_s) \frac{\mathrm{e}^{-\beta E_s}}{Z_{\mathrm{CE}}} = \Omega(E_s)\frac{\mathrm{e}^{-\beta E_s}}{Z_{\mathrm{CE}}} \propto \frac{\mathrm{e}^{-\beta(E_s - TS(E_s,\underline{X}))}}{Z_{\mathrm{CE}}} \,, \end{aligned} \tag{3.98}$$

where $\Omega(E_s)$ is the micro-canonical phase space density, which is connected to the micro-canonical entropy. We will return to this point further below.

Notation. Observe that E_s in the expression $\mathrm{Prob}_H(E_s)$ should be intended as the variable for the probability distribution, rather than the thermodynamical internal energy $E(T,\underline{X})$ which represents the *average* of the distribution:

$$E(T,\underline{X}) = \int_{-\infty}^{+\infty} \mathrm{d}E_s\, E_s\, \mathrm{Prob}_H(E_s) \,. \tag{3.99}$$

A similar reasoning would apply to any classical observable $A(\mathbf{x})$ — for instance, the kinetic energy $K(\mathbf{p})$ or the potential/interaction energy $V(\mathbf{q})$ — which has a probability distribution:

$$\mathrm{Prob}_A(a) = \int \mathrm{d}\mu\, \delta(A(\mathbf{x})-a)\, \rho_{\mathrm{CE}}(\mathbf{x}) = \int \mathrm{d}\mu\, \delta(A(\mathbf{x})-a)\, \frac{\mathrm{e}^{-\beta H(\mathbf{x})}}{Z_{\mathrm{CE}}} \,, \tag{3.100}$$

where, as you see, the quantity cannot be expressed simply in terms of the micro-canonical entropy.

Nevertheless, because momenta and positions are decoupled in $H(\mathbf{x}) = K(\mathbf{p}) + V(\mathbf{q})$, and that the kinetic energy is quadratic in the different momenta, it is relatively straightforward to calculate probability distributions involving only the velocity: you just have to perform Gaussian integrals. The well-known *Maxwell distribution* for the classical velocity comes from a similar calculation. A similar calculation for the probability distribution of the total kinetic energy $K(\mathbf{p})$ will show that the average kinetic energy is exactly given by:

$$\langle K\rangle_{\mathrm{CE}} = N\frac{d}{2}k_B T \,, \tag{3.101}$$

with a Gaussian probability distribution around the average which satisfies precisely the law of large numbers. Both are *exact results* at the classical level, independent of all interactions, [30] as you will learn from one of the problems proposed at the end of this Chapter. [31] The practical utility of the result on the average kinetic energy is quite relevant: in an NVE molecular dynamics simulation, you will be able to "measure" temperature by the average kinetic of your particles, as sketched in Fig. 3.10

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[30] The miracle is restricted to classical statistical mechanics. In the quantum case momenta and coordinates do not commute and the probability distributions of the momenta depend in general on the interactions.

[31] In school you often hear about these results in the context of *ideal gases*: they are much more general than that.

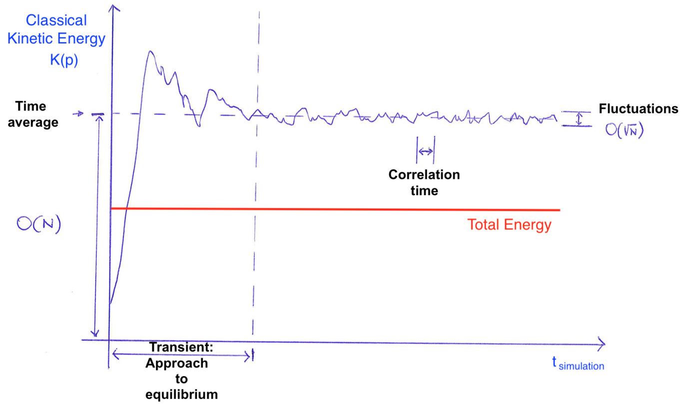

Figure 3.10: A sketch of the behaviour versus simulation time of a the kinetic energy of a classical system obeying Newton's equations, in the so-called NVE ensemble, where these variables are fixed. Kinetic energy fluctuates around an average given by $3Nk_BT/2$, while the total energy E is (in principle, at least) exactly conserved.

As you see, the probability distributions involve a nasty Dirac's delta, which might be painful to handle. One common trick is to consider the *Fourier transform* of the probability distribution:

$$g_A(k) = \int \mathrm{d}a \; \mathrm{e}^{-ika} \; \mathrm{Prob}_A(a) = \int \mathrm{d}\mu \; \mathrm{e}^{-ikA(\mathbf{x})} \; \frac{\mathrm{e}^{-\beta H(\mathbf{x})}}{Z_{\mathrm{CE}}} \;, \tag{3.102}$$

which might be easier to handle. Notice that $g_A(k)$ generates all the *moments* of the distribution $\mathrm{Prob}_A(y)$ by taking derivatives:

$$\left.\frac{\mathrm{d}^n}{\mathrm{d}k^n} g_A(k)\right|_{k=0} = (-i)^n \int \mathrm{d}\mu \; A^n(\mathbf{x}) \; \frac{\mathrm{e}^{-\beta H(\mathbf{x})}}{Z_{\mathrm{CE}}} = (-i)^n \langle A^n \rangle_{\mathrm{CE}} \;. \tag{3.103}$$

For this reason $g_A(y)$ is known as *moment generating function.*

Quantum observables. Let us now turn to the quantum case. If we have an observable represented by a Hermitian operator $\hat{A}$, von Neumann tells us that each individual measurement will give one of the possible eigenvalues a of $\hat{A}$. By writing the spectral representation of $\hat{A}$ as:

$$\hat{A} = \sum_a a \, \widehat{\Pi}^A_a \;, \tag{3.104}$$

where $\widehat{\Pi}_a$ is the *projector* [32] on the (possibly degenerate) subspace of eigenvectors associated to a, then you know that for a pure state $|\psi\rangle$, the probability of measuring the eigenvalue a is, according to von Neumann:

$$\langle\psi|\widehat{\Pi}^A_a|\psi\rangle = \sum_{j=1}^{d_a} |\langle\phi_{a,j}|\psi\rangle|^2 = \mathrm{Tr}\left(\widehat{\Pi}^A_a|\psi\rangle\langle\psi|\right) \;. \tag{3.106}$$

Hence, by linearity, for a state prepared according to the density matrix $\hat{\rho}_{\mathrm{CE}}$ you would predict that the probability of measuring the single eivenvalue a is

$$P_a = \langle\widehat{\Pi}^A_a\rangle_{\mathrm{CE}} = \mathrm{Tr}\left(\widehat{\Pi}^A_a \hat{\rho}_{\mathrm{CE}}\right) = \sum_\alpha \langle\phi_\alpha|\widehat{\Pi}^A_a|\phi_\alpha\rangle \frac{\mathrm{e}^{-\beta E_\alpha}}{Z_{\mathrm{CE}}} \;. \tag{3.107}$$

---

[32] If $|\phi_{a,j}\rangle$ are eigenstates of $\hat{A}$ associated to eigenvalue a, with a possible degeneracy $j = 1 \cdots d_a$, then

$$\widehat{\Pi}^A_a = \sum_{j=1}^{d_a} |\phi_{a,j}\rangle\langle\phi_{a,j}| \;. \tag{3.105}$$

Distribution and average of a quantum observable. This tells us that

$$\mathrm{Prob}_{\hat{A}}(x) = \sum_a \delta(a-x)\, P_a = \sum_a \delta(a-x)\ \mathrm{Tr}\left(\widehat{\Pi}^A_a \hat{\rho}_{\mathrm{CE}}\right) , \tag{3.108}$$

and, correspondingly

$$\langle \hat{A} \rangle_{\mathrm{CE}} = \int \mathrm{d}x\, x\, \mathrm{Prob}_{\hat{A}}(x) = \sum_a a P_a = \mathrm{Tr}\left(\hat{A}\, \hat{\rho}_{\mathrm{CE}}\right) . \tag{3.109}$$

In the particular case in which you consider the total energy, $\hat{A} = \widehat{H}$, since $P_\alpha = \mathrm{Tr}\left(\widehat{\Pi}_{E_\alpha} \hat{\rho}_{\mathrm{CE}}\right)$ is precisely the probability of observing the eigenstate with energy E_α — which we assume here to be non-degenerate — we deduce that:

$$\mathrm{Prob}_{\widehat{H}}(E_s) = \sum_\alpha \delta(E_\alpha - E_s) P_\alpha = \underbrace{\sum_\alpha \delta(E_\alpha - E_s)}_{\stackrel{\mathrm{def}}{=}\Omega(E_s)} \frac{\mathrm{e}^{-\beta E_s}}{Z_{\mathrm{CE}}} = \Omega(E_s) \frac{\mathrm{e}^{-\beta E_s}}{Z_{\mathrm{CE}}} . \tag{3.110}$$

As you see $\mathrm{Prob}_{\widehat{H}}(E_s)$ differs from $\mathrm{e}^{-\beta E_s}/Z_{\mathrm{CE}}$ by the (exponentially) large factor $\Omega_S(E_s)$, which is indeed related to the entropy. More about this in the next section.

3.4.1. Fluctuations of energy in the canonical ensemble

As we have seen, energy is not fixed in the canonical ensemble. The *average* energy $E(T, \underline{\mathrm{X}})$ can be directly calculated from the canonical partition function:

$$E(T, \underline{\mathrm{X}}) = \langle \widehat{H} \rangle_{\mathrm{CE}} = \frac{\sum_\alpha E_\alpha \mathrm{e}^{-\beta E_\alpha}}{Z_{\mathrm{CE}}} = -\frac{\partial \log Z_{\mathrm{CE}}}{\partial \beta} . \tag{3.111}$$

We can go beyond that, and calculate the *second cumulant* by taking a further derivative of $\log Z_{\mathrm{CE}}$:

$$\begin{aligned}
\frac{\partial^2 \log Z_{\mathrm{CE}}}{\partial \beta^2} &= \frac{\partial}{\partial \beta} \frac{\sum_\alpha (-E_\alpha \mathrm{e}^{-\beta E_\alpha})}{Z_{\mathrm{CE}}} = \frac{\sum_\alpha E_\alpha^2 \mathrm{e}^{-\beta E_\alpha} Z_{\mathrm{CE}} - \frac{\partial Z_{\mathrm{CE}}}{\partial \beta} \sum_\alpha (-E_\alpha \mathrm{e}^{-\beta E_\alpha})}{Z_{\mathrm{CE}}^2} \\
&= \frac{\sum_\alpha E_\alpha^2 \mathrm{e}^{-\beta E_\alpha}}{Z_{\mathrm{CE}}} - \frac{\sum_\alpha (-E_\alpha \mathrm{e}^{-\beta E_\alpha})}{Z_{\mathrm{CE}}} \frac{\sum_\alpha (-E_\alpha \mathrm{e}^{-\beta E_\alpha})}{Z_{\mathrm{CE}}} \\
&= \langle \widehat{H}^2 \rangle_{\mathrm{CE}} - \langle \widehat{H} \rangle_{\mathrm{CE}}^2 = \langle (\widehat{H} - \langle \widehat{H} \rangle_{\mathrm{CE}})^2 \rangle_{\mathrm{CE}} \geq 0 .
\end{aligned}$$

The variance is the specific heat. This immediately shows that the variance of the energy distribution is related to the specific heat at constant $(V, \underline{\mathrm{X}})$: [a]

$$\sigma_E^2 = \langle \widehat{H}^2 \rangle_{\mathrm{CE}} - \langle \widehat{H} \rangle_{\mathrm{CE}}^2 = -\frac{\partial E}{\partial \beta} = k_B T^2 \frac{\partial E}{\partial T} = k_B T^2 C_v . \tag{3.112}$$

---

[a] Recall that $C_v \geq 0$ was a requirement for thermodynamics stability. Here we see that, as a consistent check, its positivity emerges from the statistical relationship with the variance of the energy probability distribution.

The relationship $\frac{\partial E}{\partial T} = C_v$ — perhaps very intuitive from your basic notions of thermodynamics —

can be formally derived [33] from the definition

$$C_v(T,V,\underline{X}) = T\frac{\partial S}{\partial T}\bigg|_{V,\underline{X}} = \frac{\partial E}{\partial T}\bigg|_{V,\underline{X}} , \tag{3.113}$$

by using $F = E - TS$, $S = -\frac{\partial F}{\partial T}$. Notice that, since C_v and E are both extensive, $C_v \propto N$, this implies that the relative fluctuations of the energy decrease as $1/\sqrt{N}$ in the thermodynamic limit, unless the specific heat *diverges* (which can happen at second-order phase transition points):

$$\frac{\sigma_E}{E} \propto \frac{1}{\sqrt{N}} .$$

I remind you that $1/\sqrt{N}$ implies an amazing relative accuracy if N is of the order of the Avogadro number $\sim 10^{24}$: you measure energy to the fantastic accuracy of one part in 10^{-12}. We observe that the fact that the specific heat is proportional to the variance of the energy provides a practical way of calculating C_v from simulations, for instance by Monte Carlo.

But we can go even beyond that and argue that, in the thermodynamic limit, the full probability distribution of the energy goes — in a way entirely reminiscent of the law of large numbers — towards a Gaussian distribution centred at the average thermodynamic energy $E(T,\underline{X})$ and of width σ_E, as given above in terms of the specific heat C_v. To see this, I start from the basic definition for the distribution of energy in Eq. (3.110), using the notation E_s for the variable of the distribution to distinguish it clearly from the thermodynamical energy:

$$\mathrm{Prob}_{\hat{H}}(E_s) = \sum_\alpha \delta(E_s - E_\alpha) P_\alpha = \Omega(E_s)\frac{\mathrm{e}^{-\beta E_s}}{Z_{\mathrm{CE}}} \propto \frac{\mathrm{e}^{-\beta(E_s - TS(E_s))}}{Z_{\mathrm{CE}}} , \tag{3.114}$$

where I used the fact that the many-body density of states $\Omega(E_s)$, according to the Boltzmann hypothesis, is proportional to the micro-canonical entropy $S(E_s,\underline{X})$, i.e., $\Omega(E_s) \propto \mathrm{e}^{S(E_s)/k_B}$. The maximum of $\mathrm{Prob}_{\hat{H}}(E_s)$ is readily calculated by setting the derivative of $E_s - TS(E_s)$ to zero: [34]

$$0 = \frac{\partial}{\partial E_s}(E_s - TS(E_s,\underline{X})) \quad \Longrightarrow \quad \frac{1}{T} = \frac{\partial S}{\partial E_s}\bigg|_{E_s = E(T,\underline{X})} .$$

Hence the maximum of $\mathrm{Prob}_{\hat{H}}(E_s)$ is indeed at $E_s = E(T,\underline{X})$. Let us define $\delta E = E_s - E(T,\underline{X})$ to be the *deviation* of E_s from the average. Expanding the distribution close to the maximum we get the Gaussian form: [35]

$$\mathrm{Prob}_{\hat{H}}(E_s) \simeq \frac{1}{\sqrt{2\pi k_B T^2 C_v}}\, \mathrm{e}^{-\frac{(E_s - E)^2}{2k_B T^2 C_v}} . \tag{3.115}$$

---

[33] Indeed:

$$\frac{\partial E}{\partial T} = \frac{\partial F}{\partial T} + \frac{\partial (TS)}{\partial T} = -S + S + T\frac{\partial S}{\partial T} = T\frac{\partial S}{\partial T} .$$

[34] Note that the maximum is precisely located at the reference energy E_* we have discussed in Eq. (3.83).

[35] Notice that the expansion of the entropy $S(E+\delta E)$ gives:

$$S(E+\delta E) = S(E) + \frac{1}{T}(\delta E) + \frac{1}{2}\frac{\partial^2 S}{\partial E^2}(\delta E)^2 + \cdots$$

Next, you can show that

$$\frac{\partial^2 S}{\partial E^2} = \frac{\partial}{\partial E}\left(\frac{1}{T}\right) = -\frac{1}{T^2}\frac{1}{\frac{\partial E}{\partial T}} = -\frac{1}{T^2}\frac{1}{C_v} .$$

Imposing normalisation, or equivalently by setting $P(E_s) = \frac{\mathrm{e}^{-\beta(E_s - TS(E_s))}}{Z_{\mathrm{CE}}}$ with the partition function given by

$$Z_{\mathrm{CE}} = \int \mathrm{d}E_s\, \mathrm{e}^{-\beta(E_s - TS(E_s))} ,$$

and calculating the latter integral including the gaussian fluctuations, you end up with the expression in Eq. (3.115).

3.5. Revisiting thermodynamics: entropy, heat and work

If we are given the Hamiltonian $\widehat{H}$ of a system, the canonical ensemble average energy is simply $E = \langle \widehat{H} \rangle_{\text{CE}}$. Thermodynamics tells us that this should be intended as a function of T and of a set of extensive variables $\underline{\mathrm{X}}$ which directly appear in the Hamiltonian $\widehat{H}(\underline{\mathrm{X}})$ as "parameters" [36], for instance the volume V or the particle number N. As a consequence, the eigenvalues of $\widehat{H}$, as well as the Gibbs occupations factors $P_\alpha = \mathrm{e}^{-\beta E_\alpha}/Z_{\text{CE}}$, have to be intended to depend of $\underline{\mathrm{X}}$: $E_\alpha(\underline{\mathrm{X}})$, $P_\alpha(T, \underline{\mathrm{X}})$, with the further constraint that

$$\sum_\alpha P_\alpha(T, \underline{\mathrm{X}}) = 1 \; . \tag{3.116}$$

The same comments would apply to the classical canonical ensemble, but the calculations are a bit easier in the quantum case, where we can express averages in terms of sums over eigenstates rather than integrals in phase space. So, let us use quantum formalism.

Since $E(T, \mathbf{X}) = \sum_\alpha E_\alpha P_\alpha$ you immediately conclude that its differential should be given by:

$$\mathrm{d}E = \underbrace{\sum_\alpha E_\alpha \, \mathrm{d}P_\alpha}_{\text{đ}Q = T\mathrm{d}S} + \underbrace{\sum_\alpha P_\alpha \, \mathrm{d}E_\alpha}_{\text{đ}W} = \text{đ}Q + \text{đ}W \; . \tag{3.117}$$

We want to give now meaning to the two terms which is the one suggested in the brace below the two parts, i.e., heat and work, as sketched in Fig. 3.11. Before doing that, be aware of the fact that the natural variables for E would be $E(S, \underline{\mathrm{X}})$, while $(T, \underline{\mathrm{X}})$ are the natural variables for the Helmholtz free-energy $F(T, \underline{\mathrm{X}}) = E - TS$. Hence, we should be careful in the interpretation of the work-related part, see discussion below.

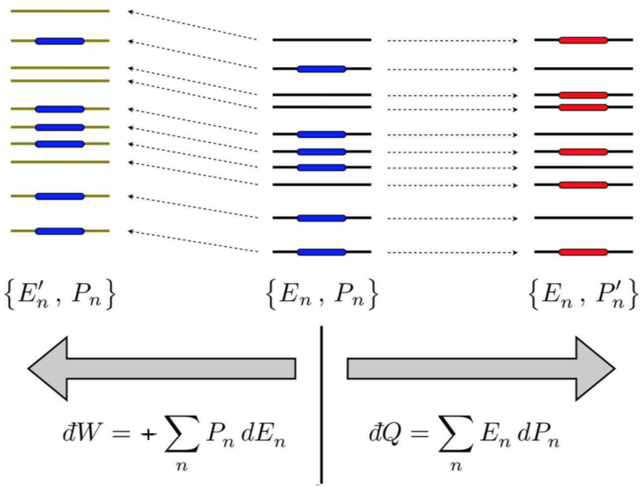

Figure 3.11: The (microscopic) statistical interpretation of Heat and Work. In the text, E_n, P_n are denoted as E_α, P_α. Figure taken from Arovas [1].

To show this, let us start from the canonical entropy. As we saw above, we can write:

$$\begin{aligned} S(T, \underline{\mathrm{X}}) &= -k_B \sum_\alpha P_\alpha \log P_\alpha \\ &\Downarrow \\ \mathrm{d}S &= -k_B \sum_\alpha \left[(\log P_\alpha) \, \mathrm{d}P_\alpha + \frac{P_\alpha}{P_\alpha} \, \mathrm{d}P_\alpha \right] = -k_B \sum_\alpha (\log P_\alpha) \, \mathrm{d}P_\alpha \\ &= -k_B \sum_\alpha (-\beta E_\alpha - \log Z_{\text{CE}}) \, \mathrm{d}P_\alpha = \frac{1}{T} \sum_\alpha E_\alpha \mathrm{d}P_\alpha \; . \end{aligned} \tag{3.118}$$

---

[36] Or, in some cases, operators, which would complicate our description a bit. For a magnetic system, you would have the total magnetisation operator appearing in $\widehat{H}$, coupled to the (intensive) magnetic field.

where we have used (twice) the fact that $\sum_\alpha \mathrm{d}P_\alpha = 0$ since the probability is normalized. Hence, we see that the first term in $\mathrm{d}E$ is indeed $T\mathrm{d}S$, the infinitesimal heat transfer: it is related to a *change in the populations* P_α of the eigenstates.

Now we turn to the second (work-related) term:

$$\sum_\alpha P_\alpha \, \mathrm{d}E_\alpha = \sum_\alpha P_\alpha \sum_i \frac{\partial E_\alpha}{\partial X_i} \, \mathrm{d}X_i = \sum_\alpha P_\alpha \sum_i \langle \phi_\alpha | \frac{\partial \widehat{H}}{\partial X_i} | \phi_\alpha \rangle \, \mathrm{d}X_i = \sum_i \underbrace{\left\langle \frac{\partial \widehat{H}}{\partial X_i} \right\rangle_{\text{CE}}}_{f_i(T,\underline{\mathrm{X}})} \mathrm{d}X_i \ ,$$

where we have invoked Hellmann-Feynman theorem and defined the generalised canonical-ensemble forces:

$$f_i(T,\underline{\mathrm{X}}) = \left\langle \frac{\partial \widehat{H}}{\partial X_i} \right\rangle_{\text{CE}} \neq \frac{\partial E(T,\underline{\mathrm{X}})}{\partial X_i} \ . \tag{3.119}$$

Observe that, quantum mechanically, we would need to calculate here the average of the *force operator*, and not the derivative of the average $E(T,\underline{\mathrm{X}})$. You might think that this is due to quantum mechanics. Not at all: [37] this is just **thermodynamics** of Legendre transforms! What we have derived is an expression for $\mathrm{d}E$ in the "wrong variables" $(T,\underline{\mathrm{X}})$:

$$\mathrm{d}E = T\mathrm{d}S + \sum_{i=1}^{r} f_i(T,\underline{\mathrm{X}}) \, \mathrm{d}X_i \qquad \text{where} \qquad f_i(T,\underline{\mathrm{X}}) \neq \left. \frac{\partial E(T,\underline{\mathrm{X}})}{\partial X_i} \right|_T \ ,$$

where we remarked that the iso-thermal (intensive) forces $f_i(T,\underline{\mathrm{X}})$ are *not* given by the corresponding derivatives of $E(T,\underline{\mathrm{X}})$. On the contrary, if we were using the "right variables" $(S,\underline{\mathrm{X}})$ we would write the differential of E as:

$$\mathrm{d}E = T\mathrm{d}S + \sum_i f_i(S,\underline{\mathrm{X}}) \, \mathrm{d}X_i \qquad \text{with} \qquad f_i(S,\underline{\mathrm{X}}) = \left. \frac{\partial E(S,\underline{\mathrm{X}})}{\partial X_i} \right|_S \ . \tag{3.121}$$

The reason why $f_i(T,\underline{\mathrm{X}})$ are not derivatives of $E(T,\underline{\mathrm{X}})$ is that in our derivation we performed *iso-entropic derivatives* since we kept the weight P_α and hence the canonical distribution *fixed* and calculated the average of the *derivative of the Hamiltonian*. We show below that the relevant derivatives are ultimately given by the derivatives of the *free-energy*: [38]

$$f_i(T,\underline{\mathrm{X}}) = \left\langle \frac{\partial \widehat{H}}{\partial X_i} \right\rangle_{\text{CE}} = \frac{\partial F(T,\underline{\mathrm{X}})}{\partial X_i} \ . \tag{3.123}$$

Indeed, we can verify [39] that the $f_i(T,\underline{\mathrm{X}})$ which appeared in our previous derivation are simply a "swift way" of writing the iso-entropic forces in the canonical variables $(T,\underline{\mathrm{X}})$:

$$f_i(T,\underline{\mathrm{X}}) = f_i(S(T,\underline{\mathrm{X}}),\underline{\mathrm{X}}) = \frac{\partial F(T,\underline{\mathrm{X}})}{\partial X_i} \ . \tag{3.125}$$

---

[37] Classically, you would write the same expression as:

$$f_i(T,\underline{\mathrm{X}}) = \left\langle \frac{\partial H}{\partial X_i} \right\rangle_{\text{CE}} \neq \frac{\partial E(T,\underline{\mathrm{X}})}{\partial X_i} \ . \tag{3.120}$$

[38] Obviously, the differential of the free-energy would directly involve the $f_i(T,\underline{\mathrm{X}})$:

$$\mathrm{d}F = -S\mathrm{d}T + \sum_i f_i(T,\underline{\mathrm{X}}) \, \mathrm{d}X_i \ . \tag{3.122}$$

[39] To verify these statements, reconsider the derivatives $\partial_{X_i} E(T,\underline{\mathrm{X}})$. From thermodynamics, we know that $E(T,\underline{\mathrm{X}}) = E(S(T,\underline{\mathrm{X}}),\underline{\mathrm{X}})$, hence:

$$\frac{\partial E(T,\underline{\mathrm{X}})}{\partial X_i} = \left. \frac{\partial E(S(T,\underline{\mathrm{X}}),\underline{\mathrm{X}})}{\partial X_i} \right|_S + T \frac{\partial S(T,\underline{\mathrm{X}})}{\partial X_i} \ ,$$

where the first derivative is intended at *fixed* S (iso-entropic derivative) and we have used the fact that $T = \frac{\partial E}{\partial S}$. On the other hand, from the canonical ensemble, we have, as outlined above, $E(T,\underline{\mathrm{X}}) = \sum_\alpha E_\alpha P_\alpha$ hence the derivative has indeed two terms:

$$\frac{\partial E(T,\underline{\mathrm{X}})}{\partial X_i} = \underbrace{\sum_\alpha \frac{\partial E_\alpha}{\partial X_i} P_\alpha}_{f_i(T,\underline{\mathrm{X}})} + \sum_\alpha E_\alpha \frac{\partial P_\alpha}{\partial X_i} \ .$$

Notice also that you might be a bit suspicious in attributing a meaning to the number derivative operator $\frac{\partial \widehat{H}}{\partial N}$, while no difficulty is encountered if you interpret this force (the chemical potential) through thermodynamics:

$$\mu(T, \underline{\mathrm{X}}, N) = \left\langle \frac{\partial \widehat{H}}{\partial N} \right\rangle_{\mathrm{CE}} \equiv \left. \frac{\partial E(S(T, \underline{\mathrm{X}}, N), \underline{\mathrm{X}}, N)}{\partial N} \right|_{S} = \frac{\partial F(T, \underline{\mathrm{X}}, N)}{\partial N} \; . \tag{3.126}$$

3.6. Problems

Problem 3.1. Consider a classical system subject to the Hamiltonian

$$H(\mathbf{x}) = K(\mathbf{p}) + V(\mathbf{q}) = \sum_{j=1}^{N} \frac{\mathbf{p}_j^2}{2m} + V(\mathbf{q}) \; ,$$

where $V(\mathbf{q})$ is an arbitrary one-body and two-body potential depending on the coordinates $\mathbf{q}$ of all particles. Assume that the system is in d dimensions, for instance with $d = 1, 2, 3$.

a) Calculate the probability distribution of the momentum $\mathbf{p}_j$ and of the velocity modulus $|\mathbf{v}_j|$ by a direct integration of the Dirac's delta.

b) Repeat the previous calculations by using the corresponding moment generating function and performing the Gaussian integrals.

c) Calculate the probability distribution of the total kinetic energy $K(\mathbf{p})$ by using the moment generating function. What happens for $N \to \infty$?

Problem 3.2. Consider a *single* free quantum particle in a cubic box of volume $V = L^d$ in d dimensions. Calculate the canonical probability distribution at temperature T for the momentum $\hat{\mathbf{p}}$ and the kinetic energy.

From the canonical entropy $S(T, \underline{\mathrm{X}}) = -k_B \sum_\alpha P_\alpha \log P_\alpha$ we immediately see (repeating some of the previous steps) that the second term above is precisely the entropic contribution to the force:

$$T \frac{\partial S(T, \underline{\mathrm{X}})}{\partial X_i} = -k_B T \sum_\alpha \frac{\partial P_\alpha}{\partial X_i} \log P_\alpha \equiv \sum_\alpha E_\alpha \frac{\partial P_\alpha}{\partial X_i} \; .$$

Hence we conclude that the generalised canonical-ensemble force is indeed the correct iso-entropic force rewritten in the canonical variables:

$$f_i(T, \underline{\mathrm{X}}) = \left\langle \frac{\partial \widehat{H}}{\partial X_i} \right\rangle_{\mathrm{CE}} \equiv \left. \frac{\partial E(S(T, \underline{\mathrm{X}}), \underline{\mathrm{X}})}{\partial X_i} \right|_{S} = \frac{\partial F(T, \underline{\mathrm{X}})}{\partial X_i} \; , \tag{3.124}$$

where we have used the fact that the iso-entropic derivative of E is just the derivative of the Helmholtz free-energy (recall the Legendre transform of derivatives).

4. Simple applications of Statistical Mechanics

We will consider here simple applications of the SM techniques to exactly solvable models. In classical physics, we have particles or waves. In quantum physics, particles have a statistics, they are fermions or bosons; waves, in turn, lead usually to a bosonic description. There is a difference, however, between ordinary bosonic particles like, e.g., He^4 or Rb^{87}, and the bosons appearing from the quantisation of waves (like photons, phonons, etc.): essentially the latter do not have a conserved particle number, which means that you do not have a chemical potential, i.e., you can always put $\mu = 0$. We begin with them, before discussing quantum ideal gases of fermions and bosons.

4.1. The quantum harmonic oscillator

Consider a quantum particle in a harmonic potential in one dimension:

$$\widehat{H} = \frac{\hat{P}^2}{2M} + \frac{1}{2} M\omega^2 \hat{X}^2 \; . \tag{4.1}$$

You probably know very well how to find the spectrum and the eigenstates of this problem from standard quantum mechanics courses. I give here a brief recap of the algebraic solution. To start with, we switch to dimensionless variables by defining a unit of length l, the so-called *oscillator length*, such that:

$$\frac{\hbar^2}{2Ml^2} = \frac{1}{2} M\omega^2 l^2 \quad \Longrightarrow \quad l = \sqrt{\frac{\hbar}{M\omega}} \; .$$

Using dimensionless length $\hat{x} = \hat{X}/l$ and momentum $\hat{p} = \hat{P}\, l/\hbar$, with commutator $[\hat{x}, \hat{p}] = i$ (i.e., effectively as if $\hbar = 1$), we rewrite the Hamiltonian as: [1]

$$\widehat{H} = \frac{\hbar\omega}{2} \left(\hat{p}^2 + \hat{x}^2 \right) \; . \tag{4.2}$$

Define now the pair of Hermitian conjugate operators: [2]

$$\begin{cases} \hat{a} &= \frac{1}{\sqrt{2}} \left(\hat{x} + i\hat{p} \right) \\ \hat{a}^\dagger &= \frac{1}{\sqrt{2}} \left(\hat{x} - i\hat{p} \right) \end{cases} \quad \Longrightarrow \quad \begin{cases} \hat{x} &= \frac{1}{\sqrt{2}} \left(\hat{a} + \hat{a}^\dagger \right) \\ \hat{p} &= \frac{1}{\sqrt{2}i} \left(\hat{a} - \hat{a}^\dagger \right) \end{cases} \; . \tag{4.4}$$

The commutator of $\hat{a}$ and $\hat{a}^\dagger$ is immediately calculated, $[\hat{a}, \hat{a}^\dagger] = 1$, and the Hamiltonian reads:

$$\widehat{H} = \hbar\omega \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right) \; . \tag{4.5}$$

---

[1] It is now clear that this procedure is totally equivalent to setting $M = 1$, $\omega = 1$, $\hbar = 1$. Summarizing, we measure lengths in units of l, masses in units of M, energies in units of $\hbar\omega$, momenta in units of $\hbar/l$, times in units of $\hbar/(\hbar\omega) = 1/\omega$, etc.

[2] In x-representation, both are quite simple operators:

$$\hat{a} = \frac{1}{\sqrt{2}} \left(x + \frac{d}{dx} \right) \qquad \text{and} \qquad \hat{a}^\dagger = \frac{1}{\sqrt{2}} \left(x - \frac{d}{dx} \right) \; . \tag{4.3}$$

Let us start finding a state $|\phi_0\rangle$ which is *annihilated* by $\hat{a}$, i.e. such that: [3]

$$\hat{a}|\phi_0\rangle = 0 \ .$$

Evidently, $|\phi_0\rangle$ is an eigenstate of $\widehat{H}$ with eigenvalue $\hbar\omega/2$. It is very simple to realize [4] that $|\phi_0\rangle$ is the *ground state* of $\widehat{H}$. Consider now the *number operator* $\hat{n} = \hat{a}^\dagger\hat{a}$, and construct the obtained by applying n operators $\hat{a}^\dagger$ to $|\phi_0\rangle$,

$$|\phi_n\rangle = \frac{\left(\hat{a}^\dagger\right)^n}{\sqrt{n!}}|\phi_0\rangle \ , \tag{4.6}$$

which turn out to be the eigenstates of $\widehat{H}$. You can show [5] that these are eigenstates of $\hat{n}$ with eigenvalue n:

$$\hat{n}|\phi_n\rangle = n|\phi_n\rangle \ .$$

Based on this we realize that

$$\widehat{H}\,|\phi_n\rangle = \hbar\omega\left(n+\frac{1}{2}\right)|\phi_n\rangle = E_n|\phi_n\rangle \ .$$

It is easy to show [6] that $\hat{a}$ and $\hat{a}^\dagger$ allow us to move up and down in the ladder of states $|\phi_n\rangle$: $\hat{a}^\dagger|\phi_n\rangle = \sqrt{n+1}|\phi_{n+1}\rangle$ and $\hat{a}|\phi_n\rangle = \sqrt{n}|\phi_{n-1}\rangle$.

ℹ **Notation.** You often find $|n\rangle$ in place of $|\phi_n\rangle$ and $|0\rangle$ in place of $|\phi_0\rangle$. The state $|0\rangle$ is called the *vacuum* of $\hat{a}$. $\hat{a}$ and $\hat{a}^\dagger$ are known as *destruction* and *creation* operators, respectively.

Let us now calculate the properties of a single oscillator at temperature T in the *canonical ensemble*, [7] described density matrix [8]

$$\hat{\rho}_{\text{CE}} = \sum_n P_n|\phi_n\rangle\langle\phi_n| = \frac{1}{Z}e^{-\beta\widehat{H}} \ , \tag{4.7}$$

where $P_n = e^{-\beta E_n}/Z$, $\beta = (k_BT)^{-1}$, $Z = \sum_n \mathrm{e}^{-\beta E_n}$ is the partition function, and $\{|\phi_n\rangle\}$ denote the energy eigenstates of $\widehat{H}$. Let us start by calculating the canonical partition function Z:

$$Z = \sum_{n=0}^{\infty} \mathrm{e}^{-\beta\hbar\omega\left(n+\frac{1}{2}\right)} = \mathrm{e}^{-\beta\hbar\omega/2}\sum_{n=0}^{\infty}\left(\mathrm{e}^{-\beta\hbar\omega}\right)^n = \frac{\mathrm{e}^{-\beta\hbar\omega/2}}{1-\mathrm{e}^{-\beta\hbar\omega}} \ , \tag{4.8}$$

where the result follows from a simple geometric series. From Z, the Helmholtz free energy F follows immediately:

$$F = -\frac{1}{\beta}\log Z = \frac{\hbar\omega}{2} - k_BT\log\frac{1}{1-\mathrm{e}^{-\beta\hbar\omega}} \ . \tag{4.9}$$

---

[3] Such a state has a simple expression in x-representation, $\phi_0(x) = \langle x|\phi_0\rangle$, since it obeys the equation:

$$\frac{1}{\sqrt{2}}\left(x+\frac{d}{dx}\right)\phi_0(x) = 0 \quad\Longrightarrow\quad \frac{d}{dx}\phi_0(x) = -x\phi_0(x) \ ,$$

which is solved by $\phi_0(x) = Ce^{-x^2/2}$, where C a normalisation constant.

[4] Simply observe that given any state $|\psi\rangle$, the expectation value of $\hat{a}^\dagger\hat{a}$ satisfies $\langle\psi|\hat{a}^\dagger\hat{a}|\psi\rangle = ||\hat{a}|\psi\rangle||^2 \geq 0$.

[5] One can prove this by recursion, or (better) by using that $[a, \left(\hat{a}^\dagger\right)^n] = n\left(\hat{a}^\dagger\right)^{n-1}$.

[6] One can show, by recursion and using $[\hat{a}, \left(\hat{a}^\dagger\right)^n] = n\left(\hat{a}^\dagger\right)^{n-1}$, that $\langle\phi_0|\hat{a}^n\hat{a}^{\dagger n}|\psi_0\rangle = n!$. From that we deduce that the correctly normalized states are $|\phi_n\rangle = \frac{(\hat{a}^\dagger)^n}{\sqrt{n!}}|\phi_0\rangle$.

[7] Notice that here the volume V does not appear (the potential itself confines the particle) and the number of particles N is also missing, since $N=1$.

[8] Observe that we are applying the statistical mechanics to a *single oscillator*. The results that we calculate describe the statistical behaviour of an ensemble of different realizations of such a single oscillator in contact with a *large bath* at temperature T.

From F, you calculate immediately S, E, and the specific heat C_v. [9]

$$\begin{aligned} S &= -\frac{\partial F}{\partial T} = k_B \log\frac{1}{1-\mathrm{e}^{-\beta\hbar\omega}} + k_B \frac{\beta\hbar\omega}{\mathrm{e}^{\beta\hbar\omega}-1} \\ E &= F+TS = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{\mathrm{e}^{\beta\hbar\omega}-1} \equiv \hbar\omega\Big(\langle\hat{n}\rangle + \frac{1}{2}\Big) \equiv \sum_n E_n P_n \qquad . \\ C_v &= T\frac{\partial S}{\partial T} = \frac{\partial E}{\partial T} = k_B \frac{(\beta\hbar\omega)^2\,\mathrm{e}^{\beta\hbar\omega}}{\left(\mathrm{e}^{\beta\hbar\omega}-1\right)^2} \end{aligned} \tag{4.11}$$

One thing that is worth noticing is the role played by the average occupation number $\langle\hat{n}\rangle$, which we can extract directly from E:

$$\langle\hat{n}\rangle = \langle\hat{a}^\dagger\hat{a}\rangle = \sum_{n=0}^{\infty} nP_n = \frac{1}{\mathrm{e}^{\beta\hbar\omega}-1} \equiv f_B(\hbar\omega) \;, \tag{4.12}$$

where we have introduced the Bose-Einstein distribution function f_B. [10]

Figure 4.1 illustrates the temperature dependence of various physical quantities. Notice the limit $T \to 0$, where the peculiar quantum behaviour shows up, as opposed to the classical regime where $k_BT \gg \hbar\omega$. Notice in particular that E approaches a constant value $\hbar\omega/2$ for $T \to 0$, due to quantum fluctuations (zero-point motion).

The exponential suppression of C_v. Correspondingly, the specific heat is exponentially suppressed:

$$C_v \approx k_B\left(\frac{\hbar\omega}{k_BT}\right)^2 \mathrm{e}^{-\hbar\omega/k_BT} \qquad\qquad \text{for} \quad T\to 0 \;. \tag{4.13}$$

This exponential suppression of C_v for $\hbar\omega > k_BT$ — the quantum regime for the oscillator — is at the root of the T^3 low-temperature law for the specific heat of solids, or of the T^4 behaviour of the total energy $E(T) = aT^4$ of the black-body problem. Both are related to a density of states $g(\omega) \propto \omega^2$ for low ω, as we will later show.

For $k_BT \gg \hbar\omega$, E approaches the classical equi-partition result $E_{\rm cl} = k_BT$ and correspondingly, the specific heat approaches the Dulong-Petit value of k_B. Worth noticing is the behaviour of the entropy S, [11] which clearly shows the inadequate description of the low-temperature regime, where $S_{\rm cl}$ becomes *negative* and, correspondingly, the free-energy has a wrong slope: it increases with T.

---

[9] The corresponding classical calculations require simple Gaussian integrals to be performed. You readily find that $Z = k_BT/(\hbar\omega)$, where $\hbar$ appears because of the factor h which normalises the phase-space volume. Hence, you derive immediately that:

$$\begin{aligned} F &= -\frac{1}{\beta}\log Z = -k_BT\log\frac{k_BT}{\hbar\omega} \\ S &= -\frac{\partial F}{\partial T} = k_B\left(1+\log\frac{k_BT}{\hbar\omega}\right) \\ E &= F+TS = k_BT \\ C_v &= T\frac{\partial S}{\partial T} = \frac{\partial E}{\partial T} = k_B \end{aligned} \tag{4.10}$$

[10] Notice that at high temperature you have

$$\langle\hat{n}\rangle = \frac{k_BT}{\hbar\omega} - \frac{1}{2} + \cdots$$

where the sub-leading constant term $-1/2$ cancels precisely the zero-point fluctuation term in the energy.

[11] Observe that the correct (quantum) entropy is *not* a concave function of T. The requirement of concavity applies to $S(E, \underline{X})$, and not to the canonical ensemble entropy.

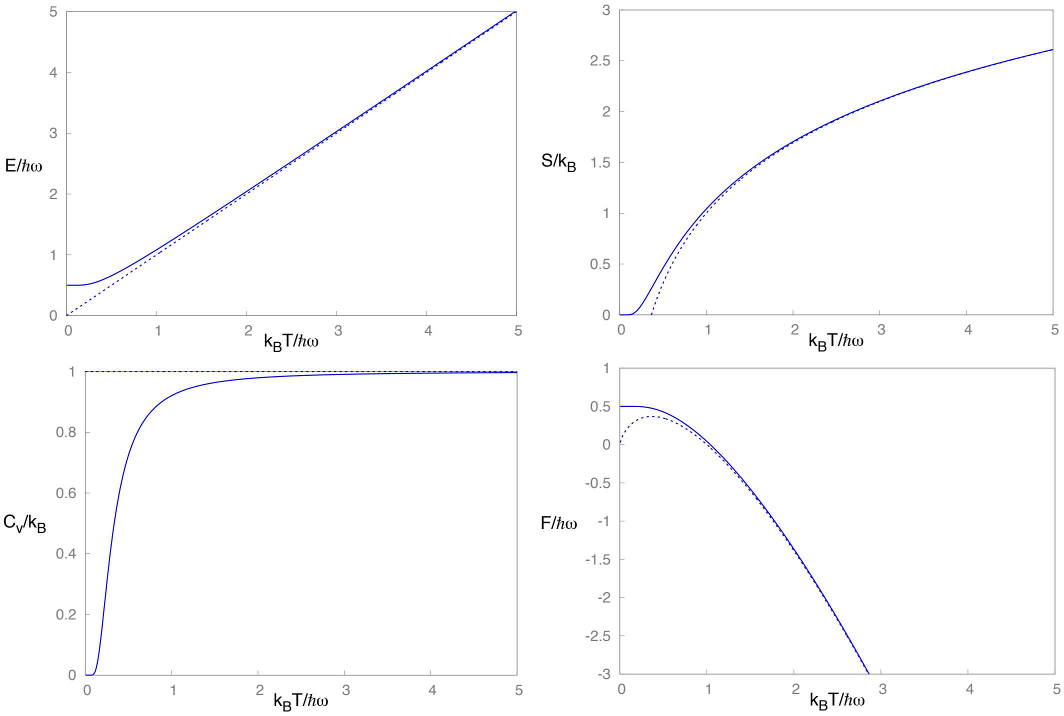

Figure 4.1.: Plot of $E/(\hbar\omega)$, S/k_B, C_v/k_B and $F/(\hbar\omega)$ for a quantum harmonic oscillator. The dashed lines are the predictions obtained with the classical canonical ensemble.

4.2. Transverse vibrations of a string

As an illustration of how to deal with waves, consider a guitar string, which we idealize as an elastic object of total mass M, length L — hence mass-per-unit-length $\mu_0 = M/L$ — which is capable of sustaining forces along the tangent: the familiar *tension* $\mathcal{T}$ of the string. A standard application of Newton's equation $F = ma$ starts from an element Δx of the string, whose shape you imagine to be given by a function $Y(x,t)$ at time t. In general, the tension $\mathcal{T}$ varies when the string is deformed: given the shape, you can think that at each point (for the deformations realized in the string) there is some tension $\mathcal{T}(x)$. According to Newton's equation, the total force along the y direction acting on a certain section $[x_0, x_0 + \Delta x]$ should be equal to the mass times the acceleration of the section. On the other hand, the forces are due to the opposite tensions (in general, different) at the two endpoints (see Fig. 4.2). Hence: [12]

$$\begin{aligned}(ma)_y &= \mu_0 \Delta x \left.\frac{\partial^2 Y}{\partial t^2}\right|_{x_0} \\ F_y &= \mathcal{T}(x_0+\Delta x)\left.\frac{\partial Y}{\partial x}\right|_{x_0+\Delta x} - \mathcal{T}(x_0)\left.\frac{\partial Y}{\partial x}\right|_{x_0} \approx \Delta x\, \frac{\partial}{\partial x}\left(\mathcal{T}(x)\frac{\partial Y}{\partial x}\right)\Big|_{x_0} + \cdots \end{aligned} \tag{4.14}$$

Dividing by Δx and omitting any reference to x_0 we end up writing:

$$\mu_0 \frac{\partial^2 Y}{\partial t^2} = \frac{\partial}{\partial x}\left(\mathcal{T}(x)\frac{\partial Y}{\partial x}\right) . \tag{4.15}$$

---

[12] Notice that we have neglected gravity (which would give a contribution proportional to $g\mu_0\,\Delta x$) as well as possible other sources of forces, including dissipation, etc. Notice also that the length of the section has, due to Pitagora, an extra factor $\sqrt{1+(\partial Y/\partial x)^2}$ which however cancels with a diminished linear mass density $\mu(x)$ in such a way that the mass of the section is roughly the original unstretched one $\mu_0\Delta x$. Observe also that we assume that the derivatives $\frac{\partial Y}{\partial x}$ are small, so that we can substitute $\sin\alpha \approx \tan\alpha = \frac{\partial Y}{\partial x}$ in calculating the y-component of the tension forces.

Now the crucial approximation consists in assuming that $\mathcal{T}(x)$, no matter what the shape and the stretching of the string is, is roughly given by the tension at rest $\mathcal{T}_0$, which you can then take out of the derivative, writing finally the familiar wave equation: [13]

$$\mu_0 \frac{\partial^2 Y}{\partial t^2} = \mathcal{T}_0 \frac{\partial^2 Y}{\partial x^2} \quad \Longrightarrow \quad \frac{1}{v^2} \frac{\partial^2 Y}{\partial t^2} = \frac{\partial^2 Y}{\partial x^2} \,, \tag{4.16}$$

where $v = \sqrt{\mathcal{T}_0/\mu_0} = \sqrt{\mathcal{T}_0 L/M}$. [14] Guitar or violin strings are held fixed at two points, $x = 0$ and $x = L$: the resulting waves are necessarily confined. *Confinement is crucial to have resonances at sharply defined frequencies.* [15]

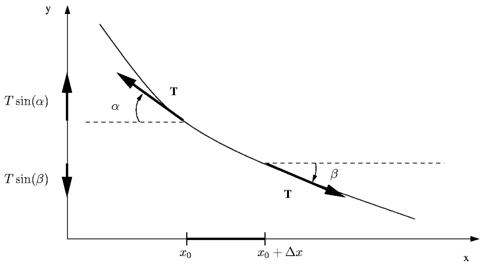

Figure 4.2: How to derive the wave equation for a string.

Let us "solve" the wave equation. First, we look for factorized solutions $Y_m(x,t) = \psi_m(x) b_m(t)$, where $\psi_m(x)$ is dimensionless and b_m is a length, m being the index for the different solutions (see below). Substituting this *Ansatz* in the wave-equation we get:

$$\frac{\psi''_m(x)}{\psi_m(x)} = \frac{1}{v^2} \frac{\ddot{b}_m(t)}{b_m(t)} \equiv -k_m^2 \,.$$

The last step follows from the fact that the left-hand is a function of x, while the central piece is a function of t, hence both must be a real constant, which must be also *negative*, $-k_m^2$, otherwise $b_m(t)$ would blow up. Hence we arrived at:

$$\left\{ \begin{array}{l} \dfrac{d^2\psi_m}{dx^2} + k_m^2 \psi_m(x) = 0 \\ \dfrac{d^2 b_m}{dt^2} + \omega_m^2 b_m(t) = 0 \end{array} \right. \,, \tag{4.19}$$

---

[13] A more realistic modelling would consist in assuming that the tension changes when the string is locally stretched, for instance assuming some Hook's type of elastic relationship. This brings, inevitably, non-linearities to the problem. Such non-linearities are quite amusing, and can even bring to instabilities in the vibration of the string: beyond a certain amplitude, the string has a natural tendency to "rotate" even if you drive it perfectly in a plane.

[14] For a two-dimensional membrane, $Z(x,y,t)$, a similar derivation would gives as a wave equation of the form

$$\frac{1}{v^2} \frac{\partial^2 Z}{\partial t^2} = \frac{\partial^2 Z}{\partial x^2} + \frac{\partial^2 Z}{\partial y^2} = \nabla^2 Z \,,$$

where $v = \sqrt{\gamma_0/\mu_0}$ where γ_0 is the surface tension (a force per unit length) and μ_0 is the mass-per-unit-area of the membrane.

[15] Imagine you have an *infinite* string obeying the wave equation in Eq. (4.16). Now you put a driving force localized at some point x_0 and with a given frequency ω_0. The equation you would write (omitting, again, any dissipation) is:

$$\frac{\partial^2 Y}{\partial t^2} - v^2 \frac{\partial^2 Y}{\partial x^2} = F_\epsilon(t)\delta(x - x_0) \,, \tag{4.17}$$

where $F_\epsilon(t) = A[\theta(-t)e^{\epsilon t} + \theta(t)] \, \sin(\omega_0 t)$. So, A is the amplitude of the forcing, and a regularising factor ϵ, which is send to $\epsilon \to 0$ at the end of the calculation, has been included to account for an "adiabatic switching-on" of the forcing. The problem can be solved by Fourier transforms and some complex plane integration to give:

$$Y(x,t) = \left\{ \begin{array}{ll} -\frac{A}{2\omega_0 v} \cos\left(\frac{\omega_0}{v}(x - x_0 + vt)\right) & \text{for } \; x < x_0 \\ -\frac{A}{2\omega_0 v} \cos\left(\frac{\omega_0}{v}(x - x_0 - vt)\right) & \text{for } \; x > x_0 \end{array} \right. . \tag{4.18}$$

As you see, simply a wave moving to the right and the left of the perturbation, but without any resonance: ω_0 can be anything you want.

where $\omega_m = vk_m$. We see that the spatial part $\psi_m(x)$ obeys a Helmholtz equation in one-dimension:

$$(\nabla^2 + k^2)\psi(x) = 0 \ . \tag{4.20}$$

The boundary conditions are such that *not all values of k are possible*: recall the bound states of a free Schrödinger particle in a box? It is the same problem!

> **Schrödinger particle in the box.** Recall that $E_k = \hbar^2 k^2/(2m)$ for a free particle, and
>
> $$-\frac{\hbar^2}{2m}\nabla^2\psi = E_k\psi(x) \qquad \Longrightarrow \qquad (\nabla^2 + k^2)\psi(x) = 0 \ , \tag{4.21}$$
>
> with boundary conditions $\psi(0) = \psi(L) = 0$.

Only the dispersion, i.e., the relationship between ω_k and k is different: for the wave equation, it is linear, $\omega_k = vk$, while the Schrödinger equation is *linear in time*, $i\hbar\partial_t\psi(x,t) = (-\frac{\hbar^2}{2m}\nabla^2)\psi(x,t)$, hence $E_k = \hbar^2k^2/(2m)$. As expected, a *discrete* spectrum naturally emerges from confinement, like for the Schrödinger problem. In the present case, for each values of k there are two possible degenerate solutions e^{ikx} and e^{-ikx} or, equivalently, $\sin(kx)$ and $\cos(kx)$, but the only solutions which satisfy the boundary conditions are $x = 0$ and $x = L$ are evidently: [16]

$$\psi_m(x) = \sqrt{2}\sin(k_m x) \qquad \text{with} \qquad k_m = \frac{m\pi}{L} \qquad \text{for} \;\; m = 1, 2, \cdots \tag{4.22}$$

and the corresponding angular frequencies are therefore $\omega_m = vk_m = vm\pi/L$, or:

$$f_m = \frac{\omega_m}{2\pi} = m\frac{v}{2L} = mf_1 \ , \tag{4.23}$$

while the wave-lengths are $\lambda_m = 2\pi/k_m = 2L/m$. [17]

But beware from thinking that, due to the analogy with the Schrödinger particle in a box, this problem has any quantum mechanics: it is simply a classical wave that we are describing! How can quantize it? Why should quantize it? The *why* is simple: nature is quantum. You do not see quantum effects in the string of your guitar, simply because you are usually not in the quantum regime. But if the "string" was a *nanotube* suspended between two points at nanoscale distances, or one of the many other nano-mechanical devices that people have learned to build and control, then quantum effects would emerge immediately! So, let us concentrate on the *how* we quantize a classical wave equation. The trick is, essentially, to look for harmonic oscillators, and quantize them in the usual way: waves are just complicated harmonic oscillators!

---

[16] Notice the non-standard normalization, with respect to the Schrödinger problem: we here assume that

$$\langle\psi_m|\psi_{m'}\rangle = \int_0^L \mathrm{d}x\, \psi_m^*(x)\psi_{m'}(x) = L\delta_{m,m'} \ .$$

The reason for this is that we want the $\psi_m(x)$ to be *dimensionless*, in such a way that the b_m has the same dimension as Y, i.e., a *length*.

[17] In music, f_1 is the *fundamental* frequency of the string, while f_2, f_3, etc. are higher *harmonics*. For the musicians among you: If f_1 is a C (DO, in italian), call it C(1), then f_2 is C(2) (the octave above), f_3 is a G(2) (SOL, in italian, in the second octave), f_4 is C(3) (a still higher octave), f_5 is E(3) (MI, in italian, in the third octave), etc. As you see, the harmonics of C have C-E-G (Do-Mi-Sol) in their "body": that is the physical reason behind the "consonance" inside a major triad chord. If you repeat a similar exercise for a two-dimensional elastic membrane held fixed by a ring, a drum, you would discover that the frequencies of the drum are not simple multiples of the fundamental frequency, but rather come from finding the zeroes of Bessel functions, obtained by separating variables for the Helmholtz equation in circular coordinates: it is much harder to play the drum, from this point of view! And if the drum had a stadium shape, you would not be able to solve the Helmholtz equation at all, except for numerical solutions: no separation of variables is possible; stadium-shaped billiards are the arena for the simplest examples of *quantum chaos*.

Indeed, we have already found the relevant oscillators: you see that the equation for b_m is simply $\ddot{b}_m = -\omega_m^2 b_m$. All we need is to decide who is the "coordinate" and who is the "momentum". We will soon see that the "coordinate" is $Q_m = b_m$, and the corresponding "momentum" $P_m = M\dot{b}_m$. To do that, let us write the "total energy" of the string, in the continuum limit:

$$\begin{aligned} H &= \frac{\mu_0}{2}\int_0^L \mathrm{d}x\, (\partial_t Y)^2 + \frac{\mathcal{T}_0}{2}\int_0^L \mathrm{d}x\, (\nabla Y)^2 \\ &= \frac{1}{2\mu_0}\int_0^L \mathrm{d}x\, \Pi^2 + \frac{\mathcal{T}_0}{2}\int_0^L \mathrm{d}x\, (\nabla Y)^2 \,, \end{aligned} \tag{4.24}$$

where you should observe that I written the kinetic energy in term of the momentum-per-unit-length:

$$\Pi(x,t) = \mu_0 \partial_t Y \,,$$

while the second term is the potential energy associated to the stretching of the string. [18] Now, let us expand Y and Π in terms of eigenmodes:

$$Y(x,t) = \sum_m \psi_m(x) b_m(t) \quad \Longrightarrow \quad \Pi(x,t) = \mu_0 \partial_t Y = \mu_0 \sum_m \psi_m(x)\, \dot{b}_m(t) \equiv \frac{1}{L}\sum_m \psi_m(x)\, P_m \,,$$

where we have defined $P_m = L\mu_0 \dot{b}_m = M\dot{b}_m$. Using the orthogonality of the $\psi_m(x)$, $\langle \psi_m | \psi_{m'} \rangle = L\delta_{m,m'}$, it is simple to rewrite the kinetic energy as:

$$\frac{1}{2\mu_0}\int_0^L \mathrm{d}x\, \Pi^2 = \frac{1}{2M}\sum_m P_m^2 \,,$$

Similarly, the potential energy, after integration by parts [19] and using again $\langle \psi_m | \psi_{m'} \rangle = L\delta_{m,m'}$, can be rewritten as:

$$\frac{\mathcal{T}_0}{2}\int_0^L \mathrm{d}x\, (\nabla Y)^2 = \frac{\mathcal{T}_0}{2}\int_0^L \mathrm{d}x\, Y(-\nabla^2 Y) = \frac{M}{2}\sum_m \omega_m^2 Q_m^2$$

where $Q_m = b_m$. Hence the classical Hamiltonian can be rewritten in terms of the eigen-mode coordinates $Q_m = b_m$ and momenta $P_m = M\dot{b}_m$ as:

$$H = \frac{1}{2M}\sum_m P_m^2 + \frac{M}{2}\sum_m \omega_m^2 Q_m^2 \,. \tag{4.25}$$

This is the expression in terms of harmonic oscillators we were looking for, whose quantisation is now obvious: [20]

$$\widehat{H} = \frac{1}{2M}\sum_m \hat{P}_m^2 + \frac{M}{2}\sum_m \omega_m^2 \hat{Q}_m^2 = \sum_m \hbar\omega_m \left(\hat{a}_m^\dagger \hat{a}_m + \frac{1}{2} \right) \,. \tag{4.26}$$

---

[18] It is worth mentioning that the continuum wave-equation might be derived from the Euler-Lagrange equations

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\delta L}{\delta \dot{Y}} = \frac{\delta L}{\delta Y} \,,$$

for the Lagrange functional

$$L[Y,\dot{Y}] = \frac{\mu_0}{2}\int_0^L \mathrm{d}x\, (\partial_t Y)^2 - \frac{\mathcal{T}_0}{2}\int_0^L \mathrm{d}x\, (\nabla Y)^2 \,.$$

This leads to the definition of Π as canonical momentum:

$$\Pi = \frac{\delta L}{\delta \dot{Y}} = \mu_0 \partial_t Y \,,$$

and to H as associated Hamiltonian.

[19] Alternatively, recall that in Quantum Mechanics $\hat{p} = -i\partial_x$ is Hermitean, hence $\langle \hat{p}\psi | \hat{p}\psi \rangle = \langle \psi | \hat{p}^2 \psi \rangle = -\langle \psi | \nabla^2 \psi \rangle$.

[20] Recall that we have to write $\hat{Q}_m = l_m(\hat{a}_m + \hat{a}_m^\dagger)/\sqrt{2}$ and $\hat{P}_m = (\hbar/l_m)(\hat{a}_m - \hat{a}_m^\dagger)/(i\sqrt{2})$, where the oscillator length of mode ω_m is $l_m = \sqrt{\hbar/(M\omega_m)}$.

Incidentally, you can rewrite Y and Π, which are now *quantum fields* as:

$$\left\{\begin{array}{rcl} \hat{Y}(x) &=& \displaystyle\sum_m \psi_m(x)\,\hat{Q}_m = \sum_m \psi_m(x)\sqrt{\frac{\hbar}{2M\omega_m}}\,\left(\hat{a}_m + \hat{a}^\dagger_m\right) \\ \hat{\Pi}(x) &=& \displaystyle\frac{1}{L}\sum_m \psi_m(x)\,\hat{P}_m = -\frac{i}{L}\sum_m \psi_m(x)\sqrt{\frac{M\hbar\omega_m}{2}}\,\left(\hat{a}_m - \hat{a}^\dagger_m\right) \end{array}\right. .$$

Notice that we have not indicated any time in $\hat{Y}(x)$. Quantum mechanically, the operatorial nature of the field is enough, as the time-dependence automatically comes from the Heisenberg evolution of the operators:

$$\hat{Y}(x,t) = \mathrm{e}^{i\widehat{H}t/\hbar}\hat{Y}(x)\mathrm{e}^{-i\widehat{H}t/\hbar} = \sum_m \psi_m(x)\,\hat{Q}_m(t) = \sum_m \psi_m(x)\sqrt{\frac{\hbar}{2M\omega_m}}\,\left(\mathrm{e}^{-i\omega_m t}\hat{a}_m + \mathrm{e}^{i\omega_m t}\hat{a}^\dagger_m\right) .$$

One thing that you should not push too far is that the number m denoting the eigenmodes can go to ∞: in practice, the wavelength of the wave being $\lambda_m = 2L/m$, there is intrinsic cut-off to a $m_{\max}$ when λ_m reaches the atomic scale. In the following, therefore, we will always assume an upper cutoff. But there is one case for which in principle such a cut-off is not there: an electromagnetic wave. Indeed, the exercise we have just carried out resembles in a quite precise way the quantisation of the electromagnetic field, which poses a few more problems, for the vectorial nature of the electric and magnetic field and their boundary conditions, but is otherwise very similar in spirit. The resulting "oscillators" are the photons, and $v = c$, the velocity of light.

Practising with this quantum string model is highly beneficial to understanding the physics of one-dimensional fermionic systems, for which there is a technique called *bosonization* that ends up with a very similar description. If you want to learn more about this, read for instance Chap.2 of the book by T. Giamarchi *Quantum Physics in One Dimension*.

4.3. Statistical mechanics of quantum oscillators

Let us now calculate the thermodynamics of our vibrating string, or indeed of any similar quantized wave, by employing canonical formalism. The Hilbert space of the problem is $\mathcal{H} = \otimes_m \mathcal{H}_m$, without any issue of symmetrization: the oscillators are considered as distinguishable. The Hamiltonian is a *sum* of independent harmonic oscillators,

$$\widehat{H} = \sum_m \widehat{H}_m = \sum_m \hbar\omega_m \left(\hat{a}^\dagger_m \hat{a}_m + \frac{1}{2}\right) , \tag{4.27}$$

where we have denoted by ω_m the generic frequency of the different modes, labelled by m. The trace factorises, hence partition function is the *product* of the Z_m of each single oscillator

$$Z = \mathrm{Tr}\,\mathrm{e}^{-\beta\widehat{H}} = \prod_m \mathrm{Tr}_m\,\mathrm{e}^{-\beta\widehat{H}_m} = \prod_m Z_m = \prod_m \left(\sum_{n_m=0}^{\infty} \mathrm{e}^{-\beta\hbar\omega_m(n_m+\frac{1}{2})}\right) . \tag{4.28}$$

The free-energy F is the *sum* of the individual free energies. We would then write:

$$\begin{aligned} F &= -\frac{1}{\beta}\log Z = \sum_m \frac{\hbar\omega_m}{2} - k_B T \sum_m \log\frac{1}{1-\mathrm{e}^{-\beta\hbar\omega_m}} \\ S &= -\frac{\partial F}{\partial T} = k_B \sum_m \log\frac{1}{1-\mathrm{e}^{-\beta\hbar\omega_m}} + \frac{1}{T}\sum_m \frac{\hbar\omega_m}{\mathrm{e}^{\beta\hbar\omega_m}-1} \\ E &= F + TS = \sum_m \frac{\hbar\omega_m}{2} + \sum_m \frac{\hbar\omega_m}{\mathrm{e}^{\beta\hbar\omega_m}-1} \equiv \sum_m \hbar\omega_m \left(\langle \hat{n}_m\rangle + \frac{1}{2}\right) \\ C_v &= T\frac{\partial S}{\partial T} = \frac{\partial E}{\partial T} = k_B\hbar^2\beta^2 \sum_m \frac{\omega_m^2\,\mathrm{e}^{\beta\hbar\omega_m}}{(\mathrm{e}^{\beta\hbar\omega_m}-1)^2} \end{aligned} \tag{4.29}$$

One simple and famous application of the last formula is the specific heat of solids due to phonons, the famous *Debye model*. You notice that the sum over the different oscillators involves only the frequencies ω_m, so that it is appropriate to rewrite everything in terms of the density of states of the modes: [21]

$$g(\omega) = \sum_m \delta(\omega - \omega_m)\ . \tag{4.30}$$

The specific heat can be expressed as:

$$C_v = \frac{\hbar^2}{k_B T^2}\int_0^{\omega_{\max}} \mathrm{d}\omega\ g(\omega)\ \frac{\omega^2\,\mathrm{e}^{\beta\hbar\omega}}{(\mathrm{e}^{\beta\hbar\omega}-1)^2}\ . \tag{4.31}$$

Without entering into too many details (you can find them in the book of Huang or Callen), the crucial aspect of the calculation is that behaviour of the density of states for $\omega \to 0$. In you assume that

$$g(\omega) = A_g\,\omega^{\alpha_g}\,\theta(\omega_{\max}-\omega) \qquad \text{with} \qquad A_g = \frac{(\alpha_g+1)}{\omega_{\max}^{\alpha_g+1}}\,N_{\text{modes}} \tag{4.32}$$

— where N_{modes} is the total number of oscillator modes [22] — the behaviour for $T \to 0$ is easy to extract by rescaling the variables. Changing variable to $x = \beta\hbar\omega$, we write:

$$C_v = (\alpha_g+1)\,N_{\text{modes}}\left(\frac{k_B T}{\hbar\omega_{\max}}\right)^{\alpha_g+1}\int_0^{\frac{\hbar\omega_{\max}}{k_B T}} \mathrm{d}x\ \frac{x^{2+\alpha_g}\,\mathrm{e}^x}{(\mathrm{e}^x-1)^2}\ . \tag{4.33}$$

For the Debye model, the important modes are the acoustic phonons which have a linear dispersion [23] $\omega \sim vk$, and a density of states (in three dimensions) with $\alpha_g = 2$. Hence, the model predicts that $C_v \sim T^3$ for $T \to 0$, as indeed found experimentally.

Why the strings of your guitar do not show any quantum effects? Let us consider a string of $L = 0.5$ m which is tuned on the fundamental A (LA, in Italian) with $f_1 = 440$ Hz. The energy of the corresponding oscillator is: [24]

$$\hbar\omega_1 = hf_1 \approx 1.8\times 10^{-9}\ \text{meV} \approx 21\times 10^{-9}\ \text{K}\ .$$

---

[21] Notice that this definition is not universal. Sometimes the volume of your sample enters explicitly in the fine structure of the splitting of the energy eigenvalues, and the sum over the levels generates a factor of V which you might prefer to single out by defining $g(\omega)$ to be the density of states per unit volume. We will do that in a short while, but sometimes (for instance in discussing Bose condensation of cold trapped atoms) we will revert to the definition given here, without volume factor.

[22] Simply observe that

$$N_{\text{modes}} = \int_0^{\omega_{\max}} \mathrm{d}\omega\, g(\omega) = A_g\frac{\omega_{\max}^{\alpha_g+1}}{\alpha_g+1}\ .$$

[23] For a more realistic description, one should distinguish between the longitudinal and two transverse acoustic phonon branches, since they have different velocities.

[24] Recall that 1 THz = 4.1 meV = 48 K.

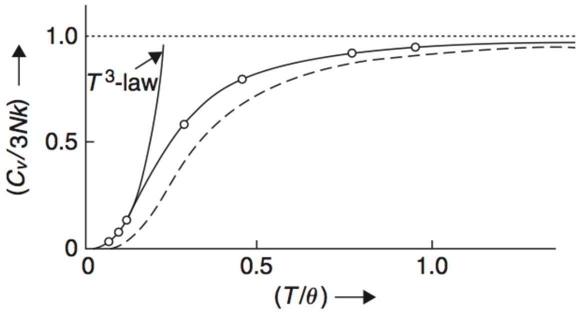

Figure 4.3.: Specific heat of Cu, compared to the Debye model fit. Figure taken from Pathria [5].

If you cut off the harmonics of the string to a generous maximum [25] $m_{\rm max} = 10^6$, this would give

$$\hbar\omega_{\rm max} = hf_{\rm max} \approx 1.8 \times 10^{-3} \text{ meV} .$$

The value of k_BT for a temperature $T = 300$ K is, in the same units, 25.85 meV. Hence $k_BT \gg \hbar\omega_{\rm max}$ and all the oscillators behave classically.

Phonons in solids are, essentially, very high frequency "strings", compared to your guitar. The energy of typical phonons and vibrations in solids and molecules can easily reach values in the meV range, i.e., hundreds of GHz. Hence k_BT can be smaller than some of the mode frequencies, and you should include quantum effects in the calculation. If the guitar string, however, was a Carbon nanotube (a very rigid object indeed) suspended between two points with $L = 10^{-6}$ m, it is not hard to figure out that quantum effects would be relevant there as well. The world of *nanomechanics*, a quite lively recent research field, is full of examples where you see quantum effects in resonating mechanical objects.

4.3.1. Calculating the single-particle density of states

Let us now learn a simple strategy to calculate the density of states $g(\omega)$ of the modes. A very clear discussion of the issues related to the discreteness of the levels, and the intrinsic averaging procedure one is performing in postulating a smooth density of states, is given in [5]. The typical problem in which density of states enter is one in which we have to calculate a sum of the following form:

$$\frac{1}{V}\sum_{\mathbf{k}} f(\omega_{\mathbf{k}}) = \int \mathrm{d}\omega \, \underbrace{\frac{1}{V}\sum_{\mathbf{k}} \delta(\omega - \omega_{\mathbf{k}})}_{g(\omega)} \, f(\omega) = \int \mathrm{d}\omega \, g(\omega) f(\omega) \; ,$$

where now we have defined the density of states per-unit-volume:

$$g(\omega) = \frac{1}{V}\sum_{\mathbf{k}} \delta(\omega - \omega_{\mathbf{k}}) \; . \tag{4.34}$$

Role of dimensionality and dispersion. We will now show that the dimensionality d and the type of dispersion $\omega_k = Ak^\alpha$ both play a role in the density of states $g(\omega)$, leading to a power-law expression of the form:

$$g(\omega) = A_g \omega^{\alpha_g} = A_g \omega^{\frac{d}{\alpha}-1} \; . \tag{4.35}$$

---

[25] This corresponds to a minimum wavelength $\lambda \sim 10^{-6}$ m, and to a maximum frequency $f_{\rm max} = 440$ MHz, well beyond the capabilities of human ears.

To show this, let us assume that the $\mathbf{k}$ values we sum are those that you typically encounter when you apply *periodic boundary conditions* in d dimensions:

$$\mathbf{k} = \frac{2\pi}{L}(n_1, \cdots, n_d) \; .$$

Then, transforming Riemann sums into integrals for large L, you easily establish that:

$$\frac{1}{V}\sum_{\mathbf{k}} f(\omega_{\mathbf{k}}) \overset{L\to\infty}{\longrightarrow} \int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^d} f(\omega_{\mathbf{k}}) \; .$$

If $\omega_{\mathbf{k}}$ depends only on $|\mathbf{k}| = k$ you switch to spherical coordinates. In d dimensions you would write then:

$$\frac{1}{V}\sum_{\mathbf{k}} f(\omega_k) \overset{L\to\infty}{\longrightarrow} \int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^d} f(\omega_k) = \Omega_d \int_0^\infty \frac{\mathrm{d}k\, k^{d-1}}{(2\pi)^d} f(\omega_k) \; ,$$

where

$$\Omega_d = \frac{2\pi^{\frac{d}{2}}}{\Gamma(\frac{d}{2})} \; ,$$

is the solid angle in d dimensions. [26] If you assume a dispersion $\omega_k = Ak^\alpha$, hence $\frac{\mathrm{d}\omega_k}{\mathrm{d}k} = \alpha A k^{\alpha-1}$ and $k(\omega) = (\omega/A)^{\frac{1}{\alpha}}$, you can easily change variables in the integral over k and transform it into an integral over ω. The result is:

$$\frac{1}{V}\sum_{\mathbf{k}} f(\omega_k) \overset{L\to\infty}{\longrightarrow} \int_0^\infty \mathrm{d}\omega\, g(\omega) f(\omega) \qquad \text{with} \qquad g(\omega) = \frac{\Omega_d}{(2\pi)^d \alpha A^{\frac{d}{\alpha}}}\, \omega^{\frac{d}{\alpha}-1} \equiv A_g \omega^{\alpha_g} \; . \tag{4.36}$$

Summarising, when the dispersion is quadratic $\omega_k = Ak^2$ (like for non-relativistic particles) we find that $g(\omega) \sim \omega^{\frac{d}{2}-1}$, while a linear dispersion (like for sound waves or light) leads to $g(\omega) \sim \omega^{d-1}$, hence the characteristic ω^2 appearing in the back-body case and in the Debye model.

4.3.2. Photons in cavities and black-body radiation

An interesting application of the previous theory has to do with the electromagnetic field and photons. As you know, this was indeed the starting point of the quantum theory: Planck found, in 1900, that the energy spectral distribution of the black-body radiation could be well fit by a phenomenological theory in which the energy of the "harmonic oscillators" making up the electromagnetic field was no longer a continuum, but rather quantized in multiples of $\hbar\omega$.

We postpone a brief introduction to the black-body problem, likely well known to most of you, to the final part of this section. Although getting the final result would take a couple of lines of algebra from the equations we already derived, let me spend a few more words on the electromagnetic field in cavities, essentially because this has to do with a quite lively branch of *quantum optics* known as *cavity QED.*

One thing that needs to be stressed is that the quantisation of the electromagnetic field regards essentially the *radiation field*, or, in other words, the *transverse* part of the field: there is where photons enter. A bit of clarification of the meaning of transverse versus longitudinal might be appropriate here. Given a general vector field $\mathbf{F}(\mathbf{x})$ in three-dimension, there is a very important theorem due to Helmholtz which allows to express it as follows:

$$\mathbf{F}(\mathbf{x}) = \underbrace{\boldsymbol{\nabla} \times \int \frac{\mathrm{d}\mathbf{x}'}{4\pi} \frac{\mathrm{curl}\,\mathbf{F}(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}}_{\mathbf{F}^{\perp}(\mathbf{x})} \underbrace{-\boldsymbol{\nabla} \int \frac{\mathrm{d}\mathbf{x}'}{4\pi} \frac{\mathrm{div}\,\mathbf{F}(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}}_{\mathbf{F}^{\parallel}(\mathbf{x})} \; . \tag{4.37}$$

---

[26] Recall that $\Gamma(1/2) = \sqrt{\pi}$ and $\Gamma(3/2) = \sqrt{\pi}/2$. Hence $\Omega_1 = 2$, $\Omega_2 = 2\pi$, $\Omega_3 = 4\pi$.

The first term, $\mathbf{F}^{\perp}$ has *zero divergence* (it is the curl of a vector field), and is known as *transverse part* of $\mathbf{F}$; the second term, $\mathbf{F}^{\parallel}$ has *zero curl* (it is the gradient of a function), and is known as *longitudinal part* of $\mathbf{F}$.

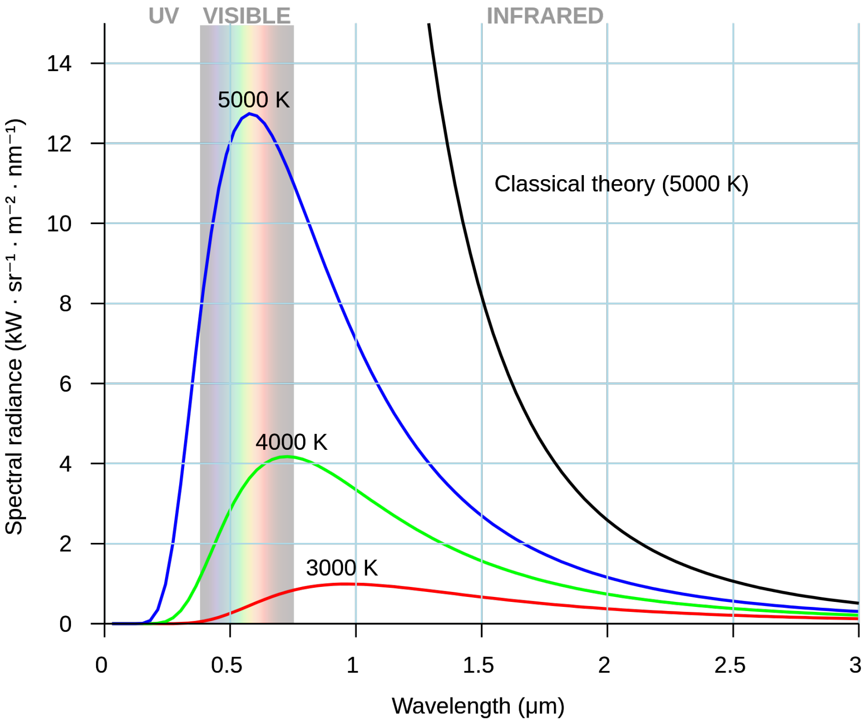

Figure 4.4.: The black-body spectral radiance, proportional to the spectral energy density $u(\lambda, T)$ at different temperatures. We plot here the curves versus the wavelength $\lambda = 2\pi/k = 2\pi c/\omega = c/f$.

In electrostatics, the electric field is purely *longitudinal* and depends on the presence of the charges. Indeed, since $\boldsymbol{\nabla} \cdot \mathbf{E} = 4\pi\rho(\mathbf{x})$ while $\boldsymbol{\nabla} \times \mathbf{E} = 0$, you can immediately write from Eq. (4.37)

$$\mathbf{E} = \mathbf{E}^{\parallel} = -\boldsymbol{\nabla} \int \frac{\mathrm{d}\mathbf{x}'}{4\pi} \frac{\boldsymbol{\nabla} \cdot \mathbf{E}(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} = -\boldsymbol{\nabla} \underbrace{\int \mathrm{d}\mathbf{x}' \frac{\rho(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|}}_{\varphi(\mathbf{x})} = -\boldsymbol{\nabla}\varphi(\mathbf{x}) \,,$$

as you well know: we can define the Coulomb potential $\varphi(\mathbf{x})$ and derive the field from it. If you eliminate the charges, you get no field: there is no life in electrostatics in a world devoid of charges.

The same happens in magnetostatics. The $\mathbf{B}$ field is always transverse, $\boldsymbol{\nabla} \cdot \mathbf{B} = 0$: this is general! In magnetostatics $\boldsymbol{\nabla} \times \mathbf{B} = 4\pi\mathbf{J}(\mathbf{x})$. Hence, we have:

$$\mathbf{B} = \boldsymbol{\nabla} \times \underbrace{\int \mathrm{d}\mathbf{x}' \frac{\mathbf{J}(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|}}_{\mathbf{A}(\mathbf{x})} = \boldsymbol{\nabla} \times \mathbf{A}(\mathbf{x}) \,.$$

If there are no currents $\mathbf{J}(\mathbf{x}) = 0$, the magnetic field vanishes.

But when you have *electrodynamics*, things change completely. The full set of Maxwell's equations reads: [27]

$$\begin{array}{rclcrcl} \boldsymbol{\nabla}\cdot\mathbf{E} & = & 4\pi\rho(\mathbf{x},t) & \qquad & \boldsymbol{\nabla}\times\mathbf{E} & = & -\dfrac{1}{c}\dfrac{\partial\mathbf{B}}{\partial t} \\ \boldsymbol{\nabla}\cdot\mathbf{B} & = & 0 & & \boldsymbol{\nabla}\times\mathbf{B} & = & 4\pi\mathbf{J}(\mathbf{x},t)+\dfrac{1}{c}\dfrac{\partial\mathbf{E}}{\partial t} \end{array} . \tag{4.39}$$

The radiation field. Even in absence of any charge $\rho = 0$ and currents $\mathbf{J} = 0$, you have solutions of the Maxwell equations with $\mathbf{E}(\mathbf{x},t)$ and $\mathbf{B}(\mathbf{x},t)$ different from zero: this is called the *radiation field*. Obviously, the radiation field is *transverse* (since $\boldsymbol{\nabla}\cdot\mathbf{E} = 0$ and $\boldsymbol{\nabla}\cdot\mathbf{B} = 0$), while

$$\boldsymbol{\nabla}\times\mathbf{E} = -\frac{1}{c}\frac{\partial\mathbf{B}}{\partial t} \qquad\qquad \boldsymbol{\nabla}\times\mathbf{B} = +\frac{1}{c}\frac{\partial\mathbf{E}}{\partial t} . \tag{4.40}$$

To study it properly, you would need the appropriate boundary conditions on the region (for instance, an electromagnetic cavity) you are interested in: moreover, the vectorial nature of the fields complicates the analysis considerably. To simplify the procedure (full details can be found in all books in quantum optics), assume that we are in an infinite space free-of-charges ($\rho = 0$ and $\mathbf{J} = 0$). We can work therefore with Fourier transforms of the fields and need not worry about boundary conditions. The four Maxwell's equations become after Fourier transforms in space:

$$\begin{array}{rclcrcl} i\mathbf{k}\cdot\mathbf{E}(\mathbf{k},t) & = & 0 & \qquad & i\mathbf{k}\times\mathbf{E}(\mathbf{k},t) & = & -\dfrac{1}{c}\dfrac{\partial\mathbf{B}(\mathbf{k},t)}{\partial t} \\ i\mathbf{k}\cdot\mathbf{B}(\mathbf{k},t) & = & 0 & & i\mathbf{k}\times\mathbf{B}(\mathbf{k},t) & = & \dfrac{1}{c}\dfrac{\partial\mathbf{E}(\mathbf{k},t)}{\partial t} \end{array} . \tag{4.41}$$

The divergence-equations impose that the fields are *transverse*, i.e., perpendicular to $\mathbf{k}$, in Fourier space. The curl-equations can be rearranged by taking a derivative with respect to time and multiplying vectorially by $\mathbf{k}$. You can reduce yourself to two *decoupled* harmonic oscillator equations: [28]

$$\begin{array}{rcl} \dfrac{\partial^2\mathbf{E}(\mathbf{k},t)}{\partial t^2} & = & -c^2k^2\,\mathbf{E}(\mathbf{k},t) \\ \dfrac{\partial^2\mathbf{B}(\mathbf{k},t)}{\partial t^2} & = & -c^2k^2\,\mathbf{B}(\mathbf{k},t) \end{array} . \tag{4.42}$$

The essence of the procedure for quantizing the electromagnetic field follows quite closely the quantisation of the string we have seen before. [29]

For the black-body radiation, $\omega_k = ck$, and you have to account for a factor 2 due to the two polarisations of transverse photons. To express the total energy you then write, transforming the sum

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[27] In SI units the Maxwell equations read:

$$\begin{array}{rclcrcl} \boldsymbol{\nabla}\cdot\mathbf{E} & = & \frac{1}{\varepsilon_0}\rho(\mathbf{x},t) & \qquad & \boldsymbol{\nabla}\times\mathbf{E} & = & -\dfrac{\partial\mathbf{B}}{\partial t} \\ \boldsymbol{\nabla}\cdot\mathbf{B} & = & 0 & & \boldsymbol{\nabla}\times\mathbf{B} & = & \mu_0\left(\mathbf{J}(\mathbf{x},t)+\varepsilon_0\dfrac{\partial\mathbf{E}}{\partial t}\right) \end{array} . \tag{4.38}$$

Here μ_0 is the vacuum permeability, $\mu_0 \approx 4\pi\cdot 10^{-7}\mathrm{H/m} = 4\pi\cdot 10^{-7}\mathrm{N/A^2}$, while $\frac{1}{4\pi\varepsilon_0} \approx 9\cdot 10^9\mathrm{Nm^2/C^2}$. Together, they are related to the velocity of light in vacuum $c = \sqrt{\mu_0\varepsilon_0}$, which is *defined* to be $c \overset{\mathrm{def}}{=} 299792458\mathrm{m/s}$ (the meter, the SI unit of length, is therefore derived from the unit of time and from c).

[28] In SI units the Maxwell equations in absence of charges and currents, using $\boldsymbol{\nabla}\times(\boldsymbol{\nabla}\times\mathbf{E}) = \boldsymbol{\nabla}(\boldsymbol{\nabla}\cdot\mathbf{E}) - \nabla^2\mathbf{E}$, read

$$\frac{\partial^2}{\partial t^2}\mathbf{E} = -\frac{1}{\mu_0\varepsilon_0}\nabla^2\mathbf{E} \qquad \text{and} \qquad \frac{\partial^2}{\partial t^2}\mathbf{B} = -\frac{1}{\mu_0\varepsilon_0}\nabla^2\mathbf{B} .$$

The Hamiltonian would read:

$$H = \frac{\varepsilon_0}{2}\int_V \mathrm{d}\mathbf{x}\,\left(|\mathbf{E}(\mathbf{x},t)|^2 + c^2|\mathbf{B}(\mathbf{x},t)|^2\right) .$$

[29] We only recall that the quantum expression for the vector potential eventually reads (in Heisenberg representation

over $\mathbf{k}$ into an integral in the usual way: [30]

$$\begin{aligned} E(T,V) &= 2V\int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3}\frac{\hbar\omega_k}{\mathrm{e}^{\beta\hbar\omega_k}-1} = 8\pi V\int_0^\infty \frac{\mathrm{d}k}{8\pi^3}\,k^2\frac{\hbar\omega_k}{\mathrm{e}^{\beta\hbar\omega_k}-1} = \frac{V}{\pi^2c^3}\int_0^\infty \mathrm{d}\omega\,\omega^2\frac{\hbar\omega}{\mathrm{e}^{\beta\hbar\omega}-1} \\ &= V\int_0^\infty \mathrm{d}\omega\,\frac{\omega^2}{\pi^2c^3}\frac{\hbar\omega}{\mathrm{e}^{\beta\hbar\omega}-1} \equiv V\int_0^\infty \mathrm{d}\omega\,\varepsilon(\omega,T) \end{aligned} \tag{4.43}$$

where we define the spectral energy density

$$\varepsilon(\omega,T) = g(\omega)\frac{\hbar\omega}{\mathrm{e}^{\beta\hbar\omega}-1} = \frac{\omega^2}{\pi^2c^3}\frac{\hbar\omega}{\mathrm{e}^{\beta\hbar\omega}-1}\ . \tag{4.44}$$

Here you recognise the density of states of the modes (see Eq. (4.36) with $A=c$, $\alpha=1$ and $d=3$ and an extra factor 2 for the two polarizations):

$$g(\omega) = \frac{\omega^2}{\pi^2c^3}\ . \tag{4.45}$$

An equivalent way of writing would be to express the spectral density in terms of the wave-length λ of the radiation. If you recall that $k=2\pi/\lambda$, and you change variable from k to λ rather than from k to ω, you can equivalently rewrite:

$$\begin{aligned} E(T,V) = 8\pi V\int_0^\infty \frac{\mathrm{d}k}{8\pi^3}\,k^2\frac{\hbar\omega_k}{\mathrm{e}^{\beta\hbar\omega_k}-1} &= V\int_0^\infty \mathrm{d}\lambda\,\frac{8\pi}{\lambda^4}\frac{hc/\lambda}{\mathrm{e}^{\beta hc/\lambda}-1} \\ &\equiv V\int_0^\infty \mathrm{d}\lambda\,u(\lambda,T)\ , \end{aligned} \tag{4.46}$$

where

$$u(\lambda,T) = \frac{8\pi hc}{\lambda^5}\frac{1}{\mathrm{e}^{hc/(\lambda k_BT)}-1}\ . \tag{4.47}$$

Historically, quite a few things were known before Planck's work, more precisely through experiments, performed by Stefan in 1879 and by Lummer & Pringsheim in 1899, and through general thermodynamical arguments due to Boltzmann and to Wien:

(1) The total energy density behaves as:

$$\frac{E(T,V)}{V} = aT^4\ , \tag{4.48}$$

with $a=4\sigma/c$ where $\sigma = 5.67\times10^{-8}$ W m^{-2} K^{-4} is the *Stefan's constant*, experimentally measured in 1879. The previous relation is known as *Stefan-Boltzmann law* because Boltzmann deduced it in 1884 from general thermodynamical arguments.

(2) The second experimentally known fact was that the spectral density $u(\lambda,T)$ shows a pronounced *maximum* at a wavelength $\lambda_{\max}=c/\nu_{\max}$ which obeys the *Wien's displacement law*:

$$\lambda_{\max}T = b \simeq 2.898\times10^{-3}\mathrm{m\,K}\ . \tag{4.49}$$

(3) The spectral density $u(\lambda,T)$ should have a universal form given by

$$u(\lambda,T) = \lambda^{-5}f_{\mathrm{Wien}}(\lambda T)\ , \tag{4.50}$$

where f_{Wien} is a *universal function* of λT. This was shown by Wien, again based on general thermodynamical arguments.

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and SI units):

$$\hat{\mathbf{A}}_{\mathrm{H}}(\mathbf{x},t) = \sum_{s=1}^{2}\int\frac{\mathrm{d}\mathbf{k}}{(2\pi)^3}\sqrt{\frac{\hbar}{2\varepsilon_0\omega_k}}\left(\boldsymbol{\epsilon}_{\mathbf{k},s}\mathrm{e}^{i\mathbf{k}\cdot\mathbf{x}-i\omega_kt}\hat{a}_{\mathbf{k},s}+\boldsymbol{\epsilon}^*_{\mathbf{k},s}\mathrm{e}^{-i\mathbf{k}\cdot\mathbf{x}+i\omega_kt}\hat{a}^\dagger_{\mathbf{k},s}\right)$$

where $\boldsymbol{\epsilon}_{\mathbf{k},s}$ are the two transverse polarization vectors, and $\omega_k=|\mathbf{k}|c$. In terms of $\hat{\mathbf{A}}$ we express the fields as $\hat{\mathbf{E}}=-\frac{\partial\hat{\mathbf{A}}}{\partial t}$ and $\hat{\mathbf{B}}=\boldsymbol{\nabla}\times\hat{\mathbf{A}}$.

[30] Notice that we neglect here the zero-point motion term, formally giving a divergent contribution in infinite space. In a confined geometry, a proper account of that term gives rise to Casimir forces.

The final formula for the average energy requires an integral [31] and reads:

$$\begin{aligned} E(T,V) &= V \int_0^{\infty} \mathrm{d}\omega \, \varepsilon(\omega,T) = V \int_0^{\infty} \mathrm{d}\omega \, \frac{\omega^2}{\pi^2 c^3} \frac{\hbar\omega}{\mathrm{e}^{\beta\hbar\omega}-1} \\ &= V \frac{\pi^2}{15} \frac{(k_B T)^4}{(\hbar c)^3} = V a T^4 \; , \end{aligned} \tag{4.52}$$

in agreement with the *Stefan-Boltzmann law.*

It is interesting to consider the classical limit of the spectral energy density $\varepsilon(\omega,T)$, obtained by assuming that $k_BT \gg \hbar\omega$, or equivalently for $u(\lambda,T)$ when $\lambda \gg hc/(k_BT)$. You would get:

$$\varepsilon_{\text{CL}}(\omega,T) \approx \frac{\omega^2}{\pi^2 c^3} \frac{\hbar\omega}{1+\beta\hbar\omega+\cdots-1} = \frac{\omega^2}{\pi^2 c^3} k_B T \; , \tag{4.53}$$

or equivalently:

$$u_{\text{CL}}(\lambda,T) \approx \frac{8\pi}{\lambda^4} k_B T \; . \tag{4.54}$$

These are the results one would obtain by treating the electromagnetic field with classical statistical mechanics. They lead to a *ultraviolet catastrophe*: the corresponding integrals over all frequencies or all wavelengths simply *diverges*, for $\omega \to \infty$ or $\lambda \to 0$, respectively.

Let us return to the correct (quantum) spectral energy density $u(\lambda,T)$ which fits very well the experimental observations. Calculating a simple derivative, we conclude that the maximum of the $u(\lambda,T)$ versus λ is realised for [32]

$$\left. \frac{\beta hc}{\lambda} \frac{1}{1-\mathrm{e}^{-\beta hc/\lambda}} \right|_{\lambda_{\max}} = 5 \qquad \Longrightarrow \qquad \frac{\beta hc}{\lambda_{\max}} \simeq 4.965 \; . \tag{4.56}$$

Rewritten differently, this reads:

$$\lambda_{\max} T = b = \frac{hc}{4.965 k_B} \approx 2.898 \times 10^{-3} \mathrm{m\,K} \; . \tag{4.57}$$

This is precisely the content of *Wien's displacement law.* For $T = 5000$ K, you get $\lambda_{\max} \approx 0.59\mu$m. Finally, Planck's form for $u(\lambda,T)$ in Eq. (4.47) satisfies Wien universal form in Eq. (4.50).

For completeness, let us sketch, before ending this section, some of the issues behind the black-body problem, to highlight the *impasse* encountered by classical physics in describing the experiments, and the brilliant ad-hoc solution given by Planck long before quantum mechanics was developed. You can view it as the first instance in which *discreteness* made its appearance in physics.

Bodies in equilibrium at temperature T absorb and emit electromagnetic radiation of different wavelengths λ, with a broad spectrum. This is essentially a consequence of the fact that electronic states in condensed

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[31] The relevant integral is

$$\mathrm{I} = \int_0^{+\infty} \mathrm{d}x \frac{x^3}{\mathrm{e}^x - 1} \; .$$

To calculate it, simply *undo* the geometric series sum leading to the Planck distribution, writing:

$$\mathrm{I} = \sum_{n=1}^{\infty} \int_0^{+\infty} \mathrm{d}x \; x^3 \mathrm{e}^{-nx} = \sum_{n=1}^{\infty} \frac{1}{n^4} \int_0^{+\infty} \mathrm{d}y \; y^3 \mathrm{e}^{-y} = \zeta(4)\Gamma(4) = \frac{\pi^4}{15} \; . \tag{4.51}$$

[32] Notice that for $\varepsilon(\omega,T)$, the maximum of $\varepsilon(\omega,T)$ for given T, as a function of ω, is verified when

$$\left. \frac{\mathrm{d}}{\mathrm{d}x} \frac{x^3}{\mathrm{e}^x - 1} \right|_{x_{\max}} = 0 \quad \Longrightarrow \quad \frac{x_{\max}}{1-\mathrm{e}^{-x_{\max}}} = 3 \quad \Longrightarrow \quad x_{\max} \approx 2.82 \; ,$$

which corresponds to

$$\hbar\omega_{\max} = h\nu_{\max} = x_{\max} k_B T \approx 2.82 k_B T \; . \tag{4.55}$$

Remarkably, the maximum you calculate is *different* from that obtained by maximising $u(\lambda,T)$.

matter group into energy bands, contrary to the sharp atomic spectral lines. Let us call $R^{\rm body}_{\rm abs}(\lambda,T){\rm d}\lambda$ and $R^{\rm body}_{\rm emi}(\lambda,T){\rm d}\lambda$ the power (energy per unit time) per unit area absorbed and emitted by a certain body in the wavelength interval $(\lambda,\lambda+{\rm d}\lambda)$. Let $R_{\rm inc}(\lambda,T){\rm d}\lambda$ be the power per unit area incident on the body. We can define the *absorption coefficient* of the body:

$$a_{\rm body}(\lambda,T)=\frac{R^{\rm body}_{\rm abs}(\lambda,T)}{R_{\rm inc}(\lambda,T)}\ . \tag{4.58}$$

In general, if the body is in equilibrium at a fixed temperature T, we must have that:

$$R^{\rm body}_{\rm abs}(\lambda,T)\equiv R^{\rm body}_{\rm emi}(\lambda,T)\ . \tag{4.59}$$

By general thermodynamics arguments, Kirckoff (1859) showed that $R^{\rm body}_{\rm emi}/a_{\rm body}$ is a *universal function of* λ *and* T. Indeed:

$$\frac{R^{\rm body}_{\rm emi}(\lambda,T)}{a_{\rm body}(\lambda,T)}=\frac{\cancel{R^{\rm body}_{\rm emi}(\lambda,T)}}{\cancel{R^{\rm body}_{\rm abs}(\lambda,T)}}\,R_{\rm inc}(\lambda,T)\equiv R_{\rm inc}(\lambda,T)\ . \tag{4.60}$$

A black-body (BB) is an idealized system such that $a_{\rm BB}(\lambda,T)\equiv 1$: it absorbs all the incident radiation, at all λ. Obviously, in equilibrium:

$$R_{\rm inc}(\lambda,T)\overset{\rm BB}{\equiv}R^{\rm BB}_{\rm abs}(\lambda,T)\overset{\rm eq}{\equiv}R^{\rm BB}_{\rm emi}(\lambda,T)\equiv R(\lambda,T)\ , \tag{4.61}$$

where we have introduced a shorter notation. Figure 4.5 shows a practical way of realizing a cavity that essentially absorbs all incoming radiation, which then thermalizes inside the cavity: the radiation emitted from the hole of the cavity is, therefore, in equilibrium, a good approximation to the black-body radiation.

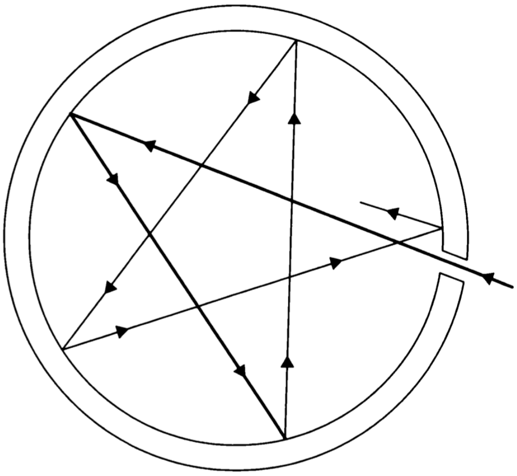

Figure 4.5: A cavity with a blackened interior, held at temperature T, and a small hole. The radiation emitted through the hole is a good approximation to the black-body radiation.

The total emissive power of a black body is given by:

$$R(T)=\int_0^\infty {\rm d}\lambda\; R(\lambda,T)\ . \tag{4.62}$$

An experimental result due to Stefan (1879), later derived through general thermodynamical arguments by Boltzmann (1884), is that:

$$R(T)=\sigma T^4\ , \tag{4.63}$$

where, empirically, the Stefan's constant is $\sigma\approx 5.67\times10^{-8}$ W/(m^2 K^4).

Measurements of $R(\lambda,T)$ by Lummer and Pringsheim (1899) allowed to confirm Wien's displacement law relating T to the $\lambda_{\rm max}$ for which $R(\lambda,T)$ has a maximum:

$$\lambda_{\rm max}T=b\ , \tag{4.64}$$

allowing also to experimentally determine $b=2.898\times10^{-3}$ m K.

Consider now the monochromatic (or spectral) energy density $u(\lambda, T)$, such that

$$E(T,V) = V \int_0^{\infty} \mathrm{d}\lambda \; u(\lambda, T) \; , \tag{4.65}$$

is the total energy of the radiation in equilibrium at temperature T in a cavity of volume V. One can show that it is related to the power emitted by the BB per unit area is:

$$u(\lambda, T) = \frac{4}{c} R(\lambda, T) \; , \tag{4.66}$$

where c is the velocity of light in vacuum. This is a convenient quantity because, as shown by Wien, again based on general thermodynamical arguments:

$$u(\lambda, T) = \lambda^{-5} f_{\mathrm{Wien}}(\lambda T) \; , \tag{4.67}$$

where f_{Wien} is a *universal function* of λT.

To know more about $f_{\mathrm{Wien}}(\lambda T)$ we need a *model*. Imagine the cavity to be a cube of volume $V = L^3$ filled with electromagnetic (transverse) waves, which are standing waves of wavenumber $\mathbf{k}$, with $k = |\mathbf{k}| = 2\pi/\lambda$. If you have a quantity $F(k)$ to be summed over all the modes of the radiation, then, accounting for the two polarisations of the transverse waves, we can write the associated density as:

$$\frac{2}{V} \sum_{\mathbf{k}} F(k) = 2 \int \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} F(k) = \frac{1}{\pi^2} \int_0^{\infty} \mathrm{d}k \, k^2 F(k) = 8\pi \int_0^{\infty} \mathrm{d}\lambda \, \frac{1}{\lambda^4} \tilde{F}(\lambda) \; , \tag{4.68}$$

where $\tilde{F}(\lambda) = F(2\pi/\lambda)$. Hence, we see that $(8\pi)/\lambda^4$ is the "density of modes" at wavelength λ. The average spectral energy density is, therefore:

$$u(\lambda, T) = \frac{8\pi}{\lambda^4} \, \bar{\epsilon}(\lambda, T) \tag{4.69}$$

where $\bar{\epsilon}$ is the average energy of every single mode of the radiation at the given λ and at temperature T.

If you model the electromagnetic field — which obeys Maxwell's equations [33] — as *classical harmonic oscillators* in equilibrium at temperature T, then classical statistical mechanics would predict:

$$\bar{\epsilon} = \frac{\int_0^{\infty} \mathrm{d}\epsilon \, \epsilon \, \mathrm{e}^{-\beta\epsilon}}{\int_0^{\infty} \mathrm{d}\epsilon \, \mathrm{e}^{-\beta\epsilon}} = -\frac{\mathrm{d}}{\mathrm{d}\beta} \log \left[\int_0^{\infty} \mathrm{d}\epsilon \, \mathrm{e}^{-\beta\epsilon} \right] = \frac{1}{\beta} = k_B T \; . \tag{4.70}$$

This classical calculation expresses the *equipartition principle.* The corresponding $f_{\mathrm{Wien}} = 8\pi k_B \lambda T$. Obviously, this result leads to an *ultraviolet catastrophe*, since the integral over λ *diverges.*

It was a bold assumption due to Planck (1900) to imagine that the integral over ϵ written above should be modified by assuming that the different values of ϵ are actually *discrete*: $\epsilon = n\epsilon_0$, with $n = 0, 1, 2, \cdots \infty$. Simply replacing the integral by a discrete sum changes the outcome of the calculation dramatically:

$$\bar{\epsilon} = \frac{\sum_{n=0}^{\infty} (n\epsilon_0) \, \mathrm{e}^{-\beta n \epsilon_0}}{\sum_{n=0}^{\infty} \mathrm{e}^{-\beta n \epsilon_0}} = -\frac{\mathrm{d}}{\mathrm{d}\beta} \log \left[\sum_{n=0}^{\infty} \mathrm{e}^{-\beta n \epsilon_0} \right] = -\frac{\mathrm{d}}{\mathrm{d}\beta} \log \left[\frac{1}{1 - \mathrm{e}^{-\beta\epsilon_0}} \right] = \frac{\epsilon_0}{\mathrm{e}^{\epsilon_0/(k_B T)} - 1} \; . \tag{4.71}$$

To be compatible with Wien's general prescription — recall, the universal function of λT —, the constant ϵ_0 should be $\epsilon_0 \sim 1/\lambda$. So, Planck took:

$$\epsilon_0 = h\nu = \frac{hc}{\lambda} \; , \tag{4.72}$$

where h is a constant with dimension [energy] × [time], and $\nu = c/\lambda$ is the frequency of the wave. Hence, we end up having:

$$u(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{\mathrm{e}^{hc/(\lambda k_B T)} - 1} \; , \tag{4.73}$$

which is exactly of the Wien's universal form, but now without ultraviolet catastrophe. The total integral over λ, together with $u(T) = (4/c)R(T)$, leads to the following explicit expression for Stefan's constant:

$$\sigma = \frac{2\pi^5}{15} \frac{k_B^4}{h^3 c^2} \; . \tag{4.74}$$

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[33] The Maxwell's equations are linear. You can show that they can be regarded as describing an infinite set of linear harmonic oscillators. See the previous discussion in this section.

Similarly, Wien's displacement law is easily established to lead to

$$\lambda_{\max} T = b = \frac{hc}{4.965 k_B} \ . \tag{4.75}$$

Since both σ and b had been experimentally measured, and c quite accurately known at that time, Planck deduced values for k_B (Boltzmann constant) and for h (Planck's constant).

4.4. Ideal quantum gases

Consider now the problem of N identical quantum particles — fermions or bosons — in a box of volume V: a *quantum fluid*. Let us try to approach this problem with the canonical ensemble. We start from a Hamiltonian $\widehat{H}$ of a rather general form, including *interactions*. In second quantisation we would introduce field operators $\widehat{\Psi}_\sigma(\mathbf{x})$ and express $\widehat{H}$ as:

$$\widehat{H} = \sum_\sigma \int d\mathbf{x}\, \widehat{\Psi}^\dagger_\sigma(\mathbf{x}) \left(-\frac{\hbar^2\nabla^2}{2m} + v(\mathbf{x}) \right) \widehat{\Psi}_\sigma(\mathbf{x}) + \sum_{\sigma,\sigma'} \frac{1}{2} \int d\mathbf{x} d\mathbf{x}'\; V_{\mathrm{int}}(|\mathbf{x}-\mathbf{x}'|)\; \widehat{\Psi}^\dagger_{\sigma'}(\mathbf{x}')\widehat{\Psi}^\dagger_\sigma(\mathbf{x})\widehat{\Psi}_\sigma(\mathbf{x})\widehat{\Psi}_{\sigma'}(\mathbf{x}') \ .$$

In turn, the field operators $\widehat{\Psi}_\sigma(\mathbf{x})$ — which obey standard commutation/anticommutation rules for bosons/fermions, for instance $[\widehat{\Psi}_\sigma(\mathbf{x}), \widehat{\Psi}^\dagger_{\sigma'}(\mathbf{x}')] = \delta_{\sigma,\sigma'}\delta(\mathbf{x}-\mathbf{x}')$ for bosons and $\{\widehat{\Psi}_\sigma(\mathbf{x}), \widehat{\Psi}^\dagger_{\sigma'}(\mathbf{x}')\} = \delta_{\sigma,\sigma'}\delta(\mathbf{x}-\mathbf{x}')$ for fermions — can be expanded in any one-particle basis set of spin-orbital wavefunctions labelled by quantum numbers (α,σ), with destruction operators $\hat{a}_{\alpha,\sigma}$, where the statistics (fermions vs bosons) requires that these operators obey the commutation/anticommutation relations

$$\text{Bosons:} \quad \begin{cases} \left[\hat{a}_{\alpha,\sigma}, \hat{a}^\dagger_{\alpha',\sigma'}\right] &= \delta_{\alpha,\alpha'}\delta_{\sigma,\sigma'} \\ \left[\hat{a}^\dagger_{\alpha,\sigma}, \hat{a}^\dagger_{\alpha',\sigma'}\right] &= 0 \\ \left[\hat{a}_{\alpha,\sigma}, \hat{a}_{\alpha',\sigma'}\right] &= 0 \end{cases} \qquad \text{Fermions:} \quad \begin{cases} \left\{\hat{a}_{\alpha,\sigma}, \hat{a}^\dagger_{\alpha',\sigma'}\right\} &= \delta_{\alpha,\alpha'}\delta_{\sigma,\sigma'} \\ \left\{\hat{a}^\dagger_{\alpha,\sigma}, \hat{a}^\dagger_{\alpha',\sigma'}\right\} &= 0 \\ \left\{\hat{a}_{\alpha,\sigma}, \hat{a}_{\alpha',\sigma'}\right\} &= 0 \end{cases} \ .$$

Assume that the orbitals actually factorize into a standard orbital wave-function $\phi_\alpha(\mathbf{x})$ times a standard spinor in such a way that $\widehat{\Psi}_\sigma(\mathbf{x}) = \sum_\alpha \phi_\alpha(\mathbf{x})\; \hat{a}_{\alpha,\sigma}$. There is large freedom in the choice of the basis $\phi_\alpha(\mathbf{x})$. [34] In general we would end-up writing (including the spin-labels in the α):

$$\widehat{H} = \sum_{\alpha,\alpha'} K_{\alpha',\alpha} \hat{a}^\dagger_{\alpha'} \hat{a}_\alpha + \frac{1}{2} \sum_{\substack{\alpha_1,\alpha_2 \\ \alpha'_1,\alpha'_2}} (\alpha'_1\alpha'_2|V_{\mathrm{int}}|\alpha_1\alpha_2)\; \hat{a}^\dagger_{\alpha'_2} \hat{a}^\dagger_{\alpha'_1} \hat{a}_{\alpha_1} \hat{a}_{\alpha_2} \ , \tag{4.77}$$

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[34] For instance, one could select plane-waves $\phi_{\mathbf{k}}(\mathbf{x}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{x}}$, where V is the volume, and write the corresponding expression for $\widehat{H}$ as:

$$\widehat{H} = \frac{1}{V}\sum_{\mathbf{k},\sigma} \frac{\hbar^2\mathbf{k}^2}{2m} \hat{a}^\dagger_{\mathbf{k},\sigma}\hat{a}_{\mathbf{k},\sigma} + \frac{1}{V}\sum_{\mathbf{k},\mathbf{q},\sigma} v(\mathbf{q}) \hat{a}^\dagger_{\mathbf{k}+\mathbf{q},\sigma}\hat{a}_{\mathbf{k},\sigma} + \frac{1}{2V}\sum_{\mathbf{k},\mathbf{k}',\mathbf{q}}\sum_{\sigma,\sigma'} V_{\mathrm{int}}(|\mathbf{q}|) \hat{a}^\dagger_{\mathbf{k}'-\mathbf{q},\sigma'}\hat{a}^\dagger_{\mathbf{k}+\mathbf{q},\sigma}\hat{a}_{\mathbf{k},\sigma}\hat{a}_{\mathbf{k}',\sigma'} \ , \tag{4.76}$$

where we have introduced the Fourier transforms of the external potential $v(\mathbf{q}) = \int d\mathbf{x}\; e^{-i\mathbf{q}\cdot\mathbf{x}} v(\mathbf{x})$, and of the interaction potential $V_{\mathrm{int}}(\mathbf{q}) = \int d\mathbf{x}\, e^{-i\mathbf{q}\cdot\mathbf{x}} V_{\mathrm{int}}(\mathbf{x})$. For the Coulomb potential in three dimensions:

$$\frac{4\pi e^2}{\mathbf{q}^2} = \int d^3\mathbf{x}\; e^{-i\mathbf{q}\cdot\mathbf{x}} \frac{e^2}{|\mathbf{x}|} \ .$$

Notice that: 1) the sums over wave-vectors run here over all $\mathbf{k}$ vectors of the form $\mathbf{k} = (k_x, k_y, k_z)$ with $k_i = (2\pi n_i)/L_i$, with all possible n_i integers, and not just in the Brillouin zone (BZ) of the crystal. 2) The choice of a plane-wave basis is optimal for the kinetic energy (which is perfectly diagonal; this term gives the usual free Fermi gas problem), but not for the external potential, which mixes states of different $\mathbf{k}$-vectors, scattering a wave with $\mathbf{k}$ in all possible waves with $\mathbf{k}+\mathbf{q}$ with amplitude $v(\mathbf{q})$. 3) The interaction potential causes an even worse mixing of states, by scattering *two* particles with wave-vectors $\mathbf{k}$ and $\mathbf{k}'$ into states $\mathbf{k}+\mathbf{q}$ and $\mathbf{k}'-\mathbf{q}$, with scattering amplitude $V_{\mathrm{int}}(|\mathbf{q}|)$. For electrons in a crystalline potential, the choice of $\phi_{n\mathbf{k}}(\mathbf{x})$ as the Bloch states of the particle in the potential $v(\mathbf{x})$, where n is a band index and $\mathbf{k}$ a wave-vector running in the BZ of the (reciprocal) lattice, evidently diagonalizes the $\mathbf{p}^2/2m + v(\mathbf{x})$ part of the Hamiltonian. One could write an expression of $\widehat{H}$ in terms of such states, introducing destruction operators $a_{n\mathbf{k},\sigma}$, but you realize that the Coulomb *many-body* mixing of states is inevitable. There is no way around it.

where

$$\begin{array}{rcl} K_{\alpha',\alpha} & = & \displaystyle\int \mathrm{d}\mathbf{x}\, \phi^*_{\alpha'}(\mathbf{x}) \left(-\frac{\hbar^2}{2m}\nabla^2 + v(\mathbf{x})\right) \phi_\alpha(\mathbf{x}) \\ (\alpha'_1\alpha'_2|V_{\mathrm{int}}|\alpha_1\alpha_2) & = & \displaystyle\int \mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2\, \phi^*_{\alpha'_1}(\mathbf{x}_1)\phi^*_{\alpha'_2}(\mathbf{x}_2)V_{\mathrm{int}}(|\mathbf{x}_1-\mathbf{x}_2|)\phi_{\alpha_1}(\mathbf{x}_1)\phi_{\alpha_2}(\mathbf{x}_2) \end{array} . \qquad (4.78)$$

The difficulty in the many-body problem is that, in general, there is no simple way to write $\widehat{H}$ as a quadratic form of the creation/destruction operators. [35] If it was not for the interaction, or in any case in which we have simplified our problem to a quadratic one, one might *diagonalize* the Hamiltonian completely by writing it as:

$$\widehat{H} = \sum_\alpha \epsilon_\alpha \hat{a}^\dagger_\alpha \hat{a}_\alpha \, . \qquad (4.79)$$

For instance, if the interactions are completely neglected, clearly the best basis-set orbitals are the ones that diagonalize the one-particle Hamiltonian leading to $K_{\alpha',\alpha}$ above:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v(\mathbf{x})\right)\phi_\alpha(\mathbf{x}) = \epsilon_\alpha\phi_\alpha(\mathbf{x}) \quad \Longrightarrow \quad K_{\alpha',\alpha} = \epsilon_\alpha\delta_{\alpha',\alpha} \, . \qquad (4.80)$$

The ideal gas case. This is the setting which we consider: an *ideal quantum gas*, with Hamiltonian

$$\widehat{H} = \sum_\alpha \epsilon_\alpha \hat{a}^\dagger_\alpha \hat{a}_\alpha \, . \qquad (4.81)$$

All eigenstates of $\widehat{H}$ are simple to write in the occupation number (of Fock) representation:

$$|\{n_\alpha\}\rangle = \prod_\alpha \frac{\left(\hat{a}^\dagger_\alpha\right)^{n_\alpha}}{\sqrt{n_\alpha!}}|0\rangle = |\underline{\alpha}\rangle \quad \Longrightarrow \quad E_{\{n_\alpha\}} = \sum_\alpha \epsilon_\alpha n_\alpha = E_{\underline{\alpha}} \, . \qquad (4.82)$$

Here $n_\alpha \in \mathbb{N}$ are integers, which, for fermions cannot exceed 1 (by Pauli principle) while they can have any value for bosons. The notation $\underline{\alpha}$ will be occasionally used to distinguish these Fock many-body states from single-particle states, denoted by α. Notice that you can set $n_\alpha = 0$ for all single-particle states which are *not occupied*. The fermionic states are nothing but the second-quantized form of *Slater determinants*.

4.4.1. The canonical impasse

Let us try to calculate the canonical partition function of the ideal gas. Since the energy of the eigenstates is a *sum* of the individual single-particle energies, it seems at first sight that we have a simple problem:

$$Z_{\mathrm{CE}}(T,V,N) = \sum_{\{n_\alpha\}}^{\sum_\alpha n_\alpha = N} \mathrm{e}^{-\beta\sum_\alpha \epsilon_\alpha n_\alpha} = \sum_{\{n_\alpha\}} \delta_{N,\sum_\alpha n_\alpha} \prod_\alpha \mathrm{e}^{-\beta\epsilon_\alpha n_\alpha} \, . \qquad (4.83)$$

We see that the different sums over the n_α are "correlated" by the presence of the delta-function restriction that imposes that the total number of particles is exactly N. So, we have to get rid of this restriction on N. How? By going over to a framework in which we do not control N, but rather its conjugate thermodynamic variable μ. We will see that this leads to a new ensemble, called *grand-canonical ensemble*. This amounts, effectively, to take a discrete Laplace's transform which eliminates the delta-function restriction, as explicitly shown later on.

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[35] Many mean-field techniques — for instance, Hartree-Fock for fermionic systems — can be seen as a way of approximately reducing the quartic interaction term to a "self-consistently calculated" quadratic piece.

4.5. The grand-canonical ensemble

To construct the new ensemble in which μ is the control variable, we start from the thermodynamic Helmholtz free-energy $F(T,\underline{X},N)$ (where $\underline{X}$ are other extensive variables, reducing to the volume V in the present simple case) and take a Legendre transform with respect to N. Recall that

$$\mu = \frac{\partial F}{\partial N} \quad \overset{\text{Invert}}{\Longrightarrow} \quad N(T,\underline{X},\mu) \ ,$$

and calculate

$$\Omega(T,\underline{X},\mu) = F - \mu N = E - TS - \mu N \ , \tag{4.84}$$

with the prescription that where you see N you should substitute $N(T,\underline{X},\mu)$. Recall that all the derivatives of F remain untouched for Ω (simply expressed in the new variables) except for the derivative with respect to the Legendre-transformed variable μ which gets an extra minus sign:

$$N = -\frac{\partial \Omega}{\partial \mu} \ . \tag{4.85}$$

For the case of a simple fluid where $F(T,V,N)$ we would write the differential of Ω and Ω itself (recalling the Euler relation $E = TS - pV + \mu N$) as:

$$\begin{aligned} \mathrm{d}\Omega &\equiv -S\mathrm{d}T - p\mathrm{d}V - N\mathrm{d}\mu \\ \Omega &= F - \mu N = E - TS - \mu N \equiv -pV \end{aligned} \ , \tag{4.86}$$

where in the last equation we should intend that $p(T,\mu)$. Notice that similarity with the Gibbs potential, $G = F + pV = -\mu N$: the grand-canonical potential Ω is nothing but (minus) the pressure-per-unit-volume (a product of the extensive variable V times its intensive generalized force $-p$).

How do we write a statistical ensemble to calculate Ω?

The gran-canonical ensemble. The analogy with the canonical ensemble suggests that a good candidate is to set

$$\text{GCE} \left\{ \begin{array}{lcl} \langle \hat{A} \rangle_{\text{GCE}}(T,\underline{X},\mu) & \equiv & \mathrm{Tr}\left[\hat{A}\,\hat{\rho}_{\text{GCE}}\right] \\ \hat{\rho}_{\text{GCE}} & = & \displaystyle\sum_{\underline{\alpha}} \frac{\mathrm{e}^{-\beta(E_{\underline{\alpha}} - \mu N_{\underline{\alpha}})}}{Z_{\text{GCE}}} |\underline{\alpha}\rangle\langle\underline{\alpha}| = \frac{\mathrm{e}^{-\beta(\widehat{H} - \mu\widehat{N})}}{Z_{\text{GCE}}} \\ Z_{\text{GCE}} & = & \displaystyle\sum_{\underline{\alpha}} \mathrm{e}^{-\beta(E_{\underline{\alpha}} - \mu N_{\underline{\alpha}})} = \mathrm{Tr}\,\mathrm{e}^{-\beta(\widehat{H} - \mu\widehat{N})} \overset{\text{Thermodynamics}}{\equiv} \mathrm{e}^{-\beta\Omega(T,\underline{X},\mu)} \end{array} \right. .$$

where $|\underline{\alpha} = |\{n_\alpha\}\rangle$ denotes the many-body Fock states, $N_{\underline{\alpha}} = \langle\underline{\alpha}|\widehat{N}|\underline{\alpha}\rangle = \sum_\alpha n_\alpha$, and $E_{\underline{\alpha}} = \langle\underline{\alpha}|\widehat{H}|\underline{\alpha}\rangle = \sum_\alpha \epsilon_\alpha n_\alpha$.

To verify that this ensemble *Ansatz* is indeed correct, let us calculate the average N: [36]

$$N = \langle\widehat{N}\rangle_{\text{GCE}} = \sum_{\underline{\alpha}} N_{\underline{\alpha}} \frac{\mathrm{e}^{-\beta(E_{\underline{\alpha}} - \mu N_{\underline{\alpha}})}}{Z_{\text{GCE}}} = \frac{1}{\beta}\frac{\partial \log Z_{\text{GCE}}}{\partial \mu} \overset{!}{\equiv} -\frac{\partial \Omega}{\partial \mu} \ ,$$

---

[36] Please observe that the notation used here is such that $\underline{\alpha}$ denotes *many-body states* of the whole system, and not the single-particle orbitals that we introduced in the previous section. Notice also that the density matrix $\hat{\rho}_{\text{GCE}}$ acts in the grand-canonical-Hilbert space, also known as Fock space $\mathcal{F}$, made by the direct sum of the Hilbert-spaces $\mathcal{H}_N$ with given N, for all $N = 0, \cdots \infty$:

$$\mathcal{F} = \oplus_{N=0}^{\infty} \mathcal{H}_N \ .$$

which is once again the correct thermodynamical relation for N. Notice that $\overset{!}{=}$ in the second line means that we have used there our *Ansatz* which states that $\log Z_{\mathrm{GCE}} = -\beta\Omega$.

Equally simple is the calculation of the average $E - \mu N$ in the ensemble. According to the prescriptions we have:

$$\begin{aligned} E - \mu N &= \langle \widehat{H} - \mu\widehat{N}\rangle_{\mathrm{GCE}} = \sum_{\underline{\alpha}} (E_{\underline{\alpha}} - \mu N_{\underline{\alpha}}) \, \frac{\mathrm{e}^{-\beta(E_{\underline{\alpha}}-\mu N_{\underline{\alpha}})}}{Z_{\mathrm{GCE}}} = -\frac{\partial \log Z_{\mathrm{GCE}}}{\partial \beta} \\ &\overset{!}{\equiv} \Omega + \beta\frac{\partial\Omega}{\partial\beta} = \Omega - T\frac{\partial\Omega}{\partial T} = \Omega + TS \;, \end{aligned} \tag{4.87}$$

which is indeed the correct thermodynamical relation for Ω.

One final thing to observe is that you can rewrite Z_{GCE} as follows:

$$Z_{\mathrm{GCE}}(T,\underline{X},\mu) = \sum_{\underline{\alpha}} \mathrm{e}^{-\beta(E_{\underline{\alpha}}-\mu N_{\underline{\alpha}})} = \sum_{N=0}^{\infty} \mathrm{e}^{\beta\mu N} Z_{\mathrm{CE}}(T,\underline{X},N) = \sum_{N=0}^{\infty} z^N Z_{\mathrm{CE}}(T,\underline{X},N) \;, \tag{4.88}$$

which can be regarded as the *discrete Laplace transform* of Z_{CE}, where $-\beta\mu$ is the "Laplace variable". Notice that one often introduces the so-called *fugacity* $z = \mathrm{e}^{\beta\mu}$ in terms which we have the last relationship above. These last remarks should clarify how the grand-canonical ensemble effectively "solves" the canonical *impasse* discussed in Sec. 4.4.1 for the non-interacting quantum gases.

4.5.1. Fluctuations of particle number in the grand-canonical ensemble

As we have seen, the *average* number of particles $N(T,\underline{X},\mu)$ can be directly calculated from the grand-canonical partition function:

$$N(T,\underline{X},\mu) = \langle\hat{N}\rangle_{\mathrm{GCE}} = \frac{\sum_{\underline{\alpha}} N_{\underline{\alpha}} \mathrm{e}^{-\beta(E_{\underline{\alpha}}-\mu N_{\underline{\alpha}})}}{Z_{\mathrm{GCE}}} = \frac{1}{\beta}\frac{\partial \log Z_{\mathrm{GCE}}}{\partial\mu} = -\frac{\partial\Omega}{\partial\mu} \;. \tag{4.89}$$

We can go beyond that, and calculate the *second cumulant* by taking a further derivative of $\log Z_{\mathrm{GCE}}$:

$$\frac{1}{\beta}\frac{\partial N}{\partial\mu} = \langle\hat{N}^2\rangle - \langle\hat{N}\rangle^2 = -\frac{1}{\beta}\frac{\partial^2\Omega}{\partial\mu^2} \;. \tag{4.90}$$

The fluctuations of N around the average. The interesting fact is that, once again, the variance of $\hat{N}$ is connected to a thermodynamical quantity, the isothermal *compressibility* κ_T, and that the relative fluctuations of N around the average are small, of order $1/\sqrt{V}$:

$$\frac{\sqrt{\langle\hat{N}^2\rangle - \langle\hat{N}\rangle^2}}{\langle\hat{N}\rangle} = \frac{\sqrt{k_B T\kappa_T}}{\sqrt{V}} \;. \tag{4.91}$$

Indeed, one can show that the iso-thermal "number" compressibility is closely related to the corresponding "volume" compressibility:

$$\frac{1}{N}\frac{\partial N}{\partial\mu} = \frac{N}{V}\kappa_T \qquad \Longrightarrow \qquad \frac{\langle\hat{N}^2\rangle - \langle\hat{N}\rangle^2}{\langle\hat{N}\rangle^2} = \frac{k_B T}{V}\kappa_T \;, \tag{4.92}$$

where the iso-thermal volume compressibility is:

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} \;, \tag{4.93}$$

where $N(T, \underline{X}, \mu)$ should be used, as usual.

To prove this remarkable identity between two seemingly unrelated thermodynamic derivatives, one needs a Jacobean gymnastics which you can find explained in some detail in App. B. Let me recall, very briefly, how the machinery works. Let $f_i(\mathbf{x})$ with $i = 1 \cdots n$ be functions of the n variables $\mathbf{x} = x_1 \cdots x_n$. We denote the Jacobean determinant as:

$$\frac{\partial(f_1, f_2, \cdots, f_n)}{\partial(x_1, x_2, \cdots, x_n)} = \det \begin{pmatrix} \frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} & \cdots & \frac{\partial f_1}{\partial x_n} \\ \frac{\partial f_2}{\partial x_1} & \frac{\partial f_2}{\partial x_2} & \cdots & \frac{\partial f_2}{\partial x_n} \\ \vdots & \vdots & \cdots & \vdots \\ \frac{\partial f_n}{\partial x_1} & \frac{\partial f_n}{\partial x_2} & \cdots & \frac{\partial f_n}{\partial x_n} \end{pmatrix} . \tag{4.94}$$

It is simple to verify that

$$\left(\frac{\partial N}{\partial \mu}\right)_{T,V} = \frac{\partial(N, T, V)}{\partial(\mu, T, V)} . \tag{4.95}$$

The usefulness of such a simple rewriting is that you can now repeatedly use the chain rules of calculus (and the fact that the determinant of a product is the product of the determinants) to show that you can rewrite:

$$\begin{aligned} \left(\frac{\partial N}{\partial \mu}\right)_{T,V} = \frac{\partial(N, T, V)}{\partial(\mu, T, V)} &= \frac{\partial(N, T, V)}{\partial(N, T, p)} \frac{\partial(N, T, p)}{\partial(V, T, p)} \frac{\partial(V, T, p)}{\partial(\mu, T, N)} \frac{\partial(\mu, T, N)}{\partial(\mu, T, V)} \\ &= \left(\frac{\partial V}{\partial p}\right)_{T,N} \cdot \frac{N}{V} \cdot \frac{\partial(V, p)}{\partial(\mu, N)} \cdot \frac{N}{V} , \end{aligned} \tag{4.96}$$

where we used that:

$$\frac{\partial(N, T, p)}{\partial(V, T, p)} = \frac{\partial(\mu, T, N)}{\partial(\mu, T, V)} = \frac{N}{V} \tag{4.97}$$

and that

$$\frac{\partial(V, T, p)}{\partial(\mu, T, N)} = \frac{\partial(T, V, p)}{\partial(T, \mu, N)} = \frac{\partial(V, p)}{\partial(\mu, N)} , \tag{4.98}$$

because a determinant does not change if you interchange two columns and two rows (this was used to move T to the first position and then get rid of it). And now comes a highly non-trivial identity: if you have a thermodynamic potential whose differential contains a term like $f_1 \, dx_1 + f_2 \, dx_2$ then, quite remarkably, it follows that:

$$\frac{\partial(f_1, x_1)}{\partial(f_2, x_2)} = -1 . \tag{4.99}$$

To apply this result to our case, notice that $d\Omega = -S dT - p dV - N d\mu$, from which you deduce that

$$-1 = \frac{\partial(-p, V)}{\partial(-N, \mu)} = \frac{\partial(p, V)}{\partial(N, \mu)} = \frac{\partial(V, p)}{\partial(\mu, N)} . \tag{4.100}$$

So, substituting back in the original expression we conclude that:

$$\left(\frac{\partial N}{\partial \mu}\right)_{T,V} = -\frac{N^2}{V^2} \left(\frac{\partial V}{\partial p}\right)_{T,N} = \frac{N^2}{V} \kappa_T . \tag{4.101}$$

4.6. Ideal quantum gas in grand-canonical ensemble

The calculation of Z_{GCE} for the ideal quantum gas is immediate since we get rid of the annoying restriction $\delta_{N,\sum_\alpha n_\alpha}$. The result is:

$$\begin{aligned} Z_{\text{GCE}} &= \sum_{\underline{\alpha}} \mathrm{e}^{-\beta(E_{\underline{\alpha}}-\mu N_{\underline{\alpha}})} = \sum_{\underline{\alpha}} \mathrm{e}^{-\beta\sum_\alpha(\epsilon_\alpha-\mu)n_\alpha} \\ &= \sum_{\{n_\alpha\}} \prod_\alpha \mathrm{e}^{-\beta(\epsilon_\alpha-\mu)n_\alpha} = \prod_\alpha \left(\sum_{n_\alpha} \mathrm{e}^{-\beta(\epsilon_\alpha-\mu)n_\alpha} \right) = \prod_\alpha \begin{cases} 1+\mathrm{e}^{-\beta(\epsilon_\alpha-\mu)} & \text{(F)} \\ \dfrac{1}{1-\mathrm{e}^{-\beta(\epsilon_\alpha-\mu)}} & \text{(B)} \end{cases} . \end{aligned} \tag{4.102}$$

> **The bosonic case.** Observe that in the bosonic case the geometric series converges only if
>
> $$\mu < \min\{\epsilon_\alpha\} \ .$$
>
> This will be important when discussing Bose-Einstein condensation, which we will see to occur precisely when $\mu \to \epsilon_{\text{min}}^{-}$.

The calculation of the grand-canonical potential is immediate:

$$\Omega(T,V,\mu) = -\frac{1}{\beta}\sum_\alpha \begin{cases} \log(1+\mathrm{e}^{-\beta(\epsilon_\alpha-\mu)}) & \text{(F)} \\ -\log(1-\mathrm{e}^{-\beta(\epsilon_\alpha-\mu)}) & \text{(B)} \end{cases} = \frac{\xi}{\beta}\sum_\alpha \log(1-\xi\mathrm{e}^{-\beta(\epsilon_\alpha-\mu)}) \ , \tag{4.103}$$

where we have introduced the statistical factor $\xi = -1$ for fermions (F) and $\xi = +1$ for bosons (B).

> **Volume dependence.** The T and μ dependence of Ω is quite transparent. Less obvious is the V dependence. But recall that the eigenvalues ϵ_α will be discrete in a finite quantization volume V, and indeed volume-dependent, $\epsilon_\alpha(V)$. For a system in a cubic box with periodic boundary conditions, $\mathbf{k} = \frac{2\pi}{L}(n_1,\cdots,n_d)$, and with a spherically symmetric dispersion $\epsilon_k = Ak^\alpha$ you easily calculate:
>
> $$\frac{\partial\epsilon_k}{\partial V} = \frac{\partial\epsilon_k}{\partial k}\frac{\partial k}{\partial L}\left(\frac{\partial V}{\partial L}\right)^{-1} = -\frac{\alpha}{d}\frac{\epsilon_k}{V} \ , \tag{4.104}$$
>
> which will be useful later on.

The whole thermodynamics follows from $\Omega(T,V,\mu)$; recall that $\mathrm{d}\Omega \equiv -S\mathrm{d}T - p\mathrm{d}V - N\mathrm{d}\mu$. The derivatives of Ω are immediate:

$$\begin{aligned} S &= -\frac{\partial\Omega}{\partial T} = \frac{1}{T}\left[-\frac{\xi}{\beta}\sum_\alpha \log(1-\xi\mathrm{e}^{-\beta(\epsilon_\alpha-\mu)}) + \sum_\alpha \frac{\epsilon_\alpha-\mu}{\mathrm{e}^{\beta(\epsilon_\alpha-\mu)}-\xi} \right] \\ p &= -\frac{\partial\Omega}{\partial V} \overset{\text{Euler}}{\equiv} -\frac{\Omega}{V} = -\frac{\xi}{\beta V}\sum_\alpha \log(1-\xi\mathrm{e}^{-\beta(\epsilon_\alpha-\mu)}) \\ N &= -\frac{\partial\Omega}{\partial\mu} = \sum_\alpha \frac{1}{\mathrm{e}^{\beta(\epsilon_\alpha-\mu)}-\xi} \equiv \sum_\alpha \langle \hat{a}_\alpha^\dagger \hat{a}_\alpha \rangle_{\text{GCE}} \\ \langle \hat{a}_\alpha^\dagger \hat{a}_\alpha \rangle_{\text{GCE}} &\equiv \frac{1}{\mathrm{e}^{\beta(\epsilon_\alpha-\mu)}-\xi} \end{aligned} \tag{4.105}$$

A few comments are in order. First, observe the important ingredient: the Fermi/Bose distribution function which gives the average of the occupation number operator, which we have highlighted in the last expression:

$$\langle \hat{a}^{\dagger}_{\alpha}\hat{a}_{\alpha}\rangle_{\text{GCE}} = \left\{ \begin{array}{l} f_F(\epsilon_\alpha-\mu) \equiv \dfrac{1}{\mathrm{e}^{\beta(\epsilon_\alpha-\mu)}+1} \\ \\ f_B(\epsilon_\alpha-\mu) \equiv \dfrac{1}{\mathrm{e}^{\beta(\epsilon_\alpha-\mu)}-1} \end{array} \right. . \tag{4.106}$$

Second, notice that we have by-passed the explicit calculation of the pressure — requiring a derivative of Ω with respect to V —, by explicitly using the Euler-derived equality $p = -\Omega/V$. A direct calculation of such a volume derivative, however, would show a non-trivial identity:

$$p = -\frac{\partial\Omega}{\partial V} = -\sum_\alpha \frac{\left(\frac{\partial\epsilon_\alpha}{\partial V}\right)}{\mathrm{e}^{\beta(\epsilon_\alpha-\mu)}-\xi} \equiv -\left\langle \sum_\alpha \frac{\partial\epsilon_\alpha}{\partial V}\hat{a}^{\dagger}_{\alpha}\hat{a}_{\alpha}\right\rangle_{\text{GCE}} = -\left\langle\frac{\partial\widehat{H}}{\partial V}\right\rangle_{\text{GCE}} , \tag{4.107}$$

where in the last equality we have introduced the partial derivative of $\widehat{H}$ with respect to V, which involves only the eigenvalues $\epsilon_\alpha(V)$ and should not be confused with the volume derivative of the average energy (which would involve also to the *occupation* of each state, hence a contribution from an entropic term): it is an *iso-entropic* derivative (recall the discussion we had in revisiting the canonical ensemble from the point of view of thermodynamics).

Relationship between Ω, E, and p. Using $\frac{\partial\epsilon_k}{\partial V} = -\frac{\alpha}{d}\frac{\epsilon_k}{V}$, it is simple to show that:

$$-\frac{\Omega}{V} \overset{\text{Euler}}{\equiv} p(T,\mu) = -\left\langle\frac{\partial\widehat{H}}{\partial V}\right\rangle_{\text{GCE}} = \frac{\alpha}{d}\frac{E}{V} \qquad \Longrightarrow \qquad -\Omega = pV = \frac{\alpha}{d}E(T,V,\mu) . \tag{4.108}$$

For non-relativistic particles, $-\Omega = pV = \frac{2}{d}E$. For the case of photons, [a] i.e., a linear dispersion in $d=3$, we have $-\Omega = pV = \frac{1}{3}E$. Physically, this means that the thermal radiation field exerts pressure on the walls of the cavity in which it is enclosed. Notice that the pressure, being intensive, cannot depend on the volume when the other two variables are intensive, hence we have $p(T,\mu)$.

---

[a] You can verify that the present grand-canonical formalism with $\mu = 0$ gives back the same formulas we derived in the canonical ensemble.

It is instructive to re-derive such non-trivial relationships via the density of states, through integration by parts. Indeed, we can rewrite the grand-canonical potential as:

$$\Omega = \frac{\xi}{\beta}\int_0^\infty \mathrm{d}\epsilon\, g(\epsilon)\, \log(1-\xi\mathrm{e}^{-\beta(\epsilon-\mu)}) , \tag{4.109}$$

where $g(\epsilon) = \sum_\alpha \delta(\epsilon-\epsilon_\alpha)$ is the density of states. [37] Consider now the integral of the density of states $G(\epsilon) = \int_0^\epsilon \mathrm{d}\epsilon' g(\epsilon')$ (i.e., the total number of states up to ϵ) and rewrite the integral by parts:

$$\begin{aligned} \Omega &= \frac{\xi}{\beta}\left[G(\epsilon)\log(1-\xi\mathrm{e}^{-\beta(\epsilon-\mu)})\Big|_0^\infty - \int_0^\infty \mathrm{d}\epsilon\, G(\epsilon)\frac{\xi\beta}{\mathrm{e}^{\beta(\epsilon-\mu)}-\xi}\right] = -\int_0^\infty \mathrm{d}\epsilon\, G(\epsilon)\frac{1}{\mathrm{e}^{\beta(\epsilon-\mu)}-\xi} \\ &\overset{!}{=} -\frac{1}{\alpha_g+1}\int_0^\infty \mathrm{d}\epsilon\, g(\epsilon)\frac{\epsilon}{\mathrm{e}^{\beta(\epsilon-\mu)}-\xi} = -\frac{\alpha}{d}E(T,V,\mu) . \end{aligned} \tag{4.110}$$

Notice that in the first step I have dropped the boundary term (assuming that the density of states extends up to ∞), while in the last steps I have assumed a power-law scaling for $g(\epsilon) = A_g\epsilon^{\alpha_g}$ which leads to $G(\epsilon) = \epsilon g(\epsilon)/(\alpha_g+1)$.

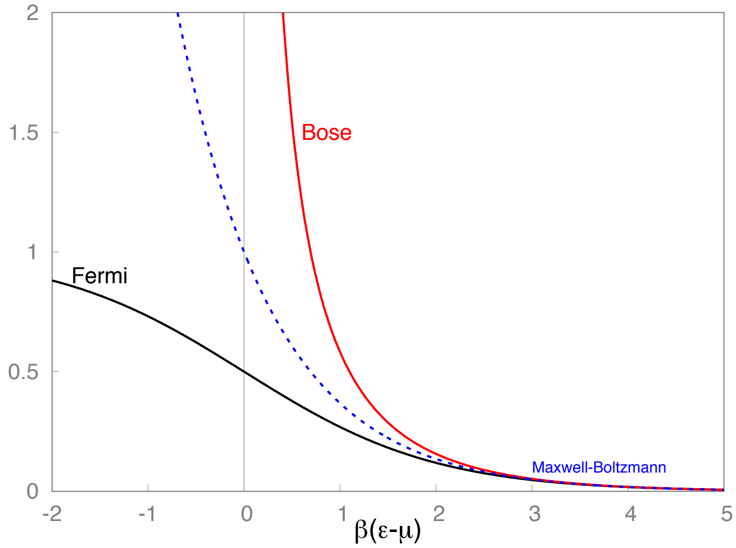

Figure 4.6.: Plot of the Fermi and Bose distribution functions, compared to the Maxwell-Boltzmann limiting distributions to which both converge in the limit of large $\beta(\epsilon_\alpha - \mu)$.

4.6.1. Maxwell-Boltzmann limit

We would expect that there should be some classical limit in which the *statistics* of our quantum particles should make no difference: after all the ideal classical gas laws should be recovered in some limit. The crucial ingredient to take care is the statistics-related factor ξ. Let us look at Ω

$$\Omega(T,V,\mu) = \frac{\xi}{\beta} \sum_\alpha \log(1 - \xi e^{-\beta(\epsilon_\alpha - \mu)}) \;, \tag{4.111}$$

from which all the thermodynamics follows. Observe that we can approximate the logarithm by its lowest-order expansion if

$$e^{-\beta(\epsilon_\alpha-\mu)} \ll 1 \;\; \forall\alpha \quad \Longrightarrow \quad \Omega = \frac{\xi}{\beta}\sum_\alpha \log(1-\xi e^{-\beta(\epsilon_\alpha-\mu)}) \approx -k_B T \sum_\alpha e^{-\beta(\epsilon_\alpha-\mu)} \equiv \Omega_{\mathrm{MB}} \;, \tag{4.112}$$

an expression that is *independent* from the statistics. In the same limit

$$e^{\beta(\epsilon_\alpha-\mu)} \gg 1 \;\; \forall\alpha \quad \Longrightarrow \quad N = \sum_\alpha \frac{1}{e^{\beta(\epsilon_\alpha-\mu)} - \xi} \approx \sum_\alpha e^{-\beta(\epsilon_\alpha-\mu)} \equiv N_{\mathrm{MB}} \;, \tag{4.113}$$

which we might express by saying that in this regime the Fermi/Bose distributions approach a common limit:

$$e^{-\beta(\epsilon_\alpha-\mu)} \ll 1 \;\; \forall\alpha \quad \Longrightarrow \quad f_F(\epsilon_\alpha-\mu) \approx f_B(\epsilon_\alpha-\mu) \approx e^{-\beta(\epsilon_\alpha-\mu)} \equiv f_{\mathrm{MB}}(\epsilon_\alpha-\mu) \;. \tag{4.114}$$

This limiting distribution, and the regime in which it applies, see Fig. 4.6, is called *Maxwell-Boltzmann.*

---

[37] Notice that we have omitted here the volume factor. Notice also that in principle there are issues associated with Bose condensation in the lowest eigenvalue; in the end, those issues will not change the result we will derive, since energy (and pressure) contribution of the Bose-condensed fraction is vanishingly small.

The classical ideal gas. We now show that in the Maxwell-Boltzmann limit the classical ideal gas equations of state are recovered. Indeed, looking at the pressure, we have:

$$-pV = \Omega \approx -(k_BT)N \quad \Longrightarrow \quad pV \approx Nk_BT \; . \tag{4.115}$$

We recover the *classical ideal gas equation of state.* For non-relativistic particles in d dimensions, since $\Omega = -\frac{2}{d}E$, we also immediately get the other ideal-gas classical relationship:

$$E = -\frac{d}{2}\Omega \approx \frac{d}{2}Nk_BT \; .$$

Let us explore a bit more the regime in which our quantum gas becomes essentially classical. One of our goals is to show that in this limit we recover the prescription on the h^{dN} factor we used in the classical partition function, and also the $1/N!$ indistinguishability factor we have inserted in a rather *ad hoc* fashion, to make the classical entropy nicely extensive.

One of the things that you should not be fooled by, is to assume that the classical limit corresponds to *high temperature* (which is true) and *hence* you can take $\mathrm{e}^{\beta(\mu-\epsilon_\alpha)} \approx 1$, which is *wrong*, because in the Maxwell-Boltzmann limit the chemical potential μ turns out to be *large and negative*, as we will now show, leading to $\mathrm{e}^{\beta(\mu-\epsilon_\alpha)} \ll 1$.

For definiteness, let us consider the usual free-particles with non-relativistic dispersion $\epsilon_{\mathbf{k}} = \hbar^2|\mathbf{k}|^2/(2m)$. Accounting for a degeneracy factor g_S related to the spin of the particles ($g_S = 2S+1$), the average number of particles N in the Maxwell-Boltzmann limit is given by:

$$\begin{aligned} N \approx g_S \sum_{\mathbf{k}} \mathrm{e}^{-\beta(\epsilon_{\mathbf{k}}-\mu)} \quad &\approx g_S \mathrm{e}^{\beta\mu} L^d \int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^d}\, \mathrm{e}^{-\beta\epsilon_{\mathbf{k}}} \\ &= g_S \mathrm{e}^{\beta\mu} V \int \frac{\mathrm{d}\mathbf{p}}{(2\pi\hbar)^d}\, \mathrm{e}^{-\beta\frac{\mathbf{p}^2}{2m}} = g_S \mathrm{e}^{\beta\mu} \overbrace{\int \frac{\mathrm{d}\mathbf{q}\,\mathrm{d}\mathbf{p}}{h^d}\, \mathrm{e}^{-\beta H_{\mathrm{cl}}(\mathbf{q},\mathbf{p})}}^{Z_1^{\mathrm{cl}}} \\ &= g_S \mathrm{e}^{\beta\mu} V \left(\frac{2\pi m k_BT}{h^2}\right)^{\frac{d}{2}} = g_S \mathrm{e}^{\beta\mu} \frac{V}{\lambda_T^d} \; . \end{aligned} \tag{4.116}$$

In the last expression, we have performed the Gaussian integral and observed that this brings-in a quantum-related length

$$\lambda_T^2 = \frac{h^2}{2\pi m k_BT} \qquad \Longrightarrow \qquad \frac{\hbar^2}{2m\lambda_T^2} = \frac{k_BT}{4\pi} \; , \tag{4.117}$$

known as *thermal de-Broglie wavelength.* The expression just above it suggests a relationship with the classical single-particle partition function, with a conspicuous factor h^d in the denominator. We can rewrite the expression we have derived as:

$$\mathrm{e}^{\beta\mu} \approx \frac{N\lambda_T^d}{g_S V} \; . \tag{4.118}$$

But in the Maxwell-Boltzmann limit we must have $\mathrm{e}^{\beta(\mu-\epsilon_{\mathbf{k}})} \ll 1 \;\; \forall \epsilon_{\mathbf{k}}$, hence:

$$\mathrm{e}^{\beta\mu} \ll 1 \quad \Longrightarrow \quad \lambda_T^d \ll g_S \frac{V}{N} = \frac{g_S}{n} \; ,$$

where $n = N/V$ is the density.

> **The classical limit.** Hence, the classical limit requires that T is large enough so that the thermal de-Broglie wavelength is much smaller than the average inter-particle separation:
>
> $$\lambda_T^d \ll g_S \frac{V}{N} = \frac{g_S}{n} \; . \tag{4.119}$$
>
> Correspondingly the chemical potential must be large and negative:
>
> $$\mu \approx -k_B T \, \log \frac{g_S V}{N \lambda_T^d} = -k_B T \, \log \frac{g_S V}{N} \Big(\frac{2\pi m}{h^2} k_B T \Big)^{\frac{d}{2}} \; . \tag{4.120}$$
>
> We see that the classical limit requires a combination of high-T/low-density, or, better, a precise relationship between the thermal length λ_T and the density.

We are not done yet. I promised we would understand the $1/N!$ (Gibbs counting). To do that, we have to get the *canonical* partition function, which is rather easy to extract in the Maxwell-Boltzmann limit. Observe that $-\beta\Omega_{\mathrm{MB}} = N_{\mathrm{MB}} = g_S \mathrm{e}^{\beta\mu} Z_1^{\mathrm{cl}}$, hence:

$$Z^{\mathrm{MB}}_{\mathrm{GCE}}(T,V,\mu) = \mathrm{e}^{-\beta\Omega_{\mathrm{MB}}} = \mathrm{e}^{g_S \mathrm{e}^{\beta\mu} Z_1^{\mathrm{cl}}} \; . \tag{4.121}$$

Next, Taylor-expand the exponential e^x with $x = g_S \mathrm{e}^{\beta\mu} Z_1^{\mathrm{cl}}$ to deduce that:

$$Z^{\mathrm{MB}}_{\mathrm{GCE}}(T,V,\mu) = \mathrm{e}^{g_S \mathrm{e}^{\beta\mu} Z_1^{\mathrm{cl}}} = \sum_{N=0}^{\infty} \mathrm{e}^{\beta\mu N} \underbrace{\frac{1}{N!} \big(g_S Z_1^{\mathrm{cl}}\big)^N}_{Z^{\mathrm{MB}}_{\mathrm{CE}}} \equiv \sum_{N=0}^{\infty} \mathrm{e}^{\beta\mu N} Z^{\mathrm{MB}}_{\mathrm{CE}}(T,V,N) \; . \tag{4.122}$$

This leads us to the conclusion that in the Maxwell-Boltzmann limit, for free gas, we should use:

$$Z^{\mathrm{MB}}_{\mathrm{CE}}(T,V,N) = \frac{g_S^N}{N!} \big(Z_1^{\mathrm{cl}}\big)^N = \frac{g_S^N}{N!} \int \frac{\mathrm{d}\mathbf{q}_1 \cdots \mathrm{d}\mathbf{q}_N \mathrm{d}\mathbf{p}_1 \cdots \mathrm{d}\mathbf{p}_N}{h^{dN}} \, \mathrm{e}^{-\beta H_{\mathrm{cl}}(\mathbf{q}_1 \cdots \mathbf{q}_N, \mathbf{p}_1 \cdots \mathbf{p}_N)} \; , \tag{4.123}$$

which coincides with our guess when $g_S = 1$ (no spin degeneracy). [38]

A word about the *entropy of mixing and the Gibbs paradox*, see for instance [5][Sec. 1.5]. As you recall, this Gibbs counting $1/N!$ makes the classical entropy nicely extensive. If you drop it, you would find the paradox — known as *Gibbs paradox* — that mixing (by removing an internal wall) two identical ideal gases at the same density and temperature leads to an increase in the total entropy. Notice that mixing two *different* gases, or even the same gas but at two different densities and/or temperatures, does lead to an increase of entropy, but this is not a paradox: indeed, mixing is irreversible. But when the two gases are identical and in identical thermodynamic conditions, removing or inserting a division wall is a perfectly reversible action. If you do the calculation *without* the Gibbs factor $1/N!$ you would find an increase of entropy also in this reversible case.

We now move to the analysis of the low-temperature behaviour of quantum ideal gases, where statistics plays a crucial role. We start with fermions.

---

[38] Obviously, this shows the validity of the Gibbs counting prescription only for free gas in a box. A similar exercise can be repeated for free particles in a parabolic confining potential, and the result would be once again the one we have stated. For general interacting quantum particles, the derivation of the classical limit is not that straightforward, as far as I can see.

4.6.2. The ideal Fermi gas

Let us start with the ideal Fermi gas. The grand-canonical potential is:

$$\begin{aligned}\Omega &= -k_BT \sum_{\alpha} \log(1+\mathrm{e}^{-\beta(\epsilon_\alpha-\mu)}) \\ &= -k_BT\, V \int_{-\infty}^{\infty} \mathrm{d}\epsilon\; g(\epsilon)\; \log(1+\mathrm{e}^{-\beta(\epsilon-\mu)}) \;, \end{aligned} \tag{4.124}$$

where we have defined as usual the density-of-states per unit volume:

$$g(\epsilon) = \frac{1}{V}\sum_{\alpha} \delta(\epsilon-\epsilon_\alpha) \tag{4.125}$$

The total number of fermions is, recalling that $f_F(\epsilon-\mu) = \frac{1}{\mathrm{e}^{\beta(\epsilon-\mu)}+1}$:

$$\begin{aligned} N = -\frac{\partial\Omega}{\partial\mu} = \sum_{\alpha}\frac{1}{\mathrm{e}^{\beta(\epsilon_\alpha-\mu)}+1} &= \sum_{\alpha} f_F(\epsilon_\alpha-\mu) \\ &= V\int_{-\infty}^{\infty}\mathrm{d}\epsilon\; g(\epsilon)\; f_F(\epsilon-\mu)\;. \end{aligned} \tag{4.126}$$

> **Inverting $N(\mu,T)$.** The grand-canonical ensemble was instrumental in doing the calculations, but we would like to express physical quantities in terms N, or the density $n=\frac{N}{V}$, rather than μ. So, we would like to invert this dependence and express $\mu(n,T)$. We will do that at low-T only: for general T, you need a numerical approach.

By considering the usual non-relativistic dispersion $\epsilon_{\mathbf{k}} = \frac{\hbar^2|\mathbf{k}|^2}{2m}$, one can write:

$$g(\epsilon) = g_S\,\frac{\Omega_d}{(2\pi)^d}\,\frac{1}{2}\left(\frac{2m}{\hbar^2}\right)^{\frac{d}{2}}\epsilon^{\frac{d}{2}-1}\;, \tag{4.127}$$

where $g_S=2$ corresponds to the spin-degeneracy factor for a spin-1/2 particle. We *define* the $T=0$ chemical potential to be ϵ_F, the so-called *Fermi energy*. The Fermi function, observe, approaches more and more a Heaviside distribution as we lower the temperature. So, at $T=0$ we have:

$$\mu(T=0) \overset{\mathrm{def}}{=} \epsilon_F \qquad \text{and} \qquad f_F(\epsilon_{\mathbf{k}}-\epsilon_F) = \Theta(\epsilon_F-\epsilon_{\mathbf{k}}) = \Theta(k_F-|\mathbf{k}|)\;,$$

where $\Theta(x)$ is the Heaviside function and we have defined, for a spherically symmetric dispersion, the Fermi momentum k_F to be simply the value of $|\mathbf{k}|$ at which $\epsilon_{k_F}=\epsilon_F$. In words: all energy levels with $\epsilon_{\mathbf{k}}<\epsilon_F$, or equivalently $|\mathbf{k}|<k_F$, are occupied with only one particle, according to the Pauli principle; but we must also account for the spin-degeneracy factor $g_S=2$.

We now impose that zero-temperature the chemical potential, ϵ_F, is such as to fit all particles:

$$\begin{aligned} N = V\int_0^{\epsilon_F}\mathrm{d}\epsilon\; g(\epsilon) &= g_S\,V\,\frac{\Omega_d}{(2\pi)^d}\,\frac{1}{d}\left(\frac{2m}{\hbar^2}\right)^{\frac{d}{2}}\epsilon_F^{\frac{d}{2}} \\ &= g_S\,V\,\frac{\Omega_d}{(2\pi)^d}\,\frac{1}{d}\,k_F^d\;, \end{aligned} \tag{4.128}$$

where $\epsilon_F = \frac{\hbar^2k_F^2}{2m}$. Notice that the expression in terms of k_F is more general: any *isotropic dispersion* $\epsilon_{|\mathbf{k}|}$ would be expressed in terms of k_F in the same way:

$$N = g_S\,V\int\frac{\mathrm{d}\mathbf{k}}{(2\pi)^d}\,\theta(k_F-|\mathbf{k}|) = g_S\,V\,\frac{\Omega_d}{(2\pi)^d}\int_0^{k_F}\mathrm{d}k\;k^{d-1} = g_S\,V\,\frac{\Omega_d}{(2\pi)^d}\,\frac{k_F^d}{d}\;. \tag{4.129}$$

A useful expression is also the fact that:

$$g(\epsilon_F) = g_S \, \frac{\Omega_d}{(2\pi)^d} \, \frac{1}{2} \left(\frac{2m}{\hbar^2}\right)^{\frac{d}{2}} \frac{\epsilon_F^{\frac{d}{2}}}{\epsilon_F} = \frac{d}{2} \frac{n}{\epsilon_F} \,, \tag{4.130}$$

where $n = N/V$ is the density of particles.

These considerations fix the limiting behaviour of $\mu(T \to 0) = \epsilon_F$: a curve for $\mu(T, n)$ will eventually, starting from $\mu(0, n) = \epsilon_F$, reach the classical expression in Eq. (4.120), $\mu \approx -k_B T \, \log \frac{g_S}{n} (\frac{2\pi m}{h^2} k_B T)^{\frac{d}{2}}$.

Let us see how to calculate the corrections to this $T = 0$ result. Consider the expressions for $N(T, V, \mu)$ or $E(T, V, \mu)$:

$$\begin{aligned} N(T,V,\mu) &= V \int_0^\infty \mathrm{d}\epsilon \; g(\epsilon) \, f_F(\epsilon - \mu) \\ E(T,V,\mu) &= V \int_0^\infty \mathrm{d}\epsilon \; g(\epsilon) \, \epsilon \, f_F(\epsilon - \mu) \,. \end{aligned} \tag{4.131}$$

More generally, one often encounters integrals of the form

$$I(T, \mu) = \int_{-\infty}^{\infty} \mathrm{d}\epsilon \; f_F(\epsilon - \mu) \; \phi(\epsilon) \,, \tag{4.132}$$

for which one would like to obtain a low-temperature expansion. A general technique to do that is provided by the Sommerfeld expansion.

The Sommerfeld expansion

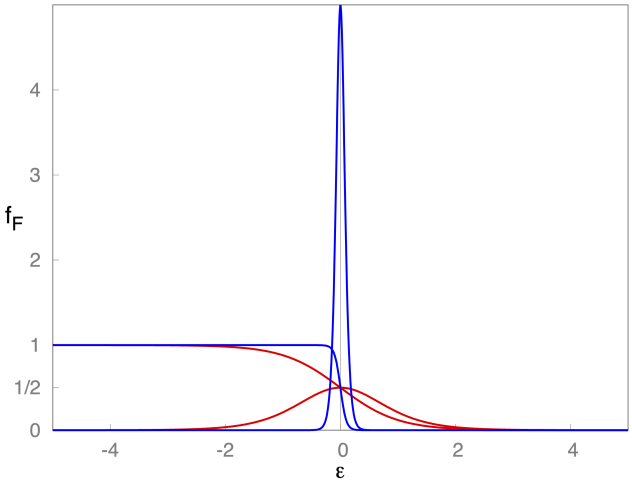

Figure 4.7: The Fermi function $f_F(\epsilon) = \frac{1}{\mathrm{e}^{\beta\epsilon}+1}$ and its derivative, or rather $-f'_F = \beta \frac{\mathrm{e}^{\beta\epsilon}}{(\mathrm{e}^{\beta\epsilon}+1)^2}$, for two values of the temperature.

I will follow here the presentation by Arovas [1]. Notice that the derivative of the Fermi function $f'_F(\epsilon)$

$$f'_F(\epsilon) = -\beta \frac{\mathrm{e}^{\beta\epsilon}}{(\mathrm{e}^{\beta\epsilon}+1)^2} \,, \tag{4.133}$$

is essentially a smoothed version of a Dirac delta function, since

$$\int_{-\infty}^{\infty} \mathrm{d}\epsilon \; f'_F(\epsilon - \mu) = f_F(+\infty) - f_F(-\infty) = -1 \,.$$

Since we will soon integrate by parts our expression for $I(T,\mu)$, let us define the primitive function of $\phi(\epsilon)$:

$$\Phi(\epsilon) = \int_{-\infty}^{\epsilon} \mathrm{d}\epsilon' \; \phi(\epsilon') \; . \tag{4.134}$$

Since the boundary term can be easily argued to vanish, the integral in $I(T,\mu)$ can be rewritten as:

$$I(T,\mu) = -\int_{-\infty}^{\infty} \mathrm{d}\epsilon \; f'_F(\epsilon-\mu) \; \Phi(\epsilon) = -\int_{-\infty}^{\infty} \mathrm{d}\epsilon \; f'_F(\epsilon) \; \Phi(\epsilon+\mu) \; . \tag{4.135}$$

Expand now $\Phi(\epsilon+\mu)$ in powers of ϵ:

$$\Phi(\epsilon+\mu) = \sum_{n=0}^{\infty} \frac{\epsilon^n}{n!} \frac{\mathrm{d}^n\Phi(\mu)}{\mathrm{d}\mu^n} = \mathrm{e}^{\epsilon \frac{\mathrm{d}}{\mathrm{d}\mu}} \Phi(\mu) \; . \tag{4.136}$$

Hence we can rewrite, changing variable to $x = \beta\epsilon$ and defining $\hat{D} = k_B T \frac{\mathrm{d}}{\mathrm{d}\mu}$:

$$\begin{aligned} I(T,\mu) &= -\int_{-\infty}^{\infty} \mathrm{d}\epsilon \; f'_F(\epsilon) \; \mathrm{e}^{\epsilon \frac{\mathrm{d}}{\mathrm{d}\mu}} \; \Phi(\mu) = \beta \int_{-\infty}^{\infty} \mathrm{d}\epsilon \; \frac{\mathrm{e}^{\beta\epsilon}}{(\mathrm{e}^{\beta\epsilon}+1)^2} \; \mathrm{e}^{\epsilon \frac{\mathrm{d}}{\mathrm{d}\mu}} \; \Phi(\mu) \\ &= \int_{-\infty}^{\infty} \mathrm{d}x \; \frac{\mathrm{e}^{x}}{(\mathrm{e}^{x}+1)(\mathrm{e}^{x}+1)} \; \mathrm{e}^{x\hat{D}} \; \Phi(\mu) = \int_{-\infty}^{\infty} \mathrm{d}x \; \frac{1}{(\mathrm{e}^{x}+1)(\mathrm{e}^{-x}+1)} \; \mathrm{e}^{x\hat{D}} \; \Phi(\mu) \\ &= \left[1 + \frac{\pi^2}{6}\hat{D}^2 + \frac{7\pi^4}{360}\hat{D}^4 + \cdots \right] \; \Phi(\mu) \\ &= \Phi(\mu) + \frac{\pi^2}{6}(k_BT)^2 \frac{\partial^2\Phi}{\partial\mu^2} + \frac{7\pi^4}{360}(k_BT)^4 \frac{\partial^4\Phi}{\partial\mu^4} + \cdots \\ &= \int_{-\infty}^{\mu} \mathrm{d}\epsilon \; \phi(\epsilon) + \frac{\pi^2}{6}(k_BT)^2 \frac{\partial\phi}{\partial\mu} + \frac{7\pi^4}{360}(k_BT)^4 \frac{\partial^3\phi}{\partial\mu^3} + \cdots \; . \end{aligned} \tag{4.137}$$

A few comments are in order. The fact that only even powers of $\hat{D}$ contribute is very simple since the remaining integrand is even in x. The integrals over x can be performed by the method of residues, the poles being given by the Fermi function, and one can even give an explicit expression for the integral of the $\hat{D}$ operator, see [1][Eq. 5.234 on page 224]. [39]

The low-T behaviour of a Fermi gas

Let us apply the Sommerfeld expansion to the density $n = N/V$, where $\phi(\epsilon) = g(\epsilon)$. Then we can write:

$$n = \frac{N}{V} = \int_{-\infty}^{\mu} \mathrm{d}\epsilon \; g(\epsilon) + \frac{\pi^2}{6}(k_BT)^2 g'(\mu) + \cdots$$

Taking then $\mu = \epsilon_F + \delta\mu$ and looking for the leading-order in T for the corrections $\delta\mu$ we can finally write:

$$n = \underbrace{\int_{-\infty}^{\epsilon_F} \mathrm{d}\epsilon \; g(\epsilon)}_{n} + g(\epsilon_F)\delta\mu + \frac{\pi^2}{6}(k_BT)^2 g'(\epsilon_F) + \cdots \; ,$$

---

[39] If you define

$$O_S(\hat{D}) = \int_{-\infty}^{\infty} \mathrm{d}x \frac{\mathrm{e}^{x\hat{D}}}{(\mathrm{e}^{x}+1)(\mathrm{e}^{-x}+1)} = (2\pi i) \sum_{n=0}^{\infty} \mathrm{Res} \frac{\mathrm{e}^{z\hat{D}}}{(\mathrm{e}^{z}+1)(\mathrm{e}^{-z}+1)} \Big|_{z_n = i(2n+1)\pi} \; ,$$

a simple application of the residue theorem leads to the expression:

$$O_S(\hat{D}) = \frac{\pi\hat{D}}{\sin(\pi\hat{D})} = \frac{1}{1 - \frac{1}{3!}(\pi\hat{D})^2 + \frac{1}{5!}(\pi\hat{D})^4 + \cdots} = 1 + \frac{\pi^2}{6}\hat{D}^2 + \frac{7\pi^4}{360}\hat{D}^4 + \cdots \; .$$

which finally leads to: [40]

$$\delta\mu = -\frac{\pi^2}{6}(k_BT)^2\frac{g'(\epsilon_F)}{g(\epsilon_F)} + \cdots = -\frac{\pi^2}{12}\frac{(k_BT)^2}{\epsilon_F} + \cdots \ , \tag{4.138}$$

where the last expression applies to a $d = 3$ dimensional non-relativistic free Fermi gas.

Consider now the *energy* $E(T, V, \mu)$. Here the function to be considered is $\phi(\epsilon) = \epsilon g(\epsilon)$. Hence we have:

$$\begin{aligned}
\frac{E}{V} &= \int_{-\infty}^{\mu} \mathrm{d}\epsilon \ \epsilon g(\epsilon) + \frac{\pi^2}{6}(k_BT)^2\frac{\partial}{\partial\mu}\big(\mu g(\mu)\big) + \cdots \\
&= \int_{-\infty}^{\mu} \mathrm{d}\epsilon \ \epsilon g(\epsilon) + \frac{\pi^2}{6}(k_BT)^2\big(g(\mu) + \mu g'(\mu)\big) + \cdots \\
&= \underbrace{\int_{-\infty}^{\epsilon_F} \mathrm{d}\epsilon \ \epsilon g(\epsilon)}_{\epsilon_{gs}} + \cancel{\epsilon_F g(\epsilon_F)\delta\mu} + \frac{\pi^2}{6}(k_BT)^2\big(g(\epsilon_F) + \cancel{\epsilon_F g'(\epsilon_F)}\big) + \cdots \\
&= \epsilon_{gs} + \frac{\pi^2}{6}(k_BT)^2 g(\epsilon_F) + \cdots
\end{aligned} \tag{4.139}$$

Let us turn to the *pressure*. Given the fact that $\Omega = -E/(\alpha_g + 1) = -2E/d$ we can write:

$$p = -\frac{\Omega}{V} = \frac{2}{d}\frac{E}{V} = \frac{2}{d}\left[\epsilon_{gs} + \frac{\pi^2}{6}(k_BT)^2 g(\epsilon_F) + \cdots\right] \tag{4.140}$$

an expression that smoothly goes towards the Maxwell-Boltzmann limit $p \approx nk_BT$ for large T.

Finally, let us consider the *entropy* and the *specific heat*. Observe that the previous expression provides Ω as a function of T and N, and not μ. Hence, you should refrain from taking the derivative with respect to T to calculate S. Rather start again from an expression in which μ appears, see Eq. (4.139):

$$\Omega(T, V, \mu) = -\frac{2}{d}V\left[\int_{-\infty}^{\mu} \mathrm{d}\epsilon \ \epsilon g(\epsilon) + \frac{\pi^2}{6}(k_BT)^2\big(g(\mu) + \mu g'(\mu)\big) + \cdots\right] \ . \tag{4.141}$$

and calculate:

$$\begin{aligned}
S(T, V, \mu) = -\frac{\partial\Omega}{\partial T} &= \frac{2}{d}V\left[\frac{\pi^2}{3}k_B^2T\big(g(\mu) + \mu g'(\mu)\big) + \cdots\right] \\
&= \frac{2}{d}V\frac{\pi^2}{3}k_B^2T\left[\cancel{g(\epsilon_F)} + (\frac{d}{2} - \cancel{1})g(\epsilon_F)\right] + \cdots \\
&= V\frac{\pi^2}{3}k_B^2T g(\epsilon_F) + \cdots
\end{aligned} \tag{4.142}$$

which is also the low-T expression for $S(T, V, N)$. From the entropy we can calculate the constant-volume specific heat:

$$\begin{aligned}
\frac{C_v}{V} &= \frac{T}{V}\frac{\partial S}{\partial T}\bigg|_{V,N} = \frac{\pi^2}{3}k_B^2T g(\epsilon_F) + \cdots = \gamma T + \cdots \\
\gamma &= \frac{\pi^2}{3}k_B^2 g(\epsilon_F) = \frac{\pi^2}{3}k_B^2\frac{d}{2}\frac{n}{\epsilon_F} \ .
\end{aligned} \tag{4.143}$$

Notice that this predicts a linear in T specific heat for metals at low T.[41]

---

[40] If $g(\epsilon) = g(\epsilon_F)(\epsilon/\epsilon_F)^{\alpha_g}$ with $\alpha_g = (d-2)/2$ then you immediately deduce that $g'(\epsilon_F)/g(\epsilon_F) = \alpha_g/\epsilon_F$.

[41] This contribution is usually much smaller than the phonon contribution (proportional to T^3), with the possible exception of heavy fermion systems.

The low-temperature behaviour of fermionic interacting systems is usually treated in the so-called *Fermi Liquid Theory*, see for instance the book by Nozières or the lecture notes by M. Fabrizio.

Concerning the *Pauli paramagnetic susceptibility*, see for instance [1][Sec. 5.8.8]:

$$\chi = \frac{\partial M}{\partial H}\bigg|_{T,V,N} = \mu_B^2 g(\epsilon_F) \ . \tag{4.144}$$

A possible exercise concerns the Landau *diamagnetic contribution* to the magnetic susceptibility, see for instance [1][Sec. 5.8.9].

4.6.3. The ideal Bose gas

Very nice treatments are given by Arovas [1] and Pathria [5]. Pathria, in particular, gives a nice discussion (see his Appendix F) of a technique to calculate the grand-canonical density of particles of a Bose gas by directly tackling the exact relevant sums through the Poisson's summation formula and related mathematical identities. Let us start from the expression for the density of particles of an ideal Bose gas:

$$n(T,\mu) = \frac{N}{V} = -\frac{1}{V}\frac{\partial \Omega}{\partial \mu} = \frac{\partial p}{\partial \mu} = \frac{1}{V}\sum_\alpha \frac{1}{\mathrm{e}^{\beta(\epsilon_\alpha-\mu)}-1} \equiv n_{\mathrm{sum}}(T,\mu) \ .$$

For a gas consisting of free non-relativistic bosons in a d-dimensional box of volume $V = L^d$ the ϵ_α would be the usual $\epsilon_{\mathbf{k}} = \hbar^2 k^2/(2m)$ and $\mathbf{k} = (2\pi/L)(n_1, \cdots, n_d)$ if, for instance, we assume periodic boundary conditions. The mimimum eigenvalue is hence $\epsilon_0 = 0$, separated from the next levels by a splitting $\Delta E = h^2/(2mL^2) \sim 1/V^{2/d}$. If $\mu < 0$ (and finite), hence the fugacity $z = \mathrm{e}^{\beta\mu} < 1$, and all the individual terms in the sum contribute

$$\frac{1}{V}\frac{1}{\mathrm{e}^{\beta(\epsilon_\alpha-\mu)}-1} < \frac{1}{V}\frac{1}{\mathrm{e}^{-\beta\mu}-1} = \frac{1}{V}\frac{z}{1-z} \sim \frac{1}{V} \ .$$

It is reasonable to expect that the sum of these small but very dense [42] contributions can be captured very well by approximating the sum with an integral, with the usual density of states technique. But we should be aware that it might happen that z gets so close to 1 (or, equivalently, that $\mu \to 0^-$) in such a way that contribution from the lowest eigenvalue $\epsilon_0 = 0$

$$\frac{N_0}{V} = \frac{1}{V}\frac{1}{\mathrm{e}^{-\beta\mu}-1} = \frac{1}{V}\frac{z}{1-z} \ ,$$

could become *finite* (i.e., $N_0 \propto V$), and we would completely miss it when we transform the sum into an integral. Indeed, you realize that

$$\lim_{\mu\to\epsilon_0^-} n_{\mathrm{sum}}(T,\mu) = +\infty \ ,$$

a very nice feature, since it allows to find a value of μ for any fixed density n you might want to allocate to the different eigenstates. So, let us tentatively transform the sum into an integral

$$n_{\mathrm{int}}(T,\mu) = \int_0^\infty \mathrm{d}\epsilon \, \frac{g(\epsilon)}{\mathrm{e}^{\beta(\epsilon-\mu)}-1} = \frac{A_g}{\beta^{\alpha_g+1}}\int_0^\infty \mathrm{d}x \, \frac{x^{\alpha_g}}{z^{-1}\mathrm{e}^x - 1} \ , \tag{4.145}$$

---

[42] For ^{4}He particles in a box of side $L = 1$ cm, the typical splitting is

$$\frac{\hbar^2}{2m_e a_B^2} 4\pi^2 \frac{m_e}{4m_p}\left(\frac{a_B}{L}\right)^2 \sim 10^{-17}\,\mathrm{eV} \sim 10^{-13}\,\mathrm{K}/k_B \ .$$

Hence, if you are summing a function whose typical scale of variation is much larger than the previous extra-tiny splitting, it is legitimate to substitute the sum with an integral. The catch is that the Bose distribution diverges for $\epsilon \to 0$ when $\mu \to 0^-$, hence the previous conclusion is risky. Indeed, it fails when Bose-condensation occurs.

where the notation "int" reminds us that this is only the regular (smooth) part of the sum obtained from the integral of the density of states, ignoring the possibly important contribution from a massive occupation of the lowest energy eigenvalue. In the final expression we have assumed a standard power-law form for the density of states $g(\epsilon) = A_g \epsilon^{\alpha_g}$, where $\alpha_g = d/2 - 1$ for free non-relativistic particles, and transformed the integral by rescaling the variables to take out the temperature dependence. Notice that for $\mu < \epsilon_0 = 0$, the singularity in the integral is entirely due to $g(\epsilon)$, and is usually integrable (for instance, $g(\epsilon) \sim 1/\sqrt{\epsilon}$ in $d = 1$). If you increase z towards 1^- (or, equivalently, $\mu \to 0^-$) this integral increases. Let us try to understand what happens if I set $z = 1$ inside the integral, which gives the maximum value that $n_{\rm int}(T, \mu)$ can reach at fixed T:

$$n_{\rm int}(T,\mu) < n_{\rm cr}(T) \equiv n_{\rm int}(T, 0^-) = \frac{A_g}{\beta^{\alpha_g+1}} \int_0^\infty {\rm d}x \, \frac{x^{\alpha_g}}{{\rm e}^x - 1} \; . \tag{4.146}$$

Here the issue is the singularity of the integrand close to $x = 0$, with the Bose distribution function contributing a crucial factor $1/x$. The density of states gives a factor $x^{d/2-1}$ so that the integrand, close to $x \to 0$, is:

$$\sim x^{\frac{d}{2}-1} \frac{1}{x} \sim x^{-1+\frac{d-2}{2}} = \begin{cases} x^{-\frac{3}{2}} & d = 1 & \Longrightarrow & \text{divergent} \\ x^{-1} & d = 2 & \Longrightarrow & \text{divergent} \\ x^{-\frac{1}{2}} & d = 3 & \Longrightarrow & \text{finite} \end{cases} \; .$$

Hence we realize that $n_{\rm int}(T, \mu)$ is *bounded* by a finite value of $n_{\rm cr}(T)$ in $d = 3$, while $n_{\rm cr} = \infty$ in $d \leq 2$. But being bound by a finite value means that *I cannot find* a chemical potential if the density of the gas happens to be $n > n_{\rm cr}(T)$. You realize that this is not a nice property of our grand-canonical approach: I can give you a high-enough density n such that all the states I have accounted for by the density of states integral would not be able to accommodate all of the particles, even if I set $\mu = 0^-$, which is the maximum value a Bose system can tolerate! Luckily, this is not a disaster at all, it is simply a pitfall of our approach of transforming a sum into an integral: we missed completely the ability that the system has to *massively occupy* the lowest-eigenvalue ϵ_0. Indeed, the original sum does diverge when $z \to 1$:

$$\lim_{\mu \to 0^-} n_{\rm sum}(T, \mu) = \lim_{\mu \to 0^-} \frac{1}{V} \sum_\alpha \frac{1}{{\rm e}^{\beta(\epsilon_\alpha - \mu)} - 1} = +\infty \; ,$$

whence whatever is the value of n, and the temperature T, I can always find a μ suitably close to 0^- such that $n = n_{\rm sum}(T, \mu)$. Before "amending" the previous replacement of $n_{\rm sum} \to n_{\rm int}$, to correctly describe Bose condensation, let us calculate the relevant integrals in a more precise fashion (although the main ingredients are already there and the essence of what we said does not change). Indeed, the integral appearing in Eq. (4.145) can be given an analytic expression in terms of the Poly-logarithmic[43]

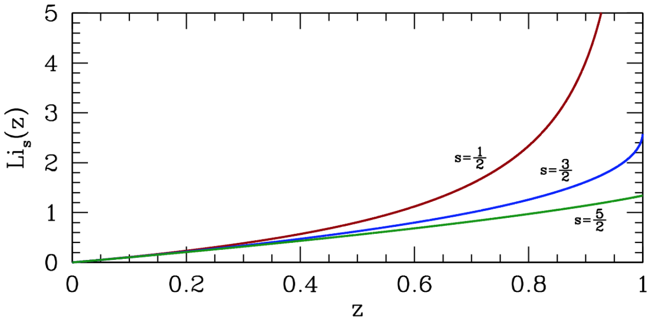

Figure 4.8.: The Poly-logarithm function $\text{Li}_s(z)$ for $s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$. Figure taken from Arovas [1].

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[43] Pathria calls them the *Bose-Einstein functions*, and denotes them by $g_\nu(z)$, see Eq. 10 in Sec. 7.1.

functions (see Fig. 4.8)

$$\mathrm{Li}_s(z) \equiv \frac{1}{\Gamma(s)} \int_0^\infty \mathrm{d}x \, \frac{x^{s-1}}{z^{-1}\mathrm{e}^x - 1} = \sum_{k=1}^\infty \frac{z^k}{k^s} \,, \tag{4.147}$$

essentially a generalisation of the Riemann zeta-function $\zeta(s)$, to which it reduces for $z = 1$, $\mathrm{Li}_s(1) \equiv \zeta(s)$. The algebra leading to this power-law expansion is quite simple. [44] Since $\xi(s)$ is *finite* for $s > 1$, while it *diverges* for $s \leq 1$, you conclude that the same occurs to $\mathrm{Li}_s(z)$ for $z \to 1^-$. Using the expression for the density of states of non-relativistic particles, including a possible spin-degeneracy factor g_S, we get:

$$\begin{array}{rcl} n_{\mathrm{int}}(T,\mu) & = & \dfrac{A_g}{\beta^{\alpha_g+1}} \, \Gamma(\alpha_g+1) \, \mathrm{Li}_{\alpha_g+1}(z) = g_S \, \lambda_T^{-d} \, \mathrm{Li}_{\frac{d}{2}}(z) \\ n_{\mathrm{cr}}(T) & \equiv & n_{\mathrm{int}}(T,0^-) = g_S \, \lambda_T^{-d} \, \mathrm{Li}_{\frac{d}{2}}(1^-) = g_S \, \lambda_T^{-d} \, \zeta(\frac{d}{2}) = g_S \left(\dfrac{2\pi m k_B T}{h^2}\right)^{\frac{d}{2}} \zeta(\frac{d}{2}) \end{array} \,. \tag{4.148}$$

The crucial ingredient to watch for is the *finite* Riemann zeta function $\zeta(\frac{3}{2}) \approx 2.612$. Hence, in $d = 3$, given a certain density n we will not be able to find a suitable chemical potential to describe it when $T < T_c$ where the critical temperature T_c is given by:

$$n_{\mathrm{cr}}(T_c) = g_S \left(\frac{2\pi m k_B T_c}{h^2}\right)^{\frac{3}{2}} \zeta(\tfrac{3}{2}) \equiv n \quad \Longrightarrow \quad k_B T_c = \frac{2\pi\hbar^2}{m} \left(\frac{n}{g_S \zeta(\frac{3}{2})}\right)^{\frac{2}{3}} \,. \tag{4.149}$$

Allowing for the correct density when $d \geq 3$. So, the solution in $d = 3$ can be written as follows:

$$\begin{array}{rclll} n & = & n_{\mathrm{int}}(T,\mu) \;=\; g_S \left(\dfrac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} \mathrm{Li}_{\frac{3}{2}}(z) & & \text{for } T > T_c \\ n & = & n_0(T) + g_S \left(\dfrac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} \zeta(\frac{3}{2}) & & \text{for } T < T_c \end{array} \,. \tag{4.150}$$

Observe that the first equation is in the grand-canonical spirit: given n and $T > T_c$ you should find the appropriate $\mu(T,n)$ that gives $n_{\mathrm{int}}(T,\mu(T,n)) \equiv n$. The second equation is essentially "canonical", in the sense that we have set $\mu = 0^-$ and, given n, we postulate that $n_0(T)$ is finite — hence $N_0 = V n_0(T)$ is a massive extensive number — in such a way as to allow the particles that do not fit in the regular part "outside the condensate". The same would hold for any $d > 3$, where the Riemann zeta function $\zeta(\frac{d}{2})$ is *finite*.

We get (by difference) that the density of particles that "condense" in the lowest eigenvalue ϵ_0 is:

$$\frac{n_0(T)}{n} = 1 - \frac{1}{n} g_S \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} \zeta(\tfrac{3}{2}) \equiv 1 - \left(\frac{T}{T_c}\right)^{\frac{3}{2}} \,. \tag{4.151}$$

Notice that the occupation of the lowest eigenvalue is macroscopic below the transition temperature, which amounts to a chemical potential which is infinitesimally close to 0^-:

$$N_0 = V n_0 = \frac{1}{z^{-1} - 1} \quad \Longrightarrow \quad z = \mathrm{e}^{\beta\mu} = \frac{1}{1 + \frac{1}{N_0}} \quad \Longrightarrow \quad \mu \approx -\frac{k_B T}{N_0} \to 0^- \,.$$

---

[44] Simply expand the function inside the integral, after a simple rewriting, using the usual geometric series:

$$\int_0^\infty \mathrm{d}x \, \frac{x^{s-1}}{z^{-1}\mathrm{e}^x - 1} = \int_0^\infty \mathrm{d}x \, x^{s-1} \frac{z\mathrm{e}^{-x}}{1 - z\mathrm{e}^{-x}} = \sum_{k=1}^\infty z^k \int_0^\infty \mathrm{d}x \, x^{s-1} \mathrm{e}^{-kx} = \sum_{k=1}^\infty \frac{z^k}{k^s} \underbrace{\int_0^\infty \mathrm{d}t \, t^{s-1} \mathrm{e}^{-t}}_{\Gamma(s)} \,.$$

No condensation is predicted for $d \leq 2$, because $\zeta(\frac{d}{2})$, and hence n_{cr}, are infinite. The condensation transition in $d = 3$ leaves a distinct feature in all thermodynamical quantities as T approaches T_c. We should stress, however, that the bosons in the condensate *do not contribute* to Ω, p, or E. The calculation of all these thermodynamical quantities (p, C_v) is in principle straightforward but in practice a bit tedious. You find plenty of details of these derivations for instance in [5][Chap.7]. I simply collect here a few useful graphs, taken from [5] and [1].

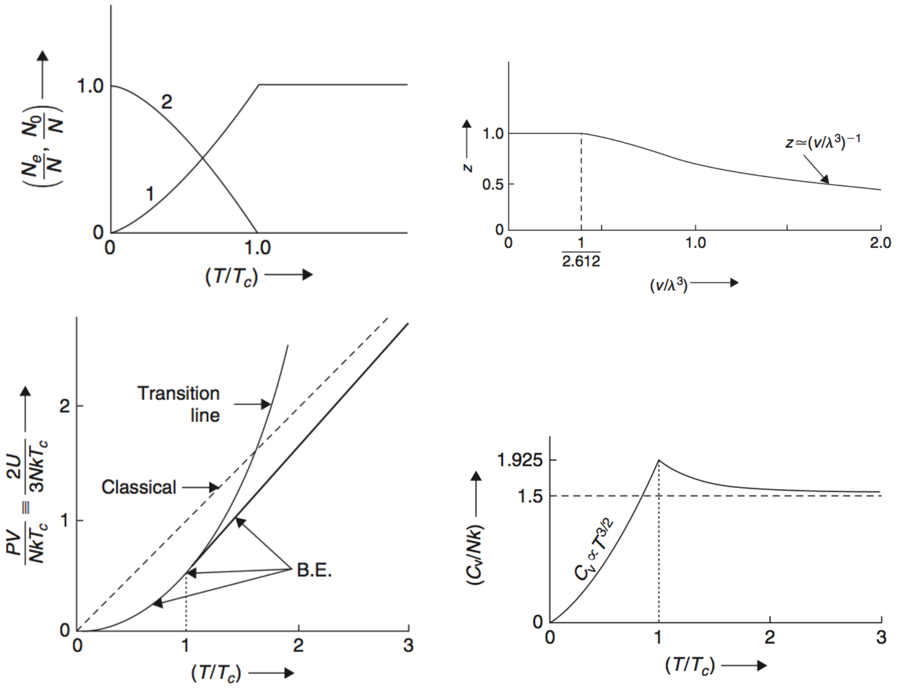

Figure 4.9.: Various thermodynamical quantities for the Bose-Einstein condensation of free non-relatistic particles in $d = 3$. Figures taken from Pathria [5].

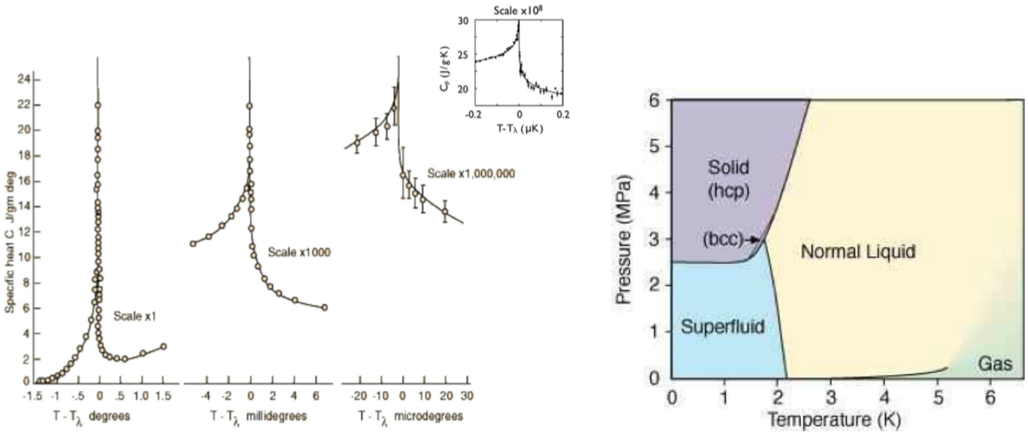

Figure 4.10.: Left: Specific heat of liquid ^{4}He in the vicinity of the λ-transition. Data from M. J. Buckingham and W. M. Fairbank, in Progress in Low Temperature Physics, C. J. Gortner, ed. (North-Holland, 1961). Inset at upper right: more recent data of J. A. Lipa et al., Phys. Rev. B 68, 174518 (2003) performed in zero gravity earth orbit, to within $\Delta T = 2$ nK of the transition. Right: pT phase diagram of ^{4}He. Figures, and left caption, from Arovas [1].

A remarkable similarity exists between these findings and the low-temperature physics of the queen of all bosonic particle fluids, ^{4}He, which becomes liquid at $T < 4.2$K and *superfluid* at a temperature $T < 2.17$K (at atmosferic pressure). The similarity, first pointed out by F. London in the late 1930s,

[45] is in some respects not perfect, because interactions are known to be important in ^{4}He, leading to a fraction of condensate of only a few percent even at the lowest temperatures. [46] Fig. 4.10 below shows the remarkable λ-transition specific-heat that the fluid shows when it becomes superfluid. Close to it, the pT phase diagram of ^{4}He.

4.7. Bose-Einstein condensation in trapped cold atomic gases

Einstein's prediction of Bose condensation was finally realized through a series of remarkable experiments with trapped ultracold atomic gases, which led to the Noble prize in physics for Cornell, Wieman and Ketterle in 2001. [47] To achieve condensation, they had to achieve temperatures of the order of nK, by *magneto-optical traps* (MOTs), followed by *evaporative cooling* in a magnetic trap. The first important step involves Doppler laser cooling, which brings the atomic cloud to temperatures in the μK range. The second step involves evaporative cooling of the atoms in a magnetic harmonic trap created by a certain combination of uniform and quadrupolar magnetic fields. Here are a few details.

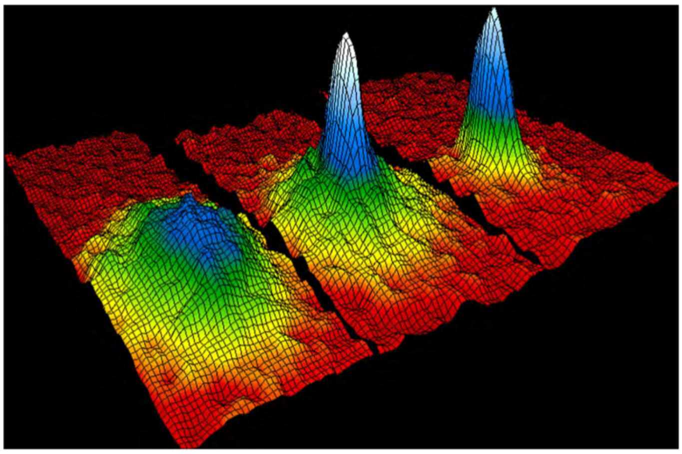

Figure 4.11: Time-of-flight images from the first observation of Bose-Einstein condensation in a dilute vapour of ^{87}Rb by Anderson *et al.* (1995) at temperatures just above and below the phase transition temperature.

Laser Doppler cooling — and also optical molasses (Nobel prize to Chu and Cohen-Tannoudji in 1997) — involves a rather simple idea. One uses three orthogonal counter-propagating laser beams that are slightly off-resonance to one of the transition lines ΔE of the atoms we are trying to cool down, more precisely $\hbar\omega < \Delta E$, where ω is the frequency of the laser beam. A stationary atom would therefore not absorb the photons of the beam. An atom moving with a certain velocity v would however see a Doppler-shifted photon: blue-shifted if the photon comes from the direction opposing the velocity v. This will lead atoms to absorb photons from the direction in which they move, receiving an extra momentum by the photon, hence reducing their velocity. The photon is then re-emitted in all possible directions: hence, on average, the original velocity in a certain definite direction is *decreased*. The limiting T which you can reach by this mechanism is essentially set by the final back-kick that an atom gets when re-emitting the photon, which is called the *recoil limit*. If $\hbar k$ is the momentum of the photon emitted (and the momentum that a rest-atom would get in emitting it), we can estimate:

$$\hbar k = \frac{\hbar\omega}{c} \approx \frac{\Delta E}{c} \qquad \Longrightarrow \qquad k_B T_{\text{eff}} \approx \frac{1}{2m}\left(\frac{\hbar\omega}{c}\right)^2 \sim 1\mu\text{K} \,,$$

---

[45] London took the density of liquid Helium $n = 2.2\times10^{22}\text{cm}^{-3}$, a mass $m = 6.65\times10^{-27}$kg, and calculated $T_c = 3.16$K, remarkably close to the Helium λ-point.

[46] In more technical terms, a free Bose gas shows full Bose condensation in the zero-momentum lowest-energy single-particle state, but would not display a superfluidity response, because interactions are important for that, as the Bogoljubov theory shows. Viceversa, a bosonic system in low dimensions might show superfluidity without having an actual "condensate fraction".

[47] Cornell and Wieman achieved Bose condensation of Rb^{87}, while Ketterle used Na^{23}, both in 1995.

for the relevant spectral lines of Rb [48] or Na atoms.

To cool below the μK range, one route is to turn off the lasers and make use of traps made of spatially-varying magnetic fields and evaporative cooling. Notice that the atoms are *neutral*, but they possess a magnetic moment $\boldsymbol{\mu}$ — emerging from the hyperfine interaction and given by the sum of the electronic angular momentum $\mathbf{J}$ and the nuclear angular momentum $\mathbf{I}$ —, hence there is a Zeeman $-\boldsymbol{\mu}\cdot\mathbf{B}$ energy contribution. For instance, the ground state of ^{87}Rb has total angular momentum (electronic and nuclear) $F = 1$.

If the magnetic field varies in space, then atoms with their magnetic moment *anti-aligned* to the field will try to go towards regions of low $|\mathbf{B}|$ to reduce their energy: they are called *low-field seeking atoms.*

A crucial fact that one should keep in mind is that the magnetic field strength $|\mathbf{B}|$ can have *no maximum*, but it can *have a minimum.* To understand that, observe that there is a theorem of electrostatics, called *Earnshaws theorem*, which states that a charged body under the action of an electric field alone cannot be at rest in stable equilibrium. This is a consequence of the Laplace equation of electrostatics and the property of electric potentials with zero Laplacian: they cannot have a maximum or a minimum.

But magnetic fields add a twist to the story, in that respect. One can show that $|\mathbf{B}(\mathbf{x})|^2$ can have minima in space, which provide attractive potential wells for the low-field seeking atoms with anti-aligned magnetic moments. Indeed, not only we have that $\boldsymbol{\nabla}\cdot\mathbf{B} = 0$ (in general) but also, in absence of currents, $\boldsymbol{\nabla}\times\mathbf{B} = 0$. Hence we have that:

$$\boldsymbol{\nabla}\times(\boldsymbol{\nabla}\times\mathbf{B}) = \boldsymbol{\nabla}(\boldsymbol{\nabla}\cdot\mathbf{B}) - \nabla^2\mathbf{B} = -\nabla^2\mathbf{B} \equiv 0 \quad\Longrightarrow\quad \nabla^2 B_i = 0\ ,$$

which is true for all components B_i of the magnetic field. Consider now B_z. Since $\nabla^2 B_z = 0$ we can apply Green's theorem [49] to show that $B_z(\mathbf{x}_c)$ at any point $\mathbf{x}_c$ is equal to the average of $B_z(\mathbf{x})$ on a sphere S of radius R around $\mathbf{x}_c$:

$$B_z(\mathbf{x}_c) = \frac{1}{4\pi R^2}\int_S B_z(\mathbf{x})\ . \tag{4.152}$$

As a consequence, it is simple to show, by contradiction [50] that $|\mathbf{B}(\mathbf{x})|^2$ cannot have a maximum. On the contrary, nothing forbids that $|\mathbf{B}(\mathbf{x})|^2$ has a *minimum* at some point $\mathbf{x}_c$. [51] There are several

---

[48] Detailed numbers for ^{87}Rb are given by Steck. Very quickly, ^{87}Rb has a nuclear spin $I = \frac{3}{2}$ and a ground state 5 $^2S_{\frac{1}{2}}$ which eventually has a total angular moment $\mathbf{F} = \mathbf{J} + \mathbf{I}$ with $F = 1$. Above, there is a close in energy $F = 2$ state. Further up, around $\hbar\omega \approx 1.6$ eV above, there are multiplets originating from 5 $^2P_{\frac{1}{2}}$, with $F = 1, 2$, and from 5 $^2P_{\frac{3}{2}}$, with $F = 0, 1, 2, 3$.

[49] Green's theorem states that:

$$\int_V (\phi\nabla^2\psi - \psi\nabla^2\phi)\,\mathrm{d}\mathbf{x} = \int_{S=\partial V} (\phi\boldsymbol{\nabla}\psi - \psi\boldsymbol{\nabla}\phi)\cdot\mathrm{d}\mathbf{S}\ .$$

Applying this to $\psi = B_z$ and $\phi = \frac{1}{|\mathbf{x}|}$, and using that $\nabla^2\frac{1}{|\mathbf{x}|} = -4\pi\delta(\mathbf{x})$, it is simple to prove the average theorem.

[50] Assume that $\mathbf{x}_c = 0$ is such a maximum. Let $\mathbf{B}(0) = \hat{\mathbf{z}}B_z(0)$ with $B_z(0) > 0$, without loss of generality. Then write $\mathbf{B}(\mathbf{x}) = \mathbf{B}(0) + \delta\mathbf{B}(\mathbf{x})$ and calculate

$$|\mathbf{B}(\mathbf{x})|^2 - |\mathbf{B}(0)|^2 = |\delta\mathbf{B}(\mathbf{x})|^2 + 2\mathbf{B}(0)\cdot\delta\mathbf{B}(\mathbf{x}) = |\delta\mathbf{B}(\mathbf{x})|^2 + 2B_z(0)\delta B_z(\mathbf{x})\ .$$

In order for it to be a maximum, we should have $B_z(0)\delta B_z(\mathbf{x}) < -|\delta\mathbf{B}(\mathbf{x})|^2 < 0$ around $\mathbf{x}_c = 0$, hence $\delta B_z(\mathbf{x}) < 0$ since $B_z(0) > 0$. But, by Laplace's average theorem, $B_z(0) > 0$ must equal its average on any sphere around $\mathbf{x}_c = 0$, hence:

$$0 = \delta B_z(0) = \frac{1}{4\pi R^2}\int_S \delta B_z(\mathbf{x})\ ,$$

which implies that $\delta B_z(\mathbf{x})$ must average to zero on such a sphere, hence definitely $\delta B_z(\mathbf{x})$ will attain *positive and negative* values around $\mathbf{x}_c = 0$.

[51] Indeed, taking $\mathbf{x}_c = 0$ and defining $\delta\mathbf{B}(\mathbf{x}) = \mathbf{B}(\mathbf{x}) - \mathbf{B}(0)$, we should have

$$|\mathbf{B}(\mathbf{x})|^2 - |\mathbf{B}(0)|^2 = |\delta\mathbf{B}(\mathbf{x})|^2 + 2\mathbf{B}(0)\cdot\delta\mathbf{B}(\mathbf{x}) = |\delta\mathbf{B}(\mathbf{x})|^2 + 2B_z(0)\delta B_z(\mathbf{x}) \geq 0\ ,$$

which is perfectly possible.

possible solutions where $|\mathbf{B}(\mathbf{x})|^2$ shows a minimum, as it is simple to realize. Take for instance a quadrupolar **B**-field of the form $\mathbf{B}(\mathbf{x}) = C_x x\,\hat{\mathbf{x}} + C_y y\,\hat{\mathbf{y}} + C_z z\,\hat{\mathbf{z}}$ with $C_x + C_y + C_z = 0$ so as to have $\boldsymbol{\nabla}\cdot\mathbf{B} = 0$. One such choice [52] would be to take $C_z = 2B_q$ and $C_x = C_y = -B_q$, resulting in

$$\mathbf{B}(\mathbf{x}) = B_q\Big(2z\,\hat{\mathbf{z}} - (x\,\hat{\mathbf{x}} + y\,\hat{\mathbf{y}})\Big) \quad\Longrightarrow\quad |\mathbf{B}(\mathbf{x})|^2 = B_q^2\left(4z^2 + (x^2+y^2)\right) . \tag{4.153}$$

To summarize, it is possible to realize magnetic field arrangements such that $|\mathbf{B}(\mathbf{x})|^2$ has a minimum in space. In some arrangements, time-varying magnetic fields are also used, like in the TOP quadrupolar trap used in the original Nobel prize-winning experiments on Rb atoms. The details of the trap configurations are beyond the scope of our discussion: quite many possibilities are there, with their tricks of the trade.

All in all, it suffices here to say that experimentalists have been able to create very cool clouds of many thousands of neutral bosonic atoms in traps that, close to their minimum for and for a limited energy range — set by the evaporative cooling process [53] —, can be thought of as harmonic:

$$V_{\mathrm{eff}}(x,y,z) = \frac{m}{2}\left(\omega_1^2x^2 + \omega_2^2y^2 + \omega_3^2z^2\right) . \tag{4.154}$$

The potential will saturate sufficiently away from the minimum, which implies that atoms with a sufficiently large velocity with actually *escape from the minimum well*: as mentioned above, such a process is called *evaporative cooling*. In typical magnetic traps, $\omega_i \sim 2\pi f$ with $f \sim 100\mathrm{Hz}$, which corresponds to an energy $\hbar\omega_i \sim 4.8\cdot 10^{-9}\mathrm{K}$. The spectrum of the harmonically trapped atoms will be given by:

$$\epsilon_{n_1n_2n_3} = \underbrace{\frac{\hbar}{2}(\omega_1+\omega_2+\omega_3)}_{\epsilon_0} + \hbar\boldsymbol{\omega}\cdot\mathbf{n} , \tag{4.155}$$

where ϵ_0 is the minimum eigenvalue. This should be contrasted with the free-particle $3d$ parabolic dispersion

$$\epsilon_{n_1n_2n_3} = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 (n_1^2+n_2^2+n_3^2) . \tag{4.156}$$

As you know, the $3d$ parabolic dispersion corresponds to a density of states $g_{3d}(\epsilon) \sim \sqrt{\epsilon}$, which is such that a transition at finite T is possible. Correspondingly, for the harmonic potential well, we can define the associated density of states to be

$$g_{\mathrm{harm}}(\epsilon) = \sum_{\mathbf{n}} \delta(\epsilon - \epsilon_0 - \hbar\boldsymbol{\omega}\cdot\mathbf{n}) . \tag{4.157}$$

I will now argue that, provided you neglect the *fine-structure* of this function, which is legitimate if T is higher than the typical separation between the various Dirac's deltas making it, $k_BT \gg \hbar\omega_i$, you can approximately show that

$$g_{\mathrm{harm}}^{\mathrm{smooth}}(\epsilon) \approx \frac{1}{2(\hbar\omega_0)^3}(\epsilon-\epsilon_0)^2 + \cdots , \tag{4.158}$$

where $\omega_0^3 \equiv \prod_i \omega_i$.

---

[52] Another possible solution is a combination of a uniform field along $\hat{\mathbf{z}}$ with a linear quadrupolar field in the xy-plane:

$$\mathbf{B}(\mathbf{x}) = B_0\hat{\mathbf{z}} + B_\perp(x\hat{\mathbf{x}} - y\hat{\mathbf{y}}) \quad\Longrightarrow\quad |\mathbf{B}(\mathbf{x})|^2 = B_0^2 + B_\perp^2\left(x^2+y^2\right) .$$

[53] The radio-frequency driven evaporative cooling mechanism used to achieve nK temperatures is based on a simple ingredient: due to the Zeeman coupling, the energy difference between a trapped $F=1, m_F=-1$ Rb atom, for instance, and the untrapped $m_F = 0, +1$ atom depends on the distance of the atom from the trap centre. By setting a certain radio-frequency drive ω_{rf} you can provoke transitions between $m_F = -1$ that have too large a velocity, visiting regions of the trap too far from the centre, and the untrapped states: after the transition, the untrapped atoms leave the trap and the average kinetic energy of the atomic cloud decreases. This is similar to blowing on a cup of hot tea.

> **Remember the harmonic oscillator DOS?** If you recall, we already encountered something similar when discussing the density of states of linearly dispersing modes $\omega_k = v|\mathbf{k}|$, like for phonons or photons. This was giving rise to T^3 corrections in the specific heat.

To show this, consider the *Laplace transform* of the density of states. Setting $\epsilon_0 \to 0$ we can write:

$$\begin{aligned}\hat{g}(\beta) = \int_0^\infty \mathrm{d}\epsilon\, \mathrm{e}^{-\beta\epsilon} \sum_{\mathbf{n}} \delta(\epsilon - \hbar\boldsymbol{\omega}\cdot\mathbf{n}) = \sum_{\mathbf{n}} \mathrm{e}^{-\hbar\beta\boldsymbol{\omega}\cdot\mathbf{n}} &= \prod_{i=1}^{3} \sum_{n_i=0}^{\infty} \mathrm{e}^{-\hbar\beta\omega_i n_i} \\ &= \prod_{i=1}^{3} \frac{1}{1-\mathrm{e}^{-\hbar\beta\omega_i}} \,. \end{aligned} \tag{4.159}$$

Consider now the Laplace transform for *small* β, which will capture the large-ϵ scale behaviour of $g_{\mathrm{harm}}(\epsilon)$. It is simple to show that

$$\hat{g}(\beta) \approx \frac{1}{\beta^3(\hbar\omega_0)^3} \,,$$

where $\omega_0^3 = \prod_i \omega_i$. It is also straightforward to verify that the Laplace transform of $g(\epsilon) = A\epsilon^2$ is indeed given, by repeated integration by parts, by:

$$\hat{g}(\beta) = A \int_0^\infty \mathrm{d}\epsilon\, \mathrm{e}^{-\beta\epsilon}\epsilon^2 = \frac{2A}{\beta^3} \,,$$

which justifies Eq. (4.158).

Returning to our general analysis of the Bose condensation, we see that an harmonic trap is essentially equivalent to $g(\epsilon) \approx A_g \epsilon^{\alpha_g}$ with $\alpha_g = 2$ and $A_g = \frac{1}{2(\hbar\omega_0)^3}$. Effectively, this is like having free non-relativistic bosons but in $d = 6$ dimensions! From Eq. (4.148) we, therefore, conclude (notice that in the present case there are no V factors) that:

$$\begin{aligned} N_{\mathrm{int}}(T,\mu) &\approx \frac{A_g}{\beta^3}\Gamma(3)\,\mathrm{Li}_3(z) = \left(\frac{k_BT}{\hbar\omega_0}\right)^3 \mathrm{Li}_3(z) \\ N_{\mathrm{cr}}(T) &\approx \left(\frac{k_BT}{\hbar\omega_0}\right)^3 \zeta(3) \end{aligned} \,. \tag{4.160}$$

The last expression defines the transition temperature T_c as that for which $N_{\mathrm{cr}}(T_c) = N$, which gives, for $N \sim 2\times 10^4$:

$$k_BT_c = \hbar\omega_0 \left(\frac{N}{\zeta(3)}\right)^{\frac{1}{3}} \approx 25.5\,\hbar\omega_0 \tag{4.161}$$

where we used $\zeta(3) \approx 1.202$. If we consider the typical value $\hbar\omega_0 \sim 4.8n\mathrm{K}$, this gives $k_BT_0 \sim 170n\mathrm{K}$, which justifies that approximation $k_BT \gg \hbar\omega_i$ used in deriving the smoothed harmonic density of states in Eq. (4.158).

4.8. Problems

Problem 4.1. Obtain the classical expressions for E, S, C_v and F for a one-dimensional harmonic oscillator starting directly from the classical partition function

$$Z_{\mathrm{CE}} = \int \frac{\mathrm{d}x\mathrm{d}p}{h}\, \mathrm{e}^{-\beta H} \,,$$

by performing the simple Gaussian integrals required. Verify that that the expressions obtained coincide with the asymptotic form of the corresponding quantum expressions in the appropriate limit

$k_BT \gg \hbar\omega$.
[Hint: you should pay attention to the correct expansion of the occupation number $\langle \hat{n} \rangle$: you should obtain a constant term which precisely cancel the zero-point motion term $\frac{1}{2}$ in the energy.]

Problem 4.2. For the one-dimensional harmonic oscillator, perform a Legendre transform from $F(T)$ to $E(S)$. Can you calculate the micro-canonical entropy $S(E)$? Try to do this problem for both the quantum and the classical case.

Problem 4.3. In general, if you have a classical probability distribution $P(\mathbf{x})$ and a classical observable $\mathbb{A}(\mathbf{x})$, the full probability distribution of the observable values is defined as:

$$\mathrm{Prob}_{\mathbb{A}}(A) = \int \mathrm{d}\mathbf{x}\, P(\mathbf{x})\, \delta(\mathbb{A}(\mathbf{x}) - A) \;. \tag{4.162}$$

Consider now the classical canonical ensemble for the Harmonic oscillator, where $\mathbf{x} = (x, p)$ and

$$P(\mathbf{x}) = \rho_{\mathrm{CE}}(\mathbf{x}) = \frac{\mathrm{e}^{-\beta H}}{Z} \;.$$

Try to calculate the probability distribution for the energy $\mathrm{Prob}_H(E)$ (the observable being $H(\mathbf{x})$), for the position $\mathrm{Prob}_x(x)$, for the momentum $\mathrm{Prob}_p(p)$, for the kinetic energy $\mathrm{Prob}_K(K)$ and for the potential energy $\mathrm{Prob}_V(V)$.

Problem 4.4. Verify that the Heisenberg operator corresponding to $\hat{Y}(x)$ is given by:

$$\hat{Y}(x,t) = \sum_m \psi_m(x)\, \hat{Q}_m(t) = \sum_m \sqrt{\frac{\hbar}{2M\omega_m}}\, \psi_m(x) \left(\mathrm{e}^{-i\omega_m t} \hat{a}_n + \mathrm{e}^{i\omega_m t} \hat{a}_n^\dagger \right) \;.$$

Calculate also the corresponding $\hat{\Pi}(x,t)$ and verify that

$$\hat{\Pi}(x,t) = \mu_0 \partial_t \hat{Y}(x,t) \;.$$

Finally, verify that $\hat{Y}(x,t)$ satisfies the same wave equation as $Y(x,t)$.

Problem 4.5. Try to calculate the average squared fluctuations of a string

$$\frac{1}{L} \int_0^L \mathrm{d}x\, \langle \hat{Y}^2(x,t) \rangle \;,$$

at temperature T and at $T = 0$. Anything remarkable to observe?

Problem 4.6. Repeat the quantisation procedure we have adopted assuming that the string obeys periodic boundary conditions in $[0, L]$. Working with ordinary plane waves, you should be able to express everything in terms of $\hat{a}_k^\dagger$ with $k = 2\pi n/L$. Pay due attention to the fact that you want to express a real field $\hat{Y}(x)$. Calculate the equal-time space-correlation function $\langle \hat{Y}(x,t)\hat{Y}(x',t) \rangle$ and the equal-space time-correlation function $\langle \hat{Y}(x,t)\hat{Y}(x,t') \rangle$, both at $T = 0$ and at finite T. Try to see what happens to the large $|x - x'|$ or $|t - t'|$ behaviours in the limit $L \to \infty$.

Problem 4.7. Show that in the Maxwell-Boltzmann limit the entropy of the gas is:

$$S_{\mathrm{MB}}(T, V, \mu) = k_B N_{\mathrm{MB}} \left(\frac{2+d}{d} - \beta\mu \right) \;.$$

This adds some insight on the reason why the chemical potential has to be large and negative in that limit. Re-express the entropy in terms of (E, V, N), to recover the result we have derived long ago for the classical ideal gas entropy.

5. Models and phase transitions

We start here with a survey of some of the traditional basic topics of a statistical mechanics course. To start with, we will need to discuss a few general facts:

Models) There is an emphasis on models which emerges clearly from glancing at any book on the subject. Why? We know pretty well how to write a very detailed Hamiltonian to describe, for instance, a condensed matter system, but we rarely adventure into the horrible experience of keeping track of all ingredients, and we resort to *simplified models.*

Phase transitions) The existence of phase transitions is quite clear on the experimental side and also from the thermodynamical point of view. But, how this basic fact emerges when you do statistical mechanics?

Universality) Many properties, close to phase transitions, seem to depend very little on details of the model: some universal features emerge, depending on the dimensionality of the space in which the model is defined, and on some symmetry properties of the basic degrees of freedom appearing.

Order parameters and correlations) We will see how a local order parameter is defined, and how its correlations are expected to behave.

5.1. Why models?

As mentioned, in condensed matter we know pretty well the Hamiltonian governing a system of atoms, with their nuclei and electrons. Yet, we resort to models, because any exact treatment of such a complex many-body problem is hopeless.

One common instance of such an idealization is the problem of a strongly correlated system, where the independent particle approximation fails. A typical model that emerges in such a case is the *Hubbard model.*

> **The Hubbard model.** You consider a *lattice* — for instance, a cubic lattice in d-dimensions with $N = L^d$ sites $\mathbf{R} = a\sum_{j=1}^{d} n_j \mathbf{e}_j$, where $n_j = 0, \cdots L-1$, $\mathbf{e}_j$ are the usual unit vectors in the direction j, and a the lattice constant — and a *single localized orbital* (technically, a Wannier orbital, to ensure orthogonality) $\phi_{\mathbf{R}}(\mathbf{x})$ sitting at each lattice site. You define the creation/annihilation operator accordingly and write the Hamiltonian as:
>
> $$\widehat{H} = -t_h \sum_{\langle \mathbf{R},\mathbf{R}'\rangle} \sum_{\sigma=\uparrow,\downarrow} \Big(\hat{c}^{\dagger}_{\mathbf{R},\sigma}\hat{c}_{\mathbf{R}',\sigma} + \text{H.c.}\Big) + U \sum_{\mathbf{R}} \hat{n}_{\mathbf{R},\uparrow}\hat{n}_{\mathbf{R},\downarrow} \;. \tag{5.1}$$
>
> Here t_h is the hopping (overlap) integral between two "neighbouring" Wannier orbitals, and U is the so-called "Hubbard" repulsion. To fully specify the model you have to tell me the density of electrons you want.

At half-filling, when $N_e = N$ (or $n = 1$), and for large U the kinetic term is strongly suppressed because doubly-occupied sites cost large energy. All states of the form:

$$|\{\sigma_{\mathbf{R}}\}\rangle = \prod_{\mathbf{R}}^{N} \hat{c}^{\dagger}_{\mathbf{R},\sigma_{\mathbf{R}}}|0\rangle \ ,$$

do not pay any repulsion penalty U. But there is a large degeneracy, 2^N, associated with the *spin*. You can do a form of *degenerate perturbation theory* to get the effective Hamiltonian which emerges for large U.

The result can be grasped from a simple *two-site* Hubbard model calculation. There is a total of six two-electron states that you can form in such a case:

$$\Big\{ \hat{c}^{\dagger}_{1,\uparrow}\hat{c}^{\dagger}_{2,\uparrow}|0\rangle, \ \ \hat{c}^{\dagger}_{1,\downarrow}\hat{c}^{\dagger}_{2,\downarrow}|0\rangle, \ \ \hat{c}^{\dagger}_{1,\uparrow}\hat{c}^{\dagger}_{2,\downarrow}|0\rangle, \ \ \hat{c}^{\dagger}_{1,\downarrow}\hat{c}^{\dagger}_{2,\uparrow}|0\rangle, \ \ \hat{c}^{\dagger}_{1,\uparrow}\hat{c}^{\dagger}_{1,\downarrow}|0\rangle, \ \ \hat{c}^{\dagger}_{2,\uparrow}\hat{c}^{\dagger}_{2,\downarrow}|0\rangle \Big\} \ .$$

Here is the 6×6 matrix for the Hubbard model in such a basis:

	$\hat{c}^{\dagger}_{1,\uparrow}\hat{c}^{\dagger}_{2,\uparrow}\|0\rangle$	$\hat{c}^{\dagger}_{1,\downarrow}\hat{c}^{\dagger}_{2,\downarrow}\|0\rangle$	$\hat{c}^{\dagger}_{1,\uparrow}\hat{c}^{\dagger}_{2,\downarrow}\|0\rangle$	$\hat{c}^{\dagger}_{1,\downarrow}\hat{c}^{\dagger}_{2,\uparrow}\|0\rangle$	$\hat{c}^{\dagger}_{1,\uparrow}\hat{c}^{\dagger}_{1,\downarrow}\|0\rangle$	$\hat{c}^{\dagger}_{2,\uparrow}\hat{c}^{\dagger}_{2,\downarrow}\|0\rangle$
$\hat{c}^{\dagger}_{1,\uparrow}\hat{c}^{\dagger}_{2,\uparrow}\|0\rangle$	0	0	0	0	0	0
$\hat{c}^{\dagger}_{1,\downarrow}\hat{c}^{\dagger}_{2,\downarrow}\|0\rangle$	0	0	0	0	0	0
$\hat{c}^{\dagger}_{1,\uparrow}\hat{c}^{\dagger}_{2,\downarrow}\|0\rangle$	0	0	0	0	$-t_h$	$-t_h$
$\hat{c}^{\dagger}_{1,\downarrow}\hat{c}^{\dagger}_{2,\uparrow}\|0\rangle$	0	0	0	0	$+t_h$	$+t_h$
$\hat{c}^{\dagger}_{1,\uparrow}\hat{c}^{\dagger}_{1,\downarrow}\|0\rangle$	0	0	$-t_h$	$+t_h$	U	0
$\hat{c}^{\dagger}_{2,\uparrow}\hat{c}^{\dagger}_{2,\downarrow}\|0\rangle$	0	0	$-t_h$	$+t_h$	0	U

Observe that due to the combinations of $+t_h$ and $-t_h$ — in turn, due to the fermionic anti-commutation relationships, only the singlet state

$$|\Psi_s\rangle = \frac{1}{\sqrt{2}}\Big(\hat{c}^{\dagger}_{1,\uparrow}\hat{c}^{\dagger}_{2,\downarrow} - \hat{c}^{\dagger}_{1,\downarrow}\hat{c}^{\dagger}_{2,\uparrow}\Big)|0\rangle$$

is effectively coupled to a symmetric doubly-occupied state

$$|\Psi_{d,+}\rangle = \frac{1}{\sqrt{2}}\Big(\hat{c}^{\dagger}_{1,\uparrow}\hat{c}^{\dagger}_{1,\downarrow} + \hat{c}^{\dagger}_{2,\uparrow}\hat{c}^{\dagger}_{2,\downarrow}\Big)|0\rangle \ ,$$

while the triplet states (with energy 0) and the anti-symmetric doubly-occupied state $|\Psi_{d,-}\rangle$ (with energy U) are totally decoupled. The Hamiltonian restricted to the 2×2 space $\{|\Psi_s\rangle, |\Psi_{d,+}\rangle\}$ is:

$$\begin{pmatrix} 0 & -2t_h \\ -2t_h & U \end{pmatrix} \qquad \Longrightarrow \qquad \lambda_{\pm} = \frac{U \pm \sqrt{U^2 + 16t_h^2}}{2} \ . \tag{5.2}$$

If $U \gg t_h$, to lowest-order in t_h/U, the ground state is a *singlet state* with energy $E_s = -4t^2/U$, while the triplet states are at energy $E_t = 0$. Further up, at energy U and $U + 4t_h^2/U$ are the two doubly occupied states.

This simple exercise suggests that, within the low-energy subspace of *singly-occupied states*, the combined effect of hopping to doubly occupied virtual states, leads to an effective spin Hamiltonian

$$\widehat{H}_{\mathrm{eff}} = \frac{4t^2}{U}\Big(\widehat{\mathbf{S}}_1 \cdot \widehat{\mathbf{S}}_2 - \frac{1}{4}\Big)$$

which favours *singlets*, while leaving triplets at zero-energy.

Remarkably, this toy problem leads to a general result that you might derive by setting up a proper *second-order degenerate perturbation theory.*

The Heisenberg model. The effective Hamiltonian for the spin-degrees of freedom of a large-U half-filled Hubbard model is given by:

$$\widehat{H} = J \sum_{\langle \mathbf{R},\mathbf{R}' \rangle} \left(\widehat{\mathbf{S}}_{\mathbf{R}} \cdot \widehat{\mathbf{S}}_{\mathbf{R}'} - \frac{1}{4} \right) , \tag{5.3}$$

where $J = 4t_h^2/U$ and $\widehat{\mathbf{S}}_{\mathbf{R}} = \frac{1}{2}\hat{\boldsymbol{\sigma}}_{\mathbf{R}}$ are spin-1/2 operators, with $\hat{\boldsymbol{\sigma}}_{\mathbf{R}}$ the Pauli matrices at site $\mathbf{R}$. Hence spin singlets emerge, out of hopping and repulsive interactions, via a mechanism that is known as *antiferromagnetic super-exchange*.

This is the isotropic version of a model that we can write, for an arbitrary spin $S \geq \frac{1}{2}$, neglecting the unimportant shift 1/4, as:

$$\widehat{H}_{\text{general}-\text{XYZ}} = \sum_{\langle \mathbf{R},\mathbf{R}' \rangle} \left(J^{xx}_{\mathbf{R}\mathbf{R}'} \widehat{\mathrm{S}}^x_{\mathbf{R}} \widehat{\mathrm{S}}^x_{\mathbf{R}'} + J^{yy}_{\mathbf{R}\mathbf{R}'} \widehat{\mathrm{S}}^y_{\mathbf{R}} \widehat{\mathrm{S}}^y_{\mathbf{R}'} + J^{zz}_{\mathbf{R}\mathbf{R}'} \widehat{\mathrm{S}}^z_{\mathbf{R}} \widehat{\mathrm{S}}^z_{\mathbf{R}'} \right) - \sum_{\mathbf{R}} \mathbf{h}_{\mathbf{R}} \cdot \widehat{\mathbf{S}}_{\mathbf{R}} . \tag{5.4}$$

Here $\widehat{\mathrm{S}}^\alpha_{\mathbf{R}}$ with $\alpha = x, y, z$ are spin-S angular momentum operators at each lattice site $\mathbf{R}$. For $S = 1/2$, and with appropriate choice of the couplings, $J^{xx}_{\mathbf{R}\mathbf{R}'} = J^{yy}_{\mathbf{R}\mathbf{R}'} = J$ and $J^{zz}_{\mathbf{R}\mathbf{R}'} = J\Delta$, we get for instance the so-called XXZ Heisenberg model:

$$\widehat{H}_{\text{XXZ}} = J \sum_{\langle \mathbf{R},\mathbf{R}' \rangle} \left(\widehat{\mathrm{S}}^x_{\mathbf{R}} \widehat{\mathrm{S}}^x_{\mathbf{R}'} + \widehat{\mathrm{S}}^y_{\mathbf{R}} \widehat{\mathrm{S}}^y_{\mathbf{R}'} + \Delta\, \widehat{\mathrm{S}}^z_{\mathbf{R}} \widehat{\mathrm{S}}^z_{\mathbf{R}'} \right) . \tag{5.5}$$

For $\Delta = 1$ we recover the fully isotropic antiferromagnetic Heisenberg model — also denoted often as XXX —, while for $\Delta = 0$ we have the so-called XY (or planar) model. For $\Delta = -1$ we have a *ferromagnetic* isotropic Heisenberg model. [1]

Still with $S = 1/2$ and with zz-couplings only we get the Ising model in transverse-field, which we write for convenience directly in terms of the Pauli operators as:

$$\widehat{H}_{\text{Ising}} = - \sum_{\langle \mathbf{R},\mathbf{R}' \rangle} J_{\mathbf{R}\mathbf{R}'} \hat{\sigma}^z_{\mathbf{R}} \hat{\sigma}^z_{\mathbf{R}'} - \sum_{\mathbf{R}} h^{\parallel}_{\mathbf{R}} \hat{\sigma}^z_{\mathbf{R}} - \sum_{\mathbf{R}} h^{\perp}_{\mathbf{R}} \hat{\sigma}^x_{\mathbf{R}} . \tag{5.6}$$

Symmetries. The *symmetries* of the previous models can be remarkably different. Let us concentrate here on internal symmetries of models that are otherwise translationally invariant, for instance, due to the uniform couplings and periodic boundary conditions.

SU(2) - The isotropic Heisenberg model

$$\widehat{H}_{\text{XXX}} = J \sum_{\langle \mathbf{R},\mathbf{R}' \rangle} \left(\widehat{\mathrm{S}}^x_{\mathbf{R}} \widehat{\mathrm{S}}^x_{\mathbf{R}'} + \widehat{\mathrm{S}}^y_{\mathbf{R}} \widehat{\mathrm{S}}^y_{\mathbf{R}'} + \widehat{\mathrm{S}}^z_{\mathbf{R}} \widehat{\mathrm{S}}^z_{\mathbf{R}'} \right) = J \sum_{\langle \mathbf{R},\mathbf{R}' \rangle} \widehat{\mathbf{S}}_{\mathbf{R}} \cdot \widehat{\mathbf{S}}_{\mathbf{R}'} , \tag{5.7}$$

for either sign of J, admits arbitrary SU(2) uniform spin rotations, associated to the fact that the total spin $\widehat{\mathbf{S}}_{\text{tot}}$ is conserved. More precisely, if $\widehat{\mathbf{S}}_{\text{tot}} = \sum_{\mathbf{R}} \widehat{\mathbf{S}}_{\mathbf{R}}$ is the total spin, then a uniform spin rotation by an angle θ around the direction $\mathbf{n}$ is associated to a unitary operator $\hat{U}_{\mathbf{n},\theta} = \mathrm{e}^{-\frac{i}{\hbar}\theta \mathbf{n}\cdot\widehat{\mathbf{S}}_{\text{tot}}}$ which transforms each spin as a "vector", i.e.,

$$\hat{U}_{\mathbf{n},\theta}\, \widehat{\mathrm{S}}^\alpha_{\mathbf{R}}\, \hat{U}^\dagger_{\mathbf{n},\theta} = \mathrm{e}^{-i\theta\mathbf{n}\cdot\widehat{\mathbf{S}}_{\text{tot}}}\, \widehat{\mathrm{S}}^\alpha_{\mathbf{R}}\, \mathrm{e}^{i\theta\mathbf{n}\cdot\widehat{\mathbf{S}}_{\text{tot}}} = \sum_{\alpha'} \mathrm{R}_{\alpha,\alpha'} \widehat{\mathrm{S}}^{\alpha'}_{\mathbf{R}} \qquad \alpha, \alpha' = x, y, z \text{ (or } 1, 2, 3) \tag{5.8}$$

---

[1] Incidentally, the sign in front of the xx and yy terms can be reversed by a simple unitary transformation on all lattices that are *bipartite*, meaning that you can sub-divide the lattice into *two sub-lattices*, call them A and B, such that spins in sub-lattice A interact with their neighbours which belong to sub-lattice B. Hyper-cubic lattices are bipartite, while the triangular lattice is not. Non-bipartite lattices give rise to geometrically frustrated antiferromagnetic models, as a rule. The transformation that changes the sign of the xx and yy terms is a rotation around the z-axis by an angle π on *one of the two sub-lattices*.

where $\mathrm{R} = \mathrm{R}(\mathbf{n}, \theta)$ is the real orthogonal 3×3 matrix describing the rotation in ordinary space. [2] Evidently, the scalar product $\widehat{\mathbf{S}}_{\mathbf{R}} \cdot \widehat{\mathbf{S}}_{\mathbf{R}'}$ is left unchanged by the rotation, and therefore $\widehat{H}_{\mathrm{XXX}}$ *commutes* with $\hat{U}_{\mathbf{n},\theta} = \mathrm{e}^{-\frac{i}{\hbar}\theta \mathbf{n}\cdot\widehat{\mathbf{S}}_{\mathrm{tot}}}$ for all $\mathbf{n}$ and all θ. Hence $\widehat{H}_{\mathrm{XXX}}$ commutes with all components of the total spin. This implies that $\widehat{H}_{\mathrm{XXX}}$, $\widehat{\mathbf{S}}^2_{\mathrm{tot}}$ and $\widehat{\mathrm{S}}^z_{\mathrm{tot}}$ form a set of three commuting operators.

SU(1) - For the planar XY model

$$\widehat{H}_{\mathrm{XY}} = J \sum_{\langle \mathbf{R},\mathbf{R}' \rangle} \left(\widehat{\mathrm{S}}^x_{\mathbf{R}} \widehat{\mathrm{S}}^x_{\mathbf{R}'} + \widehat{\mathrm{S}}^y_{\mathbf{R}} \widehat{\mathrm{S}}^y_{\mathbf{R}'} \right) \;, \tag{5.9}$$

spin-rotations $\hat{U}_{\mathbf{z},\theta} = \mathrm{e}^{-\frac{i}{\hbar}\theta \widehat{\mathrm{S}}^z_{\mathrm{tot}}}$ around the z-axis are symmetries, i.e., only $\widehat{\mathrm{S}}^z_{\mathrm{tot}}$ commutes with $\widehat{H}_{\mathrm{XY}}$.

Z$_2$ - Finally, for the transverse-field Ising model (TFIM) *in absence of longitudinal fields*

$$\widehat{H}_{\mathrm{TFIM}} = -\sum_{\langle \mathbf{R},\mathbf{R}' \rangle} J_{\mathbf{R}\mathbf{R}'} \hat{\sigma}^z_{\mathbf{R}} \hat{\sigma}^z_{\mathbf{R}'} - \sum_{\mathbf{R}} h^{\perp}_{\mathbf{R}} \hat{\sigma}^x_{\mathbf{R}} \;, \tag{5.10}$$

evidently a π rotation in spin-space around the x-axis associated to the unitary operator

$$\mathrm{e}^{-i\frac{\pi}{2}\sum_{\mathbf{R}} \hat{\sigma}^x_{\mathbf{R}}} = (-i)^N \prod_{\mathbf{R}} \hat{\sigma}^x_{\mathbf{R}} \tag{5.11}$$

commutes with the Hamiltonian, since $\hat{\sigma}^x \hat{\sigma}^z \hat{\sigma}^x = -\hat{\sigma}^z$ but the interaction term contains pairs of $\hat{\sigma}^z$, hence the two minus signs cancel. This symmetry is known as $\mathbb{Z}_2$, and the group is discrete and made of only two elements, $\{1, \hat{U}_{\mathbb{Z}_2} = \prod_{\mathbf{R}} \hat{\sigma}^x_{\mathbf{R}}\}$.

5.2. Why phase transitions?

The existence of phase transitions is quite clear experimentally. Equally clear is from a thermodynamic point of view, where phase transitions emerge from singularities in some derivatives (first- or higher-order) of the thermodynamic potentials. But where do singularities come from in statistical mechanics?

Consider for simplicity a spin system on a lattice with N sites, for instance, the transverse field Ising model:

$$\widehat{H}_{\mathrm{Ising}} = -\sum_{\langle \mathbf{R},\mathbf{R}' \rangle} J_{\mathbf{R}\mathbf{R}'} \hat{\sigma}^z_{\mathbf{R}} \hat{\sigma}^z_{\mathbf{R}'} - \sum_{\mathbf{R}} h^{\parallel}_{\mathbf{R}} \hat{\sigma}^z_{\mathbf{R}} - \sum_{\mathbf{R}} h^{\perp}_{\mathbf{R}} \hat{\sigma}^x_{\mathbf{R}} \;. \tag{5.12}$$

The Hilbert space is 2^N-dimensional, and the partition function is a *finite sum* of terms:

$$Z = \sum_{\alpha} \mathrm{e}^{-\beta E_\alpha} \qquad \Longrightarrow \qquad F = -k_B T \log \Big(\sum_{\alpha} \mathrm{e}^{-\beta E_\alpha} \Big) \;, \tag{5.13}$$

---

[2] $\mathrm{R}(\mathbf{n}, \theta)$ can be regarded as the "defining representation" of SO(3), the group of rotations in three-dimensions. You can write:

$$\mathrm{R}(\mathbf{n}, \theta) = \mathrm{e}^{-i\theta \mathbf{n}\cdot\mathbf{L}} \qquad \text{with} \qquad [\mathrm{L}_\alpha, \mathrm{L}_\beta] = i\epsilon_{\alpha\beta\gamma}\mathrm{L}_\gamma \;,$$

where $\mathrm{L}_{\alpha=x,y,z}$ are the three 3×3 Hermitean matrices

$$\mathrm{L}_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix} \qquad \mathrm{L}_y = \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix} \qquad \mathrm{L}_z = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} .$$

Observe that the same representation can be given in terms of *real antisymmetric* generators of the algebra of the group, given by $\mathbb{L}_\alpha = -i\mathrm{L}_\alpha$ such that $[\mathbb{L}_\alpha, \mathbb{L}_\beta] = \epsilon_{\alpha\beta\gamma}\mathbb{L}_\gamma$. For reference,

$$\mathrm{R}(\mathbf{z}, \theta) = \mathrm{e}^{-i\theta \mathrm{L}_z} = \mathrm{e}^{\theta \mathbb{L}_z} = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} .$$

where α labels the 2^N energy eigenstates of $\widehat{H}_{\rm Ising}$. Evidently, Z is analytic in all the parameters of the model. But the free-energy $F = -k_B T \log Z$ also *cannot* have singularities, since $\log z$ is an analytic function of z away from the branch-cut Re$z < 0$. Hence, for any finite N the free-energy depends analytically on all the parameters, and no singularities are present.

Reinforcing on this argument, suppose we consider a model in absence of longitudinal fields, say the TFIM, which we know to be $\mathbb{Z}_2$ symmetric. This means that $\hat{U}_{\mathbb{Z}_2} = \prod_{\mathbf{R}} \hat{\sigma}^x_{\mathbf{R}}$ commutes with $\widehat{H}_{\rm TFIM}$ and with the associated Gibbs density matrix $\hat{\rho}_{\rm CE}$, i.e., $\hat{U}_{\mathbb{Z}_2}\hat{\rho}_{\rm CE}\hat{U}^\dagger_{\mathbb{Z}_2} = \hat{\rho}_{\rm CE}$. Now consider the average of $\hat{\sigma}^z_{\mathbf{R}}$. Since $\hat{U}_{\mathbb{Z}_2}\hat{\sigma}^z_{\mathbf{R}}\hat{U}^\dagger_{\mathbb{Z}_2} = -\hat{\sigma}^z_{\mathbf{R}}$ you immediately deduce that

$$\langle \hat{\sigma}^z_{\mathbf{R}} \rangle = {\rm Tr}\left(\hat{\rho}_{\rm CE}\hat{\sigma}^z_{\mathbf{R}}\right) = {\rm Tr}\left(\hat{U}_{\mathbb{Z}_2}\hat{\rho}_{\rm CE}\hat{\sigma}^z_{\mathbf{R}}\hat{U}^\dagger_{\mathbb{Z}_2}\right) = {\rm Tr}\left(\hat{U}_{\mathbb{Z}_2}\hat{\rho}_{\rm CE}\hat{U}^\dagger_{\mathbb{Z}_2}\hat{U}_{\mathbb{Z}_2}\hat{\sigma}^z_{\mathbf{R}}\hat{U}^\dagger_{\mathbb{Z}_2}\right) = -\langle \hat{\sigma}^z_{\mathbf{R}} \rangle \; . \tag{5.14}$$

Hence, by symmetry, $\langle \hat{\sigma}^z_{\mathbf{R}} \rangle = 0$.

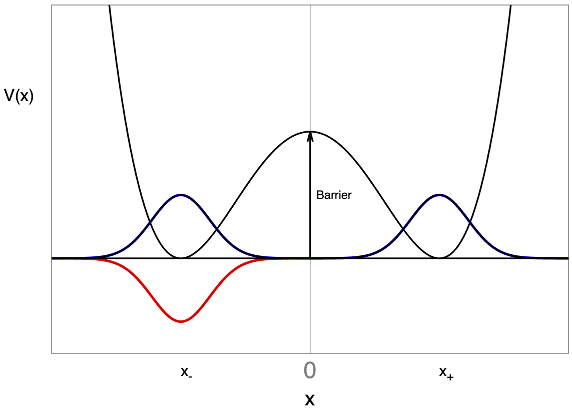

Figure 5.1: A quantum particle in a double-well symmetric potential. The ground state (blue) is an even function, superposition of the two states on the two wells. The first excited state (red) is an odd function. As the barrier increases to infinity, the states in the two wells are effectively disconnected (and degenerate).

Does this imply that no spontaneous magnetization can exist in the ground state of the Ising model? No. Indeed, if we turn off any transverse field, and consider a simple ferromagnetic model with all $J_{\mathbf{R},\mathbf{R}'} = J$ we know that there are two classical ground state, totally degenerate in energy, with spins perfectly aligned: either all spins are up $|\Psi_\uparrow\rangle = |\uparrow, \cdots, \uparrow\rangle$, or down $|\Psi_\downarrow\rangle = |\downarrow, \cdots, \downarrow\rangle$. Their energy is $E_{\rm gs} = -JNz/2$ where z is the number of nearest-neighbour. Observe that these are *not* $\mathbb{Z}_2$*-eigenstates*. Indeed, the correct common eigenstates of the classical Ising model together with the symmetry $\hat{U}_{\mathbb{Z}_2}$ are

$$|\Psi_\pm\rangle = \frac{1}{\sqrt{2}}\Big(|\uparrow, \cdots, \uparrow\rangle \pm |\downarrow, \cdots, \downarrow\rangle\Big) \qquad \text{with} \qquad \hat{U}_{\mathbb{Z}_2}|\Psi_\pm\rangle = \pm|\Psi_\pm\rangle \; , \tag{5.15}$$

and you can immediately verify that indeed these are still degenerate, with energy $E_{\rm gs} = -JNz/2$, and as prescribed by our symmetry-based "proof"

$$\langle \Psi_\pm | \hat{\sigma}^z_{\mathbf{R}} | \Psi_\pm \rangle = 0 \; , \tag{5.16}$$

for either sign of the superposition. The symmetric states $|\Psi_\pm\rangle$ are quantum superpositions of two *macroscopically distinct* broken-symmetry states $|\Psi_\uparrow\rangle$ and $|\Psi_\downarrow\rangle$. [3] This is at variance with the situation typically encountered in quantum mechanics for a single particle, for instance, where symmetries are not broken. Take for instance a double-well potential, as in Fig. 5.1, where the symmetry would be parity: the ground state is *even* (blue curve) and separated by a gap from the first excited *odd* state (red curve, partially covered by the ground state). You do not make superpositions of these states which break the parity symmetry. But the analogy with symmetry breaking in statistical mechanics emerges when you consider a barrier that *becomes infinitely large*: at that point, the gap between the

---

[3] In quantum information, you would call $|\Psi_\pm\rangle$ *cat states*, in analogy with the quantum state of Schrödinger's cat, in a quantum superposition, the poor animal, of two macroscopically distinct states of being dead or alive.

two symmetric states becomes *exponentially small* and, to all practical purposes, a particle sitting close to one of the two minima (broken-symmetry state) would not be able to *tunnel* to the other minimum.

You might object that the situation just discussed is very special: it is classical, and this perfect degeneracy would hold even for a system of a few spins. But indeed, a similar scenario holds even in presence of a transverse field $h^{\perp}$, and there you would discover that the degeneracy between $|\Psi_{+}\rangle$ and $|\Psi_{-}\rangle$ is not exact. Due to the Perron-Frobenius theorem, which we will meet again, later on, you can prove that a state $|\Psi_{+}\rangle$ with *all positive components* on the computational basis of the Hilbert space is the *unique ground state*. The other symmetric state $|\Psi_{-}\rangle$, however, turns out to be split by a quantity which is *exponentially small* in the number of spins N, hence the two are asymptotically degenerate for $N \to \infty$. For a very large system, you can still form symmetry-breaking states out of this quasi-degenerate doublet of symmetric states. Figs. 5.2-5.3 illustrate these facts for a small TFIM chain with $N = 14$ sites, whose spectrum is determined by exact diagonalisation.

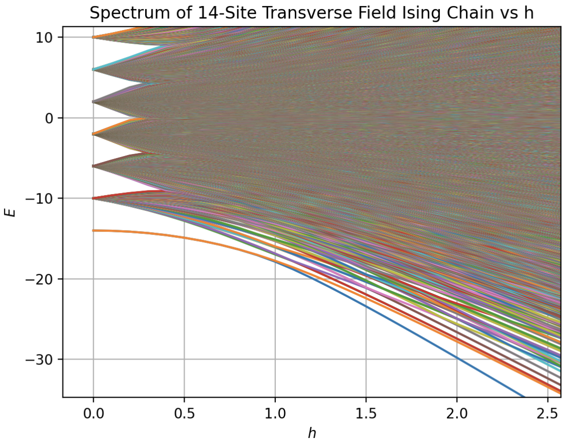

Figure 5.2: The spectrum of the TFIM for $N = 14$ sites versus the transverse field $h^{\perp}$. Observe that the classical ground states for $h^{\perp} = 0$ evolve into two states, separated by a clear gap for $h^{\perp}/J > 1$, which they merge together for $h^{\perp}/J < 1$, since they are separated by an exponentially small gap for large N.

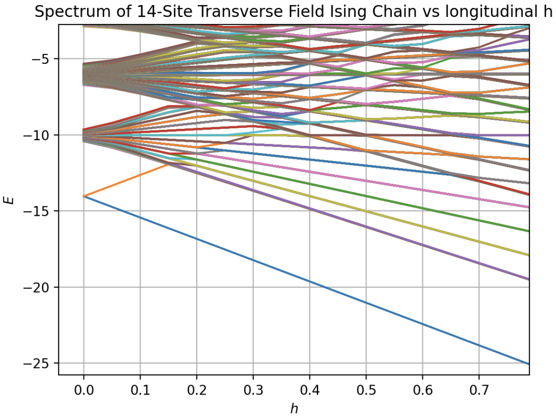

Figure 5.3: The spectrum of the TFIM for $N = 14$ sites at $h^{\perp}/J = 0.1$ versus the longitudinal field $h^{\parallel}$. Observe that the "almost doubly degenerate" ground state is Zeeman-split by the longitudinal field: the two broken-symmetry states are in this way clearly identified.

Singularities emerge in the thermodynamic limit. The mystery is solved by the fact that *singularities emerge from the thermodynamic limit* $N \to \infty$. The correct magnetization, for instance, would come out upon adding a small longitudinal field h which is *sent to* 0 *after the thermodynamic limit is taken*:

$$\langle \hat{\sigma}^{z}_{\mathbf{R}} \rangle_0 = \lim_{h \to 0} \lim_{N \to \infty} \langle \hat{\sigma}^{z}_{\mathbf{R}} \rangle \neq 0 \; . \tag{5.17}$$

Fully-connected Ising model. As a work-horse to better understand the spontaneous breaking of the $\mathbb{Z}_2$ symmetry that emerges in the thermodynamical limit, let us consider a solvable classical Ising model: the fully connected Ising ferromagnet, essentially an infinite coordination model which presents features that are “mean-field-like”, as we will discuss later on.

The model is defined by $j = 1 \cdots N$ spins (we assume N even), and every spin $\hat{\sigma}^z_j = \pm 1$ interacts ferromagnetically with every other spin $\hat{\sigma}^z_{j'}$. Including for simplicity a constant term with $j' = j$, we would write the Hamiltonian as:

$$\widehat{H} = -\frac{J}{2N}\sum_{j,j'=1}^{N} \hat{\sigma}^z_{j'}\hat{\sigma}^z_j - h\sum_{j=1}^{N}\hat{\sigma}^z_j = -\frac{J}{2N}\Big(\sum_{j=1}^{N}\hat{\sigma}^z_j\Big)^2 - h\sum_{j=1}^{N}\hat{\sigma}^z_j \ . \tag{5.18}$$

The fully-connected character of the model implies that the energy depends on the spin configuration $\underline{\sigma} = (\sigma_1, \cdots, \sigma_N)$ only through its magnetisation $M = \sum_j \sigma_j = N_+ - N_-$, where $N_\pm$ are the number of spins ± 1, with $N = N_+ + N_1$. Evidently, M can have $N+1$ values, from $+N$ down to $-N$ in steps of 2: $M = N - 2k$ with $k = 0, \cdots N$. All configurations $\underline{\sigma}$ with the same M have the same energy

$$E_M = -\frac{J}{2N}M^2 - hM \ ,$$

and therefore the same Gibbs equilibrium probability.

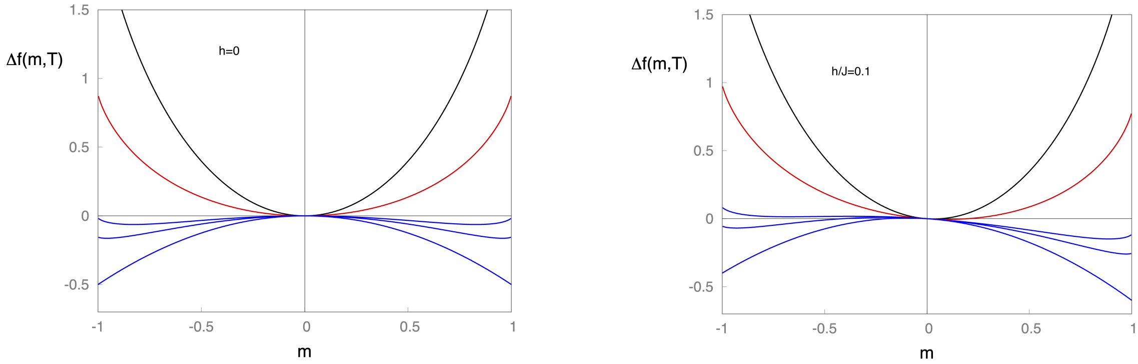

Figure 5.4.: The free-energy of the fully connected Ising ferromagnet. Temperatures are $k_B T/J = 4, 2, 0.7, 0.5, 0$ from top to bottom curves. Left panel for $h = 0$, right panel for $h/J = 0.1$.

We can organize the partition function sum as follows:

$$\begin{aligned} e^{-\beta F} = Z \ &= \ \sum_{\underline{\sigma}} e^{-\beta E_{\underline{\sigma}}} = \sum_{M}\sum_{\underline{\sigma}} \delta_{M,\sum_j \sigma_j} e^{-\beta E_M} \\ &= \ \sum_{M} \binom{N}{N_+} e^{-\beta E_M} = \sum_{M} e^{-\beta F(M,T)} \ , \end{aligned} \tag{5.19}$$

where we noticed that the number of configurations with given M is simply given by a binomial coefficient, and introduced a *constrained-magnetization* free-energy $F(M,T)$, given by

$$F(M,T) = -\frac{1}{\beta}\log\binom{N}{N_+} e^{-\beta E_M} = E_M - k_B T \log\frac{N!}{N_+!(N-N_+)!} \ . \tag{5.20}$$

Interestingly, if I ask you what is the probability of observing a given value of M, you would write:

$$P^{\rm eq}(M) = \sum_{\underline{\sigma}} P^{\rm eq}_{\underline{\sigma}}\,\delta_{M,\sum_j\sigma_j} = \frac{1}{Z}e^{-\beta E_M}\sum_{\underline{\sigma}}\delta_{M,\sum_j\sigma_j} = \frac{1}{Z}e^{-\beta E_M}\binom{N}{N_+} \equiv \frac{1}{Z}e^{-\beta F(M,T)} \ . \tag{5.21}$$

So, $F(M,T)$ gives information about the equilibrium probability distribution of the magnetization. The partition function cancels if you consider ratios, for instance:

$$\frac{P^{\rm eq}(M)}{P^{\rm eq}(M=0)} = e^{-\beta\big(F(M,T)-F(0,T)\big)} \ . \tag{5.22}$$

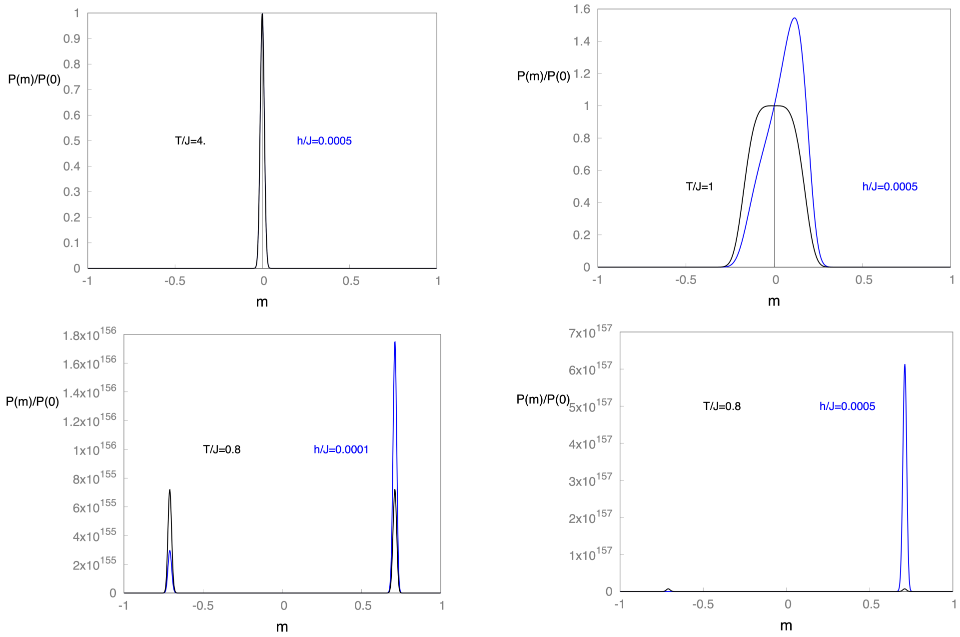

Figure 5.5.: The ratio of the probability distribution $P(m)/P(0)$ for the fully connected Ising ferromagnet. Two curves are shown: a black one, for $h=0$, and a blue one for the value of h shown in each panel. Here $N=1000$.

Using the Stirling approximation $\log N! \approx N\log N - N + \log\sqrt{2\pi N}$, and introducing the magnetisation density $m=M/N$, you would conclude that $F(M,T)\approx Nf(m,T) - k_BT\log\sqrt{\pi N(1-m^2)/2}$ where the second (sub-extensive) term is relatively unimportant, while the first extensive term defines the free-energy-per-spin $f(m,T)$, which is given by:

$$f(m,T) = -\frac{J}{2}m^2 - hm - k_BT\bigg(-\frac{1-m}{2}\log\frac{1-m}{2} - \frac{1+m}{2}\log\frac{1+m}{2}\bigg) \,, \tag{5.23}$$

and shown in Fig. 5.4. By analyzing the behaviour of $f(m,T)$ we easily discover that for large T the entropic term wins and the probability distribution $P^{\rm eq}(m)$ is peaked at $m=0$, while [4] for $T<T_c=J/k_B$ the probability distribution has two peaks $\pm m_T$, for $h=0$, with $m_T\to 1$ for $T\to 0$.

For low T, since the free-energy difference between $m=\pm m_T$ and $m=0$ (where the barrier is) is *extensive*, you would never visit the barrier at $m=0$ by starting from one of the minima at $\pm m_T$, for large N. Fig. 5.5 shows the ratio $P^{\rm eq}(m)/P^{\rm eq}(0)$ for $T=J/k_B=T_c$ and $T=0.8J/k_B<T_c$, and for various (small) fields h. Even more clear is how the ratios of probabilities of being in the two broken symmetry peaks for $T<T_c$ behaves at finite field:

$$\frac{P^{\rm eq}(+m_T)}{P^{\rm eq}(-m_T)} = \mathrm{e}^{-2\beta h m_T N} \,, \tag{5.24}$$

since all contributions apart from the field-term are even in m.

Exercise 5.1. Evaluate the free-energy per site $f(h)=F(h)/N$ for various values of N, say $N=10^2$ to $N=10^6$ by calculating numerically, with python for instance, the full partition sum. Plot the result versus h and carefully consider what happens for increasing N. For $T>T_c=J/k_B$ you should find that $f(h)=-k_BT\log 2-\frac{1}{2}\chi h^2+\cdots$ where $\chi=1/k_B(T-T_c)$, hence a parabola with a coefficient that diverges for $T\to T_c^+$. For $T<T_c$ you will find that the parabolic behaviour is truly confined

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[4] To determine T_c, expand the entropic term close to $m=0$, using $\log(1+x)=x-x^2/2+\cdots$, without forgetting the quadratic piece. You would discover that the free-energy behaves as $-k_BT\log(2)+(k_BT-J)m^2/2-hm$ for small m.

to very small h at finite N, and quickly develops a "cusp-like" feature close to $h = 0$ which becomes a true discontinuity in the derivative at $h = 0$ for $N \to \infty$. We will see later that $m = -\frac{\partial f}{\partial h}$: think about our symmetry-based proof leading to $m = 0$, and you will realize that the proper limit to take leads either to the *right* or to the *left* derivative in $h = 0$, and you get it by adding a small infinitesimal field, as discussed before.

Broken-symmetry at finite T. Before ending this discussion, let us consider the question: does the symmetry breaking that we found in the *ground state* of the one-dimensional Ising model survive at finite T? The answer is no: in one-dimension, symmetry breaking and the associated spontaneous magnetization is killed by any *arbitrarily small* T. To appreciate the reason for that, a clear manifestation of a battle between energy and entropy won by the latter, observe the excitations visible in Fig. 5.2 at $E = -10J$ (for $h^{\perp} = 0$) and at regular intervals of $+4J$ above that: they are excitations created by the so-called *domain walls* between the two broken-symmetry states. In one dimension, domain walls live in individual links and cost an energy $2J$ each, as a ferromagnetic bond with energy $-J$ is transformed into an anti-ferromagnetic bond with energy $+J$. For instance, the lowest excitations in a PBC system are obtained by creating *two domain walls*:

$$|\uparrow \cdots \uparrow\downarrow\downarrow \cdots \downarrow\uparrow \cdots \uparrow\rangle \ .$$

and cost extra energy $+4J$. But the two domain walls can stay anywhere along the chain: there are $\binom{N}{2}$ similar configurations, thus contributing a lot to the entropy of the system. If you have $2K$ domain walls, their energy cost is $4KJ$, hence linear in K, but the number of configurations $\binom{N}{2K}$ explodes exponentially. [5] All in all, a simple calculation shows that the free energy is lowered by creating a certain density of domain walls, as soon as $T > 0$. Correspondingly, the spontaneous magnetization at $T > 0$ vanishes.

The battle between energy and entropy, however, is not always won by entropy. In two dimensions, for instance, a domain wall is a closed curve surrounding an island of reversed spins into a larger region of opposite spin. If you call P the *perimeter* of the curve, the energy cost of the wall is $2JP$, hence it increases *linearly* with P. A very nice argument put forward by Rudolph Peierls, which you can read in Arovas (Sec. 6.2.5 and 7.8.2), shows that there is a region of temperatures $T > 0$ where the magnetization persists.

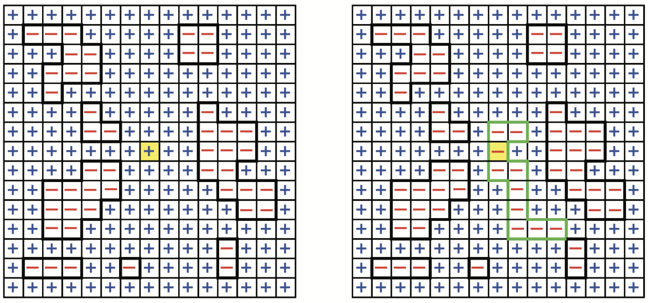

Figure 5.6: The Peierls' argument to show that the two-dimensional Ising model has a robust broken-symmetry phase surviving at finite $T < T_c$. The figure, taken from Arovas, poses the problem of how to estimate the difference in probability for the central spin being $\uparrow = +$ with respect to being $\downarrow = -$, in a large system with boundary conditions set to $+$, a device alternative to the small longitudinal field trick to test for broken symmetry.

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[5] Obviously, the number of configurations starts to decline when $2K > N/2$. When $2K = N$, there is a domain wall on each link and the configuration is unique (apart from an overall flip): the antiferromagnetic arrangement $|\uparrow\downarrow\uparrow\downarrow \cdots \uparrow\downarrow\uparrow\downarrow\rangle$.

5.3. Local order parameter and its correlation function

Consider the (classical) Ising model with longitudinal fields only:

$$\widehat{H} = -\sum_{\langle \mathbf{R},\mathbf{R}'\rangle} J_{\mathbf{R}\mathbf{R}'} \hat{\sigma}^z_{\mathbf{R}} \hat{\sigma}^z_{\mathbf{R}'} - \sum_{\mathbf{R}} h_{\mathbf{R}} \hat{\sigma}^z_{\mathbf{R}} \; . \tag{5.25}$$

Let us start from the exact expressions for the derivatives of the (classical) partition function: [6]

$$\begin{aligned} \frac{\partial Z}{\partial h_{\mathbf{R}}} &= \beta \,\mathrm{Tr}[\hat{\sigma}^z_{\mathbf{R}} \mathrm{e}^{-\beta \widehat{H}}] = \beta Z \langle \hat{\sigma}^z_{\mathbf{R}} \rangle \\ \frac{\partial^2 Z}{\partial h_{\mathbf{R}} \partial h_{\mathbf{R}'}} &= \beta^2 \,\mathrm{Tr}[\hat{\sigma}^z_{\mathbf{R}} \hat{\sigma}^z_{\mathbf{R}'} \mathrm{e}^{-\beta \widehat{H}}] = \beta^2 Z \langle \hat{\sigma}^z_{\mathbf{R}} \hat{\sigma}^z_{\mathbf{R}'} \rangle \end{aligned} \; . \tag{5.26}$$

Correlation functions. You see that

$$\langle \hat{\sigma}^z_{\mathbf{R}} \rangle = k_B T \frac{1}{Z} \frac{\partial Z}{\partial h_{\mathbf{R}}} = -\frac{\partial F}{\partial h_{\mathbf{R}}} \qquad\qquad \langle \hat{\sigma}^z_{\mathbf{R}} \hat{\sigma}^z_{\mathbf{R}'} \rangle = (k_B T)^2 \frac{1}{Z} \frac{\partial^2 Z}{\partial h_{\mathbf{R}} \partial h_{\mathbf{R}'}} \; . \tag{5.27}$$

Higher-order derivatives of the partition function Z with respect to the local fields — known as "sources" — generate the correlation functions of the model. Interestingly, you might use such a device to generate the correlation function of a model *in absence of external fields*, by setting $\{h_{\mathbf{R}} = 0\}$ *after* the derivatives have been taken.

We already discussed that, in the thermodynamic limit, the $\mathbb{Z}_2$ symmetry of the model for $\{h_{\mathbf{R}} = 0\}$ — whose averages we denote as $\langle \cdots \rangle_0$ — might be *spontaneously broken* at sufficiently low temperatures in a ferromagnetic Ising model — we assume here uniform "nearest-neighbor" couplings $J_{\mathbf{R}\mathbf{R}'} \equiv J$ —, making

$$\langle \hat{\sigma}^z_{\mathbf{R}} \rangle_0 = \lim_{h\to 0} \lim_{N\to\infty} \langle \hat{\sigma}^z_{\mathbf{R}} \rangle \neq 0 \; . \tag{5.28}$$

Such a non-vanishing $\langle \hat{\sigma}^z_{\mathbf{R}} \rangle_0$ is known as *local order parameter*. When the symmetry is spontaneously broken, the large-distance limit of the correlation function of the order-parameter tends exponentially fast to the *square* of the local order parameter:

$$\langle \hat{\sigma}^z_{\mathbf{R}} \hat{\sigma}^z_{\mathbf{R}'} \rangle_0 \overset{|\mathbf{R}-\mathbf{R}'|\to\infty}{\longrightarrow} \langle \hat{\sigma}^z_{\mathbf{R}} \rangle_0 \langle \hat{\sigma}^z_{\mathbf{R}'} \rangle_0 + O(\mathrm{e}^{-|\mathbf{R}-\mathbf{R}'|/\xi(T)}) \; , \tag{5.29}$$

where $\xi(T)$ is a temperature-dependent *correlation length.* This is true both in the broken symmetry phase, where $\langle \hat{\sigma}^z_{\mathbf{R}} \rangle_0 \neq 0$, as well as in the high-temperature symmetric phase where $\langle \hat{\sigma}^z_{\mathbf{R}} \rangle_0 = 0$. This suggests that we might define the *connected correlation functions* as

$$C^{\mathrm{conn}}_{\mathbf{R},\mathbf{R}'} = \langle \hat{\sigma}^z_{\mathbf{R}} \hat{\sigma}^z_{\mathbf{R}'} \rangle_0 - \langle \hat{\sigma}^z_{\mathbf{R}} \rangle_0 \langle \hat{\sigma}^z_{\mathbf{R}'} \rangle_0 \; , \tag{5.30}$$

which decay exponentially fast to zero both in the low-temperature and in the high-temperature phase. We will see that a power-law behaviour emerges at T_c, where $\xi(T_c) = \infty$ (in the thermodynamic limit).

You can show that the connected correlation functions are directly obtained by taking derivatives with respect to external *source fields* $h_{\mathbf{R}}$ of the *logarithm* of the partition function, or, equivalently, the *free energy.* For instance:

$$\begin{aligned} \frac{\partial}{\partial h_{\mathbf{R}'}} \frac{\partial \log Z}{\partial h_{\mathbf{R}}} = \frac{\partial}{\partial h_{\mathbf{R}'}} \frac{1}{Z} \frac{\partial Z}{\partial h_{\mathbf{R}}} &= \Big(\frac{\partial}{\partial h_{\mathbf{R}'}} \frac{1}{Z} \Big) \frac{\partial Z}{\partial h_{\mathbf{R}}} + \frac{1}{Z} \frac{\partial}{\partial h_{\mathbf{R}'}} \frac{\partial Z}{\partial h_{\mathbf{R}}} \\ &= -\frac{1}{Z^2} \frac{\partial Z}{\partial h_{\mathbf{R}'}} \frac{\partial Z}{\partial h_{\mathbf{R}}} + \frac{1}{Z} \frac{\partial^2 Z}{\partial h_{\mathbf{R}'} \partial h_{\mathbf{R}}} \\ &= -\beta^2 \langle \hat{\sigma}^z_{\mathbf{R}'} \rangle \langle \hat{\sigma}^z_{\mathbf{R}} \rangle + \beta^2 \langle \hat{\sigma}^z_{\mathbf{R}} \hat{\sigma}^z_{\mathbf{R}'} \rangle = \beta^2 C^{\mathrm{conn}}_{\mathbf{R},\mathbf{R}'} \; . \end{aligned} \tag{5.31}$$

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[6] Notice that in presence of a non-commuting transverse field, I should be more careful with my derivation, as the different terms do not commute.

Connected correlation functions. Since $\log Z = -\beta F$, we conclude the second derivative of the free-energy with respect to the source field provides directly the *connected* correlations:

$$C^{\mathrm{conn}}_{\mathbf{R},\mathbf{R}'} = -k_B T \frac{\partial^2 F}{\partial h_{\mathbf{R}'} \partial h_{\mathbf{R}}} \,. \tag{5.32}$$

Higher-order derivatives of F provide, similarly, connected correlations with more "fields" $\hat{\sigma}^z_{\mathbf{R}}$ appearing. Moreover, since $m_{\mathbf{R}} := \langle \hat{\sigma}^z_{\mathbf{R}} \rangle = -\frac{\partial F}{\partial h_{\mathbf{R}}}$, we can also write:

$$\chi_{\mathbf{R},\mathbf{R}'} \overset{\mathrm{def}}{=} \frac{\partial m_{\mathbf{R}}}{\partial h_{\mathbf{R}'}} = -\frac{\partial^2 F}{\partial h_{\mathbf{R}'} \partial h_{\mathbf{R}}} = \frac{1}{k_B T} C^{\mathrm{conn}}_{\mathbf{R},\mathbf{R}'} \,. \tag{5.33}$$

The derivatives of the free-energy with respect to a source external field $\frac{\partial F}{\partial h_{\mathbf{R}}}$, $\frac{\partial^2 F}{\partial h_{\mathbf{R}} \partial h_{\mathbf{R}'}}$, etc., are called *response functions*. The fact that two-point response functions and connected correlations are related in this way

$$C^{\mathrm{conn}}_{\mathbf{R},\mathbf{R}'} = k_B T \chi_{\mathbf{R},\mathbf{R}'} \,, \tag{5.34}$$

is strictly valid in *equilibrium*, and is an instance of a *fluctuation-dissipation relationship*. In particular, the relationship is not guaranteed to hold once you do *approximations*, such as mean-field. We will later see that connected correlations $C^{\mathrm{conn}}_{\mathbf{R},\mathbf{R}'}$, when calculated directly in the simplest mean-field approximation (Weiss mean-field) *vanish*, while a non-vanishing response function can be calculated within mean-field.

5.4. Critical exponents

I exemplify here the various critical exponents that are typically encountered at a second-order phase transition with a local order-parameter broken-symmetry low-temperature phase. For simplicity, I consider here a translationally invariant classical ferromagnetic Ising model in a uniform longitudinal field:

$$\widehat{H}_h = -J \sum_{\langle \mathbf{R},\mathbf{R}' \rangle} \hat{\sigma}^z_{\mathbf{R}} \hat{\sigma}^z_{\mathbf{R}'} - h \sum_{\mathbf{R}} \hat{\sigma}^z_{\mathbf{R}} \,. \tag{5.35}$$

The model is $\mathbb{Z}_2$ symmetric for $h = 0$: recall that you can send $\hat{\sigma}^z_{\mathbf{R}} \to -\hat{\sigma}^z_{\mathbf{R}}$ ($\forall \mathbf{R}$) by a uniform spin rotation by an angle π about the x-spin axis. The model is translationally invariant provided periodic boundary conditions (PBC) are chosen. Recall also that [7]

$$m(h=0,T) = \langle \hat{\sigma}^z_{\mathbf{R}} \rangle_0 = -\frac{1}{N} \frac{\partial F}{\partial h}\bigg|_{h=0} \tag{5.36}$$

is the order parameter, independent of $\mathbf{R}$. The first critical index tells us how m vanishes when $T \to T_c^-$, the critical temperature:

$$m(h=0,T) \sim \begin{cases} (T_c - T)^\beta & T \le T_c \\ 0 & T > T_c \end{cases} \,. \tag{5.37}$$

This order-parameter critical index is traditionally denoted as β, not to be confused with $1/k_B T$.

The connected spin-spin correlation function $C^{\mathrm{conn}}_{\mathbf{R},\mathbf{R}'}$ depends, due to translational invariance, only on the difference $\mathbf{x} = \mathbf{R}' - \mathbf{R}$. Furthermore, M. Fisher postulated that we could write for it a scaling

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[7] Indeed, observe that

$$-\frac{\partial F}{\partial h}\bigg|_{h=0} = \sum_{\mathbf{R}} \langle \hat{\sigma}^z_{\mathbf{R}} \rangle_0 = N m \,,$$

due to translational invariance.

Ansatz of the form:

$$C^{\rm conn}_{\mathbf{R},\mathbf{R}+\mathbf{x}} := C^{\rm conn}_{\mathbf{x}} = \langle \hat{\sigma}^z_{\mathbf{x}} \hat{\sigma}^z_{\mathbf{0}} \rangle_0 - m^2 \sim \frac{\mathrm{e}^{-|\mathbf{x}|/\xi(T)}}{|\mathbf{x}/a|^{d-2+\eta}} \tag{5.38}$$

where the last expression is valid for $|\mathbf{x}| \gg a$, the lattice spacing. Here d is the dimensionality of the lattice, $\xi(T)$ is the *correlation length*, and η the *anomalous exponent* for correlations. [8] The correlation length $\xi(T)$ is finite for $T \neq T_c$ — hence connected correlations decay exponentially fast for $T \neq T_c$ — but *diverges* at T_c with a critical exponent ν

$$\xi(T) \sim \frac{1}{|T-T_c|^{\nu}} \; . \tag{5.39}$$

Consequently, the connected correlations show a *power-law* behaviour at T_c:

$$C^{\rm conn}_{\mathbf{x}}\Big|_{T_c} \sim \frac{1}{|\mathbf{x}/a|^{d-2+\eta}} \; . \tag{5.40}$$

Let us now consider the two-point response function, also known as *susceptibility*, often denoted as χ. It tells us how m changes when a small h is turned on, in the present case *uniformly*, since $h_{\mathbf{R}'} = h$. The fluctuation-dissipation relation tells us that

$$\chi = \frac{\partial m}{\partial h}\bigg|_{h=0} = \sum_{\mathbf{R}'} \frac{\partial m_{\mathbf{R}}}{\partial h_{\mathbf{R}'}}\bigg|_{h=0} = \frac{1}{k_B T} \sum_{\mathbf{x}} C^{\rm conn}_{\mathbf{x}} \; . \tag{5.41}$$

We could rewrite χ in terms of a lattice Fourier transform. Quite generally, for any $f_{\mathbf{R}}$ defined on a (Bravais) lattice we introduce:

$$\left\{ \begin{array}{rcl} \hat{f}(\mathbf{q}) & \equiv & \displaystyle\sum_{\mathbf{R}} f_{\mathbf{R}}\, \mathrm{e}^{-i\mathbf{q}\cdot\mathbf{R}} \\ f_{\mathbf{R}} & \equiv & \displaystyle\frac{1}{N} \sum_{\mathbf{q}}^{\rm BZ} \hat{f}(\mathbf{q})\, \mathrm{e}^{i\mathbf{q}\cdot\mathbf{R}} \xrightarrow{N\to\infty} \Omega_c \int_{\rm BZ} \frac{\mathrm{d}\mathbf{q}}{(2\pi)^d}\, \hat{f}(\mathbf{q})\, \mathrm{e}^{i\mathbf{q}\cdot\mathbf{R}} \end{array} \right. , \tag{5.42}$$

where Ω_c denotes the volume of the direct-lattice (Wigner-Seitz) unit cell — here $\Omega_c = a^d$ for a hypercubic lattice of spacing a in d dimensions —, and we have taken the limit $N \to \infty$ in the last expression. [9] Hence, if $C^{\rm conn}(\mathbf{q})$ denotes the Fourier transform of $C^{\rm conn}_{\mathbf{x}}$, we immediately conclude that

$$\chi = \frac{\partial m}{\partial h}\bigg|_{h=0} = \frac{1}{k_B T} \sum_{\mathbf{x}} C^{\rm conn}_{\mathbf{x}} = \frac{1}{k_B T} C^{\rm conn}(\mathbf{q}=\mathbf{0}) \; . \tag{5.44}$$

To understand how χ diverges as $T \to T_c$ and in the thermodynamic limit, we directly transform the sum over $\mathbf{x}$ into an integral

$$\sum_{\mathbf{x}} C^{\rm conn}_{\mathbf{x}} \sim \int \frac{\mathrm{d}\mathbf{x}}{a^d} \frac{\mathrm{e}^{-|\mathbf{x}|/\xi(T)}}{|\mathbf{x}/a|^{d-2+\eta}} \sim (\xi/a)^{2-\eta} \int \mathrm{d}\mathbf{y}\, \frac{\mathrm{e}^{-|\mathbf{y}|}}{|\mathbf{y}|^{d-2+\eta}} \propto (\xi/a)^{2-\eta} \; ,$$

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[8] We will argue later on, when discussing mean-field, about the reason for such a power-law prefactor and the anomalous exponent.

[9] Very often, in condensed matter, one adopts a slightly different (and more symmetric) convention for the lattice Fourier (Bloch-Wannier) transform:

$$\left\{ \begin{array}{rcl} \hat{f}_{\mathbf{q}} & \equiv & \displaystyle\frac{1}{\sqrt{N}} \sum_{\mathbf{R}} f_{\mathbf{R}}\, \mathrm{e}^{-i\mathbf{q}\cdot\mathbf{R}} \\ f_{\mathbf{R}} & \equiv & \displaystyle\frac{1}{\sqrt{N}} \sum_{\mathbf{q}}^{\rm BZ} \hat{f}_{\mathbf{q}}\, \mathrm{e}^{i\mathbf{q}\cdot\mathbf{R}} \end{array} \right. , \tag{5.43}$$

which is optimal if you want to remain within a discrete and finite-N framework. If you want to go towards the continuum limit, and take also $N \to \infty$, then the equivalent definition in Eq. (5.42), which essentially implies a rescaling $\hat{f}(\mathbf{q}) \equiv \sqrt{N} \hat{f}_{\mathbf{q}}$, leads to a simpler $N \to \infty$ limit, with the sum over momenta directly transformed into an integral on the Brillouin Zone.

where only the *large-$\mathbf{x}$* behaviour matters — for small $\mathbf{x}$ the connected correlations are perfectly regular — and we rescaled variables to $\mathbf{y} = \mathbf{x}/\xi$. Hence, if $\xi \sim |T - T_c|^{-\nu}$ diverges at T_c with exponent ν, we would predict that χ also diverges at T_c:

$$\chi \sim \xi^{2-\eta} \sim |T - T_c|^{-\nu(2-\eta)} \sim |T - T_c|^{-\gamma} \qquad \text{with} \qquad \gamma = \nu(2-\eta)\ . \tag{5.45}$$

This relationship, derived by Fisher, is known as *hyperscaling.* The scaling form of the connected correlations in Eq. (5.38) implies, in terms of Fourier transforms, that one would write

$$C^{\text{conn}}(\mathbf{q}) \sim \frac{g(|\mathbf{q}|\xi)}{|\mathbf{q}|^{2-\eta}}\ , \tag{5.46}$$

where the function $g(z \to \infty) = \text{const}$, while $g(z \to 0)$ takes care of a finite value of $C^{\text{conn}}(\mathbf{q} \to 0)$ when ξ is finite.

To conclude, let me mention two further critical exponents. One tells us how the order parameter grows if we turn on a small longitudinal field h *at* T_c:

$$m(h, T_c) \sim |h|^{1/\delta}\ . \tag{5.47}$$

The second tells us about the singularities of the specific heat:

$$c_v(T) = -T\frac{\partial^2 f}{\partial T^2} \sim |T - T_c|^{-\alpha}\ . \tag{5.48}$$

We will further discuss critical exponents when doing mean-field.

The exact $d = 2$ Ising critical exponents. Let me collect here, for reference, the exact results for the critical exponents of the $d = 2$-dimensional Ising model, compared to the mean-field exponents we will later derive.

Critical index	Relation	Exact $d = 2$-Ising	Mean field
β	$m\big\vert_{h=0} \sim (T_c - T)^{\beta}$	$\beta = \frac{1}{8}$	$\beta = \frac{1}{2}$
η	$C_{\mathbf{x}}\big\vert_{T_c} \sim \dfrac{1}{\vert\mathbf{x}\vert^{d-2+\eta}}$	$\eta = \frac{1}{4}$	$\eta = 0$
ν	$\xi \sim \dfrac{1}{\vert T - T_c\vert^{\nu}}$	$\nu = 1$	$\nu = \frac{1}{2}$
γ	$\chi \sim \dfrac{1}{\vert T - T_c\vert^{\gamma}}$	$\gamma = \frac{7}{4}$	$\gamma = 1$
δ	$m\big\vert_{T_c} \sim \vert h\vert^{1/\delta}$	$\delta = 15$	$\delta = 3$
α	$C_v \sim \dfrac{1}{\vert T - T_c\vert^{\alpha}}$	$\alpha = 0$ (log)	$\alpha = 0$ (jump)

(5.49)

5.5. Universality and the role of symmetry

The two main ingredients that determine most of the features of a model close to a phase transition point — in particular, its critical exponents — are:

1) The spatial dimensionality of the lattice;

2) The symmetry — spatial, orientational, and internal — of the variables involved, although the mere *anisotropy* of the lattice is usually *not* important.

We already saw the role of the dimensionality in the Ising model case: in one-dimension broken-symmetry is only in the ground state and dies for any $T > 0$, while in two dimensions a finite magnetization persists for $0 < T \leq T_c$.

The fact that symmetry-breaking survives at finite T in two dimensions is deeply related to the *discrete* nature of the $\mathbb{Z}_2$-symmetry of the Ising model in zero longitudinal field: for *continuous* symmetries, things change remarkably.

To illustrate this, we consider an isotropic Heisenberg ferromagnet

$$\widehat{H} = -J \sum_{\langle \mathbf{R},\mathbf{R}' \rangle} \widehat{\mathbf{S}}_{\mathbf{R}} \cdot \widehat{\mathbf{S}}_{\mathbf{R}'} - h \sum_{\mathbf{R}} \widehat{\mathrm{S}}^z_{\mathbf{R}} \;, \tag{5.50}$$

where we have written the coupling to be translational invariant and to nearest-neighbor, for simplicity, and with a minus sign in front, so that positive J now means a tendency to *ferromagnetism*. The lattice is the usual hyper-cubic lattice for simplicity, with N sites and PBC. We have also added a longitudinal field along the z-direction to play the trick of testing for a ferromagnetic state by sending $h \to 0$ *after* the thermodynamic limit $N \to \infty$. In *absence of* h the system has a full SU(2) symmetry.

Once again, you could construct a symmetry-based "proof" — very similar to the one we gave for the Ising case —, to show that $\langle \widehat{\mathrm{S}}^z_{\mathbf{R}} \rangle_0 = 0$ for $h = 0$: you just observe that $\mathrm{e}^{-i\pi \widehat{\mathrm{S}}^x_{\mathrm{tot}}}$ changes sign to $\widehat{\mathrm{S}}^z_{\mathbf{R}}$ while commuting with the Hamiltonian and the Gibbs state.

Yet, we know that the ground state has *maximum total spin* $S = N/2$, and symmetry (for $h = 0$) requires a $2S + 1 = N + 1$ degenerate multiplet of states $|S, M\rangle$ with $M = -S, -S+1, \cdots S$:

$$|S, M\rangle = \begin{cases} |S, S\rangle = |\uparrow\uparrow\uparrow \cdots \uparrow\rangle \\[1ex] |S, S-1\rangle = \widehat{\mathrm{S}}^-_{\mathrm{tot}} |S, S\rangle = \frac{1}{\sqrt{N}} \Big(|\downarrow\uparrow\uparrow \cdots \uparrow\rangle + |\uparrow\downarrow\uparrow \cdots \uparrow\rangle + \cdots + |\uparrow\uparrow\uparrow \cdots \downarrow\rangle \Big) \\[1ex] \qquad\vdots \\ |S, -S\rangle = |\downarrow\downarrow\downarrow \cdots \downarrow\rangle \end{cases} \tag{5.51}$$

It is once again simple to argue that this ferromagnetic ground state breaks SU(2) symmetry: a small (infinitesimal) $h > 0$ favours the $|S, S\rangle$ state over all the other states in the multiplet.

The question, now, is if symmetry-breaking survives at finite-T or not. Let us concentrate in particular on the state $|S, S-1\rangle$ with a *single* $\downarrow$. It is a uniform superposition of spin flips at any possible sites of the lattice, like a $\mathbf{q} = 0$ state in tight-binding. This suggests that we might invoke the Fourier transform $\widehat{\mathrm{S}}^-(\mathbf{q})$

$$\widehat{\mathrm{S}}^-(\mathbf{q}) \equiv \sum_{\mathbf{R}} \mathrm{e}^{-i\mathbf{q}\cdot\mathbf{R}} \, \widehat{\mathrm{S}}^-_{\mathbf{R}} \;, \tag{5.52}$$

and consider the N states, all with magnetization $M = S - 1$, for all $\mathbf{q} \in$ BZ:

$$|\psi_{\mathbf{q}}\rangle = \frac{1}{\sqrt{N}} \widehat{\mathrm{S}}^-(\mathbf{q}) |S, S\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} \mathrm{e}^{-i\mathbf{q}\cdot\mathbf{R}} \, \widehat{\mathrm{S}}^-_{\mathbf{R}} |S, S\rangle \;, \tag{5.53}$$

with $|\psi_{\mathbf{q}=0}\rangle = |S, S-1\rangle$. Since the N states with a single spin-flip span the subspace with $M = S - 1$, and symmetry tells us that I can diagonalise the Hamiltonian in such a subspace, we consider the matrix representing $\widehat{H}$ in such a subspace. We quickly discover that the matrix is precisely of the tight-binding form with hopping matrix elements $-J/2$ in each direction $\pm \mathbf{e}_\alpha$ of the cubic lattice $(\alpha = 1, \cdots, d)$ and on-site energy Jd due to the cost a single spin flip with $2d$ neighbors. [10] The

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[10] Notice that the Hamiltonian term on each link can be written as $-J\widehat{\mathrm{S}}^z_{\mathbf{R}} \widehat{\mathrm{S}}^z_{\mathbf{R}'} - \frac{J}{2}(\widehat{\mathrm{S}}^+_{\mathbf{R}} \widehat{\mathrm{S}}^-_{\mathbf{R}'} + \widehat{\mathrm{S}}^-_{\mathbf{R}} \widehat{\mathrm{S}}^+_{\mathbf{R}'})$. The first term is diagonal, and gives energy $+J/4$, compared to $-J/4$ in absence of flip, hence a cost $+J/2$. The second term is a hopping term for the spin-flip, with matrix element $-J/2$.

energy of such states — including now the longitudinal field penalty term — is

$$E_{\mathbf{q}} - E_{\mathrm{gs}} = h + Jd - J\sum_{\alpha=1}^{d} \cos \mathbf{q}\cdot\mathbf{e}_{\alpha} = h + \frac{J}{2}a^2q^2 + \cdots \tag{5.54}$$

where the final expression follows from expanding the cosine term for small $\mathbf{q}$. For $\mathbf{q} = 0$ and $h = 0$ we recover the fact that $|\psi_{\mathbf{q}=0}\rangle = |S, S-1\rangle$ is degenerate with $|S, S\rangle$.

> **Goldstone modes.** The interesting fact that we learn from this tight-binding calculation is that these "defects" are low-energy modes for $\mathbf{q} \neq 0$: they are the *Goldstone modes* associated to the breaking of continuous symmetry, in the present case SU(2), with an energy cost that scales as q^2 for $\mathbf{q} \to 0$. The external field $h > 0$ breaks the symmetry and makes the Goldstone modes *gapped* for $\mathbf{q} \to 0$. This crucial ingredient kills symmetry-breaking at finite T in one and two-dimensions, as proved by Mermin and Wagner.

5.5.1. Mermin-Wagner theorem

In 1966 Mermin and Wagner [31] wrote a Physical Review Letter entitled "*Absence of ferromagnetism or antiferromagnetism in one- or two-dimensional isotropic Heisenberg models*, a title that might serve as an abstract: a continuous symmetry (spin isotropy) impedes order at finite temperature in one and *two* dimensions. To state what they proved, consider a Heisenberg model

$$\widehat{H} = -\sum_{\langle \mathbf{R},\mathbf{R}'\rangle} J_{\mathbf{R}-\mathbf{R}'} \widehat{\mathbf{S}}_{\mathbf{R}} \cdot \widehat{\mathbf{S}}_{\mathbf{R}'} - h\sum_{\mathbf{R}} \widehat{\mathrm{S}}^z_{\mathbf{R}} \,, \tag{5.55}$$

where we have written the coupling in translational invariant way, and with a minus sign in front, so that positive J now mean a tendency to *ferromagnetism*. The lattice is, say, the usual hypercubic lattice for simplicity, with N sites and PBC. We have also added a longitudinal field along the z-direction to play the trick of testing for a ferromagnetic state by sending $h \to 0$ *after* the thermodynamic limit $N \to \infty$. Notice that:

1) The spin S is not necessarily $S = 1/2$: any spin could be considered.

2) The coupling $J_{\mathbf{R}}$ is not necessarily restricted to nearest-neighbour: it is enough that $J_{\mathbf{R}}$ has a finite range, or more precisely that

$$C = \frac{S(S+1)}{a^2}\sum_{\mathbf{R}} \mathbf{R}^2 |J_{\mathbf{R}}| < \infty \,.$$

Next, define the candidate ferromagnetic order parameter

$$m = \frac{1}{N}\langle \sum_{\mathbf{R}} \widehat{\mathrm{S}}^z_{\mathbf{R}} \rangle \,, \tag{5.56}$$

where the average is done in presence of the external field h.

> **Bogoliubov inequality.** There is a very useful inequality first derived by Bogoliubov:
>
> $$\frac{1}{2}\langle\{\hat{A}, \hat{A}^\dagger\}\rangle\langle[[\hat{B}, \widehat{H}], \hat{B}^\dagger]\rangle \geq k_B T \big|\langle[\hat{B}, \hat{A}]\rangle\big|^2 \,. \tag{5.57}$$
>
> A simple proof of it is given in Ref. [31].

By using this Bogoliubov inequality, applied to $\hat{A} = \widehat{\mathrm{S}}^{-}_{\mathrm{tot}}(-\mathbf{q})$ and $\hat{B} = \widehat{\mathrm{S}}^{+}_{\mathrm{tot}}(\mathbf{q})$, Mermin & Wagner were able to derive the following inequality [11] for the candidate order parameter m [31][Eq. 12]:

$$m^2 < \frac{S(S+1)}{2k_B T a^d \displaystyle\int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}}{(2\pi)^d} \frac{1}{C(qa)^2 + |hm|}} \xrightarrow{d\leq 2, h\to 0} 0 \,, \tag{5.58}$$

where the final step applies to $d \leq 2$ where the integral on the denominator of the RHS *diverges* (logarithmically in $d = 2$) for $h \to 0$. A look at the integral shows the role of the Goldstone modes appearing in the denominator, which provoke the divergence of the integral in $d \leq 2$ when $h \to 0$.

5.6. Classical or quantum?

Part of the discussions we had so far — for instance, that referring to critical exponents — was referring to classical models. Other considerations — like the Mermin-Wagner theorem we just presented — seem to rely on quantum mechanics. [12]

The natural question is *if and when* quantum effects are crucial in the discussion. To illustrate the concept, consider the translationally invariant two-dimensional Ising model in a transverse field:

$$\widehat{H}_{\mathrm{TFIM}} = -J \sum_{\langle \mathbf{R},\mathbf{R}' \rangle} \hat{\sigma}^z_{\mathbf{R}} \hat{\sigma}^z_{\mathbf{R}'} \; - \; h^{\perp} \sum_{\mathbf{R}} \hat{\sigma}^x_{\mathbf{R}} \,, \tag{5.59}$$

The phase diagram of this model has been studied with different techniques. Fig. 5.7 shows the phase diagram obtained by RG in Ref. [32]. There is a line $T_c(h^{\perp})$ separating the broken-symmetry phase from the disordered state. For $h^{\perp} = 0$ the transition temperature T_c is that of the two-dimensional *classical* Ising model solved exactly by Onsager: $k_B T_c/J = 2/\sinh^{-1}(1) \approx 2.27$. At zero temperature, $T = 0$, there is a *quantum phase transtion* at $h^{\perp}_c/J \approx 3.09$ separating the ordered ferromagnetic broken-symmetry ground state from a disordered ground state for large $h^{\perp}$. [13]

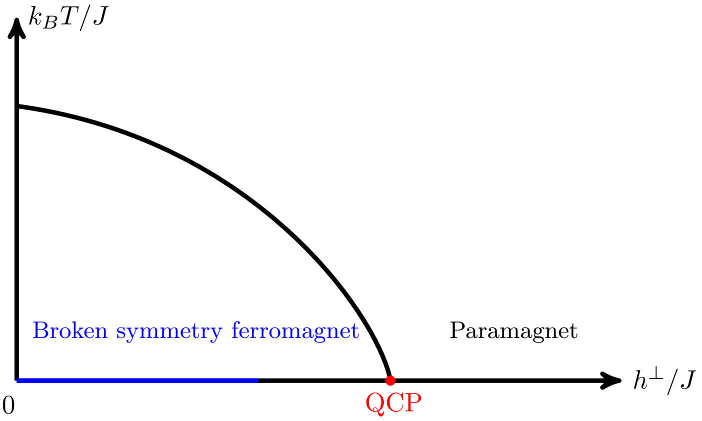

Figure 5.7: Sketch of the phase diagram of the transverse-field Ising model in two-dimensions. At $T = 0$, the quantum critical point (QCP) is close to $h^{\perp}_c/J \approx 3.09$, while for $h^{\perp} = 0$, Onsager's solution gives $k_B T_c/J = 2/\sinh^{-1}(1) \approx 2.27$. For numerical details, see Ref. [32].

You might ask yourself what are the critical exponents of the model all along the transition line $T_c(h^{\perp})$. The perhaps surprising result is that the classical two-dimensional critical exponents apply

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[11] Mermin and Wagner also show the absence of *antiferromagnetism* in the same setting. The only difference is the definition of the candidate order parameter m, the staggered magnetization, and the fact that the probing field is also staggered.

[12] Although, as pointed out by Mermin & Wagner, the proof holds for *any* spin S, and in principle, for very large S we should tend to the classical limit, where quantum fluctuations of the spin are unimportant.

[13] For very large $h^{\perp}$ the transverse field dominates, and all spin are aligned in the $+x$ direction in spin space: the ground state becomes, for $h^{\perp} \to \infty$

$$|+\rangle = \prod_{\mathbf{R}} \frac{1}{\sqrt{2}} \Big(|\uparrow_{\mathbf{R}}\rangle + |\downarrow_{\mathbf{R}}\rangle \Big) \,,$$

separated by a gap $2h^{\perp}$ from the first excited state with a spin along $-x$.

perfectly well even in presence of a transverse field $h^{\perp}$ as long as $T_c > 0$: thermal fluctuations dominate the critical region, and quantum effects are not important. The exception to this statement is the *quantum critical point*, where the critical exponents change: they become those of the *three-dimensional* classical Ising model. We will learn more about the correspondence between quantum models in d-dimensions and classical models in $d+1$ in the next chapter, when we will discuss transfer matrices and path-integral.

5.6.1. A zoo of models

Let me end this final section with a brief survey of other models that are often discussed in the literature.

Potts models. Switching to the classical world, you can think of $\sigma_{\mathbf{R}}$ being a q-valued discrete variable, $\sigma_{\mathbf{R}} = \{1, 2, \cdots q\}$ with $q \geq 2$, and write a Hamiltonian of the form: [14]

$$H_{\text{Potts}} = -\sum_{\langle \mathbf{R},\mathbf{R}'\rangle} J_{\mathbf{R},\mathbf{R}'} \delta_{\sigma_{\mathbf{R}},\sigma_{\mathbf{R}'}} - \sum_{\mathbf{R}} h_{\mathbf{R}} \delta_{\sigma_{\mathbf{R}},1} \;, \qquad \text{with } \; \sigma_{\mathbf{R}} \in \{1, \cdots, q\} \;. \tag{5.60}$$

Classical spin models. For continuous variables, for instance a unit-length two-dimensional vector $\mathbf{S}_i = (\cos\phi_i, \sin\phi_i)$ forming an angle $\phi_i \in [0, 2\pi)$ with the x-direction on each site of an arbitrary lattice, you could write an XY-model:

$$H_{\text{XY}} = -\sum_{\langle \mathbf{R},\mathbf{R}'\rangle} J_{\mathbf{R},\mathbf{R}'} \cos\left(\phi_{\mathbf{R}} - \phi_{\mathbf{R}'}\right) - h \sum_{\mathbf{R}} h_{\mathbf{R}} \cos\phi_{\mathbf{R}} \;, \qquad \text{with } \; \phi_{\mathbf{R}} \in [0, 2\pi) \;. \tag{5.61}$$

Notice that $\mathbf{S}_{\mathbf{R}} \cdot \mathbf{S}_{\mathbf{R}'} = \cos\left(\phi_{\mathbf{R}} - \phi_{\mathbf{R}'}\right)$, hence the interaction term is invariant by $O(2)$ rotations, while the external field breaks this invariance. We will have more to say about this model in $d = 2$-dimension, where it shows a Kosterlitz-Thouless transition without a local order parameter: it is one of the first instances of a model with topological objects — vortices — playing a role. Still, with continuous spins, generalizations of the XY-model involve an n-dimensional unit vector $\mathbf{S}$, leading to the so-called $O(n)$-model:

$$H_{\text{O(n)}} = -\sum_{\langle \mathbf{R},\mathbf{R}'\rangle} J_{\mathbf{R},\mathbf{R}'} \mathbf{S}_{\mathbf{R}} \cdot \mathbf{S}_{\mathbf{R}'} \;. \tag{5.62}$$

Clock models. A discrete variant of this planar-spin-vector model is the so-called p-state *clock model*, where the angles $\phi_{\mathbf{R}}$ are constrained to the p discrete values $\phi_{\mathbf{R}} = 2\pi n_{\mathbf{R}}/p$ with $n_{\mathbf{R}} = 1 \cdots p$:

$$H_{\text{p-clock}} = -\sum_{\langle \mathbf{R},\mathbf{R}'\rangle} J_{\mathbf{R},\mathbf{R}'} \cos\left(\frac{2\pi}{p}(n_{\mathbf{R}} - n_{\mathbf{R}'})\right) \;, \qquad \text{with } \; n_{\mathbf{R}} \in \{1, \cdots, p\} \;. \tag{5.63}$$

---

[14] For $q = 2$, using the identity

$$\delta_{\sigma,\sigma'} = \frac{1}{2}(1 + \sigma\sigma') \;,$$

you can rewrite the 2-state Potts model as an Ising model. For $q > 2$ the analogy with a corresponding q-Ising-spin bilinear interaction $J_{ij}\sigma_i\sigma_j$ is lost. See Arovas 7.5.3.

6. Transfer matrix and Path-Integral

In this chapter, we will deal with Ising spin systems. We will see how in principle you can write a transfer matrix, in the classical case, to express the partition function. The transfer matrix, in turn, can be rewritten as a quantum problem for a system with one dimension less in *imaginary time*. An excellent reference for this subject is the review paper by Kogut [33][Sec. III-IV].

The transfer matrix itself is a practical technique to deal with many low-dimensional classical problems, the analogue of doing exact diagonalisation in correlated lattice problems, but to get the statistical mechanics properties, rather than the low-energy states. In the two-dimensional Ising case, Onsager's exact solution amounts to diagonalizing the exact transfer matrix of the problem to extract all the important ingredients, in zero external field. We will also see how to write a path-integral representation of a transverse-field quantum Ising problem.

6.1. Transfer matrix and classical-to-quantum mapping

One-dimensional classical Ising. To illustrate the idea of a transfer matrix in the simplest setting, we consider a one-dimensional ($d = 1$) classical Ising ferromagnet with periodic-boundary conditions:

$$H[\underline{\sigma}] = -J\sum_{j=1}^{N} \sigma_j\sigma_{j+1} - h\sum_{j=1}^{N}\sigma_j \;, \tag{6.1}$$

where $\sigma_j = \pm 1$ are the two eigenvalues of $\hat{\sigma}^z_j$, and we have written H as a classical Hamiltonian depending con the configuration $\underline{\sigma} = (\sigma_1, \cdots, \sigma_N)$ of all spins. The partition function Z associated is given by

$$Z(\beta) = \sum_{\underline{\sigma}}^{\text{Configs}} \mathrm{e}^{-\beta H[\underline{\sigma}]} = \sum_{j=1}^{N}\sum_{\sigma_j=\pm 1} \mathrm{e}^{-\beta H[\underline{\sigma}]} \;. \tag{6.2}$$

Observe that we can write:

$$\begin{aligned}
\mathrm{e}^{-\beta H[\underline{\sigma}]} = \mathrm{e}^{\sum_{j=1}^{N}\left(\beta J\sigma_j\sigma_{j+1}+\beta h\sigma_j\right)} &= \prod_{j=1}^{N} \mathrm{e}^{\beta J\sigma_j\sigma_{j+1}+\beta h\sigma_j} = \prod_{j=1}^{N} \overbrace{\mathrm{e}^{\beta J\sigma_j\sigma_{j+1}+\beta h(\sigma_j+\sigma_{j+1})/2}}^{\langle\sigma_{j+1}|\mathrm{T}|\sigma_j\rangle} \\
&= \langle\sigma_1|\mathrm{T}|\sigma_N\rangle\langle\sigma_N|\mathrm{T}|\sigma_{N-1}\rangle\cdots\langle\sigma_2|\mathrm{T}|\sigma_1\rangle
\end{aligned} \tag{6.3}$$

where we have identified a 2 × 2 matrix, the *transition matrix* [1]

$$\langle\sigma_{j+1}|\mathrm{T}|\sigma_j\rangle = \begin{pmatrix} \mathrm{e}^{\beta(J+h)} & \mathrm{e}^{-\beta J} \\ \mathrm{e}^{-\beta J} & \mathrm{e}^{\beta(J-h)} \end{pmatrix} \tag{6.4}$$

and rewritten the product by using the PBC condition $\sigma_{N+1} \equiv \sigma_1$. This immediately shows that the partition function is the *trace* of a product of N transition matrices:

$$Z = \sum_{\sigma_1,\cdots,\sigma_N} \langle\sigma_1|\mathrm{T}|\sigma_N\rangle\langle\sigma_N|\mathrm{T}|\sigma_{N-1}\rangle\cdots\langle\sigma_2|\mathrm{T}|\sigma_1\rangle = \mathrm{Tr}\,\mathrm{T}^N \;. \tag{6.5}$$

---

[1] Notice that we rewrite the longitudinal field term in a manner that is symmetric in $(j, j+1)$, so that the resulting transfer matrix is symmetric.

Z comes automatically if we calculate the two eigenvalues of $\langle\sigma_{j+1}|\mathrm{T}|\sigma_j\rangle$. The calculation is elementary, for instance by noticing that:

$$\mathrm{T} = \begin{pmatrix} \mathrm{e}^{\beta(J+h)} & \mathrm{e}^{-\beta J} \\ \mathrm{e}^{-\beta J} & \mathrm{e}^{\beta(J-h)} \end{pmatrix} = \mathrm{e}^{\beta J}\cosh(\beta h)\,\mathbb{1} + \mathrm{e}^{\beta J}\sinh(\beta h)\,\hat{\sigma}^z + \mathrm{e}^{-\beta J}\hat{\sigma}^x \;, \tag{6.6}$$

from which you deduce that the two eigenvalues of T are:

$$\lambda_\pm = \mathrm{e}^{\beta J}\cosh(\beta h) \pm \sqrt{\mathrm{e}^{2\beta J}\sinh^2(\beta h) + \mathrm{e}^{-2\beta J}} \;. \tag{6.7}$$

The partition function $Z = \mathrm{Tr}\,\mathrm{T}^N = \lambda_+^N + \lambda_-^N$ is exponentially dominated by the largest eigenvalue, hence the free-energy per spin is given by:

$$f(T,h) = \lim_{N\to\infty}\frac{F}{N} = -k_BT\log\lambda_+ = -k_BT\log\left(\mathrm{e}^{\beta J}\cosh(\beta h) + \sqrt{\mathrm{e}^{2\beta J}\sinh^2(\beta h) + \mathrm{e}^{-2\beta J}}\right) \;. \tag{6.8}$$

From the free-energy you can compute the spontaneous magnetization:

$$m(T,h) = -\frac{\partial f}{\partial h} = \frac{\sinh\beta h}{\sqrt{\sinh^2\beta h + \mathrm{e}^{-4\beta J}}} \;. \tag{6.9}$$

Symmetry-breaking at finite T is lost. Observe that $m = \mathrm{sign}(h)$ for $T = 0$ ($\beta\to\infty$). On the contrary, for any finite T, the limit for $h\to 0$ of the magnetization vanishes:

$$m(T>0) = \lim_{h\to 0} m(T,h) = \lim_{h\to 0}\frac{\sinh\beta h}{\sqrt{\sinh^2\beta h + \mathrm{e}^{-4\beta J}}} = 0 \;. \tag{6.10}$$

The zero-field (linear) susceptibility is also easy to calculate:

$$\chi(T) = \frac{\partial m}{\partial h}\Big|_{h=0} = \frac{1}{k_BT}\mathrm{e}^{2J/(k_BT)} \;. \tag{6.11}$$

Observe that a Curie behaviour $\chi = \frac{1}{k_BT}$ for free spins ($J = 0$) becomes an exponentially diverging χ for $J > 0$ (ferromagnetic coupling) and an exponentially suppressed χ for $J < 0$ (antiferromagnetic coupling).

Exercise 6.1. To calculate the spin-spin correlation function, show that you can write:

$$C_{1,n+1} = \langle\hat{\sigma}_1^z\hat{\sigma}_n^z\rangle = \frac{1}{Z}\,\mathrm{Tr}\left(\mathrm{T}^{N-n}\hat{\sigma}^z\mathrm{T}^n\hat{\sigma}^z\right) \;, \tag{6.12}$$

where $0 \le n \le N$ and the transfer matrix T is given by Eq. (6.6). Next, set $h = 0$, so that $\mathrm{T} = \mathrm{e}^{\beta J}\mathbb{1} + \mathrm{e}^{-\beta J}\hat{\sigma}^x$, write explicitly the spectral decomposition of T in terms of eigenvectors $|\pm\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$ of $\hat{\sigma}^x$:

$$\mathrm{T} = \lambda_+|+\rangle\langle+| + \lambda_-|-\rangle\langle-| \;, \tag{6.13}$$

and calculate the relevant trace in this basis. Show that you get:

$$C_{1,n+1} = \frac{\lambda_+^{N-n}\lambda_-^n + \lambda_+^n\lambda_-^{N-n}}{\lambda_+^N + \lambda_-^N} \overset{N\to\infty}{\longrightarrow} \Big(\tanh(\beta J)\Big)^n = \mathrm{e}^{-n\log\mathrm{cotanh}(\beta J)} \;. \tag{6.14}$$

Two-dimensional classical Ising. We now move to the $2d$ Ising model with nearest-neighbour interactions on a square lattice, leaving comments on the generalizations to the final discussion.

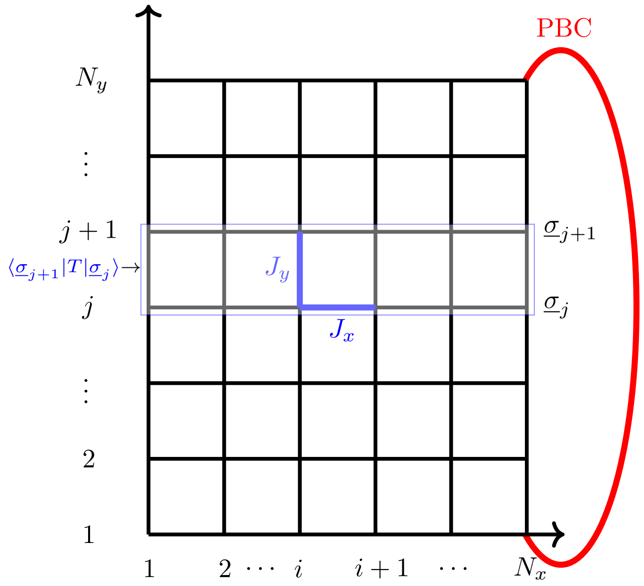

Figure 6.1: The 2-dimensional classical Ising model on a square lattice. The system has $N_x \times N_y$ sites, and PBC are enforced in the y-direction: you can think of the system as "living on a cylinder" with an axis along the x-direction. Boundary conditions along the x-direction are left unspecified: they could be *open*, *fixed*, or *periodic*. In the latter case, you might picture the system as "living on a torus". The blue lines highlight the couplings J_x, connecting sites (i,j) and $(i+1,j)$, and J_y, connecting (i,j) and $(i,j+1)$. The shaded rectangle highlights the Boltzmann weights included in the definition of the "transfer matrix" $\langle \underline{\sigma}_{j+1}|\mathrm{T}|\underline{\sigma}_j\rangle$.

Consider an Ising model with couplings J_y and J_x along the y- and x-directions of a two-dimensional square lattice. We assume the lattice to have N_x sites along x, and N_y sites along y, and we label the sites with a pair of integers (i,j), where $i = 1 \cdots N_x$ and $j = 1 \cdots N_y$. The number of sites is $N = N_x N_y$. We write the (classical) spin Hamiltonian and its canonical partition function as:

$$\begin{aligned} H[\underline{\sigma}] &= -\sum_{i,j}^{\text{Sites}} \Big(J_x \sigma_{i,j}\sigma_{i+1,j} + J_y \sigma_{i,j}\sigma_{i,j+1} \Big) - h\sum_{i,j} \sigma_{i,j} \\ Z(\beta) &= \sum_{\underline{\sigma}}^{\text{Configs}} \mathrm{e}^{-\beta H[\underline{\sigma}]} = \sum_{i,j}^{\text{Sites}} \sum_{\sigma_{i,j}=\pm 1} \mathrm{e}^{-\beta H[\underline{\sigma}]} \end{aligned} \tag{6.15}$$

We assume that the boundary conditions are periodic (PBC) in the y-direction, i.e., $\sigma_{i,N_y+1} \equiv \sigma_{i,1}$. No assumption is made on the x-direction boundary conditions, which can be open or periodic. A few notations are useful to simplify our writing. First, we denote by $\underline{\sigma}_j = (\sigma_{1,j}, \cdots, \sigma_{N_x,j})$ the *configuration of row* j of our lattice. Evidently, $\underline{\sigma}_j$ runs over 2^{N_x} possible row configurations. A full configuration $\underline{\sigma}$ of the whole system can be seen as a collection of all its row configurations: $\underline{\sigma} = (\underline{\sigma}_1, \underline{\sigma}_2, \cdots, \underline{\sigma}_{N_y})$. The number of configurations $\underline{\sigma}$ is evidently $(2^{N_x})^{N_y} = 2^N$, hence the difficulty in calculating the partition function. Consider now the following $2^{N_x} \times 2^{N_x}$ matrix

$$\langle \underline{\sigma}_{j+1}|\mathrm{T}|\underline{\sigma}_j\rangle = \exp\left(\beta \sum_{i=1}^{N_x} \Big(J_y \sigma_{i,j}\sigma_{i,j+1} + \frac{J_x}{2}\left(\sigma_{i,j}\sigma_{i+1,j} + \sigma_{i,j+1}\sigma_{i+1,j+1}\right) + \frac{h}{2}\left(\sigma_{i,j} + \sigma_{i,j+1}\right)\Big)\right) .$$

Observe that the matrix is real, *symmetric* and *positive* by construction

$$\langle \underline{\sigma}_{j+1}|\mathrm{T}|\underline{\sigma}_j\rangle = \langle \underline{\sigma}_j|\mathrm{T}|\underline{\sigma}_{j+1}\rangle \; > \; 0 \; , \tag{6.16}$$

the symmetry being due to our choice: we decided to include some Boltzmann weights in a symmetric fashion, including only *half* of the weights in $\langle \underline{\sigma}_{j+1}|\mathrm{T}|\underline{\sigma}_j\rangle$, with the understanding that the other half should be taken care of by $\langle \underline{\sigma}_{j+2}|\mathrm{T}|\underline{\sigma}_{j+1}\rangle$ and by $\langle \underline{\sigma}_j|\mathrm{T}|\underline{\sigma}_{j-1}\rangle$. Indeed, you realize that if I take a matrix product of all the T-matrices, I will include all the necessary Boltzmann weights appearing in Z:

$$Z = \sum_{\underline{\sigma}_1,\cdots,\underline{\sigma}_{N_y}} \langle \underline{\sigma}_1|\mathrm{T}|\underline{\sigma}_{N_y}\rangle \, \langle \underline{\sigma}_{N_y}|\mathrm{T}|\underline{\sigma}_{N_y-1}\rangle \cdots \langle \underline{\sigma}_{j+1}|\mathrm{T}|\underline{\sigma}_j\rangle \cdots \langle \underline{\sigma}_2|\mathrm{T}|\underline{\sigma}_1\rangle \equiv \mathrm{Tr}\, \mathrm{T}^{N_y} \; , \tag{6.17}$$

where the trace emerges from the PBC choice of boundary conditions along the y-direction.

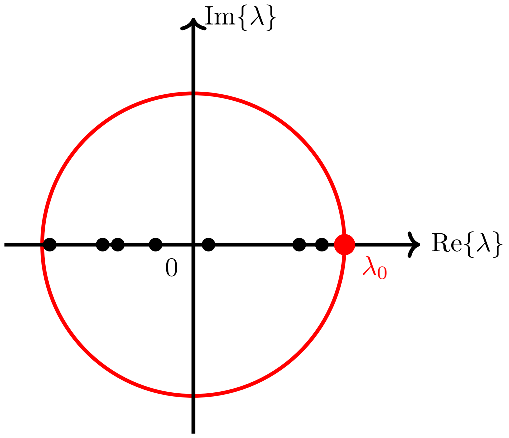

Figure 6.2: The Perron-Frobenius theorem. The red dot denotes λ_0, the Perron root, which is the maximum eigenvalue of T, real and positive. All other eigenvalues (smaller black dots) stay within the circle of radius λ_0 in the complex plane. For the symmetric T considered here, all other eigenvalues are real as well.

Since T is a positive real matrix — and even symmetric, by our construction —, we can use Perron-Frobenius theorem, which guarantees that T has a unique (positive) eigenstate $|\lambda_0\rangle$ with a *maximum eigenvalue* λ_0 — the so-called *Perron root* —, which is itself *real and positive* and greater than the modulus of any other eigenvalue, $\lambda_0 > |\lambda_{\alpha>0}|$, in general complex, but in the present case real, because T is symmetric. We can write, in terms of the eigenstates $|\lambda_\alpha\rangle$ of T, the spectral decomposition of T as:

$$\mathrm{T} = \sum_{\alpha=0}^{2^{N_x}-1} \lambda_\alpha |\lambda_\alpha\rangle\langle\lambda_\alpha| \qquad \Longrightarrow \qquad Z = \mathrm{Tr}\,\mathrm{T}^{N_y} = \sum_{\alpha=0}^{2^{N_x}-1} \lambda_\alpha^{N_y} \; ,$$

where the last equation follows because T^{N_y} is easy to calculate on the basis of the eigenvectors of T, and its trace, leading to Z is also simply the sum of all $\lambda_\alpha^{N_y}$.

Exponential dominance of the Perron root. Let us denote the maximum eigenvalue of T by $\lambda_0 \equiv \mathrm{e}^{-\epsilon E_0}$. In the limit $N_y \to \infty$, the partition sum is *exponentially dominated* by λ_0:

$$\frac{\beta F}{N_y} = -\frac{1}{N_y} \log Z \quad \xrightarrow{N_y\to\infty} \quad -\log \lambda_0 = \epsilon E_0 \; .$$

Now, let us switch to a quantum framework. We interpret the row configurations $|\underline{\sigma}_j\rangle$ as the states of a quantum spin-1/2 chain of N_x sites, $|\underline{\sigma}_j\rangle \longrightarrow |\sigma_{1,j}, \sigma_{2,j}, \cdots, \sigma_{N_x,j}\rangle_{\mathrm{Q}}$, or, omitting the j-index:

$$|\underline{\sigma}\rangle \longrightarrow |\sigma_1, \sigma_2, \cdots, \sigma_{N_x}\rangle_{\mathrm{Q}} \overset{\mathrm{def}}{=} |\underline{\sigma}\rangle_{\mathrm{Q}} \; .$$

The latter is simply an eigenstate of all the Pauli spin operators $\hat{\sigma}_i^z$:

$$\hat{\sigma}_i^z |\sigma_1, \sigma_2, \cdots, \sigma_{N_x}\rangle_{\mathrm{Q}} = \sigma_i |\sigma_1, \sigma_2, \cdots, \sigma_{N_x}\rangle_{\mathrm{Q}} \; ,$$

technically the tensor product of all the $\hat{\sigma}_i^z$ spinor states for all $i = 1 \cdots N_x$. Correspondingly, we want to find a quantum operator $\widehat{\mathrm{T}}_{\mathrm{Q}}$ which faithfully represents the matrix elements of T:

$$\langle \underline{\sigma}'|\mathrm{T}|\underline{\sigma}\rangle = \mathrm{e}^{\beta \sum_{i=1}^{N_x} \left(J_y \sigma_i \sigma_i' + \frac{J_x}{2} \left(\sigma_i \sigma_{i+1} + \sigma_i' \sigma_{i+1}'\right) + \frac{h}{2} \left(\sigma_i + \sigma_i'\right) \right)} \equiv {}_{\mathrm{Q}}\langle \underline{\sigma}'|\widehat{\mathrm{T}}_{\mathrm{Q}}|\underline{\sigma}\rangle_{\mathrm{Q}} \; . \tag{6.18}$$

The operator $\widehat{\mathrm{T}}_{\mathrm{Q}}$ is simple to construct: [2]

$$\widehat{\mathrm{T}}_{\mathrm{Q}} = \underbrace{\mathrm{e}^{\frac{\beta}{2}\sum_{i=1}^{N_x}\left(J_x\hat{\sigma}^z_i\hat{\sigma}^z_{i+1} + h\hat{\sigma}^z_i\right)}}_{L} \underbrace{\left[\prod_{i=1}^{N_x}\left(\mathrm{e}^{\beta J_y}\mathbb{1}_i + \mathrm{e}^{-\beta J_y}\hat{\sigma}^x_i\right)\right]}_{C} \underbrace{\mathrm{e}^{\frac{\beta}{2}\sum_{i=1}^{N_x}\left(J_x\hat{\sigma}^z_i\hat{\sigma}^z_{i+1} + h\hat{\sigma}^z_i\right)}}_{R} \; . \tag{6.19}$$

Consider now the ingredient appearing in the central piece, which we want to rewrite as an exponential:

$$\left(\mathrm{e}^{\beta J_y}\mathbb{1}_i + \mathrm{e}^{-\beta J_y}\hat{\sigma}^x_i\right) \equiv C\,\mathrm{e}^{\Gamma\hat{\sigma}^x_i} \equiv C\left(\mathbb{1}_i\cosh\Gamma + \hat{\sigma}^x_i\sinh\Gamma\right) \;,$$

where we used $(\hat{\sigma}^x)^{2n} = \mathbb{1}$, and $(\hat{\sigma}^x)^{2n+1} = \hat{\sigma}^x$ in the second equality, to expand the exponential. To find the constants C and Γ we write explicitly:

$$\begin{cases} C\cosh\Gamma = \mathrm{e}^{\beta J_y} \\ \\ C\sinh\Gamma = \mathrm{e}^{-\beta J_y} \end{cases} \Longrightarrow \begin{cases} \tanh\Gamma & = & \mathrm{e}^{-2\beta J_y} \\ \\ C^2 & = & \frac{2}{\sinh 2\Gamma} \end{cases} . \tag{6.20}$$

With these definitions, we can write $\widehat{\mathrm{T}}_{\mathrm{Q}}$, still exactly, as:

$$\widehat{\mathrm{T}}_{\mathrm{Q}} = C^{N_x}\mathrm{e}^{\frac{\beta}{2}\sum_{i=1}^{N_x}\left(J_x\hat{\sigma}^z_i\hat{\sigma}^z_{i+1} + h\hat{\sigma}^z_i\right)}\,\mathrm{e}^{\Gamma\sum_{i=1}^{N_x}\hat{\sigma}^x_i}\,\mathrm{e}^{\frac{\beta}{2}\sum_{i=1}^{N_x}\left(J_x\hat{\sigma}^z_i\hat{\sigma}^z_{i+1} + h\hat{\sigma}^z_i\right)} \; . \tag{6.21}$$

Although exact, this expression is not nice: the three different terms do not commute and you cannot rewrite $\widehat{\mathrm{T}}_{\mathrm{Q}}$ as the exponential of a single quantum Hamiltonian operator. Suppose, however, that the coupling constants J_x and J_y are *highly anisotropic.*

> **The high-anisotropy limit.** More precisely, we assume that:
>
> $$\textbf{High-anistropy limit:} \quad \begin{cases} \beta J_x & = & \epsilon J \\ \beta h & = & \epsilon h^{\parallel} \\ \Gamma & = & \epsilon h^{\perp} \Longrightarrow \beta J_y = -\frac{1}{2}\log\tanh\epsilon h^{\perp} \end{cases} \tag{6.22}$$
>
> where ϵ (with dimensions of "time/$\hbar$") is "**small**", and J, $h^{\parallel}$, $h^{\perp}$ (with dimensions of "energy") are suitable constants. More properly, the dimensionless combinations ϵJ, $\epsilon h^{\parallel}$, and $\epsilon h^{\perp}$ are assumed to be small. These assumptions imply that when βJ_x is "small", $\beta J_y = -\frac{1}{2}\log\tanh\epsilon h^{\perp}$ is "large", justifying the terminology "high-anisotropy limit", when $\epsilon \to 0$.

In terms of these quantities, let us now define two quantum operators:

$$\widehat{H}_z = -\sum_{i=1}^{N_x}\left(J\hat{\sigma}^z_i\hat{\sigma}^z_{i+1} + h^{\parallel}\hat{\sigma}^z_i\right) \qquad \text{and} \qquad \widehat{H}_x = -h^{\perp}\sum_{i=1}^{N_x}\hat{\sigma}^x_i \;, \tag{6.23}$$

such that the exact transfer matrix can be written as

$$\widehat{\mathrm{T}}_{\mathrm{Q}} = C^{N_x}\,\mathrm{e}^{-\frac{\epsilon}{2}\widehat{H}_z}\mathrm{e}^{-\epsilon\widehat{H}_x}\mathrm{e}^{-\frac{\epsilon}{2}\widehat{H}_z} \; . \tag{6.24}$$

In high-anisotropy limit $\epsilon \to 0$, the three exponentials can be combined by using the relationship

$$\mathrm{e}^{\epsilon\hat{A}}\mathrm{e}^{\epsilon\hat{B}} = \mathrm{e}^{\epsilon\hat{A}+\epsilon\hat{B}+\frac{\epsilon^2}{2}[\hat{A},\hat{B}]+\cdots} = \mathrm{e}^{\epsilon(\hat{A}+\hat{B})} + O(\epsilon^2) \; . \tag{6.25}$$

---

[2] With the notations in underbrace, the part denoted by "R" takes care of $\mathrm{e}^{\frac{\beta}{2}\sum_{i=1}^{N_x}(J_x\sigma_i\sigma_{i+1}+h\sigma_i)}$. Next, the action of the central operator "C" assigns a weight $\mathrm{e}^{\beta J_y}$ to the diagonal element $\sigma'_i = \sigma_i$ and a weight $\mathrm{e}^{-\beta J_y}$ to the off-diagonal element $\sigma'_i = -\sigma_i$; at the same time, the configuration is changed $|\sigma\rangle_{\mathrm{Q}} \to |\sigma'\rangle_{\mathrm{Q}}$. Finally, the action of the left operator "L" gives the remaining weights $\mathrm{e}^{\frac{\beta}{2}\sum_{i=1}^{N_x}(J_x\sigma'_i\sigma'_{i+1}+h\sigma'_i)}$.

The transfer matrix in the high-anisotropy limit. This leads us to our final expression:

$$\widehat{\mathrm{T}}_{\mathrm{Q}} \overset{\epsilon\to 0}{\simeq} C^{N_x}\, \mathrm{e}^{-\epsilon \widehat{H}_{\mathrm{Q}}} \qquad \text{with} \qquad \widehat{H}_{\mathrm{Q}} = -\sum_{i=1}^{N_x} \Big(J \hat{\sigma}^z_i \hat{\sigma}^z_{i+1} + h^{\parallel} \hat{\sigma}^z_i + h^{\perp} \hat{\sigma}^x_i \Big) \;. \tag{6.26}$$

So, in the high-anisotropy limit, the classical transfer matrix has been mapped onto the *imaginary-time* [a] evolution operator of a *quantum Ising chain in a transverse field* $h^{\perp}$. *The* y*-direction of the classical problem* — for which we chose periodic boundary conditions — *becomes the imaginary-time direction of the quantum problem.*

---

[a] The usual real-time evolution operator $\mathrm{e}^{-it\widehat{H}_{\mathrm{Q}}/\hbar}$ becomes, under the substitution $t \to -i\tau$, the imaginary-time evolution operator $\mathrm{e}^{-\tau \widehat{H}_{\mathrm{Q}}/\hbar}$, very important in numerical Quantum Monte Carlo approaches and in statistical mechanics, see [34].

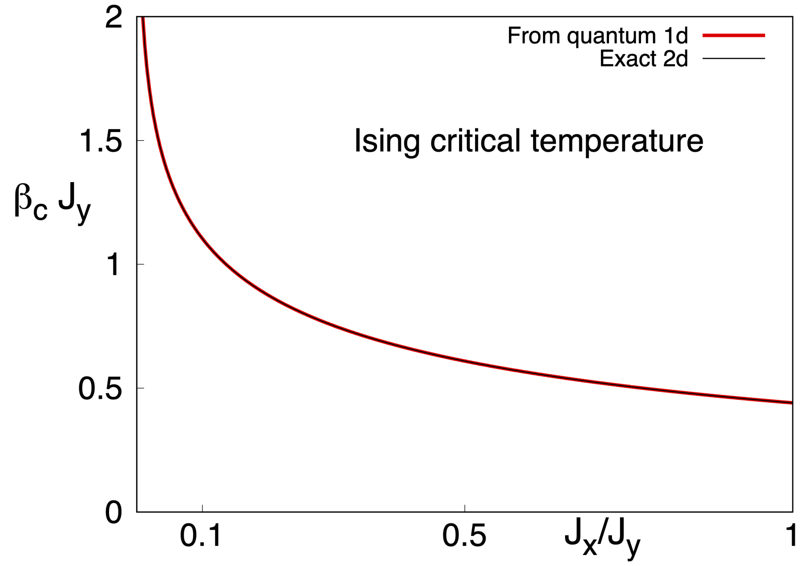

Figure 6.3: Plot of the critical coupling $\beta_c J_y = J_y/(k_B T_c)$ from the 2d Onsager's solution, Eq. (6.29), compared to the quantum-mapped prediction of Eq. (6.40), versus the anisotropy of the lattice J_x/J_y. The two predictions *coincide.*

Let us consider again the classical partition function. In the high-anisotropy limit, you rewrite it as:

$$Z = \mathrm{Tr}\, \mathrm{T}^{N_y} \equiv \mathrm{Tr}\, \widehat{\mathrm{T}}_{\mathrm{Q}}^{N_y} \overset{\epsilon\to 0}{\simeq} C^N \;\mathrm{Tr}\, \mathrm{e}^{-N_y \epsilon \widehat{H}_{\mathrm{Q}}} \;. \tag{6.27}$$

Suppose now that $\widehat{H}_{\mathrm{Q}}$ has a finite gap $\Delta_E = E_1 - E_0$ above its (non-degenerate) ground state energy $E_0 = N_x e_0$. Then for large N_y we would write:

$$Z = \mathrm{e}^{-\beta F} \overset{\epsilon\to 0}{\simeq} C^N\, \mathrm{e}^{-N_y \epsilon E_0} \big(1 + \mathrm{e}^{-N_y \epsilon \Delta_E} + \cdots \big) \approx C^N\, \mathrm{e}^{-N_y \epsilon E_0} + \cdots = C^N\, \mathrm{e}^{-N \epsilon e_0} + \cdots$$

Taking the logarithm and dividing by $N = N_y N_x$ we conclude that:

$$\beta f \;=\; \lim_{N\to\infty} \beta \frac{F}{N} = -\lim_{N\to\infty} \frac{\log Z}{N} \overset{\epsilon\to 0}{\simeq} \epsilon\, e_0 - \log C \;. \tag{6.28}$$

The constant C plays a minor role: it is simply an additive contribution to the free energy.

Singularities of $f \longleftrightarrow$ Singularities of e_0. The important point is that we expect that the *singularities* of f (in the thermodynamical limit) should be reflected by those of the *ground state energy* (per spin) e_0 of the quantum model.

Let us check this last prediction. In zero longitudinal field ($h = 0 \to h^{\parallel} = 0$) and for uniform couplings with PBC in both directions, the classical Ising model in $d = 2$ has been solved by Onsager, who succeeded in "diagonalizing" the exact transfer matrix T.

The $2d$ Ising model in zero longitudinal field. Onsager's solution predicts that the $2d$ Ising model in zero longitudinal field has a transition temperature T_c (where the free-energy f shows singularities) given by:

$$\sinh\left(2\beta_c J_x\right)\,\sinh\left(2\beta_c J_y\right) = 1\;. \tag{6.29}$$

TFIM chain: fermionic mapping. The corresponding transverse-field quantum Ising chain in $d=1$ (with PBC, and setting $L=N_x$)

$$\widehat{H}_{\text{TFIM}} = -J\sum_{j=1}^{L}\hat{\sigma}^z_j\hat{\sigma}^z_{j+1} - h^{\perp}\sum_{j=1}^{L}\hat{\sigma}^x_j\;, \tag{6.30}$$

can be easily solved by mapping the spin-operators onto spinless fermion operators — through the so-called *Jordan-Wigner transformation* [3] — leading to a simple quadratic fermion Hamiltonian:

$$\begin{aligned}
\widehat{H}_{\text{TFIM}} \longrightarrow \widehat{H} &= \sum_{k>0}^{\text{ABC}}\Big(2(h^{\perp}-J\cos k)\Big(\hat{c}^{\dagger}_k\hat{c}_k - \hat{c}_{-k}\hat{c}^{\dagger}_{-k}\Big) - 2iJ\sin k\Big(\hat{c}^{\dagger}_k\hat{c}^{\dagger}_{-k} - \hat{c}_{-k}\hat{c}_k\Big)\Big) \\
&= \sum_{k>0}^{\text{ABC}}(\hat{c}^{\dagger}_k\,,\,\hat{c}_{-k})\begin{pmatrix} 2(h^{\perp}-J\cos k) & -2Ji\sin k \\ 2Ji\sin k & -2(h^{\perp}-J\cos k)\end{pmatrix}\begin{pmatrix}\hat{c}_k \\ \hat{c}^{\dagger}_{-k}\end{pmatrix}\;.
\end{aligned} \tag{6.33}$$

Here $k=\frac{(2n-1)\pi}{L}$ with $n=1\cdots\frac{L}{2}$ are positive k-vectors for fermions on a lattice with Antiperiodic Boundary Conditions (ABC). The final form of the fermionic Hamiltonian highlights the 2×2 nature of the problem with particle annihilation ($\hat{c}_k$) and creation ($\hat{c}^{\dagger}_{-k}$) linked together into fermionic Nambu spinors, like in the BCS theory of superconductivity. Details will be studied later on, during a hands-on specific short course. Here we just sketch the main results we need.

By solving the 2×2 eigenvalue problem one can find two particle-hole symmetric bands $\epsilon_{k\pm}=\pm\epsilon_k$ with

$$\epsilon_k = 2J\sqrt{\left(\cos k - \frac{h^{\perp}}{J}\right)^2 + \sin^2 k} \geq 0\;, \tag{6.34}$$

and corresponding eigenvectors $(u_{k\pm}\,,\,v_{k\pm})^{\text{T}}$ which determine new Bogoliubov fermionic operators [4]

---

[3] For that purpose, I prefer to do a spin-rotation, writing first

$$\widehat{H}_{\text{TFIM}} = -J\sum_{j=1}^{L}\hat{\sigma}^x_j\hat{\sigma}^x_{j+1} - h^{\perp}\sum_{j=1}^{L}\hat{\sigma}^z_j\;,$$

and then mapping spins into fermions using the Jordan-Wigner (non-local) transformation:

$$\left\{\begin{array}{lcl}\hat{\sigma}^x_j &=& \hat{K}_j\,(\hat{c}^{\dagger}_j + \hat{c}_j) \\ \hat{\sigma}^y_j &=& \hat{K}_j\,i(\hat{c}^{\dagger}_j - \hat{c}_j) \\ \hat{\sigma}^z_j &=& 1-2\hat{n}_j\end{array}\right. \qquad \text{with} \qquad \hat{K}_j = \prod_{j'=1}^{j-1} \mathrm{e}^{i\pi\hat{n}_{j'}}\;. \tag{6.31}$$

It is easy to show that some nearest-neighbor spin-spin $\hat{\sigma}^x_j\hat{\sigma}^x_{j+1}$ operators transform simply into quadratic fermionic operators

$$\hat{\sigma}^x_j\hat{\sigma}^x_{j+1} = \left(\hat{c}^{\dagger}_j\hat{c}_{j+1} + \hat{c}^{\dagger}_j\hat{c}^{\dagger}_{j+1} + \text{H.c.}\right)\;. \tag{6.32}$$

Unfortunately, a longitudinal field term involving a single $\hat{\sigma}^x_j$ *cannot* be translated into a simple local fermionic operator.

[4] Define the shorthand $z_k = 2(h^{\perp}-J\cos k)$ and $y_k = 2J\,\sin k$. For the positive energy eigenvector, we have:

$$\begin{pmatrix}u_{k+}\\ v_{k+}\end{pmatrix} \equiv \begin{pmatrix}u_k\\ v_k\end{pmatrix} = \frac{1}{\sqrt{2\epsilon_k(\epsilon_k+z_k)}}\begin{pmatrix}\epsilon_k+z_k\\ iy_k\end{pmatrix}\;, \tag{6.35}$$

where we have introduced the shorthands $u_k = u_{k+}$ and $v_k = v_{k+}$. Note, in passing, that $u_{-k}=u_k$, while $v_{-k}=-v_k$, since z_k is even in k, while y_k is odd. The negative-energy eigenvector $(u_{k-}\,,\,v_{k-})^{\text{T}}$ is related to the

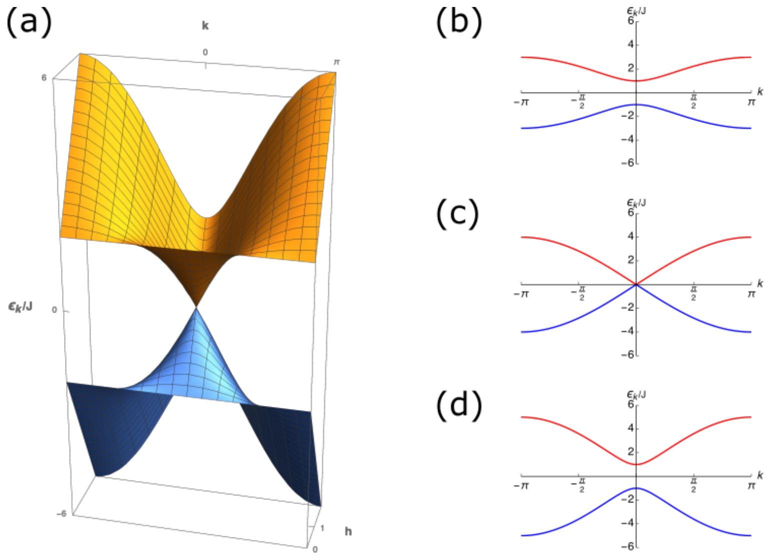

Figure 6.4.: (a) The two bands $\pm\epsilon_k$ plotted by varying the transverse field $h^\perp$ in the range $[0,2]$. (b-d) The bands $\pm\epsilon_k$ for three different transverse fields $h^\perp$: (b) $h^\perp/J = 0.5$ (inside the ferromagnetic region), (c) $h^\perp/J = 1$ (the critical point), (d) $h^\perp/J = 1.5$ (inside the paramagnetic phase). Notice the remarkable behaviour at $h^\perp = h^\perp_c = J$, clearly visible in panel (c): a gapless linear spectrum. Notice also how you can hardly distinguish the bands of the two gapped phases in (b) and (d), although their topology is distinctly different.

$\hat{\gamma}^\dagger_k = u_k \hat{c}^\dagger_k + v_k \hat{c}_{-k}$, in terms of which the fermionic Hamiltonian is perfectly diagonal:

$$\widehat{H} = \sum_{k>0}^{\text{ABC}} \epsilon_k \left(\hat{\gamma}^\dagger_k \hat{\gamma}_k + \hat{\gamma}^\dagger_{-k} \hat{\gamma}_{-k} \right) + E_0 \qquad \text{with} \qquad E_0 = -\sum_{k>0}^{\text{ABC}} \epsilon_k \; . \tag{6.37}$$

The ground state, with energy E_0, can be shown to be given by the Bogoliubov vacuum [5]

$$|\emptyset_\gamma\rangle^{\text{ABC}} = |\Psi_+\rangle = \prod_{k>0}^{\text{ABC}} \left(u_k + v_k \hat{c}^\dagger_k \hat{c}^\dagger_{-k} \right) |0\rangle \; , \tag{6.38}$$

where $\hat{\gamma}_k |\emptyset_\gamma\rangle^{\text{ABC}} = 0$. The form of the two bands $\pm\epsilon_k$, as a function of k and for several values of $h^\perp$ is noteworthy. Figure 6.4 shows plots that illustrate them.

The quantum critical point, where singularities of

$$e_0 = \lim_{L\to\infty} \frac{E_0}{L} = -\int_0^\pi \frac{\mathrm{d}k}{2\pi} \epsilon_k \; , \tag{6.39}$$

are present, is easily found to be at $(h^\perp/J)_c = 1$. Indeed, if you look at the bands in Fig. 6.4 you immediately see that they are very smooth for $h^\perp \neq J$ (panels b and d), but develop a *cusp* for $h^\perp = J$ (panel c). This corresponds, in terms of Eq. (6.22), to [6]

$$\mathrm{e}^{-2\beta_c J_y} = \tanh \beta_c J_x \; . \tag{6.40}$$

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previous one by a simple transformation:

$$\begin{pmatrix} u_{k-} \\ v_{k-} \end{pmatrix} = \begin{pmatrix} -v^*_k \\ u^*_k \end{pmatrix} = \frac{1}{\sqrt{2\epsilon_k(\epsilon_k + z_k)}} \begin{pmatrix} iy_k \\ \epsilon_k + z_k \end{pmatrix} \; . \tag{6.36}$$

[5] Incidentally, this is precisely the state $|\Psi_+\rangle$ even under the $\mathbb{Z}_2$ symmetry previously discussed. The quasi-degenerate state $|\Psi_-\rangle$ lives in a different sector of the Hilbert space, with different (PBC) values of k.

[6] Simply notice that at the critical point you can identify $\epsilon h^\perp$ with $\epsilon J = \beta J_x$.

Remarkably, all exact critical exponents of the zero-field 2d Ising model are reproduced by the quantum Ising chain. [7]

Quantitatively, you might wonder how close the two predictions for T_c are, as a function of the anisotropy of the couplings J_x/J_y (which should be "small" for the quantum mapping to be in principle valid). The two results are shown in Fig. 6.3: if you can see only one curve, you are right. Rather surprisingly, at least for me, Eq. (6.29)-(6.40) give *precisely* [8] the same T_c *for all values of the anisotropy* J_x/J_y. To summarise, not only do we expect that our quantum problem will capture the singularities of the classical model, but even quantitatively we get a perfect prediction for the critical couplings, well beyond the high-anisotropy limit.

Generalisations. Generalisations are rather simple. If you follow the steps we have taken, you realize that it was in no way crucial that the original classical Ising model was two-dimensional: any $(d+1)$ dimensional hyper-cubic lattice classical Ising model would be reduced to a corresponding d-dimensional quantum Ising problem in a transverse field. The boundary conditions on the space-like directions can be taken at will: only the direction that maps into the imaginary-time has to respect PBC. Moreover, the different couplings might be different from site to site, as long as they *remain the same along the "time-direction"*. [9]

More in details, and as a way of summary, take a classical Ising model in, say, a hyper-cubic lattice in $(d+1)$-dimensions, with the lattice sites denoted as

$$\sum_{\alpha=1}^{d} n_\alpha \mathbf{e}_\alpha + n_t \mathbf{e}_{d+1} = \mathbf{R} + n_t \mathbf{e}_{d+1} \equiv (\mathbf{R}, n_t) \ ,$$

where $\mathbf{e}_\alpha$ and $\mathbf{e}_{d+1}$ are lattice vectors in the corresponding directions, with $n_\alpha = 1, \cdots N_\alpha$ and $n_t = 1, \cdots N_t$ integers. Write the classical Ising model H as

$$H[\underline{\sigma}] = -\sum_{n_t=1}^{N_t} \sum_{\langle \mathbf{R},\mathbf{R}'\rangle} J^s_{\mathbf{R},\mathbf{R}'} \sigma_{\mathbf{R},n_t} \sigma_{\mathbf{R}',n_t} - \sum_{n_t=1}^{N_t} \sum_{\mathbf{R}} J^t_{\mathbf{R}}\, \sigma_{\mathbf{R},n_t} \sigma_{\mathbf{R},n_t+1} - \sum_{n_t=1}^{N_t} \sum_{\mathbf{R}} h_{\mathbf{R}} \sigma_{\mathbf{R},n_t} \ , \tag{6.41}$$

with PBC along the "time-like" $(d+1)$-direction and general anisotropic two-spin interactions: $J^s_{\mathbf{R},\mathbf{R}'}$ along the "space-like directions" and $J^t_{\mathbf{R}}$ along the "time direction". Let $N_s = N_1 N_2 \cdots N_d$ be the number of sites in the first d "space-like" directions, and $N = N_s N_t$ the total number of sites. Then, you can write $Z = \mathrm{Tr}\, \mathrm{T}^{N_t}$ with T a $2^{N_s} \times 2^{N_s}$ positive, symmetric, transfer matrix, whose Perron's root exponentially dominates Z in the limit $N_t \to \infty$. Moreover, in the high-anisotropy limit where:

$$\textbf{High-anistropy limit:} \quad \begin{cases} \beta J^s_{\mathbf{R},\mathbf{R}'} & = \ \epsilon J_{\mathbf{R},\mathbf{R}'} \\ \beta h_{\mathbf{R}} & = \ \epsilon h^{\parallel}_{\mathbf{R}} \\ \mathrm{e}^{-2\beta J^t_{\mathbf{R}}} & = \ \tanh \epsilon h^{\perp}_{\mathbf{R}} \end{cases} \tag{6.42}$$

the quantities on the RHS being uniformly small (formally in the limit $\epsilon \to 0$), you can write the transfer matrix as a quantum operator of the form $\mathrm{T}_{\mathrm{Q}} \longrightarrow \mathrm{e}^{-\epsilon \widehat{H}_{\mathrm{Q}}}$ with:

$$\widehat{H}_{\mathrm{Q}} = -\sum_{\langle \mathbf{R},\mathbf{R}'\rangle} J_{\mathbf{R},\mathbf{R}'} \hat{\sigma}^z_{\mathbf{R}} \hat{\sigma}^z_{\mathbf{R}'} - \sum_{\mathbf{R}} h^{\parallel}_{\mathbf{R}} \hat{\sigma}^z_{\mathbf{R}} - \sum_{\mathbf{R}} h^{\perp}_{\mathbf{R}} \hat{\sigma}^x_{\mathbf{R}} \ . \tag{6.43}$$

---

[7] We will see details of this in the hands-on short course. Interestingly, the Jordan-Wigner mapping is unable to solve the 1d quantum Ising chain precisely in the case which Onsager's solution cannot deal with: in presence of a longitudinal field.

[8] If you call $z = \mathrm{e}^{-2\beta_c J_y}$, from the Onsager relation Eq. (6.29), solving a simple quadratic equation, you get:

$$z = \mathrm{e}^{-2\beta_c J_y} = \frac{\sqrt{S^2+4}-2}{S} \quad \text{with} \quad S = 2\sinh(2\beta_c J_x) \ .$$

Straightforward algebra, using duplication formulas $\cosh(2\beta_c J_x) = \cosh^2(\beta_c J_x) + \sinh^2(\beta_c J_x)$ and $\sinh(2\beta_c J_x) = 2\sinh(\beta_c J_x)\cosh(\beta_c J_x)$, leads then to the result stated in Eq. (6.40).

[9] In the (1+1)-dimensional example we treated explicitly, with sites denoted as (i,j), you could take $J_x \to J^x_i$, $J_y \to J^y_i$, and $h \to h_i$, leading to a site-dependence of the transverse-field quantum Ising chain parameters J_i, $h^{\parallel}_i$ and $h^{\perp}_i$.

6.2. Path-integral representation of transverse-field Ising models

We now follow essentially the *inverse route* to what we did in the previous section: we will try to write the quantum partition function of a transverse-field Ising model (indeed, in any dimension and with arbitrary couplings) in terms of a "classical partition sum", as an illustration of how to write a *Suzuki-Trotter path-integral* of a quantum problem. The steps are remarkably identical to those we saw in the previous section, but *repetita iuvant.* So, consider a quantum Ising model in a transverse field:

$$\widehat{H}_{\rm Q} = \underbrace{-\sum_{\langle \mathbf{R},\mathbf{R}'\rangle} J_{\mathbf{R},\mathbf{R}'}\hat{\sigma}^z_{\mathbf{R}}\hat{\sigma}^z_{\mathbf{R}'} - \sum_{\mathbf{R}} h^{\parallel}_{\mathbf{R}}\hat{\sigma}^z_{\mathbf{R}}}_{\widehat{Z}} \underbrace{- \sum_{\mathbf{R}} h^{\perp}_{\mathbf{R}}\hat{\sigma}^x_{\mathbf{R}}}_{\widehat{X}} = \widehat{Z}+\widehat{X} \,, \tag{6.44}$$

where $\langle \mathbf{R},\mathbf{R}'\rangle$ denotes, as usual, nearest-neighbour sites on the (rather arbitrary) lattice. As a short-hand, I indicated the first term, diagonal in the basis of $\hat{\sigma}^z$ by $\widehat{Z}$ — it will be our "potential energy" — and the off-diagonal term involving $\hat{\sigma}^x$ by $\widehat{X}$ — it will be our "kinetic energy operator".

More general transverse-field models. The fact that we consider two-spin $J_{\mathbf{R},\mathbf{R}'}\hat{\sigma}^z_{\mathbf{R}}\hat{\sigma}^z_{\mathbf{R}'}$ interactions is for illustration purposes only. Indeed, you might repeat an identical construction for an arbitrary model of the form:

$$\widehat{H}_{\rm Q} = \widehat{Z} - \sum_{\mathbf{R}} h^{\perp}_{\mathbf{R}}\hat{\sigma}^x_{\mathbf{R}} = \widehat{Z}+\widehat{X} \,, \tag{6.45}$$

where $\widehat{Z}$ contains any number of $\hat{\sigma}^z_{\mathbf{R}}$. Later on, we will apply this to the Ising lattice gauge theory in a transverse field, where $\widehat{Z}$ will consist of *four spin* $\hat{\sigma}^z$ plaquette interactions.

We would like to calculate the *finite temperature* quantum partition function:

$$Z_{\rm Q} \equiv {\rm Tr}\; {\rm e}^{-\beta\widehat{H}_{\rm Q}} = {\rm Tr}\; \underbrace{{\rm e}^{-\frac{\beta}{N_t}\widehat{H}_{\rm Q}}\cdots{\rm e}^{-\frac{\beta}{N_t}\widehat{H}_{\rm Q}}}_{N_t \text{ times}} = \sum_{\underline{\sigma}_1}\langle\underline{\sigma}_1|\underbrace{{\rm e}^{-\epsilon\widehat{H}_{\rm Q}}\cdots{\rm e}^{-\epsilon\widehat{H}_{\rm Q}}}_{N_t \text{ times}}|\underline{\sigma}_1\rangle \tag{6.46}$$

So far, we have an exact expression, since we have just rewritten the exponential as a product of N_t identical terms without splitting the two non-commuting parts. The number N_t is called the *Trotter number* or *number of Trotter slices.* Notice that for fixed finite β (i.e., at finite temperature T), the quantity appearing in the exponentials is now:

$$\epsilon \equiv \frac{\beta}{N_t} = \frac{1}{k_BTN_t} = \frac{\Delta\tau}{\hbar} \,. \tag{6.47}$$

The last notation suggests that I can view ϵ as an arbitrarily small "imaginary time" $\Delta\tau$, by taking a suitably large N_t. [10] And here comes the *Suzuki-Trotter* break-up of the exponential:

$${\rm e}^{-\epsilon\widehat{H}_{\rm Q}} = {\rm e}^{-\epsilon(\widehat{Z}+\widehat{X})} = {\rm e}^{-\frac{\epsilon}{2}\widehat{Z}}{\rm e}^{-\epsilon\widehat{X}}{\rm e}^{-\frac{\epsilon}{2}\widehat{Z}} + O(\epsilon^3) \,. \tag{6.48}$$

This symmetric break-up is actually correct to order ϵ^3, while a non-symmetric form would lead to ${\rm e}^{-\epsilon(\widehat{Z}+\widehat{X})} = {\rm e}^{-\epsilon\widehat{Z}}{\rm e}^{-\epsilon\widehat{X}} + O(\epsilon^2)$. Remarkably, under the trace the two break-ups are actually totally equivalent. We now use Eq. (6.48) inside the trace expression Eq. (6.46), performing the trace by summing over the $\hat{\sigma}^z$-eigenstates configurations $|\underline{\sigma}_1\rangle$ of the Hilbert space, and inserting appropriate identities at all "time-slices" $n_t = 2\cdots N_t$, of the form

$$\sum_{\underline{\sigma}_{n_t}} |\underline{\sigma}_{n_t}\rangle\langle\underline{\sigma}_{n_t}| = \mathbb{1} \,.$$

---

[10] Notice that ϵ reabsorbs a factor of $\hbar$.

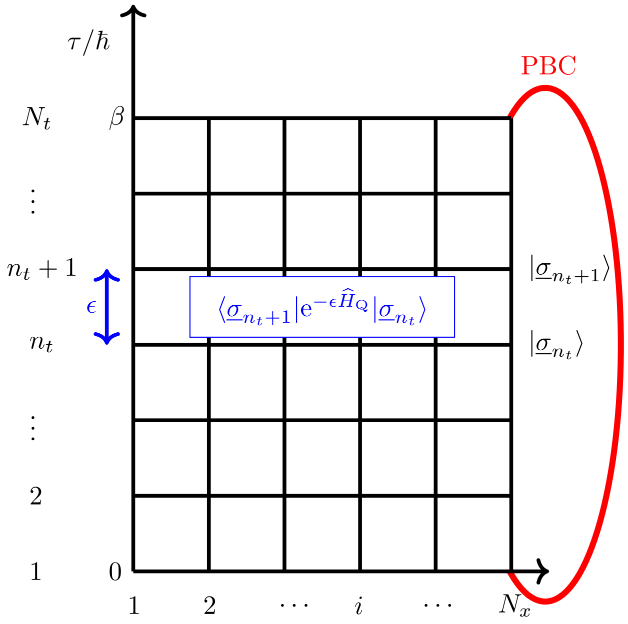

Figure 6.5: The quantum partition function, $Z_{\mathrm{Q}} \equiv \mathrm{Tr}\ \mathrm{e}^{-\beta\widehat{H}_{\mathrm{Q}}}$, expressed as $\mathrm{Tr}\left(\mathrm{e}^{-\epsilon\widehat{H}_{\mathrm{Q}}}\right)^{N_t}$. Here $\epsilon \equiv \beta/N_t$ will be assumed to be "small", so as to justify a Suzuki-Trotter decomposition of the "imaginary-time propagator" $\langle \underline{\sigma}_{n_t+1}|\mathrm{e}^{-\epsilon\widehat{H}_{\mathrm{Q}}}|\underline{\sigma}_{n_t}\rangle$. This eventually leads to the path-integral representation.

We end-up writing:

$$\begin{aligned} Z_{\mathrm{Q}} \;=\; \sum_{\underline{\sigma}_1\cdots\underline{\sigma}_{N_t}} \Big(& \langle \underline{\sigma}_1|\mathrm{e}^{-\frac{\epsilon}{2}\widehat{Z}}\mathrm{e}^{-\epsilon\widehat{X}}\mathrm{e}^{-\frac{\epsilon}{2}\widehat{Z}}|\underline{\sigma}_{N_t}\rangle \cdots \langle \underline{\sigma}_{n_t+1}|\mathrm{e}^{-\frac{\epsilon}{2}\widehat{Z}}\mathrm{e}^{-\epsilon\widehat{X}}\mathrm{e}^{-\frac{\epsilon}{2}\widehat{Z}}|\underline{\sigma}_{n_t}\rangle \cdots \\ & \cdots \langle \underline{\sigma}_2|\mathrm{e}^{-\frac{\epsilon}{2}\widehat{Z}}\mathrm{e}^{-\epsilon\widehat{X}}\mathrm{e}^{-\frac{\epsilon}{2}\widehat{Z}}|\underline{\sigma}_1\rangle\Big) \;+\; O(\epsilon^2)\,. \end{aligned} \tag{6.49}$$

The relevant matrix elements that we need to calculate are simple, since $\widehat{Z}$ is *diagonal* in the chosen basis, and $\widehat{X}$ is a *sum of commuting single-site* $\hat{\sigma}^x_{\mathbf{R}}$. More explicitly:

$$\langle \underline{\sigma}_{n_t+1}|\mathrm{e}^{-\frac{\epsilon}{2}\widehat{Z}}\mathrm{e}^{-\epsilon\widehat{X}}\mathrm{e}^{-\frac{\epsilon}{2}\widehat{Z}}|\underline{\sigma}_{n_t}\rangle = \mathrm{e}^{-\frac{\epsilon}{2}\widehat{Z}(\underline{\sigma}_{n_t+1})}\,\langle \underline{\sigma}_{n_t+1}|\mathrm{e}^{-\epsilon\widehat{X}}|\underline{\sigma}_{n_t}\rangle\,\mathrm{e}^{-\frac{\epsilon}{2}\widehat{Z}(\underline{\sigma}_{n_t})}\,.$$

In turn, the central piece can be explicitly written as:

$$\begin{aligned} \langle \underline{\sigma}_{n_t+1}|\mathrm{e}^{-\epsilon\widehat{X}}|\underline{\sigma}_{n_t}\rangle = \langle \underline{\sigma}_{n_t+1}|\prod_{\mathbf{R}}\mathrm{e}^{\epsilon h^{\perp}_{\mathbf{R}}\hat{\sigma}^x_{\mathbf{R}}}|\underline{\sigma}_{n_t}\rangle &= \prod_{\mathbf{R}}\langle \sigma_{\mathbf{R},n_t+1}|\mathrm{e}^{\epsilon h^{\perp}_{\mathbf{R}}\hat{\sigma}^x_{\mathbf{R}}}|\sigma_{\mathbf{R},n_t}\rangle \\ &= \prod_{\mathbf{R}}\langle \sigma_{\mathbf{R},n_t+1}|\big(\cosh{(\epsilon h^{\perp}_{\mathbf{R}})}\mathbb{1}_{\mathbf{R}} + \sinh{(\epsilon h^{\perp}_{\mathbf{R}})}\hat{\sigma}^x_{\mathbf{R}}\big)|\sigma_{\mathbf{R},n_t}\rangle \\ &= \prod_{\mathbf{R}}\begin{cases} \cosh{(\epsilon h^{\perp}_{\mathbf{R}})} & \text{if} \quad \sigma_{\mathbf{R},n_t+1} = \sigma_{\mathbf{R},n_t} \\ \sinh{(\epsilon h^{\perp}_{\mathbf{R}})} & \text{if} \quad \sigma_{\mathbf{R},n_t+1} = -\sigma_{\mathbf{R},n_t} \end{cases}\,. \end{aligned}$$

Let us manipulate it to make it easier to read. Remember that in the previous section we showed that

$$\mathrm{e}^{K\sigma'\sigma} = \langle \sigma'|\mathrm{e}^{K}\mathbb{1} + \mathrm{e}^{-K}\hat{\sigma}^x|\sigma\rangle = C\langle \sigma'|\mathrm{e}^{\Gamma\hat{\sigma}^x}|\sigma\rangle \qquad \text{with} \qquad \begin{cases} K &= -\frac{1}{2}\log\tanh\Gamma \\ C^2 &= \frac{2}{\sinh 2\Gamma} \end{cases}\,.$$

Hence we can write (relabelling $\Gamma \to \epsilon h^{\perp}_{\mathbf{R}}$):

$$\langle \underline{\sigma}_{n_t+1}|\mathrm{e}^{-\epsilon\widehat{X}}|\underline{\sigma}_{n_t}\rangle = \mathrm{e}^{\sum_{\mathbf{R}}\left(K^{\perp}_{\mathbf{R}}\sigma_{\mathbf{R},n_t}\sigma_{\mathbf{R},n_t+1} - \log C_{\mathbf{R}}\right)} \qquad \text{with} \qquad \begin{cases} K^{\perp}_{\mathbf{R}} &= -\frac{1}{2}\log\tanh{(\epsilon h^{\perp}_{\mathbf{R}})} \\ C^2_{\mathbf{R}} &= \frac{2}{\sinh 2\epsilon h^{\perp}_{\mathbf{R}}} \end{cases}\,. \tag{6.50}$$

Path-integral representation of quantum Ising models in a transverse field. Given a quantum Ising model in d-dimensions with $\widehat{H}_{\mathrm{Q}} = \widehat{Z} - \sum_{\mathbf{R}} h^{\perp}_{\mathbf{R}} \hat{\sigma}^x_{\mathbf{R}}$ and $\widehat{Z}$ containing only $\hat{\sigma}^z$ operators, its path-integral amounts to following classical partition sum in $(d+1)$-dimensions with a *classical effective action* $S[\boldsymbol{\sigma}]$

$$\begin{aligned} S[\boldsymbol{\sigma}] &= -\epsilon \sum_{n_t=1}^{N_t} \widehat{Z}(\underline{\sigma}_{n_t}) - \sum_{n_t=1}^{N_t} \sum_{\mathbf{R}} K^{\perp}_{\mathbf{R}}\, \sigma_{\mathbf{R},n_t} \sigma_{\mathbf{R},n_t+1} \\ Z_{\mathrm{Q}} &= \lim_{N_t\to\infty} \sum_{\underline{\sigma}_1 \cdots \underline{\sigma}_{N_t}} \mathrm{e}^{-S[\underline{\sigma}_1,\cdots,\underline{\sigma}_{N_t}]} = \lim_{N_t\to\infty} \sum_{\boldsymbol{\sigma}} \mathrm{e}^{-S[\boldsymbol{\sigma}]} \end{aligned} \;.$$

Here $\widehat{Z}(\underline{\sigma}_{n_t})$ is the eigenvalue of $\widehat{Z}$ on the classical configuration $\underline{\sigma}_{n_t}$ at the "time-slice" n_t, and the relevant [a] transverse (time-like) dimensionless coupling $K^{\perp}_{\mathbf{R}}$ is *ferromagnetic* and is given by:

$$\left\{ \begin{aligned} K^{\perp}_{\mathbf{R}} &= -\frac{1}{2} \log\tanh\left(\epsilon h^{\perp}_{\mathbf{R}}\right) > 0 \\ \epsilon &= \frac{\Delta\tau}{\hbar} \equiv \frac{\beta}{N_t} = \frac{1}{k_B T N_t} \end{aligned} \right. \;. \tag{6.51}$$

---

[a] Observe that the constant $C_{\mathbf{R}}$ plays no major role in the path-integral, and has been omitted. It will cancel anyway when considering expectation values.

7. Mean field and Ginzburg-Landau

An exact solution of a non-trivial statistical mechanics model is a rare event, mostly confined to two-dimensional (classical), or one-dimensional (quantum) models. See the excellent books by Mussardo and by Baxter if you want to learn more about exactly solvable models.

Here I will discuss a general approximate approach that yields useful information on the phase diagram you should expect for your model, although failing to quantitatively describe the behaviour close to *second-order critical points*, at least for lattices in low dimensions. This approach is known as *mean field*. It can be introduced in many ways. Here I present a useful *variational* approach leading to a mean-field description.

7.1. Variational formulation of mean field

First of all, the canonical Helmholtz free-energy obeys a minimum principle, as you already know. You can also show that a minimum principle allows getting the usual Gibbs-Boltzmann weights for the canonical ensemble in the following way. Let $\{|\phi_n\rangle\}$ be a complete basis of eigenstates of the Hamiltonian $\widehat{H}$ of the system you are considering, with E_n the corresponding energy eigenvalues. Consider a statistical ensemble defined by

$$\hat{\rho} = \sum_n p_n |\phi_n\rangle\langle\phi_n| \qquad\qquad \text{with} \quad \sum_n p_n = 1 \; . \tag{7.1}$$

If can calculate E and S for this ensemble, viewed as functionals of the weights $\{p_n\}$, as:

$$\begin{aligned} E[\{p_n\}] &= \langle \widehat{H}\rangle = \mathrm{Tr}[\hat{\rho}\widehat{H}] = \sum_n p_n E_n \\ S[\{p_n\}] &= -k_B \langle \log\hat{\rho}\rangle = -k_B\,\mathrm{Tr}[\hat{\rho}\log\hat{\rho}] = -k_B \sum_n p_n \log p_n \end{aligned} \quad . \tag{7.2}$$

One can show that the correct canonical free-energy F, with the standard Boltzmann weights $p_n = \mathrm{e}^{-\beta E_n}/Z$, verifies the inequality

$$F \le E[\{p_n\}] - TS[\{p_n\}] \; , \tag{7.3}$$

as you can immediately show by writing the Lagrange multiplier problem in presence of the constraint $\sum_n p_n = 1$. [1] But this is not all. You can also show that F is "minimal" with respect to *any density matrix* $\hat{\rho}_0$, in particular for the Gibbs density matrix

$$\hat{\rho}_0 = \frac{\mathrm{e}^{-\beta\widehat{H}_0}}{\mathrm{Tr}\,\mathrm{e}^{-\beta\widehat{H}_0}} \; ,$$

---

[1] The functional to be minimized is:

$$\sum_n p_n E_n + k_B T \sum_n p_n \log p_n - \lambda(\sum_n p_n - 1) \; .$$

Setting to 0 the simple derivative with respect to p_n, you immediately verify that the solution can be expressed in the standard Gibbs-Boltzmann form:

$$p_n = \frac{\mathrm{e}^{-\beta E_n}}{Z} \; .$$

corresponding to a *different* trial Hamiltonian $\widehat{H}_0$.

Bogoliubov-Gibbs inequality.

$$\begin{aligned} F \;\leq\; \mathrm{Tr}\left(\hat{\rho}_0 \widehat{H}\right) + k_B T\, \mathrm{Tr}\left(\hat{\rho}_0 \log \hat{\rho}_0\right) &= \langle \widehat{H} \rangle_0 - T S_0 \\ &= F_0 + \langle \widehat{H} - \widehat{H}_0 \rangle_0 \;, \end{aligned} \tag{7.4}$$

where in the second form $F_0 = E_0 - TS_0 = \langle \widehat{H}_0 \rangle_0 - TS_0$ is the free-energy corresponding to $\widehat{H}_0$.

Incidentally, this inequality generalizes to finite T the well-known Rayleigh-Ritz variational inequality of quantum mechanics

$$E_{\mathrm{gs}} \leq \langle \widehat{H} \rangle_0 = \mathrm{Tr}\left(\widehat{H} \hat{\rho}_0\right) \;,$$

which you typically meet for pure states $\hat{\rho}_0 = |\psi\rangle\langle\psi|$, but it applies to *any density matrix* $\hat{\rho}_0$. Indeed, for $T \to 0$ you have:

$$E_{\mathrm{gs}} \xleftarrow{T\to 0} F \leq \langle \widehat{H} \rangle_0 - T S_0 \xrightarrow{T\to 0} \langle \widehat{H} \rangle_0 \;. \tag{7.5}$$

To prove the Bogoliubov-Gibbs inequality, we will introduce the concept of *quantum relative entropy*, which leads to another Gibbs inequality, very interesting on its own.

Relative entropy or quantum Kullback-Leibler divergence. Given two density matrices $\hat{\rho}_1$ and $\hat{\rho}_2$, their quantum relative entropy is defined as:

$$S(\hat{\rho}_1 || \hat{\rho}_2) \stackrel{\mathrm{def}}{=} \mathrm{Tr}\left(\hat{\rho}_1 (\log \hat{\rho}_1 - \log \hat{\rho}_2)\right) \;. \tag{7.6}$$

It is the quantum analog of the classical Kullback-Leibler divergence

$$D(P_1 || P_2) = \int \mathrm{d}\mathbf{x}\, P_1(\mathbf{x}) \log \frac{P_1(\mathbf{x})}{P_2(\mathbf{x})} \;, \tag{7.7}$$

where P_1 and P_2 are probability densities. Notice that both quantities are *non-symmetric* with respect to their arguments. A crucial concept connected to the relative entropy is the Gibbs inequality

$$S(\hat{\rho}_1 || \hat{\rho}_2) \geq 0 \qquad \Longrightarrow \qquad -\,\mathrm{Tr}\, \hat{\rho}_1 \log \hat{\rho}_1 \leq -\,\mathrm{Tr}\, \hat{\rho}_1 \log \hat{\rho}_2 \;. \tag{7.8}$$

The inequality becomes an equality if and only if $\hat{\rho}_1 = \hat{\rho}_2$.

The Gibbs inequality is a consequence of a general Klein's inequality, in turn connected to the convexity preservation of the trace of positive operators. We will have more to say in later chapters. Here, I just note that the proof is simple in the classical case, or equivalently when the two density matrices have a common basis of eigenstates and differ just by the weights: $\hat{\rho}_1 = \sum_n P^{(1)}_n |\phi_n\rangle\langle\phi_n|$ and $\hat{\rho}_2 = \sum_n P^{(2)}_n |\phi_n\rangle\langle\phi_n|$. Indeed, using the concavity of $\log x$ and the fact that $\log x \leq x - 1$, you easily show that:

$$\begin{aligned} \mathrm{Tr}\left(\hat{\rho}_1 (\log \hat{\rho}_2 - \log \hat{\rho}_1)\right) &= \sum_n \Big(P^{(1)}_n \log \frac{P^{(2)}_n}{P^{(1)}_n} \Big) \\ &\leq \sum_n \Big(P^{(1)}_n \big(\frac{P^{(2)}_n}{P^{(1)}_n} - 1 \big) \Big) = \sum_n \Big(P^{(2)}_n - P^{(1)}_n \Big) = 0 \;. \end{aligned} \tag{7.9}$$

The Gibbs inequality immediately leads to a proof of the Bogoliubov-Gibbs inequality: it is enough to take $\hat{\rho}_1 = \hat{\rho}_0$, the trial density matrix, and $\hat{\rho}_2 = \hat{\rho}_{\mathrm{CE}}$, the Gibbs canonical ensemble associated to

$\widehat{H}$. Here is the proof, which uses the fact that $\log\hat{\rho}_{\rm CE} = -\beta\widehat{H} - \log Z_{\rm CE}$ and $\log Z_{\rm CE} = -\beta F$:

$$\begin{aligned} TS_0 = -k_BT\,{\rm Tr}\left(\hat{\rho}_0\log\hat{\rho}_0\right) \le -k_BT\,{\rm Tr}\left(\hat{\rho}_0\log\hat{\rho}_{\rm CE}\right) &= -k_BT\,{\rm Tr}\left(\hat{\rho}_0(-\beta\widehat{H}-\log Z_{\rm CE})\right) \\ &= {\rm Tr}\left(\hat{\rho}_0\widehat{H}\right) - F\;. \end{aligned} \tag{7.10}$$

An alternative proof of the Bogoliubov-Gibbs variational principle $F \le \langle\widehat{H}\rangle_0 - TS_0$, using a perturbative approach is given in Feynman's statistical mechanics book, Sec. 2.11. The essence of the proof is again a concavity argument. One considers an interpolating Hamiltonian

$$\widehat{H}(\alpha) = \widehat{H}_0 + \alpha(\widehat{H}-\widehat{H}_0) = \widehat{H}_0 + \alpha\widehat{V}\;, \tag{7.11}$$

such that $\widehat{H}(0)\equiv\widehat{H}_0$ and $\widehat{H}(1)\equiv\widehat{H}$, with $\widehat{V}=\widehat{H}-\widehat{H}_0$, and sets up a perturbative expansion in powers of $\alpha\widehat{V}$. For the free-energy the expansion would read:

$$F(\alpha) = F_0 + \alpha F_1 + \alpha^2F_2 + \cdots \tag{7.12}$$

where $F_0 = E_0 - TS_0 = \langle\widehat{H}_0\rangle_0 - TS_0$ is the free-energy corresponding to $\widehat{H}_0$, while F_1, F_2, etc. are the Taylor coefficients of $F(\alpha)$. The perturbative calculation is rather easy to set up and carry out. Use a basis of eigenstates of $\widehat{H}_0$, i.e., $\widehat{H}_0|n\rangle = \epsilon_n|n\rangle$, with unperturbed energies ϵ_n, and define the shorthand for the matrix elements $V_{mn} = \langle m|\widehat{V}|n\rangle$, and $p_n = {\rm e}^{-\beta\epsilon_n}/Z_0$ to be the unperturbed Boltzmann weights, where $Z_0 = \sum_n {\rm e}^{-\beta\epsilon_n} = {\rm e}^{-\beta F_0}$ is the unperturbed partition sum.

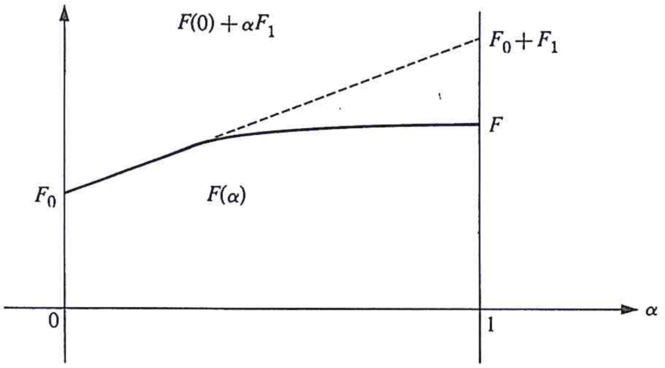

Figure 7.1: The concavity of $F(\alpha)$. Figure taken from Feynman.

Exercise 7.1. Show, by an explicit calculation, that:

$$F_1 = {\rm Tr}[\hat{\rho}_0\widehat{V}] = \langle\widehat{H}-\widehat{H}_0\rangle_0\;, \tag{7.13}$$

while:

$$\begin{aligned} F_2 &= -\frac{1}{2}{\rm e}^{\beta F_0}\sum_{m\neq n}\frac{{\rm e}^{-\beta\epsilon_m}-{\rm e}^{-\beta\epsilon_n}}{\epsilon_n-\epsilon_m}|V_{mn}|^2 - \frac{\beta}{2}\underbrace{\left(\sum_n p_n|V_{nn}|^2 - \Big(\sum_n p_nV_{nn}\Big)^2\right)}_{\ge 0} \\ &\le -\frac{1}{2}{\rm e}^{\beta F_0}\sum_{m\neq n}\frac{{\rm e}^{-\beta\epsilon_m}-{\rm e}^{-\beta\epsilon_n}}{\epsilon_n-\epsilon_m}|V_{mn}|^2 \le 0\;. \end{aligned} \tag{7.14}$$

In the previous derivation, we made use of the standard second-moment inequality [2] while the last inequality follows by inspection.

---

[2] Simply recall that

$$\sum_n p_n|V_{nn}|^2 - \Big(\sum_n p_nV_{nn}\Big)^2 \equiv \sum_n p_n\left(V_{nn} - \sum_m p_mV_{mm}\right)^2 \ge 0\;.$$

The perturbative calculation just reported shows that $F''(0) = 2F_2 \leq 0$. An entirely identical perturbative calculation, with the trick of setting up the expansion around an arbitrary point α in terms of the (small) variable γ, by writing

$$\widehat{H}(\alpha+\gamma) = \widehat{H}(\alpha) + \gamma\widehat{V} \ ,$$

shows that indeed

$$F''(\alpha) \leq 0 \qquad \forall\alpha \in [0,1] \ ,$$

which implies that the function $F(\alpha)$ is *concave*, i.e., it *stays below its tangent in* $\alpha = 0$. By looking at Fig 7.1 you realize that this immediately implies that

$$F = F(1) \leq F_0 + F_1 = F_0 + \langle \widehat{H} - \widehat{H}_0 \rangle_0 \ ,$$

which is the second form of the Bogoliubov-Gibbs variational principle in Eq. (7.4).

Applications of Bogoliubov-Gibbs inequality. You can do a lot with the Bogoliubov-Gibbs variational principle. Hartree-Fock is an application of it, with $\widehat{H}_0$ being the best (self-consistent) *quadratic Hamiltonian* for a fermionic system. $\widehat{H}_0$ can also be thought of as a *self-consistent harmonic approximation* in other contexts. For spin systems, if you restrict $\widehat{H}_0$ to be the sum of local fields on sites or sum of terms on independent larger clusters, you recover the usual Weiss mean-field (see Section below) and its improvements (Bethe-Peierls approximations).

7.1.1. The classical Ising model: Weiss mean-field

Consider the classical Ising model

$$\widehat{H} = -\sum_{\langle \mathbf{R},\mathbf{R}'\rangle} J_{\mathbf{R},\mathbf{R}'}\hat{\sigma}^z_{\mathbf{R}}\hat{\sigma}^z_{\mathbf{R}'} - \sum_{\mathbf{R}} h_{\mathbf{R}}\hat{\sigma}^z_{\mathbf{R}} \ , \tag{7.15}$$

where $\mathbf{R}$ and $\mathbf{R}'$ denote nearest-neighbour sites on a lattice or graph on which the model is defined. We now apply the Bogoliubov-Gibbs variational principle with a very simple trial Hamiltonian $\widehat{H}_0$

$$\widehat{H}_0 = -\sum_{\mathbf{R}} h^0_{\mathbf{R}}\hat{\sigma}^z_{\mathbf{R}} \ , \tag{7.16}$$

where the various $h^0_{\mathbf{R}}$ (in essence, effective magnetic fields) are used as variational parameters. This amounts to saying that our *Ansatz* for the density matrix is site-factorised and given by: [3]

$$\hat{\rho}_0 = \frac{\mathrm{e}^{-\beta\widehat{H}_0}}{\mathrm{Tr}\,\mathrm{e}^{-\beta\widehat{H}_0}} = \prod_{\mathbf{R}}\left(\frac{1}{2}\mathbb{1}_{\mathbf{R}} + \frac{m_{\mathbf{R}}}{2}\hat{\sigma}^z_{\mathbf{R}}\right) \qquad \text{with} \qquad m_{\mathbf{R}} = \tanh(\beta h^0_{\mathbf{R}}) \ , \tag{7.17}$$

where the $m_{\mathbf{R}}$ can be equivalently regarded as our set of variational parameters. Notice that this choice leads to

$$\left\{\begin{array}{rcl} \langle\hat{\sigma}^z_{\mathbf{R}}\rangle_0 & = & m_{\mathbf{R}} \\ \langle\hat{\sigma}^z_{\mathbf{R}}\hat{\sigma}^z_{\mathbf{R}'}\rangle_0 & \equiv & \langle\hat{\sigma}^z_{\mathbf{R}}\rangle_0\,\langle\hat{\sigma}^z_{\mathbf{R}'}\rangle_0 = m_{\mathbf{R}}m_{\mathbf{R}'} \end{array}\right. .$$

Hence, as you see, the site-factorisation of the trial density matrix leads to *ignoring correlations* between the spins! The variational free-energy, energy and entropy are given by:

$$\begin{aligned} F_{\mathrm{var}}[\{m_{\mathbf{R}}\}] &= E[\{m_{\mathbf{R}}\}] - TS[\{m_{\mathbf{R}}\}] \\ E[\{m_{\mathbf{R}}\}] &= \mathrm{Tr}\left(\hat{\rho}_0\widehat{H}\right) = -\sum_{\langle\mathbf{R},\mathbf{R}'\rangle} J_{\mathbf{R},\mathbf{R}'}m_{\mathbf{R}}m_{\mathbf{R}'} - \sum_{\mathbf{R}} h_{\mathbf{R}}m_{\mathbf{R}} \\ S[\{m_{\mathbf{R}}\}] &= -k_B\,\mathrm{Tr}\left(\hat{\rho}_0\log\hat{\rho}_0\right) = -k_B\sum_{\mathbf{R}}\left[\left(\frac{1+m_{\mathbf{R}}}{2}\right)\log\left(\frac{1+m_{\mathbf{R}}}{2}\right) + \left(\frac{1-m_{\mathbf{R}}}{2}\right)\log\left(\frac{1-m_{\mathbf{R}}}{2}\right)\right] \end{aligned}$$

---

[3] Recall that $\mathrm{e}^{x\hat{\sigma}^z} = \mathbb{1}\cosh x + \hat{\sigma}^z\sinh x$.

Now we can set our variational parameters $m_{\mathbf{R}}$ by requiring that $\frac{\partial F_{\text{var}}}{\partial m_{\mathbf{R}}} = 0$. The calculation is simple, since

$$0 = \frac{\partial F_{\text{var}}}{\partial m_{\mathbf{R}}} = -\sum_{\mathbf{R}'} J_{\mathbf{R},\mathbf{R}'} m_{\mathbf{R}'} - h_{\mathbf{R}} + \frac{k_B T}{2} \log \frac{1+m_{\mathbf{R}}}{1-m_{\mathbf{R}}} \ ,$$

from which it follows that

$$\beta\Big(\sum_{\mathbf{R}'} J_{\mathbf{R},\mathbf{R}'} m_{\mathbf{R}'} + h_{\mathbf{R}}\Big) = \frac{1}{2} \log \frac{1+m_{\mathbf{R}}}{1-m_{\mathbf{R}}} \equiv \tanh^{-1}(m_{\mathbf{R}}) \ ,$$

where the last equality follows easily from the hyperbolic tangent relationship:

$$\tanh\left(\frac{1}{2}\log\frac{1+x}{1-x}\right) = x \ .$$

The mean-field equations. In conclusion, the variational parameters $m_{\mathbf{R}}$ have to satisfy the following *mean-field equations*

$$m_{\mathbf{R}} = \tanh(\beta \sum_{\mathbf{R}'} J_{\mathbf{R},\mathbf{R}'} m_{\mathbf{R}'} + \beta h_{\mathbf{R}}) \ . \tag{7.18}$$

Suppose that our Ising system was an *ordered* ferromagnetic model with $J_{\mathbf{R},\mathbf{R}'} = J > 0$ on all nearest-neighbor bonds of a certain lattice with coordination z (i.e., each site has z nearest neighbors; for a cubic lattice in d-dimensions, $z = 2d$) [4] and $h_{\mathbf{R}} = h$ on all sites. Then, looking for solutions that are uniform over all sites, $m_{\mathbf{R}} = m$, we can rewrite our mean-field equations as a single relationship for m:

$$m = \tanh(z\beta J m + \beta h) \ . \tag{7.19}$$

Let us consider first the case $h = 0$, where the previous equation reduces to $m = \tanh(z\beta J m)$ which is easy to analyse graphically, as sketched in Fig. 7.2. $m = 0$ is always a (paramagnetic) solution of the previous equation. If $z\beta J < 1$, a simple inspection of the graph of $\tanh(z\beta J m)$ shows that $m = 0$ is the only solution. However, for $\beta z J > 1$ two more solutions with $\pm m \neq 0$ are allowed. Hence, the transition occurs when the slope of $\tanh(z\beta J m)$ versus m is exactly 1:

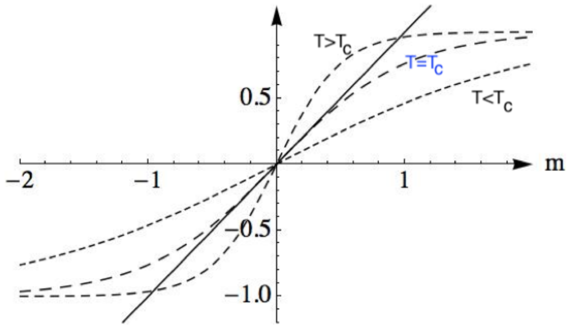

Figure 7.2: The graphical solution of the self-consistency mean-field equation $m = \tanh(z\beta J m)$ for the magnetization m of the homogeneous Ising model at $h = 0$.

$$\beta_c z J = 1 \quad \Longrightarrow \quad k_B T_c = zJ \ . \tag{7.20}$$

This critical T_c signals the temperature below which a uniform magnetisation $m(T) \neq 0$ is possible. Indeed, if you rewrite your variational free-energy per spin $f = F/N$ for a uniform m as:

$$f = -\frac{zJ}{2}m^2 - hm + k_B T\left[\left(\frac{1+m}{2}\right)\log\left(\frac{1+m}{2}\right) + \left(\frac{1-m}{2}\right)\log\left(\frac{1-m}{2}\right)\right] \tag{7.21}$$

---

[4] More generally, we could express the result in terms of the $\mathbf{q} = 0$ Fourier transform of $J_{\mathbf{R},\mathbf{R}'}$, since $\hat{J}(0) = \sum_j J_{\mathbf{R},\mathbf{R}'}$. For nearest-neighbor couplings only, $\hat{J}(0) = zJ$.

you easily realize that when $T < T_c$ and $h = 0$ indeed the solution with $m(T) \neq 0$ guarantees a lower free-energy than the paramagnetic solution with $m = 0$, whose free-energy is $f_0 = -k_B T \log 2$. Fig. 7.3 shows plots of $\Delta f = f(m) - f_0$ for values of T around T_c. To better understand the behaviour close to the critical point, you can expand the logarithms appearing in the entropic contribution, obtaining:

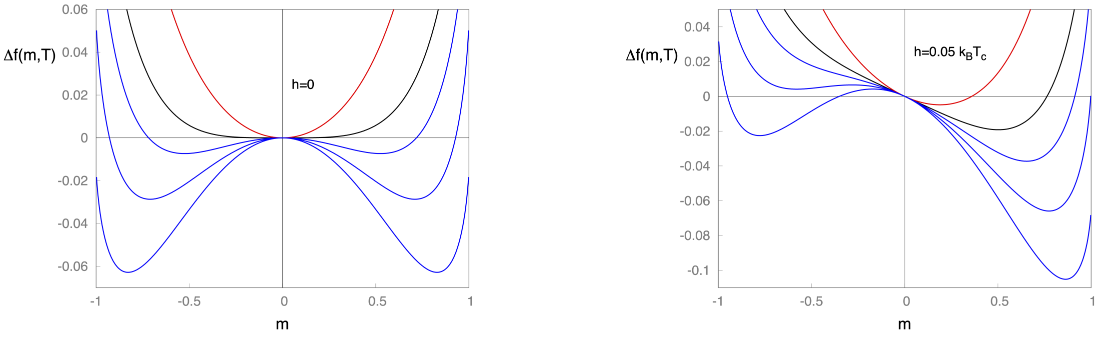

Figure 7.3.: The free-energy per spin $\Delta f = (f + k_B T \log 2)/(zJ)$ versus m, for several values of $k_B T/(zJ) = T/T_c = 1.25, 1, 0.9, 0.8, 0.7$ around the transition point in zero field $h = 0$ (left) and for a finite field $h = 0.05(zJ)$ (right).

$$
\begin{aligned}
f(m,h,T) &= -\frac{zJ}{2} m^2 - hm - k_B T \log 2 + \frac{k_B T}{2} m^2 + \frac{k_B T}{12} m^4 + \cdots \\
&= -k_B T \log 2 - hm + \frac{(k_B T - zJ)}{2} m^2 + \frac{k_B T}{12} m^4 + \cdots \\
&\equiv f_0(T) - hm + \frac{1}{2} a(T)\, m^2 + \frac{1}{4} b(T)\, m^4 + \cdots \; .
\end{aligned}
\tag{7.22}
$$

This type of expansion is known as *Landau expansion*. Notice the characteristic quadratic term $a(T)m^2$ with $a(T) = k_B(T - T_c)$ which changes sign, becoming negative, for $T < T_c$, with the accompanying positive fourth-order term $b(T)m^4$. Notice also that the only *odd power* term is of first-order in m, and originates from the energy contribution due to external field. To understand the vicinity of the critical point we can directly use the Landau expansion of the variational free-energy. The battle between the $a(T)m^2$ term and the $b(T)m^4$ ends-up giving a non-vanishing *order parameter* $m(T < T_c)$ which grows below T_c as [5]

$$
m(T < T_c) \simeq A(T_c - T)^{\frac{1}{2}} \; . \tag{7.23}
$$

When the external field is non-zero, the mean-field solution has always $m \neq 0$. Exactly at T_c, the Landau free-energy is $f(m,h,T_c) = f_0(T) - hm + \frac{1}{4} b(T_c) m^4 + \cdots$, hence setting to zero its derivative immediately gives that the magnetisation will grow like

$$
m(T_c, h) \simeq \left(\frac{h}{b(T_c)} \right)^{\frac{1}{3}} \sim h^{\frac{1}{3}} \; . \tag{7.24}
$$

Starting from high temperatures, you realize that above T_c and for small h [6] we have:

$$
m(h,T) = \frac{h}{k_B(T - T_c)} + \cdots \quad \Longrightarrow \quad \chi = \frac{\partial m}{\partial h}\bigg|_{h=0} = \frac{1}{k_B(T - T_c)} \; , \tag{7.25}
$$

---

[5] The derivative of the Landau free-energy can be written as

$$
\frac{\partial f}{\partial m} = m\Big(a(T) + b(T) m^2 + \cdots \Big) \; ,
$$

hence the ordered solution has

$$
m^2 = -\frac{a(T)}{b(T)} = \frac{3(T_c - T)}{T} \; .
$$

[6] There the Landau free-energy is $f(m,h,T > T_c) = f_0(T) - hm + \frac{k_B}{2}(T - T_c) m^2 + \cdots$ and the derivative immediately gives $m(h, T > T_c)$.

where χ is the *zero-field uniform susceptibility.*

Finally, one can calculate the full mean-field free-energy in zero-field by solving for $m(T)$ and writing

$$f(T) \equiv f(m(T), 0, T) \ .$$

Armed with $f(T)$, we can calculate the specific heat (per spin)

$$c_v = -T\frac{\partial^2 f}{\partial T^2} \ .$$

For $T > T_c$ we have $m(T) = 0$ hence $f(T > T_c) = -k_B T \log 2$ and $c_v(T > T_c) = 0$. For $T \lesssim T_c$ we find $m^2(T) \approx 3(T_c - T)/T$ hence

$$f(T \lesssim T_c) = -k_B T \log 2 - \frac{3}{4}k_B \frac{(T_c - T)^2}{T} + \cdots \ ,$$

which leads to the prediction that c_v *jumps* to $\frac{3}{2}k_B$ for $T \lesssim T_c$ in a discontinuous fashion. The full curve for $c_v(T)$ — which goes back to 0 for $T \to 0$ — is more complicated, but it can be re-expressed in terms of $m(T)$.

Exercise 7.2. Calculate $c_v(T)$ in terms of $m(T)$ by differentiating twice $f(m(T), 0, T)$ with respect to T, using the chain rule and the fact that $\partial f/\partial m = 0$. After having solved (numerically) for $m(T)$, plot $m(T)$, $f(T)$ and $c_v(T)$ versus T.

For a second-order critical point, you generally write that the *order parameter* grows like

$$m(T < T_c, h = 0) \sim (T_c - T)^{\beta} \ , \tag{7.26}$$

the uniform susceptibility diverges like

$$\chi(T) = \frac{\partial m}{\partial h}\bigg|_{h=0} \sim |T - T_c|^{-\gamma} \ , \tag{7.27}$$

the critical point order parameter grows like

$$m(h, T_c) \sim |h|^{1/\delta} \ , \tag{7.28}$$

the specific heat diverges like

$$c_v(T) \sim |T - T_c|^{-\alpha} \ , \tag{7.29}$$

with *critical exponents* β, γ, δ, α that depend on dimensionality and the symmetry of the order parameter — in brief, on what is known as the *universality class* of the problem — but not on the other microscopic details of the model. Mean-field predicts $\beta = \frac{1}{2}$, $\gamma = 1$, $\delta = 3$, and $\alpha = 0$ (a jump discontinuity) but the exact exponents, for instance, of *two-dimensional Ising model* are $\beta = \frac{1}{8}$, $\gamma = \frac{7}{4}$, $\delta = 15$, $\alpha = 0$ (a *logarithmic* divergence). More about this further below, and in our general previous discussion, where we introduced the anomalous exponent η entering in the two-point correlation function, and the exponent ν entering in the correlation length divergence, as well as their hyperscaling relation $\gamma = (2 - \eta)\nu$.

The mean-field predictions tend to come closer and closer to the true critical results as the dimensionality of the problem increases until mean-field becomes exact at and above the so-called *upper critical dimension.* Depending on whether the symmetry of the order parameter is discrete or continuous, there can also be a *lower critical dimension* at and below which no phase transition occurs at finite $T > 0$. We have seen that when discussing the Mermin-Wagner theorem.

7.1.2. Fluctuation-dissipation relationships and mean-field correlations

We already stressed the fact that, apparently, the site-factorised mean-field *Ansatz* for the density matrix completely misses correlations between spins. Should we then abandon any hope of calculating a reasonable expression for the spin-spin correlation function? The answer is a bit surprising: no.

Indeed, we discussed that the exact correlation function is related, in equilibrium, to a response function, the susceptibility, see Eq. (5.33):

$$C^{\mathrm{conn}}_{\mathbf{R},\mathbf{R}'} = k_B T \chi_{\mathbf{R},\mathbf{R}'} \;. \tag{7.30}$$

As we saw, the connected correlations $C^{\mathrm{conn}}_{\mathbf{R},\mathbf{R}'}$, when calculated directly from the trial density matrix, vanish in mean-field. But the response functions $\chi_{\mathbf{R},\mathbf{R}'}$ can be calculated in mean-field, and they *do not vanish*. Hence you can use this trick to extract our mean-field estimate for the spin-spin correlation function. To carry out this calculation, let us start from our general mean-field equations (7.18):

$$m_{\mathbf{R}} = \tanh(\beta \sum_{\mathbf{R}'} J_{\mathbf{R},\mathbf{R}'} m_{\mathbf{R}'} + \beta h_{\mathbf{R}}) = \beta \sum_{\mathbf{R}'} J_{\mathbf{R},\mathbf{R}'} m_{\mathbf{R}'} + \beta h_{\mathbf{R}} + \cdots \;,$$

where in the second step we assumed $T > T_c$, a small $h_{\mathbf{R}}$ and $m_{\mathbf{R}}$ also *small* — proportional to the small external fields —, and expanded the hyperbolic tangent. This easily leads to:

$$\sum_{\mathbf{R}'} \Big(k_B T \delta_{\mathbf{R},\mathbf{R}'} - J_{\mathbf{R},\mathbf{R}'} \Big) m_{\mathbf{R}'} = h_{\mathbf{R}} + \cdots \;. \tag{7.31}$$

Let us now assume that $J_{\mathbf{R},\mathbf{R}'} = J_{\mathbf{R}-\mathbf{R}'}$, translational invariant, where $\mathbf{R}$ are Bravais lattice sites, and introduce the usual lattice Fourier transform for lattice functions $f_{\mathbf{R}}$:

$$\begin{cases} \hat{f}(\mathbf{q}) & \equiv \displaystyle\sum_{\mathbf{R}} f_{\mathbf{R}}\, \mathrm{e}^{-i\mathbf{q}\cdot\mathbf{R}} \\ f_{\mathbf{R}} & \equiv \displaystyle\frac{1}{N}\sum_{\mathbf{q}}^{\mathrm{BZ}} \hat{f}(\mathbf{q})\, \mathrm{e}^{i\mathbf{q}\cdot\mathbf{R}} \xrightarrow{N\to\infty} \Omega_c \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}}{(2\pi)^d}\, \hat{f}(\mathbf{q})\, \mathrm{e}^{i\mathbf{q}\cdot\mathbf{R}} \end{cases} , \tag{7.32}$$

where Ω_c denotes the volume of the direct-lattice (Wigner-Seitz) unit cell, and we have taken the limit $N\to\infty$ in the last expression. Then the convolution in Eq. (7.31) is a simple product in Fourier space:

$$\underbrace{\big(k_B T - \hat{J}(\mathbf{q})\big)}_{\hat{\chi}^{-1}(\mathbf{q})} \hat{m}(\mathbf{q}) = \hat{h}(\mathbf{q}) \quad\Longrightarrow\quad \hat{m}(\mathbf{q}) = \frac{\hat{h}(\mathbf{q})}{k_B T - \hat{J}(\mathbf{q})} \equiv \hat{\chi}(\mathbf{q})\, \hat{h}(\mathbf{q}) \;. \tag{7.33}$$

Now we expand $\hat{J}(\mathbf{q})$ at small wave-vectors: [7]

$$\begin{aligned} \hat{J}(\mathbf{q}) &= \sum_{\mathbf{R}} J_{\mathbf{R}}\, \mathrm{e}^{-i\mathbf{q}\cdot\mathbf{R}} = \sum_{\mathbf{R}} J_{\mathbf{R}} \left(1 - i\mathbf{q}\cdot\mathbf{R} - \frac{1}{2}(\mathbf{q}\cdot\mathbf{R})^2 + \cdots \right) \\ &= \hat{J}(0)\left(1 - q^2 R_*^2 + O(q^4)\right) \;, \end{aligned} \tag{7.34}$$

where we have assumed inversion symmetry, which makes the linear term disappear, and simplified the quadratic term to:

$$\sum_{\mathbf{R}} R^\alpha R^\beta J_{\mathbf{R}} = \delta_{\alpha\beta} \frac{1}{d} \sum_{\mathbf{R}} \mathbf{R}^2 J_{\mathbf{R}} \overset{\mathrm{def}}{=} \delta_{\alpha\beta} 2R_*^2 \sum_{\mathbf{R}} J_{\mathbf{R}} \;.$$

---

[7] The expansion is particularly simple if we consider a cubic lattice with nearest-neighbour interactions only, for which

$$\hat{J}(\mathbf{q}) = 2J \sum_{\alpha} \cos(q_\alpha a) = 2J \sum_{\alpha} \left(1 - \frac{1}{2} q_\alpha^2 a^2 + \cdots \right) = zJ - Ja^2 q^2 + \cdots$$

The definition of R_*^2 introduced in the previous expression is essentially "the second moment" of the couplings $J_{\mathbf{R}}$: for a cubic lattice in d dimensions with nearest-neighbor couplings only, one finds $R_*^2 = \frac{a^2}{2d}$. Substituting the expansion of $\hat{J}(\mathbf{q})$ in the expression for the susceptibility $\hat{\chi}(\mathbf{q})$, recalling that $k_B T_c = \hat{J}(0)$, we find:

$$\begin{aligned}\hat{\chi}(\mathbf{q}) = \frac{1}{k_B T - \hat{J}(\mathbf{q})} &= \frac{1}{k_B T - \hat{J}(0) + \hat{J}(0) R_*^2 q^2 + O(q^4)} \\ &= \frac{1}{k_B (T - T_c) + k_B T_c R_*^2 q^2 + O(q^4)} \\ &= \frac{1}{k_B T_c R_*^2} \, \frac{1}{\xi^{-2} + q^2 + O(q^4)} \, , \end{aligned} \tag{7.35}$$

wherein the last expression we have introduced the *correlation length*

$$\xi = R_* \left(\frac{T - T_c}{T_c} \right)^{-\frac{1}{2}} \, . \tag{7.36}$$

Ornstein-Zernike lorentzian form. This Lorentzian form of $\chi(\mathbf{q})$ is usually called *Ornstein-Zernike* form (or approximation):

$$\hat{\chi}(\mathbf{q}) = \frac{A}{\xi^{-2} + q^2} \, . \tag{7.37}$$

Recall that this derivation is valid only for $T > T_c$ and small $h_{\mathbf{R}}$, which is the regime in which we were able to expand the mean-field equations and write Eq. (7.31). (For $T < T_c$ and small $h_{\mathbf{R}}$ we should expand the mean-field equations around a zero-field $m_{\mathbf{R}} \neq 0$.) Observe also that this expression for $\hat{\chi}(\mathbf{q})$ implies that (as previously derived from the uniform mean-field calculation):

$$\hat{\chi}(\mathbf{q} = 0, T) = \frac{\xi^2}{k_B T_c R_*^2} = \frac{1}{k_B (T - T_c)} \, . \tag{7.38}$$

More generally, the theory of critical phenomena developed in the 1960-1970s tells us that the correlation function diverges near T_c with an exponent ν

$$\xi(T) \sim \begin{cases} A_+ (T - T_c)^{-\nu} & \text{for } T > T_c \\ A_- (T_c - T)^{-\nu} & \text{for } T < T_c \end{cases} \, , \tag{7.39}$$

where $A_\pm$ are non-universal prefactors. Mean-field predicts $\nu = 1/2$. Similarly, the uniform susceptibility is known to diverge in general with an exponent γ (again, in general with different prefactors on the two sides of the transition):

$$\chi(T) \sim |T - T_c|^{-\gamma} \, . \tag{7.40}$$

The Ornstein-Zernike Lorentzian form for $\chi(\mathbf{q}, T)$ would suggest that $\gamma = 2\nu$, which turns out to be incorrect. In general, as we saw, a hyperscaling relation applies

$$\gamma = (2 - \eta)\nu \, , \tag{7.41}$$

where the exponent η — introduced in 1963 by M.E. Fisher — is known as *anomalous scaling exponent*: it enters in the long-distance behaviour of the connected correlation function.

If you want to get the correlation function $C^{\text{conn}}_{\mathbf{R}-\mathbf{R}'} = k_B T \chi_{\mathbf{R}-\mathbf{R}'}$, you need to calculate the inverse Fourier transform of $\hat{\chi}(\mathbf{q})$. For a translationally invariant system with nearest-neighbour Ising interactions on a d-dimensional cubic lattice, we might write the exact expression for the mean-field correlations as:

$$\begin{aligned} C^{\mathrm{conn}}_{\mathbf{R}-\mathbf{R}'} = k_B T \chi_{\mathbf{R}-\mathbf{R}'} &= k_B T\, a^d \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}}{(2\pi)^d} \frac{\mathrm{e}^{i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')}}{k_B T - \hat{J}(\mathbf{q})} \\ &= k_B T\, a^d \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}}{(2\pi)^d} \frac{\mathrm{e}^{i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')}}{k_B T - 2J\sum_\alpha \cos{(q_\alpha a)}} \;. \end{aligned} \tag{7.42}$$

To calculate the correlations for large values of $\mathbf{R}-\mathbf{R}'$, we extend the integral to all $\mathbf{q}$s — because the large $\mathbf{q}$ contribution indeed is small, as the phase-factor oscillates wildly — and approximate the denominator with its lowest-order terms, which should be the only ones important for the long-distance behaviour in the near-critical region:

$$C^{\mathrm{conn}}_{\mathbf{R}-\mathbf{R}'} \approx \frac{T}{T_c} \frac{a^d}{R_*^2} \int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^d} \frac{\mathrm{e}^{i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')}}{\xi^{-2}+q^2} \;. \tag{7.43}$$

The relevant integral which appears can then be written as:

$$G(\mathbf{x}) = \int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^d} \frac{\mathrm{e}^{i\mathbf{q}\cdot\mathbf{x}}}{\xi^{-2}+q^2} \;, \tag{7.44}$$

i.e., essentially (minus) the Green's function [8] of the operator $\nabla^2 - m^2$, with the identification $m = 1/\xi$. The integral can be computed analytically in $d=1$ and $d=3$, by the method of residues. In $d=1$ and $d=3$ we find:

$$\begin{cases} G_{1d}(x) &= \dfrac{\xi}{2}\mathrm{e}^{-x/\xi} \\[2ex] G_{3d}(\mathbf{x}) &= \dfrac{1}{4\pi|\mathbf{x}|}\mathrm{e}^{-|\mathbf{x}|/\xi} \end{cases} \tag{7.45}$$

In $d=3$ you recognize the usual screened Coulomb potential, which gives an innocuous $1/(4\pi|\mathbf{x}|)$ at exact criticality $\xi\to\infty$. In $d=2$ the angular integral involves a Bessel function, and the result is more complicated. [9] Nevertheless, we see quite clearly that close to criticality, $\xi\to\infty$, the integral has a logarithmic divergence — from the $\mathbf{q}=0$ (infrared) region — and we can estimate

$$G_{2d}(\mathbf{x}) \sim \log\left(\frac{\xi}{|\mathbf{x}|}\right)\mathrm{e}^{-|\mathbf{x}|/\xi} \;.$$

The result for $d=2$ (and that for $d=1$ as well) is very *unphysical*: the correlation function at a given finite distance $|\mathbf{R}-\mathbf{R}'|$ *should not diverge* as $T\to T_c$, i.e., when you send $\xi\to\infty$. As a remedy for this unphysical behaviour, M.E. Fisher proposed, in 1963, that the Ornstein-Zernike form should be *amendend*, in the region $|\mathbf{x}|\ll\xi$, with the *anomalous scaling* form for the correlations:

$$C(\mathbf{x}) \propto \chi(\mathbf{x}) \sim \frac{\mathrm{e}^{-|\mathbf{x}|/\xi}}{|\mathbf{x}|^{d-2+\eta}} \;. \tag{7.46}$$

An integral over space will now give a uniform susceptibility $\chi(\mathbf{q}=0,T)$ diverging as:

$$\chi(\mathbf{q}=0,T) \sim \int \mathrm{d}\mathbf{x}\, \frac{\mathrm{e}^{-|\mathbf{x}|/\xi}}{|\mathbf{x}|^{d-2+\eta}} \sim \xi^{2-\eta} \sim |T-T_c|^{-(2-\eta)\nu} \;,$$

leading to the hyperscaling relation $\gamma = (2-\eta)\nu$, as we already saw. For the $2d$ Ising model the exact solution gives $\eta = \frac{1}{4}$, $\nu = 1$, and $\gamma = \frac{7}{4}$, hence hyperscaling is satisfied. In mean-field, we get $\eta = 0$, $\nu = \frac{1}{2}$ and $\gamma = 1$.

---

[8] The Green's function

$$(\nabla^2 - m^2)\, G(\mathbf{x}) = \delta(\mathbf{x}) \;,$$

emerges in the Yukawa theory of massive mesons — essentially, $\nabla^2 - m^2$ is a time-independent Klein-Gordon equation and m is the mass of the meson — or, equivalently, as the Poisson's equation in the presence of screening of the Coulomb potential, $\xi = 1/m$ being the screening length.

[9] See Mussardo's book, Sec. 7.4, for details.

7.2. The Ginzburg-Landau description

The goal of this section is to justify the Ginzburg-Landau-Wilson expression of the free-energy *functional*

$$F[m(\mathbf{x})] = \int \mathrm{d}\mathbf{x} \left\{ f_0 + \frac{1}{2}am^2 + \frac{1}{4}bm^4 + \frac{1}{6}cm^6 - hm + \frac{1}{2}\kappa(\nabla m)^2 + \cdots \right\} , \tag{7.47}$$

where $m(\mathbf{x})$ is in general an n-component field, and $h(\mathbf{x})$ possibly space-dependent: we will concentrate in the following only in the $n = 1$ (scalar) field case, relevant to the Ising model.

This is the generalization of the *constrained-magnetization* free-energy which we previously wrote for the fully-connected Ising ferromagnet, see Eq. (5.19). In principle, such a functional should restitute the full correct partition function upon integration: [10]

$$Z = \sum_{\sigma}^{\text{Configs}} \mathrm{e}^{-\beta H[\sigma]} = \int Dm(\mathbf{x})\, \mathrm{e}^{-\beta F[m(\mathbf{x})]} . \tag{7.48}$$

Hence, you might be tempted to write a formal functional integral expression of the type:

$$\begin{aligned} Z &= \sum_{\underline{\sigma}}^{\text{Configs}} \int \mathrm{D}m(\mathbf{x}) \sum_{\mathbf{R}} \delta(m(\mathbf{x}) - \sigma_{\mathbf{R}})\, \mathrm{e}^{-\beta H[\underline{\sigma}]} = \int \mathrm{D}m(\mathbf{x})\, \mathrm{e}^{-\beta F[m(\mathbf{x})]} \\ F[m(\mathbf{x})] &= -\frac{1}{\beta} \log \left[\sum_{\sigma}^{\text{Configs}} \sum_{\mathbf{R}} \delta(m(\mathbf{x}) - \sigma_{\mathbf{R}})\, \mathrm{e}^{-\beta H[\sigma]} \right] \end{aligned} , \tag{7.49}$$

wherein the definition for Z we played the usual trick of inserting an integral with a δ-function. But you immediately realize how hard it would be — even once you have given a meaning to the formal expression for the $\delta(m(\mathbf{x}) - \sigma_{\mathbf{R}})$ by a suitable coarse-graining in space — to calculate such restricted partition sums. So, we go through to a different route, which we have also used in the fully-connected Ising ferromagnet: the Gaussian integral transformation.

Consider again the partition function of the classical Ising model, written explicitly

$$Z = \sum_{\underline{\sigma}}^{\text{Configs}} \mathrm{e}^{-\beta H[\underline{\sigma}]} = \sum_{\underline{\sigma}}^{\text{Configs}} \mathrm{e}^{\beta \sum_{\langle \mathbf{R},\mathbf{R}' \rangle} J_{\mathbf{R},\mathbf{R}'} \sigma_{\mathbf{R}} \sigma_{\mathbf{R}'} + \beta \sum_{\mathbf{R}} h_{\mathbf{R}} \sigma_{\mathbf{R}}} . \tag{7.50}$$

The whole difficulty comes from the interactions present in the "quadratic terms", which are only "*deceptively quadratic*" since the relevant variables are discrete, $\sigma_{\mathbf{R}} = \pm 1$, and not continuous variables on which to integrate (like in a Gaussian integral). But here the very useful Gaussian identity comes to rescue us:

$$\int_{-\infty}^{+\infty} \frac{\mathrm{d}y}{\sqrt{2\pi a}}\, \mathrm{e}^{-\frac{y^2}{2a} + sy} = \mathrm{e}^{\frac{as^2}{2}} , \tag{7.51}$$

with $a > 0$ (otherwise, the Gaussian integral diverges), and s any variable (including a complex one). This identity follows from the simple Gaussian integral by completing the square. [11] More generally, for many variables, you can prove, by diagonalising and reducing to one-dimensional integrals, [12] the following generalisation of the previous identity:

---

[10] The integrals appearing below are functional integrals, for which we will give a more precise definition later on, by specifying the integration measure in the case of periodic functions in a finite volume V.

[11] If you need to get to $\mathrm{e}^{-\frac{as^2}{2}}$, still with $a > 0$, you need to explicitly invoke complex numbers, setting $s \to is$ and writing:

$$\int_{-\infty}^{+\infty} \frac{\mathrm{d}y}{\sqrt{2\pi a}}\, \mathrm{e}^{-\frac{y^2}{2a} + isy} = \mathrm{e}^{-\frac{as^2}{2}} ,$$

an identity that is also useful when you are dealing with Fourier transforms. Nevertheless, care should be exercised when using such complex extensions in Quantum Monte Carlo, as they typically introduce severe sign-problems (indeed, phase-problems).

[12] See derivation in Negele-Orland, Ref. [35].

Gaussian identity. If $\mathbb{A}$ is a *positive definite* symmetric real $N \times N$ matrix, then

$$\frac{1}{\sqrt{(2\pi)^N \det \mathbb{A}}} \int \mathrm{d}\mathbf{y} \; \mathrm{e}^{-\frac{1}{2}\mathbf{y}^{\mathrm{T}}\mathbb{A}^{-1}\mathbf{y}+\mathbf{s}\cdot\mathbf{y}} = \mathrm{e}^{\frac{1}{2}\mathbf{s}^{\mathrm{T}}\mathbb{A}\,\mathbf{s}} \,. \tag{7.52}$$

Here we adopted a compact notation, writing for instance $\mathbf{s}^{\mathrm{T}}\mathbb{A}\,\mathbf{s} = \sum_{jj'} s_j A_{jj'} s_{j'}$ and $\mathbf{s}\cdot\mathbf{y} = \sum_j s_j y_j$. Once again, the variables s_j can be anything: for us, in a moment, they will be the Ising discrete variables $\sigma_{\mathbf{R}}$.

This is the strategy behind the so-called *Hubbard-Stratonovich* transformation introduced in the late 1950s to similarly transform, in a many-body context, quartic interaction terms into quadratic ones, at the expense of integrating over a fluctuating auxiliary field variable. More precisely, suppose you have a fermionic Hubbard model

$$\widehat{H} = \overbrace{-t\sum_{\langle jj'\rangle}\sum_{\sigma=\uparrow,\downarrow}(\hat{c}^{\dagger}_{j\sigma}\hat{c}_{j'\sigma} + \mathrm{H.c.})}^{\hat{K}} + \overbrace{U\sum_j \hat{n}_{j\uparrow}\hat{n}_{j\downarrow}}^{\hat{V}} = \hat{K} + \hat{V} \,, \tag{7.53}$$

and you apply a Trotter decomposition to the imaginary time propagator:

$$\mathrm{e}^{-\Delta\tau\widehat{H}} = \mathrm{e}^{-\frac{\Delta\tau}{2}\hat{V}}\mathrm{e}^{-\Delta\tau\hat{K}}\mathrm{e}^{-\frac{\Delta\tau}{2}\hat{V}} \,.$$

Then, the quartic term present in the interaction can be transformed, using $\hat{n}^2_{j\sigma} = \hat{n}_{j\sigma}$, as follows:

$$\begin{aligned}
\mathrm{e}^{-\frac{\Delta\tau}{2}\hat{V}} = \mathrm{e}^{-\frac{\Delta\tau U}{2}\sum_j \hat{n}_{j\uparrow}\hat{n}_{j\downarrow}} &= \mathrm{e}^{\frac{\Delta\tau U}{4}\sum_j(\hat{n}_{j\uparrow}-\hat{n}_{j\downarrow})^2}\mathrm{e}^{-\frac{\Delta\tau U}{4}\sum_j(\hat{n}_{j\uparrow}+\hat{n}_{j\downarrow})} \\
&= \mathrm{e}^{\frac{\Delta\tau U}{4}\sum_j(\hat{n}_{j\uparrow}-\hat{n}_{j\downarrow})^2}\mathrm{e}^{-\frac{\Delta\tau U}{4}\widehat{N}} \,.
\end{aligned} \tag{7.54}$$

Next, you rewrite, using a Gaussian identity:

$$\mathrm{e}^{\frac{g}{2}(\hat{n}_{j\uparrow}-\hat{n}_{j\downarrow})^2} = \int_{-\infty}^{+\infty}\frac{\mathrm{d}x_j}{\sqrt{2\pi}}\,\mathrm{e}^{-\frac{1}{2}x_j^2}\mathrm{e}^{\sqrt{g}\,x_j(\hat{n}_{j\uparrow}-\hat{n}_{j\downarrow})}$$

where $g = \Delta\tau U/2 > 0$. Hence, the propagator involving the interaction term is now rewritten as:

$$\mathrm{e}^{-\frac{\Delta\tau}{2}\hat{V}} = \mathrm{e}^{-\frac{\Delta\tau U}{4}\widehat{N}}\prod_{j=1}^{L}\int_{-\infty}^{+\infty}\frac{\mathrm{d}x_j}{\sqrt{2\pi}}\,\mathrm{e}^{-\frac{1}{2}x_j^2}\mathrm{e}^{\sqrt{g}\,x_j(\hat{n}_{j\uparrow}-\hat{n}_{j\downarrow})} \,,$$

which involves a much simpler *quadratic* fermion term, at the cost of having introduced, for every lattice site, an auxiliary (real) variable x_j over which we need to integrate. Notice how crucial it is that $g = \Delta\tau U/2 > 0$. [13] This procedure is at the root of Auxiliary Field QMC, as explained in the course by Prof. Sorella.

Returning to our classical Ising case, let us ask: do we have a positive-definite matrix appearing in the Ising weight of Eq. (7.50)? Observe that we can write: [14]

$$\beta\sum_{\langle\mathbf{R},\mathbf{R}'\rangle} J_{\mathbf{R},\mathbf{R}'}\sigma_{\mathbf{R}}\sigma_{\mathbf{R}'} = \frac{1}{2}\sum_{\mathbf{R},\mathbf{R}'}\sigma_{\mathbf{R}}K_{\mathbf{R},\mathbf{R}'}\sigma_{\mathbf{R}'} - \frac{1}{2}\sum_{\mathbf{R}}K_{\mathbf{R},\mathbf{R}} = \frac{1}{2}\boldsymbol{\sigma}^{\mathrm{T}}\mathbb{K}\boldsymbol{\sigma} - \frac{1}{2}\mathrm{Tr}\,\mathbb{K} \,,$$

with

$$K_{\mathbf{R},\mathbf{R}'} = \beta J_{\mathbf{R},\mathbf{R}'} = K_{\mathbf{R}',\mathbf{R}} \quad \text{for} \quad \mathbf{R} \neq \mathbf{R}' \,. \tag{7.55}$$

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[13] In the present case an even simpler *discrete Gaussian identity* can be used:

$$\mathrm{e}^{\frac{g}{2}(\hat{n}_{j\uparrow}-\hat{n}_{j\downarrow})^2} = \frac{1}{2}\sum_{\sigma_j=\pm1}\mathrm{e}^{\lambda\,\sigma_j(\hat{n}_{j\uparrow}-\hat{n}_{j\downarrow})}$$

where $\cosh\lambda = \mathrm{e}^{g/2}$.

[14] Recall that $\langle\mathbf{R},\mathbf{R}'\rangle$ is the prescription to sum over pairs with $\mathbf{R}' \neq \mathbf{R}$ and *only once*.

Since the diagonal elements $K_{\mathbf{R},\mathbf{R}}$ do not appear in the original Ising weight, I have added and subtracted them, with the last trace-term. Now, you might be tempted to think that, no, $\mathbb{K}$ is not positive definite, because even for a nearest-neighbour ferromagnetic model in $d=1$ you have that $\mathbb{K}$ is given by:

$$\mathbb{K} = \beta J \begin{pmatrix} 0 & 1 & 0 & \cdots & 0 & 1 \\ 1 & 0 & 1 & 0 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & \cdots & 1 & 0 & 1 \\ 1 & 0 & \cdots & 0 & 1 & 0 \end{pmatrix}$$

and you will immediately recognise that it has eigenvalues $2(\beta J)\cos(qa)$, with the usual wavevectors q of one-dimensional PBC boundary conditions: this is essentially, the tight-binding exercise you have repeatedly done. In general, there are negatives and positive eigenvalues. But, since the spectrum of $\mathbb{K}$ is limited from below, I can always add — and this statement is now general — a suitable constant on the diagonal of $\mathbb{K}$ such that all its eigenvalues become *positive*. This constant added to the diagonal of $\mathbb{K}$ will be exactly cancelled by the $\mathrm{Tr}\,\mathbb{K}$ term, hence I can freely do that and consider $\mathbb{K}$ to be *positive definite*.

Hence, I will now proceed by using the Gaussian integral identity in Eq. (7.52), rewriting:

$$\begin{aligned} \mathrm{e}^{\frac{1}{2}\boldsymbol{\sigma}^{\mathrm{T}}\,\mathbb{K}\boldsymbol{\sigma}} &= \frac{1}{\sqrt{(2\pi)^N \det \mathbb{K}}} \int \mathrm{d}\mathbf{y}\; \mathrm{e}^{-\frac{1}{2}\mathbf{y}^{\mathrm{T}}\mathbb{K}^{-1}\mathbf{y} + \boldsymbol{\sigma}\cdot\mathbf{y}} \\ &= \sqrt{\frac{\det \mathbb{K}}{(2\pi)^N}} \int \mathrm{d}\boldsymbol{\psi}\; \mathrm{e}^{-\frac{1}{2}\boldsymbol{\psi}^{\mathrm{T}}\mathbb{K}\boldsymbol{\psi} + \boldsymbol{\sigma}\cdot(\mathbb{K}\boldsymbol{\psi})} \;, \end{aligned} \tag{7.56}$$

where the second form is obtained by substituting $\mathbf{y} = \mathbb{K}\boldsymbol{\psi}$ and taking account of the Jacobian of the transformation. [15] Here $\int \mathrm{d}\mathbf{y} = \int \prod_{\mathbf{R}} \mathrm{d}y_{\mathbf{R}}$, and similarly $\int \mathrm{d}\boldsymbol{\psi} = \int \prod_{\mathbf{R}} \mathrm{d}\psi_{\mathbf{R}}$, and the integrals are extended from $-\infty$ to $+\infty$. The two forms are equivalent, but we will use the second to deduce the following expression for the partition function:

$$\begin{aligned} Z &= \sum_{\boldsymbol{\sigma}}^{\mathrm{Configs}} \mathrm{e}^{-\frac{1}{2}\mathrm{Tr}\,\mathbb{K}} \sqrt{\frac{\det \mathbb{K}}{(2\pi)^N}} \int \mathrm{d}\boldsymbol{\psi}\; \mathrm{e}^{-\frac{1}{2}\boldsymbol{\psi}^{\mathrm{T}}\mathbb{K}\boldsymbol{\psi} + \boldsymbol{\sigma}\cdot(\mathbb{K}\boldsymbol{\psi} + \beta\mathbf{h})} \\ &= \mathrm{e}^{-\frac{1}{2}\mathrm{Tr}\,\mathbb{K}} \sqrt{\frac{\det \mathbb{K}}{(2\pi)^N}} \int \mathrm{d}\boldsymbol{\psi}\; \mathrm{e}^{-\frac{1}{2}\boldsymbol{\psi}^{\mathrm{T}}\mathbb{K}\boldsymbol{\psi}} \prod_{\mathbf{R}} \Big(2\cosh\big(\sum_{\mathbf{R}'} \mathbb{K}_{\mathbf{R},\mathbf{R}'}\psi_{\mathbf{R}'} + \beta h_{\mathbf{R}}\big)\Big) \\ &= \mathrm{e}^{-S_0} \int \mathrm{d}\boldsymbol{\psi}\; \mathrm{e}^{-\frac{1}{2}\boldsymbol{\psi}^{\mathrm{T}}\mathbb{K}\boldsymbol{\psi}}\; \mathrm{e}^{\sum_{\mathbf{R}} \log\cosh\left(\sum_{\mathbf{R}'} \mathbb{K}_{\mathbf{R},\mathbf{R}'}\psi_{\mathbf{R}'} + \beta h_{\mathbf{R}}\right)} \\ S_0(T) &= -N\log 2 + \frac{N}{2}\log 2\pi + \frac{1}{2}(\mathrm{Tr}\,\mathbb{K} - \log\det\mathbb{K}) \;. \end{aligned} \tag{7.57}$$

Notice that in the second line we have explicitly performed the sum over the configurations, since $\boldsymbol{\sigma}$ now appears *linearly* in the exponential weight, expressing the result in terms of the hyperbolic cosine:

$$\sum_{\boldsymbol{\sigma}}^{\mathrm{Configs}} \mathrm{e}^{\boldsymbol{\sigma}\cdot(\mathbf{y}+\beta\mathbf{h})} = \prod_{\mathbf{R}} \Big(2\cosh(y_{\mathbf{R}} + \beta h_{\mathbf{R}}) \Big) \;.$$

Hence we have expressed Z in terms of the $\boldsymbol{\psi}$ as the following multidimensional integral:

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[15] Notice that:

$$\mathbf{y}^{\mathrm{T}}\mathbb{K}^{-1}\mathbf{y} = \boldsymbol{\psi}^{\mathrm{T}}\mathbb{K}^{\mathrm{T}}\mathbb{K}^{-1}\mathbb{K}\boldsymbol{\psi} = \boldsymbol{\psi}^{\mathrm{T}}\mathbb{K}\boldsymbol{\psi} \;,$$

where we have used that $\mathbb{K}^{\mathrm{T}} = \mathbb{K}$. The Jacobian of the change of variables $\mathbf{y} = \mathbb{K}\boldsymbol{\psi}$ is:

$$\mathrm{d}\mathbf{y} = |\det\mathbb{K}|\,\mathrm{d}\boldsymbol{\psi} = (\det\mathbb{K})\,\mathrm{d}\boldsymbol{\psi} \;,$$

since $\mathbb{K}$ is positive definite.

The functional integral for Z.

$$\begin{aligned} Z &= \mathrm{e}^{-S_0} \int \Big[\prod_{\mathbf{R}}^{N} \mathrm{d}\psi_{\mathbf{R}}\Big]\, \mathrm{e}^{-S[\boldsymbol{\psi},\mathbf{h}]} \\ S[\boldsymbol{\psi},\mathbf{h}] &= \frac{1}{2}\boldsymbol{\psi}^{\mathrm{T}}\mathbb{K}\boldsymbol{\psi} - \sum_{\mathbf{R}} \log\cosh\Big(\sum_{\mathbf{R}'} \mathbb{K}_{\mathbf{R},\mathbf{R}'}\psi_{\mathbf{R}'} + \beta h_{\mathbf{R}}\Big) \end{aligned} \; . \tag{7.58}$$

With these conventions, we still have an exact expression for the partition sum, and the prescription for calculating the averages of observables is evidently:

$$\Big\langle \circ \Big\rangle = \frac{\mathrm{e}^{-S_0}}{Z} \int \Big[\prod_{\mathbf{R}}^{N} \mathrm{d}\psi_{\mathbf{R}}\Big]\, \mathrm{e}^{-S[\boldsymbol{\psi},\mathbf{h}]} \Big(\circ \Big) \, . \tag{7.59}$$

In a totally equivalent way, you might shift the external field from the hyperbolic cosine into the quadratic term by setting $\mathbb{K}\boldsymbol{\phi} = \mathbb{K}\boldsymbol{\psi} + \beta\mathbf{h}$, hence changing variables from $\boldsymbol{\psi} \to \boldsymbol{\phi} = \boldsymbol{\psi} + \beta\mathbb{K}^{-1}\mathbf{h}$.

An equivalent form of functional integral for Z.

$$\begin{aligned} Z &= \mathrm{e}^{-S_0} \int \Big[\prod_{\mathbf{R}}^{N} \mathrm{d}\phi_{\mathbf{R}}\Big]\, \mathrm{e}^{-\widetilde{S}[\boldsymbol{\phi},\mathbf{h}]} \\ \widetilde{S}[\boldsymbol{\phi},\mathbf{h}] &= S[\boldsymbol{\phi} - \beta\mathbb{K}^{-1}\mathbf{h}, \mathbf{h}] \\ &= \frac{1}{2}\Big(\boldsymbol{\phi}^{\mathrm{T}}\mathbb{K}\boldsymbol{\phi} - 2\beta\boldsymbol{\phi}\cdot\mathbf{h} + \beta^2\mathbf{h}^{\mathrm{T}}\mathbb{K}^{-1}\mathbf{h}\Big) - \sum_{\mathbf{R}} \log\cosh\Big(\sum_{\mathbf{R}'} \mathbb{K}_{\mathbf{R},\mathbf{R}'}\phi_{\mathbf{R}'}\Big) \end{aligned} \; . \tag{7.60}$$

Recall now that the average magnetisation $\langle\sigma_{\mathbf{R}}\rangle$ can be obtained by a derivative of Z with respect to $h_{\mathbf{R}}$. From the form of Z in Eq. (7.58) we immediately deduce that:

$$\frac{1}{\beta}\frac{\partial Z}{\partial h_{\mathbf{R}}} = \mathrm{e}^{-S_0} \int \Big[\prod_{\mathbf{R}}^{N} \mathrm{d}\psi_{\mathbf{R}}\Big]\, \mathrm{e}^{-S[\boldsymbol{\psi},\mathbf{h}]} \, \tanh\Big(\sum_{\mathbf{R}'} \mathbb{K}_{\mathbf{R},\mathbf{R}'}\psi_{\mathbf{R}'} + \beta h_{\mathbf{R}}\Big) \, . \tag{7.61}$$

Interestingly, from the second form of Z in Eq. (7.60) we would deduce:

$$\begin{aligned} \frac{1}{\beta}\frac{\partial Z}{\partial h_{\mathbf{R}}} &= \mathrm{e}^{-S_0} \int \Big[\prod_{\mathbf{R}}^{N} \mathrm{d}\phi_{\mathbf{R}}\Big]\, \mathrm{e}^{-\widetilde{S}[\boldsymbol{\phi},\mathbf{h}]} \Big(\phi_{\mathbf{R}} - \beta\sum_{\mathbf{R}'} (\mathbb{K}^{-1})_{\mathbf{R},\mathbf{R}'} h_{\mathbf{R}'}\Big) \\ &= \mathrm{e}^{-S_0} \int \Big[\prod_{\mathbf{R}}^{N} \mathrm{d}\psi_{\mathbf{R}}\Big]\, \mathrm{e}^{-S[\boldsymbol{\psi},\mathbf{h}]} \, \psi_{\mathbf{R}} \, , \end{aligned} \tag{7.62}$$

where in the second line we have shifted back our variables to $\boldsymbol{\psi} = \boldsymbol{\phi} - \beta\mathbb{K}^{-1}\mathbf{h}$.

The local order parameter. From comparing the two expressions in Eqs. (7.61)-(7.62) we immediately conclude that the local order parameter is given by the average of the field $\psi_{\mathbf{R}}$ and is also expressed as:

$$\langle\sigma_{\mathbf{R}}\rangle = \frac{1}{\beta Z}\frac{\partial Z}{\partial h_{\mathbf{R}}} = \langle\psi_{\mathbf{R}}\rangle = \Big\langle \tanh\Big(\sum_{\mathbf{R}'} \mathbb{K}_{\mathbf{R},\mathbf{R}'}\psi_{\mathbf{R}'} + \beta h_{\mathbf{R}}\Big)\Big\rangle \, . \tag{7.63}$$

If you compare this expression to the mean-field relationship Eq. (7.18) which we report below

$$m_{\mathbf{R}} = \tanh\left(\beta\sum_{\mathbf{R}'} J_{\mathbf{R},\mathbf{R}'} m_{\mathbf{R}'} + \beta h_{\mathbf{R}}\right) ,$$

you immediately realise — recalling that $\mathbb{K}_{\mathbf{R},\mathbf{R}'} = \beta J_{\mathbf{R},\mathbf{R}'}$ — that our exact Gaussian-integral relationship reduces to the mean-field one when you approximate the *average of the hyperbolic tangent* of $\psi_{\mathbf{R}'}$ with the *hyperbolic tangent of the average* of $\psi_{\mathbf{R}'}$:

$$m_{\mathbf{R}} = \langle\psi_{\mathbf{R}}\rangle = \left\langle \tanh\left(\sum_{\mathbf{R}'} \mathbb{K}_{\mathbf{R},\mathbf{R}'}\psi_{\mathbf{R}'} + \beta h_{\mathbf{R}}\right)\right\rangle \xrightarrow{\text{MF}} \tanh\left(\sum_{\mathbf{R}'} \mathbb{K}_{\mathbf{R},\mathbf{R}'}\langle\psi_{\mathbf{R}'}\rangle + \beta h_{\mathbf{R}}\right) .$$

So, the machinery we have built is in principle capable of *going beyond mean-field systematically*, accounting for fluctuations, which are responsible for the modification of the mean-field critical exponents. To do so, however, we have to further massage our expressions to make them more "field-theory-like".

Shifting h to the quadratic term. As a first step, we use the functional form of Z in Eq. (7.60), where the external field is in the quadratic term, by changing variables $\boldsymbol{\psi} \to \boldsymbol{\phi} = \boldsymbol{\psi} + \beta\mathbb{K}^{-1}\mathbf{h}$, which we report here for convenience:

$$\begin{aligned} Z &= \mathrm{e}^{-S_0} \int \left[\prod_{\mathbf{R}}^{N} \mathrm{d}\phi_{\mathbf{R}}\right] \mathrm{e}^{-S[\boldsymbol{\phi},\mathbf{h}]} \\ S[\boldsymbol{\phi},\mathbf{h}] &= \frac{1}{2}(\boldsymbol{\phi}^{\mathrm{T}}\mathbb{K}\boldsymbol{\phi} + \beta^2\mathbf{h}^{\mathrm{T}}\mathbb{K}^{-1}\mathbf{h}) - \beta\mathbf{h}\cdot\boldsymbol{\phi} - \sum_{\mathbf{R}} \log\cosh\left(\sum_{\mathbf{R}'} \mathbb{K}_{\mathbf{R},\mathbf{R}'}\phi_{\mathbf{R}'}\right) \end{aligned} \tag{7.64}$$

where we have omitted the tilde from $\widetilde{S}[\boldsymbol{\phi},\mathbf{h}]$, as we will do from now on.

Expanding the non-linear term. Next, we expand the non-linear term up to 4^{th} order, and observe that a quadratic term originates from this expansion:

$$\log\cosh u = \frac{1}{2}u^2 - \frac{1}{12}u^4 + O(u^6) .$$

Hence:

$$-\sum_{\mathbf{R}} \log\cosh\left(\sum_{\mathbf{R}'} \mathbb{K}_{\mathbf{R},\mathbf{R}'}\phi_{\mathbf{R}'}\right) = -\frac{1}{2}\sum_{\mathbf{R}}\left(\sum_{\mathbf{R}'} \mathbb{K}_{\mathbf{R},\mathbf{R}'}\phi_{\mathbf{R}'}\right)^2 + \frac{1}{12}\sum_{\mathbf{R}}\left(\sum_{\mathbf{R}'} \mathbb{K}_{\mathbf{R},\mathbf{R}'}\phi_{\mathbf{R}'}\right)^4 + \cdots$$

Reassembling terms, [16] we can rewrite the action as:

$$S[\boldsymbol{\phi},\mathbf{h}] = \frac{1}{2}\boldsymbol{\phi}^{\mathrm{T}}\left(\mathbb{K} - \mathbb{K}^2\right)\boldsymbol{\phi} + \frac{\beta^2}{2}\mathbf{h}^{\mathrm{T}}\mathbb{K}^{-1}\mathbf{h} - \beta\mathbf{h}\cdot\boldsymbol{\phi} + S_{\mathrm{nl}}[\boldsymbol{\phi}] , \tag{7.65}$$

where the non-linear term starts with the following quartic contribution:

$$S_{\mathrm{nl}}[\boldsymbol{\phi},\mathbf{h}] = \frac{1}{12}\sum_{\mathbf{R}}\left(\sum_{\mathbf{R}'} \mathbb{K}_{\mathbf{R},\mathbf{R}'}\phi_{\mathbf{R}'}\right)^4 + \cdots . \tag{7.66}$$

---

[16] Observe that, due to the fact that $\mathbb{K} = \mathbb{K}^{\mathrm{T}}$:

$$\sum_{\mathbf{R}}\left(\sum_{\mathbf{R}'} \mathbb{K}_{\mathbf{R},\mathbf{R}'}\phi_{\mathbf{R}'}\right)^2 = \boldsymbol{\phi}^{\mathrm{T}}\mathbb{K}^2\boldsymbol{\phi} .$$

Fourier transform. We now exploit translational invariance — assuming we have a translationally invariant Ising model on some Bravais lattice — to express quantities in momentum space, through the usual lattice Fourier transform (see Eq. (7.32)):

$$\left\{ \begin{array}{rcl} \phi(\mathbf{q}) & \equiv & \displaystyle\sum_{\mathbf{R}} \phi_{\mathbf{R}}\, \mathrm{e}^{-i\mathbf{q}\cdot\mathbf{R}} \\ \phi_{\mathbf{R}} & \equiv & \displaystyle\frac{1}{N}\sum_{\mathbf{q}}^{\mathrm{BZ}} \phi(\mathbf{q})\,\mathrm{e}^{i\mathbf{q}\cdot\mathbf{R}} \stackrel{N\to\infty}{\longrightarrow} a^d \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}}{(2\pi)^d}\;\phi(\mathbf{q})\,\mathrm{e}^{i\mathbf{q}\cdot\mathbf{R}} \end{array}\right. , \tag{7.67}$$

where $a^d = \Omega_c$ denotes the volume of the direct-lattice (Wigner-Seitz) unit cell, and the last step applies when we want to take the thermodynamic limit $N \to \infty$. [17] It is simple to show that

$$\begin{aligned} \boldsymbol{\phi}^{\mathrm{T}}\mathbb{K}\boldsymbol{\phi} = \sum_{\mathbf{R},\mathbf{R}'} \phi_{\mathbf{R}}\mathbb{K}_{\mathbf{R},\mathbf{R}'}\phi_{\mathbf{R}'} &= \frac{1}{N^2}\sum_{\mathbf{q},\mathbf{q}'}^{\mathrm{BZ}}\sum_{\mathbf{R},\mathbf{R}'} \mathrm{e}^{i\mathbf{q}\cdot\mathbf{R}}\mathbb{K}_{\mathbf{R},\mathbf{R}'}\mathrm{e}^{i\mathbf{q}'\cdot\mathbf{R}'}\phi(\mathbf{q})\phi(\mathbf{q}') = \frac{1}{N}\sum_{\mathbf{q}}^{\mathrm{BZ}} K(\mathbf{q})\phi(\mathbf{q})\phi(-\mathbf{q}) \\ &\stackrel{N\to\infty}{\longrightarrow} a^d \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}}{(2\pi)^d} K(\mathbf{q})\phi(\mathbf{q})\phi(-\mathbf{q}) \;, \end{aligned} \tag{7.68}$$

where we have introduced the lattice Fourier transform of the interaction matrix:

$$\left\{ \begin{array}{rcl} \mathbb{K}_{\mathbf{R},\mathbf{R}'} & \equiv & \displaystyle\frac{1}{N}\sum_{\mathbf{q}}^{\mathrm{BZ}} K(\mathbf{q})\,\mathrm{e}^{i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')} \stackrel{N\to\infty}{\longrightarrow} a^d \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}}{(2\pi)^d} K(\mathbf{q})\,\mathrm{e}^{i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')} \\ K(\mathbf{q}) & \equiv & \displaystyle\sum_{\mathbf{R}} \mathbb{K}_{\mathbf{0},\mathbf{R}}\,\mathrm{e}^{-i\mathbf{q}\cdot\mathbf{R}} \end{array}\right. . \tag{7.69}$$

Similarly, one can transform the other quadratic term:

$$\boldsymbol{\phi}^{\mathrm{T}}\mathbb{K}^2\boldsymbol{\phi} = \frac{1}{N}\sum_{\mathbf{q}}^{\mathrm{BZ}} |K(\mathbf{q})|^2\,\phi(\mathbf{q})\phi(-\mathbf{q}) \stackrel{N\to\infty}{\longrightarrow} a^d \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}}{(2\pi)^d} |K(\mathbf{q})|^2\,\phi(\mathbf{q})\phi(-\mathbf{q}) \;, \tag{7.70}$$

the linear field term: [18]

$$\sum_{\mathbf{R}} h_{\mathbf{R}}\phi_{\mathbf{R}} = \frac{1}{N}\sum_{\mathbf{q}}^{\mathrm{BZ}} \phi(\mathbf{q})h(-\mathbf{q}) \stackrel{N\to\infty}{\longrightarrow} a^d \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}}{(2\pi)^d} \phi(\mathbf{q})h(-\mathbf{q}) \;. \tag{7.72}$$

and the quartic term:

$$\begin{aligned} \sum_{\mathbf{R}} \Big(\sum_{\mathbf{R}'} \mathbb{K}_{\mathbf{R},\mathbf{R}'}\phi_{\mathbf{R}'}\Big)^4 &= \frac{1}{N^3}\sum_{\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}}^{\mathrm{BZ}} K_4(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q})\phi(\mathbf{q}_2-\mathbf{q})\,\phi(\mathbf{q}_1+\mathbf{q})\phi(\mathbf{q}_1)\phi(\mathbf{q}_2) \\ &\stackrel{N\to\infty}{\longrightarrow} a^{3d} \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}_1\mathrm{d}\mathbf{q}_2\mathrm{d}\mathbf{q}}{(2\pi)^{3d}} K_4(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q})\phi(\mathbf{q}_2-\mathbf{q})\,\phi(\mathbf{q}_1+\mathbf{q})\phi(\mathbf{q}_1)\phi(\mathbf{q}_2) \;, \end{aligned} \tag{7.73}$$

where the 4^{th}-order coupling reads:

$$K_4(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}) = K(\mathbf{q}_2-\mathbf{q})K(\mathbf{q}_1+\mathbf{q})K(\mathbf{q}_1)K(\mathbf{q}_2) \;. \tag{7.74}$$

Long-wavelength expansion. Recall that the small $\mathbf{q}$ expansion of the interaction matrix reads:

$$K(\mathbf{q}) = K(0)(1 - R_*^2 q^2 + \cdots) \qquad \text{with} \qquad K(0) = z\beta J = \frac{T_c^0}{T} \;, \tag{7.75}$$

---

[17] Notice the asymmetric factors of $1/N$, which are indeed ideal if you want to take that limit.

[18] For the quadratic field term you get:

$$\mathbf{h}^{\mathrm{T}}\mathbb{K}^{-1}\mathbf{h} = \frac{1}{N}\sum_{\mathbf{q}}^{\mathrm{BZ}} K^{-1}(\mathbf{q})\,h(\mathbf{q})h(-\mathbf{q}) \stackrel{N\to\infty}{\longrightarrow} a^d \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}}{(2\pi)^d} K^{-1}(\mathbf{q})\,h(\mathbf{q})h(-\mathbf{q}) \;, \tag{7.71}$$

where $T_c^0 = zJ/k_B$ is the mean-field prediction for the critical temperature. Setting $K(\mathbf{q}) \to K(0)$ is safe in the quartic term: technically, the $\mathbf{q}$-corrections will be irrelevant in the RG sense.

Some care has to be devoted to the expansion of the quadratic-ϕ term, where the q^2 contributions do not cancel in the calculation of $K(\mathbf{q}) - |K(\mathbf{q})|^2$, generating a surviving q^2-term that can be interpreted as the Fourier transform of the squared *gradient* $(\nabla\phi)^2$:

$$K(\mathbf{q}) - |K(\mathbf{q})|^2 \quad \longrightarrow \quad a(T) + \kappa(T)\, q^2 \cdots \tag{7.76}$$

where the coefficient $a(T) \propto (T - T_c^0)$ *changes sign* and becomes negative below T_c^0. [19]

Fourier space integrals. By switching to Fourier transforms, we have also to modify the integral, previously an N-dimensional real integral $\prod_{\mathbf{R}} \mathrm{d}\phi_{\mathbf{R}}$. Recall that there are N $\mathbf{q}$-vectors in the BZ, but $\phi(-\mathbf{q}) = \phi^*(\mathbf{q})$. Hence in principle, we should integrate on only *half* of the wave-vectors, but with *complex* $\phi(\mathbf{q})$. Nevertheless, extending the integral to all $\mathbf{q}$ in the BZ can just be accounted for by an overall factor of 2, which is irrelevant when calculating averages. The second aspect has to do with the *notation.* We will denote the complex integral as follows

$$\int \mathrm{d}z^* \mathrm{d}z\, f(z) \overset{\text{def}}{=} \int \mathrm{d}x \mathrm{d}y\, f(x+iy) \;,$$

so that, for instance, the basic Gaussian integral (with $a > 0$) is now:

$$\int \mathrm{d}z^* \mathrm{d}z\, \mathrm{e}^{-z^* a z} = \int \mathrm{d}x \mathrm{d}y\, \mathrm{e}^{-a(x^2+y^2)} = \frac{\pi}{a} \;, \tag{7.77}$$

which generalises, for a general *positive definite Hermitean* [a] matrix $\mathbb{A}$ to:

$$\int \prod_{i=1}^{N} \Big[\mathrm{d}z_i^* \mathrm{d}z_i\Big]\, \mathrm{e}^{-\mathbf{z}^\dagger \mathbb{A}\, \mathbf{z}} = \frac{\pi^N}{\det(\mathbb{A})} \;. \tag{7.78}$$

---

[a] It is enough that $\mathbb{A}$ has a positive definite Hermitean part.

The ϕ^4 action in momentum space. What we have obtained is, essentially, a ϕ^4 field theory, which can be tackled with field-theoretical RG techniques.

$$\begin{aligned}
Z &= \mathrm{e}^{-S_0(T)} \int \Big[\prod_{\mathbf{q}}^{\mathrm{BZ}} \mathrm{d}\phi^*(\mathbf{q}) \mathrm{d}\phi(\mathbf{q})\Big]\, \mathrm{e}^{-S[\boldsymbol{\phi},\mathbf{h}]} \\
S[\boldsymbol{\phi},\mathbf{h}] &= S_2[\boldsymbol{\phi}] + S_h[\boldsymbol{\phi},\mathbf{h}] + S_{\mathrm{nl}}[\boldsymbol{\phi}] \\
S_2[\boldsymbol{\phi}] &= \frac{1}{2} a^d \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}}{(2\pi)^d} \phi^*(\mathbf{q}) \Big(a(T) + \kappa(T)\, q^2\Big) \phi(\mathbf{q}) \qquad\qquad . \\
S_h[\boldsymbol{\phi},\mathbf{h}] &= -\beta a^d \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}}{(2\pi)^d} \phi(\mathbf{q}) h(-\mathbf{q}) + \beta^2 a^d \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}}{(2\pi)^d} K^{-1}(\mathbf{q}) h(\mathbf{q}) h(-\mathbf{q}) \\
S_{\mathrm{nl}}[\boldsymbol{\phi}] &= \frac{\lambda}{4} a^{3d} \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}_1 \mathrm{d}\mathbf{q}_2 \mathrm{d}\mathbf{q}}{(2\pi)^{3d}} \phi(\mathbf{q}_2 - \mathbf{q}) \phi(\mathbf{q}_1 + \mathbf{q}) \phi(\mathbf{q}_1) \phi(\mathbf{q}_2) + \cdots
\end{aligned}$$

with $\lambda = K^4(0)/3$.

---

[19] You get:

$$a(T) = \frac{T_c^0 (T - T_c^0)}{T^2} \quad \text{and} \quad \kappa(T) = R_*^2 \frac{T_c^0 (2T_c^0 - T)}{T^2} \;.$$

7.3. Problems

Problem 7.1. Carry out a mean-field calculation for the q-state Potts model. Write your variational density matrix as:

$$\hat{\rho}_0 = \prod_{\mathbf{R}} \left(x\delta_{\sigma_{\mathbf{R}},1} + \frac{1-x}{q-1}(1-\delta_{\sigma_{\mathbf{R}},1}) \right) \ ,$$

where x is a variational parameter ($x = q^{-1}$ corresponds to all states being equally probable, while $x > q^{-1}$ signals order, with a preference for $\sigma_{\mathbf{R}} = 1$). Do a Landau expansion, and show that for $q > 2$ the transition is of *first order*.

Problem 7.2. Carry out a mean-field calculation for the classical XY model.

Problem 7.3. The fully-connected quantum Ising ferromagnet. Consider the fully-connected Ising model with $j = 1 \cdots N$ spins in presence of a transverse field term:

$$\widehat{H} = -\frac{J}{2N}\Big(\sum_{j=1}^{N} \hat{\sigma}_j^z\Big)^2 - h^{\perp} \sum_{j=1}^{N} \hat{\sigma}_j^x \ . \tag{7.79}$$

Assume N *even.*

1) Introduce now the *total spin operator* $\hat{\mathbf{S}} = \frac{1}{2}\sum_j \hat{\boldsymbol{\sigma}}_j$, and express $\widehat{H}$ in terms of $\hat{\mathrm{S}}_z$ and $\hat{\mathrm{S}}_x$. Does the model commute with the (squared) total spin operator $\hat{\mathbf{S}}^2$? What is the maximum allowed value of the total spin quantum number S? How many states belong to the subspace of maximum spin?

2) How would you represent the Hamiltonian as a matrix in the subspace of maximum spin? What is the dimension of such a matrix?

3) Diagonalise the Hamiltonian in the subsector of maximum spin. Find the quantum critical point $h_c^{\perp}/J$.

Problem 7.4. The p-spin fully connected classical Ising ferromagnet. As a generalisation of the classical fully-connected Ising ferromagnet, consider its p-spin version:

$$H = -\frac{J}{2N^{\mathrm{p}-1}}\left(\sum_{j=1}^{N} \sigma_j\right)^{\mathrm{p}} = -\frac{JN}{2}\left(\frac{1}{N}\sum_{j=1}^{N} \sigma_j\right)^{\mathrm{p}} \ , \tag{7.80}$$

with integer $\mathrm{p} \geq 2$.

1) By using the same considerations as in the $\mathrm{p} = 2$ case, show that the free-energy density of the model can be written as:

$$f(m,T) \approx -\frac{J}{2}m^{\mathrm{p}} - \frac{k_BT}{2}\left[2\log 2 - (1-m)\log(1-m) - (1+m)\log(1+m)\right] \ .$$

A plot of the free energy density for several values of the temperature is reported in Fig. 7.4.

2) The absolute minimum of the free energy is the average equilibrium magnetization $\langle m \rangle$, which is the order parameter of the phase transition: for $T > T_c$, $\langle m \rangle = 0$ and the system is in the disordered paramagnetic phase, while for $T < T_c$, $\langle m \rangle \neq 0$ and the phase is ferromagnetic. Calculate numerically, by minimizing Eq. 7.81, T_c for $\mathrm{p} = 3$ and $\mathrm{p} = 5$.

Answer: $T_c(\mathrm{p}{=}3) \approx 0.74$, $T_c(\mathrm{p}{=}5) \approx 0.725$.

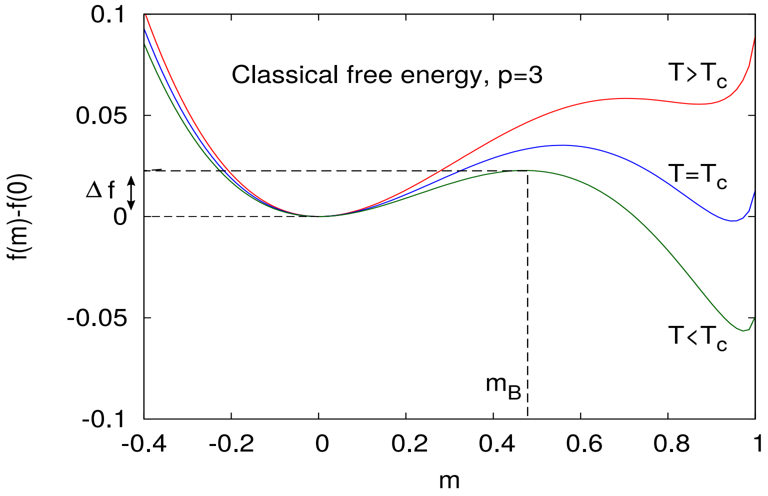

Figure 7.4.: Free energy density, versus magnetization, of the classical system for $\mathrm{p} = 3$, at temperature above, equal and below T_c. Notice the position of the barrier m_B and its height Δf for a value of the temperature $T < T_c$, and the presence of the ferromagnetic unstable minimum even for $T > T_c$.

3) An interesting feature of the classical free energy is that for $\mathrm{p} > 2$ it has a minimum in $m = 0$ for any finite temperature T, meaning that the paramagnetic state survives as a metastable state down to $T \to 0$. Compute the height of the barrier

$$\Delta f(T) = f(m_B, T) - f(0, T) \ .$$

Since we are looking at the free energy density, it follows that the barrier is extensive in the system size N. [20]

Answer: You should get: $\Delta f(T) {=} \frac{J}{2}(p{-}1)\Big(\frac{2T}{J\mathrm{p}}\Big)^{\frac{p}{\mathrm{p}-2}}$.

Problem 7.5. Mean-field for the transverse-field Ising model. Consider the transverse-field Ising model

$$\widehat{H}_{\mathrm{TFIM}} = -J \sum_{\langle \mathbf{R},\mathbf{R}' \rangle} \hat{\sigma}^z_{\mathbf{R}} \hat{\sigma}^z_{\mathbf{R}'} \; - \; h^{\perp} \sum_{\mathbf{R}} \hat{\sigma}^x_{\mathbf{R}} \ . \tag{7.81}$$

Make a mean-field variational *Ansatz* of the factorized form:

$$\widehat{H}_0 = - \sum_{\mathbf{R}} \mathbf{h}^0_{\mathbf{R}} \cdot \hat{\boldsymbol{\sigma}}_{\mathbf{R}} \ , \tag{7.82}$$

where the various $\mathbf{h}^0_{\mathbf{R}}$ (effective magnetic fields, but now *vectors*) are used as variational parameters. Our *Ansatz* for the density matrix is site-factorised and given by: [21]

$$\hat{\rho}_0 = \frac{\mathrm{e}^{-\beta \widehat{H}_0}}{\mathrm{Tr}\, \mathrm{e}^{-\beta \widehat{H}_0}} = \prod_{\mathbf{R}} \frac{1}{2} \Big(\mathbb{1}_{\mathbf{R}} + \mathbf{m}_{\mathbf{R}} \cdot \hat{\boldsymbol{\sigma}}_{\mathbf{R}} \Big) \qquad \text{with} \qquad \mathbf{m}_{\mathbf{R}} = \frac{\mathbf{h}^0_{\mathbf{R}}}{|\mathbf{h}^0_{\mathbf{R}}|} \tanh(\beta |\mathbf{h}^0_{\mathbf{R}}|) \ , \tag{7.83}$$

where the $\mathbf{m}_{\mathbf{R}}$ can be equivalently regarded as our set of variational parameters. Write the mean-field equations and determine the phase diagram as a function of T and $h^{\perp}$.

---

[20] If the system is in the paramagnetic metastable phase, with $T < T_c$, the probability of overcoming this extensive free-energy barrier will be roughly given by $\mathrm{e}^{-\beta N \Delta f} = \mathrm{e}^{-\gamma(T) N}$, which is indeed exponentially suppressed for large N, with a temperature-dependent rate $\gamma(T) = \Delta f(T)/T$ which vanishes only at $T = 0$.

[21] Recall that if $|\mathbf{n}| = 1$, then $\mathrm{e}^{a \mathbf{n} \cdot \hat{\boldsymbol{\sigma}}} = \mathbb{1} \cosh a + \mathbf{n} \cdot \hat{\boldsymbol{\sigma}} \sinh a$.

Part II.

Selected topics

8. The XY model in two dimensions

The purpose of this chapter is to give you an overview of a very important two-dimensional classical model, the XY or planar model, where no local order parameter exists — essentially, due to the continuous rotational symmetry and a classical version of the Marmin-Wagner theorem — and yet there is a remarkable phase transition: the Kosterlitz-Thouless transition, with a whole *line of critical points* where the correlation exponent changes *continuously*.

I will cover, this year, only the introductory material of Sec. 8.1, leaving the remaining material to your self-study, if interested. This material shows how deeply connected is this problem to many other interesting two-dimensional models — including discrete height models and the Coulomb gas problem — arriving at a point from which, in principle, one could set up an RG analysis. Reference for this chapter is the review paper by Kogut [33].

8.1. General and preliminary considerations

The classical XY model. Given *classical* planar spins, i.e., two-dimensional vectors of unit length $\mathbf{S}_\mathbf{x}$ at each site $\mathbf{x}$ of a square lattice, the classical Hamiltonian is given by:

$$H_{\text{XY}} = -J \sum_{\langle \mathbf{x},\mathbf{x}' \rangle} \Big(\mathbf{S}_\mathbf{x} \cdot \mathbf{S}_{\mathbf{x}'} - 1 \Big) = J \sum_{\mathbf{x}} \sum_{\nu=1,2} \Big(1 - \cos(\theta_{\mathbf{x}+\mathbf{e}_\nu} - \theta_\mathbf{x}) \Big) \,. \tag{8.1}$$

Here $\langle \mathbf{x},\mathbf{x}' \rangle$ denotes a sum over nearest-neighbor lattice sites, $\mathbf{x}' = \mathbf{x} + \mathbf{e}_\nu$ with $\mathbf{e}_1 = a(1,0)$ and $\mathbf{e}_2 = a(0,1)$. The second expression follows from the standard parameterisation of a unit vector

$$\mathbf{S}_\mathbf{x} = (\cos\theta_\mathbf{x}, \sin\theta_\mathbf{x}) \,. \tag{8.2}$$

The partition function is:

$$Z_{\text{XY}} = \int_0^{2\pi} \Big[\prod_{\mathbf{x}} \tfrac{\mathrm{d}\theta_\mathbf{x}}{2\pi} \Big] \, \mathrm{e}^{-\beta H_{\text{XY}}[\{\theta_\mathbf{x}\}]} \,. \tag{8.3}$$

We assume a system with $N = L^2$ lattice sites with periodic boundary conditions (PBC).

The most important physical quantities we will need to calculate is the spin-spin correlation function for two distant points $\mathbf{x}_1$ and $\mathbf{x}_2$:

$$\langle \mathbf{S}_{\mathbf{x}_1} \cdot \mathbf{S}_{\mathbf{x}_2} \rangle = \langle \cos(\theta_{\mathbf{x}_1} - \theta_{\mathbf{x}_2}) \rangle = \frac{1}{2} \Big(\big\langle \mathrm{e}^{i(\theta_{\mathbf{x}_1} - \theta_{\mathbf{x}_2})} \big\rangle + \text{cc} \Big) \,. \tag{8.4}$$

Two-point correlation function. The crucial average we will need is therefore:

$$\big\langle \mathrm{e}^{i(\theta_{\mathbf{x}_1} - \theta_{\mathbf{x}_2})} \big\rangle = \frac{1}{Z_{\text{XY}}} \int_0^{2\pi} \Big[\prod_{\mathbf{x}} \tfrac{\mathrm{d}\theta_\mathbf{x}}{2\pi} \Big] \, \mathrm{e}^{i(\theta_{\mathbf{x}_1} - \theta_{\mathbf{x}_2})} \, \mathrm{e}^{-\beta H_{\text{XY}}[\{\theta_\mathbf{x}\}]} \,. \tag{8.5}$$

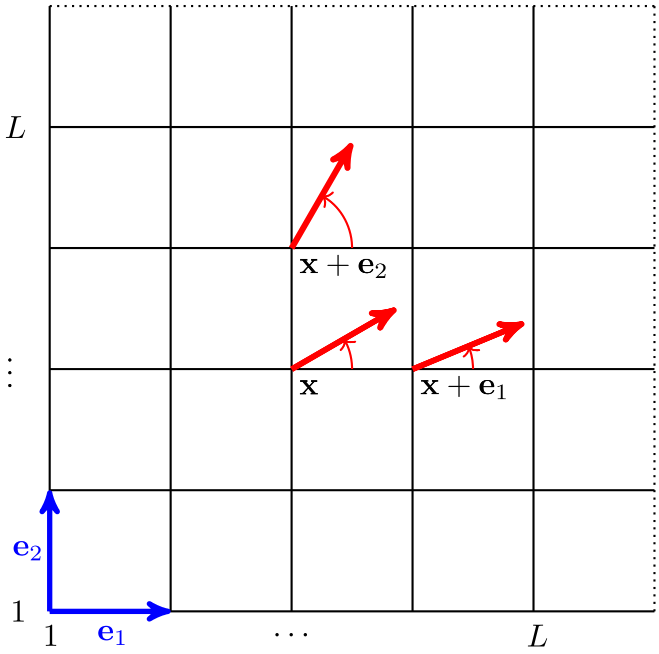

Figure 8.1: The XY model. An $L\times L$ square lattice is shown, with periodic boundary conditions: the dashed borders should be identified with the opposite border, making the geometry that a torus. The two nearest-neighbor vectors $\mathbf{e}_1$ and $\mathbf{e}_2$ are shown in blue. At each lattice site $\mathbf{x}$ a planar spin (classical unit vector on the plane) is uniquely given by the angle $\theta_{\mathbf{x}}$ formed with the x-axis: $\mathbf{S}_{\mathbf{x}} = (\cos\theta_{\mathbf{x}}, \sin\theta_{\mathbf{x}})$. Three spins at nearest-neighbor sites $\mathbf{x}$, $\mathbf{x}+\mathbf{e}_1$ and $\mathbf{x}+\mathbf{e}_2$ are shown as thick red arrows (all other spins are omitted for clarity).

The ground state has all spins aligned in a given (arbitrary) direction, which we can fix by convention to be $\theta_{\mathbf{x}} = 0$. It is useful to introduce the discrete lattice "derivative"

$$\Delta_\nu \theta_{\mathbf{x}} = \theta_{\mathbf{x}+\mathbf{e}_\nu} - \theta_{\mathbf{x}} \;, \tag{8.6}$$

which appear in the argument of the cosine function in H_{XY}.

It is quite natural to think that at small T the configurations dominating in the partition function are those for which $\Delta_\nu\theta_{\mathbf{x}}$ are small, and that it would be legitimate, at low T, to approximate H_{XY} with the so-called *spin-wave* term

$$H_{\text{XY}} \stackrel{\text{low}-T}{\longrightarrow} H_{\text{sw}} = \frac{J}{2} \sum_{\mathbf{x}} \sum_{\nu=1,2} (\Delta_\nu \theta_{\mathbf{x}})^2 \;, \tag{8.7}$$

where now $\theta_{\mathbf{x}} \in \mathbb{R}$. This spin-wave approximation does violence to the 2π-*periodicity* in $\Delta_\nu\theta_{\mathbf{x}}$ of the original H_{XY}, but it has the advantage of being easily solvable.

Discrete Laplacian. The *discrete Laplacian operator* can be defined as:

$$\left\{ \begin{array}{rcl} \mathbb{L}_{\mathbf{x},\mathbf{x}'} &=& \displaystyle\sum_{\nu=1,2} \Big(\delta_{\mathbf{x}',\mathbf{x}+\mathbf{e}_\nu} + \delta_{\mathbf{x}',\mathbf{x}-\mathbf{e}_\nu} - 2\delta_{\mathbf{x}',\mathbf{x}}\Big) \\ \displaystyle\sum_{\mathbf{x}'} \mathbb{L}_{\mathbf{x},\mathbf{x}'}\theta_{\mathbf{x}'} &=& \displaystyle\sum_{\nu=1,2} \Big(\theta_{\mathbf{x}+\mathbf{e}_\nu} + \theta_{\mathbf{x}-\mathbf{e}_\nu} - 2\theta_{\mathbf{x}}\Big) \end{array} \right. . \tag{8.8}$$

In terms of the discrete Laplacian we can rewrite:

$$\sum_{\mathbf{x}} \sum_{\nu=1,2} (\Delta_\nu\theta_{\mathbf{x}})^2 = -\sum_{\mathbf{x},\mathbf{x}'} \theta_{\mathbf{x}}\, \mathbb{L}_{\mathbf{x},\mathbf{x}'}\, \theta_{\mathbf{x}'} \;, \tag{8.9}$$

in close analogy with the standard integration by parts rule $\int \mathrm{d}\mathbf{x}\, |\boldsymbol{\nabla}\psi|^2 = -\int \mathrm{d}\mathbf{x}\, \psi^* \boldsymbol{\nabla}^2 \psi$ used when transforming the kinetic energy in quantum mechanics.

Hence, we see that the spin-wave partition function involves *gaussian integrals* provided the domain

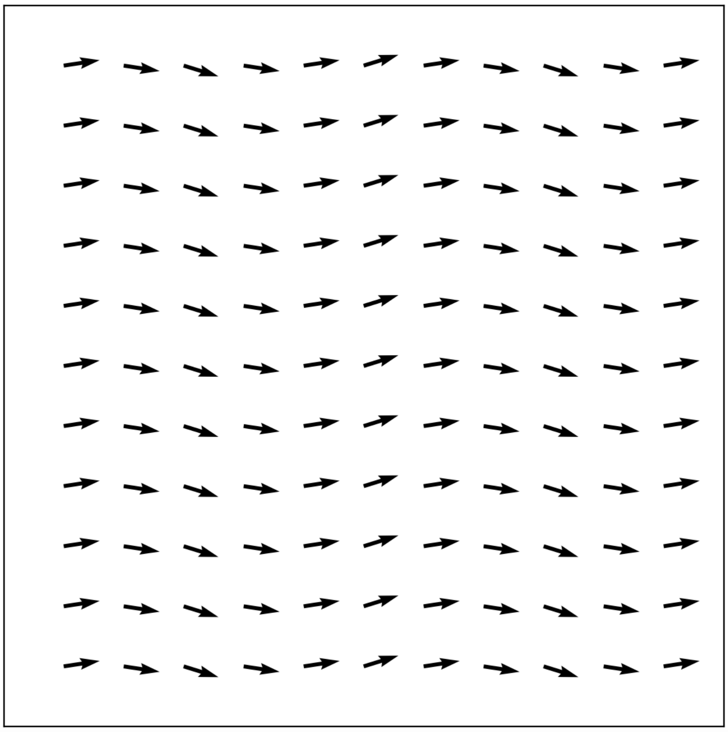

Figure 8.2: The XY model. A spin-wave excitation. Here $\theta_{\mathbf{x}} = A\cos(\frac{\pi}{3a}x)$, with $\mathbf{x} = (x, y)$, and $A = 0.3$.

of $\theta_{\mathbf{x}}$ is extended to the whole real axis:

$$Z_{\rm sw}[K] = \int_{-\infty}^{+\infty} \Big[\prod_{\mathbf{x}} \mathrm{d}\theta_{\mathbf{x}}\Big] \, \mathrm{e}^{-\beta H_{\rm sw}[\{\theta_{\mathbf{x}}\}]} = \int_{-\infty}^{+\infty} \Big[\prod_{\mathbf{x}} \mathrm{d}\theta_{\mathbf{x}}\Big] \, \mathrm{e}^{-\frac{K}{2}\sum_{\mathbf{x},\mathbf{x}'} \theta_{\mathbf{x}} \, (-\mathbb{L}_{\mathbf{x},\mathbf{x}'}) \, \theta_{\mathbf{x}'}} \;, \tag{8.10}$$

where $K = \beta J$ is the dimensionless coupling. Correspondingly, the two-point correlator reads:

$$\Big\langle \mathrm{e}^{i(\theta_{\mathbf{x}_1} - \theta_{\mathbf{x}_2})} \Big\rangle_{\rm sw} = \frac{1}{Z_{\rm sw}} \int_{-\infty}^{+\infty} \Big[\prod_{\mathbf{x}} \mathrm{d}\theta_{\mathbf{x}}\Big] \, \mathrm{e}^{i(\theta_{\mathbf{x}_1} - \theta_{\mathbf{x}_2})} \, \mathrm{e}^{-\frac{K}{2}\sum_{\mathbf{x},\mathbf{x}'} \theta_{\mathbf{x}} \, (-\mathbb{L}_{\mathbf{x},\mathbf{x}'}) \, \theta_{\mathbf{x}'}} \;. \tag{8.11}$$

We rewrite here the gaussian integral identity we will need to use, see Eq. (7.52) or (7.56), for convenience:

Gaussian integral identity. If $\mathbb{A}$ is a *positive definite* symmetric real $N \times N$ matrix defined on the lattice, then

$$\int_{-\infty}^{+\infty} \Big[\prod_{\mathbf{x}} \mathrm{d}\theta_{\mathbf{x}}\Big] \, \mathrm{e}^{\mathbf{f}\cdot\boldsymbol{\theta}} \mathrm{e}^{-\frac{1}{2}\boldsymbol{\theta}^{\rm T}\,\mathbb{A}\,\boldsymbol{\theta}} = \frac{\sqrt{(2\pi)^N}}{\det \mathbb{A}} \, \mathrm{e}^{\frac{1}{2}\mathbf{f}^{\rm T}\,\mathbb{A}^{-1}\,\mathbf{f}} \;, \tag{8.12}$$

where $\mathbf{f}\cdot\boldsymbol{\theta} = \sum_{\mathbf{x}} f_{\mathbf{x}}\theta_{\mathbf{x}}$, and $\boldsymbol{\theta}^{\rm T}\,\mathbb{A}\,\boldsymbol{\theta} = \sum_{\mathbf{x},\mathbf{x}'} \theta_{\mathbf{x}} \mathbb{A}_{\mathbf{x},\mathbf{x}'} \theta_{\mathbf{x}'}$. All prefactors cancel in calculating the averages:

$$\langle \mathrm{e}^{\mathbf{f}\cdot\boldsymbol{\theta}} \rangle \overset{\rm def}{=} \frac{\int_{-\infty}^{+\infty} \big[\prod_{\mathbf{x}} \mathrm{d}\theta_{\mathbf{x}}\big] \, \mathrm{e}^{\mathbf{f}\cdot\boldsymbol{\theta}} \mathrm{e}^{-\frac{1}{2}\boldsymbol{\theta}^{\rm T}\,\mathbb{A}\,\boldsymbol{\theta}}}{\int_{-\infty}^{+\infty} \big[\prod_{\mathbf{x}} \mathrm{d}\theta_{\mathbf{x}}\big] \, \mathrm{e}^{-\frac{1}{2}\boldsymbol{\theta}^{\rm T}\,\mathbb{A}\,\boldsymbol{\theta}}} = \mathrm{e}^{\frac{1}{2}\mathbf{f}^{\rm T}\,\mathbb{A}^{-1}\,\mathbf{f}} \;. \tag{8.13}$$

Within the spin-wave approximation, we need gaussian integrals which involve the (positive definite) matrix

$$\mathbb{A}_{\mathbf{x},\mathbf{x}'} = K(-\mathbb{L})_{\mathbf{x},\mathbf{x}'} \qquad \text{with} \qquad K = \beta J \;. \tag{8.14}$$

The Green's function. To carry out the calculation, we need to invert the discrete Laplacian, in terms of what is known as the lattice *Green's function*, or *propagator*:

$$\sum_{\mathbf{x}''}(-\mathbb{L})_{\mathbf{x},\mathbf{x}''}\mathbb{G}_{\mathbf{x}'',\mathbf{x}'} = \delta_{\mathbf{x},\mathbf{x}'} \qquad \Longrightarrow \qquad (\mathbb{A}^{-1})_{\mathbf{x},\mathbf{x}'} = K^{-1}\,\mathbb{G}_{\mathbf{x},\mathbf{x}'} \;. \tag{8.15}$$

The actual inversion is best performed in Fourier transform, exploiting translational invariance and convolutions. The lattice Fourier transform of $\mathbb{G}_{\mathbf{x},\mathbf{x}'} = \mathbb{G}_{\mathbf{x}-\mathbf{x}'}$ is defined, as usual: [1]

$$\begin{cases} \mathrm{G}(\mathbf{q}) & \equiv \displaystyle\sum_{\mathbf{x}} \mathbb{G}_{\mathbf{x},\mathbf{0}}\, \mathrm{e}^{-i\mathbf{q}\cdot\mathbf{x}} \\ \mathbb{G}_{\mathbf{x},\mathbf{0}} & = \displaystyle\frac{1}{N}\sum_{\mathbf{q}}^{\mathrm{BZ}} \mathrm{G}(\mathbf{q})\, \mathrm{e}^{i\mathbf{q}\cdot\mathbf{x}} \end{cases} \;, \tag{8.16}$$

and similarly for the lattice Laplacian

$$\mathrm{L}(\mathbf{q}) = \sum_{\mathbf{x}} \mathbb{L}_{\mathbf{x},\mathbf{0}}\, \mathrm{e}^{-i\mathbf{q}\cdot\mathbf{x}} = \sum_{\nu=1,2} 2(\cos\mathbf{q}\cdot\mathbf{e}_\nu - 1) \;. \tag{8.17}$$

Notice that $\mathrm{L}(\mathbf{q}=0)=0$. Moreover, the Fourier transform of the convolution implied by the matrix inversion, $\mathrm{L}(\mathbf{q})\,\mathrm{G}(\mathbf{q}) = -1$, gives: [2]

$$\mathrm{G}(\mathbf{q}\neq\mathbf{0}) = -\frac{1}{\mathrm{L}(\mathbf{q})} = \frac{1}{4 - 2\cos\mathbf{q}\cdot\mathbf{e}_1 - 2\cos\mathbf{q}\cdot\mathbf{e}_2} \;. \tag{8.19}$$

Green's function of Poisson's equation on the continuum. Probably more familiar to you is the concept of Green's function for differential operators on the continuum. Certainly familiar from electrostatics, and relevant in this context, is the Green's function associated with the Laplacian operator, simply a singular solution of the associated inhomogeneous (Poisson's) equation with a Dirac's delta function: [3]

$$\nabla^2 G(\mathbf{x}) = -\delta(\mathbf{x}) \qquad \Longrightarrow \qquad \widehat{G}(\mathbf{q}) = \frac{1}{|\mathbf{q}|^2} \;. \tag{8.21}$$

Here $\widehat{G}(\mathbf{q})$ denotes the Fourier transform of $G(\mathbf{x})$, obtained immediately by Fourier transforming the differential equation in real space. In *three dimensions* this gives the well-known Coulomb potential:

$$G(\mathbf{x}) = \int \frac{\mathrm{d}^3\mathbf{q}}{(2\pi)^3}\frac{\mathrm{e}^{i\mathbf{q}\cdot\mathbf{x}}}{|\mathbf{q}|^2} = \frac{1}{4\pi|\mathbf{x}|} \qquad \text{in 3d} \;. \tag{8.22}$$

In *two dimensions*, however, which is the case we are interested in, the same $\widehat{G}(\mathbf{q})$ leads to a logarithmic Coulomb potential:

$$G(\mathbf{x}) = \int \frac{\mathrm{d}^2\mathbf{q}}{(2\pi)^2}\frac{\mathrm{e}^{i\mathbf{q}\cdot\mathbf{x}}}{|\mathbf{q}|^2} = -\frac{1}{2\pi}\log|\mathbf{x}| \qquad \text{in 2d} \;. \tag{8.23}$$

---

[1] Here $\mathbf{q} = \frac{2\pi}{La}(n_1,n_2)$ are wave-vectors in the first Brillouin Zone (BZ) of the reciprocal lattice: $N = L^2$ of them, since $n_i = 0,\cdots,L-1$.

[2] The fact that $\mathrm{G}(\mathbf{q})$ is formally divergent for $\mathbf{q}=0$ forces us to some extra care in the Fourier expressions in Eq. (8.16). We will see below that the quantity $\mathrm{G}_{\mathbf{x},\mathbf{0}} - \mathrm{G}_{\mathbf{0},\mathbf{0}}$ is perfectly well defined, although the individual terms are not, since:

$$\mathrm{G}_{\mathbf{x},\mathbf{0}} - \mathrm{G}_{\mathbf{0},\mathbf{0}} = \frac{1}{N}\sum_{\mathbf{q}}^{\mathrm{BZ}} \mathrm{G}(\mathbf{q})\,(\mathrm{e}^{i\mathbf{q}\cdot\mathbf{x}} - 1) \;. \tag{8.18}$$

[3] Once the Green's function is known, you can determine the solution of *any* inhomogeneous equation. In the Poisson's equation of electrostatics $\nabla^2\varphi(\mathbf{x}) = -\varepsilon_0^{-1}\rho(\mathbf{x})$, since $\rho(\mathbf{x}) = \int \mathrm{d}\mathbf{x}'\rho(\mathbf{x}')\delta(\mathbf{x}-\mathbf{x}')$ knowing that, in three dimensions the solution of $\nabla^2 G(\mathbf{x}) = -\delta(\mathbf{x})$ is $G(\mathbf{x}) = \frac{1}{4\pi|\mathbf{x}|}$ immediately gives the solution for a general $\rho(\mathbf{x})$:

$$\varphi(\mathbf{x}) = \frac{1}{4\pi\varepsilon_0}\int \mathrm{d}\mathbf{x}'\,\frac{\rho(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|} \;. \tag{8.20}$$

For a direct proof of this, observe the interesting fact that $f(z) = \log z = \log r + i\theta$ is *analytic* with a branch cut at $\mathrm{Re}\, z \in (-\infty, 0]$. Hence, both its real part $\log r = \log |\mathbf{x}|$ and its imaginary part $\theta = \arctan y/x$ are *harmonic functions* (solutions of the Laplace equation) away from the branch cut. Interestingly:

$$\boldsymbol{\nabla} \log |\mathbf{x}| = \frac{\mathbf{x}}{|\mathbf{x}|^2} \qquad \text{and} \qquad \boldsymbol{\nabla}\theta = \frac{1}{|\mathbf{x}|^2}(-y, x) \; . \tag{8.24}$$

You can easily convince yourself that

$$\nabla^2 \log |\mathbf{x}| = 2\pi\delta(\mathbf{x}) \qquad \text{and} \qquad \nabla^2\theta = 0 \; . \tag{8.25}$$

The phase θ appearing in $z = re^{i\theta}$ will play an important role later on when discussing vortices.

Low-T spin-spin correlations. Returning to our problem of calculating the long-distance behaviour of spin-spin correlations, take $\mathbf{x}_2 = \mathbf{x}$ and $\mathbf{x}_1 = \mathbf{0}$, assuming $\mathbf{x}$ to be distant from the origin, hence $|\mathbf{x}| \gg a$. To calculate $\langle \mathrm{e}^{i(\theta_{\mathbf{x}} - \theta_{\mathbf{0}})} \rangle_{\text{sw}}$, we set $\mathbf{f}_{\mathbf{x}'} = i(\delta_{\mathbf{x}',\mathbf{x}} - \delta_{\mathbf{x}',\mathbf{0}})$ in Eq. (8.13), obtaining:

$$\langle \mathrm{e}^{i(\theta_{\mathbf{x}} - \theta_{\mathbf{0}})} \rangle_{\text{sw}} = \mathrm{e}^{\frac{1}{K}(\mathrm{G}_{\mathbf{x},\mathbf{0}} - \mathrm{G}_{\mathbf{0},\mathbf{0}})} \; . \tag{8.26}$$

We now aim at calculating the large $|\mathbf{x}|$ behaviour of this correlation function, assuming that $a \ll |\mathbf{x}| \ll La$. A *continuum approximation* is therefore very reasonable. From Eq. (8.19) we would get

$$\mathrm{G}(\mathbf{q} \to 0) \to \frac{1}{|\mathbf{q}|^2 a^2} \; . \tag{8.27}$$

Hence, we recovered the Fourier transform of a Coulomb potential in *two-dimensions*. This suggests that:

$$\mathrm{G}_{\mathbf{x},\mathbf{0}} - \mathrm{G}_{\mathbf{0},\mathbf{0}} \simeq -\frac{1}{2\pi} \log(|\mathbf{x}|/a) + \text{const} \qquad \text{for} \qquad a \ll |\mathbf{x}| \ll La \; . \tag{8.28}$$

Using this, we finally obtain:

$$\langle \mathrm{e}^{i(\theta_{\mathbf{x}} - \theta_{\mathbf{0}})} \rangle_{\text{sw}} \simeq \mathrm{e}^{-\frac{1}{2\pi K} \log(|\mathbf{x}|/a)} = \left(\frac{a}{|\mathbf{x}|} \right)^{\frac{1}{2\pi K}} \qquad \text{for} \qquad a \ll |\mathbf{x}| \ll La \; . \tag{8.29}$$

> **Spin-wave calculation of spin-spin correlations.** Summarising, based on the spin-wave approximation we expect that at low temperatures the spin-spin correlations decay as a *power-law* with a *temperature dependent exponent* $\eta(T)$:
>
> $$\langle \mathbf{S}_{\mathbf{x}} \cdot \mathbf{S}_0 \rangle_{\text{sw}} \simeq \left(\frac{a}{|\mathbf{x}|} \right)^{\eta(T)} \qquad \text{with} \qquad \eta(T) = \frac{1}{2\pi K} = \frac{k_B T}{2\pi J} \; . \tag{8.30}$$

High-T behaviour. On the other hand, the high-T expansion suggests that spin-spin correlations should decay *exponentially* in $|\mathbf{x}|$ for sufficiently large T. To show this, consider the calculation of

$$\langle \mathrm{e}^{i(\theta_{\mathbf{x}} - \theta_{\mathbf{0}})} \rangle = \frac{1}{Z} \int_0^{2\pi} \Big[\prod_{\mathbf{x}} \tfrac{\mathrm{d}\theta_{\mathbf{x}}}{2\pi} \Big] \, \mathrm{e}^{i(\theta_{\mathbf{x}} - \theta_{\mathbf{0}})} \prod_{\mathbf{x}'} \prod_{\nu=1,2} \mathrm{e}^{-K\left(1 - \cos(\theta_{\mathbf{x}'+\mathbf{e}_\nu} - \theta_{\mathbf{x}'})\right)} \; . \tag{8.31}$$

For high-T, $K = \beta J$ is small, hence we can expand the exponential and write:

$$\prod_{\mathbf{x}'} \prod_{\nu=1,2} \mathrm{e}^{K \cos(\theta_{\mathbf{x}'+\mathbf{e}_\nu} - \theta_{\mathbf{x}'})} = \prod_{\mathbf{x}'} \prod_{\nu=1,2} \left(1 + K \cos(\theta_{\mathbf{x}'+\mathbf{e}_\nu} - \theta_{\mathbf{x}'}) + \cdots \right) \; .$$

Take now, for simplicity of notation, $\mathbf{x} = n\mathbf{e}_1$. Since $\int_0^{2\pi} \frac{\mathrm{d}\theta_{\mathbf{x}}}{2\pi} \mathrm{e}^{i\theta_{\mathbf{x}}} = 0$, the first (largest) term in the product which gives a non vanishing contribution must contain a whole string of $\mathrm{e}^{-i(\theta_{\mathbf{x}'+\mathbf{e}_1} - \theta_{\mathbf{x}'})}$ joining the two points $\mathbf{x} = n\mathbf{e}_1$ and $\mathbf{x} = \mathbf{0}$:

$$\int_0^{2\pi} \Big[\prod_{\mathbf{x}} \frac{\mathrm{d}\theta_{\mathbf{x}}}{2\pi}\Big] \mathrm{e}^{i(\theta_{n\mathbf{e}_1} - \theta_{\mathbf{0}})} \prod_{j=0}^{n-1} \Big(K \frac{\mathrm{e}^{i(\theta_{j\mathbf{e}_1} - \theta_{(j+1)\mathbf{e}_1})} + \text{c.c.}}{2}\Big) = \frac{K^n}{2^n} \,.$$

Hence we conclude that for large-T:

$$\langle \mathrm{e}^{i(\theta_{n\mathbf{e}_1} - \theta_{\mathbf{0}})} \rangle_{\text{high}-T} \approx \mathrm{e}^{-n \log(2/K)} \,. \tag{8.32}$$

Spin-spin correlations at high-T. Summarizing, at high-T we have:

$$\langle \mathrm{e}^{i(\theta_{\mathbf{x}} - \theta_{\mathbf{0}})} \rangle_{\text{high}-T} \simeq \mathrm{e}^{-|\mathbf{x}|/\xi(T)} \qquad \text{with} \qquad \xi(T) = \frac{1}{\log 2/K} = \frac{1}{\log(2k_BT/J)} \,. \tag{8.33}$$

This suggests that *two distinct phases must exist.* But the low-temperature phase is not characterized by the usual *local order parameter*, since $\langle \mathbf{S}_{\mathbf{x}} \rangle = 0$, consistently with the Mermin-Wagner theorem, which forbids order at finite T in two dimensions, due to the continuous rotational symmetry.

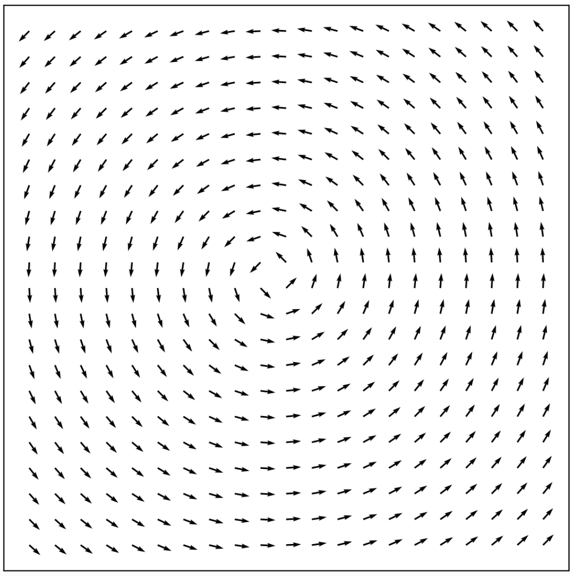

Figure 8.3: The XY model. A vortex excitation centred in the middle of a square plaquette, rather than in the origin. See text for details.

The role of vortices. Let us add some interesting physical insight that Kosterlitz and Thouless put forward in 1973. One important aspect of the low-temperature picture that the spin-wave approximation completely misses is the possibility of singular (vortex) solution of the Laplace equation, $\mathrm{Im} \log z$, with a definite *winding* around the origin. [4] More specifically, let $\mathbf{x} = (x, y)$ be seen as a complex

---

[4] It is easy to realise that, for instance the function $\mathrm{Im} \log z^{\mathrm{p}} = \mathrm{p} \arctan(y/x) = \theta_{\mathrm{p}}(\mathbf{x})$ has a gradient which *whirls* around the origin:

$$\boldsymbol{\nabla}\theta_{\mathrm{p}}(\mathbf{x}) = \mathrm{p}\left(\frac{-y}{x^2+y^2}, \frac{x}{x^2+y^2}\right) \qquad \Longrightarrow \qquad \begin{cases} \nabla^2 \theta_{\mathrm{p}} = 0 \\ \oint_{\gamma_r} \boldsymbol{\nabla}\theta_{\mathrm{p}} \cdot \mathrm{dl} = 2\pi\mathrm{p} \end{cases} \,. \tag{8.34}$$

A vortex corresponds to $\mathrm{p} = 1$, the *anti-vortex* to $\mathrm{p} = -1$. One can show that $\boldsymbol{\nabla} \wedge \boldsymbol{\nabla}\theta_{\mathrm{p}} = 2\pi\mathrm{p}\delta(\mathbf{x})$, similarly to the magnetic field generated by a very long and thin solenoid in the origin.

variable $z = x + iy = re^{i\theta}$ with $r = \sqrt{x^2 + y^2}$ and $\theta(\mathbf{x}) = \arctan(y/x)$, and take at each point $\mathbf{x}$ a unit vector $\mathbf{S}_\mathbf{x}$ orthogonal to $\mathbf{x}$, hence forming an angle $\theta_\mathbf{x} = \theta(\mathbf{x}) + \frac{\pi}{2}$ with the x-axis, as shown in Fig. 8.3. Interestingly, from $\theta(\mathbf{x}) = \arctan(y/x)$ you deduce

$$\boldsymbol{\nabla}\theta(\mathbf{x}) = \left(\frac{-y}{x^2+y^2}, \frac{x}{x^2+y^2}\right) \qquad \Longrightarrow \qquad |\boldsymbol{\nabla}\theta(\mathbf{x})|^2 = \frac{1}{|\mathbf{x}|^2} \; . \tag{8.35}$$

Notice that $\boldsymbol{\nabla}\theta(\mathbf{x})$ is reminiscent of the vector potential associated with a very long thin solenoid orthogonal to the plane in the origin. To estimate the energy cost of such a vortex configuration observe that:

$$\sum_\nu (1 - \mathbf{S}_\mathbf{x} \cdot \mathbf{S}_{\mathbf{x}+\mathbf{e}_\nu}) \approx \frac{1}{2} \sum_\nu |\Delta_\nu \theta_\mathbf{x}|^2 \sim \frac{1}{2} |\boldsymbol{\nabla}\theta(\mathbf{x})|^2 = \frac{1}{2}\frac{1}{|\mathbf{x}|^2} \; ,$$

where we substituted the finite difference derivative with a continuum derivative and used Eq. (8.35). Hence a total contribution of a vortex to the "action" (energy) can be estimated, in the continuum limit, to be:

$$H[\theta_{\text{vortex}}] \approx \frac{J}{2} \int_a^{La} \mathrm{d}^2\mathbf{x} \, |\boldsymbol{\nabla}\theta_{\text{vortex}}|^2 = \frac{J}{2} \int_a^{La} \mathrm{d}^2\mathbf{x} \, \frac{1}{|\mathbf{x}|^2} = \pi J \log L \; . \tag{8.36}$$

One might erroneously think that since this energy *diverges* for $L \to \infty$, vortex contributions can be effectively neglected. But Kosterlitz and Thouless argue, on the contrary, as follows. Let us estimate the *free-energy* contribution due to vortex configurations, taking into account that there is a configurational entropy $S_{\text{vortex}} = k_B \log L^2$ associated with the fact that you can put the centre of the vortex in *any* of the L^2 sites of the lattice. Indeed, you can estimate the extra contribution to the partition function as follows:

$$Z_{\text{vortex}} = \sum_{\text{Config}}^{1-\text{vortex}} \mathrm{e}^{-\beta H[\theta_{\text{vortex}}]} = L^2 \mathrm{e}^{-\beta H[\theta_{\text{vortex}}]} = \mathrm{e}^{-\beta(H[\theta_{\text{vortex}}] - k_B T \log L^2)} \equiv \mathrm{e}^{-\beta F_{\text{vortex}}} \tag{8.37}$$

where:

$$F_{\text{vortex}} = H[\theta_{\text{vortex}}] - TS_{\text{vortex}} = \pi J \log L - k_B T \log L^2 = (\pi J - 2k_B T) \log L \; . \tag{8.38}$$

This simple estimate shows a remarkable fact: vortices can be neglected only if $(\pi J - 2k_B T) > 0$, while for

$$k_B T > k_B T_c = \frac{\pi J}{2} \; , \tag{8.39}$$

you expect that, since $F_{\text{vortex}} \to -\infty$ for $L \to \infty$, entropy drives a proliferation of vortices! Remarkably, this picture is quite faithful, as more detailed calculations show.

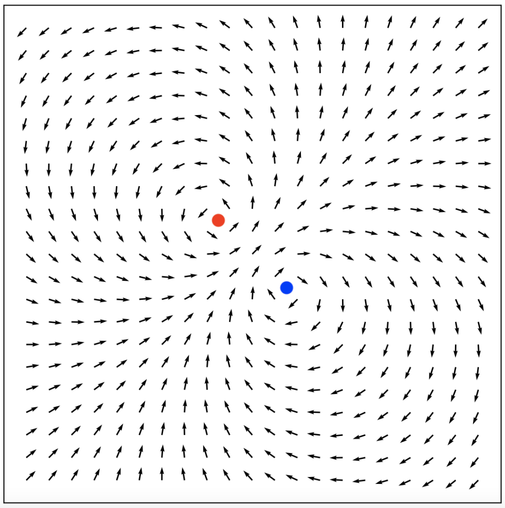

Figure 8.4: The XY model. A vortex-antivortex bound state. The vortex (red circle) is centered at $(-3/2, 3/2)$, the antivortex (blue circle) at $(3/2, -3/2)$.

The Kosterlitz-Thouless picture of the two phases of the XY model. At low-T the spin wave theory is essentially correct. Spin-spin correlations have a *power-law* decay with a *temperature-dependent* correlation exponent

$$\langle \mathbf{S}_{\mathbf{x}} \cdot \mathbf{S}_0 \rangle \simeq \left(\frac{a}{|\mathbf{x}|} \right)^{\eta(T)} \qquad \text{with} \qquad \eta(T) = \frac{k_B T}{2\pi J} \le \eta(T_c) = \frac{1}{4} \,. \tag{8.40}$$

Free vortices do not exist, although bound states of vortex-antivortex do exist, they do not disorder the system efficiently. As T increases, the vortex-antivortex bound states get larger and larger, until at T_c they *unbind*, disordering the system for $T > T_c$, with exponentially decaying spin-spin correlations:

$$\langle \mathbf{S}_{\mathbf{x}} \cdot \mathbf{S}_0 \rangle \simeq \mathrm{e}^{-|\mathbf{x}|/\xi(T)} \qquad \text{for} \qquad T > T_c = \frac{\pi J}{2 k_B} \,. \tag{8.41}$$

The critical temperature is such that:

$$k_B T_c = \frac{\pi J}{2} \qquad \longrightarrow \qquad \eta(T_c) = \frac{1}{4} \,. \tag{8.42}$$

Alternatively, $\beta_c J = 2/\pi$. For $T > T_c$ one might say that the state is a *vortex condensate* of "indefinite global vorticity".

8.2. From the Villain model to the Coulomb gas

The crucial term appearing in the partition function reads (recall $K = \beta J$):

$$\mathrm{e}^{-\beta H_{\mathrm{XY}}[\{\theta_{\mathbf{x}}\}]} = \prod_{\mathbf{x}} \prod_{\nu=1,2} \mathrm{e}^{-K\left(1-\cos(\theta_{\mathbf{x}+\mathbf{e}_\nu}-\theta_{\mathbf{x}})\right)} \,. \tag{8.43}$$

On each link of the dual lattice associated to the two points $(\mathbf{x}, \mathbf{x}+\mathbf{e}_\nu)$ we do have a periodic function of the form $\mathrm{e}^{K\cos(\Delta_\nu \theta_{\mathbf{x}})}$ for which we can use a Fourier series expansion:

$$\begin{aligned} \mathrm{e}^{K\cos\theta} &= \sum_{n\in\mathbb{Z}} \mathrm{e}^{in\theta} I_n(K) \\ I_n(K) &= \int_{-\pi}^{\pi} \frac{\mathrm{d}\theta}{2\pi}\, \mathrm{e}^{-in\theta}\, \mathrm{e}^{K\cos\theta} \,. \end{aligned} \tag{8.44}$$

Indeed, the Fourier component $I_n(K)$ is a special function: the n-th Bessel function of imaginary argument, also known as modified Bessel function. [5]

In the limit in which K is large, the function $\mathrm{e}^{K\cos\theta}$ has a large maximum, equal to e^K, at all $\theta = 2\pi m$ with $m \in \mathbb{Z}$, and one way to keep track of the periodicity in θ is to expand as usual $\cos\theta = 1 - \frac{1}{2}\theta^2 + \cdots$ in the exponent but to "periodically replicate" the resulting Gaussian as follows:

$$\mathrm{e}^{K\cos\theta} \longrightarrow \mathrm{e}^{K} \sum_{m\in\mathbb{Z}} \mathrm{e}^{-\frac{K}{2}(\theta-2\pi m)^2} \,. \tag{8.45}$$

---

[5] The integral representation of the ordinary Bessel's function $J_n(x)$ is

$$J_n(x) = \int_{-\pi}^{\pi} \frac{\mathrm{d}\theta}{2\pi}\, \mathrm{e}^{in\theta} \mathrm{e}^{-ix\sin\theta} = i^n \int_{-\pi}^{\pi} \frac{\mathrm{d}\theta}{2\pi}\, \mathrm{e}^{in\theta} \mathrm{e}^{-ix\cos\theta}$$

The modified Bessel function is defined as:

$$I_n(x) = i^{-n} J_n(ix) = \int_{-\pi}^{\pi} \frac{\mathrm{d}\theta}{2\pi}\, \mathrm{e}^{in\theta} \mathrm{e}^{x\cos\theta} \,.$$

This is an approximation — akin in some way to the spin-wave approximation —, which is quite good for sufficiently large K, and with the extra advantage that you do no violence to the periodicity. But there is another route to obtaining an expression for $\mathrm{e}^{K\cos\theta}$ when K is large, which follows directly from the Fourier series in terms of the modified Bessel's function, once you realize what is the asymptotic expression for $I_n(K)$ valid for large K.

Exercise 8.1. The large x asymptotic expansion of $I_n(x)$. Consider the integral representation of $I_n(x)$, which we report here:

$$I_n(x) = \int_{-\pi}^{\pi} \frac{\mathrm{d}\theta}{2\pi}\, \mathrm{e}^{-in\theta}\, \mathrm{e}^{x\cos\theta} \;.$$

Observe that the maximum of the integrand in $I_n(x)$ is for $\theta = 0$, and this dominates the integral for large x. Expand the cosine and argue, by performing the Gaussian integral that emerges, that for large x the asymptotic expansion of $I_n(x)$ is given by:

$$I_n(x) \approx \frac{1}{\sqrt{2\pi x}}\, \mathrm{e}^{x-\frac{n^2}{2x}} \qquad \text{for} \qquad x \gg 1 \;. \tag{8.46}$$

By inserting this asymptotic expansion of $I_n(K)$, valid for large K, into the exact Fourier series representation you would write that:

$$\mathrm{e}^{K\cos\theta} \longrightarrow \frac{\mathrm{e}^{K}}{\sqrt{2\pi K}} \sum_{n\in\mathbb{Z}} \mathrm{e}^{-\frac{n^2}{2K}+in\theta} \qquad \text{for large } \; K \;. \tag{8.47}$$

It is remarkable that these two seemingly different approximations of $\mathrm{e}^{K\cos\theta}$ for large K indeed *coincide*. To appreciate this fact, and its consequences, we need to introduce an important tool that we will use repeatedly: the Dirac-comb identity and the associated Poisson's summation formula.

Poisson's summation formula. We are all very used to the Dirac's identity

$$\delta(x) = \int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi}\, \mathrm{e}^{ikx} = \int_{-\infty}^{\infty} \mathrm{d}k\, \mathrm{e}^{2\pi ikx} \;.$$

Quite amusingly, if the integral over k is substituted by a sum at integer values $k = 2\pi m$ the Dirac's delta on the left hand side gets *periodically repeated* and the so-called Dirac-comb (or periodic delta-function) identity emerges:

$$\sum_{n\in\mathbb{Z}} \delta(x-n) = \sum_{m\in\mathbb{Z}} \mathrm{e}^{2\pi imx} \;. \tag{8.48}$$

This identity, upon integrating over an arbitrary function $g(x)$, leads to the remarkable *Poisson's summation formula*:

$$\sum_{n\in\mathbb{Z}} g(n) = \sum_{m\in\mathbb{Z}} \int_{-\infty}^{\infty} \mathrm{d}x\, \mathrm{e}^{2\pi imx} g(x) \;, \tag{8.49}$$

which relates the sum of the function evaluated at integers n with a sum of the Fourier components at $k = 2\pi m$ of the same function.

Let us now apply Poisson's summation formula to a Gaussian function

$$g(x) = \frac{1}{\sqrt{2\pi K_{\mathrm{V}}}}\, \mathrm{e}^{-\frac{x^2}{2K_{\mathrm{V}}}-ix\theta} \;.$$

We get:

$$\begin{aligned} \frac{1}{\sqrt{2\pi K_{\mathrm{V}}}} \sum_{n\in\mathbb{Z}} \mathrm{e}^{-\frac{n^2}{2K_{\mathrm{V}}} - in\theta} &= \sum_{m\in\mathbb{Z}} \int_{-\infty}^{\infty} \mathrm{d}x \, \frac{1}{\sqrt{2\pi K_{\mathrm{V}}}} \mathrm{e}^{-\frac{x^2}{2K_{\mathrm{V}}} + ix(2\pi m - \theta)} \\ &= \sum_{m\in\mathbb{Z}} \mathrm{e}^{-\frac{K_{\mathrm{V}}}{2}(\theta - 2\pi m)^2} \,, \end{aligned} \tag{8.50}$$

where the second line follows by performing the Gaussian integral. [6]

The Villain's identity. By changing $n \to -n$ we rewrite the identity we just derived as:

$$\begin{aligned} \sum_{m\in\mathbb{Z}} \mathrm{e}^{-\frac{K_{\mathrm{V}}}{2}(\theta - 2\pi m)^2} &= \frac{1}{\sqrt{2\pi K_{\mathrm{V}}}} \sum_{n\in\mathbb{Z}} \mathrm{e}^{-\frac{n^2}{2K_{\mathrm{V}}} + in\theta} \\ &= \frac{1}{\sqrt{2\pi K_{\mathrm{V}}}} \Big(1 + 2\sum_{n=1}^{\infty} \mathrm{e}^{-\frac{n^2}{2K_{\mathrm{V}}}} \cos n\theta \Big) \,. \end{aligned} \tag{8.52}$$

This identity is valid for *all values* of K_{V}. We will mostly use it in the first form, but the second is also inspiring.

In particular, taking $K_{\mathrm{V}} = K \gg 1$, we see that the two large-K expressions for $\mathrm{e}^{K\cos\theta}$ in Eq. (8.45) and (8.47) indeed coincide. But we can do more. Suppose that you assume K_{V} to be *small*, $K_{\mathrm{V}} \ll 1$, rather than large. Then, the sum over n on the RHS of the identity in Eq. (8.52) can be effectively cut-off to values of $n = \pm 1$. We then have, for the RHS:

$$\frac{1}{\sqrt{2\pi K_{\mathrm{V}}}} (1 + 2\mathrm{e}^{-\frac{1}{2K_{\mathrm{V}}}} \cos\theta + \cdots) \approx \frac{1}{\sqrt{2\pi K_{\mathrm{V}}}} \mathrm{e}^{2\mathrm{e}^{-\frac{1}{2K_{\mathrm{V}}}} \cos\theta} \,.$$

By setting

$$K = 2\,\mathrm{e}^{-\frac{1}{2K_{\mathrm{V}}}} \ll 2 \qquad \Longrightarrow \qquad K_{\mathrm{V}} = \frac{1}{2\log 2/K} \,,$$

you realise that K is *small* when $K_{\mathrm{V}} \ll 1$, and that the Villain's identity suggests an expression of the form:

$$\mathrm{e}^{K\cos\theta} \approx \sqrt{2\pi K_{\mathrm{V}}} \sum_{m\in\mathbb{Z}} \mathrm{e}^{-\frac{K_{\mathrm{V}}}{2}(\theta - 2\pi m)^2} \qquad \text{for small} \;\; K \,.$$

Hence, remarkably, a *periodic Gaussian expression* seems to be appropriate even when K is small. This led Villain, in 1975, to introduce a model where $\mathrm{e}^{K\cos\theta}$ is *always* approximated with a periodically repeated Gaussian.

---

[6] Recall the fundamental gaussian integral

$$\int_{-\infty}^{\infty} \frac{\mathrm{d}x}{\sqrt{2\pi a}} \, \mathrm{e}^{-\frac{x^2}{2a} + ikx} = \mathrm{e}^{-\frac{a}{2}k^2} \,. \tag{8.51}$$

The Villain's approximation. Villain proposed to modify the XY-model term as follows

$$\mathrm{e}^{-K(1-\cos\theta)} \longrightarrow R_{\mathrm{V}}\sqrt{2\pi K_{\mathrm{V}}}\sum_{m\in\mathbb{Z}} \mathrm{e}^{-\frac{K_{\mathrm{V}}}{2}(\theta-2\pi m)^2} = R_{\mathrm{V}}\sum_{n\in\mathbb{Z}} \mathrm{e}^{-\frac{n^2}{2K_{\mathrm{V}}}+in\theta} \;, \tag{8.53}$$

where R_{V} and K_{V} are both functions of K, chosen as to best approximate the original term, and the second equivalent form follows from the identity in Eq. (8.52). It turns out that the choice:

$$\left\{ \begin{array}{rcl} K_{\mathrm{V}} & = & \dfrac{1}{2\log I_0(K)/I_1(K)} \\ & & \\ R_{\mathrm{V}} & = & \mathrm{e}^{-K} I_0(K) \end{array} \right. \tag{8.54}$$

nicely interpolates between the large-K and small-K limits we have seen before.

The Villain model. Adopting the Villain's periodic Gaussian approximation, we trade the exact XY term by a new model, known as the Villain's model, which we can write in two equivalent ways. The first is a periodic gaussian form, where we introduce an integer value variable $m_{\mathbf{x},\nu} \in \mathbb{Z}$ on each link of the dual lattice and write the partition function as:

$$Z_{\mathrm{V}} = \left(R_{\mathrm{V}}\sqrt{2\pi K_{\mathrm{V}}}\right)^{2N} \sum_{\{m_{\mathbf{x},\nu}\in\mathbb{Z}\}} \int_0^{2\pi} \Big[\prod_{\mathbf{x}} \tfrac{\mathrm{d}\theta_{\mathbf{x}}}{2\pi}\Big] \left(\mathrm{e}^{-\frac{K_{\mathrm{V}}}{2}\sum_{\mathbf{x}}\sum_{\nu=1,2}(\Delta_\nu\theta_{\mathbf{x}}-2\pi m_{\mathbf{x},\nu})^2}\right) . \tag{8.55}$$

The second form, equivalent by the identity in Eq. (8.52), requires again an integer valued variable $n_{\mathbf{x},\nu} \in \mathbb{Z}$ for every link of the dual lattice, and writes the partition function as

$$\begin{aligned} Z_{\mathrm{V}} &= R_{\mathrm{V}}^{2N} \int_0^{2\pi} \Big[\prod_{\mathbf{x}} \tfrac{\mathrm{d}\theta_{\mathbf{x}}}{2\pi}\Big] \left(\prod_{\mathbf{x}}\prod_{\nu=1,2}\sum_{n_{\mathbf{x},\nu}\in\mathbb{Z}} \mathrm{e}^{in_{\mathbf{x},\nu}(\Delta_\nu\theta_{\mathbf{x}})}\mathrm{e}^{-\frac{1}{2K_{\mathrm{V}}}n_{\mathbf{x},\nu}^2}\right) \\ &= R_{\mathrm{V}}^{2N} \int_0^{2\pi} \Big[\prod_{\mathbf{x}} \tfrac{\mathrm{d}\theta_{\mathbf{x}}}{2\pi}\Big] \left(\sum_{\{n_{\mathbf{x},\nu}\in\mathbb{Z}\}} \mathrm{e}^{i\sum_{\mathbf{x}}\sum_\nu n_{\mathbf{x},\nu}(\Delta_\nu\theta_{\mathbf{x}})}\mathrm{e}^{-\frac{1}{2K_{\mathrm{V}}}\sum_{\mathbf{x}}\sum_\nu n_{\mathbf{x},\nu}^2}\right) . \end{aligned} \tag{8.56}$$

This second form is the one we will adopt to proceed with a series of further mappings which are very instructive. Observe indeed that $\theta_{\mathbf{x}}$ appears *linearly* in the exponential. Let us rewrite, by changing variables, the discrete equivalent of "integration by parts":

$$\begin{aligned} \sum_{\mathbf{x}}\sum_\nu n_{\mathbf{x},\nu}(\Delta_\nu\theta_{\mathbf{x}}) = \sum_{\mathbf{x}}\sum_\nu n_{\mathbf{x},\nu}(\theta_{\mathbf{x}+\mathbf{e}_\nu}-\theta_{\mathbf{x}}) &= \sum_{\mathbf{x}}\sum_\nu (n_{\mathbf{x}-\mathbf{e}_\nu,\nu}-n_{\mathbf{x},\nu})\,\theta_{\mathbf{x}} \\ &= -\sum_{\mathbf{x}}\sum_\nu (\bar{\Delta}_\nu n_{\mathbf{x},\nu})\,\theta_{\mathbf{x}} \;, \end{aligned} \tag{8.57}$$

where $\bar{\Delta}_\nu n_{\mathbf{x},\nu} = n_{\mathbf{x},\nu} - n_{\mathbf{x}-\mathbf{e}_\nu,\nu}$ is a "backward" finite difference. Hence, the integral over $\theta_{\mathbf{x}}$ simply imposes a local conservation law for the link integer variables $n_{\mathbf{x},\nu}$:

$$\int_0^{2\pi}\frac{\mathrm{d}\theta_{\mathbf{x}}}{2\pi}\,\mathrm{e}^{i\sum_\nu\bar{\Delta}_\nu n_{\mathbf{x},nu}\,\theta_{\mathbf{x}}} = \delta_{\sum_\nu\bar{\Delta}_\nu n_{\mathbf{x},nu},0} \;,$$

a constraint which is essentially a discrete version of a "zero-flux condition" for the integer vector field $(n_{\mathbf{x},1}, n_{\mathbf{x},2})$:

$$\sum_\nu \bar{\Delta}_\nu n_{\mathbf{x},\nu} = n_{\mathbf{x},1} - n_{\mathbf{x}-\mathbf{e}_1,1} + n_{\mathbf{x},2} - n_{\mathbf{x}-\mathbf{e}_2,2} \equiv 0 \qquad \forall\mathbf{x} \;. \tag{8.58}$$

One way to implement the constraint is to represent the link variables $n_{\mathbf{x},\nu}$ in terms of discrete derivatives of an integer valued height variable $h_{\mathbf{x}}$ sitting at the *lattice sites*, as follows: [7]

$$\begin{cases} n_{\mathbf{x},1} = \Delta_2 h_{\mathbf{x}} \\ n_{\mathbf{x},2} = -\Delta_1 h_{\mathbf{x}} \end{cases} \qquad \Longrightarrow \qquad \sum_{\nu} n^2_{\mathbf{x},\nu} = \sum_{\nu} (\Delta_\nu h_{\mathbf{x}})^2 \; . \tag{8.60}$$

> **The Villain model mapped into a discrete height problem.** This series of transformations allows us to rewrite the Villain partition function as
>
> $$\begin{aligned} Z_{\mathrm{V}} &= R_{\mathrm{V}}^{2N} \int_0^{2\pi} \Big[\prod_{\mathbf{x}} \frac{\mathrm{d}\theta_{\mathbf{x}}}{2\pi} \Big] \Bigg(\sum_{\{n_{\mathbf{x},\nu} \in \mathbb{Z}\}} \mathrm{e}^{i \sum_{\mathbf{x}} \sum_{\nu} n_{\mathbf{x},\nu} (\Delta_\nu \theta_{\mathbf{x}})} \mathrm{e}^{-\frac{1}{2K_{\mathrm{V}}} \sum_{\mathbf{x}} \sum_{\nu} n^2_{\mathbf{x},\nu}} \Bigg) \\ &= R_{\mathrm{V}}^{2N} \sum_{\{h_{\mathbf{x}} \in \mathbb{Z}\}} \mathrm{e}^{-\frac{1}{2K_{\mathrm{V}}} \sum_{\mathbf{x}} \sum_{\nu} (\Delta_\nu h_{\mathbf{x}})^2} \\ \longrightarrow \; Z_{\mathrm{DG}} &= \sum_{\{h_{\mathbf{x}} \in \mathbb{Z}\}} \mathrm{e}^{-\frac{1}{2K_{\mathrm{V}}} \sum_{\mathbf{x}} \sum_{\nu=1,2} (\Delta_\nu h_{\mathbf{x}})^2} \; . \end{aligned} \tag{8.61}$$
>
> The model we have arrived at is known as *discrete Gaussian* model, a discrete-height model introduced to describe the roughening transition of solid surfaces, studied by Chiu & Weeks in 1976. Notice the crucially important integer constraints for the height variables $h_{\mathbf{x}}$.

The integer constraints on $h_{\mathbf{x}}$ are hard to deal with. But we can bypass them at the cost of re-introducing integrals, using once again Poisson's summation formula. This would allow us to write the discrete Gaussian model in three equivalent forms:

$$\begin{aligned} Z_{\mathrm{DG}} &= \sum_{\{h_{\mathbf{x}} \in \mathbb{Z}\}} \mathrm{e}^{-\frac{1}{2K_{\mathrm{V}}} \sum_{\mathbf{x}} \sum_{\nu=1,2} (\Delta_\nu h_{\mathbf{x}})^2} \\ &= \sum_{\{m_{\mathbf{x}} \in \mathbb{Z}\}} \int_{-\infty}^{\infty} \Big[\prod_{\mathbf{x}} \mathrm{d}\phi_{\mathbf{x}} \Big] \, \mathrm{e}^{2\pi i \sum_{\mathbf{x}} m_{\mathbf{x}} \phi_{\mathbf{x}}} \, \mathrm{e}^{-\frac{1}{2K_{\mathrm{V}}} \sum_{\mathbf{x}} \sum_{\nu=1,2} (\Delta_\nu \phi_{\mathbf{x}})^2} \\ &= Z_{\mathrm{sw}}(K_{\mathrm{V}}^{-1}) \sum_{\{m_{\mathbf{x}} \in \mathbb{Z}\}} \mathrm{e}^{-2\pi^2 K_{\mathrm{V}} \sum_{\mathbf{x},\mathbf{x}'} m_{\mathbf{x}} G_{\mathbf{x},\mathbf{x}'} m_{\mathbf{x}'}} \; . \end{aligned} \tag{8.62}$$

The third remarkable expression — obtained by performing the Gaussian integrals over $\phi_{\mathbf{x}}$ in exactly the same way as we did when studying the spin-wave approximation to the original XY model —, involves the so-called *Coulomb gas* partition function. The $G_{\mathbf{x},\mathbf{x}'}$ which appears is once again the discrete lattice propagator associated to the discrete Laplacian in two dimensions.

---

[7] More formally, defining $n_{\mathbf{x},\nu} = \sum_{\nu'} \varepsilon_{\nu,\nu'} \Delta_{\nu'} h_{\mathbf{x}}$, with $1 = \varepsilon_{1,2} = -\varepsilon_{2,1}$ antisymmetric, you can easily see that:

$$\sum_{\nu} \Delta_\nu n_{\mathbf{x},\nu} = \sum_{\nu,\nu'} \varepsilon_{\nu,\nu'} \Delta_\nu \Delta_{\nu'} h_{\mathbf{x}} = 0 \; . \tag{8.59}$$

Observe however that the "zero-flux condition"

$$\sum_{\nu} \bar{\Delta}_\nu n_{\mathbf{x},\nu} \stackrel{\mathrm{def}}{=} \sum_{\nu} (n_{\mathbf{x}-\mathbf{e}_\nu,\nu} - n_{\mathbf{x},\nu}) = \sum_{\nu} \Delta_\nu n_{\mathbf{x}-\mathbf{e}_\nu,\nu} = 0 \; ,$$

is slightly different in form from the zero-divergence condition

$$\sum_{\nu} \Delta_\nu n_{\mathbf{x},\nu} = 0 \; .$$

Details can be found in Kleinert's book on *Gauge fields in Condensed Matter physics*, Vol. II, Chap. 4.

Summary so far. Starting from the periodic-gaussian approximation to the XY model, i.e., the Villain's model, we have proceeded through a series of exact mappings:

$$Z_{\mathrm{V}} \longrightarrow Z_{\mathrm{DG}} \longrightarrow Z_{\mathrm{CG}} = \sum_{\{m_{\mathbf{x}}\in\mathbb{Z}\}} \int_{-\infty}^{\infty} \Big[\prod_{\mathbf{x}} \mathrm{d}\phi_{\mathbf{x}}\Big]\, \mathrm{e}^{2\pi i \sum_{\mathbf{x}} m_{\mathbf{x}}\phi_{\mathbf{x}}}\, \mathrm{e}^{-\frac{1}{2K_{\mathrm{V}}}\sum_{\mathbf{x}}\sum_{\nu=1,2}(\Delta_\nu \phi_{\mathbf{x}})^2} \;, \tag{8.63}$$

where the last step follows by applying the Poisson's summation formula to the discrete heights model. The final **Coulomb gas** form, by performing the Gaussian integral over the $\phi_{\mathbf{x}}$, can be also expressed as:

$$Z_{\mathrm{CG}} = Z_{\mathrm{sw}}(K_{\mathrm{V}}^{-1}) \sum_{\{m_{\mathbf{x}}\in\mathbb{Z}\}} \mathrm{e}^{-2\pi^2 K_{\mathrm{V}} \sum_{\mathbf{x},\mathbf{x}'} m_{\mathbf{x}} G_{\mathbf{x},\mathbf{x}'} m_{\mathbf{x}'}} \;. \tag{8.64}$$

8.3. Epilogue: The RG in momentum space

The Coulomb gas form is the ideal starting point for a field-theoretical analysis based on the Renormalization Group (RG). The idea is to move to momentum space, integrate out an outer shell of the largest momenta, to obtain equations for the renormalized model parameters. The story is described in some detail in Kogut [33]. It might be an instructive seminar assignment for the final exam.

9. Ising lattice gauge theory and beyond

We have discussed broken symmetry in statistical mechanics, and the idea of a local order parameter: a symmetric Hamiltonian can give rise to states which are effectively disconnected in the thermodynamic limit, and break the symmetry. This can happen in the ground state and, for sufficiently large spatial dimensions, even at finite temperature. We have discussed already that this is at variance with the situation typically encountered in quantum mechanics for few-particle systems, where symmetries are not broken. A paradigmatic example is a particle in a double-well potential, have a look again at Fig. 5.1, where the Hamiltonian is parity symmetric, and the ground state is *even* and separated by a gap from the first excited *odd* state. As discussed, the analogy with symmetry breaking in statistical mechanics emerges when you consider a barrier that *becomes infinitely large*: the gap between the two symmetric states would become *exponentially small* and, to all practical purposes, a particle sitting close to one of the two minima (broken-symmetry state) would not be able to *tunnel* to the other minimum.

In this chapter, we will discuss models — gauge theories [1] — which display a new type of symmetry, a *local symmetry*, which cannot be spontaneously broken, much in the same way as parity is not broken for the finite double-well in quantum mechanics. As a consequence, phases in these models *cannot be distinguished by local order parameters*, which vanish due to symmetry. Topology and ground state degeneracy will be one of the *leitmotivs* of the story we are going to tell. In some sense, the planar XY model in two dimensions is nice anticipation of some of these ingredients, like the absence of a local order parameter, and the role of topology and vortex-antivortex unbinding. But we will see that there is more to that. The main reference for this chapter is the review paper by Kogut [33]. Very instructive are also the videos of the lectures given at ICTP by Xie Chen (Caltech) Lecture 1, Lecture 2.

9.1. Wegner's idea: a model with a local (gauge) symmetry

To exemplify the general discussion, take a square lattice, with nearest-neighbor lattice vectors $\mathbf{e}_1 = a(1,0)$ and $\mathbf{e}_2 = a(0,1)$. The vertices of the square lattices are denoted by $\mathbf{x}$: each is connected to $d = 2$ neighbors, $\mathbf{x}+\mathbf{e}_1$ and $\mathbf{x}+\mathbf{e}_2$, by $d = 2$ *links*, on the edges of the *plaquette* defined by the four vertices $\mathbf{x}$, $\mathbf{x}+\mathbf{e}_1$, $\mathbf{x}+\mathbf{e}_1+\mathbf{e}_2$, $\mathbf{x}+\mathbf{e}_2$, and with center at $\mathbf{x}_*$, see Fig. 9.1.

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[1] To all practical purposes the word "*gauge* theory" will be used here to mean "a theory with a *local symmetry*"

Link and plaquette notation. We will use the following shorthand notation for the links:

$$\mathbf{x},\pm 1 \longleftrightarrow (\mathbf{x},\mathbf{x}\pm\mathbf{e}_1) \qquad\qquad \mathbf{x},\pm 2 \longleftrightarrow (\mathbf{x},\mathbf{x}\pm\mathbf{e}_2)\ . \tag{9.1}$$

Notice that the same *unoriented* link can be labelled in two ways, for instance $\mathbf{x},-1 \equiv \mathbf{x}-\mathbf{e}_1, 1$. With this notation, the four links around the plaquette at $\mathbf{x}_*$, see Fig. 9.1, would be denoted as:

$$\ell_1 = \mathbf{x},1 \qquad \ell_2 = \mathbf{x}+\mathbf{e}_1, 2 \qquad \ell_3 = \mathbf{x}+\mathbf{e}_1+\mathbf{e}_2, -1 \qquad \ell_4 = \mathbf{x}+\mathbf{e}_2, -2\ . \tag{9.2}$$

Correspondingly, we define the product of *four* $\hat{\sigma}^z$ operators sitting at those links as:

$$\widehat{Z}_{\mathbf{x}_*} = \hat{\sigma}^z_{\ell_1}\,\hat{\sigma}^z_{\ell_2}\,\hat{\sigma}^z_{\ell_3}\,\hat{\sigma}^z_{\ell_4}\ . \tag{9.3}$$

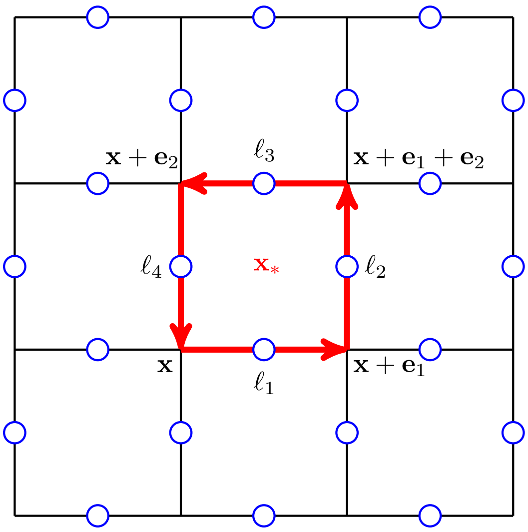

Figure 9.1: A portion of a square lattice, with a plaquette highlighted in red (the meaning of the arrows will be clarified later on). Spins are sitting on the edges of the lattice, denoted by circles. The centre of the plaquette is denoted as $\mathbf{x}_*$.

The spins are now placed on the four links around each plaquette, and you write the model as a *four spin interaction*:

$$\widehat{H} = -J\sum_{\mathbf{x}} \hat{\sigma}^z_{\ell_1}\,\hat{\sigma}^z_{\ell_2}\,\hat{\sigma}^z_{\ell_3}\,\hat{\sigma}^z_{\ell_4} = -J\sum_{\mathbf{x}_*} \widehat{Z}_{\mathbf{x}_*}\ . \tag{9.4}$$

Consider now the following operator $\widehat{G}_{\mathbf{x}}$, defined at each *internal* vertex $\mathbf{x}$ of the lattice as:

$$\widehat{G}_{\mathbf{x}} = \hat{\sigma}^x_{\mathbf{x},1}\hat{\sigma}^x_{\mathbf{x},2}\hat{\sigma}^x_{\mathbf{x},-1}\hat{\sigma}^x_{\mathbf{x},-2} \qquad \Longrightarrow \qquad \widehat{G}_{\mathbf{x}}\hat{\sigma}^z_{\mathbf{x},\nu}\widehat{G}_{\mathbf{x}} = -\hat{\sigma}^z_{\mathbf{x},\nu} \qquad \nu = \pm 1, \pm 2\ , \tag{9.5}$$

where we used $\hat{\sigma}^x\hat{\sigma}^z\hat{\sigma}^x = -\hat{\sigma}^z$. In words: $\widehat{G}_{\mathbf{x}}$ flips all spins on the links touching $\mathbf{x}$.

Internal, boundary, and corner vertices. When periodic boundary conditions (PBC) are chosen, all vertices are "internal", and they have 4 links. We will discuss later on the case of open boundary conditions (OBC), where 4 vertices sit at the corners, and have stars with two links only, while the other boundary vertices have stars with three links. Correspondingly, the operator $\widehat{G}_{\mathbf{x}}$ has a reduced number of $\hat{\sigma}^x$.

It is easy to prove that $\widehat{G}_{\mathbf{x}}$ commutes with $\widehat{H}$ for all $\mathbf{x}$: [2]

$$[\widehat{G}_{\mathbf{x}}, \widehat{H}] = 0 \qquad\qquad \forall\mathbf{x}\ . \tag{9.6}$$

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[2] To prove this, observe that $\widehat{G}^2_{\mathbf{x}} = 1$, so that we need to show $\widehat{G}_{\mathbf{x}}\widehat{H}\widehat{G}_{\mathbf{x}} = \widehat{H}$. Take now a plaquette term in the Hamiltonian: if $\mathbf{x}$ does not touch that plaquette, the commutation is trivial. The only non-trivial commutation occurs when $\mathbf{x}$ is *any* of the vertices of the plaquette. But then, since $\hat{\sigma}^x\hat{\sigma}^z\hat{\sigma}^x = -\hat{\sigma}^z$, you flip exactly *two* spins on the edges of the plaquette, and the two minus signs produce an overall $+1$.

The set of links touching $\mathbf{x}$, which enter in the definition of $\widehat{G}_{\mathbf{x}}$ is defined as the "star" at $\mathbf{x}$:

$$\mathrm{star}(\mathbf{x}) = \big\{\ell = \mathbf{x}, \pm\nu \quad \text{with} \quad \nu = 1,2 \,|\, \ell \in \text{lattice}\big\} \qquad \Longrightarrow \qquad \widehat{G}_{\mathbf{x}} = \prod_{\ell\in\mathrm{star}(\mathbf{x})} \hat{\sigma}^x_\ell \,. \tag{9.7}$$

This definition works in principle also for the possible boundary sites of systems with OBC, as we will illustrate further below.

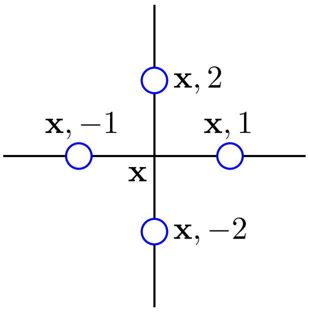

Figure 9.2: An internal vertex at $\mathbf{x}$ and the four neighboring links in a $d = 2$ dimensional (square) lattice, defining the star($\mathbf{x}$). The operator $\widehat{G}_{\mathbf{x}} = \hat{\sigma}^x_{\mathbf{x},1}\hat{\sigma}^x_{\mathbf{x},2}\hat{\sigma}^x_{\mathbf{x},-1}\hat{\sigma}^x_{\mathbf{x},-2}$ flips the four spins sitting at the blue circles on the links that enter $\mathbf{x}$.

One thing we need to discuss is the boundary conditions on the lattice. One standard choice is periodic boundary conditions (PBC), as illustrated in Fig. 9.3 (left). An alternative choice, breaking translational symmetry, is open boundary conditions (OBC), illustrated in Fig. 9.3 (right). We will later discuss the important role of boundary conditions concerning the topological aspects of the model and ground-state degeneracy.

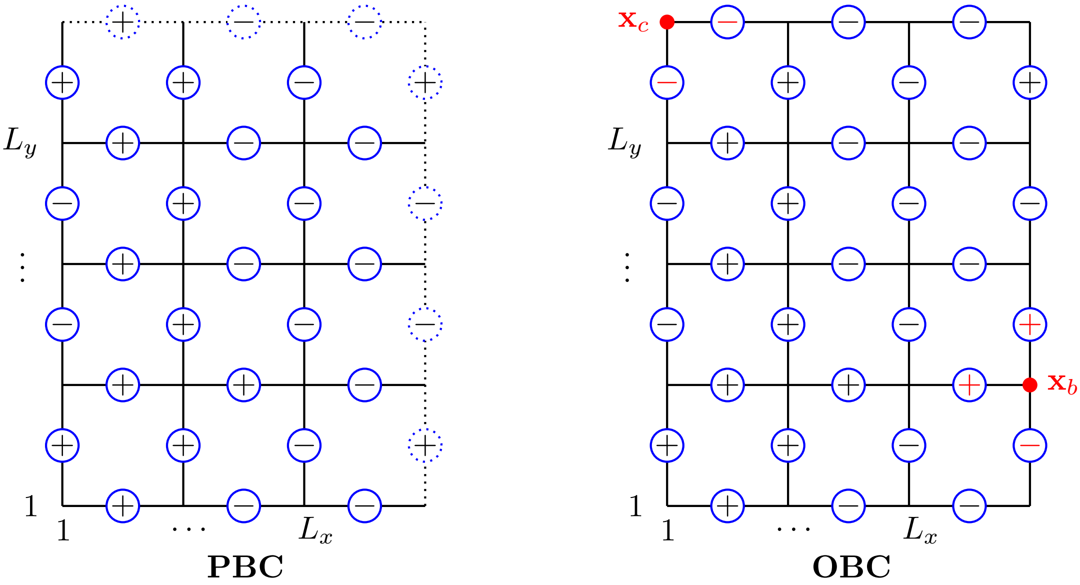

Figure 9.3.: A sketch of $d = 2$ (square) lattice, with $L_x \times L_y$ plaquettes. Here $L_x = 3$ and $L_y = 4$. The ± denote spin components along the z-axis, i.e., in the standard configuration basis. Notice that on many plaquettes the operator $\widehat{Z}_{\mathbf{x}_*}$ has eigenvalues -1: these plaquettes are called *frustrated*. **Left: The PBC case.** The dotted circles denote spins on links on the upper and right boundary, which are also drawn dotted: the spins, links, and vertices on those dotted boundaries should be *identified* with the corresponding ones on the "opposite" lower and left boundaries. Effectively, the model is defined on a 2-torus. All vertices ($N_{\mathrm{V}} = L_x \times L_y$ as well) correspond to "stars" with four links. **Right: the OBC case.** Here the corner vertices have stars with two links only, and the boundary vertices have stars with three links. Also, the spins on the boundaries are free. The configuration shown is almost identical to the PBC one on the left, except for the action of two $\widehat{G}_{\mathbf{x}}$ operators: one at the upper corner $\mathbf{x}_c$, and one on the right boundary vertex $\mathbf{x}_b$. You should remark that character of the plaquettes is not changed, consistently with gauge invariance. But the parity of the number on + and − along vertical and horizontal lines is affected.

The previous construction easily generalizes on higher dimensional hyper-cubic lattices. On a d-lattice we have d nearest-neighbor vectors $\mathbf{e}_\nu$ with $\nu = 1, \cdots, d$. Each site $\mathbf{x}$ has $2d$ links (edges) attached to it, which we denote by $\mathbf{x}, \pm\nu$. As before, $\mathbf{x}, -\nu \leftrightarrow (\mathbf{x}, \mathbf{x}-\mathbf{e}_\nu) \leftrightarrow \mathbf{x}-\mathbf{e}_\nu, \nu$. The plaquettes are always *squares* bounded by *four* edges. For each vertex $\mathbf{x}$, you can uniquely define a plaquette by choosing a direction $\nu = 1, \cdots, d-1$ and a second direction $\nu' > \nu$: hence you can do that in $\binom{d}{2} = d(d-1)/2$ ways. Boundary vertices in systems with OBC would have a different number of associated plaquettes, but we write our model for PBC, for simplicity of notation.

Wegner's Ising lattice gauge theory (LGT). For a hyper-cubic lattice in d-dimension, the classical Ising LGT model would read:

$$\widehat{H} \;=\; -J \sum_{\mathbf{x}} \sum_{\nu=1}^{d-1} \sum_{\nu'>\nu}^{d} \hat{\sigma}^z_{\ell_1}\, \hat{\sigma}^z_{\ell_2}\, \hat{\sigma}^z_{\ell_3}\, \hat{\sigma}^z_{\ell_4} = -J \sum_{\nu=1}^{d-1} \sum_{\nu'>\nu}^{d} \sum_{\mathbf{x}_*^{\nu\nu'}} \widehat{Z}_{\mathbf{x}_*^{\nu\nu'}} \tag{9.8}$$

where $\mathbf{x}_*^{\nu\nu'}$ is the center of the square plaquette surrounded by the four links labelled

$$\mathrm{plaq}(\mathbf{x}_*^{\nu\nu'}) = \big\{ \ell_1 = \mathbf{x}, \nu \;;\; \ell_2 = \mathbf{x}+\mathbf{e}_\nu, \nu' \;;\; \ell_3 = \mathbf{x}+\mathbf{e}_\nu+\mathbf{e}_{\nu'}, -\nu \;;\; \ell_4 = \mathbf{x}+\mathbf{e}_{\nu'}, -\nu' \big\} \;, \tag{9.9}$$

and the four spin interaction is:

$$\widehat{Z}_{\mathbf{x}_*^{\nu\nu'}} = \hat{\sigma}^z_{\ell_1}\, \hat{\sigma}^z_{\ell_2}\, \hat{\sigma}^z_{\ell_3}\, \hat{\sigma}^z_{\ell_4} = \prod_{\ell \in \mathrm{plaq}(\mathbf{x}_*^{\nu\nu'})} \hat{\sigma}^z_\ell \;. \tag{9.10}$$

You define the "star" at $\mathbf{x}$ to be set of all $2d$ links touching $\mathbf{x}$:

$$\mathrm{star}(\mathbf{x}) = \big\{ \ell = \mathbf{x}, \nu \quad \text{with} \quad \nu = \pm 1 \cdots \pm d \big\} \;. \tag{9.11}$$

The flip operator which commutes with $\widehat{H}$ at each vertex $\mathbf{x}$ (see Fig. 9.4) is defined as:

$$\widehat{G}_{\mathbf{x}} = \prod_{\nu=1}^{d} \Big(\hat{\sigma}^x_{\mathbf{x},\nu} \hat{\sigma}^x_{\mathbf{x},-\nu} \Big) = \prod_{\ell \in \mathrm{star}(\mathbf{x})} \hat{\sigma}^x_\ell \qquad \Longrightarrow \qquad [\widehat{G}_{\mathbf{x}}, \widehat{H}] = 0 \qquad \forall \mathbf{x} \;. \tag{9.12}$$

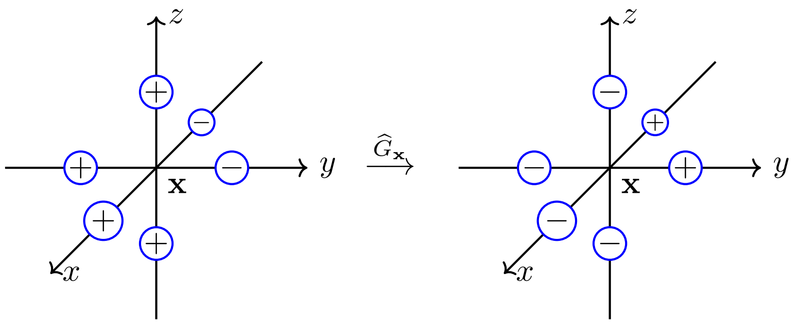

Figure 9.4: The vertex at $\mathbf{x}$ and its 6 neighboring links in a $d = 3$ dimensional cubic lattice, the star($\mathbf{x}$). The operator $\widehat{G}_{\mathbf{x}}$ flips the $2d = 6$ spins sitting at the blue circles on the links that touch $\mathbf{x}$, as exemplified with a local configuration of spins.

It is worth stressing that the presence of such an extensive set of commuting operators implies an exponentially large degeneracy of each configuration. On a hyper-cubic lattice with N_{V} vertices $\mathbf{x}$ — hence $N_{\mathrm{L}} = dN_{\mathrm{V}}$ links (or edges) on which the spins sit — there are $N_{\mathrm{C}} = 2^{N_{\mathrm{L}}} = 2^{dN_{\mathrm{V}}}$ possible different configurations. Denote by $|\mathrm{C}\rangle$ any such configurations. [3] You can apply to $|\mathrm{C}\rangle$ any product of symmetry operators $\widehat{G}_{\mathbf{x}}$, obtaining symmetry-related configurations $|\mathrm{C}'\rangle$. More precisely, you can define an equivalence class of configurations induced by the local symmetries

$$[\mathrm{C}] = \Big\{ |\mathrm{C}'\rangle = \prod_{\mathbf{x}\in \mathrm{V}} \widehat{G}_{\mathbf{x}}^{n_{\mathbf{x}}} |\mathrm{C}\rangle \quad \text{with} \quad n_{\mathbf{x}} = 0, 1 \Big\} \;. \tag{9.13}$$

---

[3] We use a ket notation for the configurations, although they are computational basis states, i.e., eigenstates of $\hat{\sigma}^z_{\mathbf{x},\nu}$, hence for all practical purposes classical Ising configurations.

All such configurations $|\mathrm{C}'\rangle$ are guaranteed by symmetry to have the same energy, which we denote as:

$$H[\mathrm{C}] = \langle \mathrm{C}'|\widehat{H}|\mathrm{C}'\rangle \qquad\qquad \forall \mathrm{C}' \in [\mathrm{C}] \; . \tag{9.14}$$

It is quite clear that the number of elements N_{gauge} in the class [C] of gauge-related configurations is totally independent of the configuration C you started from. [4] Hence, the partition function is given by

$$Z_{\mathrm{ILGT}} = \sum_{\mathrm{C}} \mathrm{e}^{-\beta\langle \mathrm{C}|\widehat{H}|\mathrm{C}\rangle} = N_{\mathrm{gauge}} \sum_{[\mathrm{C}]} \mathrm{e}^{-\beta H[\mathrm{C}]} \; . \tag{9.15}$$

Now consider any (diagonal) operator which is gauge invariant, i.e., such that

$$O[\mathrm{C}] = \langle \mathrm{C}'|\widehat{O}|\mathrm{C}'\rangle \qquad\qquad \forall \mathrm{C}' \in [\mathrm{C}] \; . \tag{9.16}$$

For such gauge-invariant operators, we might just sum over an element of the class, as the common factor N_{gauge} cancels off:

$$\langle \widehat{O}\rangle = \frac{\displaystyle\sum_{[\mathrm{C}]} O[\mathrm{C}]\mathrm{e}^{-\beta H[\mathrm{C}]}}{\displaystyle\sum_{[\mathrm{C}]} \mathrm{e}^{-\beta H[\mathrm{C}]}} \; . \tag{9.17}$$

9.2. Elitzur theorem: gauge symmetry cannot be spontaneously broken

Elitzur's theorem states that the local gauge symmetry cannot be spontaneously broken. This implies that a local order parameter calculated by the expectation value of local non-gauge-invariant objects must vanish. We exemplify this with the local magnetization $\langle \hat{\sigma}^z_{\mathbf{x},\nu}\rangle$ in the Ising LGT case, indeed the most obvious "candidate" local order parameter.

To calculate it, we use the device of adding a small external longitudinal field h, which is then sent to zero *after* the thermodynamics limit is taken. Hence, we take the Hamiltonian to be:

$$\widehat{H}_h = \underbrace{-J\sum_{\mathbf{x}_*} \hat{\sigma}^z_{\ell_1}\hat{\sigma}^z_{\ell_2}\hat{\sigma}^z_{\ell_3}\hat{\sigma}^z_{\ell_4}}_{\widehat{H}_0} - h\sum_{\mathbf{x}}\sum_{\nu=1}^{d} \hat{\sigma}^z_{\mathbf{x},\nu} \; , \tag{9.18}$$

where $\widehat{H}_0$ is the gauge-invariant Ising LGT term, and the corresponding partition function is:

$$Z_h = \sum_{\mathrm{C}} \mathrm{e}^{-\beta H_h[\mathrm{C}]} \qquad \text{with} \qquad H_h[\mathrm{C}] = H_0[\mathrm{C}] - h\sum_{\mathbf{x}',\nu'} \langle \mathrm{C}|\hat{\sigma}^z_{\mathbf{x}',\nu'}|\mathrm{C}\rangle \; , \tag{9.19}$$

where $|\mathrm{C}\rangle$ denotes computational basis states (eigenstates of $\hat{\sigma}^z$), hence classical Ising configurations, to all practical purposes. The expectation value we need is:

$$\langle \hat{\sigma}^z_{\mathbf{x},\nu}\rangle_h = \frac{1}{Z_h}\sum_{\mathrm{C}} \langle \mathrm{C}|\hat{\sigma}^z_{\mathbf{x},\nu}|\mathrm{C}\rangle \, \mathrm{e}^{-\beta H_h[\mathrm{C}]} \; . \tag{9.20}$$

---

[4] One should be careful in counting this number, since $\prod_{\mathbf{x}\in\mathrm{V}} \widehat{G}_{\mathbf{x}} = 1$ for a system with PBC. Hence, for each configuration associated to $\{n_{\mathbf{x}}\}$ we have that

$$|\mathrm{C}'\rangle = \prod_{\mathbf{x}\in\mathrm{V}} \widehat{G}^{n_{\mathbf{x}}}_{\mathbf{x}}|\mathrm{C}\rangle = \prod_{\mathbf{x}\in\mathrm{V}} \widehat{G}_{\mathbf{x}} \prod_{\mathbf{x}\in\mathrm{V}} \widehat{G}^{n_{\mathbf{x}}}_{\mathbf{x}}|\mathrm{C}\rangle = \prod_{\mathbf{x}\in\mathrm{V}} \widehat{G}^{1-n_{\mathbf{x}}}_{\mathbf{x}}|\mathrm{C}\rangle \; .$$

Indeed the number of different configurations is $N_{\mathrm{gauge}} = 2^{N_{\mathrm{V}}-1}$. What happens in the OBC case?

Now observe that $\widehat{G}^{\dagger}_{\mathbf{x}}\hat{\sigma}^z_{\mathbf{x},\nu}\widehat{G}_{\mathbf{x}} = -\hat{\sigma}^z_{\mathbf{x},\nu}$. Hence:

$$\langle\hat{\sigma}^z_{\mathbf{x},\nu}\rangle_h = \frac{1}{Z_h}\sum_{\mathrm{C}}\Big(-\langle \mathrm{C}|\widehat{G}^{\dagger}_{\mathbf{x}}\hat{\sigma}^z_{\mathbf{x},\nu}\widehat{G}_{\mathbf{x}}|\mathrm{C}\rangle\Big)\,\mathrm{e}^{-\beta H_h[\mathrm{C}]} = \frac{1}{Z_h}\sum_{\mathrm{C}}\Big(-\langle \mathrm{C}_{\mathbf{x}}|\hat{\sigma}^z_{\mathbf{x},\nu}|\mathrm{C}_{\mathbf{x}}\rangle\Big)\,\mathrm{e}^{-\beta H_h[\mathrm{C}]}\;,$$

where we defined the "locally (at $\mathbf{x}$) flipped" configuration $|\mathrm{C}_{\mathbf{x}}\rangle = \widehat{G}_{\mathbf{x}}|\mathrm{C}\rangle$. Recall that $\mathrm{star}(\mathbf{x}) = \{\mathbf{x},\pm\nu\}$ is the set of $2d$ links around the vertex $\mathbf{x}$, all flipped by $\widehat{G}_{\mathbf{x}}$. It is simple to show that

$$H_h[\mathrm{C}] = H_h[\mathrm{C}_{\mathbf{x}}] + 2h\langle \mathrm{C}_{\mathbf{x}}|\hat{m}_{\mathbf{x}}|\mathrm{C}_{\mathbf{x}}\rangle \qquad \text{with} \qquad \hat{m}_{\mathbf{x}} = \sum_{\mathbf{x}',\nu'}^{\mathrm{star}(\mathbf{x})}\hat{\sigma}^z_{\mathbf{x}',\nu'}\;. \tag{9.21}$$

Since summing over the configurations C is totally equivalent to summing over the $\mathrm{C}_{\mathbf{x}}$, we can eventually write:

$$\begin{aligned}\langle\hat{\sigma}^z_{\mathbf{x},\nu}\rangle_h &= \frac{1}{Z_h}\sum_{\mathrm{C}}\Big(-\langle \mathrm{C}|\hat{\sigma}^z_{\mathbf{x},\nu}|\mathrm{C}\rangle\Big)\,\mathrm{e}^{-\beta H_h[\mathrm{C}]}\mathrm{e}^{-2\beta h\langle \mathrm{C}|\hat{m}_{\mathbf{x}}|\mathrm{C}\rangle} \\ &= -\Big\langle\hat{\sigma}^z_{\mathbf{x},\nu}\mathrm{e}^{-2\beta h\hat{m}_{\mathbf{x}}}\Big\rangle_h\;.\end{aligned} \tag{9.22}$$

Hence, we can finally write the following inequality:

$$2\big|\langle\hat{\sigma}^z_{\mathbf{x},\nu}\rangle_h\big| = \Big|\Big\langle\hat{\sigma}^z_{\mathbf{x},\nu}\big(1-\mathrm{e}^{-2\beta h\hat{m}_{\mathbf{x}}}\big)\Big\rangle_h\Big| \le \big|\langle\hat{\sigma}^z_{\mathbf{x},\nu}\rangle_h\big|\big|\big(\mathrm{e}^{4\beta hd}-1\big)\big| \xrightarrow{h\to 0} 0\;. \tag{9.23}$$

The importance of local symmetry. Remark the difference with what global symmetries would do in statistical mechanics. There, a uniform field brings an extensive contribution in the Boltzmann weights, and the thermodynamical limit might lead to symmetry breaking. Here, the thermodynamical limit is innocuous, since only a finite (small) number of terms are involved in the local symmetry transformation.

9.3. Gauge invariant objects: the Wilson loops

The plaquette operators $\widehat{Z}_{\mathbf{x}_*}$ are not the only gauge-invariant objects you can think of. Indeed, any *product* of plaquette operators is also gauge-invariant. Indeed, see Fig. 9.5, take any *closed contour* $\mathcal{C}$ on the lattice — the contour running along the edges (or links) — and define the following Wilson loop operator:

$$\widehat{Z}_{\mathcal{C}} = \prod_{\ell\in\mathcal{C}}\hat{\sigma}^z_{\ell}\;. \tag{9.24}$$

The smallest such contour is a plaquette $\mathrm{plaq}(\mathbf{x}_*)$, and for these, you recognise the well-known plaquette operators:

$$\widehat{Z}_{\mathcal{C}=\mathrm{plaq}(\mathbf{x}_*)} \equiv \widehat{Z}_{\mathbf{x}_*}\;.$$

If you keep multiplying by a neighbouring plaquette operator, you notice that the internal links disappear since $(\hat{\sigma}^z)^2 = 1$, and only the outer contour remains.

The Wilson loop operator. The Wilson loop operator can be equivalently written as:

$$\widehat{Z}_{\mathcal{C}} = \prod_{\ell\in\mathcal{C}}\hat{\sigma}^z_{\ell} = \prod_{\mathbf{x}_*\ \text{inside}\ \mathcal{C}}\widehat{Z}_{\mathbf{x}_*}\;. \tag{9.25}$$

You can also consider contours $\mathcal{C}$ that are made of closed but disconnected pieces, in principle. As each plaquette can have eigenvalues ±1, the value of $\widehat{Z}_{\mathcal{C}}$ on a given configuration C — or, better, on the class of gauge-related configurations [C] — is also ±1.

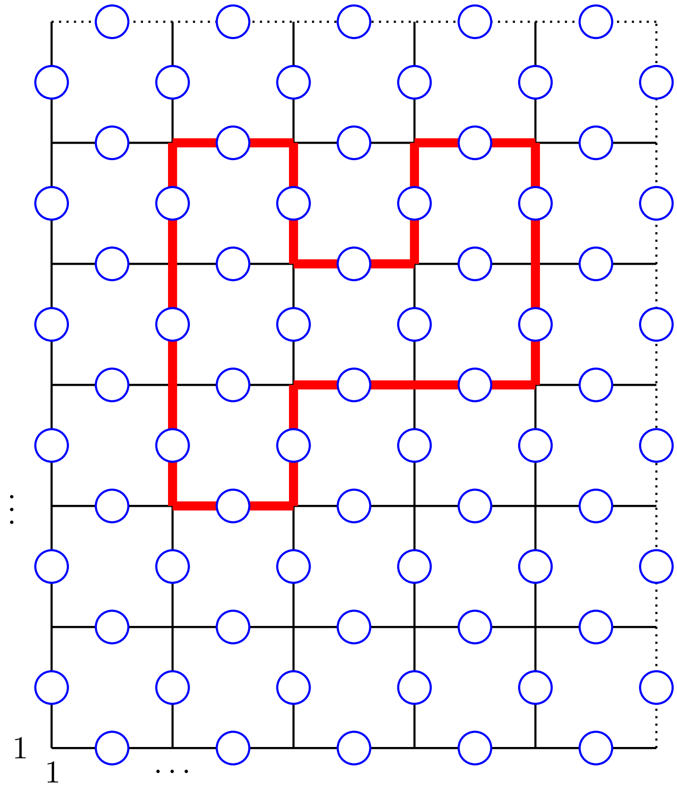

Figure 9.5: The Wilson loop. The closed contour $\mathcal{C}$ (red thick line) contains links ℓ and the Wilson loop operator is defined by $\widehat{Z}_{\mathcal{C}} = \prod_{\ell\in\mathcal{C}} \hat{\sigma}^z_\ell$. Equivalently, $\widehat{Z}_{\mathcal{C}}$ can be seen as the product of all $\widehat{Z}_{\mathbf{x}_*}$ plaquette operators where $\mathbf{x}_*$ is *inside* the contour $\mathcal{C}$. Here the area inside the loop is $A_{\mathcal{C}} = 6$, while its perimeter is $P_{\mathcal{C}} = 14$. Notice, however, that the generic situation for large loops is precisely opposite, with $A_{\mathcal{C}} > P_{\mathcal{C}}$.

Recall that, so far, the Ising LGT is a classical model, with many degenerate configurations. Energetically, it is favourable to have as many possible plaquettes with eigenvalue $+1$, as these have energy $-J$, while frustrated plaquettes — having $\widehat{Z}_{\mathbf{x}_*} = -1$, due to an odd number of spin ↓ — pay an energy penalty $+J$. But entropy plays a role.

We will now show that the classical modal has, for $d > 2$, two distinguishable phases. We will do that by analysing the characteristic behaviour of the statistical average of the Wilson loop operator $\widehat{Z}_{\mathcal{C}}$.

Area (high-T) versus perimeter law (low-T). We can easily convince ourselves that

$$\langle \widehat{Z}_{\mathcal{C}} \rangle = \begin{cases} \mathrm{e}^{-\chi_A(\beta) A_{\mathcal{C}}} & \text{high } T \\ \mathrm{e}^{-\chi_P(\beta) P_{\mathcal{C}}} & \text{low } T \quad (\text{for } d > 2) \end{cases} \tag{9.26}$$

where $A_{\mathcal{C}}$ is the *area* (in units of a^2) of the minimal surface enclosed by the contour $\mathcal{C}$, and $P_{\mathcal{C}}$ is the *perimeter* (in units of a) of the contour, i.e., the number of links belonging to $\mathcal{C}$.

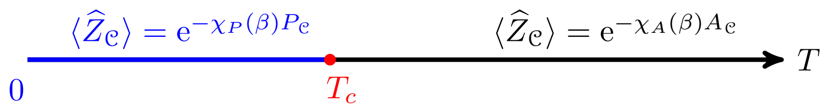

Figure 9.6: The temperature phase diagram of $\mathbb{Z}_2$ LGT for $d > 2$. At $T = 0$ the Wilson loop is trivially $\langle \widehat{Z}_{\mathcal{C}} \rangle = 1$. Explain why.

9.3.1. High-T expansion and the area law

The high-T expansion starts from the realisation that, since $\widehat{Z}_{\mathbf{x}_*}$ has eigenvalues ±1 you can equivalently write:

$$\mathrm{e}^{\beta J \widehat{Z}_{\mathbf{x}_*}} = \big(1 + \widehat{Z}_{\mathbf{x}_*} \tanh \beta J\big) \cosh \beta J \tag{9.27}$$

hence:

$$\mathrm{e}^{-\beta \widehat{H}} = (\cosh \beta J)^{N_{\mathrm{plaq}}} \prod_{\mathbf{x}_*} \big(1 + \widehat{Z}_{\mathbf{x}_*} \tanh \beta J\big) \,. \tag{9.28}$$

The thermal average we need, observing that the $\cosh \beta J$ cancels off with the partition function, is given by:

$$\langle \widehat{Z}_{\mathcal{C}} \rangle = \frac{\sum_{\mathrm{C}} \langle \mathrm{C} | \widehat{Z}_{\mathcal{C}} \prod_{\mathbf{x}_*} \big(1 + \widehat{Z}_{\mathbf{x}_*} \tanh \beta J\big) | \mathrm{C} \rangle}{\sum_{\mathrm{C}} \langle \mathrm{C} | \prod_{\mathbf{x}_*} \big(1 + \widehat{Z}_{\mathbf{x}_*} \tanh \beta J\big) | \mathrm{C} \rangle} \,. \tag{9.29}$$

For high-T, hence small βJ, the $\tanh \beta J$ produces small factors. For the partition function in the denominator, we can evidently set, to lowest order $Z = N_{\mathrm{C}}(1 + \cdots)$, where N_{C} is the number of spin configurations, and the dots $(\cdots)$ indicate terms that vanish for $\beta J \to 0$. Looking at the numerator, the $\widehat{Z}_{\mathcal{C}}$ brings about unpaired $\hat{\sigma}^z$ operators, which give zero contribution upon averaging over the configurations, $\langle \hat{\sigma}^z_{\mathbf{x},\nu} \rangle = 0$. The only escape route is that the plaquette terms contribute $\hat{\sigma}^z$ operators that can *exactly match* those appearing in $\widehat{Z}_{\mathcal{C}}$, since we can then use $(\hat{\sigma}^z)^2 = 1$. But recall that Eq. (9.25) tells us that:

$$\widehat{Z}_{\mathcal{C}} = \prod_{\mathbf{x}_* \text{ inside } \mathcal{C}} \widehat{Z}_{\mathbf{x}_*} \,.$$

Hence we need to invoke a factor $\widehat{Z}_{\mathbf{x}_*} \tanh \beta J$ for all $\mathbf{x}_*$ *inside* $\mathcal{C}$ in order for perfectly match the $\hat{\sigma}^z$ into innocuous $(\hat{\sigma}^z)^2$. Hence, the largest term (with minimal number of $\tanh \beta J$) contributing to the average will be

$$\langle \widehat{Z}_{\mathcal{C}} \rangle = (\tanh \beta J)^{A_{\mathcal{C}}} + \cdots = \mathrm{e}^{-\log(\tanh \beta J)^{-1} A_{\mathcal{C}}} + \cdots \,. \tag{9.30}$$

> **Convergence of the high-T series.** An important point is that the methods typically used to prove that high-T expansions have a finite radius of convergence do apply for the present case as well. So, we can safely tell that, for sufficiently large T, the average of the Wilson loop shows an *area law*. The leading term of the prefactor function $\chi_A(\beta)$ in Eq. (9.26) is indeed given by $\log(\tanh \beta J)^{-1}$, as predicted by Eq. (9.30).

9.3.2. Low-T expansion for $d > 2$ and the perimeter law

The low-T expansion is slightly more subtle: a naive approach would fail to appreciate that the $d = 2$ case is rather special.

We start by noticing that classical ground state is the class of configurations where all plaquettes are *unfrustrated*, i.e., they give $\widehat{Z}_{\mathbf{x}_*} \to +1$. The large degeneracy associated with the gauge freedom can be safely organized by working with class representatives, so that $[\mathrm{C}]_{\mathrm{gs}} = | + \cdots + \rangle_z$ is the configuration with all spins pointing up in the z-direction, and

$$\langle \widehat{Z}_{\mathcal{C}} \rangle = \frac{\sum_{[\mathrm{C}]} \langle \mathrm{C} | \widehat{Z}_{\mathcal{C}} \mathrm{e}^{-\beta \widehat{H}} | \mathrm{C} \rangle}{\sum_{[\mathrm{C}]} \langle \mathrm{C} | \mathrm{e}^{-\beta \widehat{H}} | \mathrm{C} \rangle} \,. \tag{9.31}$$

Each frustrated plaquette brings an increase in energy of $2J$, so that a reasonable thing to do, at low-T, is to start considering configurations with a *single flipped spin*, $[\mathrm{C}]_{1-\mathrm{flip}}$, which makes $2(d-1)$ plaquettes to become frustrated, hence:

$$H[\mathrm{C}]_{1-\mathrm{flip}} = -\big(N_{\mathrm{plaq}} - 2(d-1)\big)J + 2\big(d-1\big)J = E_{\mathrm{gs}} + 4(d-1)J \ ,$$

where $E_{\mathrm{gs}} = -JN_{\mathrm{plaq}}$ is the classical ground state energy. As usual, E_{gs} will drop off from the calculation of the average, cancelling with the partition function denominator.

The second important fact is that, while the denominator of (9.31) is blind to details, and simply gives:

$$\mathrm{Denominator} = 1 + N_{\mathrm{L}}\, \mathrm{e}^{-4(d-1)\beta J} + \text{higher flip contributions} \ ,$$

where N_{L}, the number of links, simply counts the number of possible configurations $[\mathrm{C}]_{1-\mathrm{flip}}$, the numerator is more subtle: it distinguishes configurations in which the flipped spin *is not on* $\mathcal{C}$, $N_{\mathrm{L}} - P_{\mathcal{C}}$ in number, for which $\widehat{Z}_{\mathcal{C}} \to +1$, from those in which the flipped spin *is on* $\mathcal{C}$, $P_{\mathcal{C}}$ in number, where $P_{\mathcal{C}}$ is the perimeter of the loop. Hence:

$$\mathrm{Numerator} = 1 + (N_{\mathrm{L}} - 2P_{\mathcal{C}})\, \mathrm{e}^{-4(d-1)\beta J} + \text{higher flip contributions} \ .$$

Higher-order flip contributions are more difficult to calculate. If the various flip terms were *independent* and we could neglect excluded volume effects, one might write the n-flip contribution to the numerator simply as

$$\mathrm{Numerator}_{\mathrm{n-flips}} \approx \frac{1}{n!}\Big((N_{\mathrm{L}} - 2P_{\mathcal{C}})\, \mathrm{e}^{-4(d-1)\beta J} \Big)^{n} \ ,$$

and similarly for the denominator. Within such approximation, we can sum up all terms by recognising a Taylor expansion of the exponential:

$$\langle \widehat{Z}_{\mathcal{C}} \rangle \approx \frac{\mathrm{e}^{(\cancel{N_{\mathrm{L}}} - 2P_{\mathcal{C}})\mathrm{e}^{-4(d-1)\beta J}}}{\cancel{\mathrm{e}^{N_{\mathrm{L}}\mathrm{e}^{-4(d-1)\beta J}}}} = \mathrm{e}^{-2\mathrm{e}^{-4(d-1)\beta J} P_{\mathcal{C}}} \ , \tag{9.32}$$

hence the perimeter law. A careful analysis performed by Wortis in 1972 shows that this is indeed the leading term in the function $\chi_P(\beta)$ of Eq. (9.26).

The low-T physics. This clearly shows that for $d > 2$, where the previous analysis applies, the model must have *two phases*: a high-T (disordered) phase where the area law applies and larger loops are less abundant, and a low-T phase where the perimeter law applies. At high-T loops tend to be more compact: since $A_{\mathcal{C}}$ is generally larger than $P_{\mathcal{C}}$, at least for generic large loops, this makes perfect sense.

9.3.3. The peculiar $d = 2$ case

The $d = 2$ case is rather peculiar, as you can appreciate also from the energetics of 2 spin flips. Observing Fig. 9.7 you see that, starting from the reference configuration (all spins up) a string of flipped parallel links *of any length* creates only *two frustrated plaquettes* in $d = 2$. Even more: if the system does not have PBC on the y-direction, you can even move the string of flipped spins to the lower boundary: then, only a *single frustrated* plaquette survives!

The role of cheap fluctuations. You realise that this low cost of defects compared to the large entropy gain in creating them anticipates the fact that the model is always *disordered* at any $T > 0$, hence a single phase with *area law* average Wilson loop should be expected. This is indeed the case, as one can realise in several instructive ways.

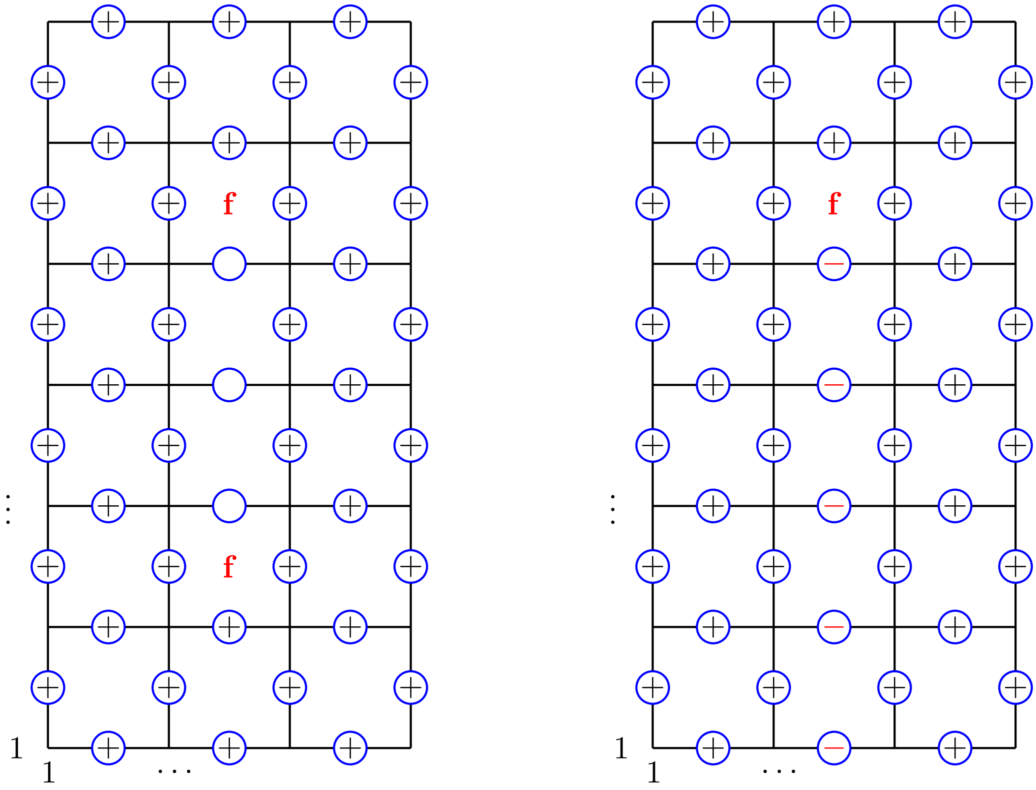

Figure 9.7.: Left: Starting from the reference configuration (all spins up) a string of flipped parallel links *of any length* creates only *two frustrated plaquettes* — denoted by **f** — in $d = 2$. Notice that this is peculiar of the $d = 2$ case, as the plaquettes coming upward, out of the plane, for instance in $d = 3$, would still be frustrated! Right: If the system does not have PBC on the y-direction, you can even move the string to the lower boundary, and only a *single frustrated* plaquette survives. The ± denote spin components along the z-axis, i.e., in the standard configuration basis.

Mapping the $d = 2$ Ising LGT into uncoupled classical Ising chains. We now show that we can indeed map the $d = 2$ classical Ising LGT into a system of uncoupled chains of ordinary classical Ising models. To do that, we adopt the strategy of *fixing a particular gauge* for the equivalent configurations.

The temporal gauge. More precisely, we fix all the spins on the *vertical links* to be +1:

$$\hat{\sigma}^z_\ell \longrightarrow +1 \qquad \text{with} \qquad \ell = \mathbf{x}, 2 \quad \forall \mathbf{x} \, . \tag{9.33}$$

This is known as *temporal gauge* [33]. [a]

---

[a] We will see later that, for a system with PBC, this implies a precise choice of a topological sector for the model, more precisely those where the non-contractible Wilson loop operator $\widehat{Z}_{\gamma_2}$ in the "temporal direction" is +1.

Consider now the plaquette operators $\widehat{Z}_{\mathbf{x}_*}$. Since the two vertical bonds are fixed to be +1, we can equivalently write

$$\widehat{Z}_{\mathbf{x}_*} \longrightarrow \hat{\sigma}^z_{\mathbf{x},1} \hat{\sigma}^z_{\mathbf{x}+\mathbf{e}_2,1} \, .$$

Hence, the plaquette terms reduce to *pairs of spins* on parallel links in the vertical direction,

$$\widehat{H}_{2d-\text{ILGT}} = -J \sum_{\mathbf{x}_*} \widehat{Z}_{\mathbf{x}_*} \longrightarrow -J \sum_{\mathbf{x}} \hat{\sigma}^z_{\mathbf{x},1} \hat{\sigma}^z_{\mathbf{x}+\mathbf{e}_2,1} \, , \tag{9.34}$$

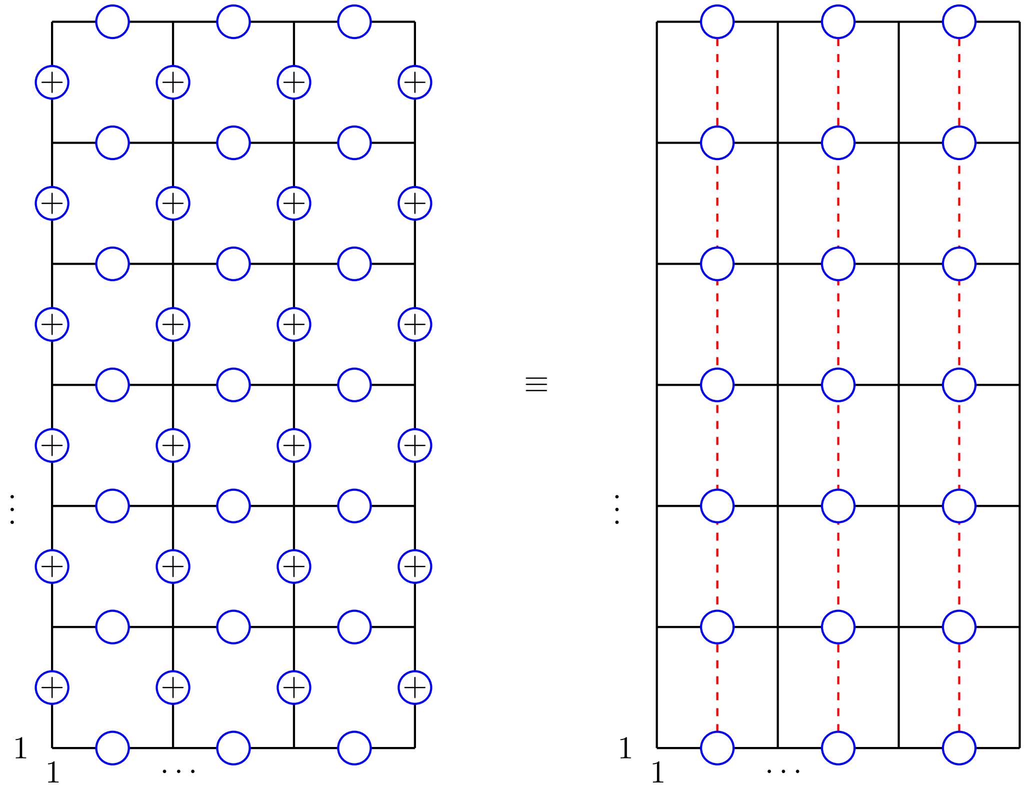

Figure 9.8.: Mapping $d = 2$ Ising LGT into uncoupled $d = 1$ ordinary Ising chains. Left: Choose a gauge — the so-called *temporal gauge* — in which the spins on the vertical links are all fixed to be $+1$. The spins on the horizontal links can be anything they want and are not indicated. Right: Ignore the pairs of parallel $+1$ spins on the vertical links altogether. The plaquette coupling becomes a simple nearest-neighbour ferromagnetic coupling $-J$ (denoted by a dashed red line) along all the vertical *uncoupled* chains.

and we have mapped the $d = 2$ classical Ising LGT into *decoupled* classical Ising chains, as shown in Fig. 9.8.

9.4. Introducing quantum fluctuations

Let us now move to a quantum model, introducing a transverse field term.

> **The quantum Ising LGT model.** For a hyper-cubic lattice in d-dimension, the quantum Ising LGT model reads:
>
> $$\widehat{H} = \widehat{H}_{\mathrm{Q-ILGT}} = -h_{\perp} \sum_{\ell} \hat{\sigma}^x_{\ell} - J \sum_{\mathbf{x}_*} \widehat{Z}_{\mathbf{x}_*} \tag{9.35}$$
>
> Quite importantly, since $\hat{\sigma}^x$ commutes with $\widehat{G}_{\mathbf{x}}$, the model is still gauge-invariant:
>
> $$[\widehat{G}_{\mathbf{x}}, \widehat{H}] = 0 \qquad\qquad \forall \mathbf{x} \; . \tag{9.36}$$

We can introduce other gauge invariant objects in the problem, which turn out to be build out of products of $\widehat{G}_{\mathbf{x}}$.

Contractible 't Hooft loop operators. Let us define, on the dual lattice defined by the plaquette centers, a contractible loop γ^* that *cuts orthogonally links on the lattice*, and the associated 't Hooft loop operator

$$\widehat{X}_{\gamma^*} = \prod_{\ell \perp \gamma^*} \hat{\sigma}^x_\ell \; . \tag{9.37}$$

You can show that these objects can be written as products of $\widehat{G}_{\mathbf{x}}$, hence they are symmetries, but not independent from the $\widehat{G}_{\mathbf{x}}$:

$$\widehat{X}_{\gamma^*} = \prod_{\mathbf{x} \,|\, \mathrm{star}(\mathbf{x}) \perp \gamma^*} \widehat{G}_{\mathbf{x}} \qquad \Longrightarrow \qquad [\widehat{X}_{\gamma^*}, \widehat{H}] = 0 \qquad \forall \gamma^* \; . \tag{9.38}$$

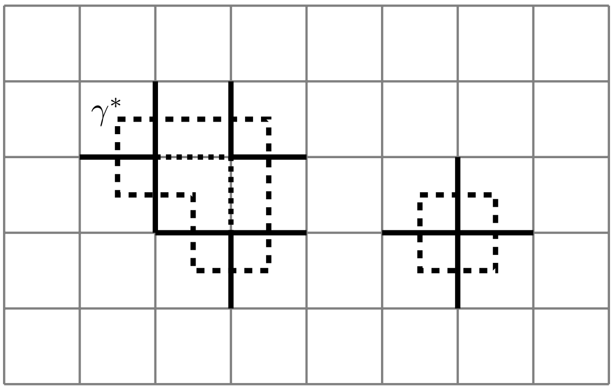

Figure 9.9: Two contractible loops γ^* on the dual lattice, and the associated 't Hooft loop operator cutting orthogonally a number of links (thick black links). On the right, the smallest loop, where $\widehat{X}_{\gamma^*} = \widehat{G}_{\mathbf{x}}$. On the left, a larger loop where $\widehat{X}_{\gamma^*}$ is a product of three $\widehat{G}_{\mathbf{x}}$: notice the internal links denoted by dotted thick lines, which are cancelled due to $(\hat{\sigma}^x_\ell)^2 = 1$. Incidentally, you can view the two loops shown as a single contractible loop γ^* made of two disjoint loops.

Let $|\psi_{\mathrm{gs}}\rangle$ denote a ground state of the model, with energy E_{gs}. Gauge symmetry implies that:

$$\widehat{H}\Big(\widehat{G}_{\mathbf{x}}|\psi_{\mathrm{gs}}\rangle\Big) = \widehat{G}_{\mathbf{x}}\widehat{H}|\psi_{\mathrm{gs}}\rangle = E_{\mathrm{gs}}\Big(\widehat{G}_{\mathbf{x}}|\psi_{\mathrm{gs}}\rangle\Big) \; . \tag{9.39}$$

Moreover, since $\widehat{G}^2_{\mathbf{x}} = 1$ you expect that, for a *translationally invariant* ground state, the eigenvalue of $\widehat{G}_{\mathbf{x}}$ can only be a sign *independent* of $\mathbf{x}$: $\widehat{G}_{\mathbf{x}}|\psi_{\mathrm{gs}}\rangle = \pm|\psi_{\mathrm{gs}}\rangle$.

Ground state value of $\widehat{G}_{\mathbf{x}}$. We will now argue that

$$\widehat{G}_{\mathbf{x}}|\psi_{\mathrm{gs}}\rangle = |\psi_{\mathrm{gs}}\rangle \qquad \forall \mathbf{x} \; , \tag{9.40}$$

a condition that defines the ground state sector(s) of the Hilbert space.

To begin, we have to discuss possible degeneracies of the ground state in the two possible phases that we expect to be present in the model. We do so in the two limits $h_\perp \to 0$ and $h_\perp \to \infty$.

9.4.1. The small $h_\perp$ phase

For $h_\perp = 0$ the classical ground states are highly degenerate, due to the large number of ways in which you can arrange unfrustrated plaquettes. Let us discuss better the question of the boundary conditions, particularly relevant at this stage.

Classification of topological sectors for PBC systems. For the model with PBC, there is a very remarkable property that emerges when you try to classify the classical ground state configurations.

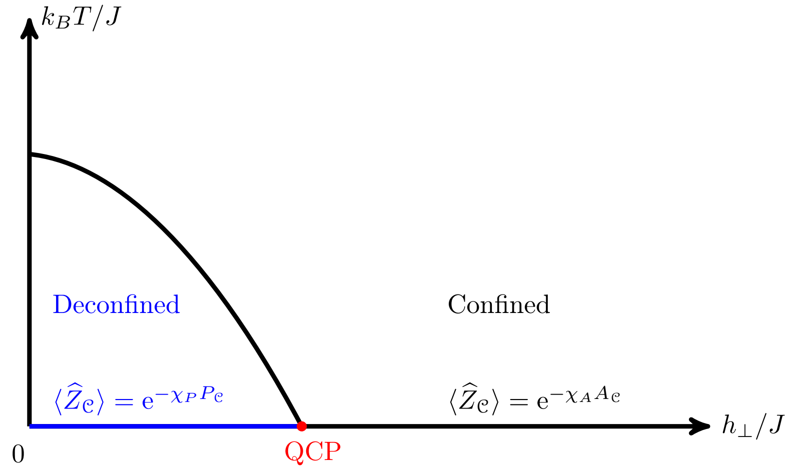

Figure 9.10: The generic phase diagram of $\mathbb{Z}_2$ quantum LGT for $d > 2$. The meaning of the words "deconfined" and "confined" will be clarified later on: it is related to the potential energy of two static excitations implanted on the ground states. For $d = 2$ the deconfined phase is strictly only at $T = 0$.

We start from the class representative where all spins on all links are $|+\rangle$, which we denote by $|\mathrm{C}_{00}\rangle$:

$$|\mathrm{C}_{00}\rangle = |+\rangle^{\otimes N_{\mathrm{L}}} \; .$$

The other elements in the class can be obtained by applying elements of $\widehat{G}_{\mathbf{x}}$, as discussed.

But some configurations will never be reached in this way: they are *topologically distinct* from $|\mathrm{C}_{00}\rangle$. To shed light on this fact, let us consider an extension of the Wilson loop operator where the loop is now *non-contractible*, i.e., goes around the torus.

Non-contractible Wilson and 't Hooft loop operators. We define γ_2 to be a closed straight contour of links that goes through the boundary in the direction $\mathbf{e}_2$, and define the associated Wilson loop operator

$$\widehat{Z}_2 \equiv \widehat{Z}_{\gamma_2} = \prod_{\ell \in \gamma_2} \hat{\sigma}^z_\ell \; . \tag{9.41}$$

On the dual lattice, we define γ_2^* to be a non-contractible loop that *cuts a line of parallel links* along the direction $\mathbf{e}_2$ — hence, running on the dual lattice defined by the plaquette centers — and the associated 't Hooft loop operator

$$\widehat{X}_2 \equiv \widehat{X}_{\gamma_2^*} = \prod_{\ell \perp \gamma_2^*} \hat{\sigma}^x_\ell \; . \tag{9.42}$$

In words, see Fig. 9.11: $\widehat{X}_{\gamma_2^*}$ creates a line of spin-flips on all parallel links in the direction $\mathbf{e}_2$. By switching $\mathbf{e}_2 \leftrightarrow \mathbf{e}_1$, similar definitions can be given for γ_1 and γ_1^*, and associated operators $\widehat{Z}_1 \equiv \widehat{Z}_{\gamma_1}$ and $\widehat{X}_1 = \widehat{X}_{\gamma_1^*}$.

Since $\widehat{G}_{\mathbf{x}}$ always *flips spin in pairs* along any direction, while obviously commutes with $\hat{\sigma}^x$, it is easy to show that:

$$\widehat{G}^\dagger_{\mathbf{x}} \widehat{Z}_\nu \widehat{G}_{\mathbf{x}} = \widehat{Z}_\nu \qquad \text{and} \qquad \widehat{G}^\dagger_{\mathbf{x}} \widehat{X}_\nu \widehat{G}_{\mathbf{x}} = \widehat{X}_\nu \qquad \forall \mathbf{x} \; . \tag{9.43}$$

However, since γ_2 and γ_2^* necessarily share a *single link* ℓ where $\hat{\sigma}^x_\ell \hat{\sigma}^z_\ell \hat{\sigma}^x_\ell = -\hat{\sigma}^z_\ell$ (and similarly for γ_1 and γ_1^*) you must have that:

$$\widehat{Z}_2 \widehat{X}_2 = -\widehat{X}_2 \widehat{Z}_2 \qquad \text{and} \qquad \widehat{Z}_1 \widehat{X}_1 = -\widehat{X}_1 \widehat{Z}_1 \; . \tag{9.44}$$

On the contrary, γ_1 and γ_2^* share no link (and similarly γ_2 and γ_1^*) hence:

$$\widehat{Z}_1 \widehat{X}_2 = \widehat{X}_2 \widehat{Z}_1 \qquad \text{and} \qquad \widehat{Z}_2 \widehat{X}_1 = \widehat{X}_1 \widehat{Z}_2 \; . \tag{9.45}$$

The two non-local Qbit operators. Summarizing, the four operators $(\widehat{Z}_1, \widehat{X}_1)$ and $(\widehat{Z}_2, \widehat{X}_2)$ both realise the Pauli algebra:

$$\{\widehat{Z}_1, \widehat{X}_1\} = 0 \qquad \{\widehat{Z}_2, \widehat{X}_2\} = 0 \; , \tag{9.46}$$

while they mutually commute:

$$[\widehat{Z}_1, \widehat{X}_2] = 0 \qquad [\widehat{Z}_2, \widehat{X}_1] = 0 \; . \tag{9.47}$$

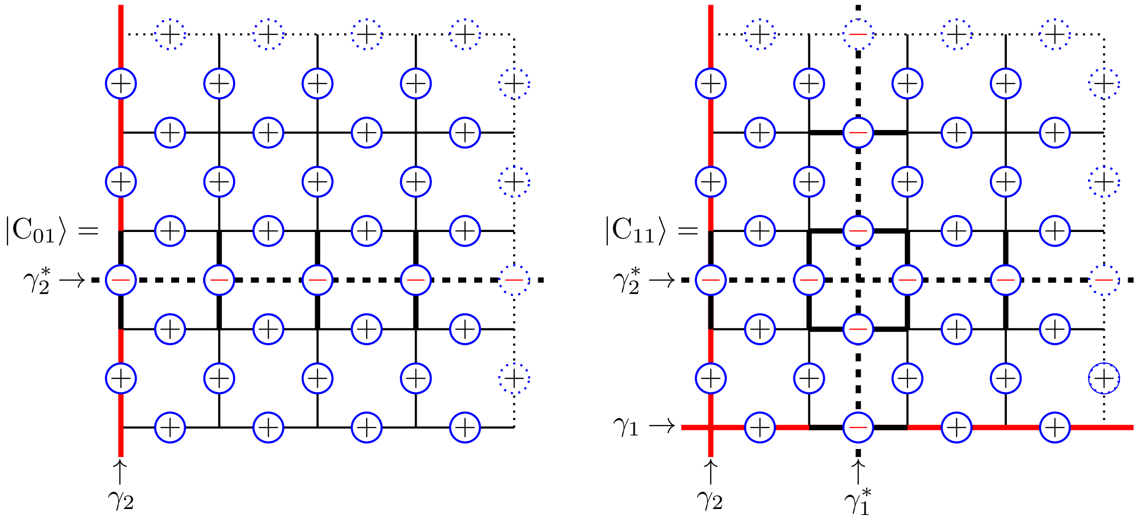

Figure 9.11.: The configurations $|C_{01}\rangle$ (left) and $|C_{11}\rangle$ (right) in a PBC system. On the left, γ_2 (red solid line) is the non-contractible Wilson loop in the direction of $\mathbf{e}_2$, associated to $\widehat{Z}_{\gamma_2}$, and γ_2^* (black dashed line) is the non-contractible t'Hooft loop cutting parallel links in the direction of $\mathbf{e}_2$, associated to $\widehat{X}_{\gamma_2^*}$. On the right, the corresponding γ_1 and γ_1^* in the other direction are shown. Here ± denote spin components along the z-axis, i.e., in the standard configuration basis. The dotted circles denote spins on links on the boundary.

The 00 sector.) Observe that $\widehat{Z}_1|\mathrm{C}_{00}\rangle = |\mathrm{C}_{00}\rangle$, and $\widehat{Z}_2|\mathrm{C}_{00}\rangle = |\mathrm{C}_{00}\rangle$, a property that, by gauge invariance holds true for all gauge-related configurations:

$$\widehat{Z}_1|C'_{00}\rangle = |C'_{00}\rangle \qquad \text{and} \qquad \widehat{Z}_2|C'_{00}\rangle = |C'_{00}\rangle \; . \tag{9.48}$$

The 01 sector.) Now apply $\widehat{X}_2$ to $|\mathrm{C}_{00}\rangle$, obtaining a configuration $|\mathrm{C}_{01}\rangle$ as shown in Fig. 9.11 (left):

$$|\mathrm{C}_{01}\rangle = \widehat{X}_2|\mathrm{C}_{00}\rangle \; .$$

By gauge invariance, the same relationship holds for all gauge-related configurations $|\mathrm{C}'_{00}\rangle$ and $|\mathrm{C}'_{01}\rangle$. Hence, due to Eqs. (9.44)-(9.45):

$$\widehat{Z}_1|C'_{01}\rangle = |C'_{01}\rangle \qquad \text{and} \qquad \widehat{Z}_2|C'_{01}\rangle = -|C'_{01}\rangle \; . \tag{9.49}$$

The 10 sector.) Similarly, for a configuration

$$|\mathrm{C}_{10}\rangle = \widehat{X}_1|\mathrm{C}_{00}\rangle$$

with a line of horizontal links all flipped to −1 but going upwards and all gauge-related partners:

$$\widehat{Z}_1|C'_{10}\rangle = -|C'_{10}\rangle \qquad \text{and} \qquad \widehat{Z}_2|C'_{10}\rangle = |C'_{10}\rangle \; . \tag{9.50}$$

The 11 sector.) Finally, there is a fourth possible reference configuration

$$|\mathrm{C}_{11}\rangle = \widehat{X}_2\widehat{X}_1|\mathrm{C}_{00}\rangle \;,$$

shown in Fig. 9.11 (right), where two lines of parallel flipped spins -1 run along the sample in the two directions. For this, and its gauge-related partners:

$$\widehat{Z}_1|C'_{11}\rangle = -|C'_{11}\rangle \qquad \text{and} \qquad \widehat{Z}_2|C'_{11}\rangle = -|C'_{11}\rangle \;. \tag{9.51}$$

This discussion implies that the classically degenerate configurations, on the PBC geometry of a torus, are divided into *four classes* which are not related by the application of local gauge-symmetry elements, and rather distinguished by a non-local quantum number: the eigenvalues of two non-contractible Wilson loops going through the boundaries, $\widehat{Z}_1$ and $\widehat{Z}_2$.

> **OBC vs PBC.** Notice that this is peculiar of the PBC system. In the OBC case, the presence of boundary star elements with two or three links allows changing the parity of the number of -1 spins along vertical or horizontal lines! You can convince yourself of that by a close inspection of Fig. 9.3 (OBC). Moreover, for a system on the sphere, for instance, all loops would be contractible, and the topological feature we described would not hold.

We might think of doing *degenerate perturbation theory* in the limit $h_\perp \to 0$ within each degenerate topologically distinct sector of configurations at $h_\perp = 0$. Notice that a single spin-flip term, for instance, $\hat{\sigma}^x_{\mathbf{x},2}|C_{00}\rangle$, does create two frustrated plaquettes, leaving the sector you started from. But to 4^{th}-order in perturbation theory, you might flip the 4 spins on the links $\ell \in \mathrm{star}(\mathbf{x})$ and return back to the state $\widehat{G}_{\mathbf{x}}|C_{00}\rangle$, with a *negative* off-diagonal matrix element $-\alpha h_\perp^4/J^3$. The calculation is a bit hard to do in practice. But it suggests that by the Perron-Frobenius theorem, a positive superposition of all gauge-related states of the form:

$$\sum_{\{n_{\mathbf{x}}\}} \psi_{\{n_{\mathbf{x}}\}} \Big(\prod_{\mathbf{x}\in\mathrm{V}} \widehat{G}_{\mathbf{x}}^{n_{\mathbf{x}}}\Big)|C_{00}\rangle \qquad \text{with} \qquad n_{\mathbf{x}} = 0,1 \;,$$

with *positive* wave-function $\psi_{\{n_{\mathbf{x}}\}} > 0$ should describe the ground state for finite small $h_\perp > 0$. Translational invariance, finally, suggests that the wave-function $\psi_{\{n_{\mathbf{x}}\}} > 0$ is *uniform* over all possible $\{n_{\mathbf{x}}\}$, hence:

$$\begin{aligned}
|\Psi_{00}\rangle &= \frac{1}{\sqrt{2^{N_\mathrm{V}}}} \sum_{\{n_{\mathbf{x}}\}} \Big(\prod_{\mathbf{x}\in\mathrm{V}} \widehat{G}_{\mathbf{x}}^{n_{\mathbf{x}}}\Big)|C_{00}\rangle = \prod_{\mathbf{x}\in\mathrm{V}} \Big(\frac{1+\widehat{G}_{\mathbf{x}}}{\sqrt{2}}\Big)|C_{00}\rangle \\
&= \frac{1}{\sqrt{2^{N_\mathrm{V}-1}}} \sum_{\gamma^*}^{\text{contractible}} \widehat{X}_{\gamma^*}|C_{00}\rangle \;.
\end{aligned} \tag{9.52}$$

The equality of these three expressions needs a few comments. The first comes from the simple relationship:

$$\prod_{\mathbf{x}\in\mathrm{V}} (1+\widehat{G}_{\mathbf{x}}) = \prod_{\mathbf{x}\in\mathrm{V}} \Big(\sum_{n_{\mathbf{x}}=0}^{1} \widehat{G}_{\mathbf{x}}^{n_{\mathbf{x}}}\Big) = \sum_{\{n_{\mathbf{x}}\}} \Big(\prod_{\mathbf{x}\in\mathrm{V}} \widehat{G}_{\mathbf{x}}^{n_{\mathbf{x}}}\Big) \;.$$

The second, with its conspicuous normalisation coefficient which reminds us that $N_{\mathrm{gauge}} = 2^{N_\mathrm{V}-1}$, is due to the following consideration. For every bipartition $\mathrm{V} = \mathrm{A} + \overline{\mathrm{A}}$ of the lattice of vertices you have that:

$$\Big(\prod_{\mathbf{x}\in\mathrm{A}} \widehat{G}_{\mathbf{x}}\Big)\Big(\prod_{\mathbf{x}\in\overline{\mathrm{A}}} \widehat{G}_{\mathbf{x}}\Big) = \prod_{\mathbf{x}\in\mathrm{V}} \widehat{G}_{\mathbf{x}} = 1 \qquad \Longrightarrow \qquad \Big(\prod_{\mathbf{x}\in\mathrm{A}} \widehat{G}_{\mathbf{x}}\Big) = \Big(\prod_{\mathbf{x}\in\overline{\mathrm{A}}} \widehat{G}_{\mathbf{x}}\Big) \;.$$

This implies that, given a configuration with a certain $\{n_{\mathbf{x}}\}$, with $n_{\mathbf{x}} = 1$ for $\mathbf{x} \in \mathrm{A}$, the configuration with $\{\bar{n}_{\mathbf{x}}\}$, where $\bar{n}_{\mathbf{x}} = 1 - n_{\mathbf{x}}$ is precisely the same, since $\bar{n}_{\mathbf{x}} = 1$ for $\mathbf{x} \in \overline{\mathrm{A}}$. Hence the configurations are included *twice* in the first two expressions. Imagine now that you keep only one of those pairs of identical configurations, pretending that the number of vertices in A is, for instance, not larger than the complement, $|\mathrm{A}| \le |\overline{\mathrm{A}}|$. [5] Observe that

$$\prod_{\mathbf{x}\in \mathrm{A}} \widehat{G}_{\mathbf{x}} = \widehat{X}_{\gamma^*} \;,$$

where γ^* is a contractible 't Hooft loop, possibly made of several disjoint loops, as in Fig. 9.9. Summing over all possible contractible γ^* you get all possible gauge related configurations — notice: without replicating them twice —, hence the normalisation that you need is now $1/\sqrt{N_{\mathrm{gauge}}}$, with $N_{\mathrm{gauge}} = 2^{N_{\mathrm{V}}-1}$.

A similar construction holds for the other topological sectors, leading to 4 possible ground states, which we could write as follows: [6]

$$|\Psi_{00}\rangle \;, \qquad |\Psi_{10}\rangle = \widehat{X}_1|\Psi_{00}\rangle \;, \qquad |\Psi_{01}\rangle = \widehat{X}_2|\Psi_{00}\rangle \;, \qquad |\Psi_{11}\rangle = \widehat{X}_1\widehat{X}_2|\Psi_{00}\rangle \;. \tag{9.54}$$

These four states, totally degenerate in the limit $h_\perp \to 0$, can be distinguished by a *non-local order parameter*: the expectation value of non-contractible Wilson loop operators. Indeed, observe that

$$\widehat{Z}_1|\Psi_{00}\rangle = |\Psi_{00}\rangle \qquad \text{and} \qquad \widehat{Z}_2|\Psi_{00}\rangle = |\Psi_{00}\rangle \;, \tag{9.55}$$

simply because $\widehat{Z}_1$ and $\widehat{Z}_2$ commute with every possible $\widehat{G}_{\mathbf{x}}$, and $\widehat{Z}_{1/2}|C_{00}\rangle = |C_{00}\rangle$. However, recall that $\widehat{Z}_1$ *anticommutes* with $\widehat{X}_1$, and similarly $\widehat{Z}_2$ anticommutes with $\widehat{X}_2$. Hence:

The expectation values of non-contractible Wilson loops. If $|\Psi_{v_1,v_2}\rangle$ with $v_1, v_2 = 0, 1$ denotes the four possible ground states, obtained with

$$|\Psi_{v_1,v_2}\rangle = \widehat{X}_1^{v_1}\widehat{X}_2^{v_2}|\Psi_{00}\rangle \;, \tag{9.56}$$

it is simple to show that:

$$\widehat{Z}_\nu|\Psi_{v_1,v_2}\rangle = (-1)^{v_\nu}|\Psi_{v_1,v_2}\rangle \qquad \Longrightarrow \qquad \langle\Psi_{v_1,v_2}|\widehat{Z}_\nu|\Psi_{v_1,v_2}\rangle = (-1)^{v_\nu} \;. \tag{9.57}$$

Kitaev (toric code) model. We will later discuss a model, introduced by Kitaev, based on precisely the ingredients discussed so far, which is *exactly solvable*. It might be viewed as the *effective Hamiltonian* inside the subsector of unfrustarted plaquettes, obtained for $h_\perp \to 0$ in 4th order perturbation theory:

$$\widehat{H}_{\mathrm{eff}} = -h_{\mathrm{eff}} \sum_{\mathbf{x}} \widehat{G}_{\mathbf{x}} - J \sum_{\mathbf{x}_*} \widehat{Z}_{\mathbf{x}_*} \;. \tag{9.58}$$

Observe that all individual terms appearing in this Hamiltonian now *commute*, hence you can find states that are *simultaneous eigenvectors* of

$$\widehat{G}_{\mathbf{x}}|\psi\rangle = |\psi\rangle \quad \forall \mathbf{x} \qquad \text{and} \qquad \widehat{Z}_{\mathbf{x}_*}|\psi\rangle = |\psi\rangle \quad \forall \mathbf{x}_* \;. \tag{9.59}$$

We will discuss at some length the physics of this model in a short while. For the time being, let us analyse the other limit $h_\perp \to \infty$.

---

[5] When $|\mathrm{A}| = |\overline{\mathrm{A}}|$, you decide arbitrarily which of the two you keep.

[6] The explicit expression in terms of configurations is simple, since $\widehat{X}_1$ and $\widehat{X}_2$ commute with all $\widehat{G}_{\mathbf{x}}$, hence, for instance, recalling that $\widehat{X}_1|C_{00}\rangle = |C_{10}\rangle$:

$$\begin{aligned} |\Psi_{10}\rangle = \widehat{X}_1|\Psi_{00}\rangle &= \frac{1}{\sqrt{2^{N_{\mathrm{V}}}}} \sum_{\{n_{\mathbf{x}}\}} \Big(\prod_{\mathbf{x}\in \mathrm{V}} \widehat{G}_{\mathbf{x}}^{n_{\mathbf{x}}}\Big)|C_{10}\rangle = \prod_{\mathbf{x}\in \mathrm{V}} \Big(\frac{1+\widehat{G}_{\mathbf{x}}}{\sqrt{2}}\Big)|C_{10}\rangle \\ &= \frac{1}{\sqrt{2^{N_{\mathrm{V}}-1}}} \sum_{\gamma^*}^{\text{contractible}} \widehat{X}_{\gamma^*}|C_{10}\rangle \;. \end{aligned} \tag{9.53}$$

9.4.2. The large $h_\perp$ phase

The ground state for $h_\perp \to \infty$ is the simple product state with all spins now aligned in the x-direction:

$$|\Psi_{\rm gs}\rangle_{h_\perp\to\infty} = \prod_\ell |+,x\rangle_\ell \qquad \text{with} \qquad |+,x\rangle_\ell = \frac{1}{\sqrt{2}}\Big(|+\rangle_\ell + |-\rangle_\ell\Big) \,. \tag{9.60}$$

It is evidently *non-degenerate*. Since $\hat{\sigma}^x_\ell |+,x\rangle_\ell = |+,x\rangle_\ell$, you deduce that, as anticipated:

$$\widehat{G}_{\mathbf{x}} |\Psi_{\rm gs}\rangle_{h_\perp\to\infty} = |\Psi_{\rm gs}\rangle_{h_\perp\to\infty} \,. \tag{9.61}$$

Obviously, on such a state, the expectation value of any Wilson loop operator vanishes exactly:

$$\langle\Psi_{\rm gs}|\widehat{Z}_{\mathcal{C}}|\Psi_{\rm gs}\rangle_{h_\perp\to\infty} = 0 \,. \tag{9.62}$$

We will adopt a convenient graphical representation for links in the states $|\pm,x\rangle_\ell$ of $\hat{\sigma}^x$: We denote by a **dotted line** a link in $|+,x\rangle_\ell$, and by a **solid line** a link in $|-,x\rangle_\ell$.

Let us consider now *excited states* in the limit $h_\perp \to \infty$ (or, equivalently, putting the plaquette coupling $J = 0$). The lowest excited state has a *single* link (anywhere in the lattice) in the state $|-,x\rangle_\ell$, shown in Fig. 9.12 (right), with an energy cost $\Delta E = 2h_\perp$. Notice that $\hat{\sigma}^z_\ell |+,x\rangle_\ell = |-,x\rangle_\ell$ is the operator that creates such an excitations.

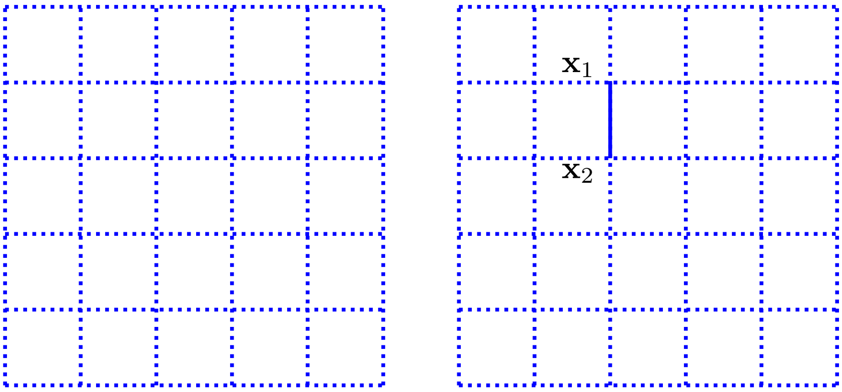

Figure 9.12: Left: The ground state $|\Psi_{\rm gs}\rangle_{h_\perp\to\infty}$ with all links in state $|+,x\rangle$ (dotted lines). Right: The lowest-energy excited states where two violations of $\widehat{G}_{\mathbf{x}} = 1$ appear at the vertices denoted as $\mathbf{x}_1$ and $\mathbf{x}_2$, and a single link (the full blue line) is in the state $|-,\mathbf{x}\rangle = \hat{\sigma}^z_\ell|+,x\rangle_\ell$.

One might analise all possible vertex configurations, $2^4 = 16$ in total, to quickly discover that 8 of them indeed satisfy $\widehat{G}_{\mathbf{x}} = 1$ because an *even number* of full lines enter the vertex. The 8 vertices satisfying $\widehat{G}_{\mathbf{x}} = 1$ are shown in Fig. 9.13.

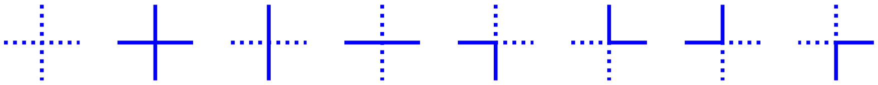

Figure 9.13.: The 8 vertices for which the constraint $\widehat{G}_{\mathbf{x}} = 1$ is satisfied.

One might further consider excited states where the vertices with $\widehat{G}_{\mathbf{x}} = -1$ — which we will consider are *charge excitations* on the background of vertices all satisfying $\widehat{G}_{\mathbf{x}} = 1$ — are placed further apart, at two distant points $\mathbf{x}_1$ and $\mathbf{x}_2$, as in Fig. 9.14. To create such an excitation, one just needs to consider a Wilson *open string* $\gamma(\mathbf{x}_1,\mathbf{x}_2)$ connecting the two points, applying the operator

$$\widehat{Z}_{\gamma(\mathbf{x}_1,\mathbf{x}_2)} = \prod_{\ell\in\gamma(\mathbf{x}_1,\mathbf{x}_2)} \hat{\sigma}^z_\ell \,. \tag{9.63}$$

The energy cost of such configurations (still assuming $h_\perp/J \to \infty$) over the ground state is now:

$$V(\mathbf{x}_1,\mathbf{x}_2) = E_{\mathbf{x}_1,\mathbf{x}_2} - E_{\rm gs} = 2h_\perp ||\mathbf{x}_2 - \mathbf{x}_1||_{\rm Manh} \tag{9.64}$$

where $||\mathbf{x}_2 - \mathbf{x}_1||_{\rm Manh}$ denotes the Manhattan distance between the two points. [7]

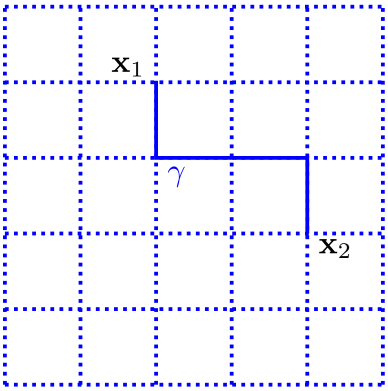

Figure 9.14: The excited state where two violations of $\widehat{G}_{\mathbf{x}} = 1$ appear at the vertices denoted as $\mathbf{x}_1$ and $\mathbf{x}_2$, with the Wilson open string $\gamma(\mathbf{x}_1, \mathbf{x}_2)$ containing the links joining these two points in the state $|-, \mathbf{x}\rangle$ (full blue line). Here $||\mathbf{x}_2 - \mathbf{x}_1||_{\rm Manh} = 4$, and the energy cost of such a configuration is $V(\mathbf{x}_1, \mathbf{x}_2) = 8h_\perp$.

Confinement. The fact that two excitations (charges) placed at two points $\mathbf{x}_1$ and $\mathbf{x}_2$ pay an energy cost

$$V(\mathbf{x}_1, \mathbf{x}_2) = \alpha ||\mathbf{x}_2 - \mathbf{x}_1|| \tag{9.65}$$

proportional to the distance between the two points is a phenomenon known as *confinement.* In the simple case shown above, a *string* of reversed links $|-, x\rangle$ (full blue lines) joins the two excitations, and the energy cost scales *linearly* with the length of the string.

9.5. Kitaev's Toric code model

Toric code model. On a $d = 2$ square lattice with PBC in both directions, Kitaev's toric code model reads: [a]

$$\widehat{H}_{\rm K} = -h_{\rm K} \sum_{\mathbf{x}} \widehat{G}_{\mathbf{x}} - J_{\rm K} \sum_{\mathbf{x}_*} \widehat{Z}_{\mathbf{x}_*} \tag{9.66}$$

---

[a] Kitaev calls A_s our $\widehat{G}_{\mathbf{x}}$, s being a "star" associated to a site (or vertex) of the lattice, and B_p our $\widehat{Z}_{\mathbf{x}_*}$, p being a "plaquette" associated to the center of the lattice squares. Since the two terms commute a common choice of parameters is to set $h_{\rm K} = J_{\rm K} = 1$, the energy unit.

We will now describe the ground states of Kitaev's model, in a way that will provide an alternative route to the description of the four topological states, see Eq. (9.56), discussed in Sec. 9.4.1.

9.5.1. The ground states

As observed several times, $[\widehat{G}_{\mathbf{x}'}, \widehat{Z}_{\mathbf{x}_*}] = 0$ for every possible $\mathbf{x}'$ and $\mathbf{x}_*$. This means that the ground states correspond to finding the common eigenstates of $\widehat{G}_{\mathbf{x}}$ and $\widehat{Z}_{\mathbf{x}_*}$ with eigenvalues $+1$:

$$\widehat{G}_{\mathbf{x}} |\psi_{\rm gs}\rangle = |\psi_{\rm gs}\rangle \quad \forall \mathbf{x} \qquad \text{and} \qquad \widehat{Z}_{\mathbf{x}_*} |\psi_{\rm gs}\rangle = |\psi_{\rm gs}\rangle \quad \forall \mathbf{x}_* \; . \tag{9.67}$$

---

[7] Recall that if $\mathbf{x} = (x, y)$, then

$$||\mathbf{x}||_{\rm Manh} = |x| + |y| \; ,$$

a particular case of a larger classes of distances $||\mathbf{x}||_n = (|x|^n + |y|^n)^{\frac{1}{n}}$ which includes the Euclidean distance for $n = 2$ and the Manhattan distance for $n = 1$. In the limit $n \to \infty$ we would obtain $||\mathbf{x}||_\infty = \max(|x|, |y|)$.

Constraints and counting of ground states. Since $\widehat{G}_{\mathbf{x}}^2 = 1$ and $\widehat{Z}_{\mathbf{x}_*}^2 = 1$, clearly both operators can have only eigenvalues ± 1. The total number of states in the Hilbert space is $2^{2L^2} = 4^{N_{\rm V}}$, where $N_{\rm V} = L^2$ is the number of vertices, the factor 2 coming from the two links at each vertex. Imposing each of the constraints, for instance $\widehat{G}_{\mathbf{x}}|\psi\rangle = |\psi\rangle$, reduces by a factor 2 the number of states. One might think that there are $2N_{\rm V}$ constraints implied by Eq. (9.67), one for each vertex $\mathbf{x}$ and one for each plaquette $\mathbf{x}_*$ (the number of plaquettes is equal to $N_{\rm V}$ in two dimensions). But in reality, since $\prod_{\mathbf{x}} \widehat{G}_{\mathbf{x}} = 1$ and $\prod_{\mathbf{x}_*} \widehat{Z}_{\mathbf{x}_*} = 1$ we have only $(N_{\rm V} - 1)$ constraints for the vertices and $(N_{\rm V} - 1)$ constraints for the plaquettes. Hence, we expect

$$\frac{4^{N_{\rm V}}}{2^{N_{\rm V}-1}\, 2^{N_{\rm V}-1}} = 4 \qquad \text{ground states .}$$

To write the ground states explicitly, we start from the reference state $|+,x\rangle = \prod_\ell |+,x\rangle_\ell$ with all links on the spin state $|+,x\rangle$. As remarked, it satisfies $\widehat{G}_{\mathbf{x}}|+,x\rangle = |+,x\rangle$, but there are many more configurations that satisfy such constraints everywhere. Indeed, you can "glue together" the 8 types of vertices in Fig. 9.13 in such a way that no vertex of the wrong type, with an odd number of solid lines, is present. A moment's reflection should convince you that we need to impose that full lines always close into *loops* $\mathcal{C}$. Since a full-line link is created by the application of $\hat{\sigma}^z_\ell$ on the state $|+,x\rangle_\ell$ you immediately realise that such a closed-loop of full lines is precisely associated with the Wilson loop operator $\widehat{Z}_{\mathcal{C}}$.

States satisfying $\widehat{G}_{\mathbf{x}} = 1$ everywhere. You immediately conclude that any state

$$|\mathcal{C}\rangle = \widehat{Z}_{\mathcal{C}}|+,x\rangle \qquad \Longrightarrow \qquad \widehat{G}_{\mathbf{x}}|\mathcal{C}\rangle = |\mathcal{C}\rangle \tag{9.68}$$

where $\mathcal{C}$ is a closed loop of full lines on the lattice, possibly made of several disconnected sub-loops. The simple reason for this result is that, as previously remarked, the Wilson loop operators are gauge invariant, $[\widehat{G}_{\mathbf{x}}, \widehat{Z}_{\mathcal{C}}] = 0$, and, trivially, $\widehat{G}_{\mathbf{x}}|+,x\rangle = |+,x\rangle$. All these states $|\mathcal{C}\rangle$ are completely degenerate, for $J_{\rm K} = 0$, and have energy $-N_{\rm V} h_{\rm K}$.

Let us now consider the effect of the other term, $-J_{\rm K}\widehat{Z}_{\mathbf{x}_*}$. As discussed, $\widehat{Z}_{\mathbf{x}_*} \equiv \widehat{Z}_{\mathcal{C}=\text{plaq}(\mathbf{x}_*)}$, the smallest closed loop $\mathcal{C}$ in the lattice: the plaquette. Hence, by applying $\widehat{Z}_{\mathbf{x}_*}$ to a loop configuration $|\mathcal{C}\rangle$ you obtain *another loop configuration* $|\mathcal{C}'\rangle$ differing from $|\mathcal{C}\rangle$ by a single plaquette loop. All in all, you realise that the best thing you can do to gain energy — recall Perron-Frobenius — is to create a *superposition of all loop configurations* with a uniform positive coefficient

$$|\Phi_{00}\rangle = \mathcal{N} \sum_{\mathcal{C}} \widehat{Z}_{\mathcal{C}}|+,x\rangle = \frac{1}{\sqrt{2^{N_{\rm V}-1}}} \sum_{\mathcal{C}} \widehat{Z}_{\mathcal{C}}|+,x\rangle \;, \tag{9.69}$$

with a suitable normalisation coefficient, which we will soon show is $\mathcal{N} = \frac{1}{\sqrt{2^{N_{\rm V}-1}}}$. Let us get to this result by the following explicit route.

Consider the alternative writing

$$|\Phi_{00}\rangle = \prod_{\mathbf{x}_*} \Big(\frac{1+\widehat{Z}_{\mathbf{x}_*}}{\sqrt{2}}\Big)|+,x\rangle = \frac{1}{\sqrt{2^{N_{\rm V}}}} \sum_{\{n_{\mathbf{x}_*}\}} \prod_{\mathbf{x}_*} \widehat{Z}_{\mathbf{x}_*}^{n_{\mathbf{x}_*}} |+,x\rangle \tag{9.70}$$

with $n_{\mathbf{x}_*} = 0,1$ on each plaquette. Arguments entirely identical to those of Sec. 9.4.1, based on the fact that $\prod_{\mathbf{x}_*} \widehat{Z}_{\mathbf{x}_*} = 1$, show that all configurations are indeed included *twice*. The fact that, given a bipartition $\mathrm{A} \cup \overline{\mathrm{A}}$ of all plaquettes, we have

$$\prod_{\mathbf{x}_* \in \mathrm{A}} \widehat{Z}_{\mathbf{x}_*} = \widehat{Z}_{\mathcal{C}}$$

completes the proof that Eqs. (9.69)-(9.70) are equivalent.

The other ground states are obtained by applying non-contractible Wilson loop operators to $|\Phi_{00}\rangle$:

> **The four ground states on the 2-torus.** Define, for $v_1, v_2 = 0, 1$, the four (degenerate) ground states
>
> $$|\Phi_{v_1,v_2}\rangle = \widehat{Z}_2^{v_2} \widehat{Z}_1^{v_1} |\Phi_{0,0}\rangle \; . \tag{9.71}$$
>
> The non-contractible 't Hooft operators act now as non-local order parameters:
>
> $$\widehat{X}_\nu |\Phi_{v_1,v_2}\rangle = (-1)^{v_\nu} |\Phi_{v_1,v_2}\rangle \qquad \Longrightarrow \qquad \langle \Phi_{v_1,v_2} | \widehat{X}_\nu | \Phi_{v_1,v_2} \rangle = (-1)^{v_\nu} \; . \tag{9.72}$$

As you see, the previous description mirrors that of Sec. 9.4.1, with a rotation from $\hat{\sigma}^z$ to $\hat{\sigma}^x$.

Obviously, on such states, the expectation value of any Wilson loop operator is exactly 1:

$$\langle \Psi_{\mathrm{gs}} | \widehat{Z}_{\mathcal{C}} | \Psi_{\mathrm{gs}} \rangle_{h_\perp \to 0} = \langle \Psi_{v_1,v_2} | \widehat{Z}_{\mathcal{C}} | \Phi_{v_1,v_2} \rangle = 1 \; , \tag{9.73}$$

for the very simple reason that any $\widehat{Z}_{\mathcal{C}}$ can be written as a product of $\widehat{Z}_{\mathbf{x}_*}$, and all of these have eigenvalues $+1$ on the ground states.

9.5.2. The excitations

Let us now discuss the excitations of Kitaev's toric code model. We will be very sketchy. For a more in-depth discussion, see the videos of the lectures given at ICTP by Xie Chen (Caltech) Lecture 1, Lecture 2.

Electric (charge) excitations. As before, electric charge excitations are associated with violations of the vertex constraint $\widehat{G}_{\mathbf{x}} = 1$, at two or more vertices. Consider, for simplicity, the case where $\widehat{G}_{\mathbf{x}} = -1$ at the two vertices $\mathbf{x}_1$ and $\mathbf{x}_2$. This excitation is created by a Wilson open string $\widehat{Z}_\gamma$, with $\gamma(\mathbf{x}_1, \mathbf{x}_2)$ the open string joining $\mathbf{x}_1$ to $\mathbf{x}_2$. Consider the associated excited state

$$|\Psi^e_{\mathbf{x}_1,\mathbf{x}_2}\rangle = \widehat{Z}_{\gamma(\mathbf{x}_1,\mathbf{x}_2)} |\Phi_{00}\rangle \; .$$

Evidently, the $-J_{\mathrm{K}} \widehat{Z}_{\mathbf{x}_*}$ terms are totally unaffected by the Wilson string (they commute), while the two vertices with $\widehat{G}_{\mathbf{x}} = -1$ imply an energy cost, over the ground state energy, of:

$$V_e(\mathbf{x}_1, \mathbf{x}_2) = 4 h_{\mathrm{K}} \qquad \forall \mathbf{x}_1, \mathbf{x}_2 \; . \tag{9.74}$$

Interestingly, this energy cost is *totally independent of the distance* $||\mathbf{x}_2 - \mathbf{x}_1||$ between the two "charges".

> **Deconfinement.** The fact that two excitations (charges) placed at two points $\mathbf{x}_1$ and $\mathbf{x}_2$ pay an energy cost
>
> $$\lim_{||\mathbf{x}_2 - \mathbf{x}_1|| \to \infty} V_e(\mathbf{x}_1, \mathbf{x}_2) = V_\infty < +\infty \tag{9.75}$$
>
> which saturates to a finite value when the distance between the two points goes to infinity is a phenomenon known as *deconfinement*. In the Kitaev model, deconfinement is extreme, since $V_e(\mathbf{x}_1, \mathbf{x}_2)$ is totally independent of the distance.

Magnetic (flux) excitations. Symmetrically, one might consider two "magnetic" excitations corresponding to *two frustrated plaquettes*. The simplest such excitations are created by applying $\hat{\sigma}^x_\ell$ on a given link, obtaining the state

$$|\Psi^m_\ell\rangle = \hat{\sigma}^x_\ell |\Phi_{00}\rangle$$

While the $-h_{\rm K}\widehat{G}_{\mathbf{x}}$ is unaffected (because they commute), this makes the two neighbouring plaquettes $\mathbf{x}^1_*$ and $\mathbf{x}^2_*$, sharing the link ℓ, frustrated because of the anti-commutation:

$$\widehat{Z}_{\mathbf{x}^{1,2}_*}\hat{\sigma}^x_\ell|\Phi_{00}\rangle = -\hat{\sigma}^x_\ell\widehat{Z}_{\mathbf{x}^{1,2}_*}|\Phi_{00}\rangle = -\hat{\sigma}^x_\ell|\Phi_{00}\rangle \; .$$

Hence this excitation costs an energy $+4J_{\rm K}$ (indeed, $+2J_{\rm K}$ for each frustrated plaquette). This can be easily generalised, once again, by considering an arbitrary 't Hooft open string $\gamma^*(\mathbf{x}^1_*,\mathbf{x}^2_*)$ joining two arbitrary plaquettes $\mathbf{x}^1_*$ and $\mathbf{x}^2_*$. The associated excited state is

$$|\Psi^m_{\mathbf{x}^1_*,\mathbf{x}^2_*}\rangle = \widehat{X}_{\gamma^*}|\Phi_{00}\rangle = \Big(\prod_{\ell\perp\gamma^*}\hat{\sigma}^x_\ell\Big)|\Phi_{00}\rangle \qquad \Longrightarrow \qquad V_m(\mathbf{x}^1_*,\mathbf{x}^2_*) = 4J_{\rm K} \qquad \forall\mathbf{x}^1_*,\mathbf{x}^2_* \; . \tag{9.76}$$

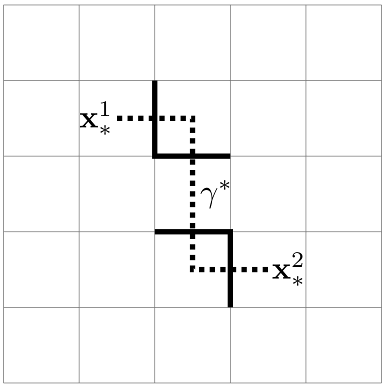

Figure 9.15: On the background of the ground state $|\Phi_{00}\rangle$ (grey thin lines), the two frustrated plaquettes obtained by applying $\hat{\sigma}^x_\ell$ on the full (black) links. The dotted line denotes the 't Hooft open string $\gamma^*(\mathbf{x}^1_*,\mathbf{x}^2_*)$ connecting the centers of the plaquettes.

Once again, the proof of this is very simple, and relies on the anticommutation of $\widehat{Z}_{\mathbf{x}^{1,2}_*}$ with $\widehat{X}_{\gamma(\mathbf{x}^1_*,\mathbf{x}^2_*)}$ due to the *single link* in common between each of the plaquette operators with the 't Hooft string. The independence of the energy cost of the excitation from the distance $||\mathbf{x}^1_* - \mathbf{x}^2_*||$ tells us, once again, that the toric code ground states show an extreme *deconfinement* also for the magnetic excitations.

9.5.3. Summary of the phase diagram for $d = 2$.

Here is a summary of the phase diagram expected for the $d = 2$ Ising quantum LGT in a transverse field. In the limit $h_\perp/J \to 0$ the physics is described by the Kitaev model: the deconfined phase has topological properties, with four ground states on the torus. In the limit $h_\perp/J \to \infty$ the physics is described by the simple product ground state $|+, x\rangle$.

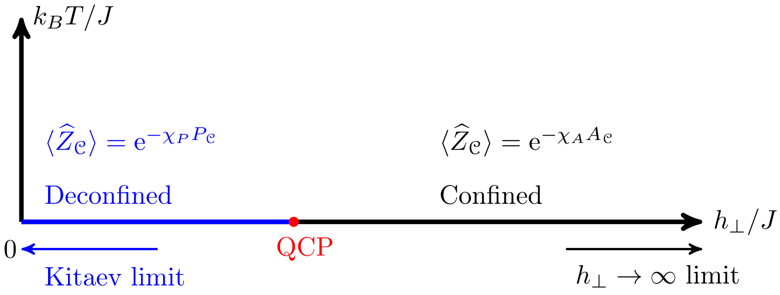

Figure 9.16: The phase diagram of $\mathbb{Z}_2$ quantum LGT for $d = 2$. From the duality mapping we know that the quantum critical point (QCP) has the exponents of the $d = 2$ Transverse Field Ising Model: the best numerical estimates give $(h_\perp/J)_c \approx 0.33$.

9.6. Path-integral of quantum Ising LGT model

The quantum Ising LGT model at finite T can be mapped, through the usual Suzuki-Trotter path-integral, into a classical model in $d+1$ dimensions. To simplify the notation we will illustrate the case for $d=2$. Figure 9.17 shows a single plaquette in $d=2$ with one its "Trotter replicas" along the imaginary time direction. Notice that spins are on links that are *horizontal*, and horizontal plaquettes, which we denote as $\mathbf{x}_*^{12}$, are only involved in the LGT interaction.

Path-integral representation of the quantum Ising LGT in a transverse field. The effective classical partition sum of the quantum Ising LGT in a transverse field is the following *classical effective action* $S[\boldsymbol{\sigma}]$ in $(d+1)$-dimensions

$$\begin{aligned} S[\boldsymbol{\sigma}] &= -\epsilon J \sum_{n_t=1}^{N_t} \sum_{\mathbf{x}} \sigma_{\ell_1,n_t}\, \sigma_{\ell_2,n_t}\, \sigma_{\ell_3,n_t}\, \sigma_{\ell_4,n_t} - K^t \sum_{n_t=1}^{N_t} \sum_{\ell} \sigma_{\ell,n_t}\sigma_{\ell,n_t+1} \\ Z_{\mathrm{Q}} &= \lim_{N_t\to\infty} \sum_{\underline{\sigma}_1\cdots\underline{\sigma}_{N_t}} \mathrm{e}^{-S[\underline{\sigma}_1,\cdots,\underline{\sigma}_{N_t}]} = \lim_{N_t\to\infty} \sum_{\boldsymbol{\sigma}} \mathrm{e}^{-S[\boldsymbol{\sigma}]} \end{aligned} .$$

As before the relevant transverse (time-like) coupling K^t is *ferromagnetic* and is given by:

$$\left\{ \begin{aligned} K^t &= -\frac{1}{2}\log\tanh\left(\epsilon h^{\perp}\right) > 0 \\ \epsilon &= \frac{\Delta\tau}{\hbar} \equiv \frac{\beta}{N_t} = \frac{1}{k_B T N_t} \end{aligned} \right. . \qquad (9.77)$$

Notice that at each $\mathbf{x}$ there are vertical links $\ell = (\mathbf{x}, \mathbf{x}+\mathbf{e}_3)$ on which there are *no spins* required by the Trotter path-integral. Such vertical links define two new plaquettes, which we denote as $\mathbf{x}_*^{13}$ and $\mathbf{x}_*^{23}$. If you introduce the spins on these links ℓ of the two plaquettes along the temporal directions, fixing them to $\hat{\sigma}_\ell^z \to +1$, you can promote the two-spin interactions in the temporal direction into *four-spin* plaquette interactions.

$$S[\boldsymbol{\sigma}] = -\sum_{\mathbf{x}_*} \left(K^s \widehat{Z}_{\mathbf{x}_*^{12}} + K^t \widehat{Z}_{\mathbf{x}_*^{13}} + K^t \widehat{Z}_{\mathbf{x}_*^{23}} \right) \qquad (9.78)$$

where the "spatial coupling" $K^s = \epsilon J$ is different from the "temporal coupling" K^t.

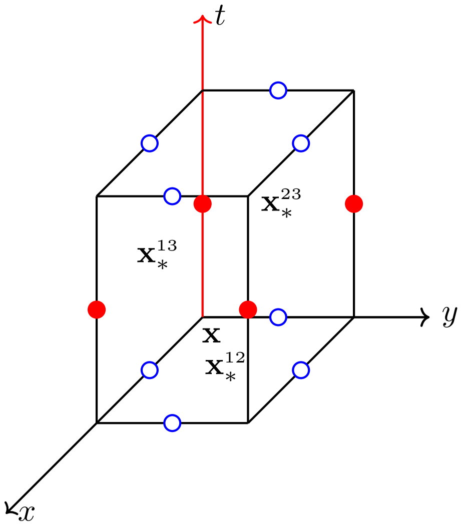

Figure 9.17: A single plaquette of a $d=2$ LGT (spins on the empty circles), with its "Trotter replica" along the "imaginary time" direction. Notice that the Suzuki-Trotter path-integral would couple only *pairs* of spins along the imaginary-time directions: the solid circles denote the positions of spins that are not present in the Suzuki-Trotter classical model. With the usual trick of "fixing the temporal gauge" you can introduce $\hat{\sigma}_\ell^z \to +1$ at all such vertical links ℓ, so that the Suzuki-Trotter classical model becomes a classical anisotropic LGT in $d+1=3$.

9.7. Duality for the quantum Ising LGT in two dimensions

Consider the quantum Ising LGT in $d = 2$. We saw that it is "equivalent", given the path-integral mapping, to a classical Ising LGT in dimension $d+1 = 3$. We will now see that, in a specific subsector where the ground states live — that of states $|\psi\rangle$ for which $\widehat{G}_{\mathbf{x}}|\psi\rangle = |\psi\rangle$ for all $\mathbf{x}$ — a nice duality mapping can be shown to exist with an ordinary transverse field quantum Ising model in the same dimensionality $d = 2$.

The duality mapping is illustrated in Fig. 9.18. Taking $\mathbf{x} = n_1\mathbf{e}_1 + n_2\mathbf{e}_2$, it is defined as follows:

$$\begin{cases} \hat{\tau}^z_{\mathbf{x}_*} = \displaystyle\prod_{\ell\,\perp\,\gamma^*(\mathbf{x}_*)} \hat{\sigma}^x_\ell = \prod_{n=0}^{n_2} \hat{\sigma}^x_{\mathbf{x}-n\mathbf{e}_2,1} \\ \\ \hat{\tau}^x_{\mathbf{x}_*} = \widehat{Z}_{\mathbf{x}_*} = \hat{\sigma}^z_{\ell_1}\,\hat{\sigma}^z_{\ell_2}\,\hat{\sigma}^z_{\ell_3}\,\hat{\sigma}^z_{\ell_4} \end{cases} \tag{9.79}$$

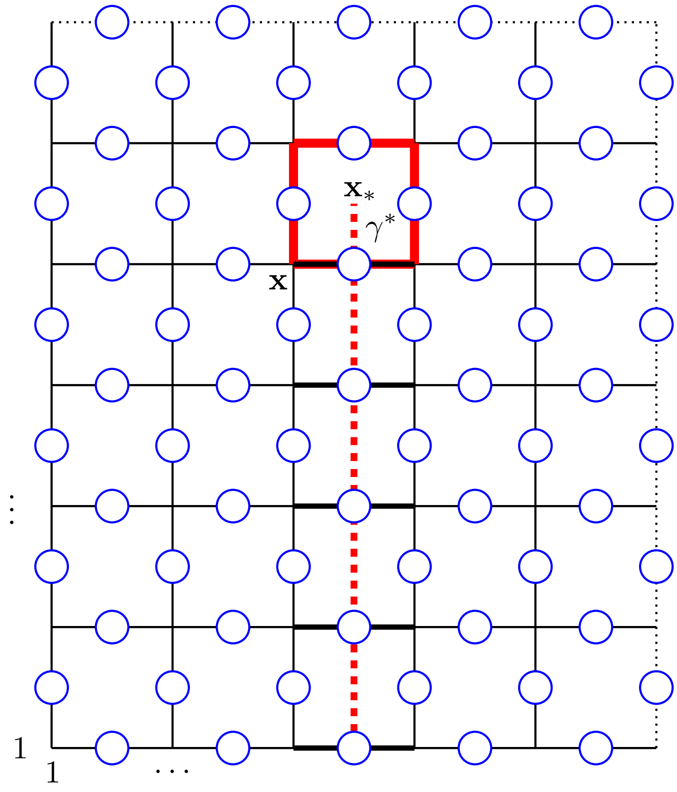

Figure 9.18: The duality mapping. In $d = 2$ the quantum Ising LGT can be mapped into the transverse field quantum Ising model in the same dimension $d = 2$. The mapping is non-local and requires using a 't Hooft open string γ^* starting from the lower edge of the system and ending at the centre $\mathbf{x}_*$ of a plaquette.

Notice the (open) 't Hooft string $\gamma^*(\mathbf{x}_*)$ on the (dual) lattice going through the centres of the plaquettes: it starts from the lower horizontal link and goes up to $\mathbf{x}_*$, cutting several horizontal links below $\mathbf{x}_*$. We start understanding the first equation for $\hat{\tau}^z_{\mathbf{x}_*}$. Since $(\hat{\sigma}^x)^2 = 1$, you deduce that

$$\hat{\tau}^z_{\mathbf{x}_*}\,\hat{\tau}^z_{\mathbf{x}_*-\mathbf{e}_2} = \hat{\sigma}^x_{\mathbf{x},1} \;. \tag{9.80}$$

Less trivial is to understand $\hat{\tau}^z_{\mathbf{x}_*}\,\hat{\tau}^z_{\mathbf{x}_*-\mathbf{e}_1}$. Let $\mathbf{x} = n_1\mathbf{e}_1 + n_2\mathbf{e}_2$. Then:

$$\widehat{G}_{\mathbf{x}} = 1 \qquad \Longrightarrow \qquad \hat{\sigma}^x_{\mathbf{x},2} = \hat{\sigma}^x_{\mathbf{x},1}\hat{\sigma}^x_{\mathbf{x},-1}\hat{\sigma}^x_{\mathbf{x},-2} = \hat{\sigma}^x_{\mathbf{x},1}\hat{\sigma}^x_{\mathbf{x},-1}\hat{\sigma}^x_{\mathbf{x}-\mathbf{e}_2,2}$$

Similarly:

$$\widehat{G}_{\mathbf{x}-\mathbf{e}_2} = 1 \qquad \Longrightarrow \qquad \hat{\sigma}^x_{\mathbf{x}-\mathbf{e}_2,2} = \hat{\sigma}^x_{\mathbf{x},1}\hat{\sigma}^x_{\mathbf{x},-1}\hat{\sigma}^x_{\mathbf{x}-2\mathbf{e}_2,2}$$

Assuming *open boundary conditions* in the y-direction, so that the bottom star contains three links only and

$$\widehat{G}_{\mathbf{x}-n_2\mathbf{e}_2} = \hat{\sigma}^x_{\mathbf{x}-n_2\mathbf{e}_2,2}\hat{\sigma}^x_{\mathbf{x}-n_2\mathbf{e}_2,1}\hat{\sigma}^x_{\mathbf{x}-n_2\mathbf{e}_2,-1} \;,$$

and proceeding iteratively until the lower edge is reached you deduce that:

$$\hat{\sigma}^x_{\mathbf{x},2} = \prod_{n=0}^{n_2} \hat{\sigma}^x_{\mathbf{x}-n\mathbf{e}_2,1}\,\hat{\sigma}^x_{\mathbf{x}-n\mathbf{e}_2,-1} \equiv \hat{\tau}^z_{\mathbf{x}_*}\hat{\tau}^z_{\mathbf{x}_*-\mathbf{e}_1} \;. \tag{9.81}$$

Hence, we have proved that:

$$\begin{cases} \hat{\sigma}^x_{\mathbf{x},1} &= \hat{\tau}^z_{\mathbf{x}_*}\hat{\tau}^z_{\mathbf{x}_*-\mathbf{e}_2} \\[2ex] \hat{\sigma}^x_{\mathbf{x},2} &= \hat{\tau}^z_{\mathbf{x}_*}\hat{\tau}^z_{\mathbf{x}_*-\mathbf{e}_1} \end{cases} \tag{9.82}$$

for all $\mathbf{x}$ of the lattice. A moment's reflection shows that all the $\hat{\sigma}^x$ on the independent links of the PBC lattice have been mapped in this way into products of nearest-neighbour $\hat{\tau}^z$ on the dual lattice. Also, our assumption of OBC was not essential at all: indeed, you can prove that $\widehat{G}_{\mathbf{x}} = 1$ at all $\mathbf{x}$, including the lower edge which, with PBC, has stars with 4 links, including the top vertical link.

Concerning $\hat{\tau}^x_{\mathbf{x}_*}$, let us understand why we need the four plaquette $\hat{\sigma}^z$. The reason is that we need that $\hat{\tau}^x_{\mathbf{x}_*}$ *anti-commutes* with $\hat{\tau}^z_{\mathbf{x}_*}$ — indeed, they share a single link — but commutes with all the other $\hat{\tau}^z$, notably, with the neighbors: $\hat{\tau}^z_{\mathbf{x}_*-\mathbf{e}_2}$, $\hat{\tau}^z_{\mathbf{x}_*-\mathbf{e}_1}$, $\hat{\tau}^z_{\mathbf{x}_*+\mathbf{e}_2}$, and $\hat{\tau}^z_{\mathbf{x}_*+\mathbf{e}_1}$. [8]

> **Mapping the two models in $d = 2$.** Hence, the mapping tells us that, in the subsector with $\widehat{G}_{\mathbf{x}} = 1$, the quantum Ising LGT maps as follows:
>
> $$\begin{aligned} \widehat{H}_{d=2-\text{Q}-\text{ILGT}} &= -h_\perp \sum_{\mathbf{x}} (\hat{\sigma}^x_{\mathbf{x},1} + \hat{\sigma}^x_{\mathbf{x},2}) - J \sum_{\mathbf{x}_*} \widehat{Z}_{\mathbf{x}_*} \\ &\mapsto -h_\perp \sum_{\mathbf{x}_*} (\hat{\tau}^z_{\mathbf{x}_*}\hat{\tau}^z_{\mathbf{x}_*-\mathbf{e}_2} + \hat{\tau}^z_{\mathbf{x}_*}\hat{\tau}^z_{\mathbf{x}_*-\mathbf{e}_1}) - J \sum_{\mathbf{x}_*} \hat{\tau}^x_{\mathbf{x}_*} = \widehat{H}_{d=2-\text{TFIM}} \;. \end{aligned} \tag{9.83}$$
>
> Notice that the couplings have been reversed: J now plays the role of a transverse field, while $h_\perp$ is the nearest-neighbour coupling.

Interestingly, as a consequence of PBC:

$$\prod_{\mathbf{x}_*} \widehat{Z}_{\mathbf{x}_*} = 1 \qquad \Longrightarrow \qquad \prod_{\mathbf{x}_*} \hat{\tau}^x_{\mathbf{x}_*} = 1 \;. \tag{9.84}$$

This shows that the $d = 2$-TFIM has $2^{N_{\text{V}}-1}$ states: those which are $\mathbb{Z}_2$ symmetric. Let us see how many degrees of freedom we can count for the original spins. Starting from $2N_{\text{V}}$ links, hence $4^{N_{\text{V}}}$ states, we have imposed $N_{\text{V}} - 1$ constraints due to the $\widehat{G}_{\mathbf{x}} = 1$ — recall that $\prod_{\mathbf{x}} \widehat{G}_{\mathbf{x}} = 1$ reduces by 1 the constraints. Hence, we arrived at:

$$\frac{4^{N_{\text{V}}}}{2^{N_{\text{V}}-1}} = 2^{N_{\text{V}}+1} \quad \text{states} \;.$$

These two counting of states, for the TFIM on the dual lattice, and the original LGT model with constraints, differ by a factor of 4. The reason is that there are *two extra constraints* on the original LGT which are effectively in place. Indeed, you can show that the mapping implies that the two non-contractible 't Hooft loop operators are constrained to be:

$$\widehat{X}_{\gamma_1^*} = \prod_{\ell \perp \gamma_1^*} \hat{\sigma}^x_\ell = 1 \qquad \text{and} \qquad \widehat{X}_{\gamma_2^*} = \prod_{\ell \perp \gamma_2^*} \hat{\sigma}^x_\ell = 1 \;, \tag{9.85}$$

which brings the total number of states, consistently, to $2^{N_{\text{V}}-1}$.

---

[8] It is simple to show that $[\hat{\tau}^z_{\mathbf{x}_*-\mathbf{e}_2}, \hat{\tau}^x_{\mathbf{x}_*}] = 0$ (they share no links), $[\hat{\tau}^z_{\mathbf{x}_*+\mathbf{e}_2}, \hat{\tau}^x_{\mathbf{x}_*}] = 0$ (they share two links), and $[\hat{\tau}^z_{\mathbf{x}_*\pm\mathbf{e}_1}, \hat{\tau}^x_{\mathbf{x}_*}] = 0$ (they share no links). Moreover, $\{\hat{\tau}^z_{\mathbf{x}_*-\mathbf{e}_1}\hat{\tau}^z_{\mathbf{x}_*}, \hat{\tau}^x_{\mathbf{x}_*}\} = 1$, and $\{\hat{\tau}^z_{\mathbf{x}_*+\mathbf{e}_1}\hat{\tau}^z_{\mathbf{x}_*}, \hat{\tau}^x_{\mathbf{x}_*}\} = 1$ because again they share a single link (the vertical sides of the plaquette).

9.8. $U(1)$ lattice gauge theory

We now consider a more general case in which the variables at each link are phase factors $\mathrm{e}^{i\theta_\ell}$ rather than Ising spin variables $\hat{\sigma}^z_\ell$. This changes the symmetry group from $\mathbb{Z}_2 = \{1, -1\}$ to $U(1)$. We will later show, in Secs. 9.8.2 and 9.8.3, the connection of this $U(1)$ lattice gauge theory with electromagnetism.

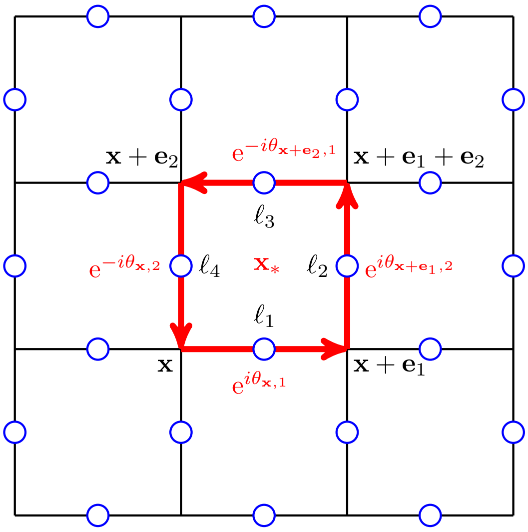

Figure 9.19: A portion of a square lattice, with a plaquette highlighted in red (the meaning of the arrows will be clarified later on). $U(1)$ variables are sitting on the edges of the lattice, denoted by circles. The center of the plaquette is denoted as $\mathbf{x}_*$.

The variables on the link and the plaquette operator. With reference to Fig. 9.19, the variable we put on each link is a $U(1)$ phase variable $\mathrm{e}^{i\theta_\ell}$. Here, the arrows will play a role. On the two links ℓ_3 and ℓ_4 the arrows go into direction $-\mathbf{e}_1$ and $-\mathbf{e}_2$, respectively, so that the system of arrows around the plaquette forms a closed-loop going counterclockwise. We will assume that:

$$\mathrm{e}^{i\theta_{\mathbf{x}+\mathbf{e}_1+\mathbf{e}_2,-1}} \equiv \mathrm{e}^{-i\theta_{\mathbf{x}+\mathbf{e}_2,1}} \qquad \text{and} \qquad \mathrm{e}^{i\theta_{\mathbf{x}+\mathbf{e}_2,-2}} \equiv \mathrm{e}^{-i\theta_{\mathbf{x},2}} \; . \tag{9.86}$$

More generally, link variables going into opposite directions are complex conjugate of each other:

$$\mathrm{e}^{i\theta_{\mathbf{x}+\mathbf{e}_\nu,-\nu}} \equiv \mathrm{e}^{-i\theta_{\mathbf{x},\nu}} \; . \tag{9.87}$$

With these definitions, the product of the link variables on the plaquette — the analogue of $\widehat{Z}_{\mathbf{x}_*}$ — is take to be:

$$\mathrm{e}^{i(\theta_{\mathbf{x},1}+\theta_{\mathbf{x}+\mathbf{e}_1,2}-\theta_{\mathbf{x}+\mathbf{e}_2,1}-\theta_{\mathbf{x},2})} = \mathrm{e}^{i(\Delta_1\theta_{\mathbf{x},2}-\Delta_2\theta_{\mathbf{x},1})} = \mathrm{e}^{i\hat{F}^{12}_{\mathbf{x}_*}} \tag{9.88}$$

where we introduced, as usual, the *discrete lattice derivatives*:

$$\Delta_1\theta_{\mathbf{x},2} = \theta_{\mathbf{x}+\mathbf{e}_1,2} - \theta_{\mathbf{x},2} \qquad \text{and} \qquad \Delta_2\theta_{\mathbf{x},1} = \theta_{\mathbf{x}+\mathbf{e}_2,1} - \theta_{\mathbf{x},1} \; , \tag{9.89}$$

and the *discrete curl*:

$$\hat{F}^{12}_{\mathbf{x}_*} = \Delta_1\theta_{\mathbf{x},2} - \Delta_2\theta_{\mathbf{x},1} \; . \tag{9.90}$$

The classical part of the Hamiltonian, in the $d = 2$ dimensional case, would be obtained by taking the Hermitian combination of the plaquette variables, involving the cosine:

$$H = J_B \sum_{\mathbf{x}_*} \left(1 - \cos \hat{F}^{12}_{\mathbf{x}_*}\right) \; . \tag{9.91}$$

We now have to look for the analogue of $\hat{\sigma}^x$: an operator that does not commute with the phase variable $\mathrm{e}^{i\theta_\ell}$. A very natural choice is to consider, on each link, the "momentum conjugate" to θ_ℓ, essentially an angular momentum:

$$\hat{L}_\ell = -i\frac{\partial}{\partial\theta_\ell} \qquad \Longrightarrow \qquad [\theta_\ell, \hat{L}_{\ell'}] = i\delta_{\ell,\ell'} \; . \tag{9.92}$$

This commutator resembles the canonical commutation rule of position and momentum in one dimension but is a bit disrespectful of the angular nature of the variable θ_ℓ which would better be involved in the $U(1)$ form $\mathrm{e}^{i\theta_\ell}$. A simple calculation, however, shows that:

Canonical commutation relation between phase and momentum.

$$[\hat{L}_\ell, \mathrm{e}^{\pm i\theta_\ell}] = \pm \mathrm{e}^{\pm i\theta_\ell} \; . \tag{9.93}$$

Quite amusingly, like the z-component of the ordinary angular momentum, $\hat{L}_\ell$ has *integer eigenvalues* $m \in \mathbb{Z}$, with eigenfunctions $\mathrm{e}^{im\theta}$, and is such that:

$$\mathrm{e}^{i\phi\hat{L}_\ell}\mathrm{e}^{i\theta_\ell}\mathrm{e}^{-i\phi\hat{L}_\ell} = \mathrm{e}^{i(\theta_\ell+\phi)} \; . \tag{9.94}$$

Consistently with Eq. (9.87), we will assume that:

$$\hat{L}_{\mathbf{x}+\mathbf{e}_\nu,-\nu} \equiv -\hat{L}_{\mathbf{x},\nu} \; . \tag{9.95}$$

Concerning the "local symmetry" $\widehat{G}_{\mathbf{x}}$, it should be an operator built from the "momenta" on the star at $\mathbf{x}$, the links touching the vertex $\mathbf{x}$. We take, again in $d = 2$ for simplicity, and recalling that $\hat{L}_{\mathbf{x},-\nu} \equiv -\hat{L}_{\mathbf{x}-\mathbf{e}_\nu,\nu}$:

$$\begin{cases} \widehat{G}_{\mathbf{x}} &= \mathrm{e}^{-i\Lambda_{\mathbf{x}}(\hat{L}_{\mathbf{x},1}+\hat{L}_{\mathbf{x},2}+\hat{L}_{\mathbf{x},-1}+\hat{L}_{\mathbf{x},-2})} = \mathrm{e}^{-i\Lambda_{\mathbf{x}}(\hat{L}_{\mathbf{x},1}+\hat{L}_{\mathbf{x},2}-\hat{L}_{\mathbf{x}-\mathbf{e}_1,1}-\hat{L}_{\mathbf{x}-\mathbf{e}_2,2})} \\ \widehat{G}_\Lambda &= \prod_{\mathbf{x}} \widehat{G}_{\mathbf{x}} = \mathrm{e}^{-i\sum_{\mathbf{x}}\Lambda_{\mathbf{x}}\sum_{\nu=1}^{2}\bar{\Delta}_\nu\hat{L}_{\mathbf{x},\nu}} = \mathrm{e}^{i\sum_{\mathbf{x}}\sum_{\nu=1}^{2}(\Delta_\nu\Lambda_{\mathbf{x}})\hat{L}_{\mathbf{x},\nu}} \; , \end{cases} \tag{9.96}$$

where $\Lambda_{\mathbf{x}}$ is an arbitrary real function defined at all the lattice points $\mathbf{x}$, and

$$\bar{\Delta}_\nu\hat{L}_{\mathbf{x},\nu} = \hat{L}_{\mathbf{x},\nu} - \hat{L}_{\mathbf{x}-\mathbf{e}_\nu,\nu} \; , \tag{9.97}$$

denotes the *backward finite difference.* The last equality expresses the discrete analogue of integration by parts:

$$\begin{aligned} \sum_{\mathbf{x}}\sum_{\nu}\Lambda_{\mathbf{x}}(\bar{\Delta}_\nu\hat{L}_{\mathbf{x},\nu}) &= \sum_{\mathbf{x}}\sum_{\nu}\Lambda_{\mathbf{x}}(\hat{L}_{\mathbf{x},\nu} - \hat{L}_{\mathbf{x}-\mathbf{e}_\nu,\nu}) = \sum_{\mathbf{x}}\sum_{\nu}\Lambda_{\mathbf{x}}\hat{L}_{\mathbf{x},\nu} - \sum_{\mathbf{x}}\sum_{\nu}\Lambda_{\mathbf{x}+\mathbf{e}_\nu}\hat{L}_{\mathbf{x},\nu} \\ &= \sum_{\mathbf{x}}\sum_{\nu}(\Lambda_{\mathbf{x}} - \Lambda_{\mathbf{x}+\mathbf{e}_\nu})\hat{L}_{\mathbf{x},\nu} = -\sum_{\mathbf{x}}\sum_{\nu}(\Delta_\nu\Lambda_{\mathbf{x}})\hat{L}_{\mathbf{x},\nu} \; . \end{aligned} \tag{9.98}$$

Gauge symmetry. Consider now a link variable, $\mathrm{e}^{i\theta_{\mathbf{x},\nu}}$ with $\nu = 1, 2$, and calculate how it is transformed by the unitary operator $\widehat{G}_\Lambda$. We get, using Eq. (9.96) and (9.94):

$$\widehat{G}_\Lambda\mathrm{e}^{i\theta_{\mathbf{x},\nu}}\widehat{G}_\Lambda^{-1} = \mathrm{e}^{i(\Delta_\nu\Lambda_{\mathbf{x}})\hat{L}_{\mathbf{x},\nu}}\mathrm{e}^{i\theta_{\mathbf{x},\nu}}\mathrm{e}^{-i(\Delta_\nu\Lambda_{\mathbf{x}})\hat{L}_{\mathbf{x},\nu}} = \mathrm{e}^{i(\theta_{\mathbf{x},\nu}+\Delta_\nu\Lambda_{\mathbf{x}})} \; . \tag{9.99}$$

We see here the analogue of gauge symmetry in electromagnetism. If we identify $\theta_{\mathbf{x},\nu} \longleftrightarrow A_\nu(\mathbf{x})$, where A_ν is the vector potential — more details on this identification later on, in Secs. 9.8.2 and 9.8.3 — the transformation induced by $\widehat{G}_\Lambda$ is the discrete analogue of the usual gauge transformation:

$$A_\nu(\mathbf{x}) \to A_\nu(\mathbf{x}) + \partial_\nu\Lambda \; . \tag{9.100}$$

As on the continuum, you can immediately verify that the (discrete) curl is left unchanged by the gauge transformation:

$$\widehat{G}_{\Lambda} \mathrm{e}^{i\hat{F}^{12}_{\mathbf{x}_*}} \widehat{G}_{\Lambda}^{-1} = \mathrm{e}^{i\hat{F}^{12}_{\mathbf{x}_*}} \; . \tag{9.101}$$

We now introduce the squared momentum term in the Hamiltonian, to get a quantum model:

$$\widehat{H} = \frac{J_E}{2} \sum_{\mathbf{x}} \sum_{\nu=1}^{2} \hat{L}^2_{\mathbf{x},\nu} + J_B \sum_{\mathbf{x}_*} \Big(1 - \cos \hat{F}^{12}_{\mathbf{x}_*} \Big) \; . \tag{9.102}$$

> **$U(1)$ lattice gauge theory.** The generalisation to a higher-dimensional case is quite clear. For a hypercubic lattice in d dimensions, we have plaquettes $\mathbf{x}_*^{\nu\nu'}$ in the planes identified by $\mathbf{e}_\nu$ and $\mathbf{e}_{\nu'}$, where it is enough to consider $\nu' > \nu$. We write, taking $J_E = Jg^2$ and $J_B = J/g^2$:
>
> $$\widehat{H} = \frac{Jg^2}{2} \sum_{\mathbf{x}} \sum_{\nu=1}^{d} \hat{L}^2_{\mathbf{x},\nu} + \frac{J}{g^2} \sum_{\nu=1}^{d-1} \sum_{\nu'>\nu}^{d} \sum_{\mathbf{x}_*^{\nu\nu'}} \Big(1 - \cos \hat{F}^{\nu\nu'}_{\mathbf{x}_*} \Big) \; . \tag{9.103}$$
>
> where g^2 is a dimensionless coupling constant. This form of the couplings will be clarified later on. Here $\hat{F}^{\nu\nu'}_{\mathbf{x}_*}$ — an antisymmetric tensor — denotes the discrete curl on the plaquette $\mathbf{x}_*^{\nu\nu'}$:
>
> $$\hat{F}^{\nu\nu'}_{\mathbf{x}_*} = \Delta_\nu \theta_{\mathbf{x},\nu'} - \Delta_{\nu'} \theta_{\mathbf{x},\nu} \; . \tag{9.104}$$
>
> The gauge symmetry is implemented by
>
> $$\left\{ \begin{array}{rcl} \widehat{G}_{\mathbf{x}} & = & \mathrm{e}^{-i\Lambda_{\mathbf{x}} \sum_{\nu=1}^{d} (\hat{L}_{\mathbf{x},\nu} - \hat{L}_{\mathbf{x}-\mathbf{e}_\nu,\nu})} = \mathrm{e}^{-i\Lambda_{\mathbf{x}} \sum_{\nu=1}^{d} \bar{\Delta}_\nu \hat{L}_{\mathbf{x},\nu}} \\ \widehat{G}_{\Lambda} & = & \prod_{\mathbf{x}} \widehat{G}_{\mathbf{x}} = \mathrm{e}^{-i \sum_{\mathbf{x}} \Lambda_{\mathbf{x}} \sum_{\nu=1}^{d} \bar{\Delta}_\nu \hat{L}_{\mathbf{x},\nu}} = \mathrm{e}^{i \sum_{\mathbf{x}} \sum_{\nu=1}^{d} (\Delta_\nu \Lambda_{\mathbf{x}}) \hat{L}_{\mathbf{x},\nu}} \end{array} \right. \tag{9.105}$$
>
> and reads:
>
> $$\mathrm{e}^{i\theta_{\mathbf{x},\nu}} \to \widehat{G}_{\Lambda} \mathrm{e}^{i\theta_{\mathbf{x},\nu}} \widehat{G}_{\Lambda}^{-1} = \mathrm{e}^{i(\theta_{\mathbf{x},\nu} + \Delta_\nu \Lambda_{\mathbf{x}})} \; . \tag{9.106}$$

9.8.1. Path-integral for $U(1)$ LGT

First of all, notice that we wrote our model as a quantum model in d-dimension. Once again, we can write an imaginary time path-integral, to map this quantum model into a classical $U(1)$ LGT in $d+1$ dimensions: as usual, with very anisotropic couplings. I will be very brief, referring to Chap. 6 for most details, concentrating on the essential ingredients, which help understand the curious choice of the couplings: $J_E = Jg^2$ as opposed to $J_B = J/g^2$.

The idea is to use a configuration basis for the Hilbert space, expressed in terms of the θ-variables for which the plaquette terms are "diagonal" (we keep calling them $\widehat{Z}$), while the $\hat{L}^2$ terms induce off-diagonal couplings between the various "Trotter replicas", and we denote them as $\widehat{X}$. Schematically, $\widehat{H} = \widehat{X} + \widehat{Z}$, and we use N_t Trotter replicas, so that $\Delta\tau = \beta/N_t$, and $\epsilon = \Delta\tau/\hbar$. The usual lattice points $\mathbf{x} = \sum_{\nu=1}^{d} n_\nu \mathbf{e}_\nu$ are now extended, with an extra vector $\mathbf{e}_t \equiv \mathbf{e}_0$ which we associate to the direction index "0". The lattice points in the Trotter replica $n_t = 1, \cdots, N_t$ are associated to $\mathbf{x} + n_t \mathbf{e}_t$, and have link variables $\mathrm{e}^{i\theta_{\mathbf{x}+n_t\mathbf{e}_t,\nu}}$ with $\nu = 1, \cdots, d$. We collectively denote by $\underline{\theta}_{n_t}$ all link variables in the n_tth-Trotter slice. Then the quantum partition function reads:

$$\begin{aligned} Z_{\mathrm{Q}} = \lim_{N_t \to \infty} \int \cdots \int \mathrm{d}\underline{\theta}_1 \cdots \mathrm{d}\underline{\theta}_{N_t} \Big(& \langle \underline{\theta}_1 | \mathrm{e}^{-\frac{\epsilon}{2}\widehat{Z}} \mathrm{e}^{-\epsilon\widehat{X}} \mathrm{e}^{-\frac{\epsilon}{2}\widehat{Z}} | \underline{\theta}_{N_t} \rangle \cdots \langle \underline{\theta}_{n_t+1} | \mathrm{e}^{-\frac{\epsilon}{2}\widehat{Z}} \mathrm{e}^{-\epsilon\widehat{X}} \mathrm{e}^{-\frac{\epsilon}{2}\widehat{Z}} | \underline{\theta}_{n_t} \rangle \cdots \\ & \cdots \langle \underline{\theta}_2 | \mathrm{e}^{-\frac{\epsilon}{2}\widehat{Z}} \mathrm{e}^{-\epsilon\widehat{X}} \mathrm{e}^{-\frac{\epsilon}{2}\widehat{Z}} | \underline{\theta}_1 \rangle \Big) \; . \end{aligned} \tag{9.107}$$

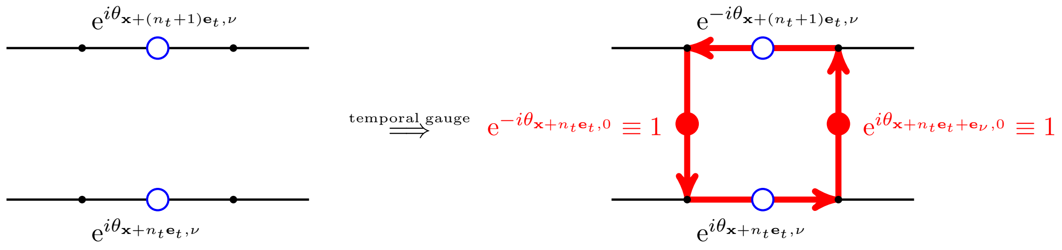

Figure 9.20.: Left: A single link in the direction $\mathbf{e}_\nu$ at site $\mathbf{x}$ in the two neighboring Trotter replicas at n_t and n_t+1. Right: The plaquette $F^{\nu 0}$ after having inserted link variables in the "time direction" complying with the temperal gauge prescription.

The plaquette terms in the ordinary "spatial directions", included in $\widehat{Z}$, contribute diagonal factors originating from:

$$\mathrm{e}^{-\frac{\epsilon J}{g^2}(1-\cos(F^{\nu\nu'}))}|\underline{\theta}_{n_t}\rangle \equiv \mathrm{e}^{-\frac{K}{g_s^2}(1-\cos(F^{\nu\nu'}))}|\underline{\theta}_{n_t}\rangle \qquad \text{where} \qquad \frac{K}{g_s^2} = \frac{\epsilon J}{g^2}\,. \tag{9.108}$$

Let us now concentrate on the kinetic term propagator $\langle\underline{\theta}_{n_t+1}|\mathrm{e}^{-\epsilon\widehat{X}}|\underline{\theta}_{n_t}\rangle$ which involves independent links in the two Trotter replicas. The basic ingredient we need to evaluated, for each link, is $\langle\theta'_\ell|\mathrm{e}^{-\frac{\epsilon J g^2}{2}\hat{L}^2_\ell}|\theta_\ell\rangle$. Here θ_ℓ is a shorthand for the link variable at ℓ in the Trotter slice n_t, $\theta_{\mathbf{x}+n_t\mathbf{e}_t,\nu}\to\theta_\ell$, and similary, for the neighboring Trotter replica link, $\theta_{\mathbf{x}+(n_t+1)\mathbf{e}_t,\nu}\to\theta'_\ell$. Let us define a shorthand for the dimensionall coupling $b=\epsilon J g^2$, which is supposed to be small. To calculate the propagator, let us insert the eigenstates $|n_\ell\rangle$ of $\hat{L}_\ell$, with $\langle\theta|n_\ell\rangle=\frac{1}{\sqrt{2\pi}}\mathrm{e}^{in_\ell\theta}$, obtaining:

$$\begin{aligned}\langle\theta'_\ell|\mathrm{e}^{-\frac{b}{2}\hat{L}^2_\ell}|\theta_\ell\rangle = \sum_{n_\ell\in\mathbb{Z}}\langle\theta'_\ell|\mathrm{e}^{-\frac{b}{2}\hat{L}^2_\ell}|n_\ell\rangle\langle n_\ell|\theta_\ell\rangle &= \frac{1}{2\pi}\sum_{n_\ell\in\mathbb{Z}}\mathrm{e}^{-\frac{b}{2}n_\ell^2}\mathrm{e}^{in_\ell(\theta'_\ell-\theta_\ell)} \\ &\approx \frac{1}{\sqrt{2\pi b}}\mathrm{e}^{-\frac{1}{b}(1-\cos(\theta'_\ell-\theta_\ell))}\,,\end{aligned} \tag{9.109}$$

where the last step follows from the discussion on the Villain's periodic gaussian approximation. [9] To form ordinary plaquette terms involving the Trotter-replicas, we need, as in the Ising LGT case, to introduce extra link variables on the links going into the imaginary time dimension, for which we assume the *temporal gauge*, as indicated in the right part of Fig. 9.20. Denoting by $\nu=0$ the links in the imaginary-time (Trotter) direction, we set $\mathrm{e}^{-i\theta_{\mathbf{x}+n_t\mathbf{e}_t,0}}\equiv 1$, where $\mathbf{e}_t\equiv\mathbf{e}_0$ is the lattice vector in the time-dimension, and similarly $\mathrm{e}^{i\theta_{\mathbf{x}+n_t\mathbf{e}_t+\mathbf{e}_\nu,0}}\equiv 1$. Then, the imaginary-time propagator generates a coupling of the form:

$$\langle\theta_{\mathbf{x}+(n_t+1)\mathbf{e}_t,\nu}|\mathrm{e}^{-\frac{\epsilon J g^2}{2}\hat{L}^2_{\mathbf{x},\nu}}|\theta_{\mathbf{x}+n_t\mathbf{e}_t,\nu}\rangle \to \mathrm{e}^{-\frac{1}{\epsilon J g^2}(1-\cos(F^{\nu0}))}\Big|_{\mathbf{x}_*^{\nu0}} \equiv \mathrm{e}^{-\frac{K}{g_\tau^2}(1-\cos(F^{\nu0}))}\Big|_{\mathbf{x}_*^{\nu0}}\,, \tag{9.111}$$

where we introduced the classical coupling $\frac{K}{g_\tau^2}=\frac{1}{\epsilon J g^2}$ in the imaginary-time direction. To summarise, we have:

$$\left\{\begin{aligned} Z_{\mathrm{Q}} &= \lim_{N_t\to\infty}\int\cdots\int \mathrm{d}\underline{\theta}_1\cdots\mathrm{d}\underline{\theta}_{N_t}\;\mathrm{e}^{-S[\underline{\theta}_1\cdots\underline{\theta}_{N_t}]} \\ S &= \sum_{\nu=0}^{d-1}\sum_{\nu'>\nu}^{d}\frac{K}{g_\nu^2}\sum_{\mathbf{x}_*^{\nu\nu'}}\left(1-\cos\hat{F}^{\nu\nu'}_{\mathbf{x}_*}\right)\,. \end{aligned}\right. \tag{9.112}$$

---

[9] You should compare this calculation with the analogue one you would carry out in the case of variables on the real line, where the result follows from a simple gaussian integral. Indeed, if $\hat{p}=-i\partial_x$ denote the dimensionless momentum operator, then:

$$\langle x'|\mathrm{e}^{-\frac{b}{2}\hat{p}^2}|x\rangle = \int_{-\infty}^{+\infty}\frac{\mathrm{d}k}{2\pi}\mathrm{e}^{-\frac{b}{2}k^2}\mathrm{e}^{ik(x'-x)} = \frac{1}{\sqrt{2\pi b}}\mathrm{e}^{-\frac{1}{2b}(x'-x)^2}\,. \tag{9.110}$$

where the couplings are highly anisotropic, with $g_0 = g_\tau$ and $g_{\nu=1\cdots d} = g_s$ and: [10]

$$\left\{\begin{array}{rcl} \dfrac{1}{\epsilon J g^2} & = & \dfrac{K}{g_\tau^2} \\ \\ \dfrac{\epsilon J}{g^2} & = & \dfrac{K}{g_s^2} \end{array}\right. \qquad \Longrightarrow \qquad \left\{\begin{array}{rcl} \dfrac{1}{g^2} & = & \dfrac{K}{g_\tau g_s} \\ \\ \epsilon J & = & \dfrac{g_\tau}{g_s} \end{array}\right. . \tag{9.113}$$

9.8.2. Connection with electromagnetism

Let us pursue explicitly the analogy between this $U(1)$ lattice gauge theory and electromagnetism. At cost of being dismissed as "inelegant", I will here present a description of how to discretise the Hamiltonian of a free electromagnetic field in three-dimension in SI units, with all ε_0 and $\hbar$ explicit.

We start from the quantum Hamiltonian of the electromagnetic fields alone — in absence of charges — in a volume V of the three-dimensional space, with periodic boundary conditions, for simplicity. The Hamiltonian is:

$$\widehat{H}_{\mathrm{em}} = \frac{\varepsilon_0}{2}\int_V \mathrm{d}\mathbf{x}\Big(\hat{\mathbf{E}}^2(\mathbf{x}) + c^2\hat{\mathbf{B}}^2(\mathbf{x})\Big) = \sum_{\mathbf{k},s}\hbar\omega_{\mathbf{k}}\Big(\hat{a}^\dagger_{\mathbf{k},s}\hat{a}_{\mathbf{k},s} + \frac{1}{2}\Big) , \tag{9.114}$$

where the (transverse) electric and magnetic field operators read:

$$\left\{\begin{array}{l} \hat{\mathbf{E}}(\mathbf{x}) = i\displaystyle\sum_{\mathbf{k},s}\sqrt{\frac{\hbar\omega_{\mathbf{k}}}{2\varepsilon_0 V}}\Big(\boldsymbol{\epsilon}_{\mathbf{k},s}\mathrm{e}^{i\mathbf{k}\cdot\mathbf{x}}\hat{a}_{\mathbf{k},s} - \boldsymbol{\epsilon}^*_{\mathbf{k},s}\mathrm{e}^{-i\mathbf{k}\cdot\mathbf{x}}\hat{a}^\dagger_{\mathbf{k},s}\Big) \\ \\ \hat{\mathbf{B}}(\mathbf{x}) = \boldsymbol{\nabla}\times\hat{\mathbf{A}} = i\displaystyle\sum_{\mathbf{k},s}\sqrt{\frac{\hbar}{2\varepsilon_0\omega_{\mathbf{k}}V}}\Big(\mathbf{k}\times\boldsymbol{\epsilon}_{\mathbf{k},s}\mathrm{e}^{i\mathbf{k}\cdot\mathbf{x}}\hat{a}_{\mathbf{k},s} - \mathbf{k}\times\boldsymbol{\epsilon}^*_{\mathbf{k},s}\mathrm{e}^{-i\mathbf{k}\cdot\mathbf{x}}\hat{a}^\dagger_{\mathbf{k},s}\Big) \end{array}\right. . \tag{9.115}$$

Here the $\boldsymbol{\epsilon}_{\mathbf{k},s}$ denote the two transverse polarisation vectors of the quantum radiation field. With the same ingredients, you write the transverse vector potential operator as: [11]

$$\hat{\mathbf{A}}(\mathbf{x}) = \sum_{\mathbf{k},s}\sqrt{\frac{\hbar}{2\varepsilon_0\omega_{\mathbf{k}}V}}\Big(\boldsymbol{\epsilon}_{\mathbf{k},s}\mathrm{e}^{i\mathbf{k}\cdot\mathbf{x}}\hat{a}_{\mathbf{k},s} + \boldsymbol{\epsilon}^*_{\mathbf{k},s}\mathrm{e}^{-i\mathbf{k}\cdot\mathbf{x}}\hat{a}^\dagger_{\mathbf{k},s}\Big) . \tag{9.118}$$

The commutation properties of the fields can be written as:

$$\Big[\hat{E}_\nu(\mathbf{x}), \hat{A}_{\nu'}(\mathbf{x}')\Big]_{V\to\infty} = i\frac{\hbar}{\varepsilon_0}\delta_{\nu\nu'}\delta(\mathbf{x}-\mathbf{x}') , \tag{9.119}$$

as you can easily verify from the canonical commutations $[\hat{a}_{\mathbf{k},s}, \hat{a}^\dagger_{\mathbf{k}',s'}] = \delta_{\mathbf{k},\mathbf{k}'}\delta_{s,s'}$.

---

[10] The dimensionless common factor K might be absorbed in g_τ and g_s, but we keep it there so that you can rescale both couplings by a common factor, keeping their ratio fixed.

[11] Observe that the (free) Heisenberg evolution operator $\hat{\mathbf{A}}_{\mathrm{H}}(\mathbf{x},t)$ is given by:

$$\hat{\mathbf{A}}_{\mathrm{H}}(\mathbf{x},t) = \sum_{\mathbf{k},s}\sqrt{\frac{\hbar}{2\varepsilon_0\omega_{\mathbf{k}}V}}\Big(\boldsymbol{\epsilon}_{\mathbf{k},s}\mathrm{e}^{i\mathbf{k}\cdot\mathbf{x}-i\omega_{\mathbf{k}}t}\hat{a}_{\mathbf{k},s} + \boldsymbol{\epsilon}^*_{\mathbf{k},s}\mathrm{e}^{-i\mathbf{k}\cdot\mathbf{x}+i\omega_{\mathbf{k}}t}\hat{a}^\dagger_{\mathbf{k},s}\Big) \tag{9.116}$$

so that the expression for $\hat{\mathbf{E}}$ and $\hat{\mathbf{B}}$ follows from:

$$\hat{\mathbf{E}} = -\frac{\partial\hat{\mathbf{A}}}{\partial t} \qquad \text{and} \qquad \hat{\mathbf{B}} = \boldsymbol{\nabla}\times\hat{\mathbf{A}} . \tag{9.117}$$

Now take the $U(1)$ lattice gauge theory, in $d = 3$, which we rewrite here:

$$\begin{aligned}\widehat{H} &= \frac{Jg^2}{2}\sum_{\mathbf{x}}\sum_{\nu=1}^{3}\hat{L}^2_{\mathbf{x},\nu} + \frac{J}{g^2}\sum_{\nu<\nu'}\sum_{\mathbf{x}_*^{\nu\nu'}}\left(1-\cos\hat{F}^{\nu\nu'}_{\mathbf{x}_*}\right) \\ &\approx \frac{Jg^2}{2}\sum_{\mathbf{x}}\sum_{\nu=1}^{3}\hat{L}^2_{\mathbf{x},\nu} + \frac{J}{2g^2}\sum_{\nu<\nu'}\sum_{\mathbf{x}_*^{\nu\nu'}}\left(\hat{F}^{\nu\nu'}_{\mathbf{x}_*}\right)^2 .\end{aligned} \tag{9.120}$$

where in the second equation, we expanded the cosine up to the second order. Now consider the following identification of variables:

$$\begin{cases} e\hat{L}_{\mathbf{x},\nu} &= -\varepsilon_0 a^2 \hat{E}_{\mathbf{x},\nu} \\ \theta_{\mathbf{x},\nu} &= \dfrac{ae}{\hbar}\hat{A}_{\mathbf{x},\nu} \end{cases} \qquad \Longrightarrow \qquad \left[\hat{E}_{\mathbf{x},\nu}, \hat{A}_{\mathbf{x}',\nu'}\right] = i\frac{\hbar}{\varepsilon_0}\delta_{\nu\nu'}\frac{1}{a^3}\delta_{\mathbf{x},\mathbf{x}'} \ , \tag{9.121}$$

which shows that Eq. (9.93) gives the correct discretisation of the canonical commutation relationship of $\hat{E}$ and $\hat{A}$ in Eq. (9.119).

The first equation in Eq. (9.121) suggests, recalling that $\hat{L}_{\mathbf{x},\nu}$ has integer eigenvalues $0, \pm 1, \pm 2, \cdots$, that the discrete *flux of the electric field* across a square of area a^2 is an integer multiple of e/ε_0, consistently with the Poisson's equation on the continuum $\frac{1}{\varepsilon_0}\hat{\rho} = \nabla\cdot\hat{\mathbf{E}}$ and Gauss' law. The second equation, which will be better understood in Sec. 9.8.3, suggests that:

$$\hat{F}^{\nu\nu'} = \Delta_\nu\theta_{\mathbf{x},\nu'} - \Delta_{\nu'}\theta_{\mathbf{x},\nu} = \frac{ae}{\hbar}\left(\Delta_\nu\hat{A}_{\mathbf{x},\nu'} - \Delta_{\nu'}\hat{A}_{\mathbf{x},\nu}\right) \longrightarrow \frac{a^2e}{\hbar}\left(\partial_\nu\hat{A}_{\nu'} - \partial_{\nu'}\hat{A}_\nu\right) \tag{9.122}$$

Hence the natural identification for the anti-symmetric field tensor is: [12]

$$\hat{F}^{\nu\nu'}_{\mathbf{x}_*} = \Delta_\nu\theta_{\mathbf{x},\nu'} - \Delta_{\nu'}\theta_{\mathbf{x},\nu} \longrightarrow \frac{a^2e}{\hbar}\hat{B}_\mu(\mathbf{x}_*^{\nu\nu'}) \qquad \mu,\nu,\nu' \text{ ciclic} . \tag{9.124}$$

Notice that, while the electric field and the vector potential stay on the *links*, the magnetic field should be imagined associated, and orthogonal, to the centre of the plaquettes: $\hat{B}_3$ in the centre of $\mathbf{x}_*^{12}$, etc. Notably, in $d = 3$ the anti-symmetric tensor $\hat{F}^{\nu\nu'}_{\mathbf{x}_*}$ has exactly *three components*, which can be identified with the three components of the magnetic field. Also, if you recall that $\phi_0 = h/e$ is the magnetic flux quantum, you realise that $\hat{F}^{\nu\nu'}_{\mathbf{x}_*} = 2\pi\phi_B/\phi_0$, where $\phi_B = a^2\hat{B}_\mu$ is the magnetic flux through the plaquette.

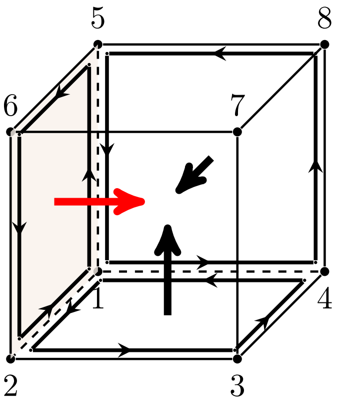

Figure 9.21: The basic cube of the 3d lattice with the three plaquettes centers at $\mathbf{x}_*^{12}$ (the xy plane), at $\mathbf{x}_*^{13}$ (the xz plane), and at $\mathbf{x}_*^{23}$ (the yz plane), with big arrows denoting the magnetic fields. Notice the closed loop arrows around the plaquettes, associated to the link variables $\mathrm{e}^{i\theta_\ell} = \mathrm{e}^{i\frac{ea}{\hbar}\hat{A}_\ell}$, which define the antisymmetric tensor $\hat{F}^{\nu,\nu'}$ with the convention of Stokes' theorem. This forces $\hat{F}^{31} = \frac{a^2e}{\hbar}\hat{B}_2 = -\hat{F}^{13}$, as signalled by the red arrow.

---

[12] Explicitly, this means:

$$\hat{F}^{12} = \frac{a^2e}{\hbar}\hat{B}_3 \qquad\qquad \hat{F}^{23} = \frac{a^2e}{\hbar}\hat{B}_1 \qquad\qquad \hat{F}^{31} = \frac{a^2e}{\hbar}\hat{B}_2 = -\hat{F}^{13} . \tag{9.123}$$

Now take the electromagnetic field Hamiltonian, and discretise it into cubes of volume a^3, with $\hat{E}_{\mathbf{x},\nu}$ on the links, and $\hat{B}_\mu$ orthogonal to the plaquette centers:

$$\begin{aligned}
\widehat{H}_{\rm em} &\to \frac{\varepsilon_0 a^3}{2}\sum_{\mathbf{x}}\sum_{\nu=1}^{3}\hat{E}^2_{\mathbf{x},\nu} + \frac{\varepsilon_0 c^2 a^3}{2}\sum_{\nu<\nu'}\sum_{\mathbf{x}_*^{\nu\nu'}}\hat{B}^2_\mu(\mathbf{x}_*^{\nu\nu'}) \\
&= \frac{\varepsilon_0 a^3}{2}\Big(\frac{e}{\varepsilon_0 a^2}\Big)^2\sum_{\mathbf{x}}\sum_{\nu=1}^{3}\hat{L}^2_{\mathbf{x},\nu} + \frac{\varepsilon_0 c^2 a^3}{2}\Big(\frac{\hbar}{a^2 e}\Big)^2\sum_{\nu<\nu'}\sum_{\mathbf{x}_*^{\nu\nu'}}(\hat{F}^{\nu\nu'}_{\mathbf{x}_*})^2 \\
&= \frac{e^2}{2\varepsilon_0 a}\sum_{\mathbf{x}}\sum_{\nu=1}^{3}\hat{L}^2_{\mathbf{x},\nu} + \frac{\varepsilon_0 c^2\hbar^2}{2e^2 a}\sum_{\nu<\nu'}\sum_{\mathbf{x}_*^{\nu\nu'}}(\hat{F}^{\nu\nu'}_{\mathbf{x}_*})^2 \, .
\end{aligned} \tag{9.125}$$

The couplings in electromagnetism. This shows that the choice for the coupling g^2 and unit J to account for the electromagnetic Hamiltonian is:

$$g^2 = \frac{e^2}{\varepsilon_0 \hbar c} = 4\pi\alpha \qquad \text{with} \qquad \alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} \approx \frac{1}{137} \, , \tag{9.126}$$

where α is the fine-structure constant, and:

$$J = \frac{\hbar c}{a} \qquad \Longrightarrow \qquad J g^2 = \frac{e^2}{\varepsilon_0 a} \qquad \text{and} \qquad \frac{J}{g^2} = \frac{\varepsilon_0 c^2 \hbar^2}{e^2 a} \tag{9.127}$$

9.8.3. Interaction of em fields with charges

It is interesting to pursue the example of electromagnetism, to understand how the "gauge field" — out of methaphore, the electromagnetic fields with their gauge freedom — interacts with the charge of electrons. We start again from the continuum description, writing the full Hamiltonian in the *transverse gauge* we have used so far, as:

$$\left\{\begin{array}{rcl}
\widehat{H} &=& \widehat{H}_{\rm matter+em} + \widehat{H}_{\rm em} \\
\widehat{H}_{\rm matter+em} &=& \displaystyle\frac{1}{2m}\sum_\sigma\int\!\mathrm{d}\mathbf{x}\,\Big((\hat{\mathbf{p}}+e\hat{\mathbf{A}})\widehat{\Psi}_\sigma(\mathbf{x})\Big)^\dagger\cdot\Big((\hat{\mathbf{p}}+e\hat{\mathbf{A}})\widehat{\Psi}_\sigma(\mathbf{x})\Big) \\
&=& \displaystyle\frac{1}{2m}\sum_\sigma\int\!\mathrm{d}\mathbf{x}\,\Big(\hat{\mathbf{p}}\widehat{\Psi}_\sigma(\mathbf{x})\Big)^\dagger\cdot\Big(\hat{\mathbf{p}}\widehat{\Psi}_\sigma(\mathbf{x})\Big) - \int\!\mathrm{d}\mathbf{x}\,\hat{\mathbf{A}}(x)\cdot\hat{\mathbf{J}}(\mathbf{x})
\end{array}\right. . \tag{9.128}$$

Here the kinetic coupling involves the kinetic momentum inside the current operator $\hat{\mathbf{J}}$:

$$\begin{aligned}
\hat{\mathbf{J}}(\mathbf{x}) &= -\frac{e}{2m}\sum_\sigma\bigg(\widehat{\Psi}^\dagger_\sigma(\mathbf{x})\Big((\hat{\mathbf{p}}+e\hat{\mathbf{A}})\widehat{\Psi}_\sigma(\mathbf{x})\Big) + \Big((\hat{\mathbf{p}}+e\hat{\mathbf{A}})\widehat{\Psi}_\sigma(\mathbf{x})\Big)^\dagger\widehat{\Psi}_\sigma(\mathbf{x})\bigg) \\
&= \hat{\mathbf{J}}_0(\mathbf{x}) + \frac{e}{m}\hat{\mathbf{A}}(\mathbf{x})\,\hat{\rho}(\mathbf{x})
\end{aligned} \, , \tag{9.129}$$

where $\hat{\mathbf{J}}_0$ and $\hat{\rho}(\mathbf{x})$ are the electronic current and charge density operators:

$$\left\{\begin{array}{rcl}
\hat{\mathbf{J}}_0(\mathbf{x}) &=& \displaystyle -\frac{e}{2m}\sum_\sigma\bigg(\widehat{\Psi}^\dagger_\sigma(\mathbf{x})\Big(\hat{\mathbf{p}}\widehat{\Psi}_\sigma(\mathbf{x})\Big) + \Big(\hat{\mathbf{p}}\widehat{\Psi}_\sigma(\mathbf{x})\Big)^\dagger\widehat{\Psi}_\sigma(\mathbf{x})\bigg) \\
\hat{\rho}(\mathbf{x}) &=& \displaystyle -e\sum_\sigma\widehat{\Psi}^\dagger_\sigma(\mathbf{x})\widehat{\Psi}_\sigma(\mathbf{x})
\end{array}\right. . \tag{9.130}$$

The previous coupling term, written for simplicity in the non-relativistic approximation, involves the substitution of $\hat{\mathbf{p}} \to (\hat{\mathbf{p}} + e\hat{\mathbf{A}})$ in the kinetic momentum, and is known as *minimal coupling.* Its great virtue is that of respecting gauge invariance. Indeed, by transforming together the vector potential $\hat{\mathbf{A}}$ and the electron field operator $\widehat{\Psi}_\sigma$:

$$\text{Gauge transformation :} \qquad \begin{cases} \hat{\mathbf{A}} & \to \quad \hat{\mathbf{A}}(\mathbf{x}) + \boldsymbol{\nabla}\Lambda(\mathbf{x}) \\ \widehat{\Psi}_\sigma & \to \quad \widehat{\Phi}_\sigma(\mathbf{x}) = \mathrm{e}^{-i\frac{e}{\hbar}\Lambda(\mathbf{x})}\widehat{\Psi}_\sigma(\mathbf{x}) \end{cases} \tag{9.131}$$

you immediately verify, using $\hat{\mathbf{p}} = -i\hbar\boldsymbol{\nabla}$, that:

$$(\hat{\mathbf{p}} + e\hat{\mathbf{A}})\widehat{\Psi}_\sigma \to (\hat{\mathbf{p}} + e(\hat{\mathbf{A}} + \boldsymbol{\nabla}\Lambda))\, \mathrm{e}^{-i\frac{e}{\hbar}\Lambda}\widehat{\Psi}_\sigma = \mathrm{e}^{-i\frac{e}{\hbar}\Lambda}(\hat{\mathbf{p}} + e\hat{\mathbf{A}})\widehat{\Psi}_\sigma \ . \tag{9.132}$$

This immediately implies the gauge invariance of the kinetic coupling $\widehat{H}_{\mathrm{matter+em}}$, and of the current operator $\hat{\mathbf{J}}$. The gauge invariance of the charge density $\hat{\rho}(\mathbf{x})$ is obvious.

The gauge transformation can be implemented by a unitary operator

$$\widehat{U}_\Lambda = \mathrm{e}^{-\frac{i}{\hbar}\int \mathrm{d}\mathbf{x}\, \left(\Lambda(\mathbf{x})\hat{\rho}(\mathbf{x}) + \varepsilon_0 \boldsymbol{\nabla}\Lambda\cdot\hat{\mathbf{E}}\right)} = \mathrm{e}^{-\frac{i}{\hbar}\int \mathrm{d}\mathbf{x}\, \Lambda(\mathbf{x})\left(\hat{\rho}(\mathbf{x}) - \varepsilon_0 \boldsymbol{\nabla}\cdot\hat{\mathbf{E}}\right)} \ , \tag{9.133}$$

where the second form follows from the divergence's theorem (essentially, integration by parts), assuming the boundary term to vanish:

$$0 = \int \mathrm{d}\mathbf{x}\ \boldsymbol{\nabla}\cdot(\Lambda\mathbf{E}) = \int \mathrm{d}\mathbf{x}\ \boldsymbol{\nabla}\Lambda\cdot\mathbf{E} + \int \mathrm{d}\mathbf{x}\ \Lambda\boldsymbol{\nabla}\cdot\mathbf{E} \ .$$

It is simple to show, using the canonical commutation relationship Eq. (9.119), that indeed: [13]

$$\widehat{U}_\Lambda \hat{A}_\nu \widehat{U}_\Lambda^{-1} = \hat{A}_\nu + \partial_\nu \Lambda \ . \tag{9.134}$$

Moreover, one can easily argue that: [14]

$$\widehat{U}_\Lambda \widehat{\Psi}_\sigma(\mathbf{x}) \widehat{U}_\Lambda^{-1} = \mathrm{e}^{-i\frac{e}{\hbar}\Lambda(\mathbf{x})}\widehat{\Psi}_\sigma(\mathbf{x}) \ . \tag{9.135}$$

Let us now discretise the coupling term, assuming the usual tight-binding approximation. For simplicity, we assume a lattice describing a crystal, with a single electronic (Wannier) orbital at each lattice site. [15] We denote by $\hat{c}^\dagger_{\mathbf{x},\sigma}$ the operator that creates an electron with spin σ in the orbital localised at lattice site $\mathbf{x}$, and by $w_{\mathbf{x}}(\mathbf{y})$ the corresponding Wannier's orbitals. This amounts to approximating the field operator as:

$$\widehat{\Psi}_\sigma(\mathbf{y}) \to \sum_{\mathbf{x}} w_{\mathbf{x}}(\mathbf{y})\ \hat{c}_{\mathbf{x},\sigma} \ . \tag{9.136}$$

In this rather drastically restricted basis set, we would express the Hamiltonian

$$\widehat{H}_{\mathrm{matter+em}} \to \sum_\sigma \sum_{\mathbf{x}} \sum_{\nu=1}^{d} \left(h_{\mathbf{x},\nu} \mathrm{e}^{-i\frac{ea}{\hbar}\hat{A}_{\mathbf{x},\nu}} \hat{c}^\dagger_{\mathbf{x}+\mathbf{e}_\nu,\sigma}\hat{c}_{\mathbf{x},\sigma} + \mathrm{H.c.} \right) \ , \tag{9.137}$$

---

[13] The $\hat{\rho}$ term has no influence. As for the other term, consider the first form $\widehat{U}^\dagger = \mathrm{e}^{\frac{i}{\hbar}\int \mathrm{d}\mathbf{x}\ \varepsilon_0 \boldsymbol{\nabla}\Lambda\cdot\hat{\mathbf{E}}} = \mathrm{e}^{\hat{O}}$, and observe that the CCR Eq. (9.119) implies (by induction):

$$[\hat{A}_\nu(\mathbf{x}), \hat{O}^n] = n(\partial_\nu\Lambda)\hat{O}^{n-1} \qquad \Longrightarrow \qquad [\hat{A}_\nu(\mathbf{x}), f(\hat{O})] = (\partial_\nu\Lambda) f'(\hat{O}) \ ,$$

for any $f(\circ)$ that can be Taylor expanded. Applying this to $f(\hat{O}) = \mathrm{e}^{\hat{O}}$, you immediately deduce the result $\mathrm{e}^{-\hat{O}}\hat{A}_\nu\mathrm{e}^{\hat{O}} = \hat{A}_\nu + \partial_\nu\Lambda$.

[14] Avoid trying the commutator route. Rather, verify that the equality is satisfied on any Fock state where the state $|\mathbf{x},\sigma\rangle$ is occupied or not.

[15] The orbitals are assumed to be orthogonal, which makes the second quantisation formalism easier.

where $h_{\mathbf{x},\nu}$ represents the amplitude for the electron to hop, conserving its spin, from orbital $w_{\mathbf{x}}$ to some neighbour $w_{\mathbf{x}+\mathbf{e}_\nu}$ on the lattice, the so-called *hopping integral.* [16] The phase factor containing the vector potential is perfectly gauge-invariant. If you change the vector potential with the discrete analogue of the gauge transformation:

$$a\hat{A}_{\mathbf{x},\nu} \to a\hat{A}_{\mathbf{x},\nu} + \Delta_\nu \Lambda_{\mathbf{x}} \qquad \Longrightarrow \qquad \mathrm{e}^{-i\frac{ea}{\hbar}\hat{A}_{\mathbf{x},\nu}} \to \mathrm{e}^{-i\frac{ea}{\hbar}\hat{A}_{\mathbf{x},\nu}}\mathrm{e}^{-i\frac{e}{\hbar}(\Lambda_{\mathbf{x}+\mathbf{e}_\nu}-\Lambda_{\mathbf{x}})} \ ,$$

then the hopping Hamiltonian is gauge invariant provided you perform a gauge transformation on the electronic operator as well:

$$\hat{c}_{\mathbf{x},\sigma} \to \mathrm{e}^{-i\frac{e}{\hbar}\Lambda_{\mathbf{x}}}\hat{c}_{\mathbf{x},\sigma} \ ,$$

equivalent to reabsorbing the gauge phase factor in the Wannier orbital $w_{\mathbf{x}}$.

> **Peierls' substitution.** This way of introducing the vector potential in a tight-binding Hamiltonian by modifying the hopping amplitudes with a phase factor is known in the literature as *Peierls' substitution*:
>
> $$h_{\mathbf{x}',\mathbf{x}} \to h^{\mathbf{A}}_{\mathbf{x}',\mathbf{x}} \equiv h_{\mathbf{x}',\mathbf{x}}\,\mathrm{e}^{-i\frac{e}{\hbar}\int_{\mathbf{x}}^{\mathbf{x}'}\mathbf{A}\cdot\mathrm{d}\mathbf{l}} \ , \tag{9.139}$$
>
> where the line-integral is calculated on a *straight line* connecting $\mathbf{x}$ to $\mathbf{x}'$. [a]
>
> ---
>
> [a] For an elementary justification of the Peierls' substitution, see for instance Feynman's Lectures on Quantum Mechanics, Chapter 21.

Very often, the Peiers' substitution is used in a context where the magnetic fields are assumed to be *classical fields*. This is the case, for instance, in the Hofstadter model, or Haldane's model. Here, we are considering models in which the gauge field has its dynamics, and responds to the motion of the electrons: a much more difficult problem.

The Peierls' minimal coupling phase factors shed light on the identification $\theta_{\mathbf{x},\nu} = \frac{ae}{\hbar}\hat{A}_{\mathbf{x},\nu}$ discussed in Eq. (9.121). As a consequence, the gauge transformations for $\theta_{\mathbf{x},\nu}$ and that for $\hat{A}_{\mathbf{x},\nu}$ are related by a factor $\frac{e}{\hbar}$:

$$\Lambda^\theta_{\mathbf{x}} = \frac{e}{\hbar}\Lambda_{\mathbf{x}} \ . \tag{9.140}$$

Also in the lattice case, the gauge transformation can be implemented by a unitary operator, obtained by discretising the continuum $\widehat{U}_\Lambda$:

$$\begin{aligned}
\widehat{U}_\Lambda \to \mathrm{e}^{-\frac{i}{\hbar}\sum_{\mathbf{x}}\left(\Lambda_{\mathbf{x}}(-e)\hat{n}_{\mathbf{x}}+\varepsilon_0 a^2\sum_\nu(\Delta_\nu\Lambda_{\mathbf{x}})\hat{E}_{\mathbf{x},\nu}\right)} \quad &= \quad \mathrm{e}^{\frac{ie}{\hbar}\sum_{\mathbf{x}}\Lambda_{\mathbf{x}}\hat{n}_{\mathbf{x}}}\ \mathrm{e}^{-\frac{i\varepsilon_0}{\hbar}a^2\sum_{\mathbf{x}}\sum_\nu(\Delta_\nu\Lambda_{\mathbf{x}})\hat{E}_{\mathbf{x},\nu}} \\
&= \quad \mathrm{e}^{i\sum_{\mathbf{x}}\Lambda^\theta_{\mathbf{x}}\hat{n}_{\mathbf{x}}}\ \mathrm{e}^{-\frac{i\varepsilon_0}{e}a^2\sum_{\mathbf{x}}\sum_\nu(\Delta_\nu\Lambda^\theta_{\mathbf{x}})\hat{E}_{\mathbf{x},\nu}} \\
&= \quad \mathrm{e}^{i\sum_{\mathbf{x}}\Lambda^\theta_{\mathbf{x}}\hat{n}_{\mathbf{x}}}\ \mathrm{e}^{i\sum_{\mathbf{x}}\sum_\nu(\Delta_\nu\Lambda^\theta_{\mathbf{x}})\hat{L}_{\mathbf{x},\nu}} \\
&= \quad \mathrm{e}^{i\sum_{\mathbf{x}}\Lambda^\theta_{\mathbf{x}}\hat{n}_{\mathbf{x}}}\ \widehat{G}_{\Lambda^\theta} \ ,
\end{aligned} \tag{9.141}$$

where we used the identification of variables in Eq. (9.121). This shows the explicit connection between the gauge transformation unitary operator and the gauge symmetry $\widehat{G}_{\Lambda^\theta}$ discussed previously.

Notice that, in presence of charges, the extra term $\mathrm{e}^{i\sum_{\mathbf{x}}\Lambda^\theta_{\mathbf{x}}\hat{n}_{\mathbf{x}}}$ appears, responsible for enforcing the Gauss' law: the electric field flux through a closed surface has to match the charges inside the surface.

---

[16] For reference, when a one-body potential $v(\mathbf{y})$ is present:

$$h_{\mathbf{x},\nu} = \int \mathrm{d}\mathbf{y}\ w^*_{\mathbf{x}+\mathbf{e}_\nu}(\mathbf{y})\Big(\frac{\hat{\mathbf{p}}^2}{2m} + v(\mathbf{y})\Big)w_{\mathbf{x}}(\mathbf{y}) \ . \tag{9.138}$$

In the main text, we considered only kinetic energy, $v \equiv 0$, and the hopping integral is independent of the site $\mathbf{x}$ and link direction.

9.8.4. A few extra remarks

Elitzur's theorem and Wilson loops First of all, Elitzur's theorem can be generalised: gauge symmetry cannot be spontaneously broken. The Wilson loops also have a very obvious counterpart: for the $U(1)$ case, you define the Wilson loop operator as:

$$\widehat{W}_{\mathcal{C}} = \prod_{\ell \in \mathcal{C}} \mathrm{e}^{i\theta_\ell} = \mathrm{e}^{i\sum_{\mathcal{C}} \theta_\ell} . \tag{9.142}$$

As before, the generic situation is that two different phases are present: a phase where the area law applies and one in which the perimeter law holds. In turn, this is connected with the concept of *confinement*: charges are bound by a linear potential in the confined phase.

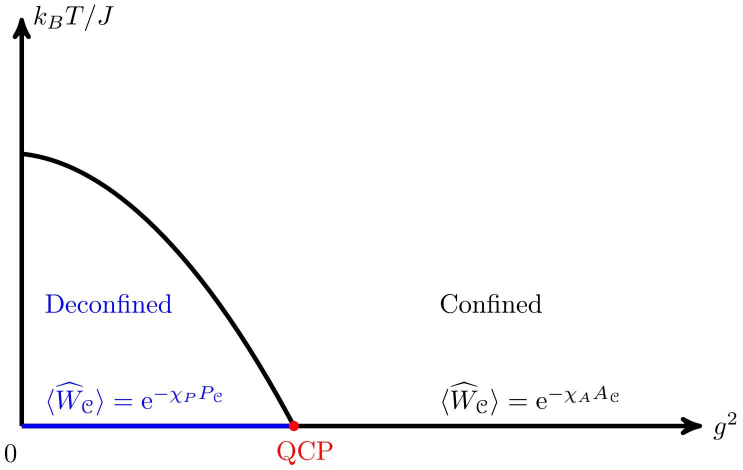

Figure 9.22: The generic phase diagram of $U(1)$ quantum LGT for $d > 2$. For $d = 2$ the deconfined phase is strictly only at $T = 0$.

Connection between area law and confinement This connection is described by Kogut [33][Sec. VIB, p. 693]. The basic idea is simple to understand in the strong coupling limit $g^2 \to \infty$. There, the ground state has $\hat{L}_\ell |n_\ell = 0\rangle = 0$ on all links. The subsector where the ground states live is that in which $\widehat{G}_\Lambda |\psi\rangle = |\psi\rangle$. The presence of two (static) extra charges of opposite sign forces a violation of the $\widehat{G}_\Lambda |\psi\rangle = |\psi\rangle$ constraint, as implied by Gauss' law. In the $g^2 \to \infty$, this requires a line where $\hat{L}_\ell |n_\ell = 1\rangle = |n_\ell = 1\rangle$ on all links between the two opposite charges, hence an extra energy:

$$V(\mathbf{x}_2, \mathbf{x}_1) = \frac{Jg^2}{2} ||\mathbf{x}_2 - \mathbf{x}_1||_{\text{Manh}} . \tag{9.143}$$

More generally, one can show a connection between the potential between the two charges and the area law, see Kogut [33][Sec. VIB, Eqs. 6.37-6.42, p. 693]. When the perimeter law holds, the potential between two opposite charges saturates to a finite value as $||\mathbf{x}_2 - \mathbf{x}_1|| \to \infty$. The approach to that limit is exponential if the propagator of the gauge field is gapped, while a Coulomb's law emerges for a gapless propagator, as appropriate for QED in $d = 3$.

The special $d = 2$ case. One can prove that the classical $U(1)$ LGT in $d = 2$ is always disordered (confining), as equivalent to one-dimensional XY models. See Kogut [33][Sec. VIB, p. 693].

From $U(1)$ to $\mathbb{Z}_n$. There are several special cases where the full $U(1)$ symmetry is made discrete, and the basic group is that of a "clock" with n states: the angles θ_ℓ on each link are restricted to the n independent multiples of $\frac{2\pi}{n}$ on the unit circle. The $\mathbb{Z}_2$ case is equivalent to the Ising case we described previously.

Part III.

Appendices

A. Problems and complements: Introduction

A.1. The Galton's board and the binomial distribution

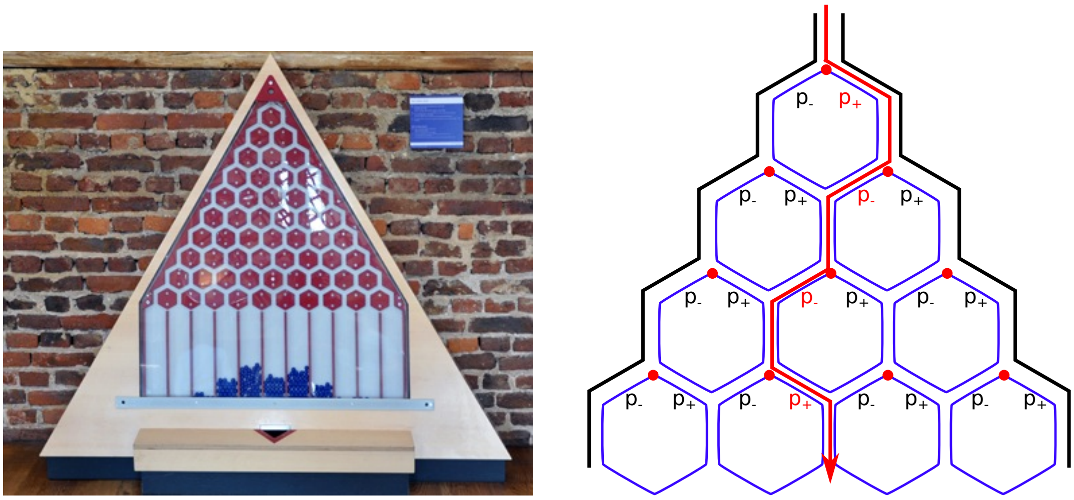

Figure A.1.: (Left) A Galton board at the *Mathematikum* exhibit in Giessen. (Right) A scheme of the game. At the apex of each hexagon, where the red dots are shown, the ball can go to the right (with probability p_+) or to the left (with p_-). The red path with an arrow (and the red letters $p_\pm$) indicate a possible path (and a choice of where to turn) for a ball entering the board from the top.

Problem A.1. Consider the Galton board in Fig. A.1. A ball inserted at the top has a probability $p_+ = 1/2$ of going to the right, at the top hexagon bifurcation, and $p_- = 1/2$ of going to the left. We assign a variable $\sigma_1 = +1$ to the event "going to the right", and $\sigma_1 = -1$ to "going to the left". The next level has two hexagons. Whatever was the path followed in the first level, there is again a probability p_+ of "going to the right" (here we say that $\sigma_2 = +1$), and p_- of "going to the left" ($\sigma_2 = -1$). And so and so forth at each of the "levels" below, until level N, with the corresponding $\sigma_N = \pm 1$. Below the last row of N hexagons, there are $N + 1$ final long tubes collecting the various balls that are inserted in the board from the top. Let us number the tubes with an integer $N_+ = 0, \cdots, N$, where $N_+ = 0$ denotes the one at the extreme left, and $N_+ = N$ that at the extreme right. A ball ends-up in the $N_+ = 0$ tube only if the path it follows is all made of left turns, i.e., $\sigma_i = -1$ for $i = 1 \cdots N$: this will happen with probability p_-^N. Similarly, the ball ends-up in the $N_+ = N$ tube by making only right turns, i.e., $\sigma_i = +1$ for $i = 1 \cdots N$, which happens with probability p_+^N.

Show that the ball ends-up in the generic N_+-tube with probability:

$$P(N_+, N) = \binom{N}{N_+} p_+^{N_+} \, p_-^{N-N_+} \, .$$

Indeed, you recognise that the board has exactly the structure of a *Pascal triangle*.[1] Correspondingly,

---

[1] To the Italian students this is better known as *Triangolo di Tartaglia*.

the Newton's binomial formula would tell us that this probability is correctly normalised :

$$1 = (p_+ + p_-)^N = \sum_{N_+=0}^{N} \binom{N}{N_+} p_+^{N_+} \, p_-^{N-N_+} \ .$$

A moment's reflection will convince you that you can think of the successive $\sigma_i = \pm$ at each of the levels $i = 1, \cdots, N$ of the board, as a *flip of a coin*. The "path" $(\sigma_1, \cdots, \sigma_N)$ can be seen as the outcome of an experiment consisting of a sequence of N coin-flips, and N_+ is the number of times you got Head ($\sigma_i = +1$). In a totally equivalent way, you can think of this problem has a *Drunkard's walk* in one dimension, $\sigma_i = +1/-1$ meaning a step to the right/left. There is no reason to restrict ourselves to $p_+ = p_- = 1/2$, as you can always think of having a "bias" in the game, making $p_+ \neq p_-$.

Let us formalise the problem in terms of probability distributions. Call $P_1(\sigma_i)$ the probability distribution of each single σ_i:

$$P_1(\sigma_i) = p_+ \delta_{\sigma_i,+1} + p_- \delta_{\sigma_i,-1} \ . \tag{A.1}$$

A full "configuration" (a "microstate") $(\sigma_1, \sigma_2, \cdots, \sigma_N)$ has a probability distribution

$$\mathbf{P}(\sigma_1, \cdots, \sigma_N) = P_1(\sigma_1) P_1(\sigma_2) \cdots P_1(\sigma_N) \ , \tag{A.2}$$

where this factorisation follows from the fact that the σ_i are *independent* and identically distributed (i.e., the same P_1 for all σ_i).

Since there is an extremely large number of microscopic configurations, 2^N, one is usually interested in the probability distribution of appropriate "macroscopic observables". In the present problem, macroscopic "observables" might be

$$\mathbb{N}_\pm = \frac{1}{2} \sum_{i=1}^{N} (1 \pm \sigma_i) \qquad \text{and} \qquad \mathbb{M} = \sum_{i=1}^{N} \sigma_i = \mathbb{N}_+ - \mathbb{N}_- \ . \tag{A.3}$$

It is simple to realise that the distributions for the observables are obtained from the full distributions of configurations by imposing a "constraint" in the form of a Kröneker (of Dirac, in the continuum case) "delta". [2] In the present case, show that you can write: [3]

$$\begin{aligned} P_{\mathbb{N}_+}(N_+, N) &= \sum_{\sigma_1, \cdots, \sigma_N} \mathbf{P}(\sigma_1, \cdots, \sigma_N) \, \delta_{N_+, \frac{1}{2}\sum_i (1+\sigma_i)} \\ &= \binom{N}{N_+} p_+^{N_+} \, p_-^{N-N_+} \ . \end{aligned} \tag{A.4}$$

The reason why we insist in writing the binomial distribution in an apparently more complicated way, in terms of a constrained sum, will be apparent in a short while, when we will discuss how to deal with such "delta-functions" by Fourier/Laplace transforms.

A.2. From the binomial distribution to the Gaussian

Problem A.2. Consider the binomial coefficient:

$$\binom{N}{N_+} = \frac{N!}{N_+!(N-N_+)!} = \mathrm{e}^{\log N! - \log N_+! - \log(N-N_+)!} \equiv \Omega(N_+, N) \ .$$

---

[2] In general, the probability distribution of an observable $\mathbb{A}(x_1, \cdots, x_N)$ will be given by

$$P_{\mathbb{A}}(A) = \int \mathrm{d}x_1 \cdots \mathrm{d}x_N \mathbf{P}(x_1, \cdots, x_N) \, \delta(\mathbb{A}(x_1, \cdots, x_N) - A) \ .$$

[3] We used here a slightly pedantic notation which distinguishes the "observable" $\mathbb{N}_+$ from the values N_+ it can attain, and indicates that the distribution depends also on N. Often, when no ambiguity arises, we will simplify the notation to $P(N_+, N)$.

Here we introduced the notation $\Omega(N_+, N)$ to refer to the "*number of available microstates*" with a given value of N_+. It is known that a good approximation for the factorial is given by the *Stirling formula*:

$$\log N! = N \log N - N + \log \sqrt{2\pi N} + O\left(\frac{1}{N}\right) . \tag{A.5}$$

By defining $N_+ = Nn_+$, where $n_+ \in [0, 1]$ is the "fraction" (or density) of $\sigma_i = +1$ spins, show that:

$$\log \Omega(N_+, N) \simeq \underbrace{N\left[-n_+ \log n_+ - (1-n_+)\log(1-n_+)\right]}_{\mathcal{S}} - \log \sqrt{2\pi N n_+(1-n_+)} . \tag{A.6}$$

Here, we have stressed that there is an "extensive" part of the $\log\Omega$, proportional to N, and much smaller corrections. [4] The extensive part of $\log\Omega$ will be defined to be the *statistical entropy*, here simply:

$$\mathcal{S}(n_+, N) = N\left[-n_+ \log n_+ - (1-n_+)\log(1-n_+)\right] . \tag{A.7}$$

Using this, show that the full binomial distribution can be approximated as:

$$P(N_+, N) \simeq \underbrace{\frac{1}{\sqrt{2\pi N n_+(1-n_+)}} e^{N[-n_+ \log n_+ - (1-n_+)\log(1-n_+)]}}_{\Omega(N_+,N)} \underbrace{e^{-N[-n_+ \log p_+ - (1-n_+)\log p_-]}}_{p_+^{N_+} p_-^{N-N_+}} . \tag{A.8}$$

Analyse the maximum of this probability distribution, and argue that it comes from a competition between the entropy contribution, which would favour $n_+ = 1/2$, and an "energy-related" term (more about this later on) which depends on the possible bias for p_+. To find the maximum, simply calculate the derivative with respect to n_+ of the quantity appearing in the exponential, and show that:

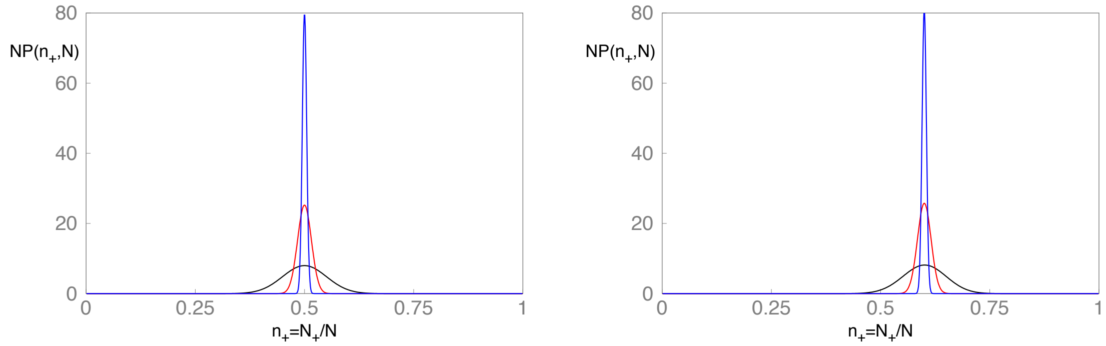

Figure A.2.: Plot of $NP(n_+, N)$ versus $n_+ = N_+/N$ for $N = 10^2, 10^3, 10^4$. Left: $p_+ = p_- = \frac{1}{2}$; Right: $p_+ = 0.6$.

$$n_+^{\max} = p_+ , \tag{A.9}$$

which is quite simple to understand: the most probable number of occurrences of +1 spins is Np_+. Calculating the second derivative, one can actually provide an expansion around the maximum. Show that this leads to the following Gaussian form:

$$P(N_+, N) \simeq \frac{1}{\sqrt{2\pi N p_+(1-p_+)}} e^{-\frac{(n_+-p_+)^2}{2\sigma_N^2}} , \tag{A.10}$$

---

[4] The term $-\log\sqrt{2\pi N n_+(1-n_+)}$ plays a role in the normalisation of the distribution, but is not important in determining neither the peak nor the width of the distribution.

where the width of the Gaussian is given by [5]

$$\sigma_N^2 = \frac{p_+(1-p_+)}{N} \ .$$

Do some plots and reproduce the results shown in Fig. A.2.

This result — originally derived for the binomial distribution, I believe, by de Moivre — represents an instance of a very important and general law of statistics, known as the *strong form of the law of large numbers.*

If you think that a relative error scaling like $1/\sqrt{N}$ is not that impressive, think a bit about what happens when $N = 10^{24}$. By making a coin flip experiments with that value of N you would determine that the *average* number of Tails is

$$n_+ \simeq 0.5 \pm O(10^{-12}) \ ,$$

a rather fantastic precision, don't you agree? [6] Statistical mechanics lives on such large numbers.

A.3. Fourier and the strong form of the law of large numbers

Problem A.3. Let us see how the strong form of the law of large numbers emerges in the limit of $N \to \infty$. The calculation we are going to perform uses Fourier transforms, but it is also very instructive to rederive similar things by using Laplace transforms, as shown below. Consider, again in the binomial case, the distribution for the magnetisation $\mathbb{M} = \sum_i \sigma_i$, which we can write as:

$$P_{\mathbb{M}}(M, N) = \sum_{\sigma_1, \cdots, \sigma_N} P_1(\sigma_1) \cdots P_1(\sigma_N) \, \delta_{M, \sum_i \sigma_i} \ . \tag{A.11}$$

Let us generalise this expression a little bit, and imagine that $P_1(x_i)$ is an arbitrary probability distribution for the single variable x_i, which could be a continuous variable (the discrete case is easily recovered from the continuous one). Let us call $\mathbb{X} = \sum_i x_i$ the observable related to the *sum* of the independently distributed measurements of the variables x_i. We can write its distribution as:

$$P_{\mathbb{X}}(X, N) = \int_{-\infty}^{+\infty} \mathrm{d}x_1 \cdots \mathrm{d}x_N \; P_1(x_1) \cdots P_1(x_N) \, \delta(X - \sum_i x_i) \ , \tag{A.12}$$

where the $\delta(\cdot)$ denotes the Dirac's delta. To cope with the Dirac's delta, take the Fourier transform of the distribution, and show that:

$$\begin{aligned} \widehat{P}_{\mathbb{X}}(k, N) &= \int_{-\infty}^{+\infty} \mathrm{d}X \mathrm{e}^{-ikX} P_{\mathbb{X}}(X, N) \\ &= \left[\int_{-\infty}^{+\infty} \mathrm{d}x_1 P_1(x_1) \, \mathrm{e}^{-ikx_1} \right]^N = \left[\widehat{P}_1(k) \right]^N \ . \end{aligned} \tag{A.13}$$

---

[5] Note that, as it is, this distribution is approximately normalised as

$$\sum_{N_+=0}^{N} P(N_+, N) \simeq 1 \ .$$

To make it approximately normalised in terms of the continuous variable n_+, and with *integrals* instead of discrete sums, you need to multiply it by N, writing:

$$\widetilde{P}(n_+, N) \simeq N P(N n_+, N) \simeq \frac{1}{\sqrt{2\pi\sigma_N^2}} \mathrm{e}^{-\frac{(n_+ - p_+)^2}{2\sigma_N^2}} \ .$$

[6] Atomic clocks have precisions ranging from 10^{-10} to 10^{-14}.

Notice how simple is the Fourier transform of the distribution for the sum of the variables: due to the factorisation of the probabilities, and taking advantage of the Dirac's delta function, you simply get the Fourier transform of the single-variable distribution $P_1(x_1)$, to the power N. If you want to recover the original distribution, you simply have to Fourier transform back:

$$P_{\mathbb{X}}(X,N) = \int_{-\infty}^{+\infty} \frac{\mathrm{d}k}{2\pi} \mathrm{e}^{ikX} \left[\widehat{P}_1(k)\right]^N = \int_{-\infty}^{+\infty} \frac{\mathrm{d}k}{2\pi} \mathrm{e}^{N[\log \widehat{P}_1(k) + ikx]} \;, \tag{A.14}$$

where we have introduced the rescaled variable $x = X/N$, related to the *average* of the individual measurements $(\sum_i x_i)/N$, in order to single-out a common (and large) factor N in the exponential.

Show that:

$$\left.\frac{\partial^n \widehat{P}_1}{\partial k^n}\right|_{k=0} = (-i)^n \int_{-\infty}^{+\infty} \mathrm{d}x \; x^n \, P_1(x) = (-i)^n \langle x^n \rangle \;.$$

which justify the name of *moment generating function* for $\widehat{P}_1(k)$.

Even more remarkable is the action of $\log \widehat{P}_1(k)$, which is known to generate the so-called *cumulants* of the distribution (do a search on the web for the *linked cluster theorem*). Show that $\partial_k \log \widehat{P}_1(0) = -i\langle x \rangle$, while the second and third derivatives indeed give the variance σ^2 and the *skewness* γ^3 of the distribution $P_1(x)$:

$$\begin{aligned} \left.\frac{\partial^2 \log \widehat{P}_1}{\partial k^2}\right|_{k=0} &= (-i)^2[\langle x^2 \rangle - \langle x \rangle^2] = -\sigma^2 \\ \left.\frac{\partial^3 \log \widehat{P}_1}{\partial k^3}\right|_{k=0} &= i[\langle x^3 \rangle - 3\langle x^2 \rangle\langle x \rangle + 2\langle x \rangle^3] = i\gamma^3 \;. \end{aligned} \tag{A.15}$$

Expand now the $\log \widehat{P}_1(k)$ around $k = 0$, and change variable to $q = k\sigma\sqrt{N}$ to show that cumulants higher than the second become irrelevant for $N \to \infty$, and conclude that:

$$P_{\mathbb{X}}(Nx,N) \;\simeq\; \frac{1}{\sqrt{2\pi N \sigma^2}} \, \mathrm{e}^{-\frac{(x-\langle x \rangle)^2}{2\sigma_N^2}} \;, \tag{A.16}$$

i.e., once again a Gaussian of width $\sigma_N = \frac{\sigma}{\sqrt{N}}$ decreasing as $1/\sqrt{N}$. [7]

A.4. The Energy comes into the game

Problem A.4. A simple rewriting of the ingredients of our binomial distribution shows that indeed the probabilities $p_\pm$ are related to the "energy" of a configuration, while the "entropy" takes care of the binomial coefficient. Let us see why. Since p_+ and p_- are such that $p_+ + p_- = 1$, show that you can always parameterise them by

$$p_\pm = \frac{\mathrm{e}^{\pm\beta h}}{Z_1} \quad \text{with} \quad Z_1 = \sum_{\sigma=\pm} \mathrm{e}^{-\beta h \sigma} \;.$$

Next, show that you can rewrite:

$$\mathbf{P}(\sigma_1, \cdots, \sigma_N) = p_+^{N_+} p_-^{N_-} = \frac{\mathrm{e}^{-\beta \mathbb{H}(\sigma_1,\cdots,\sigma_N)}}{Z} \;, \tag{A.17}$$

---

[7] Recall that, once again, as a function of the rescaled variable x we would require the normalisation $1 = N\int \mathrm{d}x P_{\mathbb{X}}(Nx,N)$. Hence the properly normalised distribution, as a function of x, would be:

$$\widehat{P}_{\mathbb{X}}(x,N) = N P_{\mathbb{X}}(Nx,N) = \frac{1}{\sqrt{2\pi\sigma_N^2}} \, \mathrm{e}^{-\frac{(x-\langle x \rangle)^2}{2\sigma_N^2}} \;.$$

where

$$\begin{aligned} \mathbb{H}(\sigma_1, \cdots, \sigma_N) &= -h \sum_{i=1}^{N} \sigma_i = -h\mathbb{M} \\ Z &= Z_1^N = \sum_{\sigma_1, \cdots, \sigma_N} \mathrm{e}^{-\beta \mathbb{H}(\sigma_1, \cdots, \sigma_N)} \ . \end{aligned} \tag{A.18}$$

We could go on and reformulate the whole problem of the Galton's board and the binomial distribution in terms of *non-interacting* Ising spins in a magnetic field.

A.5. Laplace and the saddle-point method

Problem A.5. Here we will learn a third way of approaching the calculation of the binomial distribution $P(N_+, N)$, which illustrates the use of the Laplace transform and gives a rather clean example of the use of the saddle-point technique. Many of the steps we will do are almost identical to those taken in the derivation of the law of large numbers, but the use of Laplace transform is rather ideal for later purposes, as well as the discussion of the saddle-point method. Start again from the binomial distribution function

$$P(N_+, N) = \sum_{\sigma_1, \cdots, \sigma_N} \delta_{N_+, \frac{1}{2}\sum_i (1+\sigma_i)} \, P_1(\sigma_1) \cdots P_1(\sigma_N) \ , \tag{A.19}$$

and perform a *discrete* Laplace transform [8]

$$\begin{aligned} \widehat{P}(s, N) &\overset{\text{def}}{=} \sum_{N_+=0}^{\infty} \mathrm{e}^{-sN_+} \, P(N_+, N) = \\ &= \sum_{\sigma_1, \cdots, \sigma_N} \prod_{i=1}^{N} \left[P_1(\sigma_i) \, \mathrm{e}^{-s\frac{1+\sigma_i}{2}} \right] = \prod_{i=1}^{N} \left[\sum_{\sigma_i = \pm 1} P_1(\sigma_i) \, \mathrm{e}^{-s\frac{1+\sigma_i}{2}} \right] = \\ &= \prod_{i=1}^{N} \left[p_+ \mathrm{e}^{-s} + p_- \right] = \mathrm{e}^{N \log(p_+ \mathrm{e}^{-s} + p_-)} \ . \end{aligned} \tag{A.20}$$

Here s is the Laplace variable, complex in general: Laplace transforms are usually very generously analytic functions in the complex half-plane to the right of any singularity. In the discrete case we have here, there is has a peculiarity. Indeed, you can verify that

$$\widehat{P}(s, N) = \widehat{P}(s + 2\pi i, N) \ ,$$

hence we can restrict s to the complex strip with $\mathrm{Im}s \in [-\pi, \pi]$ and even identify the two sides of the strip, i.e., we have a "cylinder" rather than a plane. Now we should return back by taking an *inverse Laplace transform.* Here, at variance with the Fourier transform which is very symmetric, the inverse Laplace transform requires an integral in the complex plane. In the general case of continuous variables this is known as Mellin's or Bromwich integral (see for instance Wikipedia), and we will encounter it explicitly when discussing the ideal gas case. Here we must use its discrete variant, which

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[8] The Krönecker deltas would require that I calculate the transform as a sum, rather than an integral. Alternatively, you can transform all the discrete variables, σ_i and N_+, into continuous variables, all $\sum_{\sigma_i}$ into integrals, and all Krönecker deltas, including those in the $P_1(\sigma_i)$, into Dirac deltas.

has the form: [9]

$$\begin{aligned} P(N_+, N) &= \int_{c-i\pi}^{c+i\pi} \frac{\mathrm{d}s}{2\pi i} \, \mathrm{e}^{sN_+} \, \widehat{P}(s, N) \\ &= \int_{c-i\pi}^{c+i\pi} \frac{\mathrm{d}s}{2\pi i} \, \mathrm{e}^{N \overbrace{[sn_+ + \log(p_+\mathrm{e}^{-s} + p_-)]}^{g(s)}} \; , \end{aligned} \tag{A.22}$$

where, as usual, we have introduced the rescaled variable $n_+ = N_+/N \in [0,1]$. The contour of integration deserves some comments. As usual with complex integral (recall Cauchy theorem), the shape of the contour can be very flexibly changed, as long as you do not cross any singularity. Here the contour should start at a point $c - i\pi$ and end at $c + i\pi$, where c is such that you stay to the *right* of any singularity, in the strip-region where the Laplace transform is analytic. For arbitrary contours, and large N, the integrand oscillates in a tremendous way. Consider the function $g(s)$ multiplying N in the exponential:

$$g(s) = sn_+ + \log(p_+\mathrm{e}^{-s} + p_-) \; . \tag{A.23}$$

Show that it has a horizontal branch-cut at $(x, \pm i\pi)$ with $x \in (-\infty, s_c)$ where

$$s_c = \log \frac{p_+}{1-p_+} \; ,$$

is the end-point of the branch cut. You better never cross it with your contour. But the interesting feature is that $g(s)$ has also a *stationary point* where $g'(s_0) = 0$. Since

$$g'(s) = n_+ - \frac{p_+\mathrm{e}^{-s}}{p_+\mathrm{e}^{-s} + p_-} \; ,$$

a simple calculation shows that the stationary point is located at: [10]

$$\mathrm{e}^{s_0} = \frac{1-n_+}{n_+} \frac{p_+}{1-p_+} \quad \Longrightarrow \quad s_0 = \log \frac{1-n_+}{n_+} \frac{p_+}{1-p_+} = s_c + \log \frac{1-n_+}{n_+} \; . \tag{A.24}$$

An important property is that this stationary point *cannot* be a maximum (or a minimum) of $g(s)$, because analytic functions cannot have maxima or minima. Hence, the stationary point *must be a*

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[9] The discrete Laplace (DL) transform is a close relative of the Z-transform (see Wikipedia) so defined

$$f_Z(z) \overset{\text{def}}{=} \sum_{n=0}^{\infty} f(n) z^{-n}$$

Indeed, by setting $z = \mathrm{e}^s$ you get:

$$f_Z(\mathrm{e}^s) = \sum_{n=0}^{\infty} \mathrm{e}^{-ns} \, f(n) \overset{\text{def}}{=} \hat{f}_{\mathrm{DL}}(s) \; ,$$

and quite generally you have that $\hat{f}_{\mathrm{DL}}(s + 2\pi i) = \hat{f}_{\mathrm{DL}}(s)$. Hence you can restrict s to the “cylinder strip” with $\mathrm{Im}s \in [-\pi, \pi]$. The inverse of the Z-transform follows quite easily from the Cauchy residue theorem:

$$f(n) = \oint_{\mathcal{C}} \frac{\mathrm{d}z}{2\pi i} \, f_Z(z) \, z^{n-1} \; ,$$

where $\mathcal{C}$ is a circle enclosing the origin and staying in the region of convergence. Indeed, the factor z^{n-1} is such that $f(n)$ appears as a residue, in the form $\frac{f(n)}{z}$. The “shape” of the circle $\mathcal{C}$ can be deformed at will, within the region of convergence. The transformation $s = \log(z)$, which results in $\mathrm{d}s = \frac{\mathrm{d}z}{z}$, is such that you can write the inverse Laplace formula as:

$$f(n) = \int_{c-i\pi}^{c+i\pi} \frac{\mathrm{d}s}{2\pi i} \, \mathrm{e}^{sn} \hat{f}_{\mathrm{DL}}(s) \; , \tag{A.21}$$

where c is related to the real part of the logarithm of the radius of the “circle” $\mathcal{C}$. Again, there is a large freedom in the choice of c and in the shape of the contour connecting the two points $c - i\pi$ and $c + i\pi$ on the “cylinder”.

[10] Notice that the stationary point is to the right of the branch-cut end-point for $n_+ < 1/2$, and to the left of it for $n_+ > 1/2$

saddle-point. [11] Consider now the behaviour of $g(s)$ close to its stationary point at s_0. Show that:

$$g''(s_0) = n_+(1-n_+) \;,$$

and, hence, expand

$$g(s) = g(s_0) + \frac{n_+(1-n_+)}{2}(s-s_0)^2 + \cdots \;,$$

from which you appreciate that the saddle point is a *minimum* when approached along the $\mathrm{Re}\, s$-direction, but a *maximum* along the $\mathrm{Im}\, s$-direction. Notice also the remarkable fact that

$$g(s_0) = \underbrace{[-n_+\log n_+ - (1-n_+)\log(1-n_+)]}_{\mathcal{S}/N} + [n_+\log p_+ + (1-n_+)\log p_-] \;, \tag{A.26}$$

which should ring a bell, if you go back and look at Eq. (A.8). Now split the contour γ into three pieces: the all-important central part γ_0 going straight-up across the saddle-point, parameterized by $s(t) = s_0 + it$ with $t \in [-t_0, t_0]$ (take $t_0 < \pi$ so that you do not hit the branch cut), plus two other L-shaped little pieces $\gamma_\rceil$ and $\gamma_\rfloor$ joining γ_0 to the points $c - i\infty$ (below) and $c + i\infty$ (above). [12] Show that the part going straight-up through the stationary point contributes:

$$\begin{aligned}\int_{\gamma_0} \frac{\mathrm{d}s}{2\pi i}\, \mathrm{e}^{Ng(s)} &= \int_{-t_0}^{t_0} \frac{\mathrm{d}t}{2\pi}\, \mathrm{e}^{Ng(s_0) - N\frac{n_+(1-n_+)}{2}t^2 + O(t^3)} \\ &= \frac{\mathrm{e}^{Ng(s_0)}}{\sqrt{2\pi N}} \int_{-\sqrt{N}t_0}^{\sqrt{N}t_0} \frac{\mathrm{d}y}{\sqrt{2\pi}}\, \mathrm{e}^{-\frac{n_+(1-n_+)y^2}{2} + O(1/\sqrt{N})} \;,\end{aligned} \tag{A.27}$$

where we have changed variable to $y = \sqrt{N}t$. In the limit of large N, when the limits of integration are extended to $\pm\infty$ and the Gaussian integral explicitly performed, show that you get:

$$\int_{\gamma_0} \frac{\mathrm{d}s}{2\pi i}\, \mathrm{e}^{Ng(s)} \simeq \frac{\mathrm{e}^{Ng(s_0)}}{\sqrt{2\pi N n_+(1-n_+)}} \overset{(A.8)}{\equiv} P(N_+, N) \tag{A.28}$$

So, our beloved Stirling-generated expression for $P(N_+, N)$ in Eq. (A.8) comes straight from the saddle-point integral! The two other contributions to the integral, $\int_{\gamma_\rfloor + \gamma_\rceil} \mathrm{e}^{Ng(s)}$, with their wildly oscillating phase for $N \to \infty$ must give very small corrections to the inverse Laplace transform!

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[11] A simple way to appreciate this is that the very fact that the derivative $g'(s)$ exists, and is independent of the direction, implies that if you write $g(s) = u(x,y) + iv(x,y)$, then u and v verify the *Cauchy-Riemann conditions*

$$\begin{cases} \frac{\partial u}{\partial x} = +\frac{\partial v}{\partial y} \\ \frac{\partial v}{\partial x} = -\frac{\partial u}{\partial y} \end{cases} . \tag{A.25}$$

These conditions, in turn, imply that both $u(x,y)$ and $v(x,y)$ have zero Laplacian: $\nabla^2 u = \nabla^2 v = 0$.

[12] If $n_+ < 1/2$ you have that $s_0 > s_c$ hence you do not cross the branch cut even if you set $t_0 = \pi$. In this case the extra contour pieces $\gamma_\rceil$ and $\gamma_\rfloor$ are not necessary, as you can set $c = s_0$.

B. Problems and complements: Thermodynamics

B.1. Convexity and concavity: a few ideal gas calculations.

It is appropriate to collect here a few basic facts about convexity, which are somewhat useful. First, the general definition. A real function $F(x)$ is convex ($\smile$-convex) if, for any two points x_1 and x_2 in its domain,[1] and any $\lambda \in [0,1]$, we have that:

$$F(\underbrace{\lambda x_2 + (1-\lambda)x_1}_{x_1+\lambda(x_2-x_1)}) \leq \underbrace{\lambda F(x_2) + (1-\lambda)F(x_1)}_{F(x_1)+\lambda(F(x_2)-F(x_1))} \; . \tag{B.1}$$

The function is *strictly* convex if the equality occurs only at the two end-points. These definitions apply both in the one-dimension case, as well as for $x \in \mathbb{R}^n$, as long as the domain in which F is defined is itself a convex set. In the one-dimensional case, applying Taylor's theorem one can show that convexity is equivalent, [2] if the function is continuously differentiable, to $F''(x) \geq 0$. Consider now the n-dimensional case. Let $g_{x_1,x_2}(\lambda)$ be the one-dimensional restriction of F to the segment joining any two points x_1 and x_2:

$$g(\lambda) = F(\lambda x_2 + (1-\lambda)x_1) \; ,$$

where we have shortened the notation to $g(\lambda)$. Quite clearly $g(\lambda)$ is convex in $[0,1]$ because F is convex:

$$g(\lambda) \leq \lambda g(1) + (1-\lambda)g(0) \; .$$

Hence it must be true that $g''(\lambda) \geq 0$. By calculating the second-derivative explicitly we get:

$$g''(\lambda) = \sum_{ij} \left[\frac{\partial^2 F(y)}{\partial y_i \partial y_j} \right]_{y=\lambda x_2+(1-\lambda)x_1} (x_2-x_1)_i \, (x_2-x_1)_j \geq 0 \; .$$

This means that the Hessian of $F(x)$ must be (semi)-positive definite. Notice that a strictly convex function has $F''(x) > 0$ but the converse is not true: for instance, $F(x) = x^4$ is strictly convex, but $F''(0) = 0$.

A very important property of (continuously differentiable) convex functions is that they "stay above" their tangent at every point. To show this, simply expand the definition for small λ, obtaining

$$F(x_1) + \lambda F'(x_1)\cdot(x_2-x_1) + O(\lambda^2) \leq F(x_1) + \lambda(F(x_2)-F(x_1)) \; .$$

Hence, we get that

$$F'(x_1)\cdot(x_2-x_1) + O(\lambda) \leq F(x_2) - F(x_1) \; .$$

But since this is true for arbitrary small λ, then we conclude that:

$$F(x_2) \geq F(x_1) + F'(x_1)\cdot(x_2-x_1) \; . \tag{B.2}$$

---

[1] Notice that the domain itself must be a convex set, i.e., it must contain $\lambda x_2 + (1-\lambda)x_1$

[2] In the proof one uses Taylor's theorem on the remainder.

Notice that, for fixed x_1, the right-hand side expresses the tangent (more generally, the tangent plane) at x_1. Notice also that if $F'(x_1) = 0$, then $F(x_2) \geq F(x_1)$, i.e., for a convex function, a stationary point is automatically a *minimum*.

Finally, it is worth mentioning that convex functions satisfy a useful inequality, known as Jensen's inequality, which "generalises" the defining property of convexity: given N points x_i and "probability weights" $p_i \geq 0$ with $\sum_i p_i = 1$, then

$$F(\sum_i p_i x_i) \;\leq\; \sum_i p_i F(x_i) \; . \tag{B.3}$$

The proof is quite simple: try it. Finally, a function $F(x)$ is *concave* (or $\frown$-convex) if the function $-F(x)$ is convex. For concave functions the various inequalities have a reversed direction.

Problem B.1. The ideal gas entropy and energy.

1) Calculate the Hessian matrix of $S_{\mathrm{ideal}}(E, V, N)$, in particular the 2×2 Hessian with respect to (E, V), and interpret the various derivatives in terms of physical quantities.

2) Calculate the Hessian matrix of $E_{\mathrm{ideal}}(S, V, N)$, in particular the 2×2 Hessian with respect to (S, V), and interpret the various derivatives.

Problem B.2. Equilibrium in ideal gases.
Consider two ideal gases making up the two subsystems 1 and 2 in the previous thermal equilibrium problem, and take the entropy of each subsystem to be given by the ideal gas entropy in Eq. (1.66) which I rewrite below with the standard factor of k_B in front:

$$S(E, V, N) = N k_B \log \frac{\mathrm{e}V}{N} \left(\frac{4\pi m \mathrm{e} E}{3h^2 N} \right)^{\frac{3}{2}} \; . \tag{B.4}$$

Do a 3D plot the total entropy as a function of the two variables E_1 and E_2 keeping all the other variabels fixed:

$$S_{\mathrm{tot}}(E_1, E_2) = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2) \; .$$

Consider now the constraint $E_1 + E_2 = E$ and draw the restriction of S_{tot} to such a line in the (E_1, E_2)-plane. Find the maximum. Verify that it is exactly what the Lagrange method tells us. Consider some explicit numerical cases, to practice a bit: for instance, you could take Argon particles (Ar mass is 40 times the proton mass) to constitute the two ideal gases, 1 mole in system 1 and, say, 2 moles in system 2, while h in the previous entropy formula is taken to be Planck's constant (this is not really relevant for most of the exercise, but useful if you want to calculate actual total entropies). We will later on derive the ideal gas equations of state from the entropy function, but for the purpose of this exercise, I assume you already now everything about ideal gases. Argon boils at 87.3 K, so let us stay away from such "low temperatures", and assume that initially system 1 has a temperature of $T_1^{\mathrm{in}} = T_0 = 273.15$ K, while system 2 is at $T_2^{\mathrm{in}} = 373.15$ K. (You can choose whatever values you want, as long as you stay, realistically, much above 87.3 K: this is just to fix some numbers.) What is the total energy E of the system (in Joules)? Take the (fixed) volume of the contaniner 1 to be $V_1 = V_0 = 22.717$ dm^3: if you calculate the corresponding pressure using the ideal gas equation of state $pV = Nk_BT$ you should find that system 1 has an initial pressure $p_0 = 10^5$ Pa (slightly below atomsferic pressure). For simplicity, assume that $V_2 = V_1$: what is the initial pressure of system 2? Now let thermal equilibrium to be established: calculate the final common temperature T^{fin} of the two gases, the final total energy of each of the two parts, as well as their (unequal) final pressures. Calculate the initial and final entropy of the system.

Problem B.3. In the same setting of Problem B.2, assume that the system has reached thermal equilibrium, and now allow the piston separating the two containers to move. What are the final pressures and volumes of the two containers? Did the final temperature change? What is the final total entropy at equilibrium?

B.2. The van der Waals equation of state

Recall that, as said mentioned in the lecture notes, one can invent an entropy function of the form:

$$S_{\mathrm{vdW}}(E,V,N) = Nk_B \log\left[A_c(v-b)\left(\varepsilon + \frac{a}{v}\right)^c\right] \tag{B.5}$$

whose equations of state lead to the van der Waals isotherms:

$$p = \frac{k_BT}{v-b} - \frac{a}{v^2} \; . \tag{B.6}$$

Here, as usual, $v = V/N$ and $\varepsilon = E/N$, while A_c is a constant with dimensions $[\text{Length}]^{-3}[\text{Energy}]^{-c}$. For a monoatomic gas you can take $c = \frac{3}{2}$ and an explicit form of $A_{\frac{3}{2}}$ can be obtained in terms of the mass m of the atoms and Planck's constant h form the ideal gas limit:

$$A_{\frac{3}{2}} = \mathrm{e}^{\frac{5}{2}}\left(\frac{4\pi m}{3h^2}\right)^{\frac{3}{2}} \; .$$

b and a are the van der Waals constants, which have been measured by fitting experimental data on many gases (see Wikipedia page). The values usually reported are referred to a mole of gas, $N = N_A$, and are more precisely given by a_m and b_m in:

$$p = \frac{RT}{V-b_m} - \frac{a_m}{V^2} \; ,$$

where $V = N_a v$ is the molar volume, $R = k_B N_A$ the ideal gas constant, $a_m = N_A^2 a$ and $b_m = N_A b$. I report in the following table the molar van der Waals constants for He, Ne, and Ar.

Gas	a_m (in Pa m^6)	b_m (in m^3)
He	0.00346	$23.7 \cdot 10^{-6}$
Ne	0.0215	$17.1 \cdot 10^{-6}$
Ar	0.1373	$32.0 \cdot 10^{-6}$

In the first problem below, more traditional, you should start practicing with the form of the isotherms predicted by Eq. (B.6). In particular, you should find that there is a temperature, the critical point temperature T_c, in which the high-temperature ever-decreasing isotherms first develops an inflection point:

$$\left.\frac{\partial p}{\partial v}\right|_{T_c} = 0 \qquad\qquad \left.\frac{\partial^2 p}{\partial v^2}\right|_{T_c} = 0 \; ,$$

which physically signals that the isothermal compressibility κ_T diverges.

Problem B.4. The van der Waals isotherms.

1) Solve the equations for the inflection point of the critical isotherm to find T_c, p_c, and v_c in terms of a and b.

2) Make a small table showing the numerical values of the critical parameters for He, Ne, Ar. Add to the table, for later use, the numerical value (in eV) of the energy-scale parameter $\epsilon_0 = p_c v_c$.

3) Switch to dimensionless variables $\tilde{p} = p/p_c$, $\tilde{v} = v/v_c$ and $\widetilde{T} = T/T_c$ and re-express the vdW isotherms in terms of the dimensionless variables.

Answer: You should get: $\tilde{p}=\frac{8\widetilde{T}}{3\tilde{v}-1}-\frac{3}{\tilde{v}^2}$.

4) Determine the lowest temperature $\widetilde{T}_{\mathrm{low}}$ at which the isotherms predict a non-negative pressure. For $\widetilde{T} < \widetilde{T}_{\mathrm{low}}$ the van der Walls isotherms make non sense at all. Plot a few isotherms in the range $\widetilde{T} \in [\widetilde{T}_{\mathrm{low}}, 1]$, including 0.9 and 0.95.

We want now to understand how to make sense of the isotherms below T_c, which show unphysical regions of *negative compressibility.* The procedure outlined below leads to the well-known Maxwell construction, in a way that clearly shows the role of the convex envelope of tangents in the relevant thermodynamic potential. For that purpose, we will make use of the *Ansatz* for $S(E, V, N)$ which we have presented above (see Callen's book for an explanation of how to get to that form). We should make clear that this form is far from perfect (we will see that it leads to several inconsistencies, in particular the absence of latent heat) but still useful to practice with. To start with, let us rewrite the expression for $S_{\mathrm{vdW}}(E, V, N)$ in terms of the entropy per particle $s = S/N$:

$$s(\varepsilon, v) = k_B \log \left[A_c (v - b) \left(\varepsilon + \frac{a}{v} \right)^c \right] .$$

Obviously, we always assume that $v > b$. Next, proceed us suggested below.

Problem B.5. The van der Waals potentials.

1) Invert the expression for $s(\varepsilon, v)$ to express $\varepsilon(s, v)$. Calculate the two equations of state

$$T(s, v) = \frac{\partial \varepsilon}{\partial s} \qquad\qquad p(s, v) = -\frac{\partial \varepsilon}{\partial v} ,$$

and re-derive the van der Walls isotherms. Notice that T as a function of s shows no sign of a phase transition (latent heat).

2) Invert $T(s, v)$ to find $s(T, v)$ and then the free-energy per particle $f(T, v) = F/N$:

$$f(T, v) = \varepsilon(s(T, v), v) - Ts(T, v) .$$

Answer: You should get: $f=ck_BT-\frac{a}{v}-ck_BT\log\Big(ck_BT[A_c(v-b)]^{\frac{1}{c}}\Big)$.

3) Express $f(T, v)$ in terms of dimensionless variables $\widetilde{T} = T/T_c$ and $\tilde{v} = v/v_c$, with the overall energy-scale $\epsilon_0 = p_c v_c$, and plot the result versus $\tilde{v}$ for the same temperatures $\widetilde{T} \in [\widetilde{T}_{\mathrm{low}}, 1]$ used previously. Notice that $f(T, v)$ *is not convex* in v (as it should), while it *is concave* in T.

Answer: A convenient form is: $f=\frac{\epsilon_0}{3}\Big\{8c\widetilde{T}\Big(1-\log\frac{8c\epsilon_0}{3}[A_cb]^{\frac{1}{c}}\Big)-\frac{9}{\tilde{v}}-8\widetilde{T}\log\widetilde{T}(3\tilde{v}-1)\Big\}$.

4) To make $f(T, v)$ *convex* in v, we should construct the convex envelops of the tangents to the curve. This implies drawing a common tangent to $f(T, v)$ through two appropriate points $v_1(T)$ and $v_2(T)$. Show that the two points v_1 and $v_2 > v_1$ should satisfy the two equations:

$$-p = \left.\frac{\partial f}{\partial v}\right|_{v_1} = \left.\frac{\partial f}{\partial v}\right|_{v_2} \qquad \text{and} \qquad f(T, v_1) - f(T, v_2) = p(v_2 - v_1) .$$

Justify geometrically the reason why these conditions univocally define the common tangent which makes the function convex.

5) Consider the function $\Phi(T,p,v) = f(T,v) + pv$ and show that the conditions for the common tangent to $f(T,v)$ can be conveniently rewritten as:

$$\left.\frac{\partial \Phi}{\partial v}\right|_{v_1} = \left.\frac{\partial \Phi}{\partial v}\right|_{v_2} = 0 \qquad \text{and} \qquad \Phi(T,p,v_1) = \Phi(T,p,v_2) \; . \tag{B.7}$$

In other words, $v_1(T,p)$ and $v_2(T,p)$ are two *minima* of the function $\Phi(T,p,v)$ for fixed T and p, and the correct values of v_1 and v_2 are obtained for the unique value of $p(T)$ for which the corresponding minimal values of Φ coincide.

6) The function $\Phi(T,p,v) = f(T,v) + pv$ can be regarded as a kind of generalized Gibbs potential, with a typical double-well structure when you plot it versus v: the actual Gibbs potential per-particle is $\mu_{\text{low}}(T,p) = \Phi(T,p,v_{\text{low}}(T,p))$ corresponding to the absolute minimum of $\Phi(T,p,v)$. One could even think of the other minimum of Φ as the Gibbs potential of the metastable phase $\mu_{\text{high}}(T,p) = \Phi(T,p,v_{\text{high}}(T,p))$. If we denote by $\mu_{1(2)}(T,p) = \Phi(T,p,v_{1(2)}(T,p)$ the chemical potentials of the two “phases”, we can say that the transition point $p(T)$ is such that:

$$\mu_1(T,p) = \mu_2(T,p) \; . \tag{B.8}$$

This uniquely defines the phase-transition line $p(T)$ in the (T,p) plane, a line terminating at the critical point (T_c,p_c). Determine numerically the phase-transition line $p(T)$. Convince yourself that the isotherms of the resulting convex $f(T,v)$ show now a plateau region where $p = p(T)$ is independent of v in the whole interval $[v_1(T,p(T)), v_2(T,p(T))]$.

7) Draw the vdW isotherm for $\widetilde{T} = 0.95$ together with the thermodynamically stable isotherm constructed as indicated above, and show that the construction indeed guarantees that the stable isotherm determines two regions of *equal area* in the unstable isotherm.

One final comment before we finish: unfortunately our *Ansatz* for S_{vdW} has lead to an entropy which shows no latent heat across the $p(T)$ line. This is an inconsistency of the *Ansatz*.

B.3. The Clausius-Clapeyron equation

The phase diagram of a substance can be quite complex. Fig.B.1 shows a sketch of the equation of state of a substance showing solid, liquid and vapour phases, with projections of the relevant lines on the (T,p), (p,v) and (T,v) planes. Fig. B.2 below shows more realistic (p,T) phase diagrams for CO_2 and water. A remarkable feature that you should notice is that the slope of the $p(T)$ transition line

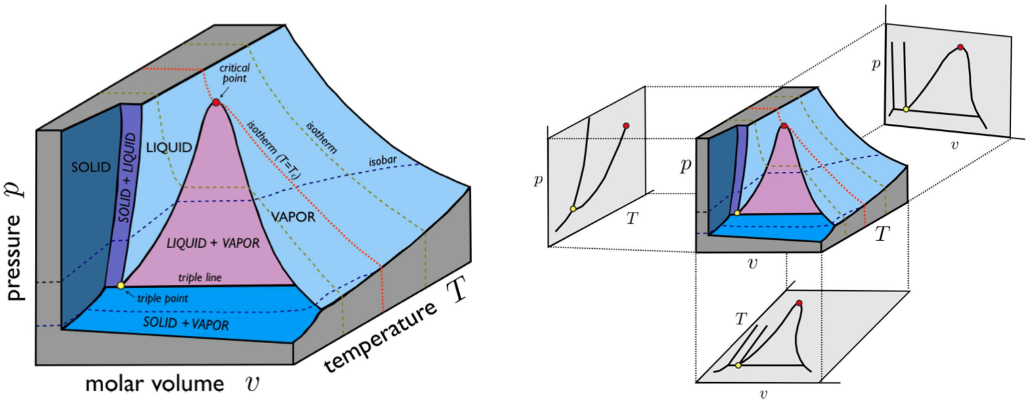

Figure B.1.: Sketch of the equation of state $f(T,v,p) = 0$ of a substance showing solid, liquid and vapour phases. Figures taken from Arovas.

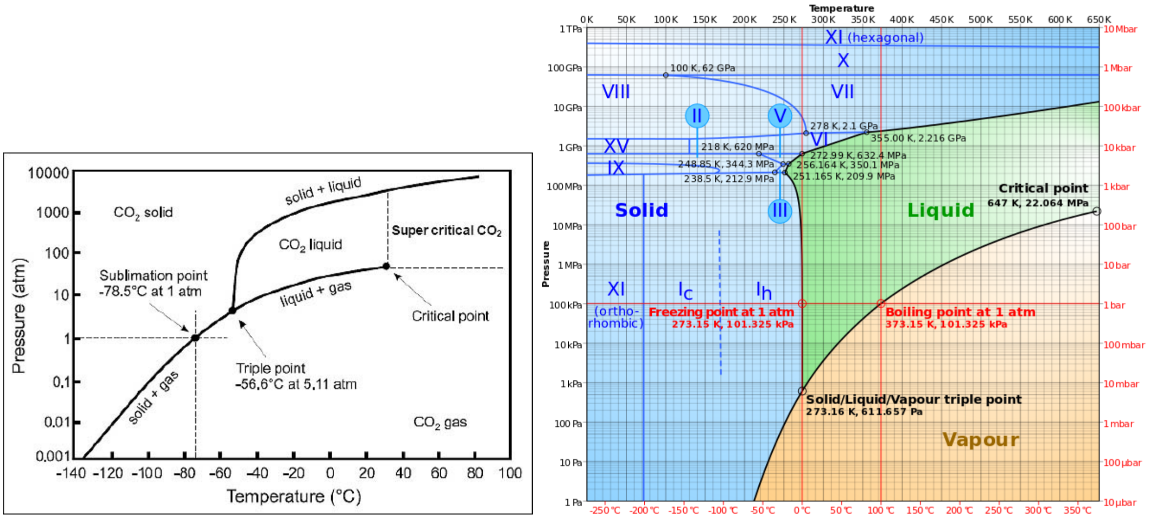

Figure B.2.: Phase diagrams in the (p, T) plane for CO_2 and water (figures taken from the web).

for the liquid-gas transition is similar in both cases, while the corresponding line for the solid-liquid transition is different. Fig. B.3 below makes the point more clear.

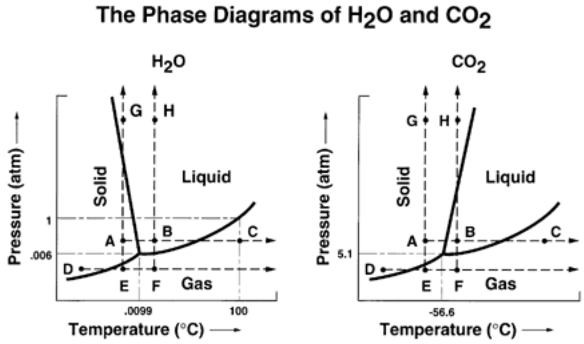

Figure B.3.: Phase diagrams in the (p, T) plane for CO_2 and water, showing in more detail the different slope of the $p(T)$ line for the solid-liquid transition (figure taken from the web).

Now question is what determines the details of the slope of the $p(T)$ transition line. We will see that the answer to that question involves the concept that at the transition line, the chemical potentials of the two phases coincide, $\mu_1(T, p) = \mu_2(T, p)$. Consider now the sketch of $p(T)$ in Fig.B.4, with the

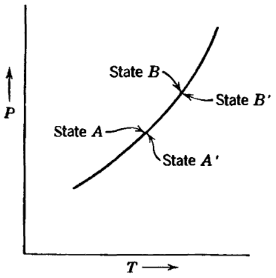

Figure B.4.: A sketch of the $p(T)$ line (figure taken from Callen).

two points $A - B$ on the coexistence line belonging to phase "1", while $A' - B'$ are the corresponding points at the same p and T, but for phase "2". We distinguish those points because, while the intensive parameters are the same, both the entropy s and the volume v are discontinuous across the transition line, indicate them by $s_i(T_{A(B)}, p_{A(B)})$ and $v_i(T_{A(B)}, p_{A(B)})$ with $i = 1, 2$. Let $\Delta p = p_B - p_A$ and $\Delta T = T_B - T_A$, which we assume to be very small.

Problem B.6. Show that the slope of the coexistence line $p(T)$ is given by:

$$\frac{dp}{dT} = \lim_{\Delta T \to 0} \frac{\Delta p}{\Delta T} = \frac{s_2(T, p(T)) - s_1(T, p(T))}{v_2(T, p(T)) - v_1(T, p(T))} = \frac{\Delta s}{\Delta v} = \frac{1}{T} \frac{\Delta Q}{\Delta v} \,, \tag{B.9}$$

where ΔQ is the *latent heat* at point $(T, p(T))$, and Δv the corresponding discontinuity in the molar volume.

B.4. Manipulating partial derivatives in thermodynamics

The algebraic manipulations involving partial derivatives are particularly nasty in thermodynamics, essentially because all variables can be promoted to become functions, and the resulting transformation of derivatives can be non-trivial. These manipulations are greatly simplified by using the following results on Jacobeans. Let $f_i(\mathbf{x})$ with $i = 1 \cdots n$ be functions of the n variables $\mathbf{x} = x_1 \cdots x_n$. We denote the following Jacobean determinant as:

$$\frac{\partial(f_1, f_2, \cdots, f_n)}{\partial(x_1, x_2, \cdots, x_n)} = \det \begin{pmatrix} \frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} & \cdots & \frac{\partial f_1}{\partial x_n} \\ \frac{\partial f_2}{\partial x_1} & \frac{\partial f_2}{\partial x_2} & \cdots & \frac{\partial f_2}{\partial x_n} \\ \vdots & \vdots & \cdots & \vdots \\ \frac{\partial f_n}{\partial x_1} & \frac{\partial f_n}{\partial x_2} & \cdots & \frac{\partial f_n}{\partial x_n} \end{pmatrix} . \tag{B.10}$$

We assume that such a determinant is different from zero, which guarantees a non-singular nature of the mapping $\mathbf{x} \to \mathbf{f}(\mathbf{x})$. The Jacobean determinant has the following three basic properties:

$$\begin{aligned} \frac{\partial(f_1, f_2, \cdots, f_n)}{\partial(x_1, x_2, \cdots, x_n)} &= \frac{\partial(f_1, f_2, \cdots, f_n)}{\partial(y_1, y_2, \cdots, y_n)} \frac{\partial(y_1, y_2, \cdots, y_n)}{\partial(x_1, x_2, \cdots, x_n)} && \text{(J1)} \\ \frac{\partial(f_1, f_2, \cdots, f_n)}{\partial(x_1, x_2, \cdots, x_n)} &= \left(\frac{\partial(x_1, x_2, \cdots, x_n)}{\partial(f_1, f_2, \cdots, f_n)} \right)^{-1} && \text{(J2)} \\ \frac{\partial(f_1, f_2, f_3, \cdots, f_n)}{\partial(x_1, x_2, x_3, \cdots, x_n)} &= -\frac{\partial(f_2, f_1, f_3, \cdots, f_n)}{\partial(x_1, x_2, x_3, \cdots, x_n)} && \text{(J3)} \end{aligned} \tag{B.11}$$

J1 follows from the chain rule of calculus and from the fact that the determinant of a product of two matrices is the product of their determinants. J2 follows from the inverse function theorem. J3, finally, follows from the alternating nature of the determinant, and can be generalised to an arbitrary permutation of the f_i, or of the x_i. The properties that make this concept particularly useful in the calculations are the following two (convince yourself of them) :

$$\begin{aligned} \left(\frac{\partial f_1}{\partial x_1} \right)_{x_2 \cdots x_n} &= \frac{\partial(f_1, x_2, \cdots, x_n)}{\partial(x_1, x_2, \cdots, x_n)} && \text{(P1)} \\ \frac{\partial(f_1, f_2)}{\partial(x_1, x_2)} &= \frac{\partial(f_1, f_2, x_3, \cdots, x_n)}{\partial(x_1, x_2, x_3, \cdots, x_n)} && \text{(P2)} \end{aligned} \tag{B.12}$$

P1 allows to transform a single partial derivative into a Jacobean, so as to be able to apply J1-J3. P2, similarly, allows to add other variables to a smaller Jacobean, to be used in the calculations.

Let us apply these mathematical results to thermodynamics. The first simple application is the relationship between inverse functions:

$$\left(\frac{\partial f_1}{\partial x_1} \right)_{x_2 \cdots x_n} \overset{P1}{=} \frac{\partial(f_1, x_2, \cdots, x_n)}{\partial(x_1, x_2, \cdots, x_n)} \overset{J2}{=} \left(\frac{\partial(x_1, x_2, \cdots, x_n)}{\partial(f_1, x_2, \cdots, x_n)} \right)^{-1} \overset{P1}{=} \left(\frac{\partial x_1}{\partial f_1} \right)^{-1}_{x_2 \cdots x_n} . \tag{B.13}$$

Next, we show how to get the triply product identity:

$$\begin{aligned}\left(\frac{\partial f_1}{\partial x_1}\right)_{f_2} \overset{P1}{=} \frac{\partial(f_1,f_2)}{\partial(x_1,f_2)} &\overset{J1}{=} \frac{\partial(f_1,f_2)}{\partial(f_1,x_1)}\frac{\partial(f_1,x_1)}{\partial(x_1,f_2)} \\ &\overset{J3}{=} -\frac{\partial(f_1,f_2)}{\partial(f_1,x_1)}\frac{\partial(x_1,f_1)}{\partial(x_1,f_2)} \overset{P1}{=} -\left(\frac{\partial f_2}{\partial x_1}\right)_{f_1}\left(\frac{\partial f_1}{\partial f_2}\right)_{x_1} . \end{aligned} \tag{B.14}$$

Contrast this non-trivial identity with the more standard chain-rule result:

$$\begin{aligned}\left(\frac{\partial f_1}{\partial x_1}\right)_{x_2,\cdots,x_n} \overset{P1}{=} \frac{\partial(f_1,x_2,\cdots,x_n)}{\partial(x_1,x_2,\cdots,x_n)} &\overset{J1}{=} \frac{\partial(f_1,x_2,\cdots,x_n)}{\partial(y_1,x_2,\cdots,x_n)}\frac{\partial(y_1,x_2,\cdots,x_n)}{\partial(x_1,x_2,\cdots,x_n)} \\ &\overset{P1}{=} \left(\frac{\partial f_1}{\partial y_1}\right)_{x_2,\cdots,x_n}\left(\frac{\partial y_1}{\partial x_1}\right)_{x_2,\cdots,x_n} . \end{aligned} \tag{B.15}$$

To get a feeling for the power of the technique, consider the following problem. Suppose someone asks you to show that:

$$\left(\frac{\partial E}{\partial T}\right)_S = \left(\frac{\partial E}{\partial T}\right)_V - \left(\frac{\partial E}{\partial V}\right)_T\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial S}{\partial V}\right)_T^{-1} . \tag{B.16}$$

How would you do that?

Problem B.7. By using the Jacobean properties show that:

$$\left(\frac{\partial f_1}{\partial x_1}\right)_{f_2} = \frac{\partial(f_1,f_2)}{\partial(x_1,x_2)}\left(\frac{\partial f_2}{\partial x_2}\right)^{-1} . \tag{B.17}$$

Apply the identity with $f_1 = E$, $f_2 = S$, $x_1 = T$, $x_2 = V$ to establish the previous non-trivial relationship.

Assume that you have a thermodynamical potential $E(\mathbf{x})$ and write its differential as:

$$\mathrm{d}E = f_1\,\mathrm{d}x_1 + f_2\,\mathrm{d}x_2 + \cdots = \sum_{i=1}^{n} f_i(\mathbf{x})\,\mathrm{d}x_i , \tag{B.18}$$

where $f_i(\mathbf{x}) = \partial_{x_i}E(\mathbf{x})$. If you consider

$$\frac{\partial(f_1,f_2)}{\partial(x_1,x_2)} = \det\begin{pmatrix} \partial^2_{x_1x_1}E & \partial^2_{x_2x_1}E \\ \partial^2_{x_1x_2}E & \partial^2_{x_2x_2}E \end{pmatrix} , \tag{B.19}$$

you recognise that this is simply the determinant of the (partial) Hessian of E. A remarkable and incredibly useful identity emerges if we interchange x_1 and f_2:

$$\frac{\partial(f_1,x_1)}{\partial(f_2,x_2)} = -1 . \tag{B.20}$$

To prove this identity, we apply the Jacobean machinery as follows:

$$\begin{aligned}\frac{\partial(f_1,x_1)}{\partial(f_2,x_2)} &\overset{J1}{=} \frac{\partial(f_1,x_1)}{\partial(x_1,x_2)}\frac{\partial(x_1,x_2)}{\partial(f_2,x_2)} \\ &\overset{J3}{=} -\frac{\partial(x_1,f_1)}{\partial(x_1,x_2)}\frac{\partial(x_1,x_2)}{\partial(f_2,x_2)} \overset{J2}{=} -\frac{\partial(x_1,f_1)}{\partial(x_1,x_2)}\left(\frac{\partial(f_2,x_2)}{\partial(x_1,x_2)}\right)^{-1} \\ &\overset{P1}{=} -\frac{\partial_{x_2}f_1}{\partial_{x_1}f_2} = -\frac{\partial^2_{x_2x_1}E}{\partial^2_{x_1x_2}E} = -1 , \end{aligned} \tag{B.21}$$

where the last equality follows from the equality of mixed second derivatives of E, which we assume to hold, given a sufficient regularity of $E(\mathbf{x})$.

Let us apply this identity to the case of a simple homogenous fluid, where $\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \cdots$. Hence, we get:

$$\frac{\partial(T,S)}{\partial(-p,V)} = -1 \quad \Longrightarrow \quad \frac{\partial(T,S)}{\partial(p,V)} = 1\;. \tag{B.22}$$

If you recall that the *Maxwell relations* originate from the equality of the mixed second derivatives of a thermodynamical potential, you should not be surprised to learn that the identity just shown leads directly to the Maxwell relation for the energy (ME). Indeed:

$$1 = \frac{\partial(T,S)}{\partial(p,V)} = \frac{\partial(T,S)}{\partial(S,V)}\,\frac{\partial(S,V)}{\partial(p,V)} = -\frac{\partial(S,T)}{\partial(S,V)}\left(\frac{\partial(p,V)}{\partial(S,V)}\right)^{-1} = -\frac{\left(\frac{\partial T}{\partial V}\right)_S}{\left(\frac{\partial p}{\partial S}\right)_V}\;,$$

from which you easily derive:

$$\text{ME:} \qquad \left(\frac{\partial p}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S\;. \tag{B.23}$$

Similar techniques will lead to the Maxwell relations for the other thermodynamic potential.

Problem B.8. Try to prove the following identities:

1. Show that
$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p\;, \tag{B.24}$$
which requires the Maxwell relation for the free-energy $F = E - TS$.
2. Show that
$$\left(\frac{\partial E}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p - p\left(\frac{\partial V}{\partial p}\right)_T\;, \tag{B.25}$$
which requires the Maxwell relation for the Gibbs free-energy $G = E - TS + pV$.
3. Show that, if $H = E + pV$ is the Entalpy:
$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V + V\left(\frac{\partial p}{\partial V}\right)_T\;, \tag{B.26}$$
which requires the Maxwell relation for the free-energy.
4. Show that
$$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V\;. \tag{B.27}$$
Which Maxwell relation is behind this identity?

Finally, let us consider an application of these techniques to show the following relationship between specific heats.

Problem B.9. Consider the specific heat at constant p, $C_p = T\left(\frac{\partial S}{\partial T}\right)_p$, and that at constant V, $C_v = T\left(\frac{\partial S}{\partial T}\right)_V$. Show that:

$$C_p - C_v = -T\frac{\left(\frac{\partial V}{\partial T}\right)_p^2}{\left(\frac{\partial V}{\partial p}\right)_T} = VT\,\frac{\alpha_p^2}{\kappa_T}\;, \tag{B.28}$$

where $\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ is the coefficient of thermal expansion (at constant pressure), and $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$ is the coefficient of isothermal compressibility.

C. Problems and complements: Statistical Mechanics

C.1. A micro-canonical master equation: the approach to equilibrium

Rather than going through the Boltzmann's equation and H-theorem, a traditional topic which you can find in many books (see for instance Huang), I prefer to illustrate to you a somewhat related micro-canonical master equation approach that sheds some light on some of the issues involved in the way a system approaches its "equilibrium" and maximizes entropy. For that, I took inspiration from some remarks contained in the final chapter of Callen [3], with appropriate modifications.

I must stress that, while the usual Boltzmann equation addressed the distribution $f(\mathbf{q},\mathbf{p},t)$ in the single-particle phase space $(\mathbf{q},\mathbf{p}) \in \mathbb{R}^6$: [1]

$$\left(\frac{\partial}{\partial t} + \frac{\mathbf{p}}{m}\cdot\frac{\partial}{\partial \mathbf{q}} + \mathbf{F}\cdot\frac{\partial}{\partial \mathbf{p}}\right) f(\mathbf{q},\mathbf{p},t) = \left(\frac{\partial f}{\partial t}\right)_{\mathrm{coll}} \;, \tag{C.1}$$

we will rather start directly from the Liouville's equation for the distribution $\rho(\mathbf{q},\mathbf{p},t)$ in the many-particle phase space $(\mathbf{q},\mathbf{p}) = (\mathbf{q}_1,\cdots,\mathbf{q}_N,\mathbf{p}_1,\cdots,\mathbf{p}_N) \in \mathbb{R}^{6N}$:

$$\frac{\partial}{\partial t}\rho(\mathbf{q},\mathbf{p},t) = \{H(\mathbf{q},\mathbf{p}),\rho(\mathbf{q},\mathbf{p},t)\}_{\mathrm{PB}} \;, \tag{C.2}$$

where $\{f,g\}_{\mathrm{PB}} = \partial_{\mathbf{q}} f \cdot \partial_{\mathbf{p}} g - \partial_{\mathbf{p}} f \cdot \partial_{\mathbf{q}} g$ denotes the Poisson's brackets. To make the notation more compact we will again use the abbreviation $x = (\mathbf{q},\mathbf{p})$ for the generic point in phase-space. One should observe that, while the Boltzmann equation contains non-linearities through the so-called collision term, the Liouville's equation is *linear* in the distribution $\rho(x,t)$, with all non-linearities appearing through the Hamiltonian $H(x)$. Let us coarse-grain the micro-canonical phase space $\Omega(E)$ into a very large number $N_c \sim \mathrm{e}^{Ns(E)}$ of small phase-space cells (e.g., of volume h^{3N}) C_j, with $j = 1 \cdot N_c$. Let

$$P_j(t) = \int \mathrm{d}\mu\, \rho(x,t)\, \chi_{C_j}(x) \;, \tag{C.3}$$

be the probability of finding a many-particle trajectory in cell C_j at time t: here $\chi_{C_j}(x)$ is the characteristic function of the cell C_j. It is physically reasonable, although mathematically not rigorous,

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[1] Notice that the non-linearities enter in the Boltzmann equation through the collision term, see Huang for a detailed exposition. $\mathbf{F}$ is the external force acting on the system, which you might include, if it can be derived from a potential, in the Hamiltonian of the system.

that we can write a first-order-in-time (linear) master equation for the $P_j(t)$ in the following form: [2]

$$\begin{array}{rcl} \dot{P}_i(t) & = & \sum_j \widetilde{T}_{ij}\, P_j(t) - \left(\sum_{j'} \widetilde{T}_{j'i} \right) P_i(t) \\ & = & \sum_j \mathbb{T}_{ij}\, P_j(t) \\ & \text{or} & \\ \dot{\mathbf{P}} & = & \mathbb{T} \cdot \mathbf{P} \end{array} \qquad . \tag{C.4}$$

where the second form uses a shorter vectorial notation. Here $\widetilde{T}_{ij} = \widetilde{T}_{i \leftarrow j} > 0$ is the (positive) rate of making a transition from cell j to cell $i \neq j$, and you should observe that the diagonal term $\widetilde{T}_{ii}$ gives contributions that cancel and can be set to zero without loss of generality, $\widetilde{T}_{ii} = 0$. In the second form, we have grouped the two terms, describing transitions *into* C_i and transitions *out of* C_i into a single matrix $\mathbb{T}_{ij}$ defined in this way:

$$\mathbb{T}_{ij} = \widetilde{T}_{ij} - \delta_{ij} \sum_{j'} \widetilde{T}_{j'i} = \begin{cases} \widetilde{T}_{ij} & i \neq j \\ -\sum_{j'}^{\neq i} \widetilde{T}_{j'i} & i = j \end{cases} \quad . \tag{C.5}$$

One very general property of the matrix $\mathbb{T}$, which is required by the fact that the total probability has to be conserved (i.e., $\sum_i \dot{P}_i = 0$) is that:

$$\sum_i \mathbb{T}_{ij} = 0 \qquad \forall j \; . \tag{C.6}$$

A real matrix with *positive off-diagonal elements* such that, for each column, the sum over the rows *vanishes*, as expressed by Eq. (C.6), is called a *stochastic matrix.* [3] One further property which we will require is that the matrix $\mathbb{T}$ does not single-out invariant subspaces: it has no invariant cycles and is *irreducible.* [4] Technically, starting from any cell j you can reach any cell i by an appropriate power of $\mathbb{T}$:

$$\forall\, i, j\; \exists\, k \;\; \text{such that} \;\; \left[\mathbb{T}^k \right]_{ij} \neq 0 \; .$$

Notice that, in general, $\sum_j \mathbb{T}_{ij} \neq 0$, and the matrix $\mathbb{T}$ is *not symmetric*. Recall that all the cells corresponds to the same energy: they live in the micro-canonical shell. [5] Suppose that the Hamiltonian dynamics of our system is *time-reversal invariant*, which is rather generally true in absence of external magnetic fields. Recall that time-reversal invariance leaves the positions unchanged, but reverses the momenta. A standard Hamiltonian with quadratic momenta would hence be time-reversal invariant: $H(\mathbf{q}, -\mathbf{p}) = H(\mathbf{q}, \mathbf{p})$.

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[2] Since the resulting master equation is in essence *Markovian*, what is implied is some time-coarse-graining and a Markovian assumption on the dynamics. Notice, however, that the usual Markovian nature of similar master equations originates from having integrated away other degrees of freedom in a stochastic framework. Here, we are just coarse-graining in space the Liouville's equation of a closed dynamical system. These aspects are rather subtle. If you consider the entropy of the phase-space distribution $\rho(x,t)$, you can easily show that the Liouville's equation conserves such an entropy. This is the classical analogue of the fact that $S = -k_B \operatorname{Tr}[\hat{\rho}(t) \log \hat{\rho}(t)]$ is *constant* (does not depend on t) if $\hat{\rho}(t)$ evolves unitarily according to the von Neumann equation. Matteo Wauters tells us that the procedure of coarse-graining a partial differential equation to transform into a set of ordinary differential equations is well known in mathematics, and introduces subtle "diffusive terms" that make the coarse-grained time-evolution of the system *non equivalent* to the continuous one: even non-ergodic problems might be transformed, in that way, into completely "mixing" master equations. This, I believe, is at the roots of the fact that the entropy associated to the Markovian master equation we will write *increases* with t.

[3] One often deals with *discrete-time processes*, for which we would write:

$$\mathbf{P}(t + \Delta t) = \underbrace{(\mathbb{1} + \Delta t \mathbb{T})}_{\mathbb{M}} \cdot \mathbf{P}(t) = \mathbb{M} \cdot \mathbf{P}(t) \; .$$

Clearly, the Δt can be chosen in such a way that $\mathbb{M}$ has non-negative elements. The stochasticity condition reads now $\sum_i \mathbb{M}_{ij} = 1$.

[4] For a short introduction to the theory of Markov chains see Sethna [4] or the book by van Kampen.

[5] Callen states that time-reversal invariance in the micro-canonical shell implies that $\mathbb{T}_{ij} = \mathbb{T}_{ji}$, but that is too swift a conclusion, I believe.

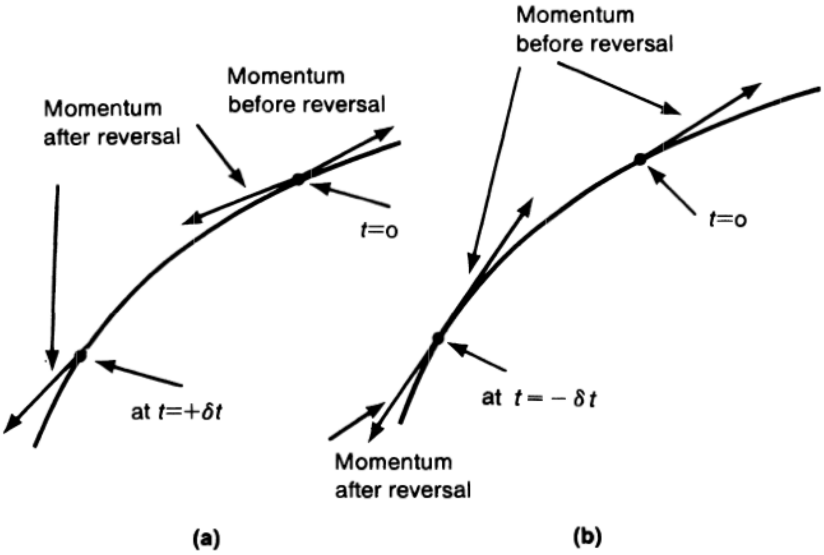

Figure C.1.: Figure taken from Sakurai's book *Modern Quantum Mechanics*, illustrating the idea behind Time Reversal (TR) invariance, with a classical-like trajectory picture. (a, Left) The TR operation (inversion of momenta/spins) is applied at time $t = 0$ to a state, and then the system is evolved for a time $+\delta t$. (b, Right) The system is propagated backward in time, up to time $-\delta t$, and then the TR operation (inversion of momenta/spins) is applied. The two states coincide if the system is TR-invariant.

We therefore make a specific choice of our phase-space cells which is "time-reversal compliant", by splitting the phase space into two big regions, $\mathcal{R}_+ \cup \mathcal{R}_-$, and imposing that for every cell $i \in \mathcal{R}_+$, there is a time-reversed cell i_R with reversed momenta belonging to $\mathcal{R}_-$, and viceversa. The crucial consequence that time-reversal implies for our transition-rate matrix is that

$$\mathbb{T}_{ij} = \mathbb{T}_{j_R i_R} \; . \tag{C.7}$$

With the splitting of cells we have chosen, we can rewrite our master equation Eq. (C.4) as follows:

$$\left\{ \begin{array}{lcl} \dot{P}_i & = & \sum\limits_{j\in\mathcal{R}_+} \left(\mathbb{T}_{ij} P_j + \mathbb{T}_{ij_R} P_{j_R} \right) \\ \dot{P}_{i_R} & = & \sum\limits_{j\in\mathcal{R}_+} \left(\mathbb{T}_{i_R j} P_j + \mathbb{T}_{i_R j_R} P_{j_R} \right) \end{array} \right. . \tag{C.8}$$

If you define the two block matrices $\mathbb{A}_{ij} = \mathbb{T}_{ij}$ and $\mathbb{B}_{ij} = \mathbb{T}_{ij_R}$, where $i, j \in \mathcal{R}_+$, then you immediately realize that time-reversal invariance, via Eq. (C.7), implies that:

$$\begin{pmatrix} \dot{\mathbf{P}} \\ \dot{\mathbf{P}}_R \end{pmatrix} = \begin{pmatrix} \mathbb{A} & \mathbb{B} \\ \mathbb{C} & \mathbb{A}^T \end{pmatrix} \cdot \begin{pmatrix} \mathbf{P} \\ \mathbf{P}_R \end{pmatrix} = \mathbb{K} \cdot \begin{pmatrix} \mathbf{P} \\ \mathbf{P}_R \end{pmatrix} \tag{C.9}$$

The notation we have used is as follows: $\mathbf{P}$ and $\mathbf{P}_R$ are two $L = \frac{N_c}{2}$-dimensional vectors with elements $(\mathbf{P})_i = P_i$ and $(\mathbf{P}_R)_i = P_{i_R}$, for $i \in \mathcal{R}_+$; the matrices $\mathbb{A}$, $\mathbb{B} = \mathbb{B}^T$ and $\mathbb{C} = \mathbb{C}^T$ are $\frac{N_c}{2} \times \frac{N_c}{2} = L \times L$ square matrices with elements $\mathbb{A}_{ij} = \mathbb{T}_{ij}$, $\mathbb{B}_{ij} = \mathbb{T}_{ij_R}$, $\mathbb{C}_{ij} = \mathbb{T}_{i_R,j}$, for $i, j \in \mathcal{R}_+$. The matrix $\mathbb{K}$ is $N_c \times N_c = 2L \times 2L$, with the blocks written in terms of $\mathbb{A}$, $\mathbb{B}$ and $\mathbb{C}$. It is straightforward to realize that the matrix $\mathbb{K}$ is *stochastic*, exactly as the general matrix $\mathbb{T}$ must be: [6]

$$\sum_i \mathbb{K}_{ij} = 0 \qquad \forall j \; . \tag{C.10}$$

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[6] Indeed, if $j \in \mathcal{R}_+$ then

$$\sum_i \mathbb{K}_{ij} = \sum_{i\in\mathcal{R}_+} \left([\mathbb{A}]_{ij} + [\mathbb{C}]_{ij} \right) = \sum_{i\in\mathcal{R}_+} \left(\mathbb{T}_{ij} + \mathbb{T}_{i_R j} \right) = \sum_i \mathbb{T}_{ij} = 0 \, ,$$

and similarly for $j_R \in \mathcal{R}_-$. These requirements fix some constraints on $\mathbb{A}$, $\mathbb{C}$, and $\mathbb{B}$.

Notice that this implies that $\mathbb{K}$ has the vector $(1,\cdots,1)$ as *left eigenvector*, with eigenvalue 0:

$$(1,\cdots,1)\cdot\mathbb{K}=0\ ,$$

a property generally shared by all master equations (recall that it is related to the conservation of the total probability). The non-trivial consequence of time-reversal symmetry, is that the matrix $\mathbb{K}$ has also a vanishing sum-of-columns, for each row, while still being *non-symmetric* in general:

$$\sum_j \mathbb{K}_{ij}=0 \qquad \forall i\ . \tag{C.11}$$

To prove this, simply observe that for $i\in\mathcal{R}_+$:

$$\sum_j \mathbb{K}_{ij}=\sum_{j\in\mathcal{R}_+}(\mathbb{T}_{ij}+\mathbb{T}_{ij_R})=\sum_{j\in\mathcal{R}_+}(\mathbb{T}_{j_Ri_R}+\mathbb{T}_{ji_R})=\sum_j \mathbb{T}_{ji_R}=0\ .$$

Notice that in the second equality we have used the time-reversal property $\mathbb{T}_{ij}=\mathbb{T}_{j_Ri_R}$ and $\mathbb{T}_{ij_R}=\mathbb{T}_{ji_R}$. The final equality follows from the fact that sum-of-rows $\sum_j\mathbb{T}_{ji_R}=0$, because $\mathbb{T}$ is stochastic. A similar conclusion holds for $i\in\mathcal{R}_-$. Hence a stochastic $\mathbb{K}$ which respects Time-Reversal-Invariance (TRI) is automatically *doubly stochastic*, that is also the sum-of-colums is zero. Here is an explicit example with a 4×4 matrix: [7]

$$\mathbb{K}=\left[\begin{array}{cc|cc} -14 & 7 & 4 & 3\\ 2 & -21 & 3 & 16\\ \hline 3 & 9 & -14 & 2\\ 9 & 5 & 7 & -21 \end{array}\right] \tag{C.12}$$

Notice that $\mathbb{K}$ is *non-symmetric*, but doubly stochastic. [8]

The remarkable consequence of Eq. (C.11) is that $\mathbb{K}$ has the *right* eigenvector $(1\cdots1)^T$ with zero eigenvalue:

$$\mathbb{K}\cdot\begin{pmatrix}1\\ \vdots\\ 1\end{pmatrix}=0\ .$$

My guess (I still do not have a full proof of this statement, see discussion and problem below) [9] is that the equal-population vector

$$\mathbf{P}^{\rm eq}=\frac{1}{N_c}\begin{pmatrix}1\\ \vdots\\ 1\end{pmatrix}\ ,$$

is the $t\to\infty$ limit of the solution of our micro-canonical time-reversal-invariant master equation for any initial $\mathbf{P}_i(0)$.

The difficulty I still have is that, while $(1,\cdots,1)$ is both a left and a right eigenvector, the matrix $\mathbb{K}$ is still *non-symmetric*. The standard approach to such master equations is to *assume* what is called the *detailed balance condition*

$$\mathbb{K}_{ij}P^{\rm eq}_j=\mathbb{K}_{ji}P^{\rm eq}_i \qquad \forall i,j\ . \tag{C.13}$$

Detailed balance is a *sufficient* condition to reach equilibrium, which is also very useful to reduce yourself to a standard symmetric eigenvalue problem. In our case, detailed balance would imply

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[7] You realize that the number of parameters in the choice of $\mathbb{A}$, $\mathbb{B}$ and $\mathbb{C}$ is $L(2L+1)$, and the number of constraints for imposing stocasticity is $2L$, hence the number of free parameter for a TRI stochastic matrix is $L(2L-1)$. For $L=2$ you get a 6-dimensional space.

[8] A symmetric stochastic matrix is automatically (trivially) doubly stochastic.

[9] Sethna in [4][p.170] says that there is a proof also for the general non-symmetric case, but he does not give a reference for that.

that the matrix $\mathbb{K}$ is symmetric, $\mathbb{K}_{ij} = \mathbb{K}_{ji}$, which is not our case. Hence, we cannot *assume* detailed balance. [10] To show the simple consequences of having a symmetric $\mathbb{K}$, let us assume for a while that this is indeed the case. Then, the Perron-Frobenius theorem [4], see for instance `https://en.wikipedia.org/wiki/Perron-Frobenius_theorem`, would imply that the equal population vector we have discovered (which has all *positive components*) is the *unique* eigenvector with maximum eigenvalue $E_0 = 0$, all the other eigenvectors $\mathbf{P}_\lambda$ having negative eigenvalues $-E_\lambda$. Hence, if you expand your initial vector $\mathbf{P}(0)$ in terms of the eigenvectors:

$$\mathbf{P}(0) = \mathbf{P}^{\mathrm{eq}} + \sum_{\lambda>0} c_\lambda \mathbf{P}_\lambda \;,$$

you can immediately solve the master equation as:

$$\mathbf{P}(t) = \mathbf{P}^{\mathrm{eq}} + \sum_{\lambda>0} c_\lambda \mathrm{e}^{-E_\lambda t} \mathbf{P}_\lambda \;.$$

Hence, we would immediately conclude that, indeed, the final $t \to \infty$ probability distribution is the one associated to the $E_0 = 0$ eigenvalue (equal population over all cells). A similar result should hold for the general non-symmetric $\mathbb{K}$ we are dealing with, but I do not have a reference for that.

Returning to Boltzmann, you might have heard about his famous H-theorem. Essentially, Boltzmann introduced a function, which is strictly related to the entropy of a probability distribution which we have already encountered, which would read in the present case as:

$$\mathrm{H}(t) = \sum_i P_i(t) \log P_i(t) = -\mathbb{S}[\{P_i(t)\}] \;. \tag{C.16}$$

The content of Boltzmann's H-theorem is that H is a *non increasing* function of time:

$$\frac{\mathrm{dH}}{\mathrm{d}t} \le 0 \;. \tag{C.17}$$

Let us see how this result comes about. Take the derivative of $\mathrm{H}(t)$:

$$\begin{aligned}
\frac{\mathrm{dH}}{\mathrm{d}t} &= \sum_i \dot{P}_i \left(\log P_i + 1\right) \overset{\sum_i \dot{P}_i = 0}{=} \sum_i \dot{P}_i \log P_i \\
&= \sum_{ij} \mathbb{K}_{ij} P_j \log P_i \overset{\sum_i \mathbb{K}_{ij} = 0}{=} \sum_{ij} \mathbb{K}_{ij} P_j \left(\log P_i - \log P_j\right) \\
&= \frac{1}{2} \sum_{ij} \mathbb{K}_{ij} P_j \left(\log P_i - \log P_j\right) + \frac{1}{2} \sum_{ij} \mathbb{K}_{ji} P_i \left(\log P_j - \log P_i\right) \\
&= -\frac{1}{2} \sum_{ij} \left(\mathbb{K}_{ji} P_i - \mathbb{K}_{ij} P_j\right) \left(\log P_i - \log P_j\right) \\
&= -\frac{1}{2} \sum_{i \neq j} \left(\mathbb{K}_{ji} P_i - \mathbb{K}_{ij} P_j\right) \left(\log P_i - \log P_j\right) \;.
\end{aligned} \tag{C.18}$$

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[10] The detailed balance assumption is very often adopted in the theory of Markov chains and is at the basis of the proof that, for instance, a Metropolis Monte Carlo will sooner or later sample the correct equilibrium distribution. To see how detailed balance allows symmetrization, observe that the new matrix:

$$[\mathbb{H}]_{ij} = -\frac{1}{\sqrt{P_i^{\mathrm{eq}}}} \, \mathbb{K}_{ij} \, \sqrt{P_j^{\mathrm{eq}}} \;, \tag{C.14}$$

is symmetric, as implied by Eq. (C.13). Hence, by working with the new vector ψ_i such that $\mathbf{P}_i = \sqrt{\mathbf{P}_i^{\mathrm{eq}}}\,\psi_i$, you transform the master equation into an *imaginary time Schrödinger equation* of the form:

$$-\dot{\psi}_i = \sum_j [\mathbb{H}]_{ij} \, \psi_j \;. \tag{C.15}$$

You can prove that the spectrum of $\mathbb{H}$ is reversed with respect to that of $\mathbb{K}$, in particular $\mathbb{H}$ has eigenvalues $E_\lambda \ge 0$, while the eigenvectors are related in a very simple way.

And now comes the final part of the proof, which is I still miss in the general case of a non-symmetric $\mathbb{K}_{ij}$. Indeed, **if we have a symmetric** $\mathbb{K}_{ij} = \mathbb{K}_{ji}$, then you can rewrite:

$$\frac{\mathrm{dH}}{\mathrm{d}t} = -\frac{1}{2}\sum_{i\neq j} \mathbb{K}_{ij}\,(P_i - P_j)\,(\log P_i - \log P_j) \leq 0 \;, \tag{C.19}$$

where the final result follows from the fact that $(x-y)(\log x - \log y) \geq 0$ and $\mathbb{K}_{ij} \geq 0$ for $i \neq j$. At equilibrium $\mathrm{H}(t \to \infty)$ would then attain its *minimum value* given by $\mathrm{H} = -\log N_c$. Once again, a crucial missing step is to prove that the same result holds even when $\mathbb{K}$ is not symmetric, as in our case.

Assuming that the result holds true, which I am quite convinced, notice how the microscopic reversibility of the motion implied by time-reversal invariance, is in no way in contradition with the fact that $\mathrm{H}(t)$ is a decreasing function — or, equivalently, that entropy is an increasing function — of time.

Problem C.1. A micro-canonical time-reversal invariant master equation without detailed balance. Generate three random $L \times L$ (L an integer parameter of your choice) matrices $\mathbb{A}$, $\mathbb{B} = \mathbb{B}^T$, $\mathbb{C} = \mathbb{C}^T$ *non-negative elements* except for the diagonal elements of $\mathbb{A}$, impose the stochasticity constraints such that in such a way that the $2L \times 2L$ matrix $\mathbb{K}$

$$\mathbb{K} = \begin{pmatrix} \mathbb{A} & \mathbb{B} \\ \mathbb{C} & \mathbb{A}^T \end{pmatrix} \;,$$

is stochastic: $\sum_i \mathbb{K}_{ij} = 0$. Verify that the resulting $\mathbb{K}$ is automatically doubly-stochastic, i.e., $\sum_j \mathbb{K}_{ij} = 0$. Verify that $(1, \cdots, 1)$ is both right and left eigenvector of $\mathbb{K}$ with eigenvalue 0. Show that, starting from any initial condition $\mathbf{P}(0)$, the master equation

$$\dot{\mathbf{P}}(t) = \mathbb{K} \cdot \mathbf{P}(t) \;,$$

converges towards the equilibrium solution $\mathbf{P}^{\mathrm{eq}} = \frac{1}{2L}(1, \cdots, 1)^T$. Try different choices of $\mathbb{A}$, $\mathbb{B}$, $\mathbb{C}$. Verify if and when the Boltzmann H-theorem holds.

Bibliography

[1] D. Arovas. *Lecture Notes on Thermodynamics and Statistical Mechanics*, 2013.

[2] Luca Peliti. *Statistical Mechanics in a Nutshell.* Princeton University Press, 2011.

[3] Herbert B. Callen. *Thermodynamics And An Introduction To Thermostatistics.* Wiley, 2 edition, 1985.

[4] James P Sethna. *Statistical mechanics : entropy, order parameters, and complexity.* Oxford master series in statistical, computational, and theoretical physics. Oxford University Press, 2006.

[5] R. K. Pathria and P. D. Beale. *Statistical Mechanics.* Butterworth-Heinemann, 3rd edition edition, 2011.

[6] David MacKay. *Information Theory, Inference, and Learning Algorithms.* Cambridge University Press, 2003.

[7] A. I. Khinchin. *Mathematical Foundations of Statistical Mechanics.* Dover Publications, 1949.

[8] Joel L. Lebowitz and Oliver Penrose. Modern ergodic theory. *Phys. Today*, 26:23–29, 1973.

[9] R. Balescu. *Equilibrium and Non-Equilibrium Statistical Mechanics.* John Wiley & Sons, 1975.

[10] Adrian Patrascioi. The ergodic hypothesis. *Los Alamos Science*, 15:263–279, 1987.

[11] J.V. José and E.J. Saletan. *Classical Dynamics: A Contemporary Approach.* Cambridge University Press, 1998.

[12] J. G. Sinai. Ergodicity of Boltzmann's Gas Model. In T. A. Bak, editor, *Statistical Mechanics: Foundations and Applications*, page 559, 1967.

[13] Yakov G Sinai. Dynamical systems with elastic reflections. *Russian Mathematical Surveys*, 25(2):137, 1970.

[14] E. Fermi, J. Pasta, and S. Ulam. Studies of non linear problems. *Los Alamos Report No. LA-1940*, 1955.

[15] A.N. Kolmogorov. *Dokl. Akad. Nauk SSSR (N.S.)*, 98:527, 1954.

[16] V.I. Arnold. *Russ. Math. Surveys*, 18:9, 1963.

[17] J. Moser. *Nachr. Akad. Wiss. Göttingen Math.-Phys. Kl. II*, 1962:1, 1962.

[18] Giulio Biroli and Marc Mézard. Lattice glass models. *Phys. Rev. Lett.*, 88:025501, Dec 2001.

[19] G. Parisi, M. Mézard, and M. Virasoro. *Spin Glass Theory and Beyond.* World Scientific, 1987.

[20] T. Erber, B. Schweizer, and A. Sklar. Mixing transformations on metric spaces. *Communications in Mathematical Physics*, 29(4):311–317, 1973.

[21] A. Messiah. *Quantum mechanics.* Number v. 1 in Quantum Mechanics. North-Holland, 1965.

[22] J. von Neumann. Beweis des ergodensatzes und desh-theorems in der neuen mechanik. *Zeitschrift für Physik*, 57(1-2):30–70, 1929.

[23] J. von Neumann. Proof of the Ergodic Theorem and the H-Theorem in Quantum Mechanics. *Eur. Phys. J. H*, 35:201, 2010.

[24] Asher Peres. Ergodicity and mixing in quantum theory. i. *Phys. Rev. A*, 30:504, 1984.

[25] Mark Srednicki. Chaos and quantum thermalization. *Phys. Rev. E*, 50:888–901, 1994.

[26] M. Rigol, V. Dunjko, and M. Olshanii. Thermalization and its mechanism for generic isolated quantum systems. *Nature*, 452:854–858, 2008.

[27] Marcos Rigol and Mark Srednicki. Alternatives to eigenstate thermalization. *Phys. Rev. Lett.*, 108:110601, Mar 2012.

[28] Marlon Brenes, Silvia Pappalardi, John Goold, and Alessandro Silva. Multipartite entanglement structure in the eigenstate thermalization hypothesis. *Phys. Rev. Lett.*, 124:040605, Jan 2020.

[29] Anatoli Polkovnikov. Quantum ergodicity: fundamentals and applications, 2013. Available at: `http://physics.bu.edu/ asp/teaching/PY_747.pdf`.

[30] Mark Srednicki. Thermal fluctuations in quantized chaotic systems. *J. Phys. A*, 29:L75–L79, 1996.

[31] N. D. Mermin and H. Wagner. Absence of ferromagnetism or antiferromagnetism in one- or two-dimensional isotropic heisenberg models. *Phys. Rev. Lett.*, 17:1133–1136, Nov 1966.

[32] Zvi Friedman. Ising model with a transverse field in two dimensions: Phase diagram and critical properties from a real-space renormalization group. *Phys. Rev. B*, 17:1429–1432, Feb 1978.

[33] John B. Kogut. An introduction to lattice gauge theory and spin systems. *Rev. Mod. Phys.*, 51:659–713, Oct 1979.

[34] R. P. Feynman. *Statistical mechanics: A set of lectures.* Benjamin, 1972.

[35] J. W. Negele and H. Orland. *Quantum many-particle systems.* Addison-Wesley, 1988.