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Statistical Physics

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Part I

Ideal Quantum Gases

Chapter A

Grand canonical ensemble and quantum statistical mechanics

A.1 Grand canonical ensemble

A.1.1 Introduction

Grand canonical ensemble is easier to use for describing statistical mechanics of quantum system for two main reasons :

- Quantum particles may be *fermions* or *bosons* implying that it will be easier to use a description in term of occupation of states.
- In some cases, we can *create* of *destroy* quantum particles, example being photons, phonons. Implying that the number of particles is not fixed.

To summarize that, we can see that there is situation or quantum problem where the grand canonical is clearly the good ensemble. There are other situation, example being in condensed matter (free electron metal), usually in that case you know the number of quantum particles you have in your system, then in that case it's just easier to use the grand canonical ensemble.

The idea of the Grand-canonical ensemble is we allow an exchange of heat and matter, thus fixing the temperature T, the chemical potential μ and the volume V.

A.1.2 Grand canonical distribution

On the statistical physics point of view, the question is the following : What is the distribution probability of the Grand canonical ensemble ?

$$P^{\rm GC}_{l_{(T,\mu,V)}}=?$$

Remark :

• in the microcanonical ensemble :

$$P_{l_{(E,N,V)}}^{\rm MC} = \frac{1}{\Omega}$$

Where Ω are the micro-states.

• in the canonical ensemble :

$$P_{l_{(T,N,V)}}^{C} = \frac{e^{-\beta E_l}}{Z_{c_{(T,N,V)}}}$$

Where Z_c is the canonical partition function.

A system at equilibrium will have a probability distribution that is maximizing Shannon entropy respecting the external constraints. And Shannon entropy is given by

$$S = -k_B \sum_{l} P_l \ln(P_l)$$

In the Grand canonical ensemble we have to maximize a function

$$\phi(\{P_l\}) = -k_B \sum_{l} P_l \ln(P_l) - \lambda_0 \left(\sum_{l} P_l - 1\right) - \lambda_E \left(\sum_{l} P_l E_l - \langle E \rangle\right) - \lambda_N \left(\sum_{l} P_l N_l - \langle N \rangle\right)$$

The technique we will use is the Lagrange multiplicators : λ_0 is a parameter to impose a condition, here it's the normalized probability distribution, λ_E , and λ_N will ensure that the chemical potential is fixed.

The idea of Lagrange multiplicators is the following

$$\frac{\partial \phi}{\partial P_l} = 0 \Rightarrow -k_B \left(\ln(P_l) + 1 \right) - \lambda_0 - \lambda_E E_l - \lambda_N N_l = 0$$
$$\frac{\partial \phi}{\partial \lambda_0} = 0 \qquad \qquad \frac{\partial \phi}{\partial \lambda_E} = 0 \qquad \qquad \frac{\partial \phi}{\partial \lambda_N} = 0$$

Remark : There is no summation in the end since l is a mute index, hence ∂_{P_l} is just the derivation on one of the micro-state, not all.

Hence we can have an expression for P_l ,

$$P_{l} = e^{-\left(1 + \frac{\lambda_{0}}{k_{B}}\right)} e^{\frac{\lambda_{E}}{k_{B}}\left(E_{l} + \frac{\lambda_{N}}{\lambda_{E}}N_{l}\right)}$$

We introduced three parameters $(\lambda_0, \lambda_E, \lambda_N)$. We prefer to us (Z, T, μ) . Then,

$$Z \equiv \exp\left(1 + \frac{\lambda_0}{k_B}\right) \qquad \qquad T \equiv -\frac{1}{\lambda_E} \qquad \qquad \mu \equiv -\frac{\lambda_N}{\lambda_E}$$

Meaning

$$P_{l_{(T,V,\mu)}}^{\rm GC} = \frac{1}{Z_{(T,V,\mu)}^{\rm GC}} e^{-\beta(E_l - \mu N_l)}$$

With

$$Z_{(T,V,\mu)}^{\rm GC} = \sum_{l} e^{-\beta(E_l - \mu N_l)}$$

A.1.3 Grand potential

We will define

$$\Omega(T, V, \mu) \equiv -k_B T \ln Z_{(T, V, \mu)}^{\rm GC}$$

It is the exact same definition as the free energy in the canonical ensemble, but here we will call it the grand canonical potential. It has to be an extensive quantity.

Using Euler theorem, we know that

$$\Omega = V\omega(T,\mu)$$

where ω is a function only of the intensive quantity.

$$\Omega = V \left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu} \qquad \qquad \bar{p} = -\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu}$$

A.1.4 Average number of particles

$$\begin{split} \langle N \rangle &= \sum_{l} N_{l} P_{l} = \sum_{l} N_{l} \frac{1}{Z_{(T,V,\mu)}} e^{-\beta(E_{l}-\mu N_{l})} \\ &= \frac{1}{Z_{(T,V,\mu)}} \sum_{l} N_{l} e^{-\beta(E_{l}-\mu N_{l})} \\ &= \frac{1}{Z_{(T,V,\mu)}} \sum_{l} \frac{1}{\beta} \frac{\partial}{\partial \mu} \left(e^{-\beta(E_{l}-\mu N_{l})} \right) \\ &= \frac{1}{Z_{(T,V,\mu)}} \frac{1}{\beta} \frac{\partial}{\partial \mu} \left(\sum_{l} e^{-\beta(E_{l}-\mu N_{l})} \right) \\ &= \frac{1}{Z_{(T,V,\mu)}} \frac{1}{\beta} \frac{\partial}{\partial \mu} Z_{(T,V,\mu)} \\ &= \frac{1}{\beta} \frac{\partial}{\partial \mu} \left(\ln Z_{(T,V,\mu)} \right) \\ &= - \left(\frac{\partial \Omega}{\partial \mu} \right)_{T,V} \end{split}$$

Hence,

$$\langle N \rangle = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V}$$

We now are interested in the fluctuation around its mean value,

$$\Delta N2 \equiv \langle (N - \bar{N})^2 \rangle$$

 $\mathbf{Remark}:$

$$|N^{2}\rangle = \sum_{l} \frac{N_{l}^{2}}{Z_{(T,V,\mu)}} e^{-\beta(E_{l}-\mu N_{l})} = \frac{1}{\beta^{2}} \frac{1}{Z_{(T,V,\mu)}} \frac{\partial^{2} Z_{(T,V,\mu)}}{\partial \mu^{2}}$$

Hence,

$$\Delta N^2 = \frac{1}{\beta^2} \left[\frac{1}{Z_{(T,V,\mu)}} \frac{\partial^2 Z_{(T,V,\mu)}}{\partial \mu^2} - \left(\frac{\partial Z_{(T,V,\mu)}}{\partial \mu} \right)^2 \right] = \frac{1}{\beta^2} \frac{\partial^2}{\partial \mu^2} \ln Z$$

Hence we get,

$$\Delta N^2 = (k_B T)^2 \left(\frac{\partial^2}{\partial \mu^2} \ln Z\right) = k_B T \left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V}$$

This relationship is called the *fluctuation-dissipation theorem* or the *linear response theorem*. This translates to particle fluctuations being described by how the system responds to a disturbance in its chemical potential.

A.1.5 Average energy

$$\begin{split} \langle E \rangle &= \sum_{l} E_{l} P_{l} \\ &= \sum_{l} E_{l} \frac{1}{Z} e^{-\beta (E_{l} - \mu N_{l})} \\ &= -\frac{\partial \ln Z}{\partial \beta} + \mu k_{B} T \frac{\partial \ln Z}{\partial \mu} \end{split}$$

Remark :

$$\langle E - \mu N \rangle = \frac{1}{Z} \sum_{l} (E_l - \mu N_l) e^{-\beta (E_l - \mu N_l)} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \mu}$$

We then deduce that

$$\langle E \rangle = \mu \langle N \rangle - \frac{\partial \ln Z}{\partial \mu}$$

hence,

$$\langle E \rangle = \mu k_B T \frac{\partial \ln Z}{\partial \mu} - \frac{\partial \ln Z}{\partial \beta}$$

It is also possible to calculate the variance,

$$\Delta E^2 = \left(\frac{\partial}{\partial\beta} - \frac{\mu}{\beta}\frac{\partial}{\partial\mu}\right) \left[\left(\frac{\partial}{\partial\beta} - \frac{\mu}{\beta}\frac{\partial}{\partial\mu}\right) \ln Z \right] = \left(\frac{\partial}{\partial\beta} - \frac{\mu}{\beta}\frac{\partial}{\partial\mu}\right)^2 \ln Z$$

A.1.6 Average entropy

$$S = -k_B \sum_{l} P_l \ln(P_l)$$

= $-k_B \sum_{l} P_l (-\ln Z - \beta(E_l - \mu N_l))$
= $k_B \ln Z + \beta k_B \left(\sum_{l} P_l E_l - \mu \sum_{l} P_l N_l \right)$
= $k_B \ln Z + \frac{1}{T} (\langle E \rangle - \mu \langle N \rangle)$
= $-\frac{\Omega}{T} + \frac{1}{T} \langle E \rangle - \frac{\mu}{T} \langle N \rangle$

We can re-write it

$$\Omega = \langle E \rangle - TS - \mu \langle N \rangle$$

In thermodynamics, it is the definition of the grand-potential function. First principle,

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

The conservsion to statistical mechanics should be written

$$\mathrm{d}E = \langle T \rangle \mathrm{d}S - \langle p \rangle \mathrm{d}V + \langle \mu \rangle \mathrm{d}N$$

Now we want to "exchange" the role of the variable, mathematically it is done using a *Legendre* transformation

$$F = E - TS$$

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

If we take the definition of the grand-potential,

$$\Omega = E - TS - \mu N$$

hence,

$$\mathrm{d}\Omega = -S\mathrm{d}T - p\mathrm{d}V - N\mathrm{d}\mu = -\langle S\rangle\mathrm{d}T - \langle p\rangle\mathrm{d}V - \langle N\rangle\mathrm{d}\mu$$

So it is totally consistent with the thermodynamics.

A.1.7 Average pressure

From the first principle, we get

$$\langle p \rangle = -\frac{\partial \Omega}{\partial V}$$

We can also get,

$$\Omega(T,\mu,V) = -\langle p \rangle V$$

A.2 Quantum statistics

A.2.1 Generalities

We call λ an individual state, meaning the quantum state in which a particle is in. Generally, we have $\lambda = (\vec{k}, s)$, where \vec{k} represent the quantum numbers n, l, m.. and s the spin.

Example : For a free particle, we usually need 4 quantum numbers n_x , n_y , n_z and s, meaning we can represent it with \vec{k} and s, where $\vec{k} = 2\pi \left(\frac{n_x}{L_x}, \frac{n_y}{L_y}, \frac{n_z}{L_z}\right)$

We will write down few definitions :

- n_{λ} : the number of particles in the state λ .
- ε_{λ} : energy of single state λ .

- $l = (\lambda_1, ..., \lambda_N) = \{n_\lambda\}$: a microstate.
- $N_l = \sum_{\lambda} n_{\lambda}$: number of particles in the microstate l
- $E_l = \sum_{\lambda} n_{\lambda} \varepsilon_{\lambda}$: total energy in the microstate l.

Example : For non-relativistic massive particles, the dispersion relation is

$$\varepsilon_{\lambda} = \frac{\hbar^2 k_{\lambda}^2}{2m}$$

Hence the grand-canonical partition function is given by

$$\Xi = \sum_{l} e^{-\beta(E_{l}-\mu N_{l})}$$
$$= \sum_{l=\{n_{\lambda}\}} e^{-\beta \sum_{\lambda} (\varepsilon_{\lambda}-\mu)n_{\lambda}}$$
$$= \sum_{l=\{n_{\lambda}\}} \prod_{\lambda} e^{-\beta(\varepsilon_{\lambda}-\mu)n_{\lambda}}$$
$$= \prod_{\lambda} \sum_{n_{\lambda}} e^{-\beta(\varepsilon_{\lambda}-\mu)n_{\lambda}}$$
$$= \prod_{\lambda} \xi_{\lambda}$$

where ξ_{λ} is the individual grand-partition function. Hence, we can write,

$$\Xi(T,V,\mu) = \prod_{\lambda} \xi_{\lambda}$$

We can get the probability to be in the microstate l,

$$P_{l} = \frac{1}{\Xi} e^{-\beta(E_{l} - \mu N_{l})}$$
$$= \prod_{\lambda} \frac{e^{-\beta(\varepsilon_{\lambda} - \mu)n_{\lambda}}}{\xi_{\lambda}}$$
$$= \prod_{\lambda} P_{\lambda}$$

where P_{λ} is the probability that a particle is in an individual state λ . We can get the grand potential,

$$\Omega(T, V, \mu) = -k_B T \ln Z = -k_B T \sum_{\lambda} \ln \xi_{\lambda}$$

The average value of particle,

$$\langle N \rangle = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V,\mu} = k_B T \sum_{\lambda} \frac{\partial}{\partial\mu} \ln \xi_{\lambda} = \sum_{\lambda} \langle n_{\lambda} \rangle$$

with

$$\langle n_{\lambda} \rangle = k_B T \frac{\partial}{\partial \mu} (\ln \xi_{\lambda})$$

A.2.2 Fermions and bosons

We define fermions and bosons as follow :

- Fermions : the wavefunction is anti-symmetrical when you exchange two particles. It is not possible to have two fermions in the same state λ , meaning that $n_{\lambda} \in \{0, 1\}$.
- **Bosons**: the wavefunction is symmetrical when you exchange two particles. It is possible to have two bosons in the same state λ , meaning that $n_{\lambda} \in \mathbb{N}$.

Elementary particles :

- All leptons (electron, quarks, muon, tau,...) are fermions.
- Bosons are the vector of intereaction (photons, gluons...)

Composite particles : We have to determine the total spin of the particle. For atoms, number of protons is equal to the number of electrons, hence we just have to count the number of neutrons. Even number of neutron mean boson, odd number of neutrons mean fermion.

Example : He^4 is a boson and He^3 is a fermion.

A.2.3 Density of states

We have discrete summation to perform for all the quantities we need as shown before. When *it is possible* we will be happy to replace them by integrals.

Let's take an easy example : free particle in a box of volume $V = L_x l_y L_z$,

The box is of volume $V = L_x L_y L_z$ and the particle has a mass m. In the box, Schrödinger's equation is given by

$$-\frac{\hbar^2}{2m}\Delta\psi = E\psi$$

We can perform a variable split,

$$\psi(x, y, z) = \psi_x(x)\psi_y(y)\psi_z(z) \propto e^{ik_x x} e^{ik_y y} e^{ik_z z}$$

with $\varepsilon_{\lambda} = \hbar^2 k_{\lambda}^2 / 2m$. We can distinguish two solutions based on the boundaries conditions.

Periodic conditions

Hard wall conditions $\psi(0, y, z) = \psi(L_x, y, z) = 0$

 \longrightarrow not meant for particles transport

 $\psi(x, y, z) = \psi(x + L, y, z)$

 \rightarrow meant for particles transport

$$c_x = \frac{2\pi}{L_x} n_x, \qquad n_x \in \mathbb{Z}$$

 \rightarrow propagation in the both directions

 $k_x = \frac{\pi}{L_x} n_x, \qquad n_x \in \mathbb{N}$

 \longrightarrow superposition of two waves in each opposite directions

$$\varepsilon_{\lambda} = \frac{\hbar^2}{2m} \left[\left(\frac{2\pi n_x}{L_x} \right)^2 + \left(\frac{2\pi n_y}{L_y} \right)^2 + \left(\frac{2\pi n_z}{L_z} \right)^2 \right] \qquad \varepsilon_{\lambda} = \frac{\hbar^2}{2m} \left[\left(\frac{\pi n_x}{L_x} \right)^2 + \left(\frac{\pi n_y}{L_y} \right)^2 + \left(\frac{\pi n_z}{L_z} \right)^2 \right]$$

We now want to perform summations as integrals. If the lengths of the system become big, meaning that $\frac{(2)\pi}{L_i} \to 0$ and we can consider that the gap between two values of k_i , Δk_i is becoming really negligeable, meaning that k_i is continuous. The volume that a point \vec{k} occupy in phase space is

$$\left(\frac{2\pi}{L_x}\right) \left(\frac{2\pi}{L_y}\right) \left(\frac{2\pi}{L_z}\right)$$

$$\left(\frac{\pi}{L_x}\right) \left(\frac{\pi}{L_y}\right) \left(\frac{\pi}{L_z}\right)$$

hence we get the density of states

$$\mathcal{D}(\vec{k})d^{3}\vec{k} = \frac{d^{3}\vec{k}}{\left(\frac{2\pi}{L_{x}}\right)\left(\frac{2\pi}{L_{y}}\right)\left(\frac{2\pi}{L_{z}}\right)} = \frac{V}{(2\pi)^{3}}d^{3}\vec{k}$$

where we need to integrate over all the space, with the spin, we get

$$\mathcal{D} = g_s \frac{V}{(2\pi)^3}$$

hence we get the density of states

$$\mathcal{D}(\vec{k})d^{3}\vec{k} = \frac{d^{3}\vec{k}}{\left(\frac{\pi}{L_{x}}\right)\left(\frac{\pi}{L_{y}}\right)\left(\frac{\pi}{L_{z}}\right)} = \frac{V}{\pi^{3}}d^{3}\vec{k}$$

where we integrate over 1/8 of the space, with the spin, we get

$$\mathcal{D} = g_s \frac{V}{(\pi)^3}$$

with $g_s = 2s + 1$ is the spin degeneracy.

It is possible to use other coordinates for \vec{k} , we can use spherical coordinates in phase space, meaning, instead of using (k_x, k_y, k_z) , we use (k, ϕ_k, θ_k) . In this case we get $d^3\vec{k} = k^2 \sin \theta_k dk d\theta_k d\phi_k$. If the problem is isotropic (all the directions are equivalent) using this set of coordinates is really useful.

Let's consider periodic conditions,

$$\iiint \mathcal{D}(\vec{k}) \mathrm{d}^{3}\vec{k} = \iiint \mathcal{D}(\vec{k}) k^{2} \sin \theta_{k} \mathrm{d}k \mathrm{d}\theta_{k} \mathrm{d}\phi_{k}$$
$$= \int \mathrm{d}k g_{s} \frac{V}{(2\pi)^{3}} 4\pi k^{2}$$
$$= \int_{0}^{+\infty} \mathrm{d}k g_{s} \frac{V}{2\pi^{2}} k^{2}$$

For all the isotropic case, if we know the dispersion relation, $\varepsilon(k)$ it is possible to use the variable ε .

The important case is when $\varepsilon(k) = \hbar^2 k^2/2m$,

$$\mathcal{D}(\vec{k}) \mathrm{d}^3 \vec{k} = \mathcal{D}(\varepsilon) \mathrm{d}\varepsilon = KV \sqrt{\varepsilon} \mathrm{d}\varepsilon$$

with $K = \frac{g_s}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2}$.

if we work with dimensionless quantity, we can use $x^2 = \beta \varepsilon$,

$$\mathcal{D}(\vec{k}) \mathrm{d}^{3} \vec{k} = \mathcal{D}(\varepsilon) \mathrm{d}\varepsilon = \mathcal{D}(x) \mathrm{d}x = g_{s} \frac{V}{\Lambda_{T}^{3}} \frac{4}{\sqrt{\pi}} x^{2} \mathrm{d}x$$

with Λ_T the thermal De Broglie wavelength,

$$\Lambda_T = \left(\frac{\hbar^2}{2\pi m k_B T}\right)^{1/2}$$

This quantity has the dimension of a length. It does correspond to the spatial spreading of the wave packet associated to a particle,



There is two limit cases,

- $\Lambda_T \xrightarrow[T \to 0]{} \infty$: the particle is totally delocated and the quantum effects are important.
- $\Lambda_T \xrightarrow[T \to \infty]{} 0$: the particle is totally localized and the quantum effects are negligeable.

There is three characteristic lengths,

- The average distance between particles $d \equiv 1/\rho^{1/3}$ with $\rho = N/V$.
- Thermal De Broglie wavelength Λ_T , the average size of a particle wavefunction.
- a_0 the range of the interaction between particles.

We can distinguish three cases

- $\Lambda_T \ll a_0 \ll d$: the system is classical and is described by classical interactions.
- $a_0 \ll \Lambda_T \ll d$: the system is classical but the particles quantum interact, we speak about quantum collisions.
- $a_0 \ll d \sim \Lambda_T$: particles are quantum and undergo quantum collisions.

Chapter B

Ideal quantum gases: Fermions

B.1 Generalities

B.1.1 Fermi-Dirac distribution

We remind ourselves that the grand-partition function for an individual state is given by

$$\xi_{\lambda} = \sum_{n_{\lambda}} e^{-\beta(\varepsilon_{\lambda} - \mu)n_{\lambda}}$$

avec $\lambda = (\vec{k}, s)$. For fermions, there is at max one particle in the state λ . We then get that $n_{\lambda} \in \{0, 1\}$ so we get,

$$\xi_{\lambda} = 1 + e^{-\beta(\varepsilon_{\lambda} - \mu)}$$

We define the occupation probability of a single state λ as the mean value of the number of particle in that single state

$$\bar{n}^{\rm FD}(\varepsilon_{\lambda}) = \frac{e^{-\beta(\varepsilon_{\lambda}-\mu)}}{\xi_{\lambda}} = \frac{1}{e^{\beta(\varepsilon_{\lambda}-\mu)}+1}$$

From Pauli's exclusion principle, two fermions can't be in the same state, so we get that $\bar{n}^{\text{FD}}(\varepsilon_{\lambda}) \leq 1$. We define Fermi's energy as the chemical potential at the null temperature :

$$\varepsilon_F = \mu(T=0)$$

It is the energy of the highest occupied state at the null temperature.

B.1.2 General relations

We consider an ideal gas of fermions. The grand-canonical partition function is

$$\Xi(T,V,\mu) = \prod_{\lambda} \xi_{\lambda}$$



Figure (B.1) – Fermi-Dirac distribution n_{λ}^{FD} as a function of $\varepsilon/\mu(T)$ for different temperatures. Solid red line: degenerate Fermi gas limit.

The grand potential is

$$\Omega = -k_B T \sum_{\lambda} \ln\left(1 + e^{-\beta(\varepsilon_{\lambda} - \mu)}\right)$$

We can then write the average value of the energy

$$\langle E \rangle = \sum_{\lambda} \bar{n}^{\rm FD}(\varepsilon_{\lambda})\varepsilon_{\lambda}$$

And the average value of particles,

$$\langle N \rangle = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V} = \sum_{\lambda} \bar{n}_{\lambda}^{\mathrm{FD}}(\varepsilon_{\lambda}) = \sum_{\lambda} \frac{1}{e^{\beta(\varepsilon_{\lambda}-\mu)}+1}$$

and the average value of pressure,

$$\langle p \rangle = -\frac{\Omega}{V}$$

We will restrict ourselves for non-relativistic massive particles in 3D, hence we know the dispersion relation,

$$\varepsilon_{\lambda} = \frac{\hbar^2 k^2}{2m}$$

And we can write the density of states,

$$\mathcal{D}(\vec{k})\mathrm{d}^{3}\vec{k} = KV\sqrt{\varepsilon}\mathrm{d}\varepsilon = g_{s}\frac{V}{\Lambda_{T}^{3}}\frac{4}{\sqrt{\pi}}x^{2}\mathrm{d}x$$

With the density of states introduced, we can transform the sums by integrals and the quantities we introduced earlier can be written differently,

$$\Omega(T, V, \mu) = -k_B T K V \int_0^{+\infty} \mathrm{d}\varepsilon \sqrt{\varepsilon} \ln\left(1 + e^{-\beta(\varepsilon - \mu)}\right)$$
$$\langle N \rangle = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V} = K V \int_0^{+\infty} \mathrm{d}\varepsilon \frac{\sqrt{\varepsilon}}{e^{\beta(\varepsilon - \mu)} + 1}$$
$$\langle E \rangle = K V \int_0^{+\infty} \mathrm{d}\varepsilon \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon - \mu)} + 1}$$

Introducing $z = e^{\beta\mu}$ the fugacity, we can rewrite Ω ,

$$\Omega(T, V, \mu) = -k_B T g_s \frac{V}{\Lambda_T^3} \frac{4}{\sqrt{\pi}} \int_0^{+\infty} \mathrm{d}x x^2 \ln\left(1 + z e^{-x^2}\right)$$

We will perform an integration by parts,

$$\Omega(T, V, \mu) = -\frac{2}{3}k_B T g_s \frac{V}{\Lambda_T^3} \frac{4}{\sqrt{\pi}} \int_0^{+\infty} \mathrm{d}x \frac{x^4}{z^{-1} e^{x^2} + 1}$$
$$\langle N \rangle = g_s \frac{V}{\Lambda_T^3} \frac{4}{\sqrt{\pi}} \int_0^{+\infty} \mathrm{d}x \frac{x^2}{z^{-1} e^{x^2} + 1}$$

$$\langle E \rangle = k_B T g_s \frac{V}{\lambda_T^3} \frac{4}{\sqrt{\pi}} \int_0^{+\infty} \mathrm{d}x \frac{x^4}{z^{-1} e^{x^2} + 1}$$

We can define a *Bose function*,

$$f_n(z) = \frac{4}{\sqrt{\pi}} \int_0^{+\infty} \mathrm{d}x \frac{x^n}{z^{-1}e^{x^2} + 1}$$

Hence, replacing the integrals by the function $f_n(z)$,

$$\Omega(T, V, \mu) = -\frac{2}{3}k_B T g_s \frac{V}{\Lambda_T^3} \frac{4}{\sqrt{\pi}} f_4(z)$$
$$\langle N \rangle = g_s \frac{V}{\Lambda_T^3} \frac{4}{\sqrt{\pi}} f_2(z)$$

$$\langle E \rangle = k_B T g_s \frac{V}{\Lambda_T^3} \frac{4}{\sqrt{\pi}} f_4(z)$$

We remark that the grand potential Ω and the mean value of energy $\langle E \rangle$ are both dependent of $f_4 t(z)$, so taking the quotient allow us to write,

$$\frac{\Omega}{\langle E\rangle}=-\frac{2}{3}$$

Meaning,

$$\langle E \rangle = \frac{3}{2} \langle p \rangle V$$

We find back the state equation for an ideal gas.

B.2 High temperature limit

We define Fermi's temperature linked to the Fermi's energy following $k_B T_F = \varepsilon_F$. We say that we are in the high temperature regime if we have $T \gg T_F$. In this case, we have $\Lambda_T \to 0$.

We remind ourselves the quantities,

$$\langle E \rangle = k_B T g_s \frac{V}{\Lambda_T^3} \frac{4}{\sqrt{\pi}} f_4(z) \qquad \langle N \rangle = g_s \frac{V}{\Lambda_T^3} \frac{4}{\sqrt{\pi}} f_2(z) \qquad \langle p \rangle = \frac{3}{2} \frac{\langle E \rangle}{V}$$

with $f_n(z)$ being,

$$f_n(z) = I(n) \sum_{i=1}^{+\infty} \frac{(-1)^{i+1}}{i^{\frac{n+1}{2}}} z^i \qquad \text{with} \qquad I(n) = \frac{4}{\sqrt{\pi}} \int_0^{+\infty} \mathrm{d}x x^n e^{-x^2}$$

Hence we can make the approximations,

$$f_2(z) \approx \left(z - \frac{z^2}{2^{3/2}} + \cdots\right), \qquad f_4(z) \approx \frac{3}{2} \left(z - \frac{z^2}{2^{5/2}} + \cdots\right)$$

And so, the quantitise becomes,

$$\langle E \rangle = \frac{3}{2} k_B T g_s \frac{V}{\Lambda_T^3} \frac{4}{\sqrt{\pi}} \left(z - \frac{z^2}{2^{5/2}} + \cdots \right), \qquad \langle N \rangle = g_s \frac{V}{\Lambda_T^3} \frac{4}{\sqrt{\pi}} \left(z - \frac{z^2}{2^{3/2}} + \cdots \right)$$

First order approximation

Making a first order approximation, we can define the density of particles in the system,

$$\rho \equiv \frac{\langle N \rangle}{V} = g_s \frac{1}{\Lambda_T^3} z \iff z \approx \left(\rho \frac{\Lambda_T^3}{g_s} \right)$$

Hence we can re-write the mean value of the energy,

$$\langle E \rangle = \frac{3}{2} k_B T g_s \frac{V}{\Lambda_T^3} z = \frac{3}{2} \langle N \rangle k_B T$$
$$\langle N \rangle = g_s \frac{V}{\Lambda_T^3} z$$

$$\langle p \rangle = \frac{2}{3} \frac{\langle E \rangle}{V} \approx \langle N \rangle \frac{k_B T}{V}$$

So we get that for the first order approximation we find back the classical results for ideal gases. The equation for $\langle N \rangle$ gives us an expression for the chemical potential μ ,

$$\mu = k_B T \ln\left(\frac{n\Lambda_T^3}{g_s}\right)$$

And we verify that for $T \to +\infty$, μ goes to $-\infty$.

Second order approximation

Now we will push our approximation up to the second order. In order to do that, we need to express z in function of the system's parameters. We get,

$$\rho \equiv \frac{\langle N \rangle}{V} \approx g_s \frac{1}{\Lambda_T^3} \left(z - \frac{1}{2^{3/2}} z^2 \right)$$

Meaning that,

$$z \approx \rho \frac{\lambda_T^3}{g_s} + \frac{1}{2^{3/2}} \left(\frac{\rho \Lambda_T^3}{g_s}\right)^2 + \cdots$$

Now that we know the value of z, we need to get the mean value of the energy,

Calculation :

$$\begin{split} \langle E \rangle &= \frac{3}{2} k_B T g_s \frac{V}{\Lambda_T^3} \left(z - \frac{z^2}{2^{5/2}} + \cdots \right) \\ &= \frac{3}{2} k_B T g_s \frac{V}{\Lambda_T^3} \left\{ \rho \frac{\Lambda_T^3}{g_s} + \frac{1}{2^{3/2}} \left(\frac{\rho \Lambda_T^3}{g_s} \right) - \frac{1}{2^{5/2}} \left(\frac{\rho \Lambda_T^3}{g_s} \right)^2 + \cdots \right\} \\ &= \frac{3}{2} k_B T V \left\{ \rho + \frac{1}{2^{5/2}} \rho \left(\frac{\rho \Lambda_T^3}{g_s} \right) + \cdots \right\} \\ &= \frac{3}{2} \langle N \rangle k_B T \left\{ 1 + \frac{1}{2^{5/2}} \left(\frac{\rho \Lambda_T^3}{g_s} \right) + \cdots \right\} \end{split}$$

1

Finally, we get,

$$\langle E \rangle = \frac{3}{2} \langle N \rangle k_B T \left\{ 1 + \frac{1}{2^{5/2}} \left(\frac{\rho \Lambda_T^3}{g_s} \right) + \cdots \right\}$$

So we can write,

$$\beta \langle p \rangle \approx \rho \left(1 + \frac{1}{2^{5/2}} \left(\frac{\rho \Lambda_T^3}{g_s} \right) + \cdots \right) > \beta \langle p \rangle_{\text{Classical Ideal Gas}}$$

The pressure of a quantum ideal gas of fermion is higher than that of a classical ideal gas. This comes from Pauli's exclusion principle. Indeed, fermions do not have the possibility of sharing the same state. Thus, if there is an overlap of the wave function, the fermions will undergo *effective repulsion* which will contribute to the total pressure of the system.

Using the expression of $\langle E \rangle$ we can express the heat capacity,

$$C_V = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_V \approx \frac{3}{2} \langle N \rangle k_B \left\{ 1 - \frac{1}{2^{7/2}} \left(\frac{\rho \Lambda_T^3}{g_s}\right) + \cdots \right\}$$

In all the quantities we get, we see the apparition of $\rho \Lambda_T^3/g_s$, so we can define a characteristic temperature T_0 such that

$$\frac{\rho \Lambda_T^3}{g_s} = \left(\frac{T_0}{T}\right)^{3/2} \qquad \text{where} \qquad T_0 = \frac{\hbar^2}{2\pi m k_B} \left(\frac{\rho}{g_s}\right)^{2/3} \propto T_F$$

where T_F is the Fermi temperature.

Since z is

$$z \approx \frac{\rho \Lambda_T^3}{g_s} + \frac{1}{2^{3/2}} \left(\frac{\rho \Lambda_T^3}{g_s}\right)^2$$

we can get an expression for the chemical potential μ ,

$$\mu = k_B T \ln z \approx k_B T \left\{ \ln \left(\frac{\rho \Lambda_T^3}{g_s} \right) + \frac{1}{2^{3/2}} \left(\frac{\rho \Lambda_T^3}{g_s} \right) \right\}$$

B.3 Low temperature limit

B.3.1 Degenerate Fermi gas

For a fermion gas at null temperature (meaning $T \ll T_F$), we get

$$\bar{n}^{\rm FD}(\varepsilon) = \Theta(\varepsilon_F - \varepsilon)$$

where Θ is Heaviside's function.

The chemical potential in this area is defined as the Fermi energy of the system. This is therefore the maximum energy that a fermion can have at zero temperature. Indeed, because the thermal agitation is no longer present, it is no longer possible to fluctuate in energy and exceed this value.



$$\langle N \rangle = KV \int_0^{+\infty} \mathrm{d}\varepsilon \sqrt{\varepsilon} \frac{1}{e^{\beta(\varepsilon-\mu)} + 1}$$

$$\langle E \rangle = KV \int_0^{+\infty} \mathrm{d}\varepsilon \varepsilon^{3/2} \frac{1}{e^{\beta(\varepsilon-\mu)} + 1}$$

$$\langle p \rangle = -\frac{\Omega}{V}$$

So, let's take the limit for $T \to 0$,

$$\langle N \rangle = KV \int_0^{\varepsilon_F} \mathrm{d}\varepsilon \varepsilon^{1/2} = \frac{2}{3} KV \varepsilon_F^{3/2}$$

Meaning,

$$\varepsilon_F = \left(\frac{3}{2}\frac{\rho}{K}\right)^{2/3} = \frac{\hbar^2}{2m} \left(\frac{6\pi^2}{g_s}\frac{\langle N \rangle}{V}\right)^{2/3}$$

Do the numerical application for the free electrons of a piece of copper (each atoms give one electron to the free-electron gas).

We can write Fermi's temperature as $T_F \equiv \varepsilon_F / k_B$.

$$\langle E \rangle = \frac{2}{5} K V \varepsilon_F^{5/2} = \frac{3}{5} \langle N \rangle \varepsilon_F$$

We also remember ourselves that $\langle E \rangle = \frac{3}{2} \langle p \rangle V$ (general result)

$$\langle p \rangle = \frac{2}{5} \langle N \rangle \varepsilon_F$$

We obtain a very important result, that $\langle p \rangle \neq 0$. It is purely a quantum effect. It is related to Pauli's principle. If the pressure would be 0, it would violated Pauli's principle. Those results are for $T \ll T_F$.

B.3.2 Low temperature expansion (Sommerfeld expansion)

According to the forms of $\langle N \rangle$ and $\langle E \rangle$, we will have to calculate the integral of the form

$$Y_{\alpha}(T,\mu) = \int_{0}^{+\infty} \mathrm{d}\varepsilon \varepsilon^{\alpha} \left(-\frac{\mathrm{d}\bar{n}^{\mathrm{FD}}}{\mathrm{d}\varepsilon}\right)$$

Remark : We will use a technique called *méthode du point col* to calculate this integral.

Note that the derivative of the Fermi-Dirac function tends towards a Dirac peak centered on μ when the temperature becomes zero. Thus, only the part in the neighborhood of μ will contribute to the integral.



We therefore carry out a limited expansion of ε^{α} in the vicinity of $\mu.$

$$\varepsilon^{\alpha} \approx \mu^{\alpha} + \alpha \mu^{\alpha-1}(\varepsilon - \mu) + \frac{1}{2}\alpha(\alpha - 1)\mu^{\alpha-2}(\varepsilon - \mu)^2 + \cdots$$

So now,

$$Y_{\alpha}(T,\mu) = \int_{0}^{+\infty} \mathrm{d}\varepsilon \left[\mu^{\alpha} + \alpha \mu^{\alpha-1}(\varepsilon - \mu) + \frac{1}{2}\alpha(\alpha - 1)\mu^{\alpha-2}(\varepsilon - \mu)^{2} + \cdots \right] \left(-\frac{\mathrm{d}n}{\mathrm{d}\varepsilon} \right)$$
$$\approx \mu^{\alpha} \int_{0}^{+\infty} \mathrm{d}\varepsilon \left(-\frac{\mathrm{d}n}{\mathrm{d}\varepsilon} \right) + \alpha \mu^{\alpha-1} \int_{0}^{+\infty} \mathrm{d}\varepsilon(\varepsilon - \mu) \left(-\frac{\mathrm{d}n}{\mathrm{d}\varepsilon} \right) + \frac{1}{2}\alpha(\alpha - 1)\mu^{\alpha-2} \int_{0}^{+\infty} \mathrm{d}\varepsilon(\varepsilon - \mu)^{2} \left(-\frac{\mathrm{d}n}{\mathrm{d}\varepsilon} \right)$$

$$-\frac{\mathrm{d}n}{\mathrm{d}\varepsilon} = -\frac{\mathrm{d}}{\mathrm{d}\varepsilon} \left(\frac{1}{e^{\beta(\varepsilon-\mu)}+1} \right) = \frac{\beta e^{\beta(\varepsilon-\mu)}}{\left(e^{\beta(\varepsilon-\mu)}+1\right)^2}$$
$$Y_{\alpha}(T,\mu) \approx \mu^{\alpha}\beta \int_{-\infty}^{+\infty} \mathrm{d}\varepsilon \frac{e^{\beta(\varepsilon-\mu)}}{\left(e^{\beta(\varepsilon-\mu)}+1\right)^2} + \cdots$$

We also know

$$\int_{\mathbb{R}} \mathrm{d}x \frac{e^x}{(e^x+1)^2} = 1, \qquad \int_{\mathbb{R}} \mathrm{d}x \frac{xe^x}{(e^x+1)^2} = 0, \qquad \int_{\mathbb{R}} \mathrm{d}x \frac{x^2 e^x}{(e^x+1)^2} = \frac{\pi^2}{3}$$

if we take $x \equiv \beta(\varepsilon - \mu)$, then

$$Y_{\alpha}(T,\mu) \approx \mu^{\alpha} \int_{-\infty}^{+\infty} \mathrm{d}x \frac{e^x}{(e^x+1)^2} + \cdots$$

and this integral is just a number and is equal to 1,

$$Y_{\alpha}(T,\mu) \approx \mu^{\alpha} + \frac{1}{2}\alpha(\alpha-1)\mu^{\alpha-2}(k_BT)^2 \int_{-\infty}^{+\infty} \frac{x^2e^x}{(e^x+1)^2} + \cdots$$

and this integral is just a number and is equal to $\pi^2/3$,

$$Y_{\alpha}(T,\mu) \approx \mu^{\alpha} + \frac{\pi^2}{6} \alpha(\alpha-1)\mu^{\alpha-2}(k_B T)^2$$
$$= \mu^{\alpha} \left(1 + \frac{\pi^2}{6} \alpha(\alpha-1) \left(\frac{k_B T}{\mu}\right)^2 + \cdots\right)$$

And so,

$$\begin{split} \langle N \rangle &= KV \int_{0}^{+\infty} \mathrm{d}\varepsilon \sqrt{\varepsilon} \bar{n}^{\mathrm{FD}}(\varepsilon) \qquad \text{take} \qquad u = \bar{n}^{\mathrm{FD}}(\varepsilon), \quad u' = \mathrm{d}\bar{n}^{\mathrm{FD}}/\mathrm{d}\varepsilon, \quad v' = \varepsilon^{1/2}, \quad v = 2\varepsilon^{3/2}/3 \\ &= KV \left(\left[\frac{2}{3} \varepsilon^{3/2} \bar{n}^{\mathrm{FD}} \right]_{0}^{+\infty} + \frac{2}{3} \int_{0}^{+\infty} \mathrm{d}\varepsilon \varepsilon^{3/2} \left(-\frac{\mathrm{d}\bar{n}^{\mathrm{FD}}}{\mathrm{d}\varepsilon} \right) \right) \\ &= \frac{2}{3} KV \int_{0}^{+\infty} \mathrm{d}\varepsilon \varepsilon^{3/2} \left(-\frac{\mathrm{d}\bar{n}^{\mathrm{FD}}}{\mathrm{d}\varepsilon} \right) \\ &= \frac{2}{3} KV Y_{3/2}(T, \mu) \\ &\approx \frac{2}{3} KV \mu^{3/2} \left(1 + \frac{\pi^{2}}{8} \left(\frac{k_{B}T}{\mu} \right)^{2} + \cdots \right) \end{split}$$

And with the same idea,

$$\begin{split} \langle E \rangle &= \frac{2}{5} KV \int_0^{+\infty} \mathrm{d}\varepsilon \varepsilon^{5/2} \left(-\frac{\mathrm{d}\bar{n}^{\mathrm{FD}}}{\mathrm{d}\varepsilon} \right) \\ &= \frac{2}{5} KV Y_{5/2}(T,\mu) \\ &\approx \frac{2}{5} KV \mu^{5/2} \left(1 + \frac{5}{8} \pi^2 \left(\frac{k_B T}{\mu} \right)^2 + \cdots \right) \end{split}$$

In the thermodynamic limit, we can try to express every quantity as a function of (T, N, V) assuming $N = \langle N \rangle$.

We want to approximate μ as a function of T,N,V and we will introduce this expression into $\langle E \rangle$

$$\mu \approx \varepsilon_F \left\{ 1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\varepsilon_F} \right)^2 + \cdots \right\}$$
$$\approx \varepsilon_F \left\{ 1 - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 + \cdots \right\}$$

$$\langle E \rangle \approx \frac{3}{5} \langle N \rangle \varepsilon_F \left\{ 1 + \frac{5}{12} \pi^2 \left(\frac{k_B T}{\varepsilon_F} \right)^2 + \cdots \right\}$$

It is then easy to deduce the thermal capacity of the gas,

$$C_V = \left(\frac{\partial \langle E \rangle}{\partial T}\right) \approx \frac{1}{2} \langle N \rangle \pi^2 \frac{k_B T}{T_F} \propto T$$

Thus, at first order, CV is linear with temperature.

B.4 Conclusions



We recall the form of the chemical potential for a fermion gas in the figure below.

If $T ggT_0$, T_F , we find the properties obtained in the case of classical calculations, while providing a correction. If $T llT_0$, T_F , if T = 0, we obtain important results, such as the fact that the pressure is not zero, the existence of the Fermi level, etc. If the temperature is low but not zero, then we obtain a first order correction in T/T_F for the energy, the thermal capacity and the other canonical quantities of the system.

Note that the two characteristic temperatures T_0 and T_F are of the same order of magnitude and proportional. Indeed, we show that

$$\frac{T_0}{T_{\rm F}} = \frac{1}{\pi} \left(\frac{4\pi}{3}\right)^{2/3}.$$

It is then advisable to be interested in only one of them, the temperature of Fermi.

- a gas of electrons, of mass $m_e = 9.1 \ times 10^{-31} \ \text{kg}$, of density $\rho_e \ simeq 10^{29} e^-/\text{m}^3$, we get $T_F \simeq 10^4 \ \text{K}$. At room temperature, for a metal, the approximation T = 0 is therefore very good.
- a fermionic atom gas, of mass $m_{atom} \simeq 10^3 \sim 10^4 m_{\rm e}$ at the same density $\rho_{\rm e}$, we therefore have $T_{\rm F} \simeq 1 \sim 10$ K. It is therefore difficult to observe quantum effects for an ideal gas of a fermionic atom.

Chapter C

Ideal quantum gases: Bosons

C.1 Generalities

C.1.1 Bose-Einstein distribution

For bosons, the number of bosons per energy state is not limited. The individual partition function is therefore written

$$\xi_{\lambda} = \sum_{n_{\lambda}=0}^{+\infty} e^{-\beta(\varepsilon-\mu)n_{\lambda}} = \frac{1}{1 - e^{-\beta(\varepsilon_{\lambda}-\mu)}}$$

We can then calculate the probability for a particle to occupy a microstate of energy ε_{λ} ,

$$\bar{n}_{\lambda}^{\mathrm{BE}} = k_B T \frac{\partial}{\partial \mu} \left(\ln \xi_{\Lambda} \right) = \frac{1}{e^{\beta(\varepsilon_{\lambda} - \mu)} - 1}$$

and so the Bose-Einstein distribution is

$$\bar{n}_{\lambda}^{\rm BE} = \frac{1}{e^{\beta(\varepsilon_{\lambda} - \mu)} - 1}$$

C.1.2 General relations

$$\Omega = k_B T \ln Z = -k_B T \sum_{(\lambda)} \ln(\xi_{\rm BE})$$

$$\langle E \rangle = \sum_{(\lambda)} \bar{n}_{\lambda}^{\rm BE} \varepsilon_{\lambda}$$



Figure (C.1) – Bose-Einstein distribution for different chemical potentials. We notice that the distribution diverges for $\epsilon = \mu$.

$$\begin{split} \langle N \rangle &= \sum_{(\lambda)} \bar{n}^{\rm BE}_\lambda \\ \langle p \rangle &= -\frac{\Omega}{V} \end{split}$$

C.2 Ideal quantum gas bosons of mass m

C.2.1 Generalities

Density of states

$$\mathcal{D}_{(\vec{k})} \mathrm{d}^3 \vec{k} = g_s \frac{V}{\Lambda_T^3} \frac{4}{\sqrt{\pi}} x^2 \mathrm{d}x$$

with $x^2 = \beta \varepsilon$.

$$\Omega = -\frac{2}{3}k_B T g_s \frac{V}{\Lambda_T^3} \frac{4}{\sqrt{\pi}} \int_0^{+\infty} \mathrm{d}x \frac{x^4}{z^{-1} e^{x^2} - 1} \equiv -\frac{2}{3}k_B T g_s \frac{V}{\Lambda_T^3} \tilde{f}_4(z)$$
$$\langle N \rangle = g_s \frac{V}{\Lambda_T^3} \frac{4}{\sqrt{\pi}} \int_0^{+\infty} \mathrm{d}x \frac{x^2}{z^{-1} e^{x^2} - 1} \equiv g_s \frac{V}{\Lambda_T^3} \tilde{f}_2(z)$$

$$\langle E \rangle = k_B T g_s \frac{V}{\Lambda_T^3} \frac{4}{\sqrt{\pi}} \int_0^{+\infty} \mathrm{d}x \frac{x^4}{z^{-1} e^{x^2} - 1} \equiv k_B T g_s \frac{V}{\Lambda_T^3} \tilde{f}_4(z)$$
$$\langle p \rangle = -\frac{\Omega}{V}$$

$$\tilde{f}_n(z) = \frac{4}{\sqrt{\pi}} \int_0^{+\infty} \mathrm{d}x \frac{x^n}{z^{-1}e^{x^2} - 1}$$

We have

$$f_n(z) = -\tilde{f}_n(-z)$$

$$\Omega = -\frac{2}{3} \langle E \rangle \Longleftrightarrow pV = \frac{2}{3} \langle E \rangle$$

 $\tilde{f}_n(z)$ are defined for $z \in]-\infty, 1]$, but $z = e^{\beta \mu} \ge 0$. For bosons, $z \in [0, 1] \Leftrightarrow \mu \in]-\infty, 0]$.

C.2.2 High temperature limit

In the high temperature (low density) limit, we can do Taylor expansion of the function $\tilde{f}_n(z)$ (for $z \ll 1$)

$$\rho \frac{\Lambda_T^3}{g_s} \approx z + \frac{1}{2^{3/2}} z^2 + \cdots$$
$$\langle E \rangle \approx \frac{3}{2} k_B T g_s \frac{V}{\Lambda_T^3} \left(z + \frac{1}{2^{5/2}} z^2 + \cdots \right)$$
$$\langle E \rangle \approx \frac{3}{2} N k_B T \left(1 - \frac{1}{2^{5/2}} \rho \frac{\Lambda_T^3}{g_s} \right)$$
$$\approx \frac{3}{2} N k_B T \left(1 - \frac{1}{2^{5/2}} \left(\frac{T_0}{T} \right)^{3/2} + \cdots \right)$$

$$C_V \approx \left(\frac{\partial E}{\partial T}\right)$$
$$\approx \frac{3}{2} N k_B \left(1 + \frac{1}{2^{7/2}} \left(\frac{T_0}{T}\right)^{3/2} + \cdots\right)$$

Average pressure,

$$\langle p \rangle = \rho \left(1 - \frac{1}{2^{5/2}} \left(\frac{T_0}{T} \right)^{3/2} + \cdots \right)$$

$$\mu_{(T)} = k_B T \ln z \approx k_B T \left[\ln \left(\rho \frac{\Lambda_T^3}{g_s} \right) - \frac{1}{2^{3/2}} \left(\rho \frac{\Lambda_T^3}{g_s} \right) + \cdots \right]$$



Figure (C.2) – Left: Chemical potential of the Bose-Einstein ideal gas as a function of temperature and (Right) as a function of $(\rho \Lambda_T^3/g_s)$: high temperature limit (blue dotted line) and ideal gas (green dashed-dotted line). The red dot corresponds to the Bose temperature.

C.2.3 Low temperature limit: Bose condensation

See tutorial

When T is decreasing (ρ is increasing) the chemical potential is increasing ($\mu \leq 0$) and can may be reach 0.

$$\frac{\langle N \rangle}{V} \frac{\Lambda_T^3}{g_s} = \tilde{f}_2(z)$$

What is happening if $\mu = 0 \iff z = 1$? $\tilde{f}_2(1)$ is it defined? The answer is yes,

$$f_2(1) \approx 2.612$$

This define a specific temperature (Bose temperature) T_B (or a specific density $\rho_B = 1/v_B$) as

$$\left(\rho \frac{\Lambda_T^3}{g_s}\right)_B = \tilde{f}_2(1) \approx 2.612$$

for $T < T_B$ (or $\rho > \rho_B$) we have a problem to satisfy the relation

$$\rho \frac{\Lambda_T^3}{g_s} = \tilde{f}_2(z)$$

Because the left-term is changing with T (or ρ) and the right-term is constant for $T < T_B$ (or $\rho > \rho_B$)

$$\langle N \rangle = \sum_{\varepsilon_{\lambda}} \bar{n}_{\lambda}^{\text{BE}}(\varepsilon_{\lambda})$$
$$= \sum_{\lambda} \frac{1}{z^{-1}e^{\beta\varepsilon_{\lambda}} - 1}$$

The first term in this discrete sum is N_0 , the number of particle in the ground state.

$$N_0 = \frac{z}{1-z}$$

When z = 1, then N_0 goes to $+\infty$. $N_0 \to +\infty$, also mean that $N_0 \propto N$, meaning that $N_0/N \to \text{cst}$ in the thermodynamical limit.

For $T < T_B$ (or $\rho > \rho_B$) meaning z = 1, and the fundamental state start to be macroscopically occupied. This is called the Bose condensation (condensation in the space of states).

$$\langle N \rangle = \sum_{\varepsilon_{\lambda}} \bar{n}_{\lambda}^{\text{BE}}(\varepsilon_{\lambda})$$

$$= \sum_{\lambda} \frac{1}{z^{-1}e^{\beta\varepsilon_{\lambda}} - 1}$$

$$= N_{0} + \sum_{\varepsilon_{\lambda} \neq 0} \bar{n}_{\lambda}^{\text{BE}}(\varepsilon_{\lambda})$$

and we can perform the continuous limit for that summation.

C.3 Ideal quantum gas of massless bosons

C.3.1 Black body radidation

A black body is :



Figure (C.3) – Relative number of bosons in the ground state $(N_0/N, \text{ red solid line})$ and in the excited states $(1 - N_0/N, \text{ blue dotted})$ as a function of the temperature T, scaled with the Bose temperature T_B .

- adsorption of all wavelength
- emit radiation after thermalisation (inelastic interactions between photons and atoms)

We have to describe a gas of photons at temperature T

$$\bar{n}^{\mathrm{BE}}(\varepsilon_{\lambda}) = \frac{1}{e^{\beta(\varepsilon_{\lambda}-\mu)} - 1}$$

With

$$\varepsilon_{\lambda} = |\vec{p}|c = \hbar \omega$$
 and not $\frac{p^2}{2m}$

The number of photons is not fixed, we have creation and annihilation of photons. The number of photons will adapt to minimize the free energy

$$\mu = \left(\frac{\partial F}{\partial N}\right) = 0 \text{ at equilibrium}$$

$$\bar{n}^{\mathrm{BE}}(\varepsilon_{\lambda}) = \frac{1}{e^{\beta \varepsilon_{\lambda}} - 1}$$

$$\mathcal{D}(k)\mathrm{d}^{3}\vec{k} = 2\frac{V}{(2\pi)^{3}}\mathrm{d}^{3}\vec{k}$$

Where the 2 stands for the degeneracy of photons. Using ω , $c = \omega/k$,

$$\mathcal{D}(\omega)\mathrm{d}\omega = \mathcal{D}(\vec{k})\mathrm{d}^{3}\vec{k} = \frac{2V}{8\pi^{3}}4\pi k^{2}\mathrm{d}k = \frac{V}{\pi^{2}c^{3}}\omega^{2}\mathrm{d}\omega$$

Let's introduce Stefan's constant

$$\sigma = \frac{\pi^2 k_B^4}{60\hbar^3 c^2}$$

$$\langle N \rangle = \sum_{\lambda} \frac{1}{e^{\beta \varepsilon_{\lambda}} - 1} = \frac{V}{\pi^2 c^3} \int_0^{+\infty} \frac{\omega^2}{e^{\beta \hbar \omega} - 1} \mathrm{d}\omega$$

Assuming $x = \beta \hbar \omega$,

$$\langle N \rangle = \frac{V}{\pi^2 c^3} \frac{1}{(\beta \hbar)^3} \int_0^{+\infty} \frac{x^2}{e^x - 1} dx = \frac{V}{\pi^2} \left(\frac{k_B T}{c \hbar}\right)^3 \int_0^{+\infty} dx \frac{x^2}{e^x - 1}$$
$$\langle N \rangle = \frac{V}{\pi^2} \left(\frac{k_B T}{\hbar c}\right)^3 \int_0^{+\infty} \frac{x^2}{e^x - 1} dx = \frac{60\sigma T^3}{\pi^4 k_B c} \int_0^{+\infty} dx \frac{x^2}{e^x - 1}$$
$$\langle E \rangle = \frac{60\sigma T^4 V}{\pi^4 c} \int_0^{+\infty} dx \frac{x^3}{e^x - 1}$$
$$\Omega = -\frac{1}{3} \frac{60\sigma T^4}{\pi^4 c} V \int_0^{+\infty} dx \frac{x^3}{e^x - 1}$$

$$\langle E \rangle = -3\Omega = 3pV$$

average density of energy in an interfal of frequency $\mathrm{d}\omega,$

$$\bar{u}_{\omega}(T) = \frac{1}{V} \bar{n}^{\text{BE}}(\hbar\omega) \mathcal{D}(\hbar\omega) \hbar\omega \qquad \qquad \omega \to \omega + d\omega$$
$$= \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1}$$
$$= \frac{60}{\pi^4} \frac{\hbar\sigma T^4}{k_B T c} \frac{(\hbar\omega/k_B T)^3}{e^{\beta\hbar\omega} - 1}$$
$$= \frac{60}{\pi^4} \frac{\hbar\sigma T^4}{k_B T c} f(x)$$



Figure (C.4) – Energy spectral density $\bar{u}_{\omega}(T)$ as a function of ω for different temperatures T: blue solid line (ambient temperature T = 300 K), red solid line (T = 3000 K, temperature of a filament bulb) and green solid line (T = 6000 K, temperature of the surface of the sun). Black dashed line : Rayleigh-Jeans law represented at the corresponding temperatures. Red dotted lines : displacement of the maximum.

with

$$f(x) = \frac{x^3}{e^x - 1}$$

with $x = \hbar \omega / k_B T$. $\bar{u}_{\omega}(T)$ is maximum for $\hbar \omega_M / k_B T = 2.822$ Meaning that

$$\omega_M = 2.822 \frac{k_B T}{\hbar}$$

This law is known as the Wien displacement law (1896).

$$\lim_{x \ll 1} f(x) \approx x^2$$

and so we get,

$$\bar{u}_{\omega}(T) \approx \frac{k_B T}{\pi^2 c^3} \omega^2$$

And this is kown as the Rayleigh-Jeans approximation Experimental observations
SCHEMA1

We want to know the energy that is going through this hole per unit time, meaning what is $d^2E/dSdt = ?$

$$d^{2}E = \iiint \bar{u}(T)d^{3}\vec{r}\frac{1}{4\pi r^{2}}d\vec{S}\cdot\vec{u}_{r}$$
$$= \int_{0}^{2\pi}d\varphi \int_{0}^{\pi/2}d\theta\sin\theta \int_{0}^{cdt}dr r^{2}\bar{u}(T)\frac{1}{4\pi r^{2}}\cos\theta dS$$

with

$$\bar{u}(T) = \frac{\bar{E}}{V} = \frac{\pi^2}{15} \frac{(k_B T)^4}{(\hbar c)^3} = \frac{4}{c} \sigma T^4$$

Remark : this integral is over the volume $d^3\vec{r}$, it is at fixed $d\vec{S}$.

And so we get,

$$\frac{\mathrm{d}^2 E}{\mathrm{d}S\mathrm{d}t} = \sigma T^4$$

It is the Stefan-Boltzmann law (1879).

Part II

Phase transitions: the Ising model

Chapter A

Generalities on Ising model

A.1 A brief history of Ising model

Pierre Curie (1895) made the distinction between two situations : the diamagnetic (materials that don't have any magnetization in absence of an external magnetic field) and paramagnetic/ferromagnetic. One important idea introduced by Curie, is that paramagnetic and ferromagnetic belong in the same family, up-to-a phase transition. Pierre Weiss introduced a very important idea, the idea of molecular field, that lead to a more general idea in physics, being the mean field approximation.

One very important model is the Ising model. The ising model was introduced by W. Lenz in 1920 and it was the PhD topic of Ising. Physicists spent 100 years on that model.

During Ising's PhD he realised that there is no phase transition in 1D.

Peierls (1936) demonstrate that in 2D there is phase transition.

A very important physicist, Onsager (who will won the Nobel prize if chemistry in 1968) who found the exact solution for the Ising model in 2D without external field (h = 0).

Renormalisation group theory (Wilson, 1970)

A.2 Ising Hamiltonian

A.2.1 Introduction-Notations

In order to discretize the space, in discrete points, we define a lattice in a space of dimension d. WIth coordinance z (number of nearest neighbour of one sites)

SCHEMA2

The cubic lattice in 3D has z = 6, the cubic lattice in 2D has z = 4, the cubic lattice in 1D has z = 2 and for an hypercubic lattice in dimension d has z = 2d.

We will denote a the microscopic length scale.

Let's take the idea of Lenz,

Let's assume that we have a "magnetic" dipole on each site that can take only two values $s_i = \pm s/$ In the lecture we will assume that s = 1, meaning,

$$s_i = \pm 1$$

Remark : If we have an electron with spin
$$s_i = \pm 1/2$$
, then,

$$\mu_i = g\mu_B s_i$$

where g is the Landé factor, $\mu_B = e\hbar/2m$ is Bohr's magneton. For an electron, g = 2. Meaning that,

$$\mu_i = \pm \mu_B$$

In the ising model,

$$\mu_i = \mu_B s_i$$

with $s_i = \pm 1$.

$$H_{\text{ising}} = -\sum_{i=1}^{N} h_i s_i - \sum_{i=1}^{N} \sum_{j=1}^{N} J_{i,j} s_i s_j$$

with h_i the external "magnetic" field. h_i is not necessarily uniform, if it was uniform, then $h_i = h$ for all $i \in \{1, ..., N\}$. $J_{i,j}$ describe the interaction between spins.

Ising model consider only the case of nearest neighbors.

$$H_{\text{ising}} = -\sum_{\langle i,j \rangle} Js_i s_j - \sum_{i=1}^N s_i h_i$$

where $\langle i, j \rangle$ is the nearest neighbors pairs, this number is Nz/2. $J_{i,j} = J$ isotropic interaction. This interaction $_Js_is_j$ is called the exchange interaction. It is a pure quantum mechanic interaction.

A.2.2 Interaction with an external field

A.2.3 Coupling between spins: exchange energy

A.2.4 Ising hamiltonians

Chapter B

General relations

B.1 Partition function and free energy

Let's suppose we are in the canonical ensemble $(T, V, \{h_i\})$. The partition function will be,

$$Z = \sum_{l} e^{-\beta H_{\text{ising}}} = \sum_{\{s_i = \pm 1\}} e^{-\beta H_{\text{ising}}}$$

with $l = (s_1, ..., s_N)$. The number of microstate is 2^N .

$$Z(T,h) = \sum_{\{s_i=\pm 1\}} \exp\left[-\beta \left(-J \sum_{\langle i,j \rangle} s_i s_j - \sum_{i=1}^N h_i s_i\right)\right]$$

 $F(T,h) = -k_B T \ln Z$

B.2 Average energy and heat capacity

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = \frac{\partial (\beta F)}{\partial \beta} = F - T \frac{\partial F}{\partial T} \Big|_{\{h_i\}}$$

Heat capacity,

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

B.3 Average magnetization and susceptibility

 $m_i \equiv \langle s_i \rangle$ average magnetization of one site,

$$m_i = \sum_l s_i P_l = -\left(\frac{\partial F}{\partial h_i}\right)_{T, h_{k \neq i}}$$

Remark : if *h* is uniform, $\partial F / \partial h \Big|_T = \sum_i m_i$.

$$\chi_{ij} = \left(\frac{\partial m_i}{\partial h_j}\right)_{T,V,N,h_k} = \frac{\partial^2 F}{\partial h_i \partial h_j}$$

B.4 Correlation function

$$c_{i,j} = \langle s_i s_j \rangle - \langle s_i \rangle \langle s_j \rangle$$

= $\langle (s_i - \langle s_i \rangle) (s_j - \langle s_j \rangle) \rangle$
= $\frac{1}{\beta^2} \left(\frac{\partial^2 \ln Z}{\partial h_i \partial h_j} \right)_{T,h_{k \neq i,j}}$
= $\frac{1}{\beta} \left(\frac{\partial m_i}{\partial h_j} \right)$
= $\frac{1}{\beta} \chi_{ij}$

This is a way to measure the correlation in the system.

Proof :

$$Z = \sum_{l} e^{-\beta E_{l}}$$
$$= \sum_{s_{1}=\pm 1} \sum_{s_{2}=\pm 1} \cdots \sum_{s_{N}=\pm 1} e^{\beta J \sum_{\langle ij \rangle} s_{i}s_{j} + \beta \sum_{i} h_{i}s_{i}}$$
$$F = -k_{D}T \ln Z$$

$$\begin{split} \langle E \rangle &= \sum_{l} E_{l} \frac{e^{-\beta E_{l}}}{Z} \\ &= -\frac{\partial \ln Z}{\partial \beta} \\ &= \frac{\partial}{\partial \beta} (\beta F) \\ &= F + \frac{1}{k_{B}T} \frac{\partial F}{\partial T} \frac{\partial T}{\partial \beta} \\ &= F - T \frac{\partial F}{\partial T} \end{split}$$

$$C_V = \frac{\partial \langle E \rangle}{\partial T}$$

= $\frac{\partial F}{\partial T} - \frac{\partial F}{\partial T} - T \frac{\partial^2 F}{\partial T^2}$
= $-T \frac{\partial^2 F}{\partial T^2}$

$$m_{i} = \langle s_{i} \rangle$$

$$= \sum_{s_{1}} \cdots \sum_{s_{N}} s_{i} \frac{e^{\beta J \sum_{\langle jk \rangle} s_{j} s_{k} + \beta \sum_{j} h_{j} s_{j}}}{Z}$$

$$= \frac{1}{\beta} \frac{\partial \ln Z}{\partial h_{i}}$$

$$= -\frac{\partial F}{\partial h_{i}}$$

$$c_{ij} = \langle s_i s_j \rangle - \langle s_i \rangle \langle s_j \rangle$$
$$\stackrel{?}{=} \frac{1}{\beta} \chi_{ij}$$
$$= -\frac{1}{\beta} \frac{\partial^2 F}{\partial h_i \partial h_j}$$
$$= \frac{1}{\beta^2} \frac{\partial^2 \ln Z}{\partial h_i \partial h_j}$$

$$\begin{split} \frac{1}{\beta^2} \frac{\partial^2 \ln Z}{\partial h_i \partial h_j} &= \frac{1}{\beta} \frac{\partial}{\partial h_i} \left(\frac{\sum_{\{s_k\}} s_j e^{\beta(\cdots)}}{\sum_{\{s_k\}} e^{\beta(\cdots)}} \right) \\ &= \frac{\sum_{\{s_k\}} \beta s_i s_j e^{\beta(\cdots)}}{Z} - \frac{\sum_{\{s_k\}} \sum_{\{s_p\}} s_i s_j e^{\beta(\cdots)} e^{\beta(\cdots)}}{Z^2} \\ &= \langle s_i s_j \rangle - \langle s_i \rangle \langle s_j \rangle \end{split}$$

Chapter C

Mean-field approximation

It has already been said that there is only a solution to the problem if d = 1 (Ising, 1925) and d = 2 and without magnetic fields (Onsager, 1944). Apart from these cases, there is no solution and we have to make some approximations. We will therefore do the mean fields approximation to solve the system. It was performed by Pierre Weiss in 1907.

C.1 General relations

C.1.1 Partition function and free energy

We can always decompose a variable as the sum of its mean value and the fluctuations around the mean value. So we have

$$s_i = \langle s_i \rangle + \delta s_i = m_i + \delta s_i$$

where $m_i = \langle s_i \rangle$ as defined above, and δs_i are the fluctuations of s_i around m_i . We can therefore rewrite the correlation function,

$$c_{ij} = \langle s_i s_j \rangle - \langle s_i \rangle \langle s_j \rangle$$

= $\langle (m_i + \delta s_i)(m_j + \delta s_j) \rangle - m_i m_j$
= $\langle \underline{m}_i \overline{m_j} + \underline{m}_i \delta \overline{s_j} + \underline{m}_j \delta \overline{s_i} + \delta s_i \delta s_j \rangle - \underline{m}_i \overline{m_j}$

We have $\langle m_i \delta s_j \rangle = \langle m_i \rangle \langle s_j \rangle$ because the fluctuation of one spin is independent of the average value of another spin. However, the fluctuations of two different spins are not necessarily decorrelated and the term $\langle \delta s_i \delta s_j \rangle$ is not necessarily zero. So we get,

$$c_{ij} = \langle \delta s_i \delta s_j \rangle$$

The mean field approximation consists in assuming that the fluctuations of the spins around their average value are negligible: $\delta s \ll m$. We can then remove the order terms δs^2 from the equations. In this case, we have

$$c_{ij} = 0$$

We can now rewrite the hamiltonian,

$$\begin{split} H &= -\sum_{\langle ij \rangle} Js_i s_j - \sum_i h_i s_i \\ &= -J \sum_{\langle ij \rangle} \left(m_i + \delta s_i \right) \left(m_j + \delta s_j \right) - \sum_i h_i s_i \\ &\approx -J \sum_{\langle ij \rangle} \left(m_i m_j + m_i \delta_j + m_j \delta s_i \right) - \sum_i h_i s_i \\ &= -J \sum_{\langle ij \rangle} m_i m_j - 2J \sum_{\langle ij \rangle} m_j \delta s_i - \sum_i h_i s_i \\ &= -J \sum_{\langle ij \rangle} m_i m_j - 2J \sum_{\langle ij \rangle} m_j (s_i - m_i) - \sum_i h_i s_i \\ &= J \sum_{\langle ij \rangle} m_i m_j - 2J \sum_{\langle ij \rangle} m_j s_i - \sum_i h_i s_i \end{split}$$

We can transform the second sum by counting the first neighbors of each atom. However, by doing this, each atom is counted twice. We must then divide the result by two. Thus, we obtain

$$H = J \sum_{\langle ij \rangle} m_i m_j - 2J \sum_i \sum_{j \in \text{nearest neighbourg}(i)} m_j m_i - \sum_i h_i s_i$$

So we get,

$$H = J \sum_{\langle ij \rangle} m_i m_j - \sum_i \sum_{j \in \text{nearest neighbourg}(i)} (Jm_j + h_i) s_i$$

The Hamiltonian is finally written

$$H = J \sum_{\langle ij \rangle} m_i m_j - \sum_i h_{\text{eff},i} s_i \qquad \text{with} \qquad h_{\text{eff},i} = h_i + J \sum_{j \in \text{nearest neighbourg}(i)} m_j$$

where $h_{\text{eff},i}$ is the effective field felt by spin *i*. It takes into account the interactions between *i* and its first neighbors, and accounts for the field disturbance that this implies.

The fact of neglecting the fluctuations of the spins is called approximation of mean fields because, considering a spin i subjected to the magnetic field h_i , s_i is equal to its average value, that is to say that the spin field is at all points equal to its average value allowed by the magnetic field.

It is now possible to calculate the partition function of the system,

$$Z = \sum_{s_1} \cdots \sum_{s_N} e^{-\beta H}$$

= $\sum_{s_1} \cdots \sum_{s_N} e^{-\beta J \sum_{\langle ij \rangle} m_i m_j + \beta \sum_i h_{\text{eff},i} s_i}$
= $e^{-\beta J \sum_{\langle ij \rangle} m_i m_j} \sum_{\{s_k\}} \prod_i e^{\beta h_{\text{eff},i} s_i}$
= $e^{-\beta J \sum_{\langle ij \rangle} m_i m_j} \prod_i \sum_{s_i = \pm 1} e^{\beta h_{\text{eff},i} s_i}$
= $e^{-\beta J \sum_{\langle ij \rangle} m_i m_j} \prod_i 2 \cosh(\beta h_{\text{eff},i})$

which makes it possible to find an expression for free energy. Indeed, we have

$$F = -k_B T \ln Z$$

= $J \sum_{\langle ij \rangle} m_i m_j - k_B T \sum_i \ln(2 \cosh(\beta h_{\text{eff},i}))$

Example : if our field is homogeneous, $h_i = h_j = h$,

$$F = J \frac{1}{2} \sum_{i} \sum_{j \in \mathrm{nn}(i)} m^2 - Nk_B T \ln(2 \cosh(\beta h_{\mathrm{eff},i}))$$
$$= \frac{NzJ}{2} m^2 - Nk_B T \ln(2 \cosh(\beta h_{\mathrm{eff},i})) \qquad \qquad h_{\mathrm{eff},i} = h + zJm$$

But, we don't know m.

C.1.2 Self-constitent equations

At this level, we cannot solve the system. Indeed, it was assumed that we already knew m_i , which is not true. We have in fact, by deriving the previous equation,

$$m_i = -\frac{\partial F}{\partial h_i} = k_B \mathcal{T} \frac{2\beta \sinh(\beta h_{\text{eff},i})}{2 \cosh(\beta h_{\text{eff},i})}$$

We then get,

$$m_i = \tanh(\beta h_{\text{eff},i}) = \tanh\left(\beta \left[\sum_{j \in \text{nn}(i)} Jm_j + h_i\right]\right)$$

which is a self-consistent equation. It is therefore necessary to use numerical methods to find a solution.

C.2 Phase transition without magnetic field

C.2.1 Average magnetization and critical temperature

For a zero magnetic field, h = 0, we have

$$m = \tanh(\beta z J m)$$

We can solve this equation graphically. The equation is written

 $\operatorname{arctanh}(m) = \beta z J m$

This equation depends on the temperature T of the system. So, graphically, there are three regimes that depend on temperature. We define a critical temperature T_C defined by

$$k_B T_C = z J$$

The three regimes are represented in the following figure.



Figure (C.1) – Solution of the self-consistent equation for zero field h = 0 and for different temperatures : $T > T_C$ green solid line $(m = 0), T < T_C$ blue solid line $(m = -m_0, 0, m_0)$ and $T = T_C$ red dashed line.

If $T > T_C$, there is only one solution: m = 0, if $T < T_C$, there are three solutions: m = 0, $m = \pm_0$. Ultimately, if $T = T_C$, there is only one solution : m = 0.

In the case $T < T_C$, the system is spontaneously magnetized, although the field is bare. It's that called the ferromagnetic phase of the system. The magnetization is shown below in depending on the temperature.



It is a so-called "second order phase transition". It is a spontaneous symmetry breaking.

C.2.2 Free energy and Landau expansion

CM stands for *champ moyen*

$$F_{CM} = \frac{NzJ}{2}m^2 - Nk_BT\ln(2\cosh(\beta h_{\text{eff},i})) \qquad h_{\text{eff},i} = h + zJm$$

$$\frac{\Delta F_{CM}}{Nk_B T_C} = \frac{1}{2}m^2 - \frac{T}{T_C}\ln\left[\cosh\left(\frac{T}{T_C}\left(m + \frac{h}{zJ}\right)\right)\right] \qquad \Delta F_{CM} = F_{CM}(m) - F_{CM}(0)$$

For h = 0,

Which can be summarized in the fig,



indeed the solution m = 0 for $T < T_C$ is unstable because it is a maximum of the free energy and $m = \pm m_0(T)$ are stable solutions because they are minima of F.



Figure (C.2) – Free energy F as a function of the magnetisation m for different temperatures : $T > T_C$ green solid line $(m = 0), T < T_C$ blue solid line $(m = -m_0, 0, m_0)$ and $T = T_C$ red dashed line.

Remark :

$$k_B T_C = z J$$

For d = 1, we find that z = 2.

For d = 2, we fin that z = 4, meaning $k_B T_C = 4J$ (and it is way greater than the exact value that we will calculate latter on).

$$\frac{\Delta F_{CM}}{Nk_B T_C} = \frac{1}{2}m^2(T) - \frac{T}{T_C}\ln\left(\cosh\left(\frac{T_C}{T}m\right)\right)$$

We will try to make a Taylor expansion close to $T \approx T_C$, meaning $m \approx 0$.

$$\cosh(x) \approx 1 + \frac{x^2}{2} + \frac{x^4}{24} + \cdots$$

 $\ln(1+x) = x - \frac{x^2}{2} + \cdots$

$$\frac{\Delta F_{CM}}{Nk_BT_C} \approx \frac{1}{2} \left(\frac{T - T_C}{T}\right) m^2 + \frac{1}{12} \left(\frac{T_C}{T}\right)^3 m^4$$



C.2.3 Average energy and heat capacity

We are still on the case h = 0,



And we now that

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

We have a second order phase transition (continuous phase transition) because the discontinuity appears at the second order of derivation of the free energy (no latent heat)

$$\delta Q = C \mathrm{d}T + \iota \mathrm{d}K$$

C.3 Magnetic field effect

Self-consitent equation,

$$\operatorname{arctanh}(m) = \beta(zJm + h)$$
$$= \frac{T_C}{T} \left(m + \frac{h}{zJ}\right)$$

$$\Delta F_{CM} = Nk_B T_C \left(\frac{1}{2}m^2 - \frac{T}{T_C}\ln(\cosh(\beta(zJ+h)))\right)$$
$$\approx \Delta F_{CM}(h=0) - hm$$





C.4 Critical exponents

We are working close to the critical point, meaning $T \approx T_C$, which means $T - T_C/T_C \ll 1$, and the magnetization $m \approx 0$, we are at a very small magnetic field $h \approx 0$.

The self consistent equation look like this,

$$m = \tanh(\beta(zJm + h))$$

In a first case, we will study for h = 0,

$$m = \tanh\left(\frac{T_C}{T}m\right)$$

We can perform a Taylor expansion,

$$m \approx \frac{T_C}{T}m - \frac{1}{3}\left(\frac{T_C}{T}m\right)^3$$

m = 0 is a solution, we can then divide by m supposing $m \neq 0$,

$$1 = \frac{T_C}{T} - \frac{1}{3} \left(\frac{T_C}{T}\right)^3 m^2$$

Meaning,

$$m \propto (T_C - T)^{1/2}$$

for $T < T_C$. We can write the exponent as β meaning here $\beta = 1/2$, it is our first critical exponant. Meaning

$$m \propto (T_C - T)^{\beta}$$

In the mean-field approximation, $\beta_{MF} = 1/2$.

Now we introduce $h \neq 0$, so the self consistent equation is

$$m = \tanh(\beta(zJm + h))$$
$$\approx \beta zJm + \beta h$$

We can rewrite,

$$m\left(1-\frac{T_C}{T}\right) \approx \frac{h}{k_B T}$$

$$m \approx \frac{1}{k_B(T - T_C)}h$$

So for a very small magnetic field, the magnetization is linear to the magnetic field.

$$\chi = \left(\frac{\partial m}{\partial h}\right) \frac{1}{k_B} (T - T_C)^{-1}$$

We can write the exponant as γ , meaning $\gamma_{MF} = 1$.

$$m_{h=0,T} \propto (T_C - T)^{\beta} \qquad \qquad \beta_{MF} = \frac{1}{2}$$

$$m_{h,T=T_C} \propto h^{1/\delta} \qquad \qquad \delta_{MF} = 3$$

$$\chi_{h=0,T} \propto |T - T_c|^{-\gamma} \qquad \qquad \gamma_{MF} = 1$$

$$C_{h=0,T} \propto (T_C - T)^{\alpha} \qquad \qquad \alpha_{MF} = 0$$

In 3D, numerical simulation gives $\beta=0.325$

C.5 Conclusions

Chapter D

Exact solution for the Ising model

D.1 1d-Ising model: exact solution (see Tutorials)

see Tutorials

D.2 2d-Ising model: exact solution for critical temperature (Onsager 1944)

D.2.1 General relation

Ising model with h = 0,

$$Z_{\text{Ising}} = \sum_{\{s_i = \pm 1\}} e^{\beta J \sum_{\langle i,j \rangle} s_i s_j}$$

$$e^{\beta J s_i s_j} = \cosh(\beta J)(1 + s_i s_j \tanh(\beta J))$$

In our case, $s_i s_j = \pm 1$ For the case $s_i s_j = 1$,

$$\cosh(\beta J)(1 + \tanh(\beta J)) = \frac{1}{2} \left(e^{\beta J} + e^{-\beta J} \right) \left(1 + \frac{e^{\beta J} - e^{-\beta J}}{e^{\beta J} + e^{-\beta J}} \right)$$
$$= e^{\beta J}$$
$$= e^{\beta J s_i s_j}$$

Let's call $K \equiv \beta J$,

$$e^{Ks_is_j} = \cosh(K)(1 + s_is_j \tanh K)$$

$$Z(K) = \sum_{\{s_i = \pm 1\}} e^{K \sum_{\langle i,j \rangle} s_i s_j}$$

=
$$\sum_{\{s_i = \pm 1\}} \prod_{\langle i,j \rangle} e^{K s_i s_j}$$

=
$$\sum_{\{s_i = \pm 1\}} \prod_{\langle i,j \rangle} \cosh(K) (1 + s_i s_j \tanh(K))$$

D.2.2 High temperature expansion



where \mathcal{R} is the square lattice and l_G is the graph length. This is an exact result. We call this the high-temperature limite, because at $T \to +\infty$, $\beta \to 0$, meaning $K \ll 1$, which mean $\tanh K \ll 1$, and so the graph of large length contributes less.

Remark : Order 0 in tanh K:

$$\sum_{s_i=\pm 1\}} 1 = 2^N$$

{

Order 1 in $\tanh K$:

$$\sum_{\{s_i=\pm 1\}} s_{10}s_{11} \tanh K = \tanh K \sum_{\{s_i=\pm 1\}} s_{10}s_{11} = 0$$

Order 2 in $\tanh K$:

$$\sum_{s_i=\pm 1\}} s_{10} s_{11} s_{10} s_{43} \tanh^2 K = 0$$

It is 0 both for connected and disconnected graphs. The contribution is non-zero only for closed-connected graphs.

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 $l_G = 0$, empty graph, 1 term.

D.2.3 Low temperature expansion



At T = 0,

$$H = -J\sum_{\langle i,j\rangle} s_i s_j$$

$$E(T=0) = -\frac{NzJ}{2} = -2NJ$$

Length	Graph	Number
4		N
	• •	
6	• • •	2N
	• • •	
8	• • •	$N\left(N-5 ight)/2$
		2N
	• • •	4N
		Ν

Figure (D.1) – Different graphs contributing to the partition function of the two-dimensional Ising model.



 $T \neq 0,$ but very small, the first excited state, one spin is flipped,

$$E = -2NJ + 2J \times 4$$

Remark :

The interaction between the flipped spin and its neighbour is 2J, and it has 4 neighbours, meaning $4 \times 2J$.

One first order excited state correspond to a closed graph on the dual lattice \mathcal{R}^* .

$$Z(K) = \sum_{\{s_i=\pm 1\}} e^{-\beta H}$$

=
$$\sum_{\text{closed graph on } \mathcal{R}^*} e^{-\beta(2NJ+2Jl_G)}$$

=
$$(e^K)^{2N} \sum_{\text{closed graph on } \mathcal{R}^*} (e^{-2K})^{l_G}$$

when $K \to +\infty$, $e^{-2K} \ll 1$, which is equivalent to $T \to 0$, so we only have to consider the first excited state.

D.2.4 Low and high temperature limit connection

$$Z_{\text{high-temp}}(K) = 2^{N} (\cosh(K))^{2N} \sum_{\text{closed graph} \in \mathcal{R}} (\tanh K)^{l_{G}}$$
$$Z_{\text{low-temp}}(\tilde{K}) = (e^{\tilde{K}})^{2N} \sum_{\text{closed graph} \in \mathcal{R}^{*}} \left(e^{-2\tilde{K}}\right)^{l_{G}}$$

Remark : For the square lattice in 2D, the lattice and the dual lattice are the same.

If we choose K and \tilde{K} like $\tanh K = e^{-2\tilde{K}}$,

$$Z_{\text{high-temp}}(K) = 2^N (\cosh(K))^{2N} \frac{Z_{\text{low-temp}}(K)}{(e^{\tilde{K}})^{2N}}$$

And with a more symetric expression, we can write,

$$\frac{Z_{\text{high-temp}}(K)}{\sinh(2K)^{N/2}} = \frac{Z_{\text{low-temp}}(\tilde{K})}{\sinh(2\tilde{K})^{N/2}}$$

At a critical point $K_C = \beta_C J = J/k_B T_C$, we will have a non-analytical behaviour of $Z(K\tilde{K}_C)$, then \tilde{K}_C given $e^{-2\tilde{K}_C} = \tanh(K_C)$ will be also a critical point. If we assume that the Ising model has only one critical point, it should be for $e^{-2K_C} = \tanh(K_C)$. With $x_c = e^{2K_C}$,

$$\frac{1}{x_c^2} = \frac{x_c - \frac{1}{x^c}}{x_c + \frac{1}{x_c}}$$

Meaning,

$$K_C = \frac{1}{2} \ln \left(1 + \sqrt{2} \right) \approx 0.440687$$

Meaning,

$$k_B T_C \approx 2.269 \text{ J}$$

And whitin the mean-field approximation, we found $k_B T_C = 4$ J.

 \mathbf{Remark} :

Kramers and Wannier (1941) and three years latter (1944) Onsager gives the exact solution.

Chapter E

Critical phenomena: a deeper view

E.1 Correlations in mean-field approximation

E.1.1 Correlation function

The correlation function is defined,

$$C_{ij} \equiv \langle s_i s_j \rangle - \langle s_i \rangle \langle s_j \rangle$$
$$= \frac{1}{\beta^2} \left(\frac{\partial^2 \ln Z}{\partial h_i \partial h_j} \right)$$
$$= \frac{1}{\beta} \left(\frac{\partial m_i}{\partial h_j} \right)$$
$$= \frac{1}{\beta} \chi_{ij}$$

Within the mean-field approximation, we assumed that,

$$C_{ij} \approx 0 \Longrightarrow m_i \approx \beta \left(h_i + \sum_j J_{ij} m_j \right)$$

A system of N non-linear self-consistent equations.

Remark : this is an \approx for the self-consistent equation because it is close to the critical point (linearized).

We can write it a different way,

$$h_i = \frac{1}{\beta}m_i - \sum_j J_{ij}m_j$$

vector

$$\vec{h} = (h_i)_{i=1,...,N}$$
 $\vec{m} = (m_i)_{i=1,...,N}$

$$\vec{h} = M\vec{m}$$
 with the matrix $M = \left(\frac{1}{\beta}\delta_{ij} - J_{ij}\right)$

Meaning we need to find the inverse M^{-1} ,

$$\vec{m} = M^{-1}\vec{h}$$

We will write $A = M^{-1}$ for notation conveniance

$$C_{ij} = \frac{1}{\beta} A_{ij}$$

with

$$\sum_{k=1}^{N} A_{ik} \left(\frac{1}{\beta} \delta_{kj} - J_{kj} \right) = \delta_{ij}$$

$$\beta \sum_{k=1}^{N} C_{ik} \left(\frac{1}{\beta} \delta_{kj} - J_{kj} \right) = \delta_{ij}$$

E.1.2 Correlation length

$$\beta \sum_{k} \left(\frac{\delta_{k,j}}{\beta} - J_{k,j} \right) C_{i,k} = \delta_{i,j}$$

Continuous approximation (we are interested in what is happening close to T_c , where we expect the correlation to be long-range).



$$S_{i} \longrightarrow S(\vec{r}_{i})$$

$$C_{i,j} \longrightarrow C(\vec{r}_{i},\vec{r}_{j}) = C(\vec{r}_{i}-\vec{r}_{j}) = C(|\vec{r}_{i}-\vec{r}_{j}|)$$

$$J_{i,j} \longrightarrow J(\vec{r}_{i},\vec{r}_{j}) = J(\vec{r}_{i}-\vec{r}_{j})$$

$$\delta_{i,j} \longrightarrow \delta_{\text{Dirac}}^{(d)}(\vec{r}_{i},\vec{r}_{j}) = \delta_{\text{Dirac}}^{(d)}(\vec{r}_{i}-\vec{r}_{j})$$

Meaning, now,

$$\beta \int \mathrm{d}^{(d)} \vec{r}_k \left(\frac{\delta(\vec{r}_i - \vec{r}_k)}{\beta} - J(\vec{r}_i - \vec{r}_k) \right) C(\vec{r}_k - \vec{r}_j) = \delta^{(d)}(\vec{r}_i - \vec{r}_j)$$

where we call $\vec{r_i} - \vec{r} - k \equiv \vec{r'}$ and $\vec{r} - \vec{r'} \equiv \vec{r_k} - \vec{r_j}$.

$$\beta \int \mathbf{d}^{(d)} \vec{r}' \underbrace{\left(\frac{\delta(\vec{r}')}{\beta} - J(\vec{r}')\right)}_{A(\vec{r})} C(\vec{r} - \vec{r}') = \delta^{(d)}(\vec{r})$$
Convolution product *

And we know that the Fourier transform of a convolution product is the convolution product of the Fourier transform. We're gonna use the convention,

$$\begin{cases} f(\vec{r}) \equiv \frac{V}{(2\pi)^d} \int d^{(d)} \vec{k} \tilde{f}(\vec{k}) e^{-j\vec{k}\cdot\vec{r}} \\ \tilde{f}(\vec{k}) \equiv \frac{1}{V} \int d^{(d)} \vec{r} f(\vec{r}) e^{+j\vec{k}\cdot\vec{r}} \end{cases}$$

So,

$$\begin{split} \beta \tilde{A}(\vec{k}) \tilde{C}(\vec{k}) &= \underbrace{\tilde{\delta}(\vec{k})}_{=1} \end{split}$$

$$\tilde{C}(\vec{k}) &= \frac{1}{\beta} \frac{1}{\tilde{A}(\vec{k})} \end{split}$$

So, what is $\tilde{A}(\vec{k})$?



$$\tilde{A}(\vec{k}) = \frac{1}{\beta} - 2J \sum_{\nu=1}^{d} \cos(k_{\nu}a)$$
$$\tilde{C}(\vec{k}) = \frac{1}{1 - 2\beta J \sum_{\nu} \cos(k_{\nu}a)}$$

we're interested in $r \gg a$, meaning $k_{\nu}a \ll 1$,

$$\tilde{C}(\vec{k}) \simeq \frac{1}{1 - 2\beta J \left(\sum_{\nu=1}^{d} \left(1 - \frac{1}{2}(k_{\nu}a)^{2}\right)\right) + \cdots}$$
$$\approx \left(1 - \frac{2dJ}{k_{B}T} + \beta J(ka)^{2}\right)^{-1}$$
$$\tilde{C}(\vec{k} \propto \frac{1}{\left(\frac{1}{\xi^{2}} + k^{2}\right)} \frac{1}{\beta Ja^{2}}$$

with

$$\xi^2 = \frac{\beta J a^2}{(1 - 2dJ\beta)} \iff \xi^2 = \frac{T_c}{T - T_c} a^2$$

with T_c the critical temperature,

$$T_c = \frac{2dJ}{k_B}$$

And now, if we perform the inverse Fourier transform, we get

$$C(\vec{r}) \simeq \frac{1}{(2\pi)^d \beta J a^2} \int d^{(d)} \vec{k} \frac{1}{\frac{1}{\xi^2} + k^2} e^{j\vec{k} \cdot \vec{r}}$$

• For $T = T_c$,

$$\frac{1}{\xi^2} = 0$$

Meaning,

$$C(\vec{r}) \simeq \frac{1}{(2\pi)^d \beta J a^2} \int \mathrm{d}^{(d)} \vec{k} \frac{1}{k^2} e^{j\vec{k} \cdot \vec{r}}$$

we can define $\vec{u}=\vec{k}|\vec{r}|=\vec{k}r$

$$\begin{split} C(\vec{r}) \simeq \frac{1}{(2\pi)^d \beta J a^2} \frac{1}{r^{d-2}} \underbrace{\int \mathrm{d}^{(d)} \vec{u} \frac{1}{u^2} e^{-i\vec{u} \cdot \vec{u}_r}}_{\text{is not depending on } r} \\ \propto \frac{1}{r^{d-2}} \end{split}$$

We see that it behaves like a power-law, meaning there is no characteristic length scale, meaning a scaling invariance at T_c .

Remark : we see that this exponent d-2 is probably different than d-2 within an exact calculation.

We define a new critical exponent η ,

$$C(r) \simeq \frac{1}{r^{d-2+\eta}} \iff \eta_{\rm MFA} = 0$$

• $T \neq T_c$,

We can show that

$$C(r) = \frac{1}{r^{d-2}}e^{-r/\xi}$$

We have an exponential decay over the characteristic length ξ , with

$$\xi = a \left(\frac{T_c}{|T - T_c|} \right)^{1/2}$$

This define a new critical exponent, $\nu, \xi \equiv |T - T_c|^{-\nu}$ which here is equal to $\nu_{\text{MFA}} = 1/2$.



E.2 Validity of mean-field approximation

E.2.1 Interaction range

It has already been said that the more reliable the number of particles interacting with each other, the more important the correlations in the interactions will be. In the limit where this number becomes too low, the average field approximation is no longer valid. Conversely, if a spin interacts with all the other spins in the network, then the approximation will give an exact solution to the problem.

Note that in this situation, it is no longer an Ising model, which consists in assuming only the correlations between first neighbors. It is then interesting to ask when does the approximation begin to cease to be valid.

E.2.2 Ginzburg criteria

In order to obtain a criterion on the field of application of the mean field, it is judicious to study the fluctuations at the mean value of the relevant physical quantities, placing oneself at the critical point. For this, we can consider the free energy or the magnetization of the system.

• Free energy

$$F_{\text{mean}} = ?$$
$$\Delta F \simeq \frac{k_B T}{\xi^d} \simeq |T - T_c|^{d\nu}$$
$$C = T \frac{\partial^2 F_{\text{mean}}}{\partial T^2} \propto |T - T_c|^{-\alpha}$$

Meaning,

$$F_{\rm mean} \propto |T - T_c|^{2-\alpha}$$

$$\frac{\Delta F}{F_{\rm mean}} \simeq |T - T_c|^{d\nu - 2 + \alpha}$$

and the smaller this ratio, the better the average field approximation. It all depends only on $d\nu - 2 + \alpha$.

- If $d\nu 2 + \alpha > 0$, then $T \sim T_c$ we have the ratio that tends to 0 and hence the approximation is good.
- If $d\nu 2 + \alpha < 0$, this ratio diverges and the approximation is no longer applicable.

We see that there is then a critical dimension of the system, $d_{c,sup} = (2 - \alpha)/\nu$ at which point the mean-field approximation starts to look good. In the MFA, $\alpha = 0$ and $\nu = 1/2$, meaning this $d_{c,sup} = 4$. Meaning the Ising model is good for d = 4 and above.

• We can do the same reasoning with magnetization,

$$\left(\frac{\Delta m}{m_0}\right)^0 \simeq |T - T_c|^{\nu(d-2+\eta)-2\beta}$$

and again,

$$d_{c, \text{sup}} = \frac{2\beta}{\nu} + 2 - \eta \stackrel{\text{MFA}}{=} 4$$

which also gives the critical dimension $d_{c,\sup} = 4$.

E.3 Introduction to Landau theory

E.3.1 General idea

At the critical point, the model's behavior is universal. The emerging properties of collective phenomena are therefore also universal. In fact, we find exactly the same behavior for the Ising model, the liquid gas transition, and a large number of other network models. To study these systems in general, Landau proposes to act in stages.

First, it is necessary to identify the relevant parameters of the system. For example, for a magnetic system, this would be magnetization or polarizability. These parameters can be scalars, vectors, or more generally tensors. We will consider that the model is continuous and the considered parameter will be $s(\vec{r})$ the value of the spin projection at position \vec{r} .

Second, we must construct an effective phenomenological Hamiltonian $H_L[s\vec{r})$ depends on the relevant parameters. We can choose it as simply as possible, as long as the symmetries of the system are respected. It is therefore a phenomenological model. For the Ising model, the symmetry is the system is invariant if, in the absence of magnetic fields, all the spins are reversed: $s(\vec{r}) \rightarrow -s(\vec{r})$ describes exactly the same system if h = 0.

The main assumption is that the Hamiltonian is developable as a convergent series of the parameter of order $s(\vec{r})$ near the critical temperature:

$$H_L[S(\vec{r})] = \int_{v_d} \mathrm{d}^d \vec{r} \left\{ \frac{1}{2} a_2(T) S^2(\vec{r}) + \frac{1}{4} a_4(T) S^4(\vec{r}) + \frac{1}{2} b_2(T) (\vec{\nabla} S(\vec{r}))^2 - h(\vec{r}) S(\vec{r}) \right\}$$

There is no odd power term of $s(\vec{r})$ since the invariance by spin change must be preserved in the Hamiltonian. In addition, the terms a_2 and a_4 are dependent on all the parameters of the system. We use the term $(\vec{\nabla}S(\vec{r}))^2$ not to restrict ourselves to a homogeneous system. The non-homogeneity of the latter is therefore included in this quantity. Finally, in the presence of a magnetic field, the term $-h(\vec{r})S(\vec{r})$ expresses the interaction between the spins and the fields.

E.3.2 Landau approximation

Landau hypothesizes that the thermal fluctuations are small, even if we are quite close to the critical point. This assumes that the effective hamiltonian varies quite rapidly around the $m(\vec{r})$ value of $s(\vec{r})$ that minimizes the hamiltonian and that one can then compute the integral that gives the partition function by the neck method as :

$$Z = \int \mathcal{D}[S(\vec{r})] e^{-\beta H_L[S(\vec{r})]}$$
$$\approx e^{-\beta H_L[m(\vec{r})]}$$

And so the free energy F,

$$F = -k_B T \ln Z = H_L[m(\vec{r})]$$

we have to find $m(\vec{r})$ that is minimizing $H_L[S(\vec{r})]$

E.3.3 Second order transition

We will now place ourselves in the case where the external magnetic field is zero. The average magnetization is then uniform and the gradient terms are zero,



Figure (E.1) – Free energy ΔF as a function of the order parameter (magnetisation $m(\vec{r})$) within the Landau theory of second order phase transitions.

We can recover the free energy of the Ising model within the mean-field approximation,

$$\Delta F_{\rm CM} = \frac{1}{2} N k_B T_c (T - T_c) m^2 + \frac{1}{12} N k_B T_c m^4$$

By analogy with Landau's development we can thus pose :

$$\begin{cases} a_2(T) = Nk_B T_c(T - T_c) = r_0(T - T_c) \\ a_3(T) = 0 \\ a_4(T) = 2Nk_B T_c = u_0 \end{cases}$$

One thus chooses a simple Landau development which gives back the Ising model in average field in the neighborhood of T_c :

$$\Delta F = \frac{1}{2}r_0(T - T_c)m^2 + \frac{1}{4}u_0m^4 - hm$$

The shape of the free energy is shown in Fig. E.1. It is of course similar to Ising's in medium field and the discussion is similar. One must look for the minimums of the free energy by solving the equation :

$$r_0(T - T_c)m + u_0m^3 = h$$

when h = 0 we must distinguish two cases :

• For $T > T_c$, there is only one stable solution m = 0. There is no average magnetization of the system.

• For $T < T_c$, the solution m = 0 becomes unstable and two stable solutions appear :

$$m = \pm m_0 = \pm \sqrt{\frac{r_0(T - T_c)}{u_0}}$$

There is a symmetry break and the system has a non-zero average magnetization. We also obtain the value of the first critical exponent $\beta = 1/2$.

The case $h \neq 0$ is discussed as before and leads to the calculation of the magnetic susceptibility :

$$\chi_m = \left(\frac{\partial m}{\partial h}\right)_{h=0} = \frac{1}{r_0(T - T_c) + 3u_0m^2} = \begin{cases} (r_0(T - T_c))^{-1} & \text{if } T > T_c \\ (2r_0(T_c - T))^{-1} & \text{if } T < T_c \end{cases}$$

Meaning the critical exponent is $\gamma = 1$.

We also obtain the behavior of m as a function of h,

$$m \sim h^{1/3} \Longrightarrow \delta = 1/3$$

Finally, the heat capacity can be calculated,

$$C = -T \frac{\partial^2 F}{\partial T^2} = -T_c \left[\frac{1}{2} r'' m_0^2(T) + r' \frac{\partial m_0^2(T)}{\partial T} + \frac{1}{2} r \frac{\partial^2 m_0^2(T)}{\partial T^2} + \frac{1}{4} u_0 \frac{\partial^2 m_0^4(T)}{\partial T^2} \right] = \begin{cases} 0 & \text{if } T > T_c \\ \frac{r_0^2 T_c}{2u_0} & \text{if } T < T_c \end{cases}$$

which leads to $\alpha = 0$.

This approach makes it possible to find all the critical exponents of the mean field. If we now take into account a non-homogeneous field, it leads to the calculation of the correlation function and gives the results of the mean field.

E.3.4 First order transition

It is possible to generalize Landau's formalism to many situations. In particular, first-order phase transitions can be described by introducing a 6-order term in limited development :

$$\Delta F = \frac{1}{2}a_2(T - T_0)m^2 - \frac{1}{4}a_4m^4 + \frac{1}{6}a_6m^6$$

with a_2 , a_4 and a_6 positive coefficients. The minimums of free energy are given by the equation :

$$m(a_2(T - T_0) - a_4m^2 + a_6m^4) = 0$$

whose solutions are given by

$$\begin{split} m_{\min} &= 0, & \forall T, \\ m_{\min}^2 &= \sqrt{\frac{a_4 + \sqrt{a_4^2 - 4a_2a_6(T - T_0)}}{2a_6}} = m_0^2 & \text{if } T < T^{**} = T_0 + \frac{a_4^2}{4a_2a_6} \end{split}$$

We can now watch when the lateral minimums cancel each other out. We get $\Delta F(m_0) = 0$ for :

- m = 0 for all T,
- $m = \pm M_0$ when $T = T^* = T_0 + 3a_4^2/(16a_2a_6) < T^{**}$.

The shape of the free energy is given by Fig. E.2



Figure (E.2) – Free energy ΔF as a function of the order parameter (magnetisation $m(\vec{r})$) within the Landau theory of first order phase transitions.

- For $T > T^{**}$ the null order parameter is the only stable solution.
- For $T^* < T < T^{**}$, there are 3 possibilities for the order parameter $(m = 0, m = \pm m_0)$. The solution m = 0 is the most stable and both solutions $m = \pm m_0$ are metastable.
- For $T_0 < T < T^*$ the order parameter can take the two values $\pm m_0$ which are now stale. The solution m = 0 is now metastable.
- For $T < T_0$ the two values $\pm m_0$ are stable and the solution m = 0 is unstable.

It can be seen that the order parameter is no longer continuous at the phase transition and that a hysteresis cycle occurs due to the existence of metastable states. We can also show that entropy is discontinuous at the phase transition which results in the existence of latent heat $L = T\Delta S$.

We can finally notice that the introduction of a term in $S(\vec{r})^3$ in Landau's hamiltonian also leads to a first-order transition. This is for example the case of the isotropic-nematic transition in liquid crystals, the order parameter being then $\langle s \rangle = 1/2(3\cos^2\theta - 1)$ (with θ is the angle that makes a molecule with the \vec{n} director vector).

Generally speaking, if the Landau development contains odd terms, the transition cannot be of the second order. If there are only even terms, the transition can be of the second order, but it is not necessarily second order as we have just seen.



Figure (E.3) – Order parameter $(m(\vec{r}))$ for a first order phase transition.

E.3.5 Tricritical line and tricritical point

It is possible to generalize Landau's formalism to many different problems. We deal in this part with a situation where there are two control parameters noted T and x (for example temperature and chemical composition...) and such as :

$$\Delta F = \frac{1}{2}a_2(T - T_0)m^2 + \frac{1}{4}a_4(x - x_c)m^4 + \frac{1}{6}a_6m^2$$

with a_2 , a_4 and a_6 positive coefficients.

If $x > x_c$ the term in m^4 increases with m and we can neglect the term in m^6 . We then find a transition of the second order with a critical temperature for all $x > x_c$ as :

$$T_c = T_0$$

If $x < x_c$ we must keep the term of degree 6 in the development. We then return to the discussion in the previous section on first order phase transition with temperature,

$$T^* = T_0 + \frac{3a_4^2}{16a_2a_6}(x_c - x)^2, \qquad T^{**} = T_0 + \frac{a_4^2}{4a_2a_6}(x_c - x)^2$$


Figure (E.4) – Phase diagram for a system with a second order phase line, a first order phase line and a tricritical point.

The minimum of free energy are given by the equation,

$$m(a_2(T - T_0) - a_m^2 + a_6m^4) = 0$$

whose solutions are given by

$$\begin{split} m_{\min} &= 0 & \forall T, \\ m_{\min}^2 &= \sqrt{\frac{a_4 + \sqrt{a_4^2 - 4a_2a_6(T - T_0)}}{2a_6}} = m_0^2 & \text{if } T < T^{**} = T_0 + \frac{a_4^2}{4a_2a_6} \end{split}$$

E.4 Conclusion

In tutorials we saw that there is an analogy between the Ising model $(s_i = \pm 1)$ and a fluid model on lattice $(n_i \in \{0, 1\})$ with in particular the correspondence $\rho_l - \rho_v \leftrightarrow m$. We can thus define the critical exponent β as : $\rho_l - \rho_v \sim (T_c - T)^{\beta}$. We recall that the mean field predicts $\beta = 1/2$, but that more elaborate theories (renormalization group) predict $\beta \simeq 0.325 \pm 0.0015$ in dimension 3.



Figure (E.5) – Phase diagram in reduced variables $(T/T_c \text{ vs } \rho/\rho_c)$ for different molecular fluids. The fit corresponds to a critical exponent $\beta = 1/3$ (mean field prediction 1/2). From Guggenheim E. A., Journal of Chemical Physics, 13), 253.

Part III

Realistic classical fluids

Chapter F

Classical Fluids

F.1 Generalities

F.1.1 Introduction

A real fluid of particles of mass m;, at temperature T. We have $N \gg 1$ particles. A particle i is associated to a position $\vec{r_i}$ and an impulsion $\vec{p_i} = m\vec{v_i}$.

$$H[\vec{r}_1, \cdots, \vec{r}_N, \vec{p}_1, \cdots, \vec{p}_N] = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + \underbrace{U(\vec{r}_1, \cdots, \vec{r}_N)}_{\text{interaction between particles}} + \underbrace{U_{\text{ext}}(\vec{r}_1, \cdots, \vec{r}_N, \vec{p}_1, \cdots, \vec{p}_N)}_{\text{interaction with external field}}$$

In this lecture, we will assume,

$$U_{\text{ext}} = 0$$

•

$$U(\vec{r}_1, \cdots, \vec{r}_N) = \sum_{i=1}^N \sum_{j=1, j \neq i}^N u(r_{ij})$$

is the interaction potential between two particles, and we assume that u is a function of $r_{ij}=|\vec{r_i}-\vec{r_j}|.$

Example : Lennard-Jones potential,

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

F.1.2 Partition function

The classical partition function of a classic fluid,

$$Z(T, V, N) = \sum_{\nu} e^{-\beta E_{\nu}}, \qquad E_{\nu} = H[\vec{r}_1, \cdots, \vec{r}_N, \vec{p}_1, \cdots, \vec{p}_N]$$

The idea is to write it,

$$Z(T,V,N) = \frac{1}{N!} \frac{1}{h^{3N}} \int_{v} \mathrm{d}^{3}\vec{r_{1}} \int_{v} \mathrm{d}^{3}\vec{r_{2}} \cdots \int_{v} \mathrm{d}^{3}\vec{r_{N}} \int \mathrm{d}^{3}\vec{p_{1}} \cdots \int \mathrm{d}^{3}\vec{p_{N}} e^{-\beta H[\vec{r_{1}},\cdots,\vec{r_{N}},\vec{p_{1}},\cdots,\vec{p_{N}}]}$$

Notation : We introduce the notations,

$$\vec{r}^{N} = (\vec{r}_{1}, \vec{r}_{2}, \cdots, \vec{r}_{N}) \qquad d^{3}\vec{r}^{N} = d^{3}\vec{r}_{1}d^{3}\vec{r}_{2}\cdots d^{3}\vec{r}_{N}$$
$$\vec{p}^{N} = (\vec{p}_{1}, \vec{p}_{2}, \cdots, \vec{p}_{N}) \qquad d^{3}\vec{p}^{N} = d^{3}\vec{p}_{1}d^{3}\vec{p}_{2}\cdots d^{3}\vec{p}_{N}$$

$$Z(T, V, N) = \frac{1}{h^{3N}N!} \int_{v} \mathrm{d}^{3} \vec{r}^{N} \int \mathrm{d}^{3} \vec{p}^{N} \exp\left[-\beta \left(\sum_{i=1}^{N} \frac{p_{i}^{2}}{2m} + U(\vec{r}^{N})\right)\right]$$
$$= \frac{1}{h^{3N}N!} \left(\int \mathrm{d}^{3} \vec{p} \exp\left[-\beta \frac{p^{2}}{2m}\right]\right)^{N} \int \mathrm{d}^{3} \vec{r}^{N} \exp\left[-\beta U(\vec{r}^{N})\right]$$

if $U(\vec{r}^N) = 0$, meaning no interactions,

$$Z_{\text{ideal}} = \frac{1}{h^{3N}N!} \underbrace{\left(\int \mathrm{d}^{3}\vec{p} \exp\left(-\beta\frac{p^{2}}{2m}\right)\right)^{N}}_{\text{Gaussian integrals}} \times V^{N} = \frac{V^{N}}{N!\Lambda_{(T)}^{3N}}$$

with $\Lambda_{(T)}$ the De Broglie wavelength.

$$\bar{E} = \frac{3}{2}Nk_BT$$
$$\bar{p} = \frac{N}{V}k_BT \iff \beta\bar{p} = \rho$$
$$C_V = \frac{3}{2}Nk_B$$

$$Z(T, V, N) = Z_{\text{ideal}} \frac{1}{V^N} \int d^3 \vec{r}^N e^{-\beta U(\vec{r}^N)} = Z_{\text{ideal}} Z_{\text{conf}}$$

Remark : Sometimes, people use

$$Q = \int \mathrm{d}^3 \vec{r}^N e^{-\beta U(\vec{r}^N)}$$

F.1.3 Probability density

In the canonical ensemble,

$$P_l = \frac{1}{Z} e^{-\beta E_l}$$

What is the probability to be in a microstate $(\vec{r}_1, \cdots, \vec{r}_N, \vec{p}_1, \cdots, \vec{p}_N)$? $d\mathcal{P}(\vec{r}^N, \vec{p}^N)$ is the probability to be in an elementary volume $d^3\vec{r}^N d^3\vec{p}^N$ around point (\vec{r}^N, \vec{p}^N) on phase space,

$$\mathrm{d}\mathcal{P}(\vec{r}^N,\vec{p}^N) == f(\vec{r}^N,\vec{p}^N)\mathrm{d}^3\vec{r}^N\mathrm{d}^3\vec{p}^N$$

where f is called the density of probability. This quantity is very important in out-of-equilibrium statistical mechanics.

$$f(\vec{r}^{N}, \vec{p}^{N}) = \frac{e^{-\beta H(\vec{r}^{N}, \vec{p}^{N})}}{\int d^{3}\vec{r}^{N} \int d^{3}\vec{p}^{N} e^{-\beta H(\vec{r}^{N}, \vec{p}^{N})}}$$

the average value of a quantity $A(\vec{r}^N, \vec{p}^N)$,

$$\langle A(\vec{r}^N, \vec{p}^N) \rangle = \int \mathrm{d}^3 \vec{r}^N \mathrm{d}^3 \vec{p}^N A(\vec{r}^N, \vec{p}^N) f(\vec{r}^N, \vec{p}^N)$$

$$f(\vec{r}^{N}, \vec{p}^{N}) = \underbrace{\frac{e^{-\beta \sum_{i=1}^{N} \frac{p_{i}^{2}}{2m}}}{\int d^{3}\vec{p}^{N} e^{-\beta \sum_{i=1}^{N} \frac{p_{i}^{2}}{2m}}}_{\phi(\vec{p}^{N})}}_{\phi(\vec{p}^{N})} \times \underbrace{\frac{e^{-\beta U(\vec{r}^{N})}}{\int d^{3}\vec{r}^{N} e^{-\beta U(\vec{r}^{N})}}}_{P(\vec{r}^{N})}$$

Chapter G

Many-body probability distribution

G.1 One body distribution density

What is the probability to find particle 1 at a position $\vec{r_1}$, for all $(\vec{p_1}, \cdots, \vec{p_N})$

$$P^{(\frac{1}{N})}(\vec{r}_{1}) = \int d^{3}\vec{r}_{2}\cdots d^{3}\vec{r}_{N} \int d^{3}\vec{p}_{1}\cdots d^{3}\vec{p}_{N}f(\vec{r}^{N},\vec{p}^{N})$$
$$= \frac{\int d^{3}\vec{r}_{2}\cdots d^{3}\vec{r}_{N}e^{-\beta U(\vec{r}^{N})}}{\int d^{3}\vec{r}^{N}e^{-\beta U(\vec{r}^{N})}}$$

A more interesting quantity is,

$$\rho^{(\frac{1}{N})}(\vec{r_1}) = NP^{(\frac{1}{N})}(\vec{r_1})$$

the probability distribution to find one particle at $\vec{r_1} (+\delta \vec{r_1})$. As $U(\vec{r}^N) = U(\vec{r_1}, \cdots, \vec{r_N})$ in only the function of the $\vec{r_{ij}} = |\vec{r_j} - \vec{r_i}|$. We have only N - 1 independent $\vec{r_{ij}}$.

Let us define

$$\vec{u}_j = \vec{r}_j - \vec{r}_1$$

for $j \neq 1$. $\vec{u}_1 = \vec{r}_1$.

$$\mathbf{d}^3 \vec{r_1} = \mathbf{d}^3 \vec{u_1}, \qquad \qquad \mathbf{d}^3 \vec{r_j} = \mathbf{d}^3 \vec{u_j}$$

$$\rho^{\left(\frac{1}{N}\right)}(\vec{r}_{1}) = N \frac{\int d^{3}\vec{r}_{1} \cdots d^{3}\vec{r}_{N} e^{-\beta U(\vec{r}^{N})}}{\int d^{3}\vec{r}_{1} \cdots \int d^{3}\vec{r}_{N} e^{-\beta U(\vec{r}^{N})}} \\
= N \frac{\int d^{3}\vec{u}_{1} \cdots \int d^{3}\vec{u}_{N} e^{-\beta U(\vec{u}_{2}, \cdots, \vec{u}_{N})}}{\int d^{3}\vec{r}_{1} \int d^{3}\vec{u}_{2} \cdots \int d^{3}\vec{u}_{N} e^{-\beta U(\vec{u}_{2}, \cdots, \vec{u}_{N})}} \\
= \frac{N}{V}$$

A more formal definition of $\rho^{(\frac{1}{N})}(\vec{r})$ will be,

$$\rho^{(\frac{1}{N})}(\vec{r}) = \langle \hat{\rho}(\vec{r}) \rangle$$

with $\hat{\rho}$ the density operator,

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

It does make the link between discrete and continuous quantity,

$$\int \hat{\rho}(\vec{r},t) \mathrm{d}^3 \vec{r} = N$$

$$\langle \hat{\rho}(\vec{r}) \rangle = \int \mathrm{d}^3 \vec{r}^N \int \mathrm{d}^3 \vec{p}^N f(\vec{r}^N, \vec{p}^N) \hat{\rho}(\vec{r}) = \rho^{(\frac{1}{N})}(\vec{r})$$

G.2 Two bodies probability distribution

$$P^{(\frac{2}{N})}(\vec{r_1}, \vec{r_2}) = \frac{\int d^3 \vec{r_3} \cdots d^3 \vec{r_N} e^{-\beta U(\vec{r^N})} \int d^3 \vec{p^N} e^{-\beta K(\vec{p^N})}}{\int d^3 \vec{r^N} e^{-\beta U} \int d^3 \vec{p^N} e^{-\beta K}} = \frac{\int d^3 \vec{r_3} \cdots d^3 \vec{r_N} e^{-\beta U(\vec{r^N})}}{\int d^3 \vec{r^N} e^{-\beta U}}$$

$$\rho^{(\frac{2}{N})}(\vec{r}_1, \vec{r}_2) = N(N-1)P^{(\frac{2}{N})}(\vec{r}_1, \vec{r}_2)$$
$$= \frac{N(N-1)\int d^3\vec{r}_3 \cdots \int d^3\vec{r}_N e^{-\beta U(\vec{r}^N)}}{\int d^3\vec{r}_1 \cdots \int d^3\vec{r}_N e^{-\beta U(\vec{r}^N)}}$$

It can then be shown that,

$$\rho^{\left(\frac{2}{N}\right)}(\vec{r},\vec{r'}) = \left\langle \hat{\rho}^{\left(\frac{2}{N}\right)}(\vec{r},\vec{r'}) \right\rangle$$

with,

$$\hat{\rho}^{\left(\frac{2}{N}\right)}(\vec{r},\vec{r}') = \sum_{i} \sum_{j \neq i} \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_j)$$

Example : for an ideal gas, there is no interactions, meaning $U(\vec{r}^N) = 0$,

$$\rho^{\left(\frac{2}{N}\right)}(\vec{r_1}, \vec{r_2}) = N(N-1)\frac{V^{N-2}}{V^N} = \frac{N(N-1)}{V^2} \approx \left(\frac{N}{V}\right)^2 = \rho^2$$

We see that,

$$\rho^{(\frac{2}{N})}(\vec{r_1}, \vec{r_2}) \approx \rho^{(\frac{1}{N})}(\vec{r_1}) \rho^{(\frac{1}{N})}(\vec{r_2})$$

There is no correlation.

G.3 Pair correlation function

G.3.1 Definition

Pair correlation function $g(\vec{r}, \vec{r'})$ is defined as,

$$g(\vec{r}, \vec{r}') = \frac{\rho^{(\frac{2}{N})}(\vec{r}, \vec{r}')}{\rho^2}$$

with this definition, no correlations is equivalent to say that $g(\vec{r}, \vec{r}') = 1$.

Peoples define also a quantity, $h(\vec{r}, \vec{r'})$ as,

$$h(\vec{r}, \vec{r'}) = g(\vec{r}, \vec{r'}) - 1$$

In many cases, for example for pair wise interactions, $g(\vec{r}, \vec{r'})$ (or h) are function of the relative distance $|\vec{r} - \vec{r'}|$

Remark : we can also define the van Hoove correlation function,

$$G(\vec{r}, \vec{r'}) = \frac{1}{N} \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(\vec{r} - \vec{r_i}) \delta(\vec{r'} - \vec{r_j}) \right\rangle$$
$$= \delta(\vec{r} - \vec{r'}) + \rho g(\vec{r}, \vec{r'})$$

G.3.2 Link with scattering experiments



What is $I(\theta)$?

G.3.2.1 Inelastic experiment

You look for $\omega_d \neq \omega_i$ meaning dynamical properties of the sample

G.3.2.2 Elastic experiment

You look for $\omega_d = \omega_i$ meaning structural information. Transfer vector,

$$\vec{q} = \vec{k}_d - \vec{k}_i = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)$$

$$I(\theta) = I(q) = N|f(q)|^2 S(q)$$

with $|f(q)|^2$ the form factor (depending on the individual objects) and S(q) the structure factor,

$$S(q) = 1 + \rho \int \mathrm{d}^3 \vec{r} g(\vec{r}) e^{i\vec{q}\cdot\vec{r}}$$

it is more or less the Fourier transform of the pair correlation function.

G.3.3 Interpretation of $g(\vec{r})$

An intuitive interpretation of $g(\vec{r})$ is the following, $dn(\vec{r}) = \rho g(\vec{r}) d^3 \vec{r}$ is the number of particles in $d^3 \vec{r}$ knowing that there is a particle at $\vec{r} = \vec{0}$.

For a solid,



For an ideal gas,



In a liquid,



Reversible work theorem A fluid of N-2 particles, at equilibrium,



The force exerted on particle (1) is,

$$\vec{F}_{\rightarrow 1} = -\vec{\nabla}_{\vec{r}_1} U(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$$
$$\langle \vec{F}_{\rightarrow 1} \rangle = \langle -\vec{\nabla}_{\vec{r}_1} U(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) \rangle$$

$$\begin{split} \langle \vec{F}_{\to 1} \rangle &= \int d^{3}\vec{r}_{3} \cdots \int d^{3}\vec{r}_{N} \int d^{3}\vec{p}_{3} \cdots \int d^{3}\vec{p}_{N} (-\vec{\nabla}U(\vec{r}^{N}))f(\vec{r}_{3}, \cdots, \vec{r}_{N}) \\ &= \frac{\int d^{3}\vec{r}_{3} \cdots \int d^{3}\vec{r}_{N} (-\vec{\nabla}_{\vec{r}_{1}}U(\vec{r}^{N}))e^{-\beta U(\vec{r}^{N})}}{\int d^{3}\vec{r}_{3} \cdots \int d^{3}\vec{r}_{N} e^{-\beta U(\vec{r}^{N})}} \\ &= \frac{\vec{\nabla}_{\vec{r}_{1}} \ln\left(\int d^{3}\vec{r}_{3} \cdots \int d^{3}\vec{r}_{N} e^{-\beta U(\vec{r}^{N})}\right)}{\beta} \\ &= -\vec{\nabla}_{\vec{r}_{1}} \left(-k_{B}T \ln\left[\frac{\int d^{3}\vec{r}_{3} \cdots \int d^{3}\vec{r}_{N} e^{-\beta U(\vec{r}^{N})}}{\int d^{3}\vec{r}_{N} e^{-\beta U(\vec{r}^{N})}} \times N(N-1)\right]\right) \\ &= -\vec{\nabla}_{\vec{r}_{1}} \left(-k_{B}T \ln(g(\vec{r}_{1},\vec{r}_{2}))\right) \\ &= -\vec{\nabla}_{\vec{r}_{1}} \left(-k_{B}T \ln(g(\vec{r}_{1},\vec{r}_{2}))\right) \\ &= -\vec{\nabla}_{\vec{r}} \underbrace{(-k_{B}T \ln(g(\vec{r})))}_{W(\vec{r})} \\ \end{array}$$

Meaning that,

$$g(\vec{r}) = e^{-\beta W(\vec{r})}$$

Remark : when $|\vec{r}| + \infty$, we have $W(\vec{r}) \to 0$, that is consistent with $g(\vec{r}) \to 1$.

For a diluted system,

$$W(\vec{r}) = u(\vec{r}) + \delta u(\vec{r})$$

where $u(\vec{r})$ is the energy between two particles

G.4 Average energy and state equation

G.4.1 Interaction potential

I

$$U(\vec{r}^{N}) = \frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1\\j \neq i}}^{N} u(r_{ij})$$

with u the interaction potential between two particles, and $r_{ij} = |\vec{r_i} - \vec{r_j}|$.

G.4.2 Average energy

$$\langle E(\vec{r}^N, \vec{p}^N) \rangle = \langle K(\vec{p}^N) \rangle + \langle U(\vec{r}^N) \rangle$$

$$= \frac{3}{2} N k_B T + \langle U(\vec{r}^N) \rangle$$

$$\langle U(\vec{r}^N) \rangle = \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1\\j \neq i}}^N \langle u(r_{ij}) \rangle = \frac{N(N-1)}{2} \langle u(r_{ij}) \rangle \simeq \frac{N^2}{2} \langle u(r_{ij}) \rangle$$

So the question is, what is $\langle u(r_{ij}) \rangle$?

$$\langle u(r_{12}) \rangle = \frac{\int d^3 \vec{r_1} \cdots \int d^3 \vec{r_N} u(r_{12}) e^{-\beta U(\vec{r^N})}}{\int d^3 \vec{r_1} \cdots \int d^3 \vec{r_N} e^{-\beta U(\vec{r^N})}}$$

$$= \frac{\int d^3 \vec{r_1} \int d^3 \vec{r_2} u(r_{12}) \cdots \int d^3 \vec{r_N} e^{-\beta U(\vec{r^N})}}{\int d^3 \vec{r_1} \cdots \int d^3 \vec{r_N} e^{-\beta U(\vec{r^N})}}$$

$$= \int d^3 \vec{r_1} \int d^3 \vec{r_2} u(r_{12}) \frac{\rho^{(\frac{2}{N})}(\vec{r_1}, \vec{r_2})}{N(N-1)}$$

$$= \int d^3 \vec{r_1} \int d^3 \vec{r_2} u(r_{12}) \frac{\rho^2}{N(N-1)} g(\vec{r_1}, \vec{r_2})$$

Meaning,

$$\begin{split} \langle U(\vec{r}^N) \rangle &= \frac{N(N-1)}{2} \frac{\rho^2}{N(N-1)} \int d^3 \vec{r}_1 \int d^3 \vec{r}_2 u(r_{12}) g(\vec{r}_1, \vec{r}_2) \\ &= \frac{N(N-1)}{2} \frac{\rho^2 V}{N(N-1)} \int d^3 \vec{r} u(r) g(\vec{r}) \\ &= \frac{1}{2} N \rho \int d^3 \vec{r} u(r) g(r) \end{split}$$

This is an exact result but we don't know g(r). We can then ask ourselves what is the state equation ?

G.4.3 State equation

How to calculate the pressure ?

$$\langle p \rangle \equiv p = -\left(\frac{\partial F}{\partial V}\right) \Big|_{T,N}$$

 $Z = Z_{\text{ideal}} Z_{\text{configuation}}$

$$\langle p \rangle = k_B T \frac{\partial}{\partial V} \left[\ln(Z_{\text{ideal}}) + \ln(Z_{\text{configuration}}) \right]$$

= $\frac{Nk_B T}{V} + k_B T \frac{1}{Z_{\text{configuration}}} \left(\frac{\partial Z_{\text{configuration}}}{\partial V} \right) \Big|_{T,N}$

We can write it,

$$\beta p = \rho + \frac{1}{Z_{\text{configuration}}} \left(\frac{\partial Z_{\text{configuration}}}{\partial V} \right) \Big|_{T,N}$$

$$\left(\frac{\partial Z_{\text{configuration}}}{\partial V}\right)\Big|_{T,N} = \frac{\partial}{\partial V}\left(\frac{1}{V^N}\int \mathrm{d}^3\vec{r}^N e^{-\beta U(\vec{r}^N)}\right)$$

We want to work on that. What are the dependence on the temperature and the volume on that quantity? temperature is onto β , but the volume is onto $1/V^N$ and onto the integral (in an implicit manner). We want to perform a change of variables,

$$\vec{r_i} \longrightarrow \vec{u_i} = \frac{\vec{r_i}}{V^{1/3}}$$

$$\left(\frac{\partial Z_{\text{configuration}}}{\partial V}\right)\Big|_{T,N} = \frac{\partial}{\partial V}\left(\int_{v_0} \mathrm{d}^3 \vec{u}^N e^{-\beta U(V^{1/3}\vec{u}^N)}\right)$$

where v_0 is the renormalized volume of intergration.

$$\left(\frac{\partial Z_{\text{configuration}}}{\partial V}\right)\Big|_{T,N} = \int \mathrm{d}^{3}\vec{u}^{N} \left(-\beta \frac{\partial U}{\partial V}(V^{1/3}\vec{u}^{N})\right) e^{-\beta U(V^{1/3}\vec{u}^{N})}$$

Reminder : Let's assume f a field $f(\vec{r}) = f(x, y, z)$,

$$\mathrm{d}f = \frac{\partial f}{\partial x} \bigg|_{y,z} \mathrm{d}x + \frac{\partial f}{\partial y} \bigg|_{z,x} \mathrm{d}y + \frac{\partial f}{\partial z} \bigg|_{x,y} \mathrm{d}z = \vec{\nabla}f \cdot \mathrm{d}\vec{r}$$

$$\mathrm{d}U = \sum_{i=1}^{N} \vec{\nabla}_{\vec{r}_i} U(\vec{r}^N) \cdot \mathrm{d}\vec{r}_i$$

$$d\vec{r}_{i} = d(V^{1/3}\vec{u})$$

= $\frac{1}{3}V^{-2/3}\vec{u}_{i}dV$
= $\frac{1}{3}\frac{1}{V^{2/3}}\frac{V^{1/3}\vec{u}_{r}}{V^{1/3}}dV$
= $\frac{1}{3}\frac{1}{V}\vec{r}_{i}dV$

$$\frac{\partial U}{\partial V}(V^{1/3}\vec{u}_1,\cdots,V^{1/3}\vec{u}_N) = \frac{1}{3V}\sum_{i=1}^N \vec{\nabla}_{r_i}U(\vec{r}^N)\cdot\vec{r}_i$$

$$\begin{split} \left(\frac{\partial Z_{\text{configuration}}}{\partial V}\right) &= -\frac{1}{3V}\beta \int \mathrm{d}^{3}\vec{u}^{N}\sum_{i=1}^{N}\vec{\nabla}_{r}U(\vec{r}^{N})\vec{r}_{i}e^{-\beta U} \\ &= -\frac{1}{3V}\beta\frac{1}{V^{N}}\int \mathrm{d}^{3}\vec{r}^{N}\sum_{i=1}^{N}\vec{\nabla}_{\vec{r}_{i}}U\vec{r}_{i}e^{-\beta U} \end{split}$$

$$\begin{aligned} \frac{1}{Z_{\text{configuration}}} \left(\frac{\partial Z_{\text{configuration}}}{\partial V} \right) &= -\frac{1}{3V} \beta \frac{1}{Z_{\text{configuration}}} \frac{1}{V^N} \sum_{i=1}^N \int \mathrm{d}^3 r_N (\vec{r_i} \cdot \vec{\nabla}_{r_i} U) e^{-\beta U(\vec{r^N})v} \\ &= -\beta \frac{1}{3V} \sum_{i=1}^N \left\langle \vec{r_i} \vec{\nabla}_{\vec{r_i}} U(\vec{r^N}) \right\rangle \end{aligned}$$

$$-\vec{\nabla}_{\vec{r}_i} U(\vec{r}^N) = -\vec{\nabla}_{\vec{r}_i} \left(\sum_{\substack{j=1\\j\neq i}}^N u(r_{ij}) \right)$$

Meaning,

$$\vec{\nabla}_{\vec{r}_i} U(\vec{r}^N) = \sum_{\substack{j=1\\j\neq i}}^N \vec{f}_{ji}$$

where $\vec{f}_{ji} = -\vec{\nabla}_{\vec{r}_i} u(r_{ij})$ is the force exerted by particle j on particle i.

$$\begin{split} -\sum_{i=1}^{N} \left\langle \vec{r}_{i} \vec{\nabla}_{\vec{r}_{i}} U \right\rangle \right\rangle &= \sum_{i=1}^{N} \sum_{\substack{j=1\\j \neq i}}^{N} \vec{r}_{i} \cdot \vec{f}_{ji} \\ &= \frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1\\j \neq i}}^{N} \vec{r}_{i} \vec{f}_{ji} + \frac{1}{2} \sum_{j=1}^{N} \sum_{\substack{i=1\\i \neq j}}^{N} \vec{r}_{j} \vec{f}_{ij} \\ &= \frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1\\j \neq i}}^{N} \left(\vec{r}_{i} \vec{f}_{ji} + \vec{r}_{j} \vec{f}_{ij} \right) \end{split}$$

but we have $\vec{f}_{ji} = -\vec{f}_{ij}$ (Newton's reciprocal action principle)

$$\frac{1}{Z_{\text{configuration}}} \left(\frac{\partial Z_{\text{configuration}}}{\partial V}\right) = \frac{\beta}{3V} \sum_{i=1}^{N} \sum_{\substack{j=1\\j \neq i}}^{N} \frac{1}{2} \langle \vec{f}_{ij} \cdot (\vec{r}_j - \vec{r}_i) \rangle$$

$$\begin{split} \beta p &= \rho + \frac{\beta}{3V} \sum_{i=1}^{N} \sum_{\substack{j=1\\j\neq i}}^{N} \frac{1}{2} \langle \vec{f}_{ij} \cdot (\vec{r}_j - \vec{r}_i) \rangle \\ &= \rho + \frac{\beta}{6} \frac{N}{V} \sum_{\substack{j=1\\j\neq i}}^{N} \langle \vec{f}_{ij} \cdot (\vec{r}_j - \vec{r}_i) \rangle \\ &= \rho \left(1 + \frac{\beta}{6} \sum_{\substack{j=1\\j\neq i}}^{N} \langle \vec{f}_{ij} \cdot \vec{r}_{ij} \rangle \right) \end{split}$$

Which is the so-called the Kirchwood virial expression.

$$\beta p = \rho \left(1 - \frac{\beta}{6} \sum_{j=1}^{N} \left\langle \frac{\partial u(r_{ij})}{\partial r_{ij}} \cdot r_{ij} \right\rangle \right)$$

We used $u(\vec{r}_{ij}) = u(r_{ij})$.

$$\left\langle \frac{\partial u(r_{12})}{\partial r_{12}} \cdot r_{12} \right\rangle = \int \mathrm{d}^3 \vec{r_1} \int \mathrm{d}^3 \vec{r_2} \left(\frac{\partial u(r_{12})}{\partial r_{12}} \right) r_{12} \underbrace{\frac{\int \mathrm{d}^3 \vec{r_3} \cdots \int \mathrm{d}^3 \vec{r_N} e^{-\beta U}}{\int \mathrm{d}^3 \vec{r'N} e^{-\beta U}}}_{\equiv \rho^2 g(r_{12})/N(N-1)}$$

$$= \int \mathrm{d}^3 \vec{r_1} \int \mathrm{d}^3 \vec{r_2} \left(\frac{\partial u(r_{12})}{\partial r_{12}} \right) r_{12} g(r_{12}) \frac{\rho^2}{N(N-1)}$$

$$= \frac{V}{N(N-1)} \rho^2 \int \mathrm{d}^3 \vec{r} r \frac{\partial u}{\partial r} g(r)$$

$$\beta p = \rho \left(1 - \frac{1}{6} \frac{1}{k_B T} \rho \int d^3 \vec{r} \vec{r} \frac{\partial u}{\partial r} g(r) \right)$$

We can't do more because we need $g(r) = e^{-\beta W(r)}$ but we don't know it.

$$g(r) = e^{-\beta W(r)}$$

For a sufficiently diluted fluid it's $W(r) \sim u(r)$,

$$g(r) \simeq e^{-\beta U(r)}$$

Meaning,

$$\beta p \simeq \rho \left(1 - \frac{1}{6} \frac{1}{k_B T} \rho \int_0^{+\infty} \mathrm{d}r 4\pi r^2 r \frac{\partial u}{\partial r} e^{-\beta u} \right)$$
$$= \rho - \rho^2 \underbrace{\left(\frac{1}{6} \frac{1}{k_B T} \int_0^{+\infty} \mathrm{d}r 4\pi r^3 \frac{\mathrm{d}u}{\mathrm{d}r} e^{-\beta u} \right)}_{\text{only depends on temperature } \equiv -B_2(T)} + \cdots$$
$$= \rho + B_2(T)\rho^2 + \cdots$$

We can write the Viriel expansion,

$$\beta p \equiv \sum_{n=1}^{+\infty} B_n(T) \rho^n$$

$$B_1(T) = 1$$

$$B_2(T) = \frac{1}{2} \int_v d^3 \vec{r} \left(1 - e^{-\beta U(r)} \right) = 2\pi \int_0^{+\infty} dr r^2 \left(1 - e^{-\beta U(r)} \right)$$

G.4.4 Applications

(a) Hard-sphere potential,



The function $f(r) \equiv 1 - e^{-\beta U(r)}$ is the Meyer function

$$B_2(T) = 2\pi \int_0^\sigma r^2 \mathrm{d}r = \frac{2}{3}\pi\sigma^3$$

 B_2 is not depending on T on that case.

(b) Square well potential,



$$B_2(T) = \frac{2\pi}{3}\sigma^3 \left[1 - \left(e^{+\beta u_0} - 1 \right) \left(\lambda^3 - 1 \right) \right]$$