Lecture notes on Statistical Physics
L3 Physique – École Normale Supérieure - PSL

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Chapter 1

Introduction to statistical physics: 'more is different'

1.1 Context and Goals

This course is an introduction to statistical physics. The aim of statistical physics is to model systems with an extremely large number of degrees of freedom. To give an example, let us imagine that we want to model 1L of pure water. Let's say that one molecule of water has a typical size of $\sigma = 3\dot{A}$ of space. We then have a density

$$\rho \sim \frac{1}{\sigma^3} \sim 3 \cdot 10^{28}\,\mathrm{m}^{-3} \quad \text{so} \quad N = \rho \cdot 10^{-3}\,\mathrm{m}^3 = 3 \cdot 10^{25} \text{ molecules in 1L}$$

Then to describe each molecule we need 3 spatial coordinates, 3 velocity coordinates and 3 angles. Let's say that we only care about an approximate position so we divide our volume on each direction in 256 pieces, then we need 1 byte per coordinate. We do the same thing for speeds and angles. We then need 9 bytes per molecule to characterize their microscopic state, so in total we need something in the order of 10^{15} terabytes for one single configuration. That is a lot of hard drives, just for one configuration. And this is therefore impossible to capture so much information, in particular if one wants to follow the trajectories of all molecules. One the other hand, we know that if this liter of water is at 30° Celcius it is liquid, but it is a solid at -10°C and a gas at 110°C. Hence we don't really need the complete information about microscopic states to know how the full system of particle behave, a few variables (temperature, pressure, etc.) are sufficient. Therefore, the objective of this lecture is to show how the macroscopic thermodynamic properties relate to and emerge from the microscopic description of the group of many interacting particles. To do so, we will perform statistical averages and apprehend the system in terms of probabilities to observe the various states: this is statistical physics.

Overall, one idea behind the simplifications of statistical physics is that fluctuations are small compared to mean values. Mean behavior emerge from the statistical averages. But as we will highlight several times in the lectures, there is more than this obvious result when many particles interact. We will show that a group of N particles can behave collectively in a manner which is not 'encoded' trivially in the individual behavior of each particle, i.e. that groups of individuals have a behavior of their own, which goes beyond the 'DNA' of each individual. Consider the liquid to ice transition of water: ice and liquid water are constituted by the very same water molecules, interacting in the same way. So the transition reflects that at low temperature, an assembly of (many) water molecules preferentially organize into a well structured phase (crystalline), while at larger temperature they remain strongly disordered phase (liquid). And this huge change is only tuned by a single parameter (at ambiant pressure): the temperature. This transition reflects that the symmetries of the collective assembly (for $N \to \infty$) 'breaks the underlying symmetries' of the microscopic interactions. Hence 'more is different'[1] and there are bigger principles at play which we want to uncover.

The contents of the lectures are as follow. We will start by studying on simple examples what are the emerging laws and how 'more is different'. We will then study statistical physics in the framework of ensembles, which allows calculating thermodynamic potentials and predicting how a system behave as a function of temperature, pressure, etc. We will introduce and discuss in details the three main ensembles of statistical physics, namely the micro-canonical, canonical and grand-canonical ensembles. We will also see how we can create mechanical energy from entropy [2]. The course will then explore phase transitions from thermodynamics and we will explore

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[1] This is the title of a seminal paper by PW Anderson in 1972: P. W. Anderson, 'More is different' *Science*, **177** (4047), 393-396 (1972).

[2] A typical example which we will consider is osmosis: a tank of water with salty water on one side and pure water on the other. We place a filter in the middle that lets pass only water and not salt, then the entropy of the system will generate a mechanical force on the barrier.

exhaustively the model of Van Der Waals for the liquid-vapour phase transition. Finally, we will introduce quantum statistical physics.

1.2 Statistics and large numbers.

As a first example, we consider a simple statistical model. We take a volume V that we partition in V_1 and V_2, and we want to know what is the probability of finding $n = N_1$ particles in the 1^{st} volume. We assume that a particle has a probability $p = \frac{V_1}{V}$ to be in V_1 and $q = 1 - p = \frac{V_2}{V}$ to be in V_2. To have n particles in the first volume, we need to realize n times the previous probability and $N - n$ times its complementary, and since order does not matter we also get an extra binomial term. In summary, we have :

$$\mathbb{P}(n = N_1) = \mathrm{Bin}(p = \frac{V_1}{V}, n) = \binom{N}{n} p^n (1-p)^{N-n} = \binom{N}{n} p^n q^n$$

As a sanity check, one can verify the following sum rules:

$$\sum_{n=0}^{N} \mathbb{P}(n = N_1) = \sum_{n=0}^{N} \mathrm{Bin}(\frac{V_1}{V}, n) = (p + 1 - p)^N = 1$$

Let us now calculate the average and standard deviation which we compute as follows:

$$\langle n \rangle = \sum_{n=0}^{N} n\mathbb{P}(n = N_1) = \sum_{n=0}^{N} n \binom{N}{n} p^n q^{N-n} = p\frac{\partial}{\partial p} \sum_{n=0}^{N} \binom{N}{n} p^n q^{N-n} = p\frac{\partial}{\partial p}(p+q)^N = Np$$

The simple mathematical trick in the above equation can be generalized by introducing the generating function:

$$\hat{p}(z) = \sum_{n=0}^{N} z^n p(n)$$

It is easy to show that:

$$\hat{p}(1) = 1 \quad \text{and} \quad \langle n^k \rangle = \left(z\frac{\partial}{\partial z} \right)^k \hat{p}(z) \Bigg|_{z=1}$$

From this we can get the standard deviation:

$$\langle n^2 \rangle = z\frac{\partial}{\partial z} z \left(zNp(zp+q)^{N-1} \right) \Big|_{z=1} = z\left(Np(zp+q)^{N-1} + zp^2 N(N-1)(zp+q)^{N-2} \right) \Big|_{z=1} = Np + Np^2(N-1)$$

Which then gives:

$$\Delta n^2 = \langle n^2 \rangle - \langle n \rangle^2 = Npq$$

This quantifies the fluctuations around the mean value. For the large system we are considering, see e.g. the $\sim 10^{26}$ particles contained in 1L of liquid water, we have

$$\frac{\Delta n}{\langle n \rangle} = \frac{1}{\sqrt{10^{26}}} = 10^{-13} \ll 1$$

showing that the fluctuations are negligible.

Now let us focus on the distribution function $p(n)$ in the ' thermodynamic limit', $N \to +\infty$. Since we are dealing with small values pf $p(n)$, we calculate the log of $p(n)$:

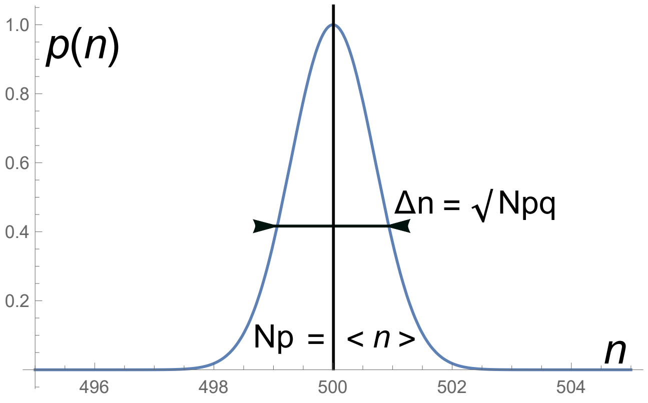
$$\log(p(n)) = N\log N - N - \Big[n\log n - n + (N-n)\log(N-n) - (N-n) \Big] + n\log p + (N-n)\log q$$

The maximum n^* of this function is

$$\frac{\partial}{\partial n} \log(p(n)) \Bigg|_{n^*} = -\log n + \log(N-n) + \log p - \log q \Bigg|_{n^*} = 0 \Leftrightarrow \frac{n^*}{N-n^*} = \frac{p}{1-p} \Leftrightarrow n^* = Np$$

and we indeed recover the previous value for the mean as the point of maximal probability. We then expand around this value n^* as:

$$\begin{aligned} \log(p(n)) &= \log(p(n^*)) + \frac{\partial}{\partial n} \log p(n) \Bigg|_{n^*} (n-n^*) + \frac{1}{2}\frac{\partial^2}{\partial n^2} \log(p(n)) \Bigg|_{n^*} (n-n^*)^2 + \cdots \\ &= \log(p(n^*)) - \frac{1}{2Npq}(n-n^*)^2 \end{aligned}$$

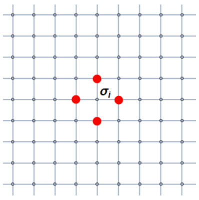


Rewriting this we get that:

$$p(n) = A \exp\left(-\frac{1}{2Npq}(n-n^*)^2\right) \quad \text{and normalization gives} \quad A = \frac{1}{\sqrt{2\pi Npq}}$$

We see that $p(n)$ approaches a Gaussian as $N \to +\infty$.

1.3 Emergent Laws: example of a voting model.



As we have announced in the introduction, 'more is different' and a collective behavior may emerge in an assembly of particles, which is not trivially encoded in its microscopic description. As we quoted, this is refered to as a 'symmetry breaking', which may occurs when the number of particles goes to infinity, $N \to +\infty$ We will illustrate this concept on the example of a voting model: 'the majority vote model'. We will show that the outcome of a vote does not reflect obviously the voting of individuals when they interact, even only within their close neighbours.

We consider a square lattice with N voters/nodes, illustrated on the figure. To each node we associate a 'vote', which is here described as a parameter that can take two values: $\sigma_i = +1/-1$. We then make the system evolve by finite time steps Δt which can correspond to a day for example. People are discussing politics among each other (but only with their neighbours) and the evolution consists of each voter/node having a probability $1-q$ of taking the majoritary opinion of its neighbors and a probability q of taking the minoritary one. Now we define the following:

$$w_i := \text{ probability that } i \text{ changes opinion} \quad S_i := \text{ neighboring opinion } = \text{sign}(\sigma_{i\uparrow} + \sigma_{i\downarrow} + \sigma_{i\leftarrow} + \sigma_{i\rightarrow})$$

We can see case by case [*we leave the demonstration as an exercise*] that we can rewrite:

$$w_i = \frac{1}{2}(1 - (1-2q)\sigma_i S_i)$$

And note that this formula is also well-behaved for $S_i = 0$.

The question now is: how does the opinion of i evolve ? We know that σ_i will stay the same with a probability $1 - w_i$ and change by a quantity $-2\sigma_i$ (from 1 to -1 or vice-versa) with probability w_i, so we get:

$$\frac{\Delta\sigma_i}{\Delta t} = 0 \cdot (1 - w_i) - 2\sigma_i w_i = -\sigma_i + (1-2q)\sigma_i^2 S_i = -\sigma_i + (1-2q)S_i$$

and we deduce

$$\frac{d\sigma_i}{dt} = -\sigma_i + (1-2q)S_i$$

with $S_i = \text{sign}\left(\sum_{k\in\mathcal{N}(i)} \sigma_k\right)$. Now let's call $m = \langle\sigma_i\rangle$ the average opinion. Furthermore, one can rewrite S_i, which is defined in terms of a sign function, in terms of individual values for the neighbouring 'vote':

$$S_i = \frac{3}{8}(\sigma_{i\uparrow} + \sigma_{i\downarrow} + \sigma_{i\leftarrow} + \sigma_{i\rightarrow}) - \frac{1}{8}(\sigma_{i\uparrow}\sigma_{i\downarrow}\sigma_{i\leftarrow} + \sigma_{i\downarrow}\sigma_{i\leftarrow}\sigma_{i\rightarrow} + \sigma_{i\leftarrow}\sigma_{i\rightarrow}\sigma_{i\uparrow} + \sigma_{i\rightarrow}\sigma_{i\uparrow}\sigma_{i\downarrow})$$

We leave it as an exercise to the reader to check case by case that this formula works.

Now we are interested in the *average* properties of the vote. We want to calculate an average vote, denoted as $\langle\sigma_i\rangle$ for node i. Note that on average the vote is the same for every node so that $\langle\sigma_i\rangle = m$ is independent of i. This is a very complicated matter to calculate this quantity exactly from the previous equations since there are couplings between neighbouring sites. But one can do some approximations which capture the main behaviors at play: we will do what is called the 'mean field approximation' which will be justified and explained later in the lectures. It simply consists of saying that every node behaves more or less like all the others, and identify to the mean value, here m. Accordingly, average of products like $\sigma_{i\downarrow}\sigma_{i\leftarrow}\sigma_{i\rightarrow}$ will be approximated by their 'uncoupled' version: $\langle\sigma_{i\downarrow}\sigma_{i\leftarrow}\sigma_{i\rightarrow}\rangle \simeq \langle\sigma_{i\downarrow}\rangle\cdot\langle\sigma_{i\leftarrow}\rangle\cdot\langle\sigma_{i\rightarrow}\rangle \simeq m^3$. More concretely the 'uncoupling' of the dynamical equation leads to :

$$\frac{d\langle\sigma_i\rangle}{dt} = -\langle\sigma_i\rangle + (1-2q)\left[\frac{3}{8}\sum_{k\in\mathcal{N}(i)}\langle\sigma_k\rangle - \frac{1}{8}\Big(\langle\sigma_{i\uparrow}\sigma_{i\downarrow}\sigma_{i\leftarrow} + \cdots\}\Big)\right] \approx -m + (1-2q)\left[\frac{3}{2}m - \frac{1}{2}m^3\right]$$

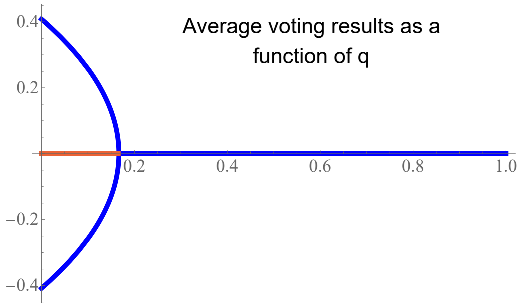
Now we call $\gamma = (1-2q)$ and so we obtain:

$$\frac{dm}{dt} = (-1+\frac{3}{2}\gamma)m - \frac{\gamma}{2}m^3$$

We are interested in the stationary states, $dm/dt = 0$, which writes

$$\frac{dm}{dt} = 0 \Leftrightarrow m(-1+\frac{3\gamma}{2} - \frac{\gamma}{2}m^2) = 0 \Rightarrow \begin{cases} m = 0 \\ m^2 = -\frac{2\varepsilon}{\gamma} \end{cases}$$

Now if $\varepsilon > 0$ then $m = 0$ is the only solution, otherwise $m = 0$ and $m = \pm\sqrt{\frac{2\varepsilon}{\gamma}}$ are the two solutions. Furthermore $\varepsilon = 3(q - \frac{1}{6})$ so we see that the critical value is $q_c = 1/6$ for the parameter q such that for $q < q_c$ a non-trivial solution $m \neq 0$ for the global solution emerge. It is also quite straight-forward to check that all solutions are stable with the exception of $m = 0$ when $q < q_c$.



As a side note, we mention that the numerical solution of the full model gives qualitatively similar results (changing the critical value q_c for the transition as well as the dependence of $m(q)$ in particular close to q_c); cf for example C. Castellano, S. Fortunato, & V. Loreto 'Statistical physics of social dynamics' **Reviews of modern physics**, **81**, 591 (2009). This shows that the previous mean-field approximation describes at least qualitatively the behavior at stake.

What is emerging from this example is that depending on q, the system may collectively break the underlying microscopic symmetry (which do not promote one solution or the other) to yield a non-zero average for the vote for values of q below a critical value q_c. This is *not* contained a priori in the microscopic equations. This emerging solution is a result of the collective, statistical behavior. Hence *more is different*, as put forward by PW. Anderson in his article.

This is a fundamental aspect of statistical physics and at the core of the understanding of phase transitions in many-body systems. We will come back to this aspect later in the lectures.

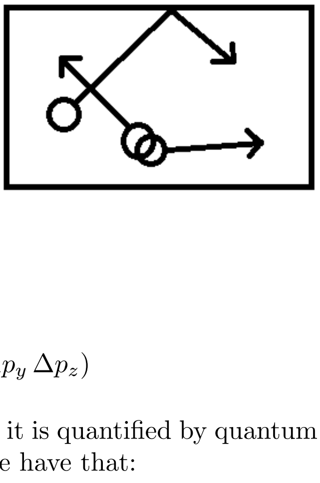
Chapter 2

Combinatorics and emergent laws.

In this chapter we will make a first study of ideal systems in order to grab the phenomena at play. A more thorough and detailed analysis of ideal systems will then come in the next chapter.

2.1 Perfect Gas

2.1.1 Combinatorics of an elementary system without interactions.



To start with we consider a fixed volume V with a fixed number of particles N that don't interact with each other, so we ignore collisions between parrticles altogether (we however need to consider collisions with the confining container). The system is also completely isolated from the 'outside'. Then each particle is described by its position and velocity (or momentum):

$$\begin{cases} \overrightarrow{r_i} = (x_i, y_i, z_i)(t) \\ \overrightarrow{p_i} = m(v_{x_i}, v_{y_i}, v_{z_i})(t) \end{cases}$$

So our system is evolving in a 6 dimensional phase space, which we denote as Γ. We then subdivide this space in elementary cells of size $\Delta\Gamma$, writing:

$$\Gamma = \Big\{ \{\overrightarrow{r_1}, \overrightarrow{p_1}\}, \{\overrightarrow{r_2}, \overrightarrow{p_2}\}, \cdots \Big\} \quad \text{and} \quad \Delta\Gamma = (\Delta x\, \Delta y\, \Delta z\, \Delta p_x\, \Delta p_y\, \Delta p_z)$$

The size of $\Delta\Gamma$ will be without importance in the following but we will see later that it is quantified by quantum effects. Now let α be a microscopic state, since the system is completely isolated we have that:

$$\epsilon_\alpha = \frac{1}{2} m v_\alpha^2 = \frac{1}{2} \frac{p_\alpha^2}{m}$$

Now we make the following postulate: **all the configurations of the phase space are equiprobable**, which seems quite natural for the system at stake. Hence, if we divide the phase-space into M cells in total, each cell has a probability of $p = \frac{1}{M}$ to be occupied by a microscopic state, *i.e.* a particle with a given position and velocity. The question we want to answer is what is the most probable configuration for our system. Similarly as in the previous chapter we get that:

$$\mathbb{P}(n_1, n_2, \cdots, n_m) = \frac{N!}{n_1! n_2! \cdots n_m!} \left(\frac{1}{M}\right)^N$$

where n_i is the number of particles in a state i. Furthermore we have the following constraints on the fixed total number of particles and total energy:

$$n_1 + n_2 + \cdots + n_m = N \quad \text{and} \quad n_1\epsilon_1 + n_2\epsilon_2 + \cdots n_m\epsilon_m = E$$

To maximize the probability under these constraints, the easiest way is to use Lagrangian multipliers; we refer to the Appendix in Chapter 10 for details on the method. We introduce accordingly the function

$$F(n_1, \cdots, n_m) := \log \mathbb{P}(n_1, \cdots, n_m) - \mu \left(\sum_{i=1}^{m} n_i - N \right) - \beta \left(\sum_{i=1}^{m} n_i \epsilon_i - E \right)$$

where μ and β are the Lagrangian multipliers, and minimize F versus each n_i. Using Stirling's formula we immediately get that:

$$\frac{\partial F}{\partial n_i} = 0 = -\log n_i - \mu - \beta\epsilon_i$$

so the most probable state is

$$n_i = e^{-\mu-\beta\epsilon_i}$$

Then the Lagrange parameters μ and β are fixed by the initial constraints: $N = \sum_{i=1}^m n_i = N(\mu,\beta)$ and $E = \sum_{i=1}^m n_i\epsilon_i = E(\mu,\beta)$.

2.1.2 Distribution of Energy

Perfect Gas

Let us now come back to the perfect has. We want first to estimate how many particles have a given energy: $\epsilon = \frac{1}{2}mv^2$. Using the previous result we find that:

$$\#\text{particles with energy } \epsilon = C\, d^3\vec{r}\, d^3\vec{v}\, e^{-\beta\frac{1}{2}mv^2}$$

Using the normalization to determine C we get that:

$$\int C\, d^3\vec{r}\, d^3\vec{v}\, e^{-\beta\frac{1}{2}mv^2} = N \Rightarrow CV\left(\sqrt{\frac{2\pi}{\beta m}}\right)^3 = N$$

So we get the following result:

$$\#\text{ particles with } (\vec{r},\vec{v}) = d^3\vec{r}\, d^3\vec{v}\, \rho\left(\frac{\beta m}{2\pi}\right)^{3/2} \exp\big[-\beta\frac{1}{2}mv^2\big] \quad \text{with } \rho = N/V$$

This is the so-called Maxwell-Boltzmann distribution.

Average Energy

From the previous computation we can calculate the average energy as

$$\begin{aligned} E &= \int d^3\vec{r}\int d^3\vec{v}\left(\frac{1}{2}mv^2\right)\rho\left(\frac{\beta m}{2\pi}\right)^{3/2}\exp\left(-\beta\frac{1}{2}mv^2\right) = N\left(\frac{\beta m}{2\pi}\right)^{3/2}\int d^3\vec{v}\left(\frac{1}{2}mv^2\right)\exp\left(-\frac{\beta}{2}mv^2\right) \qquad (2.1)\\ (\cdots) &= \frac{3}{2}\frac{N}{\beta} \end{aligned}$$

In the absence of any interaction between particle, we expect that the energy is purely thermal and $E \sim T$ so $\beta \sim \frac{1}{T}$. More precisely we will see that $\beta = \frac{1}{k_BT}$ with the prefactor $k_B = 1.38\cdot 10^{-23}$ J/K being the Boltzmann constant. This leads to the simple result:

$$E = \frac{3}{2}Nk_BT$$

Note that the definition of temperature is somewhat arbitrary. It is defined such that under ambiant pressure, ice melts at 0° Celcius and 273 Kelvin, and liquid water boils at 100°C, and 373K.

2.1.3 Elements of kinetic theory and law of Boyle-Mariotte.

The law of Boyle-Mariotte highlights that the pressure P and volume V of a gas system are related accoring to the relationship

$$P \times V = cst$$

for a given temperature.

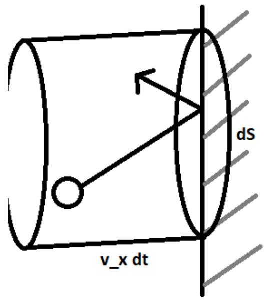
Formally this takes the form of the equation of state for the perfect gas as

$$PV = Nk_BT$$

where T is in Kelvin and the prefactor k_B is the Boltzmann constant ($k_B = R/\mathcal{N}$ with $R = 8.31\text{J.mol}^{-1}.\text{K}^{-1}$ the universal constant of gases and $\mathcal{N}$ the Avogadro number). Let us derive this result using kinetic theory.

Pressure

The pressure is the force acting on surfaces, which is due to collisions of the particles bouncing on the surface.



When a particle bounces on the surface, its momentum will change by

$$(\Delta\vec{p})_x = -2mv_x$$

and the average force sums up all momentum changes of particles bouncing on the surface:

$$\vec{F}_{\text{wall}} = \sum_{i \text{ colliding during } \Delta t} \frac{\Delta p_i}{\Delta t}$$

For a given time step Δt, we need to determine how many particles are colliding with the wall. Reminding that all particles maintain the same velocity in this time step Δt (since they don't experience collision between them), this number is given by the number of particles contained contaned in a cylinder of base ΔS and height $v_x\Delta t$ (with $v_x > 0$). We thus deduce

$$dF_x = -\int_{v_x>0} d^3\vec{v}\, \frac{\Delta p_x}{\Delta t}(v_x \Delta t\, dS) C f(\vec{v})$$

where f is the previous Maxwell-Boltzmann distribution, and the pressure is

$$P = \frac{dF_x}{dS} = \rho \int_{v_x>0} d^3\vec{v}\, 2mv_x^2 f(\vec{v})$$

We can rewrite this result as

$$P = \rho\langle 2mv_x^2\rangle_{v_x>0}$$

This can be calculated using the expression for the Maxwell-Boltzmann distribution, to obtain

$$\langle v_x^2\rangle_{v_x>0} = \frac{1}{2\beta m}$$

Plugging this back in the equation for the pressure we obtain

$$P = \rho \times 2m\langle v_x^2\rangle_{v_x>0} = \frac{\rho}{\beta}$$

and using the previous value for $\beta = 1/k_BT$, we get $PV = \frac{N}{\beta}$ leading to the final result

$$PV = Nk_BT$$

Orders of magnitude

The thermal energy at 300K is $k_BT = 4\,10^{-21}$ J and one gets

$$v \sim \sqrt{\frac{k_BT}{m}} \sim 10^2 \text{ m/s}$$

The atmospheric pressure is $P = 10^5$ Pa for the molar density of air (corresponding to a volume per mole of 22.4 liter).

The force exerted on a 1m^2 window is 10^5 N (corresponding to the weight of a few elephants...). Although this might seem huge one has to remember that the same force is exerted on both sides of the window, which explains why the window isn't exploding. Furthermore one might wonder if a pressure fluctuation on one side may lead to a intermittent force imbalance and break the window ? Actually the pressure fluctuations are $\frac{\Delta P}{P} = \frac{\Delta N}{N} \sim \frac{1}{\sqrt{N}} \sim 10^{-13}$ and may only lead to force fluctuations of the order of 10^{-8} N according to the previous results. Fortunately this clearly is not enough to break a window. We are somewhat lucky that fluctuations are small, otherwise life would be a bit more complicated.

2.1.4 Barometric Law

We now consider the same problem but we now add gravity (or any other time-independent potential $V(\vec{r})$). The modification is quite easy to make, it suffices to change the energy of a cell as follows:

$$\epsilon_i = \frac{1}{2}mv_i^2 + V(\vec{r}_i) = \frac{1}{2}mv_i^2 + mgz_i$$

Then the Maxwell-Boltzmann distribution is re-written as follows:

$$\#\text{ particles with } (\vec{r},\vec{v}) \propto \exp\Big[-\beta\Big(\frac{1}{2}mv^2 + mgz\Big)\Big]$$

And so we get that:

$$\rho(z) = \rho_0 \exp(-\beta mgz)$$

If we compute this with the usual balance of forces method from mechanics we get the same result:

$$0 = -P(z+dz)dS + P(z)\,\mathrm{d}S - \rho mg\,\mathrm{d}S\,\mathrm{d}Z = -\frac{\partial P}{\partial z}\,\mathrm{d}S\,\mathrm{d}z - \rho mg\,\mathrm{d}S\,\mathrm{d}z$$

So we get that:

$$\begin{cases} \frac{\partial P}{\partial z} = -\rho mg \\ P = \rho k_B T \end{cases} \Rightarrow \frac{\partial \rho}{\partial z} = -\frac{mg}{k_B T}\rho \Rightarrow \rho = \rho_0 \exp\left[-\frac{mgz}{k_B T}\right]$$

2.2 Introduction to the notions of statistical ensembles and fundamental postulate.

From the previous discussion, one may conclude that, while the previous approach would be sufficient to consider ideal systems, one needs more powerful tools to adress the statistical properties of many-body interacting systems in the large number $N \to \infty$. Such a tool is provided by the ensemble theory, which we will introduce in the following.

But we first need to say a few words about the dynamics of systems. This will incidently hint at some constraints on the theory of ensemble we will build.

2.2.1 Dynamics

Let us consider a system of N particles, so that our system is described by $2N$ vectors, positions and velocties: $\overrightarrow{r_i}(t)$, $\overrightarrow{v_i}(t)$. In dynamical systems, one prefers to use equivalently $2N$ 'canonical' variables: $\overrightarrow{q_i}(t)$, $\overrightarrow{p_i}(t)$, which in the present case are the position and momentum (see below). We introduce the Hamiltonian $\mathcal{H}(\{\overrightarrow{q_i}, \overrightarrow{p_i}\}, t)$, and the equations of motion of our system are:

$$\begin{cases} \dot{\overrightarrow{q_i}} = \frac{\partial \mathcal{H}}{\partial \overrightarrow{p_i}} \\ \dot{\overrightarrow{p_i}} = -\frac{\partial \mathcal{H}}{\partial \overrightarrow{q_i}} \end{cases}$$

$$\mathcal{H} = \frac{1}{2}\frac{\overrightarrow{p}^2}{m} + V(\overrightarrow{q}) \quad \text{then we get that} \quad \dot{\overrightarrow{q_i}} = \frac{\partial \mathcal{H}}{\partial \overrightarrow{p}} = \frac{\overrightarrow{p_i}}{m}$$

We then introduce the phase space $\Gamma = \{\overrightarrow{q_i}, \overrightarrow{p_i}\}$ and subdivide it in base elements $\mathrm{d}\Gamma = \prod_{i=1}^{N} \mathrm{d}\overrightarrow{q_i}\mathrm{d}\overrightarrow{p_i}$. We then introduce the microscopic density $\rho(\Gamma, t)$, which one can define as

$$\rho(\Gamma, t) = \prod_{i=1}^{N} \delta(\overrightarrow{q_i} - \overrightarrow{q_i}(t))\delta(\overrightarrow{p_i} - \overrightarrow{p_i}(t))$$

Sturm-Lioumville equation.

Let us establish the dynamical equation for $\rho(\Gamma, t)$. We calculate accordingly

$$\begin{aligned} \frac{\partial \rho}{\partial t} = \sum_i \Big(-\frac{\partial \overrightarrow{q_i}}{\partial t}\Big)\Big(\boldsymbol{\nabla}_{q_i}\delta(\overrightarrow{q_i} - \overrightarrow{q_i}(t))\delta(\overrightarrow{p_i} - \overrightarrow{p_i}(t))\Big) \prod_{j=1, j\neq i}^{N} \delta(\overrightarrow{q_j} - \overrightarrow{q_j}(t))\delta(\overrightarrow{p_j} - \overrightarrow{p_j}(t)) \\ + \Big(-\frac{\partial \overrightarrow{p_i}}{\partial t}\Big)\Big(\boldsymbol{\nabla}_{q_i}\delta(\overrightarrow{q_i} - \overrightarrow{q_i}(t))\delta(\overrightarrow{p_i} - \overrightarrow{p_i}(t))\Big) \prod_{j=1, j\neq i}^{N} \delta(\overrightarrow{q_j} - \overrightarrow{q_j}(t))\delta(\overrightarrow{p_j} - \overrightarrow{p_j}(t)) \end{aligned}$$

where we used

$$\frac{\partial}{\partial t}\delta(x - x(t)) = -\frac{\partial x}{\partial t}\delta'(x - x(t)) = -\dot{x}\boldsymbol{\nabla}_x \delta(x - x(t))$$

We then rewrite this result as:

$$\frac{\partial \rho}{\partial t} = -\left(\sum_i \dot{\overrightarrow{q_i}}\boldsymbol{\nabla}_{q_i}\rho + \dot{\overrightarrow{p_i}}\boldsymbol{\nabla}_{p_i}\rho\right) = -\sum_i \left(\frac{\partial \rho}{\partial \overrightarrow{q_i}}\frac{\partial \mathcal{H}}{\partial \overrightarrow{p_i}} - \frac{\partial \rho}{\partial \overrightarrow{p_i}}\frac{\partial \mathcal{H}}{\partial \overrightarrow{q_i}}\right)$$

We then introduce what is called the Poisson bracket:

$$\{A, B\} = \sum_i \left(\frac{\partial A}{\partial \overrightarrow{q_i}}\frac{\partial B}{\partial \overrightarrow{p_i}} - \frac{\partial A}{\partial \overrightarrow{p_i}}\frac{\partial B}{\overrightarrow{q_i}}\right)$$

We can then write the Sturm-Liouville equation:

$$\frac{\partial \rho}{\partial t} = \{\mathcal{H}, \rho\}$$

Note that one can re-write:

$$\frac{\partial \rho}{\partial t} = -\sum_i \boldsymbol{\nabla}_{q_i}(\dot{\overrightarrow{q_i}}\rho) + \boldsymbol{\nabla}_{p_i}(\dot{\overrightarrow{p_i}}\rho)$$

because

$$(\boldsymbol{\nabla}_{q_i}\dot{\overrightarrow{q_i}} + \boldsymbol{\nabla}_{p_i}\dot{\overrightarrow{p_i}})\rho = \left(\frac{\partial^2 \mathcal{H}}{\partial \overrightarrow{q_i}\partial \overrightarrow{p_i}} - \frac{\partial^2 \mathcal{H}}{\partial \overrightarrow{q_i}\partial \overrightarrow{p_i}}\right)\rho = 0$$

This leads to the final result

$$\frac{\partial \rho}{\partial t} = -\boldsymbol{\nabla}(\overrightarrow{v}\rho)$$

shich shows that probabilities are conserved.

An important result of this conservation equation is that **any function that depends only on the hamiltonian $\mathcal{H}$ is a stationary solution of the Liouville equation**, or in mathematics terms:

$$\rho \equiv \rho_0(\mathcal{H}) \quad \text{verifies} \quad \frac{\partial \rho}{\partial t} = \{\mathcal{H}, \rho\} = 0$$

2.2.2 Ensembles and postulate

We want to move from a microscopically dynamic system to a probabilistic description. To do so, one imagines many different 'representative' trajectories of the system in the phase space, following the same dynamics but starting from different initial conditions.

Starting from a given set of M initial conditions, the trajectory of the system will explore a number of microscopic states in the phase space. We then consider how the trajectories do fill the phase space when averaged over the 'M' replica. We then state that the density of probability for the system to be in a state '$\Gamma = \{\vec{q_i}, \vec{p_i}\}$' in the phase space corresponds to the average presence of the trajectories of the system around this state 'Γ', i.e:

$$\rho(\Gamma) = \frac{1}{M}\sum_\alpha \rho_\alpha(\Gamma)$$

where α runs over the sets of M initial conditions, i.e. the replica. One can then define averages like:

$$\langle A \rangle = \int \mathrm{d}\Gamma \rho(\Gamma) A(\Gamma)$$

with $d\Gamma = \Pi_i d\vec{q_i}\, d\vec{p_i}$. In order to calculate such averages, one needs to have an expression for the density $\rho(\Gamma)$ at equilibrium. A hint for $\rho(\Gamma)$ is given by the previous Sturm-Liouville theorem, showing that any expression for the density $\rho \equiv \rho(\mathcal{H})$ which is a functional of the hamiltonian is a stationary solution. We shall come back to this later on. However, note that the density ρ is expected to depend on the global conditions imposed: i.e. whether the energy is fixed, or the temperature; whether the number of particle is fixed or the chemical potential, etc. This introduces the notion of 'ensembles':

Ensembles

The study of statistical physics separates into multiple 'ensembles', depending on such global conditions. We are going to consider:

- The micro-canonical (N, V, E) ensemble: the energy of the system is fixed and the system is isolated, so N and V don't vary either.

- The canonical (N, V, T) ensemble: Instead of fixing the energy we know fix the temperature. So N, V, T are fixed.

- The grand-canonical ensemble (μ, V, T): we fix the chemical potential instead of the number of particles. So μ, V, T are fixed.

Many other ensembles can be introduced depending on the global conditions and globally conserved parameters.

Fundamental Postulate

This is the key postulate which will allow us to calculate the statistical properties of systems. It generalizes the results we discussed above on the various simple examples (perfect gas, etc.).

In an isolated system at equilibrium, all the microscopic states are equally probable.

Remark that this means that at equilibrium $\rho_{\text{eq}}(\Gamma)$ becomes independent of Γ and we have instead that:

$$\boxed{\rho_{\text{eq}} = \frac{1}{\text{number}(\#)\text{ of microscopic states}}}$$

which, as we will see, depends on the energy E. Note as well that this agrees with the microscopic dynamics since it does satisfy the previous Liouville equation. If ρ depends only of E it can be written as a function of $\mathcal{H}$ and so is a stationary solution of the Liouville equation.

This postulate is in some sens the most 'simple' that one can propose. But in spite of its apparent simplicity, it is extrememy powerful and agrees with all experimental results.

Based on this postulate, we will first build the microcanonical ensemble in the next chapter. Hereafter we will build the canonical and grand-canonical ensembles.

Chapter 3

Microcanonical ensemble.

In the microcanoncal ensemble we consider situations in which the system is isolated: the total energy, the volume and the number of particles are fixed.

3.1 Microcanonical partition function.

We made the following postulate:

$$\rho_{\mathrm{eq}}(\Gamma) = \frac{1}{\Omega} \quad \text{where} \quad \Omega = \#\text{ microstates of energy } E$$

Another way to write this is:

$$\Omega = \sum_{\text{microstates } s|N(s)=N, V(s)=V, E(s)=E} 1$$

Now to simplify calculus we introduce an uncertainty on the energy ΔE. So instead of requiring a strict equality we only require that $E \leq \mathcal{H}(\Gamma) \leq E + \Delta E$. Although not obvious at first we will see that in the end ΔE has no impact on the physics and is simply a calculus trick. We also define the average of a quantity as:

$$\langle A \rangle = \int \mathrm{d}\Gamma A(\Gamma)\rho(\Gamma) = \frac{\int_{E\leq\mathcal{H}(\Gamma)\leq E+\Delta E} \mathrm{d}\Gamma \cdot A(\Gamma)}{\int_{E\leq\mathcal{H}(\Gamma)\leq E+\Delta E} \mathrm{d}\Gamma \cdot 1}$$

We now introduce the partition function. We divide our phase space into small elements with volume:

$$\Delta\Gamma = \Delta\overrightarrow{q_i}\Delta\overrightarrow{p_i} = h^3 \quad \text{where } h \text{ is Planck's constant.}$$

As to now, h just fixes the dimension of an elementary cell in phase space. Now instead of summing on all of our microstates as we did before we are going to use this subdivision and re-write:

$$\boxed{\Omega = \frac{1}{N!}\int_{E\leq\mathcal{H}(E)\leq E+\Delta E} \frac{\mathrm{d}\Gamma}{h^{3N}} \cdot 1} \tag{3.1}$$

Ω is the partition function.

This is a central quantity in statistical physics. Here this expression corresponds to the classical partition function and we will discuss at the end of the lectures its quantum counterpart.

Note that we add the $N!$ term because our integral does not take into consideration the *undiscernability of the particles* and we thus force it by considering all permutations between particles, hence divide by a $N!$ factor. Note though that the adding of this $N!$ is not so obvious and hides some physics subtleties [1]. In the quantum framework, indiscernability is built-in without requiring to enforce it.

3.2 Entropy and Temperature.

We define the entropy, as done by Boltzmann in 1872, by:

$$S = k_B \log\Omega \quad \text{with } k_B \text{ being the Boltzmann constant.} \tag{3.2}$$

---

[1] This point is still being discussed, cf. D. Frenkel, Molecular Physics, 112 2325 (2014)

Then the temperature is defined by:

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{V,N}$$

We will see this more in detail later, but we just mention that the entropy is an extensive variable and T is an intensive variable so when we consider two systems 1, 2 in equilibrium, we have:

$$S_{1\cup 2} = S_1 + S_2 \quad \text{while} \quad T_{1\cup 2} = T_1 = T_2$$

3.3 Entropy of the perfect gas.

A perfect gas is a gas with no interactions, which translates to:

$$\mathcal{H}(\Gamma) = \sum_{i=1}^{N} \frac{\overrightarrow{p_i}^2}{2m}$$

Now what we have to compute is:

$$\Omega = \frac{1}{N!}\frac{1}{h^{3N}} \int_{E \leq \sum_{i=1}^{N} \frac{\overrightarrow{p_i}^2}{2m} \leq E+\Delta E} \mathrm{d}\Gamma$$

We then decompose $\mathrm{d}\Gamma$ in its two fundamental building blocks and use the fact that the positions are independent of the energy. We then get:

$$\Omega = \frac{1}{N!}\frac{1}{h^{3N}} \int_{V\times V\times\cdots} \mathrm{d}\overrightarrow{r_1}\cdots\mathrm{d}\overrightarrow{r_N} \int_{2mE\leq\sum_i \overrightarrow{p_i}^2 \leq E+\Delta E} \mathrm{d}\overrightarrow{p_1}\cdots\mathrm{d}\overrightarrow{p_N} = \frac{V^N}{N! h^{3N}}\Delta\mathcal{V}(E)$$

where we introduced the volume $\Delta\mathcal{V}(E)$ defined as:

$$\Delta\mathcal{V}(E) = \int_{2mE\leq\sum_i \overrightarrow{p_i}^2 \leq E+\Delta E} \mathrm{d}\overrightarrow{p_1}\cdots\mathrm{d}\overrightarrow{p_N}$$

To do so we use our ΔE term in the following way, we say that:

$$\mathcal{V}(E) = \int_{0\leq\sum_i \overrightarrow{p_i}^2 \leq 2mE} \mathrm{d}\overrightarrow{p_1}\cdots\mathrm{d}\overrightarrow{p_N} \quad \text{and} \quad \Delta\mathcal{V}(E) = \mathcal{V}(E+\Delta E) - \mathcal{V}(E)$$

Note that this corresponds simply to the volume of a hyper-sphere of dimension $3N$, for which we know the explicit formula:

$$\mathcal{V}(E) = \frac{\pi^{\frac{3N}{2}}}{(\frac{3N}{2})!} R^{3N} \quad \text{here with} \quad R = \sqrt{2mE}$$

Then we write:

$$\Delta\mathcal{V} = \mathcal{V}(E+\Delta E) - \mathcal{V}(E) \approx \Delta E\,\mathcal{V}'(E) \quad \text{with} \quad \mathcal{V}'(E) = \frac{\pi^{\frac{3N}{2}}}{(\frac{3N}{2})!}\frac{3N}{2}\frac{(2mE)^{\frac{3N}{2}}}{E}$$

We can then deduce that:

$$\Omega = \frac{V^N}{N! h^{3N}} \frac{\pi^{\frac{3N}{2}}}{(\frac{3N}{2})!} (2mE)^{\frac{3N}{2}} \frac{\frac{3N}{2} N \Delta E}{E}$$

We can now compute the entropy of our system:

$$S = k_B \log\Omega$$

And if we write $\Omega = \omega^N \frac{3N\Delta E}{E}$ we then get:

$$\log\Omega = N\log\omega + \log\left(\frac{3N\Delta E}{E}\right) \approx N\log\omega$$

Note that the second term $\log(\frac{3N\Delta E}{E})$ is of order $\log N$ and completely negligeable as compared to the first term scaling in N (just compare 10^{23} to $\log 10^{23} \approx 50$). Now we get:

$$\begin{aligned} S &\approx k_B \log\left[\frac{V^N}{N! h^{3N}} \frac{\pi^{\frac{3N}{2}}}{(\frac{3N}{2})!} (2mE)^{\frac{3N}{2}}\right] \\ &= k_B N \left(\log V\left(\frac{2\pi m E}{h^2}\right)^{\frac{3}{2}} - \log N + 1 - \frac{3}{2}\log N + \frac{3}{2}\right) \end{aligned}$$

so that one deduces

$$S = k_B N \left(\log \left(\frac{V}{N} \left(\frac{\frac{4\pi}{3} mE/N}{h^2} \right)^{3/2} \right) + \frac{5}{2} \right)$$

This is the so-called Sackur-Tetrode formula.

We now introduce a few variables:

- $\rho = \frac{N}{V}$, the numeric density not to be confused with the previous $\rho(\Gamma)$, the phase space density.
- $\lambda = \sqrt{\frac{h^2}{\frac{4\pi}{3} m \frac{E}{N}}}$ which is called the De Broglie wavelength.

The De Broglie wavelength indeed has the unit of a length and actually corresponds to the length under which quantum effects dominate and become non-negligible. For a perfect gas at 300K this gives $\lambda \sim 10^{-11}$m, and the distance in between particles $\frac{1}{\rho^{1/3}} \sim \text{nm} \gg \lambda$. Now re-writing the formula we have:

$$S = k_B N \left(\log \frac{1}{\rho \lambda^3} + \frac{5}{2} \right) \tag{3.3}$$

Note that if we had not included the $N!$ indiscernability term earlier, $\rho = N/V$ would be replaced by $1/V$ in the expression for S and $S \sim N \log V$. Hence the entropy would not behave as an extensive variable, which is not acceptable.

Temperature

Now that we have the entropy we can try and compute the temperature. We have the formula:

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_{V,N} \qquad \text{and} \qquad S = k_B N \left(\log \left(\alpha E^{3/2} \right) + \frac{5}{2} \right)$$

with α a term independent of temperature. This then gives:

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_{N,V} = k_B N \frac{3}{2E} \Rightarrow E = \frac{3}{2} N k_B T$$

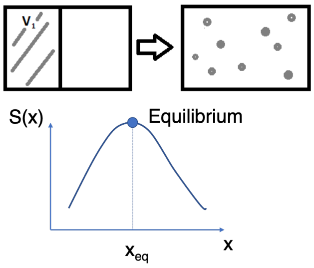
3.4 General Properties of Entropy.

3.4.1 Evolution towards equilibrium: increase of entropy.

We are as always considering an isolated system where at $t = 0$ we add a constraint 'x' imposed on the global state of the system. When we remove the constraint the number of possible microstates increases and therefore:

$$\Omega_f \geq \Omega_i \quad \text{so} \quad S_f \geq S_i \quad \text{and} \quad \Delta S \geq 0$$

When the constraint x is released, entropy increases in the path towards equilibrium: $S(x)$ is therefore maximal at equilibrium. Then a general property that we are going to look at now is that the **equilibrium is found by maximizing the entropy**, as a function of the constraint x.

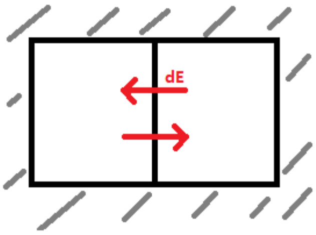


3.4.2 Thermodynamic equilibrium.

We consider the following system: we take a fixed isolated volume and separate it in two systems V_1, N_1, E_1 and V_2, N_2, E_2 separated by an impermeable barrier. However energy can be exchanged in between the two systems. So we have V_1, V_2 and N_1, N_2 constant, and $E = E_1 + E_2$ constant.

Then the number of microstates is given as follows ($\star$)

$$\Omega = \Omega_1 \times \Omega_2$$



So we have that:

$$S_{1 \cup 2} = k_B \log \Omega = k_B \log \Omega_1 + k_B \log \Omega_2 \Rightarrow S_{1 \cup 2} = S_1 + S_2$$

We now look for the equilibrium. So we are trying to maximize the following function:

$$S_{1\cup 2}(E_1, E_2 = E - E_1, V_1, V_2, N_1, N_2) = S_1(E_1) + S_2(E - E_1)$$

We see immediately that we need to maximize for E_1 so:

$$\text{equilibrium} = \max_{E_1} S(E_1)$$

So we obtain:

$$0 = \frac{\partial}{\partial E_1} S_{1\cup 2} = \left.\frac{\partial S_1}{\partial E_1}\right|_{\text{eq}} - \left.\frac{\partial S_2}{\partial E_2}\right|_{\text{eq}} = \frac{1}{T_1} - \frac{1}{T_2} \Rightarrow T_1 = T_2$$

Alternative (more rigorous) method.

Actually the previous description and factorization ($\Omega = \Omega_1 \times \Omega_2$) in ($\star$) is not obvious, because, while $E = E_1 + E_2$ is indeed constant, the energy E_1 is not fixed. In practice one should rather write:

$$\Omega(E) = \sum_{E_1} \Omega_1(E_1)\Omega_2(E - E_1) = \int \frac{\mathrm{d}E_1}{\Delta E}\, \Omega_1(E_1)\Omega_2(E - E_1)$$

In order to evaluate this integral, we will use the so-called saddle point method. The idea is that the functions $\Omega_i(E_i)$ are very sensitive functions of the energy: this is because $\Omega \sim e^{N\times s}$, with $s \sim \mathcal{O}(1)$ the entropy per particle and $N \sim 10^{23}$, so that any variation in s leads to a huge variation in Ω. Hence the integrand is extremely spiked at its maximum value and the integral is dominated by this maximum. To make this explicit, we thus write:

$$\Omega(E) = \int \frac{\mathrm{d}E_1}{\Delta E_1} e^{\frac{S_1(E_1)}{k_B} + \frac{S_2(E-E_1)}{k_B}}$$

and find the point where the integrand is maximum as a function of E_1. This maximum occurs for an energy E_1^* such that

$$\max_{E_1} S_1(E_1) + S_2(E - E_1) \Rightarrow \frac{1}{T_1}(E_1^*) = \frac{1}{T_2}(E_1^*)$$

Denote E_1^* the value for which the maximum is reached. Now we expand the integrand around its maximal value taken at $E_1 = E_1^*$:

$$S_1 + S_2(E_1) \simeq S_1(E_1^*) + S_2(E - E_1^*) + \left.\frac{\partial}{\partial E_1}(S_1 + S_2)\right|_{E_1^*} (E_1 - E_1^*) + \frac{1}{2}\left.\frac{\partial^2}{\partial E_1^2}(S_1 + S_2)\right|_{E_1^*} (E_1 - E_1^*)^2 + \dots$$

Then plugging this back in the integral we get:

$$\Omega(E) = e^{\frac{S_1(E_1^*) + S_2(E - E_1^*)}{k_B}} \int \frac{\mathrm{d}E_1}{\Delta E} e^{\frac{1}{2k_B} \left.\frac{\partial^2 (S_1+S_2)}{\partial E_1^2}\right|_{E_1^*} (E_1 - E_1^*)^2}$$

This is a Gaussian integral that we can compute exactly and we get :

$$\Omega(E) = e^{\frac{S}{k_B}} \sqrt{\frac{2\pi k_B}{\left|\left.\frac{\partial^2 S}{\partial E_1^2}\right|_{E_1^*}\right| \Delta E^2}}$$

Note that we take the absolute value because the entropy function is concave and its second derivative versus the energy is negative. We then deduce:

$$S_{\text{eq}} = k_B \log \Omega = \underbrace{S_1(E_1^*) + S_2(E - E_1^*)}_{\sim N} + \overbrace{\log \sqrt{\frac{2\pi k_B}{\left|\left.\frac{\partial^2 S}{\partial E_1^2}\right|_{E_1^*}\right| \Delta E^2}}}^{\sim \log N}$$

The last term is $\mathcal{O}(\log N)$ since $\frac{\partial^2 S}{\partial E_1^2} \sim 1/N$. Therefore in the thermodynamic limit $N \to \infty$, one gets:

$$S_{\text{eq}} = S_1(E_1^*) + S_2(E - E_1^*) \quad \text{with } E_1^* \text{ such that} \quad \frac{1}{T_1} = \frac{1}{T_2}$$

We therefore recover the above results, justifiying *a posteriori* the previous factorization ($\star$).

3.4.3 Pressure and chemical potential.

We can rewrite the previous results under a differential form as:

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}E \quad \text{when all the other parameters are fixed.}$$

More generally, if the systems depends on a state parameter X, then we define the thermodynamic force F, conjugate to X, by the following relation:

$$\mathrm{d}S = -\frac{F}{T}\mathrm{d}X \quad \text{so equivalently} \quad F = -T\left.\frac{\partial S}{\partial X}\right|_{\text{other parameters fixed}}$$

We will see that this formula is very general and identifies well with the standard expression for pressure and other forces. Now we write:

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}E - \sum_{\alpha}\frac{F_\alpha}{T}\mathrm{d}X_\alpha \quad \text{or equivalently} \quad \mathrm{d}E = T\mathrm{d}S + \sum_{\alpha}F_\alpha \mathrm{d}X_\alpha$$

Pressure.

If we say that we can make the volume vary, we have $X = V$ and we expect to get pressure as a conjugate force: $\delta W = -P\mathrm{d}V$. Indeed we get the expected formula:

$$P = -T\left.\frac{\partial S}{\partial V}\right|_{E,N} \Rightarrow \mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V$$

Chemical potential.

The chemical potential is a force that comes from the fact that the number of particles can vary. So we have $X = N$ then:

$$F = \mu = -T\left.\frac{\partial S}{\partial N}\right|_{E,V}$$

So we can write:

$$\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N$$

Equilibrium.

When we studied the previous system we only made the energy vary, but we could make the number of particles vary as well as the volume. Then we have that:

$$S = S_1 + S_2 = S_1(E_1, V_1, N_1) + S_2(E - E_1, V - V_1, N - N_1)$$

Then to maximize the entropy we have to cancel all the partial derivatives:

$$\left.\frac{\partial S}{\partial E_1}\right|_{\text{eq}} = 0 \Rightarrow \frac{1}{T_1} - \frac{1}{T_2} = 0$$
$$\left.\frac{\partial S}{\partial V_1}\right|_{\text{eq}} = 0 \Rightarrow \frac{P_1}{T_1} - \frac{P_2}{T_2} = 0$$
$$\left.\frac{\partial S}{\partial N_1}\right|_{\text{eq}} = 0 \Rightarrow -\frac{\mu_1}{T_1} + \frac{\mu_2}{T_2} = 0$$

So at equilibrium we require that:

$$\boxed{T_1 = T_2 \quad \text{and} \quad P_1 = P_2 \quad \text{and} \quad \mu_1 = \mu_2}$$

3.5 Examples

3.5.1 Back to the perfect gas.

Now back to the perfect gas, we have that:

$$S = k_B N \left(\log \left[\frac{V}{N} \left(\frac{4\pi m E}{3Nh^2} \right)^{3/2} \right] + \frac{5}{2} \right)$$

And applying the definitions we get that:

$$\begin{aligned} E &= \frac{3}{2} N k_B T \\ P &= \frac{N}{V} k_B T \\ \mu &= k_B T \log\left(\frac{N}{V} \lambda^3 \right) \qquad \text{where} \qquad \lambda = \sqrt{\frac{h^2}{2\pi m k_B T}} \end{aligned}$$

3.5.2 Ideal polymers and entropic forces

Let us consider a simple model of polymers, where we neglect interactions between monomers. We assume that the polymer is constituted of N connected monomers, with random orientations. We want to calculate the statistics of the polymers.

Length scales

Starting from an initial position of an initial monomer $\vec{R}_0 = 0$, the position of the other end of the polymer is

$$\vec{R}_N = \sum_{i=1}^{N} a \vec{u}_i$$

with a the length of a monomer, and $\vec{u}_i$ is a unit vector giving the direction of the monomer. In this model of an ideal polymer, this is a random variable. We deduce

$$\langle \vec{R}_N \rangle = \sum_{i=1}^{N} a \langle \vec{u}_i \rangle = 0$$

where $\langle . \rangle$ denotes an average over configurations of the polymer. Now,

$$\langle \vec{R}_N^2 \rangle = \langle \left(\sum_{i=1}^{N} a \vec{u}_i \right)^2 \rangle = a^2 \sum_{i,j} \langle \vec{u}_i \cdot \vec{u}_j \rangle$$

But, for $i \neq j$, $\langle \vec{u}_i \cdot \vec{u}_j \rangle = \langle \vec{u}_i \rangle \cdot \langle \vec{u}_j \rangle = 0$ since monomers are assumed independent in this model. For $i = j$, $\langle \vec{u}_i \cdot \vec{u}_j \rangle = \langle \vec{u}_i^2 \rangle = 1$. We deduce

$$\langle \vec{R}_N^2 \rangle = a^2 \times N$$

The end-to-end length of the polymer is therefore $\sim a \times \sqrt{N}$.

Statistics

Beyond the length scales, it is interesting to get further insights into the statistics of the polymer, i.e., the probability that the polymer is of a given length $\vec{R}$.

Let us consider a 1-dimensional version of this problem, the 3D generalization is obvious. In 1D, the length of the polymer is $X = a \sum_i \epsilon_i$, where $\epsilon_i = \pm 1$. We introduce N_+ the number of steps in the forward direction ($\epsilon_i > 0$), and N_- the number of steps in the forward direction ($\epsilon_i > 0$). One can rewrite the previous result as

$$X = a(N_+ - N_-)$$

with $N = N_+ + N_-$ the number of monomers.

The statistics follows from the simple combinatorics

$$p(X) = \binom{N}{N_+} p_0^{N_+} (1 - p_0)^{N_-}$$

with p_0 the probability that the direction is positive. We will assume that $p_0 = 1/2$ to simplify. Since one has simply $N_+ = (N + X/a)/2$ and $N_- = (N - X/a)/2$ Then

$$p(X) = \frac{N!}{\left(\frac{N+X/a}{2}\right)!\left(\frac{N-X/a}{2}\right)!}\left(\frac{1}{2}\right)^N$$

We introduce the reduced variable $x = X/Na$; one has for typical configurations that $x \ll 1$ (since $x \sim 1/\sqrt{N}$). Then using the Stirling formula to calculate $\log p(X)$, and expanding for small x, one obtains

$$p(X) = A \exp\left(-\frac{X^2}{2Na}\right)$$

where the factor A is obtained by normalization: $A = (2\pi Na^2)^{-1/2}$.

Entropic forces

Let us consider that we fix the end-to-end length of the polymer X. This parameter therefore acts as a 'constraint'. We can then calculate the entropy $S(X)$ as $S = k_B \log \Omega$, where Ω is the number of configurations for a given length X:

$$\Omega = \frac{N!}{N_+\, N_-!} = \frac{N!}{\left(\frac{N+X/a}{2}\right)!\left(\frac{N-X/a}{2}\right)!}$$

Using the previous results, we then immediatly deduce

$$S(X) = cst - \frac{k_B}{2Na^2}X^2$$

Since $dS = \frac{1}{T}dE - \frac{F}{T}dX$ then, the corresponding thermodynamic force F is obtained as $F = -T\left(\frac{\partial S}{\partial X}\right)_E$, i.e.

$$F = \frac{k_B T}{Na^2}X$$

This shows that the polymer behaves as a spring with a stiffness of entropic origin: $K = \frac{k_B T}{Na^2}$.

This points to the so-called 'entropic forces'. We will come back to this question in Chapter 6.

Chapter 4

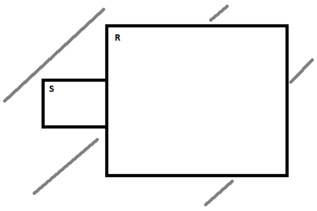
Canonical Ensemble.

The previous microcanonical ensemble corresponds to a situation where the system is insulated and the energy is fixed. But in practice, systems exchange energy with their surroundings and it is usually more relevant experimentally to fix the temperature. This corresponds to the N, V, T ensemble where the temperature, number of particle and volume are fixed.

Also, as we will also show in this chapter, calculating the partition function in the canonical ensemble prooves usually to be simpler than in the microcanonical ensemble (remember that results do not depend on the thermodynamic ensemble in the thermodynamic limit).

4.1 Principles and canonical probabilities.

To model a system of the canonical ensemble, we consider a system $\mathcal{S}$ connected to a huge reservoir R which, together, are isolated from the rest of the universe. Since the reservoir is huge, we consider it always at equilibrium: indeed fluctuations in $\mathcal{S}$ will negligibly influence the huge reservoir R. We set T_0 to be the temperature of the reservoir and the total energy is fixed:



$$E_{tot} \equiv E_{\mathcal{S}+R} = E_{\mathcal{S}} + E_R$$

Now we want to find what is the probability of a microstate s of the system $\mathcal{S}$ (say, with an energy E_s). We recall the main postulate of statistical physics:

In an isolated system all the microstates are equiprobable.

Then, since the total system $\mathcal{S} + R$ is in a microcanonical ensemble,

$$p_s = \frac{\Omega_R(E_R = E_{\text{tot}} - E_s)}{\Omega_{\text{tot}}}$$

The term $\Omega_R(E_R = E_{\text{tot}} - E_s)$ counts the *number of microstates of the reservoir* R associated with the (single) microstate s of the system $\mathcal{S}$ for that energy E_s, so that the total energy of the $R + \mathcal{S}$ system is E_{tot}. The probability to find the system in a microstate s is then equal to the ratio between this number to the total number of microstates of the $\mathcal{S} + R$ system.

The reservoir is supposed to be at equilibrium and we can thus rewrite :

$$\Omega_R(E_{\text{tot}} - E_s) = \exp\left[\frac{S_R}{k_B}(E_{\text{tot}} - E_s)\right]$$

Now since $\mathcal{S}$ is much smaller than the reservoir R, then $E_s \ll E_{\text{tot}} \sim E_R$ so we expand the entropy S_R for small E_S to write:

$$S_R(E_{\text{tot}} - E_s) \approx S_R(E_{\text{tot}}) - \underbrace{\left.\frac{\partial S_R}{\partial E}\right|_{\text{eq}}}_{\frac{1}{T_0}} E_S + \cdots$$

We then get the central result for the probability of a microstate s of the system $\mathcal{S}$ at temperature T_0:

$$\boxed{p_s = \frac{1}{Z}\exp\left(-\frac{E_s}{k_B T_0}\right)}$$

This is the Boltzmann-Gibbs distribution. The normalization of probability requires that:

$$\boxed{Z = \sum_s \exp\left(-\frac{E_s}{k_B T_0}\right)}$$

where the sum is over all *microstates* s of the system $\mathcal{S}$; Z is the partition function for the canonical ensemble.

4.2 Canonical partition function and Free Energy.

The free energy is defined as $F = E - TS$ with $T = T_0$. We now show that $F = -k_B T \log Z$.

First we compute what is the probability that the system $\mathcal{S}$ has an energy E within $\mathrm{d}E$, which we denote $p(E)\mathrm{d}E$. We are doing something similar to what was done previously for the micro-canonical ensemble. One has to count all microstates corresponding to the energy E_s. Then:

$$p(E)\mathrm{d}E = \frac{1}{Z} e^{-\frac{E}{k_B T_0}} \qquad \underbrace{\omega(E)}_{\#\text{ microstates of energy}E} \qquad \mathrm{d}E$$

ω counts the 'degeneracy', i.e. the number of micro-states associated to a given energy. By definition of the entropy, one has:

$$\omega(E) = e^{\frac{S(E)}{k_B}}$$

Plugging this back in, we get that:

$$p(E)\mathrm{d}E = \frac{1}{Z} e^{-\frac{E - T_0 S(E)}{k_B T_0}} \mathrm{d}E \quad \text{and} \quad \int p(E)\mathrm{d}E = 1$$

and we obtain:

$$Z = \int \mathrm{d}E e^{-\frac{E - T_0 S(E)}{k_B T_0}}$$

Now as previously we are going to use the saddle-point method since we expect that the integral is dominated by the maximum of the integrand. We accordingly calculate the maximum of the term in the exponential, i.e. the minimum of

$$\min_E (E - T_0 S(E))$$

Let us introduce $f(E) = E - T_0 S(E)$. Calculating the derivative with respect to E, we get:

$$0 = \frac{\partial f}{\partial E} = 1 - T_0 \frac{\partial S}{\partial E}\bigg|_{E^*} = 1 - \frac{T_0}{T_s} \Rightarrow T_s = T_0$$

Now we expand $f(E)$ around its minimum as

$$f(E) = f(E^*) + \cancelto{0}{f'(E^*)}(E - E^*) + \frac{1}{2} f''(E^*)(E - E^*)^2 + \dots$$

Plugging this back in the integral, one gets:

$$Z = \int \mathrm{d}E\, e^{-\frac{E^* - T_0 S(E^*)}{k_B T_0}} \times e^{-\frac{1}{2}\frac{f''(E^*)}{k_B T_0}(E - E^*)^2} = e^{-\frac{E^* - T_0 S(E^*)}{k_B T_0}} \sqrt{\frac{2\pi k_B T_0}{f''(E^*)}}$$

Therefore, in the thermodynamic limit $N \to \infty$, we can deduce that:

$$-\log Z = \frac{(E - TS)\Big|_{\text{eq}}}{k_B T_0} + \mathcal{O}(\log N) \approx \frac{(E - TS)\Big|_{\text{eq}}}{k_B T_0}$$

Altogether one has

$$\boxed{F = E - TS\Big|_{\text{eq}} = -k_B T_0 \log Z}$$

While in the microcanonical systems, we showed that the entropy is maximal at equilibirium, in the canonical systems, *the free energy* $F = E - T\,S$ *is minimal at equilibrium.*

Note that the general definition of the partition function is

$$Z = \sum_{microstates\, s} e^{-\frac{E_s}{k_B T}}$$

But for continuous (classical) systems we rather write:

$$\boxed{Z = \frac{1}{N!}\frac{1}{h^{3N}}\int \mathrm{d}\Gamma e^{-\frac{\mathcal{H}(\Gamma)}{k_B T}}}$$

As for the microcanonical ensemble, the factorial term $N!$ stems from indiscernability and the term h^{-3N} allows discretizing the energy levels and allow counting.

4.3 Fluctuations and thermodynamics.

For now we have always looked at the peak of functions and neglecting the small variations around them. Let us now estimates these fluctuations around equilibrim. From the previous computation we have :

$$p(E) \propto e^{-\frac{1}{2k_B T_0} f''(E^*)(E-E^*)^2}$$

and one can calculate the second moment of the energy distribution $\langle(\Delta E)^2\rangle$:

$$\langle(\Delta E)^2\rangle = \int \mathrm{d}E (E-E^*)^2 p(E) = \frac{\int \mathrm{d}E(E-E^*)^2 e^{-\frac{1}{2k_B T_0} f''(E^*)(E-E^*)^2}}{\int \mathrm{d}E e^{-\frac{1}{2k_B T_0} f''(E^*)(E-E^*)^2}}$$

In practice, we will often have to compute quantities of this form (moments of a gaussian distribution), and we will use the general result:

$$\langle x^2\rangle = \frac{\int \mathrm{d}x e^{-\alpha x^2} x^2}{\int \mathrm{d}x e^{-\alpha x^2}} = \frac{-\frac{\partial}{\partial\alpha}\int \mathrm{d}x e^{-\alpha x^2}}{\int \mathrm{d}x e^{-\alpha x^2}} = -\frac{\partial}{\partial \alpha}\log \underbrace{\int \mathrm{d}x e^{-\alpha x^2}}_{\sqrt{\frac{\pi}{\alpha}}} = \frac{1}{2\alpha}$$

Now if we apply this to our case we have $x = E - E^*$ and $\alpha = \frac{1}{2k_B T_0} f''(E^*)$. So we get that:

$$\langle(\Delta E)^2\rangle = \langle(E-E^*)^2\rangle = \frac{k_B T_0}{f''(E^*)}$$

It remains only to compute f'' and we have:

$$f'' = \frac{\partial^2}{\partial E^2}\left(E - T_0 S(E)\right) = 0 - T_0 \left.\frac{\partial^2 S}{\partial E^2}\right|_{\mathrm{eq}} = -T_0 \frac{\partial}{\partial E}\left(\frac{1}{T(E)}\right) = \frac{T_0}{T_{\mathrm{eq}}^2}\left.\frac{\partial T}{\partial E}\right|_{\mathrm{eq}} \quad \text{where } T_{\mathrm{eq}} = T_0$$

We introduce the heat capacity (at fixed volume):

$$C_v = \left.\frac{\partial E}{\partial T}\right|_{\mathrm{eq},N,V}$$

Then we get that:

$$\boxed{\langle \Delta E^2\rangle = k_B T_0^2 C_V}$$

Now to check the validity of our previous approximations in using the saddle-point approximation for the partition function, we can calculate how peaked is the energy around its mean-value:

$$\frac{\Delta E}{E} \sim \frac{\sqrt{\langle\Delta E^2\rangle}}{E} \sim \frac{\sqrt{kT^2 C_V}}{E} \sim \frac{1}{\sqrt{N}} \to 0$$

This validates therefore the previous derivations.

Alternative method

Another way to derive the above results is to use the general probability of a microstate:

$$p_s = \frac{1}{Z} e^{-\frac{E_s}{k_B T}} \qquad \text{with} \qquad Z = \sum_s e^{-\frac{E_s}{k_B T}}$$

So we get for the mean energy $\langle E \rangle \equiv \bar{E}$:

$$\bar{E} = \sum_s E_s p_s = \sum_s E_s \frac{1}{Z} e^{-\frac{E_s}{k_B T}} = \sum_s \frac{1}{Z}\left(-\frac{\partial}{\partial \beta} e^{-\beta E_s}\right) = \frac{1}{Z} \cdot -\frac{\partial}{\partial \beta} \sum_s e^{-\beta E_s} = -\frac{1}{Z}\frac{\partial}{\partial \beta} Z$$

So we have that:

$$\bar{E} = -\frac{\partial}{\partial \beta} \log Z \text{ and } \qquad F = -k_B T \log Z$$

So we can re-write this as:

$$\boxed{\bar{E} = \frac{\partial}{\partial \beta}(\beta F)}$$

Now reminding the thermodynamic formula

$$F = E - TS \Rightarrow \beta F = \beta E - \frac{S}{k_B}$$

one can write the previous equation as:

$$\bar{E} = -T^2 \frac{\partial}{\partial T}\left(\frac{F}{T}\right) \qquad \text{since} \qquad \mathrm{d}\beta = \mathrm{d}\frac{1}{k_B T} = \frac{1}{k_B}\frac{-\mathrm{d}T}{T^2}$$

Now looking at the fluctuations, and using the same method, we also get that:

$$\bar{E^2} = \sum_s E_s^2 p_s = \sum_s E_s^2 \frac{e^{-\beta E_s}}{Z} = \frac{1}{Z}\frac{\partial^2}{\partial \beta^2} Z$$

Putting the two results together we have that:

$$\langle (E-\bar{E})^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right)^2 = \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right)$$

which we can re-write as:

$$\langle (E-\bar{E})^2 \rangle = \frac{\partial^2}{\partial \beta^2}(-\beta F)$$

Now,

$$\bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} \qquad \text{and} \qquad \langle (E-\bar{E})^2 \rangle = -\frac{\partial}{\partial \beta}\bar{E}$$

So we get that:

$$\langle (E-\bar{E})^2 \rangle = k_B T^2 \frac{\partial E}{\partial T} = k_B T^2 C_V$$

Thermodynamics.

Let's gather the various thermodynamics results. Remember that thermodynamics does fix the extensive quantities, like the energy, to be equal to their average values.

In this chapter we introduced the free energy:

$$F = E - TS$$

We saw that the energy of the system has very small fluctuations around its mean value and it is obtained from the free energy according to:

$$E = \bar{E} = -T^2 \frac{\partial}{\partial T}\left(\frac{F}{T}\right)$$

The entropy can be expressed as:

$$S = \frac{E-F}{T} = -T\frac{\partial}{\partial T}\left(\frac{F}{T}\right) - \frac{F}{T} = \frac{F}{T} - \frac{\partial F}{\partial T} - \frac{F}{T} = -\frac{\partial F}{\partial T}$$

Differential form.

The differential form of the energy is given by:

$$\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N + \sum_\alpha \mathcal{F}_\alpha \mathrm{d}X_\alpha$$

Then since $F = E - TS$ we also get that:

$$\mathrm{d}F = \mathrm{d}E - S\mathrm{d}T - T\mathrm{d}S = -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}N + \sum_\alpha \mathcal{F}_\alpha \mathrm{d}X_\alpha$$

And we have that:

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V,X_\alpha} \qquad \text{and} \qquad P = -\left.\frac{\partial F}{\partial V}\right|_{N,T,X_\alpha} \qquad \text{and} \qquad \mathcal{F}_\alpha = \left.\frac{\partial F}{\partial X_\alpha}\right|_{N,V,T,X_{\beta\neq\alpha}}$$

4.4 The perfect gas.

4.4.1 Partition Function.

For a perfect gas, all interactions between particles are omitted/neglected and the hamiltonian reduces to

$$\mathcal{H} = \sum_i \frac{\vec{p_i}^2}{2m} + 0$$

Then the (classical) partition function is then given by:

$$Z = \frac{1}{N!}\frac{1}{h^{3N}} \int \mathrm{d}\vec{r_1} \cdots \mathrm{d}\vec{r_N} \mathrm{d}\vec{p_1} \cdots \mathrm{d}\vec{p_N} e^{-\beta\mathcal{H}(\vec{p_i},\vec{r_i})}$$

Since the Hamiltonian is independent of positions we immediately calculate the integral over positions to obtain:

$$Z = \frac{1}{N!}\frac{1}{h^{3N}} V^N \int \mathrm{d}\vec{p_1} \cdots \mathrm{d}\vec{p_N} e^{-\beta \sum_i \frac{\vec{p_i}^2}{2m}}$$

Finally, the exponentials of kinetic terms do factorize and we get the same integral to a power of N, as:

$$Z = \frac{1}{N!}\frac{1}{h^{3N}} V^N \left(\int \mathrm{d}\vec{p_1} e^{\frac{-\beta\vec{p_1}^2}{2m}}\right)^N = \frac{1}{N!}\frac{1}{h^{3N}} V^N \left(2\pi m k_B T\right)^{3/2}$$

Once again we introduce the De Broglie wavelength:

$$\lambda = \sqrt{\frac{h^2}{2\pi m k_B T}}$$

And the perfect gas partition function takes the expression:

$$Z = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N$$

4.4.2 Thermodynamics.

We now check that this result is consistent with the standard thermodynamic theory of the perfect gas. First the free energy is:

$$\begin{aligned} F = -k_B T \log Z = -k_B T \log\left(\frac{V^N}{N!\lambda^{3N}}\right) &= -k_B T N \left(\log\frac{V}{\lambda^3} - (\log N - 1)\right) \\ = k_B T N(\log\rho\lambda^3 - 1) \quad &\text{where } \rho = \frac{N}{V} \end{aligned}$$

We introduce the free energy per unit volume, $f = \frac{F}{V}$, which takes the following compact expression for the perfect (ideal) gas :

$$f_{id} = k_B T\left(\rho\log(\rho\lambda^3) - \rho\right)$$

The average energy is (omitting the $\bar{E}$ notation to simplify):

$$E = -T^2 \frac{\partial}{\partial T}\left(\frac{F}{T}\right) = -Nk_B T^2 \frac{\partial}{\partial T}\left(\log \rho\lambda^3 - 1\right)$$

Now we compute the derivative:

$$\frac{\partial}{\partial T}\log \lambda^3 = -\frac{3}{2T}$$

and deduce

$$E = \frac{3}{2}Nk_B T$$

Then the entropy is given by:

$$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N} = -Nk_B(\log \rho\lambda^3 - 1) - Nk_B T\frac{\partial}{\partial T} = -Nk_B(\log \rho\lambda^3 - 1 - \frac{3}{2}) = -Nk_B(\log \rho\lambda^3 - \frac{5}{2})$$

For the pressure we have:

$$P = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = Nk_B T\frac{\partial}{\partial V}\left(\log \rho\lambda^3 - 1\right) = \frac{N}{V}k_B T = \rho k_B T$$

Finally for the chemical potential we have:

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V} = k_B T\frac{\partial}{\partial N}\left(N\log \frac{N}{V}\lambda^3 - N\right) = k_B T\log \rho\lambda^3$$

Note that if we consider back the interactions of a system, as long as the interactions do not depend on velocity, one has:

$$Z = Z_{\text{ideal}} \cdot Z_{\text{interactions}} \quad \text{and} \quad F = F_{\text{id}} + F_{\text{int}}$$

4.5 Equipartition and consequences.

4.5.1 Kinetic energy

Imagine we have a Hamiltonian of the form:

$$\mathcal{H} = \sum_i \frac{1}{2m}\vec{p_i}^2 + V(\vec{r_1}, \cdots, \vec{r_N})$$

Then the average of any kinetic term derives as:

$$\begin{aligned}
\langle\frac{1}{2m}p_{1,x}^2\rangle &= \frac{\int \mathrm{d}\vec{r_1}\cdots\mathrm{d}\vec{r_N}\mathrm{d}\vec{p_1}\cdots\mathrm{d}\vec{p_N}\frac{1}{2}\frac{p_{1,x}^2}{m}e^{-\frac{\sum_i \frac{1}{2m}\vec{p_i}^2 + V(\vec{r_1},\cdots,\vec{r_N})}{k_B T}}}{\int \mathrm{d}\vec{r_1}\cdots\mathrm{d}\vec{r_N}\mathrm{d}\vec{p_1}\cdots\mathrm{d}\vec{p_N}e^{-\frac{\sum_i \frac{1}{2m}\vec{p_i}^2 + V(\vec{r_1},\cdots,\vec{r_N})}{k_B T}}} \\
&= \frac{\int \mathrm{d}\vec{r_1}\cdots\mathrm{d}\vec{r_N}e^{-\beta V(\vec{r_1},\cdots,\vec{r_N})}\int \mathrm{d}\vec{p_1},\cdots,\mathrm{d}\vec{p_N}\frac{1}{2m}p_{1,x}^2 e^{-\sum_i \frac{p_i^2}{2mk_B T}}}{\int \mathrm{d}\vec{r_1},\cdots,\mathrm{d}\vec{r_N}e^{-\beta V(\vec{r_1},\cdots,\vec{r_N})}\int \mathrm{d}\vec{p_1}\cdots\mathrm{d}\vec{p_N}e^{-\sum_i \frac{p_i^2}{2mk_B T}}} \\
&= \frac{\int \mathrm{d}p_{1,x}\frac{p_{1,x}^2}{2m}e^{-\beta\frac{p_{1,x}^2}{2m}}}{\int \mathrm{d}p_{1,x}e^{-\beta\frac{{p_{1,x}}^2}{2m}}} = \frac{-\frac{\partial}{\partial\beta}\int \mathrm{d}p_{1,x}\exp\left(-\beta\frac{p_{1,x}^2}{2m}\right)}{\int \mathrm{d}p_{1,x}\exp\left(-\beta\frac{p_{1,x}^2}{2m}\right)} \\
&= -\frac{\partial}{\partial\beta}\log\underbrace{\int \mathrm{d}p_{1,x}e^{-\beta\frac{p_{1,x}^2}{2m}}}_{\sqrt{2m\frac{\pi}{\beta}}} = \frac{1}{2\beta}
\end{aligned}$$

So finally we obtain:

$$\langle\frac{1}{2m}p_{1,x}^2\rangle = \frac{1}{2}k_B T$$

4.5.2 Generalization

This result can be generalized to any quadratic hamiltonian. Indeed the Hamiltonian takes the form:

$$\mathcal{H} = \frac{1}{2}\alpha\dot{q}^2 + V(q)$$

then one can show immediately that:

$$\langle\frac{1}{2}\alpha\dot{q}^2\rangle = \frac{1}{2}k_BT$$

In fact this results is even generalizable to some Hamiltonian of the form:

$$\mathcal{H} = \frac{1}{2}\alpha(y)\dot{q}^2 + V(y,q)$$

In conclusion the take-away message is that each quadratic term averages to $\frac{1}{2}k_BT$, hence $\frac{1}{2}k_BT$ **per degree of freedom for which the Hamiltonian has a quadratic dependence**.

4.5.3 Calorific capacity

Perfect Gas.

In a perfect mono-atomic gas we previously had:

$$\mathcal{H} = \sum_i \frac{p_i^2}{2m} \quad \text{and} \quad E = \frac{3}{2}Nk_BT \quad \text{and} \quad C_V = \frac{3}{2}Nk_B$$

Solid.

We model a solid as a lattice of atoms where every bond between atoms is a spring. Then we have 3 extra-degrees of freedom per atom coming from the elasticity of the spring. So for each atom we have 6 degrees of freedom, and each of these have a quadratic dependence in the Hamiltonian so by the previous reasoning we get that:

$$\bar{E} = \frac{6}{2}Nk_BT = 3Nk_BT \quad \text{and} \quad C_V = 3Nk_B$$

Di-atomic gas.

We can model a di-atomic gas by each particle being two atoms connected by a spring. Then we have 3 degrees of freedom from translation, 2 degrees of freedom from Euler's angles and 2 degrees of freedom from the spring. So in total we have $7N$ degrees of freedom that are quadratic in the Hamiltonian so we get:

$$E = \frac{7}{2}Nk_BT \quad \text{and} \quad C_V = \frac{7}{2}Nk_B$$

4.6 Example: classic model of paramagnetism

We consider a simple model for a paramagnetic system. Each particle (with fixed position) has a magnetic moment $\vec{\mu_c}$, and we neglect the interactions between the magnetic dipoles to consider only the interaction with an extenally applied magntique field, $\vec{B}$. The hamiltonian is simply:

$$\mathcal{H} = -\sum_i \vec{\mu_i}\cdot\vec{B}$$

and the partition function is defined as:

$$Z = \int \frac{\mathrm{d}\Omega_1}{4\pi}\cdots\frac{\mathrm{d}\Omega_N}{4\pi}e^{-\frac{1}{k_BT}\mathcal{H}}$$

Note that we did not include the $N!$ term because here the particles are discernable, since they are each fixed at a given position. Then we can re-write the equation above as:

$$Z = z_1^N \quad \text{with } z_1 = \int \frac{\mathrm{d}\Omega_1}{4\pi}e^{\frac{\vec{\mu_1}\cdot\vec{B}}{k_BT}} = \int \frac{\sin\theta\mathrm{d}\theta\mathrm{d}\varphi}{4\pi}e^{\frac{\mu B\cos\theta}{k_BT}} = \frac{1}{2}\int_{-1}^{1}\mathrm{d}x e^{\frac{\mu B}{k_BT}x} = \frac{k_BT}{\mu B}\sinh\left(\frac{\mu B}{k_BT}\right)$$

Then the average magnetic moment is

$$\langle \mu_{1,z} \rangle = \frac{\int \frac{\mathrm{d}\Omega}{4\pi} \mu \cos\theta e^{\frac{\mu B}{k_B T}\cos\theta}}{\int \frac{\mathrm{d}\Omega}{4\pi} e^{\frac{\mu B}{k_B T}\cos\theta}} = \mu \frac{\int \sin\theta \mathrm{d}\theta \cos\theta \exp\left(\frac{\mu B}{k_B} T \cos\theta\right)}{\int \sin\theta \mathrm{d}\theta \exp\left(\frac{\mu B}{k_B T}\cos\theta\right)} = \mu \frac{\int_{-1}^{1} \mathrm{d}x x e^{\frac{\mu B}{k_B T} x}}{\int_{-1}^{1} \mathrm{d}x e^{\frac{\mu B}{k_B T} x}}$$

Integrating by parts we obtain that:

$$\langle \mu_z \rangle = \mu \frac{\cosh \frac{\mu B}{k_B T} - \frac{k_B T}{\mu B} \sinh \frac{\mu B}{k_B T}}{\sinh \frac{\mu B}{k_B T}} = \mu \mathcal{L}\left(\frac{\mu B}{k_B T}\right)$$

where we introduced Langevin's function:

$$\mathcal{L}(x) = \frac{1}{\tanh x} - \frac{1}{x}$$

One of the properties of Langevin's function that for $x \ll 1$ we have $\mathcal{L}(x) \approx \frac{x}{3}$, so for small magnetic interactions we have:

$$\langle \mu_z \rangle = \frac{\mu^2}{3 k_B T} B \quad \text{and } \chi = \frac{\mu^2}{3 k_B T} \text{ is called the magnetic susceptibility}$$

Note that this very simple model forgets about interactions. We will come back to the role of interactions in a later chapter and show that this leads to phase transition of the material and symmetry breaking.

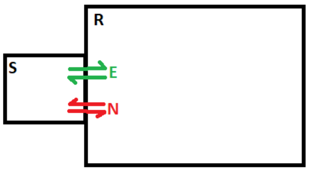
Chapter 5

Grand canonical ensemble.

We now introduce a further Gibbs ensemble, in which the system under consideration exchanges both energy and particles with the external world. This corresponds to the μ, V, T ensemble where the temperature, chemical potential and volume are fixed. We will define the associated partition function and thermodynamic potential.

5.1 Principles and grand canonical partition function.

In the grand canonical ensemble we allow for an exchange of energy E and particles N between the system $\mathcal{S}$ and the reservoir R. The total system $\mathcal{S}+R$ is isolated. The probability of a microstate s derives from the same analysis as done for the canonical ensemble. In the present case, both the total energy



$$E_{tot} \equiv E_{\mathcal{S}+R} = E_{\mathcal{S}} + E_R$$

and total number of particles

$$N_{tot} \equiv N_{\mathcal{S}+R} = N_{\mathcal{S}} + N_R$$

are fixed. Now we want to find what is the probability of a microstate s of the system $\mathcal{S}$ (say, with an energy E_s and number of particles N_s). Then, since the total system $\mathcal{S}+R$ is in a microcanonical ensemble, and the probability of a microstate s of the system $\mathcal{S}$ is accordingly

$$p_s = \frac{\Omega_R(E_R = E_{\text{tot}} - E_s, N_R = N_{tot} - N_s)}{\Omega_{\text{tot}}}$$

since all the microstates of the isolated system are equiprobable.

The term $\Omega_R(E_R = E_{\text{tot}} - E_s, N_R = N_{\text{tot}} N_s)$ counts the *number of microstates of the reservoir* R associated with the (single) microstate s of the system $\mathcal{S}$ for that energy E_s and number of particles N_s, such that the total energy of the $R+\mathcal{S}$ system is E_{tot} and total number of particles is N_{tot}. The probability to find the system in a microstate s is then equal to the ratio between this number to the total number of microstates of the $\mathcal{S}+R$ system.

Now since the reservoir is supposed to be at equilibrium, we can rewrite :

$$\Omega_R(E_{\text{tot}} - E_s, N_{\text{tot}} - N_s) = \exp\left[\frac{S_R}{k_B}(E_{\text{tot}} - E_s, N_{\text{tot}} - N_s)\right]$$

Now since $\mathcal{S}$ is much smaller than the reservoir R, then $E_s \ll E_{\text{tot}} \sim E_R$ and $N_s \ll N_{\text{tot}}$, and we expand the entropy S_R for small E_s and small N_s to write:

$$S_R(E_{\text{tot}} - E_s, N_{\text{tot}} - N_s) \approx S_R(E_{\text{tot}}, N_{\text{tot}}) - \underbrace{\left.\frac{\partial S_R}{\partial E}\right|_{\text{eq}}}_{\frac{1}{T_0}} E_s - \underbrace{\left.\frac{\partial S_R}{\partial N}\right|_{\text{eq}}}_{-\frac{\mu_0}{T_0}} N_s \cdots$$

where T_0 and μ_0 are the temperature and chemical potential of the reservoir, respectively. In the following we drop the label "0" to simplify notations. We then get the central result for the probability of a microstate s of the system $\mathcal{S}$ at temperature T:

$$\boxed{p_s = \frac{e^{\frac{1}{k_B T}(\mu N_s - E_s)}}{\Theta}}$$

Here Θ is the grand canonical partition function which is defined as:

$$\boxed{\Theta(\mu, V, T) = \sum_{\text{microstates } s} e^{\frac{1}{k_B T}(\mu N_s - E_s)}}$$

An alternative way of writing the grand canonical partition function is to sum over the number of particles of the system $\mathcal{S}$:

$$\Theta = \sum_s e^{\frac{1}{k_B T}(\mu N_s - E_s)} = \sum_N \sum_{s(N)} e^{\frac{1}{k_B T}(\mu N_s - E_s)} = \sum_N e^{\frac{\mu N}{k_B T}} \underbrace{\sum_{s(N)} e^{-\frac{E_s}{k_B T}}}_{Z_N}$$

$$\boxed{\Theta(\mu, V, T) = \sum_{N=0}^{+\infty} e^{\beta\mu N} Z_N = \sum_{N=0}^{+\infty} e^{\beta(\mu N - F_N)}}$$

where $F_N = -k_B T \log Z_N$ the free energy of the system $\mathcal{S}$ calculated for a fixed number N of particles.

5.2 Grand Potential.

We define the grand potential as:

$$\Omega(\mu, V, T) = -k_B T \log \Theta$$

(do not confuse the notation $\Omega(\mu, V, T)$ with the number of micro-states).

We now show that

$$\Omega(\mu, V, T) = F - \mu N = -p(\mu, T) \times V$$

Expression of Ω.

The probability that the system $\mathcal{S}$ has N particles is

$$p_N = \frac{e^{\beta\mu N} Z_N}{\Theta}$$

Normalization requires that $\sum_{N=1}^{+\infty} p_N = 1$, showing again that $\Theta = \sum_{N=1}^{+\infty} e^{\beta\mu N} Z_N$, as obtained above.

We can see immediately that p_N is very spiked to its average value, i.e $\Delta N \ll \bar{N}$. Then, as done previously we use the saddle point method to calculate this serie. First we re-write:

$$\Theta = \sum_N e^{\beta\mu N} Z_N = \sum_N e^{\beta(\mu N - F_N)}$$

Writing the sum as a continuous integral, we rewrite it as

$$\Theta = \int \mathrm{d}N \, e^{\beta(\mu N - F_N)}$$

The maximum of the exponential is obtained for:

$$\frac{\partial}{\partial N} = 0 \Leftrightarrow \mu = \left.\frac{\partial F}{\partial N}\right|_{N^*}$$

And we write:

$$[\mu N - F_N](N) \approx \mu N^* - F_{N^*} + \cancelto{0}{\left.\frac{\partial}{\partial N}(\mu N - F_N)\right|_{N^*}} (N - N^*) + \frac{1}{2}\frac{\partial^2}{\partial N^2}(\mu N - F_N)\bigg|_{N^*} (N - N^*)^2 + \cdots$$

Then plugging this back in the integral we have:

$$\Theta \approx \int \mathrm{d}N e^{\beta(\mu N^* - F_{N^*})} e^{\frac{\beta}{2}\frac{\partial^2}{\partial N^2}(\mu N - F_N)\big|_{N^*}(N-N^*)^2} = e^{\beta(\mu N^* - F_{N^*})} \underbrace{\sqrt{\frac{2\pi k_B T}{-\frac{\partial^2}{\partial N^2}(\mu N - F_N)\big|_{N^*}}}}_{\sim\sqrt{N}}$$

Hence we obtain the result:

$$\boxed{\Omega = -k_B T \log \Theta \approx F - \mu N}$$

This result can be further simplified to $\Omega = -pV$. To do so, we first start by deriving the Gibbs-Duhem relation.

Relation of Gibbs-Duhem.

The relation of Gibbs-Duhem says that μ, P, T are not independent variables. We already showed:

$$\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}N, \quad \mu = \left.\frac{\partial F}{\partial N}\right|_{T,V}, \quad P = -\left.\frac{\partial F}{\partial V}\right|_{T,N}$$

Since F is an extensive variable we know that we can write it as:

$$F(N,V,T) = Vf(\frac{N}{V},T) = Vf(\rho,T)$$

Then:

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{V,T} = V\frac{1}{V}\left.\frac{\partial f}{\partial \rho}\right|_{T} = \left.\frac{\partial f}{\partial \rho}\right|_{T}$$

And similarly:

$$P = -\left.\frac{\partial F}{\partial V}\right|_{N,T} = -\frac{\partial}{\partial V}\left[Vf(\frac{N}{V},T)\right] = -f(\rho,T) - V\left.\frac{\partial}{\partial V}f(\frac{N}{V},T)\right|_{T,N} = -f - V\left.\frac{\partial}{\partial \rho}f(\rho,T)\right|_{T}\left.\frac{\partial \rho}{\partial V}\right|_{T} = -f + \rho\left.\frac{\partial f}{\partial \rho}\right|_{T}$$

So we can re-write this was:

$$P = -f + \mu\rho \text{ therefore } PV = -F + \mu N$$

Therefore going back to our previous result we get that:

$$\boxed{\Omega = F - \mu N = -pV}$$

We now introduce the free enthalphy which is given by:

$$\boxed{G = F + PV = \mu N \quad \text{so} \quad \mu = \frac{G}{N}}$$

Differential version of Gibbs-Duhem.

To write the Gibbs-Duhem in differential form, we start from

$$\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}N$$

and we do a Legendre transformation to get:

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}\rho + \mu\mathrm{d}N \text{ and we have } \mathrm{d}G = \mathrm{d}(\mu N) = N\mathrm{d}\mu + \mu\mathrm{d}N$$

So finally we get the following relation:

$$\boxed{N\mathrm{d}\mu = -S\mathrm{d}T + V\mathrm{d}P}$$

Average number of particles.

With T fixed the previous equation can be written as:

$$\bar{N} = V\left.\frac{\partial P}{\partial \mu}\right|_{T} = -\left.\frac{\partial \Omega}{\partial \mu}\right|_{T,V}$$

5.3 Alternative calculation of the grand canonical partition function

We consider two volumes which can exchange particles. The temperature is fixed to T and the volumes and number of each container are V_1, N_1 and $V_2\,N_2$; $V = V_1 + V_2$ is the total volume and $N = N_1 + N_2$ is the total number of particles (both fixed). The total system is thus treated in the canonical ensemble but we are interested in the statistics and grand partition function of the container 1. We will assume in the calculation that the container 2 is much larger than the container 1.

The partition function for the overall system (with fixed N) is

$$\begin{aligned} Z(N,V,T) &= \frac{1}{h^{3N}N!} \times \sum_{N_1=0}^{N_1=N} \frac{N!}{N_1!N_2!} \int d\Gamma_1 \int d\Gamma_2 \; e^{-\beta \mathcal{H}(\Gamma_1)+\mathcal{H}(\Gamma_2)} \\ &= \sum_{N_1=0}^{N_1=N} Z_1(N_1,V_1,T) \times Z_2(N_2,V_2,T) \end{aligned} \tag{5.1}$$

Note that the factor $N!/N_1!N_2!$ in the first line can be interpreted as the number of combinations to distribute N_1 particles in the container 1 and N_2 particles in the container 2, given $N = N_1 + N_2$. Hence we deduce that

$$\sum_{N_1=0}^{N_1=N} Z_1(N_1,V_1,T) \times \frac{Z_2(N_2,V_2,T)}{Z_N(N,V,T)} = 1 \tag{5.2}$$

Introducing the free energy $F(N,V,T) = -k_B T \log Z_N$, one has

$$\frac{Z_2}{Z_N} = \frac{Z(N_2,V_2,T)}{Z(N,V,T)} = \frac{\exp[-\beta F(N-N_1, V-V_1, T)]}{\exp[-\beta F(N,V,T)]} \tag{5.3}$$

Note that we implicitly assume that the two systems are made of identical particles and same hamiltonian, so that the partition functions are identical (but for different number of particles and volume).

Now assuming that the container 2 is much larger than the container 1 and $N_1 \ll N$, one can write

$$F(N-N_1, V-V_1, T) \simeq F(N,V,T) - \frac{\partial F}{\partial N} \times N_1 - \frac{\partial F}{\partial V} V_1 \tag{5.4}$$

Using $\frac{\partial F}{\partial N}\big|_{V,T} = \mu$ and $\frac{\partial F}{\partial V}\big|_{V,T} = -P$, this gives

$$\sum_{N_1=0}^{N_1=N} Z_1(N_1,V_1,T) \times e^{-\beta[-\mu N_1 + PV_1]} = 1 \tag{5.5}$$

so that

$$\sum_{N_1=0}^{N_1=N} Z_1(N_1,V_1,T) \times e^{\frac{\mu N_1}{k_B T}} = e^{\frac{PV_1}{k_B T}} \tag{5.6}$$

One recognizes the grand partition function for the system 1 which is defined here as

$$\Theta_1(\mu, V_1, T) = \sum_{N_1=0}^{N} e^{\beta \mu N_1} Z(N_1, V_1, T)$$

so that

$$\Theta_1(\mu, V_1, T) = e^{\frac{PV_1}{k_B T}} \tag{5.7}$$

and the grand potential $\Omega = -k_B T \log \Theta$ reduces to

$$\Omega_1 = -P\, V_1 \tag{5.8}$$

5.4 Fluctuations and statistics.

We showed previously that:

$$p_N \approx \frac{1}{\Theta} \exp[\beta(\mu N^* - F_{N^*})] \exp\left[\frac{1}{2k_B T} \frac{\partial^2}{\partial N^2} (\mu N - F_N) \bigg|_{N^*} (N-N^*)^2 \right]$$

From this we can deduce that:

$$\langle (N-N^*)^2 \rangle = \frac{k_B T}{-\frac{\partial^2}{\partial N^2} (\mu N - F_N) \Big|_{N^*}}$$

And we can re-write:

$$-\frac{\partial^2}{\partial N^2} = \frac{\partial^2 F_N}{\partial N^2}\bigg|_{T,V} = \frac{\partial}{\partial N}\mu\bigg|_{T,V} \quad \text{with in the last equality } \mu = \frac{\partial F}{\partial N}$$

Using Gibbs-Duhem with fixed temperature, one gets

$$N\mathrm{d}\mu = V\mathrm{d}P \Rightarrow \frac{\partial \mu}{\partial N}\bigg|_T = \frac{V}{N}\frac{\partial P}{\partial N}\bigg|_T \text{ then } \frac{\partial^2 F}{\partial N^2} = \frac{\partial \mu}{\partial N}|_{T,V} = \frac{V}{N}\frac{\partial P}{\partial N}\bigg|_T$$

We define the compressibility factor as:

$$\chi_T = \frac{1}{V}\frac{\partial V}{\partial P}\bigg|_T$$

Then:

$$\frac{\partial P}{\partial N} = \frac{\partial P}{\partial \rho}\frac{\partial \rho}{\partial N} = \frac{1}{V}\frac{\partial P}{\partial \rho} \text{ and } \frac{\partial P}{\partial V} = \frac{\partial P}{\partial \rho}\frac{\partial \rho}{\partial V} = -\frac{N}{V^2}\frac{\partial P}{\partial \rho}$$

so that

$$\frac{\partial P}{\partial N} = \frac{1}{V}\frac{-V^2}{N}\frac{\partial P}{\partial V} = -\frac{V}{N}\frac{\partial P}{\partial V} = \frac{1}{N\chi_T}$$

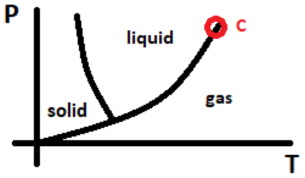
and

$$\frac{\partial^2 F}{\partial N^2}\bigg|_{T,V} = \frac{V}{N}\frac{\partial P}{\partial N}\bigg|_T = \frac{V}{N^2\chi_T}$$

Altogether we can re-write the result above as:

$$\boxed{\langle (N - N^*)^2\rangle = N\rho\chi_T k_B T}$$

This is a main result that contains a lot of physics. First of all one may note that $\Delta N = \sqrt{\langle (N-N^*)^2\rangle} \sim \sqrt{N}$ so that $\frac{\Delta N}{N} \sim \frac{1}{\sqrt{N}} \to 0$. This relationship also demonstrates that χ_T must be positive. This is what is called a condition of stability. The states that violate this condition are unstable. Furthermore, if we look at a system close to the critical point where the transition in between liquid and gas stops (meaning that we cannot really differentiate our system as a liquid or a solid) then $\frac{\partial P}{\partial V} \overset{(C)}{\to} 0$ so $\chi_T \overset{(C)}{\to} \infty$ therefore:



$$\langle (N - N^*)^2\rangle \overset{(C)}{\to} \infty$$

So we see that the fluctuations diverge at a critical point.

5.5 Alternative Approach (again).

The probability to find the system with N particles is

$$p_N = \frac{e^{\beta(\mu N - F_N)}}{\Theta}$$

and by definition

$$\bar{N} = \langle N\rangle = \sum_N N p_N = \sum_N N\frac{e^{\beta(\mu N - F_N)}}{\Theta}$$

So we can re-write:

$$\bar{N} = \frac{1}{\beta\Theta}\frac{\partial}{\partial \mu}\underbrace{\sum_N e^{\beta(\mu N - F_N)}}_{\Theta} = \frac{k_B T}{\Theta}\frac{\partial \Theta}{\partial \mu} = k_B T\frac{\partial}{\partial \mu}\log\Theta$$

Therefore

$$\bar{N} = -\frac{\partial}{\partial \mu}\Omega \text{ where } \Omega = -k_B T\log\Omega$$

Similarly we have that:

$$\langle N^2\rangle = \sum_N N^2 p_N = \frac{1}{\beta^2\Theta}\frac{\partial^2}{\partial \mu^2}\Theta$$

So we get that:

$$\langle (N - N^*)^2\rangle = \langle N^2\rangle - \langle N\rangle^2 = (kT)^2\left[\frac{1}{\Theta}\frac{\partial^2\Theta}{\partial \mu^2} - \frac{1}{\Theta^2}\left(\frac{\partial \theta}{\partial \mu}\right)^2\right] = (k_B T)^2\frac{\partial}{\partial \mu}\left(\frac{1}{\Theta}\frac{\partial \Theta}{\partial \mu}\right) = k_B T\frac{\partial^2}{\partial \mu^2}\Omega = k_B T\frac{\partial \bar{N}}{\partial \mu}$$

This is the same result as above.

5.6 The perfect gas in the grand canonical ensemble

In a system with no interaction we have:

$$\Theta = \sum_s e^{\frac{\mu N_s}{k_B T} - \frac{E_s}{k_B T}} = \sum_N e^{\beta\mu N} Z_N$$

We already calculated Z_N for the perfect gas so we know:

$$Z_N = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N \qquad \text{where} \qquad \lambda = \sqrt{\frac{h^2}{2\pi m k_B T}}$$

So we get that:

$$\Theta = \sum_N e^{\beta\mu N} \cdot \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N = \sum_N = \frac{1}{N!}\left(\frac{Ve^{\beta\mu}}{\lambda^3}\right)^N = \exp\left(\frac{Ve^{\beta\mu}}{\lambda^3}\right)$$

Which gives:

$$\Omega = -k_B T \log\Theta = -k_B T \frac{V}{\lambda^3} e^{\beta\mu}$$

Pressure.

We know that $\Omega = -PV$ so we get immediately that:

$$P(\mu, T) = \frac{k_B T}{\lambda^3} e^{\beta\mu}$$

Number of particles.

We have that:

$$N = -\frac{\partial\Omega}{\partial\mu} = \frac{V}{\lambda^3} e^{\beta\mu}$$

So:

$$\rho(T, \mu) = \frac{N}{V} = \frac{e^{\beta\mu}}{\lambda^3}$$

Note that we obtain results that are completely equivalent to all the results obtained in the canonical ensemble.

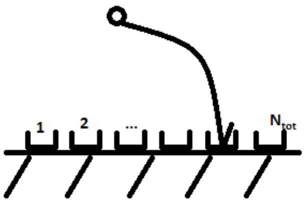
5.7 Example: Adsorption on a surface.

We consider a situation where molecules adsorb on a surface. The process is modelled using a simplified view where the surface consists of N_{tot} sites of adsorption, containing 0 or 1 molecule at most, and the adsorption energy of one molecule is fixed to ϵ_0. We assume that the atmosphere is a reservoir of molecules so that their chemical potential is fixed to the value μ.

We introduce N_{tot} variables n_i which will be equal to 1 if the exist a particle in the site on the surface i and 0 otherwise. For a given microstate $s = \{n_i\}$, the energy of the system is:

$$E_s = \sum_i n_i \epsilon_0, \qquad \text{and} \qquad N_s = \sum_i n_i$$

Now we can follow two routes to obtain the physical properties of the system, based on the two expressions of the partition function:



$$\Theta = \sum_s e^{\beta(\mu N_s - E_s)} \qquad \text{and} \qquad \Theta = \sum_N e^{\beta\mu N} Z_N$$

Method 1: Following the first description, i.e. a summation over microstates, we can write:

$$\Theta = \sum_s e^{\beta(\mu N_s - E_s)} = \sum_{\{n_i=0,1\}} e^{\beta\mu(\sum_i n_i - \sum_i n_i \epsilon_0)} = \sum_{n_1=0}^{1}\sum_{n_2=0}^{1}\cdots\sum_{n_{N_{tot}}=0}^{1}\prod_i e^{\beta(\mu-\epsilon_0)n_i}$$

The key point is that the sum factorizes because all sites are independent, so that the partition function can be rewritten as

$$\Theta = \sum_{n_1=0}^{1} e^{\beta(\mu-\epsilon_0)n_1} \sum_{n_2=0}^{1} e^{\beta(\mu-\epsilon_0)n_2} \ldots \sum_{n_{N_{tot}}=0}^{1} e^{\beta(\mu-\epsilon_0)n_{N_{tot}}}$$

This can be rewritten in a compact form as

$$\Theta = \prod_i \sum_{n_i=0,1} e^{\beta(\mu-\epsilon_0)n_i} = \prod_i (1+e^{\beta(\mu-\epsilon_0)})$$

And we arrive at the final result:

$$\Theta = (1+e^{\beta(\mu-\epsilon_0)})^{N_{\text{tot}}}$$

Method 2: Alternatively we can calculate the partition function by summing the free energy over the number of particles, as

$$\Theta = \sum_N e^{\beta\mu N} Z_N$$

And by definition we have:

$$Z_N = \sum_{\{s|N\text{fixed}\}} e^{-\beta E_s} = e^{-\beta N\epsilon_0} \times \#\text{ number of ways to adsorb N particles over the } N_{tot} \text{ sites}$$

In terms of combinatorics, we have the simple result for the number of ways to choose N sites among N_{tot}:

$$\#\text{ nb of ways} = \binom{N_{\text{tot}}}{N} = \frac{N_{\text{tot}}!}{N!(N_{\text{tot}}-N)!}$$

So we have:

$$\Theta = \sum_N \binom{N_{\text{tot}}}{N} e^{\beta(\mu-\epsilon_0)N} \times 1^{N_{\text{tot}}-N} = \left(1+e^{\beta(\mu-\epsilon_0)}\right)^{N_{\text{tot}}}$$

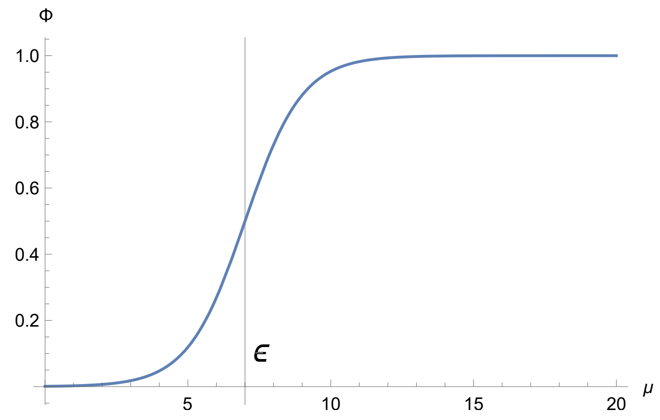
So we indeed get the same result. Note that the second method is easier so long as we can calculate the expression of Z_N.

Now, we can deduce the thermodynamics from the partition function. The average number of adsorbed particles is

$$\bar{N} = -\frac{\partial\Omega}{\partial\mu} = N_{\text{tot}} k_B T \frac{\partial}{\partial\mu}\log\left(1+e^{\beta(\mu-\epsilon_0}\right)$$

so that we obtain the fraction of adsorbed sites on the surface

$$\Phi = \frac{\bar{N}}{N_{\text{tot}}} = k_B T \frac{\beta e^{\beta(\mu-\epsilon_0)}}{1+e^{\beta(\mu-\epsilon_0)}} = \frac{1}{1+e^{\beta(\epsilon_0-\mu)}}$$



5.8 Conclusion on ensembles.

We can then summarize the different results for the various ensembles with the following table:

Conditions	Ensemble	Partition function	Potential
N,V,E	Micro Canonical	$\Omega = \sum_s \delta_{E_s,E} = \frac{1}{N!}\frac{1}{h^{3N}}\int_{E\leq\mathcal{H}(-\leq E+\Delta E} \mathrm{d}\Gamma$	$S = k_B\log\Omega = S(E,V,N)$
N,V,T	Canonical	$Z = \sum_s \exp\left(-\frac{E_s}{k_BT}\right)$	$F = -k_BT\log Z = F(N,V,T) = E-TS$
μ,V,T	Grand Canonical	$\Theta = \sum_s \exp\left(\frac{\mu N_s - E_s}{k_BT}\right)$	$\Omega = -k_BT\log\Theta = \Omega(\mu,V,T) = F-\mu N = -P(\mu,T)V$

Note that in the various derivation of these results, we followed the saddle-point method to focus on the states of highest probability. Accordingly that we implicitly wrote the following relations:

$$\boxed{F = \min_E \left(E - TS(E,V,N)\right), \quad \Omega = \min_N \left(F(N,V,T) - \mu N\right), \quad G = \min_V \left(F(N,V,T) + PV\right)}$$

The interpretation is quite natural in terms of constraints: for each ensemble, one might consider a number of states where we constrain the value of an extensive quantity: the energy, number of particles or volume. Then, when this constraint is relaxed, the global thermodynamic equilibrium is obtained by calculating the minimum of the corresponding functional over the constraint.

One may construct of course other ensembles. For example, an interesting ensemble is the isobaric ensemble (N, P, T), for which the microstate probability is

$$p_s = \frac{1}{Y} e^{-\left(\frac{E_s}{k_B T} + \frac{PV_s}{k_B T}\right)}$$

and the partition functiion is

$$Y = \sum_s e^{-\frac{E_s + PV_s}{k_B T}} = \sum_V e^{-\frac{PV}{k_B T}} Z(N,V,T).$$

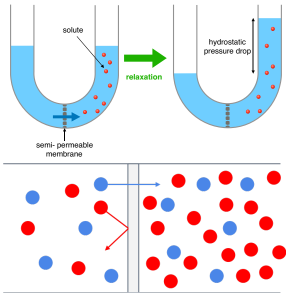
The corresponding potential is the Gibbs enthalpy $G = -k_B T \log Y = F + PV = \min_V (F(N,V,T) + PV)$. Furthermore remember that the Gibbs Duhem equation shows that $F + PV = \mu N$, so that $G = \sum_{\text{species } i} \mu_i N_i$.

Chapter 6

Ideal systems and entropic forces.

Ideal systems are systems in which the interactions are negligeable (perfect gas, ideal polymers, etc.). Hence, from a naive point of view, one would not expect any complex phenomena to emerge in such systems. However, entropic effects introduce much subtleties in spite of the absence of interactions and can lead to the building up of entropic forces. A good example was given above by the ideal polymer: we have shown that in spite of the absence of any interaction, the polymer exhibit an entropic stiffness proportional to the thermal energy $k_B T$ $K = \frac{k_B T}{N a^2}$. Similiar effects occurs in many situations. One prominent example is osmosis and osmotic forces[1] In general, maximization of entropy can lead to mechanical restoring forces: indeed, reducing the degrees of freedom of a system by external constraint generate force to re-establish a larger exploration of the phase space. These are entropic forces, that we want to illustrate by a few examples in this chapter.

6.1 Osmosis.



Osmosis is striking because of its simplicity, subtlety and consequences. The prototypical configuration to highlight osmosis is the following: two solutions, one with fresh water and one with salty water (say, $NaCl$), are separated by a semi-permeable membrane, which lets water pass but not salt. Starting from this configuration, the fresh water will start moving to the salty water side, trying to balance the concentration on both sides in order to reach equilibrium. To stop this flux we could add a piston to the right hand side that would add a pressure of

$$\Delta\Pi = k_B T \Delta C_{\text{solution}}$$

where C_{solution} is the total ions concentration (which is here twice the salt concentration since the salt solutions contains both sodium and chlorine salts). This is the osmotic pressure and this formula is called the van 't Hoff formula, which we will demonstrate below. It is of pure entropic origin.

To give an idea of the orders of magnitude, if we have a salinity contrast of 1 mole of salt between the two reservoirs, we get an osmotic pressure of $\Delta\Pi = 48$bar ! This is huge and corresponds to the hydrostatic pressure ~ 500m below the level of the sea (or equivalently that of a dam 500m high).

We will now explore more thoroughly this phenomenon and demonstrate more specifically the van 't Hoff formula using statistical physics. We assume to simplify that we are using ideal molecules (which water is not), but the principles are general. We consider N_1 molecules of type 1 and N_2 molecules of type 2 and we neglect interactions. For now we fix the the volume and the temperature. Since the two systems are independent the partition function is simply the product of the two partition functions::

$$Z(N_1, N_2, V, T) = \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^{N_1} \frac{1}{N_2!}\left(\frac{V}{\lambda_T^3}\right)^{N_2}$$

Intestingly we can rewrite this expression in a more transparent way;

$$Z(N_1, N_2, V, T) = \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^{N} \frac{N!}{N_1! N_2!} \equiv Z_{\text{id}}(N, V, T) \cdot Z_{\text{mix}}(N_1, N_2)$$

where

$$Z_{\text{id}} = \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^{N}, \quad \text{and } Z_{\text{mix}} = \frac{N!}{N_1! N_2!} = \binom{N}{N_1}$$

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[1] See. e.g. *Osmosis, from molecular insights to large scale applications*, S. Marbach and L. Bocquet, Chemical Society Reviews 48, 3102-3144 (2019); https://www.phys.ens.fr/∼lbocquet/172article.pdf

This highlights the combination of the ideal term (as if the systems 1 and 2 would be identical) and the mixing term. The free energy thus takes the form

$$F(N_1, N_2, V, T) = F_{\mathrm{id}}(N, V, T) + F_{\mathrm{mix}}(N_1, N_2, T)$$

where

$$F_{\mathrm{id}}(N, V, T) = -k_B T \log Z_{\mathrm{id}} = -k_B T \log\left(\frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N\right), \text{ and } F_{\mathrm{mix}}(N_1, N_2, T) = -k_B T \log Z_{\mathrm{mix}} = -k_B T \log\left(\frac{N!}{N_1! N_2!}\right)$$

Using the Stirling formula, the mixing term rewrites

$$F_{\mathrm{mix}}(N_1, N_2, T) = -k_B T\,(N \log N - N - N_1 \log N_1 + N_1 - N_2 \log N_2 + N_2) = k_B T N (x_1 \log x_1 + x_2 \log x_2)$$

where:

$$x_i = \frac{N_i}{N_1 + N_2} \quad \text{and} \quad x_1 + x_2 = 1$$

is the molar fraction.

Let us come back to the situation above in which two systems with different concentrations of solute are put in contact. In this configuration, the solvent is in chemical equilibrium across the semi-permeable membane (since it can be exchanged across the membrane), but not the solute since the membrane is impermeable to it. To write chemical equilibrium of the 'solvent' (here labelled as '1'), we first calculate the chemical potential, $\mu(T, P, x_1)$. Several routes are possible and, for illustration, we choose here to first calculate the Gibbs-Free energy, defined as: $G = \min_V (F(N_1, N_2, V, T) + PV)$.

The minimum of $F(N_1, N_2, V, T) + PV$ versus V leads to the condition $\frac{\partial F}{\partial V} + P = 0$, which defines the volume versus the imposed pressure P. Since F_{mix} is independent of V we obtain:

$$\frac{\partial F_{\mathrm{id}} + F_{\mathrm{mix}}}{\partial V} = \frac{\partial F_{\mathrm{id}}}{\partial V} = -P \Rightarrow \frac{k_B T}{V} N = P \Rightarrow V = \frac{N k_B T}{P}$$

The Gibbs enthalpy thus takes the expresion :

$$G = F_{\mathrm{id}}\left(N_1, N_2, V = \frac{N K_B T}{P}, T\right) + P \times \frac{N k_B T}{P} + F_{\mathrm{mix}}(N_1, N_2, T)$$

so that

$$G = \underbrace{N k_B T \log\left(\frac{P}{k_B T} \lambda_T^3\right)}_{G_0(T,P,N)} + N k_B T (x_1 \log x_1 + x_2 \log x_2)$$

Here we supposed that the two systems were ideal but more generally we can write the Gibbs enthalpy as:

$$\boxed{G(T, P, N_1, N_2) = G_0(T, P, N) + G_{\mathrm{mix}}(N_1, N_2, T)}$$

and for dilute solutions of the specie '2' ($N_2 \ll N_1$), one expects $G_0(T, P, N) \simeq N_1 \mu_1^0(T, P) + N_2 \mu_2^0(T, P)$.

The chemical potentials are defined as

$$\mu_i(T, P, x_s) = \left.\frac{\partial G}{\partial N_i}\right|_{N_{j \neq i}, T, P}$$

Now to make the link with our initial problem more transparent, we write $N_1 \equiv N_w$ the number of molecules of water and $N_2 \equiv N_s$ the number of solute molecules, assuming further that $N_s \ll N_w$. In the latter limit, G simplifies to

$$G \simeq G_0(T, P, N_s + N_w) + k_B T \left(N_s \log \frac{N_s}{N_w} - N_s\right)$$

and the water chemical potential thus writes

$$\mu_w(T, P, x_s) = \left.\frac{\partial G}{\partial N_w}\right|_{N_s, T, P} = \mu_0(T, P) - k_B T \frac{N_s}{N_w} \approx \mu_0(T, P) - k_B T x_s$$

Equilibrium between the two reservoirs can be reached only if one applies an excess pressure on the 'salty' side, in order to avoid the flux of water from the fresh water side. The pressure is therefore not the same on both sides. On the fresh water side (no salt), we have therefore $x_s = 0$ and the pressure is P; on the salty water side, the salt fraction is $x_s = N_s/N_w$ and the pressure is $P + \Delta\Pi$. Thermodynamic equilbrium imposes that the chemical of water is equal on both sides, so that:

$$\mu_w(T, P, x_s = 0) = \mu_w(T, P + \Delta\Pi, x_s) \Leftrightarrow \mu_0(T, P) = \mu_0(T, P + \Delta\Pi) - k_BTx_s$$

For small x_s we can expand the expression in $\Delta\Pi$ using

$$\mu_w(T, P + \Delta\Pi) - \mu_w(T, P) = \frac{\partial\mu_w}{\partial P}\Delta\Pi$$

Using the Gibbs-Duhem equation we have that $N\mathrm{d}\mu = V\mathrm{d}P$ so that $\frac{\partial\mu}{\partial P} = \frac{V}{N_w}$. Inserting this result into the previous equation leads to the expression for the osmotic pressure $\Delta\Pi$

$$\Delta\Pi = k_BT\frac{N_s}{V} = k_BTC_s$$

This concludes the proof of the van 't Hoff equation.

Alternative demonstration.

Another way to approach the problem is to write a force balance. One thing to note is that the semi-permeable membrane, though crucial to the problem, disappears in the final van 't Hoff equation. So we can simplify the mathematical description of the membrane and replace it by a simple potential barrier $\mathcal{U}_s(x)$. This potential does not act on water but only on the salt molecules, and it is peaked at $x = 0$ with a maximal value $\max\mathcal{U}_s \gg k_BT$, so that it repels strongly the salt molecules.

Now in the reservoir containing the salt, we write Boltzmann's law for salt particles in the presence of the potential to obtain

$$c_s(x) = \underbrace{C_s}_{x=+\infty} \exp\left(-\frac{\mathcal{U}_s(x)}{k_BT}\right)$$

We can now calculate the force due to the filter and acting on the fluid (water+salt). The barrier acts on the salt molecules but due to action-reaction principle, this force acts on the fluid globally. This force can be decomposed as

$$\frac{F}{A} = \sum_{\text{salt}} \underbrace{f_i}_{\text{force on a molecule of salt}} = \sum_{\text{salt}}\left(-\frac{\partial\mathcal{U}_s}{\partial x}\right)$$

Which we can re-write as:

$$\frac{F}{A} = \int \mathrm{d}x\, c_s(x)\times\left(-\frac{\partial\mathcal{U}_s}{\partial x}\right) = \int \mathrm{d}x\, C_s e^{-\frac{\mathcal{U}_s(x)}{k_BT}}(-\partial_x\mathcal{U}_s) = \int \mathrm{d}x\, C_s k_BT\partial_x e^{-\frac{\mathcal{U}_s(x)}{k_BT}} = k_BTC_s\left(\underbrace{e^{-\frac{\mathcal{U}_s(\infty)}{k_BT}}}_{1} - \underbrace{e^{-\frac{\mathcal{U}_s(0)}{k_BT}}}_{0}\right)$$

So we finally get that:

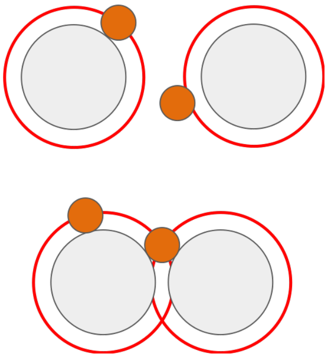
$$\frac{F}{A} = \Delta\Pi = k_BTC_s$$

We see here two different perspectives for osmotic forces. The first is to consider it as a thermodynamic equilibrium condition for the solvent, which has to equilibrate its chemical potential shifted by the salt : the only solution is to modulate the pressure. The second perspective is merely mechanical and shows that the osmotic force is simply the 'push' due to the membrane acting on the fluid to repel the salt (to avoid the crossing of the solute).

6.2 Depletion forces.

Depletion forces are entropic forces which emerge in mixtures of colloidal particles with different sizes. To be more specific, let us consider a system containing a suspension of 'large' and 'small' particles, typically in experiments experiments are performed with suspensions of colloids ($\sim 1\mu$m in size) and much smaller polymers, all suspended in a solvent, water or else. We assume that the only interaction between particles is the exclusion originating in their hard cores. What is observed is that the large particle do attract each other, in spite of no direct attractive interaction put in. This is a signature of depletion, entropic forces, originating in the 'excluded volume' around particles.

Let us denote as R the radius of the colloids and R_g the radius of the polymers ($R \gg R_g$). Now if we consider a single, isolated colloid surrounded by polymer,



we see that polymers are excluded from a spherical volume around the colloid. Quantitatively the excluded volume for the polymer is $V^0_{\text{exl}} = \frac{\pi}{6}\left(2(R+R_g)\right)^3 = \frac{\pi}{6}D^3$. Now if we consider two colloids which arre far apart (as on the top figure above), we simply add the excluded volumes so that:

$$V_{\text{accessible}} = V - 2V^0_{\text{excluded}}$$

But now, let us consider a situation where the colloid are near enough that a polymer cannot enter in the space between the two colloids (see figure). Then there is an overlap in the exclusion volumes induced by each colloid, so that $V_{\text{excl}} < 2V^0_{\text{excl}}$.

Quantitatively, the excluded volume follows from simple geometry. If we consider two colloids which are separated by a distance h, then one can estimates that

$$V_{\text{excl}} = 2 \times \frac{\pi}{6}D^3 - V_{\text{overlap}} = 2\left(\frac{\pi}{6}D^3 - \frac{\pi}{3}\underbrace{((R+R_g)-(R+\frac{h}{2}))}_{d=R_g-\frac{h}{2}}{}^2(3(R+R_g)-d)\right)$$

This can be re-written as:

$$V_{\text{excl}} = \frac{\pi D^3}{6}\left(1 + \frac{3}{2}\frac{r}{D} - \frac{1}{2}\left(\frac{r}{D}\right)^2\right), \qquad \text{with } r = 2R+h \text{ and } D = 2(R+R_g)$$

Now, how does this result translate into an interaction force between the two colloids ? The physics at play is clear: if the colloid are left free, reducing their distance increase the free volume for the polymers and the polymer entropy increases accordingly. Hence there should be a force driving the colloids together.

Let us therefore assume that the colloids are fixed and we study the phase space of polymers. The free/accessible volume for the polymers is

$$V_{\text{accessible}} = V_{\text{free}} = V - V_{\text{excl}}(r)$$

So the partition function for the polymers in the remaining volume V_{free} is:

$$Z = \frac{1}{N!}\left(\frac{V - V_{\text{excl}}(r)}{\lambda_T^3}\right)^{N_p}$$

The potential is given by $F = -k_BT\log Z$ and the thermodynamic force is:

$$\mathcal{F} = -\frac{\partial F}{\partial r} = k_BTN_p\frac{\partial}{\partial r}\log(V - V_{\text{excl}}(r)) = k_BT\frac{N_p}{V - V_{\text{excl}}} \times \left(-\frac{\partial}{\partial r}V_{\text{excl}}(r)\right)$$

If we write $c_p = \frac{N_p}{V-V_{\text{excl}}}$ the polymer concentration, we get:

$$\mathcal{F} = k_BTc_p\left(-\frac{\partial V_{\text{excl}}}{\partial r}\right)$$

with the expression of $V_{\text{excl}}(r)$ given above. Now we saw earlier that for $r > D$ we have that $V_{\text{excl}} = 2V^0_{\text{excl}}$ which is a constant while for $r < D$ the exluded volume will decrease (i.e. the function is increasing). Therefore this shows that the force is going to be 0 when $r > D$ and negative (i.e. attractive) when $r < D$. The physical understanding of this is that when the colloids are closer together the phase space of the polymers becomes bigger and therefore the the entropy increases. This is another example of an entropic force. Such effects play an essential role in colloidal systems and in Nature.

6.3 Forces induced by thermal fluctuations.

In line with previous examples, we are interested in forces induced by restrictions on the phase space. Here we discuss forces induced by space limitations on fluctuations. There are three main configurations: Casimir - Fisher-De Gennes - Helfrisch, we will focus specifically on Helfrisch-type of forces, with a simplified description, altough capturing the main ingredients.

Casimir

The Casimir forces caracterize the fluctuations of, for example, an electromagnetic field in between two conducting plates separated by a distance D in vaccum. Modes are quantified by the confinement, as a trivial calculation shows. But Casimir and many others showed that this leads to an attractive force due to the fluctuations of the electromagnetic field:

$$\frac{F}{A} = \frac{-\pi^2}{240}\frac{\hbar c}{D^4}$$

This is clearly a quantum effect.

'Critical' forces - Fisher-De Gennes.

De Gennes and Fischer showed later that a similar type of fluctuation-induced forces occured in confined fluids close to a critical point For more detail one can go see the original paper by de Gennes and Fischer Comptes Rendus Academie des Sciences (1978); this effect was evidenced experimentally only recently, see C. Bechinger *et al.*, Nature 2007. A fluctuation induced (attractive) force builds up between the confining surfaces, with expression

$$\frac{F}{A} \sim -\frac{k_BT}{D^3}$$

This is an entropic force, as highlighted by the k_BT amplitude.

Helfrisch forces.

Helfrisch studies a superposition of membranes separated by a distance D, showing that entropic effects leads to a repulsive force, in the form:

$$\frac{F}{A} \propto \frac{(k_BT)^2}{\kappa D^3}$$

where κ is the bending rigidity of the membrane.

The principle is that an elastic membrane will be able to explore some configurations of its phase space thanks to the ambient temperature, having a characteristic height $\langle h^2\rangle_{free}$. When we confine the membrane in a well of width D such that $D^2 < \langle h^2\rangle_{free}$, i.e. we apply a corresponding constraint, the membrane will be forced out to fit into the confining space (so that in the end $\langle h^2\rangle_{confined} \approx D^2$). Hence the system will therefore apply a force that will tend to go back to equilibrium. So overall we expect to find a repulsive (entropic) force in between the membranes.

Simplified Model.

The general calculation is somewhat cumbersome, so we will make a simplifying analysis which captures the main physical ingredients. The steps are the following. First, instead of a real elastic membrane, we will consider a 1D elastic string. Second we will put this string into a (parabolic) confining potential which will *mimick* the confinement of width D and we will explore its fluctuations in this confined situation. We will make a translation between the two situations. And we will finally calculate the free energy in this confined situation.

We start by considering that the system is characterized by the following hamiltonian defined on a lattice:

$$\mathcal{H} = \underbrace{\sum_i \frac{1}{2}\tilde{k}(h_{i+1}-h_i)^2}_{\text{string energy}} + \underbrace{V(h)}_{\text{confining constaint}} \qquad \text{and we take} \qquad V(h) = \sum_i \frac{1}{2}\tilde{K}h_i^2$$

where $\{h_i\}$ is the height of the string at the point $x = i \times a$ with a a lattice spacing. The Hamiltonian is therefore a function of all h_i, $\mathcal{H}(h_1, \cdots, h_N) \equiv H(\{h\})$ and we call such 'function of function' a functional. We will consider equivalently the lattice (discrete) model and its the continous version using the equivalence

$$H(\{h\}) = \sum_i \frac{1}{2}\tilde{k}(h_{i+1}-h_i)^2 + \frac{1}{2}\tilde{K}h_i^2 \quad \text{and} \quad \sum_i = \int \frac{\mathrm{d}x}{a}$$

so that

$$H(\{h\}) = \int_0^L \mathrm{d}x \left[\frac{1}{2}k(\boldsymbol{\nabla} h)^2 + \frac{1}{2}Kh^2\right] \qquad \text{with } \boldsymbol{\nabla} = \frac{\mathrm{d}}{\mathrm{d}x}$$

where a is the lattice size in the discrete case and L its length.

The probability of finding the string in a given state is given by the canonical probability:

$$p(\{h\}) \equiv p(h_1, \cdots, h_N) \propto \exp\left[-\frac{1}{k_BT}\mathcal{H}(\{h\})\right]$$

The partition function is defined accordingly as

$$Z = \int \mathrm{d}h_1 \cdots \mathrm{d}h_N \exp\left[-\frac{\mathcal{H}(\{h\})}{k_B T}\right]$$

and the free energy is $F = -k_B T \log Z$. For any observable A, the average is therefore defined as

$$\langle A \rangle = \frac{\int \mathrm{d}h_1 \cdots \mathrm{d}h_N A(\{h\}) \exp\left[-\frac{\mathcal{H}(\{h\})}{k_B T}\right]}{\int \mathrm{d}h_1, \cdots \mathrm{d}h_N \exp\left[-\frac{\mathcal{H}(\{h\})}{k_B T}\right]}$$

Note that it is simpler (and better defined) to consider the discrete variables to compute averages.

Average extension.

Let us first compute the fluctuation of the string height $\langle h^2 \rangle$. We have:

$$\langle h^2 \rangle = \frac{1}{L} \int_0^L \mathrm{d}x \langle h^2(x) \rangle$$

The height is averaged over the probability distribution with the previous Hamiltonian, which takes the form:

$$p(\{h\}) = \frac{1}{Z} \exp\left[-\frac{1}{k_B T} \int \mathrm{d}x \left(\frac{1}{2} k (\boldsymbol{\nabla} h)^2 + \frac{1}{2} K h^2\right)\right]$$

The difficulty comes the gradient terms, i.e. (in the discretized version) from the interaction between nearest neighbors. We need to 'diagonalize' the hamiltonian by changing of variables: this can be achieved using the Fourier space. As we will see, modes in to the Fourier space do separate and allows calculating the averages and partition function. We first recall a few definitions of the Fourier transforms (see also the mathematical memo in Chapter 10):

$$h_q = \int \mathrm{d}x h(x) e^{iqx} \quad \text{and} \quad h(x) = \int \frac{\mathrm{d}q}{2\pi} h_q e^{-iqx}$$

We will also use Parceval theorem:

$$\int \mathrm{d}x f(x)^2 = \int \frac{\mathrm{d}q}{2\pi} |f_q|^2$$

Furthermore Fourier transforming the gradient corresponds to $\boldsymbol{\nabla} \xrightarrow{\mathrm{FT}} -iq$ since

$$\int \mathrm{d}x \frac{\partial h}{\partial x} e^{iqx} = -iq \int \mathrm{d}x h e^{iqx} = -iq h_q$$

Back to the hamiltonian, we find that with Fourier variables, it simplifies to (making a FT and applying Parceval):

$$\int \mathrm{d}x \left(\frac{1}{2} k (\boldsymbol{\nabla} h)^2 + \frac{1}{2} K h^2\right) = \int \frac{\mathrm{d}q}{2\pi} \frac{1}{2} (kq^2 + K) |h_q|^2$$

In order to make averages, it will proove useful to come back to discretized variables, i.e. here discretized modes in Fourier space. Since the length of the string is L, the Fourier modes are discretized as $q_n = \frac{2\pi}{L} n$, and the discretization of the integral takes the form:

$$\int \frac{\mathrm{d}q}{2\pi} (\cdot) = \frac{1}{L} \sum_n (\cdot)$$

Gathering the previous results, we therefore obtain:

$$\exp\left[-\frac{1}{k_B T} \int \mathrm{d}x \left(\frac{1}{2} k (\boldsymbol{\nabla} h)^2 + \frac{1}{2} K h^2\right)\right] = \exp\left[-\frac{1}{k_B T} \underbrace{\int \frac{\mathrm{d}q}{2\pi} \frac{1}{2} (kq^2 + K) |h_q|^2}_{\frac{1}{L} \sum_{\{q_n\}} \frac{1}{2} (kq^2 + K) |h_{q_n}|^2}\right]$$

so that

$$p(\{h\}) = \frac{1}{Z} \prod_{\{q_n\}} \exp\left[-\frac{1}{2 k_B T L} (k q_n^2 + K) |h_{q_n}|^2\right]$$

The probability distribution therefore takes the form of a product of probability for each mode, as $p(\{h\}) = \prod_{\{q_n\}} p_0(h_{q_n})$ (p_0 being a gaussian), which shows that the h_{q_n} variables are *statistically independent*; and furthermore they have a *gaussian* probability distribution since their weight is of the form $\exp\left[(\cdot)|h_{q_n}|^2\right]$, with a quadratic dependence in the exponential. We can therefore make use of the results we derived in Chap 4 (section 5) for the equipartition, to write immediately:

$$\frac{1}{2L}(kq_n^2 + K)\langle |h_{q_n}|^2\rangle = \frac{1}{2}k_BT \cdot 2$$

Note that we have a factor of 2 on the right hand side because h_{q_n} is a complex variable so it has two degrees of freedom: its real and imaginary part. So finally we get:

$$\langle |h_q|^2\rangle = \frac{2k_BTL}{kq^2+K}$$

Note that (to recall where equipartition comes from), the steps of the calculation are:

$$\langle |h_{q_n}|^2\rangle = \frac{1}{z}\int dh_{q_n}^R \int dh_{q_n}^I \left([(h_{q_n}^R)^2 + (h_{q_n}^I)^2) \exp\left[-\alpha(q_n)\left[(h_{q_n}^R)^2 + (h_{q_n}^I)^2\right)\right]\right.$$

where we introduced the average over the real and imaginary parts of h_{q_n}, $\alpha(q_n) = \frac{1}{2k_BTL}(kq_n^2+K)$ and z is the normalization factor for the gaussian $z = \int dh_{q_n}^R \int dh_{q_n}^I \exp\left[-\alpha(q_n)\left[(h_{q_n}^R)^2 + (h_{q_n}^I)^2\right)\right]$.

Coming back to the original question we have:

$$\langle h^2\rangle_K = \frac{1}{L}\int_0^L \mathrm{d}x\langle h(x)^2\rangle = \frac{1}{L}\int_{-\infty}^{+\infty}\frac{\mathrm{d}q}{2\pi}\langle |h_q|^2\rangle = \frac{1}{L}\int\frac{\mathrm{d}q}{2\pi}\frac{2k_BTL}{kq^2+K} = \frac{k_BT}{\pi}\int \mathrm{d}q\frac{1}{kq^2+K} = \frac{k_BT}{\pi K}\int\sqrt{\frac{K}{k}}\frac{\mathrm{d}u}{1+u^2}$$

where we added the index K to highlight that this average is made with a confining well of strength K. So finally we get that:

$$\langle h^2\rangle_K = \frac{k_BT}{\sqrt{kK}}$$

Note that the fluctuations of the membrane increase linearly with temperature and diverge as $1/\sqrt{K}$ as the strength of the confining potential decreases $K \to 0$. This is a general result for elastic membranes, and they exhibit very important fluctuations.

Now, we want to come back to our initial question where we consider a membrane confined in a well of width D. We need to translate the previous results obtained for a string in a harmonic well to a 'physical' confinement of width D. This can be enforced by imposing that in the confined situation above, the fluctuations of h match the width D: $\langle h^2\rangle_K = D^2$. We therefore make the translation between the two problems as

$$\frac{k_BT}{\sqrt{kK}} = D^2 \Rightarrow K = \frac{1}{k}\left(\frac{k_BT}{D^2}\right)^2$$

Free Energy.

The final step is to calculate the free energy $\mathcal{F}$ for the confined membrane/string. In practice, we will calculate $\Delta\mathcal{F} = \mathcal{F}(D) - \mathcal{F}(D \to \infty)$, i.e. the difference to the unconfined case. We have:

$$Z(\{h\}) = \int \mathrm{d}h_1\cdots\mathrm{d}h_N \exp\left[\underbrace{-\frac{1}{k_BT}\sum_i\left(\frac{1}{2}\tilde{k}(h_{i+1}-h_i)^2 + \frac{1}{2}\tilde{K}h_i^2\right)}_{=\mathbf{H}^T\mathbf{A}\mathbf{H}}\right]$$

Note that the terms inside the exponential could be written as a matrix, which can be rewritten in terms of a diagonal coupling matrix A: this is the general route to calculate this gaussian integral. This is actually equivalent to the Fourier Transform, which performs such a diagonalization:

$$Z(\{h\}) = \int \mathrm{d}h_1\cdots\mathrm{d}h_N \exp\left[-\frac{1}{k_BT}\sum_{q_n}\frac{1}{2}(kq_n^2+K)|h_{q_n}|^2\right] = \prod_{q_n}\int \mathrm{d}h_{q_n}\exp\left[-\frac{1}{2k_BT}(kq_n^2+K)|h_{q_n}|^2\right]$$

The last gaussian term can be calculated exactly

$$\int \mathrm{d}h_{q_n}\exp\left[-\frac{1}{2k_BT}(kq_n^2+K)|h_{q_n}|^2\right] = \frac{2\pi k_BT}{kq_n^2+K}$$

(remember that the integral involves a real and a imaginary part of the variable). So finally we get that:

$$Z = \prod_{q_n} \left(\frac{2\pi k_B T}{k q_n^2 + K} \right)$$

The free energy follows immediately

$$\mathcal{F}(K) = -k_B T \log Z = -k_B T \sum_{q_n} \log \frac{2\pi k_B T}{k q_n^2 + K} = -k_B T L \int \frac{\mathrm{d}q}{2\pi} \log \left(\frac{2\pi k_B T}{k q^2 + K} \right)$$

Which gives:

$$\Delta \mathcal{F} = \mathcal{F}(D) - \mathcal{F}(D \to \infty) = \mathcal{F}(K) - \mathcal{F}(K = 0) = -k_B T L \int \frac{\mathrm{d}q}{2\pi} \log \left(\frac{k q^2}{k q^2 + K} \right)$$

So we get that:

$$\frac{\Delta \mathcal{F}}{L} = k_B T \underbrace{\int \frac{\mathrm{d}q}{2\pi}}_{u=\sqrt{\frac{k}{K}}q} \log \left(1 + \frac{K}{k q^2} \right) = C k_B T \sqrt{\frac{K}{k}}$$

where C is a numerical constant. Now using the previous conversion, $\frac{k_B T}{\sqrt{kK}} = D^2$, we get that:

$$\frac{\Delta \mathcal{F}}{L} = C \left(\frac{k_B T}{D} \right)^2$$

and the force per unit area

$$P(D) = -\frac{\partial \mathcal{F}}{\partial V} = -\frac{\partial}{\partial D} \left(\frac{\mathcal{F}}{\mathcal{A}} \right) = \frac{2C (k_B T)^2}{k D^3}$$

These are the 'Hellfrisch' results for the algebraic decay of the repulsion entropic force between membranes (up to a prefactor which we are not intereted in). Although much simpler than the full calculation, the above result captures the physics at play in the constrained membrane.

Overal, this is intersting to see how fluctuations can induce long range force due to entropic terms.

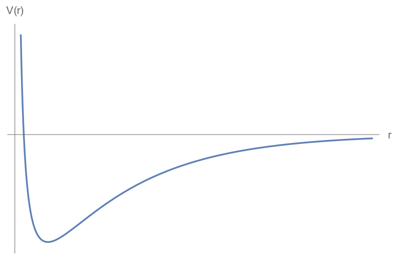
Chapter 7

Systems in interaction and phase transitions.

7.1 Introduction.

Up to now we have merely considered ideal systems with no interactions between particles or magnets. Such description is expected to remain valid for low density systems $\rho \to 0$, as one can neglect interactions when particles are far away. But interactions become key for high density systems – hence for condensed matter –, in particular to describe phase changes. However partition functions become highly difficult to calculate for interacting systems and, except in rare cases, cannot be evaluated exactly. One of this rare situation is the Ising model in 1 and 2 dimensions, and these results have played, and still play, a key role in physics. However, various approximation schemes have been developped, such as the virial expansion or the mean-field approximation, which captures at least some qualitative features of the collective properties and phase change.

Let us start by discussing briefly interactions between particles. A typical shape for the interaction potential between molecules is like the one sketched in the graph enclosed, highlighting typically a short-range repulsion and a long-range interaction – here an attraction–. A typical example is the Lennard-Jones potential



$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

The short range $1/r^{12}$ is purely heuristic and accounts for the Pauli exclusion principles between the electronic cloud of atoms. But the long-range $1/r^6$ attraction is universal and accounts for van der Waals interactions due to mutual polarisation of molecules. A typical value for σ is a few angtröms and $\epsilon \sim 10 - 100$meV. Another, even simpler, example is the hard sphere potential:

$$V(r) = \begin{cases} +\infty \text{ if } r < \sigma \\ 0 \quad\quad \text{if } r > \sigma \end{cases}$$

This potental captures the short-range repulsion in its simplest form. This can also be re-written as $e^{-\beta V(r)} = H(r-\sigma)$, with H the heaviside function. The hard sphere model has played a very important role as a model system for liquid matter. It allows calculating a number of properties with exact or approximate results. One counter-intuitive results for the hard sphere system is that it exhibits a liquid-crystal phase transition, even though it has no attractive interaction. The transition is purely entropic by nature. For further discussion of the hard sphere model, see the book by Hansen and McDonald, *Theory of Simple Liquids*, Elsevier (2013).

The above models corresponds to two-body interactions (i.e. the particles interact by pairs) and the Hamiltonian takes the form

$$\mathcal{H} = \sum_i \frac{\vec{p}_i^2}{2m} + \sum_{i<j} V(|\vec{r}_i - \vec{r}_j|)$$

Many-body interaction potential can occur in some systems, including three-body or even higher level interactions, but we will not discuss these in this lecture. Once the hamiltonian is given, one needs to calculate the partition function to obtain the collective and thermodynamic properties of the system, according to

$$Z = \frac{1}{N!h^{3N}} \int \mathrm{d}\vec{r}_1 \cdots \mathrm{d}\vec{r}_N \mathrm{d}\vec{p}_1 \cdots \mathrm{d}\vec{p}_N e^{-\beta\mathcal{H}}$$

here in its classical version; quantum effects will be considered in the next chapter. Calculating this partition function is obviously a formidable challenge, even for the hard sphere interaction.

Magnetic systems constitutes another important class of systems, which we will also discuss explicitly. We consider interacting spins, and the interactions typically tend to align the spins (some interactions may tend to anti-align the spins, leading to antiferromagnetic ordering). A simple way to describe the interaction is according to the Hamiltonian

$$\mathcal{H} = -\frac{4J_{ij}}{h^2}\vec{s}_i \cdot \vec{s}_j$$

with J_{ij} a coupling term between two spins $\vec{s}_i$. The physical origin of J_{ij} is a quantum exchange mechanism (a combination between the coulombic interaction and Pauli principle); typically, $J \sim 1\text{eV}$. Based on this interaction, one construct the Heisenberg's model of magnetic systems:

$$\mathcal{H} = -\frac{4}{h^2}\sum_{i<j} J_{ij}\vec{s}_i \cdot \vec{s}_j - \gamma\vec{B}\cdot\sum_i \vec{s}_i$$

An even simpler model is to assume that the value of the spin takes only two extreme values $\pm\frac{\hbar}{2}$, while restricting interactions to only nearest neighbors. This is the Ising model. Writing $\vec{s}_i = \frac{\hbar}{2}S_i$, $S_i = \pm 1$ we obtain the Ising hamiltonian

$$\mathcal{H} = -J\sum_{\langle i,j\rangle} S_i S_j - \mu\, B\sum_i S_i$$

where the notations $\langle i,j\rangle$ denotes a sum over pairs of nearest neighbors. For such spin models, the partition function writes

$$Z = \sum_{\{s_i\}} e^{-\beta H(\{s_i\})}$$

with the sum over microscopic states $\{s_i\} = \{S_i = \pm 1\}$ for the Ising model.

Again, calculating this partition function is extremely difficult and in most cases impossbile. The Ising model can be easily solved in dimension 1. And one of the great achievement of the 20^{th} century in physics is the exact solution for the 2 dimensional model. This is a formidable tour de force achieved by Lars Onsager in 1944, see below. The 3D model was not solved up to now.

In the following, our objective then is to compute exact expression for Z whenever possible, or at least build 'reasonable' approximations of it.

7.2 Interactions and partition functions.

7.3 Magnetic systems.

7.3.1 Ising model: exact Results in 1D and 2D.

As mentioned above, the Ising model is a canonical model in physics for magnetic systems, but even beyond for any system and phase change. For example, we will discuss in Sec. 8.4 a model for capillary adsorption which reduces to an Ising model.

We recall the Ising hamiltonian

$$\mathcal{H} = -J\sum_{\langle i,j\rangle} S_i S_j - \mu\, B\sum_i S_i$$

Quantities of interest are the partition function and the average magnetization. The latter is defined as $m = \langle\frac{1}{N}\sum_{i=1}^{N} S_i\rangle$, the average spin in the system. It follows from

$$m = \frac{1}{Z}\sum_{\{S_i\}}\left(\frac{1}{N}\sum_{i=1,N} S_i\right)e^{-\beta H(\{S_i\})},$$

or equivalently $m = -\frac{1}{N\mu}\frac{\partial\mathcal{F}}{\partial B}\Big|_{B=0}$, where $\mathcal{F} = -k_BT\log Z$ the free energy.

General results:

1D.

In 1 dimension, the calculation of the partition function is quite straightforward and follows from the transfer matrix method. We will report this calculation in section 8.4 in the context of the capillary adsorption and we only give the main outcomes here. The average magnetization is

$$m = \frac{\sinh\left(\frac{\mu B}{k_B T}\right)}{\sqrt{\sinh^2(\frac{\mu B}{k_B T}) + \exp\left(-\frac{4J}{k_B T}\right)}}$$

and the free energy is

$$\mathcal{F} = -N k_B T \left\{ \frac{J}{k_B T} + \log\left[\cosh\frac{\mu B}{k_B T} + \left[\sinh^2\frac{\mu B}{k_B T} + \exp\left(\frac{-4J}{k_B T}\right)\right]^2\right]\right\}$$

In one dimension, the Ising model exhibits **no phase transition**. For $B = 0$, then $m = 0$ for any temperature, except for $T = 0$.

2D.

The two dimensional version of the Ising model was calculated by Onsager in 1944. Onsager computed the partition function in 2 dimensions [Physical Review **65** 117 (1944) [1]] and Yang published in 1952 (8 years later !) the calculation of the mean polarization [Physical Review **85** 808 (1952)[2]].

The result for the partition function has the following expression (for $B = 0$):

$$Z = \left(2\cosh\frac{2J}{k_B T} e^I\right)^N, \quad I = \frac{1}{2\pi}\int_0^\pi \mathrm{d}\phi \log\frac{1+\sqrt{1-x^2\sin^2\theta}}{2}, \quad x = \frac{2\sinh\left(\frac{2J}{k_B T}\right)}{\cosh^2(\frac{2J}{k_B T})}$$

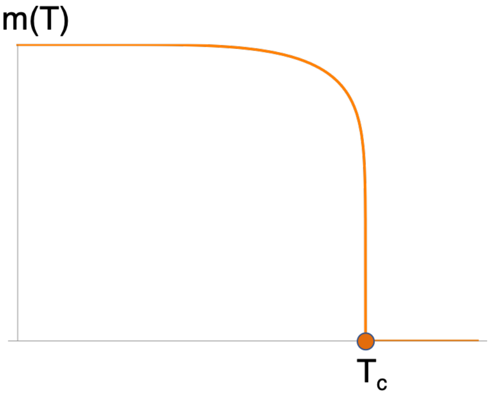
The model exhibits a second order phase transition (for $B = 0$) between a disordered phase $m = 0$ at high temperature and an ordered phase $m \neq 0$ at low temperature. The phase transition occurs at a temperature T_C defined implicitly as:

$$\sinh\frac{2J}{k_B T_C} = 1$$

Accordingly $T_c = 2.269 \dot{\times} \frac{J}{k_B}$. The temperature dependence of the average magnetization is given as

$$m(T) = \begin{cases} \pm\left(1 - \frac{1}{\sinh^4(\frac{2J}{k_B T})}\right)^{1/8} & \text{for } T < T_c \\ 0 \quad \text{for } T > T_c \end{cases}$$

and is shown in the enclosed figure



Note that there is a symmetric solution $-m$ which we do not plot here. Note the steep dependence of the magnetization close to T_c and one can verify that $m(T \sim T_C) \sim |T - T_C|^{1/8}$. This highlights the exact critical exponent for the temperature dependence of the order parameter for the 2D Ising model.

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[1] https://journals.aps.org/pr/abstract/10.1103/PhysRev.65.117

[2] https://journals.aps.org/pr/abstract/10.1103/PhysRev.85.808

The role played by these results in physics is absolutely tremendous. It shows exactly how order builds up collectively, with a symmetry breaking, in a model where only short range interactions occurs between particles (here spins). It acts as a benchmark result for a second order phase transition. It provides exact results for the critical exponent, etc. As mentioned above, there is no solution ini 3D, and actually no solution in 2D with a magentic field.

7.3.2 Mean field approximation.

There is therefore a need to make proper approximation schemes in order to calculate the partition function. One of the simplest and quite natural approximation scheme is the so-called 'mean-field' calculation. We already used it in the first lecture for the voter model. As we will show, this approach provides qualitatively correct results (sometimes even quantitative in specific models) but fails close to the transition point. Hence, it is always a good starting point since it captures most of the qualitative behavior (i.e. the existence of a phase change and symmetry breaking), but not in the detailed resulting laws: e.g. magnetization versus temperature, critical exponents, or the value of the critical temperaturer itself.

The idea of the mean field approximation is to say that "fluctuations are small". So the value for any microscopic quantity X is assumed to remain close to its average $\bar{X}$.

To implement the mean-field approximation, let us first consider a magnetic system *without any interactions*, i.e. $J = 0$, but under a magnetic field $B \neq 0$. The hamiltonian is therefore

$$\mathcal{H} = -\mu B \sum_i S_i,$$

and the partition function factorizes naturally

$$Z = \sum_{\{S_i\}} e^{\mu B\beta \sum_i S_i} = \sum_{S_1=\pm 1} e^{\mu B\beta S_1} \times \sum_{S_2=\pm 1} e^{\mu B\beta S_2} \times \cdots = \left(2\cosh\frac{\mu B}{k_B T}\right)^N$$

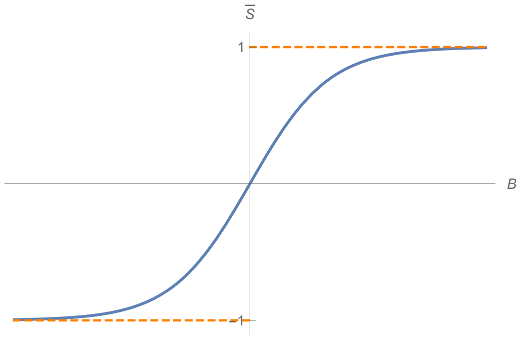
The averaged magnetization therefore takes the expression

$$m = \frac{\sum_{\{S_i\}} \frac{1}{N}\sum_i S_i e^{\mu B\beta\sum_i S_i}}{\sum_{\{S_i\}} e^{\mu B\beta\sum_i S_i}} = \frac{1}{N}\frac{\partial}{\partial x}\log Z \quad \text{with} \quad x = \beta\mu B$$

so that

$$m = \tanh\left(\frac{\mu B}{k_B T}\right)$$

This result is reported on the following graph ($\bar{S} \equiv m$).



Now let us come back to the interacting Ising model with the hamiltonian (now with $B = 0$):

$$\mathcal{H}_0 = -J \sum_{<i,j>=1} S_i S_j$$

Since in the mean field approximation, we assume that the spins do not deviate much from their average, we hence write $S_i = \bar{S} + \delta S_i$, with $\delta S_i << \bar{S}$ and $\bar{S} \equiv m$ is the average value for the spin. When introduced in the Hamiltonian, one has:

$$\begin{aligned}\mathcal{H} &= -\frac{J}{2}\sum_{i,j \text{ neighbors}} (m+\delta S_i)(m+\delta S_j) - \mu B\sum_i S_i \\ &= -\frac{J}{2}qNm^2 - \frac{J}{2}\sum_{i,j}(m\,\delta S_i + m\,\delta S_j) - \frac{J}{2}\overset{\text{negligeable}}{\cancel{\sum_{i,j}\delta S_i\delta S_j}} - \mu B\sum_i S_i\end{aligned}$$

where q is the number of neighbors in the lattice.

In the mean-field approximation, we therefore neglect the second order terms $\delta S_i \delta S_j$ in the hamiltonian. Once this approximation is done, we come back to the original spin variables $S_i = \bar{S} + \delta S_i$ (again we use equally $\bar{S} \equiv m$ as notations). We end up with the mean-field approximation for the hamiltonian

$$\begin{aligned}\mathcal{H} &= -\frac{J}{2}qNm^2 + JqNm^2 - qJm\sum_i S_i - \mu B\sum_i S_i = \frac{J}{2}qNm^2 - (qJm + \mu B)\sum_i S_i \\ &\equiv \frac{J}{2}qNm^2 - \mu B_{\text{eff}}\sum_i S_i\end{aligned}$$

with

$$\mu B_{\text{eff}} = \mu B + qJm$$

The externally applied field B adds up to the self-consistent field qJm induced by the other spins. Now, in this effective hamiltonian, spins are independent. We can then use the previous result for the independent spins and we can calculate the average magnetization as:

$$m = \tanh\left[\frac{\mu B_{\text{eff}}(m)}{k_B T}\right] = \tanh\left[\frac{\mu B + qJm}{k_B T}\right]$$

where the term $\frac{J}{2}qNm^2$ in the hamiltonian disappears when computing the average in the canonical ensemble. Finally if we restrict ourself to $B = 0$, we obtain the self-consistent equation:

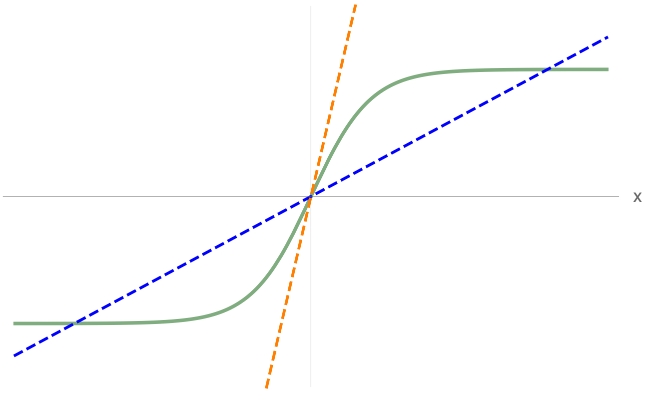
$$\frac{k_B T}{qJ}x = \tanh x$$

with $x = \frac{qJ}{k_B T}m$. We can further introduce the parameter $\alpha = \frac{k_B T}{qJ} \equiv \frac{T}{T_c}$, with $T_c = \frac{qJ}{k_B}$. We thus get the self-consistent equation for x or m

$$\tanh x = \alpha \cdot x$$

.

This equation for m can be solved numerically but one can learn a lot from a graphical construction. We plot both $\tanh x$ and $\alpha \cdot x$, see the figure below.



There are two different possibilities:

- if $\alpha > 1$ (orange dashed line, corresponding to $T > T_c$), then the line $\alpha \cdot x$ only crosses $\tanh x$ for $x = 0$: hence the only solution to the previous equation is $m = 0$. This corresponds to temperature $T > T_C$.
- if $\alpha < 1$ (blue dashed line, corresponding to $T < T_c$) then the line $\alpha \cdot x$ crosses $\tanh x$ at three different points: one at $x = 0$ and two intersections at non-vanishing values of x, say $\pm x_{sol}$. One can actually verify (see also below) that the solution corresponding to $m = 0$ is thermodynamically unstable (exhbiting a negative second derivative of the free energy) and we can discard it.

Hence the critical temperature $T_c = \frac{qJ}{k_B}$ is the transition temperature separating a disordered phase ($m = 0$) at high temperatures $T > T_c$ and the ordered phase ($m \neq 0$) at low temperature $T < T_c$. The system thus gets magnetized for $T < T_c$ and this corresponds to a ferromagnetic state. For $T > T_c$ the system is in a paramagnetic state, meaning it does not exhibit a permanent magnetic moment ($m = 0$), but can orientate and exhibit a small magnetization under an externally applied magnetic field.

We can obtain some analytical results close to the critical point. Indeed for $\alpha \simeq 1$, the solution x_{sol} is small and we expand

$$\tanh x \approx x - \frac{x^3}{3}$$

The self-consistent equation then writes

$$\alpha x = x - \frac{x^3}{3} \Leftrightarrow x_{sol}^2 = 3(1-\alpha) \quad \text{for } \alpha < 1$$

with solutions

$$m(T) = \frac{k_BT}{qJ}\left(1 - \frac{T}{T_c}\right)^{1/2}$$

for $T < T_c$ and $m = 0$ for $T > T_c$. This shows that $m(T) \propto (T_c - T)^{1/2}$ close to the critical point and the corresponding critical exponent for mean-field is 1/2. This is to be compared to the exact 2D result for the same exponent which is 1/8 (see above).

The magnetic susceptibility is a measure of how much a material will become magnetized under an applied magnetic field. Similar calculations, but including the B terms, do show that

$$\chi = \left.\frac{\mathrm{d}m}{\mathrm{d}B}\right|_{B=0} \sim \frac{1}{|T_c - T|} \xrightarrow{T=T_c} \infty$$

7.3.3 Mean field free-energy.

An alternative route to obtain this result is to calculate directly the free-energy. We know that for non-interacting spins we have:

$$H = -\mu B \sum_i S_i, \quad Z = \left(2\cosh\frac{\mu B}{k_BT}\right)^N, \quad F = -k_BTN\log\left(2\cosh\frac{\mu B}{k_BT}\right)$$

So when we take into account the interactions at the mean-field level, we calculate similarly

$$H = H_{MF} = \underbrace{\frac{JqNm^2}{2}}_{\text{cst}} - \mu B_{\text{eff}} \sum_i S_i, \quad Z_{MF} = \sum_{\{S_i\}} e^{-\beta H_{MF}(\{S_i\})} = e^{-\frac{JqNm^2}{2k_BT}}\left(2\cosh\frac{\mu B_{\text{eff}}}{k_BT}\right)^N$$

which thus gives:

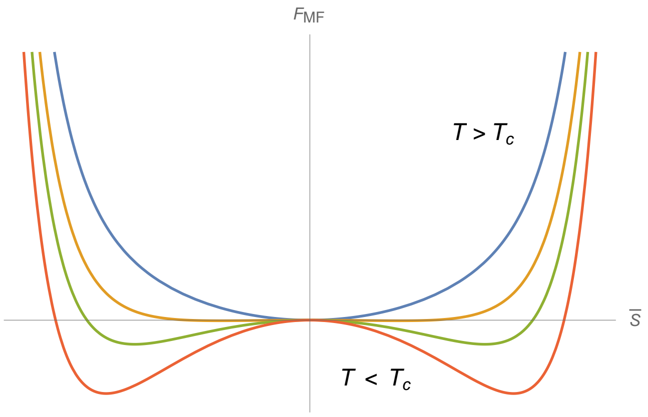
$$F_{MF}(m,T) = -k_BT\log Z_{MF} = \frac{1}{2}JqNm^2 - Nk_BT\log\left(2\cosh\left(\frac{\mu B + Jqm}{k_BT}\right)\right)$$

This expression can be viewed as the free-energy of the system constrained to a magnetization m, $F_{MF}(m)$. At equilibrium, with constant temperature and volume, the free-energy is minimal with respect to the constraint m. This imposes:

$$\frac{\partial F_{MF}}{\partial m} = 0 = N\left(Jqm - k_BT\frac{Jq}{k_BT}\tanh\left(\frac{Jqm}{k_BT}\right)\right) \Rightarrow m = \tanh\left(\frac{Jqm}{k_BT}\right)$$

We thus recovers the previous results.

Now, let us plot this free energy as a function of m for various temperatures, see graph below. For $T < T_c$, $F_{MF}(m)$ exhibits only a single minimum for $m = 0$. Now for $T < T_c$, $F_{MF}(m)$ exhibits two minima for non-vanishing m, and a maximum at $m = 0$. Interstingly, as T decreases across T_c, the curvature of F_{MF} at $m = 0$ (second derivative) reverses, making this solution unstable for $T < T_c$.



7.3.4 Bragg-Williams approach.

We now present an alternative mean field description, called Bragg-Williams approach. As we will see, this gives a different free-energy (one has to remember that the mean field is only an approximation) but the same transition.

To procede, we directly make estimates of the energy and the entropy of the system. Let us introduce the following conventions: $< i, j >$ indicates a sum over all pair of nearerst neighbours spins. The energy is approximated as:

$$E = \langle H \rangle = -J \langle \sum_{<i,j>} S_i S_j \rangle \approx -J \frac{Nq}{2} m^2$$

where the factor $Nq/2$ counts the number of pairs with q nearest neighbors. The entropy is calculated here in terms of the number of configurations to produce a state with a given magnetization m:

$$\mathcal{S}(m) = k_B \log \Omega = k_B \log(\#\{\text{configurations } s | m(s) = m\})$$

So the problem is reduced to counting how many ways there are to generate m. Now if we introduce N_+ and N_- the number of spins up and down we can write:

$$m = \frac{N_+ - N_-}{N}, \quad \text{so} \quad N_+ = N\left(\frac{1+m}{2}\right), \quad N_- = N\left(\frac{1-m}{2}\right)$$

Now the number of possible configurations is simply given by:

$$\Omega = \binom{N}{N_+} = \frac{N!}{N_+! N_-!}$$

From this we get:

$$\begin{aligned}
\mathcal{S} = k_B \log \frac{N!}{N_+! N_-!} &= k_B \left(N \log N - N - N_+ \log N_+ + N_+ - N_- \log N_- + N_-\right) \\
&= -k_B N \left(\frac{N_+}{N} \log \frac{N_+}{N} + \frac{N_-}{N} \log \frac{N_-}{N}\right) = -k_B N \left(\frac{1+m}{2} \log \frac{1+m}{2} + \frac{1-m}{2} \log \frac{1-m}{2}\right)
\end{aligned}$$

So in total we get:

$$F_{BW}(m) = -\frac{JqNm^2}{2} + Nk_BT \left(\frac{1+m}{2} \log \frac{1+m}{2} + \frac{1-m}{2} \log \frac{1-m}{2}\right)$$

As we quoted earlier, one can remark that this expression of the free-energy is not the same as the one we found previously in the previous mean-field approach; however the minima and the corresponding solutions for the magnetization will be the same.

Let us calculate these minima:

$$0 = \frac{\partial F_{BW}}{\partial m} = -JNqm + \frac{Nk_BT}{2} \log \frac{1+m}{1-m}$$

We deduce $\frac{1+m}{1-m} = \exp\left(\frac{2Jqm}{k_BT}\right)$, and then:

$$m = \frac{\exp\left(2\frac{Jqm}{k_BT}\right) - 1}{\exp\left(2\frac{Jqm}{k_BT}\right) + 1} = \tanh\left(\frac{qJm}{k_BT}\right)$$

So we indeed get the same minima as in the previous mean-field description and therefore the same transition point. Note that the Bragg-Williams approach writes the free energy as

$$F = \langle H \rangle - T\mathcal{S}_0$$

where $\mathcal{S}_0$ is the entropy of a 'reference', non-interacting, system. It is therefore making an 'expansion' around the non-interacting model.

7.3.5 Landau description of phase transitions

Landau generalized the description of phase transitions from the consideration of the functional dependence of the free energy in terms of the order parameter. As we showed above, the (mean-field) free energy was obtained to be a function of the magnetization m. Close to the critical point, $T \sim T_c$, we have

$$F_{MF}(m) \overset{T \sim T_C}{\approx} \frac{1}{2}\alpha(T)(T - T_C)m^2 + \frac{1}{4}\beta(T)m^4 + \cdots$$

Such an expansion is called a Landau free energy. This one is generic for second order phase transition, with an order parameter showing an underlying microscopic symmetry $m \to -m$ (see below).

For first order transitions, a typical free energy expansion is

$$F_{MF}(\phi) = \frac{1}{2}\alpha(T)\phi^2 + \frac{1}{3}\beta(T)(T - T^*)\phi^3 + \frac{1}{4}\gamma(T)\phi^4 + \cdots$$

For the liquid-gas transition, the order parameter ϕ is the density (or any equivalent function of the density).

The difference between the expansions for the first and second order transition is the symmetry of terms involved of the various expansion, here the presence of cubic terms in the expansion. As mentioned above, the presence or not of these terms is determined by the microscopical symmetries. For example the spin system we studied previously exhibits an up/down symmetry, i.e the hamiltonian is not changed if one reverses all the spins and so is the free energy. In contrast, the liquid-gas transition has no similar symmetry, hence there is a third order term in the expansion of the free energy in the order parameter (the density difference), as shown above. In the appendix in Chapter 11, we show, for the van der Waals model of the liquid-gas transition, how the Landau expansion emerge from the detailed free energy.

Overal the Landau expansion assumes an analytic expansion (in mathematical sense) in the order parameter, which is not fully justified, in particular close to a critical point. But this framework is extremely useful to describe the properties of matter. Accordingly, applications of the Landau description are numerous: supraconductivity, liquid crystals, super fluidity, etc. For more details on this approach, we refer to the book by Chaikin-Lubensky, *Principles of condensed matter physics*, Cambridge University Press.

7.4 Lattice models.

We discussed above lattice models of spins. But it is easy to introduce lattice models of liquids, or more generally matter, where quantities are discretized on a lattice. We can then 'map' the model to the Ising models and/or make mean-field descriptions, etc.

Let us build a simple lattice model for a liquid. We describe the system on a lattice, and count the number of particles on each site via a spin variable: $S_i = 1$ is the lattice's node contains a particle, and $S_i = 0$ for no particle. We also assume that the interactions in between particles are only acting over short lengths, and we consider only nearest neighbors. We denote the energy of interaction as $-\epsilon_\times$. The Hamiltonian is then given by:

$$H = H(\{S_i\}) = -\epsilon_\times \sum_{\langle i,j \rangle} S_i S_j$$

with the notation $\langle i, j\rangle$ corresponding to nearest neighbours. We can also put the whole system in an external potential, say with an energy $-\epsilon_0$, acting on all particles. This gives an extra term to the Hamiltonian:

$$H_{\text{ext}} = -\epsilon_0 \sum_i S_i$$

Finally the total number of particles is given by:

$$N = \sum_i S_i$$

Note that this model is both extremely crude and simple, but also very rich in terms of properties and predictions. It is obvious that it will present a (liquid-gas) phase transition, with a critical point, since it is very close to the Ising model.

Here we discuss such lattice models in the context of *capillary condensation*, which is the liquid-gas transition shifted by confinement.

7.4.1 Application to a 1D model of capillary condensation.

Sketch of capillary condensation

Capillary condensation is the liquid-vapor phase transition, which is shifted in the confinement. A system of particles (for example water) is confined between two surfaces separated by a distance D and is in contact with an external reservoir of vapor (for example, with controled water humidity). Now let us assume that the confining surfaces have a strong interaction with the fluid, so that they 'prefer' to be wet by the dense liquid. One says that they are 'wetting'. Then a competition occurs: volume effects versus surface effects. In the volume, the stable thermodynamic phase is the vapour; but at surface, the liquid is favored energetically. The ratio of volume versus surface is a length. And we will see that there is indeed a characteristic confinement D_c, such that for $D > D_c$ the bulk phase is stable (vapor), but for $D < D_c$ a phase transition occurs towards the liquid phase. Hence, the shifted liquid-vapour transition.

We will explore exhaustively the capillary condensation in Section 8.5.5.

But here we make a first, crude, approach to the problem using a 1D lattice description. It will be partly infructious and we will not predict a true phase transition, which is expected in 1 dimension. This is however an exact statistical physics calculation and it highlights the transfer matrix method which allows solving the 1D Ising model.

1D model and the transfer matrix method.

We consider a 1D lattice system composed of M interacting sites – characterized by the energy of interaction $\epsilon_\times$ – and interacting with an external 'surface' via an interaction energy $-\epsilon_0$. The occupation of the site by a liquid molecule is determined by the variable $S_i = 0, 1$. We assume that the system is periodic, so that $S_{M+1} = S_1$. The Hamiltonian is given by:

$$\mathcal{H}_{1D} = -\epsilon_\times \sum_{i=1}^{M} S_i S_{i+1} - \epsilon_0 \sum_{i=1}^{M} S_i$$

The total number of particles is $N = \sum_i S_i$. Hence investigating the properties in N, V, T (canonical) ensemble would require to fix this quantity and this makes the calculation particularly cumbersome in terms of combinatorics. Hence we will make use of the grand-canonical ensemble μ, V, T which is particularly relevant for this problem. Accordingly the grand-partition function is defined as

$$\begin{aligned}\Theta &= \sum_{\{S_i\}} e^{\frac{\mu N(\{S_i\})}{k_B T}} e^{-\frac{\mathcal{H}(\{S_i\})}{k_B T}} = \sum_{S_1=0,1} \sum_{S_2=0,1} \sum_{S_3=0,1} \cdots\, e^{\frac{\mu}{k_B T}\sum_i S_i} e^{-\frac{\mathcal{H}(\{S_i\})}{k_B T}} \\ &= \sum_{S_1=0,1} \cdots \sum_{S_M=0,1} \exp\left(\frac{\epsilon_\times}{k_B T}\sum_{i=1}^{M} S_i S_{i+1} + \frac{\epsilon_0 + \mu}{k_B T}\sum_{i=1}^{M} S_i\right) \end{aligned} \tag{7.1}$$

Let us introduce the following notation

$$T(S_i, S_j) = \exp\left(\frac{\epsilon_\times}{k_B T} S_i S_j + \frac{\epsilon_0 + \mu}{k_B T}\frac{S_i + S_j}{2}\right)$$

and the partition function can then be rewritten as

$$\Theta = \sum_{S_1=0,1} \cdots \sum_{S_M=0,1} \prod_{i=1}^{M} T(S_i, S_{i+1})$$

Now $T(S_i, S_j)$ can be considered as the element of a 2×2 matrix:

$$\Pi = \begin{pmatrix} T(1,1) & T(1,0) \\ T(0,1) & T(0,0) \end{pmatrix}$$

for the various values of $S_i = 0, 1$, $S_j = 0, 1$. Now using this matrix, we can rewrite the previous sum in terms of product of matrices. For example, fixing S_i, S_j we have the relationship

$$\sum_{S_k} T(S_i, S_k) T(S_k, S_j) = (\Pi^2)(S_i, S_j)$$

Similarly, extending to a further term, we have

$$\sum_{S_k, S_m} T(S_i, S_k) T(S_k, S_m) T(S_m, S_j) = (\Pi^3)(S_i, S_j)$$

etc. In general we have that for any matrix A,

$$(A^n)_{i,j} = \sum_{i_1,i_2,\ldots i_{n-1}} A_{i,i_1} A_{i_1,i_2} \cdots A_{i_{n-1},j}$$

so that

$$\mathrm{Tr}(A^n) = \sum_{\{i_k\}} A_{i_1,i_2} A_{i_2,i_3} \cdots A_{i_n,i_1}$$

Then in the previous sum for the partition function, we can perform all the intermediate sums to obtain in the end:

$$\Theta = \sum_{S_1=0,1} (\Pi^M)(S_1,S_1) = \mathrm{Tr}\big(\Pi^M\big)$$

(noting that due to periodicity, S_1 appears at the two ends of the line of spins). Now we diagonalize Π^M to compute the trace. The matrix itself is:

$$\Pi = \begin{pmatrix} \exp\Big(\frac{\epsilon_\times}{k_BT} + \frac{\epsilon_0+\mu}{k_BT}\Big) & \exp\Big(\frac{\epsilon_0+\mu}{2k_BT}\Big) \\ \exp\Big(\frac{\epsilon_0+\mu}{2k_BT}\Big) & 1 \end{pmatrix} \equiv \begin{pmatrix} a & b \\ b & 1 \end{pmatrix}$$

The eigen values follows immediately as

$$\lambda_\pm = \frac{1 + a \pm \sqrt{(1-a)^2 + 4b^2}}{2}$$

with a and b defined above. The partition function is therefore

$$\Theta = \lambda_+^M + \lambda_-^M$$

For large system size $M \to \infty$, the largest eigenvalue dominates, $\Theta \approx \lambda_+^M$ and the grand potential follows as

$$\Omega(\mu, T, M) = -k_BT \log\Theta = -Mk_BT \log(\lambda_+(\mu,T))$$

From the expression of the partition function, one can calculate any thermodynamic property. For example, the average density is calculated as

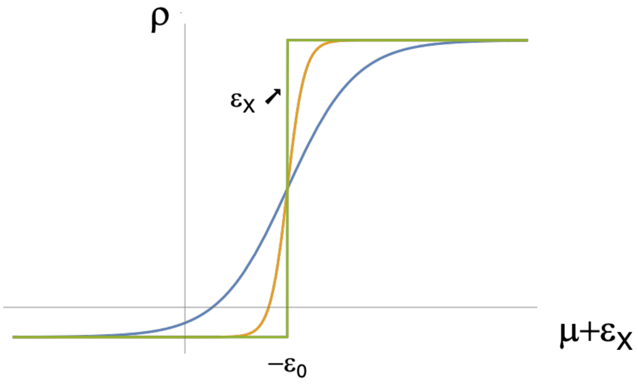
$$N = -\frac{\partial\Omega}{\partial\mu} = Mk_BT \frac{\frac{\partial^2}{\partial\mu\partial\lambda_+(\mu,T)}}{\lambda_+(\mu,T)} \Rightarrow \rho = \frac{N}{L} = \frac{k_BT}{a}\frac{\frac{\partial\lambda_+}{\partial\mu}}{\lambda_+}$$

leading to

$$\rho(\mu,T) = \frac{1}{2a}\left[1 + \frac{\sinh\Big(\frac{\epsilon_0+\epsilon_\times+\mu}{2k_BT}\Big)}{\sqrt{\exp\Big(-\frac{\epsilon_\times}{k_BT}\Big) + \sinh^2\big(\frac{\epsilon_0+\epsilon_\times+\mu}{2k_BT}\big)}}\right]$$

We plot the density as a function of the chemical potential in the figure below. This plot does not highlight any discontinuity or change of slope, meaning that there is no pecularity in the thermodynamic potential. In other words, there is NO phase transition in this model. The model predicts a smooth transition from a low density (gaseous system) to a high density (liquid system) for $\mu \simeq -(\epsilon_0 + \epsilon_\times)$. The transition becomes steeper as $\epsilon_\times$ increases and only in the peculiar limit $\epsilon_\times \to \infty$ we get a step-function for the density, meaning a phase transition.

Altogether, one should however appreciate that this is an *exact* result, which accounts for the strong corrrelation between particles. The absence of phase transition is due to the 1D nature of the problem. In Sec. 8.5.5 below, we will come back to the phenomenon of capillary condensation, and discuss the underlying thermodynamics.



7.5 Dense Liquids and Phase Transitions.

7.5.1 Structures in liquids.

A liquid is a dense and disordered phase. To give some orders of magnitude, the density is typically $\rho \sim \frac{1}{\sigma^3}$ where σ is the size of one molecule. For water for example: $\rho = 3\cdot 10^{28}\,\text{molecules.m}^{-3}$ (to compare with $\sigma^{-3} = 1/(3\cdot 10^{-10})^3 = 3{\cdot}10^{28}\,\text{molecules.m}^{-3}$). There are therefore strong interactions between molecules, which makes the calculation of the statistical properties really difficult, and in particular the partition functions. We discussed already in section 8.1 the typical interactions occuring between molecules and atoms and quoted the examples of Lennard-Jones or hard sphere potentials. For a given pair interaction potential $V(\vec r)$, the classical (canonical) partition function will write

$$Z = \frac{1}{N!\,h^{3N}}\int \mathrm{d}\vec r_1\cdots\mathrm{d}\vec r_N \mathrm{d}\vec p_1\cdots\mathrm{d}\vec p_N e^{-\beta\{\sum_i \frac{\vec p_i^{\,2}}{2m}+\sum_{i<j}V(\vec r_i-\vec r_j)\}}$$

The kinetic part factorizes from the potential part and can be integrated out explicitly to give

$$Z = \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N \times \frac{1}{V^N}\int \mathrm{d}\vec r_1\cdots\mathrm{d}\vec r_N e^{-\beta\sum_{i<j}V(\vec r_i-\vec r_j)}$$

with λ_T the thermal de Broglie length scale, $\lambda_T = \sqrt{h^2/2\pi m k_B T}$. This highlights the ideal part of the partition function $Z_{\text{id}} = \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N$. The remaining potential part is the most interesting and contains most of the phase behavior... but is unfortunately highly difficult to calculate.

So we now discuss a number of tools to describe dense liquids, as well as various approximation schemes to evaluate the partition function of interacting particles and their thermodynamic properties.

Structure and density correlations.

We start by considering the structure inside liquids. Since the system is packed, the position of each molecules is strongly correlated to that of its neighbours. We introduce here the correlation functions, an in particular the pair correlation function $g(r)$, which are proper descriptors of the liquid structure.

Let us formally introduce correlation functions from the microscopic density ,

$$\hat\rho(\vec r) = \sum_{i=1}^{N}\delta(\vec r-\vec r_i)$$

This is as such a distribution in mathematical terms (see Chap. 10.3). The integration over the volume V leads to the simple result:

$$\int \mathrm{d}^3\vec r\,\hat\rho(\vec r) = \sum_{i=1}^{N}\int \mathrm{d}^3\vec r\delta(\vec r-\vec r_i) = N$$

The statistical average of the microscopic density reduces $\rho^{(1)}(\vec r) = \langle\hat\rho(\vec r)\rangle$ to the usual numerical density $\rho = N/V$ in an homogeneous system

$$\rho^{(1)}(\vec r) = \langle\sum_{i=1}^{N}\delta(\vec r-\vec r_i)\rangle = \rho$$

One can then define a two-body density distribution according to:

$$\rho^{(2)}(\vec{r},\vec{r}') = \langle \hat{\rho}(\vec{r})\hat{\rho}(\vec{r}')\rangle = \langle \sum_{i,j} \delta(\vec{r}-\vec{r}_i)\delta(\vec{r}'-\vec{r}_j)\rangle$$

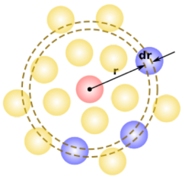
For $|\vec{r}-\vec{r}'| \to +\infty$, the two regions of the system become uncorrelated and $\rho^{(2)}(\vec{r},\vec{r}') \to \rho^2$. The two-point correlation function is accordingly defined as

$$G(\vec{r},\vec{r}') = \langle (\hat{\rho}(\vec{r})-\rho)(\hat{\rho}(\vec{r}')-\rho)\rangle$$

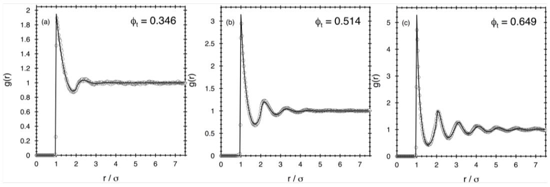
In a translationally invariant system, $G(\vec{r},\vec{r}') = G(\vec{r}-\vec{r}')$ and one can rewrite

$$G(\vec{r},\vec{r}') = \rho\,\delta(\vec{r}-\vec{r}') + \rho^2(g(\vec{r}-\vec{r}')-1)$$

where we introduced $g(\vec{r})$, the pair correlation function; the first term comes from the $i=j$ contribution in the previous sum. In a homogeneous and isotropic system, this function only depends on the distance $r=|\vec{r}|$ between molecules. It has accordingly a simple interpretation: $\rho g(r)$ is the density of particules at a distance r from a particle situated at $r=0$. In other words, $\rho g(r) \times (4\pi r^2 dr)$ *is the probability to find a molecule at a distance r within dr from a central molecule.* The pair correlation function thus describes the modulation of the density around a given particle. In a dense liquid we expect the following behavior for $g(r)$ for various densities (the volume fraction being defined as $\phi = \frac{\pi}{6}\rho\sigma^3$), showing that the density oscillation increase when the density increases. This is the signature of an increasing local structure inside the liquid, with a particle enclosed in a 'cage' formed by its neighbours. The oscillations correspond to the first, second, third, etc. layers of neighbours. The effect gets stronger as the particle density increases.



(wikipedia)



D. Aarts, R. Dullens (Oxford)

When the density is moderate, corresponding to a 'dense gas' with weak interactions, the probability to find a particles around a fixed center will be given by the simple Boltzmann weight in terms of interaction potential, $e^{-\frac{V(r)}{k_BT}}$. One thus concludes that

$$g(r) = e^{-\frac{V(r)}{k_BT}}$$

for low to intermediate densities.

For more details on fluid structure, we refer to Hansen and McDonald, *Theory of Simple Liquids*, Elsevier (2013).

Link with thermodynamics and virial Expansion

The knowledge of the pair correlation function $g(r)$ is central in liquid and it allows computing many properties of the fluid. For example one can obtain an (exact) virial formula for the pressure in terms of $g(r)$ as

$$\frac{P}{k_BT} = \rho - \frac{\rho^2}{6k_BT}\int \mathrm{d}\vec{r}\,g(r)\,\vec{r}\cdot\vec{\nabla}V$$

(not demonstrated here, see Hansen and Mc Donald cited above).

The previous exact formula illustrates how the pressure expands naturally as a function of density. For example, if one assumes that $g(r)$ is independent of ρ (which is only valid at low densities), then the previous formula simply gives terms in ρ and ρ^2. The first correction of g in density will lead to a term in ρ^3, etc. In full generality, one can write

$$\frac{P}{k_BT} = \rho + B_2\rho^2 + B_3\rho^3 + \cdots \text{ where } B_i \text{ is called the virial coefficients.}$$

The term B_2 only takes into account 2 body interactions and its expression is:

$$\boxed{B_2 = \frac{1}{2}\left(\int \mathrm{d}^3\vec{r}\left[1-e^{-\frac{V(r)}{k_BT}}\right]\right)}$$

A simple derivation of this result is to use the previous virial formula and injecting the first correction for $g(r)$, $g(r) = e^{-\frac{V(r)}{k_BT}}$ valid for low density (and which is independent of the density):

$$-\frac{1}{6k_BT}\int \mathrm{d}\vec{r}\,\vec{r}\cdot\underbrace{\vec{\nabla} v e^{-\frac{V(r)}{k_BT}}}_{k_BT\left(1-e^{-\frac{V(r)}{k_BT}}\right)} = \frac{-1}{6k_BT}\int \mathrm{d}\vec{r}\,\vec{r}\cdot\vec{\nabla}\left[1-e^{-\frac{V(r)}{k_BT}}\right] = \underbrace{\int_{R\to+\infty}\mathrm{d}\vec{S}\,\vec{r}(1-e^{-\frac{V(r)}{k_BT}})}_{\to 0} + \frac{1}{6}\int \mathrm{d}^3\vec{r}(1-e^{-\frac{V(r)}{k_BT}})\underbrace{\vec{\nabla}\cdot\vec{r}}_{3}$$

hence the previous result, $B_2 = \frac{1}{2}\int \mathrm{d}^3\vec{r}(1-e^{-\frac{V(r)}{k_BT}})$.

An alternative derivation is to expand the partition function as a function of the density (Mayer development). We first write $Z = Z_{\mathrm{id}} \times Z_{\mathrm{ex}}$ where:

$$Z_{\mathrm{id}} = \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N \quad \text{and} \quad Z_{\mathrm{ex}} = \frac{1}{V^N}\int \mathrm{d}^3\vec{r}_1\cdots\mathrm{d}^3\vec{r}_N\, e^{-\beta\sum_{i<j}V(\vec{r}_{ij})}$$

Then we re-write:

$$Z_{\mathrm{ex}} = \langle e^{-\sum_{i<j}\beta V(r_{ij})}\rangle_v \quad \text{where} \quad \langle\cdot\rangle_v = \frac{1}{V^N}\int \mathrm{d}\vec{r}_1\cdots\mathrm{d}\vec{r}_N(\cdot)$$

To proceed further and illustrate the density expansion, one can make a crude factorization approximation for Z_{ex} to write

$$Z_{\mathrm{ex}} = \langle\prod_{i<j} e^{-\beta V(r_{ij})}\rangle_v \approx \prod_{i<j}\langle e^{-\beta V(r_{ij})}\rangle_v$$

in which we only keep the two-body interaction terms. This approximation is best understood by introducing the Mayer function defined as $\exp[-\beta V(r_{ij})] \equiv 1 + f(r_{ij})$. In the expansion, this amounts to keeping only the terms that are linear in f: $\langle\prod_{i<j} e^{-\beta V(r_{ij})}\rangle_v = \langle\prod_{i<j}[1+f(r_{ij})]\rangle_v \simeq 1 + \langle\sum_{i<j} f(r_{ij})\rangle_v + \dots$

Using this result, we can then calculate

$$\langle e^{-\beta V(r_{ij})}\rangle_v = \frac{1}{V^N}\int \mathrm{d}\vec{r}_1\cdots\mathrm{d}\vec{r}_N e^{-\beta V(r_{ij})} = \frac{1}{V^2}\underbrace{\int \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2 e^{-\beta V(\vec{r}_{12})}}_{\vec{r}_{12}=\vec{r}_1-\vec{r}_2=\vec{r}} = \frac{1}{V}\int \mathrm{d}\vec{r}\;\underbrace{e^{-\beta V(\vec{r})}}_{1+(e^{-\beta V(r)}-1)} = 1 - \frac{1}{V}\left(\int \mathrm{d}\vec{r}(1-e^{-\beta V(\vec{r})})\right)$$

Back to the free-energy, $F = -k_BT\log Z = F_{\mathrm{id}} + F_{\mathrm{ex}}$, we get

$$F = -k_BT\log Z = F_{\mathrm{id}} - k_BT\log\underbrace{\prod_{i<j}\left[1-\frac{1}{V}\left(\int \mathrm{d}\vec{r}(1-e^{-\beta V(r)})\right)\right]}_{\left(1-\frac{1}{V}\int \mathrm{d}\vec{r}1-e^{-\beta V(r)}\right)^{\frac{N(N-1)}{2}}} = F_{\mathrm{id}} - \frac{k_BT}{2}N^2\log\underbrace{\left(1-\frac{1}{V}\int \mathrm{d}\vec{r}[1-e^{-\beta V(r)}]\right)}_{\approx\frac{-1}{V}\left(\int \mathrm{d}\vec{r}1-e^{-\beta V(r)}\right)}$$

and we recover the previously announced result:

$$P = -\frac{\partial F}{\partial V} = P_{\mathrm{id}} + P_{\mathrm{ex}} = \rho k_BT + k_BT\rho^2\frac{1}{2}\int \mathrm{d}\vec{r}(1-e^{-\frac{V(r)}{k_BT}}) + \dots$$

These are the two first terms in the virial expansion for the pressure. Increasing the density requires to add more and more terms in the density expansion. At very high density, this expansion is not very efficient in capturing the strong correlations, in particular those originating in volume exclusion, and requires to involve high order terms in the expansion. We will follow an alternative method below to account for these effects.

7.5.2 Virial expansion and Van der Waals fluid.

The idea here is to split the potential in two pieces: a short range interaction term ('$r < \sigma$') and a long range interaction term ('$r > \sigma$'). The second virial coefficient $B_2(T)$ thus writes as:

$$B_2 \approx B_{\mathrm{SR}} + B_{\mathrm{LR}} \quad \text{where} \quad B_{\mathrm{SR}} = \frac{1}{2}\int_{r=0}^{\sigma}(1-\underbrace{e^{-\beta V(r)}}_{\approx 0}) \text{ and } B_{\mathrm{LR}} = \frac{1}{2}\int_{r=\sigma}^{+\infty}\underbrace{(1-e^{-\beta V(r)})}_{\approx\beta V(r)}$$

where we assumed that the potential is strong and repulsive for the short rand part, and weak in the long rang part. Hence we get that:

$$B_2 = \frac{1}{2}\frac{4\pi\sigma^3}{3} + \frac{1}{2k_BT}\int_{\sigma}^{+\infty}V(r)\mathrm{d}\vec{r} = b - \frac{a}{k_BT}$$

We call b the excluded volume and a is positive if the long range potential is attractive.

State equation.

From the virial expansion we immediately get:

$$\frac{P}{k_BT} = \rho + (b - \frac{a}{k_BT})\rho^2$$

so that:

$$\frac{P}{k_BT} = (\rho + b\rho^2) - \frac{a\rho^2}{k_BT}$$

Excluded Volume.

As we quoted above, one issue is that the second term $b\rho^2$ originates in the short range part, i.e. excluded volume where correlation are very strong. The virial expansion is therefore ill-justified for this term.

Let us come back on the origin of this contribution. Physically this excluded volume term stems from the fact that the volume accessible to particles is restricted by the presence of the other particles. A simple way to account for this effect is to simply replace the bare volume with the free volume accessible to particles, i.e:

$$V^N \to V_{\text{free}}^N = [V - \frac{N}{2}V_0]^N \text{ where } V_0 \text{ is the volume of 1 particle.}$$

The $N/2$ term avoids double-counting of pairs of particles. Keeping only these terms (we forget for now the other interaction terms in the partition function), we obtain the following expression for the partition function

$$Z = Z_{\text{id}} \times Z_{\text{ex}} \text{ with } Z_{\text{id}} = \frac{V^N}{N!\,\lambda^{3N_T}} \text{ and } Z_{\text{ex}} = \left(1 - \frac{N}{2}\frac{V_0}{V}\right)^N$$

The free energy follows directly

$$F = -k_BT \log Z = -k_BT \log Z_{\text{id}} - k_BT \log Z_{\text{ex}}$$

and the pressure is deduced as:

$$P = -\frac{\partial F}{\partial V} = \rho k_BT + Nk_BT\frac{\partial}{\partial V}\log\left(1 - \frac{NV_0}{2V}\right) = \rho k_BT + \frac{\rho^2 k_BT}{1 - \frac{\rho V_0}{2}}\frac{V_0}{2} = \frac{\rho k_BT}{1 - b\rho}$$

Where $b = \frac{V_0}{2}$ is the excluded volume. As expected the pressure does strongly increases with density, and diverges when the density increase reaches $\frac{1}{b}$, corresponding to the situation where particles fill the complete volume V (no free volume).

Van der Waals equation of state and free energy

Adding this excluded volume contribution to the virial contribution associated with the long range forces, one obtains the corresponding van der Waals equation of state:

$$P(\rho, T) = \frac{\rho k_BT}{1 - b\rho} - a\rho^2$$

The corresponding free energy for the van der Waals model is

$$f = \frac{F}{V} = k_BT[\rho \log \frac{\rho\lambda_T^3}{1 - b\rho} - \rho] - a\rho^2$$

and the chemical potential $\mu = \frac{\partial F}{\partial N} = \frac{\partial f}{\partial \rho}|_{V,T}$ is

$$\mu = k_BT \log(\rho\lambda_T^3) + \frac{\partial}{\partial \rho}\left[k_BT \log \frac{1}{1 - b\rho} - a\rho^2\right] = k_BT \log\left(\frac{\rho\lambda_T^3}{1 - b\rho}\right) + k_BT\frac{\rho b}{1 - b\rho} - 2a\rho$$

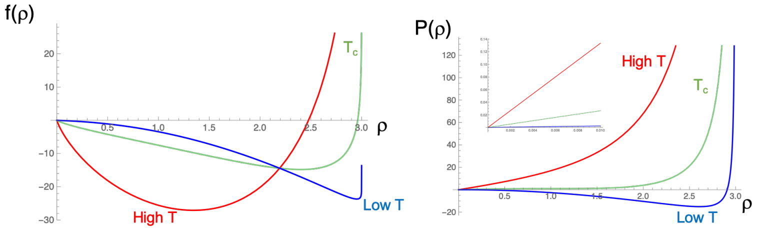
7.5.3 Liquid-gas phase transition of the van der Waals fluid.

Note that we provide in the Chapter 11 a Mathematica file calculating numerically the phase diagram for the van der Waals fluid, including the spinodal, phase coexistence, as well as the corresponding Landau expansion of the free energy.

The previous van der Waals model for dense fluids is a canonical model to study the liquid-gas phase transition. In spite of its simplicity, the model captures qualitatively most of the physics of the transition, including the existence of a critical point, metastable states, etc. Of course the region very close to the critical point would require more advanced descriptions, which go beyond the purpose of this lecture.

The existence of a liquid-gas phase transition originates in the long range attractive interactions. In practice, this can be understood from the previous expression of the free energy: the corresponding $-a\rho^2$ contribution to the free energy density is a *concave* contribution, opposing the *convex* entropic and excluded volume terms (the first and second contribution). Hence, when this term becomes dominant, the free energy may become concave and the system hence unstable. As a rule of thumb, this occurs when $a\rho^2 \gg k_BT\rho$ for densities $\rho \sim 1/b$, hence for temperature $k_BT \ll \frac{a}{b}$. One expects therefore a critical temperature $T_c \sim \frac{a}{k_Bb}$ below which phase separation occurs and not above.

A similar estimate can be obtained using the pressure, since in the above parameters sets, the pressure will obey $\frac{\partial P}{\partial \rho} < 0$ and the system is accordingly thermodynamically unstable in this region.



(in unit or ρ_c and T_c)

Spinodal and critical point.

We start by analyzing the spinodal limit. To do so, we search for the unstable region, which is such that $\frac{\partial^2 f}{\partial \rho^2} < 0$, and the boundaries of the spinodal curve in the phase diagram are defined by $\frac{\partial^2 f}{\partial \rho^2} = 0$, or $\frac{\partial P}{\partial \rho} = 0$. For a given temperature, this will give two values for the density, $\rho^V_{\text{spin}}(T)$ and $\rho^L_{\text{spin}}(T)$ delimiting the spinodal region. Calculating

$$0 = \frac{\partial P}{\partial \rho} = \frac{k_BT}{1-b\rho} + \frac{\rho k_BTb}{(1-b\rho)^2} - 2a\rho$$

one deduces that ρ^V_{spin} and ρ^L_{spin} are the two solutions of the equation

$$k_BT = 2a\rho_{\text{spin}}(1-b\rho_{\text{spin}})^2 \equiv T_{\text{spin}}$$

From the corresponding solutions, one can also calculate the spinodal pressure $P_{\text{spin}}(\rho_{\text{spin}}(T), T)$ as a function of temperature (or equivalently $P_{\text{spin}}(\rho, T_{\text{spin}}(\rho))$ for a given density). We plot below the boundaries of the spinodal in the ρ, P variables.

The curves $\rho^V_{\text{spin}}(T)$ and $\rho^L_{\text{spin}}(T)$ (or corresponding pressures) join at a maximal temperature T_c where $\rho^V_{\text{spin}}(T_c) = \rho^L_{\text{spin}}(T_c)$. This is the critical point. In terms of the pressure, this critical point is defined according to

$$\boxed{\left.\frac{\partial P}{\partial \rho}\right|_C = 0 \quad \text{and} \quad \left.\frac{\partial^2 P}{\partial \rho^2}\right|_C = 0}$$

For the van der Waals fluid, one obtains

$$\frac{\partial^2 P}{\partial \rho^2} = \frac{2k_BT}{(1-b\rho)^2} - 2a$$

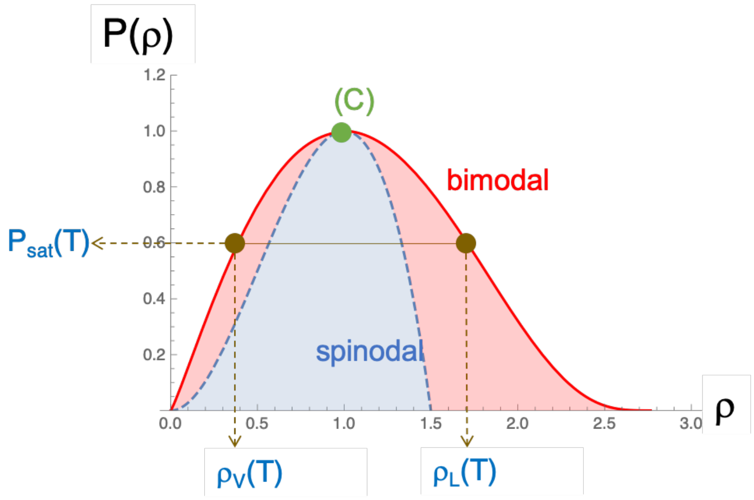
and the critical point conditions write

$$\begin{cases} k_BT_c = 2a\rho_c(1-b\rho_c)^2 \\ bk_BT_c = a(1-b\rho_c)^3 \end{cases} \Rightarrow \begin{cases} b = \frac{1}{2\rho_c}(1-b\rho_c) \\ \rho_c = \frac{1}{3b} \end{cases} \Rightarrow \begin{cases} \rho_c = \frac{1}{3b} \\ k_BT_c = \frac{8a}{27b} \\ P_c = \frac{a}{27b^2} \end{cases}$$

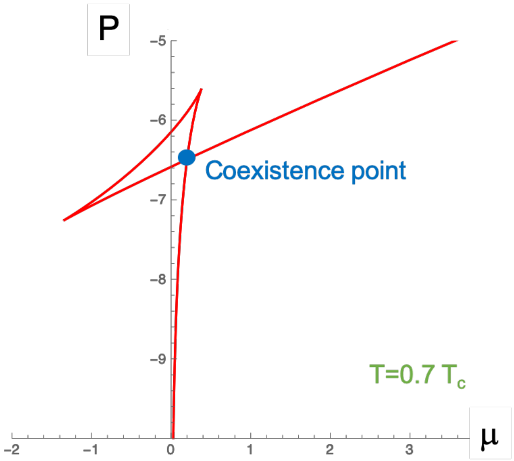
Coexistence.

The coexistence curve is obtained by solving the equilibrium conditions, i.e. equality of pressures and chemical potentials in the gas and liquid phase.

$$P(\rho_l, T) = P(\rho_g, T) \equiv P_{\text{sat}}(T) \quad \text{and} \quad \mu(\rho_l, T) = \mu(\rho_g, T) \equiv \mu_{\text{sat}}(T)$$



An illustrative way to highlight the coexistence, and this condition of equality of pressure and chemical potential, is to make a parametric plot of $P(\rho,T)$ versus $\mu(\rho,T)$ using density ρ as a variable for a fixed temperature T. This is shown in the enclosed figure for a temperature below the critical temperature. The curve intersects itself in the μ, P plane, demonstrating that there are two densities ρ_g and ρ_l for which the pressure and chemical potential are equal. This is the coexistence condition.



To get quantitative results, the condition of equal pressure and chemical potential can be solved numerically in order to obtain the values for ρ_g and ρ_L for any temperature. The numerical solution using Mathematica is presented in Chapter 11.

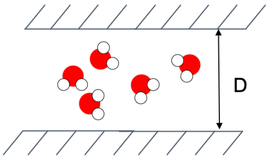
We plot the resulting curve for the phase diagram in the ρ, P variables, see graph above, together with the spinodal curve. This coexistence curve is also called the 'bimodal'.

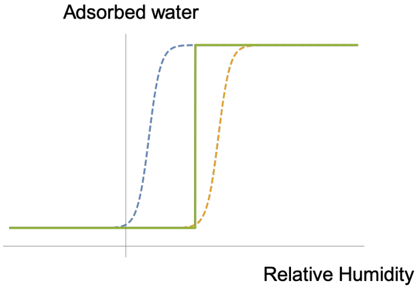
7.5.4 Thermodynamics of capillary condensation.

We come back in this section on the question of the capillary condensation, which is the liquid-gas phase transition in confinement. This extends naturally the above discussion concerning the liquid-gas phase transition.

We consider a system of particles confined in a slit, and in equilibrium with a large (external) reservoir which fixes the chemical potential of the fluid to $\mu_{\rm res}$. For example, one may consider water in a porous material (with pores), in contact with a reservoir of water vapor with fixed relative humidity, RH. In this case, the chemical potential of water is fixed to $\mu(RH) = \mu_{\rm sat}(T) + k_B T \log(RH)$; $RH = P_v/P_{\rm sat}(T)$. The 'saturating' values of the chemical potential are those corresponding to the coexistence point at temperature T.

The physical principle underlying the capillary condensation is a surface-to volume balance. The stable phase in the reservoir is the vapor, so the particles in the bulk of the pore will involve a free energy term favoring the vapour and proportional to the volume V, generically as $\Delta f \times V$. Now, if we assume that the surfaces are 'wetting', this means that they favor the liquid and there is a surface free energy which is lower for the liquid as compared to the vapor; we usually write this as $\gamma_{SL} < \gamma_{SV}$, with γ the surface free energy. The corresponding free energy gain writes as $\mathcal{A}(\gamma_{SL} - \gamma_{SV})$ where $\mathcal{A}$ is the area of the 'wetting' surface.





Hence in confinement, the system will undergo a transition from the vapour to the liquid when the gain outweighs the cost i.e. $V\delta f \sim \mathcal{A}\delta\gamma$. This highlights a threshold confinement $H_c \sim \frac{V}{\mathcal{A}} \sim \frac{\Delta\gamma}{\Delta f}$ below which surface effects overcome the bulk terms and liquid 'condenses' in the confinement. This is the essence of the capillary condensation.

Let us formalize this a bit. We will follow two different routes, highlighting various aspects of the capillary condensation.

Density functional approach.

Let us first introduce a density functional approach. To model the system we assume that the fluid interacts with the surface via an external potential $V_{\text{ext}}(z)$ which depends only on the distance between fluid particles and the surface surface. Including this external potential, the grand potential Ω, constrained to the value ρ of the density, takes the form:

$$\Omega(\{\rho\}|\mu, V, T) = \int \mathrm{d}^3\vec{r}\,[f(\rho(\vec{r}) - \mu\rho(\vec{r}) + \rho(\vec{r})V_{\text{ext}}(\vec{r})]$$

Note that here we introduced the full density profile $\rho(\vec{r})$ as a parameter. This means that Ω depends on the value of the density at each point of the sample, as $\Omega(\rho_1, \rho_2, \rho_3, \dots)$ where $\rho_i = \rho(\vec{r}_i)$ is the density at point $\vec{r}_i$: the grand potential is accordingly a density functional, see Chapter 10 for more details.

Here we make a crude simplification and write that the density is homogeneous, $\rho(\vec{r}) \approx \rho_0 = \text{cst}$. This then simplifies the integral as follows:

$$\int \mathrm{d}^3\vec{r}\rho(\vec{r})V_{\text{ext}}(\vec{r}) \approx 2\mathcal{A}\cdot\rho_0\int_0^{+\infty}\mathrm{d}zV_{\text{ext}}(z)$$

with $\mathcal{A}$ the lateral area. The factor 2 come from the two surfaces and we assume that the distance D between the surfaces is larger than the range of the potential $V_{\text{ext}}(z)$. Defining

$$-\alpha = \int_0^{+\infty}\mathrm{d}zV_{\text{ext}}(z) < 0$$

we hence obtain

$$\Omega(\rho, \mu, V, T) = V \times (f(\rho_0) - \mu\rho_0) - 2\rho_0\alpha\,\mathcal{A}$$

Now the distance between walls is $D = V/\mathcal{A}$, so that

$$\Omega(\rho_0|\mu, V, T) = V\left[f(\rho_0) - \underbrace{\left(\mu + \frac{2\alpha}{D}\right)}_{\mu_{\text{app}}}\rho_0\right]$$

This equation highlights that the confined fluid behaves as a bulk fluid, but with a shifted chemical potential

$$\mu_{\text{app}} = \mu + \frac{2\alpha}{D}.$$

From the discussion on the fluid phase transition above, we know that for chemical potential below μ_{sat} ($\equiv \mu_{\text{coex}}$), the vapor phase is stable in the reservoir, while for chemical potential above μ_{sat} the liquid phase is stable in the reservoir. Now in confinement, this discussion is made according to the apparent chemical potential $\mu_{\text{app}} = \mu + \frac{2\alpha}{D}$. We define

$$\Delta\mu = \mu_{\text{sat}} - \mu$$

Since the vapor phase is the stable phase in the reservoir, then $\Delta\mu > 0$. In confinement, there will be therefore a vapour to liquid transition when $\mu_{\text{app}} > \mu_{\text{sat}}$, i.e. the transition in confinement happens for

$$\Delta\mu = \frac{2\alpha}{D}$$

As a final step, let us rewrite α in terms of the surface free energies γ_{SL} and γ_{SV}. In the considered model we have that $\gamma_{SL} = \rho_L \cdot (-\alpha)$ and $\gamma_{SV} = \rho_V \cdot (-\alpha)$. Hence combining the two expressions, we can write α as:

$$\alpha = \frac{\gamma_{SV} - \gamma_{SL}}{\rho_L - \rho_V} > 0$$

Altogether capillary condensation occurs at a threshold chemical potential

$$\Delta\mu = \frac{2\Delta\gamma}{\Delta\rho D}$$

Equivalently, if one introduces the threshold confinement

$$D_c = \frac{2\Delta\gamma}{\Delta\rho\Delta\mu}$$

then the vapour to liquid transition occurs for $D < D_c$.

Finally let us relate the chemical potential to the 'humidity' in the reservoir. As we wrote in the introduction, the relative humidity denoted RH is given by $RH = \frac{P_v}{P_{\text{sat}}}$, and the expression for the chemical potential (approximated to an ideal gas) then writes:

$$\mu = \mu_{\text{sat}} + k_B T \log\frac{P_v}{P_{\text{sat}}}$$

Hence we can re-write:

$$\Delta\mu = k_B T \log\big(RH^{-1}\big)$$

The threshold confinement is accordingly

$$D_c = \frac{2\Delta\gamma}{\Delta\rho\, k_B T \log\big(RH^{-1}\big)}$$

This is usually called a Kelvin length.

Thermodynamical approach.

Let us now follow a slightly different thermodynamic approach. Here the chemical potential of the fluid is fixed in the reservoir, so the proper thermodynamic potential is the grand potential, $\Omega(\mu, V, T)$. One can calculate the grand potential assuming the vapour phase fills the pore, which we denote as Ω_V, as well as the potential assuming the vapour phase fills the pore, Ω_L. Their expressions are

$$\Omega_V = -P_v V + 2\gamma_{SV} S \quad \wedge \quad \Omega_L = -P_L V + 2\gamma_{SL}\mathcal{A}$$

And P_V and P_L both depend on μ and T and we will provide expression below. The potential difference $\Delta\Omega = \Omega_L - \Omega_V$ is given by:

$$\Delta\Omega = -(P_L - P_V)V - 2(\gamma_{SV} - \gamma_{SL})\mathcal{A}$$

and accordingly

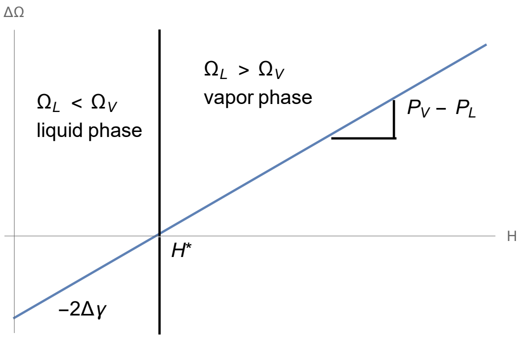
$$\frac{\Delta\Omega}{\mathcal{A}} = -(P_L - P_V)D - 2\Delta\gamma$$

This is a linear function of D which crosses "0" for a threshold distance D_c such that $\Delta\Omega(D_c) = 0$. Hence this gives $D_c = \frac{2\Delta\gamma}{P_V - P_L}$; see enclosed figure. Let us now calculate $P_V - P_L$ as a function of the chemical potential μ, T. We know that:

$$\mu = \mu_{\text{sat}} + k_B T \log\frac{P_V}{P_{\text{sat}}} \Rightarrow P_V = P_{\text{sat}} \exp\left(-\frac{\Delta\mu}{k_B T}\right) \approx P_{\text{sat}} - \rho_V \Delta\mu \quad \text{with } \rho_V = \frac{P_{\text{sat}}}{k_B T}$$

Now for P_L we cannot use the perfect gas approximation because the pressure and density are way too high. However we can use the Gibbs-Duhem relation, which gives:

$$\rho \mathrm{d}\mu = \mathrm{d}P$$



Assuming that the liquid is incompressible then we have that $\rho = \rho_L$ and independent of μ, and we can rewrite the above equation as:

$$\rho_L \underbrace{(\mu - \mu_{\text{sat}})}_{-\Delta\mu} \approx P_L - P_{\text{sat}}$$

So overall we get that:

$$P_V - P_L = P_V - P_{\text{sat}} + P_{\text{sat}} - P_L = -\rho_V \Delta\mu + \rho_L \Delta\mu = (\rho_L - \rho_V)\Delta\mu$$

Putting everything together we obtain that:

$$D_c = \frac{2\Delta\gamma}{(P_V - P_L)} = \frac{2\Delta\gamma}{\Delta\rho\Delta\mu}$$

which identifies with the previous expression, as expected.

Applications.

Putting numbers, D_c is in the range of nanometers and increases with humidity, diverging at $RH = 1$ (100% humidity). There are many example and applications for capillary condensation in many different fields: porous media, membranes, granular systems, biology, protein folding (for which it is merely the reverse capillary evaporation phenomenon in hydrophobic confinement), etc.

Chapter 8

Statistical ensembles and thermodynamics.

In the previous chapters, we have introduced the basic tools of statistical physics and we have showed some links with thermodynamics and thermodynamic functions. In this chapter, we summarize and discuss more thoroughly thermodynamic principles on their own. While there is an intimate relationship between the two fields, it is crucial to handle properly the principles of thermodynamics when investigating many-body systems using statisticial physics. We will in particular discuss the thermodynamics of phase transitions.

For further details, we refer to the book by H.B. Callen, Callen, (1998) *Thermodynamics and an Introduction to Thermostatistics.*

8.1 Back to thermodynamic principles.

8.1.1 Definitions.

We start by a few definitions to lay down the vocabulary:

- **State variables**: variables which characterize the thermodynamic state of a system $(N, P, T, \mu, \cdots)$. One of the big surprises of thermodynamics is that very few variables are required to describe very complex systems. This is due to the fact that the systems are very large and therefore can usually be considered as being only small variations away from their average values.

- **Order parameters**: these are the parameters that characterize/'quantify' the state of the system. This allows to answer the question: is the system a liquid or a solid, a magnet or not, etc.

  For example in spin system, i.e. a succession of up/down magnetic moments, the mean value of the magnetic moments, m, is an order parameter. Indeed it will tell if the system is polarized ($m \neq 0$) or not ($m = 0$). Another example is the liquid/solid transition. If we define:

  $$\rho_G = \frac{1}{N} \sum_i e^{i\vec{G}\cdot\vec{r_i}}$$

  where $\vec{G}$ is the vector of the reciprocal lattice of the solid (i.e. $\vec{r_i} \cdot \vec{G} = 2\pi k$ where $\vec{r_i}$ are the lattice position of the atoms in the crystal): ρ_G is going to be 0 for a liquid (no ordering) and 1 for a crystal (perfect ordering). For the liquid/gas transition, the density is an order parameter.

- **State function**: a state function is a function of state variables.

- **Reversible transformation**: A transformation that can be done both ways, i.e. it is a process whose direction can be "reversed" by inducing infinitesimal changes to some property of the system via its surroundings. Throughout the entire reversible process, the system is in thermodynamic equilibrium with its surroundings. An alternative definition of a reversible process is a process that, after it has taken place, can be reversed and, when reversed, returns the system and its surroundings to their initial states.

- **Intensive parameters:** it is any physical property that doesn't depend on the system size or amount of matter (ex. $T, \mu, \rho, P,$).

- **Extensive parameters:** It is any physical property that is proportional to the size of the system or the quantity of matter in it (ex. V, E, S, F, G, H).

8.1.2 Principles.

First Principle:

The variation of energy of a system is the sum of the work and heat that it receives:

$$\mathrm{d}E = \delta W + \delta Q \quad \text{and} \quad \Delta E = W + Q$$

While the conservation of energy is a general principle in physics, this first principle implies some further information. First that at the macroscopic scale, energy is conveyed in various forms: work ('ordered' form of energy) or heat ('disordered' form of energy). Second, an underlying principle is that the energy E is a state function: $E = E(S, V, N)$. This is not obvious.

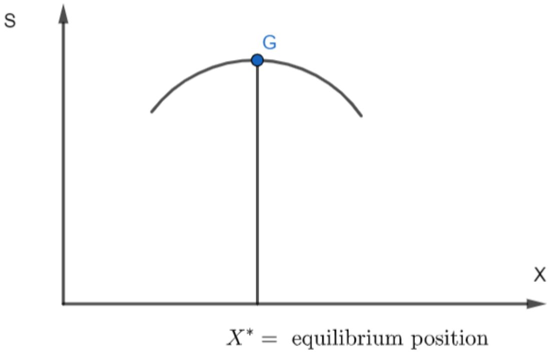
Note also that we are going to use the banker's convention, i.e. what is coming in is positive and what is going out is negative. So $\delta Q > 0$ and $\delta W > 0$ is the quantity of received heat (resp. work) for the system.

Second Principle:

There exists a function S, called the entropy, which is a function of the extensive parameters characterizing the macroscopic state, and such that, in all transformations towards an equilibrium state in an isolated system, $\Delta S \geq 0$. The entropy is a state function.

Another formulation of this principle is in terms of constraints (Callen type):
Consider a system under a given constraint. The values taken by the extensive state parameters when the constraint is freed are those that maximize the entropy over all the constrained equilibrium states.

Let us precise the meaning of this version of the second principle. Let X be a constraint, and the entropy of the system is a function $S = S(E, V, N, X)$. The second principle states that the equilibrium without constraint is defined as the one possessing the maximal entropy versus X: $S_{max} = \max_X S(X)$. The value taken by X at equilibrium, $X = X^\star$, is the one maximizing the function $S(X)$.



Link with heat exchange.

For a given system $\mathcal{S}$ that performs a reversible transformation we have that:

$$\mathrm{d}S = \frac{\delta Q}{T}$$

Instead, for an irreversible transformation we have that:

$$\mathrm{d}S > \frac{\delta Q}{T}$$

with T being the temperature of the system that is exchanging heat with $\mathcal{S}$.

The first relation is to be thought in terms of the differential relations that we obtained for the energy and entropy in Chapter 3:

$$\mathrm{d}E = T\mathrm{d}S + \sum_i X_i dx_i$$

where we introduced the generalized forces (X_i) and corresponding variables x_i. In a reversible transformation, the work naturally identifies with $\delta W = \sum_i X_i dx_i$, so that the entropy variation is given in terms of the heat exchange: $\delta Q = T\mathrm{d}S$. Note that the second relation comes from the fact that if we consider a system $\mathcal{S}$ in contact with a much larger system R, the whole being isolated, then the huge system R can be considered always at equilibrium and for this 'reservoir', $\delta Q = T_0 \mathrm{d}S_R$. Since the whole $\mathcal{S} + R$ is isolated, we have during any transformation:

$$\begin{cases} \mathrm{d}E_{\text{tot}} = \mathrm{d}E_S + \mathrm{d}E_R \\ \mathrm{d}S_{\text{tot}} \geq 0 \end{cases}$$

so that

$$\mathrm{d}S_{\text{tot}} = \mathrm{d}S_s + \underbrace{\mathrm{d}S_R}_{-\frac{\delta Q}{T_0}} \geq 0 \Rightarrow \mathrm{d}S_s \geq \frac{\delta Q}{T_0}$$

8.1.3 Thermodynamic and heat engines.

A heat engine is a system that exchanges work and heat in cycles. Note that engines have to verify some rules that follow from the thermodynamics principles. A particularly important one is the impossibility of perpetual motion of the second kind:

A machine that does a cycle with only one source of heat cannot produce work.

Proof

The key to the proof is to remark that over a cycle, the system under consideration satisfies

$$\begin{cases} \Delta E = 0 \\ \Delta S = 0 \end{cases}$$

This is because both E and S are state functions and one comes back to the initial state at the end of a cycle. Denoting T_0 the temperature of the heat reservoir, we also have the following equations:

$$\begin{cases} \Delta E = Q + W = 0 \\ 0 = \Delta S \geq \frac{Q}{T_0} \end{cases} \Rightarrow Q \leq 0 \wedge W \geq 0$$

So the system necessarily receives work and cannot not produce any.

Two heat sources engine.

We now consider an engine M that takes some heat Q_1 from a thermal bath with temperaturer T_1 and outputs work W and heat Q_2 to a thermal bath with temperature T_2. As above, we can write the general conditions:

$$\begin{cases} \Delta E = 0 = Q_1 - Q_2 - W \\ \Delta S = 0 \geq \frac{Q_1}{T_1} - \frac{Q_2}{T_2} \end{cases}$$

Now let's introduce the efficiency of the engine, defined as $\nu = \frac{W}{Q_1}$, i.e. how much work is produced from the heat Q_1. From our equations above we obtain :

$$\begin{cases} Q_2 = Q_1 - W \\ \frac{Q_2}{T_2} \geq \frac{Q_1}{T_1} \end{cases} \Rightarrow 1 - \nu \geq \frac{T_2}{T_1} \Rightarrow \nu \leq 1 - \frac{T_2}{T_1}$$

Hence there is an upper bound on efficiency, and it is impossible to have a perfectly efficient engine, except in the asymptotic limit $T_1 \to \infty$.

This concludes our short reminders on basic thermodynamics, but the reader is strongly invited to read more about it in Callen book or any other good book on thermodynamics.

8.2 Thermodynamics and ensembles.

8.2.1 Conclusion on the different ensembles.

We have:

microcanonical	isolated system	N, V, E	$S(N, V, E)$
canonical	fixed temperature system	N, V, T	$F(N, V, T) = E - TS$
grand canonical	T, μ fixed system	μ, V, T	$\Omega(\mu, V, T) = F - \mu N$
isobaric	T, P fixed system	N, P, T	$G(N, P, T) = F + PV$

A key aspect is the state variables on which each thermodynamics potential is depending. We also have the differential equations:

$$\begin{cases} \mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N \\ \mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}N \\ \mathrm{d}\Omega = -S\mathrm{d}T - P\mathrm{d}V - N\mathrm{d}\mu \\ \mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \mu\mathrm{d}N \end{cases}$$

8.2.2 Maxwell relations

From the above we immediately get that:

$$\left.\begin{array}{l} P = -\frac{\partial F}{\partial V}\Big|_{T,N} \\ \\ \mu = \frac{\partial F}{\partial N}\Big|_{V,T} \end{array}\right\} \quad \left.\frac{\partial P}{\partial N}\right| = -\frac{\partial^2 F}{\partial N \partial V} = -\frac{\partial^2 F}{\partial V \partial N} = -\frac{\partial \mu}{\partial V}$$

So we have:

$$\left.\begin{array}{l} -S = \frac{\partial F}{\partial T} \\ -P = \frac{\partial F}{\partial V} \end{array}\right\} \quad \frac{\partial S}{\partial V} = -\frac{\partial^2 F}{\partial T \partial V} = -\frac{\partial^2 F}{\partial V \partial T} = \frac{\partial P}{\partial T}$$

8.2.3 Equilibrium and release of constraints.

We consider an isolated system and add constraint X to the system. Remember that we stated previously that equilibrium was defined for:

$$S_{\text{eq}} = \max_X \{S(X)\}$$

Intuitively this result states that at equilibrium the system does explore as much of its phase space as possible so that $S = k_B T \log \Omega$ is maximal.

We can extend the results to systems which are not isolated. Let us for example consider a system $\mathcal{S}$ in contact with a thermostat at temperature T_0. The system is described by an extensive variable X, for example the volume. Now, let us imagine that the system is split in two subsystems, $\mathcal{S}_1$ and $\mathcal{S}_2$, characterized by the sub-variables X_1 and X_2 such that $X = X_1 + X_2$. For example, if X is the volume, the system is separated into two volumes V_1, and V_2. We consider the dependence of the partition function Z and free energy as a function of X_1, here considered as a variable (or a constraint). The probability to find the system with a value X_1 is

$$p(X_1) = \frac{1}{Z_{1\cup 2}} \sum_{\text{micro states } s_1, s_2} e^{-\beta E_{s_1}} e^{-\beta E_{s_2}} \delta_{X_{s_1} = X_1} \delta_{X_{s_2} = X_2 = X - X_1}$$

where the δ (Kronecker) terms do fix the values of the variable X of the microstate to the imposed ones, X_1 and $X_2 = X - X_1$. The sums over the microstates do factorize and the previous expression can be rewritten as

$$p(X_1 = V_1) = \frac{Z_1(X_1) Z_2(X_2 = X - X_1)}{Z_{1\cup 2}}$$

Now, using $Z_1(X_1) = e^{-\beta F(X_1)}$ and $Z_2(X_2) = e^{-\beta F(X_2)}$, one can rewrite

$$\boxed{p(X_1) = \frac{1}{Z_{\text{tot}}} e^{-\beta F_{\text{tot}}(X_1)}}$$

with $F_{\text{tot}}(X_1) = F_1(X_1) + F_2(X - X_1)$. This shows that the probability of occurence of the variable X_1 is given in terms of the constrained free energy.

Consequences.

The probability is maximal when the free energy $F_{\rm tot}(X_1)$ is minimal. This occurs for

$$\frac{\partial F_{\rm tot}}{\partial X_1} = 0 = \frac{\partial F_1}{\partial X_1} - \frac{\partial F_2}{\partial X_2}$$

Since $\frac{\partial F_i}{\partial X_i} = x_i$, the intensive parameters associated to X_i, then the equilibrium condition imposes

$$\boxed{x_1 = x_2}$$

For $X \equiv V$ the volume, then $x_i = -p_i$, the pressure, and the equilibrium condition is $p_1 = p_2$. For $X \equiv N$ the number of particles, then $x_i = -\mu_i/T$ and the equilibrium condition is $\mu_1 = \mu_2$.

Example of Application.

We consider a system in contact with a bath at T, μ. Then the proper thermodynamic potential characterizing the system is the Grand potential: $\Omega = \Omega(\mu, V, T) = F - \mu N$.

Let us assume that in practice we actually know an expression for the free energy F. Let us introduce the free energy per unit volume $f(\rho)$, defined as $f(\rho) = F/V$, with $\rho = \frac{N}{V}$. For an ideal system we have shown previously

$$f_{\rm id}(\rho) = k_B T(\rho \log \rho\lambda_T^3 - \rho)$$

And more generally the free energy is the sum of the ideal term and an interaction term:

$$f(\rho) = f_{\rm id}(\rho) + f_{\rm int}(\rho)$$

For example, a simple model for $f_{\rm int}(\rho)$ within the van der Waals fluid is $f_{\rm int}(\rho) = -k_B T\rho \log(1 - b\rho) - a\rho^2$, with b an excluded volume and a a parameter characterizing the van der Waals attractive interactions. This will be studied in the next chapter 8. Now we introduce a constrained grand potential $\Omega_c = V \times \omega_c(\rho)$, in which the density is fixed to its value $\rho = N/V$ by

$$\omega_c(\rho) = f(\rho) - \mu\rho$$

In practice, this quantity is *not* the equilibrium grand potential, since the density should be fixed to its equilibrium density for a given chemical potential μ and temperature T. The density ρ or number of particles N should be therefore considered here as a constraint.

Now, at equilibrium the grand potential will be minimum against the number of particles N (or density ρ): $\min_N \Omega$. This imposes:

$$\frac{\partial \Omega_c}{\partial N} = 0 \Rightarrow \left.\frac{\partial \omega_c}{\partial \rho}\right|_{\rm eq} = 0$$

so that

$$\left.\frac{\partial f}{\partial \rho}\right|_{\rm eq} = \mu.$$

More generally, the constrained grand potential is a functional (i.e. a function of function) of the density field $\rho(\vec{r})$

$$\Omega_c = \Omega_c(\{\rho\}) = \int d\vec{r}\, \omega_c(\vec{r}) = \int d\vec{r}\ [f(\{\rho(\vec{r})\}) - \mu\, \rho(\vec{r}))]$$

and the minimization of the grand potential versus the constraint $\rho(\vec{r})$, should be done as a functional minimization

$$\frac{\delta \Omega_c}{\delta \rho}(\vec{r}) = 0$$

The functional minimization is described in the Mathematical memo in Chapter 10. Using $\Omega_c = F - \mu N = \int d\vec{r}\,(f(\rho) - \mu\rho)$, this equation rewrites in a more transparent form

$$\frac{\partial f}{\partial \rho} = \mu$$

which states that at equilibrium the chemical potential is homogeneous and equal to the imposed chemical potential.

This back-and-forth considerations between ensembles will be proove very useful to investigate phase transitions, see chapter 8.

8.3 Stability conditions and fluctuations.

As a final point, we also explore the stability condition imposed by the second principle. At equilibrium S must be maximal, meaning that the entropy as a function of an (extensive) constraint X, $S(X)$, should be a *concave* function of X. This imposes at equilibrium

$$\left.\frac{\partial S}{\partial X}\right|_{\mathrm{eq}} = 0 \quad \wedge \quad \left.\frac{\partial^2 S}{\partial X^2}\right|_{\mathrm{eq}} \leq 0$$

Similarly, F is minimal at equilibrium and therefore F must be a convex function of (extensive) constraints X, so that:

$$\left.\frac{\partial F}{\partial X}\right|_{\mathrm{eq}} = 0 \quad \wedge \quad \left.\frac{\partial^2 F}{\partial X^2}\right|_{\mathrm{eq}} \geq 0$$

Another way of stating the same thing, is to use the properties of convex functions which shows that

$$2F(\frac{N}{2},\frac{V}{2},T) = F(N,V,T) \leq F(\frac{N}{2}-n,\frac{V}{2}-v,T) + F(\frac{N}{2}+n,\frac{V}{2}+v,T)$$

We note as a side remark that:

$$\frac{\partial^2 F}{\partial T^2} \leq 0 \quad \text{idem for } G, H, P, \cdots$$

which is general for intensive variables.

Example.

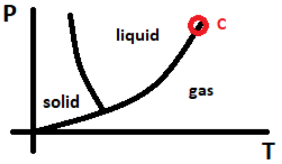
An example is the compressibility factor:

$$\chi_T = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T \propto \left(\left.\frac{\partial^2 F}{\partial V^2}\right|_T\right)^{-1} \geq 0 \quad \text{and} \quad P = -\frac{\partial F}{\partial V}$$

Note that this is in agrreement with:

$$N k_B T \rho \chi_T = \langle \Delta N^2 \rangle > 0$$

8.4 Thermodynamics and phase transitions.



We now discuss the phenomena of phase transitions in the context of thermodynamics. In this section, we will have a general discussion and explain the general principles of phase transitions and the corresponding concepts: first and second order transitions, latent heat, spinodals, double tangent, critical points, etc. We will then apply these concepts to specific phase transitions in the next chapter.

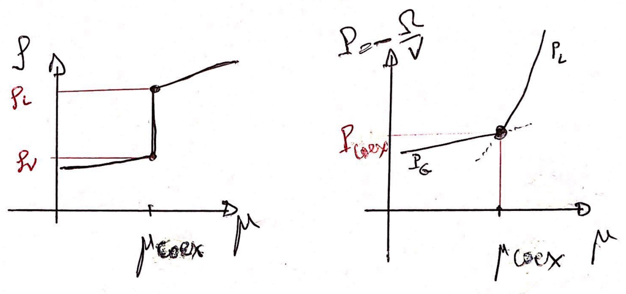
A prototypical example is the liquid-solid-gas transition, leading to a phase diagram as shown on the enclosed figure: depending on the values of the pressure and temperature, the system is in one or the other phase, solid, liquid or gas. It is already remarkable that changing only very few factors (pressure or temperature) leads to such drastic changes in the state of the system; and reversly that one can predict the state of the system only by knowing such a few number of quantities. Phase change occurs at the boundaries of the various regions in the phase space. A number of remarkable behaviors occurs at these boundaries. This is what we study in this section, in the context of general thermodynamics. We will examplify the corresponding behaviors in the next chapter 8, in the context of the statistical physics of interacting systems.

8.4.1 Order parameters and transitions orders.

We have already discussed order parameters, which allows to distinguish the phases under scrutinity: liquid from gas; as characterized by their density; a magnetic or not state, by measuring the mean magnetic moment: $m = \frac{1}{N}\sum_i S_i$, etc. In the following we assume that the system is characterized by an order parameter Φ: for example $\Phi = 1$ in a given phase 1 and $\Phi = 0$ in another phase 2. Let us now consider the transition between these two phases, which occurs as the temperature, pressure, chemical potential, or any other state variable is varied. A key aspect is that one may classify transitions into two main types: first order and second order transition. This only depends on the behavior of the order parameter Φ at the transition.

1st Order Transition.

In a first order transition, the order parameter Φ makes a discontinuous jump at the transition. Then **the discontinuity in the order parameter will induce a discontinuity or even a divergence in the first derivatives of the thermodynamic potential.**

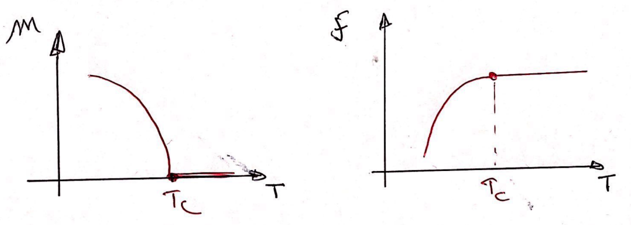


First order transition

To give a concrete example of this behavior, let us consider a system of particles in the grand canonical ensemble. At the liquid-gas transition, the density – which is the order parameter – exhibits a jump $\Delta\rho$ from the gas to the liquid density when the chemical potential is varied from below to above the saturating chemical potential. Now, the number of particles (i.e. the density) is given by $N = -\frac{\partial\Omega}{\partial\mu}\Big|_{T,V}$, so that the density jump in $\rho = N/V$ induces a discontinuity in the first derivative of the grand potential.

2nd Order Transition.

In second order transition, the order parameter Φ is continuous at the transition. The first order derivative of the thermodynamic potential is continous but **there is a discontinuity or even a divergence of the second derivative of the thermodynamic potentials**.



Second order transition

8.4.2 Description of first order transitions, spinodal and coexistence

Instead of making a general and abstract discussion, we illustrate the general concepts emerging for first order transitions in the case of the liquid-gas transition. All concepts can be applied to any other type of first order transitions by a proper translation of quantities.

At the liquid-gas transition, the thermodynamic equilibrium conditions are verified between the liquid and gas phase:

$$P_l = P_g \quad \text{and} \quad \mu_l = \mu_g$$

Solving these joint equations for a given temperature allows to obtain the density of the coexisting gas and liquid phases, $\rho_l(T)$, $\rho_g(T)$. One deduces accordingly the coexistence pressure and chemical potential, P_{coex}, μ_{coex}, which are by definition equal in the coexisting phases. The values are sometimes coined the 'saturation' pressure and chemical potential.

The transition occurs at the coexistence (or saturation) point. The density ρ is discontinuous, and this leads to a discontinuity of the first derivative of the grand potential, Ω. Ω has therefore a different behavior for $\mu < \mu_{\text{coex}}$ and $\mu > \mu_{\text{coex}}$, as if it is given by two functions, one for the liquid phase and one for the gaseous phase, the system staying to the minimal value (for Ω, so the maximal value for P) of the two. We therefore get a singularity at the crossing point of the two functions.

Latent Heat.

At the transition the entropy is discontinous:

$$S = -\left.\frac{\partial \Omega}{\partial T}\right|_{V,\mu}$$

and one introduces a new quantity to characterize this entropy jump, the latent heat of the transition:

$$L_{l \leftrightarrow g} = T(S_{\text{gas}} - S_{\text{liquid}})$$

Clapeyron Relation.

If we take two pairs of close points symmetric with respect to the transition curve on the P, T graph : A and A' on the liquid side and B and B' on the gas side. Because A and B are at equilibrium, we get that $\mu_A = \mu_B$ and same for A' and B', $\mu_{A'} = \mu_{B'}$. Now on each side of the transition curve (on the liquid and gas sides), the Gibbs-Duhem relation can be written as

$$\mathrm{d}\mu = \frac{V}{N}\mathrm{d}P - \frac{S}{N}\mathrm{d}T$$

so that one has the relationships

$$\mathrm{d}\mu_A = \mu_{A'} - \mu_A = \frac{V_g}{N}\mathrm{d}P - \frac{S_g}{N}\mathrm{d}T \quad \text{and} \quad \mathrm{d}\mu_B = \mu_{B'} - \mu_B = \frac{V_l}{N}\mathrm{d}P - \frac{S_l}{N}\mathrm{d}T$$

But due to equilibrium, $\mathrm{d}\mu_A = \mathrm{d}\mu_B$ and

$$v_g \mathrm{d}P - s_g \mathrm{d}T = v_l \mathrm{d}P - s_l \mathrm{d}T$$

where we use $v = \frac{V}{N}$ and $s = \frac{S}{N}$, then on the transition curve:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{s_g - s_l}{v_g - v_l} = \frac{T l_{g \leftrightarrow l}}{\Delta v} \quad \text{with} \quad l_{g \leftrightarrow l} = \frac{L_{l \leftrightarrow g}}{N}$$

Transition and free-energy variations

Let us analyze more in detail what is happening at the transition in terms of the free energy. To do so, let us consider the problem in the grand canonical ensemble. At equilibrium the grand potential $\Omega = -PV$ is a function of (μ, V, T). To simplify the discussion, we fix the temperature and tune the chemical potential to control the state of the system. The transition then occurs for a given chemical potential $\mu_{\text{coex}}(T)$. Across the first order transition at μ_{coex}, Ω varies continuously from its values in the gas side to the values on the liquid side, with a discontinuity in the first derivative; See above figure.

Now, similarly to what we discussed previously, we consider a *constrained* grand potential, where we fix the density ρ as a constraint. We define accordingly $\omega_c(\rho) = \frac{\Omega_c}{V}(\rho|\mu, V, T)$. In practice, the function $\omega(\rho|\mu, T)$ is constructed from a given free energy, according to

$$\omega_c(\rho|\mu, T) = f(\rho, T) - \mu\rho$$

where $f(\rho, T) = F(N, V, T)/V$ is the free energy per unit volume; its expression is independent of μ. Then $\omega_c(\rho)$ will exhibit two minima which correspond to ρ_g and ρ_l. For $\mu < \mu_{\text{coex}}$, the minimum associated with ρ_g is the global minimum, while for $\mu > \mu_{\text{coex}}$ then the minimum associated with ρ_l is the global minimum; see figure below. The value of the equilibrium grand potential is $\omega_(\rho = \rho_{\text{min}}, \mu, T)$, i.e. the value of the constrained grand potential taken at the value of the density at the minimum. When $\mu = \mu_{\text{coex}}$ the two minima are equivalent and the corresponding value is $\omega_{\text{coex}} = -P_{\text{coex}}$.

From this graphical analysis, one can sketch the behavior of the density ρ as a function of the chemical potential: increasing μ, the density will increase smootly in both phases, but exhibit a discontinuity from ρ_g to ρ_l at $\mu = \mu_{\text{coex}}$.

Spinodals and spinodal transition

We previously discussed the stability conditions for the free energy, namely

$$\left.\frac{\partial^2 \mathcal{F}}{\partial V^2}\right|_{T,N} \geq 0$$

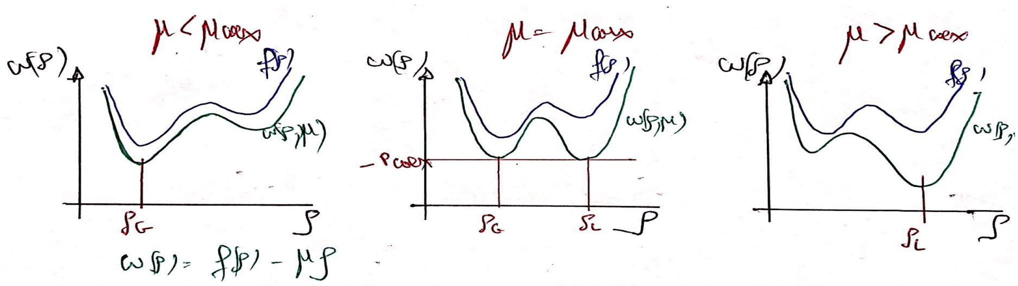


Figure 8.1: Graphs of the constrained grand potential per unit volume $\omega(\rho)|\mu, V, T) = f(\rho, T) - \mu\rho$ as a function of density for various different values of the chemical potential μ. The equilibrium density is the minimum of $\omega(\rho)|\mu, V, T)$ over the constrained density ρ.

In terms of the free energy per unit volume, $f(\rho, T) = \frac{\mathcal{F}}{V}(N, V, T)$, this rewrites

$$\boxed{\left.\frac{\partial^2 f}{\partial \rho^2}\right|_T \geq 0}$$

This can be demonstrated easily. First, the pressure

$$P = -\frac{\partial \mathcal{F}}{\partial V} = -\frac{\partial}{\partial V}\left(V f(\frac{N}{V})\right) = -f(\rho) + \rho f'(\rho)$$

Note that this result also comes directly from the definition of the grand potential as

$$P = -\frac{\Omega}{V} = -\frac{F - \mu N}{V} = -f + \underbrace{\mu}_{\frac{\partial f}{\partial \rho}} \rho$$

Then we deduce

$$\frac{\partial^2 \mathcal{F}}{\partial V^2} = -\frac{\partial P}{\partial V} = -\frac{\partial}{\partial \rho}\left(-f + \rho f'(\rho)\right)\frac{-N}{V^2} = \frac{N}{V^2}\left[-f + \rho f'' + f\right]$$

Then the stability condition can be rewritten as:

$$0 \leq \frac{\partial^2 \mathcal{F}}{\partial V^2} = \frac{1}{V}\rho^2 \frac{\partial^2 f}{\partial \rho^2} \quad \text{CQFD}$$

We then conclude that stability imposes that the free energy $f(\rho)$ must be convex function of ρ. Any region in the phase diagram where the free energy is a concave functon of density is *unstable*. **The spinodal curve is then defined as the points for which** $f''(\rho, T) = 0$:

$$\boxed{\left.\frac{\partial^2 f}{\partial \rho^2}\right|_T = 0}$$

This corresponds to the limit of stability of the system.

Coexistence and double Tangent construction.

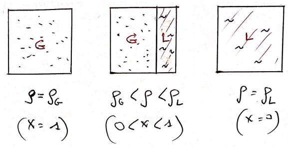
Previoulsy, we discussed the behavior of the density in the grand canonical ensemble, where μ, V, T are fixed: when the chemical potential is increased across μ_{coex}, the density increases with a sharp discontinuity from ρ_g to ρ_l at the transition.

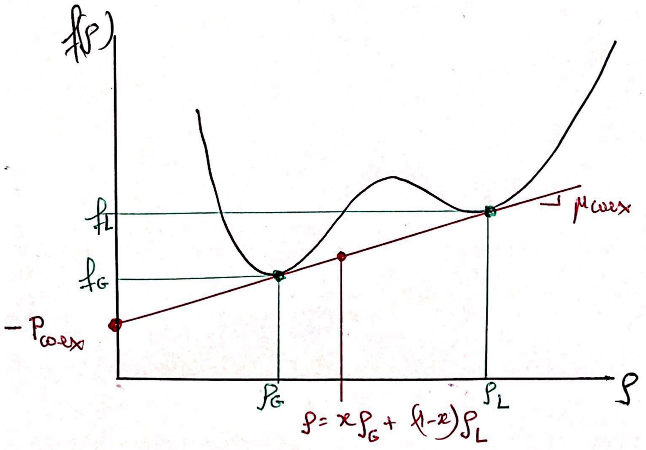
Now, what happens if we rather consider the problem in the canonical ensemble, where N, V, T are fixed ? Overall the global phase behavior should not depend on the ensemble, and indeed the transition behavior can be obtained in any ensemble. But there is a difference at the transition. Indeed, if one fixes both N and V, it is not possible a priori to accomodate the density jump at the transition, with the gas density ρ_g being very different from the liquid density ρ_l. The way this 'paradox' is solved is that the system becomes *inhomogeneous* at the transition: the overall volume separates into two subsystems, where a liquid volume coexists with a gas volume. This is the phase coexistence.

In practice, introducing the fraction x of gas, the fixed total density ρ of the system will be split into the two contributions (gas and liquid) according to

$$\rho = x\rho_g + (1 - x)\rho_l;$$

In other words, $x = (\rho_l - \rho)/(\rho_l - \rho_g)$ is the fraction of gas. When increasing ρ from ρ_g to ρ_l, the fraction x of gas in the volume will vary smoothly from 1 to 0. A key point is that **the gas volume will have a fixed density ρ_g and the liquid volume will have a fixed density ρ_l**. The values for ρ_g and ρ_l are those obtained from the equilibrium conditions: $P_g = P_l$, $\mu_g = \mu_l$.





Double tangent construction

This has a graphical interpretation which is very useful to draw the phase diagram, which is the so-called **double-tangent construction**. We plot the free energy density $f(\rho)$ as a function of the density and construct graphically the line which is the "double tangent" to the curve $f(\rho)$, see the graph above. It is easy to realize that this double-tangent touches the curve $f(\rho)$ in the points ρ_v and ρ_l defined by the equilibrium conditions.

Indeed the general equation of a tangent to the curve $f(\rho)$ at the point ρ_0 takes the form

$$y = f'(\rho_0)(x - \rho_0) + f(\rho_0),$$

For $x = 0$ the value crossese the vertical axes at $y = -f'(\rho_0)\rho_0 + f(\rho_0)$: this is nothing but the pressure at the density ρ_0, since $P(\rho_0) = f(\rho_0) - f'(\rho_0)\rho_0$. Also the slope of the tangent is $f'(\rho_0) = \mu$ the chemical potential. Hence, the double tangent corresponds to the densities ρ_v and ρ_l which have the same slope and same y-intercept, i.e. same pressure and chemical potential. The double-tangent thus corresponds to $P_g = P_l \equiv P_{\rm coex}$ and $\mu_g = \mu_l = \mu_{\rm coex}$.

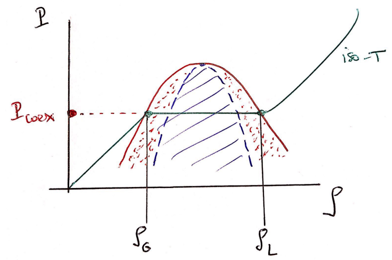
Furthermore the free energy for any phase separated state with a gas fraction x is equal to

$$f_{\rm mix}(\rho) = xf(\rho_v) + (1-x)f(\rho_L) \leq f_{\rm hom}(\rho).$$

As can be seen on the graph above, this 'mixed' free energy, which adds up the gas and liquid contribution, is lower than the homogeneous free energy for the same density $f(\rho)$. This is why the system phases separates, since it gains free energy by separating itself into two phases. In other words the system does 'convexify' the free energy function by phase separating.

Conclusion.

Altogether, we introduced a number of concepts for first order phase transitions: spinodals, phase coexistence, etc. This is summarized in the general phase diagram enclosed. On this graph the red line is the coexistence line, while the dashed blue line is the spinodal. The blue region within the spinodal curve is unstable, while the dotted red zone corresponds to a metastable region: the system is not stable thermodynamically but mechanically stable. The green line is an isothermal path in the phase diagram, $P(\rho, T)$.

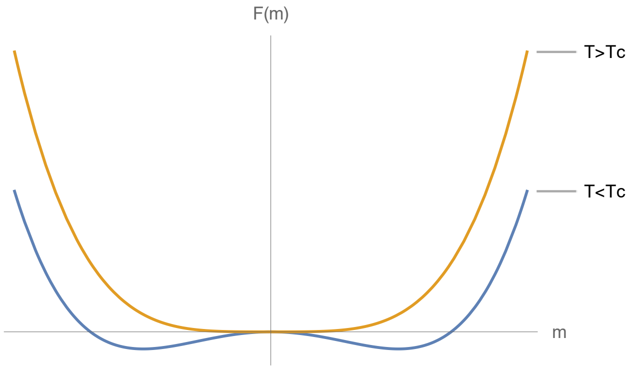


8.4.3 Description of second order transitions

We discuss here the general characteristics of second order phase transitions. As above, we describe the behavior on a prototypical example, which is the phase transition in magnetic systems. We measure here the average magnetic moment (or spin) m as a function of the temperature (and magnetic field). As shown in the graph in the previous section, for a vanishing magnetic field $B = 0$, the systems exhibits a transition from a disordered phase at high temperature, with $m = 0$, to an ordered phase at low temperature $m \neq 0$. The transition occurs at a temperature T_c and is continuous ($m(T)$ is a continuous function below and above the phase transition). This is a second order phase transition.

Free energy behavior

We plot in the curve below the typical behavior for the free energy $F(m)$ above and below the transition temperature, $T > T_c$ and $T < T_c$. For $T > T_c$ the free energy has a single minimum at $m = 0$; for $T < T_c$ it exhibits two minima $\pm m$ (one being the symmetric of the other, which is a consequence of an intrinsic symmetry of the system). An important feature of second order phase transitions is that the susceptibility of the system diverges at the transition point. The susceptibility quantifies how the system reacts to the magnetic field (for low field):



$$\chi = \left.\frac{\mathrm{d}m_{\mathrm{eq}}}{\mathrm{d}B}\right|_{B=0}$$

Let us show this result. To calculate the susceptibility, one has to introduce the effect of the magnetic field on the system, which is described by the free energy

$$\tilde{F}(m, B) = F(m) - mB$$

At equilibrium,

$$\frac{\partial \tilde{F}}{\partial m} = 0 \Leftrightarrow \left.\frac{\partial F}{\partial m}\right|_{m_{\mathrm{eq}}(B)} = B$$

For low magnetic field, we make a first order expansion in m and get:

$$\left.\frac{\partial F}{\partial m}\right| \underbrace{(m_{\mathrm{eq}}(B+\mathrm{d}B))}_{m_{\mathrm{eq}}(B)+\mathrm{d}m_{\mathrm{eq}}} = B + \mathrm{d}B \Rightarrow \cancel{\left.\frac{\partial F}{\partial m}\right| m_{\mathrm{eq}}}(B) + \left.\frac{\partial^2 F}{\partial m^2}\right| \times \mathrm{d}m_{\mathrm{eq}} = \cancel{B} + \mathrm{d}B$$

This shows that:

$$\chi = \left.\frac{\mathrm{d}m_{\mathrm{eq}}}{\mathrm{d}B}\right|_{B=0} = \left(\left.\frac{\partial^2 F}{\partial m^2}\right|_{B=0}\right)^{-1}$$

Now, when $T \to T_c$, the second derivative of the free energy vanishes $\left.\frac{\partial^2 F}{\partial m^2}\right|_{B=0} \to 0$. This can be easily understood from the previous graph of $F(m)$ since going from a single minimum $m = 0$ for $T > T_c$ to two symmetric minima $m \neq 0$ for $T < T_c$, will make the second derivative vanish at $T = T_c$.

A immediate consequence is

$$\chi = \left.\frac{\partial m}{\partial B}\right|_{B=0} \xrightarrow{T \to T_c} \infty$$

and this shows that the susceptibility χ diverges at the transition point. This is a key behavior of second order phase transitions.

Transitions of the second order, critical exponents.

In second order phase transitions, one can pass continuously from one phase to the other. The transition occurs via a diverging length scales. At the transition point, one can show that this leads to 'scaling laws' for the various thermodynamic quantities. In particular, one can write

$$C_V \sim |T - T_C|^{-\alpha}, m \sim |T - T_C|^{\beta}, \chi = -\left.\frac{\partial \Phi}{\partial B}\right|_{B=0} \sim |T - T_C|^{-\gamma}$$

This is associated with the divergence of the correlation length in the system, which goes to infinity at T_c. What is remarkable is that these critical exponents $(\alpha, \beta, \gamma, \cdots)$ are universal and depend only on the symmetries of the problem.

We will not discuss further this aspect in the present lecture.

Chapter 9

Quantum statistics.

In this last chapter, we introduce the general concepts of quantum statistics. This should be considered as an introduction to the field, and we leave further insights in the domain to subsequent advanced quantum physics and condensed matter courses.

In some sense, quantum statistics is somewhat easier than classical statistics because contrary to the classical case everything is always discrete and it is easier to count microscopic states. For example questions around the $N!$ factors (indiscernability and Gibbs Paradox) or the discretization of the phase space are no longer specific issues. However we will merely focus here on non-interacting particles. First because interactions between particles becomes very difficult to handle in quantum description. But the main reason is that quantum effects, in particular originating in the symmetrization or antisymmetrization of the wave function, already leads to highly non-trivial behaviors.

9.1 Quantum states and partition functions.

We could summarize quantum physics by saying that we are passing from the concept of 'particles' to the concept of 'waves'. Atoms are described as wave packets. We have already introduced the De Broglie wavelength:

$$\lambda_T = \sqrt{\frac{h^2}{2\pi m k_B T}}$$

We are in a 'classical' case when $\lambda_T < [\text{ distance between particles } \sim \rho^{-1/3}]$. However when $\lambda_T \sim \rho^{-1/3}$ i.e. 'low temperatures' orvery high densities, quantum effects show up. We denote by $|\psi\rangle_i$ the wavefunction associated to the state i and we have $\hat{H}|\psi\rangle_i = E_i |\psi\rangle_i$. The difficulty of the quantum aspects comes from the fact that we have a 'double statistics'. We first have a statistics due to the quantum effects and uncertainty, to which we add the statistics and combinatorics of the many-body problem itself.

Let us assume that we have a probability p_i to observe a certain state i. This quantity depends on the statistical ensemble considered and we give its expression in the next section. But a few general results can be already obtained. If we consider the states $|\psi\rangle_i$ with associated probabilities p_i, the average of a variable A is then calculated as

$$\bar{A} = \sum_{\text{quantum states} i} p_i \langle\psi_i| A |\psi_i\rangle$$

We then introduce the 'density operator' as

$$\rho = \sum_{\text{quantum states} i} p_i |\psi_i\rangle\langle\psi_i|$$

so that averages can be rewritten in a compact form as

$$\bar{A} = \mathrm{Tr}(\rho A)$$

The proof is quite simple: denoting as $|k\rangle$ an orthonormal basis of our Hilbert space, then

$$\mathrm{Tr}(\rho A) = \sum_k \langle k| \rho A |k\rangle = \sum_{k,i} p_i \langle k|\psi_i\rangle \langle\psi_i| A |k\rangle = \sum_i p_i \langle\psi_i| A \underbrace{\left(\sum_k |k\rangle\langle k|\right)}_{\mathrm{Id}} |\psi_i\rangle = \sum_i p_i \langle\psi_i| A |\psi_i\rangle = \bar{A}$$

Note also that:

$$p_i = \langle\psi_i| \rho |\psi_i\rangle \quad \wedge \quad \langle\psi_i| \rho |\psi_j\rangle = 0 \text{ if } i \neq j$$

Let us consider a basis $|u_i\rangle$ of quantum eigenstates for the Hamiltonian $\mathcal{H}$ of the system, it verifies

$$\mathcal{H}\,|u_i\rangle = E_i\,|u_i\rangle$$

In this basis the elements of the density operator are

$$\rho_{ij} = \langle u_i|\,\rho\,|u_j\rangle = p_{ij} = p_i\,\delta_{i,j}$$

9.1.1 Statistical Ensembles

We now describe the statistical probability p_i. This follows the same lines as for the classical description of statistical ensembles, which we discussed in the previous chapters.

Micro-canonical ensemble

$$\rho_{ij} = \frac{1}{\Omega}\,\delta_{i,j} \quad \text{if} \quad E < E_i < E + \Delta E; \quad 0 \quad \text{otherwise}$$

where:

$$\Omega = \sum_{\substack{\text{quantum state } i \\ E \le E_i \le E+\Delta E}} 1$$

The probability of a quantum microstate i is accordingly $p_i = \frac{1}{\Omega}$.

Canonical ensemble

Extending on the classical case, the density operator takes the form

$$\rho = \frac{1}{Z} e^{-\beta\mathcal{H}}$$

where

$$Z = \sum_{\text{quantum states } i} e^{-\beta E_i} = \mathrm{Tr}\left[e^{-\beta H}\right]$$

In the basis $|u_i\rangle$ of eigen states of the hamiltonian $\mathcal{H}$, one has therefore

$$\rho_{ij} = \frac{1}{Z} e^{-\beta E_i}\,\delta_{i,j}$$

and the probability of the microscopic state i with energy E_i is:

$$p_i = \frac{1}{Z} e^{-\beta E_i}$$

The average of a quantity A is therefore

$$\bar{A} = \mathrm{Tr}(\rho A) = \frac{1}{Z} e^{-\beta E_i}\,A_{ii}$$

Grand Canonical ensemble

Extending again on the classical case, we write similarly that:

$$p_i = \frac{1}{\Theta} e^{\frac{-E_i+\mu n_i}{k_B T}} \qquad \text{with } n_i \text{ the occupation number of the state } i$$

The grand partition function is accordingly:

$$\Theta = \sum_{\text{quantum state } i} e^{-\beta(E_i+\mu n_i)} = \mathrm{Tr}\left[e^{-\beta(H-\mu N)}\right]$$

The main focus is on the quantum states i rather than on particles.

9.2 Two examples: harmonic oscillator and black body radiation

We will now examplify these principles on two examples: the harmonic oscillator and the black body. These example highlights two main notions of quantum statistics: (i) the discretized/quantized states and (ii) the density of state.

9.2.1 Harmonic Oscillator.

We consider the so-called Einstein model of a vibrating crystal. This model extends on the classical oscillator models, the predictions of which – in particular for the thermal capacitance - do not match the experimental results at low temperature.

We consider N sites on a lattice, each site being associated with a harmonic oscillator with characteristic frequency ω_0 (in all three directions). All the oscillators are assumed to independent. There are accordingly $6N$ degrees of freedom in total and in the classical description one would predict that the energy is $E = 3Nk_BT$ and the thermal capacitance $C = dE/dt = 3Nk_B$. The predictions of the quantum statistics depart form this prediction, as we will see.

Partition function.

The oscillators being independent, one can write

$$Z = \sum_{\text{states } i} e^{-\beta E_i} = \left(\sum_{\text{1D states } i} e^{-\beta E_i} \right)^{3N} \equiv z^{3N}$$

where the last sum is over the eigenstates of a 1D harmonic oscillator.

The energy levels of a harmonic oscillator are discretized according to

$$E_n = \hbar\omega_0 \left(\frac{1}{2} + n \right).$$

We do not demonstrate this classical result here. The partition function for a 1D harmonic oscillator then takes the form

$$z = \sum_{n=0}^{+\infty} e^{-\beta\hbar\omega_0(\frac{1}{2}+n)} = e^{-\frac{\hbar\omega_0}{2k_BT}} \sum_{n=0}^{+\infty} \underbrace{q^n}_{q=e^{-\beta\hbar\omega_0}} = \frac{e^{-\beta\frac{\hbar\omega_0}{2}}}{1-e^{-\beta\hbar\omega_0}}$$

The free energy follows immediately as

$$F = -k_BT \log Z = -\frac{3N}{2}\hbar\omega_0 + 3Nk_BT \log\left[1 - e^{-\beta\hbar\omega_0}\right]$$

Mean occupation number.

The mean occupation number is defined as

$$\langle n \rangle = \frac{1}{z} \sum_{n=0}^{+\infty} n e^{-\beta\hbar\omega_0(\frac{1}{2}+n)} = \frac{\sum_n n e^{-\alpha n}}{\sum_n e^{-\alpha n}} = -\frac{\partial}{\partial\alpha} \log \underbrace{\sum_n e^{-\alpha n}}_{\frac{1}{1-e^{-\alpha}}} \quad \text{where } \alpha = \frac{\hbar\omega_0}{k_BT}$$

This leads to

$$\langle n \rangle = \frac{1}{e^{\beta\hbar\omega_0} - 1}$$

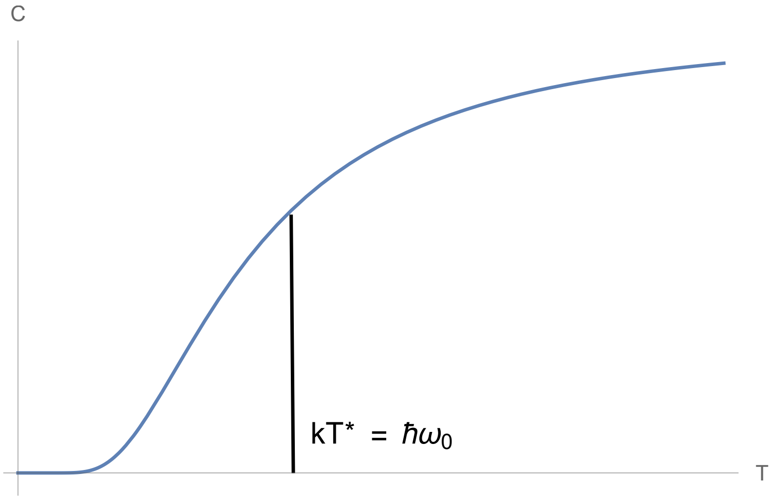
Then the average total energy is also given by:

$$E_{\text{tot}} = 3N\hbar\omega_0(\langle n \rangle + \frac{1}{2}) = 3N\hbar\omega_0 \left[\frac{1}{e^{\alpha}-1} + \frac{1}{2} \right] = 3N\frac{\hbar\omega_0}{2} \frac{1}{\tanh\frac{\hbar\omega_0}{2k_BT}}$$

We remark that $E_{\text{tot}} = 3Nk_BT$ in the limit $\frac{\hbar\omega_0}{k_BT} \ll 1$ (i.e. as T goes to ∞) and one recovers, as expected, the classical case. However in the quantum case the thermal capacitance is given by:

$$C = \frac{\mathrm{d}E}{\mathrm{d}T} = 3Nk_B \left[\frac{\frac{\hbar\omega_0}{2k_BT}}{\sinh\left(\frac{\hbar\omega_0}{2k_BT}\right)} \right]^2$$

which depends strongly on the temperature and vanishes at low temperature. This is due to the fact that exciting the oscillators requires a finite, discrete energy step, $\hbar\omega_0$, with a probability $\propto \exp\left[-\frac{\hbar\omega_0}{k_BT}\right]$. For low T, we actually get that the thermal capacitance behaves as $C \sim \frac{1}{T^2} e^{-\frac{\hbar\omega_0}{k_BT}}$. The thermal capacitance decreases strongly for low T, in contrast with the classical result which predicts a constant capacitance. So this is in fair agreement with the experimental results, but the decrease is too strong. This discrepancy is due to the over-simplified model of the crystal which only involve a single harmonic frequency. However, solids exhibit a spectrum of harmonic frequencies, with the excitation of phonon modes, and this has to be properly modeled to reproduce the experimental results. This modelling goes beyond the present course.



9.2.2 Photon gas and black-body radiation.

We consider a second example, which played a seminal role in quantum physics. This concerns the behavior of a gas of photons in thermalizing box. In this box at fixed temperature T, photons are emitted and adsorbed at the surface, and a thermodynamic equilibrium is established for the population of photons inside the box.

A photon exhibits a wave/particle duality and its energy writes

$$\epsilon = \hbar\omega = |\vec{p}|c,\ \vec{p} = \hbar\vec{k},\ \omega = ck$$

where ω is its frequency, $\vec{p}$ its momentum, and $\vec{k}$ the wave vector. Furthermore photons can have two polarizations.

The chemical potential of the photons is zero since they are created and adsorbed by the box. In other words, if one calculates the free energy for a given number of particles F_N, then the number of photons in the box N will verify $\mu = \frac{\partial F}{\partial N} = 0$.

$$Z_N = \sum_{\text{microstates with } N \text{ photons}} e^{-\beta E_s}$$

The grand canonical function is accordingly

$$\Theta = \sum_{\text{microstates} s} e^{\frac{\mu N - E_s}{k_B T}}$$

since $\mu = 0$.

In order to calculate the partition function, we will make a slight change in perspective to rewrite the sum over microstates in terms of a sum of occupied energy levels. Indeed the previous picture of a microstate corresponds to:

$$\begin{gathered}\text{photon 1} \rightarrow \text{quantum state } \lambda_1\\ \text{photon 2} \rightarrow \text{quantum state } \lambda_2\\ \ldots\\ \text{photon N} \rightarrow \text{quantum state } \lambda_N\end{gathered}$$

Now we can equivalently describe the microstate as

$$\begin{gathered}\text{quantum state } \lambda_1 \rightarrow n_1 \text{ photons}\\ \text{quantum state } \lambda_2 \rightarrow n_2 \text{ photons}\\ \ldots\\ \text{quantum state } \lambda_N \rightarrow n_N \text{ photons}\end{gathered}$$

Remember that photons are indistinguishable. **Defining a microstate therefore corresponds to the repartition of the occupation numbers n_i of each quantum level.** In other words, each microstate will be characterized by the numbers $n_1, n_2, ..$ and this allows us to re-write the partition function as

$$\Theta = \sum_{\text{microstates} s} e^{-\beta E_s} = \sum_{n_1}\sum_{n_2}\sum_{n_3}\ldots e^{-\beta E(n_1,n_2,n_3,\ldots)}$$

Now the energy of the microstate is

$$E_s = n_1\epsilon_1 + n_2\epsilon_2 + \cdots$$

and

$$\Theta = \sum_{n_1}\sum_{n_2}\sum_{n_3}\dots e^{-\beta\sum_i n_i\epsilon_i}$$

and one deduces

$$\begin{aligned}\Theta &= \sum_{n_1} e^{-\beta n_1\epsilon_1}\sum_{n_2} e^{-\beta n_2\epsilon_2}\sum_{n_3} e^{-\beta n_3\epsilon_3}\dots\\ &= \prod_{\text{quantum states } i}\left(\sum_{n_i} e^{-\beta n_i\epsilon_i}\right) \qquad (9.1)\end{aligned}$$

Remark that the grand-canonical formalism is crucial for the factorization. We then introduce a crucial quantity:

$$\boxed{\zeta_i = \sum_{n_i} e^{-\beta n_i\epsilon_i}}$$

This allows us to re-write:

$$\Theta = \prod_{\text{quantum states } i}\zeta_i$$

Furthermore the probability of finding the system in the microstate s, defined by its occupation numbers n_i, is given by:

$$\mathbb{P}(s) = \frac{e^{-\beta n_1\epsilon_1}}{\zeta_1}\frac{e^{-\beta n_2\epsilon_2}}{\zeta_2}\cdots$$

For the photon gas, the function ζ_i involves a sum from $n_i = 0 \to \infty$ and

$$\zeta_i = \sum_{n_i=0}^{+\infty} e^{-\beta n_i\epsilon_i} = \frac{1}{1-e^{-\beta\epsilon_i}}$$

Plugging this back in the partition function gives:

$$\Theta = \prod_{\text{quantum states } i}\frac{1}{1-e^{-\beta\epsilon_i}}$$

and we deduce the grand potential

$$\Omega = -k_BT\log(\Theta) = -k_BT\log\prod_{\text{quantum states } i}\frac{1}{1-e^{-\beta\epsilon_i}} = k_BT\sum_{\text{quantum states}}\log\left(1-e^{-\beta\epsilon_i}\right)$$

We need now to specify to energy of the quantum levels. For the photon gas, the energy is quantified in terms of electromagnetic modes with wave vectors $\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$ where L is the size of the box and the corresponding energy is

$$\epsilon_{n_x,n_y,n_z} = \frac{2\pi}{L}\hbar c\sqrt{n_x^2+n_y^2+n_z^2}$$

so that

$$\Omega = 2\cdot k_BT\sum_{n_x,n_y,n_z}\log\left(1-e^{-\beta\frac{2\pi}{L}\hbar c\sqrt{n_x^2+n_y^2+n_z^2}}\right)$$

where the factor 2 stems from the two polarizations. This sum can be calculated by going to a continuum version, using

$$\sum_{\text{quantum states}}(\cdot) = 2\sum_{n_x,n_y,n_z}(\cdot) = 2\int\frac{\mathrm{d}^3\vec{k}}{(2\pi/L)^3}(\cdot)$$

This is valid for $L\to\infty$. This yields finally

$$\Omega = k_BT\cdot 2\cdot\int\frac{\mathrm{d}^3\vec{p}}{(\frac{2\pi}{L})^3\hbar^3}\log\left(1-e^{-\beta|\vec{p}|c}\right) = k_BT\frac{8\pi V}{h^3}\int_0^{+\infty}p^2\mathrm{d}p\log\left(1-e^{-\beta pc}\right)$$

We deduce the pressure as:

$$P = -\frac{\Omega}{V} = -k_BT\frac{8\pi}{h^3}\int_0^{+\infty}p^2\mathrm{d}p\log\left(1-e^{-\beta pc}\right)$$

The average energy can be calculated as:

$$\langle E\rangle = \sum_{\text{quantum states } i} \langle n_i\rangle \epsilon_i \text{ with } \langle n_i\rangle = \frac{\sum_{n_i} n_i e^{-\beta n_i \epsilon_i}}{\sum_{n_i} e^{-\beta n_i \epsilon_i}} = -\frac{1}{\beta}\frac{\partial}{\partial \epsilon_i}\log \zeta_i = \frac{1}{e^{\beta\epsilon_i}-1}$$

Then by passing from the sum to the integral, this leads to the following for the energy:

$$\langle E\rangle = 2V\int \frac{\mathrm{d}^3p}{(2\pi)^3\hbar^3}\frac{pc}{e^{\beta pc}-1} = \frac{8\pi Vc}{h^3}\int_0^{+\infty}\mathrm{d}p\frac{p^3}{e^{\beta pc}-1}$$

An integral by part shows immediately that $\Omega = -\langle E\rangle/3$. Furthermore using the analytical formula,

$$\int_0^\infty \frac{x^3\mathrm{d}x}{e^x-1} = \frac{\pi^4}{15},$$

we deduce that

$$\frac{\langle E\rangle}{V} = \frac{\pi^2}{15}\frac{(k_BT)^4}{(\hbar c)^3}$$

Spectral density.

The spectral density $u(\omega)$ is defined as $u(\omega) = n(\omega)\hbar\omega$, with $n(\omega)d\omega$ the density of states within $d\omega$. It obeys

$$\langle E\rangle = \int_0^\infty \mathrm{d}\omega\, u(\omega)$$

This leads to

$$\boxed{u(\omega) = \frac{h}{2\pi^3c^3}\frac{\omega^3}{e^{\beta\hbar\omega}-1}}$$

This is called Planck's Law. The maximum of $u(\omega)$ occurs with $\hbar\omega_{\max} = 2.82k_BT$. For the sun, the measured maximum occurs at a wavelength $\lambda_{\max} \sim 500$nm, and assuming that it behaves as a black body, this points to a surface temperature of the sun of $T \sim 5700K$. For the human body, with $T \sim 300$K, the maximum occurs at a wavelength $\lambda_{\max} \sim 10\mu$m corresponding to infra-red (hence the infra-red night vision).

Emitted Power.

One of the fundamental assumptions of black body radiation is that the emitted power is perfectly balanced by the received power. The received power can be calculated as the integral over all angles θ of the power received by a unit surface from a direction θ. The latter is $\epsilon(\omega)\times n(\omega)\times c\cos\theta$, with $\epsilon(\omega) = \hbar\omega$. The total flux rewrites, using $u(\omega) = n(\omega)\hbar\omega$,

$$\mathcal{P} = \int \frac{2\pi\sin\theta d\theta}{4\pi}\int d\omega\, u(\omega)\, c\cos\theta$$

per unit solid angle, and one deduces that $\mathcal{P} = \frac{1}{4}\langle\frac{E}{V}\rangle \times c$. This shows that:

$$\mathcal{P} = \sigma T^4, \text{ where } \sigma = \frac{2}{15}\frac{\pi^5k_B^4}{h^3c^2}$$

This is the law of Stefan and its gives the emitted power per unit surface. The prefactor is calculated as $\sigma = 5.67\,10^{-8}\mathrm{W.m^{-2}.K^{-4}}$.

9.3 Bosons and fermions without interactions.

9.3.1 Indiscernability and symetrisation.

In particles without interactions we can always split the Hamiltonian as

$$\mathcal{H} = \mathcal{H}^{(1)} + \mathcal{H}^{(2)} + \cdots,$$

A solution to the Schrödniger equation, $\mathcal{H}|\psi\rangle = E|\psi\rangle$ can then be written as

$$|\psi\rangle = |\psi_{\lambda_1}(1)\rangle \otimes |\psi_{\lambda_2}(2)\rangle \otimes \cdots,$$

where the energy is $E = E_{\lambda_1} + E_{\lambda_2} + \cdots$, with E_{λ_2} the eigenvalue of the equation $\mathcal{H}^{(i)}|\psi_{\lambda_i}\rangle = E_i|\psi_{\lambda_i}\rangle$. The solution $|\psi\rangle = |\psi_{\lambda_1}(1)\rangle \otimes |\psi_{\lambda_2}(2)\rangle \otimes \cdots$, corresponds to particle 1 in quantum state λ_1, etc.

However, this description consider the particles as discernable and does not respect indiscernability: the state of the system i should not be altered if one exchanges one particle by another. Let us describe the state of the system as $|\psi(1,2,3,\cdots,N)\rangle$ where i characterizes the state of the i-particle (maybe including its spin variable as well). Then, if one permutes two particles, the wave function should be equal up to a phase c:

$$|\psi(1,2,3,\cdots,N)\rangle = c\,|\psi(2,1,3,\cdots,N)\rangle$$

We then permute a second time, and this leads to the condition

$$|\psi(1,2,3,\cdots,N)\rangle = c^2\,|\psi(1,2,\cdots N)\rangle \Rightarrow c^2 = 1$$

So if $c = 1$ the function is symmetric since $|\psi(1,2)\rangle = |\psi(2,1)\rangle$: these particles are called **boson**. if $c = -1$ then the function is anti-symmetric since $|\psi(1,2)\rangle = -\,|\psi(2,1)\rangle$, these particles are **fermions**. A remarkable result of quantum mechanics is the spin-statistics theorem[1]: bosons are particles with integer spins; fermions are particles with semi-integer spins. For example, photons and Helium 4 particles are bosons. Electrons, protons, neutrons, Helium 3 particles are fermions.

> An important consequence is the *Pauli principle*: one cannot describe a antisymmetric quantum state with fermions in the same state. Hence, **two fermions cannot be in the same individual quantum state.**

If two fermions share the same spatial wavefunction, they must have different spin.

Example: 2 level system with 2 particles

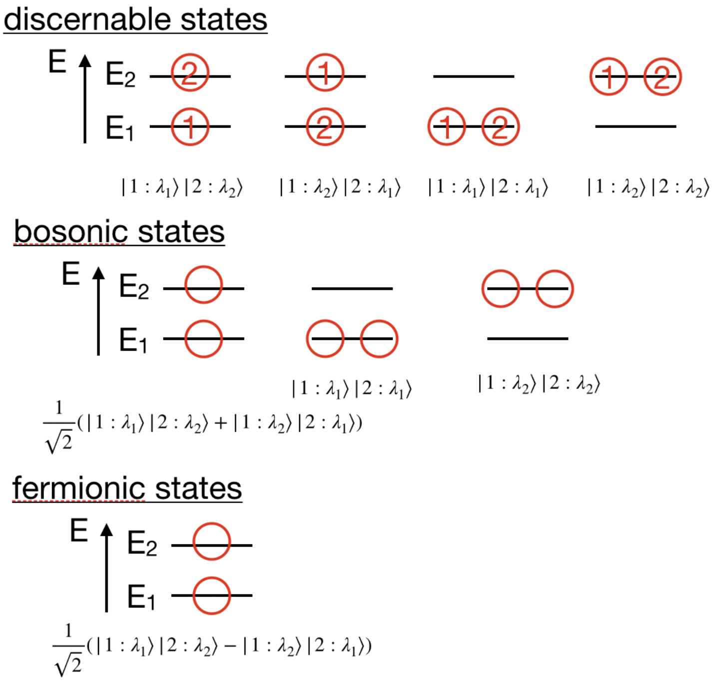
We have two particles in a system with two energy levels λ_1, λ_2. Then for the bosonic case the symmetrized wave function is

$$|\psi\rangle = \frac{1}{\sqrt{2}}\left(|1:\lambda_1\rangle \otimes |2:\lambda_2\rangle + |1:\lambda_2\rangle \otimes |2:\lambda_1\rangle\right)$$

As for the fermionic case the antisymmetrized wave function is

$$|\psi\rangle = \frac{1}{\sqrt{2}}\left(|1:\lambda_1\rangle \otimes |2:\lambda_2\rangle - |1:\lambda_2\rangle \otimes |2,\lambda_1\rangle\right)$$

In summary, for two particles in a two energy level system, one has the following possible states:



Note that if one includes spin, the wave function combines the orbital and spin wave function, $|\psi\rangle = |\varphi\rangle\otimes|\chi\rangle$ and the (anti-)symmetry principle applies overal to this combination. This implies for example that two fermions can coexist in a given energy level provided their spin are different.

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[1] Pauli, Phys. Rev. **58** 716 (1940)

These considerations generalize to N independent fermions and the anti-symmetrization of the wave function takes the form of a matrix determinant, the so-called Slater determinant, as:

$$|\psi\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} |\psi(1:\lambda_1)\rangle & |\psi(1:\lambda_2)\rangle & & |\psi(1:\lambda_N)\rangle \\ |\psi(2:\lambda_1)\rangle & \cdots & & \\ & & \ddots & \\ & & & |\psi(N:\lambda_N)\rangle \end{vmatrix}$$

The notation $|\psi(i:\lambda_j)\rangle$ indicates the wave function of the particle i in the λ_j quantum state.

For N independent bosons, the symmetrization of the wave function writes

$$|\psi(1,2,\cdots,N)\rangle = C \sum_{\sigma\in\mathfrak{S}_N} \bigotimes_{i=1}^{N} |\psi(\sigma(i):\lambda_i)\rangle$$

where σ is a permutation and the normalization constant is equal to $C = (N!\prod_i N_j)^{-1/2}$, with N_j the number of particles in the same quantum state λ_j.

We conclude by the question of indiscernability. Indiscernability is naturally accounted for in the quantum framework. In the classical calculations we introduced the $N!$ term to take into account the indiscernability of the particles. This is an approximation which is valid in the classical limit. It can be derived explicitly in the classical limit. We refer to the book by Kardar, "Statistical Mechanics of Particles", Chap. 7.2 (p184) for a discussion about this question, which we do not reproduce here.

9.3.2 Grand canonical partition function

The symmetrization or anti-symmetrization of the wave function makes calculations of the partition function really difficult when the number of particles is fixed, even for non-interacting particles.

However these calculations become far easier in the grand canonical ensemble. The general form of the grand partition function is:

$$\Theta = \sum_{\text{microstates } s} e^{\beta(\mu N_s - E_s)}$$

And we again take the point of view that we already introduced for the gas of photons, and which describes the microscopic quantum states in terms of the occupation number of quantum levels. This means that we now describe the quantum microstate as

$$\begin{gathered}\text{quantum state } \lambda_1 \to n_1 \text{ particles}\\ \text{quantum state } \lambda_2 \to n_2 \text{ particles}\\ \cdots\end{gathered}$$

and the microstate is fully defined by the set of occupation numbers $\{n_1, n_2, \dots\}$. The total number of particles for a given microstate is:

$$N_s = \sum_i n_i$$

and the energy

$$E_s = \sum_i n_i \epsilon_i.$$

wherre ϵ_i is the energy of the quantum level i (eigenvalue of the one-particle hamiltonian) and the sum runs over an (a priori) infinite number of quantum levels i. Fixing N_s would lead to considerable combinatoric difficulties and working in the grand canonical ensemble – where N_s is not fixed – allows to bypass this difficulty. We can therefore rewrite the previous sum over microstates s as a sum over the occupation of quantum levels:

$$\Theta = \sum_{n_1}\sum_{n_2}\cdots e^{\beta(\mu\sum_i n_i - \sum_i n_i\epsilon_i)}$$

where i denotes the i-th quantum state and n_i its occupation number. There is an infinite number of sums, as many as the number of energy levels. For non-interacting systems, this sum factorizes as

$$\boxed{\Theta = \prod_i \underbrace{\sum_{n_i} e^{\beta(n_i(\mu-\epsilon_i))}}_{\zeta_i} \equiv \prod_i \zeta_i}$$

Fermions

For fermions the problem is further simplified since the exclusion principle gives that $n_i = 0$ or $n_i = 1$, since two fermions cannot be in the same quantum level. Then ζ_i simplify immediately to:

$$\boxed{\zeta_i = \sum_{n_i=0}^{1} e^{\beta(n_i(\mu-\epsilon_i))} = 1 + e^{\beta(\mu-\epsilon_i)}}$$

The partition function hence follows as

$$\Theta = \prod_{i=1}^{\infty} \left(1 + e^{\beta(\mu-\epsilon_i)}\right)$$

We can also calculate the average occupation number of a given level i, $\langle n_i \rangle$, as

$$\langle n_i \rangle = \frac{\sum_{n_i=0,1} n_i e^{\beta(\mu-\epsilon_i)n_i}}{\sum_{n_i=0,1} e^{\beta(\mu-\epsilon_i)n_i}}$$

And this shows that the average occupation number in the quantum state i is

$$\boxed{\langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i-\mu)} + 1}}$$

This important result is called the Fermi-Dirac distribution for fermions.

Bosons

For the bosons, there is no restriction on the occupation number of a given quantum level and we have that $n_i = 0, \dots \infty$. Hence we obtain:

$$\zeta_i = \sum_{n_i=0}^{+\infty} e^{\beta(\mu-\epsilon_i)n_i} = \frac{1}{1 - e^{\beta(\mu-\epsilon_i)}}$$

We deduce the partition function hence follows as

$$\Theta = \prod_{i=1}^{\infty} \frac{1}{1 - e^{\beta(\mu-\epsilon_i)}}$$

The average occupation number of a given level for bosons is then

$$\langle n_i \rangle = \frac{\sum_{n=0}^{\infty} n e^{\beta(\mu-\epsilon_i)n}}{\sum_{n=0}^{\infty} e^{\beta(\mu-\epsilon_i)n}} = -\frac{1}{\beta}\frac{\partial}{\partial \epsilon_i} \log \zeta_i$$

leading to the Bose distribution for bosons

$$\boxed{\langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i-\mu)} - 1}}$$

Average number of particles

Following the same lines we can calculate the average number of particles in the system as:

$$\langle N \rangle = \sum_i \langle n_i \rangle = \sum_i \frac{1}{e^{\beta(\epsilon_i-\mu)} \pm 1}$$

where + is for fermions and − for bosons.

Average Energy.

Similarly the average energy of the system is :

$$\langle E \rangle = \sum_i \langle n_i \rangle \epsilon_i = \sum_i \frac{\epsilon_i}{e^{\beta(\epsilon_i-\mu)} \pm 1}$$

All these results apply generally to non-interacting bosons and fermions. To be more specific, one needs to specify the quantum energy levels ϵ_i. In the following we apply these results to free particles (bosons and fermions) confined in a box. Accordingly the indivudal particle hamiltonian reduces to its kinetic part $\mathcal{H} = \frac{\hat{p}^2}{2m}$.

9.4 Gas of fermions.

The energy levels of a free fermion are given simply by $\epsilon(\vec{k}) = \frac{(\hbar k)^2}{2m} = \frac{p^2}{2m}$. One can assume periodic boundary conditions on the box of size L (to simplify) and the wave number k is accordingly quantified as

$$\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z).$$

with $n_x, n_y, n_z = 0, \dots \infty$; for each quantum numbers n_x, n_y, n_z, there is also a finite number of spin states, say typically two values for spin 1/2.

Then we get the following expression for the grand potential:

$$\Omega = -k_B T \sum_i \log(\zeta_i) = -k_B T \sum_i \log\Big(1 + e^{\beta(\mu - \epsilon_i)}\Big) \underset{\sum \to \int}{=} -2k_B T \int \frac{\mathrm{d}^3\vec{k}}{(2\pi/L)^3} \log[1 + e^{\beta(\mu - \frac{(\hbar k)^2}{2m})}]$$

where the factor 2 stems from the 2 spin values.

The pressure is found by taking $P = -\frac{\Omega}{V}$ and the density is:

$$\rho(\mu, T) = \frac{\langle N \rangle}{V} = \frac{1}{V} \sum_i \frac{1}{e^{\beta(\epsilon_i - \mu)} + 1} = 2 \int \frac{\mathrm{d}^3\vec{k}}{(2\pi)^3} \frac{1}{e^{\beta(\frac{(\hbar k)^2}{2m} - \mu)} + 1}$$

We introduce the fugacity as $z = e^{\beta\mu}$.

High Temperatures.

In this regime, $z \to 0$ at high temperatures. Then the formula for the pressure simplifies to:

$$P = \rho k_B T \left(1 + \frac{\rho \lambda_T^3}{2^{7/2}} + \cdots\right)$$

Low Temperatures.

At low temperature, the distribution $\langle n \rangle(\epsilon)$ reduces to a step function

$$\langle n \rangle(\epsilon) \xrightarrow{T \to 0} \Theta(\mu - \epsilon)$$

where Θ here is the heavy side step function.

We introduce ϵ_F the Fermi energy, which is the value of the chemical potential calculated in terms of the density at low temperature. We define accordingly $\epsilon_F = \frac{(\hbar k_F)^2}{2m}$. Using the previous result for $\langle n \rangle(\epsilon)$, one can calculate the averaged density $\rho = N/V$ as

$$\langle n \rangle \overset{T \to 0}{=} 2 \int_{k < k_F} \frac{\mathrm{d}^3\vec{k}}{(2\pi)^3} \cdot 1$$

giving

$$\rho = \frac{1}{3\pi^2} k_F^3$$

This gives reversly k_F as a function of the average density ρ:

$$k_F = \left(3\pi^2 \rho\right)^{1/3}$$

The average energy can be estimated as well as

$$E \overset{T \to 0}{=} 2V \int_{k < k_F} \frac{\mathrm{d}^3\vec{k}}{(2\pi)^3} \frac{(\hbar k)^2}{2m}$$

This leads to $E/V = \frac{\hbar^2}{10\pi^2 m} \left(3\pi^2 \rho\right)^{5/3}$. The pressure follows as

$$P = \frac{2}{3} \frac{(3\pi^2)^{5/3}}{10\pi^2} \frac{\hbar^2}{m} \rho^{5/3}$$

Note that the temperature does not appear in this expression, meaning that there is a finite pressure at vanishing temperature ! This is a consequence of the Fermi exclusion.

9.5 Gas of bosons and condensation of Bose-Einstein.

We now focus on a gas of free bosons. As we will highlight there is a singularity in the free energy emerging at a finite temperature, pointing to the existence of a phase transitionn in this non-interacting system. This is the so-called Bose-Einstein condensation.

9.5.1 Grand potential and pressure

For bosons the grand potential writes

$$\Omega = -k_BT\log\Theta = -k_BT \sum_{\text{quantum state i}} \log\frac{1}{1-e^{-\beta(\epsilon_i-\mu)}}.$$

and the pressure is accordingly

$$p = \frac{k_BT}{V}\sum_{\text{quantum state i}} \log\left(\frac{1}{1-e^{-\beta(\epsilon_i-\mu)}}\right).$$

We follow the same lines as for fermions, and write that the energy level of individual quantum state is

$$\epsilon(\vec{k}) = \frac{p^2}{2m} = \frac{(\hbar\vec{k})^2}{2m}$$

with the wave number quantified as $\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$. The sum over quantum states i is calculated as

$$\sum_{\text{Q state } i} (\cdot) = \int \frac{\mathrm{d}^3\vec{k}}{\left(\frac{2\pi}{L}\right)^3}(\cdot)$$

and we obtain:

$$P = \frac{k_BT}{V}\int \frac{\mathrm{d}^3\vec{k}}{\left(\frac{2\pi}{L}\right)^3}\log\frac{1}{\left(1-e^{-\frac{\epsilon(\vec{k})-\mu}{k_BT}}\right)}$$

We then get (using $V = L^3$):

$$\beta P = \int \frac{\mathrm{d}^3\vec{k}}{(2\pi)^3}\log\left(\frac{1}{1-ze^{-\frac{\hbar^2k^2}{2mk_BT}}}\right) = \int_0^{+\infty}\frac{4\pi}{(2\pi)^3}k^2\mathrm{d}k\log\left(\frac{1}{1-ze^{-\frac{\hbar^2k^2}{2mk_BT}}}\right)$$

Now making the change of variables $x^2 = \frac{\hbar^2k^2}{2mk_BT}$, we find :

$$\beta P = \frac{1}{2\pi^2}\left(\frac{2mk_BT}{\hbar^2}\right)^{3/2}\int_0^{+\infty} x^2\mathrm{d}x\log\left(\frac{1}{1-ze^{-x^2}}\right)$$

We introduce the de Broglie wave length $\lambda_T = (h^2/2\pi mk_BT)^{1/2}$ and rewrite the pressure as

$$\beta P = \frac{4}{\sqrt{\pi}}\frac{1}{\lambda_T^3}\int_0^{+\infty} x^2\mathrm{d}x\log\left(\frac{1}{1-ze^{-x^2}}\right)$$

Now we introduce some special functions $g_\alpha(x)$ as

$$g_\alpha(X) = \sum_{l=1}^{+\infty}\frac{X^l}{l^\alpha}$$

This allows to rewrite the pressure in simple terms. Indeed expanding the log as a power serie we obtain:

$$\log\left(\frac{1}{1-X}\right) = \sum_{l=1}^{+\infty}\frac{X^l}{l}$$

and plugging this into the integral we get that:

$$\int_0^{+\infty}\mathrm{d}x\,x^2\log\left(\frac{1}{1-ze^{x^2}}\right) = \sum_{l=1}^{+\infty}\frac{1}{l}\int_0^{+\infty}\mathrm{d}x\,x^2z^le^{\ell x^2} = \sum_{\ell=1}^{+\infty}\frac{z^\ell}{\ell}\int_0^{+\infty}\mathrm{d}x\,x^2e^{-\ell x^2}$$

From which we get the final result:

$$\boxed{\beta P(z) = \frac{1}{\lambda_T^3} g_{5/2}(z)}$$

with $z = \exp[\beta\mu]$ the fugacity.

We can make similar estimate for the density $\rho = N/V$, or calculate directly

$$\rho = \left.\frac{\partial P}{\partial \mu}\right|_T = z\left.\frac{\partial \beta\rho}{\partial z}\right|_T = z\frac{\partial}{\partial z}\left.\left[\frac{1}{\lambda_T^3} g_{5/2}(z)\right]\right|_T$$

Using

$$z\frac{\partial}{\partial z} g_{5/2}(z) = z\sum_{\ell=1}^{+\infty} \frac{1}{\ell^{5/2}} \ell z^{\ell-1} = g_{3/2}(z)$$

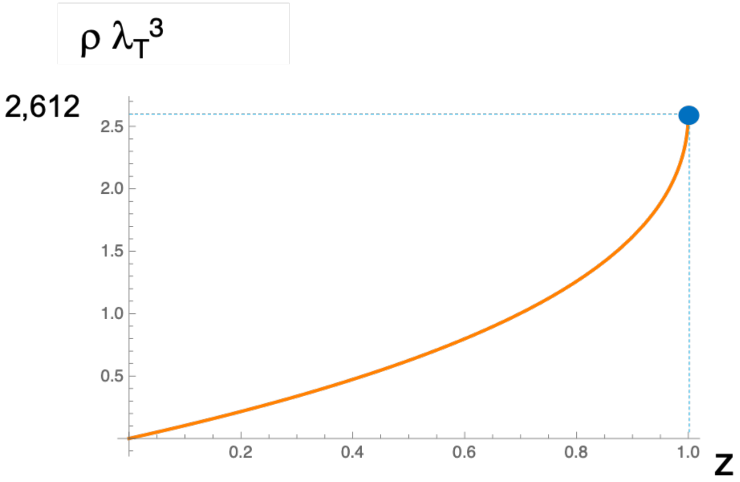
we then obtain the final result for the density:

$$\boxed{\rho = \frac{1}{\lambda_T^3} g_{3/2}(z)}$$

We have therefore the pressure and density as a function of the chemical potential μ (or fugacity $z = \exp[\beta\mu]$) and temperature T.

9.5.2 Bose Einstein Condensation.

As we will immediately observe, a singularity occurs when $z = 1$. Indeed let us plot the density as a function of the fugacity, or in dimensionless form $\rho(z)\lambda_T^3 = g_{3/2}(z)$, see enclosed figure.



The function $g_{3/2}(z)$ has a vertical asymptote for $z = 1$ at its value $g_{3/2}(z = 1) = 2.612\ldots$ and it is not defined (infinite) for $z > 1$. The curve for the density then stops at a maximal value $\rho_{\max} = \lambda_T^3 \times g_{3/2}(1)$. This raises mathematical issues when one wants to solve the equation ρ as a function of z in order to get the equation of state $P(\rho, T)$. There are indeed two behaviors depending on the temperature:

- For ρ and T such that $\rho\lambda_T^3 < g_{3/2}(1) = 2.612$ then the parametric solution $\rho(\mu)$ (or $\rho(z)$) can be inverted as $\mu(\rho)$ (or $z(\rho)$). This can be done e.g. graphically on the previous graph. The equation of state follows immediately, as $P(\rho, T)$.
- For ρ and T such that $\rho\lambda_T^3 > g_{3/2}(1) = 2.612$, then there is no solution for ρ as a function of $z = e^{\beta\mu}$.

This defines a Bose-Einstein temperature as

$$\rho\left(\frac{h^2}{2\pi m k_B T_{BE}}\right)^{1/2} = 2.612\ldots$$

Now what occurs for $T < T_{BE}$? The origin of the problem comes from the fundamental level. There is indeed a singularity of the Bose distribution which diverges as the fugacity $z \to 1$ for the fundamental state $\epsilon = 0$. The ocupation number of this fundamental state writes

$$\langle n\rangle_0 = \frac{1}{\frac{1}{z} - 1} = \frac{z}{1 - z} \xrightarrow{z\to 1} \infty$$

Hence there is an infinite number of particles in the fondamental state when $z = 1$. In the previous representation, where the number of particles was written as

$$N = \sum_{\text{Q states } i} \frac{1}{e^{\beta(\varepsilon-\mu)} - 1}$$

there is therefore a mathematical difficulty when passing from the discrete sum to the continuous integral, since we assumed that no singularity occured. However if the number of elements in the fundamental state diverges, then this cannot hold anymore and we have to separate the fundamental state from the rest of the terms in the sum. One should therefore separate the sum as

$$N = N_0 + \sum_{\vec{k} \neq \vec{0}}$$

where $N_0 = \frac{1}{\frac{1}{z}-1}$ and the second term now behaves in a regular way. In other words:

$$N = N_0 + \underbrace{V \int \frac{\mathrm{d}^3\vec{k}}{(2\pi)^3} \langle n_{\vec{k}} \rangle}_{\frac{1}{\lambda_T^3} g_{3/2}(z)}$$

with $N_0 = \langle n_{\epsilon=0} \rangle = \frac{z}{1-z}$ which diverges for $z = 1$. An important remark is that 'diverging' here means that N_0 becomes *macroscopic* when $z = 1$. In other words, N_0 is proportional to the volume V: $N_0 \simeq 1/(1-z) \propto V$.

From the previous equation, we deduce the number of particles in the fundamental state as

$$\frac{N_0}{V} = \frac{N}{V} \left(1 - \frac{g_{3/2}(z)}{\rho \lambda_T^3}\right)$$

For $\rho\lambda_T^3 > g_{3/2}(1)$ (z saturates to 1), we now obtain

$$\frac{N_0}{N} \approx 1 - \frac{2.612}{\rho \lambda_T^3}$$

In terms of the Bose-Einstein temperature defined above, this leads to

$$\begin{cases} \frac{N_0}{N} = 1 - \left(\frac{T}{T_{\mathrm{BE}}}\right)^{3/2}, & T < T_{\mathrm{BE}} \\ \frac{N_0}{N} = 0, & T > T_{\mathrm{BE}} \end{cases}$$

This demonstrates that the fundamental state becomes macroscopically filled ! This is a very important result, which had and still has a strong importance in physics.

Pressure.

Thermodynamic quantities can be calculated for $T < T_{\mathrm{BE}}$ following the same lines. However it can be shown that the fundamental state does not contribute to the pressure. If we perform the same separation as before between the fundamnental state and the rest ($\vec{k} = \vec{0}$ and $\vec{k} \neq \vec{0}$), we get:

$$P = \frac{k_B T}{V} \sum_{\text{Q states } i} \log[\frac{1}{1 - e^{-\beta(\epsilon_i - \mu)}}] = \frac{k_B T}{V} \log[\frac{1}{1-z}] + \frac{k_B T}{V} L^3 \int \frac{\mathrm{d}^3\vec{k}}{(2\pi)^3} \log[\frac{1}{1 - e^{-\frac{\epsilon(\vec{k})-\mu}{k_B T}}}]$$

The integral term is exactly the same as previously, and only the first term adds a contribution. However:

$$\frac{k_B T}{V} \log \frac{1}{1-z} \approx \frac{k_B T}{V} \log N_0 \sim \frac{\log V}{V} \ll 1$$

So we can neglect this term and the pressure is entirely determined by the non-singular, integral term. We thus obtain

$$\rho\lambda_T^3 < 2.612 \Rightarrow \beta P = \frac{1}{\lambda_T^3} g_{5/2}(z), \quad \rho\lambda_T^3 > 2.612 \Rightarrow \beta P = \frac{1}{\lambda_T^3} g_{5/2}(1)$$

Energy.

The energy is given by:

$$E = \frac{3}{2} PV$$

with the previous result for the pressure. One can deduce the thermal capacitance.

Conclusions.

The application of these concepts are numerous and Bose-Einstein condensation occurs in many different systems and was exhaustively investigated experimentally. A classical example is the transition observed for Helium 4 at 2.18 Kelvins from an ordinary liquid towards a superfluid, which can be considered as a kind of Bose-Einstein condensation. However interactions are never negligeable.

Chapter 10

Appendix: Mathematical memo

Notes in french

Ces notes n'ont pas vocation de rigueur et doivent être utilisées comme un mémo pratique pour quelques outils techniques utilisés usuellement en physique. Je renvoie vers les ouvrages appropriés pour des dévloppements plus poussés et rigoureux. Voir par exemple le cours de méthode mathématiques pour physicien de J-B Zuber: https://www.lpthe.jussieu.fr/∼zuber/Cours/L3_2013.pdf

10.1 Multiplicateurs de Lagrange

La méthode des mulitplicateurs de Lagrange est utilisée lorsque l'on veut maximiser ou minimiser une fonction à plusieurs variables en présence d'une contrainte.

Le principe: Les solutions $\{\tilde{x}_i\}$ qui extrémalisent une fonction à plusieurs variables $z = f(x_1, x_2, \ldots, x_n)$ en présence d'une contrainte implicite $C(x_1, x_2, \ldots, x_n) = 0$, sont les extréma de la fonction

$$F(x_1, x_2, \ldots, x_n) = f(x_1, x_2, \ldots, x_n) - \lambda \times C(x_1, x_2, \ldots, x_n)$$

dans laquelle la contrainte C est libérée. Le paramètre λ (multiplicateur de Lagrange) est calculé *in fine* pour que la contrainte soit vérifiée. C'est la méthode des multiplicateurs de Lagrange.

10.1.1 Un exemple typique

On considère un cylindre de hauteur h et de rayon a. On veut connaitre les dimensions du cylindre qui maximise la surface sachant que le volume est fixé. Cela revient donc à maximiser la fonction

$$S(a,h) = 2\pi a^2 + 2\pi a\, h$$

avec la contrainte $V = \pi a^2\, h$=cste. La solution évidente est de calculer h en fonction de a, $h = V/\pi a^2$ et de remplaxer dans l'équation précédente pour obtenir une fonction à un seul paramètre: $S(a) = 2\pi a^2 + 2\pi a \frac{V}{\pi a^2}$. La solution optimale est $h = 2a$ et $a = (V/2\pi)^{1/3}$.

Mais une solution alternative est de "libérer" la contrainte. Pour cela on extrémalise la fonction à deux variables

$$[S - \lambda V](a,h)$$

avec λ un paramètre fixe, dont on calcule la valeur à la fin.

Vérifions:

$$\begin{aligned} \frac{\partial}{\partial a}[S - \lambda V](a,h) = &\quad 4\pi a + 2\pi h - \lambda\, 2\pi a\, h = 0 \\ \frac{\partial}{\partial h}[S - \lambda V](a,h) = &\quad 2\pi a - \lambda\, \pi a^2 = 0 \end{aligned} \tag{10.1}$$

On en déduit $\lambda = 2/a$, puis $h = 2a$, d'où $a = (V/2\pi)^{1/3}$.

10.1.2 Justification simple

On veut extrémaliser $z = f(x_1, x_2, \ldots, x_n)$ avec la contrainte implicite $C(x_1, x_2, \ldots, x_n) = 0$. Supposons que l'on peut inverser la contrainte implicite pour écrire $x_n = \phi(x_1, x_2, \ldots, x_{n-1})$. On a alors $z = f(x_1, \ldots, x_{n-1}, \varphi(x_1, x_2, \ldots, x_{n-1}))$. À un extremum, les dérivées partielles vérifient

$$\forall i = \{1, n-1\}\ \frac{\partial z}{\partial x_i} = \frac{\partial f}{\partial x_i} + \frac{\partial \varphi}{\partial x_i} \times \frac{\partial f}{\partial x_n} = 0 \tag{10.2}$$

dont la solution donne les valeurs des $\tilde{x}_i$ correspondant à l'extremum recherché. Cela est bien équivalent à optimiser la fonction

$$F(x_1, x_2, \ldots, x_n) = f(x_1, x_2, \ldots, x_n) - \lambda \times (x_n - \varphi(x_1, ..., x_{n-1}))$$

où la contrainte $x_n = \phi(x_1, x_2, \ldots, x_{n-1})$ est relaxée. On le vérifie simplement: le calcul des dérivées partielles donne

$$\forall i = \{1, n-1\} : \ \frac{\partial F}{\partial x_i} = \frac{\partial}{\partial x_i}[f - \lambda(x_n - \varphi(x_1, ..., x_{n-1}))] = \frac{\partial f}{\partial x_i} + \lambda \frac{\partial \varphi}{\partial x_i} = 0$$

et

$$i = n : \ \frac{\partial F}{\partial x_n} = \frac{\partial f}{\partial x_n} - \lambda = 0$$

Donc les $\tilde{x}_i$ correspondant à un extremum vérifient bien l'équation Eq.(10.2).

10.1.3 Interprétation géométrique

Supposons que $\vec{x_0} = \{\tilde{x}_1, \cdots, \tilde{x}_n\}$ soit un extrémum recherché de la fonction $z = f(x_1, x_2, \ldots, x_n)$ avec la contrainte implicite $C(x_1, x_2, \ldots, x_n) = 0.$. Alors pour $d\vec{x}$ autour de $\vec{x_0}$ on a $dz \equiv df = \frac{\partial f}{\partial x_i} \cdot x_i = 0$, soit

$$\vec{\nabla} f|_{\vec{x_0}} \cdot d\vec{x} = 0$$

Mais par construction $dC = 0$ le long de la courbe $C = 0$ et on en déduit

$$\vec{\nabla} C|_{\vec{x_0}} \cdot d\vec{x} = 0$$

Donc les vecteurs $\vec{\nabla} f$ et $\vec{\nabla} C$ sont tous deux perpendiculaires à $d\vec{x}$ et on en déduit qu'il existe un coefficient λ tel que $\vec{\nabla} f = \lambda \vec{\nabla} C$.

10.2 Transformée de Fourier

On considère un champ $A(\vec{r})$, fonction de l'espace (3D) et on définit:

$$A(\vec{k}) = \int d^3\mathbf{r} \, A(\vec{r}) \, e^{i\vec{k}\cdot\vec{r}} \tag{10.3}$$

$$A(\vec{r}) = \int \frac{d^3\mathbf{k}}{(2\pi)^3} \, A(\vec{k}) \, e^{-i\vec{k}\cdot\vec{r}} \tag{10.4}$$

- Transformées usuelles:

Table 10.1: Quelques transformées à 1D

Fonction	Fourier transform	comment
1	$\delta(x)$	cf distributions
$\delta(x)$	$\frac{1}{2\pi}$	”
$\delta(x-a)$	$\frac{1}{2\pi} e^{ika}$	”
$e^{-a\|x\|}$	$\frac{2a}{k^2+a^2}$	a¿0
$\frac{2a}{x^2+a^2}$	$2\pi e^{-\|k\|a}$	a¿0
e^{-ax^2}	$\sqrt{\frac{\pi}{a}} e^{-k^2/(4a)}$	a¿0
$\cos ax$	$\frac{1}{2}(\delta(x-a) + \delta(x+a))$	
$\sin ax$	$\frac{1}{2i}(\delta(x-a) - \delta(x+a))$	
$\frac{1}{x}$	$i\pi \mathrm{sign}(x)$	

- Opérateurs vectoriels:

$$\begin{aligned} \vec{\nabla} A \quad & \rightarrow -i\vec{k} A(\vec{k}) \\ \vec{\nabla} \cdot \vec{A} \quad & \rightarrow -i\vec{k} \cdot A(\vec{k}) \\ \Delta A \quad & \rightarrow -k^2 \cdot A(\vec{k}) \end{aligned}$$

Table 10.2: Quelques transformées à 3D

Fonction	Fourier transform	comment
$\frac{1}{4\pi r}$	$\frac{1}{k^2}$	
$\frac{\exp(-ar)}{4\pi r}$	$\frac{1}{k^2+a^2}$	

- Produit de convolution: On définit un produit de convolution entre deux fonctions par

$$[f \star g](\vec{r}) = \int d^3\mathbf{r}'\, f(\vec{r}-\vec{r'})g(\vec{r'}) \tag{10.5}$$

La transformée de Fourier d'un produit de convolution est le produit des transformées de Fourier:

$$\int d^3\mathbf{r'}\, [f \star g](\vec{r})e^{-i\vec{k}\cdot\vec{r}} = f(\vec{k}) \times g(\vec{k}) \tag{10.6}$$

- Parseval (1D et 3D)

$$\begin{aligned} \textstyle\int dx\, |f(x)|^2 &= \int \frac{dk}{2\pi}\, |f(k)|^2 \\ \textstyle\int d^3\mathbf{r}\, |f(\vec{r})|^2 &= \int \frac{d^3\mathbf{k}}{(2\pi)^3}\, |f(\vec{k})|^2 \end{aligned} \tag{10.7}$$

- Transformée de Fourier et passage continu-discret:

Pour un système de taille L, périodique, on écrit un développement de $A(\vec{r})$ en série de Fourier:

$$A(\vec{r}) = \frac{1}{L^3}\sum_{\vec{k}} A_{\vec{k}}\, e^{-i\vec{k}\cdot\vec{r}} \tag{10.8}$$

avec $\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$ et $A_{\vec{k}} = \int_{L^3} d^3\mathbf{r}\, A(\vec{r})\, e^{i\vec{k}\cdot\vec{r}}$.

Dans la limite des grandes taille $L \to \infty$, on écrit alors:

$$A(\vec{r}) = \frac{1}{L^3}\sum_{\vec{k}} A_{\vec{k}}\, e^{-i\vec{k}\cdot\vec{r}} \simeq \int \frac{d^3\mathbf{k}}{(2\pi)^3}\, A(\vec{k})\, e^{-i\vec{k}\cdot\vec{r}} \tag{10.9}$$

On utilise de façon générale l'équivalence

$$\frac{1}{(2\pi)^3}\int d^3\mathbf{k} \longleftrightarrow \frac{1}{L^3}\sum_{\vec{k}} \tag{10.10}$$

pour le passage discret – continu.

10.3 Distributions

Une distribution f est une fonctionnelle qui s'applique à une fonction quelconque φ sous la forme

$$\forall\varphi, \langle f, \varphi\rangle = \int_{-\infty}^{+\infty} dx\, f(x)\, \varphi(x) \tag{10.11}$$

La distribution de Dirac est notée δ_{x_0} ou encore $\delta(x-x_0)$ est telle que $\langle\delta_{x_0}, \varphi\rangle = \varphi(x_0)$, ce qui se réecrit

$$\int dx\, \delta(x-x_0)f(x) = f(x_0) \tag{10.12}$$

La distribution de Dirac peut être vue comme une fonction 'test' de support (largeur) infiniment petit et de hauteur infinie, de sorte que son intégrale est égale à 1:

$$\int dx\, \delta(x-x_0) = 1.$$

Par exemple c'est la limite d'une gaussienne lorsque la largeur tend vers zero:

$$\lim_{\sigma\to 0} \frac{1}{\sqrt{2\pi\sigma}} \exp\left(-\frac{x^2}{2\sigma}\right) = \delta(x) \tag{10.13}$$

Propriétés utiles:

- Dilatation
$$\delta(\alpha\, x) = \frac{1}{|\alpha|}\, \delta(x) \tag{10.14}$$
- Convolution
$$\delta \circ f(x) = \delta(f(x)) = \sum_{x_i} \frac{1}{|f'(x_i)|}\, \delta(x - x_i) \tag{10.15}$$
avec x_i les zéros de la fonction $f(x)$, ici supposés isolés et à dérivée non-nulle.
- La distribution de Dirac est la dérivée de la fonction de Heavisde $\delta(x - x_0) = H'_(x - x_0)$ avec H la fonction de Heavisde :
$$\begin{aligned} H(x) &= 1 \quad x > 0 \\ H(x) &= 0 \quad x < 0 \end{aligned} \tag{10.16}$$
- La dérivée d'une distribution quelconque f est définie par
$$\int dx\, f'(x)\varphi(x) = -\int dx\, f(x)\varphi'(x)$$
et donc
$$\int dx\, \delta'(x)\varphi(x) = -\int dx\, \delta(x)\varphi'(x) = -\varphi'(0) \tag{10.17}$$
- Transformée de Fourier de la distribution de Dirac: à une dimension:
$$\int dx\, \delta(x - x_0)\, e^{i\vec{k}\, x} = e^{ik\, x_0} \tag{10.18}$$
ce qui se généralise à toute dimension
$$\int d\vec{r}\, \delta(\vec{r} - \vec{r}_0)\, e^{i\vec{k}\cdot\vec{r}} = e^{i\vec{k}\cdot\vec{r}_0} \tag{10.19}$$

10.4 Fonctionelles, dérivées fonctionnelles

Une fonctionnelle est une "fonction de fonction", elle fait correspondre à une fonction un nombre réel:

$$A(\vec{r}) \to \mathcal{F}[A(\vec{r})] \tag{10.20}$$

- exemples: $I[A] = \int d^3\mathbf{r}\, A(\vec{r})$, $\int d^3\mathbf{r} d^3\mathbf{r}' A(\vec{r} - \vec{r'})A(\vec{r} + \vec{r'})$, $\int d^3\mathbf{r}\, (\nabla A(\vec{r}))^2$.
- Si on se place sur un réseau, une fonctionnelle s'interprète comme une fonction de l'ensemble des valeurs de A en tout point du réseau: $\mathcal{F}[A(\vec{r})] = \mathcal{F}[A_1, A_2, \ldots, A_n]$.
$$\delta\mathcal{F} = \sum_i \frac{\partial\mathcal{F}}{\partial A_i}\delta A_i + \ldots \tag{10.21}$$
soit,
$$\delta\mathcal{F} = \int d^3\mathbf{r}\, \left(\frac{\partial\mathcal{F}}{\partial A(\vec{r})}\right) \delta A(\vec{r}) + \ldots \tag{10.22}$$

Quelques exemples d'application:

- pour $I[A] = \int d^3\mathbf{r}\, A(\vec{r})$, on obtient
$$\frac{\delta I}{\delta A(\vec{r})} = 1 \tag{10.23}$$

- de façon identique, pour $I[A] = \int d^3\mathbf{r}\, A^n(\vec{r})$, on obtient
$$\frac{\delta I}{\delta A(\vec{r})} = nA^{n-1}(\vec{r}) \tag{10.24}$$

- pour $\mathcal{F}[A] = \int d^3\mathbf{r}\, \frac{1}{2}(\vec{\nabla}A)^2$,
$$\frac{\delta \mathcal{F}}{\delta A(\vec{r})} = -\Delta A \tag{10.25}$$
avec $\Delta = \nabla^2$ le laplacien. On peut montrer ce résultat soit par intégration par partie ou discrétisation sur un réseau.

- Un exemple utile en physique est la dérivée fonctionnelle de l'énergie libre avec un terme en gradient carré de la densité:
$$\mathcal{F}(\{\rho(\vec{r})\}) = \int d^3\mathbf{r}\ \frac{1}{2}m(\vec{\nabla}\rho)^2 + f(\rho)$$
alors
$$\frac{\delta \mathcal{F}(\{\rho(\vec{r})\})}{\delta \rho(\vec{r})} = -m\nabla^2\rho + \frac{df}{d\rho}(\rho)$$

10.5 Exemples de résolution d'EDP

10.5.1 Résolution d'une équation de Poisson et fonction de Green

On cherche à résoudre une équation de type
$$\Delta G = -\delta(\vec{r}) \tag{10.26}$$
C'est une équation universelle que l'on trouve dans de nombreux problèmes en électrostatique, écoulements hydrodynamiques, équation de diffusion, etc.

Par application de la transformée de Fourier, on obtient
$$k^2\tilde{G}(\vec{k}) = 1 \tag{10.27}$$
et $\tilde{G}(\vec{k}) = 1/k^2$. D'où, par transformée inverse,
$$G(\vec{r}) = \int \frac{d^3\mathbf{k}}{(2\pi)^3}\, \frac{1}{k^2}\, e^{-i\vec{k}\cdot\vec{r}} \tag{10.28}$$
Ce qui donne
$$G(\vec{r}) = \frac{1}{4\pi|\vec{r}|} \tag{10.29}$$

Remarques:
- G est la fonction de Green associée à l'opérateur Laplacien.
- le résultat peut aisément être généralisé à l'équation avec 'écrantage'
$$(\Delta + \kappa^2)G = -\delta(\vec{r}) \tag{10.30}$$
dont la solution en Fourier est $\tilde{G}(\vec{k}) = 1/(k^2 + \kappa^2)$ et l'inversion conduit à
$$G(\vec{r}) = \frac{e^{-\kappa r}}{4\pi|\vec{r}|} \tag{10.31}$$
- La solution pour une distribution quelconque de "charge" $\rho_0(\vec{r})$
$$\Delta G = -\rho_0(\vec{r}) \tag{10.32}$$
$$G(\vec{r}) = \frac{1}{4\pi}\int d\vec{r'}\, \frac{\rho_0(\vec{r'})}{|\vec{r} - \vec{r'}|} \tag{10.33}$$

10.5.2 Résolution d'une équation de Diffusion

L'équation de diffusion s'écrit

$$\frac{\partial c}{\partial t} = D\Delta c \tag{10.34}$$

(avec D le coefficient de diffusion) et on suppose que la condition initiale est $c(\vec{r}, t = 0) = \delta(\vec{r})$. La transformée de Fourier spatiale de l'équation de diffusion donne

$$\frac{\partial \tilde{c}}{\partial t}(\vec{k}, t) = -Dk^2 c(\vec{k}, t) \tag{10.35}$$

de solution

$$\tilde{c}(\vec{k}, t) = \tilde{c}(\vec{k}, t = 0)\, e^{-Dk^2 t} \tag{10.36}$$

et pour la condition initiale donnée, $\tilde{c}(\vec{k}, t = 0) = 1$. On en déduit par transformée de Fourier inverse que

$$c(\vec{r}, t) = \frac{1}{(4\pi Dt)^{3/2}} \exp\left[-\frac{r^2}{4Dt}\right] \tag{10.37}$$

La solution de cette équation peut être interprété comme la fonction de Green – ou propagateur – associé à l'équation de diffusion ci-dessus.

Pour une condition initiale quelconque $c(\vec{r}, t = 0) = c_0(\vec{r})$, il suffit de remarquer que

$$c_0(\vec{r}) = \int d\vec{r'}\, c_0(\vec{r'})\delta(\vec{r} - \vec{r'}) \tag{10.38}$$

et par linéarité de l'EDP, on en déduit donc que la solution est la superposition des poids $c_0(\vec{r'})$, propagés par la fonction de Green de l'équation Eq.(10.37), de sorte que

$$c(\vec{r}, t) = \int d\vec{r'}\, c_0(\vec{r'}) \times \frac{1}{(4\pi Dt)^{3/2}} \exp\left[-\frac{(\vec{r} - \vec{r'})^2}{4Dt}\right] \tag{10.39}$$

Chapter 11

Appendix: Mathematica calculations of van der Waals phase transitions

Théorie de van der Waals de la transition liquide - gaz

ρ représente ρ / ρ_C
T représente T / T_C
f est en unité $P_c = \frac{3}{8} \rho_c k_B T_C$

μ est en unité $\frac{P_c}{\rho_c} = \frac{3}{8} k_B T_C$

Energie libre volumique

$$f[\rho\_,\ T\_] := \frac{8}{3}\, T \rho \left(\mathrm{Log}\left[\frac{\rho}{3-\rho}\right] - 1\right) - 3\rho^2$$

$$P[\rho\_,\ T\_] := \frac{8}{3}\, \frac{\rho\, T}{1 - \frac{\rho}{3}} - 3\rho^2$$

```
(*Plot[{f[ρ,5],f[ρ,1],f[ρ,0.1]},{ρ,0,3},
 PlotStyle→{RGBColor[1,0,0],RGBColor[0.5,0.8,0.5],
   RGBColor[0,0,1]},AxesLabel→{"ρ","f(ρ)"}]*)
```

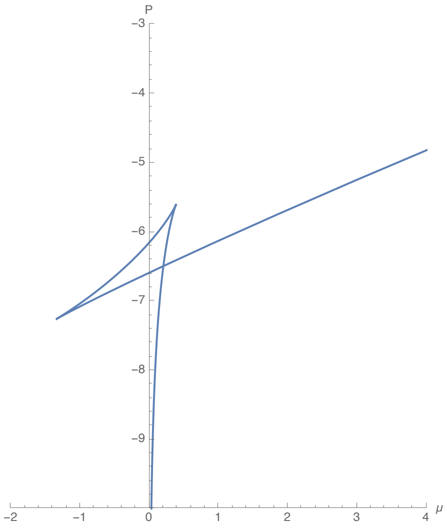
```
(*Plot[{P[ρ,5],P[ρ,1],P[ρ,0.1]},{ρ,0,3},
 PlotStyle→{RGBColor[1,0,0],RGBColor[0.5,0.8,0.5],
   RGBColor[0,0,1]},TicksStyle→None,
 AxesLabel→{"ρ","P"}]*)
```

Pression et potentiel chimique

$$P[\rho\_,\ T\_] := \frac{8}{3}\, \frac{\rho\, T}{1 - \frac{\rho}{3}} - 3\rho^2$$

$$\mu[\rho\_,\ T\_] := \frac{f[\rho,\ T] + P[\rho,\ T]}{\rho}$$

```
T = 0.7;
ParametricPlot[{P[ρ, T], μ[ρ, T]}, {ρ, 0, 3},
 PlotRange → {{-2, 4}, {-10, -3}},
 AxesLabel → {"μ", "P"}]
```



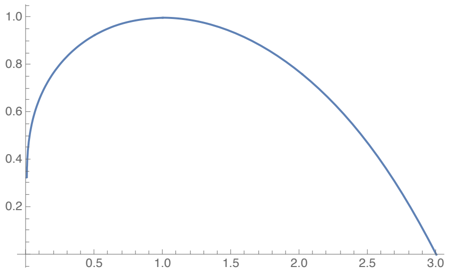
Bimodale

```
ρv0 = 0.0001;
ρL0 = 2.9;
Tin = 0.25;
Tfin = 1.;
binroot =
 FindRoot[{(μ[ρv, T] == μ[ρL, T]),
    (P[ρv, T] == P[ρL, T])}, {ρv, {ρv0, ρv0 + 0.00005}},
   {ρL, {ρL0, ρL0 - 0.005}}, MaxIterations -> 50,
   AccuracyGoal -> 11];

ρv1 = First[ρv /. binroot];
   ρL1 = First[ρL /. binroot];
```

```
ρv0 = 0.0001;
ρL0 = 2.9;
Tin = 0.25;
Tfin = 1.;
nn = 20;
BimodaleV = {};
BimodaleL = {};
Do[T = (Tin + j / nn * (Tfin - Tin));

binroot =
   FindRoot[{(μ[ρv, T] == μ[ρL, T]),
      (P[ρv, T]  == P[ρL, T])},
     {ρv, {ρv0, ρv0 + 0.00005}},
     {ρL, {ρL0, ρL0 - 0.005}}, MaxIterations -> 50,
     AccuracyGoal -> 11];
     ρv1 = First[ρv /. binroot];
     ρL1 = First[ρL /. binroot];
     Print[T, "   ", CForm[ρv1], "    ", CForm[ρL1]];

     BimodaleV = Append[BimodaleV, {ρv1, T}];
     BimodaleL = Append[BimodaleL, {ρL1, T}];
     ρv0 = ρv1; ρL0 = ρL1,
  {j, 0, nn}];

BimodV = Interpolation[BimodaleV];
BimodL = Interpolation[BimodaleL];
```

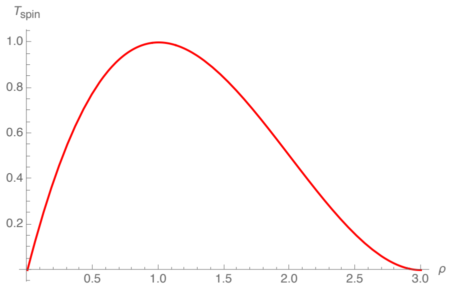
```
0.25   0.00005125899541706119    2.7583061357378464
0.2875   0.00025624753872846627    2.7179245146584794
0.325   0.0008696978713965782    2.6761648069902737
0.3625   0.002268063182512048    2.6328877234215526
0.4   0.004910889713098212    2.5879374843271177
0.4375   0.009288455165865314    2.541139779437889
0.475   0.01588546651588045    2.4922980969586646
0.5125   0.02516664910024084    2.4411880577329903
0.55   0.03758004533956086    2.3875492814007457
0.5875   0.05357225433669696    2.3310739522766357
0.625   0.0736120792887917    2.2713906104979906
0.6625   0.09822223583914359    2.208040592879236
0.7   0.12802230166578657    2.1404425485057135
0.7375   0.16379088709441406    2.06783654645015
0.775   0.2065637240860893    1.9891910218399123
0.8125   0.2578037865070602    1.9030365801328064
0.85   0.31972996451885616    1.8071403273364057
0.8875   0.3960459485384905    1.6977792593253787
0.925   0.4939195068540769    1.5677626899039274
0.9625   0.6317070512248043    1.3987089566614364
1.   1.008077270390525    1.008077270392827
```

```
TBimod[ρ_] := BimodV[ρ] /; ρ  < 1
TBimod[ρ_] := BimodL[ρ] /; ρ  > 1
Plot[TBimod[ρ], {ρ, 0.001, 3}]
```



Spinodale

```
Tspin[ρ_] := 9/4 ρ (1 - ρ/3)^2
Plot[Tspin[ρ], {ρ, 0, 3},
 PlotStyle → RGBColor[1, 0, 0],
 AxesLabel → {"ρ", "T_spin"}]
```

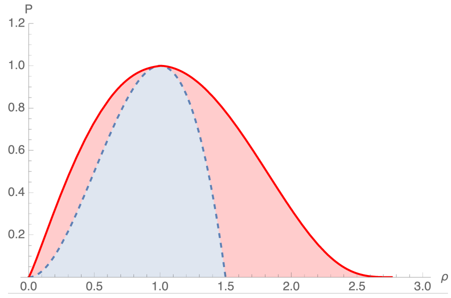


Bilan : bimodale et spinodale

$$\mathrm{Pspin}[\rho\_] := \frac{8}{3}\,\frac{\rho\,\frac{9}{4}\,\rho\,\left(1-\frac{\rho}{3}\right)^2}{1-\frac{\rho}{3}} - 3\,\rho^2$$

$$\mathrm{Pbimod}[\rho\_] := \frac{8}{3}\,\frac{\rho\,\mathrm{TBimod}[\rho]}{1-\frac{\rho}{3}} - 3\,\rho^2$$

```
Plot[{Pspin[ρ], Pbimod[ρ]}, {ρ, 0, 3},
 PlotStyle → {Dashed, RGBColor[1, 0, 0]},
 PlotRange → {0, 1.2}, Filling → {1 → Axis, 2 → {1}},
 AxesLabel → {"ρ", "P"}]
```



Développement de Landau de l' énergie libre

Potentiel chimique au point critique (en unité ρ_C, T_C, P_C)

```
ρc = 1;
Tc = 1;
Pc = P[ρc, Tc];
μc = μ[ρc, Tc];
```

Grand potentiel au point critique

```
ωc = f[ρc, Tc] - μc ρc
```

C' est $-P_c$ dans le système d' unités réduites

```
δω[μ_, T_, ρ_] := f[ρ, T] - μ ρ - ωc

FullSimplify[Series[δω[μc + Δμ, Tc + ΔT, ρc + ξ],
   {ξ, 0, 4}]]
```

$$\frac{1}{3}\,(-3\,\Delta\mu - 8\,\Delta T\,(1 + \mathrm{Log}[2])) + \frac{1}{3}\,(-3\,\Delta\mu + \Delta T\,(4 - 8\,\mathrm{Log}[2]))\,\zeta + 3\,\Delta T\,\zeta^2 + \frac{3}{8}\,(1 + \Delta T)\,\zeta^4 + O[\zeta]^5$$

```
ClearAll[T];
Series[f[ρ, T], {ρ, ρc, 4}, {T, 1, 1}]
```

$$\left(\left(-\frac{17}{3} - \frac{8\,\mathrm{Log}[2]}{3}\right) + \left(-\frac{8}{3} - \frac{8\,\mathrm{Log}[2]}{3}\right)(T-1) + O[T-1]^2\right) + \left(\left(-\frac{14}{3} - \frac{8\,\mathrm{Log}[2]}{3}\right) + \left(\frac{4}{3} - \frac{8\,\mathrm{Log}[2]}{3}\right)(T-1) + O[T-1]^2\right)(\rho-1) + \left(3\,(T-1) + O[T-1]^2\right)(\rho-1)^2 + \left(\frac{3}{8} + \frac{3\,(T-1)}{8} + O[T-1]^2\right)(\rho-1)^4 + O[\rho-1]^5$$

Energie libre de Landau : analogie magnétique

```
h[μ_, T_] := μ - μ[ρc, T]
```

attention ici potentiel chimique calculé à T et non T_c

cf : $\Delta\mu - \frac{\Delta T}{3}(4 - 8\,\mathrm{Log}[2]) = \mu - \mu[\rho_c, T]$

avec $\mu[\rho_c, T] = -6 + 4\,T - \frac{8}{3}\,T\,(1 + \mathrm{Log}[2])$

$$\delta\omega_{\mathrm{LANDAU}}[h\_, T\_, \xi\_] := -h\,\xi + 3\,(T-1)\,\xi^2 + \frac{3}{8}\,T\,\xi^4$$

Analogie avec système *magnétique* :

$h = \mu - \mu[\rho_c, T]$: h joue le rôle d' un champ extérieur

$\zeta = \frac{\rho - \rho_c}{\rho_c}$ joue le rôle du paramètre d' ordre

---

```
Plot[{δωLANDAU[0, .5, ϕ], δωLANDAU[2.1, 0.5, ϕ],
  δωLANDAU[3, 0.5, ϕ]}, {ϕ, -3, 3}]
```