
Statistical Mechanics of Complex Systems

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Introduction

If you find any mistake/typo/missing thing, please write at francesco.manzali@studenti.unipd.it (or even just for feedback).

Francesco Manzali, 20/02/2019

About the missing lectures. Lectures 18/03, 19/03, 23/03, 25/03 and 26/03 are still missing, because of lack of time. I will try to keep up with the new lectures (especially the ones about different topics), and then return back to these lessons. If you want to help with transcription, please write to francesco.manzali@studenti.unipd.it

The contract is complete. Your wish has surpassed entropy. Now release your new power!
-Kyubey - Puella Magi Madoka Magica

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Statistical Mechanics

1.1 Introduction

Many interesting systems, such as the climate, cells and organisms, cities and societies, are inherently very difficult to model, and fall under the denomination of **complex systems**. One of their key feature is **emergence**, i.e. the presence of “cooperative” behaviours that originate from interactions of the system’s parts, and that cannot be explained by any single element of the system by itself¹.

(Lesson 1 of
9/3/20)
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It does not suffice to consider a large and *complicated* system to create a *complex* system. For example, a gas trapped in a piston is *complicated* - as it involves a large number of molecules -, but not *complex* - as it always reacts to changes in the same way: if the gas is compressed or expanded, the piston will just move towards the previous equilibrium state at a predictable rate.

Complicated vs.
complex

True complex systems react “**globally**” to small perturbations. Living organisms and packs of animals are one of the most evident case of complex system: for example see how **bird/fish flocks** alter their movement when approached by a predator. Most of them can’t even *see* the threat - yet they know, by observing each other, where to go next in order to avoid it.

Examples of
complex systems
1. Living

Non-living physical system at equilibrium can exhibit complex behaviours while being much simpler to analyse. One such example is given by **critical opalescence**, where a fluid is normally transparent to light, but if heated above a certain *critical temperature* T_c it suddenly becomes opaque. As we will see, this is due the fact that, close to T_c , density fluctuations in the fluid become really high - producing internal boundaries that refract or reflect rays of light, so that they cannot cross the fluid unaffected.

2. Physical

This behaviour depending on a **critical temperature** is a feature shared by many complex system.

Critical
temperature

For example, consider the **Ising model**, consisting in a set of locally interacting magnetic spins $\{S_i\}_{i=1,\dots,n}$. By simulation, we can show that, depending on the temperature, it exhibits two phases:

¹^The definitions here are deliberately fuzzy, as we are dealing with a huge class of very diverse systems. In fact, there is no single “clear-cut” definition for a “complex system”.

- **High temperature:** the spins S_i are randomly distributed, while the magnetization m , defined as:

$$m = \frac{1}{n} \sum_{i=1}^n S_i$$

is null. If the system is slightly perturbed, it relaxes quickly to $m = 0$

- **Low temperature:** the spins are all directed in the same direction, and a slight perturbation relaxes quickly to $m = 1$.

At the **critical temperature** T_c , exactly between the two phases, the system relaxes *very slowly* after a perturbation - taking order of magnitudes more time to return to the equilibrium magnetization state ($m = 0$). Spatially, the perturbation generates wild fluctuations of the spin states that propagate throughout the entire system, meaning that distant points become highly correlated, *as if* they were directly interacting, even when there are *no forces* between them). This is exactly what happens in the bird flock case, where the entire group “changes shape” at once reacting to the predator movement. So, in general, **locally perturbing** a complex system will produce changes over **all spatial and temporal scales**.

Thus, certain physical systems at equilibrium behave, at the critical temperature, **similarly** to complex living systems - and so become very interesting to study.

Living vs physical systems

1.1.1 Ingredients for a complex physical system

First of all, we wish to understand the *ingredients* of **physical** complex systems, the key aspects that are needed for emergent behaviours, and that distinguish truly *complex* systems from merely *complicated* ones. From the previous examples we saw that we should focus on *fluctuations*, and especially in how much the system changes (globally) after a perturbation. So, to have emergent behaviour we need:

Ingredients of emergent behaviour

- **Many degrees of freedom** (not necessary elementary particles, but “properties” that can be changed).
- **Interactions** among the degrees of freedom. The simplest kind is the pairwise *symmetric* interaction - but there are also more complex possibilities (e.g. *mediated* or *many-body* interactions)
- **Balance between Energy and Entropy.** A physical system **at equilibrium** exhibits long-range correlations, and thus complex behaviour, only when cooled at a **critical temperature** T_c , such that energy \mathcal{E} and entropy S are “balanced”:

$$\text{Energy}(T_c) \approx T_c \cdot \text{Entropy}(T_c) \quad (1.1)$$

The **energy** is defined as $\mathcal{E} = U + K$, where K is the kinetic energy of the system’s components, and U the potential term given by the interactions. On the other hand, the **entropy** S is proportional to the

Energy

Entropy

number of configurations (*realizations*) of the system's microstates that share the same macrostate, i.e. that lead to the same values of macroscopic observables (e.g. energy). In other words, S increases if there are “more configurations” of the system's components that lead to the same “overall result”.

To give some intuition for (1.1), consider a closed system (i.e. one that can exchange energy, but not particles) in a heat bath at constant temperature T . By consequence of the second law of thermodynamics, processes inside a closed system tend to maximise S if \mathcal{E} is constant, or minimize \mathcal{E} if S is constant². If \mathcal{E} nor S are constant, a *compromise* must be done, and another quantity (a thermodynamic potential) is minimized instead. For example, in the case of a system of fixed volume V , it is the **Helmholtz free energy**:

$$F = \mathcal{E} - TS \tag{1.2} \quad \text{Helmholtz free energy}$$

Physically, F quantifies the amount of the system's energy that can be used to perform useful work.

Now, note that if T is low, F is dominated by \mathcal{E} , meaning that the system at equilibrium will be in one of the minima of \mathcal{E} (ordered state). However, if T is sufficiently high, S prevails, and the system will reorganize itself so to occupy one of the states with maximum S - which are usually very different from the low energy ones (disordered state). *Intuition for criticality*

The critical temperature T_c sits at the boundary between these two phases, where little perturbations produce significant effects on the entire system's volume - which is exactly the kind of complex behaviour we are studying. In fact, fluctuations towards high S produces *disordered patches*, while ones in the opposite side lead to *ordered patches* - which then influence the neighbouring regions through the local interactions between degrees of freedom. These *wild fluctuations* allow the system to visit the regions of phase space that are specific of both low and high temperature (which are usually separated) *at the same time*.

In other words, a system at T_c is “tuned to respond to change”, and it does so over all spatial and temporal scales.

Unfortunately, (1.1) and the free energy (1.2) are only defined at **equilibrium**, leaving out all the interesting cases of non-equilibrium systems (e.g. living organisms). Finding a generalization of F that works also in non-equilibrium states is one of the current goals of research in statistical mechanics. *The non-equilibrium problem*

The desire to do so can only increase after observing that **all** physical systems at **criticality** exhibit very similar emergent/cooperative behaviours, depending only on system's dimensionality, and the symmetry and range (long/short) of interactions. This is, in essence, the concept of **universality**, one of the key ideas of theoretical physics. *Universality*

Universality allows to study many different systems with **minimal models** (or *null* models), where all the non-necessary details are left out, and only the *few* parameters relevant for criticality are analysed. These are way simpler to solve and model than the full cases, and so provide the opportunity of a deeper theoretical understanding.

Minimal models

1.1.2 The non-equilibrium case

While physical systems at criticality and living organisms are both examples of complex systems, the latter show remarkable and yet unexplained differences, leading to a list of deep questions in the field of Statistical Mechanics.

Unanswered questions

For examples, physical systems need to be *fine-tuned* to show an emergent behaviour, because they need to be inside a very specific patch of the phase-space sitting between different phases. Living systems, however, need not this kind of tuning - they are, in a sense, “always critical”. For example, a bird flock does not need a specific temperature nor a certain wind speed to react readily to a predator: it just does.

So, it is fair to ask at which point the analogy between non-equilibrium living organisms and equilibrium critical states must stop. *Do bird flocks share the same core mechanism of an Ising model, with just another layer of complexity on top - or are they just superficially similar, but inherently completely different?* If the former is true, how can they “self-tune” to be “always critical”?

More importantly: *does universality even hold for non-equilibrium complex systems?* If this were true, it would enable a generation of theorists to model all of these magnificent behaviours with a single framework.

In any case, even after confirming the analogy with critical systems, we must remember that we are not aiming for *specific predictions*, but seeking a general, understandable, explanation for complex phenomena. For example, with the critical system analogy we do not wish to predict tomorrow’s forecast, but rather unveil the typical patterns of Earth’s climate over millennia. For a specific application, such as weather forecasting or establishing the efficacy of a drug, it is best to use numerical models with thousands of parameters, *fitting* reality to the further decimal place. On the other hand, modelling with few parameters a critical system can give insight on the behaviour of many non-equilibrium system (as we noted before), such as:

Examples of systems with critical-like behaviours

- Bird and fish flocks
- Certain kinds of brain activity
- Ecosystems with high biodiversity (such as natural forests)
- Written communication (mails, text messages, social connections, memes...)
- River basins

²See “principle of minimum energy” and “principle of maximum entropy”.

1.1.3 Statistical Mechanics

Statistical mechanics is the branch of physics that deals with many-body systems, borrowing concepts from statistics, probability theory and quantum mechanics. It can be divided in:

- **Equilibrium Statistical Mechanics**, which extends classical thermodynamics, linking macroscopic observables (e.g. *pressure*, *temperature*) and thermodynamic quantities (e.g. *heat capacity*) to microscopic behaviour.
- **Non-equilibrium Statistical Mechanics** (or Statistical Dynamics), which models irreversible processes driven by imbalances - such as chemical reactions or flows of particles/heat.

In a more recent sense, Statistical Mechanics can be extended to generic (not necessarily inanimate) systems with many degrees of freedom formed by interacting parts. In this sense, Statistical Mechanics becomes the natural environment in which to study complex systems and emergent behaviour.

1.2 Review of Mathematical Methods

1.2.1 Continuous Random Variables

(Lesson 2 of
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Let X be a *continuous* random variable with probability distribution $p(x)$. Then:

- The probability of X assuming values in the interval $[a, b)$ is given by:

$$\mathbb{P}[a \leq X < b] = \int_a^b p(x) dx$$

- The probability distribution $p(x)$ represents the *infinitesimal* probability of X assuming a value *very close to* x :

$$\mathbb{P}(x \leq X < x + dx) = p(x) dx$$

- The expected value of a function of X (also called an **observable**) $O(X)$ is given by sampling many $X_i \sim p$ all **independently** and **identically**, and then computing the limit:

$$\begin{aligned} \langle O \rangle &= \lim_{n \rightarrow \infty} \frac{1}{n} \sum_{i=1}^n O(X_i) = \\ &= \int_{\mathbb{R}} p(x) O(x) dx \equiv \mathbb{E}[O(X)] \end{aligned}$$

Physically, this corresponds to *repeating many time the same measurement of O* , and averaging the results.

Exercise 1.2.1 (Some example distributions):

Consider the following distributions:

$$\text{Uniform} \quad p_1(x) = \begin{cases} 1 & 0 \leq x \leq 1 \\ 0 & \text{otherwise} \end{cases} \quad (1.3a)$$

$$\text{Exponential} \quad p_2(x) = \frac{1}{m} \exp\left(-\frac{x}{m}\right) \theta(x); \quad \theta(x) = \begin{cases} 1 & x > 0 \\ 0 & x < 0 \end{cases} \quad (1.3b)$$

$$\text{Gaussian} \quad p_3(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(x-m)^2}{2\sigma^2}\right) \quad (1.3c)$$

Evaluate $\langle X \rangle$, $\langle X^2 \rangle$ and $\text{Var}(X) = \langle X^2 \rangle - \langle X \rangle^2$ with the above three distributions (1.3a-1.3c). Are the three distributions correctly normalized, that is:

$$\int_{\mathbb{R}} p_i(x) dx \stackrel{?}{=} 1 \quad \forall i = 1, 2, 3$$

Solution.

1. The distribution is already normalized:

$$\int_{\mathbb{R}} p_1(x) dx = \int_0^1 1 dx = 1$$

The first two moments are:

$$\begin{aligned} \langle X \rangle &= \int_{\mathbb{R}} x p_1(x) dx = \int_0^1 x dx = \frac{x^2}{2} \Big|_0^1 = \frac{1}{2} \\ \langle X^2 \rangle &= \int_{\mathbb{R}} x^2 p_1(x) dx = \int_0^1 x^2 dx = \frac{x^3}{3} \Big|_0^1 = \frac{1}{3} \end{aligned}$$

And so the variance can be computed as:

$$\text{Var}(X) = \langle X^2 \rangle - \langle X \rangle^2 = \frac{1}{3} - \frac{1}{4} = \frac{1}{12}$$

2. We proceed exactly in the same way:

$$\begin{aligned} \int_{\mathbb{R}} p_2(x) dx &= \int_0^{+\infty} \frac{1}{m} \exp\left(-\frac{x}{m}\right) dx = -\exp\left(-\frac{x}{m}\right) \Big|_0^{+\infty} = 1 \\ \langle X \rangle &= \int_{\mathbb{R}} x p_2(x) dx = \int_0^{+\infty} \frac{x}{m} \exp\left(-\frac{x}{m}\right) dx = \\ &= \cancel{-x \exp\left(-\frac{x}{m}\right) \Big|_0^{+\infty}} + \int_0^{+\infty} \exp\left(-\frac{x}{m}\right) dx = -m \exp\left(-\frac{x}{m}\right) \Big|_0^{+\infty} = m \\ \langle X^2 \rangle &= \int_{\mathbb{R}} x^2 p_2(x) dx = \int_0^{+\infty} \frac{x^2}{m} \exp\left(-\frac{x}{m}\right) dx = \\ &= \cancel{-x^2 \exp\left(-\frac{x}{m}\right) \Big|_0^{+\infty}} - \cancel{2mx \exp\left(-\frac{x}{m}\right) \Big|_0^{+\infty}} - 2m \int_0^{+\infty} \exp\left(-\frac{x}{m}\right) dx = \end{aligned}$$

$$= -2m^2 \exp\left(-\frac{x}{m}\right) \Big|_0^{+\infty} = 2m^2$$

$$\text{Var}(X) = \langle X^2 \rangle - \langle X \rangle^2 = 2m^2 - m^2 = m^2$$

where in (a) and (b) we performed (multiple) integrations by parts.

3. As before:

$$\int_{\mathbb{R}} \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(x-m)^2}{2\sigma^2}\right) dx \underset{y=\frac{x-m}{\sqrt{2\sigma}}}{=} \int_{\mathbb{R}} \frac{dy}{\sqrt{\pi}} e^{-y^2} = \frac{\sqrt{\pi}}{\sqrt{\pi}} = 1$$

$$\langle X \rangle = \int_{\mathbb{R}} \frac{x}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(x-m)^2}{2\sigma^2}\right) dx = \int_{\mathbb{R}} \frac{\sqrt{2}\sigma y + m}{\sqrt{2\pi}\sigma} e^{-y^2} \cancel{\sqrt{2}\sigma} dy =$$

$$\underset{(a)}{=} \frac{m}{\sqrt{\pi}} \int_{\mathbb{R}} e^{-y^2} dy = m$$

In (a) we noted that the ye^{-y^2} term is an *odd* function integrated over a symmetric domain, and so it vanishes.

$$\langle X^2 \rangle = \int_{\mathbb{R}} \frac{x^2}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(x-m)^2}{2\sigma^2}\right) dx = \int_{\mathbb{R}} \frac{(\sqrt{2}\sigma y + m)^2}{\sqrt{2\pi}\sigma} e^{-y^2} \cancel{\sqrt{2}\sigma} dy =$$

$$= \int_{\mathbb{R}} \frac{2\sigma^2}{\sqrt{\pi}} y^2 e^{-y^2} dy + \int_{\mathbb{R}} \cancel{\frac{2\sqrt{2}\sigma m}{\sqrt{\pi}} ye^{-y^2}} dy + m^2 \int_{\mathbb{R}} \frac{1}{\sqrt{\pi}} e^{-y^2} dy =$$

$$= \frac{2\sigma^2}{\sqrt{\pi}} \int_{\mathbb{R}} y^2 e^{-y^2} dy + m^2$$

For the last integral, we note that:

$$\int_{\mathbb{R}} y^2 e^{-y^2} dy = -\frac{d}{ds} \int_{\mathbb{R}} e^{-sy^2} dy \Big|_{s=1}$$

and:

$$\int_{\mathbb{R}} e^{-sy^2} dy \underset{t=\sqrt{s}y}{=} \int_{\mathbb{R}} \frac{dt}{\sqrt{s}} e^{-t^2} = \sqrt{\frac{\pi}{s}}$$

meaning that:

$$\int_{\mathbb{R}} e^{-y^2} e^{-y^2} dy = -\frac{d}{ds} \sqrt{\frac{\pi}{s}} \Big|_{s=1} = \frac{\sqrt{\pi}}{2} s^{-3/2} \Big|_{s=1} = \frac{\sqrt{\pi}}{2}$$

Substituting in the previous expression we finally get:

$$\langle X^2 \rangle = \frac{2\sigma^2}{\sqrt{\pi}} \frac{\sqrt{\pi}}{2} + m^2 = \sigma^2 + m^2$$

$$\text{Var}(X) = \langle X^2 \rangle - \langle X \rangle^2 = \sigma^2$$

Exercise 1.2.2 (Variance properties):

Show that:

1. $\text{Var}(X) \equiv \langle (X - \langle X \rangle)^2 \rangle = \langle X^2 \rangle - \langle X \rangle^2$
2. $\min_a \langle (X - a)^2 \rangle = \text{Var}(X)$

Solution.

1. By using the linearity of the average:

$$\begin{aligned} \text{Var}(X) &= \langle (X - \langle X \rangle)^2 \rangle = \langle X^2 - 2X\langle X \rangle + \langle X \rangle^2 \rangle = \\ &= \langle X^2 \rangle - 2\langle X \rangle \langle X \rangle + \langle X \rangle^2 = \langle X^2 \rangle - \langle X \rangle^2 \end{aligned}$$

2. First we expand the square, and use again the linearity of the average:

$$\langle (X - a)^2 \rangle = \langle X^2 \rangle - 2a\langle X \rangle + a^2$$

To *minimize* this expression, we differentiate wrt a and set the derivative to 0:

$$\frac{d}{da} [\langle X^2 \rangle - 2a\langle X \rangle + a^2] = -2\langle X \rangle + 2a \stackrel{!}{=} 0 \Rightarrow a = \langle X \rangle$$

And substituting in the expression above we have:

$$\min_a \langle (X - a)^2 \rangle = \langle X^2 \rangle - 2\langle X \rangle \langle X \rangle + \langle X \rangle^2 = \langle X^2 \rangle - \langle X \rangle^2 = \text{Var}(X)$$

Exercise 1.2.3:

Consider the following pdf:

$$p(x) = (\alpha + 1)x^{-\alpha}\theta(x - 1)$$

For what values of $\alpha \in \mathbb{R}$ is it normalizable? Which moments $\langle x^k \rangle$, with $k \in \mathbb{R}$, are well defined?

Solution. We start by checking the normalization:

$$\int_{\mathbb{R}} p(x) dx = \int_1^{+\infty} (\alpha + 1)x^{-\alpha} dx$$

If $\alpha = 1$:

$$\int_1^{+\infty} \frac{1}{x} dx = \ln x \Big|_1^{+\infty} = +\infty$$

If $\alpha \neq 1$:

$$\int_1^{+\infty} \frac{1}{x^\alpha} dx = \frac{1}{1-\alpha} x^{1-\alpha} \Big|_1^{+\infty} = \begin{cases} +\infty & \alpha < 1 \\ -\frac{1}{1-\alpha} & \alpha > 1 \end{cases}$$

And so the integral certainly converges to a non-zero value for $\alpha > 1$:

$$\int_{\mathbb{R}} p(x) dx = \frac{\alpha + 1}{\alpha - 1} = A \quad \alpha > 1$$

meaning that $p(x)/A$ is normalized.

Note that the integral converges also for $\alpha = -1$, where the prefactor $(\alpha + 1)$ vanishes. However, in this case the integral is 0, and so it cannot be normalized to 1.

The k -th moment, with $k \in \mathbb{R}$ is given by:

$$\langle X^k \rangle = \int_1^{+\infty} (\alpha + 1)x^{k-\alpha} dx \quad \alpha > 1$$

This converges if $-(k - \alpha) = -k + \alpha > 1$, i.e. if $k < \alpha - 1$, to:

$$\langle X^k \rangle = -\frac{\alpha - 1}{1 - \alpha + k}$$

1.2.2 Discrete Random Variables

A discrete random variable X can only assume values inside a *discrete*, **countable** (or *denumerable*) set E . The probability of X assuming a value $\omega \in E$ is denoted by:

$$\mathbb{P}(X = \omega) \equiv \mathbb{P}_\omega$$

Given an observable $O(X)$, its possible outcomes are $O(X = \omega) \equiv O_\omega \quad \forall \omega \in E$, and its expected value is given by their average:

$$\langle O(X) \rangle = \sum_{\omega \in E} \mathbb{P}_\omega O_\omega$$

Exercise 1.2.4 (Examples of discrete random variables):

- a. Let X_i be a discrete random variable with only two possible values $E_i = \{0, 1\}$, with probabilities:

$$\mathbb{P}(X_i = 0) \equiv p; \quad \mathbb{P}(X_i = 1) = 1 - p$$

Consider n random variables $\{X_i\}_{i=1, \dots, n}$ that are **independently** and **identically distributed** like X (i.i.d.). Their sum is a new discrete random variable X that assumes values between 0 and n (included):

$$X = X_1 + \dots + X_n; \quad E_n = \{0, 1, \dots, n\}$$

Show that:

- i. The distribution of X is the **binomial distribution**:

$$p(k) = \mathbb{P}(X = k) = \binom{n}{k} p^k (1-p)^{n-k}; \quad \binom{n}{k} = \frac{n!}{k!(n-k)!} \quad (1.4)$$

- ii. $p(k)$ so defined is properly normalized:

$$\sum_{k=0}^n \mathbb{P}(X = k) = 1$$

- iii. Evaluate $\langle X \rangle$, $\langle X^2 \rangle$, $\text{Var}(X)$.

- b. As before, consider a set of n i.i.d. discrete random variables $\{X_i\}_{i=1,\dots,n}$, each following the same **Poisson distribution**:

$$\mathbb{P}(X_i = k) = \frac{\lambda^k}{k!} e^{-\lambda} \quad k \in \mathbb{N}; \quad E_i = \mathbb{N} \quad (1.5)$$

Consider their sum:

$$X = X_1 + \dots + X_n$$

Show that:

- i. The distribution of the sum X is:

$$\mathbb{P}(X = k) = \frac{(n\lambda)^k}{k!} e^{-n\lambda}$$

- ii. It is properly normalized:

$$\sum_{k=0}^{+\infty} \mathbb{P}(X = k) = 1$$

- iii. Evaluate $\langle X \rangle$, $\langle X^2 \rangle$, $\text{Var}(X)$.

Notice that the binomial distribution (1.4) in the case of *rare events* $p = \lambda/n$ with $k \ll n$ becomes:

$$\begin{aligned} \binom{n}{k} p^k (1-p)^{n-k} &= \frac{n(n-1) \cdots (n-k+1)}{k!} \left(\frac{\lambda}{n}\right)^k \left(1 - \frac{\lambda}{n}\right)^{n-k} \approx \\ &\approx \frac{n^k}{k!} \left(\frac{\lambda/n}{1 - \lambda/n}\right)^k \left(1 - \frac{\lambda}{n}\right)^n = \\ &= \frac{\lambda^k}{k!} \left(1 - \frac{\lambda}{n}\right)^{-k} \left(1 - \frac{\lambda}{n}\right)^n = \\ &= \frac{\lambda^k}{k!} \left[\exp\left(k \frac{\lambda}{n} + k \frac{\lambda^2}{n^2} + \dots\right) \right] \left[\exp\left(-n \frac{\lambda}{n} + \dots\right) \right] \approx \\ &\approx \frac{\lambda^k}{k!} e^{-\lambda} \end{aligned}$$

which is a Poisson distribution (1.5). This argument can be made more precise using more sophisticated methods, by introducing a scalar product in the space of distributions and prove *convergence in total variation*.

Solution.

1. $X = k$ if and only if there are exactly k variables $X_i = 1$, and the others are 0. This can happen in $\binom{n}{k}$ distinct ways. As the X_i are independent, the probability of any configuration is just the product of the probabilities of each state. In the case we are interested on, we have always exactly k states $X_i = 1$, and $n - k$ with $X_i = 0$, and so the total probability of each configuration will be $p^k(1 - p)^{n-k}$. Putting it all together we arrive to the binomial distribution:

$$p(k) = \mathbb{P}(X = k) = \binom{n}{k} p^k (1 - p)^{n-k}$$

2. Applying the binomial theorem we have:

$$\sum_{k=0}^n \mathbb{P}(X = k) = \sum_{k=0}^n \binom{n}{k} p^k (1 - p)^{n-k} = (p + [1 - p])^n = 1^n = 1$$

3. By direct computation:

$$\begin{aligned} \langle X \rangle &= \sum_{k=0}^n k \mathbb{P}(X = k) = \sum_{k=0}^n k \frac{n!}{(n-k)! k!} p^k (1 - p)^{n-k} = \\ &= \sum_{k=1}^n \frac{n(n-1)!}{(n-k)! (k-1)!} p^k (1 - p)^{n-k} = \\ &= n \sum_{k=1}^n \binom{n-1}{k-1} p^k (1 - p)^{n-k} = \end{aligned}$$

Now we factor out a p and sum and subtract a 1 so that everywhere we have $k - 1$:

$$= np \sum_{k=1}^n \binom{n-1}{k-1} p^{k-1} (1 - p)^{(n-1)-(k-1)}$$

And finally we shift the index of summation:

$$= np \sum_{k=0}^{n-1} \binom{n-1}{k} p^k (1 - p)^{(n-1)-k} =$$

Applying the binomial theorem leads to the result:

$$= np[p + (1 - p)]^{n-1} = np1^{n-1} = np$$

For the second moment we repeat the first few steps:

$$\begin{aligned} \langle X^2 \rangle &= \sum_{k=0}^n k^2 \mathbb{P}(X = k) = \sum_{k=0}^n k^2 \frac{n!}{(n-k)! k!} p^k (1 - p)^{n-k} = \\ &= \sum_{k=1}^n k \frac{n(n-1)!}{(n-k)! (k-1)!} p p^{k-1} (1 - p)^{(n-1)-(k-1)} = \\ &= np \sum_{k=0}^{n-1} (k+1) \binom{n-1}{k} p^k (1 - p)^{(n-1)-k} \end{aligned}$$

Expanding the multiplication:

$$= np \left[\sum_{k=0}^{n-1} k \binom{n-1}{k} p^k (1 - p)^{(n-1)-k} + \right.$$

$$+ \underbrace{\sum_{k=0}^{n-1} \binom{n-1}{k} p^k (1-p)^{(n-1)-k}}_1 =$$

Let $m = n - 1$ for simplicity. Note that for the first term we can repeat the same trick as before:

$$\begin{aligned} &= np \sum_{k=1}^m k \frac{m(m-1)!}{(m-k)!k(k-1)!} p p^{k-1} (1-p)^{(m-1)-(k-1)} + np = \\ &= np^2 m \sum_{k=1}^m \binom{m-1}{k-1} p^{k-1} (1-p)^{(m-1)-(k-1)} + np = \end{aligned}$$

And we shift once again the index of summation:

$$\begin{aligned} &= np^2 m \underbrace{\sum_{k=0}^{m-1} \binom{m-1}{k} p^k (1-p)^{(m-1)-k}}_1 + np = \\ &= np^2(n-1) + np = n^2 p^2 + np(1-p) \end{aligned}$$

Finally we can compute the variance:

$$\text{Var}(X) = \langle X^2 \rangle - \langle X \rangle^2 = n^2 p^2 + np(1-p) - n^2 p^2 = np(1-p)$$

Alternatively, we can re-derive the same results by using properties of the expectation and the variance. In fact X is a sum of X_i , each with:

$$\begin{aligned} \langle X_i \rangle &= 0 \cdot (1-p) + 1 \cdot p = p \\ \langle X_i^2 \rangle &= 0^2 \cdot (1-p) + 1^2 \cdot p = p \\ \text{Var}(X_i) &= \langle X_i^2 \rangle - \langle X_i \rangle^2 = p - p^2 = p(1-p) \end{aligned}$$

Then:

$$\begin{aligned} \langle X \rangle &= \sum_{i=1}^n \langle X_i \rangle = \sum_{i=1}^n p = np \\ \text{Var}(X) &= \sum_{i=1}^n \text{Var}(X_i) = \sum_{i=1}^n p(1-p) = np(1-p) \end{aligned}$$

1.2.3 Characteristic Functions

The **characteristic function** of a random variable X is defined as the Fourier transform of its pdf:

$$\varphi_X(\alpha) = \int_{\mathbb{R}} dx p(x) e^{i\alpha x} = \langle e^{i\alpha X} \rangle \quad (1.6)$$

$\varphi_X(\alpha)$ can be used to *generate* moments of X . Note that:

$$\varphi_X(\alpha) = \langle e^{i\alpha x} \rangle = \left\langle \sum_{n=0}^{+\infty} \frac{(i\alpha x)^n}{n!} \right\rangle \stackrel{(a)}{=} \sum_{n=0}^{+\infty} \frac{(i\alpha)^n}{n!} \langle x^n \rangle =$$

$$= 1 + i\alpha\langle x \rangle - \frac{\alpha^2}{2}\langle x^2 \rangle + \dots$$

where in (a) we used the linearity of the expected value. Then, by differentiating k times with respect to α and evaluating the derivative at $\alpha = 0$, all terms except the k -th vanish - meaning that the result is proportional to $\langle x^k \rangle$.

Explicitly:

$$\begin{aligned}\langle X \rangle &= -i \frac{\partial}{\partial \alpha} \varphi(\alpha) \Big|_{\alpha=0} \\ \langle X^2 \rangle &= (-i)^2 \frac{\partial^2}{\partial \alpha^2} \varphi(\alpha) \Big|_{\alpha=0} \\ &\vdots \\ \langle X^k \rangle &= \left(-i \frac{\partial}{\partial \alpha} \right)^k \varphi(\alpha) \Big|_{\alpha=0}\end{aligned}\tag{1.7}$$

In general, for a given distribution $\langle X^k \rangle$ may or may not exist - as it could possibly be a non-converging integral. Thanks to formula (1.7) we know that the k -th moment of a random variable X exists *if and only if* the k -th α -derivative of its respective characteristic function $\varphi_X(\alpha)$ exists.

Example 1 (Characteristic function of the gaussian):

Let's compute the characteristic function for the gaussian pdf. By definition (1.6), we have:

$$\varphi_m(\alpha) = \int_{\mathbb{R}} \frac{dx}{\sigma\sqrt{2\pi}} \exp\left(i\alpha x - \frac{(x-m)^2}{2\sigma^2}\right)$$

To simplify the integral, we perform a change of variables $x = y + m$, with unit jacobian:

$$\varphi_m(\alpha) = e^{im\alpha} \int_{\mathbb{R}} \frac{dy}{\sigma\sqrt{2\pi}} \exp\left(i\alpha y - \frac{y^2}{2\sigma^2}\right) = e^{im\alpha} \varphi_0(\alpha)\tag{1.8}$$

So we need to compute just $\varphi_0(\alpha)$. To do this, we rewrite: $e^{i\alpha y} = \cos(\alpha y) + i \sin(\alpha y)$, so that:

$$\varphi_0(\alpha) = \int_{\mathbb{R}} \frac{dy}{\sigma\sqrt{2\pi}} \exp\left(-\frac{y^2}{2\sigma^2}\right) (\cos(\alpha y) + i \sin(\alpha y)) =$$

Note that the sin term is an odd function, integrated over a symmetric domain, and so it vanishes, leaving only the cos term:

$$= \int_{\mathbb{R}} \frac{dy}{\sigma\sqrt{2\pi}} \exp\left(-\frac{y^2}{2\sigma^2}\right) \cos(\alpha y)$$

To compute this integral, we note that the derivative of $\varphi_0(\alpha)$ is proportional to $\varphi_0(\alpha)$ by a negative constant - meaning that we can reduce this problem to the solution of a differential equation. Explicitly:

$$\frac{d}{d\alpha} \varphi_0(\alpha) = - \int_{\mathbb{R}} \frac{dy}{\sigma\sqrt{2\pi}} \exp\left(-\frac{y^2}{2\sigma^2}\right) y \sin(\alpha y) =$$

We wish to have the same integrand as before, meaning that we need to convert the $\sin(\alpha y)$ to a $\cos(\alpha y)$. This can be done by integrating by parts. First, note that we can rewrite $y \exp(Ay)$ as a derivative of itself, adjusting the prefactor:

$$= \sigma^2 \int_{\mathbb{R}} \frac{dy}{\sigma\sqrt{2\pi}} \left[\frac{\partial}{\partial y} \exp\left(-\frac{y^2}{2\sigma^2}\right) \right] \sin(\alpha y) =$$

And finally we integrate by parts:

$$\begin{aligned} &= -\sigma^2 \int_{\mathbb{R}} \frac{dy}{\sigma\sqrt{2\pi}} \exp\left(-\frac{y^2}{2\sigma^2}\right) \frac{\partial}{\partial y} \sin(\alpha y) + \underbrace{\sigma^2 \exp\left(-\frac{y^2}{2\sigma^2}\right) \sin(\alpha y) \Big|_{-\infty}^{+\infty}}_0 = \\ &= -\alpha\sigma^2 \int_{\mathbb{R}} \frac{dy}{\sigma\sqrt{2\pi}} \exp\left(-\frac{y^2}{2\sigma^2}\right) \cos(\alpha y) = -\alpha\sigma^2 \varphi_0(\alpha) \end{aligned}$$

So we have transformed the integral in a first-order ordinary differential equation:

$$\frac{d}{d\alpha} \varphi_0(\alpha) = -\alpha\sigma^2 \varphi_0(\alpha) \Rightarrow \varphi_0(\alpha) = C \exp\left(-\frac{\alpha^2\sigma^2}{2}\right)$$

To compute the integration constant we note that:

$$\varphi_0(\alpha = 0) = \langle 1 \rangle + \sum_{n=1}^{+\infty} \frac{(i\alpha)^n \langle x^n \rangle}{n!} \Big|_{\alpha=0} = \langle 1 \rangle = 1$$

and so $C = 1$, leading to:

$$\varphi_0(\alpha) = \exp\left(-\frac{\alpha^2\sigma^2}{2}\right) \quad (1.9)$$

Then, substituting (1.9) in (1.8) we arrive at the final result:

$$\varphi_m(\alpha) = \exp\left(i\alpha m - \frac{\alpha^2\sigma^2}{2}\right)$$

Thanks to (1.7) we can use $\varphi_m(\alpha)$ to compute the gaussian moments:

$$\begin{aligned} \langle X \rangle &= -i \frac{\partial}{\partial \alpha} \varphi_m(\alpha) \Big|_{\alpha=0} = m \\ \langle X^2 \rangle &= \left(-i \frac{\partial}{\partial \alpha}\right)^2 \varphi_m(\alpha) \Big|_{\alpha=0} = -i \frac{\partial}{\partial \alpha} \left[(m + i\alpha\sigma^2) \exp\left(i\alpha m - \frac{\alpha^2\sigma^2}{2}\right) \right] \Big|_{\alpha=0} = \\ &= m^2 + \sigma^2 \end{aligned}$$

And finally the variance:

$$\text{Var}(X) = \langle X^2 \rangle - \langle X \rangle^2 = \sigma^2$$

Exercise 1.2.5 (Characteristic functions):

- a. Calculate the characteristic function of the uniform distribution (1.3a) and of the exponential distribution (1.3b), and re-obtain the results of exercise 1.2.1.
- b. Do the same for the binomial distribution (1.4) and the Poisson distribution (1.5), replicating the results of ex. 1.2.4. In the discrete case the definition of the characteristic function involves a *sum* instead of the integral:

$$\varphi(\alpha) = \sum_{\omega \in E} \mathbb{P}_{\omega} e^{i\omega\alpha}$$

- c. Verify the following useful formulas:

$$-i \frac{\partial}{\partial \alpha} \ln \varphi(\alpha) \Big|_{\alpha=0} = \langle X \rangle \quad (1.10a)$$

$$\left(-i \frac{\partial}{\partial \alpha} \right)^2 \ln \varphi(\alpha) \Big|_{\alpha=0} = \text{Var}(X) \quad (1.10b)$$

1.2.4 Generating functions

As we saw in (1.7) the characteristic function $\varphi_X(\alpha)$ can be manipulated by differentiation to obtain information about X . There are several other functions that share this same mechanism, and that are so-called **generating functions**.

One such example is given by the **probability generating function** for a discrete non-negative random variable X with $E = \mathbb{N}$, which is defined as the following:

$$G(z) \equiv \sum_{k=0}^{\infty} z^k \mathbb{P}(X = k) \quad (1.11)$$

Differentiating $G(z)$ and evaluating at $z = 1$ produces the *factorial moments* of X , i.e. the expected values of $X!/(X-l)!$:

$$\begin{aligned} \langle X \rangle &= \sum_{k=0}^{+\infty} k \mathbb{P}(X = k) = \frac{\partial}{\partial z} G(z) \Big|_{z=1} \\ \langle X(X-1) \rangle &= \frac{\partial^2}{\partial z^2} G(z) \Big|_{z=1} \\ &\vdots \\ \langle X(X-1) \cdots (X-l+1) \rangle &= \frac{\partial^l}{\partial z^l} G(z) \Big|_{z=1} \end{aligned}$$

We can produce the standard *moments* by applying a more complex operator to $G(z)$:

$$\left(z \frac{\partial}{\partial z} \right)^l G(z) \Big|_{z=1} = \langle X^l \rangle$$

Example 2 (Poisson generating function):

Consider the Poisson distribution:

$$\mathbb{P}(X = k) = \frac{\lambda^k}{k!} e^{-\lambda} \quad k \in \mathbb{N}$$

Its probability generating function is given by (1.11):

$$G(z) = \sum_{k=0}^{+\infty} z^k \mathbb{P}(X = k) = e^{\lambda(z-1)}$$

Note that:

$$G(1) = \sum_{k=0}^{+\infty} \mathbb{P}(X = k) = 1$$

by normalization. Then, by differentiation:

$$\begin{aligned} \langle X \rangle &= \left. \frac{\partial}{\partial z} G(z) \right|_{z=1} = \lambda \\ \langle X(X-1) \rangle &= \left. \frac{\partial^2}{\partial z^2} G(z) \right|_{z=1} = \lambda^2 = \langle X^2 \rangle - \langle X \rangle \end{aligned}$$

And so $\langle X^2 \rangle = \lambda^2 + \lambda$, leading to:

$$\text{Var}(X) = \langle X^2 \rangle - \langle X \rangle^2 = \lambda^2 + \lambda - \lambda^2 = \lambda$$

1.2.5 Change of variables

Often we know a functional relation between two random variables $Y = f(X)$, and we wish to compute the distribution of $Y \sim p_y$ given that of $X \sim p_x$.

To do this, note that the expected value of any generic observable $O(Y)$ can be computed in two ways: by using the distribution p_x and the correspondence $X \mapsto f(X)$, or directly with the distribution p_y :

$$\langle O(Y) \rangle = \int_{\mathbb{R}} dx O(f(x)) p_x(x) \quad (1.12a)$$

$$\langle O(Y) \rangle = \int_{\mathbb{R}} dy O(y) p_y(y) \quad (1.12b)$$

The trick is now to introduce a δ in (1.12a):

$$\begin{aligned} \langle O(Y) \rangle &= \int_{\mathbb{R}} dx O(f(x)) p_x(x) \underbrace{\int_{\mathbb{R}} dy \delta(y - f(x))}_1 = \\ &= \int_{\mathbb{R}} dy \int_{\mathbb{R}} dx p_x(x) O(f(x)) \delta(y - f(x)) = \\ &= \int_{\mathbb{R}} dy O(y) \int_{\mathbb{R}} dx p_x(x) \delta(y - f(x)) \stackrel{(1.12b)}{=} \int_{\mathbb{R}} dy O(y) p_y(y) \end{aligned}$$

As the equivalence holds for any arbitrary function $O(y)$, the two integrands must be the same, meaning that:

$$p_y(y) = \int_{\mathbb{R}} dx p_x(x) \delta(y - f(x)) = \langle \delta(y - f(X)) \rangle_{X \sim p_x} \quad (1.13)$$

Note that in the last expression the average is computed over the random variable X , whereas y is just a generic real number.

In the special case where the equation $y = f(x)$ is invertible, meaning that it has *only one solution* $x(y) = f^{-1}(y)$ for any value of y , we can obtain a simpler formula for the change of variables. We start by expanding $f(x)$ in Taylor's series around $x(y)$ in the rhs of (1.13):

$$\begin{aligned} \delta(y - f(x)) &= \delta[y - [f(x(y)) + (x - x(y))f'(x(y)) + \dots]] = \\ &= \delta[(x - x(y))f'(x(y))] = \frac{\delta(x - x(y))}{|f'(x)|} \end{aligned}$$

Leading to the formula:

$$p_y(y) = \frac{p_x(x(y))}{|f'(x(y))|} \quad (1.14)$$

The same formula can be obtained by graphical reasoning, as shown in fig. 1.1. The idea is that if $y \in [y, y + dy]$ with probability $p_y(y) dy$, then - as $y = f(x)$ is invertible - x must be in $[x, x + dx]$ with *the same probability* $p_x dx$, and with $x = x(y)$. So:

$$p_y(y) dy = p_x(x) dx \Rightarrow p_y(y) = p_x(x) \left| \frac{dx}{dy} \right| = p_x(x(y)) \left| \frac{dy}{dx} \right|^{-1} = \frac{p_x(x(y))}{|f'(x(y))|}$$

where the absolute value is needed because probabilities must be positive³

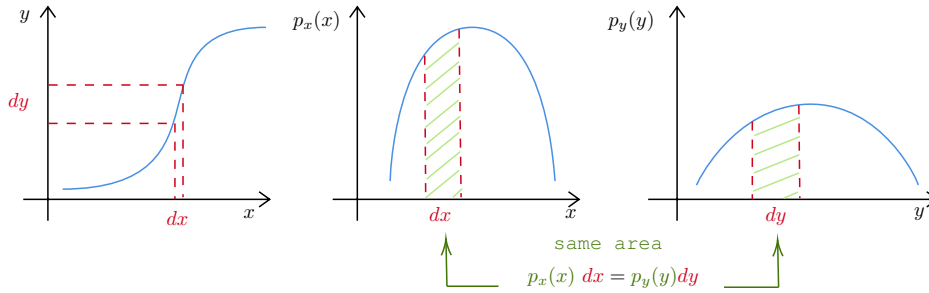


Figure (1.1) – If $y = f(x)$ is invertible on its range, then it is either strictly increasing or decreasing. This means that the preimage $f^{-1}(I)$ of an interval $I = [y, y + dy]$ is again an interval $J = [x, x + dx]$. Clearly, the probability of y being in I (which is the area in the central graph) must be the same of the probability of x being in J (the area in the graph to the right). By equating these two areas, we can derive formula (1.14)..

1.2.6 Generating probability distributions

Changes of random variables can be used to *simplify* the problem of sampling from a certain pdf. For example, suppose we are able to efficiently generate

³Formally, one should start by noting that if $y = f(x)$ is invertible, then it is either monotonically increasing or decreasing. The same reasoning can be applied to both cases, up to a sign difference. So, we can “unify” the two formulas by adding the absolute value.

random numbers that are **uniformly** distributed between 0 and 1, and that we denote with $Y \sim \mathcal{U}([0, 1])$, with:

$$p_y(y) = \begin{cases} 1 & y \in [0, 1] \\ 0 & \text{otherwise} \end{cases} = \mathbb{I}_{[0,1]} \quad (1.15)$$

We would like to determine a transformation $f(x)$ such that X has an exponential distribution:

$$p_x(x) = ae^{-ax}\theta(x) \quad a > 0 \quad (1.16)$$

Using formula (1.14) we impose:

$$\left| \frac{dy}{dx} \right| p_y(y) \stackrel{(1.15)}{=} \left| \frac{dy}{dx} \right| = p_x(x) = ae^{-ax}$$

Then the desired transformation $f(x) \equiv y(x)$ can be obtained by integrating and inverting:

$$y(x) = e^{-ax} \Rightarrow x = -\frac{1}{a} \ln y$$

Since $y \in [0, 1]$, we have that $x \geq 0$. Thus, if we generate y_i uniformly in $[0, 1]$, and then apply:

$$x_i = -\frac{1}{a} \ln y_i$$

the resulting x_i are distributed according to (1.16).

Exercise 1.2.6 (Inverse transform method):

If $Y \sim \mathcal{U}([0, 1])$, find the transformation f such that:

- a. $p_x(x) = x^{-2}\mathbb{I}_{[1,\infty)}(x)$
- b. $p_x(x) = |\beta|x^{\beta-1}\mathbb{I}_{[1,\infty)}(x)$, with $\beta < 0$
- c. $p_x(x) = \beta x^{\beta-1}\mathbb{I}_{(0,1]}(x)$, with $\beta > 0$
- d. $p_x(x) = \frac{1}{1+x^2} \frac{1}{\pi}$ (**Cauchy's distribution**), with $Y \sim \mathcal{U}([-\pi/2, \pi/2])$.

1.2.7 Gaussian Integrals

In Statistical Mechanics, many integrals involve **gaussian** functions.

These can be computed analytically in some quite general cases, as we now show, starting from the simplest case:

(Lesson 3 of
12/3/20)
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2020

$$I(b) \equiv \int_{\mathbb{R}} dx e^{-ax^2+bx} = \sqrt{\frac{\pi}{a}} \exp\left(\frac{b^2}{4a}\right) \quad a \in \mathbb{R}^+, b \in \mathbb{C} \quad (1.17)$$

Proof. When $b \in \mathbb{R}$, we can just *complete the square* in the exponential argument:

$$-ax^2 + bx = -a \left(x - \frac{b}{2a} \right)^2 + \frac{b^2}{4a}$$

So that the integral becomes:

$$I(b) = \int_{\mathbb{R}} dx \exp \left[-a \underbrace{\left(x - \frac{b}{2a} \right)^2}_{y^2} + \frac{b^2}{4a} \right]$$

We then *extract* the constant term from the integral, and change variables:

$$y = \left(x - \frac{b}{2a} \right) \sqrt{a}$$

So that $I(b)$ reduces to computing the integral of a standard gaussian:

$$I(b) = \frac{1}{\sqrt{a}} \exp \left(\frac{b^2}{4a} \right) \underbrace{\int_{\mathbb{R}} dy e^{-y^2}}_{\sqrt{\pi}} = \sqrt{\frac{\pi}{a}} \exp \left(\frac{b^2}{4a} \right)$$

In the case of $b = i\alpha$ (pure imaginary) we have:

$$I(i\alpha) = \varphi_0(\alpha)$$

where φ_0 is the characteristic function for the gaussian (with $a = 1/(2\sigma^2) \Rightarrow \sigma = (2a)^{-1/2}$) already computed in example 1 at pag. 17, which confirms the result (1.17).

Exercise 1.2.7 (General case):

Prove formula (1.17) in the most general case, where $b = \beta + i\alpha$.

Hint: translate the integration path in the complex plane, close it with the real line and apply the Cauchy Integral theorem.

It is useful to generalize (1.17) to the multidimensional case.

Let $\mathbf{x} \in \mathbb{R}^d$ and A a $d \times d$ **symmetric** and **positive definite** matrix, i.e. such that:

$$\mathbf{x}^T A \mathbf{x} \equiv \sum_{i,j=1}^d x_i A_{ij} x_j > 0 \quad \forall \mathbf{x} \neq \mathbf{0} \quad (1.18)$$

The multi-dimensional Gaussian integral is defined as:

$$I(A) \equiv \int_{\mathbb{R}^d} d^d \mathbf{x} e^{-\mathbf{x}^T A \mathbf{x}}$$

To solve it, the idea is to *decouple* all the n components, so that the integral becomes the product of n gaussian integrals of the type (1.17).

This is done by using the spectral decomposition of A . As it is symmetric, it has d eigenvectors $\mathbf{v}_\alpha = (v_{1\alpha}, \dots, v_{d\alpha})^T$ of eigenvalue λ_α (with $\alpha = 1, \dots, d$) that form an orthonormal basis of \mathbb{R}^d (spectral theorem):

$$\mathbf{v}_\alpha^T \mathbf{v}_\beta = \delta_{\alpha\beta}$$

If we then use the definition of eigenvector:

$$A\mathbf{v}_\alpha = \lambda_\alpha \mathbf{v}_\alpha$$

we arrive to:

$$\mathbf{v}_\beta^T A \mathbf{v}_\alpha = \lambda_\alpha \delta_{\alpha\beta} \quad (1.19)$$

Let V be the matrix with the orthonormal eigenvectors of A as columns: $V = (v_{\alpha\beta})_{\alpha,\beta=1,\dots,d}$. Then (1.19) can be put in matrix form:

$$V^T A V = \Lambda \stackrel{(a)}{\Rightarrow} A = V \Lambda V^T \quad (1.20)$$

where $\Lambda = \text{diag}(\{\lambda_\alpha\}_{\alpha=1,\dots,d}) = (\delta_{\alpha\beta} \lambda_\alpha)_{\alpha\beta=1,\dots,d}$, and in (a) we used the fact that V is an orthogonal matrix (as its columns are orthogonal to each other), and so $V^{-1} = V^T$. Equation (1.20) gives the **spectral decomposition** of A .

Substituting in the integral we get:

$$I(A) = \int_{\mathbb{R}^d} d^d \mathbf{x} e^{-\mathbf{x}^T A \mathbf{x}} = \int_{\mathbb{R}^d} d^d \mathbf{x} \exp(-\mathbf{x}^T V \Lambda V^T \mathbf{x})$$

Then we change variables $\mathbf{y} = V^T \mathbf{x} \Leftrightarrow \mathbf{x} = V \mathbf{y}$. The determinant of the jacobian is unitary, because V is orthogonal. In fact, starting from $V^T V = \mathbb{I}$, we have:

$$\begin{aligned} 1 = \det \mathbb{I} &= \det(V^T V) \stackrel{(a)}{=} (\det V^T)(\det V) \stackrel{(b)}{=} (\det V)(\det V) = (\det V)^2 \\ &\Rightarrow |\det V| = 1 \end{aligned} \quad (1.21)$$

where in (a) we applied Binet's formula, and in (b) $\det V^T = \det V$.

So we arrive to:

$$I(A) = \int_{\mathbb{R}^d} d^d \mathbf{y} e^{-\mathbf{y}^T \Lambda \mathbf{y}} = \prod_{\alpha=1}^d \int_{\mathbb{R}} dy_\alpha e^{-y_\alpha^2 \lambda_\alpha} \stackrel{(a)}{=} \prod_{\alpha=1}^d \sqrt{\frac{\pi}{\lambda_\alpha}}$$

where in (a) we use (1.17), as all components are now decoupled. To use (1.17) we need all λ_α to be positive - which is indeed true, because the matrix A is positive definite:

$$0 \stackrel{(1.18)}{<} \mathbf{v}_\alpha^T A \mathbf{v}_\alpha = \lambda_\alpha \mathbf{v}_\alpha^T \mathbf{v}_\alpha = \lambda_\alpha \|\mathbf{v}_\alpha\|^2 \Leftrightarrow \lambda_\alpha > 0$$

Finally, note that:

$$\det(A) \stackrel{(1.20)}{=} \det(V \Lambda V^T) = \cancel{\det(V^T)} \det(\Lambda) \cancel{\det(V)} \stackrel{(1.21)}{=} \det \Lambda = \prod_{\alpha=1}^d \lambda_\alpha$$

And so we can rewrite:

$$I(A) = \int_{\mathbb{R}^d} d^d \mathbf{x} e^{-\mathbf{x}^T A \mathbf{x}} = \prod_{\alpha=1}^d \sqrt{\frac{\pi}{\lambda_\alpha}} = \pi^{d/2} (\det A)^{-1/2} \quad (1.22)$$

Exercise 1.2.8 (Generalization):

Prove that:

$$I(A, \mathbf{b}) \equiv \int_{\mathbb{R}^d} d^d \mathbf{x} e^{-\mathbf{x}^T A \mathbf{x} + \mathbf{b}^T \mathbf{x}} = \pi^{d/2} (\det A)^{-1/2} \exp \left(\frac{1}{4} \mathbf{b}^T A^{-1} \mathbf{b} \right) \quad (1.23)$$

where A is a **symmetric, positive definite** $d \times d$ real matrix, and $\mathbf{b} \in \mathbb{C}^d$.

1.2.8 Saddle Point approximation

Let $f(\mathbf{x})$ be a function with a single minimum at \mathbf{x}_0 and such that:

$$I_f = \int_D e^{-Nf(\mathbf{x})} d^d \mathbf{x} \quad D \subset \mathbb{R}^d \quad (1.24)$$

Suppose that \mathbf{x}_0 is not on the boundary of D , meaning that there exists some $r > 0$ so that the sphere centred on \mathbf{x}_0 of radius r is entirely inside D :

$$\exists r > 0 \text{ s.t. } \{\mathbf{x} \in \mathbb{R}^d : |\mathbf{x} - \mathbf{x}_0| < r\} \subset D$$

We want to show that:

$$I_f \equiv \int_D e^{-Nf(\mathbf{x})} d^d \mathbf{x} = e^{-Nf(\mathbf{x}_0)} \left(\frac{2\pi}{N} \right)^{d/2} [\det(\partial_\alpha \partial_\beta f(\mathbf{x}_0))]^{-1/2} \cdot \left[1 + O\left(\frac{1}{N}\right) \right] \quad N \gg 1 \quad (1.25)$$

where $\partial_\alpha \partial_\beta f(\mathbf{x}_0)$ is the Hessian of $f(\mathbf{x})$ evaluated at $\mathbf{x} = \mathbf{x}_0$.

In other words, I_f for a *large enough* N , is equal (up to the gaussian pre-factor) to the maximum of the integrand $e^{-Nf(\mathbf{x})}$, which is obtained evaluating at the minimum of the function \mathbf{x}_0 .

To prove (1.25) we start by Taylor expanding $f(\mathbf{x})$ around its minimum \mathbf{x}_0 :

$$\begin{aligned} f(\mathbf{x}) = f(\mathbf{x}_0) &+ \sum_{\alpha=1}^d [x_\alpha - (\mathbf{x}_0)_\alpha] \partial_\alpha f(\mathbf{x}_0) + \frac{1}{2} \sum_{\alpha, \beta=1}^d [x_\alpha - (\mathbf{x}_0)_\alpha] [x_\beta - (\mathbf{x}_0)_\beta] \partial_\alpha \partial_\beta f(\mathbf{x}_0) + \\ &+ \frac{1}{3!} \sum_{\alpha, \beta, \gamma=1}^d [x_\alpha - (\mathbf{x}_0)_\alpha] [x_\beta - (\mathbf{x}_0)_\beta] [x_\gamma - (\mathbf{x}_0)_\gamma] \partial_\alpha \partial_\beta \partial_\gamma f(\mathbf{x}_0) + \dots \end{aligned}$$

Since \mathbf{x}_0 is a stationary point for f , all first derivatives vanish: $\partial_\alpha f(\mathbf{x}_0) = 0$.

Substituting in the integral we get:

$$\begin{aligned} I_f = \int_D d^d \mathbf{x} \exp \left(-N \left[f(\mathbf{x}_0) + \frac{1}{2} \sum_{\alpha, \beta=1}^d [x_\alpha - (\mathbf{x}_0)_\alpha] [x_\beta - (\mathbf{x}_0)_\beta] \partial_\alpha \partial_\beta f(\mathbf{x}_0) + \right. \right. \\ \left. \left. + \frac{1}{3!} \sum_{\alpha, \beta, \gamma=1}^d [x_\alpha - (\mathbf{x}_0)_\alpha] [x_\beta - (\mathbf{x}_0)_\beta] [x_\gamma - (\mathbf{x}_0)_\gamma] \partial_\alpha \partial_\beta \partial_\gamma f(\mathbf{x}_0) + \dots \right] \right) \end{aligned}$$

Note that $f(\mathbf{x}_0)$ is constant and can be brought outside the integral. The second term can be recognized as a multi-dimensional gaussian integral. In fact,

the Hessian $\partial_\alpha \partial_\beta f(\mathbf{x}_0)$ is surely symmetric (Schwartz theorem) and positive definite (\mathbf{x}_0 is a minimum). This suggests the following change of variable:

$$\mathbf{y} = \sqrt{N}(\mathbf{x} - \mathbf{x}_0); \quad \det \left| \frac{\partial \mathbf{x}}{\partial \mathbf{y}} \right| = N^{-d/2} \quad (1.26)$$

leading to:

$$I_f = \frac{\exp(-Nf(\mathbf{x}_0))}{N^{d/2}} \int_{D'} d^d \mathbf{y} \exp \left(-\frac{1}{2} \mathbf{y}^T A \mathbf{y} \right) \cdot \exp \left(-\frac{1}{3! \sqrt{N}} \sum_{\alpha, \beta, \gamma=1}^d y_\alpha y_\beta y_\gamma \partial_\alpha \partial_\beta \partial_\gamma f(\mathbf{x}_0) + O\left(\frac{1}{N}\right) \right)$$

where the matrix A is the Hessian: $A_{\alpha\beta} \equiv \partial_\alpha \partial_\beta f(\mathbf{x}_0)$, and D' is the new integration domain. Finally, we expand the second exponential to first order ($e^{-z} = 1 - z + \dots$):

$$I_f = \frac{\exp(-Nf(\mathbf{x}_0))}{N^{d/2}} \int_{D'} d^d \mathbf{y} \exp \left(-\frac{1}{2} \mathbf{y}^T A \mathbf{y} \right) \cdot \left(1 - \frac{1}{3! \sqrt{N}} \sum_{\alpha, \beta, \gamma=1}^d y_\alpha y_\beta y_\gamma \partial_\alpha \partial_\beta \partial_\gamma f(\mathbf{x}_0) + O\left(\frac{1}{N}\right) \right) \quad (1.27)$$

Note that the yellow term is *even* in \mathbf{y} , while the blue one is *odd*. So, when integrating, the third derivatives vanish, and only the even terms remain:

$$I_f = \frac{\exp(-Nf(\mathbf{x}_0))}{N^{d/2}} \int_{D'} d^d \mathbf{y} \exp \left(-\frac{1}{2} \mathbf{y}^T A \mathbf{y} \right) \left(1 + O\left(\frac{1}{N}\right) \right) =$$

All that's left is to compute the Gaussian integral:

$$\stackrel{(1.22)}{=} e^{-Nf(\mathbf{x}_0)} \left(\frac{2\pi}{N} \right)^{d/2} (\det A)^{-1/2} \quad (1.28)$$

Note that we are implicitly assuming that D' is symmetric about \mathbf{x}_0 (for the symmetry argument), and also that $D' = \mathbb{R}^d$ (for the gaussian integral). This is indeed true in the limit $N \rightarrow \infty$. In fact, we required that the original domain D contains a (small) spherical neighbourhood of \mathbf{x}_0 . Then, the change of variables (1.26) “stretches” D , such that the size of the resulting D' scales with N . It can be shown that approximating D' with the entire \mathbb{R}^d leads to an error that *vanishes exponentially*, and which is $\ll O(1/N)$. This is explored explicitly in the $d = 1$ in ex. 1.2.10.

To summarize, the saddle point approximation essentially states that an integral of the form I_N can be approximated, provided that N is large, with the value of the integrand calculated at its maximum (up to a multiplicative factor).

Exercise 1.2.9 (Gamma function):

The Γ function is defined as:

$$\Gamma(n) = \int_0^{+\infty} dx x^{n-1} e^{-x}$$

Show that:

- a. $\Gamma(n+1) = n\Gamma(n)$. Since $\Gamma(1) = 1$, we have that $\Gamma(n+1) = n!$ when $n \in \mathbb{N}$, meaning that the Γ function is a *generalization* of the factorial to the real case.
- b. $\Gamma(n+1) = \sqrt{2\pi n} \exp(n \ln n - n)(1 + O(1/n))$. This leads to **Stirling's approximation**:

$$\ln n! \underset{n \gg 1}{\approx} n \ln n - n + \frac{1}{2} \ln(2\pi n) + O\left(\frac{1}{n}\right)$$

Exercise 1.2.10 (Motivation of the saddle-point result):

Consider a one-dimensional example of the saddle-point approximation (1.24), with $f(x) = x^2$ and $D = [-r, r]$ (a small *neighbourhood* of $x = 0$ with radius $r > 0$). Show that the *error* in computing I_f over $F = \mathbb{R}$ rather than D decreases exponentially as $N \rightarrow \infty$:

$$0 < \int_{-\infty}^{+\infty} e^{-Nx^2} dx - \int_{-r}^{+r} e^{-Nx^2} dx < \frac{2}{\sqrt{N}} e^{-r^2 N}$$

In particular, this means that if we had kept track of that error in the d dimensional case (1.28) we would have had extra terms of order less than $N^{-d/2} e^{-r^2 N}$, which is $\ll O(1/N)$ - and so are irrelevant in the final result.

Exercise 1.2.11 (Saddle-point of a monotone increasing function):

Let $f(x)$ in (1.24) be a monotone increasing function $f: \mathbb{R} \rightarrow \mathbb{R}$. Show that:

$$\int_a^b e^{-Nf(x)} dx = \frac{e^{-Nf(a)}}{Nf'(a)} \left(1 + O\left(\frac{1}{N}\right) \right)$$

1.2.9 Gaussian averages

The multi-dimensional gaussian distribution is given by:

$$p_G(\mathbf{x}) \equiv \frac{(\det A)^{1/2}}{(2\pi)^{d/2}} \exp\left(-\frac{\mathbf{x}^T A \mathbf{x}}{2}\right) \quad (1.29)$$

The result we obtained in (1.22) confirms that (1.29) is properly normalized.

Then, by using (1.23) we can derive its characteristic function:

$$\varphi(\boldsymbol{\alpha}) = \langle e^{i\boldsymbol{\alpha} \cdot \mathbf{x}} \rangle = \int_{\mathbb{R}^d} d^d \mathbf{x} p_G(\mathbf{x}) e^{i\boldsymbol{\alpha} \cdot \mathbf{x}} = \exp \left(-\frac{1}{2} \boldsymbol{\alpha}^T A^{-1} \boldsymbol{\alpha} \right)$$

Then the first moment of the k -th component of (1.29) is:

$$\begin{aligned} \langle X_k \rangle &= \int_{\mathbb{R}^d} d^d \mathbf{x} x_k p_G(\mathbf{x}) = -i \frac{\partial}{\partial \alpha_k} \varphi(\boldsymbol{\alpha}) \Big|_{\boldsymbol{\alpha}=0} = \\ &= i \sum_{j=1}^d A_{kj}^{-1} \alpha_j \exp \left(-\frac{1}{2} \boldsymbol{\alpha}^T A^{-1} \boldsymbol{\alpha} \right) \Big|_{\boldsymbol{\alpha}=0} = 0 \quad k = 1, 2, \dots, d \end{aligned}$$

And the second moment of the k, l components is:

$$\begin{aligned} \langle X_k X_l \rangle &= \int_{\mathbb{R}^d} d^d \mathbf{x} x_k x_l p_G(\mathbf{x}) = \left(-i \frac{\partial}{\partial \alpha_l} \right) \left(-i \frac{\partial}{\partial \alpha_k} \right) \exp \left(-\frac{1}{2} \boldsymbol{\alpha}^T A^{-1} \boldsymbol{\alpha} \right) = \\ &= \exp \left(-\frac{1}{2} \boldsymbol{\alpha}^T A^{-1} \boldsymbol{\alpha} \right) \left[A_{kl}^{-1} - \sum_{m,n=1}^d A_{km}^{-1} A_{ln}^{-1} \alpha_m \alpha_n \right] \Big|_{\boldsymbol{\alpha}=0} = \\ &= A_{kl}^{-1} \end{aligned}$$

1.2.10 Central Limit Theorem

One of the most important results in statistics is the **Central Limit Theorem**, which states that the sum $S_n \equiv \sum_{i=1}^n X_i$ of n i.i.d. random variables $X_i \sim p(x)$ with $\langle X_i \rangle = \mu$ and *finite variance*:

$$\sigma^2 \equiv \langle X_i^2 \rangle - \langle X_i \rangle^2 < \infty$$

converges *in distribution* to a random variable with *gaussian* distribution.

More precisely, we consider a shifted and rescaled version of S_n :

$$Z_n \equiv \frac{S_n - n\mu}{\sigma\sqrt{n}}$$

such that $\langle Z_n \rangle = 0$ and $\text{Var}(Z_n) = 1$. Then the CDF of Z_n is that of a standard gaussian, in the limit of large n :

$$\mathbb{P}(Z_n < a) \xrightarrow{n \rightarrow \infty} \int_{-\infty}^a \frac{dx}{\sqrt{2\pi}} \exp \left(-\frac{x^2}{2} \right)$$

Equivalently⁴, this means that the pdf of Z_n is a standard gaussian $\mathcal{N}(0, 1)$ (with 0 mean and unit variance):

$$p_n(z) = \langle \delta(Z_n - z) \rangle \xrightarrow{n \rightarrow \infty} \frac{1}{\sqrt{2\pi}} \exp \left(-\frac{z^2}{2} \right) = \mathcal{N}(0, 1)$$

Proof. We start from the change of random variable formula:

$$p_n(z) = \langle \delta(Z_n - z) \rangle$$

⁴^The CDF for a random variable always exists. If it is differentiable, then we can compute the pdf - so the CLT theorem is actually more general in its CDF form. However, we will always work in the “nice cases” where the pdfs exist.

and we use the Fourier representation of the Dirac's delta:

$$\delta(x) = \int_{\mathbb{R}} \frac{d\alpha}{2\pi} e^{i\alpha x}$$

leading to:

$$p_n(z) = \langle \int_{\mathbb{R}} \frac{d\alpha}{2\pi} e^{i\alpha(Z_n - z)} \rangle = \int_{\mathbb{R}} \frac{d\alpha}{2\pi} e^{-i\alpha z} \langle e^{i\alpha Z_n} \rangle \quad (1.30)$$

As the X_i are all i.i.d., we can factorize the average:

$$\langle e^{i\alpha Z_n} \rangle = \langle \exp\left(-\frac{i\alpha n\mu}{\sigma\sqrt{n}}\right) \prod_{i=1}^n \exp\left(\frac{i\alpha X_i}{\sigma\sqrt{n}}\right) \rangle = \exp\left(-\frac{i\alpha\sqrt{n}\mu}{\sigma}\right) \prod_{i=1}^n \underbrace{\langle \exp\left(\frac{i\alpha X_i}{\sigma\sqrt{n}}\right) \rangle}_{\varphi(\alpha/(\sigma\sqrt{n}))}$$

and we recognize the *characteristic function* $\varphi(\alpha)$ of the X_i . Thus:

$$\langle e^{i\alpha Z_n} \rangle = \exp\left(-\frac{i\alpha\mu\sqrt{n}}{\sigma}\right) \left[\varphi\left(\frac{\alpha}{\sigma\sqrt{n}}\right) \right]^n \quad (1.31)$$

Then we rewrite the characteristic function by expanding the exponential:

$$\begin{aligned} \varphi(\alpha) &= \int_{\mathbb{R}} dx p(x) e^{i\alpha x} = \int_{\mathbb{R}} dx p(x) \left(1 + i\alpha x - \frac{\alpha^2 x^2}{2} + \dots \right) = \\ &= 1 + i\alpha\mu - \frac{\alpha^2}{2}(\sigma^2 + \mu^2) + O(\alpha^3) \end{aligned}$$

where we used $\langle X^2 \rangle = \sigma^2 + \mu^2$.

Note that we are implicitly assuming that the cubic moment of p exists - but in a more careful proof this would not be necessary.

To proceed, we need to rewrite $\varphi(\alpha)$ as an exponential:

$$\varphi(\alpha) = e^{\ln \varphi(\alpha)}$$

and we use the logarithm expansion $\ln(1+x) = x - x^2/2 + x^3/3 + \dots$ to compute:

$$\ln \varphi(\alpha) = i\alpha\mu - \frac{\alpha^2}{2}\sigma^2 + O(\alpha^3)$$

Substituting back in (1.31) we arrive to:

$$\langle e^{i\alpha Z_n} \rangle = \exp\left(-\frac{\alpha^2}{2} + O\left(\frac{1}{n}\right)\right)$$

And finally we can go back to (1.30), and compute the resulting gaussian integral in the large n limit:

$$p_n(z) = \int_{\mathbb{R}} \frac{d\alpha}{2\pi} \exp\left(-i\alpha z - \frac{\alpha^2}{2} + O\left(\frac{1}{\sqrt{n}}\right)\right) \xrightarrow{n \rightarrow \infty} \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{z^2}{2}\right) \quad \square$$

This concludes the proof.

Note that:

$$S_n = \frac{1}{n} \sum_{i=1}^n X_i \xrightarrow{n \rightarrow \infty} \mu = \langle X_i \rangle \text{ almost surely}$$

That is, the sample average of a *large number of samples* will be very close to the population average μ with a high probability. This convergence is, in a sense, the “probabilistic equivalent” of the usual convergence in \mathbb{R} .

However, Z_n converges *in distribution* (or weakly) to a random variable X with gaussian distribution.

1.3 Statistical Ensembles

The goal of **equilibrium statistical mechanics** is to **connect** the macroscopic behaviour of a system to the dynamics of its microscopical constituents. This allows to *rederive* the results of thermodynamics from a very different approach: instead of focusing directly on the observables, we try to deeply understand the *nature* of the system at hand.

We start our analysis from the case of a completely **isolated** system of N particles, encased in a volume V , which does not exchange particles nor energy with the outside world [1, Chapter 3].

Denote with \mathbf{r}_i and \mathbf{v}_i , with $i = 1, \dots, N$, the positions and velocities of the system’s particles, and with m_i their mass. We can organize all the positions and momenta in two $3N$ -dimensional vectors:

$$\begin{aligned} \mathbf{Q} &\equiv \left(\underbrace{x_1, y_1, z_1}_{\mathbf{r}_1}, \underbrace{x_2, y_2, z_2}_{\mathbf{r}_2}, \dots, \underbrace{x_N, y_N, z_N}_{\mathbf{r}_N} \right) \in \mathbb{R}^{3N} \\ \mathbf{P} &\equiv \left(\underbrace{p_{1x}, p_{1y}, p_{1z}}_{\mathbf{p}_1 = m_1 \mathbf{v}_1}, \underbrace{p_{2x}, p_{2y}, p_{2z}}_{\mathbf{p}_2 = m_2 \mathbf{v}_2}, \dots, \underbrace{p_{Nx}, p_{Ny}, p_{Nz}}_{\mathbf{p}_N = m_N \mathbf{v}_N} \right) \in \mathbb{R}^{3N} \end{aligned}$$

Let \mathbf{F}_i be the force acting on the i -th particle. In the classical case, the system’s dynamics is entirely determined by Newton’s laws of motion, which - for the i -th particle - state:

$$\begin{cases} \dot{\mathbf{r}}_i = \frac{d\mathbf{r}_i}{dt} = \frac{\dot{\mathbf{p}}_i}{m_i} \\ \dot{\mathbf{p}}_i = \frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i(\mathbf{Q}) \end{cases} \quad (1.32)$$

For a macroscopic system, N is in the order of 10^{23} (Avogadro’s number), meaning that:

1. It is not feasible to solve so many equations at the same time.
2. Even if we were able to solve 1, there would be no way to measure the required $6N$ initial conditions with a sufficient accuracy, nor to *store* such amount of information.

3. Even if 1 and 2 could be solved, the system's dynamics would likely prove to be **chaotic**, meaning that even for a simple choice of interaction, the trajectories would be extremely sensitive to initial conditions. In practice this would severely limit the timescale at which the model is accurate.

Furthermore, merely solving the dynamics with numerical methods does not produce any **understanding** of the system's behaviour - and so this huge computational task would give very little insight in the phenomena of interest. In fact, we are more interested in *global* observables, such as pressure or temperature, and not in the exact impact positions of molecules on a container's wall.

So, instead of tackling the system in (1.32) directly, in Statistical Mechanics we take a different approach. Consider the system's *phase space*, which is the space of coordinates $\Gamma = (\mathbf{Q}, \mathbf{P}) \in \mathbb{R}^{6N}$. Equations (1.32) describe a trajectory in phase-space. Given the chaotic dynamics of the particles, we suppose that, at **equilibrium**, the system can reach any state in the phase-space (compatibly with energy conservation), independently of the starting condition.

Moreover, we assume that all *possible states* (the ones with same energy) have the **same probability** of happening. We denote this postulate with \mathcal{H} .

All these states are “possible versions” of the same system. In principle, at any given time the system is at a given point $(\mathbf{Q}_0, \mathbf{P}_0)$, and follows a uniquely determined trajectory in phase-space. However, from the macroscopic point of view, all of these states are completely undistinguishable. So, with our imperfect knowledge, we can best describe the system only with a *probability distribution*, and talk about *expected values* of observables given that pdf. We call this distribution, made of “copies” of the system with very different microscopical dynamics but same macroscopic observables, a **statistical ensemble**. The \mathcal{H} postulate tells us that this pdf should be *uniform* - meaning that every state in the ensemble is treated equally. We call this specific pdf **microcanonical ensemble**.

So, let's find an expression for that probability distribution. We start by allowing the system to have an energy in an interval $(\mathcal{E}, \mathcal{E} + \delta E)$, and we will then take the limit $\delta \mathcal{E} \downarrow 0$.

This follows closely what can be done experimentally. In practice, we may not know the *exact* value of \mathcal{E} - every measurement will have a certain *uncertainty*. So, to us, systems with very similar energies will look the same - meaning that we need to account for that uncertainty in the statistical ensemble that we are constructing⁵. In principle, by repeating measurements for an *infinite* time, we could *restrict* the possible energy interval to a single value \mathcal{E}' .

So, if the energy is in $(\mathcal{E}, \mathcal{E} + \delta \mathcal{E})$, the possible states (\mathbf{Q}, \mathbf{P}) in phase-space are contained in a *thin energy shell* in that high-dimensional space, comprised between the hypersurfaces at fixed \mathcal{E} and $\mathcal{E} + \delta \mathcal{E}$. Then \mathcal{H} states that we can describe an isolate system with a **uniform distribution** over such energy shell.

⁵Recall that we introduced a probability distribution at first because of our imperfect knowledge of the microscopical states

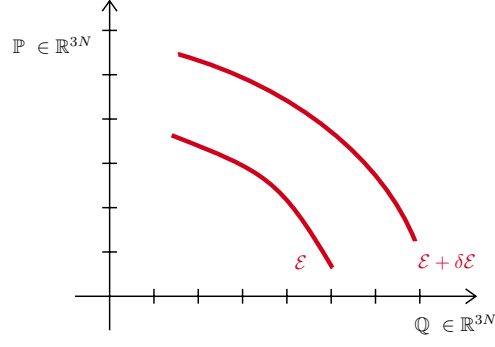


Figure (1.2) – Energy shell between \mathcal{E} and $\mathcal{E} + \delta\mathcal{E}$ in the microcanonical ensemble.

The energy associated with a certain microstate is given by the **Hamiltonian** function:

$$H(\mathbf{Q}, \mathbf{P}) = \sum_{i=1}^N \frac{\|\mathbf{p}_i\|^2}{2m_i} + U(\mathbf{Q}) \quad (1.33)$$

where $U(\mathbf{Q})$ is the potential energy associated with the (conservative) forces \mathbf{F}_i :

$$\mathbf{F}_i(\mathbf{Q}) = -\nabla_{\mathbf{r}_i} U = \left(-\frac{\partial U}{\partial x_i}, -\frac{\partial U}{\partial y_i}, -\frac{\partial U}{\partial z_i} \right)^T$$

We can rewrite Newton's equations (1.32) by using the Hamiltonian as follows:

$$\begin{aligned} \dot{q}_\alpha &= \frac{\partial H(\mathbf{Q}, \mathbf{P})}{\partial p_\alpha} & q_\alpha &\in \{x_i, y_i, z_i : i = 1, \dots, N\} \\ \dot{p}_\alpha &= -\frac{\partial H(\mathbf{Q}, \mathbf{P})}{\partial q_\alpha} & p_\alpha &\in \{p_{xi}, p_{yi}, p_{zi} : i = 1, \dots, N\} \end{aligned}$$

So the energy shell D between \mathcal{E} and $\mathcal{E} + \delta\mathcal{E}$ can be written as:

$$D \equiv \{(\mathbf{Q}, \mathbf{P}) : \mathcal{E} \leq H(\mathbf{Q}, \mathbf{P}) < \mathcal{E} + \delta\mathcal{E}\} \subset \mathbb{R}^{6N}$$

Then, as consequence of \mathcal{H} , we construct a uniform distribution over D :

$$\begin{aligned} \mathcal{P}(\mathbf{Q}, \mathbf{P}) &= \frac{1}{\mathcal{Z}} [\theta(\mathcal{E} + \delta\mathcal{E} - H(\mathbf{Q}, \mathbf{P})) - \theta(\mathcal{E} - H(\mathbf{Q}, \mathbf{P}))] = \\ &= \begin{cases} \frac{1}{\mathcal{Z}} & \mathcal{H} \in [\mathcal{E}, \mathcal{E} + \delta\mathcal{E}] \\ 0 & \text{otherwise} \end{cases} \end{aligned} \quad (1.34)$$

where \mathcal{Z} is just the normalization constant:

$$\mathcal{Z} = \int_{\mathbb{R}^{6N}} \underbrace{d^{3N}\mathbf{q} d^{3N}\mathbf{p}}_{d\Gamma} [\theta(\mathcal{E} + \delta\mathcal{E} - \mathcal{H}) - \theta(\mathcal{E} - \mathcal{H})] \quad (1.35)$$

where $H \equiv H(\mathbf{Q}, \mathbf{P})$ for brevity.

We then expand the difference of θ functions to first order:

$$\theta(\mathcal{E} + \delta\mathcal{E} - H) - \theta(\mathcal{E} - H) = \delta\mathcal{E} \frac{\partial}{\partial \mathcal{E}} \theta(\mathcal{E} - H) \approx \delta\mathcal{E} \delta(\mathcal{E} - H) \quad (1.36)$$

where we used the *distributional derivative* for the Heaviside function, which is the Dirac delta δ .

We neglect all higher orders in $\delta\mathcal{E}$, as, as we will then send $\delta\mathcal{E} \rightarrow 0$.

Substituting (1.36) in (1.35) we get:

$$\mathcal{Z} = \int_{\mathbb{R}^{6N}} d\mathbf{\Gamma} \delta(\mathcal{E} - H) \delta\mathcal{E} \equiv \Omega(\mathcal{E}) \delta\mathcal{E} \quad (1.37)$$

where we defined:

$$\Omega(\mathcal{E}) = \int_{\mathbb{R}^{6N}} d\mathbf{\Gamma} \delta(\mathcal{E} - H(\mathbf{Q}, \mathbf{P})) \quad (1.38)$$

We now substitute (1.36) and (1.37) in (1.34), leading to:

$$P(\mathbf{Q}, \mathbf{P}) = \frac{1}{\mathcal{Z}} \delta\mathcal{E} \cdot \delta(\mathcal{E} - H(\mathbf{Q}, \mathbf{P})) \underset{\delta\mathcal{E} \rightarrow 0}{=} \frac{\delta(\mathcal{E} - H(\mathbf{Q}, \mathbf{P}))}{\Omega(\mathcal{E}, V, N)} \quad (1.39)$$

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Then, we can compute the (microcanonical) average for any given observable $O(\mathbf{Q}, \mathbf{P})$ as follows:

$$\langle O \rangle = \int_{\mathbb{R}^{6N}} d\mathbf{\Gamma} P(\mathbf{Q}, \mathbf{P}) O(\mathbf{Q}, \mathbf{P}) \underset{\delta\mathcal{E} \rightarrow 0}{=} \frac{1}{\Omega} \int_{\mathbb{R}^{6N}} d\mathbf{\Gamma} \delta(\mathcal{E} - H(\mathbf{Q}, \mathbf{P})) O(\mathbf{Q}, \mathbf{P}) \quad (1.40)$$

1.3.1 Ideal gas

Now that we have obtained the microcanonical distribution, we can use it to compute thermodynamic quantities, such as energy, temperature, pressure.

To make explicit calculations we need to fix the *specifics* of the system we are working with, and in particular its **Hamiltonian** (1.33).

So, we start by considering the simplest possible case, where there are *no interactions* between the N particles, meaning that:

$$U_{\text{int}}(\mathbf{Q}) = 0 \quad (1.41)$$

Thus the Hamiltonian involves only *translational* kinetic energies:

$$H(\mathbf{Q}, \mathbf{P}) = \sum_{i=1}^N \frac{\|\mathbf{p}_i\|^2}{2m} = \frac{\|\mathbf{P}\|^2}{2m} \equiv H(\mathbf{P}) \quad (1.42)$$

This is the key hypothesis of the (monoatomic⁶) **ideal gas** model, which approximates the behaviour of real gases at sufficiently high temperature and low pressure.

However, *some amount of interaction* needs to be present if we want the gas to reach equilibrium. Otherwise, the $\|\mathbf{p}_i\|$ of each particle i would be conserved, meaning that the velocity distribution would remain always that of the initial state. So, more precisely, we consider:

$$0 \neq U(\mathbf{Q}) \ll |\mathcal{E}|$$

⁶^If we consider molecules we need also to account the *rotational kinetic energies*.

In this way we can study equilibrium and still neglect U_{int} in our calculations, as the kinetic energy always *prevails*.

Note that H in (1.42) depends only on \mathbb{P} , and so also the probability density of *configurations*, which can be obtained by *marginalizing* the joint pdf $\mathcal{P}(\mathbf{Q}, \mathbb{P})$ over \mathbb{P} , must be independent of \mathbf{Q} - and so it must be uniform over the “allowed” domain V_N :

$$P(\mathbf{Q}) = \int_{\mathbb{R}^{3N}} d^{3N}\mathbb{P} \mathcal{P}(\mathbf{Q}, \mathbb{P}) = \frac{1}{\Omega} \int_{\mathbb{R}^{3N}} d^{3N}\mathbb{P} \delta\left(\mathcal{E} - \frac{\|\mathbb{P}\|^2}{2m}\right) = \frac{1}{A} \mathbb{1}_{V_N}(\mathbf{Q}) \quad (1.43)$$

Here V_N is the subset of \mathbf{Q} containing the *possible* configurations, which are constrained to have a **fixed volume**:

$$V_N = \{Q_N \in \mathbb{R}^{3N} : (x_i, y_i, z_i) \in V, i = 1, \dots, N\}$$

And A is the normalization factor, given by:

$$A = \int_{V_N} d^{3N}\mathbf{Q} = \int_{V_N} \prod_{i=1}^N dx_i dy_i dz_i = \prod_{i=1}^N \underbrace{\int_V dx dy dz}_V = V^N \quad (1.44)$$

Substituting in (1.43) we arrive to:

$$\mathbb{P}(\mathbf{Q}) = \frac{1}{V^N} \mathbb{1}_{V_N}(\mathbf{Q}) = \begin{cases} \frac{1}{V^N} & \mathbf{r}_i \in V \forall i \\ 0 & \text{otherwise} \end{cases} \quad (1.45)$$

In the definition of Ω (1.38) we can then integrate over the \mathbf{Q} , which just leads to a factor of V^N , leading to:

$$\begin{aligned} \Omega(\mathcal{E}, V, N) &= \int_{\mathbb{R}^{6N}} d\Gamma \delta\left(\mathcal{E} - \frac{\|\mathbb{P}\|^2}{2m}\right) = \underbrace{\int_{V_N} d\mathbf{Q}}_{V^N} \underbrace{\int_{\mathbb{R}^{3N}} d\mathbb{P} \delta\left(\mathcal{E} - \frac{\|\mathbb{P}\|^2}{2m}\right)}_{\Omega_1(\mathcal{E}, N)} = \\ &\equiv V^N \Omega_1(\mathcal{E}, N) \end{aligned} \quad (1.46)$$

Fixed volume constraint. The constraint on the volume V is part of the *specification* of the system. In fact, more precisely, it appears as part of the potential term $U(\mathbf{Q})$ in H , describing the interaction between the gas particles and the walls.

Explicitly, we can write $U(\mathbf{Q})$ as a sum of two terms:

$$U(\mathbf{Q}) = U_{\text{int}}(\mathbf{Q}) + \sum_{i=1}^N u(\mathbf{r}_i)$$

Here $U_{\text{int}}(\mathbf{Q})$ describes the *particle-particle* interactions, and is such that $0 \neq |U_{\text{int}}(\mathbf{Q})| \ll \mathcal{E}$ as we have seen above. The second term, on the other hand, represents the *particle-wall* interactions. In particular, $u(\mathbf{r})$ is a **confining**

potential:

$$u(\mathbf{r}) = \begin{cases} 0 & \mathbf{r} \in V \\ +\infty & \mathbf{r} \notin V \end{cases}$$

So, all configurations with at least a particle $\notin V$ are assigned a *infinite* energy H , meaning that:

$$\delta(\mathcal{E} - H(\mathbf{Q}, \mathbf{P})) = \delta\left(\mathcal{E} - \frac{\mathbf{P}^2}{2m} - U(\mathbf{Q})\right)_{|U_{\text{int}}| \ll \mathcal{E}} \approx \delta\left(\mathcal{E} - \frac{\mathbf{P}^2}{2m} - \sum_{i=1}^N u(\mathbf{r}_i)\right) = 0 \quad \forall \mathcal{E}$$

as \mathcal{E} is always finite. It follows that the integrand of (1.43) is *null* outside V_N , and *constant* (as it does not depend on \mathbf{Q}) on the inside, leading back to:

$$\mathbb{P}(\mathbf{Q}) = \frac{1}{\Omega} \int_{\mathbb{R}^{3N}} d^{3N} \mathbf{P} \delta\left(\mathcal{E} - \frac{\mathbf{P}^2}{2m} - \sum_{i=1}^N u(\mathbf{r}_i)\right) = \frac{1}{V^N} \mathbb{1}_{V_N}(\mathbf{Q})$$

Probability distribution of the number of particles in half the volume

Consider the volume V as divided in two halves, V_L and V_R . To simplify notation, we *double* the number of particles in the entire system, meaning that now V contains $2N$ particles. We expect that, at any given instant, V_L and V_R will contain roughly N particles - half of the total number - up to some slight fluctuation.

We can *quantify* this argument by using the microcanonical ensemble.

Consider the probability P_m that, at a given instant at **equilibrium**, $N + m$ particles are found in V_R , with $m > 0$. According to (1.45), the probability of any configuration \mathbf{Q}_0 is the same. This means that configurations are distributed uniformly in V_{2N} , and - as all particles are independent - that each particle is uniformly distributed in V . So, for any given i , $\mathbf{r}_i \in V_R$ with probability $1/2$, because $V_R = V/2$ by definition.

Then P_m can be seen as the probability of *tossing* $2N$ coins and obtaining exactly $N + m$ heads, which is given by a binomial distribution:

$$P_m = \binom{2N}{N+m} \left(\frac{1}{2}\right)^{N+m} \left(1 - \frac{1}{2}\right)^{N-m} = \binom{2N}{N+m} 2^{-2N} \quad -N \leq m \leq N \quad (1.47)$$

When both $N \pm m$ are $\gg 1$ we can use the Stirling's approximation:

$$\ln n! = n \ln n - n + \frac{1}{2} \ln(2\pi n) + O\left(\frac{1}{n}\right) \quad (1.48)$$

to evaluate $\ln P_n$:

$$\begin{aligned} \ln P_m &= \ln \frac{2N!}{(2N - N - m)!(N + m)!} 2^{2N} = \\ &= -2N \ln 2 + \ln(2N)! - \ln(N + m)! - \ln(N - m)! = \end{aligned}$$

$$\begin{aligned}
&= -2N \ln 2 + \underbrace{2N \ln 2N}_{2N \ln 2 + 2N \ln N} - 2N + \frac{1}{2} \ln(4\pi N) + \\
&\quad - (N+m) \ln(N+m) + N - m - \frac{1}{2} \ln(2\pi(N+m)) + \\
&\quad - (N-m) \ln(N-m) + N + m - \frac{1}{2} \ln(2\pi(N-m)) + O\left(\frac{1}{N}\right) = \\
&= 2N \ln N + \frac{1}{2} \ln(4\pi N) - \frac{1}{2} \ln(2\pi[N+m]) - \frac{1}{2} \ln(2\pi[N-m]) \\
&\quad - (N+m) \ln(N+m) - (N-m) \ln(N-m) + O\left(\frac{1}{N}\right)
\end{aligned}$$

We then split the two highlighted terms, and group all terms with π :

$$\begin{aligned}
&= \frac{1}{2} \ln(4\pi N) - \ln(2\pi) + 2N \ln N - \frac{1}{2} \ln(N+m) - \frac{1}{2} \ln(N-m) + \\
&\quad - (N+m) \ln(N+m) - (N-m) \ln(N-m) + O\left(\frac{1}{N}\right) =
\end{aligned}$$

As both $N \pm m \gg 1$, $m/N \ll 1$, and so we can expand the logarithms:

$$\begin{aligned}
\ln(N+m) &= \ln\left(N\left(1+\frac{m}{N}\right)\right) = \ln N + \ln\left(1+\frac{m}{N}\right) = \\
&= \ln N + \frac{m}{N} - \frac{m^2}{2N^2} + O\left(\frac{1}{N^2}\right) \\
\ln(N-m) &= \ln N - \frac{m}{N} - \frac{m^2}{2N^2} + O\left(\frac{1}{N^2}\right)
\end{aligned}$$

In particular we substitute the second order expansion in the $N \ln(\dots)$ terms, and the first order expansion everywhere else, so that at the end all the error terms will be $O(1/N)$:

$$\begin{aligned}
P_m &= \frac{1}{2} \ln(4\pi N) - \ln(2\pi) + 2N \ln N - \ln N - \cancel{\frac{1}{2} \frac{m}{N}} + \cancel{\frac{1}{2} \frac{m}{N}} + O\left(\frac{1}{N}\right) + \\
&\quad - N \ln(N+m) - N \ln(N-m) - m \ln(N+m) + m \ln(N-m) = \\
&= \frac{1}{2} \ln(4\pi N) - \ln(2\pi) + \cancel{2N \ln N} - \ln N + \\
&\quad - \cancel{2N \ln N} - \cancel{N \frac{m}{N}} + \cancel{N \frac{m}{N}} + N \frac{m^2}{N^2} - m \left(\ln N + \frac{m}{N} \right) \\
&\quad - m \left(\ln N - \frac{m}{N} \right) + O\left(\frac{1}{N}\right) = \\
&= \ln\left(\frac{\sqrt{4\pi N}}{2\pi N}\right) + \frac{m^2}{N} - 2 \frac{m^2}{N} + O\left(\frac{1}{N}\right) = \\
&= -\frac{1}{2} \ln(\pi N) - \frac{m^2}{N} + O\left(\frac{1}{N}\right)
\end{aligned}$$

We can finally write:

$$P_m = e^{\ln P_m} \underset{N \gg 1}{=} \frac{1}{\sqrt{\pi N}} \exp\left(-\frac{m^2}{N}\right) = \mathcal{N}\left(0, \sqrt{\frac{N}{2}}\right) \quad (1.49)$$

Let N_R be the random variable representing the number of particles in V_R . We expect $N_R \approx N$ most of the time (here N is a number, not a r.v.). We then

define $M = N_R - N$ as the *difference* from the *expected state*, and note that M is a discrete random variable following the distribution given by P_m . So:

$$\langle M \rangle = 0; \quad \text{Var}(M) = \frac{N}{2} \quad (1.50)$$

Numbers and random variables. Sometimes we will denote a random variable (e.g. M) with the *same symbol* used for the values it assumes (m), and then write:

$$\langle m \rangle = 0; \quad \text{Var}(m) = \frac{N}{2} \quad (1.51)$$

This isn't rigorous mathematically, as M and m are very different *objects*: the former is a random variable, i.e. a measurable function from the sample space Ω to a measurable space E , while the latter is just a number. However, most of the times the correct *meaning* can be inferred from the context, and writing (1.51) frees us from defining another object (M) and reduces the cluttering in the notation. In general, whenever an expected value or variance is used, we are talking about random variables, and not numbers.

We know from probability theory that, most of the time, we will find M as being *close* to its mean. Quantitatively, the probability of M being inside a region $[-3\sigma, +3\sigma]$, with $\sigma = \sqrt{N/2}$ is given by:

$$\mathcal{P}(M \in [-3\sigma, +3\sigma]) = \int_{-3\sigma}^{3\sigma} \exp\left(-\frac{m^2}{2\sigma^2}\right) \frac{dm}{\sigma\sqrt{2\pi}} = \int_{-3}^3 \exp\left(-\frac{x^2}{2}\right) \frac{dx}{\sqrt{2\pi}} \approx 0.997$$

This means that, at any given time at equilibrium, with probability $p = 99.7\%$, the number of particles contained in V_R is inside $[N - 3\sigma, N + 3\sigma]$, i.e.:

$$N_R \in \left[N - 3\sqrt{\frac{N}{2}}, N + 3\sqrt{\frac{N}{2}} \right]$$

Dividing by the total number of particles $2N$ we can find the *fraction* of particles in the *right half*:

$$\frac{m}{2N} \in \left[\frac{1}{2} - \frac{3}{2\sqrt{2}} \frac{1}{\sqrt{N}}, \frac{1}{2} + \frac{3}{2\sqrt{2}} \frac{1}{\sqrt{N}} \right]$$

For $N \sim 10^{23}$, this fraction differs from $1/2$ less than 3.35×10^{-12} . So, in general, the two halves will contain *almost* the same number of particles, and significant deviations are so rare that they just never happen⁷.

This also means that the approximation $m/N \ll 1$ that we did to derive (1.49) is, effectively, always verified. In other words, even if $m \in \mathbb{Z}$ in (1.49) but is "capped" to $|m| \leq N$ in (1.47), the results are the same - because all values of m that are a significant fraction of N result in a negligible P_m . *Mathematically*, (1.49) is not the same of (1.47) due to approximations, but *physically* they are.

⁷Quantitatively, the probability that they happen even once during the entire age of the universe is negligible.

Exercise 1.3.1:

1. Using Stirling's approximation, prove that (1.47) becomes the gaussian (1.49) if $N \pm m \gg 1$.

(Already done in the notes)

2. Use the Central Limit Theorem to re-derive (1.49).

Hint: Introduce a random variable X_i which is -1 if the i -th particle is on the left volume and $+1$ if it is in the right volume. X_i are i.i.d. with $\mathbb{P}(X_i = \pm 1) = 1/2$ and $M = \frac{1}{2} \sum_{i=1}^N X_i$ is the number of particles exceeding N in V_R .

Velocity distribution

Velocity is related to momentum by $\mathbf{p}_i = m\mathbf{v}_i$, and we can find the momentum distribution $\rho_p(\mathbf{p})$ of a single particle from the joint pdf in (1.39), with a change of random variables:

$$\rho_p(\mathbf{p}) = \langle \delta^3(\mathbf{p}_i - \mathbf{p}) \rangle = \int_{\mathbb{R}^{6N}} d\Gamma \delta^3(\mathbf{p}_i - \mathbf{p}) \mathcal{P}(\mathbf{Q}, \mathbb{P}) =$$

We now factorize the integration over configurations \mathbf{Q} and that over momenta \mathbb{P} , apply the volume constraint to the former and arrive to:

$$\stackrel{(1.39)}{=} \frac{1}{\Omega(\mathcal{E}, V, N)} \underbrace{\int_{V_N} d\mathbf{Q}}_{V^N} \int_{\mathbb{R}^{3N}} d^{3N}\mathbb{P} \delta^3(\mathbf{p}_i - \mathbf{p}) \delta\left(\mathcal{E} - \frac{\|\mathbb{P}\|^2}{2m}\right) \quad (1.52)$$

Since all particles have the same mass and $d^{3N}\mathbb{P} = \prod_{i=1}^N d^3\mathbf{p}_i$, there is no way to distinguish them, meaning that all \mathbf{p}_i distribute the same. So, whatever i we choose in (1.52) we will get the same result at the end. For simplicity, let's fix $i = N$:

$$\rho_p(\mathbf{p}) = \frac{1}{\Omega} V^N \int_{\mathbb{R}^{3N}} d^{3N}\mathbb{P} \delta^3(\mathbf{p}_N - \mathbf{p}) \delta\left(\mathcal{E} - \frac{\|\mathbb{P}\|^2}{2m}\right)$$

Then we split the integration in two parts: one over the first $N - 1$ particles, and the other over the last one:

$$= \frac{1}{\Omega} V^N \int_{\mathbb{R}^{3(N-1)}} d^{3(N-1)}\mathbb{P}' \int_{\mathbb{R}^3} d^3\mathbf{p}_N \delta^3(\mathbf{p}_N - \mathbf{p}) \delta\left(\mathcal{E} - \frac{\|\mathbb{P}\|^2}{2m}\right)$$

where:

$$\mathbb{P}' = (p_{1x}, p_{2x}, p_{1z}, p_{2x}, p_{2y}, p_{2z}, \dots, p_{N-1,x}, p_{N-1,y}, p_{N-1,z}) \in \mathbb{R}^{3(N-1)}$$

We do the same for the norm of \mathbb{P} :

$$\mathbb{P}^2 = \|\mathbb{P}'\|^2 + \|\mathbf{p}_N\|^2 \quad (1.53)$$

leading to:

$$\rho_p(\mathbf{p}) = \frac{V^N}{\Omega} \int_{\mathbb{R}^{3(N-1)}} d^{3(N-1)}\mathbb{P}' \int_{\mathbb{R}^3} d^3\mathbf{p}_N \delta^3(\mathbf{p}_N - \mathbf{p}) \delta\left(\mathcal{E} - \frac{\|\mathbf{p}_N\|^2}{2m} - \frac{\|\mathbb{P}'\|^2}{2m}\right)$$

Finally we can integrate over \mathbf{p}_N and eliminate the δ^3 :

$$\begin{aligned}
&= \frac{V^N}{\Omega} \underbrace{\int_{\mathbb{R}^{3(N-1)}} d^{3(N-1)} \mathbb{P}' \delta \left(\mathcal{E} - \frac{\|\mathbf{p}\|^2}{2m} - \frac{\|\mathbb{P}'\|^2}{2m} \right)}_{\Omega_1(\mathcal{E}-p^2/(2m), N-1)} = \\
&\stackrel{(1.46)}{=} \frac{V^N}{V^N \Omega_1(\mathcal{E}, N)} \Omega_1 \left(\mathcal{E} - \frac{\|\mathbf{p}\|^2}{2m}, N-1 \right) = \frac{\Omega_1 \left(\mathcal{E} - \frac{\|\mathbf{p}\|^2}{2m}, N-1 \right)}{\Omega_1(\mathcal{E}, N)} \quad (1.54)
\end{aligned}$$

The result in (1.54) shows that the distribution of momenta $\rho_p(\mathbf{p})$ for a particle depends only on $\|\mathbf{p}\|^2$ - the modulus, not the direction of the argument - meaning that it is **rotation invariant**. In other words, $\rho_p(\mathbf{p})$ is a **isotropic distribution**: it “looks the same” in every direction.

To proceed we need to explicitly compute Ω_1 . This problem will be tackled in full detail later on, and for now we limit ourselves to just *extracting* the dependence of Ω_1 on energy \mathcal{E} . So we start from the definition in (1.46):

$$\Omega_1(\mathcal{E}, N) = \int_{\mathbb{R}^{3N}} d^{3N} \mathbb{P} \delta \left(\mathcal{E} - \frac{\|\mathbb{P}\|^2}{2m} \right)$$

The idea is to change variables so that we can factor \mathcal{E} inside the δ . So we extract a factor $\sqrt{2m\mathcal{E}}$ from \mathbb{P} :

$$\mathbb{P} = \sqrt{2m\mathcal{E}} \mathbb{X} \quad \frac{d^{3N} \mathbb{P}}{d^{3N} \mathbb{X}} = (\sqrt{2m\mathcal{E}})^{3N}$$

So that:

$$\Omega_1(\mathcal{E}, N) = (2m\mathcal{E})^{\frac{3N}{2}} \int_{\mathbb{R}^{3N}} d^{3N} \mathbb{X} \delta(\mathcal{E}[1 - \|\mathbb{X}\|^2])$$

We can then *extract* a constant factor from the δ as follows:

$$\delta(ax) = \frac{1}{|a|} \delta(x) \quad \forall a \in \mathbb{R}$$

leading to:

$$\begin{aligned}
\Omega_1(\mathcal{E}, N) &= (2m\mathcal{E})^{\frac{3N}{2}} |\mathcal{E}|^{-1} \underbrace{\int_{\mathbb{R}^{3N}} d^{3N} \mathbb{X} \delta(1 - \|\mathbb{X}\|^2)}_{\Omega_1(N)} = \\
&= \mathcal{E}^{\frac{3N}{2}-1} (2m)^{\frac{3N}{2}} \Omega_1(N) \quad (1.55)
\end{aligned}$$

where we dropped the modulus because $\mathcal{E} > 0$ since $\mathbb{P}^2/(2m) > 0$.

In this way we have *extracted* the dependence on \mathcal{E} from $\Omega_1(\mathcal{E}, N)$. The computation of the remaining integral $\Omega_1(N)$ will be tackled at another time.

Substituting (1.55) in (1.54) leads to:

$$\begin{aligned}
\rho_p(\mathbf{p}) &= \left(\mathcal{E} - \frac{\|\mathbf{p}\|^2}{2m} \right)^{\frac{3(N-1)}{2}-1} \mathcal{E}^{-\frac{3N}{2}+1} \cdot \frac{\Omega_1(N-1)}{\Omega_1(N)} (2m)^{-\frac{3}{2}} = \\
&= \left(1 - \frac{\|\mathbf{p}\|^2}{2m\mathcal{E}} \right)^{\frac{3N}{2}-1} \left(\mathcal{E} - \frac{\|\mathbf{p}\|^2}{2m} \right)^{-3/2} (2m)^{-3/2} \frac{\Omega_1(N-1)}{\Omega_1(N)} \quad (1.56)
\end{aligned}$$

We now take the **thermodynamic limit** $N \rightarrow \infty$. We expect \mathcal{E} to be proportional to N - as more particles means more kinetic energy. So, to get a meaningful limit, we need to fix the *energy per particle* ϵ :

$$\epsilon = \frac{\mathcal{E}}{N} \text{ constant } \quad \forall N \quad (1.57)$$

Substituting (1.57) in (1.56) we get:

$$\rho_p(\mathbf{p}) = \left(1 - \frac{\|\mathbf{p}\|^2}{2mN\epsilon}\right)^{\frac{3N}{2}-1} \left(N\epsilon - \frac{\|\mathbf{p}\|^2}{2m}\right)^{-3/2} (2m)^{-3/2} \frac{\Omega_1(N-1)}{\Omega_1(N)} \quad (1.58)$$

The first term of (1.58) becomes an exponential in the $N \rightarrow \infty$ limit, as consequence of the following theorem:

Theorem 1.3.1. *Let $f(x)$ and $g(x)$ be two functions such that $\lim_{x \rightarrow a} f(x) = \infty$ and $\lim_{x \rightarrow a} g(x) = 0$, with $\lim_{x \rightarrow a} f(x)g(x) = \lambda$ and $|\lambda| < \infty$, with $a \in \mathbb{R}$ or $a = \pm\infty$. Then:*

$$\lim_{x \rightarrow a} (1 + g(x))^{f(x)} = e^\lambda$$

In fact:

$$\left(1 - \underbrace{\frac{\|\mathbf{p}\|^2}{2mN\epsilon}}_{g(N)}\right)^{\overbrace{\frac{3N}{2}-1}^{f(N)}}$$

and $g(N) \rightarrow 0$, $f(N) \rightarrow \infty$, with:

$$\begin{aligned} \lim_{N \rightarrow \infty} g(N)f(N) &= \lim_{N \rightarrow \infty} -\frac{\|\mathbf{p}\|^2}{2mN\epsilon} \left(\frac{3N}{2} - 1\right) = \lim_{N \rightarrow \infty} -\frac{3}{2\epsilon} \frac{\|\mathbf{p}\|^2}{2m} + \frac{\|\mathbf{p}\|^2}{2mN\epsilon} = \\ &= -\frac{3}{2\epsilon} \frac{\|\mathbf{p}\|^2}{2m} \end{aligned}$$

and so:

$$\left(1 - \frac{\|\mathbf{p}\|^2}{2mN\epsilon}\right)^{\frac{3N}{2}-1} \underset{N \rightarrow \infty}{\sim} \exp\left(-\frac{3}{2\epsilon} \frac{\|\mathbf{p}\|^2}{2m}\right)$$

In the second term of (1.58) we ignore the part not scaling with N , and so:

$$\left(N\epsilon - \frac{\|\mathbf{p}\|^2}{2m}\right)^{-3/2} \underset{N \rightarrow \infty}{\sim} (N\epsilon)^{-3/2}$$

Putting everything together we arrive to:

$$\rho_p(\mathbf{p}) = \exp\left(-\frac{3}{2\epsilon} \frac{\|\mathbf{p}\|^2}{2m}\right) \underbrace{N^{-3/2} \frac{\Omega_1(N-1)}{\Omega_1(N)} (2m\epsilon)^{-3/2}}_{\text{Constant } C} \quad (1.59)$$

We can compute the constant term C by enforcing normalization:

$$\int_{\mathbb{R}^3} d^3\mathbf{p} \rho_p(\mathbf{p}) = C \int_{\mathbb{R}^3} d^3\mathbf{p} \exp\left(-\frac{3}{2\epsilon} \frac{\|\mathbf{p}\|^2}{2m}\right) \stackrel{!}{=} 1$$

meaning that:

$$\begin{aligned} C^{-1} &= \int_{\mathbb{R}^3} d^3\mathbf{p} \exp\left(-\frac{3}{2\epsilon} \frac{\|\mathbf{p}\|^2}{2m}\right) = \int_{\mathbb{R}} dp_x \int_{\mathbb{R}} dp_y \int_{\mathbb{R}} dp_z \exp\left(-\frac{3}{2\epsilon} \frac{p_x^2 + p_y^2 + p_z^2}{2m}\right) = \\ &= \left[\int_{\mathbb{R}} dp \exp\left(-\frac{3}{2\epsilon} \frac{\|\mathbf{p}\|^2}{2m}\right) \right]^3 = \left(\frac{4\pi\epsilon m}{3}\right)^{3/2} \end{aligned} \quad (1.60)$$

In particular:

$$\lim_{N \rightarrow \infty} N^{-3/2} \frac{\Omega_1(N-1)}{\Omega_1(N)} = \left(\frac{3}{2\pi}\right)^{3/2}$$

We will verify this relation when we will compute explicitly $\Omega_1(N)$.

Substituting (1.60) back in (1.59) we get:

$$\rho_P(\mathbf{p}) = \left(\frac{3}{4\pi\epsilon m}\right)^{3/2} \exp\left(-\frac{\|\mathbf{p}\|^2}{2m} \frac{3}{2\epsilon}\right) \quad \epsilon = \frac{\mathcal{E}}{N} \quad (1.61)$$

Or, equivalently, using the change of variable $\mathbf{p} = m\mathbf{v}$, the velocity distribution is given by:

$$\rho_v(\mathbf{v}) = \rho_p(\mathbf{p}) \underbrace{\left| \frac{d^3\mathbf{p}}{d^3\mathbf{v}} \right|}_{m^3} = \left(\frac{3m}{4\pi\epsilon}\right)^{3/2} \exp\left(-\frac{1}{2}m\|\mathbf{v}\|^2 \frac{3}{2\epsilon}\right) \quad (1.62)$$

In order to relate $\epsilon = \mathcal{E}/N$ to the temperature T , at least for this particular instance, we can calculate the gas pressure P (which is left as exercise), and then use the equation of state of the ideal gas known from experiments:

$$PV = nRT \quad (1.63)$$

where n is the number of moles in the gas, which is equal to N/N_A , with $N_A = 6.205 \times 10^{23}$ being Avogadro's number, $R = 8.315 \text{ J K}^{-1}$ the gas constant and $[T] = \text{K}$.

Exercise 1.3.2 (Pressure of an ideal gas):

Determine the pressure P of an ideal gas using eq. (1.61) or (1.62). In particular, determine:

- The flux of particles with velocity in the $d = 3$ interval $(v_x, v_x + dv_x) \times (v_y, v_y + dv_y) \times (v_z, v_z + dv_z)$
- The variation of the total momentum, $\Delta \mathbf{P}$, of the gas due to the collisions with an area A of the walls during a time interval Δt_i .
- The force undergone by the gas is therefore:

$$\lim_{\Delta t \rightarrow 0} \frac{\Delta \mathbf{P}}{\Delta t}$$

which must be equal in absolute value to $\mathbf{P} \cdot \mathbf{A}$.

See also exercise 3.4 of the textbook. Hint: use the result from exercise 1.3.3.

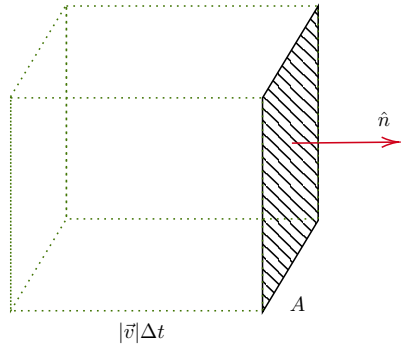


Figure (1.3) – Flux for a beam of particles perpendicular to a surface A .

Flux. Consider a beam of particles with velocity \mathbf{v} and numerical density $n_d = N/V$ (number of particles per unit volume). The number N_c of particles crossing a *flat* area A , with unit normal $\hat{\mathbf{n}} \parallel \mathbf{v}$, during a time interval Δt , is given by the total number of particles inside the green region in fig. 1.3, meaning that:

$$N_c = n_d \cdot \underbrace{\|\mathbf{v}\| \Delta t A}_{\text{Volume of the region}} \equiv \|\mathbf{J}\| \Delta t A \quad (1.64)$$

The quantity $\|\mathbf{J}\|$ defined by the relation (1.64) is called **flux**, and represents the number of particles crossing a unit area during a unit time interval. Comparing the left and right hand sides, we obtain the vector relation:

$$\mathbf{J} \equiv n_d \mathbf{v}$$

Exercise 1.3.3 (Flux: general case):

Show that for a generic $\hat{\mathbf{n}}$ (not necessarily $\parallel \mathbf{v}$), the number of particles crossing A during the time interval Δt is given by:

$$N_c = \Delta t A \mathbf{J} \cdot \hat{\mathbf{n}}$$

The comparison with the equation of state (1.63) of the ideal gas leads to identify:

$$T = \frac{2}{3} \frac{\mathcal{E}}{nR} \Leftrightarrow \mathcal{E} = \frac{3}{2} nRT \quad (1.65)$$

This result will be obtained also later when we will derive the equation of state directly from Statistical Mechanics.

Substituting (1.65) in (1.61) leads to:

$$\rho_p(\mathbf{p}) = (2\pi m k_B T)^{-3/2} \exp\left(-\frac{\|\mathbf{p}\|^2}{2m} \frac{1}{k_B T}\right)$$

where $k_B = R/N_A = 1.3807 \times 10^{-23} \text{ J K}^{-1}$ is the Boltzmann constant.

Equivalently, the velocity distribution is given by:

$$\rho_v(\mathbf{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m\|\mathbf{v}\|^2}{2k_B T}\right) \quad (1.66)$$

Exercise 1.3.4 (Speed averages):

- a. Use (1.66) to calculate the average speed, $\langle \|\mathbf{v}\| \rangle$, of particles in a gas at temperature T . Apply this for H_2 , He , N_2 , O_2 .

In order to calculate m , remember that $N_A \cdot m$ is the molar mass M_{mol} of the atom (or molecule) of a given gas. So, for example, $M_{\text{O}_2} = 2 \cdot 16 \text{ g} = 32 \text{ g}$ is the mass of a mole of O_2 , whereas $M_{\text{He}} = 2 \text{ g}$.

- b. Determine also $\langle v_\alpha \rangle$, $\langle |v_\alpha| \rangle$, and $\langle \|\mathbf{v}\|^2 \rangle$, with $\alpha \in \{x, y, z\}$. Compare $\langle |\mathbf{v}| \rangle$ with $\sqrt{\langle \|\mathbf{v}\|^2 \rangle}$ and notice how they depend on m and T .
- c. Determine the mean kinetic energy of a particle of H_2 , He , N_2 and O_2 at $T = 300 \text{ K}$.
- d. Determine the number of collisions n_c with a wall per unit time and unit area. Show that:

$$n_c = \frac{N}{V} \frac{\langle |v_\alpha| \rangle}{2} = \frac{P}{\sqrt{2\pi R M_{\text{mol}} T}} N_A$$

Show that at atmospheric pressure $P = 1 \text{ atm} = 1.013 \times 10^5 \text{ N m}^{-2}$, $T = 300 \text{ K}$ for a gas of O_2 , we have $n_c = 2.7 \times 10^{23} \text{ s}^{-1} \text{ m}^{-2}$.

Exercise 1.3.5:

- *Do exercise 3.3 in the textbook.*

Entropy and the Emergence of Time

(Lesson 14 of
8/4/20)
Compiled: June 2,
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Irreversibility is one of the fundamental aspects of reality as we know it - it describes why it is easy for things to break, scatter or decay, and why it is hard - or in certain cases impossible - to return them to their previous unscathed state. Irreversible processes are a key indicator of the *directionality* of time, physical remainders of the difference between the past we remember and the future we try to predict.

Statistical Mechanics allows us to understand - at least in part - why irreversibility exists, and where does it come from. In that regard, we will start our discussion by stating two important results: Liouville's theorem and the Poincaré Recurrence theorem.

The first deals with the evolution of ensembles, showing that patches of phase-space *flow* like incompressible fluids. This will provide both a stochastic origin of irreversibility and also a more convincing motivation for the microcanonical equiprobability postulate.

On the other hand, the Poincaré recurrence theorem will reveal the illusory nature of irreversibility, as given sufficient time everything can be reversed. However, Poincaré recurrence works on *unfathomably long* time scales - completely hiding its effects from our experience.

When talking about irreversibility, it is almost impossible not to include **entropy**, and the consequences of the *second law of thermodynamics*. After revising the two different definitions we gave of S - the one from classical thermodynamics, and the other from Statistical Mechanics - we will introduce a *third* point of view, originating from **information theory**, which will prove extremely useful - allowing us to re-derive the entire equilibrium statistical mechanics from a variational point of view, while offering several applications to other fields (social sciences, image reconstruction, etc.).

2.1 The Liouville theorem

Consider a physical system of N particles, with positions \mathbf{Q} and momenta \mathbf{P} :

$$\begin{aligned}\mathbf{Q} &= (q_{1x}, q_{1y}, q_{1z}, \dots, q_{Nx}, q_{Ny}, q_{Nz}) \\ \mathbf{P} &= (p_{1x}, p_{1y}, p_{1z}, \dots, p_{Nx}, p_{Ny}, p_{Nz})\end{aligned}$$

As we saw before, it is impossible to determine exactly \mathbf{Q} and \mathbf{P} . Practically, we can only measure with precision some *macroscopic quantities* (such as energy, volume, pressure...) and infer the possible *ranges* for the values of \mathbf{Q} and \mathbf{P} which are compatible with our observations, thus constructing a **probability distribution** $\rho(\mathbf{Q}, \mathbf{P})$ over the $6N$ -dimensional **phase space** Γ . We call the ρ so derived a *statistical ensemble*.

Statistical ensembles

In this chapter we are particularly interested in the *time evolution* of an initial $\rho_0(\mathbf{Q}, \mathbf{P})$.

Time evolution of an ensemble

We can obtain it by *sampling* M points from the initial ρ_0 - each representing a possible realization of *entire* system - then letting them evolve for some time t and seeing how they are distributed at the end. $M\rho(\mathbf{Q}, \mathbf{P}, t)$ will be the phase-space *density* of system-points in a tiny neighbourhood of (\mathbf{Q}, \mathbf{P}) . So, if we consider a tiny cube of volume $d^{3N}\mathbf{Q} d^{3N}\mathbf{P}$ centred at (\mathbf{Q}, \mathbf{P}) , the *total number* of system-points in it at instant t will be:

$$M\rho(\mathbf{Q}, \mathbf{P}, t) d^{3N}\mathbf{Q} d^{3N}\mathbf{P}$$

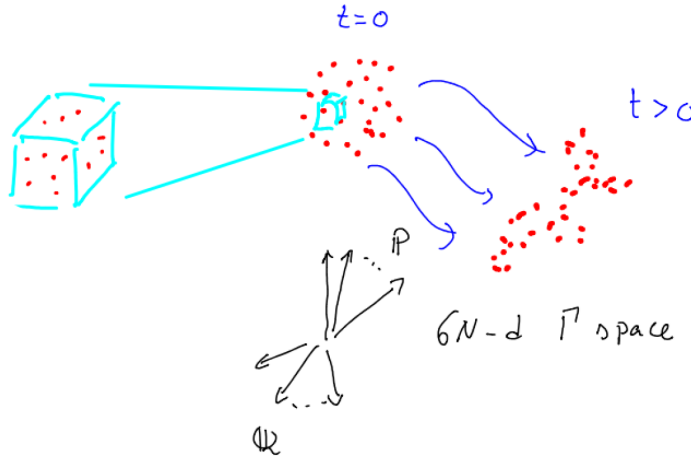


Figure (2.1) – Evolution of an ensemble of system-points in phase space

So, by computing how each system-point moves, and then measuring their *density* in phase-space, we can estimate the final probability distribution $\rho(\mathbf{Q}, \mathbf{P}, t)$, i.e. the *time evolution* of the original ensemble.

Each system-point initially at $(\mathbf{Q}(0), \mathbf{P}(0))$ *evolves* in time according to the Hamilton equations:

Evolution of a system-point

$$\dot{q}_\alpha = \frac{\partial H(\mathbf{Q}, \mathbf{P})}{\partial p_\alpha} \quad \alpha \in \{1x, 1y, 1z, \dots, Nx, Ny, Nz\} \quad (2.1)$$

$$\dot{p}_\alpha = -\frac{\partial H(\mathbf{Q}, \mathbf{P})}{\partial q_\alpha} \quad (2.2)$$

In the simplest case of N point-particles interacting through conservative forces depending only on positions, H is given by:

$$H(\mathbf{Q}, \mathbf{P}) = \sum_{i=1}^{3N} \frac{\|\mathbf{p}_i\|^2}{2m_i} + U(\mathbf{Q})$$

In this case (2.1) reduces to the second Newton's law:

$$m_\alpha \ddot{q}_\alpha = -\frac{\partial U(\mathbf{Q})}{\partial q_\alpha} \quad m_\alpha \equiv m_i \text{ if } \alpha \in \{ix, iy, iz\} \quad (2.3)$$

More complicated H can be constructed to describe the motion of more involved systems, such as *rigid bodies*, or to account more general forces, such as *magnetic ones* (which depend also on \mathbf{P}).

Liouville's theorem states that the probability density *along a trajectory* does not change during the time evolution:

Liouville's theorem

$$\frac{d}{dt}\rho(\mathbf{Q}(t), \mathbf{P}(t), t) = \frac{\partial \rho}{\partial t} + \sum_{\alpha=1}^{3N} \left(\frac{\partial \rho}{\partial q_\alpha} \dot{q}_\alpha + \frac{\partial \rho}{\partial p_\alpha} \dot{p}_\alpha \right) = 0 \quad (2.4)$$

where $(\mathbf{Q}(t), \mathbf{P}(t))$ is the solution of (2.1) with given initial conditions, and $\frac{d}{dt}$ denotes a *total derivative*, taking into account the time-dependence of also \mathbf{Q} and \mathbf{P} .

In other words, (2.4) means that if we follow a system-point during its evolution, and measure the *density* of other system-points travelling in its neighbourhood, we will find it unchanging. System-points *do not* “coalesce” together, nor “disperse” in phase-space - they behave like droplets of water, flowing and spreading, but never expanding nor compressing. In physical terms: probability in phase-space *flow* like an *incompressible fluid*.

Substituting (2.1) in (2.4) and rearranging we get:

$$\begin{aligned} \frac{\partial \rho}{\partial t}(\mathbf{Q}(t), \mathbf{P}(t), t) = & - \sum_{\alpha=1}^{3N} \left[\frac{\partial \rho}{\partial q_\alpha}(\mathbf{Q}(t), \mathbf{P}(t), t) \frac{\partial H}{\partial p_\alpha}(\mathbf{Q}(t), \mathbf{P}(t)) + \right. \\ & \left. - \frac{\partial \rho}{\partial p_\alpha}(\mathbf{Q}(t), \mathbf{P}(t), t) \frac{\partial H}{\partial q_\alpha}(\mathbf{Q}(t), \mathbf{P}(t)) \right] \end{aligned} \quad (2.5)$$

Note that in (2.4) we can fix any point (\mathbf{Q}, \mathbf{P}) and then find some appropriate initial conditions $(\mathbf{Q}(0), \mathbf{P}(0))$ such that the trajectory will pass through that point at time t , i.e. $(\mathbf{Q}(t), \mathbf{P}(t)) = (\mathbf{Q}, \mathbf{P})$.

So we can remove the time-dependence of $\mathbf{Q}(t)$ and $\mathbf{P}(t)$ in (2.5), leading to:

Liouville operator for time evolution

$$\begin{aligned} \frac{\partial}{\partial t}\rho(\mathbf{Q}, \mathbf{P}, t) = & - \sum_{\alpha=1}^{3N} \left[\frac{\partial \rho}{\partial q_\alpha}(\mathbf{Q}, \mathbf{P}, t) \frac{\partial H}{\partial p_\alpha}(\mathbf{Q}, \mathbf{P}) - \frac{\partial \rho}{\partial p_\alpha}(\mathbf{Q}, \mathbf{P}, t) \frac{\partial H}{\partial q_\alpha}(\mathbf{Q}, \mathbf{P}) \right] = \\ \equiv & -\{\rho, H\} = i\hat{L}\rho \end{aligned} \quad (2.6)$$

Where $\{\cdot, \cdot\}$ are the so-called **Poisson bracket**:

$$\{f, g\} \equiv \sum_{i=1}^n \left(\frac{\partial f}{\partial q_i} \frac{\partial g}{\partial p_i} - \frac{\partial f}{\partial p_i} \frac{\partial g}{\partial q_i} \right)$$

and \hat{L} is a linear operator called as the *Liouvillian* (or **Liouville operator**):

$$i\hat{L} \equiv \{\cdot, H\}$$

We can then use (2.6) as an evolution equation to compute $\rho(\mathbf{Q}, \mathbf{P}, t)$ given an initial condition $\rho(\mathbf{Q}, \mathbf{P}, 0) \equiv \rho_0(\mathbf{Q}, \mathbf{P})$ for any $t > 0$.

Since it is a linear differential equation in time, its formal solution can be written in terms of the *exponential* of the operator \hat{L} :

$$\rho(\mathbf{Q}, \mathbf{P}, t) = e^{-i\hat{L}t} \rho_0(\mathbf{Q}, \mathbf{P})$$

Proof. The idea is to compute explicitly the derivative in (2.6).

Proof of Liouville's theorem

The probability density $\rho(\mathbf{Q}, \mathbf{P}, t)$ at a given instant t can be obtained by *counting* all system-points that arrive at (\mathbf{Q}, \mathbf{P}) *from every possible origin* $(\mathbf{Q}_0, \mathbf{P}_0)$, weighting each of them with its “origin probability” $\rho_0(\mathbf{Q}_0, \mathbf{P}_0)$:

$$\rho(\mathbf{Q}, \mathbf{P}, t) = \int_{\Gamma} \underbrace{d^{3N} \mathbf{q}_0 d^{3N} \mathbf{p}_0}_{d\Gamma_0} \delta^{3N}(\mathbf{Q}(t) - \mathbf{Q}) \delta^{3N}(\mathbf{P}(t) - \mathbf{P}) \rho_0(\mathbf{Q}_0, \mathbf{P}_0) \quad (2.7)$$

In this notation, δ^{3N} is the *product* of $3N$ δ s. For example, for the positions we have:

$$\delta^{3N}(\mathbf{Q}(t) - \mathbf{Q}) \equiv \prod_{\alpha=1}^{3N} \delta(q_{\alpha}(t) - q_{\alpha})$$

and a similar expression holds for the momenta.

On the other hand, $\mathbf{Q}_0, \mathbf{P}_0$ are the initial conditions for the motion $(\mathbf{Q}(t), \mathbf{P}(t))$, i.e. $(\mathbf{Q}(t=0), \mathbf{P}(t=0)) = (\mathbf{Q}_0, \mathbf{P}_0)$. So, in the integral (2.7) the $(\mathbf{Q}(t), \mathbf{P}(t))$ **depend** (implicitly) on the origin coordinates $(\mathbf{Q}_0, \mathbf{P}_0)$.

In the following, to simplify notation, we denote $d\Gamma_0 \equiv d^{3N} \mathbf{q}_0 d^{3N} \mathbf{p}_0$.

Differentiating (2.7) with respect to t we get:

$$\begin{aligned} \frac{\partial}{\partial t} \rho(\mathbf{Q}, \mathbf{P}, t) &= \frac{\partial}{\partial t} \int_{\Gamma} d\Gamma_0 \delta^{3N}(\mathbf{Q}(t) - \mathbf{Q}) \delta^{3N}(\mathbf{P}(t) - \mathbf{P}) \rho_0(\mathbf{Q}_0, \mathbf{P}_0) = \\ &\stackrel{(a)}{=} - \int_{\Gamma} d\Gamma_0 \rho_0(\mathbf{Q}_0, \mathbf{P}_0) \sum_{\alpha=1}^{3N} \left[\dot{q}_{\alpha}(t) \frac{\partial}{\partial q_{\alpha}} + \dot{p}_{\alpha}(t) \frac{\partial}{\partial p_{\alpha}} \right] \cdot \\ &\quad \cdot \delta^{3N}(\mathbf{Q}(t) - \mathbf{Q}) \delta^{3N}(\mathbf{P}(t) - \mathbf{P}) \end{aligned} \quad (2.8)$$

The $-$ sign comes from the definition of *distributional derivative* - see the following green box for more information.

Derivative of the Dirac-delta. δ is a *distribution*, and so its derivative is defined by its *action* on test functions $\varphi \in \mathcal{S}(\mathbb{R})$:

$$\langle \delta', \varphi \rangle \equiv -\langle \delta, \varphi' \rangle = -\varphi'(0) \quad \forall \varphi \in \mathcal{S}(\mathbb{R})$$

This definition is motivated by the following *formal* manipulation:

$$\langle \delta', \varphi \rangle = \int_{\mathbb{R}} dx \delta'(x) \varphi(x) \underset{\text{by parts}}{=} \left. \varphi(x) \delta(x) \right|_{x=-\infty}^{x=+\infty} - \int_{\mathbb{R}} dx \delta(x) \varphi'(x) = -\varphi'(0)$$

The same relation can be generalized to partial derivatives in higher dimension. For example, let $\mathbf{r} = (x, y, z)^T$. Then:

$$\left\langle \frac{\partial}{\partial x} \delta^3, \varphi \right\rangle \equiv -\frac{\partial}{\partial x} \varphi(\mathbf{0}) \quad \forall \varphi \in \mathcal{S}(\mathbb{R}^3)$$

If the argument of the delta is shifted, so it will be in the result. Let $\delta_{\mathbf{r}_0}^3 \equiv \delta(\mathbf{r} - \mathbf{r}_0)$. Then:

$$\left\langle \frac{\partial}{\partial x} \delta_{\mathbf{r}_0}^3, \varphi \right\rangle \equiv -\frac{\partial}{\partial x} \varphi(\mathbf{r}_0) \quad (2.9)$$

Let's consider the time-derivative of just one of the δs in (2.8):

$$\frac{\partial}{\partial t} \delta(q_\alpha(t) - q_\alpha)$$

To compute it, we apply it to a test function $\varphi(x) \in \mathcal{S}(\mathbb{R})$, and apply definition (2.9):

$$\begin{aligned} \left\langle \frac{\partial}{\partial t} \delta(q_\alpha(t) - q_\alpha), \varphi \right\rangle &= -\frac{\partial}{\partial t} \varphi(q_\alpha(t)) = -\left(\frac{\partial}{\partial q_\alpha} \varphi(q_\alpha(t)) \right) \dot{q}_\alpha(t) = \\ &\equiv -\langle \dot{q}_\alpha(t) \frac{\partial}{\partial q_\alpha} \delta(q_\alpha(t) - q_\alpha), \varphi \rangle \end{aligned} \quad (2.10)$$

And so we get the following identity between operators:

$$\delta(q_\alpha(t) - q_\alpha) = -\dot{q}_\alpha(t) \frac{\partial}{\partial q_\alpha} \delta(q_\alpha(t) - q_\alpha)$$

Another way to see (2.10) is by *formally* writing:

$$\left\langle \frac{\partial}{\partial t} \delta(q_\alpha(t) - q_\alpha), \varphi \right\rangle = \int_{\mathbb{R}} dq_\alpha \frac{\partial}{\partial t} \delta(q_\alpha(t) - q_\alpha) \varphi(q_\alpha)$$

Here the ∂_t acts on *everything* on its right, i.e. $\partial_t \delta(\cdots) \varphi$ is to be intended as first applying δ to the φ , and then ∂_t to the result. As ∂_t acts on the entire integral, we can bring it out:

$$\begin{aligned} &= \frac{\partial}{\partial t} \int_{\mathbb{R}} dq_\alpha \delta(q_\alpha(t) - q_\alpha) \varphi(q_\alpha) = \\ &= \frac{\partial}{\partial t} \varphi(q_\alpha(t)) = (2.10) \end{aligned}$$

To extend to more dimensions (e.g. 3), we need to use gradients when applying the chain rule. For example, for $d = 3$ and $\mathbb{R}^3 \ni \mathbf{r} \mapsto \varphi(\mathbf{r})$:

$$\left\langle \frac{\partial}{\partial t} \delta^3(\mathbf{r}(t) - \mathbf{r}), \varphi \right\rangle = -\frac{\partial}{\partial t} \varphi(\mathbf{r}(t)) = -\nabla_{\mathbf{r}} \varphi(\mathbf{r}(t)) \cdot \dot{\mathbf{r}}(t) =$$

$$= - \sum_{i=1}^3 \dot{r}_i(t) \frac{\partial}{\partial r_i} \varphi(\mathbf{r}(t))$$

In operatorial terms:

$$\frac{\partial}{\partial t} \delta^3(\mathbf{r}(t) - \mathbf{r}) = -\dot{\mathbf{r}}(t) \cdot \nabla_{\mathbf{r}} \delta(\mathbf{r}(t) - \mathbf{r})$$

In step (a) of (2.8) we are dealing with $6N$ coordinates at once:

$$\begin{aligned} \frac{\partial}{\partial t} \delta^{6N}[(\mathbf{Q}(t), \mathbf{P}(t)) - (\mathbf{Q}, \mathbf{P})] &= -(\dot{\mathbf{Q}}(t), \dot{\mathbf{P}}(t)) \cdot \nabla_{(\mathbf{Q}, \mathbf{P})} \delta^{6N}[(\mathbf{Q}(t), \mathbf{P}(t)) - (\mathbf{Q}, \mathbf{P})] = \\ &= - \left\{ \sum_{\alpha=1}^{3N} \left[\dot{q}_{\alpha}(t) \frac{\partial}{\partial q_{\alpha}} + \dot{p}_{\alpha}(t) \frac{\partial}{\partial p_{\alpha}} \right] \right\} \delta^{3N}(\mathbf{Q}(t) - \mathbf{Q}) \delta^{3N}(\mathbf{P}(t) - \mathbf{P}) \end{aligned}$$

where $(\mathbf{Q}(t), \mathbf{P}(t))$ denotes the $6N$ -dimensional vector with the first $3N$ entries equal to the ones of $\mathbf{Q}(t)$, and the last ones equal to those of $\mathbf{P}(t)$.

In (2.8) we then use (2.1) to rewrite the $\dot{q}_{\alpha}(t)$ and $\dot{p}_{\alpha}(t)$:

$$\begin{aligned} \frac{\partial}{\partial t} \rho(\mathbf{Q}, \mathbf{P}, t) &= - \int_{\Gamma} d\Gamma_0 \rho_0(\mathbf{Q}_0, \mathbf{P}_0) \sum_{\alpha=1}^{3N} \left[\frac{\partial H}{\partial p_{\alpha}}(\mathbf{Q}(t), \mathbf{P}(t)) \frac{\partial}{\partial q_{\alpha}} + \right. \\ &\quad \left. - \frac{\partial H}{\partial q_{\alpha}}(\mathbf{Q}(t), \mathbf{P}(t)) \frac{\partial}{\partial p_{\alpha}} \right] \delta^{3N}(\mathbf{Q}(t) - \mathbf{Q}) \delta^{3N}(\mathbf{P}(t) - \mathbf{P}) = \end{aligned}$$

The two δ s fix the arguments of H and its derivatives to (\mathbf{Q}, \mathbf{P}) :

$$\begin{aligned} &= - \int_{\Gamma} d\Gamma_0 \rho_0(\mathbf{Q}_0, \mathbf{P}_0) \sum_{\alpha=1}^{3N} \left[\frac{\partial H}{\partial p_{\alpha}}(\mathbf{Q}, \mathbf{P}) \frac{\partial}{\partial q_{\alpha}} - \frac{\partial H}{\partial q_{\alpha}}(\mathbf{Q}, \mathbf{P}) \frac{\partial}{\partial p_{\alpha}} \right] \cdot \\ &\quad \cdot \delta^{3N}(\mathbf{Q}(t) - \mathbf{Q}) \delta^{3N}(\mathbf{P}(t) - \mathbf{P}) = \end{aligned}$$

Now the sum (highlighted in blue) is independent of the integration variable, and so can be brought outside the integral:

$$\begin{aligned} &= - \sum_{\alpha=1}^{3N} \left[\frac{\partial H}{\partial p_{\alpha}}(\mathbf{Q}, \mathbf{P}) \frac{\partial}{\partial q_{\alpha}} - \frac{\partial H}{\partial q_{\alpha}}(\mathbf{Q}, \mathbf{P}) \frac{\partial}{\partial p_{\alpha}} \right] \cdot \\ &\quad \cdot \underbrace{\int_{\Gamma} d\Gamma_0 \rho_0(\mathbf{Q}_0, \mathbf{P}_0) \delta^{3N}(\mathbf{Q}(t) - \mathbf{Q}) \delta^{3N}(\mathbf{P}(t) - \mathbf{P})}_{\rho(\mathbf{Q}, \mathbf{P}, t)} \quad (2.11) \end{aligned}$$

This last result (2.11) can be rewritten as:

$$\frac{\partial}{\partial t} \rho(\mathbf{Q}, \mathbf{P}, t) = -\{\rho(\mathbf{Q}, \mathbf{P}, t), H(\mathbf{Q}, \mathbf{P})\}$$

which is exactly eq. (2.6). By computing the total derivative:

$$\frac{d}{dt} \rho(\mathbf{Q}(t), \mathbf{P}(t), t)$$

and using (2.6) we can then derive also (2.4), thus completing the proof. \square

Exercise 2.1.1 (Liouville's theorem):

Show that (2.6) implies (2.4).

Solution. We start by computing the total derivative of $\rho(\mathbf{Q}(t), \mathbf{P}(t), t)$ with respect to time t :

$$\begin{aligned} \frac{d}{dt}\rho(\mathbf{Q}(t), \mathbf{P}(t), t) &= \sum_{\alpha=1}^{3N} \left[\frac{\partial \rho}{\partial q_{\alpha}}(\mathbf{Q}(t), \mathbf{P}(t), t) \dot{q}_{\alpha}(t) + \frac{\partial \rho}{\partial p_{\alpha}}(\mathbf{Q}(t), \mathbf{P}(t), t) \dot{p}_{\alpha}(t) \right] + \\ &\quad + \frac{\partial \rho}{\partial t}(\mathbf{Q}(t), \mathbf{P}(t), t) \end{aligned}$$

We rewrite \dot{q}_{α} and \dot{p}_{α} through the Hamilton equations (2.1):

$$\begin{aligned} &= \sum_{\alpha=1}^{3N} \left[\frac{\partial \rho}{\partial q_{\alpha}}(\mathbf{Q}(t), \mathbf{P}(t), t) \frac{\partial H}{\partial p_{\alpha}}(\mathbf{Q}(t), \mathbf{P}(t)) + \right. \\ &\quad \left. - \frac{\partial \rho}{\partial p_{\alpha}}(\mathbf{Q}(t), \mathbf{P}(t), t) \frac{\partial H}{\partial q_{\alpha}}(\mathbf{Q}(t), \mathbf{P}(t)) \right] + \\ &\quad + \frac{\partial \rho}{\partial t}(\mathbf{Q}(t), \mathbf{P}(t), t) \end{aligned}$$

Using (2.6) for the last term we have:

$$\begin{aligned} \frac{\partial \rho}{\partial t}(\mathbf{Q}(t), \mathbf{P}(t), t) &= - \sum_{\alpha=1}^{3N} \left[\frac{\partial \rho}{\partial q_{\alpha}}(\mathbf{Q}(t), \mathbf{P}(t), t) \frac{\partial H}{\partial p_{\alpha}}(\mathbf{Q}(t), \mathbf{P}(t)) + \right. \\ &\quad \left. - \frac{\partial \rho}{\partial p_{\alpha}}(\mathbf{Q}(t), \mathbf{P}(t), t) \frac{\partial H}{\partial q_{\alpha}}(\mathbf{Q}(t), \mathbf{P}(t)) \right] \end{aligned}$$

which leads to a total cancellation, and so:

$$\frac{d}{dt}\rho(\mathbf{Q}(t), \mathbf{P}(t), t) \equiv 0 \quad \forall t$$

as desired.

2.1.1 Measure theoretic version

We can express the results of Liouville's theorem in terms of the (hyper)volumes occupied by system-points in phase-space [2, Appendix A]. As we have noted before, an ensemble *evolves* like an *incompressible fluid*. So, as a cup of water *does not change its total volume* after being stirred or scattered or dispersed, so do the ensembles experiencing Hamiltonian evolution.

Let's make this more precise. Consider a Lebesgue-measurable subset $A_0 \subset \Gamma$ of phase-space. Then we have a way to compute its *measure* (a generalization of "volume") with the integral:

$$V(A_0) \equiv \int_{A_0} d^{3N} \mathbf{q} d^{3N} \mathbf{p} \equiv \int_{A_0} d\Gamma_0$$

Let A_0 evolve for a time t according to Hamilton equations (2.1), and call its

*Measure-theoretic
Liouville's
theorem*

evolved version A_t . Then we can restate **Liouville's theorem** as the equality:

$$V(A_0) = V(A_t) \quad \forall t$$

Before providing a formal proof, consider the following *heuristic* considerations. *Heuristic proof*
Let A be a sufficiently small region of phase-space (obtained, for example, by partitioning a larger region B), so that the density of system-points in it is (approximately) constant: $\rho(\mathbf{Q}, \mathbf{P}, t) \approx \text{const} \neq 0$. Let A_t be its *evolved* version after time t . The fraction ΔN_t of system-points inside A_t is given by:

$$\Delta N_t = \rho(\mathbf{Q}(t), \mathbf{P}(t), t) V(A_t)$$

and remains constant by definition. Differentiating with respect to t :

$$0 \equiv \frac{d}{dt} \Delta N_t = \underbrace{\frac{d\rho}{dt} \cdot V(A_t)}_{0 \text{ by Liouville's theorem}} + \rho(\mathbf{Q}(t), \mathbf{P}(t), t) \frac{d}{dt} V(A_t)$$

Dividing by ρ we obtain:

$$\frac{dV}{dt} = 0$$

Meaning that the volume of A_t does not change, and so:

$$V(A_t) = V(A_0)$$

Proof. A more **rigorous proof** is given by the following. *Formal proof*

We can express the two regions A_0 and A_t as uniform densities:

$$\rho_0(\mathbf{Q}, \mathbf{P}) = \mathbb{1}_{A_0}(\mathbf{Q}, \mathbf{P}); \quad \rho(\mathbf{Q}, \mathbf{P}, t) = \mathbb{1}_{A_t}(\mathbf{Q}, \mathbf{P})$$

Then, the volume of A_0 is given by:

$$V(A_0) = \int_{\Gamma} d^{3N} \mathbf{q} d^{3N} \mathbf{p} \rho_0(\mathbf{Q}, \mathbf{P}) =$$

And we rename the integration variables to \mathbf{q}_0 and \mathbf{p}_0 :

$$= \int_{\Gamma} d^{3N} \mathbf{q}_0 d^{3N} \mathbf{p}_0 \rho_0(\mathbf{Q}_0, \mathbf{P}_0) \quad (2.12)$$

By Liouville's theorem (2.4), the local density does not change along a path. In particular, consider the path starting at $(\mathbf{Q}, \mathbf{P}_0)$ and arriving at $(\mathbf{Q}(t; \mathbf{Q}_0, \mathbf{P}_0), \mathbf{P}(t; \mathbf{Q}_0, \mathbf{P}_0))$ at time t , i.e. such that:

$$\mathbf{Q}(t; \mathbf{Q}_0, \mathbf{P}_0) \Big|_{t=0} = \mathbf{Q}_0; \quad \mathbf{P}(t; \mathbf{Q}_0, \mathbf{P}_0) \Big|_{t=0} = \mathbf{P}_0$$

Then:

$$\rho(\mathbf{Q}(t; \mathbf{Q}_0, \mathbf{P}_0), \mathbf{P}(t; \mathbf{Q}_0, \mathbf{P}_0), t) = \rho_0(\mathbf{Q}_0, \mathbf{P}_0)$$

Substituting in (2.12) leads to:

$$V(A_0) = \int_{\Gamma} d^{3N} \mathbf{q}_0 d^{3N} \mathbf{p}_0 \rho(\mathbf{Q}(t; \mathbf{Q}_0, \mathbf{P}_0), \mathbf{P}(t; \mathbf{Q}_0, \mathbf{P}_0), t)$$

Then we change variables, passing from the origins $(\mathbf{Q}_0, \mathbf{P}_0)$ to an arbitrary end-point (\mathbf{Q}, \mathbf{P}) :

$$(\mathbf{Q}, \mathbf{P}) = (\mathbf{Q}(t; \mathbf{Q}_0, \mathbf{P}_0), \mathbf{P}(t; \mathbf{Q}_0, \mathbf{P}_0)) \quad (2.13)$$

leading to:

$$V(A_0) = \int_{\Gamma} d^{3N} \mathbf{q} d^{3N} \mathbf{p} \rho(\mathbf{Q}, \mathbf{P}, t) J^{-1}$$

where the determinant J of the jacobian of the change of variables is given by:

$$J = \det \left| \frac{\partial(\mathbf{Q}, \mathbf{P})}{\partial(\mathbf{Q}_0, \mathbf{P}_0)} \right|$$

If $J = 1$, then (2.13) would become:

$$V(A_0) = \int_{\Gamma} d^{3N} \mathbf{q} d^{3N} \mathbf{p} \underbrace{\rho(\mathbf{Q}, \mathbf{P}, t)}_{\mathbb{1}_{A_t}(\mathbf{Q}, \mathbf{P})} = V(A_t)$$

thus concluding the theorem.

So, all that's left is to verify that the following determinant is unitary:

$$J(t) = \det \left| \frac{\partial(\mathbf{Q}(t; \mathbf{Q}_0, \mathbf{P}_0), \mathbf{P}(t; \mathbf{Q}_0, \mathbf{P}_0))}{\partial(\mathbf{Q}_0, \mathbf{P}_0)} \right|$$

where $\mathbf{Q}(t)$ and $\mathbf{P}(t)$ are obtained with the Hamilton equations (2.1).

For simplicity of notation, let's define:

$$(\mathbf{Q}_0, \mathbf{P}_0) \equiv \mathbf{y}; \quad (\mathbf{Q}(t; \mathbf{Q}_0, \mathbf{P}_0), \mathbf{P}(t; \mathbf{Q}_0, \mathbf{P}_0)) \equiv \mathbf{x}(t, \mathbf{y}) \quad (2.14)$$

And so:

$$J(t) = \det \left| \frac{\partial(x_1, \dots, x_{6N})}{\partial(y_1, \dots, y_{6N})} \right|$$

We already know that $J(0) = 1$, because $\mathbf{x}(0, \mathbf{y}) = \mathbf{y}$. So, if we prove that $J(t)$ is constant, i.e. it does not depend on t , we will have $J(t) \equiv 1$, as desired. The idea is thus to *differentiate* $J(t)$ and use Hamilton equations (2.1).

In general, for a matrix $A(t)$ with rows $(\mathbf{A}_1(t), \dots, \mathbf{A}_n(t))^T$, we have:

$$\begin{aligned} \frac{d}{dt} \det A(t) &= \frac{d}{dt} \det \begin{vmatrix} | - & \mathbf{A}_1(t) & - | \\ | - & \mathbf{A}_2(t) & - | \\ & \vdots & \\ | - & \mathbf{A}_n(t) & - | \end{vmatrix} = \\ &= \det \begin{vmatrix} | - & \mathbf{A}'_1(t) & - | \\ | - & \mathbf{A}_2(t) & - | \\ & \vdots & \\ | - & \mathbf{A}_n(t) & - | \end{vmatrix} + \det \begin{vmatrix} | - & \mathbf{A}_1(t) & - | \\ | - & \mathbf{A}'_2(t) & - | \\ & \vdots & \\ | - & \mathbf{A}_n(t) & - | \end{vmatrix} + \dots + \det \begin{vmatrix} | - & \mathbf{A}_1(t) & - | \\ & \vdots & \\ | - & \mathbf{A}_{n-1}(t) & - | \\ | - & \mathbf{A}'_n(t) & - | \end{vmatrix} = \end{aligned}$$

$$= \sum_{i=1}^n \det[(\mathbf{A}_1(t), \dots, \mathbf{A}_{i-1}(t), \mathbf{A}'_i(t), \mathbf{A}_{i+1}(t), \dots, \mathbf{A}_n(t))^T] \quad (2.15)$$

For a proof of (2.15) see the green box at pag. 55.

In our case, (2.15) leads to:

$$\frac{d}{dt} J(t) = \sum_{i=1}^{6N} \det \left| \frac{\partial(x_1, \dots, x_{i-1}, \dot{x}_i, x_{i+1}, \dots, x_{6N})}{\partial(y_1, \dots, y_{i-1}, y_i, y_{i+1}, \dots, y_{6N})} \right| \equiv \sum_{i=1}^{6N} \det A_i \quad (2.16)$$

where $x_i = q_i$ for $1 \leq i \leq 3N$, and p_i for $3N < i \leq 6N$. In either case, when we differentiate and compute \dot{x}_i , we will have, as consequence of (2.1) one of the two results:

$$\dot{q}_\alpha = \frac{\partial H}{\partial p_\alpha}; \quad \dot{p}_\alpha = -\frac{\partial H}{\partial q_\alpha}$$

which are both functions of (\mathbf{Q}, \mathbf{P}) , i.e. of \mathbf{x} . Thus, the (i, k) elements of such matrices can be computed by the chain-rule:

$$\frac{\partial \dot{x}_i}{\partial y_k} = \sum_{j=1}^{6N} \frac{\partial \dot{x}_i}{\partial x_j} \frac{\partial x_j}{\partial y_k} \quad (2.17)$$

In vector notation:

$$\frac{\partial \dot{x}_i}{\partial \mathbf{y}} = \sum_{j=1}^{6N} \frac{\partial \dot{x}_i}{\partial x_j} \frac{\partial x_j}{\partial \mathbf{y}} \quad (2.18)$$

Note that $\frac{\partial \dot{x}_i}{\partial \mathbf{y}}$ is the i -th row of the matrix A_i , which, according to (2.18), can be written as a sum of $6N$ rows. As all other rows of A_i remain unchanged, we can use the *row-linearity* of the determinant (see (2.19) and (2.20)):

$$\begin{aligned} \det A_i &= \det \begin{vmatrix} | & \frac{\partial x_1}{\partial \mathbf{y}} & | \\ & \vdots & \\ | & \frac{\partial x_{i-1}}{\partial \mathbf{y}} & | \\ | & \sum_{j=1}^{6N} \frac{\partial \dot{x}_i}{\partial x_j} \frac{\partial x_j}{\partial \mathbf{y}} & | \\ | & \frac{\partial x_{i+1}}{\partial \mathbf{y}} & | \\ & \vdots & \\ | & \frac{\partial x_{6N}}{\partial \mathbf{y}} & | \end{vmatrix} = \sum_{j=1}^{6N} \frac{\partial \dot{x}_i}{\partial x_j} \det \begin{vmatrix} | & \frac{\partial x_1}{\partial \mathbf{y}} & | \\ & \vdots & \\ | & \frac{\partial x_{i-1}}{\partial \mathbf{y}} & | \\ | & \frac{\partial x_j}{\partial \mathbf{y}} & | \\ | & \frac{\partial x_{i+1}}{\partial \mathbf{y}} & | \\ & \vdots & \\ | & \frac{\partial x_{6N}}{\partial \mathbf{y}} & | \end{vmatrix} = \\ &= \sum_{j=1}^{6N} \frac{\partial \dot{x}_i}{\partial x_j} \underbrace{\det \left| \frac{\partial(x_1, \dots, x_{i-1}, \mathbf{x}_j, x_{i+1}, \dots, x_{6N})}{\partial(y_1, \dots, y_{i-1}, y_i, y_{i+1}, \dots, y_{6N})} \right|}_{\delta_{ij} J} \end{aligned}$$

The determinant in the sum argument is obtained by replacing the i -th row of the jacobian in J with the j -th. But if there are two repeated rows, the determinant will be 0. So the only non-zero possibility is when $j = i$, and in that case the determinant will be exactly J . This leads to a Kronecker delta δ_{ij} that we can use to collapse the sum, leading to:

$$\det A_i = \frac{\partial \dot{x}_i}{\partial x_i} J$$

Substituting this last result back in (2.16) we get:

$$\frac{dJ}{dt} = J \sum_{i=1}^{6N} \frac{\partial \dot{x}_i}{\partial x_i}$$

We then undo the change of variables (2.14), splitting the first and last $3N$ terms of the sum:

$$\sum_{i=1}^{6N} \frac{\partial \dot{x}_i}{\partial x_i} = \sum_{\alpha=1}^{3N} \left[\frac{\partial}{\partial q_\alpha} \dot{q}_\alpha + \frac{\partial}{\partial p_\alpha} \dot{p}_\alpha \right] \stackrel{(2.1)}{=} \sum_{\alpha=1}^{3N} \left[\frac{\partial}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha} + \frac{\partial}{\partial p_\alpha} \left(-\frac{\partial H}{\partial q_\alpha} \right) \right] = 0$$

And so:

$$\frac{dJ}{dt} \equiv 0$$

meaning that $J(t)$ is constant, and then - as noted before:

$$J(t) = J(0) = 1$$

which proves Liouville's theorem. □

Derivative of a determinant (*Proof of (2.15)*) .

We start by noting that the determinant of a matrix A is a linear function of its rows or columns. For example, if $A \in \mathcal{M}(\mathbb{R}^{d \times d})$ has rows $\{\mathbf{A}_i\}_{i=1,\dots,n}$, then the following two relations hold:

$$\det |(\mathbf{A}_1, \dots, \mathbf{A}_{i-1}, \lambda \mathbf{A}_i, \mathbf{A}_{i+1} \dots, \mathbf{A}_n)^T| = \lambda \det |(\mathbf{A}_1, \dots, \mathbf{A}_{i-1}, \mathbf{A}_i, \mathbf{A}_{i+1} \dots, \mathbf{A}_n)^T| \quad \forall 1 \leq i \leq n; \forall \lambda \in \mathbb{R} \quad (2.19)$$

$$\begin{aligned} \det |(\mathbf{A}_1, \dots, \mathbf{A}_{i-1}, \mathbf{A}_i + \mathbf{w}, \mathbf{A}_{i+1} \dots, \mathbf{A}_n)^T| &= \\ \det |(\mathbf{A}_1, \dots, \mathbf{A}_{i-1}, \mathbf{A}_i, \mathbf{A}_{i+1} \dots, \mathbf{A}_n)^T| + \\ + \det |(\mathbf{A}_1, \dots, \mathbf{A}_{i-1}, \mathbf{w}, \mathbf{A}_{i+1} \dots, \mathbf{A}_n)^T| &\quad \forall 1 \leq i \leq n; \forall \mathbf{w} \in \mathbb{R}^d \end{aligned} \quad (2.20)$$

This property is proved geometrically in fig. 2.2.

We then proceed by computing the time derivative of $\det A(t)$ as the limit of the difference quotient:

$$\frac{d}{dt} \det A(t) \equiv \lim_{\Delta t \rightarrow 0} \frac{\det A(t + \Delta t) - \det A(t)}{\Delta t} =$$

In terms of rows:

$$= \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \left(\det \begin{vmatrix} | - & \mathbf{A}_1(t + \Delta t) & - | \\ & \vdots & \\ | - & \mathbf{A}_n(t + \Delta t) & - | \end{vmatrix} - \det \begin{vmatrix} | - & \mathbf{A}_1(t) & - | \\ & \vdots & \\ | - & \mathbf{A}_n(t) & - | \end{vmatrix} \right)$$

We sum and subtract the determinant of the first addend with *only* the first row changed:

$$\begin{aligned}
&= \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \left(\det \begin{vmatrix} \mathbf{A}_1(t + \Delta t) & - \\ \mathbf{A}_2(t + \Delta t) & - \\ \vdots & \\ \mathbf{A}_n(t + \Delta t) & - \end{vmatrix} - \det \begin{vmatrix} \mathbf{A}_1(t) & - \\ \mathbf{A}_2(t + \Delta t) & - \\ \vdots & \\ \mathbf{A}_n(t + \Delta t) & - \end{vmatrix} + \right. \\
&\quad \left. \det \begin{vmatrix} \mathbf{A}_1(t) & - \\ \mathbf{A}_2(t + \Delta t) & - \\ \vdots & \\ \mathbf{A}_n(t + \Delta t) & - \end{vmatrix} - \det \begin{vmatrix} \mathbf{A}_1(t) & - \\ \mathbf{A}_2(t) & - \\ \vdots & \\ \mathbf{A}_n(t) & - \end{vmatrix} \right) \quad (2.21)
\end{aligned}$$

Focus on the first two terms. They are determinants of two matrices that differ only for a single row. So we can apply linearity (2.20) *in reverse* and gather them in a single determinant:

$$\begin{aligned}
&\lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \left(\det \begin{vmatrix} \mathbf{A}_1(t + \Delta t) & - \\ \mathbf{A}_2(t + \Delta t) & - \\ \vdots & \\ \mathbf{A}_n(t + \Delta t) & - \end{vmatrix} - \det \begin{vmatrix} \mathbf{A}_1(t) & - \\ \mathbf{A}_2(t + \Delta t) & - \\ \vdots & \\ \mathbf{A}_n(t + \Delta t) & - \end{vmatrix} \right) = \\
&= \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \det \begin{vmatrix} \mathbf{A}_1(t + \Delta t) - \mathbf{A}_1(t) & - \\ \mathbf{A}_2(t + \Delta t) & - \\ \vdots & \\ \mathbf{A}_n(t + \Delta t) & - \end{vmatrix} = \det \begin{vmatrix} \mathbf{A}'_1(t) & - \\ \mathbf{A}_2(t) & - \\ \vdots & \\ \mathbf{A}_n(t) & - \end{vmatrix}
\end{aligned}$$

We can then reiterate the same argument on the last two terms of (2.21), arriving at the end to:

$$\frac{d}{dt} A(t) = \sum_{i=1}^n \det[(\mathbf{A}_1(t), \dots, \mathbf{A}_{i-1}(t), \mathbf{A}'_i(t), \mathbf{A}_{i+1}(t), \dots, \mathbf{A}_n(t))^T]$$

Alternative proof for Liouville's theorem [1, Chapter 4.1].

As particles move in *continuous* trajectories, i.e. they do not “teleport” between spatially distant regions, the probability density describing their ensemble must be **locally conserved**. Mathematically, this means that $\rho(\mathbf{Q}, \mathbf{P})$ satisfies a *continuity equation*:

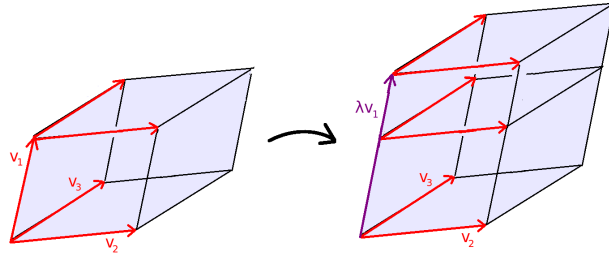
$$\frac{\partial \rho}{\partial t}(\mathbf{Q}, \mathbf{P}) = -\nabla \cdot \mathbf{J}(\mathbf{Q}, \mathbf{P}) = -\nabla \cdot [\rho(\mathbf{Q}, \mathbf{P}) \mathbf{v}(\mathbf{Q}, \mathbf{P})] \quad (2.22)$$

In other words, the local *change* of ρ over time is equal to the opposite of the *outward flux* $\nabla \cdot \mathbf{J}$ at that point, i.e. the rate of particles traversing a tiny closed surface encompassing (\mathbf{Q}, \mathbf{P}) in the outward direction (as consequence of Gauss' theorem). If that flux is positive, then “probability is escaping” (\mathbf{Q}, \mathbf{P}) , and so ρ will decrease. Otherwise, if the outward flux is negative, then “probability is gathering” at (\mathbf{Q}, \mathbf{P}) , and so ρ will rise.

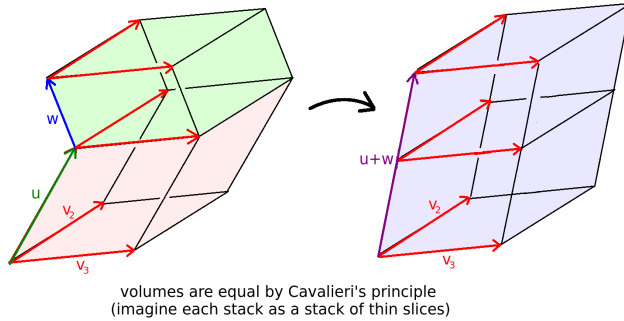
The flux field \mathbf{J} is given by $\rho \mathbf{v}$, where $\mathbf{v} = (\dot{\mathbf{Q}}, \dot{\mathbf{P}})^T$. So (2.22) can be rewritten

$$\det([\mathbf{v}_1 | \mathbf{v}_2 | \mathbf{v}_3]) = \text{Volume} \left(\begin{array}{c} \text{parallelepiped spanned by } \mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_3 \end{array} \right)$$

(a) Geometrically, the determinant is equal to the (signed) *hyper*-volume of the parallelepiped spanned by the column (or row) vectors. Here we consider the $d = 3$ case, with $A = (\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_3)^T$.



(b) If we scale one of the edges by λ , the entire volume scaled by the same factor λ . Thus $\det |(\lambda \mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_3)^T| = \lambda \det |(\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_3)^T|$



(c) The quantity $\det |(\mathbf{u} + \mathbf{w}, \mathbf{v}_2, \mathbf{v}_3)^T|$ is the blue volume on the right, which is equal to the sum of the red volume on the left ($\det |(\mathbf{u}, \mathbf{v}_2, \mathbf{v}_3)^T|$) and the green one ($\det |(\mathbf{w}, \mathbf{v}_2, \mathbf{v}_3)^T|$), as consequence of Cavalieri's principle. In fact the left figure is obtained from the right one by merely *shifting* some thin slices - which does not change the total volume, as moving around some coins in a stack does not change their number.

Figure (2.2) – Geometrical proof of the row/column-linearity of the determinant, taken from [3].

as:

$$\begin{aligned}\frac{\partial \rho}{\partial t} &= - \sum_{\alpha=1}^{3N} \left(\frac{\partial(\rho \dot{q}_{\alpha})}{\partial q_{\alpha}} + \frac{\partial(\rho \dot{p}_{\alpha})}{\partial p_{\alpha}} \right) = \\ &= - \sum_{\alpha=1}^{3N} \left(\frac{\partial \rho}{\partial q_{\alpha}} \dot{q}_{\alpha} + \rho \frac{\partial \dot{q}_{\alpha}}{\partial q_{\alpha}} + \frac{\partial \rho}{\partial p_{\alpha}} \dot{p}_{\alpha} + \rho \frac{\partial \dot{p}_{\alpha}}{\partial p_{\alpha}} \right)\end{aligned}\quad (2.23)$$

Using Hamilton equations (2.1) we can cancel two terms. In fact:

$$\frac{\partial \dot{q}_{\alpha}}{\partial q_{\alpha}} \stackrel{(2.1)}{=} \frac{\partial}{\partial q_{\alpha}} \frac{\partial H}{\partial p_{\alpha}} = \frac{\partial^2 H}{\partial q_{\alpha} \partial p_{\alpha}} \stackrel{(a)}{=} \frac{\partial^2 H}{\partial p_{\alpha} \partial q_{\alpha}} = \frac{\partial}{\partial p_{\alpha}} \frac{\partial H}{\partial q_{\alpha}} \stackrel{(2.1)}{=} \frac{\partial}{\partial p_{\alpha}} (-\dot{p}_{\alpha}) = -\frac{\partial \dot{p}_{\alpha}}{\partial p_{\alpha}}$$

And so (2.23) becomes:

$$\frac{\partial \rho}{\partial t} + \sum_{\alpha=1}^{3N} \left(\frac{\partial \rho}{\partial q_{\alpha}} \dot{q}_{\alpha} + \frac{\partial \rho}{\partial p_{\alpha}} \dot{p}_{\alpha} \right) = \frac{d\rho}{dt} = 0$$

which is Liouville's theorem.

2.1.2 Consequences of Liouville's theorem

As system-points flow like an incompressible fluid, a *uniform ensemble* will remain *uniform* indefinitely. Intuitively, a uniform ensemble is just a fluid with a constant definite density. Hamiltonian dynamics just “stir” around that fluid, but cannot change its local density anywhere: there cannot be points becoming “denser” or “more rarefied”. This means that a uniform ensemble (i.e. the **microcanonical ensemble**) is **stationary** - and thus is suitable to describe the equilibrium condition. However, at least for now, nothing guarantees that a generic isolate system at equilibrium will reach exactly the stationary state given by the microcanonical. We have proved that it is a *possible solution*, but not *the unique solution*!

Microcanonical ensemble is stationary

An other interesting consequence of incompressible flow is that there are no **attractors**, there are no points in phase space to which many paths “converge” over time. So, when we observe a pendulum stopping due to friction in the same place independently of initial conditions, it must not be because it is converging to some definite region of phase-space. Rather, the phase-space paths in which the pendulum loses energy to random air particles are *so much more* than the few where all molecules “hit the pendulum at the right times” to keep it going indefinitely.

Damping with no attractors

Liouville's theorem also provides an intuitive explanation for the *second law of thermodynamics*, following an argument by Jaynes [4][5].

Liouville's theorem and irreversibility

Consider a physical system evolving from a macrostate A to another macrostate B . If the process $A \rightarrow B$ is reproducible, then the volume W_A of microstates compatible with A must *fit* in the volume W_B of microstates compatible with B , i.e. $W_A \leq W_B$. In fact, if it were instead $W_A > W_B$, the evolution $A \rightarrow B$ would not be reliable: at any t , the volume W_t of the evolved ensemble $A(t)$ is the same as W_A (by Liouville's theorem) - and so if we require all of $A(t)$ to end up in B (which is necessary for the evolution to happen reliably), then we

would be trying to “squeeze” too much (incompressible) “fluid” W_A in a “too small bucket” W_B .

Entropy in Statistical Mechanics is the logarithm of the volume in phase-space associated with a certain macrostate, and so from $W_A \leq W_B$ follows $S_A \leq S_B$, i.e. the second law of thermodynamics.

In the case the inequality holds strictly, then the inverse process $B \rightarrow A$ cannot happen reliably. We can estimate the “rate of success” of an inverse transition as the ratio W_A/W_B . Intuitively, if we try to fill a bucket of 1l with 3l of water, only 1 in 3 molecules will make it to the end - and the others will be left outside the bucket. Then, we note that even the tiniest difference in entropy would make W_A/W_B negligible, because $S = k_B \ln W$, and so the ratio decays exponentially:

$$p = \frac{W_A}{W_B} = \exp\left(-\frac{S_B - S_A}{k_B}\right)$$

This means that not only the process $B \rightarrow A$ cannot happen reliably, but that it is *so* unreliable that it never happens!

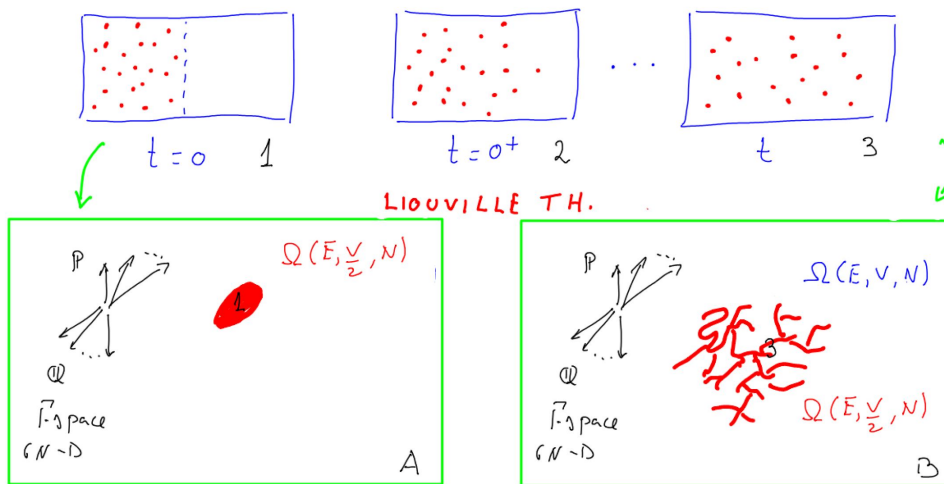


Figure (2.3) – A gas, initially constrained to the left side of a box (state A), is released at $t = 0$, and quickly fills the entire volume (state B). In phase-space, the ensemble associated with A occupies a volume $\Omega(\mathcal{E}, V/2, N)$, which evolves by *flowing* like an incompressible fluid due to Liouville’s theorem. Denote with A_t its evolved version at time t , which in general will be *spread* in some complex way. Consider a symmetrized version of A_t , obtained by reversing all momenta, and denoted with \bar{A}_t . Clearly it has the same volume $\Omega(\mathcal{E}, V/2, N)$ (by symmetry), and if we pick any microstate in it and let it evolve for an interval of time t it will go back to state A, because of the reversibility of Hamiltonian mechanics. However, experimentally we have no control on the choice of microstate: when constructing B, we effectively pick at random a microstate from a larger set $\Omega(\mathcal{E}, V, N)$, which contains many more paths than the ones coming from A (there is a plethora of ways to obtain a box full of gas). The probability of picking a microstate in \bar{A}_t is given by the ratio $\Omega(\mathcal{E}, V/2, N)/\Omega(\mathcal{E}, V, N) = 2^{-N}$, which is negligible. So, while $A \rightarrow B$ happens every time we run the experiment, $B \rightarrow A$ is never observed.

Note: to be more precise, we should account also for the microstates in B that reach state A in a time $\leq t$, which is a set much larger than the sole \bar{A}_t . This makes the discussion much more complex - but the result remains the same.

2.2 Poincaré Recurrence Theorem

The **Poincaré Recurrence Theorem** states that a mechanical system enclosed in a **finite volume** and possessing a **finite** amount of **energy** will, after a *finite time*, return to an arbitrary small neighbourhood of almost any¹ given initial state in phase-space [2, Chapter 1.7]. In general, the smaller the neighbourhood chosen, the larger will be the first arrival time.

Proof. Omitted. □

In other words, the Poincaré Recurrence theorem states that everything is *reversible*, given enough time. This seems in **contradiction** with experience. For example, suppose we start with a gas contained in one half of a box (state A), and let it expand freely in the entire box (state B). This process is clearly irreversible: the gas will not *spontaneously* return to the initial state.

If we reverse time, we will obtain a motion $B \rightarrow A$ that it is still physically possible, but that in practice never happens. This clearly defines a *preferred direction* for time evolution - a so-called “arrow of time”.

Similarly, if we see a video of an egg crashing on the floor, and that of an egg “recomposing” itself after being destroyed, we can surely tell which one has been time-reversed.

However, Poincaré Recurrence is mathematically proved - and indeed must happen. The key to resolve the apparent contradiction with experience lies in the *amount* of time T required to observe such recurrence. For any macroscopic system, T is orders of magnitude larger than the age of the universe. So, while recurrence *will happen*, it will do so *so far in the future* that it will not matter anymore to anyone!

Recurrence can be observed and verified for systems of few particles. For example, consider just $N = 2$ particles, moving *at random*² in a box. At a given moment, each of them is inside the left half of the box with probability $1/2$. So, the two will be in the left side with probability $1/4$. If we do not care about which side the particles are grouped in, we need to *double* this result: the probability that $N = 2$ particles lie in the same side of a box is $1/2$.

If we repeat the same computation for $N = 3$, we will obtain $p = 1/8 \cdot 2 = 1/4$. So, by adding more particles, the “grouping probability” quickly decreases, but it is always non-zero. So, given infinite time, the particles will spontaneously return to an half-box configuration an infinite number of times.

2.2.1 Heuristic estimate of recurrence time

To get a sense of the time scales proper of Poincaré recurrence, consider the following heuristic computation.

¹∧ Apart of a set of zero measure.

²∧ In classical mechanics, particles follow deterministic trajectories given by Hamilton equations. Here we are implicitly assuming that the resulting motions are comparable with random motion.

We start with a box filled by N particles of an **ideal gas**. Let's discretize time, and denote with X_n the *macrostate* of the system at time t_n . X_{n+1} depends only on the previous state X_n , and so we can model the system as a Markov chain.

If the chain is regular, i.e. if it is possible to start in any state i and reach every other state j given sufficient time, then, due to Kac's lemma (the *basic limit theorem* for Markov chains), the Markov chain will reach, for $t \rightarrow \infty$ a *stationary state*, where the probability π_i of being in state i is given by:

$$\pi_i = \frac{1}{\langle T_i \rangle} \quad (2.24)$$

where T_i is the time it takes to visit state i for the first time.

Let i be a macrostate with all particles occupying the left side of the box, corresponding to a region A_0 of microstates in phase-space. Then T_i is the time needed for the set of N particles starting in the left side of the box to *regroup* for the first time in the same side.

If the deterministic motion is sufficiently chaotic, on the long run it can be considered like if it was random - meaning that all microstates are equiprobable. Then, at stationarity, the probability of the system being in A_0 is given by a ratio of phase-space volumes:

$$\mathbb{P}(V/2) = \frac{\Omega(\mathcal{E}, V/2, N)}{\Omega(\mathcal{E}, V, N)} = \frac{(V/2)^N \Omega(\mathcal{E}, 1, N)}{V^N \Omega(\mathcal{E}, 1, N)} = 2^{-N} \quad (2.25)$$

In other words, the microstates with all particles in the left side occupy a phase-space volume of $\Omega_1 \equiv \Omega(\mathcal{E}, V/2, N)$, inside a larger volume of physically possible states $\Omega_2 \equiv \Omega(\mathcal{E}, V, N)$. So, if we pick a microstate at random inside Ω_2 , it will be in Ω_1 with probability³ Ω_1/Ω_2 .

Then we take the inverse of the stationary probability to find the number of time step necessary for recurrence. Before doing that, we need to properly specify the size of a single discretised time step. One possibility is to use the characteristic time needed for a gas molecule to visit regions of phase-space sufficiently "separated" - for example the time interval τ needed to traverse the entirety of the volume. Assuming a square box, the particles needs to travel a length of $V^{1/3}$, and it does so at a mean velocity $\langle |v_x| \rangle$, given by Maxwell's distribution. Then:

$$\tau \approx \frac{V^{1/3}}{\langle |v_x| \rangle}$$

where:

$$\langle |v_x| \rangle = \frac{1}{\int_{\mathbb{R}} dv_x \exp\left(-\beta m \frac{v_x^2}{2}\right)} \int_{\mathbb{R}} dv_x |v_x| \exp\left(-\beta m \frac{v_x^2}{2}\right) = \sqrt{\frac{2k_B T}{\pi m}} = \sqrt{\frac{2RT}{\pi M_{\text{mol}}}}$$

³Intuitively, the probability that a coin will drop inside the area of a carpet, is the ratio between the carpet's area and the room's area.

And so the first return time to i is:

$$\langle T_{\frac{V}{2}} \rangle \stackrel{(2.24)}{=} \frac{\tau}{\mathbb{P}(V/2)} \approx \frac{V^{1/3} 2^N}{\langle |v_x| \rangle}$$

Numerically, consider 1 mol of O_2 ($M_{\text{O}_2} = 32 \text{ g mol}^{-1}$), corresponding to $N = N_A = 6.2 \times 10^{23}$ molecules in a box of length $V^{1/3} \approx 0.4 \text{ m}$, at atmospheric pressure $P = 1 \text{ atm}$ and room temperature $T = 300 \text{ K}$. Then $\langle |v_x| \rangle \approx 500 \text{ m s}^{-1}$, and $\langle T_{\frac{V}{2}} \rangle \approx 10^{1.86 \times 10^{23} - 11} \text{ y}$, which is so much higher than the age of the universe $T_{\text{univ}} = 14 \times 10^9 \text{ y}$.

So, based on this heuristic calculation, we might think that irreversibility is just a matter of **time scales**: everything is theoretically reversible, but we will never see it reverse any time soon.

(Lesson 14 of
9/4/20)
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2.3 Asymptotic Evolution

Liouville's theorem showed us that a uniform ensemble, such as the *micro-canonical ensemble* for a isolate system, is **stationary**, thus suitable to describe equilibrium.

However, we would like to prove that it *is* in fact, the only suitable description. Intuitively, this requires that the Liouville's evolution “thoroughly stirs” phase-space, so that the trajectory followed by *almost*⁴ any point in phase-space passes arbitrarily close to any other point in phase-space. In such case, it can be shown that all states can be treated “equally”, and so we can compute the expected values of observables by using the microcanonical ensemble, as we previously postulated. A system satisfying this condition is said to be **ergodic**. Unfortunately, it is usually very difficult to prove.

To make the argument formal, consider any observable $O(\mathbf{Q}, \mathbf{P})$ and compute its average at time t over all the initial conditions compatible with some ensemble ρ_0 :

$$\langle O(\mathbf{Q}(t), \mathbf{P}(t)) \rangle = \int_{\Gamma} d^{3N} \mathbf{q}_0 d^{3N} \mathbf{p}_0 \rho_0(\mathbf{Q}_0, \mathbf{P}_0) O(\mathbf{Q}(t; \mathbf{Q}_0, \mathbf{P}_0), \mathbf{P}(t; \mathbf{Q}_0, \mathbf{P}_0)) =$$

We change variables $(\mathbf{Q}(t), \mathbf{P}(t)) \rightarrow (\mathbf{Q}, \mathbf{P})$ by introducing two δ s:

$$\begin{aligned} &= \int_{\Gamma} d^{3N} \mathbf{q}_0 d^{3N} \mathbf{p}_0 \rho_0(\mathbf{Q}_0, \mathbf{P}_0) \cdot \\ &\quad \cdot \int_{\Gamma} d^{3N} \mathbf{q} d^{3N} \mathbf{p} \delta^{3N}(\mathbf{Q} - \mathbf{Q}(t; \mathbf{Q}_0, \mathbf{P}_0)) \delta^{3N}(\mathbf{P} - \mathbf{P}(t; \mathbf{Q}_0, \mathbf{P}_0)) O(\mathbf{Q}, \mathbf{P}) = \end{aligned}$$

In this way we can bring $O(\mathbf{Q}, \mathbf{P})$ outside the inner integral:

$$\begin{aligned} &= \int_{\Gamma} d^{3N} \mathbf{q} d^{3N} \mathbf{p} O(\mathbf{Q}, \mathbf{P}) \cdot \\ &\quad \cdot \int_{\Gamma} d^{3N} \mathbf{q}_0 d^{3N} \mathbf{p}_0 \rho_0(\mathbf{Q}_0, \mathbf{P}_0) \delta^{3N}(\mathbf{Q} - \mathbf{Q}(t; \mathbf{Q}_0, \mathbf{P}_0)) \delta^{3N}(\mathbf{P} - \mathbf{P}(t; \mathbf{Q}_0, \mathbf{P}_0)) = \end{aligned}$$

⁴∧Up to a set of null measure

And so we have rewritten the average of O in terms of the *evolved* distribution $\rho(\mathbf{Q}, \mathbf{P}, t)$:

$$\stackrel{(2.7)}{=} \int_{\Gamma} d^{3N} \mathbf{q} d^{3N} \mathbf{p} O(\mathbf{Q}, \mathbf{P}) \rho(\mathbf{Q}, \mathbf{P}, t)$$

For an ergodic system, in the limit $t \rightarrow \infty$ this is equivalent to using the microcanonical ensemble:

$$\langle O(\mathbf{Q}(t), \mathbf{P}(t)) \rangle \xrightarrow{t \rightarrow \infty} \int_{\Gamma} d^{3N} \mathbf{q} d^{3N} \mathbf{p} O(\mathbf{Q}, \mathbf{P}) \rho_{\text{MC}}(\mathbf{Q}, \mathbf{P}) \quad (2.26)$$

where:

$$\rho_{\text{MC}} = \begin{cases} \text{const} & \mathcal{E} \leq \mathcal{H}(\mathbf{Q}, \mathbf{P}) \leq \mathcal{E} + \delta\mathcal{E} \\ 0 & \text{otherwise} \end{cases}$$

This is equivalent to saying that the time average of an observable over a single trajectory is equal to the microcanonical ensemble average, which is the argument used in [1, Chapter 4.2]:

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T O(\mathbf{Q}(t), \mathbf{P}(t)) dt = \int_{\Gamma} d\Gamma O(\mathbf{Q}(t), \mathbf{P}(t)) \rho_{\text{MC}}(\mathbf{Q}, \mathbf{P}) \quad (2.27)$$

The full proof that (2.26) and (2.27) follow from *ergodicity* is quite involved. Here, we focus only on its last part. Namely, we suppose that:

1. Hamilton dynamics lead, in the large time limit, to a *stationary distribution*
 $\rho_{\text{st}}: \lim_{t \rightarrow \infty} \rho(\mathbf{Q}, \mathbf{P}, t) = \rho_{\text{st}}(\mathbf{Q}, \mathbf{P})$

And then show that:

2. The stationary distribution coincides with the microcanonical ensemble:
 $\rho_{\text{st}} = \rho_{\text{MC}}$

This can be done by using Liouville's theorem (2.4), which states that the local probability density is a constant of motion:

$$\frac{d}{dt} \rho_{\text{st}}(\mathbf{Q}(t), \mathbf{P}(t)) = 0$$

For a generic system, there are only 7 possible constants of motion: the energy H , three components of the total momentum \mathbf{P} and the three components of the angular momentum \mathbf{L} . So ρ_{st} is necessarily a function of them:

$$\rho_{\text{st}}(\mathbf{Q}, \mathbf{P}) = \mathcal{F}(H, \mathbf{L}, \mathbf{P})$$

However, if our system is at rest and not rotating, $\mathbf{P} = \mathbf{0} = \mathbf{L}$, and so the only remaining constant is H :

$$\rho_{\text{st}}(\mathbf{Q}, \mathbf{P}) = \mathcal{F}(H)$$

For an isolated system the energy is constant: $H(\mathbf{Q}(t), \mathbf{P}(t)) \equiv \mathcal{E}$, and thus $\rho_{\text{st}} = \text{const}$ on the hypersurface $H = \mathcal{E}$, implying that:

$$\rho_{\text{st}} = \rho_{\text{MC}}$$

(In fact, recall that we chose ρ_{MC} as the uniform distribution in phase-space over the hypersurface $H = \mathcal{E}$).

2.4 Three kinds of entropy

In its classical and original interpretation, **entropy** quantifies the **irreversibility** of a process. More precisely, it is a function of state, depending on macroscopic observables of an equilibrium system. For a reversible process, the *total* entropy - i.e. that of the system and anything it has interacted with - remains the same. For any irreversible transformation, however, it increases. The more the process is “difficult” to reverse, the more the total entropy will rise.

It is not clear from this definition alone *where does entropy come from*, or if it is a real “physical” quantity and not some mathematical abstraction.

Fortunately, decades of analysis have given entropy new and clearer meanings. Boltzmann proved a connection between the thermodynamical S and the amount of *states* in phase-space available to a system, leading to the interpretation of entropy as some sort of “disorder”. Irreversibility is then merely the fact that while “macroscopically ordered states” are few, states of “maximum disorder” are the most - by an incredible margin. So, inevitably, any system will tend to explore the latter, just as an artifact of chance.

An even more general interpretation of entropy comes from *information theory*, where S is a measure of the experimenter’s ignorance about the system. Shifting from an ontological property to an epistemological one has several benefits: for example it allows to search for *the most general* probability distributions compatible with some given conservation laws and experimental results. This is done by *maximizing* the experimenter’s ignorance - rejecting every bias except a few experimentally observable “truths”. Surprisingly, this *MaxEnt* principle provides a variational re-derivation of all equilibrium statistical mechanics, where *informational entropy* plays the role the *action* had in re-deriving classical mechanics (or, with some extensions, even relativistic mechanics, QM or QFT).

Informational entropy can be defined also for non-equilibrium states - but its respective variational principle does not hold anymore in general. It can be adapted to a few restricted cases - such as the flow of heat from the equator to the poles of a planet - but unfortunately not to general complex systems.

Even if MaxEnt is not the desired solution to non-equilibrium dynamics, it still can be applied in a variety of situations outside statistical mechanics: for example in pattern recognition tasks, or in image reconstruction.

In this section, we will start by revising the first two definitions of entropy - the one from classical thermodynamics, and that from statistical mechanics. Then we will introduce the third kind of entropy - *information entropy* - and motivate its definition as the only function satisfying some reasonable requirements. We will then introduce the MaxEnt principle, and employ it to re-derive statistical mechanics, and in particular all the results we previously got for the microcanonical and canonical ensembles. We will then go even further, deriving and discussing the **grandcanonical ensemble**, in which we allow both energy and particles to flow in and out the system.

Finally, we will examine the relation linking *entropy* and *information* in the first place - demonstrating with Landauer’s principle that even an “irreversible

processing of information”, such as erasing a bit-sized register, *increase* the entropy of the universe!

1. **Thermodynamic entropy.** In classical thermodynamics, entropy is a mysterious quantity introduced to characterize the second law.

The difference in entropy $S(B) - S(A)$ between two equilibrium states A and B is defined as:

$$S(B) - S(A) = \int_A^B \left(\frac{dQ}{T} \right)_R \quad (2.28)$$

where A and B are connected by a reversible transformation R . The system is at **equilibrium** at every point on the path $A \rightarrow B$, possessing a definite temperature T_{sys} , and exchanging an infinitesimal amount of heat dQ with a thermal bath at the *same* temperature $T = T_{\text{sys}}$.

The second law of thermodynamics states that the same integral, if done along any path, will lead to a result which is *lower* than that of the reversible case:

$$\int_A^B \frac{dQ}{T} \leq S(B) - S(A) \quad (2.29)$$

T is the temperature of the heat bath in thermal contact with the system during the path $A \rightarrow B$. Note that if the latter does not traverse equilibrium points, then T_{sys} will not be defined. (2.29) holds as an equality if and only if the transformation $A \rightarrow B$ is reversible.

For an isolated system, $dQ \equiv 0$, and so (2.29) leads to:

$$S(B) \geq S(A)$$

with the equality holding only for **reversible** transformations.

Thus, an isolated system is in thermal equilibrium if and only if it has the **maximum possible entropy** compatible with the given macroscopic constraints (e.g. energy, volume, number of particles...). In this case, in fact, it cannot do any other transformation to increase the entropy. A similar argument will prove to be the key for introducing the MaxEnt principle later on.

2. **Statistical Mechanics entropy.**

In Statistical Mechanics we define the entropy as the logarithm of the volume of microstates in phase-space corresponding to the observed macrostate (with definite macroscopic observables), scaled by k_B :

$$S(\mathcal{E}, V, N) = k_B \ln \Omega(\mathcal{E}, V, N) \quad (2.30)$$

where:

$$\Omega(\mathcal{E}, V, N) = \int_{\Gamma} d\Gamma \delta(H(\mathbf{Q}, \mathbf{P}; N, V) - \mathcal{E})$$

The definition (2.30) is compatible with (2.28) because for both of them the following holds:

$$dS = \frac{d\mathcal{E}}{T} + \frac{P}{T} dV - \frac{\mu}{T} dN$$

This means that the derivative of S with respect to \mathcal{E} at constant V and N is $1/T$, and similarly:

$$\left(\frac{dS}{d\mathcal{E}}\right)_{V,N} = \frac{1}{T}; \quad \left(\frac{dS}{dV}\right)_{\mathcal{E},N} = \frac{P}{T}; \quad \left(\frac{dS}{dN}\right)_{\mathcal{E},V} = -\frac{\mu}{T}$$

Furthermore, for an isolated system the only possible transformation (apart from chemical reactions, or nuclear decays) is a **free expansion**, where $V \rightarrow V' > V$. The initial entropy is $S_{\text{in}} = S(\mathcal{E}, V, N)$, and at the end it will be $S_{\text{fin}}(\mathcal{E}, V', N)$. Note that:

$$\begin{aligned} \Omega(\mathcal{E}, V', N) &= \int_{\underbrace{V' \times \dots \times V'}_{N \text{ times}}} d\mathbf{Q} \int_{\mathbb{R}^{3N}} d\mathbf{P} \delta(H(\mathbf{Q}, \mathbf{P}; N) - \mathcal{E}) \\ &> \int_{\underbrace{V \times \dots \times V}_{N \text{ times}}} d\mathbf{Q} \int_{\mathbb{R}^{3N}} d\mathbf{P} \delta(H(\mathbf{Q}, \mathbf{P}; N) - \mathcal{E}) \end{aligned}$$

since the integration domain for the configuration space is *larger* after the expansion ($V' > V$).

Taking the logarithm of both sides, we note:

$$S_{\text{final}} > S_{\text{initial}}$$

which is exactly the result we would have obtained from classical thermodynamics. In other words, the entropy defined in (2.30) is compatible with the second law of thermodynamics.

3. Information entropy. A third definition of entropy comes from **information theory**.

Consider a discrete event space $E = \{i\}_{i=1,\dots,N}$, with probabilities $p_i \geq 0$, such that $\sum_i p_i = 1$.

We want to quantify the amount of information $I(p_i)$ acquired by the observation of event i occurring.

For example, if $p_i = 1$, i.e. the event occurs with certainty, we will not gain any new information by its occurrence: we already knew that it would occur! In other words, if now the sky is free of clouds and it is a beautiful sunny day, the fact that it will be still sunny in 15 minutes is almost sure, and it will not be surprising when it indeed happens. On the other hand, we would not expect that in 15 minutes it will start to rain. Such a unlikely scenario, if it occurs, will give *a lot* of new information to us: for example that we were ignoring little dark clouds on the horizon, or did not properly account of the air currents.

Equivalently, we can quantify the *gain in information* by measuring the minimum length of a message needed to precisely communicate to someone that a certain event has occurred. To *optimize* the sending of data, we can in fact create a code such that the shorter combinations of characters refer to likely events, while the longer ones to *unlikely* events. In this way, on average, we will have to send *shorter* messages. Then, in this scenario, a likely event holds *less information* because it can be coded with *shorter messages* (assuming that the code we are using for transmission is the *most efficient* possible).

In other words, $I(p_i)$ encodes the amount of *surprise* held by event i occurring. Then, clearly a *gain* in information must be non-negative:

$$I(p) \geq 0 \quad (2.31a)$$

It will be minimum (0) for an event that is completely expected:

$$I(p = 1) = 0 \quad (2.31b)$$

And it will be higher the rarer the event:

$$I(p) \text{ is a decreasing function of } p \quad (2.31c)$$

Furthermore, if we have two independent events occurring with probability p_1 and p_2 , it is reasonable that the gain of information obtained by both of them happening to be just the *sum* of the information gains of each of them happening separately:

$$I(\mathbb{P}[1 \wedge 2]) = I(p_1 \cdot p_2) = I(p_1) + I(p_2) \quad (2.31d)$$

Assuming $I(p)$ to be differentiable, differentiating (2.31d) with respect to p_2 leads to:

$$p_1 \frac{d}{dx} I(x) \Big|_{x=p_1 p_2} = \frac{dI}{dp_2}$$

If we now set $p_2 = 1$ and $p_1 = x$ we get:

$$x \frac{d}{dx} I(x) = I'(1) \Leftrightarrow I(x) = I'(1) \ln x + c$$

By (2.31b) $I(1) = 0$, and so the integration constant c must be 0. From (2.31a) we also find that $I'(1) < 0$.

We now define the **information entropy** of an ensemble (i.e. a pdf) as the **average** of $I(p)$. Suppose the set E contains exactly K elements (i.e. $|E| = K$), then:

$$S_I(p_1, \dots, p_k) = \langle I(p_1) \rangle = -|I'(1)| \sum_{i=1}^k p_i \ln p_i \quad (2.31e)$$

We will show that in order for (2.31e) to be compatible with (2.28) and (2.30) we have to choose:

$$I'(1) = -k_B$$

Thus (2.31e) becomes:

$$S_I(p_1, \dots, p_k) = \langle I(p_i) \rangle = -k_B \sum_{i=1}^k p_i \ln p_i \quad (2.31f)$$

Or, in the continuum case:

$$S_I[\rho] = -k_B \int_{\Gamma} d\Gamma \rho(\mathbf{Q}, \mathbf{P}) \ln \rho(\mathbf{Q}, \mathbf{P}) \quad (2.31g)$$

Since $\lim_{x \rightarrow 0} x \ln x = 0$, we define, by continuity, $0 \ln 0 = 0$.

We now show that (2.31g) agrees with the Statistical Mechanics entropy (2.30).

- **Microcanonical case.** The microcanonical ensemble is given by:

$$\rho_{MC}(\mathbf{Q}, \mathbf{P}) = \frac{\mathbb{1}_{[\mathcal{E}, \mathcal{E} + \delta\mathcal{E}]}(H(\mathbf{Q}, \mathbf{P}))}{\int_{\Gamma} d\Gamma \mathbb{1}_{[\mathcal{E}, \mathcal{E} + \delta\mathcal{E}]}(H)}$$

The information entropy is then:

$$S_I[\rho_{MC}] = -k_B \int_{\Gamma} d\Gamma \frac{\mathbb{1}_{[\mathcal{E}, \mathcal{E} + \delta\mathcal{E}]}(H)}{\int_{\Gamma} d\Gamma \mathbb{1}_{[\mathcal{E}, \mathcal{E} + \delta\mathcal{E}]}(H)} [\ln \mathbb{1}_{[\mathcal{E}, \mathcal{E} + \delta\mathcal{E}]}(H) - \ln \int_{\Gamma} d\Gamma \mathbb{1}_{[\mathcal{E}, \mathcal{E} + \delta\mathcal{E}]}(H)] =$$

Note that $\mathbb{1}_{[\mathcal{E}, \mathcal{E} + \delta\mathcal{E}]} \ln \mathbb{1}_{[\mathcal{E}, \mathcal{E} + \delta\mathcal{E}]}$ is either $1 \log 1 = 0$ if (\mathbf{Q}, \mathbf{P}) is inside the energy shell, or $0 \log 0 = 0$ otherwise. The logarithm of the integral does not depend on the integration variables, and so can be factored out:

$$\begin{aligned} &= k_B \left[\ln \int_{\Gamma} d\Gamma \mathbb{1}_{[\mathcal{E}, \mathcal{E} + \delta\mathcal{E}]}(H) \right] \frac{\int_{\Gamma} d\Gamma \mathbb{1}_{[\mathcal{E}, \mathcal{E} + \delta\mathcal{E}]}(H)}{\int_{\Gamma} d\Gamma \mathbb{1}_{[\mathcal{E}, \mathcal{E} + \delta\mathcal{E}]}(H)} \\ &= k_B \ln \underbrace{\int_{\Gamma} d\Gamma \mathbb{1}_{[\mathcal{E}, \mathcal{E} + \delta\mathcal{E}]}(H)}_{\Omega(\mathcal{E}, V, N) \delta\mathcal{E}} = k_B \ln \Omega(\mathcal{E}, V, N) + \underbrace{k_B \ln \delta\mathcal{E}}_{\text{Irrelevant constant}} \end{aligned}$$

leading to (2.30) up to a constant, which is irrelevant, as only differences in entropy have physical meaning.

- **Canonical case.** The canonical ensemble is given by:

$$\rho_c(\mathbf{Q}, \mathbf{P}) = \frac{1}{Z(T, V, N)} e^{-\beta H(\mathbf{Q}, \mathbf{P})} \quad Z(T, V, N) = \int_{\Gamma} d\Gamma e^{-\beta H(\mathbf{Q}, \mathbf{P})} = e^{-\beta A(T, V, N)}$$

where $A(T, V, N)$ is the Helmholtz **free energy**.

The corresponding information entropy is then:

$$\begin{aligned} S_I[\rho_c] &= -k_B \int_{\Gamma} \rho_c(\mathbf{Q}, \mathbf{P}) \ln \rho_c(\mathbf{Q}, \mathbf{P}) d\Gamma = \\ &= -k_B \int_{\Gamma} d\Gamma \rho_c [-\beta H + \beta A] = \frac{1}{T} \langle H \rangle_c - \frac{1}{T} A \end{aligned}$$

Recall that:

$$A = \langle H \rangle_c - TS_c \Rightarrow$$

and substituting above we obtain:

$$S_I(\rho_c) = S_c$$

where:

$$S_c(T, V, N) = -\frac{\partial A}{\partial T}$$

What is the max $S_I(p_1, \dots, p_k)$, given $\sum_i p_i = 1$?

2.5 Information Entropy and Ignorance

The definition we gave of information entropy in the last section, as the average “surprise” of data sampled from a distribution, may seem quite arbitrary and contrived.

In fact, more in general, we can interpret S_I as a measure of the amount of **ignorance** or **uncertainty** contained in a probability distribution. In other words, if $S_I[\rho]$ is maximum, then ρ possess the *least amount of bias*.

While it is not easy to exactly define what we mean by “ignorance”, we can still find some key properties any *ignorance*-measure should have, and use them to fix the functional form of S_I .

So, let’s suppose $S_I(\mathbf{p})$ to be a measure of the *uncertainty* of the discrete distribution $\mathbf{p} = (p_1, \dots, p_\Omega)$, with $\sum_{i=1}^\Omega p_i = 1$. We require the following 3 properties:

- **Uniform distribution = maximum ignorance**, i.e.:

$$S_I\left(\frac{1}{\Omega}, \dots, \frac{1}{\Omega}\right) > S_I(p_1, \dots, p_\Omega) \quad (2.32)$$

for all \mathbf{p} that are non-uniform (i.e. such that not all p_i are the same).

Clearly, if not all p_i are the same, then some states are more probable than others, meaning that we possess some bias towards them. The uncertainty is maximum for a uniform distribution, as in that case we have no bias towards any state at all.

- **Impossible events do not alter the uncertainty:**

$$S_I(p_1, \dots, p_\Omega, 0) = S_I(p_1, \dots, p_\Omega)$$

If a state is never visited, then it makes no difference on the amount of knowledge we possess about the distribution.

- **Rule for updating knowledge.** ...

2.6 MaxEnt Principle

The main *idea* of the **MaxEnt** principle is to find the **most general** probability distribution **compatible** with a set of **constraints** - i.e. *conservation laws* or *measurements* - by **maximizing** the **information entropy** S_I subject to these constraints. As S_I can be interpreted as a measure of *ignorance*, the MaxEnt principle merely suggests to choose the most “unbiased” distribution, i.e. the one with “just enough information” to satisfy the constraints, without containing any further assumption.

Main idea

In Statistical Mechanics, when constructing a macrostate we may *control* only a few macroscopic parameters $\{O_i\}$ - i.e. the energy, the volume, etc. Still, the majority of the system’s degrees of freedom are *not* under control: we cannot

*MaxEnt in
Statistical
Mechanics*

choose the exact *microstate* the system will be in. At any given moment, the system is *in a single definite microstate* - but we do not know which one. Thus we assign *probabilities* to each microstate, expressing our degree of belief about them⁵, i.e. how much we suspect that a certain microstate may be the “real” one. There are many possible choices for these probabilities. For sure, they must be compatible with our previous observations $\{O_i\}$ - and so any microstate which would lead to some different value for the measurements must have a probability 0. Apart from this, our assignment of probabilities will be arbitrary. However, note that many possible choices of p_i , while compatible with the observed $\{O_i\}$ are *biased* towards some measurement values B_j that we do not have under control. MaxEnt tells us to choose p_i such that this *bias* is removed: if we have not measured any B_j , then the p_i we choose must weigh each possible value of B_j **equally**, i.e. *maximize* our ignorance about any other observable which is not under our control. Practically, if we have fixed energy and volume, we know nothing about pressure⁶, and so we must choose a microstate pdf (i.e. an ensemble) which treats all possible p equally.

MaxEnt and Bayesian statistics. MaxEnt is often used as a way to construct **prior** distributions, encoding all the “available” knowledge about some system. Then, in the framework of Bayesian statistics, subsequent observations can be used to “update” the prior pdf through Bayes theorem, allowing inference (or learning) from data.

2.6.1 Single constraint: probability normalization

Mathematically, to maximize a function (S_I) subject to some constraints we use the method of Lagrange multipliers.

Brief refresher of Lagrange multipliers. Suppose we have two functions $F, g: \mathbb{R}^2 \rightarrow \mathbb{R}$, with $F(x, y)$ being the function to maximize, and $g(x, y) = c \in \mathbb{R}$ a constraint.

A stationary point (x_0, y_0) of F subject to the constraint $g(x, y) = c$ is such that if we move slightly from (x_0, y_0) along the contour $g(x, y) = c$, the value of $F(x, y)$ does not change (to first order). This happens if the contour of F passing through the stationary point $F(x, y) = F(x_0, y_0)$ is parallel at (x_0, y_0) to that of $g(x, y) = c$, meaning that at (x_0, y_0) the gradients of F and g are parallel:

$$\nabla_{x,y} F = \lambda \nabla_{x,y} g \quad \lambda \in \mathbb{R}$$

(Here we assume that $\nabla_{x,y} g(x_0, y_0) \neq \mathbf{0}$). Rearranging:

$$\nabla_{x,y} (F(x, y) - \lambda g(x, y)) = \mathbf{0}$$

Together with the constraint equation $g(x, y) = c$, we have now 3 equations

⁵^In the Bayesian sense

⁶^Except in the ideal gas case, but here we are talking in general

in 3 unknowns (x, y, λ) that can be solve to yield the desired stationary point (x_0, y_0) .

This procedure can be extended to the n -dimensional case $F(\mathbf{x})$, with d constraints $\mathbf{g}(\mathbf{x}) = (g_1(\mathbf{x}), \dots, g_d(\mathbf{x})) = (c_1, \dots, c_d) = \mathbf{c}$:

$$\nabla_{\mathbf{x}} \left(F(\mathbf{x}) - \sum_{i=1}^d \lambda_i g_i(\mathbf{x}) \right) = \mathbf{0}$$

The parameters $\boldsymbol{\lambda} = (\lambda_1, \dots, \lambda_d)$ are called the **Lagrange multipliers**.

For example, consider a discrete distribution over a (disjoint) partition of state-space Ω in K states $\{A_i\}_{i=1, \dots, K}$, with $\mathbb{P}[A_i] = p_i$. Without further knowledge, the only constraint we have on the $\{p_i\}$ is the one given by normalization:

*First example of
MaxEnt*

$$\sum_{i=1}^K p_i \stackrel{!}{=} 1$$

We choose $\{p_i\}$ following the MaxEnt principle:

$$\mathbf{p}: \max_{\sum_i p_i = 1} S_I(p_1, \dots, p_K)$$

which is solved with Lagrange multipliers:

$$\begin{aligned} 0 &= \frac{\partial}{\partial p_j} \left(S_I(\mathbf{p}) + \lambda \sum_{i=1}^K p_i \right) = -k_B \left[\frac{\partial}{\partial p_j} \sum_{i=1}^K p_i \log p_i \right] + \lambda = \\ &= -k_B \left[\sum_{i=1}^K \delta_{ij} \log p_j + p_i \delta_{ij} \frac{1}{p_j} \right] + \lambda = \\ &= -k_B (\log p_j + 1) + \lambda = 0 \quad \forall j = 1, \dots, K \end{aligned}$$

Rearranging:

$$\ln p_j = \frac{\lambda}{k_B} - 1 \Rightarrow p_j = \exp \left(\frac{\lambda}{k_B} - 1 \right) = \text{constant} \quad \forall j = 1, \dots, K$$

Then by imposing the normalization:

$$\sum_{i=1}^K p_i = 1 \Leftrightarrow K \exp \left(\frac{\lambda}{k_B} - 1 \right) = 1 \Leftrightarrow \underbrace{\exp \left(\frac{\lambda}{k_B} - 1 \right)}_{p_j} = \frac{1}{K} \Leftrightarrow p_j = \frac{1}{K}$$

As expected, the “most ignorant” distribution over n states is the **uniform** distribution.

Interestingly, note that the maximum entropy is given by:

$$\begin{aligned} \mathbf{p}: \max_{\sum_i p_i = 1} S_I(\mathbf{p}) &= -k_B \sum_{i=1}^K \frac{1}{K} \ln \frac{1}{K} = -k_B K \frac{1}{K} (-\ln K) = k_B \ln K \\ &\propto \ln \text{“Volume of space of possible events”} \end{aligned}$$

2.6.2 Multiple constraints

In general, we will have some additional constraint on the $\{p_i\}_{i=1,\dots,K}$. For example, suppose we have m functions $\{G^{(a)}\}_{a=1,\dots,m}$, each assigning some value to each state: $A_k \mapsto G^{(a)}(A_k) \equiv G_k^{(a)} \in \mathbb{R}$. As each state A_k is chosen with a probability p_k , the $G^{(a)}$ are random variables.

Suppose we have a collection (*data*) of states sampled from the (unknown) distribution $\{p_i\}$, and we measure the averages of $G^{(a)}$ over such collection, obtaining:

$$\langle G^{(a)} \rangle_{\text{data}} = g^{(a)} \quad a = 1, \dots, m \quad (2.33)$$

We want to determine the $\{p_i\}$ that are compatible with those measurements:

$$g^{(a)} = \sum_{i=1}^K p_i G_i^{(a)} \quad a = 1, \dots, m \quad (2.34)$$

without adding any “unnecessary” hypothesis other than the constraints (2.34).

Applying the MaxEnt principle, we choose the $\mathbf{p} = (p_1, \dots, p_K)^T$ that maximizes $S_I(\mathbf{p})$ while satisfying the $m + 1$ constraints given by:

$$\sum_{i=1}^K p_i G_i^{(a)} = g^{(a)} \quad a = 1, \dots, m \quad (2.35a)$$

and the normalization:

$$\sum_{i=1}^K p_i = 1 \quad (2.35b)$$

This can be done by using $m + 1$ Lagrange’s multipliers, one for each of the $(m + 1)$ constraints (2.35a-2.35b). So, the maximizing \mathbf{p}_{\max} is chosen such that:

$$\mathbf{p}_{\max} \text{ s.t. } 0 \stackrel{!}{=} \frac{\partial}{\partial p_j} \left[S_I(\mathbf{p}) - \sum_{a=1}^m \lambda_a \underbrace{\sum_{i=1}^K p_i G_i^{(a)}}_{g^{(a)}} - \lambda \sum_{i=1}^K p_i \right]_{\mathbf{p}=\mathbf{p}_{\max}} \quad \forall j = 1, \dots, K$$

If we let $G_i^{(0)} \equiv 1$ and $\lambda_0 \equiv \lambda$, then we can write all the constraints with a single sum:

$$\mathbf{p}_{\max}: 0 = \frac{\partial}{\partial p_j} \left[S_I(\mathbf{p}) - \sum_{a=0}^m \lambda_a \sum_{i=1}^K p_i G_i^{(a)} \right]_{\mathbf{p}=\mathbf{p}_{\max}} \quad (2.36)$$

Inserting the expression for the Shannon entropy in (2.36):

$$S_I(\mathbf{p}) = -k_B \sum_{i=1}^K p_i \ln p_i$$

leads to:

$$-k_B \left(\ln p_j + \frac{p_j}{p_j} \right) - \sum_{a=0}^m \lambda_a G_j^{(a)} = 0 \Rightarrow p_j^{\max} = \exp \left(-\frac{\lambda_0}{k_B} - 1 - \sum_{a=1}^m \frac{\lambda_a}{k_B} G_j^{(a)} \right) \quad (2.37)$$

We can immediately determine λ_0 from the normalization condition:

$$1 \stackrel{!}{=} \sum_{j=1}^K p_j^{\max} = \exp\left(-\frac{\lambda_0}{k_B} - 1\right) \underbrace{\sum_{j=1}^K \exp\left(-\sum_{a=1}^m \frac{\lambda_a}{k_B} G_j^{(a)}\right)}_{Z(\lambda_1, \dots, \lambda_m) \equiv Z(\boldsymbol{\lambda})} \quad (2.38)$$

And so:

$$Z(\boldsymbol{\lambda}) \equiv \sum_{j=1}^K \exp\left(-\sum_{a=1}^m \frac{\lambda_a}{k_B} G_j^{(a)}\right) \stackrel{(2.38)}{=} \exp\left(1 + \frac{\lambda_0}{k_B}\right) \quad (2.39a)$$

$$p_j^{\max} \equiv p_j(\boldsymbol{\lambda}) \stackrel{(2.37)}{=} \frac{1}{Z(\boldsymbol{\lambda})} \exp\left(-\sum_{a=1}^m \frac{\lambda_a}{k_B} G_j^{(a)}\right) \quad (2.39b)$$

with $\boldsymbol{\lambda} = (\lambda_1, \dots, \lambda_m)^T$.

To find $\{\lambda_a\}_{a=1, \dots, m}$ we need to impose the constraints (2.35a):

$$\langle G^{(a)} \rangle_{\mathbf{p}} \equiv \sum_{j=1}^K p_j^{\max} G_j^{(a)} \stackrel{(2.39b)}{=} \frac{1}{Z(\boldsymbol{\lambda})} \sum_{j=1}^K G_j^{(a)} \exp\left(-\sum_{a=1}^m \frac{\lambda_a}{k_B} G_j^{(a)}\right) = \quad (2.40)$$

Note that the sum looks like $Z(\boldsymbol{\lambda})$, except for the factor $G_j^{(a)}$ that can be “extracted” by differentiating with respect to λ_a and adjusting the constants:

$$= -\frac{k_B}{Z(\boldsymbol{\lambda})} \frac{\partial}{\partial \lambda_a} \underbrace{\sum_{j=1}^K \exp\left(-\sum_{a=1}^m \frac{\lambda_a}{k_B} G_j^{(a)}\right)}_{Z(\boldsymbol{\lambda})} = -\frac{k_B}{Z(\boldsymbol{\lambda})} \frac{\partial}{\partial \lambda_a} Z(\boldsymbol{\lambda}) =$$

Which can be written as the derivative of $\log Z(\boldsymbol{\lambda})$:

$$\langle G^{(a)} \rangle_{\mathbf{p}} = -k_B \frac{\partial}{\partial \lambda_a} \ln Z(\boldsymbol{\lambda}) \quad (2.41)$$

Thus the $\boldsymbol{\lambda}$ are the solutions of the following equations:

$$g_a = \langle G^{(a)} \rangle_{\mathbf{p}} \stackrel{(2.41)}{=} -k_B \frac{\partial}{\partial \lambda_a} \ln Z(\boldsymbol{\lambda}) \quad (2.42)$$

We can rewrite this system as an optimization problem, i.e. see $\boldsymbol{\lambda}$ as the minimum of some function $h(\mathbf{x})$:

$$\nabla_{\mathbf{x}} h(\mathbf{x}) \Big|_{\mathbf{x}=\boldsymbol{\lambda}} = 0 \quad (2.43)$$

This is useful, as it is computationally easier to find a minimum than solve the non-linear equations (2.42).

In practice, we start by rewriting (2.42) in vector form:

$$\mathbf{g} = -k_B \nabla_{\boldsymbol{\lambda}} \ln Z(\boldsymbol{\lambda}) \quad (2.44)$$

and bring both terms inside the gradient:

$$0 = \nabla_{\boldsymbol{\lambda}} [\mathbf{g} \cdot \boldsymbol{\lambda} + k_B \ln Z(\boldsymbol{\lambda})]$$

It is also convenient to divide by k_B , so that the arguments inside the brackets become dimensionless:

$$0 = \nabla_{\mathbf{x}} \left[\underbrace{\frac{\mathbf{g} \cdot \mathbf{x}}{k_B} + k_B \ln Z(\mathbf{x})}_{h(\mathbf{x})} \right]_{\mathbf{x}=\boldsymbol{\lambda}} \quad (2.45)$$

So, we define:

$$h(\mathbf{x}) \equiv \frac{\mathbf{g} \cdot \mathbf{x}}{k_B} + k_B \ln Z(\mathbf{x}) \quad (2.46)$$

And clearly (2.42) are equivalent to the minimization problem (2.43), by construction, i.e.:

$$\left. \frac{\partial h}{\partial x_a}(\mathbf{x}) \right|_{\mathbf{x}=\boldsymbol{\lambda}} \stackrel{!}{=} 0 \Leftrightarrow g_a = -k_B \left. \frac{\partial}{\partial x_a} \ln Z(\mathbf{x}) \right|_{\mathbf{x}=\boldsymbol{\lambda}}$$

Legendre transform. Note that $h(\mathbf{x})$ so defined is the (non-standard) Legendre transform of $\ln Z(\mathbf{x})$ with respect to \mathbf{x} .

Recall that the Legendre transform of a **convex** function $F(x)$ is given by:

$$H(s(x)) = xs(x) - F(x) \quad s(x) = \frac{dF}{dx}(x)$$

This definition is best remembered when rearranged in a more symmetric form:

$$H(s) + F(x) = xs$$

with x and s being *conjugate* variables, i.e. $\frac{dF}{dx} = s$ and $\frac{dH}{ds} = x$.

The definition naturally extends to the multidimensional case:

$$H(\mathbf{s}(\mathbf{x})) = \mathbf{x} \cdot \mathbf{s}(\mathbf{x}) - F(\mathbf{x}) \quad (2.47)$$

Let^a $F(\mathbf{x}) = \ln Z(\mathbf{x})$, then the gradient of $F(\mathbf{x})$ with respect to \mathbf{x} leads to the following *conjugate variable* \mathbf{g} , according to (2.44):

$$-\frac{\mathbf{g}}{k_B} = \nabla_{\mathbf{x}} \ln Z(\mathbf{x})$$

So the Legendre transform of $F(\mathbf{x})$ with respect to \mathbf{x} is given by applying the definition (2.47):

$$h(\mathbf{g}(\mathbf{x})) = -\frac{\mathbf{g}}{k_B} \cdot \mathbf{x} - \ln Z(\mathbf{x})$$

Often, in Statistical Mechanics, we redefine the Legendre transform as its opposite $h(\mathbf{x}) \rightarrow -h(\mathbf{x})$, so that the annoying $-$ signs are removed:

$$h(\mathbf{x}) = \frac{\mathbf{g}}{k_B} \cdot \mathbf{x} + \ln Z(\mathbf{x})$$

We call such Legendre transform $h(\mathbf{x})$ *non-standard*, in the sense that it has an added $-$, as if the definition were:

$$-H(\mathbf{s}(\mathbf{x})) = \mathbf{x} \cdot \mathbf{s} \cdot \mathbf{x} - F(\mathbf{x})$$

^a^The convexity of $F(\mathbf{x})$ is proved below

All that's left is to show that $h(\mathbf{x})$ has **at most** one minimum corresponding to the solution (2.42), meaning that everything is well defined. The proof proceeds in two parts:

1. We prove that $h(\mathbf{x})$ is convex in general, and *strictly* convex in all the applications we are interested in.
2. Then, we show that a strictly convex function has at most one minimum.

Proof. For the **first** step, we proceed by direct computation of the second derivative:

$$\begin{aligned} \frac{\partial^2 h}{\partial x_a \partial x_b}(\mathbf{x}) &= \frac{\partial^2}{\partial x_a \partial x_b} \ln Z(\mathbf{x}) \stackrel{(2.42)}{=} -\frac{\partial}{\partial x_a} \langle G^{(b)} \rangle \frac{1}{k_B} = \\ &\stackrel{(2.40)}{=} -\frac{\partial}{\partial x_a} \frac{1}{k_B} \frac{\overbrace{\sum_{j=1}^K G_j^{(b)} \exp\left(-\frac{\boldsymbol{\lambda} \cdot \mathbf{G}_j}{k_B}\right)}^{\text{Num}}}{\underbrace{\sum_{j=1}^K \exp\left(-\frac{\boldsymbol{\lambda} \cdot \mathbf{G}_j}{k_B}\right)}_{\text{Den}}} = \end{aligned}$$

With $\mathbf{G}_j \equiv (G_j^{(1)}, \dots, G_j^{(m)})^T$. To compute the derivative, we split the fraction as $A/B = A \cdot 1/B$ and apply Leibniz rule:

$$\begin{aligned} &= \cancel{\frac{1}{k_B}} \left[\cancel{\frac{1}{k_B} \sum_{j=1}^K G_j^{(a)} G_j^{(b)} \exp\left(-\frac{\boldsymbol{\lambda} \cdot \mathbf{G}_j}{k_B}\right)} \frac{\sum_{j=1}^K G_j^{(b)} \exp\left(-\frac{\boldsymbol{\lambda} \cdot \mathbf{G}_j}{k_B}\right)}{\underbrace{\sum_{j=1}^K \exp\left(-\frac{\boldsymbol{\lambda} \cdot \mathbf{G}_j}{k_B}\right)}_{\frac{1}{\text{Den}} \frac{\partial \text{Num}}{\partial x_a}}} - \frac{\sum_{j=1}^K G_j^{(b)} \exp\left(-\frac{\boldsymbol{\lambda} \cdot \mathbf{G}_j}{k_B}\right)}{\underbrace{\sum_{j=1}^K \exp\left(-\frac{\boldsymbol{\lambda} \cdot \mathbf{G}_j}{k_B}\right)}_{\frac{1}{\text{Den}} \frac{\partial \text{Num}}{\partial x_a}}} \frac{\cancel{\frac{1}{k_B} \sum_{j=1}^K G_j^{(a)} \exp\left(-\frac{\boldsymbol{\lambda} \cdot \mathbf{G}_j}{k_B}\right)}}{\underbrace{\sum_{j=1}^K \exp\left(-\frac{\boldsymbol{\lambda} \cdot \mathbf{G}_j}{k_B}\right)}_{\frac{1}{\text{Den}} \frac{\partial \text{Num}}{\partial x_a}}} \right] = \\ &= \frac{1}{k_B^2} \left[\langle G^{(a)} G^{(b)} \rangle_{\mathbf{p}} - \langle G^{(a)} \rangle_{\mathbf{p}} \langle G^{(b)} \rangle_{\mathbf{p}} \right] = \\ &= \frac{1}{k_B^2} [\langle G^{(a)} G^{(b)} \rangle_{\mathbf{p}} - \langle G^{(a)} \rangle_{\mathbf{p}} \langle G^{(b)} \rangle_{\mathbf{p}} + \langle G^{(a)} \rangle_{\mathbf{p}} \langle G^{(b)} \rangle_{\mathbf{p}} - \langle G^{(a)} \rangle_{\mathbf{p}} \langle G^{(b)} \rangle_{\mathbf{p}}] = \\ &= \frac{1}{k_B^2} \langle [G^{(a)} - \langle G^{(a)} \rangle_{\mathbf{p}}] [G^{(b)} - \langle G^{(b)} \rangle_{\mathbf{p}}] \rangle_{\mathbf{p}} = \frac{1}{k_B^2} \text{Cov}(G^{(a)}, G^{(b)})_{\mathbf{p}} \end{aligned}$$

This means that the Hessian of $h(\mathbf{x})$ is, up to a constant, the covariance matrix of the observables $\{G^{(a)}\}_{a=1, \dots, m}$ which is **positive semi-definite**, meaning that $h(\mathbf{x})$ is **convex**.

In fact, let $\mathbf{G} = (G^{(1)} - \langle G^{(1)} \rangle, \dots, G^{(m)} - \langle G^{(m)} \rangle)^T$ be the vector of 0-mean observables. Then the covariance matrix can be written as $\langle \mathbf{G} \mathbf{G}^T \rangle_{\mathbf{p}}$. For any vector $\mathbf{w} \in \mathbb{R}^m \setminus \{0\}$, we have:

$$\mathbf{w}^T \langle \mathbf{G} \mathbf{G}^T \rangle \mathbf{w} = \langle \mathbf{w}^T \mathbf{G} \mathbf{G}^T \mathbf{w} \rangle = \langle \mathbf{w}^T \mathbf{G} (\mathbf{w}^T \mathbf{G})^T \rangle = \langle \|\mathbf{w}^T \mathbf{G}\|^2 \rangle \geq 0 \quad (2.48)$$

Where $\mathbf{w}^T \mathbf{G}$ is a scalar, and $\|\cdot\|^2$ is the L_2 norm. (2.48) proves that the covariance matrix is positive semi-definite.

Note that equality is reached if and only if:

$$\langle \|\mathbf{w}^T \mathbf{G}\|^2 \rangle_{\mathbf{p}} = \text{Var}_{\mathbf{p}}(\mathbf{w}^T \mathbf{G}) = \text{Var}_{\mathbf{p}}\left(\sum_{a=1}^m w_a G^{(a)}\right) = 0$$

for some vector $\mathbf{w} \in \mathbb{R}^m \setminus \{\mathbf{0}\}$. This means that a certain linear combination of the observables has variance 0 - i.e. it is constant. As this rarely happens in a reality, we can assume the covariance matrix, and thus the Hessian of $h(\mathbf{x})$ to be **positive definite**, meaning that $h(\mathbf{x})$ is **strictly** convex.

We can now deal with the **second** part of the proof. Consider a scalar function (for simplicity) $f: \mathbb{R} \rightarrow \mathbb{R}$ which is a strictly convex, and has a local minimum at x_1 .

Suppose that x_2 is a local minimum too, with $x_1 \neq x_2$ and $f(x_1) \leq f(x_2)$. Then by definition of (strict) convexity:

$$f(hx_1 + (1-h)x_2) < hf(x_1) + (1-h)f(x_2) \quad 0 < h < 1 \quad (2.49)$$

As h is positive:

$$f(x_1) \leq f(x_2) \Rightarrow hf(x_1) \leq hf(x_2) \quad (2.50)$$

Substituting (2.50) in (2.49) leads to:

$$f(hx_1 + (1-h)x_2) < hf(x_1) + (1-h)f(x_2) \stackrel{(2.50)}{\leq} hf(x_2) + (1-h)f(x_2) = f(x_2)$$

meaning that:

$$f(hx_1 + (1-h)x_2) < f(x_2) \quad \forall h \in (0, 1) \quad (2.51)$$

However, x_2 is by hypothesis a local minimum, and so there is a neighbourhood \mathcal{D} of x_2 such that $f(x) > f(x_2) \forall x \in \mathcal{D} \setminus \{x_2\}$. This contradicts (2.51) when h is sufficiently close to 1, meaning that x_2 cannot be a local minimum of $f(x)$ which is *distinct* from x_1 . So, $f(x)$ can only have up to one minimum, which concludes the proof. \square

Once we have found the $\boldsymbol{\lambda}$, we can finally compute the maximum value of $S_I(\mathbf{p})$:

*Maximum
constrained entropy*

$$\begin{aligned} S_I(\mathbf{p}^{\max}) &= -k_B \sum_{j=1}^K p_j^{\max} \log p_j^{\max} = \\ &\stackrel{(2.39a)}{=} k_B \sum_{j=1}^K \frac{1}{Z(\boldsymbol{\lambda})} \exp\left(-\sum_{a=1}^m \frac{\lambda_a}{k_B} G_j^{(a)}\right) \left[\sum_{a=1}^m \frac{\lambda_a}{k_B} G_j^{(a)} - \ln Z(\boldsymbol{\lambda}) \right] = \end{aligned} \quad (2.52)$$

In the first term we exchange the sums to recognize $\langle G^{(a)} \rangle$:

$$= k_B \underbrace{\sum_{a=1}^m \frac{1}{Z(\boldsymbol{\lambda})} \sum_{j=1}^K \frac{\lambda_a}{k_B} G_j^{(a)} \exp\left(-\sum_{a=1}^m \frac{\lambda_a}{k_B} G_j^{(a)}\right)}_{(2.40): \lambda_a \langle G^{(a)} \rangle} + \quad (2.53)$$

$$\begin{aligned}
& + k_B \ln Z(\boldsymbol{\lambda}) \underbrace{\frac{\sum_{j=1}^K \exp \left(- \sum_{a=1}^m \frac{\lambda_a}{k_B} G_j^{(a)} \right)}{Z(\boldsymbol{\lambda})}}_1 = \\
& = k_B \ln Z(\boldsymbol{\lambda}) + \sum_{a=1}^m \lambda_a \langle G^{(a)} \rangle_{\mathbf{p}} \equiv S(\boldsymbol{\lambda})
\end{aligned}$$

2.6.3 Types of constraints

In the previous example, we met two different types of constraints:

- **First class** (*soft constraints*), as the ones in (2.35a). These correspond to observables $G^{(a)}$ that are fixed *on average*:

$$\sum_{i=1}^K p_i G_i^{(a)} \stackrel{!}{=} g^{(a)} \quad (2.54)$$

One example may be the energy of a system in thermal equilibrium with the environment. The *total* energy is strictly conserved - but many different *partitions* are physically possible. However, on average the smaller system will have a definite energy, which can be experimentally measurable.

We denote with $\boldsymbol{\lambda} = (\lambda_1, \dots, \lambda_m)^T$ the Lagrange multipliers corresponding to the constraints (2.54), i.e. the *conjugate variables* of the $g^{(a)}$. In fact, recall from (2.42) that:

$$g_a = \langle G^{(a)} \rangle_{\mathbf{p}} = -k_B \frac{\partial}{\partial \lambda_a} \ln Z(\boldsymbol{\lambda}) \quad a = 1, \dots, m \quad (2.55)$$

- **Second class** (*hard class*), such as the probability normalization constraint (2.35b). These correspond to *exact* conservation laws, that are satisfied at all times with no uncertainty:

$$h_b \stackrel{!}{=} \text{const.} \quad b = 1, \dots, n \quad (2.56)$$

For example, in an isolate system the energy, volume and number of particles are strictly fixed to \mathcal{E} , V and N . We denote with $\boldsymbol{\gamma} = (\gamma_1, \dots, \gamma_n)^T$ the *conjugate variables* of the h_b , which are defined following (2.42) as:

$$\gamma_b = k_B \frac{\partial \ln Z}{\partial h^{(b)}} \quad (2.57)$$

In general, the entropy S will depend on both kinds of constraints:

$$S(\boldsymbol{\lambda}, \mathbf{h}) = k_B \ln Z(\boldsymbol{\lambda}, \mathbf{h}) + \sum_{a=1}^m \lambda_a \langle G^{(a)} \rangle_{\mathbf{p}} \quad (2.58)$$

Let's consider an infinitesimal change $\boldsymbol{\lambda} \rightarrow \boldsymbol{\lambda} + d\boldsymbol{\lambda}$, $\mathbf{h} \rightarrow \mathbf{h} + d\mathbf{h}$. The entropy change dS is given by its differential:

$$\begin{aligned}
dS = \sum_{a=1}^m \underbrace{k_B \frac{\partial \ln Z}{\partial \lambda_a}}_{(2.42): -g^{(a)}} d\lambda_a + \sum_{b=1}^n \underbrace{k_B \frac{\partial \ln Z}{\partial h_b}}_{(2.57): \gamma_b} dh_b + \sum_{a=1}^m \lambda_a \underbrace{d\langle G^{(a)} \rangle_{\mathbf{p}}}_{(2.40): dg^{(a)}} + \sum_{a=1}^m \underbrace{\langle G^{(a)} \rangle}_{(2.40): g^{(a)}} d\lambda_a = \\
\end{aligned} \quad (2.59)$$

$$= \sum_{b=1}^n \gamma_b dh_b + \sum_{a=1}^m \lambda_a dg^{(a)}$$

If $G^{(1)} = H$, the system energy, we call $\lambda_1 = 1/T$ and:

$$g^{(1)} = \langle H \rangle_p \equiv U \quad (2.60)$$

From (2.59):

$$dU = \underbrace{T dS}_{\delta Q} - \underbrace{\left[T \sum_{a=2}^m \lambda_a dg^{(a)} + T \sum_{b=1}^m \gamma_b dh_b \right]}_{\delta W} = \delta Q + \delta W \quad (2.61a)$$

which is the **first law** of thermodynamics.

If $h_1 = H \equiv U$ (fixed) then we identify $\gamma_1 = 1/T$ and again from equation (2.59):

$$dU = \underbrace{T dS}_{\delta Q} - \underbrace{\left[T \sum_{a=1}^m \lambda_a dg^{(a)} + T \sum_{b=2}^m \gamma_b dh_b \right]}_{\delta W} = \delta Q + \delta W \quad (2.61b)$$

which is again the first law of thermodynamics. Thus $\mathcal{E} = \mathcal{E}(\mathbf{g}, \mathbf{h})$ and:

$$\lambda_a = -\frac{1}{T} \frac{\partial \mathcal{E}}{\partial g^{(a)}} \quad \gamma_b = -\frac{1}{T} \frac{\partial \mathcal{E}}{\partial h_b} \quad (2.61c)$$

Summarizing, in case (2.61a) we have $a \geq 2$, $b \geq 1$ and $\lambda_1 = 1/T$, while in (2.61b) we have $a \geq 1$, $b \geq 2$ and $\gamma_1 = 1/T$.

Equations (2.42) and (2.57) are, respectively:

$$\begin{cases} g^{(a)} = \langle G^{(a)} \rangle = -k_B \frac{\partial}{\partial \lambda_a} \ln Z(\boldsymbol{\lambda}, \mathbf{h}) \\ \gamma_b = k_B \frac{\partial}{\partial h_b} \ln Z(\boldsymbol{\lambda}, \mathbf{h}) \end{cases} \quad (2.61d)$$

And from (2.61c):

$$\begin{aligned} \text{if } h_b = V & \quad \frac{\partial \mathcal{E}}{\partial V} = -P \Rightarrow T\gamma_b = P \stackrel{(2.61d)}{=} k_B T \frac{\partial \ln Z}{\partial V} \\ \text{if } h_b = N & \quad \frac{\partial \mathcal{E}}{\partial N} = \mu \Rightarrow T\gamma_b = \mu \stackrel{(2.61d)}{=} k_B T \frac{\partial \ln Z}{\partial N} \end{aligned} \quad (2.61e)$$

If $g^{(1)} = H$, then:

$$\langle H \rangle \stackrel{(2.61d)}{=} -k_B \frac{\partial}{\partial (1/T)} \ln Z = -\frac{\partial}{\partial \beta} \ln Z$$

If $g^{(2)} = N$, then from (2.61c) we have:

$$-T\lambda_2 = \frac{\partial \mathcal{E}}{\partial N} = \mu \quad (2.61f)$$

and so (2.61d) implies that:

$$\langle N \rangle = -k_B \frac{\partial}{\partial \lambda_2} \ln Z = k_B T \frac{\partial}{\partial \mu} \ln Z \quad (2.61g)$$

Exercise 2.6.1 (Linear combination of constraints):

Show that if we have an extra constraint that is a linear combination of the other ones, i.e.:

$$G^{(m+1)} = \sum_{a=1}^m \alpha_a G^{(a)} \quad (2.62)$$

then $\lambda_{m+1} = 0$. In other words, redundant constraints are “not needed” to find the solution.

However, if $G^{(m+1)}$ is non-linear, then in general $\lambda_{m+1} \neq 0$.

Solution.

Let $\{\mathbf{p}^{\max}\} = (p_1^{\max}, \dots, p_K^{\max})^T$ be the probability distribution satisfying a set of m constraints:

$$\langle G^{(a)} \rangle_{\mathbf{p}^{\max}} \equiv \mathbf{g}_a(\mathbf{p}^{\max}) = \sum_{i=1}^K p_i^{\max} G_i^{(a)} \stackrel{!}{=} g_a \quad a = 1, \dots, m \quad (2.63)$$

for some $\mathbf{g} = (g_1, \dots, g_m) \in \mathbb{R}^m$, such that $S_I(\mathbf{p}^{\max})$ is maximum. In other words, $(\mathbf{p}^{\max}, \boldsymbol{\lambda}^{\max})$ is the solution of the system:

$$\begin{cases} \nabla S_I(\mathbf{p}) = \sum_{a=1}^m \lambda_a \nabla \mathbf{g}_a(\mathbf{p}) \\ \mathbf{g}_a(\mathbf{p}) = g_a \quad \forall a = 1, \dots, m \end{cases} \quad (2.64)$$

Let's introduce another constraint which is a linear combination of the previous m ones:

$$\alpha_1 \langle G^{(1)} \rangle + \dots + \alpha_m \langle G^{(m)} \rangle \stackrel{!}{=} \alpha_1 g_1 + \dots + \alpha_m g_m \quad (2.65)$$

with $\boldsymbol{\alpha} = (\alpha_1, \dots, \alpha_m)^T \in \mathbb{R}^m \setminus \{\mathbf{0}\}$. Clearly (2.65) is immediately satisfied by \mathbf{p}^{\max} , because of (2.63), and so adding (2.65) does not lead to a different solution for the pdf.

In this case, the first K equation of systems (2.64) become:

$$\begin{aligned} \nabla S_I(\mathbf{p}) &= \sum_{a=1}^m \lambda_a \nabla \mathbf{g}_a(\mathbf{p}) + \lambda_{m+1} \nabla \mathbf{g}_{m+1}(\mathbf{p}) = \\ &\stackrel{(a)}{=} \sum_{a=1}^m \lambda_a \nabla \mathbf{g}_a(\mathbf{p}) + \lambda_{m+1} \sum_{a=1}^m \alpha_a \nabla \mathbf{g}_a(\mathbf{p}) = \\ &= \sum_{a=1}^m (\lambda_a + \alpha_a \lambda_{m+1}) \nabla \mathbf{g}_a(\mathbf{p}) \end{aligned} \quad (2.66)$$

where in (a) we applied the linearity of the gradient:

$$\begin{aligned} \mathbf{g}_{m+1}(\mathbf{p}) &= \sum_{a=1}^m \alpha_a \mathbf{g}_a(\mathbf{p}) \\ \Rightarrow \nabla \mathbf{g}_{m+1}(\mathbf{p}) &= \nabla \sum_{a=1}^m \alpha_a \mathbf{g}_a(\mathbf{p}) = \sum_{a=1}^m \alpha_a \nabla \mathbf{g}_a(\mathbf{p}) \end{aligned}$$

which works only because the constraint $\mathbf{g}_{m+1}(\mathbf{p})$ is a **linear** combination of the other constraints in the first place.

As \mathbf{p}^{\max} has not changed, also $\nabla S_I(\mathbf{p}^{\max})$ remains the same, meaning that we can directly equate the right hand sides of (2.64) and (2.66), evaluated at their respective solutions $(\mathbf{p}^{\max}, \boldsymbol{\lambda}^{\max})$ and $(\mathbf{p}^{\max}, \boldsymbol{\lambda}'^{\max})$:

$$\sum_{a=1}^m \lambda_a^{\max} \nabla \mathbf{g}_k(\mathbf{p}^{\max}) = \sum_{a=1}^m (\lambda_a^{\max} + \alpha_a \lambda_{m+1}'^{\max}) \nabla \mathbf{g}_a(\mathbf{p}^{\max})$$

One immediate solution is given by $\lambda_a'^{\max} = \lambda_a^{\max}$ with $a = 1, \dots, m$ and $\lambda_{m+1}'^{\max} = 0$ - which is the one we expected.

Note, however, that this solution is not unique. For example: $\lambda_a'^{\max} = \lambda_a^{\max} - \alpha_a \lambda_{m+1}'^{\max}$ with $a = 1, \dots, m$ is a solution for any value of $\lambda_{m+1}'^{\max} \in \mathbb{R}$. This makes sense, as the system is overdetermined. Moreover, the linear dependence of the observables $\{G^{(a)}\}_{a=1, \dots, m+1}$ makes their covariance matrix singular, meaning that it isn't positive definite (but positive *semi*-definite), and so $h(\mathbf{x})$ (2.46) is convex and not strictly convex, thus it may have more than one minimum.

2.7 Variational Statistical Mechanics

All the ensembles from **equilibrium** Statistical Mechanics can be derived by maximizing the information entropy $S_I(\mathbf{p})$ with some appropriate constraints.

2.7.1 Derivation of the MC ensemble

We start our discussion with the **microcanonical ensemble**, describing an isolate system with fixed energy \mathcal{E} , volume V and number of particles N .

As we did in section 1.3, we construct the microcanonical distribution ρ_{MC} through a limiting process. In particular:

1. We consider the energy $H(\mathbf{Q}, \mathbf{P})$ fluctuating in a small interval $[\mathcal{E}, \mathcal{E} + \delta\mathcal{E}]$, with $\delta\mathcal{E} \rightarrow 0$. In other words, only the phase-space coordinates (\mathbf{Q}, \mathbf{P}) corresponding to an energy $H(\mathbf{Q}, \mathbf{P})$ “sufficiently close to” \mathcal{E} are allowed:

$$H(\mathbf{Q}, \mathbf{P}) \in [\mathcal{E}, \mathcal{E} + \delta\mathcal{E}] \equiv \mathcal{I}$$

2. We discretize the phase-space Γ in $6N$ -dimensional non-overlapping **cells** $[\mathcal{C}_i]$. If $[\mathcal{C}_i]$ is sufficiently small, i.e. when its **volume** $|c_i| \approx 0$, then any function $f(\mathbf{Q}, \mathbf{P})$ will be approximately *constant* for all points $(\mathbf{Q}, \mathbf{P}) \in [\mathcal{C}_i]$, and so we evaluate it at the cell's centre $(\mathbf{Q}_i, \mathbf{P}_i)$.

For example, the energy $H(\mathbf{Q}, \mathbf{P})$ becomes:

$$H(\mathbf{Q}, \mathbf{P}) = H(\mathbf{Q}_i, \mathbf{P}_i) + (\text{negligible}) \text{ terms when } |c_i| \approx 0 \quad \forall (\mathbf{Q}, \mathbf{P}) \in [\mathcal{C}_i]$$

For simplicity, let's denote $H(\mathbf{Q}_i, \mathbf{P}_i) \equiv H_i$ (and similarly for other functions).

Consider the probability distribution $\rho_d(\mathbf{Q}, \mathbf{P})$ of microstates. For $|c_i| \approx 0$, it is (approximately) constant inside each $[\underline{c}_i]$, and equal to ρ_i . Moreover, it is non-zero only for $[\underline{c}_i]$ corresponding to energies inside \mathcal{I} . Putting everything together, we can write:

$$\rho_d(\mathbf{Q}, \mathbf{P}) = \sum_{[\underline{c}_i] \in \Gamma} \mathbb{1}_{[\underline{c}_i]}(\mathbf{Q}, \mathbf{P}) \mathbb{1}_{\mathcal{I}}(H_i) \rho_i \quad \mathbb{1}_{[\underline{c}_i]}(\mathbf{Q}, \mathbf{P}) = \begin{cases} 1 & (\mathbf{Q}, \mathbf{P}) \in [\underline{c}_i] \\ 0 & \text{otherwise} \end{cases} \quad (2.67)$$

So the average of a generic observable O can be computed as:

$$\begin{aligned} \langle O \rangle_d &= \int_{\Gamma} d^{3N} \mathbf{Q} d^{3N} \mathbf{P} \rho_d(\mathbf{Q}, \mathbf{P}) O(\mathbf{Q}, \mathbf{P}) = \\ &\stackrel{(2.67)}{=} \int_{\Gamma} d^{3N} \mathbf{Q} d^{3N} \mathbf{P} \sum_{[\underline{c}_i] \in \Gamma} \mathbb{1}_{[\underline{c}_i]}(\mathbf{Q}, \mathbf{P}) \mathbb{1}_{\mathcal{I}}(H_i) \rho_i O(\mathbf{Q}, \mathbf{P}) = \\ &= \sum_{[\underline{c}_i] \in \Gamma} \rho_i \mathbb{1}_{\mathcal{I}}(H_i) \int_{\Gamma} d^{3N} \mathbf{Q} d^{3N} \mathbf{P} \mathbb{1}_{[\underline{c}_i]}(\mathbf{Q}, \mathbf{P}) O(\mathbf{Q}, \mathbf{P}) = \\ &\stackrel{(a)}{=} \sum_{[\underline{c}_i] \in \Gamma} \rho_i \mathbb{1}_{\mathcal{I}}(H_i) \underbrace{\int_{[\underline{c}_i]} d^{3N} \mathbf{Q} d^{3N} \mathbf{P} O_i}_{|c_i|} \\ &= \sum_{[\underline{c}_i] \in \Gamma} |c_i| \rho_i O_i \mathbb{1}_{\mathcal{I}}(H_i) \end{aligned} \quad (2.68)$$

where in (a) we considered $O(\mathbf{Q}, \mathbf{P})$ equal to the constant $O_i \equiv O(\mathbf{Q}_i, \mathbf{P}_i)$ inside the cell $[\underline{c}_i]$.

If we let $O = \ln \rho_d$, then $S_I[\rho_d] = \langle O \rangle_d$ is the information entropy of the pdf:

$$S_I[\rho_d] = -k_B \int_{\Gamma} d^{3N} \mathbf{Q} d^{3N} \mathbf{P} \rho_d(\mathbf{Q}, \mathbf{P}) \ln \rho_d(\mathbf{Q}, \mathbf{P}) = \quad (2.69)$$

$$\stackrel{(2.68)}{=} -k_B \sum_{[\underline{c}_i] \in \Gamma} \mathbb{1}_{\mathcal{I}}(H_i) |c_i| \rho_i \ln \rho_i = -k_B \sum_{\substack{[\underline{c}_i] \in \Gamma \\ H_i \in \mathcal{I}}} |c_i| \rho_i \ln \rho_i \quad (2.70)$$

The only constraint that is left to impose is the **normalization**:

$$1 \stackrel{!}{\stackrel{(2.35b)}}{=} \int_{\Gamma} d^{3N} \mathbf{Q} d^{3N} \mathbf{P} \rho_d(\mathbf{Q}, \mathbf{P}) = \langle 1 \rangle_d \stackrel{(2.68)}{=} \sum_{[\underline{c}_i] \in \Gamma} |c_i| \mathbb{1}_{\mathcal{I}}(H_i) \rho_i = \sum_{\substack{[\underline{c}_i] \in \Gamma \\ H_i \in \mathcal{I}}} |c_i| \rho_i \quad (2.71)$$

So the values $\{\rho_i^{\max}\}$ that maximize $S_I[\rho_d]$ subject to (2.71) are the solutions of the Lagrange equations:

$$0 = \frac{\partial}{\partial \rho_j} \left[S_I[\rho_d] - \lambda_0 \sum_{\substack{[\underline{c}_i] \in \Gamma \\ H_i \in \mathcal{I}}} |c_i| \rho_i \right] = -k_B (\ln \rho_j^{\max} + 1) |c_j| - \lambda_0 |c_j|$$

Rearranging:

$$\rho_j^{\max} = \exp \left(-1 - \frac{\lambda_0}{k_B} \right) = \text{const.} \quad (2.72)$$

And so, by applying the normalization (2.71):

$$\sum_{\substack{[C_i] \in \Gamma \\ H_i \in \mathcal{I}}} |c_i| \rho_i^{\max} \stackrel{!}{=} 1 \Rightarrow p_i^{\max} \sum_{\substack{[C_i] \in \Gamma \\ H_i \in \mathcal{I}}} |c_i| \stackrel{!}{=} 1 \Rightarrow p_i^{\max} = \frac{1}{\sum_{\substack{[C_i] \in \Gamma \\ H_i \in \mathcal{I}}} |c_i|} \equiv \bar{\rho}$$

Equivalently:

$$\sum_{\substack{[C_i] \in \Gamma \\ H_i \in \mathcal{I}}} |c_i| = \frac{1}{\bar{\rho}} \quad (2.73)$$

In the limit $\max_i |c_i| \rightarrow 0$, the left hand side of (2.73) tends to the integral:

$$\int_{\Gamma} d^{3N} \mathbf{Q} d^{3N} \mathbf{P} \mathbb{1}_{\mathcal{I}}(H(\mathbf{Q}, \mathbf{P})) \underset{\substack{(1.35) \\ (??) \\ \text{pag.??}}}{=} \delta \mathcal{E} \cdot \Omega(\mathcal{E}, V, N)$$

while the right hand side remains the same constant, so that:

$$\delta \mathcal{E} \cdot \Omega(\mathcal{E}, V, N) = \frac{1}{\bar{\rho}} \quad (2.74)$$

Where:

$$\Omega(\mathcal{E}, V, N) = \lim_{\delta \mathcal{E} \rightarrow 0} \frac{\int_{\Gamma} d^{3N} \mathbf{Q} d^{3N} \mathbf{P} \mathbb{1}_{\mathcal{I}}(H)}{\delta \mathcal{E}} = \int_{\Gamma} d^{3N} \mathbf{Q} d^{3N} \mathbf{P} \delta(\mathcal{H} - \mathcal{E})$$

We can finally compute the entropy at the maximum:

$$S_I[\rho_d^{\max}] = -k_B \int_{\Gamma} d\Gamma \bar{\rho} \ln \bar{\rho} = -k_B \ln \bar{\rho} \underbrace{\int_{\Gamma} d\Gamma \bar{\rho}}_1 = -k_B \ln \bar{\rho} \quad (2.75)$$

Which in the limit $\max_i |c_i| \rightarrow 0$ becomes:

$$\begin{aligned} S_I[\rho_d^{\max}] &\stackrel{(2.74)}{=} -k_B \ln \frac{1}{\delta \mathcal{E} \Omega(\mathcal{E}, V, N)} = k_B \ln(\delta \mathcal{E} \cdot \Omega(\mathcal{E}, V, N)) = \\ &= k_B \ln \Omega(\mathcal{E}, V, N) + \underbrace{k_B \ln \delta \mathcal{E}}_{\text{Irrelevant term}} \end{aligned}$$

which corresponds exactly to the microcanonical entropy in Statistical Mechanics, up to a irrelevant constant, which is not a problem as only differences in entropy have physical meaning.

Similarly, we can use (2.74) to rewrite the average (2.68) as follows:

$$\langle O \rangle_d = \frac{\sum_{[C_i] \in \Gamma} |c_i| O_i \mathbb{1}_{\mathcal{I}}(H_i)}{\sum_{[C_i] \in \Gamma} |c_i| \mathbb{1}_{\mathcal{I}}(H_i)} \xrightarrow{\max_i |c_i| \rightarrow 0} \frac{1}{\delta \mathcal{E} \Omega(\mathcal{E}, V, N)} \int_{\Gamma} d^{3N} \mathbf{Q} d^{3N} \mathbf{P} O(\mathbf{Q}, \mathbf{P}) \mathbb{1}_{\mathcal{I}}(H) \quad (2.76)$$

$$\xrightarrow{\delta \mathcal{E} \rightarrow 0} \frac{1}{\Omega(\mathcal{E}, V, N)} \int_{\Gamma} d^{3N} \mathbf{Q} d^{3N} \mathbf{P} O(\mathbf{Q}, \mathbf{P}) \delta(H - \mathcal{E}) \quad (2.77)$$

which is again equivalent to the previously obtained results (1.40, pag. 33).

2.7.2 Derivation of the C ensemble

In the case of the **canonical ensemble** we do not need any limiting procedure, as we are not dealing with a “infinitely thin” hyper-surface of constant energy, meaning that Dirac Deltas appear and all functions are well behaved.

So, let’s consider a system with fixed volume V and number of particles N that is put in thermal contact with a larger environment at a fixed temperature T . As energy exchanges are now possible, the system’s energy H will not be conserved. However, experimentally, we see that at equilibrium the *average* value of H is *well defined*, with $\text{Var}(H)$ vanishingly small.

We represent this situation with a constraint of the first class (2.35a):

$$U \stackrel{!}{=} \langle H \rangle = \int_{\Gamma} \underbrace{d^{3N}\mathbf{Q} d^{3N}\mathbf{P}}_{d\Gamma} H(\mathbf{Q}, \mathbf{P}) \rho(\mathbf{Q}, \mathbf{P}) \quad (2.78)$$

And the usual normalization constraint (second class):

$$1 \stackrel{!}{=} \int_{\Gamma} d\Gamma \rho(\mathbf{Q}, \mathbf{P}) \quad (2.79)$$

However, now we are dealing with a *continuous* pdf ρ , and not discrete probabilities p_i or ρ_i as seen in the previous cases, meaning that we need to introduce some results from the calculus of variations⁷.

In fact, the information entropy S_I is now a functional, i.e. a mapping between functions (which, in this case, are pdfs over phase-space $\rho: \Gamma \rightarrow [0, 1]$) and real numbers, defined by:

$$S_I[\rho] = -k_B \int_{\Gamma} d^{3N}\mathbf{Q} d^{3N}\mathbf{P} \rho(\mathbf{Q}, \mathbf{P}) \ln \rho(\mathbf{Q}, \mathbf{P}) \quad (2.80)$$

We want to maximize $S_I[\rho]$ subject to the constraints (2.78) and (2.79). The method of Lagrange multipliers naturally extends to the maximization of functionals, by just replacing derivatives with *functional* derivatives.

Recall that the functional derivative (or *Gateaux derivative*, or *first variation*) of a functional \mathcal{F} evaluated at ρ is defined as:

$$\delta\mathcal{F}[\rho] = \lim_{\tau \rightarrow 0} \frac{f(\rho + \tau s) - f(\rho)}{\tau} = \left. \frac{d}{d\tau} f(\rho + \tau s) \right|_{\tau=0} \quad (2.81)$$

where $s: \Gamma \rightarrow \mathbb{R}$ is a “perturbation of ρ ”, i.e. some function vanishing at ∞ .

Thus, the Lagrange multipliers method leads to:

$$0 \stackrel{!}{=} \delta[S_I[\rho] - \lambda_1 \int_{\Gamma} d^{3N}\mathbf{Q} d^{3N}\mathbf{P} \rho \cdot H - \lambda_0 \int_{\Gamma} d^{3N}\mathbf{Q} d^{3N}\mathbf{P} \rho]$$

The functional derivative is linear (as the usual one), and so we may compute separately the variation of each term, starting from $\delta S_I[\rho]$:

$$\delta S_I[\rho] \stackrel{(2.81)}{=} \left. \frac{d}{d\tau} S_I(\rho + \tau s) \right|_{\tau=0} = -k_B \left. \frac{d}{d\tau} \int_{\Gamma} d\Gamma (\rho + \tau s) \ln(\rho + \tau s) \right|_{\tau=0} = \quad (2.82)$$

⁷See www2.math.uconn.edu/~gordina/NelsonAaronHonorsThesis2012.pdf for a refresher

$$\begin{aligned}
&= -k_B \int_{\Gamma} d\mathbf{\Gamma} \left[s \ln(\rho + \tau s) + \frac{s}{\rho + \tau s} (\rho + \tau s) \right] \Big|_{\tau=0} = \\
&= -k_B \int_{\Gamma} d\mathbf{\Gamma} s [1 + \ln(\rho)] \\
\delta \lambda_1 \int_{\Gamma} d\mathbf{\Gamma} \rho H &= \lambda_1 \frac{d}{d\tau} \int_{\Gamma} d\mathbf{\Gamma} (\rho + \tau s) H \Big|_{\tau=0} = \lambda_1 \int_{\Gamma} d\mathbf{\Gamma} s H \\
\delta \lambda_0 \int_{\Gamma} d\mathbf{\Gamma} \rho &= \lambda_0 \frac{d}{d\tau} \int_{\Gamma} d\mathbf{\Gamma} (\rho + \tau s) \Big|_{\tau=0} = \lambda_0 \int_{\Gamma} d\mathbf{\Gamma} s
\end{aligned}$$

Putting everything back together leads to:

$$0 \stackrel{!}{=} \int_{\Gamma} d^{3N} \mathbf{Q} d^{3N} \mathbf{P} s(\mathbf{Q}, \mathbf{P}) [-k_B - k_B \ln \rho(\mathbf{Q}, \mathbf{P}) - \lambda_1 H(\mathbf{Q}, \mathbf{P}) - \lambda_0]$$

This relation holds for *any* possible $s: \Gamma \rightarrow \mathbb{R}$ (that vanishes at ∞), which can only happen if the function multiplying s vanishes everywhere:

$$0 \stackrel{!}{=} -k_B - k_B \ln \rho(\mathbf{Q}, \mathbf{P}) - \lambda_1 H(\mathbf{Q}, \mathbf{P}) - \lambda_0$$

And rearranging leads to:

$$\rho(\mathbf{Q}, \mathbf{P}) = \exp \left(-1 - \frac{\lambda_0}{k_B} \right) \exp \left(-\frac{\lambda_1}{k_B} H(\mathbf{Q}, \mathbf{P}) \right) \quad (2.83)$$

As λ_1 is the conjugate variable of the energy, $\lambda_1 = 1/T$, and so $\lambda_1/k_B = 1/(k_B T) \equiv \beta$, which is generally known by experiment (it is easier to measure the temperature T of the environment than the energy of the system). To find λ_0 we only need to impose the normalization constraint (2.79):

$$\begin{aligned}
1 &\stackrel{!}{=} \int_{\Gamma} d\mathbf{\Gamma} \rho(\mathbf{Q}, \mathbf{P}) = \exp \left(-1 - \frac{\lambda_0}{k_B} \right) \underbrace{\int_{\Gamma} d\mathbf{\Gamma} \exp(-\beta H(\mathbf{Q}, \mathbf{P}))}_{Z(T, V, N)} \\
&\Rightarrow \exp \left(1 + \frac{\lambda_0}{k_B} \right) = Z(T, V, N)
\end{aligned}$$

Substituting back in (2.83) we get:

$$\rho(\mathbf{Q}, \mathbf{P}) = \frac{e^{-\beta H(\mathbf{Q}, \mathbf{P})}}{Z(T, V, N)} \quad (2.84a)$$

with:

$$\beta = \frac{1}{k_B T} \quad Z = \int_{\Gamma} d^{3N} \mathbf{Q} d^{3N} \mathbf{P} e^{-\beta H(\mathbf{Q}, \mathbf{P})} = e^{-\beta A(T, V, N)}$$

From (2.61c-2.61g) and (2.84a):

$$P = -\frac{\partial A}{\partial V}(T, V, N) \quad \mu = \frac{\partial A}{\partial N}(T, V, N) \quad (2.84b)$$

$$\mathcal{E} = \langle H \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{\partial}{\partial \beta} [\beta A(T, V, N)] \quad (2.84c)$$

The maximum entropy is then:

$$S_I[\rho] = -k_B \int_{\Gamma} d\mathbf{\Gamma} \rho \ln \rho \stackrel{(2.84a)}{=} -k_B \int_{\Gamma} d\mathbf{\Gamma} \frac{e^{-\beta H}}{Z} (-\beta H - \log Z) =$$

$$\begin{aligned}
&= -k_B \left[\int_{\Gamma} d\Gamma \frac{e^{-\beta H}}{Z} (-\beta H) - \log Z \underbrace{\int_{\Gamma} d\Gamma \frac{e^{-\beta H}}{Z}}_1 \right] = \\
&= -k_B (-\beta \langle H \rangle_{\rho} - \log Z) = \frac{1}{k_B T} k_B \langle H \rangle_{\rho} + k_B \log Z = \\
&= \frac{\langle H \rangle}{T} + k_B \log Z
\end{aligned}$$

Exercise 2.7.1 (2):

Fix the correct constants for the volume element $d\Gamma \propto d^{3N}\mathbf{Q} d^{3N}\mathbf{P}$ and the case of identical particles.

Solution. As only differences in entropy are physical, Z is defined up to a multiplicative constant. So we can divide the volume element $d\Gamma$ by h^{3N} , making it dimensionless. In this way, Z becomes proportional the number of *cells* of hyper-volume h^{3N} occupied by the ensemble in phase-space (this choice can be fully motivated by quantum mechanical arguments, as it amounts to a “quantization” of Γ).

Moreover, to resolve the Gibbs paradox, we need to count all permutations of identical particles as one. So, for a system of N particles, this amounts to rescaling $d\Gamma$ by $N!$

At the end, the final definition of $Z(T, V, N)$ becomes:

$$Z(T, V, N) = \int_{\Gamma} \frac{d^{3N}\mathbf{Q} d^{3N}\mathbf{P}}{h^{3N} N!} e^{-\beta H(\mathbf{Q}, \mathbf{P})}$$

2.7.3 Derivation of the G-C ensemble

In the **grandcanonical ensemble** we consider a system exchanging both heat Q and particles δN with a larger environment. Let’s assume, for simplicity, that all particles are identical.

At equilibrium, it is experimentally observed that the average number of particles $\langle N \rangle$ inside the system is fixed to a certain value \mathcal{N} , and does not fluctuate much. This is similar to what happened with energy in the canonical ensemble, and so we need to add a similar *soft* constraint:

$$\langle H_N \rangle \stackrel{!}{=} \mathcal{E}; \quad \langle N \rangle \stackrel{!}{=} \mathcal{N} \quad (2.85)$$

where:

$$H_N(\mathbf{Q}_N, \mathbf{P}_N) = \frac{\|\mathbf{P}\|^2}{2m} + U(\mathbf{Q}_N) \quad \mathbf{Q}_N, \mathbf{P}_N \in \mathbb{R}^{3N}$$

is the Hamiltonian of N particles interacting with with the potential U .

We search for a distribution $\rho_N(\mathbf{Q}, \mathbf{P})$ such that:

$$\rho_N(\mathbf{Q}_N, \mathbf{P}_N) \frac{d\Gamma_N}{N! h^{3N}} = \begin{array}{l} \text{Probability to find } N \text{ particles of the system with} \\ \text{coordinates within a volume element} \\ d^{3N}\mathbf{Q}_N d^{3N}\mathbf{P}_N \equiv d\Gamma_N \text{ in phase space} \end{array} \quad (2.86)$$

The normalization constraint (2.35b) is:

$$1 \stackrel{!}{=} \sum_{N=0}^{\infty} \int_{\Gamma_N} \rho_N(\mathbf{Q}_N, \mathbf{P}_N) \frac{d\Gamma_N}{N!h^{3N}} \equiv \langle 1 \rangle_{\text{g.c.}} \quad (2.87)$$

whereas the constraints in (2.85) become:

$$\mathcal{E} \stackrel{!}{=} \langle H_N \rangle = \sum_{N=0}^{\infty} \int_{\Gamma_N} \rho_N(\mathbf{Q}_N, \mathbf{P}_N) H_N(\mathbf{Q}_N, \mathbf{P}_N) \frac{d\Gamma_N}{N!h^{3N}} \quad (2.88a)$$

$$\mathcal{N} \stackrel{!}{=} \langle N \rangle = \sum_{N=0}^{\infty} N \underbrace{\int_{\Gamma_N} \rho_N(\mathbf{Q}_N, \mathbf{P}_N) \frac{d\Gamma_N}{N!h^{3N}}}_{\substack{\text{Marginalized distribution:} \\ \text{probability that the system} \\ \text{contains } N \text{ particles}}} \quad (2.88b)$$

The grand-canonical average of a generic observable $O_N(\mathbf{Q}_N, \mathbf{P}_N)$ is:

$$\langle O \rangle_{\text{g.c.}} = \sum_{N=0}^{\infty} \int_{\Gamma_N} \rho_N(\mathbf{Q}_N, \mathbf{P}_N) O_N(\mathbf{Q}_N, \mathbf{P}_N) \frac{d\Gamma_N}{N!h^{3N}} \quad (2.89)$$

In the case of $O_N = \log \rho_N$ the average is the information entropy:

$$S_I[\rho_{\text{g.c.}}] = -k_B \sum_{N=0}^{\infty} \int_{\Gamma_N} \frac{d\Gamma_N}{h^{3N}N!} \rho_N(\mathbf{Q}_N, \mathbf{P}_N) \ln \rho_N(\mathbf{Q}_N, \mathbf{P}_N) \quad (2.90)$$

The Lagrange multipliers equations are:

$$0 \stackrel{!}{=} \delta[S_I[\rho_{\text{g.c.}}] - \lambda_0 \langle 1 \rangle_{\text{g.c.}} - \lambda_1 \langle H \rangle_{\text{g.c.}} - \lambda_2 \langle N \rangle_{\text{g.c.}}] =$$

With similar calculations as in (2.82) we get:

$$= - \sum_{N=0}^{\infty} \int_{\Gamma_N} \frac{d\Gamma_N}{N!h^{3N}} \delta \rho_N(\mathbf{Q}_N, \mathbf{P}_N) \left[k_B + k_B \ln \rho_N(\mathbf{Q}_N, \mathbf{P}_N) + \lambda_0 + \right. \\ \left. + \lambda_1 H_N(\mathbf{Q}_N, \mathbf{P}_N) + \lambda_2 N \right] \quad (2.91)$$

where $\delta \rho_N: \Gamma \rightarrow \mathbb{R}$ is a “perturbation” of ρ_N .

Equation (2.91) holds for any $\delta \rho_N$, meaning that the expression in the square brackets must vanish everywhere:

$$0 \stackrel{!}{=} k_B + k_B \ln \rho_N(\mathbf{Q}_N, \mathbf{P}_N) + \lambda_0 + \lambda_1 H_N(\mathbf{Q}_N, \mathbf{P}_N) + \lambda_2 N$$

leading to:

$$\rho_N(\mathbf{Q}_N, \mathbf{P}_N) = \underbrace{\exp\left(-\frac{\lambda_0 + 1}{k_B}\right)}_{1/\Theta} \exp\left(-\frac{\lambda_1}{k_B} H_N(\mathbf{Q}_N, \mathbf{P}_N) - \frac{\lambda_2}{k_B} N\right)$$

λ_1 is the conjugate variable to the energy, and so $\lambda_1 \equiv -1/T$. On the other hand, λ_2 is the conjugate variable of the number of particles N , and so we define $\lambda_2 \equiv -\mu/T$, where μ is called **chemical potential**.

So we can rewrite ρ_N as follows:

$$\rho_N(\mathbf{Q}_N, \mathbf{P}_N) = \frac{1}{\Theta} \exp \left(-\beta H_N(\mathbf{Q}_N, \mathbf{P}_N) + \beta \mu N \right); \quad \beta = \frac{1}{k_B T} \quad (2.92)$$

Then, from the normalization constraint (2.87):

$$\begin{aligned} 1 &\stackrel{!}{=} \sum_{N=0}^{\infty} \int_{\Gamma_N} \rho_N(\mathbf{Q}_N, \mathbf{P}_N) \frac{d\Gamma_N}{N! h^{3N}} = \\ &= \frac{1}{\Theta} \sum_{N=0}^{\infty} \int_{\Gamma_N} \frac{d\Gamma_N}{N! h^{3N}} \exp \left(-\beta H_N(\mathbf{Q}_N, \mathbf{P}_N) + \beta \mu N \right) \end{aligned}$$

Rearranging:

$$\begin{aligned} \exp \left(1 + \frac{\lambda_0}{k_B} \right) &\equiv \Theta(T, \mu, V) = \\ &= \sum_{N=0}^{\infty} \int_{\Gamma_N} \frac{d\Gamma_N}{h^{3N} N!} \exp \left(-\beta H_N(\mathbf{Q}_N, \mathbf{P}_N) \right) \exp(+\beta \mu N) = \\ &= \sum_{N=0}^{\infty} \underbrace{\left[\underbrace{e^{\beta \mu}}_z \right]^N \int_{\Gamma_N} \frac{d\Gamma_N}{h^{3N} N!} \exp \left(-\beta H_N(\mathbf{Q}_N, \mathbf{P}_N) \right)}_{Z(T, V, N)} \quad (2.93) \end{aligned}$$

$$= \sum_{N=0}^{\infty} z^N Z(T, V, N); \quad z = e^{\beta \mu} \quad (2.94)$$

$\Theta(T, \mu, V)$ is the **grand canonical partition function**. $Z(T, V, N)$ is the partition function of a canonical ensemble of N particles in a volume V at temperature T , with corresponding Helmholtz free energy $A_N(T, V, N)$: And so:

$$Z(T, V, N) = \int_{\Gamma_N} \frac{d\Gamma_N}{h^{3N} N!} e^{-\beta H_N(\mathbf{Q}_N, \mathbf{P}_N)} \equiv e^{-\beta A_N(T, V, N)} \quad (2.95)$$

Finally, we can find T and μ (related to the Lagrange multipliers λ_1 and λ_2) by imposing the constraints (2.88a-2.88b), leading to:

$$\mathcal{N} \stackrel{!}{=} \langle N \rangle = k_B T \frac{\partial}{\partial \mu} \ln \Theta(T, \mu, V) \quad (2.96)$$

$$\mathcal{E} \stackrel{!}{=} \langle H \rangle = -\frac{\partial}{\partial \beta} \ln \Theta(T, \mu, V) \quad (2.97)$$

as it is immediate to verify using the definitions (2.89) and (2.94).

The maximum entropy can be obtained by substituting ρ_N given by (2.92) in the formula for S_I (2.90):

$$\max_{\rho} S_I[\rho] \equiv S_{GC}(T, \mu, V) = k_B \ln \Theta(T, \mu, V) + \frac{\langle H \rangle}{T} - \frac{\mu}{T} \langle N \rangle$$

We then define:

$$\Phi(T, \mu, V) \equiv -k_B T \ln \Theta = \mathcal{E} - T S_{GC} - \mu \mathcal{N} \quad (2.98)$$

Large V limit

From (2.94) and (2.95) we have:

$$e^{-\beta\Phi(T,\mu,V)} = \Theta = \sum_{N=0}^{\infty} e^{\beta(\mu N - A(T,V,N))} \quad (2.99)$$

Then from (2.61c-2.61g):

$$P = \frac{\partial}{\partial V} \Phi(T, \mu, V) \quad (2.100)$$

$$\langle H \rangle = \frac{\partial}{\partial \beta} [\beta \Phi(T, \mu, V)] = \mathcal{E}(T, \mu, V) \quad (2.101)$$

$$\langle N \rangle = -\frac{\partial}{\partial \mu} \Phi(T, \mu, V) = \mathcal{N}(T, \mu, V) \quad (2.102)$$

where the last two equations coincide with (2.96) and (2.97).

Since \mathcal{E} and \mathcal{N} in (2.101) and (2.102) are expected to be extensive, whereas μ and β are intensive, we must have that Φ is extensive, i.e.:

$$\Phi(T, \mu, V) = V\varphi(T, \mu) \quad (2.103)$$

Using (2.100) we have $\varphi(T, \mu) = -P$, the grand canonical pressure (since it depends on μ and T).

Thus we have:

$$e^{-\beta PV} \stackrel[(2.98)]{(2.94)} = \sum_N e^{\beta\mu N - A(T,V,N)} \quad (2.104)$$

The large V limit

From (2.84b) the canonical chemical potential is:

$$\mu_C(T, V, N) = \frac{\partial}{\partial N} A(T, V, N)$$

which is intensive since both N and A are intensive:

$$\mu_c(T, V, N) \equiv \mu_c(T, V) + O\left(\frac{1}{N}\right)$$

Exercise 2.7.2 (2):

Prove the last chain using:

$$A(T, V, N) = Na\left(T, \frac{V}{N}\right) + O(\ln N)$$

as was shown in chapter 2.

In (2.102) we can replace the sum $\sum_{N=0}^{\infty}$ with an integration $\int_0^{\infty} dN$ as the leading contributions are the large N , and we can verify “a posteriori” that if V is macroscopic, then $N/V \rightarrow \text{const.}$ when $V \rightarrow \infty$. Then, applying the saddle-point approximation:

$$-\beta\Phi = \beta P(\mu, T)V = \beta[\mu\tilde{N} - A(T, V, \tilde{N})] + O(\ln V)$$

and so \tilde{N} is such that:

$$\begin{aligned}\mu &= \left. \frac{\partial}{\partial N} A(T, V, N) \right|_{N=\tilde{N}} = \mu_c(T, V, N) \Big|_{\tilde{N}} = \\ &= \mu_c(T, V) + O\left(\frac{1}{N}\right)\end{aligned}$$

Then:

$$PV = \mu\tilde{N} - A(T, V, \tilde{N})$$

with \tilde{N} satisfying:

$$\mu = \left. \frac{\partial A}{\partial N} \right|_{N=\tilde{N}}$$

Finally, from (2.102):

$$\begin{aligned}\mathcal{N} = \langle N \rangle &= -\frac{\partial}{\partial \mu} \Phi = \frac{\partial}{\partial \mu} (PV) = \\ &= \tilde{N} + \underbrace{\frac{\partial}{\partial N} (\mu N - A(T, V, N)) \Big|_{N=\tilde{N}}}_{=0} \frac{\partial \tilde{N}}{\partial \mu} = \tilde{N}\end{aligned}$$

What remains to be proved is that this is really a maximum, by computing the second derivative.

(Lesson 16 of
16/4/20)
Compiled: June 2,
2020

2.7.4 Remark on the Legendre Transform

We saw that the *Free energy* $A(T, V, N)$ is the Legendre transform of the **energy** with respect to the **entropy**:

$$d\mathcal{E} = -P dV + T dS + \mu dN \quad (2.105)$$

$$\left(\frac{\partial \mathcal{E}}{\partial S} \right)_{VN} = \mathcal{E} - TS \quad (2.106)$$

Then we solve for $S(T, V, N)$ and write

$$: A(T, V, N) = \mathcal{E} - TS \quad (2.107)$$

$$dA = -P dV - S dT + \mu dN \quad (2.108)$$

$$\left(\frac{\partial A}{\partial N} \right)_{VT} = \mu \quad (2.109)$$

And we solve for $N(T, \mu, V)$. The Legendre transform of A wrt N (or equivalently the Legendre transform of E wrt both S and N) is:

$$\Phi(T, \mu, V) = A - N\mu \quad (2.110)$$

$$d\Phi = -P dV - S dt - N d\mu \quad (2.111)$$

Note that Φ is extensive since A and N are, and so $\Phi(T, \mu, V) = V\varphi(T, \mu)$. Then:

$$-P = \left(\frac{\partial \Phi}{\partial V} \right)_{T, \mu} = \varphi(T, \mu) \quad (2.112)$$

$$\Phi(T, \mu, V) = -P(T, \mu)V \quad (2.113)$$

where $P(T, \mu)$ is the *grand-canonical* pressure.

Exercise 2.7.3 (4):

Determine Φ for the Ideal Gas and show that:

$$P(T, \mu)V = \langle N \rangle k_B T$$

which is the equation of state in the GC ensemble.

2.7.5 Fluctuation of the number of particles

This is related to the correction of the saddle-point approximation.

$$\begin{aligned} e^{\beta PV} &\stackrel{(2.94)}{=} \sum_N e^{\beta \mu N - \beta A(T, V, N)} = \\ &\stackrel{(2.98)}{=} e^{\beta \bar{N} \mu - \beta A(T, V, \bar{N})} \int dN \exp \left(-\frac{(N - \bar{N})^2}{2\sigma_N^2} \right) + \dots \end{aligned} \quad (2.114)$$

where:

$$\sigma_N^2 = \langle (N - \bar{N})^2 \rangle = \left(\beta \frac{\partial^2 A}{\partial N^2} \right)_{N=\bar{N}}^{-1} \quad (2.115)$$

Since from exercise 3 above we have:

$$A(T, V, N) = Na(T, v) + O(\ln N) \quad v = \frac{V}{N} \quad (2.116)$$

(In the following the subindex c refers to “Canonical Ensemble”).

$$\begin{aligned} \left(\frac{\partial^2 A}{\partial N^2} \right)_{\bar{N}} &= \frac{\partial}{\partial N} \underbrace{\left[a - v \frac{\partial a}{\partial v} \right]}_{\frac{\partial A}{\partial N} \equiv \mu_c(T, v)} \Big|_{\bar{N}} = -\frac{v^2}{V} \frac{\partial}{\partial v} \mu_c(T, V) \Big|_{\bar{v}} = \frac{v^3}{V} \frac{\partial^2 a}{\partial v^2} \Big|_{\bar{v}} = \\ &= -\frac{v^3}{V} \frac{\partial P_C}{\partial v} \Big|_{v=\bar{v}} \quad \bar{v} \equiv \frac{\bar{N}}{V} \end{aligned} \quad (2.117)$$

where we have used:

$$P_c \stackrel{(2.108)}{=} -\frac{\partial A}{\partial V} = -\frac{\partial a}{\partial v} \quad (2.118)$$

From equations (2.115) and (2.117) we have:

$$\sigma_N^2 = \frac{k_B T V}{\bar{v}^2} k_T = \bar{N} \frac{k_B T}{\bar{v}} k_T \Rightarrow \frac{\sigma_N}{\sqrt{\bar{N}}} \propto \frac{1}{\sqrt{\bar{N}}} \quad (2.119)$$

where:

$$k_T \equiv \bar{v} \left(-\frac{\partial P_c}{\partial v}(T, v) \right)_{\bar{v}} \quad (2.120)$$

is the **isothermal compressibility**.

Exercise 2.7.4 (5):

Show that in the special example of the Ideal Gas we have:

$$k_T(T, v) = \frac{k_B T}{v} \quad (2.121)$$

In chapter 2 we found the energy fluctuation in the canonical ensemble to be:

$$\sigma_{\mathcal{E}}^2 = \langle (H - \langle H \rangle)^2 \rangle = k_B T^2 C_v(T, V, N) \Rightarrow \frac{\sigma_F}{\langle H \rangle} \propto \frac{1}{\sqrt{N}} \quad (2.122)$$

where C_V is the heat capacity ($\propto N$).

Equations (2.120) and (2.122) are two instances of the famous fluctuation dissipation theorem (another instance is the Einstein relation we found in chapter 4).

In both cases above we see that the fluctuations $\sigma_N/\langle N \rangle$ and $\sigma_{\mathcal{E}}/\langle H \rangle$, ($\langle H \rangle \propto N$) tend to 0 in the thermodynamic limit unless the isothermal compressibility and the heat capacity diverges. Typically this is what happens at a phase transition as we will see in the next chapter.

2.7.6 Absence of macroscopic motion in equilibrium

The MaxEnt principle allows us to prove that in equilibrium there cannot exist macroscopic motion of matter. Indeed, divide the 3D system in macroscopically small regions such that *at stationarity* the part of the system occupying the j -th cell has a momentum \mathbf{p}_j , a mass M_j , a total energy \mathcal{E}_j and thus an internal energy:

$$E_j - \frac{P_j^2}{2M_j} = E_j^{\text{Internal}}$$

and an entropy:

$$S_h(E_j - P_j^2/(2M_j))$$

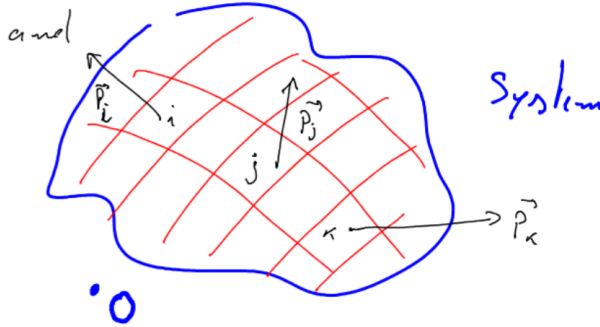


Figure (2.4) – Each macroscopic region of the system at equilibrium shares the same momentum and angular momentum.

We assume that the volume of the cell is fixed and also the number of particles that it contains (thus we will not display their dependence in S_j). If interparticle forces are short range, the total entropy is:

$$S = \sum_j S_j \left(\mathcal{E}_j - \frac{P_j^2}{2M_j} \right) \quad (2.123)$$

The system is isolated and so:

$$\sum_j \mathcal{E}_j = \mathcal{E}, \quad \sum_j \mathbf{p}_j = \mathbf{P}, \quad \sum_j \mathbf{r}_j \times \mathbf{P}_j = \mathbf{L} \quad (2.124)$$

are conserved but otherwise undetermined. Assuming the MaxEnt principle we have to maximize S wrt \mathbf{p}_j under the 7 constraints (2.124), and so we have to determine the stationary conditions for the following system:

$$\mathcal{F} = \sum_j S_j \left(\mathcal{E}_j - \frac{P_j^2}{2M_j} \right) + \mathbf{a} \sum_j \mathbf{p}_j + \mathbf{b} \sum_j \mathbf{r}_j \times \mathbf{p}_j - c \sum_j \mathcal{E}_j$$

$$\frac{\partial \mathcal{F}}{\partial \mathcal{E}_j} = 0 \Leftrightarrow \frac{\partial S_j}{\partial E_j} \left(\mathcal{E}_j - \frac{P_j^2}{2M_j} \right) = c \quad \forall j \quad (2.125)$$

$$\nabla_{\mathbf{p}_j} \mathcal{F} = 0 \Leftrightarrow \underbrace{\frac{\partial}{\partial E_j} S_j \left(\mathcal{E}_j - \frac{P_j^2}{2M_j} \right)}_{1/T} \quad \frac{\mathbf{p}_j}{M_j} = \mathbf{a} + \mathbf{b} \times \mathbf{r}_j \quad (2.126)$$

$$\mathbf{v}_j = \frac{\mathbf{p}_j}{M_j} = (\mathbf{a} + \mathbf{b} \times \mathbf{r}_j)T \quad (2.127)$$

which tells us that all parts have a common uniform translation velocity $\mathbf{a}T$ and a uniform rotatory motion with angular velocity $\mathbf{\Omega} = \mathbf{b}T$. Thus the system behaves like a rigid body as far as the macroscopic motion is concerned.

He⁴ is exceptional since it cannot rigidly rotate.

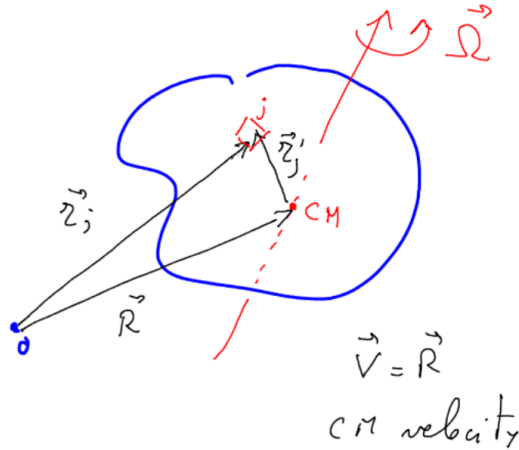


Figure (2.5)

$$\begin{aligned}
\mathbf{r}_j &= \mathbf{R} + \mathbf{r}'_j \\
\mathbf{v}_j &= \dot{\mathbf{r}}_j = \dot{\mathbf{R}} + \dot{\mathbf{r}}'_j = \mathbf{V} + \boldsymbol{\Omega} \times \mathbf{r}'_j = \underbrace{\mathbf{V} - \boldsymbol{\Omega} \times \mathbf{R}}_{\mathbf{aT}} + \underbrace{\boldsymbol{\Omega} \times \mathbf{r}_j}_{\mathbf{bT}}
\end{aligned}$$

2.8 Non Equilibrium Entropy

May we define the entropy in non equilibrium like we did in (??).

$$S_I[\rho(t)] = -k_B \int d\Gamma \rho(\mathbf{Q}, \mathbf{P}, t) \ln \rho(\mathbf{Q}, \mathbf{P}, t) \quad (2.128)$$

where the non-equilibrium probability distribution is time independent and, of course, satisfies the Liouville Theorem (??, ch. 5):

$$\begin{aligned}
\frac{\partial}{\partial t} \rho(\mathbf{Q}, \mathbf{P}, t) &= - \sum_{\alpha} \left[\frac{\partial \rho}{\partial q_{\alpha}}(\mathbf{Q}, \mathbf{P}, t) \frac{\partial H}{\partial p_{\alpha}}(\mathbf{Q}, \mathbf{P}) - \frac{\partial \rho}{\partial p_{\alpha}}(\mathbf{Q}, \mathbf{P}, t) \frac{\partial H}{\partial q_{\alpha}}(\mathbf{Q}, \mathbf{P}) \right] = \\
&\equiv -\{\rho, H\}
\end{aligned} \quad (2.129)$$

with a given initial condition $\rho(\mathbf{Q}, \mathbf{P}, t=0)$.

Let us consider our paradigm of irreversible transformation:

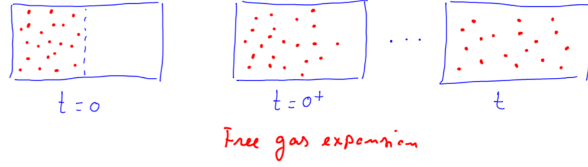


Figure (2.6) – Irreversible transformation: free gas expansion.

and let us calculate dS_I / dt using (2.128) and (2.129) (compare with exercise 5.7 of Sethna).

For a generic functional F (S_I is a particular instance):

$$F[\rho] = \int f(\rho(\mathbf{Q}, \mathbf{P}, t)) \underbrace{d^{3N}\mathbf{Q} d^{3N}\mathbf{P}}_{d\Gamma} \quad (2.130)$$

we have:

$$\begin{aligned}
\frac{d}{dt} F[\rho] &= \int \frac{\partial}{\partial t} f(\rho(\mathbf{Q}, \mathbf{P}, t)) d\Gamma = \int d\Gamma f'(\rho) \frac{\partial \rho}{\partial t} = \\
&\stackrel{(2.129)}{=} - \int d\Gamma f'(\rho) \boldsymbol{\nabla} \rho \cdot \mathbf{V} = - \int d\Gamma \boldsymbol{\nabla} f(\rho) \cdot \mathbf{V}
\end{aligned} \quad (2.131)$$

$$\boldsymbol{\nabla} \rho = \left(\frac{\partial \rho}{\partial q_{\alpha}}, \frac{\partial \rho}{\partial p_{\alpha}} \right)^T \in \mathbb{R}^{6N} \quad (2.132)$$

$$\mathbf{V} = \left(\frac{\partial H}{\partial p_{\alpha}}, -\frac{\partial H}{\partial q_{\alpha}} \right)^T \in \mathbb{R}^{6N} \quad (2.133)$$

Notice that:

$$\nabla \cdot \mathbb{V} = \sum_{\alpha} \left(\frac{\partial}{\partial q_{\alpha}} \frac{\partial H}{\partial p_{\alpha}} - \frac{\partial}{\partial p_{\alpha}} \frac{\partial H}{\partial q_{\alpha}} \right) = 0 \quad (2.134)$$

$$\Rightarrow \nabla f \cdot \mathbb{V} = \nabla \cdot (f \mathbb{V}) - f \nabla \cdot \mathbb{V} = \nabla \cdot (f \mathbb{V}) \quad (2.135)$$

Thus (2.131) becomes:

$$\frac{d}{dt} F[\rho] = - \int d\Gamma \nabla \cdot (f \mathbb{V}) = - \oint_{\substack{\text{Surface} \\ \text{in } \Gamma \text{ at } \infty}} d\mathbf{\Sigma} \cdot \mathbb{V} f = 0 \quad (2.136)$$

In our case $f(\rho) = -k_B \rho \ln \rho$. Since $\int \rho d\Gamma = 1$, then $\rho \rightarrow 0$ when $\mathbf{Q}, \mathbf{P} \rightarrow \infty$ and so $f(\rho) \rightarrow 0$ on the surface at ∞ in the last integral. In summary:

$$\frac{d}{dt} S_I[\rho(t)] = 0 \quad (2.137)$$

that is the information entropy does not change in the irreversible process of the free expansion (and any other process!).

This is because ρ encodes *full information* about the system, and during the deterministic evolution we do not lose any of it, meaning that our *ignorance* does not rise.

If we *discard* some of the information, we will see the entropy rise. For example, consider the marginal probability distribution $\rho_D(\mathbf{Q}, t)$, and suppose it evolves as a diffusion process:

$$\dot{\rho}_D(\mathbf{Q}, t) = D \nabla^2 \rho_D(\mathbf{Q}, t) \quad (2.138)$$

We now compute:

$$\begin{aligned} dvt S_I[\rho_D(t)] &= -k_B \frac{d}{dt} \int \rho_d \ln \rho_d d^{3N} \mathbf{Q} = \\ &= -k_B \int \left[\frac{\partial \rho_D}{\partial t} \ln \rho_d + \rho_d \frac{\partial \rho_d}{\partial t} \frac{1}{\rho_d} \right] d^{3N} \mathbf{Q} \end{aligned}$$

Note that the last term:

$$-k_B \int d^{3N} \mathbf{Q} \frac{\partial}{\partial t} \rho_D(\mathbf{Q}, t) = -k_B \frac{\partial}{\partial t} \underbrace{\int d^{3N} \mathbf{Q} \rho_D(\mathbf{Q}, t)}_{=1} = 0$$

Thus:

$$\frac{d}{dt} S_I[\rho_D(t)] = -k_B \int d^{3N} \mathbf{Q} \frac{\partial}{\partial t} \rho_D \ln \rho_D = \quad (2.139)$$

$$= -k_B D \int d^{3N} \mathbf{Q} (\nabla^2 \rho_D) \ln \rho_D = k_B D \int d^{3N} \mathbf{Q} \frac{(\nabla \rho_D)^2}{\rho_D} \geq 0 \quad (2.140)$$

where we have integrated by parts and assumed that $(\nabla \rho_D) \ln \rho_D \rightarrow 0$ when $\mathbf{Q} \rightarrow \infty$. This is due to the fact that $-D \nabla \rho_D$ is the probability flux and this has to be 0 at infinity if the probability has to be conserved. Then:

$$0 = \frac{\partial}{\partial t} \int \rho_D d^{3N} \mathbf{Q} = D \int \nabla^2 \rho_D d^{3N} \mathbf{Q} = D \int d\mathbf{\Sigma} \cdot \nabla \rho_0 \quad (2.141)$$

As expected, now the entropy *rises* during the irreversible transformation.

Clearly, the diffusion assumption is *ad-hoc*. To obtain a definition of entropy for the non-equilibrium case which is truly general we need a different approach altogether. One possible way is to divide the system in macroscopically small parts, so that each of them $d^3\mathbf{r}$, has a well defined energy density $\epsilon(\mathbf{r}, t)$, number of particles density $n(\mathbf{r}, t)$ and velocity $u(\mathbf{r}, t)$ and so it can be considered “in equilibrium”. This is, in essence, the hypothesis of **local thermal equilibrium** (lte).

Recall that, for a macroscopic system, we have:

$$S(\mathcal{E}, V, N) = Vs \left(\frac{\mathcal{E}}{V}, \frac{N}{V} \right) \quad (2.142)$$

This suggests to define the entropy of the system outside equilibrium but in lte (and with short range interparticle forces) as:

$$S(\epsilon, n, u) = \int d^3\mathbf{r} s \left(\underbrace{\epsilon(\mathbf{r}, t) - \frac{m}{2} u^2(\mathbf{r}, t)}_{\substack{\text{Internal energy of the} \\ \text{subsystem in } d^3\mathbf{r} \\ \text{centred at } \mathbf{r}}}, n(\mathbf{r}, t) \right) \quad (2.143)$$

This S *never decreases* over time!

Notice that (2.143) does not take into account all the details of the evolution like it did $S_I[\rho]$. Thus the set of configurations (\mathbf{Q}, \mathbf{P}) at time t which derives from initial configurations at time $t = 0$ where all the particles were on the left side of a box have an essentially zero measure (from the Liouville theorem) and thus when included in (2.143) have the same $\epsilon(\mathbf{r}, t)$, $u(\mathbf{r}, t)$, $n(\mathbf{r}, t)$ as the almost totality of configurations that will “never” have the possibility to lead the gas again the left half of the box once the momenta $\mathbf{P} \rightarrow -\mathbf{P}$. This means that even changing $t \rightarrow -t$ will make S in (2.143) to decrease in time.

2.8.1 Maxwell demon

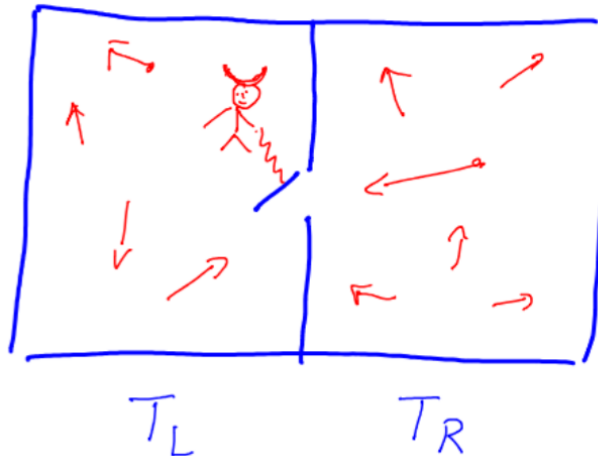


Figure (2.7)

The demon is a device that allows fast particles from the right to go to the left.

$$0 \leq \Delta S_{\text{tot}} = \underbrace{\Delta S_{\text{env}} + \Delta S_{\text{sys}}}_{\text{might be } \leq 0} + \Delta S_{\text{demon}}$$

The second principle of thermodynamics may appear violated when considering only the system and the environment. However, it must apply when we consider also the *demon*. In other words, the act of storing information (or, more precisely, *deleting it*), produces entropy. See ex. 5.2.

Ising Model

(Lesson 19 of
22/04/20)
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Statistical Mechanics, at its core, allows us to understand and quantify macroscopic phenomena starting from microscopic dynamics. In particular, it provides a window in how surprisingly *complex emergent* behaviours arise from the interaction of many relatively *simple* components.

One such example is given by **phase transitions**, i.e. abrupt changes of a system's properties when surpassing a well-defined threshold. For instance, water becomes ice when its temperature dips below $T = 0^\circ\text{C}$, or steam when $T = 100^\circ\text{C}$ is reached.

Phase transitions

Perhaps one of the simplest models describing a phase-transition is the **Ising Model**. At its origin, it was meant as an explanation of **ferromagnetism**. Certain materials possess no net magnetic moment above a certain temperature T_c (the **Curie** temperature), and develop a temporary induced magnetization only in the presence of an external magnetic field (**paramagnetic** phase). However, when T dips below T_c , they exhibit **spontaneous magnetization**, even in the absence of any external field, and behave like *permanent magnets* (**ferromagnetic** phase).

*Ferromagnetism
and paramagnetism*

Classical Statistical Mechanics, by itself, cannot explain this kind of behaviour. In fact, if we suppose that magnetization arises from *tiny current loops*, its (canonical) thermal average is predicted to be always 0, regardless of temperature¹. This is because paramagnetism and ferromagnetism are inherently **quantum** phenomena, arising from the alignment of intrinsic magnetic dipoles of atoms, i.e. **spins**.

*Quantum nature of
ferromagnetism*

In 1920, Wilhelm Lenz proposed a model of interacting spins on a lattice to his student Ernst Ising, who then found an analytic solution for the one-dimensional case in 1924. Underwhelmingly, the model did not exhibit any kind of phase transition - but it was still able to capture the attention of many researcher.

An analytic solution for the $d = 2$ generalization was found by Lars Onsager in 1944, requiring a long and sophisticated mathematical derivation. In this case, however, the model was complex enough to capture a **phase transition** - a very important result for Statistical Mechanics.

The Ising Model a lot of research and applications. Nowadays, the Ising Model

Applications

¹^This is consequence of the Bohr-van Leeuwen theorem. See [6]

is relevant for simulating the behaviour of gases on a discretized grid (**lattice gases**), more complex **spin glasses**, and also the activity of **neural networks** (e.g. Hopfield networks). Also higher dimensional cases are of interest - for example the $d = 4$ model is relevant for modelling *spacetime* (3 dimensions for space plus 1 for time). While no analytic solution for $d > 2$ is known, efficient numerical methods are available, and will be examined in a later chapter.

3.1 Lattice gas

The Ising Model can be introduced as a purely classical model when applied to the behaviour of gas particles in a discretized grid (lattice), completely bypassing the need to deal with quantum effects which are often difficult to interpret.

Consider a system \mathcal{S} of N particles of mass m enclosed in a volume V . Its state is completely specified by $3N$ positions and $3N$ momenta:

$$\begin{aligned}\mathbf{Q} &= (q_{1x}, q_{1y}, q_{1z}, \dots, q_{Nx}, q_{Ny}, q_{Nz}) = (\mathbf{q}_1, \dots, \mathbf{q}_N) \in \mathbb{R}^{3N} \\ \mathbf{P} &= (p_{1x}, p_{1y}, p_{1z}, \dots, p_{Nx}, p_{Ny}, p_{Nz}) = (\mathbf{p}_1, \dots, \mathbf{p}_N) \in \mathbb{R}^{3N}\end{aligned}$$

Suppose that the particles interact through a potential $V_N(\mathbf{Q})$ depending only on the spatial coordinates. The Hamiltonian is then given by:

$$\mathcal{H}_N(\mathbf{Q}, \mathbf{P}) = \sum_{i=1}^N \frac{\|\mathbf{p}_i\|^2}{2m} + V_N(\mathbf{Q}) \quad (3.1)$$

The system is at equilibrium with a much larger environment, with which it exchanges both energy and particles. Denoting with P the grand-canonical pressure, the grand-canonical partition function is given by:

$$e^{\beta PV} = \sum_{N=0}^{+\infty} \frac{1}{N!} \int_{\Gamma_N} \prod_{i=1}^N \frac{d^3 \mathbf{q}_i d^3 \mathbf{p}_i}{h^3} \exp(-\beta[\mathcal{H}_N(\mathbf{Q}, \mathbf{P}) - \mu N]) \quad (3.2)$$

where μ is the system's chemical potential, representing the energy cost of adiabatically adding one particle to \mathcal{S} such that the resulting $N + 1$ system is still at equilibrium. Physically, the value of μ *fixes* the average number of particles $\langle N \rangle$ in \mathcal{S} : if we “forcefully empty \mathcal{S} ”, making $N = 0$, particles will flow in \mathcal{S} from the environment until the “cost” of adding a new particle reaches μ , and then N will only slightly oscillate.

Since in (3.1) momenta and positions are independent, the integral over \mathbf{P} in (3.2) is just a gaussian integral, resulting in:

$$\int_{\mathbb{R}^{3N}} \frac{d^{3N} \mathbf{P}}{h^{3N}} \exp\left(-\beta \sum_{i=1}^N \frac{\|\mathbf{p}_i\|^2}{2m}\right) = \left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3N}{2}} \equiv \lambda^{-3N} \quad (3.3)$$

where:

$$\lambda = \sqrt{\frac{\beta h^2}{2\pi m}} \underset{\substack{\beta=1/k_B T \\ \hbar=h/2\pi}}{=} \sqrt{\frac{2\pi \hbar}{mk_B T}}$$

is called the **thermal wavelength**², and has dimensions of a length (in fact $[d^3\mathbf{p}/h^3] = 1/\text{m}^3$).

Substituting (3.3) back in (3.2) leads to:

$$\begin{aligned} e^{\beta PV} &= \sum_{N=0}^{+\infty} \frac{1}{N!} \int_{V^N} d^{3N}\mathbf{Q} e^{-\beta V_N(\mathbf{Q})} \left(\underbrace{\frac{e^{\beta\mu}}{\lambda^3}}_z \right)^N = \\ &= \sum_{N=0}^{+\infty} \frac{z^N}{N!} \int_{V^N} d^{3N}\mathbf{Q} e^{-\beta V_N(\mathbf{Q})} \end{aligned} \quad (3.4)$$

We now **discretize** the system's volume V in small cubic *sites*, each with edges of size a (fig. 3.1). Space is thus divided in cells, each labelled by its 3-dimensional integer indices $\mathbf{x}_i \in \mathbb{Z}^3$.

1. Lattice discretization

More in general, we may consider a d -dimensional system, of d -volume³ V . Then, each cell i will be labelled by d indices: $\mathbf{x}_i \in \mathbb{Z}^d$. In fact, many physical systems can be modelled with $d \neq 3$ dimensions. For example, oxygen interacting with a graphite plane is intrinsically a $d = 2$ system.

Also, cells may be of different shapes: it suffices that they are all equal and that they *tessellate* the entire space. For instance, in $d = 2$ we may subdivide a plane in triangles instead of squares, or with tetrahedra instead of cubes in $d = 3$. In our case we will focus on the simplest choice, the cubic one.

Suppose now that $V_N(\mathbf{Q})$ may be written as sum of two-body interactions:

2. Pair-wise close-range potential

$$V_N(\mathbf{Q}) = \sum_{i < j}^N v(q_{ij}) \quad q_{ij} \equiv \|\mathbf{q}_i - \mathbf{q}_j\| \quad (3.5)$$

where $v(q_{ij})$ is the potential of two particles i and j separated by a (relative) distance q_{ij} . If the gas is made of neutral particles, then $v(q)$ is a close-range attractive interaction, with the shape of a **Lennard-Jones potential** (fig. 3.2).

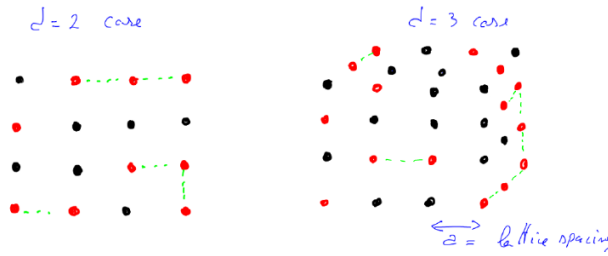


Figure (3.1) – Examples of cubic lattices in $d = 2$ and $d = 3$.

²^It is the average de Broglie wavelength of particles of an ideal gas at temperature T , i.e. of particles with energy of order $k_B T$.

³^If $d = 1$, then V is a length, if $d = 2$ it is an area, and if $d = 3$ it is the usual volume. For higher dimensions it is a *hyper*-volume.

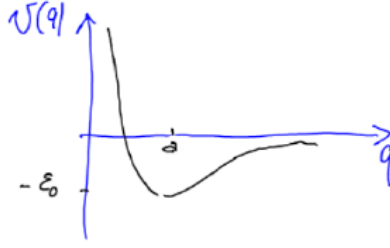


Figure (3.2) – Shape of the Lennard-Jones potential. Two particles separated by a sufficiently small distance $q \sim a$ are weakly attracted to each other, and repelled if $q \rightarrow 0$ (as if they were *hard spheres*). As $v(q)$ quickly vanishes for $q \rightarrow \infty$, particles that are too far from each other *do not interact*. Physically, such $v(q)$ is due to interactions of the electronic clouds of neutral atoms. For q too small, the (Pauli) repulsion of electrons dominates. Due to quantum fluctuations, the electronic clouds are not completely uniform: sometimes an electron “spends more time on one side”, producing a short-lived polarization. If $q \sim a$, one such “instantaneous dipole” may induce a temporary dipole in the other atom. It is this correlation between temporary polarizations that leads to a weak attractive force between the atoms (van der Waals force).

If we choose the lattice step length a as the position of the minimum of $v(q)$, then on average at most one particle will occupy a given cell at any time - because two particles in the same site would be separated by $q < a$, for which $v(q)$ is strongly repulsive. Moreover, only particles in neighbouring cells are sufficiently close to interact with each other.

So, in **approximation**, we consider a model in which cells can contain **at most one particle** at a time (at its centre), and interactions between non-neighbouring cells are neglected. Thus the distance q between two particles must be a multiple of a , and the interaction potential is given by:

3. *Discretized potential*

$$v(q) = \begin{cases} +\infty & q = 0 \\ -\epsilon_0 & q = a \\ 0 & \text{otherwise} \end{cases}$$

We then define the **occupancy** n_i of cell i as a binary variable:

$$n_i = \begin{cases} 1 & \text{Site } i \text{ contains a particle} \\ 0 & \text{Site } i \text{ is empty} \end{cases}$$

If we know all $\{n_i\}$, then the system (in this discretized approximation) is completely determined. Note that dealing with occupancies *automatically* takes into account the indistinguishability of particles: $n_i = 1$ regardless if cell i is occupied by particle #3 or #42.

Shortcomings of the lattice model. In summary, the lattice model is a way to deal with the complex integration in 3.4, making the following approximations:

1. **Discretization:** space is divided in small cubic units, each containing **at most one particle**.

2. **Close-range pair-wise interaction:** the only possible interactions are between pairs of neighbouring cells.

As a consequence of these approximation, there is a **maximum density** in the system, corresponding to the case when all cells are occupied - meaning that the system cannot be compressed over a certain threshold.

Moreover, there is no way to understand if, in the densest case, particles are still moving from one cell to the other, “exchanging places” with each other, or if they just stay forever in their original site: in both cases, all the n_i will be equal to 1, and remain constant. In other words, there is no difference between the **liquid** phase and the **solid** one, meaning that the model **cannot appreciate the liquid-solid phase transition**, and so it is not very good for explaining the usual three phases of matter. However, it can describe accurately the liquid-vapour transition, and - more importantly - it leads to the Ising Model, which is very important in physical mechanics.

There are of course more complex methods that relax the lattice approximation, dealing directly with the grand partition function in the continuum. In general they apply perturbation theory to the pair-wise potential, and through quite involved expansions (e.g. Virial expansion, or Mayer cluster expansion) they lead to equations of state capturing both the solid-liquid transition and the liquid-vapour transition. These are all well-known techniques (Mayer worked in the 1940s), with not much conceptual difficulty, apart of some very long and uninspiring computations. For more information, see [7].

We can now write $V_N(\mathbf{Q})$ as function of the $\{n_i\}$. We consider two particles occupying neighbouring cells as being separated by a distance of a , and experiencing a potential $V(a) = -\epsilon_0$. Then the total potential experienced at cell i is given by summing a contribution of $V(a)$ for each occupied neighbouring cell:

$$V(\mathbf{x}_i) = -\epsilon_0 \sum_{\langle j,i \rangle} n_j$$

The notation $\langle j,i \rangle$ represents a sum over all cells j that are the nearest neighbours of cell i . Then $\sum_{\langle j,i \rangle} n_j$ is exactly to the number of cells *around* i that are occupied. In particular, the total number N of particles in the system is the number of occupied cells:

$$N = \sum_x n_x \tag{3.6}$$

Then, the total potential $V_N(\mathbf{Q})$ can be approximated as the sum of $V(\mathbf{x}_i)$ terms over all cells i that are occupied, leading to:

$$V_N(\{\sigma_i\}) = -\epsilon_0 \sum_{\langle x,y \rangle} n_x n_y \tag{3.7}$$

Note that the product $n_x n_y$ is 1 if and only if both cells are occupied.

So, in other words, V_N is obtained by multiplying the average potential of an interaction ($-\epsilon_0$) by the number of such pairwise interactions, i.e. the number of pairs of neighbouring cells $\langle x,y \rangle$ that are both occupied.

Note that not all sites are treated equally: the ones at the **boundaries** of V have a lower number of neighbours than the ones in the **bulk**. If we consider this asymmetry, letting cells at the margins interact only with their neighbours, the system is said to have **open boundaries**. Alternatively, boundaries may be removed by “connecting” sites at one margin with the ones from the opposite side (**periodic boundaries**). In this way, all cells have exactly the same number of neighbours, and can then be treated the same, achieving **translational invariance**.

Open and periodic boundary conditions

Periodic boundary conditions alter the system’s **topology**. For example, in $d = 1$, the *open* case can be represented as a segment, while the *periodic* one as a circle (fig. 3.3). In $d = 2$, open boundaries result in a *planar* topology, while periodic conditions produce a *toroidal* surface (fig. 3.4).

Periodic boundaries and topology

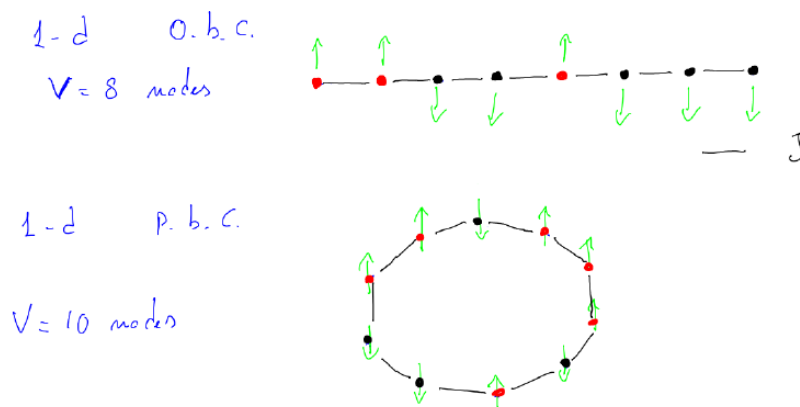


Figure (3.3) – Ising model in $d = 1$ with **open** boundaries (top), or **periodic** boundaries (bottom). Periodic conditions are obtained by *deforming* the initial line to “attach” its two ends.

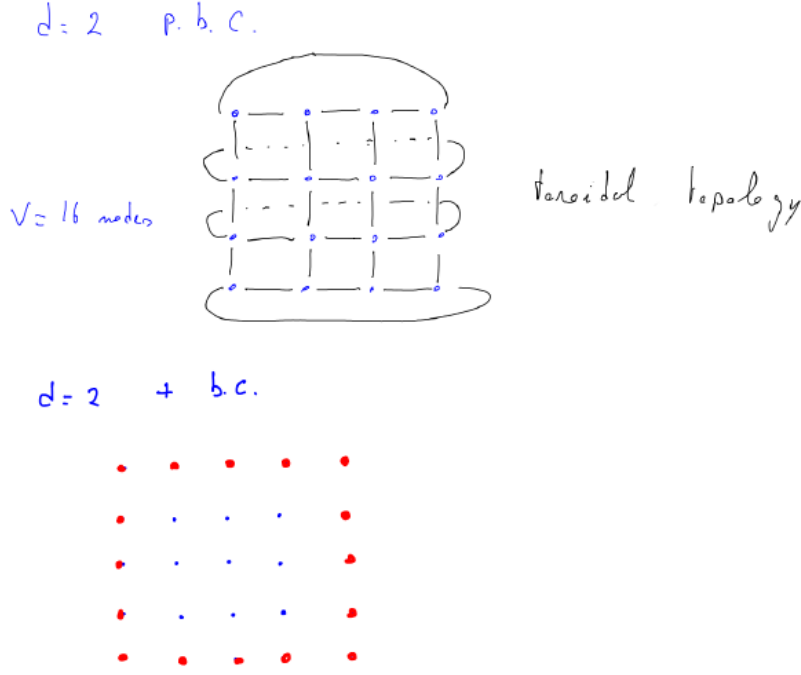


Figure (3.4) – Ising model in $d = 2$, with **periodic** boundaries (top) or **open** boundaries (bottom). Starting from a square, two opposite edges are attached together, forming a cylinder. Then the two circles at the boundaries are attached, deforming the cylinder into a torus.

Boundaries may also be **fixed** to a particular *state*: for example to be always empty or full of particles.

It is now useful to *shift* the occupancies n_i so that they assume symmetrical values. So, we define a “spin-like” occupancy σ_i as follows:

$$\sigma_i = \begin{cases} +1 & \text{Cell } i \text{ is occupied} \\ -1 & \text{Cell } i \text{ is empty} \end{cases} \quad (3.8)$$

Clearly $\sigma_i = 2n_i - 1$, and so:

$$n_i = \frac{1 + \sigma_i}{2}$$

And so we may rewrite (3.6) and (3.7) as follows:

$$N = \sum_x \frac{1 + \sigma_x}{2} \quad (3.9)$$

$$V_N(\{\sigma_i\}) = -\epsilon_0 \sum_{\langle x,y \rangle} n_x n_y \quad (3.10)$$

We can then use (3.10) and (3.9) to approximate (3.4) on the lattice:

$$\begin{aligned} Z_{\text{g.c.}} &\equiv e^{\beta PV} \stackrel{(3.4)}{=} \sum_{\{\sigma\}} \exp(-\beta V_N(\sigma) + N(\sigma) \ln z) = \\ &\stackrel{(3.10)}{\stackrel{(3.9)}}{=} \sum_{\{\sigma\}} \exp \left(\beta \epsilon_0 \sum_{\langle x,y \rangle} \frac{1 + \sigma_x}{2} \frac{1 + \sigma_y}{2} + \ln z \sum_x \frac{1 + \sigma_x}{2} \right) \end{aligned} \quad (3.11)$$

In fact the sum over all possible unique⁴ configurations of N particles over all values of N is equivalent to the sum over all possible occupancies $\boldsymbol{\sigma} = \{\sigma_i\}$:

$$\sum_{N=0}^{+\infty} \int_{V^N} \frac{d^{d \cdot N} \mathbf{Q}}{N!} \xrightarrow{\text{discretization}} \sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_{\text{last}}=\pm 1} = \sum_{\{\boldsymbol{\sigma}\}}$$

The choice of using spin-like variables (3.8) has lead to the appearance of constant terms, independent of the system's state, in (3.11), that we now extract. Consider the argument of the exponential, and expand the sums:

$$\frac{\beta \epsilon_0}{4} \left[\sum_{\langle x,y \rangle} 1 + \sum_{\langle x,y \rangle} (\sigma_x + \sigma_y) + \sum_{\langle x,y \rangle} \sigma_x \sigma_y \right] + \frac{\ln z}{2} \left(\sum_x 1 + \sum_x \sigma_x \right) \quad (3.12)$$

Summing ones over all cells is just the total number of cells in the lattice, each with volume a^d :

$$\sum_x 1 = N_{\text{cells}} = \frac{V}{a^d}$$

For simplicity, let's choose our units so that $a = 1$, and thus:

$$\sum_x 1 = V \quad (3.13)$$

Similarly $\sum_{\langle x,y \rangle} 1$ counts the number of *pairs* of neighbours. Graphically, if we represent cells as nodes in a graph, each connected to its neighbours by edges, then $\sum_{\langle x,y \rangle} 1$ is just the number of edges (fig. 3.3). Let's consider, for simplicity, a system with periodic boundary conditions - so that all cells have the same number q of neighbours (this is also true for a system with open boundaries, in the limit of a lattice of infinite size). Then, the number of pairs (edges) will be:

$$\sum_{\langle x,y \rangle} 1 = \text{N. of pairs} = \frac{N_{\text{cells}} q}{2} = \frac{V q}{2}$$

where the division by 2 accounts for the fact that edges are *undirected* - i.e. if a is connected to b , then b is connected to a by the same edge. Without this division, we would be counting every edge *twice*.

For a cubic lattice (with no boundaries), each cell has exactly 2 neighbours in each *direction*. So the total number of neighbours q will be twice the number of dimensions d :

$$\sum_{\langle x,y \rangle} 1 = \frac{2Vd}{2} = Vd \quad (3.14)$$

Finally, consider the second sum:

$$\sum_{\langle x,y \rangle} \sigma_x + \sigma_y$$

⁴Due to the division by $N!$, configurations where only N cells are occupied are considered distinguishable only if the occupied cells are different. In other words, permuting the position of two particles is not counted.

Practically, to compute it we may inspect each edge (x, y) , and sum the values σ_x and σ_y of the *spins* at its extrema. When we are done, each value σ_x at a node will have been considered exactly q times - one for every neighbour of x :

$$\sum_{\langle x, y \rangle} \sigma_x + \sigma_y = \sum_x \sigma_x \text{dg}(x) \quad (3.15)$$

where $\text{dg}(x)$ is the **degree** of node x , i.e. the number of connections (edges) involving cell x . In our case, $\text{dg}(x) = q = 2d$:

$$\sum_{\langle x, y \rangle} \sigma_x + \sigma_y = 2d \sum_x \sigma_x$$

This relation will allow to highlight the common factor $\sum_x \sigma_x$.

Substituting (3.13), (3.14) and (3.15) back in (3.12) leads to:

$$\begin{aligned} & \beta \frac{\epsilon_0}{4} \left[Vd + 2d \sum_x \sigma_x + \sum_{\langle x, y \rangle} \sigma_x \sigma_y \right] + \frac{\ln z}{2} \left(V + \sum_x \sigma_x \right) = \\ & = \left[\underbrace{\beta \frac{\epsilon_0}{4} \sum_{\langle x, y \rangle} \sigma_x \sigma_y}_J + \underbrace{\left[\frac{\beta \epsilon_0 d}{2} + \frac{\ln z}{2} \right] \sum_x \sigma_x}_{\beta b} \right] + V \left(\beta \frac{\epsilon_0}{4} d + \frac{\ln z}{2} \right) \end{aligned} \quad (3.16)$$

The term in the first set of square parentheses is the only one depending on σ , and thus the one capturing the *essence* of the Ising Model. The last one is just a scaling factor given by the current application (lattice gas).

For simplicity, let's define:

$$J \equiv \frac{\epsilon_0}{4}; \quad \beta b \equiv \frac{\beta \epsilon_0 d}{2} + \frac{\ln z}{2} \quad (3.17)$$

In this way we may collect a β in (3.16):

$$\beta \left[J \sum_{\langle x, y \rangle} \sigma_x \sigma_y + b \sum_x \sigma_x \right] + \beta V \left(Jd + \frac{\ln z}{2\beta} \right)$$

Substituting back in (3.11):

$$Z_{\text{g.c.}} \equiv e^{\beta PV} = \underbrace{\left(\sum_{\{\sigma\}} \exp \left[\beta \left(J \sum_{\langle x, y \rangle} \sigma_x \sigma_y + b \sum_x \sigma_x \right) \right] \right)}_Z \exp \left(\beta V \left[Jd + \frac{\ln z}{2\beta} \right] \right) \quad (3.18)$$

We define the Ising Model partition function Z to contain the only relevant factor:

$$Z_{\text{Ising}} \equiv \sum_{\{\sigma\}} \exp \left[\beta \left(J \sum_{\langle x, y \rangle} \sigma_x \sigma_y + b \sum_x \sigma_x \right) \right] \equiv e^{-\beta V f(T, b)} \quad (3.19)$$

where $f(T, b)$ (defined by the above relation) is the model's **free energy density**. Then, taking the logarithm of both terms in (3.18):

$$\beta P \mathcal{V} \stackrel{(3.19)}{=} -\beta \mathcal{V} f(T, b) + \beta \mathcal{V} J d + \beta \mathcal{V} \frac{\ln z}{2\beta} \quad (3.20)$$

Rearranging the definition of b (3.17):

$$b = \frac{\epsilon_0 d}{2} + \frac{\ln z}{2\beta} \Rightarrow \frac{\ln z}{2\beta} = b - \frac{\epsilon_0 d}{2}$$

and substituting in (3.20) we get the grand-canonical pressure of the lattice gas:

$$\begin{aligned} P_{\text{g.c.}} &= -f(T, b) + \frac{\epsilon_0}{4} d + b - \frac{\epsilon_0 d}{2} = -f(T, b) - \frac{\epsilon_0}{4} d + b = \\ &= -f(T, b) + b - Jd \end{aligned} \quad (3.21)$$

The physical interpretation of J and b depends on which application we are considering. In the lattice gas, J is clearly proportional to the strength of interaction between gas molecules occupying neighbouring cells, while b depends on the chemical potential μ (through z), the temperature and the system's dimensionality.

A clearer meaning for b is found when the Ising Model is applied to ferromagnetism. In this case, the $\{\sigma_i\}$ represent the direction (up or down) of the particle's *spins*, i.e. their *intrinsic* magnetic momenta (of pure quantum origin). Then $b \sum_x \sigma_x$ measures the correlation between the *spin directions* and b . In particular, configurations for which the majority of σ_i have the same sign of b (i.e. are “parallel” to b) have a higher probability (as each term in the sum over states in Z is the probability associated with a particular configuration $\boldsymbol{\sigma}$). So, b can be interpreted as an **external magnetic field**, pushing each particle to align its spin to it.

On the other hand, for a quantum system (such as a ferromagnet), J is called the **exchange energy**, and measures the overlap of electronic clouds of neighbouring atoms.

From (3.19) we can extract the Hamiltonian for the Ising Model:

$$Z_{\text{Ising}} \equiv \sum_{\{\boldsymbol{\sigma}\}} e^{-\beta \mathcal{H}(\boldsymbol{\sigma})} \Rightarrow \mathcal{H}(\boldsymbol{\sigma}) = -J \sum_{\langle x, y \rangle} \sigma_x \sigma_y - b \sum_x \sigma_x \quad (3.22)$$

$\beta \mathcal{H}(\boldsymbol{\sigma})$ is called the **reduced Hamiltonian**:

$$\begin{aligned} \beta \mathcal{H}(\boldsymbol{\sigma}) &= - \underbrace{\beta J}_{K} \sum_{\langle x, y \rangle} \sigma_x \sigma_y - \underbrace{\beta b}_h \sum_x \sigma_x \\ &= -K \sum_{\langle x, y \rangle} \sigma_x \sigma_y - h \sum_x \sigma_x \end{aligned}$$

Intuitively, $\mathcal{H}(\boldsymbol{\sigma})$ is the sum of two interactions:

- **Spin-spin interactions:** $-J \sum_{\langle x, y \rangle} \sigma_x \sigma_y$. If $J > 0$, the term is minimized if $\sigma_x \sigma_y > 0$, i.e. if neighbouring spins are all *parallel* to each other (**ferromagnetic order**). If $J < 0$, spins tend instead to be *anti-parallel* to each other (**anti-ferromagnetic order**), as can be seen in fig. 3.5.

- **Spin-field interaction:** $-b \sum_x \sigma_x$, which is minimized if spins are aligned (parallel) to the magnetic field b (when applying the model to a ferromagnet).

In particular, if $h = 0$ (and so $b = 0$), then there is no “preferred direction” for the alignment of spins. This results in two equivalent *ground states*, as $H(\boldsymbol{\sigma}) = H(-\boldsymbol{\sigma})$. For instance, if $J > 0$, the two possibilities are all $\sigma_i = +1$ (up), or all $\sigma_i = -1$ (down).

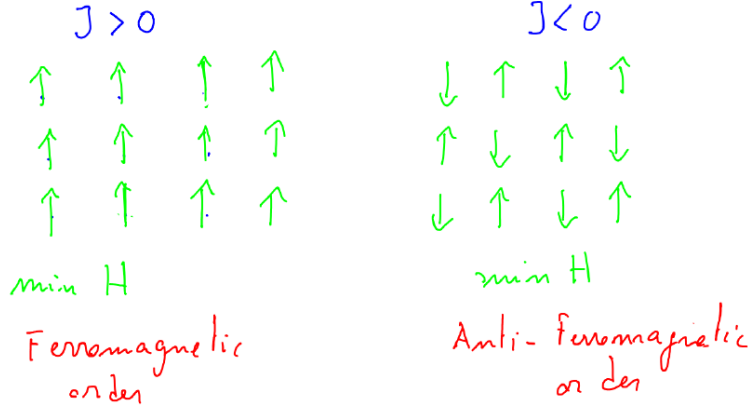


Figure (3.5) – The spin-spin interaction energy when all neighbouring spins are ordered in a (anti)parallel way, depending on the sign of J .

3.2 Ising Partition Function

Our next goal is to compute explicitly the Ising partition function (3.19):

$$Z(K, h) = \sum_{\{\boldsymbol{\sigma}\}} \exp \left(K \sum_{\langle x, y \rangle} \sigma_x \sigma_y + h \sum_x \sigma_x \right) = e^{-\beta V f(K, h)} \quad \begin{matrix} K = \beta J \\ h = \beta b \end{matrix} \quad (3.23)$$

Note that the sum is over $2^{N_{\text{cells}}} = 2^V$ (as the lattice step a is set to 1) possible states (spin configurations).

We define the **magnetization** m as the average *alignment* of spins:

Magnetization

$$\begin{aligned} m &\equiv \frac{1}{V} \langle \sum_x \sigma_x \rangle = \frac{1}{V} \frac{1}{Z} \sum_{\{\boldsymbol{\sigma}\}} \exp \left(K \sum_{\langle x, y \rangle} \sigma_x \sigma_y + h \sum_x \sigma_x \right) \sum_x \sigma_x = \\ &= \frac{1}{V} \frac{\partial}{\partial h} \ln Z(K, h) \stackrel{(3.23)}{=} -\beta \frac{\partial}{\partial h} f(K, h) \end{aligned} \quad (3.24)$$

The average number of particles $\langle N \rangle$ in a grand-canonical ensemble is given by:

Average number of particles $\langle N \rangle$

$$\langle N \rangle_{\text{g.c.}} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z_{\text{g.c.}} = \frac{1}{\beta} \frac{\partial z}{\partial \mu} \frac{\partial}{\partial z} \ln Z_{\text{g.c.}} \quad (3.25)$$

with:

$$\frac{\partial z}{\partial \mu} = \frac{\partial}{\partial \mu} \frac{e^{\beta \mu}}{\lambda^3} = \beta \underbrace{\frac{e^{\beta \mu}}{\lambda^3}}_z = \beta z$$

and so:

$$\langle N \rangle_{\text{g.c.}} = \frac{1}{\beta} \beta z \frac{\partial}{\partial z} \ln Z_{\text{g.c.}} = z \frac{\partial}{\partial z} \ln Z_{\text{g.c.}} \quad (3.26)$$

Let v be the average volume per particle, i.e. $\langle N \rangle/V$. Then the average **density** of particles is v^{-1} : *Particle density*

$$\begin{aligned} v^{-1} &\equiv \frac{\langle N \rangle}{V} \stackrel{(3.26)}{=} \frac{z}{V} \frac{\partial}{\partial z} \ln Z_{\text{g.c.}} \stackrel{(3.18)}{=} \frac{z}{V} \frac{\partial}{\partial z} \beta PV = \\ &\stackrel{(3.21)}{=} \frac{z}{V} \frac{\partial}{\partial z} [-\beta V f(T, b(z)) + \beta V b(z) - \beta V Jd] = \\ &\stackrel{(3.23)}{=} \frac{z}{V} \frac{\partial}{\partial z} [\ln Z_{\text{Ising}} + \beta V b] \end{aligned} \quad (3.27)$$

as the third term does not depend on z . It is useful to change variables from $z \rightarrow \ln z$, as b is a function of $\ln z$:

$$z \frac{\partial}{\partial z} = z \frac{\partial(\ln z)}{\partial z} \frac{\partial}{\partial(\ln z)} = \cancel{z} \frac{1}{\cancel{z}} \frac{\partial}{\partial(\ln z)} = \frac{\partial}{\partial(\ln z)}$$

So that:

$$\frac{z}{V} \frac{\partial}{\partial z} \beta V b = \beta \frac{\partial b}{\partial(\ln z)} \stackrel{(3.17)}{=} \beta \frac{1}{2\beta} = \frac{1}{2} \quad (3.28)$$

With another change of variable $z \rightarrow h$ we can rewrite $z \partial_z \ln Z_{\text{Ising}}$ as a function of the magnetization m :

$$\frac{z}{V} \frac{\partial}{\partial z} \ln Z_{\text{Ising}} = \frac{\partial h}{\partial(\ln z)} \underbrace{\frac{1}{V} \frac{\partial}{\partial h} \ln Z_{\text{Ising}}}_m = \left(\frac{\partial(\ln z)}{\partial(h)} \right)^{-1} m \stackrel{(a)}{=} \frac{m}{2} \quad (3.29)$$

where the derivative in (a) can be computed by isolating $\ln z$ in the definition of b (3.17):

$$b = \frac{\epsilon_0 d}{2} + \frac{\ln z}{2\beta} \Rightarrow 2\beta b = \underbrace{\epsilon_0}_{4J} d + \ln z \Rightarrow \ln z = 2\beta(b - 2Jd) = 2(h - 2Kd) \Rightarrow \frac{\partial(\ln z)}{\partial h} = 2$$

Substituting (3.28) and (3.29) back in (3.27) leads to:

Particle density and magnetization

$$v^{-1} = \frac{m}{2} + \frac{1}{2} = \frac{m+1}{2} \quad (3.30)$$

So a higher m corresponds (in the lattice gas model) to a higher particle density. Intuitively, a high m means that, *on average*, cells are more occupied - meaning that particles will be, in general, closer together. Note that $m \in [-1, +1]$ (which happens, respectively, when all spins point *up* or *down*, i.e. if all cells are occupied or empty), and so $v^{-1} \in [0, 1]$ as expected.

Assuming periodic boundary conditions, the system is **translational invariant**: there is no “preferred” position in the lattice - all cells are exactly equal to each

Consequences of translational invariance

other. This means that $\langle \sigma_x \rangle \equiv \bar{\sigma}$ must be independent of x , and so it is equal to the magnetization m :

$$m = \frac{1}{V} \langle \sum_x \sigma_x \rangle = \frac{1}{V} \sum_x \langle \sigma_x \rangle = \frac{1}{V} \cancel{V} \bar{\sigma} = \bar{\sigma} = \langle \sigma_x \rangle$$

On the other hand, the 2-point correlation function $\langle \sigma_x \sigma_y \rangle$ must depend only on the distance $\|\mathbf{r}_x - \mathbf{r}_y\|$ between the two cells, because of translational invariance.

Note that for any finite V , the sum in (3.23) is a sum over a finite number 2^V of states. As each term is an analytic function, Z is also an analytic function, and so it is $\ln Z = -\beta V f(K, h)$, and in particular the free energy $f(K, h)$. However, we expect phase-transitions to correspond to points at which the free energy is non-analytic - which would explain the *sudden* changes in the system's properties that are experimentally observed during such a transition.

So, in any finite lattice we won't be able to see any phase-transition. Conversely, to observe a phase-transition, an **infinite lattice** is required, which is obtained when $V \rightarrow \infty$, i.e. in the **thermodynamic limit**.

Example 3 (Non-interacting spins):

Let's examine the simplest possible case in the Ising Model, occurring when $J = 0$ (or, equivalently, $K = 0$). The Hamiltonian becomes:

$$\mathcal{H}(\boldsymbol{\sigma}) = -h \sum_x \sigma_x \quad (3.31)$$

meaning that spins (or cells) are completely independent from each other (**decoupled**). In fact, the partition function factorizes:

$$Z = \sum_{\{\boldsymbol{\sigma}\}} \exp\left(h \sum_x \sigma_x\right) = \sum_{\sigma_1=\pm 1} e^{h\sigma_1} \dots \sum_{\sigma_V=\pm 1} e^{h\sigma_V}$$

Noting that:

$$\sum_{\sigma_i=\pm 1} e^{h\sigma_i} = \frac{e^h + e^{-h}}{2} = 2 \cosh h$$

the partition function becomes:

$$Z = (2 \cosh h)^V \quad (3.32)$$

Then the **free energy** f is:

$$Z = e^{-\beta V f(h)} \Rightarrow f(h) = -\frac{\ln Z}{\beta V} \stackrel{(3.32)}{=} -\frac{\ln(2 \cosh h)}{\beta} \quad (3.33)$$

The **magnetization**:

$$m(h) \stackrel{(3.24)}{=} -\beta \frac{\partial}{\partial h} f(h) = \frac{\partial}{\partial h} \ln(\cosh h) = \frac{\sinh h}{\cosh h} = \frac{e^h - e^{-h}}{e^h + e^{-h}} = \tanh h \quad (3.34)$$

A plot of $m(h)$ can be seen in fig. 3.6.

Inverting (3.34) allows to express h as a function of m :

$$h = \beta b = \tanh^{-1} m$$

This can be solved by letting $t = e^h$, and so:

$$\begin{aligned} m = \tanh h &= \frac{t + 1/t}{t - 1/t} = \frac{t^2 - 1}{t^2 + 1} \Rightarrow m(t^2 + 1) = t^2 - 1 \\ \Rightarrow t^2(m + 1) &= -(m - 1) \Rightarrow t = \pm \sqrt{\frac{1 + m}{1 - m}} \end{aligned}$$

As $t = e^h > 0$, only the positive solution is acceptable, leading to:

$$e^h = \sqrt{\frac{1 + m}{1 - m}} \Rightarrow h = \ln \sqrt{\frac{1 + m}{1 - m}} = \frac{1}{2} \ln \frac{1 + m}{1 - m} \quad (3.35)$$

Substituting back:

$$h = \beta b = \tanh^{-1} m = \frac{1}{2} \ln \frac{1 + m}{1 - m} \quad -1 < m < +1 \quad (3.36)$$

We can also express the free energy (3.33) as function of m . First note that:

$$\begin{aligned} \ln \cosh h &= \frac{1}{2} \ln(\cosh h)^2 = \frac{1}{2} \ln \frac{\cosh^2 h}{\underbrace{\cosh^2 h - \sinh^2 h}_1} = \\ &= -\frac{1}{2} \ln \frac{\cosh^2 h - \sinh^2 h}{\cosh^2 h} = -\frac{1}{2} \ln(1 - \tanh^2 h) = \\ &\stackrel{(3.36)}{=} -\frac{1}{2} \ln(1 - m^2) \end{aligned} \quad (3.37)$$

and so:

$$\begin{aligned} f &\stackrel{(3.33)}{=} -\frac{\ln(2 \cosh h)}{\beta} \Rightarrow \beta f = -\ln(\cosh h) - \ln 2 = \\ &\stackrel{(3.37)}{=} \frac{1}{2} \ln(1 - m^2) - \frac{1}{2} \ln 2 = \frac{1}{2} \ln \frac{1 - m^2(h)}{4} \end{aligned} \quad (3.38)$$

Note that the free energy is an **even** function of the magnetization, whereas m is an **odd** function of h .

Finally, from (3.34) note that the derivative of f with respect to b is $-m$:

$$\frac{\partial f}{\partial b} = \frac{\partial^2 f}{\partial h \partial \frac{\partial h}{\partial b}} \stackrel{h=\beta b}{=} -\frac{m}{\beta} \stackrel{(3.34)}{=} -m$$

So, the **(non-standard) Legendre transform** of $f(b)$ with respect to b is $\gamma(m)$ defined by the following relation:

$$-\gamma(m) + f(b(m)) = \frac{\partial f}{\partial b} \cdot b(m) = -mb(m) \Rightarrow \gamma(m) = f + bm \quad (3.39)$$

$b(m)$ is obtained rearranging (3.36):

$$\frac{h}{\beta} = b = \frac{1}{2\beta} \ln \frac{1+m}{1-m} \quad (3.40)$$

Then substituting (3.38) and (3.40) in (3.39) leads to:

$$\begin{aligned} \gamma(m) &= \frac{1}{2\beta} \ln \frac{1-m^2}{4} + \frac{m}{2\beta} \ln \frac{1+m}{1-m} = \\ &= \frac{1}{2\beta} \left[\ln \frac{1-m}{2} \ln \frac{1+m}{2} + m \left(\ln \frac{1+m}{2} + \ln 2 - \ln \frac{1-m}{2} - \ln 2 \right) \right] = \\ &= \frac{1}{2\beta} \left[\ln \frac{1-m}{2} + \ln \frac{1+m}{2} + m \left(\ln \frac{1+m}{2} - \ln \frac{1-m}{2} \right) \right] = \\ &= \frac{1}{2\beta} \left[(1+m) \ln \frac{1+m}{2} + (1-m) \ln \frac{1-m}{2} \right] = \\ &= \left[\frac{1-m}{2} \ln \frac{1-m}{2} + \frac{1+m}{2} \ln \frac{1+m}{2} \right] \beta^{-1} \end{aligned}$$

Note that, due to the properties of the Legendre transform, we have:

$$\frac{\partial \gamma(m)}{\partial m} = b$$

Then, the **entropy density** is obtained by differentiating f (or equivalently its Legendre transform γ , as T is not involved in the transformation):

$$s = -\frac{\partial f}{\partial T} = -\frac{\partial \gamma}{\partial T} = -k_B \left[\frac{1-m}{2} \ln \frac{1-m}{2} + \frac{1+m}{2} \ln \frac{1+m}{2} \right] \quad (3.41)$$

This can be derived also from the definition of the Shannon Entropy. Recall that the probability of a certain spin configuration σ is:

$$\rho(\sigma) = \frac{1}{Z} e^{-\beta \mathcal{H}(\sigma)}$$

As spins are decoupled, $\rho(\sigma)$ factorizes:

$$\rho(\sigma) \stackrel{(3.31)}{\stackrel{(3.32)}{=}} \prod_x \frac{e^{h\sigma_x}}{2 \cosh h} \equiv \prod_x \rho_1(\sigma_x) \quad \rho_1(\sigma_x) \equiv \frac{e^{h\sigma_x}}{2 \cosh h} \quad (3.42)$$

Any generic function $g(\sigma)$ of a binary variable $\sigma \in \{\pm 1\}$ can be written as:

$$g(\sigma) = \frac{g(+1) + g(-1)}{2} + \sigma \frac{g(+1) - g(-1)}{2}$$

In fact:

$$\begin{aligned} g(+1) &= \frac{g(+1) + \cancel{g(-1)}}{2} + \frac{g(+1) - \cancel{g(-1)}}{2} = g(+1) \\ g(-1) &= \frac{\cancel{g(+1)} + g(-1)}{2} - \frac{\cancel{g(+1)} - g(-1)}{2} = g(-1) \end{aligned}$$

In particular, if $g(\sigma) = \exp(h\sigma)$:

$$e^{h\sigma} = \frac{e^h + e^{-h}}{2} + \sigma \frac{e^h - e^{-h}}{2} = \cosh h + \sigma \sinh h \quad (3.43)$$

And so:

$$\rho_1(\sigma) \stackrel{(3.42)}{=} \frac{e^{h\sigma}}{2 \cosh h} \stackrel{(3.43)}{=} \frac{\cosh h + \sigma \sinh h}{2 \cosh h} = \frac{1 + \sigma \tanh h}{2} \stackrel{(3.34)}{=} \frac{1 + \sigma m}{2} \quad (3.44)$$

The ρ_1 so defined is already normalized:

$$\sum_{\sigma=\pm 1} \rho_1(\sigma) = \frac{1+m}{2} + \frac{1-m}{2} = 1 \quad (3.45)$$

We are now ready to compute the **information entropy**:

$$\begin{aligned} S_I[\rho] &= -k_B \sum_{\{\sigma\}} \rho(\sigma) \ln \rho(\sigma) \stackrel{(3.42)}{=} -k_B \sum_{\{\sigma\}} \left(\prod_{x=1}^V \rho_1(\sigma_x) \right) \ln \left(\prod_{y=1}^V \rho_1(\sigma_y) \right) = \\ &= -k_B \sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_V=\pm 1} \prod_{x=1}^V \rho_1(\sigma_x) \sum_{y=1}^V \ln \rho_1(\sigma_y) = \\ &\stackrel{(a)}{=} -k_B \sum_{y=1}^V \sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_V=\pm 1} \left(\prod_{x \neq y} \rho_1(\sigma_x) \right) \rho_1(\sigma_y) \ln \rho_1(\sigma_y) = \\ &\stackrel{(b)}{=} -k_B \sum_{y=1}^V \sum_{\sigma_y=\pm 1} \rho_1(\sigma_y) \ln \rho_1(\sigma_y) \underbrace{\prod_{x \neq y} \sum_{\sigma_x=\pm 1} \rho_1(\sigma_x)}_1 = \\ &\stackrel{(c)}{=} -k_B \sum_{y=1}^V \sum_{\sigma_y=\pm 1} \rho_1(\sigma_y) \ln \rho_1(\sigma_y) = -k_B V \sum_{\sigma_y=\pm 1} \rho_1(\sigma_y) \ln \rho_1(\sigma_y) \end{aligned} \quad (3.46)$$

In (a) we exchange the sum over cells y with the one over states σ . Then, we split the product over x (highlighted in blue) in two factors: one with $x \neq y$, and the other with $x = y$. Then, in (b) we exchange the order of the sums over cell states, bringing the one over σ_y first, and factoring out everything that depends only on σ_y . The remaining term is a product of ρ_1 , and thanks to the spin-independence we can bring all the other sum over states inside it, and then apply normalization (3.45) to reach the result in (c). Due to translational invariance, the inner sum evaluates to a constant, and so $\sum_{y=1}^V$ amounts merely to multiplying by the number of cells V .

Finally, substituting (3.44) in the last step (3.46) and dividing by V leads back to (3.41):

$$s = \frac{S_I[\rho]}{V} = -k_B \left[\frac{1+m}{2} \ln \frac{1+m}{2} + \frac{1-m}{2} \ln \frac{1-m}{2} \right] \quad (3.47)$$

The grand-canonical pressure is given by:

$$\begin{aligned} P &\stackrel{(3.21)}{=} [-f(T, b) + b - Jd] \Big|_{J=0} \stackrel{(3.38)}{=} -\frac{1}{2\beta} \ln \frac{1-m^2}{4} + \frac{1}{2\beta} \ln \frac{1+m}{1-m} = \\ &\stackrel{(3.40)}{=} \frac{1}{2\beta} \left[-\ln \frac{1-m}{2} - \cancel{\ln \frac{1+m}{2}} + \cancel{\ln \frac{1+m}{2}} - \ln \frac{1-m}{2} \right] = -\beta^{-1} \ln \frac{1-m}{2} = \end{aligned}$$

$$\begin{aligned}
&= -\beta^{-1} \ln \frac{2 - 1 - m}{2} = -\beta^{-1} \ln \left(1 - \frac{m+1}{2} \right) \stackrel{(3.30)}{=} -\beta^{-1} \ln(1 - v^{-1}) = \\
&= -\beta^{-1} \ln \left(1 - \frac{\langle N \rangle}{V} \right) \xrightarrow{v^{-1} \rightarrow 0} -\beta^{-1} \left(-\frac{\langle N \rangle}{V} \right) = k_B T \frac{\langle N \rangle}{V}
\end{aligned}$$

So, in the limit of *low density* $v^{-1} \rightarrow 0$, i.e. of a rarefied gas, we get the equation of state for an ideal gas in the grand-canonical ensemble.

However, if we consider the full equation, we note a singularity for $v^{-1} \rightarrow 1$ (densest case, where all cells are filled), corresponding to the *liquid phase*. A plot of $P(v)$ is shown in fig. 3.7, and compared with the one of a real gas. In particular, no *phase-transition* is captured by such *free* Ising Model: as we will see, spin-spin interactions are fundamental. However, even with $J = 0$, the model is able to describe two phases: that of a rarefied gas and of a liquid.

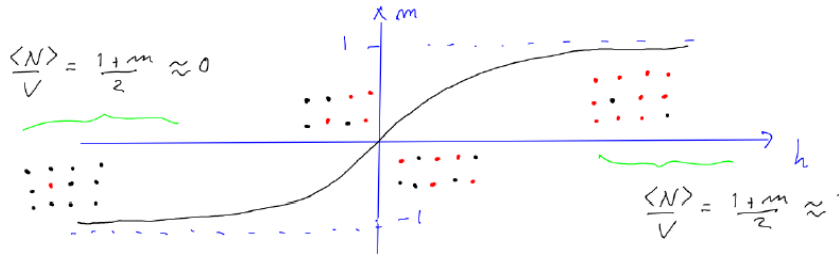


Figure (3.6) – Magnetization m as function of $h = \beta b$ for the Ising Model with decoupled spins ($J = 0$). For $h \rightarrow \pm\infty$, $m = \tanh h \rightarrow \pm 1$. For the negative magnetization, the lattice is almost “empty”, while for $m \rightarrow +1$ it is almost full.

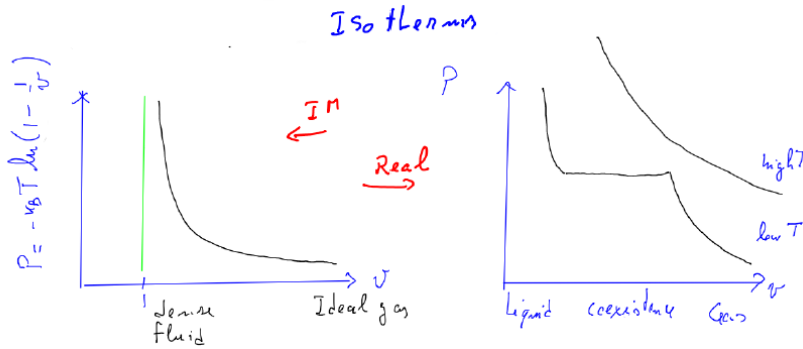


Figure (3.7) – Isothermal curves $P(v)$ for the lattice gas (left) and a real gas (right), where v is the average volume per particle (the reciprocal of the density v^{-1}). In the Ising Model pressure *diverges* when density approaches its maximum $v^{-1} \rightarrow 1$. However, in the real case there is a range of temperatures at which, for a range of values of v , the liquid and gas phases are coexisting (which is where the phase transition is happening). So the model is able to capture *some* of the behaviour (the dilute “ideal gas” state and the *liquid* phase), but not all.

Exercise 3.2.1 (2-point correlation):

Show that:

$$\langle \sigma_x \sigma_y \rangle = (\tanh h)^2 = \langle \sigma_x \rangle \langle \sigma_y \rangle$$

We have shown that, in the absence of spin-spin interactions, the Ising Model does not predict any phase transition.

So, let's study the **interacting case** $J \neq 0$ in one dimension $d = 1$. In this case, the volume V , which coincides with the number of cells (as we have fixed the lattice step a to 1 with a choice of units), is more properly a length $L \equiv V$.

For simplicity, we start from the case of **no external field** $b = 0$ and **open boundary conditions** (fig. 3.8).

(Lesson 20 of
23/04/20)
Compiled: June 2,
2020

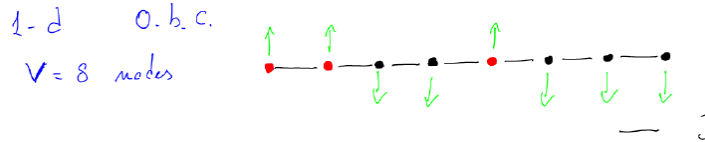


Figure (3.8) – One-dimensional Ising Model with **open** boundary conditions.

The partition function is given by:

$$\begin{aligned} Z_L(K) &\stackrel{(3.23)}{=} \sum_{\{\sigma\}} \exp \left(K \sum_{\langle x,y \rangle} \sigma_x \sigma_y \right) = \sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_{L-1}=\pm 1} \sum_{\sigma_L=\pm 1} e^{K\sigma_1\sigma_2} e^{K\sigma_2\sigma_3} \cdots e^{K\sigma_{L-1}\sigma_L} = \\ &\stackrel{(a)}{=} \sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_{L-1}=\pm 1} e^{K\sigma_1\sigma_2} \cdots e^{K\sigma_{L-2}\sigma_{L-1}} 2 \cosh(K\sigma_{L-1}) \end{aligned}$$

where in (a) we summed over the last spin σ_L . Note that \cosh is even, and so (thanks to our choice of *symmetric* spin-like variables):

$$2 \cosh(K\sigma_{L-1}) = 2 \cosh(\pm K) = 2 \cosh(K)$$

and so:

$$Z_L(K) = 2 \cosh K \underbrace{\sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_{L-1}=\pm 1} e^{K\sigma_1\sigma_2} \cdots e^{K\sigma_{L-2}\sigma_{L-1}}}_{Z_{L-1}(K)} = 2 \cosh(K) Z_{L-1}(K)$$

Reiterating:

$$Z_L(K) = (2 \cosh K)^L \stackrel{(3.23)}{\equiv} e^{-\beta L f(K)} \quad (3.48)$$

Taking the logarithm of both sides:

$$L \ln(2 \cosh K) = -\beta L f(K) \Rightarrow -\beta f(K) = \ln(2 \cosh K)$$

1-d p.b.c.
V = 10 nodes

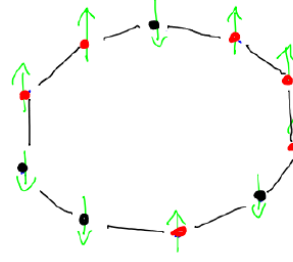


Figure (3.9) – One-dimensional Ising Model with **periodic** boundary conditions.

If we had chosen **periodic boundary conditions** instead (fig. 3.9) and $h \neq 0$, the partition function would have been:

$$Z \stackrel{(3.23)}{=} \sum_{\{\sigma\}} \exp \left(K \sum_{\langle x,y \rangle} \sigma_x \sigma_y + h \sum_x \sigma_x \right) = \quad (3.49)$$

$$= \sum_{\sigma_1 = \pm 1} \cdots \sum_{\sigma_L = \pm 1} e^{K\sigma_1\sigma_2} \cdots e^{K\sigma_{L-1}\sigma_L} e^{K\sigma_L\sigma_1} e^{h\sigma_1} \cdots e^{h\sigma_L} \quad (3.50)$$

Note how the last spin σ_L interacts with the first one σ_1 . We can rewrite the spin-spin interactions more compactly as:

$$e^{K\sigma_1\sigma_2} \cdots e^{K\sigma_{L-1}\sigma_L} e^{K\sigma_L\sigma_1} = \prod_{i=1}^L e^{K\sigma_i\sigma_{i+1}} \quad \sigma_{L+1} \equiv \sigma_1 \quad (3.51)$$

With a trick, we can rewrite also the terms $e^{h\sigma_i}$ as a product over *pairs* (σ_i, σ_{i+1}) . Thanks to p.b.c., each cell is *connected* to exactly 2 neighbouring cells (in $d = 1$) and so a product over pairs contains the product of *squares* of each node - because each cell is multiplied by itself once for every neighbour:

$$\prod_{i=1}^L e^{h\sigma_i} = \prod_{\langle i,j \rangle} \exp \left(h \frac{\sigma_i + \sigma_j}{2} \right) = \prod_{i=1}^L \exp \left(h \frac{\sigma_i + \sigma_{i+1}}{2} \right) \quad \sigma_{L+1} \equiv \sigma_1 \quad (3.52)$$

Substituting (3.51) and (3.52) back in (3.49) leads to:

$$Z = \sum_{\{\sigma\}} \prod_{i=1}^L \exp \left(K\sigma_i\sigma_{i+1} + h \frac{\sigma_i + \sigma_{i+1}}{2} \right) \quad (3.53)$$

Let's define a **matrix** \mathbf{T} with entries equal to the factors in (3.53):

$$T_{\sigma\sigma'} \equiv \exp \left(K\sigma\sigma' + h \frac{\sigma + \sigma'}{2} \right) \quad (3.54)$$

As $\sigma, \sigma' \in \{\pm 1\}$, \mathbf{T} is a 2×2 matrix:

$$\mathbf{T} = \begin{matrix} & \begin{matrix} \sigma'=+1 & \sigma'=-1 \end{matrix} \\ \begin{matrix} \sigma=+1 \\ \sigma=-1 \end{matrix} & \begin{pmatrix} e^{K+h} & e^{-K} \\ e^{-K} & e^{K-h} \end{pmatrix} \end{matrix}$$

\mathbf{T} is called the **transfer matrix** for the $d = 1$ Ising Model with periodic boundaries.

Substituting (3.54) in (3.53) leads to:

$$\begin{aligned} Z &= \sum_{\{\sigma\}} \prod_{i=1}^L T_{\sigma_i \sigma_{i+1}} = \sum_{\sigma_1=\pm 1} \sum_{\sigma_2=\pm 1} \cdots \sum_{\sigma_{L-1}=\pm 1} \sum_{\sigma_L=\pm 1} T_{\sigma_1 \sigma_2} T_{\sigma_2 \sigma_3} \cdots T_{\sigma_{L-1} \sigma_L} T_{\sigma_L \sigma_1} = \\ &\stackrel{(a)}{=} \sum_{\sigma_1=\pm 1} (\underbrace{\mathbf{T} \cdots \mathbf{T}}_{L \text{ times}})_{\sigma_1 \sigma_1} = \sum_{\sigma_1=\pm 1} (\mathbf{T}^L)_{\sigma_1 \sigma_1} = \text{Tr } \mathbf{T}^L \end{aligned}$$

In (a), note that all the sums except the first one lead to a *chain* of matrix multiplications:

$$\sum_a A_{ia} B_{aj} = C_{ij}$$

So, at the end, Z is the sum of the diagonal elements of \mathbf{T}^L , i.e. its **trace**.

\mathbf{T} is symmetric, and so it is diagonalizable, and its eigenvalues are **real** numbers. Moreover, the trace is basis independent, and so we may compute it in the basis where \mathbf{T} is diagonal. Let \mathbf{P} be the invertible matrix needed for diagonalizing \mathbf{T} , then $\mathbf{P} \mathbf{T} \mathbf{P}^{-1} = \text{diag}(\lambda_1, \lambda_2)$, where λ_1 and λ_2 are the *eigenvalues* of \mathbf{T} . Raising both sides to the L -th power, we get:

$$(\mathbf{P} \mathbf{T} \mathbf{P}^{-1})^L = \mathbf{P} \mathbf{T} \mathbf{P}^{-1} \mathbf{P} \mathbf{T} \mathbf{P}^{-1} \mathbf{P} \mathbf{T} \mathbf{P}^{-1} \cdots \mathbf{P} \mathbf{T} \mathbf{P}^{-1} = \mathbf{P} \mathbf{T}^L \mathbf{P}^{-1} = \begin{pmatrix} \lambda_1^L & 0 \\ 0 & \lambda_2^L \end{pmatrix}$$

Then:

$$\text{Tr}(\mathbf{P} \mathbf{T}^L \mathbf{P}^{-1}) = \text{Tr}(\mathbf{P}^{-1} \mathbf{P} \mathbf{T}^L) = \text{Tr}(\mathbf{T}^L) = \text{Tr} \begin{pmatrix} \lambda_1^L & 0 \\ 0 & \lambda_2^L \end{pmatrix} = \lambda_1^L + \lambda_2^L$$

And so:

$$Z = \text{Tr } \mathbf{T}^L = \lambda_1^L + \lambda_2^L \stackrel{(3.23)}{\equiv} e^{-\beta L f(K, h)}$$

Taking the logarithm of both sides:

$$\ln Z = -\beta L f(K, h) = \ln(\lambda_1^L + \lambda_2^L)$$

and dividing by L :

$$\frac{\ln Z}{L} = -\beta f(K, h) = \frac{1}{L} \ln(\lambda_1^L + \lambda_2^L)$$

Suppose (without loss of generality) that $\lambda_1 < \lambda_2$. Then:

$$-\beta f(K, h) = \frac{1}{L} \ln \left(\lambda_2^L \left[1 + \left(\frac{\lambda_1}{\lambda_2} \right)^L \right] \right) = \frac{1}{L} \ln \lambda_2 + \frac{1}{L} \ln \left[1 + \left(\frac{\lambda_1}{\lambda_2} \right)^L \right]$$

In the thermodynamic limit $L \rightarrow \infty$, the larger eigenvalue λ_2 *dominates*, and $(\lambda_1/\lambda_2)^L \rightarrow 0$, so that:

$$-\beta f(K, h) = \ln \lambda_2 + \frac{1}{L} \ln \left[1 + \left(\frac{\lambda_1}{\lambda_2} \right)^L \right] \xrightarrow{L \rightarrow +\infty} \ln \lambda_2 \quad (3.55)$$

The eigenvalues can be computed (as usual) as the roots of the *secular* (or *characteristic*) equation:

$$0 = \det(\mathbf{T} - \lambda \mathbf{I}) = \det \begin{vmatrix} e^{K+h} - \lambda & e^{-K} \\ e^{-K} & e^{K-h} - \lambda \end{vmatrix} = (e^{K+h} - \lambda)(e^{K-h} - \lambda) - e^{-2K} =$$

$$= \lambda^2 - \lambda e^K \frac{e^h + e^{-h}}{2} + \frac{e^{2K} - e^{-2K}}{2} = \lambda^2 - \lambda e^K \cosh h + 2 \sinh 2K$$

which are:

$$\lambda_{1,2} = e^K \cosh h \mp \sqrt{e^{2K} \cosh^2 h - 2 \sinh 2K} =$$

$$= e^K \cosh h \mp \sqrt{e^{2K} \sinh^2 h + e^{-2K}}$$

The **magnetization** is given by:

$$m \stackrel{(3.24)}{=} -\frac{\partial}{\partial h}(\beta f) \stackrel{L \rightarrow \infty}{\stackrel{(3.55)}{=}} \frac{\partial}{\partial h} \ln \lambda_2 = \frac{\partial}{\partial h} \ln \left(e^K \cosh h + \sqrt{e^{2K} \sinh^2 h + e^{-2K}} \right) =$$

$$= \frac{1}{e^K \cosh h + \sqrt{e^{2K} \sinh^2 h + e^{-2K}}} \left(e^K \sinh h + \frac{2e^{2K} \sinh h \cosh h}{2\sqrt{e^{2K} \sinh^2 h + e^{-2K}}} \right) =$$

$$= \frac{1}{e^K \cosh h + \sqrt{e^{2K} \sinh^2 h + e^{-2K}}} \frac{e^K \sqrt{e^{2K} \sinh^2 h + e^{-2K}} + e^{2K} \cosh h}{\sqrt{e^{2K} \sinh^2 h + e^{-2K}}} =$$

$$\stackrel{(a)}{=} \frac{1}{e^K \cosh h + \sqrt{e^{2K} \sinh^2 h + e^{-2K}}} \frac{e^K \cosh h + \sqrt{e^{2K} \sinh^2 h + e^{-2K}}}{\sqrt{\sinh^2 h + e^{-4K}}} =$$

$$= \frac{\sinh h}{\sqrt{\sinh^2 h + e^{-4K}}} \stackrel{(b)}{=} \frac{\tanh h}{\sqrt{1 - \frac{1-e^{-4K}}{\cosh^2 h}}} \quad (3.56)$$

where in (a) we divided numerator and denominator by e^K , and in (b) by $\cosh h$ and applied the identity $\cosh^2 h - \sinh^2 h = 1 \Rightarrow \sinh^2 h = \cosh^2 h - 1$.

Note that if $K = 0$, and so $J = 0$ (non-interacting case), (3.56) leads back to $m = \tanh h$, the result we already found in (3.34). Moreover, if $K > 0$ (ferromagnetic interaction), $m(K, h) > m(0, h)$ - meaning that spins align more easily to the external field if they can interact with their neighbours.

Again, if $h = 0$, $m(K, h = 0) = 0$, and so the system is unable to magnetize in absence of an external field.

In fact, consider any average spin, e.g. $\langle \sigma_0 \rangle$:

$$\langle \sigma_0 \rangle = \sum_{\{\sigma\}} \exp \left(K \sum_{\langle x, y \rangle} \sigma_x \sigma_y \right)$$

For any *finite* system ($L < +\infty$) the sum over all states is a *finite* sum, meaning that it evaluates to some finite number. Moreover, it is **odd** under the change of variables $\sigma_x \leftrightarrow \sigma'_x = -\sigma_x$:

$$\langle \sigma_0 \rangle = \sum_{\{\sigma\}} \exp \left(K \sum_{\langle x, y \rangle} \sigma_x \sigma_y \right) \sigma_0 = - \sum_{\{\sigma\}} \exp \left(K \sum_{\langle x, y \rangle} \sigma_x \sigma_y \right) \sigma_0 = -\langle \sigma_0 \rangle \quad (3.57)$$

and so $\langle \sigma_0 \rangle = 0$. Clearly, this argument holds for any spin (by translation invariance), and so in general $\langle \sigma_k \rangle = 0 \forall k$.

3.3 Spontaneous magnetization

To observe the rise of a **spontaneous magnetization** (which is the experimental result we wish to model), i.e. a non zero m with no external field ($h = 0$), we need to be careful in the *order* of limits. In (3.57) taking $h = 0$ first leads to $m = 0$ for any finite V - and so also in the thermodynamic limit. The idea is then to *exchange* the two limits:

$$m(T) = \lim_{h \rightarrow 0^+} \lim_{V \rightarrow +\infty} \langle \sigma \rangle_{V,h} \quad (3.58)$$

So, first compute the magnetization $\langle \sigma \rangle$ for a finite volume V and in presence of an external field $h \neq 0$. Then perform the thermodynamic limit $V \rightarrow \infty$, and only then let go the field $h \rightarrow 0^+$. The $m(T)$ so defined is the **spontaneous magnetization** of the system, and it can be non-zero.

The idea is that the *presence* of $h \neq 0$ *breaks* the symmetry ($\sigma \leftrightarrow -\sigma$) of the system, invalidating argument (3.57) and thus allowing a spontaneous magnetization.

Equivalently, one can break the symmetry without using $h \neq 0$, but by imposing some *fixed* boundary conditions, for example by setting all spins at the boundaries set to $+1$. In this case, the magnetization for a finite volume V is denoted with $\langle \sigma \rangle_V^+$ (**plus** boundary condition). We can then take the thermodynamic limit:

$$m(T) = \lim_{V \rightarrow +\infty} \langle \sigma \rangle_V^+ \quad (3.59)$$

The boundary effect will vanish when $V \rightarrow \infty$, but it will always break the symmetry of the Hamiltonian ($\sigma \leftrightarrow -\sigma$).

Intuitively, (3.58) and (3.59) *break* the symmetry in the “same direction” (the first with $h > 0$, and the latter with $\sigma_i = +1$ at the boundaries), and so we expect them to lead to the same result at the end. For now, no instances in which (3.58) and (3.59) lead to different results are known.

Clearly, we can also consider the limits *from the other direction*, i.e. from $h < 0$, or with **down** boundary conditions ($\sigma_i = -1$ at the boundaries). The resulting magnetization will be the opposite:

$$\lim_{h \downarrow 0^+} m(K, h) = - \lim_{h \uparrow 0^-} m(K, h)$$

For the Ising Model in $d = 1$, $m(T) = 0$. In fact, in computing m in (3.56) we first considered the thermodynamic limit $L \rightarrow \infty$ for the free energy (3.55) with $h \neq 0$. Then, taking $h \rightarrow 0$ (as already observed), leads to $m = 0$. So, unfortunately, the $d = 1$ Ising Model **does not** suffice to capture the effect of spontaneous magnetization (and thus of a phase-transition), even when spin-spin interactions are considered.

No
phase-transitions in
 $d = 1$

To observe a phase-transition, we need to find where the free energy $f(K, h)$ is non-analytic. In general, it can be shown that $\forall d > 1$, and $\forall h \neq 0$, $f(K, h)$ is analytic everywhere. The only singular points happen at $h = 0$ for $T < T_c$, where T_c is called the **critical temperature**.

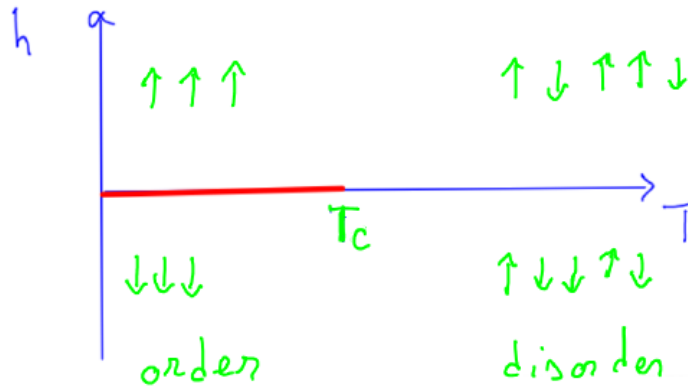


Figure (3.10) – Phase-diagram showing all parameters (h, T) for which the Ising Model’s free energy $f(K, h)$ is non-analytic, which lie on the red segment with $h = 0$ and $T = (0, T_c]$. Taking the limit $h \rightarrow 0^\pm$ when $T < T_c$ will lead to a non-zero magnetization m (positive if $h \downarrow 0^+$, negative if $h \uparrow 0^-$) - in other words the system “spontaneously organizes” in absence of an external field (**ordered phase**). The same limit when $T > T_c$ leads to $m = 0$ - here thermal fluctuations are too high, and the system remains in a random state (**disordered phase**).

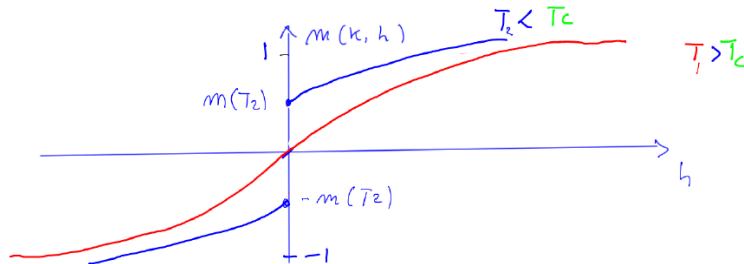


Figure (3.11) – Magnetization at constant temperature T as function of the field strength h (i.e. along a vertical line in fig. ??). If $T > T_c$, as for the red line, the result is the same we obtained in the non-interacting case (fig. 3.6), or the $d = 1$ model. On the other hand, for $T < T_c$ (blue line), a singularity appears at $h = 0$, with two possible limits for the magnetization.

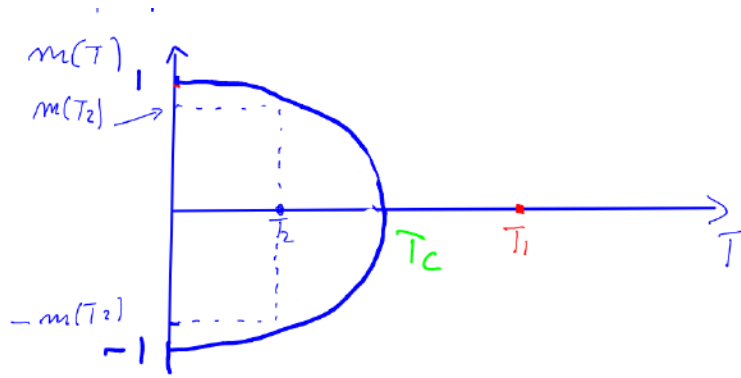


Figure (3.12) – Bifurcation plot for the **spontaneous magnetization** $m(T)$, i.e. the intercept at $h = 0$ of the curves in fig. 3.11 at various temperatures. For $T > T_c$, all curves $m(h)$ cross the origin, and so lead to no spontaneous magnetization $m(T) = 0$. Conversely, for $T < T_c$, two opposite values of $m(T)$ are possible, depending on the taken limit $h \rightarrow 0^\pm$. Note that the region “inside the arc” is not reachable (**unphysical region**): for example at $T = T_2$ it is impossible to obtain a magnetization $|m| < |m(T_2)|$.

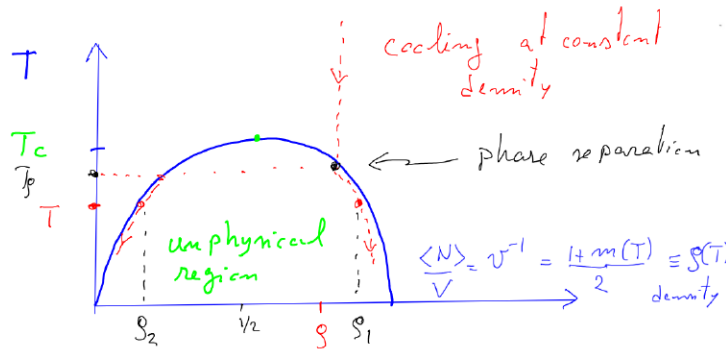


Figure (3.13) – The analogue of the magnetization m in the lattice gas is the **density** $\rho = v^{-1} = \langle N \rangle / V = (1 + m(T)) / 2$.

Consider the lattice gas model, with a fraction ρ of occupied cells. Suppose we want to keep $\langle N \rangle$ fixed. This can be done by changing the chemical potential, which is the conjugate variable to N , and in the lattice gas model takes the role the external magnetic field had in the ferromagnetic Ising Model (in fact the magnetic field b is a function of $\ln z$, which contains μ).

Lowering the temperature (moving along the red dashed line), to keep ρ fixed, μ has to change. When it reaches the blue curve, a *phase separation* is observed, and the gas divides in two parts: one of low density ρ_2 , and one with higher density ρ_1 . Graphically, until the blue curve is reached, the gas is “well mixed”: every region has almost the same density. After, it is divided in mostly empty regions and very dense regions (fig. 3.14).

⚠ This part is still under revision!

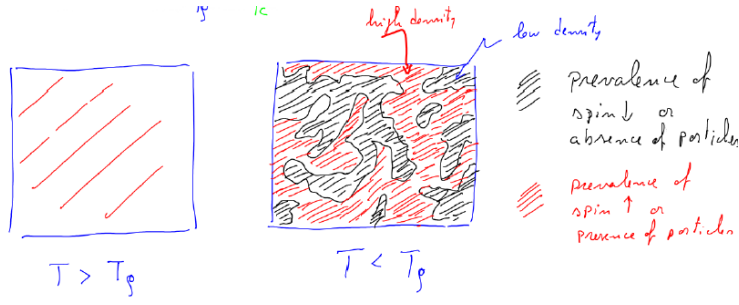


Figure (3.14) – The lattice gas is well-mixed for $T > T_\rho$ (left figure), but separates in two phases with different densities for $T < T_\rho$.

Let f_i be the fraction of volume occupied by the fluid with density ρ_i satisfies:

$$f_1\rho_1 + f_2\rho_2 = \rho$$

and ρ is fixed and remains constant. Also $f_1 + f_2 = 1$. Then:

$$\rho_1 = \frac{1 + m(T)}{2}; \quad \rho_2 = \frac{1 - m(T)}{2}$$

leading to:

$$f_1(T) = 1 - f_2(T) = \frac{1}{2} \left(1 + \frac{2\rho - 1}{m(T)} \right)$$

$$\rho = \begin{cases} \frac{1+m(T_\rho)}{2} & \rho > \frac{1}{2} \\ \frac{1-m(T_\rho)}{2} & \rho < \frac{1}{2} \end{cases}$$

T_ρ is defined as the temperature at which the red dashed line intercepts the blue curve, i.e. at which phase separation occurs.

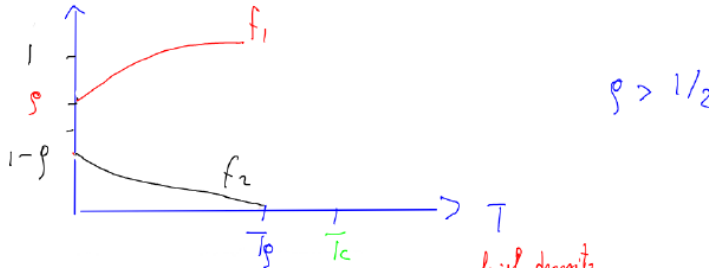


Figure (3.15)

Spinoidal decomposition: try to enter in the unphysical region by rapidly cooling the gas.

So we have found that the both the non-interacting case and the $d = 1$ Ising Model do not present any kind of phase transition. To proceed, we need to considerate a higher dimensional case. One possible way is through numerical simulations, or by considering the exact solution of the $d = 2$ case, for which the critical temperature turns out to be:

$$T_c = \frac{2\epsilon_0/k_B}{\ln(1 + \sqrt{2})}$$

Often one considers the *adimensional* critical parameter k_c , defined as:

$$k_c \equiv \frac{\epsilon_0}{k_B T_c} = \frac{1}{2} \ln(1 + \sqrt{2}) = 0.44 \dots$$

which is such that $\sinh(2k_c) = 1$. For details see [7].

The specific heat at $b = 0$ is:

$$c_v(b = 0, T) \underset{T \sim T_c}{\propto} -\ln \left| 1 - \frac{T}{T_c} \right|$$

The magnetization is 0 above T_c , and for $T < T_c$ is given by:

$$m(T) = \left[1 - \frac{1}{\sinh^4(2K)} \right]^{1/8} \theta(T_c - T) \propto \theta(T_c - T)(T_c - T)^{1/8}$$

The exponent $1/8$ is also called the β exponent (not to be confused with $1/k_B T$). We will study this kind of *power laws* for criticality in a later chapter. They are of particular importance because of their **universality** - i.e. very different systems sharing certain fundamental symmetries have the same behaviour when approaching T_c . (As anticipated, criticality is important to model complex systems).

No rigorous *exact* result is known for the case $h \neq 0$.

Another possibility to go on is to study low/high temperatures expansion of the Ising Model.

3.3.1 Low temperature expansion

Consider the partition function for the Ising Model in d dimensions:

$$Z = \sum_{\{\sigma\}} \exp \left(K \sum_{\langle x,y \rangle} \sigma_x \sigma_y + h \sum_x \sigma_x \right) = e^{-\beta V f(K,h)} \quad \begin{matrix} h=\beta b \\ K=\beta J \end{matrix} \quad (3.60)$$

The idea is to *approximate* Z with a truncated sum, considering only the most *relevant* states. Suppose $h \neq 0$ - for instance $h > 0$. Then, at very low temperature, we expect almost all spins to be aligned towards h . In this situation, the *most probable* configurations σ comprehend the one where all spins are aligned ($\sigma_i \equiv +1$), followed by the ones where only a few spins are *flipped*. Each of them *refines* the value of Z - and if a sufficient number of terms is considered, we can understand the low-temperature behaviour of the system.

In general, however, it is not clear how to find the **radius of convergence** of such a series. In practice, the low-temperature approximation works well for $T \sim 0$, and breaks down when approaching T_c , where Z is non-analytic.

So, let's start computing some terms. In the following we will assume for simplicity **periodic** boundary conditions, meaning that every cell has exactly $2d$ neighbours.

When no spins are flipped $\sigma_i \equiv +1$, the exponential becomes:

$$\mathcal{N}_0 = \exp \left(K \underbrace{\sum_{\langle x,y \rangle} 1}_A + h \underbrace{\sum_x 1}_B \right) \stackrel{(3.14)}{=} \exp(KVd + hV) \quad (3.61)$$

Let's fix $d = 2$ to allow some visualization. Then:

$$\mathcal{N}_0 = \exp[V(2K + h)] \quad (3.62)$$

Suppose now we flip one spin $\sigma_i = -1$ (it does not matter which, as the system is transitionally invariant), and consider how much each of the two sums A and B in (3.61) changes (fig. 3.16).

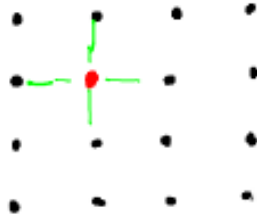


Figure (3.16) – Square lattice with one flipped spin (in red). The affected interactions are represented by the green edges.

B is just the sum over spins. As σ_i was $+1$ and now it is -1 , the change ΔB is $-1 - (+1) = -2$, so $B = N \rightarrow N - 2$.

On the other hand, changing one spin in A affects all the pairs (σ_j, σ_i) involving it, which are $2d = 4$ in our case (the green edges in fig. 3.16). The total change will then be $\Delta A = 4(-1 - (+1)) = 4 \cdot (-2) = -8$, and so $A = 2V \rightarrow 2V - 8$. So, the exponential after one flipped spin will be:

$$\mathcal{N}_1 = \exp((2V - 8)K + (V - 2)h) \quad (3.63)$$

We can then begin to write Z (3.60) by summing all these terms. Note that while there is only one possible configuration σ resulting in the term \mathcal{N}_0 , there are V possibilities for \mathcal{N}_1 - because we can flip *any* of the V spins in the system:

$$Z = \mathcal{N}_0 + V\mathcal{N}_1 + \dots$$

Things start to become more difficult when considering *two* flipped spins σ_i and σ_j at once. Now their distance *matters* - and in particular if they are neighbouring or not.

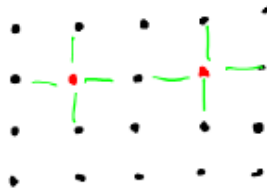


Figure (3.17) – Square lattice with two flipped non-neighbouring spins (in red).

Suppose σ_i and σ_j are **not neighbours** - meaning that they are independent (3.17). Then the change in the sums A and B will just be *twice* that produced by flipping only one spin, and the exponential will be:

$$\mathcal{N}_{2,\text{far}} = \exp[(2V - 16)K + (V - 4)h] \quad (3.64)$$

How many configurations $\{\sigma\}$ generate such term? The first spin to flip σ_i may be anyone of the V spins in the system, but the second σ_j cannot be in the same position, not in one of the 4 neighbouring cells, leaving available only $V - 5$ places. Thus, so far we have $V(V - 5)$ configurations. Exchanging σ_i and σ_j will not alter anything - as they are both -1 - and so we need to divide by 2 the previous total, leading to $V(V - 5)/2$:

$$Z = \mathcal{N}_0 + V\mathcal{N}_1 + \frac{V(V - 5)}{2}\mathcal{N}_{2,\text{far}} + \dots$$

If the two flipped spins are instead **neighbours**, then B will change the same (by -4), but for A we need to account only 6 changed interactions, and not 8: one *edge* is in common between the two spins, contributing with a $\sigma_i\sigma_j = (-1)(-1) = +1$, as if it was never changed, leaving 3 affected edges for each spin (fig. 3.18).

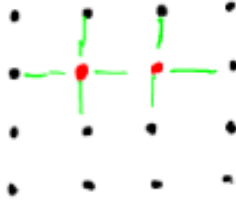


Figure (3.18) – Square lattice with two flipped neighbouring spins (in red).

So the new exponential term will be:

$$\mathcal{N}_{2,\text{close}} = \exp[(2V - 12)K + (V - 4)h]$$

The first spin can go in V places, but the second one must be its neighbour, leaving only 4 possibilities. Dividing by 2 to account for their permutation leaves us with $2V$ configurations forming $\mathcal{N}_{2,\text{close}}$:

$$\begin{aligned} Z &= \mathcal{N}_0 + V\mathcal{N}_1 + \frac{V(V - 5)}{2}\mathcal{N}_{2,\text{far}} + 2V\mathcal{N}_{2,\text{close}} + \dots = \\ &= e^{2VK + hV} + Ve^{(2V-8)K + (V-2)h} + \frac{V(V - 5)}{2}e^{(2V-16)K + (V-4)h} + 2Ve^{(2V-12)K + (V-4)h} + \dots \end{aligned}$$

Note that substituting $\sigma \leftrightarrow -\sigma$ is equivalent to changing the sign of h . In fact, any term of the sum in (3.60) changes by:

$$\exp\left(K \sum_{\langle x,y \rangle} \sigma_x \sigma_y + h \sum_x \sigma_x\right) \xrightarrow{\sigma \leftrightarrow -\sigma} \exp\left(K \sum_{\langle x,y \rangle} (\not\sigma_x)(\not\sigma_y) - h \sum_x \sigma_x\right)$$

So, by changing the sign of h in all the terms we already found, we can construct their *reflections* - i.e. the ones starting from all spins *down* and flipping *up* 1 or 2 of them. Adding them to Z we get:

$$Z = e^{V(2K+h)} \left[1 + Ve^{-8K-2h} + \frac{V(V-5)}{2} e^{-16K-4h} + 2Ve^{-12K-4h} + O(e^{-16K-6h}) \right] + \\ + e^{V(2K-h)} \left[1 + Ve^{-8K+2h} + \frac{V(V-5)}{2} e^{-16K+4h} + 2Ve^{-12K+4h} + O(e^{-16K+6h}) \right]$$

In fact, considering 3 spin-flips leads to new terms of order $O(e^{-16K-6h})$ (if they happen to be all neighbouring, as there are 8 affected interactions), or higher (if they are further apart, for up to 12 affected interactions).

Starting with $h > 0$ and taking first the thermodynamic limit $V \rightarrow \infty$ and then $h \downarrow 0^+$ we note that only the first series of terms *dominates*. In fact, for any $h > 0$:

$$\lim_{V \rightarrow \infty} \frac{e^{V(2K-h)}}{e^{V(2K+h)}} = \lim_{V \rightarrow \infty} e^{-2h} = 0 \quad \forall h > 0$$

So in the thermodynamic limit we can ignore the terms in the second row. Taking the logarithm and dividing by V we get the series expansion of the free energy:

$$\frac{\ln Z}{V} = -\beta f(K, h) = 2K + h + \frac{1}{V} \ln \left[1 + Ve^{-8K-2h} + \frac{V(V-5)}{2} e^{-16K-4h} + 2Ve^{-12K-4h} + \dots \right]$$

For $T \rightarrow 0$, $\beta \rightarrow \infty$, and so $K = \beta J \rightarrow \infty$, meaning that $e^{-K} \rightarrow 0$ and so we may expand in series the logarithm:

$$\ln(x) \approx x - \frac{x^2}{2} + O(x^3)$$

leading to:

$$-\beta f(K, h) = 2K + h + \underbrace{e^{-8K-2h} + \frac{V-5}{2} e^{-16K-4h} + 2e^{-12K-4h}}_{\text{First term}} \\ - \frac{1}{2V} (Ve^{-8K-2h})^2 + O(e^{-16K-6h}) = \\ = 2K + h + e^{-8K-2h} + 2e^{-12K-4h} - \frac{5}{2} e^{-16K-4h} + O(e^{-16K-6h})$$

The spontaneous magnetization is then:

$$m \stackrel{(3.24)}{=} \frac{1}{V} \frac{\partial \ln Z}{\partial h} \Big|_{h=0} \stackrel{(3.58)}{=} 1 - 2e^{-8K-2h} - 8e^{-12K-4h} + 10e^{-16K-4h} + \dots \Big|_{h=0} = \\ = 1 - 2e^{-8K} - 8e^{-12K} + 10e^{-16K} + \dots \quad (3.65)$$

and is plotted in fig. 3.19.

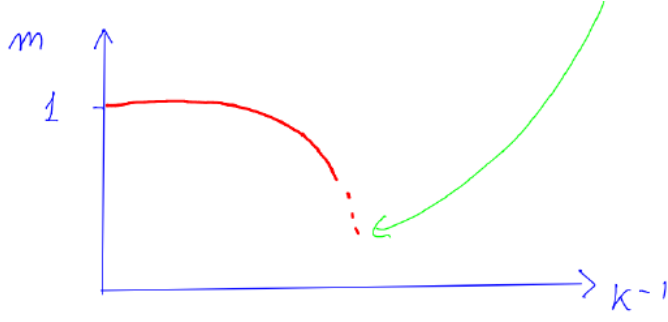


Figure (3.19) – Plot of the spontaneous magnetization as function of temperature $T \propto K^{-1} = 1/(\beta J)$. For $T \rightarrow 0$ ($K \rightarrow \infty$) m goes to 1. From Onsager’s exact solution we know that m reaches 0 at T_c , but this cannot be observed in this expansion, as the radius of convergence never includes T_c .

More terms. For more terms of the expansion in (3.65) see [8]. There also next nearest neighbours interactions are considered, with an interaction strength J_2 - so, to reconstruct our case, let $J_2 = 0$ and thus $y = e^{-4J_2\beta} = 1$. So, formula (3) in [8] may be adapted as:

$$M(x) = 1 - 2x^2y^2 + \sum_{m,n} a(m,n)x^m y^n \Big|_{y=1} \quad x = e^{-4K}$$

Borrowing coefficients from table 1 in [8] we get:

$$M(K) = 1 - 2e^{-8K} - 8e^{-12K} + (-8 + 18 - 24 - 20)e^{-16K} + \dots$$

So the first coefficients in (3.65) are correct, but the one for e^{-16K} not. In fact, to refine it, we should also consider the case of 3 and 4 neighbouring flips, which add terms of the same order e^{-16K} , but are much more difficult to compute.

Fortunately, there are more sophisticated methods for generating more terms, as can be seen in [9]

3.3.2 Correlation functions

Until now we analysed the *magnetization*, i.e. the average local spin alignment:

$$m_x \equiv \langle \sigma_x \rangle$$

This can be interpreted as a **one-point** correlation function, measuring how much a spin σ_x is “correlated” with itself.

If we instead compare σ_x with a *different* spin σ_y , we get the **two-point** correlation function⁵:

$$G_{x,y}^{(2)} = \text{Cov}[\sigma_x, \sigma_y] = \langle \sigma_x \sigma_y \rangle - \langle \sigma_x \rangle \langle \sigma_y \rangle \quad (3.66)$$

⁵Also known as the **connected** correlation function (or Ursell function), as we are subtracting the *trivial* product $\langle \sigma_x \rangle \langle \sigma_y \rangle$

If σ_x and σ_y are independent, then immediately $\langle \sigma_x \sigma_y \rangle = \langle \sigma_x \rangle \langle \sigma_y \rangle$, and so $G_{x,y}^{(2)} = 0$. In general, however, the converse is not true: if the two-point correlation is 0, the two spin may still be interacting.

Consider each spin interacting with a local field h_x in the Ising Model. The partition function is then:

$$Z(\mathbf{h}) = \sum_{\{\boldsymbol{\sigma}\}} \exp \left(-\beta \mathcal{H}(\boldsymbol{\sigma}) + \sum_x h_x \sigma_x \right) \equiv e^{-\beta F(\mathbf{h})}$$

with F being the corresponding **free energy**. This is a generalization of the case (3.60), where $h_x \equiv h$ for all spins. Being able to *vary* the local field experienced by a single spin allows us to write correlation functions as derivatives of Z .

For the one-point correlation we get the same formula previously found in (3.24):

$$m_x = -\frac{\partial}{\partial h_x} (\beta F(\mathbf{h})) \quad (3.67)$$

On the other hand, for the two point correlation we get:

$$G_{xy}^{(2)} = -\frac{\partial^2}{\partial h_x \partial h_y} (\beta F(\mathbf{h})) = \langle (\sigma_x - \langle \sigma_x \rangle) (\sigma_y - \langle \sigma_y \rangle) \rangle \stackrel{(3.67)}{=} \frac{\partial m_y}{\partial h_x} \quad (3.68)$$

Similarly, for a 3-point correlation:

$$G_{xyz}^{(3)} = -\frac{\partial^3}{\partial h_x \partial h_y \partial h_z} (\beta F(\mathbf{h})) = \langle (\sigma_x - \langle \sigma_x \rangle) (\sigma_y - \langle \sigma_y \rangle) (\sigma_z - \langle \sigma_z \rangle) \rangle$$

and in general:

$$G_{x_1, \dots, x_n}^{(n)} = -\frac{\partial^n}{\partial h_{x_1} \dots \partial h_{x_n}} (\beta F)$$

We define the **susceptibility** as the derivative of the magnetization m with respect to the field h (when $h_x \equiv h \forall x$): Susceptibility χ

$$\chi \equiv \frac{\partial m}{\partial h}$$

Inserting the definition of the magnetization (3.24) and computing the averages leads to:

$$\begin{aligned} \chi \equiv \frac{\partial m}{\partial h} &= \frac{\partial}{\partial h} \langle \sum_x \sigma_x \rangle \frac{1}{V} = \frac{1}{V} \sum_x \frac{\partial}{\partial h} \langle \sigma_x \rangle = \frac{1}{V} \sum_x \frac{\partial}{\partial h} \frac{\overbrace{\sum_{\{\boldsymbol{\sigma}\}} \sigma_x \exp \left(-\beta \mathcal{H}(\boldsymbol{\sigma}) + \sum_y h \sigma_y \right)}^{\text{Num}}}{\underbrace{Z(\mathbf{h})}_{\text{Den}}} = \\ &= \frac{1}{V} \sum_x \frac{\overbrace{\sum_{\{\boldsymbol{\sigma}\}} \exp \left(-\beta \mathcal{H}(\boldsymbol{\sigma}) + \sum_y h \sigma_y \right) \sum_y \sigma_y}^{(\partial_h \text{Num})/\text{Den}}}{Z(\mathbf{h})} + \end{aligned}$$

$$\begin{aligned}
& -\frac{1}{V} \sum_x \underbrace{\frac{\sum_{\{\sigma\}} \sigma_x \exp\left(-\beta \mathcal{H}(\sigma) + \sum_y h \sigma_y\right)}{Z(\mathbf{h})} \cdot \frac{\sum_{\{\sigma\}} \exp\left(-\beta \mathcal{H}(\sigma) + \sum_y h \sigma_y\right) \sum_y \sigma_y}{Z(\mathbf{h})}}_{-(\text{Num } \partial_h \text{Den})/\text{Den}^2} = \\
& = \frac{1}{V} \left[\left\langle \sum_{x,y} \sigma_x \sigma_y \right\rangle - \left\langle \sum_x \sigma_x \right\rangle \left\langle \sum_y \sigma_y \right\rangle \right]
\end{aligned}$$

So, rewriting the last step result in terms of (3.68) we get:

*Fluctuation
dissipation theorem*

$$\chi = \sum_x G_{x,y} \quad (3.69)$$

This is the **fluctuation dissipation theorem**. In other words, the “total” *correlation* between one spin σ_x and every other spin σ_y is equal to the “responsivity” of m_x to a change in h , i.e. how much the alignment of σ_x varies when the external field $b = h/\beta$ is adjusted.

\mathcal{H} is translational invariant if it does not change when *translating* spins:

$$\mathcal{H}(\sigma) = \mathcal{H}(\sigma')$$

with $\sigma'_x = \sigma_{x+x_0}$ for any x and x_0 fixed.

In this case, as we previously noted, the magnetization is constant: $m = \langle \sigma_x \rangle$, and the two-point correlation depends only on the distance between the two spins: $\langle \sigma_x \sigma_y \rangle = \langle \sigma_{x-y} \sigma_0 \rangle$.

Finally, we compute the Legendre transform $\Gamma(m)$ of βF with respect to h :

$$\Gamma(\mathbf{m}) = \beta F(\mathbf{j}) + \sum_x h_x m_x$$

where the $\{h_x\}$ have been calculated as a function of the local magnetizations $\{m_x\}$ by inverting (3.67). By property of the Legendre transform:

$$\frac{\partial \Gamma}{\partial m_x} = h_x$$

Differentiating both sides with respect to h_y leads to:

$$\delta_{xy} = \sum_z \frac{\partial^2 \Gamma}{\partial m_x \partial m_z} \frac{\partial m_z}{\partial h_y} \stackrel{(3.66)}{=} \sum_z \frac{\partial^2 \Gamma}{\partial m_x \partial m_z} G_{zy}$$

Thus $\frac{\partial^2 \Gamma}{\partial m_x \partial m_y}$ is the inverse of the two-point correlation function G_{xy} .

Exercise 3.3.1 (Ising Model):

Consider a 1-dimensional Ising Model with nearest-neighbour ferromagnetic interaction in an external uniform field with energy function given by:

$$\mathcal{H}(\boldsymbol{\sigma}) = -J \sum_{x=1}^N \sigma_x \sigma_{x+1} - B \sum_{x=1}^N \sigma_x \quad J > 0$$

where periodic boundary conditions are used, i.e. $\sigma_{N+1} \equiv \sigma_1$. Define $K = \beta J$ and $\beta B = h$.

Part A. Using the transfer matrix $T(\sigma, \sigma') = \exp(K\sigma\sigma' + h(\sigma + \sigma')/2)$ and its spectral decomposition, determine:

1. The **partition function** $Z(K, h)$
2. The **free energy** per node in the thermodynamic limit and its plot for $h = 0$ versus $1/K$
3. The **entropy** per node in the thermodynamic limit and its plot for $h = 0$ versus $1/K$
4. The **mean energy** per node in the thermodynamic limit and its plot for $h = 0$ versus $1/K$
5. The **specific heat** per node in the thermodynamic limit and its plot for $h = 0$ versus $1/K$
6. The **average magnetization** at x , $\langle \sigma_x \rangle$, in the thermodynamic limit and its plot for $h = 0, 0.1, 0.2, 0.5, 1$ versus $1/K$ and for $K = 1$ versus h in the range $(-5, 5)$
7. The **two-point correlation function** $\langle \sigma_x \sigma_{x+y} \rangle$ in the thermodynamic limit and its plot for $h = 0$ and $K = 1$ versus y .

Part B. Consider the same model with **open** boundary conditions (node 1 is linked only to node 2, and node N only to node $N - 1$):

$$\mathcal{H}(\boldsymbol{\sigma}) = -J \sum_{x=1}^{N-1} \sigma_x \sigma_{x+1} - B \sum_{x=1}^N \sigma_x$$

Show that the partition function for this case can be formally written as:

$$Z(K, h) = \mathbf{v}^T \mathbf{T}^N \mathbf{v} \equiv \sum_{\substack{\sigma_1 = \pm 1 \\ \sigma_N = \pm 1}} v(\sigma_1) \mathbf{T}^N(\sigma_1, \sigma_N) v(\sigma_N)$$

where $v(\sigma) = e^{h\sigma/2}$. Show that the free energy per node in the thermodynamic limit is the same as above.

Part C. Same as in part B with fixed boundary conditions $\sigma_1 = 1 = \sigma_2$, and $v(\sigma) = e^{h\sigma/2}$ for both $\sigma = \pm 1$.

Part D. How would you try to solve the Ising model in 1-dimension with nearest neighbour and next-to-nearest neighbour interaction and periodic boundary condition ($\sigma_{N+1} = \sigma_1$ and $\sigma_{N+2} = \sigma_2$):

$$\mathcal{H}(\boldsymbol{\sigma}) = - \sum_{x=1}^N (J_1 \sigma_x \sigma_{x+1} + J_2 \sigma_x \sigma_{x+2}) - B \sum_{x=1}^N \sigma_x$$

Solution. WIP

Variational methods

Exactly solvable models are rare. For example, the Ising Model, describing in a very simplified manner a discrete set of local interacting binary variables, has been exactly solved only for $d = 1$ in general, and for $d = 2$ only in absence of an external field ($h = 0$). The latter, in particular, requires long and sophisticated derivations.

Even for other models, the trend is the same: whenever we wish to study *emergent phenomena* the problem usually becomes analytically intractable.

One possibility is then to resort to **numerical simulations**. However, these are often time-consuming, require significant computational power, and can be hard to interpret - as interesting “high level” characteristics (such as the conditions for phase transitions) are drowned in lots of irrelevant “low-level” data.

So we may resort to **approximate computations** instead. The idea is to find a simple model that is able to capture, at least *qualitatively*, features from a more complex one, while still admitting an exact solution. This can then give hints on *what to look for* in a full numerical simulation, thus allowing a deeper understanding.

One quick way to compute approximations is through **variational methods**. In essence, we consider some parametrized pdf $f_{\theta}(\mathbf{x})$, and tweak the parameters θ so that it becomes “closer and closer” to the target pdf $f(\mathbf{x})$ of the full model. If we choose a sufficiently *simple* form for f_{θ} , we will be able to perform exact computations, while still retaining some sort of “correspondance” with the more complex model.

In the following, we will first introduce a notion of “**distance**” between pdfs (**relative entropy**), giving a mathematical meaning to the notion of “closeness” between probability distributions. Then we will explicitly state the *variational method* as a **minimization problem**, and, using the Ising Model as an example, we will see a popular choice for the parametrization of f_{θ} : the **mean-field approximation**.

(Lesson 21 of
27/04/20)
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4.0.1 Relative Entropy

Given two (discrete) probability distributions $\{p_i\}_{i \in \mathcal{D}}$ and $\{q_i\}_{i \in \mathcal{D}}$, with $p_i, q_i > 0$ and $\sum_i p_i = \sum_i q_i = 1$, we define the **relative entropy** (or Kullback–Leibler divergence) of $\{p_i\}$ with respect to $\{q_i\}$ as follows:

$$S_R(\{p_i\}, \{q_i\}) = - \sum_{i \in \mathcal{D}} p_i \ln \frac{p_i}{q_i} \leq 0 \quad (4.1)$$

In a sense, relative entropy measures the *closeness* between the two distributions - as it is maximum ($S_R = 0$) when the two coincide, i.e. $p_i = q_i \forall i$. Note, however, that S_R is not a *distance function* in the proper sense, as it does not satisfy the triangular inequality.

The fact that $S_R = 0$ is the maximum point of S_R , i.e. $S_R \leq 0$, can be proven as follows. First we define an auxiliary function $f(x)$ over $(0, \infty)$: *Proof that $S_R \leq 0$*

$$f(x) = -x \ln x \quad x > 0$$

Such function $f(x)$ is **concave**. In fact:

$$\begin{aligned} f'(x) &= -1 - \ln x \\ f''(x) &= -\frac{1}{x} < 0 \quad x > 0 \end{aligned}$$

So, we may apply Jensen's inequality. For any choice of a set of non-negative numbers $\{\lambda_i\}$ summing to 1, the following relation holds:

$$f\left(\sum_i \lambda_i x_i\right) \geq \sum_i f(x_i) \lambda_i \quad \sum_i \lambda_i = 1 \wedge \lambda_i \geq 0$$

And letting $\lambda_i = q_i$ and $x_i = p_i/q_i$ completes the proof:

$$S_R = \sum_i q_i f\left(\frac{p_i}{q_i}\right) \leq f\left(\sum_i q_i \frac{p_i}{q_i}\right) = f(1) = 0$$

with the equality holding if and only if $p_i = q_i$.

4.0.2 Approximation as an optimization problem

Let's consider, for simplicity, a system with **discrete** states $\{\sigma_i\}_{i \in \mathcal{D}}$, each with energy $\mathcal{H}(\sigma_i)$, and an associated probability q_i given by a Boltzmann distribution:

$$\rho(\sigma_i) \equiv q_i = \frac{e^{-\beta \mathcal{H}(\sigma_i)}}{Z} = e^{-\beta(\mathcal{H}(\sigma) - F)} \quad Z = \sum_{\{\sigma\}} e^{-\beta \mathcal{H}(\sigma)} \equiv e^{-\beta F}$$

where F is the system's **free energy** function.

In general, the $\{q_i\}$ are difficult to explicitly compute, because Z is generally a sum over a huge number of terms (2^V in the case of the Ising Model) with no analytical form.

So, the idea is to approximate ρ with another “easier” distribution ρ_0 , the **variational ansatz**, which is parametrized as a Boltzmann distribution with a different Hamiltonian \mathcal{H}_0 (and so also a different free energy F_0):

$$\rho_0(\boldsymbol{\sigma}_i) \equiv p_i = \frac{e^{-\beta\mathcal{H}_0(\boldsymbol{\sigma}_i)}}{Z_0} = e^{-\beta(\mathcal{H}_0(\boldsymbol{\sigma})-F_0)} \quad Z_0 = \sum_{\{\boldsymbol{\sigma}\}} e^{-\beta\mathcal{H}_0(\boldsymbol{\sigma})} \equiv e^{-\beta F_0} \quad (4.2)$$

The *closeness* of $\{p_i\}$ to $\{q_i\}$ is given by their **relative entropy** (4.1):

$$\begin{aligned} 0 \leq \sum_i p_i \ln \frac{p_i}{q_i} &= \sum_{\{\boldsymbol{\sigma}\}} \frac{e^{-\beta\mathcal{H}_0(\boldsymbol{\sigma})}}{Z_0} \ln \frac{e^{-\beta\mathcal{H}_0(\boldsymbol{\sigma})} \overbrace{Z}^{e^{-\beta F}}}{\underbrace{Z_0}_{e^{-\beta F_0}} e^{-\beta\mathcal{H}(\boldsymbol{\sigma})}} = \\ &= \frac{1}{Z_0} \sum_{\{\boldsymbol{\sigma}\}} e^{-\beta\mathcal{H}_0(\boldsymbol{\sigma})} \beta[\mathcal{H}(\boldsymbol{\sigma}) - \mathcal{H}_0(\boldsymbol{\sigma}) - F + F_0] = \\ &= \beta\langle\mathcal{H} - \mathcal{H}_0\rangle_0 - \beta(F - F_0) \end{aligned} \quad (4.3)$$

where $\langle\cdots\rangle_0$ denotes the average according to the ansatz distribution:

$$\langle f(\boldsymbol{\sigma}) \rangle_0 \equiv \frac{1}{Z_0} \sum_{\{\boldsymbol{\sigma}\}} e^{-\beta\mathcal{H}_0(\boldsymbol{\sigma})} f(\boldsymbol{\sigma})$$

The expression (4.3) is called the **Gibbs-Bogoliubov-Feynman inequality**¹, and holds as an equality if and only if $\rho = \rho_0 \Leftrightarrow \mathcal{H} = \mathcal{H}_0$.

Rearranging (4.3):

$$\beta F \leq \beta F_0 + \beta\langle\mathcal{H} - \mathcal{H}_0\rangle_0 = \beta\langle\mathcal{H}\rangle_0 + \beta(F_0 - \langle\mathcal{H}_0\rangle_0) \quad (4.4)$$

Note that F_0 does not depend on $\boldsymbol{\sigma}$, as it's $\propto \ln Z_0$, and so we can bring it inside the average, and expand it:

$$\beta(F_0 - \langle\mathcal{H}_0\rangle_0) = \beta\langle F_0 - \mathcal{H}_0 \rangle_0 = \sum_{\{\boldsymbol{\sigma}\}} \rho_0(\boldsymbol{\sigma}) \beta(F_0 - \mathcal{H}_0(\boldsymbol{\sigma}))$$

Then, from (4.2) note that:

$$\rho_0(\boldsymbol{\sigma}) = e^{-\beta(\mathcal{H}_0(\boldsymbol{\sigma})-F_0)} \Rightarrow \ln \rho_0(\boldsymbol{\sigma}) = \beta(F_0 - \mathcal{H}_0(\boldsymbol{\sigma}))$$

and substituting above:

$$\beta(F_0 - \langle\mathcal{H}_0\rangle_0) = -\frac{1}{k_B} \underbrace{\left(-k_B \sum_{\{\boldsymbol{\sigma}\}} \rho_0(\boldsymbol{\sigma}) \ln \rho_0(\boldsymbol{\sigma}) \right)}_{S[\rho_0]} = -\frac{S[\rho_0]}{k_B} \quad (4.5)$$

where $S[\rho_0]$ is the **information entropy** of ρ_0 :

$$S[\rho_0] = -k_B \sum_{\{\boldsymbol{\sigma}\}} \rho_0(\boldsymbol{\sigma}) \ln \rho_0(\boldsymbol{\sigma})$$

¹Physically, it is completely equivalent to the second law of thermodynamics.

Thus, substituting (4.5) back in the inequality (4.4) leads to:

$$\beta F \leq \beta \langle \mathcal{H} \rangle_0 - \frac{S[\rho_0]}{k_B} = \beta \langle \mathcal{H} \rangle_0 - \beta TS[\rho_0] \quad (4.6)$$

And dividing by β :

$$F \leq F_V \equiv \langle \mathcal{H} \rangle_0 - TS[\rho_0]$$

where F_V is called the **Variational Free Energy** (VFE).

So, the true free energy F is always less or equal to the variational one F_V . An optimal estimate of F is obtained by minimizing F_V with respect to ρ_0 .

Clearly, if we do not require any constraint on ρ_0 , thus allowing arbitrary complexity, then the minimum is obtained when $\rho_0 = \rho$: the most accurate approximation of a model is the model itself. Realistically ρ is mathematically intractable, and we need to *bound* the “complexity” of ρ_0 , with the effect that it won’t be able to perfectly replicate ρ , and so the minimum for F_V will be larger than F (but hopefully still somewhat close).

One possible way to constrain the “complexity” of ρ_0 is to *force it* to be separable:

$$\rho_0(\boldsymbol{\sigma}) = \prod_x \rho_x(\sigma_x) \quad (4.7)$$

In this way, all degrees of freedom of the system become **decoupled**. In a sense, correlations and complex behaviours are “averaged” between each component - and in fact the approximation in (4.7) is known as the **mean field** ansatz.

4.1 Mean Field Ising Model

Consider a d -dimensional nearest-neighbour Ising Model, where we allow each spin to interact with a **local** magnetic field b_x , leading to the Hamiltonian:

$$\mathcal{H}(\boldsymbol{\sigma}) = -J \sum_{\langle x,y \rangle} \sigma_x \sigma_y - \sum_x b_x \sigma_x$$

To understand its behaviour, we use the **mean-field** approximation (4.7), and choose a parametrization inspired by the non-interacting Ising Model (3.44, pag. 112):

$$\rho_0(\boldsymbol{\sigma}) = \prod_x \rho_x(\sigma_x) \quad \rho_x(\sigma_x) = \frac{1 + m_x \sigma_x}{2} \quad m_x \in [-1, 1] \quad (4.8)$$

where the $\{m_x\}$ are the *variational parameters* that will be *tweaked* to make $\rho_0(\boldsymbol{\sigma})$ closer to the real probability distribution $\rho(\boldsymbol{\sigma})$ of the Ising Model, by minimizing the **variational free energy** F_V . The constraint $m_x \in [-1, 1]$ comes from requiring all probabilities to be non-negative $\rho_x(\sigma_x) \geq 0$.

Before proceeding, note that (4.8) is already normalized:

$$\sum_{\sigma_x = \pm 1} \rho_x(\sigma_x) = \frac{1 + m_x}{2} + \frac{1 - m_x}{2} = \frac{1}{2} + \frac{1}{2} = 1$$

and that each *variational parameter* m_x corresponds to the **local magnetization** of spin σ_x in the mean-field model:

$$\begin{aligned}
\langle \sigma_x \rangle_0 &= \sum_{\{\sigma\}} \rho_0(\sigma) \sigma_x = \sum_{\{\sigma\}} \prod_y \frac{1 + m_y \sigma_y}{2} \sigma_x = \\
&\stackrel{(a)}{=} \sum_{\sigma_x = \pm 1} \left(\underbrace{\prod_{y \neq x} \sum_{\sigma_y = \pm 1} \frac{1 + m_y \sigma_y}{2}}_1 \right) \frac{1 + m_x \sigma_x}{2} \sigma_x = \\
&= \sum_{\sigma_x = \pm 1} \sigma_x \frac{1 + m_x \sigma_x}{2} = \frac{1 + m_x}{2} - \frac{1 - m_x}{2} = m_x \quad (4.9)
\end{aligned}$$

where in (a) we split the product in the case $y \neq x$ and $y = x$. Also note that the average is over ρ_0 and not the “true” pdf ρ .

Choice of parametrization. The distribution $\rho_x(\sigma_x)$ in (4.8) is the most general discrete distribution for a binary variable such as σ_x , just rewritten to highlight the average m_x .

In fact, consider a generic **binary** variable σ . Its distribution is:

$$\mathbb{P}[\sigma = +1] = p_+ \quad \mathbb{P}[\sigma = -1] = p_-$$

Due to normalization, $p_+ + p_- = 1$, and so there is only **one free parameter** needed to completely specify the pdf:

$$\mathbb{P}[\sigma = +1] = p \quad \mathbb{P}[\sigma = -1] = 1 - p$$

If we then rewrite p as function of the average $\langle \sigma \rangle = m$, we get:

$$m = \sum_{\sigma = \pm 1} \sigma \mathbb{P}[\sigma] = p - (1 - p) = 2p - 1 \Rightarrow p = \frac{1 + m}{2}$$

And so:

$$\mathbb{P}[\sigma = +1] = \frac{1 + m}{2} \quad \mathbb{P}[\sigma = -1] = \frac{1 - m}{2}$$

Which can be rewritten more compactly as:

$$\rho(\sigma) = \frac{1 + m\sigma}{2}$$

So we are not making any additional hypothesis other than that of a separable $\rho(\sigma)$ (given by the mean field approximation).

For simplicity, we work with βF_V , denoting $\beta J \equiv K$ and $\beta b_x \equiv h_x$. From the variational principle (4.6):

$$\beta F \leq \min_{\mathbf{m}} \beta F_V(\mathbf{m}, \mathbf{h}) = \min_{\mathbf{m}} \left(\beta \langle \mathcal{H} \rangle_0 - \frac{S[\rho_0]}{k_B} \right) \quad (4.10)$$

The average of \mathcal{H} according to the ansatz is:

$$\langle \mathcal{H} \rangle_0 = \langle -J \sum_{\langle x, y \rangle} \sigma_x \sigma_y - \sum_x b_x \sigma_x \rangle_0 = -J \sum_{\langle x, y \rangle} \langle \sigma_x \sigma_y \rangle_0 - \sum_x b_x \langle \sigma_x \rangle_0$$

We already computed $\langle \sigma_x \rangle_0 = m_x$ in (4.9). For the two-point correlation, as ρ_0 is separable and thus σ_x and σ_y are decoupled, we get:

$$\langle \sigma_x \sigma_y \rangle_0 = \langle \sigma_x \rangle_0 \langle \sigma_y \rangle_0 = \sum_{\sigma_x} \frac{1 + m_x \sigma_x}{2} \sigma_x \sum_{\sigma_y} \frac{1 + m_y \sigma_y}{2} \sigma_y = m_x m_y$$

Thus:

$$\langle \mathcal{H}(\boldsymbol{\sigma}) \rangle_0 = -J \sum_{\langle x, y \rangle} m_x m_y - \sum_x b_x m_x = \mathcal{H}(\mathbf{m}) \quad (4.11)$$

This is valid more in general when applying the mean field approximation to even more complex Hamiltonians, as it is a consequence of the separability of ρ_0 .

On the other hand, the entropy of ρ_0 can be directly computed. Noting that $\rho_x(\sigma_x)$ is exactly the same pdf we used in the non-interacting Ising Model, we can borrow the results (3.46) and (3.47, pag. 112) from there:

$$\begin{aligned} -\frac{S[\rho_0]}{k_B} &= \sum_{\{\boldsymbol{\sigma}\}} \rho_0(\boldsymbol{\sigma}) \ln \rho_0(\boldsymbol{\sigma}) = \sum_x \sum_{\sigma_x} \frac{1 + m_x \sigma_x}{2} \ln \frac{1 + m_x \sigma_x}{2} = \\ &= \sum_x \left(\frac{1 + m_x}{2} \ln \frac{1 + m_x}{2} + \frac{1 - m_x}{2} \ln \frac{1 - m_x}{2} \right) \equiv \sum_x s_0(m_x) \end{aligned} \quad (4.12)$$

where we defined a *local entropy* s_0 as:

$$s_0(m) \equiv \frac{1 + m}{2} \ln \frac{1 + m}{2} + \frac{1 - m}{2} \ln \frac{1 - m}{2} \quad (4.13)$$

Substituting these results (4.11) and (4.12) back in (4.10) we arrive to:

$$\begin{aligned} \beta F_V(\mathbf{m}, \mathbf{h}) &= \beta H(\mathbf{m}) + \sum_x s_0(m_x) = \\ &= -K \sum_{\langle x, y \rangle} m_x m_y - \sum_x h_x m_x + \sum_x \left[\frac{1 + m_x}{2} \ln \frac{1 + m_x}{2} + \frac{1 - m_x}{2} \ln \frac{1 - m_x}{2} \right] \end{aligned} \quad (4.14)$$

where the first line holds for a generic Hamiltonian $\mathcal{H}(\boldsymbol{\sigma})$, and the second is specific for the Ising Model we are studying.

Then, we minimize $F_V(\mathbf{m}, \mathbf{h})$ with respect to \mathbf{m} , denoting the minimum as $F_V(\mathbf{M}, \mathbf{h})$:

$$\begin{aligned} \frac{\partial}{\partial m_x} \beta F_V \Big|_{\mathbf{m}=\mathbf{M}} &\stackrel{!}{=} 0 \quad (4.15) \\ 0 &\stackrel{!}{=} \frac{\partial}{\partial m_x} \left[-K \sum_{\langle x, y \rangle} m_x m_y - \sum_x h_x m_x + \sum_x \left(\frac{1 + m_x}{2} \ln \frac{1 + m_x}{2} + \frac{1 - m_x}{2} \ln \frac{1 - m_x}{2} \right) \right]_{\mathbf{m}=\mathbf{M}} = \\ &= -K \sum_{y \in \langle x, y \rangle} M_y - h_x + \frac{1}{2} \ln \frac{1 + M_x}{2} + \cancel{\frac{1 + M_x}{2} \ln \frac{1 + M_x}{2}} - \frac{1}{2} \ln \frac{1 - M_x}{2} - \cancel{\frac{1 - M_x}{2} \ln \frac{1 - M_x}{2}} = \\ &= -K \sum_{y \in \langle x, y \rangle} M_y - h_x + \frac{1}{2} \ln \left(\frac{1 + M_x}{2} \frac{2}{1 - M_x} \right) \end{aligned}$$

where the sum is over all nodes y neighbouring x , i.e. the ones included in some pair of neighbours $\langle y, x \rangle$ involving x .

Using the identity (3.35, pag. 110)

$$\tanh^{-1} M_x = \frac{1}{2} \ln \frac{1 + M_x}{1 - M_x}$$

and rearranging leads to:

$$M_x(\mathbf{h}, K) = \tanh \left[K \sum_{y \in \langle y, x \rangle} M_y + h_x \right] \quad (4.16)$$

4.1.1 Physical meaning of the variational parameters M_x

It would be interesting to associate some physical meaning to the variational solution, and in particular understand what the M_x represent.

So, we found that:

$$\min_{\mathbf{m}} F_V(\mathbf{m}, \mathbf{h}) \equiv F_V(\mathbf{M}, \mathbf{h})$$

with the \mathbf{M} given by solving the N equations (4.16), one for each node.

The *magnetization* given by the variational free energy is:

$$\begin{aligned} \langle \sigma_x \rangle_V &= - \frac{\partial}{\partial h_x} [\beta F_V(\mathbf{M}, \mathbf{h})] = -\beta \left[\underbrace{\sum_y \frac{\partial F_V(\mathbf{m}, \mathbf{h})}{\partial m_y}}_{0 \text{ (4.15)}} \frac{\partial m_y}{\partial h_x} - \underbrace{\frac{\partial F_V(\mathbf{m}, \mathbf{h})}{\partial h_x}}_{M_x \text{ (4.14)}} \right]_{\mathbf{m}=\mathbf{M}} = \\ &= M_x \end{aligned} \quad (4.17)$$

Note that the variational free energy F_V is **not** the *ansatz free energy* F_0 , and so $\langle \sigma_x \rangle_V$ and $\langle \sigma_x \rangle_0$ are different averages, and (4.17) should not be confused with (4.9).

So, M_X is the best estimate of the *true magnetization* σ_x , as it is obtained with the F_V closest to the real F .

4.1.2 Uniform case

Suppose the magnetic field is uniform $h_x \equiv h$. In this case, the system is **translationally invariant**. So, it is reasonable to consider the *ansatz* where also all the local magnetizations are the same: $m_x \equiv m$, and search for a single value of m .

Given these assumptions, (4.14) becomes:

$$\beta F_V(m, h) = -K m^2 \sum_{\langle x, y \rangle} 1 - m h \sum_x 1 + \left[\frac{1+m}{2} \ln \frac{1+m}{2} + \frac{1-m}{2} \ln \frac{1-m}{2} \right] \sum_x 1$$

Then $\sum_x 1$ is just the number of nodes N , and $\sum_{\langle x, y \rangle} 1$ is the number of possible pairs, which is Nd for a d -dimensional cubic lattice (each node contributes with one pair for every possible *direction*). Dividing by N :

$$\beta \frac{F_V(m, K, h)}{N} = -K d m^2 + \frac{1+m}{2} \ln \frac{1+m}{2} + \frac{1-m}{2} \ln \frac{1-m}{2} - h m \quad (4.18)$$

The equation for M_X (4.16) becomes:

$$M(h, K) = \tanh \left[KM \sum_{y \in \langle y, x \rangle} 1 + h \right]$$

The sum is over all *neighbours* of x , which are $2d$ for a d -dimensional cubic lattice (2 for every *direction*), leading to:

$$M(h, K) = \tanh(2dKM + h) \quad (4.19)$$

A. No external field

Let's start with the case of no external field $h = 0$. In this case, the variational free energy (4.18) is an **even** function of m : Case 1. $h = 0$

$$F_V(m, 0) = F_V(-m, 0)$$

We can then study the solutions of (4.19):

$$M = \tanh(2dKM) \quad M(K, 0) \equiv M(K) \quad (4.20)$$

Clearly $M = 0$ is always a solution. Depending on $2dK$, there can be two more solutions, as can be seen by plotting each side and looking for intersections (4.1).

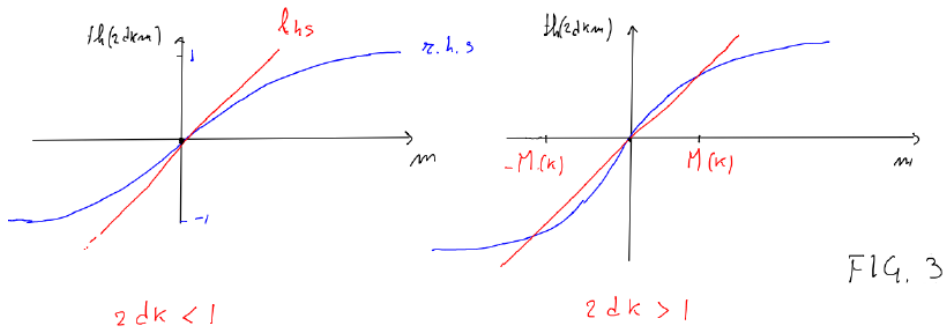


Figure (4.1) – Solutions of (4.19) are intersections of the two curves.

The plots in (4.1) can be obtained by expanding $\tanh x$ in Taylor series around $x = 0$. The first three derivatives are:

$$\begin{aligned} \frac{d}{dx} \tanh x &= 1 - \tanh^2 x \\ \frac{d^2}{dx^2} \tanh x &= -2 \tanh x (1 - \tanh^2 x) \\ \frac{d^3}{dx^3} \tanh x &= -2(1 - \tanh^2 x) + 4 \tanh^2 x (1 - \tanh^2 x) \end{aligned}$$

So:

$$\tanh x = \tanh 0 + x \frac{d}{dx} \tanh x \Big|_{x=0} + \frac{x^2}{2} \frac{d^2}{dx^2} \tanh x \Big|_{x=0} + \frac{x^3}{3!} \frac{d^3}{dx^3} \tanh x \Big|_{x=0} + \dots =$$

$$= x - \frac{2x^3}{3 \cdot 2 \cdot 1} + O(x^5) = x - \frac{x^3}{3} + O(x^5) \quad (4.21)$$

For small x , $\tanh x$ is linear, and in particular $\tanh(2dKM)$ is a line passing through the origin with slope $2dK$. If that slope is **less** than the one of $y = M$, i.e. 1, then the only intersection is at $M = 0$ (left of fig. 4.1). However, if $2dK > 1$, then there will be two other solutions (right of fig. 4.1).

In summary:

- $2dK < 1 \Rightarrow K < K_c \equiv 1/2d$, (4.20) has only one solution $M = 0$.
- If $2dK > 1 \Rightarrow K > K_c$, there are 3 solutions: $M = 0, \pm M(K)$.

In the case $K > K_c$, we need to understand which of the three solution leads to the absolute minimum of F_V . So, let's proceed by expanding $\beta F_V(m, 0)/N \equiv f(m)$ (4.18) for small m . The first four coefficients are:

$$\begin{aligned} f(0) &= \frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2} = -\frac{1}{2} \ln 2 - \frac{1}{2} \ln 2 = -\ln 2 \\ f'(0) &= -2Kd + \frac{1}{2} \ln \frac{1+m}{2} + \frac{1}{2} - \frac{1}{2} \ln \frac{1-m}{2} - \frac{1}{2} \Big|_{m=0} = 0 \\ f''(0) &= -2Kd + \frac{1}{4} \frac{2}{1+m} + \frac{1}{4} \frac{2}{1-m} \Big|_{m=0} = 1 - 2Kd \\ f^{(3)}(0) &= -\frac{1}{2(1+m)^2} + \frac{1}{2(1-m)^2} \Big|_{m=0} = 0 \\ f^{(4)}(0) &= -\frac{1}{2} \frac{-2}{(1+m)^3} + \frac{1}{2} (-2) \frac{-1}{(1-m)^3} \Big|_{m=0} = 2 \end{aligned}$$

Clearly all odd terms vanish because $F_V(m, 0)$ is **even**. Then:

$$\begin{aligned} \frac{\beta F_V(m, h=0)}{N} &= f(0) + m f'(0) + \frac{m^2}{2} f''(0) + \frac{m^3}{3!} f^{(3)}(0) + \frac{m^4}{4!} f^{(4)}(0) + \dots = \\ &= -\ln 2 + \frac{1-2Kd}{2} m^2 + \frac{m^4}{12} + O(m^6) \end{aligned} \quad (4.22)$$

Let's focus on the highlighted quadratic term. We distinguish three cases:

1. When $2Kd < 1$ ($K < K_c$) the coefficient is positive, meaning that, for $x \sim 0$, F_V behaves like a convex parabola (left of fig. 4.2). As $K = \beta J = J/k_B T$, this holds for $T > T_c = 2dJ/k_B$, where T_c is called the system's **critical temperature**.

Note how, in this case, the variational free energy has a single global minimum at $m = 0$.

2. Now, if we let $2Kd = 1$ ($K = K_c = 1/2d$, or $T = T_c = 2dJ/k_B$), then the quadratic coefficient vanishes, and for $m \sim 0$ the variational free energy has the shape of a *quartic* (m^4), meaning that it is close to 0 and “very flat” for $m \rightarrow 0$. Still, there is only one global minimum at $m = 0$.
3. However, if $2Kd > 1$, then F_V is like a **concave** parabola near the origin. So $m = 0$ becomes a local maximum, and $m = \pm M(K)$ are two equivalent local minima.

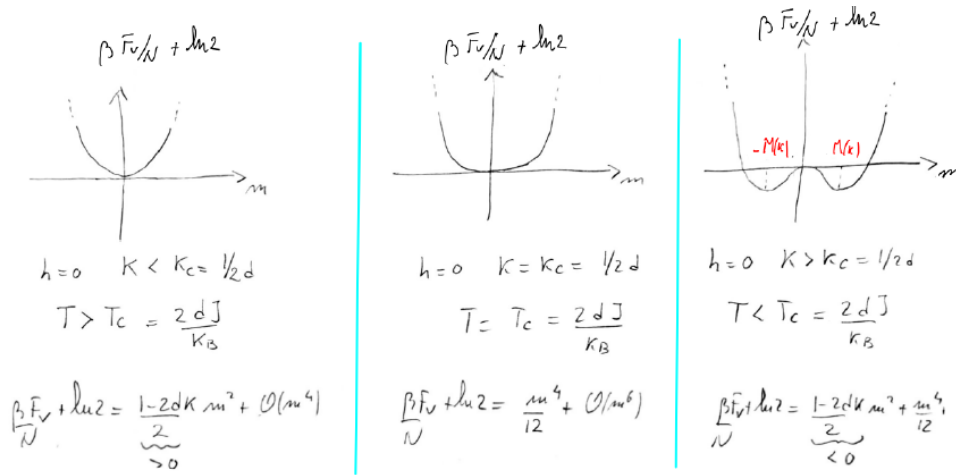


Figure (4.2)

Thus, depending on the **temperature**, the system's behaviour changes *fundamentally*.

Once we have found the solution M for the minimum, the **best estimate** of the exact *free energy* βF is given by 4.18 evaluated at $m = M$ and $h = 0$:

$$\beta \frac{F_V(M, K, 0)}{N} = -KdM + \frac{1+M}{2} \ln \frac{1+M}{2} + \frac{1-M}{2} \ln \frac{1-M}{2} \quad (4.23)$$

Physical meaning of $M(K)$

When $T < T_c$, we found that the free energy is best approximated by a function with two local minima at $\pm M(K)$ - which we have interpreted as estimates of the system's **magnetization**. So, this mechanism could explain the experimentally observed phenomenon of **spontaneous magnetization**.

$M(K)$ and the spontaneous magnetization

Explicitly, we defined the spontaneous magnetization *per node* m_S (3.58) as:

$$-\lim_{h \downarrow 0} \frac{1}{N} \lim_{N \uparrow \infty} \frac{\partial}{\partial h} (\beta F) = \lim_{h \downarrow 0} \left\langle \frac{\sum_x \sigma_x}{N} \right\rangle = m_S \quad (4.24)$$

In particular, the thermodynamic limit must be taken **before** the $h \rightarrow 0$ limit. We can now use the variational free energy to compute an estimate of m_S . Note that in (4.18), the free energy density *does not* depend on N , so the limit of $N \rightarrow \infty$ is trivial. Then we just need to differentiate with respect to h and set $m = M$, the minimum found by solving (4.20). Thus, the *variational estimate* of m_S is given by:

$$\begin{aligned} m_S \Big|_{\text{var.}} &= -\lim_{h \downarrow 0} \frac{\partial}{\partial h} \frac{F_V(M, K, h)}{N} = -\lim_{h \downarrow 0} \left[\underbrace{\frac{\partial F_V}{\partial m}(m, K, h)}_{0 \text{ (4.15)}} \frac{\partial M}{\partial h} + \underbrace{\frac{\partial F_V}{\partial h}(m, K, h)}_{-m \text{ (4.18)}} \right]_{m=M} = \\ &= \lim_{h \downarrow 0} M(K, h) = M(k) \end{aligned} \quad (4.25)$$

where $M(K, h)$ is the solution of (4.19), which, in the limit $h \rightarrow 0$, becomes one of the solutions we found in the $h = 0$ case, since it is an analytic function. So $m_S = 0$ if $2dK < 1$, and $\neq 0$ otherwise.

We can then study how the solution $M(K)$ of (4.20) varies as a function of $K^{-1} = k_B T/J$. This can be done numerically - but to get some understanding we consider the case near criticality $K \approx K_c = 1/2d$. From fig. 4.1 and fig. 4.2 we expect $M \approx 0$ when $K \approx K_c$.

So, using the expansion of $\tanh x$ (4.21) for small x , (4.20) becomes:

$$M = 2dKM - \frac{(2dK)^3 M^3}{3} + O(M^5)$$

One solution is clearly $M = 0, \forall K$.

For the other **solutions**, we suppose that $K > K_c = 1/2d$, e.g. $K = K_c + \delta$ with $\delta \approx 0^+$, and then divide by M to get:

M(K) near criticality

$$\begin{aligned} M^2 &= \frac{3}{(2dK)^3} (2dK - 1) + O(M^4) = \\ &= \frac{6d}{(K/K_c)^3} (K - K_c) + O(M^4) = \\ &= \frac{6d}{[(K_c + \delta)/K_c]^3} (K_c + \delta - K_c) + O(M^4) = \\ &= 6d \frac{\delta}{(1 + \delta/K_c)^3} + O(M^4) = \\ &= 6d\delta + O(\delta^2) \end{aligned}$$

For $\delta \approx 0$, $\delta/(1 + \delta/K_c)^3 \approx \delta$, and so M^2 is of order δ , meaning that M^4 is of order δ^2 .

Taking the square root:

$$M(K) = \sqrt{6d}(K - K_c)^\beta + O(K - K_c) \quad (4.26)$$

where $\beta = 1/2$ is the **critical exponent**. Note that the behaviour of the spontaneous magnetization near criticality is given by a power law in the distance to the critical point K_c : this happens more in general, not only for the Ising Model, and does not depend on the details of the model (**universality**). (4.26) also produces a **singularity** at $K = K_c$, where $M(K)$ starts rising from 0 in a non-smooth manner (fig. 4.3).

Critical exponent and universality

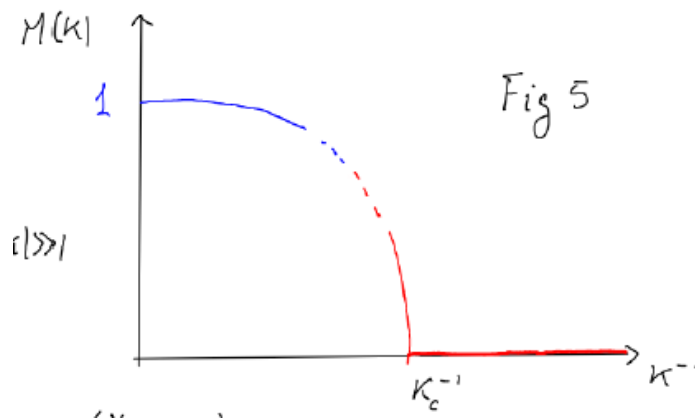


Figure (4.3) – Plot of the spontaneous magnetization $M(K)$ (estimated from the variational free energy) as function of temperature ($K^{-1} \propto T$). From fig. 4.2 we know that $M(K) = 0$ for $K < K_c$. The red curve at $K \approx K_c$ is given by (4.26), while the blue curve at $K \rightarrow \infty$ derives from (??) Note the **singularity** at $K = K_c$, the critical point.

The result in (4.26) is an estimate given by the mean field approximation. However, the same kind of relation *holds* in the true model, just with a different exponent β . For the $d = 2$ case, $\beta = 1/8$ can be exactly determined, while for $d > 2$ one resorts to numerical methods, obtaining $\beta \approx 0.31$ at $d = 3$, and - surprisingly - $\beta = 1/2$ for $d > 3$. Again, this is not a specific behaviour: the mean field approximation happens to become **exact** in $d \geq 4$ in many cases, as we will see later on.

The validity of the mean field approximation

If we instead study the behaviour at low temperatures ($K \gg 1$), we expect from fig. 4.1 to see $M \approx 1$, meaning that the argument $2dKM(k)$ of the tangent in (4.20) becomes very large. So we expand $\tanh x$ accordingly:

$$\begin{aligned} \tanh x &= \frac{e^x - e^{-x}}{e^x + e^{-x}} \stackrel{(a)}{=} \frac{1 - e^{-2x}}{1 + e^{-2x}} = (1 - e^{-2x})(1 - e^{-2x} + e^{-4x} + \dots) = \\ &= 1 - 2e^{-2x} + 2e^{-4x} + O(e^{-6x}) \end{aligned}$$

where in (a) we used the geometric series expansion:

$$\frac{1}{1+x} = 1 - x + x^2 - x^3 + \dots$$

And substituting in (4.20) we get:

$$M(K) = 1 - 2e^{-4dKM(k)} + O(e^{-8dKM(k)}) \stackrel{(b)}{=} 1 - 2e^{-4dK} + O(e^{-12dK}) \quad (4.27)$$

where in (b) we substituted $M(k) \approx 1$ in the right side, noticing that all other terms are of order e^{-12dK} or higher. This result agrees with the low temperature expansion we did in the $d = 2$ case in (3.65, pag. 125). So the spontaneous magnetization quickly approaches 1 when $K^{-1} \rightarrow 0$ ($T \rightarrow 0$).

B. External field

If $h \neq 0$, from (4.18) we have:

2. Case $h \neq 0$

$$\beta \frac{F_V(m, K, h)}{N} = \beta \frac{F_V(m, K, 0)}{N} - hm$$

So the variational equations (4.15) become:

$$\begin{aligned} h &= \frac{\partial}{\partial m} \left[\beta \frac{F_V(m, K, 0)}{N} \right]_{m=M} = (\tanh^{-1} m - 2dKm) \Big|_{m=M} = \\ &\stackrel{M \approx 0}{=} M(1 - 2dK) + \frac{M^3}{3} + \frac{M^5}{5} + \frac{M^7}{7} + \dots \end{aligned} \quad (4.28)$$

Depending on the sign of $1 - 2dK$, i.e. if $2dK$ is lower or higher than 1, the slope at the origin will be either positive or negative, leading to the plots in fig. 4.4.

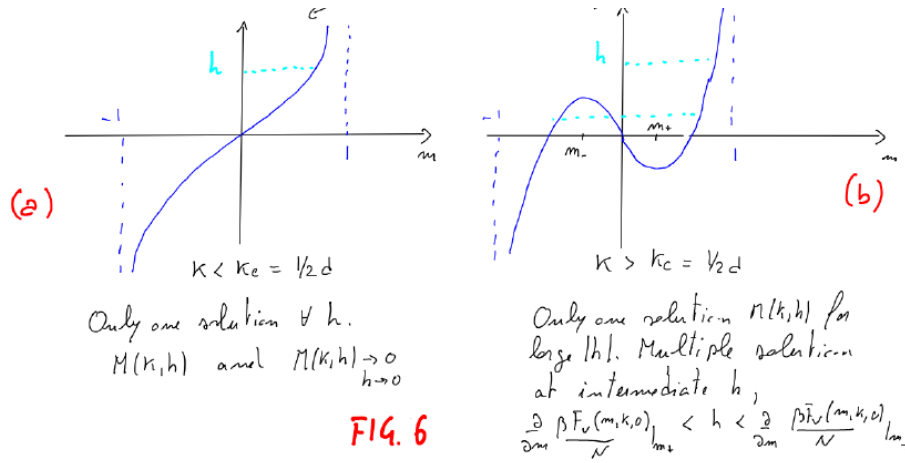


Figure (4.4) – Plot of the right hand side of (4.28), i.e. the variational estimate of magnetization, as function of m .

So there are two cases:

1. If $K < K_c = 1/2d$, then the right side of (4.28) is strictly increasing, and so admits only one intersection with an horizontal line $y = h$, meaning that there is only one solution for $M(h, K)$ (in general $\neq 0$). If we then let $h \rightarrow 0$, $M(K, h) \rightarrow 0$ smoothly, and so $m_S = 0$, as expected.
2. If $K > K_c$, instead, the plot is the one on the right of fig. 4.4, and multiple intersections with $y = h$ are possible if h lies in a certain range:

$$\frac{\partial}{\partial m} \frac{\beta F_V(m, K, 0)}{N} \Big|_{m_+} < h < \frac{\partial}{\partial m} \frac{\beta F_V(m, K, 0)}{N} \Big|_{m_-}$$

where m_{\pm} are the local minima/maxima of the right side of (4.28).

In the $K > K_c$ case, in order to understand which of the possible multiple solutions $\{M_i\}_{i=1,2,3}$ corresponds to the minimum of F_V we refer to fig. 4.5.

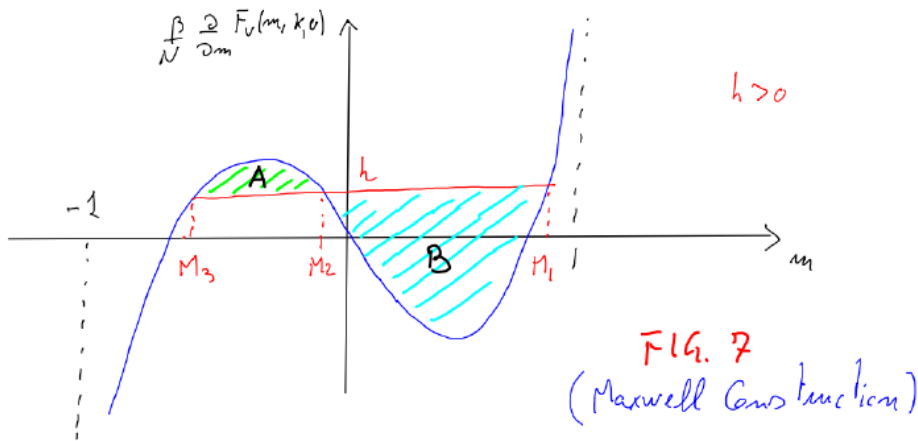


Figure (4.5)

To simplify notation, let's denote as f_i the free variational energy evaluated at a solution M_i :

$$f_i = \frac{\beta F_V(M_i, K, h)}{N} = \frac{\beta F_V(M_i, K, 0)}{N} - h M_i$$

Then note that differences of f_i can be rewritten as integrals, which can be roughly evaluated by looking at fig. 4.5. Then, for $h > 0$:

$$f_1 - f_2 = \int_{M_2}^{M_1} \left(\frac{\beta}{N} \frac{\partial}{\partial m} F_V(m, K, 0) - h \right) dm = -\text{Area of } \mathbf{B} < 0 \Rightarrow f_1 < f_2$$

$$f_2 - f_3 = \int_{M_3}^{M_2} \left(\frac{\beta}{N} \frac{\partial}{\partial m} F_V(m, K, 0) - h \right) dm = -\text{Area of } \mathbf{A} < 0 \Rightarrow f_2 < f_3$$

$$f_1 - f_3 = \int_{M_3}^{M_1} \left(\frac{\beta}{N} \frac{\partial}{\partial m} F_V(m, K, 0) - h \right) dm = \text{Area of } \mathbf{A} - \text{Area of } \mathbf{B} < 0 \Rightarrow f_1 < f_3$$

Summarizing:

1. For $h > 0$, the area of \mathbf{B} is always bigger than that of \mathbf{A} . So, at the end, $f_1 < f_2 < f_3$.
2. For $h = 0$, the two areas \mathbf{A} and \mathbf{B} become equal, and f_1 and f_3 are two degenerate minima.
3. On the other hand, if $h < 0$, all inequalities are reversed, and $f_3 < f_2 < f_1$. So, when h changes sign, the system *jumps* to a different minimum.

Intuitively, a $h > 0$ leads to a *preference* for a positive magnetization, and, conversely, $h < 0$ for a negative magnetization.

A plot of the solution $M(K, h)$ corresponding to the minimum of F_V as a function of h is shown in fig. 4.6.

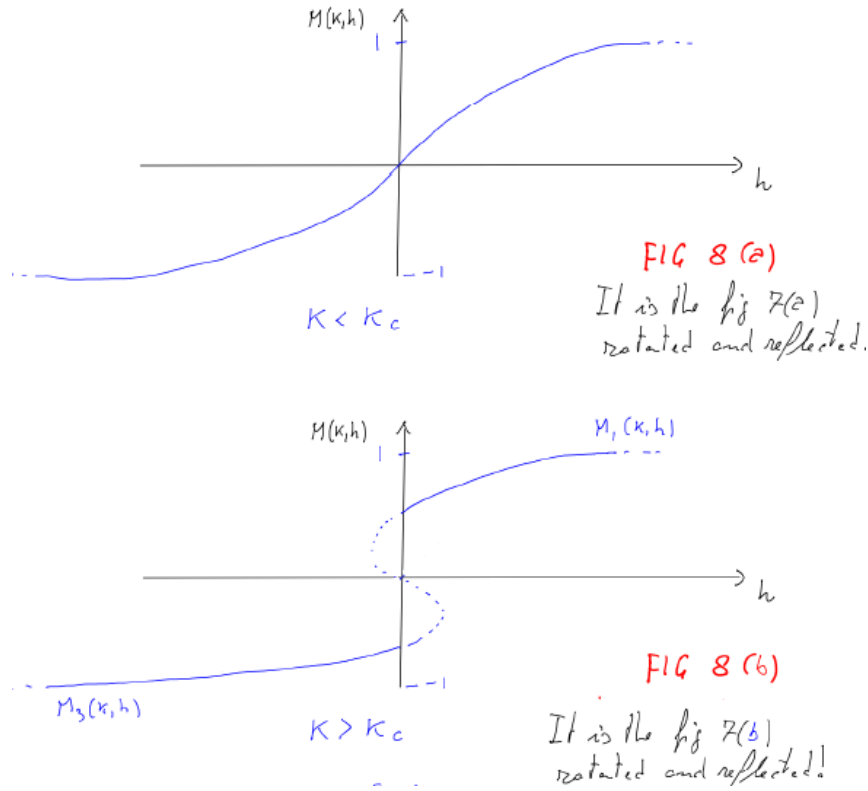


Figure (4.6) – Plot of $M(K, h)$ (variational estimate of magnetization, obtained by minimizing F_V) as a function of the external field h , which can be obtained by rotating and reflecting fig. 4.4. If $K < K_c$ (top) the magnetization varies continuously as a function of h . If $K > K_c$, instead, (bottom) there is a discontinuity at $h = 0$, given by the system's transition to a different minimum (M_3 instead of M_1)

All of these results about criticality are summarized in fig. 4.7.

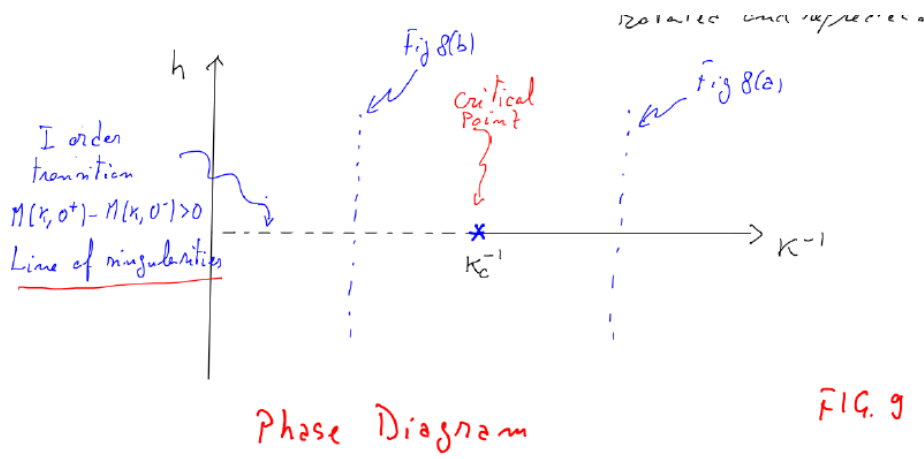


Figure (4.7) – Phase diagram representing all the singular points of $M(K, h)$ as a dashed line. Any curve surpassing the dashed part (left of K_c^{-1}) has a discontinuity (first-order transition). One such path is the one in the bottom plot of fig. 4.6. On the other hand, a curve surpassing $h = 0$ at the right of K_c^{-1} , however, is smooth; and one such example is given by the top curve of fig. 4.6. So, starting at a point (h, K^{-1}) with $h > 0$, we can construct *two kinds* of paths arriving to the phase with $h < 0$: one passing through a high-temperature state and without phase-transitions, and one with a phase-transition at a low temperature. Something analogous happens for the vapour-liquid transition: it can be observed as an abrupt change (phase transition) at sufficiently low temperatures, or as a completely smooth process if pressure is increased such that phase differences are removed (the “gas looks like a liquid”).

We conclude by stressing that the **singularities** at $h = 0$ and $K > K_c$ emerge from the variational principle as a consequence of the minimization.

Remarks on the mean-field approximation. The Mean Field (MF) model predicts a phase transition in all $d > 0$. However we know that this is not true in $d = 1$, where no phase transition is observed (pag. 118). Still, for $d > 1$ the MF is at least qualitatively correct. Impressively, such a simple model agrees *exactly* with simulation at $d \geq 4$, at least for the behaviour of magnetization near criticality.

Mean Field and symmetry breaking. For $h = 0$, the Ising Model Hamiltonian:

$$\mathcal{H}(\sigma) = -J \sum_{\langle x, y \rangle} \sigma_x \sigma_y$$

is **symmetric** with respect to the transformation $\sigma_x \rightarrow -\sigma_x \forall x$, i.e. $\mathcal{H}(\sigma) = -\mathcal{H}(\sigma)$. In any **finite** system ($N < \infty$), this symmetry implies that $\langle \sigma_x \rangle = -\langle \sigma_x \rangle \Rightarrow \langle \sigma_x \rangle = 0$, meaning that no spontaneous magnetization can be observed. However, in the **infinite volume**, this symmetry is **spontaneously broken** below some critical temperature and $\langle \sigma_x \rangle \neq 0$.

We have shown how this occurs in the mean field approximation. Specifically, the symmetry that is broken for the Ising model is \mathbb{Z}_2 .

If we instead consider the Hamiltonian:

$$H(\boldsymbol{\sigma}) = -J \sum_{\langle x,y \rangle} \boldsymbol{\sigma}_x \cdot \boldsymbol{\sigma}_y$$

where $\boldsymbol{\sigma}_x \in \mathbb{R}^n$ and $\|\boldsymbol{\sigma}_x\| = 1$, then the group symmetry is $O(n)$, the orthogonal group, and $H(R\boldsymbol{\sigma}) = H(\boldsymbol{\sigma})$, where R is a $n \times n$ matrix such that $\|R\boldsymbol{\sigma}\| = \|\boldsymbol{\sigma}\|^2 = 1$, i.e. a orthogonal (“rotation”) matrix satisfying $R^T R = R R^T = \mathbb{I}$. There are rigorous results establishing that discrete symmetries like \mathbb{Z}_2 cannot be spontaneously broken in $d = 1$ (Landau arguments) whereas continuous symmetries, like $O(n)$, cannot be spontaneously broken in $d \leq 2$ (Mermin-Wagner theorem). In both cases only short-range interactions are assumed.

4.2 Critical Behaviours and Scaling Laws

In the last section, we were able to finally describe a **phase-transition**, by analysing the Ising Model in the mean field approximation in $d > 1$. Mathematically, we observed how the **spontaneous magnetization** $M(K, h)$, when K is chosen in the proximity of the *critical parameter* K_c needed for the phase-transition, is described by a **power law** (4.26).

This happens to be a very general kind of behaviour, proper of **not only mean field** models. Scaling laws such as (4.26) were originally formulated from empirical evidence, and then given a theoretical foundation in the 1960s by Widom, Kadanoff and Kenneth Wilson, leading to the field of **renormalization group theory**. In this framework, all critical phenomena can be treated on equal ground, and general results can be mathematically proven.

The importance of scaling laws, and especially the values of their *critical exponents* (such as β for the IM) resides in their **universality**, i.e. in the fact that they are *largely independent* on the “model’s details”. In other words, the very same scaling law can describe two systems that - from the outside - seem completely different - but that share some fundamental characteristic (e.g. symmetry).

So, let’s continue using the Ising Model in the mean field approximation as a *concrete* example, and let’s focus on deriving and understanding scaling laws for various quantities of interest.

4.2.1 Spontaneous magnetization

We start with (re)deriving the power law for the **spontaneous magnetization**. Recall the expression for the variational free energy (4.18):

$$\beta \frac{F_V(m, K, h)}{N} = -K d m^2 + \frac{1+m}{2} \ln \frac{1+m}{2} + \frac{1-m}{2} \ln \frac{1-m}{2} - h m \quad (4.29)$$

F_V is closest to the *true* “unapproximated” free energy F when it’s minimum:

$$\frac{\partial}{\partial m} F_V(m, K, h) \stackrel{!}{=} 0 \Rightarrow_{(4.19)} m(h, K) = \tanh(2dKm + h) \quad (4.30)$$

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Power laws

Let's solve (4.30) for h and expand² for $m \approx 0$, which holds near the critical temperature $T \approx T_c$:

$$\begin{aligned}
h &= -2dKm + \tanh^{-1} m \stackrel{(3.35)}{=} -2dKm + \frac{1}{2} \ln \frac{1+m}{1-m} \stackrel{(\text{??})}{=} -2dKm + \frac{1}{2} [\ln(1+m) - \ln(1-m)] = \\
&= -2dKm + \frac{1}{2} \left[m - \frac{m^2}{2} + \frac{m^3}{3} - \frac{m^4}{4} + \frac{m^5}{5} + \dots - \left(-m - \frac{m^2}{2} - \frac{m^3}{3} - \frac{m^4}{4} - \frac{m^5}{5} + \dots \right) \right] = \\
&= m(1 - 2dK) + \frac{m^3}{3} + \frac{m^5}{5} + \dots \tag{4.31}
\end{aligned}$$

When $h = 0$ and $K \geq K_c = 1/2d$, then³ $1 - 2dK < 0$. We already know that 1. $h = 0$ the solution $m = 0$ is a local *maximum* of F_V , and the minima are given by the other *two* solutions. Dividing by m and rearranging leads to:

$$(2dK - 1) = \frac{m^2}{3} + \frac{m^4}{5} + \dots \Rightarrow m^2 = 3(2dK - 1) - \frac{m^4}{5} + \dots$$

If $(2dK - 1)$ is of order $O(m^2)$, then m^4 is of order $O[(2dK - 1)^2]$, and so:

$$m^2 = 3(2dK - 1) + O[(2dK - 1)^2]$$

And substituting $K_c = 1/2d$:

$$m^2 = 3 \left(\frac{K}{K_c} - 1 \right) + \dots = 3 \frac{K - K_c}{K_c} + O \left(\left[\frac{K - K_c}{K_c} \right]^2 \right) \tag{4.32}$$

Then, using $K = J/k_B T$ and $K_c = J/k_B T_c$ leads to the equivalent relation in terms of temperatures:

$$\begin{aligned}
m^2 &= 3 \frac{J/k_B T - J/k_B T_c}{J/k_B T_c} + \dots = 3 \frac{1/T - 1/T_c}{1/T_c} + \dots = 3 \left(\frac{T_c - T}{T} \right) \underbrace{\frac{T}{T_c}}_{\approx 1} + \dots = \\
&= 3 \underbrace{\frac{T_c - T}{T_c}}_{-t} + O \left(\left[\frac{T_c - T}{T_c} \right]^2 \right) = 3|t| + O(t^2) \quad t \equiv \frac{T - T_c}{T_c}
\end{aligned}$$

Taking the square root leads to the power law for the magnetization:

$$m = \sqrt{3}|t|^\beta \theta(-t) \quad \beta = \frac{1}{2} \tag{4.33}$$

Here, the Heaviside function $\theta(-t)$ ensures that $m = 0$ for $T > T_c$.

Let's now consider (4.31) in the case $h \neq 0$. To “see” the phase-transition, we 2. $h \neq 0$ fix⁴ any $K \geq K_c$, for example (and for simplicity) $K = K_c = 1/2d$. In this case, $1 - 2dK = 0$ and the linear term in (4.31) vanishes:

$$h = \frac{m^3}{3} + \frac{m^5}{5} + \dots \stackrel{m \sim 0}{=} \frac{m}{3} |m|^{\delta-1} \quad \delta = 3 \tag{4.34}$$

²^For notational simplicity, we do not denote with M the value of m that solves (4.30), as was instead done in the previous section.

³^Consider fig. 4.7, pag. 146. When $h = 0$, we are “moving” along a horizontal line, encountering the singularity at $K = K_c$.

⁴^Referring to fig. 4.7, 146, we are “moving” along a vertical line with $K = K_c$

After collecting a m , all the powers are even, and so we can insert a modulus⁵. The exponent of the leading order is then $\delta = 3$.

4.2.2 Susceptibility (at $h = 0$)

Near criticality, also the susceptibility χ , measuring “how much” the system reacts to a change in the external field, obeys a power law.

Recall that the susceptibility χ is defined as:

$$\chi^{-1} \equiv \frac{\partial h}{\partial m} \quad (??)$$

Using the expression (4.31) for h and expanding around $m = 0$ we get:

$$\chi^{-1} = \frac{\partial h}{\partial m} \stackrel{(4.31)}{=} -2dK + \frac{1}{1-m^2} = 1 - 2dK + m^2 + O(m^4)$$

And using (4.33) to compute m^2 we arrive to:

$$\chi^{-1} \Big|_{h=0} \stackrel{(4.33)}{=} \begin{cases} 1 - 2dK = \frac{K_c - K}{K_c} = \frac{T - T_c}{T} = t + O(t^2) & T > T_c \ (m = 0) \\ 1 - 2dK + m^2 = \frac{K_c - K}{K_c} + 3\frac{K - K_c}{K_c} = 2|t| + O(t^2) & T < T_c \end{cases}$$

Taking the reciprocal we finally get the power law for χ :

$$\chi = A_{\pm} |t|^{-\gamma} \quad \gamma = 1 \quad (4.35)$$

with $A_+ = 1$ for $t > 0$, and $A_- = 1/2$ for $t < 0$. A plot of $\chi(T)$ is shown in fig. 4.8, and shows how it diverges for $T \rightarrow T_c$. In other words, near criticality, a small change in h produces a *infinite* change of m - i.e. the system is *globally* sensitive to the external field.

This kind of *global reaction* to *small changes* is a defining characteristic of complex systems, such as living organisms - with the difference that they seems to “always” be near criticality. One example is a bird flock - which can be hundreds of meters in size - reacting almost instantaneously to a predator (very small in comparison).

4.2.3 Specific heat (at $h = 0$)

Another quantity of interest is the **specific heat**, defined as:

$$C \equiv \frac{\partial \langle \mathcal{H} \rangle}{\partial T}$$

Recalling that:

$$-\langle \mathcal{H} \rangle = \frac{\partial}{\partial \beta} \ln Z$$

⁵^This is done so that the resulting expression is meaningful for any real δ . Otherwise, we would have problems when a negative m is elevated to a fractional exponent, such as $1/2$, leading to results that are complex - meaning that we would have to add more specifications. The notation $m|m|^{\delta-1}$ naturally solves this kind of trouble.

we get:

$$C = \frac{\partial \langle \mathcal{H} \rangle}{\partial T} = -\frac{\partial \beta}{\partial T} \frac{\partial^2}{\partial \beta^2} \ln Z = \frac{1}{k_B T^2} \frac{\partial^2}{\partial \beta^2} (-\beta F)$$


The specific heat *per node* at $h = 0$ is then:

$$\begin{aligned} c &= \frac{C}{N} \stackrel{(4.29)}{=} -k_B \beta^2 \frac{\partial^2}{\partial \beta^2} [-K d m^2 + \frac{1+m}{2} \ln \frac{1+m}{2} + \frac{1-m}{2} \ln \frac{1-m}{2}] = \\ &\stackrel{m \approx 0}{\stackrel{(4.22)}}{=} -k_B \beta^2 \frac{\partial^2}{\partial \beta^2} \left(\frac{1-2dK}{2} m^2 + \frac{m^4}{12} + O(m^6) \right) = \\ &= -k_B \beta^2 \frac{\partial^2}{\partial \beta^2} \left(-\frac{1}{2} \left(\frac{K}{K_c} - 1 \right) m^2 + \frac{m^4}{12} + O(m^6) \right) \end{aligned}$$

For $K < K_c$ ($T > T_c$), $m \equiv 0$ (4.33) and so $c = 0$. Otherwise, for $K > K_c$ ($T < T_c$), using (4.32) leads to:

$$\begin{aligned} c &= -k_B \beta^2 \frac{\partial^2}{\partial \beta^2} \left(-\frac{3}{2} \left(\frac{K}{K_c} - 1 \right)^2 + \frac{9}{12} \left(\frac{K}{K_c} - 1 \right)^2 + O \left(\left[\frac{K}{K_c} - 1 \right]^3 \right) \right) = \\ &= \cancel{k_B} \beta^2 \frac{\partial^2}{\partial \beta^2} \left(\cancel{\frac{3}{4}} \left[\frac{K}{K_c} - 1 \right]^2 + \dots \right) \approx \frac{3}{4} k_B \beta^2 \frac{\partial}{\partial \beta} \frac{2J}{K_c} \left(\frac{K}{K_c} - 1 \right) = \frac{3}{2} k_B \overbrace{\frac{J \beta^2}{K_c}}^{K^2} = \\ &\stackrel{K \approx K_c}{=} \frac{3}{2} k_B \end{aligned}$$

In summary:

 In the slides it is $3/4$ instead.

$$c(T) = \begin{cases} 0 & T > T_c \\ \frac{3}{2} k_B & T < T_c \end{cases} \propto |t|^{-\alpha} \quad \alpha = 0 \quad (4.36)$$

Here we would expect $C(T)$ to diverge near the critical temperature, with some exponent α , but this does not happen in the mean-field approximation (and so we say $\alpha = 0$). However, in Onsanger's exact solution for the $d = 2$ case, $c(T)$ diverges logarithmically.

Mean field and specific heat. The fact that $\alpha = 0$ in (??) in the mean-field approximation can be justified by examining $c(T)$ on the complex plane - as a purely abstract function (clearly a *complex* temperature does not make any physical sense). See [] for more details.

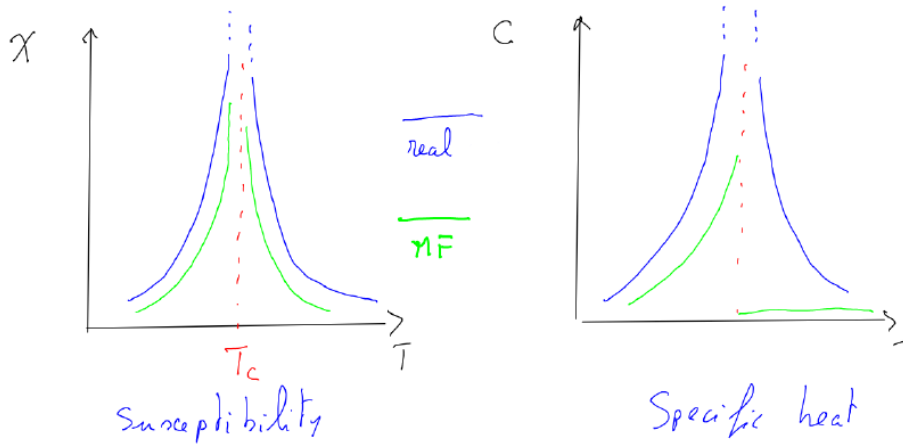


Figure (4.8) – Plot of the susceptibility χ (left) and the specific heat per node c (right) as functions of temperature T . Both quantities *diverge* for $T \rightarrow T_c$ in the real case - but this behaviour is captured by the mean field approximation only for χ , and not for c - for which only a *finite* jump discontinuity is predicted. Even in the case of χ , in a real system it diverges more rapidly than in the mean field model.

4.3 Scaling ansatzs

We can use the power laws we have just found to write an **equation of state** connecting the external field h , the magnetization m and distance to criticality t . We start from (4.31), highlight a t and collect a m^3 :

$$h = m^3 \left[\frac{1}{3} + \overbrace{\frac{K_c - K}{K_c}}^t m^{-2} + O(m^2) \right] \quad K \sim K_c; h \sim 0$$

As in the mean-field $\beta = 1/2$ (4.33), we can rewrite $m^{-2} = m^{-1/\beta}$. We then use (4.34) to write $m^3 = m|m|^{\delta-1}$, leading to the **scaling ansatz**, first conjectured by Widom in 1960:

$$h = m|m|^{\delta-1} h_s(t|m|^{-1/\beta}) \quad t = \frac{T - T_c}{T_c} \quad (4.37)$$

Where h_s (the “scaling function”) has the following form in the mean field approximation:

$$h_s(x) = \frac{1}{3} + x \quad (4.38)$$

Expression (4.37) is certainly a valid relation between h , m and t near criticality in the mean field approximation - but we *suppose*⁶ that it holds in more general cases, perhaps with different choices of exponents β, δ or scaling function h_s . In particular, we make the hypothesis that h_s *should be “similar”* to (4.38), and in particular should be **non-decreasing** and vanishing at a **negative** point x_0 (fig. 4.9).

⁶That is why it is called an *ansatz*.

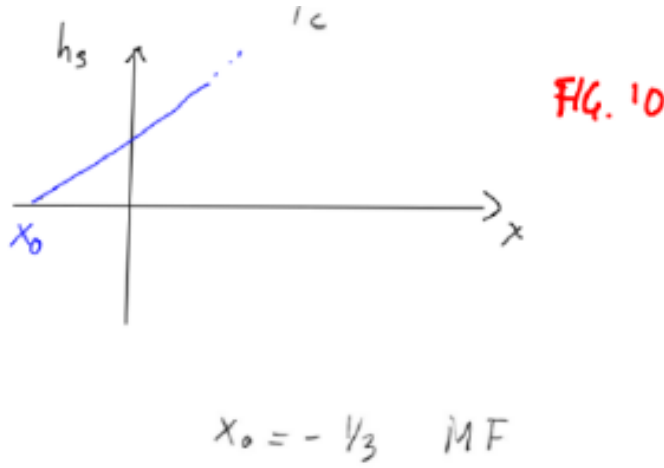


Figure (4.9) – Plot of the scaling function h_S for the Mean Field case.

Equation (4.37) summarizes the previous scaling laws, in particular (4.33), (4.34) and (4.35) in all cases ($h = 0$ or $h \neq 0$, $T < T_c$ or $T > T_c$). So, if we assume that an equation of state of the form (4.37) holds indeed in a more general case, and not only in the mean field approximation, we have a way to re-derive all the scaling laws.

Explicitly, assuming h_S monotonically increasing with $h_S(x_0) = 0$ and $x_0 < 0$:

1. **Magnetization.** If $h = 0$, equation (4.37) becomes:

$$0 = m|m|^{\delta-1}h_S(t|m|^{-1/\beta})$$

The possible solutions are $m = 0$ or $t|m|^{-1/\beta} = x_0 < 0$. The second one is acceptable only if $t < 0$, and in that case:

$$-|t||m|^{-1/\beta} = -|x_0| \Rightarrow |m| = \left| \frac{t}{x_0} \right|^\beta$$

However, the second one is present only if $t < 0$, and so:

$$m = \begin{cases} 0 & t > 0 \\ |t|^\beta / |x_0|^\beta & t < 0 \end{cases} \quad (4.39)$$

In the mean field, $\beta = 1/2$ and $x_0 = -1/3$, and so (4.39) is equivalent to (4.33).

2. **Susceptibility.** Differentiating (4.37) with respect to m and evaluating at $h = 0$ leads to:

$$\begin{aligned} \chi^{-1}(h=0) &= \frac{\partial h}{\partial m} \Big|_{h=0} \stackrel{(4.37)}{=} \delta|m|^{\delta-1}h_S(\underbrace{t|m|^{-1/\beta}}_x) + m|m|^{\delta-1}h'_S(t|m|^{-1/\beta}) \frac{t|m|^{-1/\beta}}{m} \left(-\frac{1}{\beta} \right) = \\ &= |m|^{\delta-1} \left[\delta h_S(x) - \frac{x}{\beta} h'_S(x) \right]_{h=0} \quad x \equiv t|m|^{-1/\beta} \end{aligned}$$

For $t < 0$, the scaling is given by:

$$\chi^{-1} \propto |m|^{\delta-1} \underset{(4.39)}{\propto} |t|^{\beta(\delta-1)} = |t|^{\gamma_-} \quad \gamma_- \equiv \beta(\delta-1)$$

In the mean field, $\beta = 1/2$ and $\delta = 3$, and so $\gamma_- = 1$, and $\chi \propto |t|^{-1}$, which is the same result we got in (4.35).

In essence, the scaling ansatz (4.37) comes from the peculiar scaling of m in a neighbourhood of criticality (fig. 4.10), and in particular:

- a) For $h = 0$ fixed and $t = (T - T_c)/T_c \approx 0$ (i.e. varying in the vicinity of the critical point), $m \propto (-t)^\beta$ for $t \lesssim 0$ (4.33).
- b) For $t = 0$ fixed and h varying, $|m| \propto |h|^{1/\delta}$ (4.34).

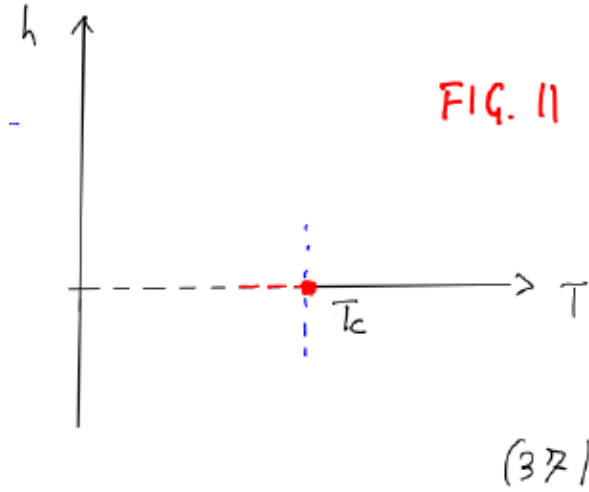


Figure (4.10) – Phase diagram in h and T . Singularities of F_V are represented as the black dots at the left of T_c . The scaling ansatz describes how m changes when approaching the critical point *horizontally* (along the red path), i.e. at $h = 0$ and varying T , or *vertically*, i.e. at $T = T_c$ and varying h .

In principle it is natural to say that h should depend on two independent variables - t and m - but the choice of the *form* of (4.37) arises from some **non-trivial** dimensional analysis arguments. The idea comes from observing that certain *ratios* of quantities - due to their scaling behaviour near criticality (a) and b)) - are “dimensionless”⁷, in the sense that, near criticality, they *do not depend* anymore on the distance from the critical point and are “devoid” of singularities. Some of them are $h/m|m|^{\delta-1}$, $t/|m|^{1/\beta}$ and $t|h|^{-1/\delta\beta}$ - and so (4.37) is written as a function of such arguments.

⁷^Not in the sense that being *pure numbers*, i.e. not having physical dimensions (e.g. kg, T, K etc.) - which is a matter of the so-called naïve dimensional analysis. The “non-trivial” dimensional analysis deals with *scaling* and *local behaviours*.

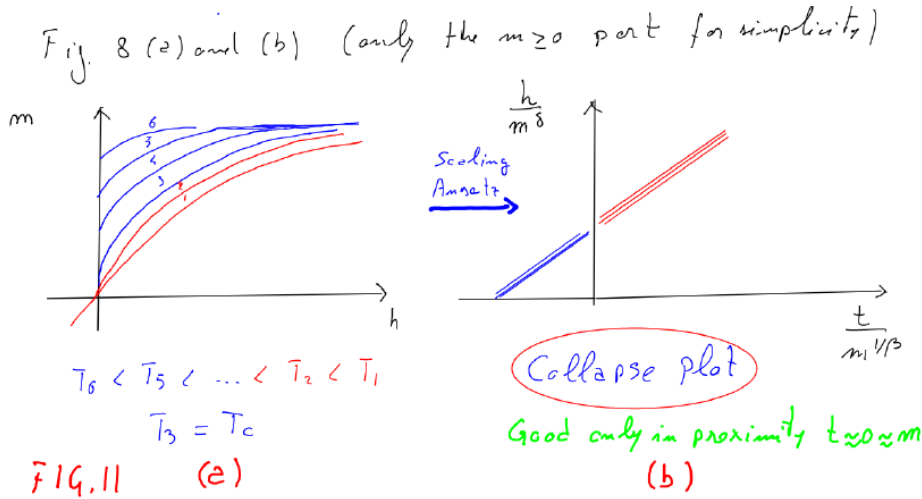


Figure (4.11) – (a): $m(h)$ for different values of $K(T)$. When $T > T_c$ (hot system), $m(h)$ passes through the origin (red lines), while if $T < T_c$ (cold system), there is a nonzero spontaneous magnetization, i.e. $m(0) \neq 0$. As $m(h)$ is an odd function, only the first quadrant is shown for simplicity. If we instead plot “dimensionless” variables (b), all these curves *collapse* into a single line (at least for $K(T)$ close to $K_c = K(T_c)$, i.e. $t \approx 0 \approx m$). This happens in the mean field approximation, and motivates a generalization to more complex systems giving rise to the scaling ansatz (4.37).

4.3.1 Two-point correlation function

By shining a light on a fluid and measuring its scattering we can estimate how the density (and thus the refraction index) changes from point to point, and in particular its *correlation* between different points. That’s why it is important to compute correlation functions, especially the **two-point correlation** one:

$$g(\mathbf{r}) \equiv \langle \sigma_x \sigma_y \rangle - \langle \sigma_x \rangle \langle \sigma_y \rangle$$

Ising Model in $d = 1$

Before computing $g(\mathbf{r})$ in a generic dimension using the mean field model, we study a simpler case - namely, the $d = 1$ IM with $h = 0$ and **open boundary** conditions.

We previously obtained:

$$\langle \sigma_x \rangle \stackrel{(3.57, \text{ pag.117})}{=} 0 \quad (4.40)$$

For the correlation, we proceed by explicitly computing the average:

$$\langle \sigma_x \sigma_y \rangle = \sum_{\sigma} \sigma_x \sigma_y \frac{1}{Z} \exp \left(K \sum_z \sigma_z \sigma_{z+1} \right) =$$

Factoring the exponential over neighbouring pairs:

$$= \sum_{\sigma} \sigma_x \sigma_y \frac{1}{Z} \prod_z \exp(K \sigma_z \sigma_{z+1}) =$$

As $\sigma_z \sigma_{z+1}$ is a binary variable (it can be only ± 1), we can rewrite it using (3.43, pag. 111):

$$= \sum_{\sigma} \frac{\sigma_x \sigma_y}{Z} \prod_z (\cosh K + \sigma_z \sigma_{z+1} \sinh K)$$

Then we expand $Z = (2 \cosh K)^N$ (3.48, pag. 114) and simplify the $\cosh K$:

$$\begin{aligned}
&= \sum_{\sigma} \sigma_x \sigma_y \frac{\prod_z \cosh K (1 + \sigma_z \sigma_{z+1} \tanh K)}{(2 \cosh K)^L} = \\
&= \sum_{\sigma} \sigma_x \sigma_y \frac{\cancel{(\cosh K)^N} \prod_z (1 + \sigma_z \sigma_{z+1} \tanh K)}{(\cancel{2 \cosh K})^N} = \\
&= \frac{1}{2^N} \sum_{\sigma} \sigma_x \sigma_y \prod_z (1 + \sigma_z \sigma_{z+1} \tanh K)
\end{aligned}$$

To proceed, let's denote $\tanh K \equiv A$ for simplicity, and expand both the sum and the product, assuming $x < y$:

$$= \frac{1}{2^N} \sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_N=\pm 1} \sigma_x \sigma_y (1 + \sigma_1 \sigma_2 A) \cdots (1 + \sigma_{x-1} \sigma_x A) \cdots (1 + \sigma_{y-1} \sigma_y A) \cdots (1 + \sigma_{N-1} \sigma_N A)$$

We can *factor out* all elements except the last, and perform the sum over σ_N :

$$= \frac{1}{2^N} \left[\sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_{N-1}=\pm 1} \sigma_x \sigma_y (1 + \sigma_1 \sigma_2 A) \cdots (1 + \sigma_{N-2} \sigma_{N-1} A) \right] \left[\sum_{\sigma_N=\pm 1} (1 + \sigma_{N-1} \sigma_N A) \right]$$

Note that:

$$\sum_{\sigma_N=\pm 1} (1 + \sigma_{N-1} \sigma_N A) = 1 + \cancel{\sigma_{N-1} A} + 1 - \cancel{\sigma_{N-1} A} = 2$$

Leading to:

$$= \frac{1}{2^N} \sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_{N-1}=\pm 1} \sigma_x \sigma_y (1 + \sigma_1 \sigma_2 A) \cdots (1 + \sigma_{N-2} \sigma_{N-1} A) \cdot 2$$

We can then sum over σ_{N-1} , which will result in another factor 2, and reiterate until we arrive at the sum over σ_y :

$$= \frac{1}{2^N} \sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_y=\pm 1} \sigma_x (1 + \sigma_1 \sigma_2 A) \cdots \sigma_y (1 + \sigma_{y-1} \sigma_y A) \cdot 2^{N-y}$$

If we now compute the sum over σ_y , the result will be different due to the added factor:

$$\sum_{\sigma_y=\pm 1} \sigma_y (1 + \sigma_{y-1} \sigma_y A) = 1 + \sigma_{y-1} A - (1 - \sigma_{y-1} A) = 2\sigma_{y-1} A$$

Beside the usual factor 2, now we have also a factor A and a σ_{y-1} :

$$= \frac{1}{2^N} \sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_{y-1}=\pm 1} \sigma_x (1 + \sigma_1 \sigma_2 A) \cdots \sigma_{y-1} (1 + \sigma_{y-2} \sigma_{y-1} A) \cdot 2^{N-y+1} A$$

Due to the added σ_{y-1} , also the *next* sum will produce (beside the 2) also an A and a σ_{y-2} , and so on. This continues until we arrive at the sum over σ_x :

$$= \frac{1}{2^N} \sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_x=\pm 1} (1 + \sigma_1 \sigma_2 A) \cdots \sigma_x^2 (1 + \sigma_{x-1} \sigma_x A) \cdot 2^{N-x} A^{y-x}$$

Note the σ_x^2 : one σ_x was there from the start, the other was produced by summing over σ_{x+1} . However, as $\sigma_x = \pm 1$, $\sigma_x^2 \equiv 1$ in any case, thus making the sum “go back to normal”:

$$\sum_{\sigma_x=\pm 1} \underbrace{\sigma_x^2}_1 (1 + \sigma_{x-1}\sigma_x A) = 1 + \cancel{\sigma_{x-1}A} + 1 - \cancel{\sigma_{x-1}A} = 2$$

From now on, all the remaining sums will just produce a factor 2 each, and nothing more. So, at the end:

$$\langle \sigma_x \sigma_y \rangle = \frac{1}{2^{\mathcal{N}}} A^{y-x} 2^{\mathcal{N}} = (\tanh K)^{y-x}$$

Here we supposed $x < y$. If $y < x$ instead, nothing really changes in the argument apart from the sign of the exponent. So, in general, we may write:

$$\langle \sigma_x \sigma_y \rangle = (\tanh K)^{|y-x|} \quad (4.41)$$

Denoting with $r = |y - x|$ the **distance** between the *two points* x and y , we can finally compute the correlation function $g(r)$, and rewrite it as an exponential:

$$g(r) = \underbrace{\langle \sigma_x \sigma_y \rangle}_{(4.41)} - \underbrace{\langle \sigma_x \rangle \langle \sigma_y \rangle}_0 \quad (4.40) = (\tanh K)^{|r|} \equiv \exp\left(-\frac{|r|}{\xi(K)}\right) \quad (4.42)$$

where $\xi(K)$ is called the **correlation length**, and measures the *decay* of correlations. In other words, spins are significantly correlated only when they are $|r| < \xi(K)$ positions apart.

Note that:

$$\xi(K) = -\frac{1}{\ln \tanh K}$$

diverges when $K \rightarrow \infty$, i.e. when $T \rightarrow 0$. At very low temperature, the one-dimensional Ising model becomes *fixed* in a extremely correlated configuration - as if $T = 0$ were its the **critical temperature**. Still, note that this does not agree with the mean field model, for which $K_c = 1/2d = 1/2 \Rightarrow T_c = 2J/k_B$.

The divergence of the correlation length $\xi(K)$ is fundamental for **universality**: as all microscopical parts of the system can interact with the *whole* system, the “exact specifics” do not matter anymore, but only the most *fundamental* characteristics of the system.

General case: the correlation ansatz

The exponential behaviour of the two-point correlation function (4.42) motivates an *ansatz* for models in $d \geq 2$. More precisely, when $t \neq 0$ (i.e. $T \neq T_c$) the two-point correlation function is hypothesized to have the form:

$$g(\mathbf{r}, t) = r^{-\tau} \exp\left(-\frac{\tau}{\xi(t)}\right) \quad r = \|\mathbf{r}\| \quad (4.43)$$

Correlation ansatz

with the correlation length diverging near the critical point:

$$\xi(t) = C_{\pm} |t|^{-\nu} \quad t \approx 0, h = 0 \quad (4.44)$$

for some proper choices of parameters τ , ν and C_{\pm} . In more general cases, $\xi(t)$ may also depend (weakly) on the *direction* of \mathbf{r} , meaning that the system is not isotropous.

At the critical point $t = (T - T_c)/T_c = 0$, with $h = 0$, the correlation *does not diverge* anymore, but it's described instead by a power law:

$$g(\mathbf{r}, t) \sim \|\mathbf{r}\|^{-(d-2+\eta)} \quad (4.45) \quad \begin{array}{l} \text{Correlation ansatz} \\ \text{at } t = 0 \end{array}$$

where the added exponent η is called the **anomalous dimension**.

We can combine (4.43) and (4.45) by writing an *equation of state* for the correlation length $\xi(K)$, as a function of the only two “dimensionless” scaling variable r/ξ and $t|h|^{-1/\beta\delta}$:

$$\xi(t, h) = |t|^{-\nu} \hat{\xi}(t|h|^{-1/\beta\delta}) \quad (4.46)$$

leading to the **complete** ansatz for the two-point correlation ansatz:

$$g(\mathbf{r}, t, h) = r^{-(d-2+\eta)} \tilde{g}\left(\frac{r}{\xi}, th^{-1/\beta\delta}\right) \quad (4.47) \quad \begin{array}{l} \text{The “complete”} \\ \text{correlation ansatz} \end{array}$$

Before proceeding, we note that (4.47) leads to an interesting relation between γ (the exponent defining the scaling for the susceptibility) and η, δ , i.e. the exponents appearing in the correlation ansatz.

Recall the fluctuation dissipation theorem (3.69, 128):

$$\begin{aligned} \chi &= \frac{\partial}{\partial h} \left\langle \frac{\sum_x \sigma_x}{N} \right\rangle = \frac{1}{N} [\langle \sum_{xy} \sigma_x \sigma_y \rangle - \langle \sum_x \sigma_x \rangle^2] = \\ &= \frac{1}{N} \sum_{xy} \left(\underbrace{\langle \sigma_x \sigma_y \rangle - \langle \sigma_x \rangle \langle \sigma_y \rangle}_{g(x-y, t, h)} \right) = \sum_{\mathbf{r}} g(\mathbf{r}, t, h) \end{aligned}$$

At $h = 0$ and $t \approx 0$, \tilde{g} varies slowly, because it is defined as a function of “dimensionless” variables. So we can consider the continuum limit, and substitute the sum over \mathbf{r} with an integral:

$$\begin{aligned} \chi &= \int d^d \mathbf{r} \tilde{g}\left(\frac{r}{\xi}\right) r^{-(d-2+\eta)} \underset{r/\xi=\mathbf{x}}{=} \xi^{2-\eta} \underbrace{\int d^d \mathbf{x} \tilde{g}(\mathbf{x}) x^{-(d-2+\eta)}}_{\text{Constant in } h, t} = \\ &= \xi^{2-\eta} \cdot \text{Const.} \underset{(4.44)}{\propto} |t|^{-\nu(2-\eta)} \end{aligned}$$

and comparing with (4.35) leads to the following **scaling relation**:

$$\gamma = \nu(2 - \eta) \quad (4.48)$$

4.3.2 Hyperscaling

Finally, we proceed yet further in finding new ansatzs.

In the previous section, we found that the correlation length ξ can be regarded as new scale length that emerges spontaneously near criticality.

So, naïvely we know that the free energy **density** f scales as L^{-d} , where L is the physical length scale of the system and d its dimension. However, near criticality, we may *guess* that the “most important” length scale becomes instead ξ , leading to the ansatz:

$$f(T, h = 0) = \frac{F(T, h = 0)}{N} = \xi^{-d} \cdot \text{Const.} + \text{Less Singular Terms}$$

As $\xi \sim |t|^{-\nu}$ (4.46), then, near criticality:

$$f(T, h = 0) \sim |t|^{d\nu}$$

Differentiating two times with respect to T we can derive a similar relation for the heat capacity:

$$C = -T \frac{\partial^2}{\partial T^2} F(T, h = 0) = \text{Const} \cdot |t|^{d\nu-2} + \text{l.s.t}$$

Comparing with (4.36), we find a relation for the exponent α , known as the **hyper-scaling relation** :

$$\alpha = 2 - d\nu \quad (4.49)$$

The *hyper* comes from the fact that (4.49) is the only relation thus far that *explicitly* involves the dimension d of the system. Moreover, it is known to hold only below some **critical dimension** d_U (the “upper” dimension), and violated in $d > d_U$. In case of the Ising Model, $d_U = 4$.

4.3.3 Summary of scaling relations

We have introduced a total of 6 exponents:

1. β , regulating the magnetization m as a function of temperature (4.39)
2. γ , for the susceptibility χ as a function of temperature (4.35)
3. δ , regulating the magnetization m as a function of the magnetic field h (4.34)
4. α , for the specific heat c versus temperature (4.36)
5. η , dealing with the *decay* of the two-point correlation function near the critical point as a function of the distance t from it (4.47)
6. ν , describing the divergence of the correlation length near criticality as a function of t (4.46)

and 4 scaling relations between them:

$$\beta(\delta - 1) = \gamma \quad (4.50a)$$

$$\nu(2 - \eta) = \gamma \quad (4.50b)$$

$$\beta(\delta + 1) = 2 - \alpha \quad (4.50c)$$

$$d\nu - 2 = \alpha \quad (4.50d)$$

meaning that, at the end, only 2 exponents are independent.

4.3.4 Correlation function in the Mean Field

(Lesson 27 of
11/05/20)
Compiled: June 2,
2020

We want to verify (4.47) in the case of the mean field approximation.

So, we start with a *separable* variational ansatz (4.8, pag. 134):

$$\rho_0(\boldsymbol{\sigma}) = \prod_x \rho_x(\sigma_x) \quad \rho_x(\sigma_x) = \frac{1 + m_x \sigma_x}{2} \quad m_x \in [-1, 1] \quad (4.51)$$

In this case, spins are independent, and so:

$$\langle \sigma_x \sigma_y \rangle_0 = \sum_{\{\boldsymbol{\sigma}\}} \rho_0(\boldsymbol{\sigma}) \sigma_x \sigma_y = \langle \sigma_x \rangle_0 \langle \sigma_y \rangle_0 \stackrel{(4.9)}{=} m_x m_y$$

More in general, the n -point correlator between m **distinct** x_1, \dots, x_m spins is the product of the *local magnetizations* m_{x_i} :

$$\langle \sigma_{x_1} \cdots \sigma_{x_n} \rangle_0 = \prod_{i=1}^n m_{x_i}$$

This means that the correlation function G_{xy} is trivial:

$$G_{xy} \equiv \langle \sigma_x \sigma_y \rangle - \langle \sigma_x \rangle \langle \sigma_y \rangle = m_x m_y - m_x m_y = 0$$

A more interesting (and accurate) result can be obtained if we start from the **exact** partition function:

$$Z(\mathbf{h}) = \sum_{\{\boldsymbol{\sigma}\}} \exp \left(-\beta H(\boldsymbol{\sigma}) + \sum_x h_x \sigma_x \right)$$

The magnetization m_{x_1} at position x_1 can be obtained by deriving $\ln Z(\mathbf{h})$ with respect to the local field h_{x_1} at that position (3.67):

$$\frac{\partial}{\partial h_{x_1}} \ln Z(\mathbf{h}) = \frac{\sum_{\{\boldsymbol{\sigma}\}} \exp \left(-\beta H(\boldsymbol{\sigma}) + \sum_x h_x \sigma_x \right) \sigma_{x_1}}{Z(\mathbf{h})} = \langle \sigma_{x_1} \rangle = m_{x_1}$$

And if we differentiate once more, with respect to h_{x_2} with $x_2 \neq x_1$ (see the steps preceding (3.69) at pag. 128):

$$\begin{aligned} \frac{\partial^2}{\partial h_{x_1} \partial h_{x_2}} \ln Z(\mathbf{h}) &= \frac{\partial}{\partial h_{x_1}} \langle \sigma_{x_1} \rangle = \frac{\sum_{\{\boldsymbol{\sigma}\}} \exp \left(-\beta H(\boldsymbol{\sigma}) + \sum_x h_x \sigma_x \right) \sigma_{x_1} \sigma_{x_2}}{Z} + \\ &\quad - \frac{\sum_{\{\boldsymbol{\sigma}\}} \exp \left(-\beta H(\boldsymbol{\sigma}) + \sum_x h_x \sigma_x \right) \sigma_{x_1}}{Z} \cdot \frac{\sum_{\{\boldsymbol{\sigma}\}} \exp \left(-\beta H(\boldsymbol{\sigma}) + \sum_x h_x \sigma_x \right) \sigma_{x_2}}{Z} = \\ &= \langle \sigma_{x_1} \sigma_{x_2} \rangle - \langle \sigma_{x_1} \rangle \langle \sigma_{x_2} \rangle \end{aligned}$$

And so we get an exact result for the two-point correlation function:

$$G_{x_1 x_2} \equiv \frac{\partial m_{x_1}}{\partial h_{x_2}} = \langle \sigma_{x_1} \sigma_{x_2} \rangle - \langle \sigma_{x_1} \rangle \langle \sigma_{x_2} \rangle \quad (4.52)$$

In the mean field, local magnetizations obey equation (4.16):

$$m_x(\mathbf{h}, K) = \tanh \left[K \sum_{y \in \langle y, x \rangle} m_y + h_x \right] \quad (4.53)$$

where the sum is over all nodes y that are neighbours of x . Solving for h_x leads to:

$$h_x = \tanh^{-1} m_x - \sum_y K_{xy} m_y \quad K_{xy} \equiv_{(a)} K \delta_{|\mathbf{r}_x - \mathbf{r}_y|, a} = \begin{cases} K & |\mathbf{r}_x - \mathbf{r}_y| = a \\ 0 & \text{otherwise} \end{cases} \quad (4.54)$$

Here we denote with \mathbf{r}_x the position of node x in the lattice, so that $|\mathbf{r}_x - \mathbf{r}_y|$ is the distance between spins x and y . Neighbouring cells are separated only by the grid step a , and we use this fact to rewrite in (a) the sum over neighbours of x as a sum over *all nodes* by adding an appropriate Kronecker delta.

Differentiating both sides of (4.54) with respect to h_z leads to:

$$\begin{aligned} \delta_{xz} = \frac{\partial h_x}{\partial h_z} &= \frac{1}{1 - m_x^2} \underbrace{\frac{\partial m_x}{\partial h_z}}_{G_{xz} \text{ (4.52)}} - \sum_y K_{xy} \underbrace{\frac{\partial m_y}{\partial h_z}}_{G_{yz} \text{ (4.52)}} = \\ &= \sum_y \underbrace{\left[\frac{\delta_{xy}}{1 - m_x^2} - K_{xy} \right]}_{A_{xy}} G_{yz} \end{aligned}$$

This can be rewritten in matrix form as follows:

$$\mathbb{1} = \mathbf{A} \mathbf{G} \quad (4.55)$$

where the entries of A are:

$$\mathbf{A} = \begin{pmatrix} \frac{1}{1 - m_1^2} - K_{11} & -K_{12} & -K_{13} & \cdots \\ -K_{21} & \frac{1}{1 - m_2^2} - K_{22} & -K_{23} & \cdots \\ -K_{31} & -K_{32} & \frac{1}{1 - m_3^2} - K_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \quad A_{xy} = \frac{\delta_{xy}}{1 - m_x^2} - K_{xy}$$

In the case of a **cubic lattice** with **periodic boundary conditions** the system is translationally invariant, and so it is reasonable to assume a **uniform magnetization**, i.e. $h_x \equiv h$ and $m_x \equiv m(h, T)$. This leads to:

$$A_{xy} = \frac{\delta_{xy}}{1 - m^2} - K_{xy} = \begin{cases} \frac{1}{1 - m^2} & x = y \\ -K & |\mathbf{r}_x - \mathbf{r}_y| = a \end{cases}$$

And from (4.55) we obtain:

$$\mathbf{G}^{-1} = \mathbf{A} \Leftrightarrow (\mathbf{G}^{-1})_{xy} = A_{xy} = \frac{\delta_{xy}}{1 - m^2} - K_{xy}$$

Note that the entries of \mathbf{G}^{-1} depend only on *differences of positions* (in K_{xy}), meaning that \mathbf{G}^{-1} is translationally invariant. Explicitly, the (reciprocal of the) correlation between spins that are *the same distance apart* is the same, and so:

$$(\mathbf{G}^{-1})_{xy} \equiv G^{-1}(\mathbf{r}_x, \mathbf{r}_y) = G^{-1}(\mathbf{r}_x + \mathbf{n}a, \mathbf{r}_y + \mathbf{n}a) \quad \mathbf{n} \in \mathbb{Z}^d$$

Choosing \mathbf{n} so that $\mathbf{r}_y = -\mathbf{n}a$ we get:

$$G^{-1}(\mathbf{r}_x, \mathbf{r}_y) = G^{-1}(\mathbf{r}_x - \mathbf{r}_y, 0) \equiv G^{-1}(\mathbf{r}_x - \mathbf{r}_y) \quad (4.56)$$

Translational invariance implies that \mathbf{G}^{-1} is diagonalized by the Fourier basis.

This can be quickly shown in the *continuum limit*, i.e. if we treat \mathbf{r}_x and \mathbf{r}_y as continuous variables. Then, ignoring the normalization constants:

*Translational
invariance and
Fourier basis*

$$\begin{aligned} \mathcal{F}[G^{-1}](\mathbf{p}, \mathbf{q}) &\propto \int_{\mathbb{R}^d} d^d \mathbf{r}_x e^{i\mathbf{p} \cdot \mathbf{r}_x} \int_{\mathbb{R}^d} d^d \mathbf{r}_y e^{i\mathbf{q} \cdot \mathbf{r}_y} G^{-1}(\mathbf{r}_x, \mathbf{r}_y) = \\ &\stackrel{(4.56)}{=} \int_{\mathbb{R}^{2d}} d^d \mathbf{r}_x d^d \mathbf{r}_y e^{i\mathbf{p} \cdot \mathbf{r}_x} e^{i\mathbf{q} \cdot \mathbf{r}_y} G^{-1}(\mathbf{r}_x - \mathbf{r}_y) = \\ &= \int_{\mathbb{R}^{2d}} d^d \mathbf{t} d^d \mathbf{r}_y e^{i\mathbf{p} \cdot \mathbf{t}} e^{i\mathbf{r}_y \cdot (\mathbf{p} + \mathbf{q})} G^{-1}(\mathbf{t}) = \\ &= \underbrace{\int_{\mathbb{R}^d} d^d \mathbf{t} e^{i\mathbf{p} \cdot \mathbf{t}} G^{-1}(\mathbf{t})}_{\mathcal{F}[G^{-1}](\mathbf{p})} \underbrace{\int_{\mathbb{R}^d} d^d \mathbf{r}_y e^{i\mathbf{r}_y \cdot (\mathbf{p} + \mathbf{q})}}_{\delta^d(\mathbf{p} + \mathbf{q})} = \tilde{G}^{-1}(\mathbf{p}) \delta^d(\mathbf{p} + \mathbf{q}) \end{aligned} \quad (4.57)$$

And so $\mathcal{F}[G^{-1}](\mathbf{p}, \mathbf{q})$ can be nonzero only if $\mathbf{p} = -\mathbf{q}$, meaning that can be seen as a (infinite) diagonal matrix⁸. Then, the inverse of a diagonal matrix is obtained by replacing each element in the diagonal with its reciprocal:

$$\mathcal{F}[G^{-1}](\mathbf{p}, \mathbf{q}) = \frac{1}{\mathcal{F}[G^{-1}](\mathbf{p})} \delta^d(\mathbf{p} + \mathbf{q})$$

However, \mathbf{r}_x and \mathbf{r}_y are constrained to **discrete** positions in the cubic lattice - in other words $G^{-1}(\mathbf{r}_x, \mathbf{r}_y)$ should really be a function $\mathbb{Z}^d \times \mathbb{Z}^d \rightarrow \mathbb{R}$. By adding some Dirac deltas, we can extend the domain to $\mathbb{R}^d \times \mathbb{R}^d$, essentially making the function vanish for all non-integers arguments:

$$G^{-1}(\mathbf{r}_x, \mathbf{r}_y) = \sum_{\mathbf{n}, \mathbf{m} \in \mathbb{Z}^d} G^{-1}(\mathbf{r}_x, \mathbf{r}_y) \delta^d(\mathbf{r}_x - \mathbf{n}a) \delta^d(\mathbf{r}_y - \mathbf{m}a) \quad \mathbf{r}_x, \mathbf{r}_y \in \mathbb{R}^d$$

G^{-1} has a period of a for all its arguments, and so its Fourier transform will have⁹ a period of $2\pi/a$.

With a **symmetric** choice for the normalization, the Fourier transform becomes:

$$\begin{aligned} \mathcal{F}[G^{-1}](\mathbf{p}, \mathbf{q}) &= \left(\frac{a}{2\pi}\right)^d \int_{\mathbb{R}^d} d^d \mathbf{p} e^{-i\mathbf{p} \cdot \mathbf{r}_x} \int_{\mathbb{R}^d} d^d \mathbf{q} e^{-i\mathbf{q} \cdot \mathbf{r}_y} \\ &\cdot \sum_{\mathbf{n}, \mathbf{m} \in \mathbb{Z}^d} G^{-1}(\mathbf{r}_x, \mathbf{r}_y) \delta^d(\mathbf{r}_x - \mathbf{n}a) \delta^d(\mathbf{r}_y - \mathbf{m}a) = \end{aligned}$$

⁸ A discrete matrix $\mathcal{M}_{N \times N}(\mathbb{R})$ is diagonal if it has entries $A_{xy} = A_x \delta_{xy}$. Here we have some sort of “continuous matrix” - which should really be intended as the matrix representation in the Fourier basis of a linear operator on $L^2(\mathbb{R}^d)$. So, in a sense, it is a $\infty \times \infty$ matrix “centred in $\mathbf{0}$ ”. In the $d = 1$ case, it can be thought as of a *plane*, with entries at every point (p, q) , and the diagonal being the second-fourth quadrant bisector $p = -q$.

⁹ See https://www.gnu.org/software/gnustro/manual/html_node/Dirac-delta-and-comb.html for the proof.

$$\begin{aligned}
& \stackrel{(a)}{=} \left(\frac{a}{2\pi}\right)^d \sum_{\mathbf{n} \in \mathbb{Z}^d} \sum_{\mathbf{m} \in \mathbb{Z}^d} e^{-ia\mathbf{p} \cdot \mathbf{n}} e^{-ia\mathbf{q} \cdot \mathbf{m}} \underbrace{G^{-1}(\mathbf{n}a, \mathbf{m}a)}_{G^{-1}([\mathbf{n}-\mathbf{m}]a)} = \\
& \stackrel{t=\mathbf{n}-\mathbf{m}}{=} \left(\frac{a}{2\pi}\right)^d \sum_{\mathbf{t} \in \mathbb{Z}^d} \sum_{\mathbf{m} \in \mathbb{Z}^d} e^{-ia\mathbf{p} \cdot \mathbf{t}} e^{-ia\mathbf{m} \cdot (\mathbf{p}+\mathbf{q})} G^{-1}(\mathbf{t}a) = \\
& = \left(\frac{a}{2\pi}\right)^d \underbrace{\sum_{\mathbf{t} \in \mathbb{Z}^d} e^{-ia\mathbf{p} \cdot \mathbf{t}} G^{-1}(\mathbf{t}a)}_{1\text{st}} \underbrace{\sum_{\mathbf{m} \in \mathbb{Z}^d} e^{-ia\mathbf{m} \cdot (\mathbf{p}+\mathbf{q})}}_{2\text{nd}}
\end{aligned}$$

where in (a) we used the deltas to collapse the integrals.

For the second sum, recall that¹⁰:

$$(2\text{nd}) = \frac{1}{F} \sum_{k=-\infty}^{+\infty} \exp\left(\pm i \frac{2k\pi f}{F}\right) = \sum_{n=-\infty}^{+\infty} \delta(f - nF)$$

In our case:

$$\left(\frac{2\pi}{a} \frac{a}{2\pi}\right)^d \sum_{\mathbf{m} \in \mathbb{Z}^d} \exp\left(-i \frac{2\pi \mathbf{m} \cdot (\mathbf{p} + \mathbf{q})}{2\pi/a}\right) = \left(\frac{2\pi}{a}\right)^d \sum_{\mathbf{m} \in \mathbb{Z}^d} \delta\left(\mathbf{p} + \mathbf{q} - \mathbf{m} \frac{2\pi}{a}\right)$$

Regarding the remaining sum, recall that $\mathbf{t}a = \mathbf{r}_x - \mathbf{r}_y$:

$$(1\text{st}) = G^{-1}(\mathbf{t}a) \equiv G^{-1}(\mathbf{r}_x - \mathbf{r}_y) = A_{xy} = \frac{\delta_{xy}}{1 - m^2} - K\delta_{|\mathbf{r}_x - \mathbf{r}_y|, a}$$

Note that $x = y$ if and only if $\mathbf{r}_x - \mathbf{r}_y = 0$, i.e. $\mathbf{t} = \mathbf{0}$, and so $\delta_{xy} = \delta_{\mathbf{t}, \mathbf{0}}^d$, which denotes a d -dimensional Kronecker delta:

$$\delta_{\mathbf{t}, \mathbf{0}}^d = \begin{cases} 1 & \mathbf{t} = \mathbf{0} \Leftrightarrow t_1 = \dots = t_d = 0 \\ 0 & \text{otherwise} \end{cases}$$

Similarly:

$$\delta_{|\mathbf{r}_x - \mathbf{r}_y|, a} = \delta_{\|\mathbf{t}\|, a} = \delta_{\|\mathbf{t}\|, 1}$$

Substituting in the sum:

$$\sum_{\mathbf{t} \in \mathbb{Z}^d} e^{-ia\mathbf{p} \cdot \mathbf{t}} \left(\frac{\delta_{\mathbf{t}, \mathbf{0}}^d}{1 - m^2} - K\delta_{\|\mathbf{t}\|, 1} \right) = \underbrace{e^{-ia\mathbf{p} \cdot \mathbf{0}}}_1 \frac{1}{1 - m^2} - K \sum_{\substack{\mathbf{t} \in \mathbb{Z}^d \\ \|\mathbf{t}\|=1}} e^{-ia\mathbf{p} \cdot \mathbf{t}}$$

For a integer valued vector $\mathbf{t} \in \mathbb{Z}^d$, a unitary norm can be obtained if and only if *exactly one* of its components is ± 1 . Thus:

$$\sum_{\substack{\mathbf{t} \in \mathbb{Z}^d \\ \|\mathbf{t}\|=1}} e^{-ia\mathbf{p} \cdot \mathbf{t}} = \sum_{\mu=1}^d \left[e^{-ia\mathbf{p} \cdot \mathbf{t}_+^\mu} + e^{-ia\mathbf{p} \cdot \mathbf{t}_-^\mu} \right] = \left(\mathbf{t}_\pm^\mu = (0, \dots, \pm 1, \dots, 0) \right)$$

¹⁰See equation 4 in <http://fourier.eng.hmc.edu/e102/lectures/ExponentialDelta.pdf> for the proof.

$$= \sum_{\mu=1}^d \left[e^{-iap_{\mu}} + e^{iap_{\mu}} \right] = \sum_{\mu=1}^d 2 \cos(ap_{\mu})$$

And so at the end we get:

$$\mathcal{F}[G^{-1}](\mathbf{p}, \mathbf{q}) = \left(\frac{1}{1-m^2} - 2K \sum_{\mu=1}^d \cos(ap_{\mu}) \right) \sum_{\mathbf{m} \in \mathbb{Z}^d} \delta^d \left(\mathbf{p} + \mathbf{q} - \mathbf{m} \frac{2\pi}{a} \right)$$

which is periodic with period $2\pi/a$ in each component of both arguments - and so \mathbf{p} and \mathbf{q} vary within¹¹ $(-\pi/a, +\pi/a)^d$. This means that:

$$p_{\mu} + q_{\mu} \in \left(-\frac{2\pi}{a}, +\frac{2\pi}{a} \right) \quad \forall \mu = 1, \dots, d$$

And so:

$$\sum_{\mathbf{m} \in \mathbb{Z}^d} \delta^d(\mathbf{p} + \mathbf{q} - \mathbf{m} \frac{2\pi}{a}) = \delta^d(\mathbf{p} + \mathbf{q})$$

because all other δ s with some $m_{\mu} \neq 0$ vanish. Thus $\mathcal{F}[G^{-1}](\mathbf{p}, \mathbf{q})$ is **diagonal**, and its matrix inverse is:

$$\tilde{G}(\mathbf{p}, \mathbf{q}) = \frac{1}{(1-m^2)^{-1} - 2K \sum_{\mu=1}^d \cos(ap_{\mu})} \delta^d(\mathbf{p} + \mathbf{q})$$

Symmetric normalization. We are using a *symmetric* normalization for the direct and inverse Fourier transforms (here for $d = 1$ for simplicity):

$$\begin{aligned} \mathcal{F}[f(x)](p) &\equiv \tilde{f}(p) = \sqrt{\frac{a}{2\pi}} \sum_{x=-\infty}^{+\infty} e^{ixp} f(x) \\ \mathcal{F}^{-1}[\tilde{f}(p)](x) &= \sqrt{\frac{a}{2\pi}} \int_{-\pi/a}^{+\pi/a} \tilde{f}(p) e^{ixp} dp \end{aligned}$$

Where the factor is exactly $1/\sqrt{T}$, with T being the period of $\tilde{f}(p)$, which is $2\pi/a$ in our case.

This is done so that \mathcal{F} is a **unitary** linear operator mapping elements (i.e. functions) of $L_2(\mathbb{R})$ to elements of $L_2([-\pi/a, \pi/a])$. This is necessary to avoid altering the determinant of the matrix during transformation.

Physically, this is the only way to make both G^{-1} and \tilde{G}^{-1} adimensional - as they should be.

To find G_{xy} we anti-transform. Applying the definition of the inverse transform of the DTFT (with a symmetric choice for normalization) leads to:

$$G(\mathbf{r}_x, \mathbf{r}_y) = \left(\frac{a}{2\pi} \right)^d \int_{(-\frac{\pi}{a}, +\frac{\pi}{a})^{2d}} d^d \mathbf{q} d^d \mathbf{p} e^{i\mathbf{p} \cdot \mathbf{r}_x} e^{i\mathbf{q} \cdot \mathbf{r}_y} \frac{\delta^d(\mathbf{p} + \mathbf{q})}{(1-m^2)^{-1} - 2K \sum_{\mu=1}^d \cos(ap_{\mu})} =$$

¹¹^The extrema are **not** contained. This can be proved by considering the *discrete finite case*, i.e. a lattice with a finite number N of spins, computing the DFT and taking the thermodynamic limit $N \rightarrow \infty$.

$$\begin{aligned}
& \underset{\mathbf{q}=-\mathbf{p}}{=} \left(\frac{a}{2\pi}\right)^d \int_{(-\frac{\pi}{a}, +\frac{\pi}{a})^d} d^d \mathbf{p} e^{i\mathbf{p} \cdot (\mathbf{r}_x - \mathbf{r}_y)} \underbrace{\frac{1}{(1-m^2)^{-1} - 2K \sum_{\mu=1}^d \cos(ap_\mu)}}_{\tilde{G}(\mathbf{p})} \\
& \hspace{15em} (4.58)
\end{aligned}$$

The integral's cubic domain is also called the **first Brillouin zone**¹² of the cubic lattice with grid step a . $\tilde{G}(\mathbf{p})$ are then the **eigenvalues** of the matrix G_{xy} (when $N \rightarrow \infty$), and $(a/2\pi)^{d/2} e^{i\mathbf{p} \cdot \mathbf{r}_x}$ are the (orthonormal) eigenvectors.

Note that for $|\mathbf{x} - \mathbf{y}| \gg a$, i.e. spins that are very far apart, the oscillation of the complex exponential $e^{i\mathbf{p} \cdot (\mathbf{r}_x - \mathbf{r}_y)}$ is very rapid, i.e. a tiny difference in \mathbf{p} amounts to a high change in phase. Then the integrand will *oscillate* rapidly about 0, making the integral vanish. Thus, the only significant contributions are when $\mathbf{p} \approx \mathbf{0}$, i.e. the ones with a “stationary phase”¹³. So, we can expand $\tilde{G}(\mathbf{p})$ in series:

$$\begin{aligned}
\tilde{G}(\mathbf{p}) &= \left[\frac{1}{1-m^2} - 2K \sum_{\mu=1}^d \cos(ap_\mu) \right] = \left[\frac{1}{1-m^2} - 2K \sum_{\mu=1}^d \left(1 - \frac{(ap_\mu)^2}{2} + O(p_\mu^4) \right) \right] = \\
&= \underbrace{\left[\frac{1}{1-m^2} - 2dK \right]}_A + K \|\mathbf{p}\|^2 a^2 + O(\|\mathbf{p}\|^4) \approx \left[Ka^2 \left(\|\mathbf{p}\|^2 + \frac{A}{Ka^2} \right) \right]^{-1} = \\
&= \frac{1}{Ka^2} \frac{1}{\|\mathbf{p}\|^2 + Ka^2/A}
\end{aligned}$$

Recall that a has dimension of length, ($[a] = \text{L}$) and that \mathbf{p} of the reciprocal of length ($[\|\mathbf{p}\|] = \text{L}^{-1}$), while the constant A defined in the above expression is a pure number. Then $[A/Ka^2] = \text{L}^{-2}$ and so we denote it $\xi^{-2} = A/ka^2$, where now $[\xi] = \text{L}$ is the **correlation** length:

$$\tilde{G}(\mathbf{p}) \approx \frac{1}{Ka^2} \frac{1}{\|\mathbf{p}\|^2 + \xi^{-2}} \quad \xi^{-2} \equiv \frac{A}{Ka^2} = \frac{a^{-2}}{K} \left[\frac{1}{1-m^2} - 2dK \right] \quad (4.59)$$

In the mean field approximation, m is given by the solution of (4.53), which near criticality is given by (4.26, pag. 141):

$$m^2(K) = \begin{cases} 3 \frac{K - K_c}{K_c} & K > K_c \\ 0 & K < K_c \end{cases}$$

with $K_c = 1/2d$.

¹²^Lattices are at the foundation of solid state physics. In particular, the Fourier transform of a lattice - represented as a “grid of δs ” - is still a lattice in the space of *frequencies*, and it's called the **reciprocal lattice**. The first Brillouin zone is just how the first unit cell of the lattice appears after the Fourier transform. In the case of a cubic lattice, it is still cubic, but with a different length.

¹³^This is in fact a generalization of the *saddle-point approximation* to complex integrals with an oscillating term

Then, substituting in the definition of ξ , for $K < K_c$ we get:

$$\xi^{-2} = \frac{a^{-2}}{K^2} \left[\frac{1}{1-m^2} - \frac{K}{K_c} \right]_{K < K_c} \stackrel{K < K_c}{=} \frac{a^{-2}}{K} \left[1 - \frac{K}{K_c} \right] = \frac{a^{-2}}{K} \left(\frac{K_c - K}{K_c} \right) = \frac{a^{-2}}{K} \frac{|K - K_c|}{K_c}$$

And for $K > K_c$, expanding around $m \approx 0$:

$$\xi^{-2} = \frac{a^{-2}}{K^2} \left[1 + m^2 + O(m^4) - \frac{K}{K_c} \right]_{K > K_c} \stackrel{K > K_c}{\approx} \frac{a^{-2}}{K} \left[1 + 3 \frac{K - K_c}{K_c} - \frac{K}{K_c} \right] = 2 \frac{a^{-2}}{K} \frac{|K - K_c|}{K_c}$$

So, in both cases, we have:

$$\xi^{-2} \propto \left| \frac{K - K_c}{K_c} \right| \quad K \approx K_c$$

Meaning that the correlation length diverges near criticality:

$$\xi \propto \left| \frac{K_c}{K - K_c} \right|^{1/2} \quad K \approx K_c$$

This is consistent with (4.46, pag. 157):

$$\xi \propto |t|^{-\nu}$$

with $\nu = 1/2$ in the mean field approximation.

Substituting back in (4.59) and collecting a $\|\mathbf{p}\|^2$:

$$\tilde{G}(\mathbf{p}) \approx \frac{1}{ka^2 \|\mathbf{p}\|^2} \left(1 + \frac{1}{(\xi \|\mathbf{p}\|)^2} \right)^{-1} = \|\mathbf{p}\|^{-2} \tilde{g}(\|\mathbf{p}\| \xi) \quad (4.60)$$

All that's left is to verify that (4.60) is indeed compatible with a correlation function given by the ansatz (4.47). So, let $h = 0$ for simplicity, and assume that:

$$G_{xy} = \|\mathbf{r}_x - \mathbf{r}_y\|^{-(d-2+\eta)} \hat{g} \left(\frac{\|\mathbf{r}_x - \mathbf{r}_y\|}{\xi} \right) \quad (4.61)$$

The Fourier transform of (4.61), up to normalization, is given by:

$$\tilde{G}(\mathbf{p}) \propto \int_{\mathbb{R}^d} d^d \mathbf{r} \|\mathbf{r}\|^{-(d-2+\eta)} \hat{g} \left(\frac{\|\mathbf{r}\|}{\xi} \right) e^{i\mathbf{r} \cdot \mathbf{p}}$$

By rescaling $\mathbf{r} = \mathbf{v}/\|\mathbf{p}\|$ we can make \hat{g} a function of $\|\mathbf{p}\| \xi$ as in (4.60):

$$\begin{aligned} \tilde{G}(\mathbf{p}) &\propto \int_{\mathbb{R}^d} \frac{d^d \mathbf{v}}{\|\mathbf{p}\|^d} \left\| \frac{\mathbf{r}}{\|\mathbf{p}\|} \right\|^{-(d-2+\eta)} \hat{g} \left(\frac{\|\mathbf{v}\|}{\|\mathbf{p}\| \xi} \right) \exp \left(i \mathbf{v} \cdot \underbrace{\frac{\mathbf{p}}{\|\mathbf{p}\|}}_{\hat{\mathbf{p}}} \right) = \\ &= \|\mathbf{p}\|^{-(2-\eta)} \underbrace{\int_{\mathbb{R}^d} d^d \mathbf{v} \|\mathbf{v}\|^{-(d-2+\eta)} \hat{g} \left(\frac{\|\mathbf{v}\|}{\|\mathbf{p}\| \xi} \right) e^{i\mathbf{v} \cdot \hat{\mathbf{p}}}}_{\tilde{g}(\|\mathbf{p}\| \xi)} = \\ &= \|\mathbf{p}\|^{-2+\eta} \tilde{g}(\|\mathbf{p}\| \xi) \end{aligned}$$

And so (4.61) is compatible with (4.60). Moreover, we see that $\eta = 0$ in the mean field approximation (but in general it can be $\neq 0$).

As a bonus, we see that the scaling relation (4.48, pag. 157) is respected in the mean field:

$$\gamma = \nu(2 - \eta)$$

As we have found $\gamma = 1$, $\nu = 1/2$ and $\eta = 0$.

Finally, notice that:

$$\sum_y G_{xy} = \langle \sigma_x \sum_y \sigma_y \rangle - \langle \sigma_x \rangle \langle \sum_y \sigma_y \rangle \stackrel{(a)}{=} \frac{\partial}{\partial h} \langle \sigma_x \rangle = \chi$$

where in (a) we used the fluctuation-dissipation theorem (3.69, pag. 128). Then, the sum over all y is equal to the Fourier transform evaluated at $\mathbf{p} = \mathbf{0}$. First we rewrite it as:

$$\sum_y G_{xy} \equiv \sum_{\mathbf{r}_y \in \mathbb{Z}^d} G(\mathbf{r}_x, \mathbf{r}_y) = \sum_{\mathbf{t} \in \mathbb{Z}^d} G(\mathbf{r}_x - \mathbf{r}_y, 0) = \sum_{\mathbf{t} \in \mathbb{Z}^d} G(\mathbf{t})$$

Then, evaluating $\tilde{G}(\mathbf{0})$ gives the desired sum:

$$\tilde{G}(\mathbf{0}) = \sum_{\mathbf{t} \in \mathbb{Z}^d} G(\mathbf{t}) e^{-i\mathbf{p} \cdot \mathbf{t}} \Big|_{\mathbf{p}=\mathbf{0}} = \sum_{\mathbf{t} \in \mathbb{Z}^d} G(\mathbf{t}) \stackrel{(4.58)}{=} \left(\frac{1}{1 - m^2} - 2Kd \right)$$

4.3.5 Example in a real system

An example of the emergence of scaling laws in real complex systems can be seen by examining some features of a **forest**, in which many trees *compete* for a set of resources (elements in soil, light, etc.).

We start from the simplifying assumption that each tree of a certain “size” r (which can be measured as its height, or the diameter of its trunk) mainly *competes* with trees of similar or bigger size - as everything much smaller will have a negligible effect on it.

Then we measure the distance r_i between the tree of size r and the closest *bigger* tree, which will follow some distribution $\mathbb{P}(r_i|r)$. In particular, we consider the *accumulated* distribution given by:

$$\mathbb{P}^>(r_i|r) \equiv \int_{r_i}^{\infty} P(r'_i|r) dr'_i$$

After some sophisticated analysis, a reasonable *ansatz* for $\mathbb{P}^>$ is found:

$$\mathbb{P}^>(r_i|r) = F\left(\frac{r_i}{r^{2/3}}\right) \quad (4.62)$$

For each r , $\mathbb{P}^>(r_i|r)$ is plotted in fig. ??.

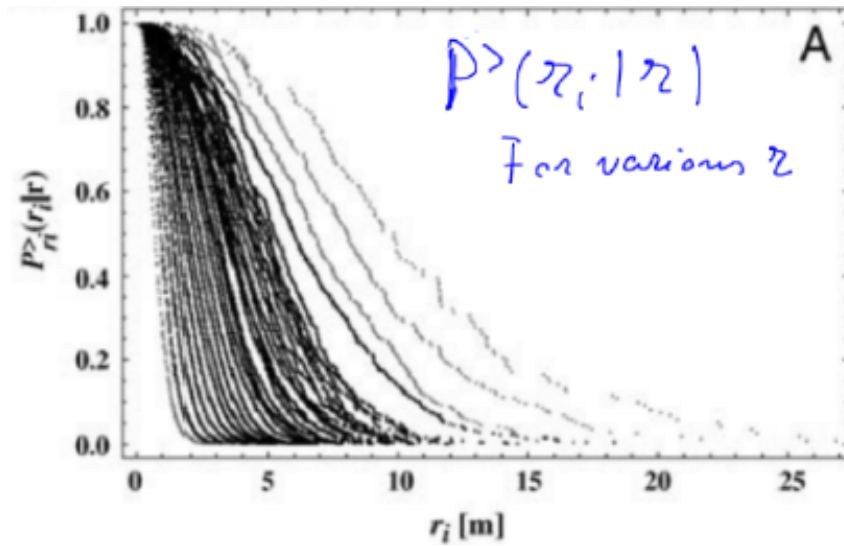


Figure (4.12) – Plot of the *accumulated* probabilities for r_i for various tree sizes r .

If the ansatz in (4.62) is correct, then by rescaling the x axis to $r_i/r^{2/3}$ we should see all curves “collapsing” into one. This indeed happens in fig. 4.13.

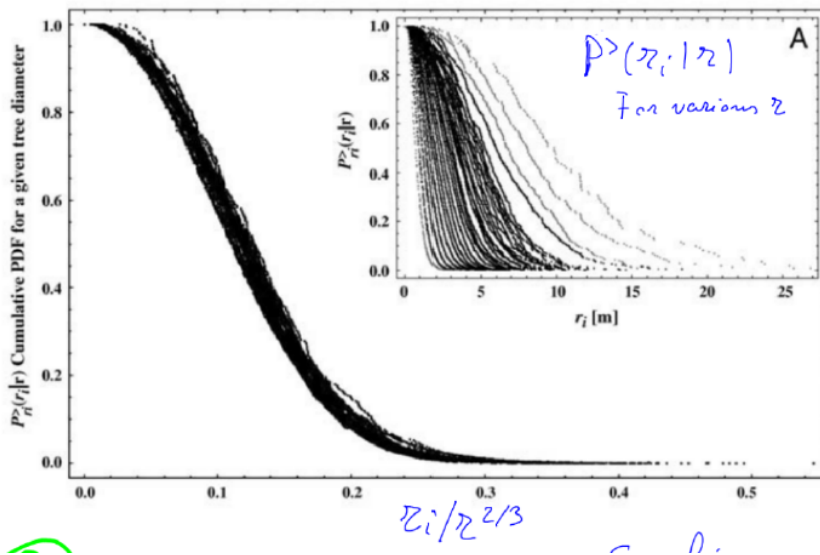


Figure (4.13) – All curves from fig. 4.12 collapse (approximately) into one when rescaling the x axis according to ansatz (4.62)

This means that there is some kind of *emergent behaviour* in the forest: the distribution of tree sizes is not completely random, but exhibits a *scaling behaviour*, which is similar to the one we studied in the Ising model. In a sense, the forest has “self-tuned” to a state “near criticality”. Yet, it is not clear *why* this is the case - for example what is the evolutionary advantage in this kind of “self tuning”.

Beyond Mean Field and Universality

Many years of study of phase transitions have shown that there are few *types* of critical behaviours, meaning that many systems exhibit the same kind of behaviour near criticality.

A summary of the critical exponents for several *classes* of models is shown in fig. 5.1.

Table 1-1 Values of critical exponents

Expo- nent	Mean field theory	Ising model $d = 2$	Ising model $d = 3^\dagger$	Heisenberg model $d = 3^\dagger$	Spherical model $\epsilon > 0$
α α'	0	0	0.12	-0.06	$-\frac{\epsilon}{2 - \epsilon}$
β	$\frac{1}{2}$	$\frac{1}{8}$	0.31		$\frac{1}{2}$
γ γ'	1	$\frac{7}{4}$	1.25	1.38 not defined	$\frac{2}{2 - \epsilon}$
ν ν'	$\frac{1}{2}$	1	0.64	0.7	$\frac{1}{2 - \epsilon}$
δ	3	15	5.0		$\frac{6 - \epsilon}{2 - \epsilon}$
η	0	$\frac{1}{4}$	0.04	0.05	0

[†]Approximate results from numerical extrapolations of high-temperature and low-temperature series. The uncertainties are higher for $n = 3$ than $n = 1$ and for the primed indices.

Figure (5.1) – Values of critical exponents for several models. As these exponents do not depend on all the details of each model, there is no need to fully specify each Hamiltonian. For example, the IM in $d = 2$ could have more complex couplings between spins (other than the nearest neighbour ones we considered until now).

Here there is no need to **fully specify** the **Hamiltonian** of each model: for instance, when talking about a Ising Model in $d = 2$, the exponents are the same no matter how complex the spin couplings may be (for example, not only nearest neighbours may be interacting).

Moreover, if we consider higher and **higher dimensions**, the exponents **tend** to the values obtained in the **mean field** approximation. For example, δ is 15 in $d = 2$, and 5 in $d = 3$, which is closer to the MF value of 3.

There is also a dependence on the **symmetries** of each model. As an example we may consider the Heisenberg model, a generalization of the IM in which each spin is a 3-vector. Now the system is globally *rotationally symmetric*, meaning that the symmetry group is $O(3)$. In the Ising Model with *binary* spins, the spin-flip symmetry is instead described by the \mathbb{Z}_2 group. So, even if the two models are studied in the same number of dimension (e.g. $d = 3$), the scaling exponents will be different, as can be seen in fig. 5.1.

From this analysis, we find that the critical exponents do not depend on the specificity of the Hamiltonian, but only on two *general* characteristics:

- The **dimensionality** of the model
- The **symmetries** of the Hamiltonian

5.1 From discrete to continuous variables

Consider a Ising Model, with a general Hamiltonian including also more complex spin-spin interactions:

$$-\beta H(\boldsymbol{\sigma}) = \sum_{x,y} K_{xy} \sigma_x \sigma_y + \sum_{x,y,z,t} K_{xyzt} \sigma_x \sigma_y \sigma_z \sigma_t + \dots \quad (5.1)$$

The term K_{xy} (and similarly the others) could include not only neighbouring spins, but also next-to-neighbouring spins and so on. One important constraint is to allow only interaction between an **even** number of spins, so that the Hamiltonian has still a *spin-flip* symmetry:

1. *Symmetry*

$$H(\boldsymbol{\sigma}) = H(-\boldsymbol{\sigma})$$

which is described by the cyclic group \mathbb{Z}_2 .

The partition function is given by:

$$Z = \sum_{\{\boldsymbol{\sigma}\}} e^{-\beta H(\boldsymbol{\sigma})}$$

This is a function of **discrete** binary variables $\sigma_x = \pm 1$. We can write it as a function of *continuous* variables φ_x by *zeroing* all values where $\varphi_x \neq \pm 1$ with a Dirac delta:

$$Z = \int_{\mathbb{R}^N} \left[\prod_x d\varphi_x \delta(\varphi_x^2 - 1) \right] e^{-\beta H(\boldsymbol{\varphi})} \quad (5.2)$$

The Dirac delta can then be written as the limit in which a smooth function (e.g. a gaussian) becomes more and more “peaked” (fig. 5.2):

$$\delta(\varphi_x^2 - 1) = \lim_{\lambda \rightarrow +\infty} e^{-\lambda(\varphi_x^2 - 1)^2} \mathcal{N}(\lambda) \quad (5.3)$$

where $\mathcal{N}(\lambda)$ is a normalization constant. In fact, the integral of the δ is always fixed:

$$\int_{-\infty}^{+\infty} d\varphi \delta(\varphi^2 - 1) \stackrel{(a)}{=} \int_{-\infty}^{+\infty} d\varphi \frac{\delta(\varphi - 1) + \delta(\varphi + 1)}{2|\varphi|} = \frac{1}{2|1|} + \frac{1}{2|-1|} = 1 \quad (5.4)$$

where in (a) we used the composition formula for the δ :

$$\delta(g(x)) = \sum_i \frac{\delta(x - x_i)}{|g'(x_i)|}$$

with the sum over all (simple) roots x_i of $g(x)$.

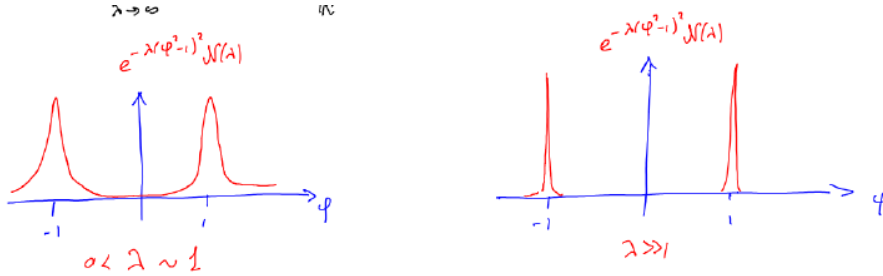


Figure (5.2) – The $\delta(\varphi_x^2 - 1)$ can be seen as the limit of a smooth function with two peaks in ± 1 , which become more and more sharp as $\lambda \rightarrow +\infty$, while maintaining the area under the curve fixed to 1.

Imposing (5.4) in (5.3) leads to the following expression for the normalization $\mathcal{N}(\lambda)$:

$$\mathcal{N}(\lambda) = \left[\int_{-\infty}^{+\infty} d\varphi e^{-\lambda(\varphi^2-1)^2} \right]^{-1}$$

Then, substituting (5.3) into the partition function (5.2) we get:

$$Z = \lim_{\lambda \rightarrow \infty} \mathcal{N}(\lambda)^N \int_{\mathbb{R}^N} \left[\prod_x d\varphi_x \right] \exp \left(-\beta H(\varphi) - \lambda \sum_x (\varphi_x^2 - 1)^2 \right) \quad (5.5)$$

Experimentally, we observe that near criticality the details of the system do not matter for describing its behaviour - and so we expect that the system with finite λ (e.g. $\lambda \sim 1$) will behave *similarly* to the one with $\lambda \rightarrow +\infty$. Mathematically, studying the first case allows us to deal with *smooth* functions.

So, removing the limit from (5.5) is equivalent to study the following Hamiltonian:

$$-\beta H_{\text{tot}}(\varphi) = -\beta H(\varphi) - \lambda \sum_x (\varphi_x^2 - 1)^2$$

Let's now assume that all spin-spin interactions are **translationally invariant**, meaning that the interaction terms K_{xy} , K_{xyzt} and so on are all functions of *distances*.

2. *Translational invariance*

Explicitly, let's focus for instance on K_{xy} . Translational invariance means that we can write it as:

$$K_{xy} = K_2(\mathbf{r}_x - \mathbf{r}_y)$$

for some function K_2 . Then, due to the \mathbb{Z}_2 symmetry, $K_2(\mathbf{r}_x - \mathbf{r}_y) = K_2(\mathbf{r}_y - \mathbf{r}_x)$. In fact, if the two spins are the same (both $+1$ or -1), then exchanging them will not make any difference. If they are different, i.e. one $+1$ and the other -1 , exchanging them is equivalent to a *spin-flip*, and so the result will still be the same.

Thus, if we rewrite $\mathbf{r} = \mathbf{r}_x - \mathbf{r}_y = \mathbf{n}a$, with $\mathbf{n} \in \mathbb{Z}^d$, then $K_2(\mathbf{r})$ is an **even** function, and depends only on $\|\mathbf{r}\|$ due to translational invariance.

This means that all averages of only one component of \mathbf{r} are zero:

$$\sum_{\mathbf{r}} K_2(\|\mathbf{r}\|) r_\alpha = 0 \quad \alpha = 1, \dots, d \quad (5.6)$$

because K_2 is even, while r_α is odd.

We also assume interactions to be **short range**. This means that the average of two components of \mathbf{r} is proportional to a^2 :

3. *Short range interactions*

$$\sum_{\mathbf{r}} K_2(\|\mathbf{r}\|) r_\alpha r_\beta = \frac{\delta_{\alpha\beta}}{d} \sum_{\mathbf{r}} K_2(\|\mathbf{r}\|) \|\mathbf{r}\|^2 \propto a^2 < \infty \quad (5.7)$$

The $\delta_{\alpha\beta}$ comes from the fact that we expect different directions to be independent (**isotropy**), and the d is just a normalization for the Kronecker delta.

Similar relations are expected to hold for all higher order interaction terms (K_{xyzt} and so on).

With all these assumptions, we can simplify the Hamiltonian (5.1). For instance, the K_{xy} term becomes:

$$\sum_{xy} K_2(\mathbf{r}_x - \mathbf{r}_y) \varphi(\mathbf{r}_x) \varphi(\mathbf{r}_y)$$

with $\varphi(\mathbf{r}_x) \equiv \varphi_x$ and $\varphi(\mathbf{r}_y) \equiv \varphi_y$. In this notation, x and y are *numeric* indices for the spins, and $\mathbf{r}_x, \mathbf{r}_y \in \mathbb{Z}^d a$ are their positions in the lattice. Then $\varphi(\mathbf{r}_x) \in \mathbb{R}$ refers to the *spin* of the cell x at position \mathbf{r}_x .

Changing variables to $\mathbf{r} = \mathbf{r}_x - \mathbf{r}_y$ leads to:

$$\sum_y \varphi(\mathbf{r}_y) \sum_{\mathbf{r}} K_2(\mathbf{r}) \varphi(\mathbf{r}_y + \mathbf{r})$$

Now we use the fact that K_2 is **short range**, and so the dominant contributions to the sum are the ones with small \mathbf{r} . Near **criticality**, we expect the correlation length to diverge, meaning that spins that are far apart can be highly correlated. Qualitatively, this leads to spin configurations that are “smooth”, in the sense that neighbouring spins are similarly aligned. Mathematically, this allows us to treat $\varphi(\mathbf{r})$ as a smooth function of the position \mathbf{r} , and in particular to expand it in series around $\mathbf{r} = \mathbf{0}$:

4. *Criticality*

$$\sum_y \varphi(\mathbf{r}_y) \sum_{\mathbf{r}} K_2(\mathbf{r}) \left[\varphi(\mathbf{r}_y) + \sum_{\alpha=1}^d r_\alpha \frac{\partial}{\partial r_\alpha} \varphi(\mathbf{r}) \Big|_{\mathbf{r}=\mathbf{r}_y} + \frac{1}{2} \sum_{\alpha,\beta=1}^d r_\alpha r_\beta \frac{\partial^2}{\partial r_\alpha \partial r_\beta} \varphi(\mathbf{r}) \Big|_{\mathbf{r}=\mathbf{r}_y} + \dots \right] =$$

We can then exchange some of the sums to use (5.6) and (5.7):

$$\begin{aligned} &= \sum_y \varphi(\mathbf{r}_y) \underbrace{\sum_{\mathbf{r}} K_2(\mathbf{r})}_{c_2} \varphi(\mathbf{r}_y) + \sum_y \varphi(\mathbf{r}_y) \sum_{\alpha=1}^d \underbrace{\left(\sum_{\mathbf{r}} K_2(\mathbf{r}) r_\alpha \right)}_{0 \text{ (5.6)}} \frac{\partial \varphi}{\partial r_\alpha}(\mathbf{r}_y) + \\ &\quad + \sum_y \varphi(\mathbf{r}_y) \sum_{\alpha,\beta=1}^d \underbrace{\left(\sum_{\mathbf{r}} \frac{r_\alpha r_\beta}{2} K_2(\mathbf{r}) \right)}_{\propto \delta_{\alpha\beta} a^2 \text{ (5.7)}} \frac{\partial^2 \varphi}{\partial r_\alpha \partial r_\beta}(\mathbf{r}_y) + \dots = \end{aligned}$$

And inserting a coefficient c_3 to account for the proportionality:

$$\begin{aligned} &= c_2 \sum_y \varphi(\mathbf{r}_y)^2 + c_3 a^2 \sum_y \varphi(\mathbf{r}_y) \underbrace{\sum_{\alpha=1}^d \frac{\partial^2 \varphi}{\partial r_\alpha^2}(\mathbf{r}_y)}_{\nabla^2 \varphi(\mathbf{r}_y)} = \\ &= c_2 \sum_y \varphi(\mathbf{r}_y)^2 + c_3 a^2 \sum_y \varphi(\mathbf{r}_y) \nabla^2 \varphi(\mathbf{r}_y) \end{aligned}$$

Taking the **continuum limit** $a \rightarrow 0$ (an “infinitely dense” lattice) the summation becomes an integral. We then *rescale* the integration variable from $\mathbf{r}_y = \mathbf{y}a$, resulting in an additional a^{-d} factor, so that the integrand is adimensional:

$$\underset{a \rightarrow 0}{=} \int_{\mathbb{R}^d} d^d \mathbf{y} a^{-d} \left[c_2 \varphi(a\mathbf{y})^2 + c_3 a^2 \varphi(a\mathbf{y}) \nabla^2 \varphi(a\mathbf{y}) + \dots \right] =$$

Finally, integrating by parts two times the highlighted term, and ignoring the resulting surface terms, leads to:

$$= \int_{\mathbb{R}^d} d^d \mathbf{y} a^{-d} \left[c_2 \varphi^2(a\mathbf{y}) - c_3 a^2 (\nabla \varphi(a\mathbf{y}))^2 + \dots \right]$$

A similar procedure can be done also for the other interaction terms. For instance, consider the *quartic* term:

$$\sum_{x,y,z,t} K_{xyzt} \varphi(\mathbf{r}_x) \varphi(\mathbf{r}_y) \varphi(\mathbf{r}_z) \varphi(\mathbf{r}_t)$$

Translational invariance implies that:

$$K_{xyzt} = K_4(\mathbf{r}_x - \mathbf{r}_y, \mathbf{r}_z - \mathbf{r}_y, \mathbf{r}_t - \mathbf{r}_y)$$

And so we can rewrite the term in the Hamiltonian as follows:

$$\begin{aligned} &\sum_{xyzt} K_{xyzt} \varphi(\mathbf{r}_x) \varphi(\mathbf{r}_y) \varphi(\mathbf{r}_z) \varphi(\mathbf{r}_t) = \\ &\underset{\substack{\mathbf{r}_1 \equiv \mathbf{r}_x - \mathbf{r}_y \\ \mathbf{r}_2 \equiv \mathbf{r}_z - \mathbf{r}_y \\ \mathbf{r}_3 \equiv \mathbf{r}_t - \mathbf{r}_y}}{=} \sum_y \varphi(\mathbf{r}_y) \sum_{\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3} K_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \varphi(\mathbf{r}_y + \mathbf{r}_1) \varphi(\mathbf{r}_y + \mathbf{r}_2) \varphi(\mathbf{r}_y + \mathbf{r}_3) \end{aligned}$$

And then expand around $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3 = \mathbf{0}$.

After all these manipulations, the Hamiltonian will look like:

$$-\beta H_{\text{tot}}(\varphi) = \int_{\mathbb{R}^d} d^d \mathbf{y} a^{-d} \left[-c_3 a^2 (\nabla \varphi)^2 + \hat{c}_2 \varphi^2 + \hat{c}_4 \varphi^4 + \dots \right]$$

$$+ d_2 a^2 (\nabla \varphi)^2 + \dots \Big]$$

The yellow term comes from the binary interactions, the blue ones from the quartic interactions, and the green includes contributions from both of them.

As $\varphi \in \mathbb{R}$, through a change of variables we can *fix* one of the coefficients - for example c_3 to $1/2$. So we consider the transformation $\varphi = \zeta \phi$, with $\zeta \in \mathbb{R}$ constant such that:

$$c_3 a^{2-d} (\nabla \varphi)^2 = c_3 a^{2-d} \zeta^2 (\nabla \phi)^2 \stackrel{!}{=} \frac{1}{2} (\nabla \phi)^2 \Rightarrow \zeta^2 = \frac{a^{d-2}}{c_3}$$

After this, the Hamiltonian becomes:

$$-\beta H_{\text{tot}}(\varphi) \equiv -\beta \mathcal{H}(\phi) = - \int_{\mathbb{R}^d} d^d \mathbf{y} \left[\frac{1}{2} (\nabla \phi)^2 + \frac{\mu}{2} \phi^2 + g_4 \phi^4 + g_6 \phi^6 + \dots + \right. \quad (5.8)$$

$$\left. + f_2 (\nabla \phi)^2 \phi^2 + \dots \right] \quad (5.9)$$

It is not important to specify exactly the dependence of these new coefficients $\mu, g_4, g_6, f_2, \dots$ on the old ones $c_3, \hat{c}_2, \hat{c}_4, d_2, \dots$. For now, let's just observe their order on a :

$$\mu \propto a^{-2}; \quad g_4 \propto a^{d-4}; \quad g_6 \propto a^{2(d-3)}; \quad g_8 \propto a^{3d-8}; \quad f_2 \propto a^{d-2}$$

When taking the continuum limit $a \rightarrow 0$, μ always diverges, while the other coefficients either vanish or diverge depending on d . For instance:

- $d > 4$: only μ is diverging
- $3 < d < 4$: μ and g_4 diverge
- $8/3 < d < 3$: μ, g_4, g_6 diverge

In particular, this means that for $d > 4$, a purely gaussian model can be used to describe the system, and it's able to capture all the behaviour of the system near criticality:

$$-\beta H_G(\phi) = - \int_{\mathbb{R}^d} d^d \mathbf{x} h_g(\phi, \partial_\alpha \phi) \quad h_G(\phi) = \frac{1}{2} [(\nabla \phi)^2 + \phi^2]$$

This is the essence of **universality**: a critical system can be described with few parameters, which depend only on the symmetry and the dimensionality (assuming short-range interactions).

From a physical point of view, we are interested only in the $d = 3$ (general systems) and $d = 2$ cases (interfaces/surfaces of systems). However, all other possibilities are still relevant theoretically. In particular, the concept of *fractional dimensions* enables *perturbative expansions*. The idea is that for $d \lesssim 4$ we can write $d = 4 - \epsilon$, with $\epsilon \approx 0$. This means that g_4 is “less important” than μ , and can be treated perturbatively starting from a Gaussian model, leading to results that agree well with experiments. In particular, this has lead to very powerful *renormalization group techniques*, which are able to shed light onto the so-called “universality classes”, i.e. very general “types” of models with similar critical behaviour.

5.2 Back to the discrete world

In summary, the continuum limit $a \rightarrow 0$ has shown to us that only a **finite number of terms** in the **Hamiltonian** are **important**.

Thus, a **discrete model** with just the “right terms” so that its continuum limit matches just the first terms of (5.8) is enough to describe *all the systems* in the same *universality class* near criticality!

One such example is the Nearest Neighbour Ising Model that we have already studied. In the same universality class we find the “Next neighbour” Ising Model, in which a spin may interact with a *neighbour* of its *neighbours* (fig. 5.3). Explicitly, the Hamiltonian is given by:

$$-\beta H(\boldsymbol{\sigma}) = K \sum_{\langle x,y \rangle} \sigma_x \sigma_y + L \sum_{\langle\langle x,y \rangle\rangle} \sigma_x \sigma_y$$

where the second sum is over all x and y that *share* a neighbour z (i.e. that are “neighbours of neighbours”).

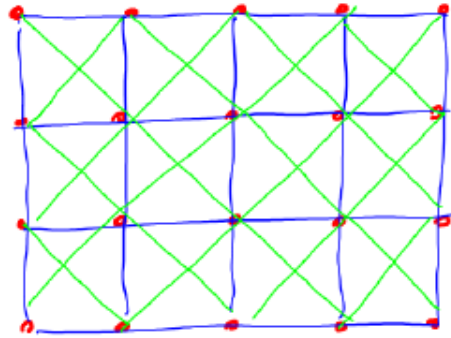


Figure (5.3) – Diagram of the interactions in a Next Neighbour Ising Model. Spins in the lattice are represented as red dots, the usual *nearest neighbour* interactions are in **blue**, and the *next neighbour* interactions are in **green**.

Results from renormalization group theory show that the phase diagram of this kind of model is that of fig. 5.4.

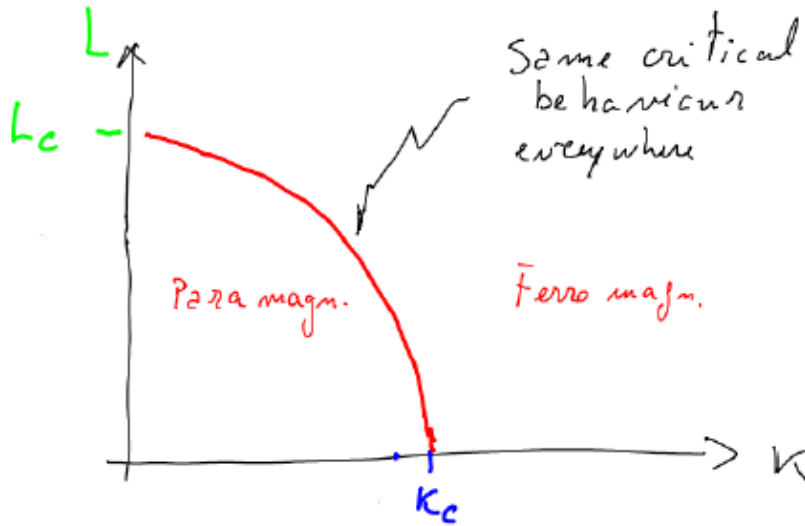


Figure (5.4) – Phase diagram of the Next Neighbour Ising Model.

When the system is near criticality (i.e. along the red line of fig. 5.4) its behaviour is described by the **same set of critical exponents** that appear in the Nearest Neighbour Ising Model we previously examined.

Let's add *another term* to the Hamiltonian, describing *quartic* interactions:

$$-\beta H(\sigma) = K \sum_{\langle x,y \rangle} \sigma_x \sigma_y + L \sum_{\langle\langle x,y \rangle\rangle} \sigma_x \sigma_y + M \sum_{[xyzt]} \sigma_x \sigma_y \sigma_z \sigma_t \quad (5.10)$$



Figure (5.5) – Types of interactions in (5.10)

In this case, the phase diagram is shown in fig. 5.6. Near the *red surface*, at which a second order transition happens, the system's behaviour is again described by the same critical exponents that appear in the Nearest Neighbour Ising Model! They are only different when crossing the *green surface* (corresponding to a first order transition, for which there is no universality in principle) and the boundary between the two surfaces, called the *tri-critical line* (which belongs to a *different* universality class).

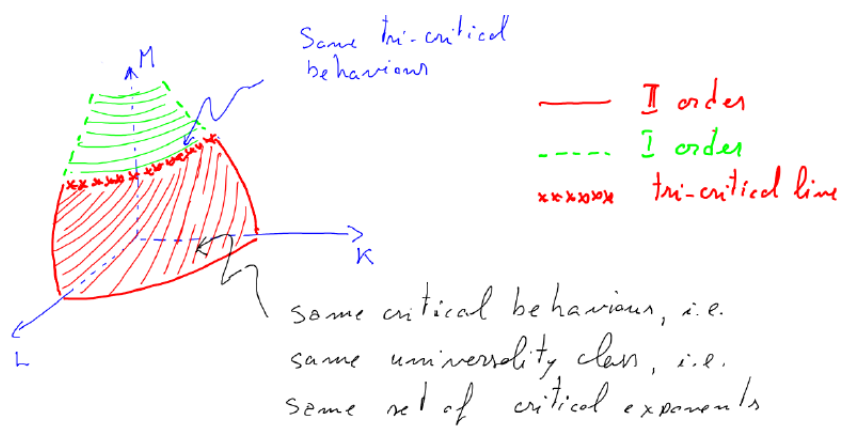


Figure (5.6) – Phase diagram for the model (5.10)

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