Statistical Mechanics

Notes from Prof. E. Ercolessi's Lectures

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Contents

Chapter 1

Prerequisites

1.1　Prerequisites of Thermodynamics

In thermodynamics there are **extensive** quantities, that grows with the system size, and **intensive** quantities, which does not. **Conjugation** between them, means *tuning* intensive variables to make extensive one change.

　　Note that we always refer to quasi-static transformations

1.1.1　The laws of thermodynamics

0th Law Equilibrium (empirical) temperature.

　　We call:　　$\mathcal{M}_A$: space of state of A　　$\mathcal{M}_B$: space of state of B.
The total phase space is $\mathcal{M}_A \times \mathcal{M}_B = \{(a, b)\}$, where (a, b) denotes all possible couples.

　　At equilibrium, not all couples are possible. At equilibrium:

$$F_{AB}(a, b) = 0 \iff (a, b)$$

so there is a constraint. This is an equivalence relation:

$$A \sim A \qquad A \sim B \iff B \sim A \qquad A \sim B \ \& \ B \sim C \implies A \sim C$$

$$F_{AB}(a, b) = f_A(a) - f_B(b) = 0$$

This condition define the *empirical temperature* $t_A = t_B$ at equilibrium.

　　The transitive property allow us to choose anything as a measure (e.g. thermometer).

1st Law Internal energy E

　　There is an internal energy, which can change in different ways, but it always conserved (*conservation of energy*).

$$dE = \delta Q - \delta \mathcal{L} + \mu dN$$

where δQ is heat, $\delta \mathcal{L}$ is work, N is number of particles and μ is the chemical potential: the energy needed to add/remove a particle.

　　d means that $\oint dE = 0$ on any cycle, so the integral does not depend on the path. δ no, so $\delta Q, \delta \mathcal{L}$ is not necessary 0.

　　E.g. Classical fluids:
$\delta \mathcal{L} = pdV$: the work derive from the compression/expansion. So the variation of the energy: $dE = \delta Q - pdV + \mu dN$.

2nd Law Entropy S

In a reversible process:

$$\oint \frac{\delta Q}{T} = 0 \qquad \text{in general:} \quad \frac{deltaQ}{T} = dS$$

Putting the two laws together,

$$\oint \frac{\delta Q}{T} \leq 0 \implies dS \geq \frac{\delta Q}{T} \quad (= 0 \text{ for reversible})$$

So, **a system evolves towards the maximum of entropy**

3rd Law For any isothermal process, $\Delta S \xrightarrow[T \to 0]{} 0$

1.1.2 Thermodynamic potentials (for reversible processes)

Let's see the relation between these quantities:
  Internal energy $dE = TdS - pdV + \mu dN$
The internal energy can be changed by changing S, V, N so $E = E(S, V, N)$ and:

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

All terms in couple are conjugate variables: $T \leftrightarrow S, p \leftrightarrow V, \mu \leftrightarrow N$
E, S, V, N are extensive variables, so if

$$\begin{cases} N \to \lambda N \\ V \to \lambda V \\ S \to \lambda S \end{cases} \implies E = \lambda E$$

where λ is a scaling factor.
  So:

$$\boxed{E(\lambda S, \lambda V, \lambda N) = \lambda E(S, V, N)}$$

Homogeneous function of degree 1 (linear)
  That requires: $E(S, V, N) = TS - pV + \mu N \qquad dE = TdS - pdV + \mu dN$

Usually it's easier to work with T then S (there are no experiment where you can tune the entropy S), so thermodynamic potentials are introduced. These are other function which are more convenient to work with:

- Internal energy:
  $$E(S, V, N) = TS - pV + \mu N \qquad\qquad dE = TdS - pdV + \mu dN$$

- Helmotz free energy:
$$F(T,V,N) = E - TS = -pV + \mu N \qquad\qquad dF = -SdT - pdV + \mu dN$$

- Entalpy:
$$H(S,p,N) = E + pV = ST + \mu N \qquad\qquad dH = TdS + Vdp + \mu dN$$

- Gibbs free energy:
$$G(T,p,V) = E - TS + pV = \mu N \qquad\qquad dG = -SdT + Vdp + \mu dN$$

- Granpotential:
$$\Omega(T,V,\mu) = E - TS - \mu N = -pV \qquad\qquad d\Omega = -SdT - pdV - Nd\mu$$

1.1.3   Thermodynamic limit

$N,V \to \infty$ with $n = N/V$ fixed In this limit, all the thermodynamic potential diverges, so (e.g) E has no meaning. What we can calculate is the ratio with the number of particle (e.g E/N : internal energy for particle). Things do not change because they depend on N, except for Ω which doesn't.

$$e \equiv \frac{E}{N} \qquad s \equiv \frac{S}{N} \qquad v \equiv \frac{V}{N} \qquad f \equiv \frac{F}{N} \qquad g \equiv \frac{G}{N} \qquad \omega \equiv \frac{\Omega}{N}$$

1.1.4   Equation of state - μ-n relation

From the granpotential, one can derive $p = -\frac{\partial \Omega}{\partial V}$, which, written for a particular model (e.g. classical gas) gives the *equation of state* of the system/model.

Also, the μ-n relation is very important: $N = -\frac{\partial \Omega}{\partial \mu}$

1.1.5   Variational principles

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Suppose we set up an experiment in which S,V,N are constant. Then $dE = 0$, which implies that the system evolves towards the minimum of energy E.

The same happen if T,V,N are constant, in which case $dF = 0$, so the system evolves towards the minimum of Helmotz free energy. Etc... .

So the problem becomes a problem of minimization.

We'll see that the minimization of F and Ω are the most important.

For reversible processes, $dF = -SdT + pdV + \mu dN$, from which:

$$S = -\frac{\partial F}{\partial T}\bigg|_{V,N} \qquad p = -\frac{\partial F}{\partial V}\bigg|_{T,N} \qquad \mu = \frac{\partial F}{\partial T}\bigg|_{T,V}$$

The minimum is found with the hessian matrix:

$$\text{Hess}(F) = \begin{pmatrix} \dfrac{\partial^2 F}{\partial T^2} & \dfrac{\partial^2 F}{\partial T \partial V} & \dfrac{\partial^2 F}{\partial T \partial N} \\[2mm] \dfrac{\partial^2 F}{\partial V \partial T} & \dfrac{\partial^2 F}{\partial V^2} & \dfrac{\partial^2 F}{\partial V \partial N} \\[2mm] \dfrac{\partial^2 F}{\partial N \partial T} & \dfrac{\partial^2 F}{\partial N \partial V} & \dfrac{\partial^2 F}{\partial N^2} \end{pmatrix}$$

In fact, the condition to have a minimum is that all the 3 eigenvalues of the hessian matrix should be > 0.

That is the same as saying that going in every direction the "gradient" increase

We won't prove this, but because of the way $F = F(T, V, N)$, it us sufficient that

$$\frac{\partial^2 F}{\partial T^2} < 0 \qquad \frac{\partial^2 F}{\partial V^2} > 0 \qquad \frac{\partial^2 F}{\partial T \partial N} \leq 0$$

The same can be done changing the variables and it also works with other different from F (e.g. E etc.)

1.2   Prerequisites of Classical Mechanics

To represent a classical system we need:

1) Coordinates: position q, momenta p.
For 1 particle. If a particle lives in $\mathbb{R}^d \implies \vec{q} \in \mathbb{R}^d \quad \vec{p} \in \mathbb{R}^d$.
So the phase space $\mathcal{M}_1$ is $\{(q, p)\} \in \mathbb{R}^d \times R^d = 2\mathbb{R}^d$

For N particles living in $\mathbb{R}^d$, the phase space is:

$$\mathcal{M}_N = \{(q_1, p_1, q_2, p_2, \ldots, q_n, p_N)\} = \{(q_i, p_i) \quad i = 1, \ldots, N\} = \mathbb{R}^{2dN}$$

2) Observable: An observable is given by a smooth real function from the phase space to a real number.

$$f(q_i, p_i) : \mathcal{M}_N \to \mathbb{R}$$

e.g. $\mathcal{H}$, angular momentum, kinetic energy T are all observables

3) Measure: (ideal, without errors) A measure of an observable on a state $(\bar{q}_i \bar{p}_i)$ is given by the value of the function at that particular point: $f(\bar{q}_1, \bar{p}_1)$

4) Evolution: The evolution of a system is fixed by a special observable, called Hamiltonian $\mathcal{H}$, through Hamilton's *equation of motion*:

$$\dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i} \qquad \dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i} \qquad \text{(they give Newton's law)} \tag{1.1}$$

In general, $\mathcal{H} = \mathcal{H}(q_i, p_i, t)$, but we only study the case where the hamiltonian is time-independent.

The equation 1.1 are equation of the first order in t $(q_i(t)p_i(t))$, so the solution is uniquely fixed by the initial conditions $(\bar{q}_i, \bar{p}_i)$. Because of that we have two theorems:

Conservation of volumes (even id the shape is changed). Since each point of the phase space is a state, the volume counts the number of states. In other words, giving a volume is the same as giving a subset.

Conservation of energy. If $\mathcal{H}$ does not depend explicitly on time, the hamiltonian is constant for each curve of motion:

$$E = \mathcal{H}(q_i(t), p_i(t)) = \mathcal{H}(\bar{q}_i, \bar{p}_i) = \mathcal{H}(q_i(t = 0), p_i(t = 0))$$

1.2.1   On the notion of "state"

We will call one of these states $(q_i(t), p_i(t))$ a **microstate** at time t. Fixing an initial microstate, completely determine the trajectory in phase space, backward and forward in time.

If the initial conditions are changed a little, allowing the system to "choose" them between a given set, we enter the field of *complex systems*

In general, there is a (huge) number of possible microstates corresponding to the same macroscopic set of thermodynamic variables (the **macrostate**).

In order to study this, we can think of having an **ensemble**: a large number of copies of the system, all with the same Macroscopic State but with different microscopic realizations.

1.2.2 Probability distribution

Given an ensemble, in the limit in which the number of copies becomes very large, we can construct the probability with which, at a fixed time, a given microstate $\{q_i(t), p_i(t)\}$ appears, thus recovering a **probability density distribution** on $\mathcal{M}_N$:

$$\rho(q_i(t), p_i(t)) \qquad \mathcal{M}_N \to \mathbb{R}^+(0, 1)$$

Which is:

- Positive: $\quad \rho(p_i(t), p_i(t)) \geq 0$

- Normalized:

$$\int_{\mathcal{M}_N} \rho(q_i, p_i) \left(\prod_{I=1}^N dq_i dp_i \right) = 1$$

  (implicit vector used: dq_i, dp_i should be $d^3\vec{q}_i, d^3\vec{p}_i$)

- For a subset $U \subset \mathcal{M}_N$, the probability to find the system in the subset U is: $\int_U \rho(q_i, p_i) d\Gamma$

To have an a-dimensional quantity, we replace:

$$d\Gamma \equiv \prod_i dq_i dp_i \qquad \text{with} \quad d\Omega \equiv \frac{\prod_i dq_i dp_i}{h}$$

where h is a constant with the dimension of an action (here we don't say anything about it, it's just the dimension of a little state of sides dq_i, dp_i but in quantum mechanics, it will be Plank's constant).

1.2.3 Liouville's theorem

The conservation of volumes is the Liouville's theorem.
Given a region Ω_0 in which there is some density probability $\rho(q_i, p_i) \in \Omega_0$, there is a density current $\vec{J}$ of particles moving out of Ω_0:

$$\vec{J} = \rho\vec{v} \qquad \text{where } \vec{v} = (\dot{q}_i, \dot{p}_i) \text{ is a velocity in phase space}$$

If there is a conservation of the total probability density: $\frac{\partial \rho}{\partial t} + \vec{\nabla}(\vec{J}) = 0$ That means

$$\frac{d\rho}{dt} = \frac{\partial t}{\partial h} ot + \vec{\nabla}(\rho \vec{v}) = 0$$

which is the Liouville's theorem

We can also use the Poisson's bracket's to write $\vec{\nabla}(\rho \vec{v}) = \{\rho, \mathcal{H}\}$, reminding that $\{f, g\} = \sum_i \left(\frac{\partial f}{\partial q_i} \frac{\partial g}{\partial p_i} - \frac{\partial g}{\partial q_i} \frac{\partial f}{\partial p_i} \right)$

DEFINITION: A system is called **stationary** iff $\frac{\partial \rho}{\partial t} = 0$. Stationarity is a necessary condition for **equilibrium**: $\frac{d\rho}{dt} = 0$, which is what we want to study. From the previous condition follows that at equilibrium: $\{\rho, \mathcal{H}\} = 0$ which can happen if

1. $\rho = const$

2. $\rho = \rho(\mathcal{H}(q_i, p_i))$

giving, respectively, the cases of the microcanonical and canonical/grancanonical distributions.

DEFINITION: Given an observable f, we can define its:

$$\textbf{average} \quad \langle f \rangle_\rho = \int_{\mathcal{M}_N} f(q_i, p_i) \rho(q_i, p_i) \left(\prod_{i=1}^{N} \frac{dq_i dp_i}{h} \right)$$

$$\textbf{standard deviation} \quad (\Delta t)^2 = \langle f^2 \rangle_\rho - (\langle f \rangle_\rho)^2$$

The subscript ρ, indicates that we need to have defined a probability density distribution, to evaluate these two.

1.2.4 Time-Independent Hamiltonians

For time-independent hamiltonians, the energy is conserved. That means that all the trajectories will be on a $(2M-1)$hypersurface in the phase space (where M is the total number of degree of freedom). The whole space can thus be foliated into different sheets according to different energies like in the figure.

So we can compute every integrals integrating firstly over an hypersurface of constant energy and then over all the possible energies:

$$\int (\dots) \prod dq_i dp_i = \int_0^\infty d\mathcal{H} \int_{\mathcal{H}} ds_{\mathcal{H}}(\dots)$$
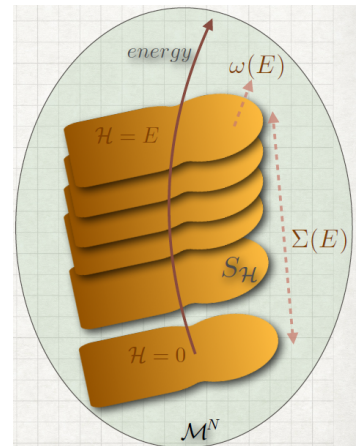
DEFINITION: Volume ($\sim$ number of state) in phase space with energy lower than a certain value ($0 \leq \mathcal{H}(q_i, p_i) \leq E$):

$$\Sigma(E) \equiv \int_{0 \leq \mathcal{H} \leq E} \prod_i dq_i dp_i = \int_0^E d\mathcal{H} \int_{S_\mathcal{H}} dS_\mathcal{H} = \int_0^E d\mathcal{H} \omega(\mathcal{H})$$

DEFINITION: The density of state is the "area" of the hypersurface $S_\mathcal{H}$

$$\omega(E) \equiv \int_{S_\mathcal{H}} dS_\mathcal{H} = \frac{\partial \Sigma}{\partial E}$$

Σ, ω aren't property of the space, but they depends on $\mathcal{H}$ because the surfaces depend on $\mathcal{H}$.

In the case of time-independent hamiltonians:

$$\langle f \rangle_E \equiv \frac{1}{\omega(E)} \int_{S_E} dS_E f$$

$$\text{time average} \qquad \langle f \rangle_\infty \equiv \lim_{T \to \infty} \frac{1}{T} \int_{t_0}^{t_0+T} dt f(q_i(t), p_i(t))$$

the latter exists for almost all initial conditions and it is independent of t_0

DEFINITION: A system is said to be **ergodic** over the surface S_E iff almost all points $(q_i, p_i) \in S_E$ pass through a neighbourhood $U \in S_E$ during the evolution. In other words, starting from any point, if you let the system evolve for a long time, every region will be explored.

THEOREM: A system is ergodic iff, for almost all initial points: $\langle f \rangle_\infty = \langle f \rangle_E$
This tell that the time spent on a region is proportional to the area of that region.

In the following we will consider only ergodic systems.

Chapter 2

Classical Statistical Mechanics

2.1   Microcanonical Ensemble

Recap:

$$\text{Phase space} \quad \mathcal{M}_N = \{(q_i, p_i) \quad i = 1 \ldots N\}$$
$$\text{Hamiltonian} \quad \mathcal{H}(q_i, p_i) : \mathcal{M}_N \to \mathbb{R}$$

The microcanonical ensemble represents a closed system that doesn't exchange either energy or matter with the environment, so in which the energy E, the number of particles N and the volume V are fixed. The evolution occurs on the hypersurface $S_E \subset \mathcal{M}_N \quad \mathcal{H}(q_i, p_i) = E$

To describe the system we need the probability distribution of the microcanonical ensemble. We assume (a priori) a uniform probability:

DEFINITION: The probability distribution of the microcanonical ensemble is:

$$\rho_{mc}(q_i, p_i) = C\delta(\mathcal{H}(q_i, p_i) - E)$$

where C is a constant we can obtain from the normalization:

$$1 = \int_{\mathcal{M}_N} C\delta(\mathcal{H} - E) = \int_{S_E} C dS_E = C\omega(E) \implies C = \frac{1}{\omega(E)}$$

(reminding that $\omega(E)$ is the area of $S_{\mathcal{H}} = E$). So:

$$\rho_{mc}(q_i, p_i) = \frac{1}{\omega(E)}\delta(\mathcal{H} - E) \tag{2.1}$$

Working with S is difficult (e.g. it creates some problems when integrating), so we give an operative definition. We can write the volume of a phase space:

$$\Sigma(E) = \int_{0 \leq \mathcal{H}(q_i, p_i) \leq E} d\Gamma = \int_0^E d\mathcal{H}\omega(\mathcal{H})$$

from which,

$$\Gamma(E) = \int_{E \leq \mathcal{H} \leq E + \Delta E} d\Gamma = \int_E^{E+\Delta E} \omega(E')dE' \stackrel{(if \ \Delta E \ small)}{\simeq} \omega(E)\Delta E$$

So we can see that the microcanonical probability density function (2.1) is the limit for $\Delta E \to 0$ of:

$$\rho_{mc}(q_i, p_i) = \begin{cases} \dfrac{1}{\Gamma(E)} & E \leq \mathcal{H} \leq E + \Delta E \\ 0 & \text{otherwise} \end{cases}$$

2.1.1 Microcanonical entropy S_{mc}

We will see that it coincide with the thermodynamic entropy.

$$S_{mc}(E, V, N) \equiv k_B \log \omega(E)$$

1) We could actually define the entropy in three different ways:

1. $S_{mc}^{(1)} = k_B \log \omega(E)$

2. $S_{mc}^{(2)} = k_B \log \Gamma(E)$

3. $S_{mc}^{(3)} = k_B \log \Sigma(E)$

which in general are different quantities. However in the thermodynamic limit ($N, V \to \infty$, with $n = N/V \, const$), they represent the same quantity:

$$s_{mc} = \frac{S_{mc}^{(1)}}{N} = \frac{S_{mc}^{(2)}}{N} = \frac{S_{mc}^{(3)}}{N}$$

So while doing calculations, we can use one of the three.

2) Entropy should be extensive, so it should be additive: $S_{mc}^A + S_{mc}^B = S_{mc}^{A \cup B}$

PROOF: To prove it, let's call the phase space of the two systems: $\mathcal{M}_1, \mathcal{M}_2$. So $\mathcal{M}_{AB} = \mathcal{M}_1 \times \mathcal{M}_2$

$$d\Gamma_1 = \prod_{i=1}^{N_1} dq_i dp_i \qquad d\Gamma_2 = \prod_{j=1}^{N_2} dq_i dp_i \qquad \Longrightarrow \qquad d\Gamma = d\Gamma_1 d\Gamma_2$$

If $\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 \implies E = E_1 + E_2 + E_{int}$.
Here we make an assumption: there could be interactions in the wall that divides the two systems, however, since E_1 and E_2 both scale with the volume (L^3) while E_{int} scale like the area of interaction (L^2), we neglect the interaction term, because it disappears in the thermodynamic limit.
We can foliate the phase space with surfaces each at different energy

$$\omega(E) = \int_{\mathcal{M}_1 \times \mathcal{M}_2} d\Gamma \delta(\mathcal{H} - E)$$

$$= \left(\int_0^\infty d\mathcal{H}_1 \int dS_{\mathcal{H}_1} \right) \left(\int_0^\infty d\mathcal{H}_2 \int dS_{\mathcal{H}_2} \right) \delta(\mathcal{H}_1 + \mathcal{H}_2 - E)$$

$$= \int d\mathcal{H}_1 \int d\mathcal{H}_2 \delta(\mathcal{H}_1 + \mathcal{H}_2 - E) \int_{\mathcal{H}_1 = E_1} ds_{\mathcal{H}_1} \int_{\mathcal{H}_2 = E_2} dS_{\mathcal{H}_2}$$

$$= \int d\mathcal{H}_1 \int d\mathcal{H}_2 \delta(\mathcal{H}_1 + \mathcal{H}_2 - E) \, \omega_1(E_1) \, \omega_2(E_2)$$

$$= \int_0^E dE_1 \quad \omega_1(E_1) \, \omega_2(E_2 = E - E_1)$$

The integrand is ≥ 0 and defined in a compact interval $[0, E)$, so it has a maximum. Let $E_1^*, E_2^* = E - E_1^*$ be the value of energy for which the integrand is maximum. So:

$$\omega(E) \leq \left(\int_0^E dE_1 \right) \omega_1(E_1^*) \, \omega_2(E_2^*) \leq E_1^* \, \omega_1(E_1^*) \, \omega_2(E_2^*)$$

and for ΔE small enough:

$$\Delta E \, \omega_1(E_1^*) \, \omega_2(E_2^*) \leq \Delta E \, \omega(E) \leq E_1^* \, \omega_1(E_1^*) \, \omega_2(E_2^*) \, \Delta E$$

Reminding that $\Gamma(E) \sim \omega(E)\Delta(E)$:

$$\Gamma_1(E_1^*)\Gamma_2(E_2^*) \leq \Gamma(E) \leq \frac{E}{\Delta E}\Gamma_1(E_1^*)\Gamma_2(E_2^*)$$

$$\log\Gamma_1 + \log\Gamma_2 \leq \log\Gamma \leq \log\Gamma_1 + \log\Gamma_2 + \log\frac{E}{\Delta E} \qquad (\times k_B)$$

$$S_{mc}^1 + S_{mc}^2 \leq S_{mc} \leq S_{mc}^1 + S_{mc}^2 + k_B \log\frac{E}{\Delta E}$$

In the thermodynamic limit, dividing everything by N and letting $N \to \infty$, the last term approaches zero and can be neglected. So we find:

$$S_{mc}(E) = S_{mc}^1(E_1^*) + S_{mc}^2(E_2^* = E - E_1^*)$$

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3) In the thermodynamic limit, this entropy coincides with the thermodynamic entropy: $s_{mc} = s_{th}$

PROOF: At equilibrium, $E = E_1^* + E_2^*$, where $\omega_1(E_1) \, \omega_2(E - E_1)$ is maximized.

$$\Gamma(E_1^*)\Gamma(E_2^*) \rightarrow d\left(\Gamma(E) = \Gamma_1(E_1)\Gamma_2(E_2)\right)\big|_{E_1=E_1^*, E_2=E_2^*} = 0$$

$$\left(\frac{\partial \Gamma_1}{\partial E_1}dE_1\right)\Gamma_2 + \Gamma_1\left(\frac{\partial \Gamma_2}{\partial E_2}dE_2\right)\bigg|_{E_1^*, E_2^*} = 0$$

$$(dE_2 \rightarrow dE_1) \qquad \frac{\Gamma_1}{\Gamma_1\Gamma_2}\left(\frac{\partial \Gamma_1}{\partial E_1}\Gamma_2\bigg|_{E_1^*, E_2^*} = \Gamma_1\frac{\partial \Gamma_2}{\partial E_2}\bigg|_{E_1^*, E_2^*}\right)$$

$$\frac{1}{\Gamma_1}\frac{\partial \Gamma_1}{\partial E_1}\bigg|_{E_1^*} = \frac{1}{\Gamma_2}\frac{\partial \Gamma_2}{\partial E_2}\bigg|_{E_2^*}$$

$$\frac{\partial}{\partial E_1}k_B\log\Gamma_1(E_1)\bigg|_{E_1^*} = \frac{\partial}{\partial E_2}k_B\log\Gamma_2(E_2)\bigg|_{E_2^*}$$

$$\frac{\partial}{\partial E_1}S_{mc}^1\bigg|_{E_1^*} = \frac{\partial}{\partial E_2}S_{mc}^2\bigg|_{E_2^*}$$

since this is calculated at E_1^*, E_2^*, it is calculated at the equilibrium (N, V fixed).

The same thing happens in thermodynamic: if $T_1 = T_2$,

$$dE = TdS_{th} - pdV + \mu dN \implies \frac{1}{T} = \frac{\partial S_{th}}{\partial E}\bigg|_{V,N}$$

So the equilibrium in thermodynamics requires this condition:

$$\boxed{\frac{\partial S_{th}^1}{\partial E_1} = \frac{\partial S_{th}^2}{\partial E_2}}$$

So we find that:

$$S_{th}(E, V, N) = S_{mc}(E, V, N) = k_B\log\Gamma(E)$$

(equal and not only proportional, because k_B is the constant appositely chosen to make them equal)

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4) We saw that

$$\langle f\rangle_{mc} = \int_{\mathcal{M}_N}\left(\prod dp_i dq_i\right)f(q_i, p_i)\rho_{mc}(q_i, p_i)$$

We can now prove the Universal Boltzmann's formula (works in the TD-limit):

$$S_mc = -k_B\langle\log\rho_mc\rangle_{mc}$$

PROOF: Working from the Universal Boltzmann's formula, we can arrive to the definition of entropy

$$-k_B \left\langle \log \rho_m c \right\rangle_{mc} = -k_B \int_{\mathcal{M}_N} d\Gamma (\log \rho_{mc}) \rho_{mc} \qquad \rho_{mc} = \frac{1}{\omega(E)} \delta(\mathcal{H} - E) \implies \rho_{mc}|_{S_c} = \frac{1}{\omega(E)}$$

$$= -k_B \int_{S_E} \frac{1}{\omega(E)} (-\log \omega(E))$$

$$= k_B \frac{1}{\omega(E)} \log \omega(E) \int_S dS_E$$

$$= k_B \log \omega(E) = S_{mc}$$

So we have proved that, in the TD-limit:

$$S_{mc} = k_B \log \Sigma = k_B \log \Gamma = k_B \log \omega = -k_B \left\langle \log \rho_{mc} \right\rangle_{mc}$$

2.1.2   One example/exercise (1.1, 1.2): Perfect gas

We consider a gas of N non-relativistic and non-interacting monoatomic particles in 3D, confined in a volume V.

$$\mathcal{M}_N = \{\{(\vec{q}_i, \vec{p}_i)\}_{i=1}^N : \vec{q}_i \in V, \vec{p}_i \in \mathbb{R}^3\} \qquad \mathcal{H}(q_i, p_i) = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}$$

The volume of states is:

$$\Sigma(E) = \int \prod_{i=1}^N \frac{d^3 q_i d^3 p_i}{h^3}$$

where the integral is calculated on:

$$0 \le \mathcal{H}(q_i, p_i) \le E \qquad 0 \le \sum_{i=1}^N \vec{p}_i^2 \le 2mE \qquad 0 \le \sum_{i=1}^N \left(p_i^{(x)^2} + p_i^{(y)^2} + p_i^{(z)^2} \right) \le 2mE$$

So it is the volume of a $3N$-dimensional sphere of radius $\sqrt{2mE}$. So:

$$\Sigma(E) = \frac{1}{h^{3N}} \left(\int_V d^3 q_i \right)^N \int_{0 \le \sum \vec{p}_i^2 \le 2mE} \prod_i \vec{p}_i^2$$

$$= \frac{V^N}{h^{3N}} \Omega_{3N}(R = \sqrt{2mE})$$

$$= \frac{V^N}{h^{3N}} \frac{2\pi^{3N/2}}{(3N)\Gamma(3N/2)} (R = \sqrt{2mE})^{3N}$$

where $\Gamma(x) = \int_0^\infty dt \; t^{x-1} e^{-t}$ is the Euler's Γ-function, which can be seen as a generalization of the factorial. In fact, one can prove (integrating by parts) that

$\Gamma(n) = (n-1)! \qquad \Gamma(x+1) = x\Gamma(x) \qquad \log\Gamma(x) \simeq x\log x - x$

The previous formula is composed by an angular part (the Euler's Γ-function) and a radial part (which scale with $3N$). So finally we have that:

$$\Sigma(E) = \frac{2}{3}\left(\frac{V}{h^3}\right)^N \frac{(2\pi mE)^{3N/2}}{N\Gamma(3N/2)}$$

Calculating the derivative, one can also get the density of the states and $d\Gamma$:

$$\omega(E) = \frac{\partial\Sigma}{\partial E} = \frac{3N}{2E}\Sigma(E) \qquad \Gamma(E) = \omega(E)\Delta E = \frac{3N}{2E}\Sigma(E)\Delta E$$

and we can check that in the TD-limit, the different ways of defining the entropy are the same:

$$\frac{\log\Gamma}{N} = \frac{\log\omega}{N} + \frac{\log\cancel{\Delta E}}{\cancel{N}} = \frac{\log\Sigma}{N} + \frac{\log\cancel{\Delta E}}{\cancel{N}} + \frac{\log\cancel{\frac{3N}{2E}}}{\cancel{N}}$$

where the terms can be cancelled in the limit of $N \to \infty$ (for the last one, since $E \sim N$, the ratio $3N/2E$ is constant).

We can then find the entropy for a perfect gas (supposing distinguishable particle)

$S_{dis} = k_B \log\Sigma(E)$

$$= k_B\left[N\log\left(V\left(\frac{2\pi mE}{h^2}\right)^{3/2}\right) - \cancel{\log N} - \log\Gamma\left(\frac{3N}{2}\right) + \cancel{\log\frac{2}{3}}\right] \qquad (TD - limit)$$

$$= k_B\left[N\log\left(V\left(\frac{2\pi mE}{h^2}\right)^{3/2}\right) - \frac{3N}{2}\log\frac{3N}{2} + \frac{3N}{2}\right] \qquad (Stirling)$$

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

This formula has a problem: it is not extensive: if $N \to 2N$ and $V \to 2V$ we expect $S \to 2S$, but we actually have $S \to 2S + N\log 2$.

The solution is to consider indistinguishable particles. That means that the states:
$(q_1, p_1, q_2, p_2, \dots, q_n, p_n) \qquad (q_2, p_2, q_1, p_1, \dots, q_n, p_n)$
which are different points in the phase space $\mathcal{M}_N$, should be counted only once. We have $N!$ of this equivalent vectors, so $\Sigma(E) \to \Sigma(E)/N!$, and we get:

$$S_{ind} = k_B \log \frac{\Sigma(E)}{N!}$$
$$= k_B \left[\log \Sigma(E) - \log N! \right]$$
$$= k_B \left[\frac{5}{2} N + N \log \left(\frac{V}{N} \left(\frac{4\pi mE}{3Nh^2} \right)^{3/2} \right) \right] \tag{2.2}$$

which is an extensive quantity.

So for an ideal gas in 3D microcanonical we have:

$$d\Omega = \prod_{i=1}^{N} \frac{d^d q_i d^d p_i}{h^d} \qquad \text{distinguishable particles}$$

$$d\Omega = \frac{1}{N!} \prod_{i=1}^{N} \frac{d^d q_i d^d p_i}{h^d} \qquad \text{indistinguishable particles}$$

From the entropy, knowing that $TdS = dE + pdV - \mu dN$, we can get:

- $$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_{V,N} = [\dots] = \frac{3}{2} \frac{Nk_B}{E}$$

  $$\boxed{E = \frac{3}{2} Nk_B T} \qquad \text{Thermal energy of an ideal gas} \tag{2.3}$$

  (where the 3 stands for the number of dimension)

- $$\frac{p}{T} = \left. \frac{\partial S}{\partial V} \right|_{E,N} = \frac{Nk_B}{V} \implies \boxed{pV = k_B NT}$$

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

Substituting 2.3 in 2.2 we get:

$$S = \frac{5}{2} Nk_B + k_B N \log \left[\frac{V}{N} \left(\frac{2\pi mk_B T}{h^2} \right)^{3/2} \right] = \frac{5}{2} Nk_B + 3Nk_B \log \left(\frac{d}{\lambda_T} \right)$$

where we have defined the *thermal wavelength* λ_T and the average inter-particle distance d as:

$$\lambda_T \equiv \sqrt{\frac{h^2}{2\pi mk_B T}} \qquad v = \frac{V}{N} = \frac{1}{n} \simeq d^3$$

These formulas have a problem: it might happen that for low temperature $T, d \underset{\sim}{<} \lambda_T, S < 0$!. So something break down when $d \sim \lambda_T$, but there will be a quantum mechanical solution. However, what we have found is true until $d > \lambda_T$, otherwise we have interaction effects.

2.2   Canonical Ensemble

$$\begin{aligned}\text{System} \quad & \mathcal{S} = \{(q_i^{(1)}, p_i^{(1)})\}, \quad V_1 \ll V_2, \quad N_1 \ll N_2 \\ \text{Environment} \quad & \varepsilon = \{(q_i^{(2)}, p_i^{(2)})\}, \quad V_2, N_2\end{aligned}$$

We have a system and an environment with a wall in between them that permits heat and energy to pass but not particles. Energy is exchanged, but the total energy $E \equiv E_1 + E_2 = const.$ (with $E_1 \ll E$), so that the universe $\mathcal{U} = \mathcal{S} \cup \varepsilon$ is microcanonical. The phase space is $\mathcal{M}_{\mathcal{U}} = \mathcal{M}_1 \times \mathcal{M}_2$ and:

$$d\Omega_{\mathcal{U}} = d\Omega_1 d\Omega_2 \propto \left(\prod_{i=1}^{N_1} dq_i^{(1)} dp_i^{(1)}\right) \left(\prod_{j=1}^{N_2} dq_j^{(2)} dp_j^{(2)}\right)$$

$$\rho_{mc}\left(q_i^{(1)}, p_i^{(1)}; q_j^{(2)}, p_j^{(2)}\right) = \frac{\delta(\mathcal{H}_1 + \mathcal{H}_2 - E)}{\omega(E)}$$

The whole universe is described with a microcanonical probability distribution function, and the (canonical) probability distribution describing the system only is obtained by integrating out the environment d.o.f. So:

$$\rho_c^{(\mathcal{S})}\left(q_i^{(1)}, p_i^{(1)}\right) \propto \int \rho_{mc}(\ ) d\Omega_2 \qquad \delta \text{ is selecting only the surface with } E_2 = E - E_1$$

$$= \frac{1}{\omega(E)} \int_{E_2 = E - E_1} d\Omega_2$$

$$= \frac{\omega(E_2 = E - E_1)}{\omega(E)}$$

So $\rho_c^{(\mathcal{S})}\left(q_i^{(1)}, p_i^{(1)}\right) \sim \omega_2(E_2 = E - E_1)$ and we know that $S = k_B \log \omega$, so:

$$\log \rho_c \sim \log \omega_2(E_2) \sim S_2(E_2 = E - E_1)$$

$$(E_1 \ll E) \qquad \simeq S_2(E) + \left.\frac{\partial S_2}{\partial E_2}\right|_{E_2 = E} (-E_1) + \dots$$

$$= S_2(E) - \frac{E_1}{T_2(= T_1 = T)}$$

$$\implies \log \rho_c \sim \log \omega_2 \sim \frac{1}{k_B}\left(S(E) - \frac{E_1}{T}\right)$$

$$\implies \rho_c\left(q_i^{(1)}, p_i^{(1)}\right) = e^{S_2(E)/k_B}\ e^{-E_1/k_B T} \simeq e^{-E_1/k_B T}$$

since the first term is a constant.

We can see that it depends only on the system (E_1). Defining $\beta = 1/k_B T$:

$$\rho_c\left(q_i^{(1)}, p_i^{(1)}\right) = (const)\ e^{-\beta\mathcal{H}\left(q_i^{(1)}, p_i^{(1)}\right)}$$

We have eliminated the environment, so we will avoid writing the subscript $^{(1)}$ from now on:

$$\rho_c(q_i, p_i) = \frac{1}{Z_N} e^{-\beta\mathcal{H}(q_i, p_i)}$$

where he have defined the **canonical partition function** Z_N, which can be determined with the normalization:

$$1 = \int_{\mathcal{M}_1} \rho_c d\Omega = \frac{1}{Z_N} \int_{\mathcal{M}_\mathcal{S}} \prod_{i=1}^{N} \left(\frac{dq_i dp_i}{h^d}\right) e^{-\beta\mathcal{H}(q_i, p_i)}$$

$$\implies Z_N \equiv \int_{\mathcal{M}_\mathcal{S}} \left(\prod_{i=i}^{N} \frac{dq_i dp_i}{h^d}\right) e^{-\beta\mathcal{H}(q_i, p_i)}$$

$Z_N = Z_N(T, V)$ depends on N, T, V.

This expression is valid for distinguishable particles. For indistinguishable particles there is a $1/N!$ factor. For simplicity we write:

$$d\Omega = \frac{1}{\xi_N} \prod_{i=1}^{N} \frac{dq_i dp_i}{h^d} \qquad \text{with } \xi_N = \begin{cases} 1 & \text{distinguishable} \\ N! & \text{indistinguishable} \end{cases}$$

Using the fact that we can foliate the phase space, we can write (assuming the lowest bound to be 0):

$$Z_N(V, T) = \int_{\mathcal{M}} d\Omega e^{-\beta\mathcal{H}} = \int_0^\infty dE \int_{S_\mathcal{H}=E} dS_\mathcal{H} e^{-\beta\mathcal{H}} = \int_0^\infty dE\ \omega(E) e^{-\beta E}$$

In systems with a discrete set of energies values E_j: $Z_N = \sum_j e^{-\beta\epsilon_j} g_j$

1) For more species $A, B, \ldots$ of particles, we can assume that there is no interaction among different species: $\mathcal{H} = \mathcal{H}_A + \mathcal{H}_B$. So:

$$Z_N = \int d\Omega_A d\Omega_B \ldots\ e^{-\beta(\mathcal{H}_A + \mathcal{H}_B + \ldots)}$$

$$= \left(\int d\Omega_A e^{-\beta\mathcal{H}_A}\right) \left(\int d\Omega_B e^{-\beta\mathcal{H}_B}\right) \ldots$$

$$= Z_{N_A}^A Z_{N_B}^B \ldots$$

So if the species are distinguishable and independent one from the others (not interacting), the partition function is the product of the partition function of all the species.

2) Given an observable $f(q_i, p_i)$, the canonical average is:

$$\langle f \rangle_c \equiv \int_\mathcal{S} d\Omega \rho_c(q_i, p_i) f(q_i, p_i) = \frac{1}{Z_N} \int_\mathcal{S} d\Omega e^{-\beta\mathcal{H}(q_i, p_i)} f(q_i, p_i)$$

2.2.1 Thermodynamic quantities

We recover the thermodynamic potentials, by defining:

1)

$$F(T, V, N) = -\frac{1}{\beta} \log Z_N(T, V) \qquad (\iff Z_N = e^{-\beta F})$$

2)

$$E = \langle \mathcal{H} \rangle_c = -\frac{\partial \log Z_N}{\partial \beta}$$

PROOF: We can see that both Z_N (microscopic description) and F (macroscopic) depend on N, V, T. This leads us to think that it must be related, We will see that: $Z_N = e^{-\beta F} \quad F = -\frac{1}{\beta} \log Z$

$$e^{-\beta F} = Z_N = \int d\Omega e^{-\beta \mathcal{H}} \implies \int d\Omega e^{-\beta(\mathcal{H} - F)} = 1$$

Differentiating both sizes $\left(\frac{\partial}{\partial \beta} \right)$:

$$\int d\Omega e^{-\beta(\mathcal{H} - F)} \left[F - \mathcal{H} + \beta \frac{\partial F}{\partial \beta} \right] = 0$$

As an exercise, since $\beta = \frac{1}{k_B T} \qquad \beta \frac{\partial}{\partial \beta} = -T \frac{\partial}{\partial T}$

$$\implies F = \frac{\int d\Omega \mathcal{H} e^{-\beta \mathcal{H}}}{e^{-\beta F} = Z_N} + T \left. \frac{\partial F}{\partial T} \right|_{V,N} = \langle \mathcal{H} \rangle_c + T \frac{\partial F}{\partial T}$$

While in thermodynamic we have $F_{th} = E_{th} - TS \qquad S = - \left. \frac{\partial F_{th}}{\partial T} \right|_{V,N}$.
These two expressions are the same if we identify:

$$F_{th} = F = -\frac{1}{\beta} \log Z_N \qquad S_{th} = - \left. \frac{\partial F}{\partial T} \right|_{V,N} \qquad E = \langle \mathcal{H} \rangle_c = \frac{\int d\Omega \mathcal{H} e^{-\beta \mathcal{H}}}{\int d\Omega e^{-\beta \mathcal{H}}}$$

A useful formula in exercises:

$$E = \langle \mathcal{H} \rangle_c = \frac{1}{\int e^{-\beta \mathcal{H}} = Z_N} \frac{\partial}{\partial \beta} \left(\int e^{-\beta \mathcal{H}} \right) = -\frac{\partial}{\partial \beta} \log Z_N$$

3) We saw the universal Boltzmann's formula in the microcanonical. In the canonical it is the same (that's why it's called *universal*):

$$\boxed{S = -k_B \langle \log \rho_c \rangle_c}$$

PROOF:

$$-k_B \left\langle \log \rho_c \right\rangle_c = -k_B \int d\Omega \rho_c \log \rho_c$$

$$= -kB \int d\Omega \frac{e^{-\beta\mathcal{H}}}{Z}(-\beta\mathcal{H} - \log Z)$$

$$= k_B \left[\beta \int d\Omega \frac{e^{-\beta\mathcal{H}}}{Z}\mathcal{H} + \log Z \frac{\overbrace{\int d\Omega e^{-\beta\mathcal{H}} = Z}}{Z} \right]$$

$$= k_B \left[\frac{1}{k_B T} \left\langle \mathcal{H} \right\rangle_c + \log Z \right] \qquad \left(F = -\frac{1}{\beta}\log Z \implies \log Z = \frac{1}{k_B T}F \right)$$

$$= \frac{E - F}{T} = S$$

2.2.2   Equipartition theorem

THEOREM: Let $\xi_1 \in [a, b]$ denote one of the canonical coordinates (q) or momenta (p) and ξ_j ; $(j \neq 1)$ all other variables. Suppose that the following condition holds:

$$\int \left(\prod_{j\neq 1} d\xi_j \right) \left[\xi_1 e^{-\beta\mathcal{H}} \right]_a^b = 0$$

Then:
$$\left\langle \xi_1 \frac{\partial \mathcal{H}}{\partial \xi_1} \right\rangle_c = k_B T$$

PROOF:
$$1 = \int d\Omega \rho_c = \int d\xi_1 \left(\prod_j d\xi_j \right) \frac{e^{-\beta\mathcal{H}}}{Z}$$

But we can write the differential $d_{\xi_1} = \frac{d}{d\xi_1}\partial\xi_1$:

$$d\xi_1 e^{-\beta\mathcal{H}(\xi_1,\xi_j)} = d_{\xi_1}\left(\xi_1 e^{-\beta\mathcal{H}} \right) - \xi_1(-\beta)e^{-\beta\mathcal{H}}\frac{\partial\mathcal{H}}{\partial\xi_1}d\xi_1$$

So we obtain:

$$1 = \int \left(\prod_{j\neq 1} d\xi_j \right) d_{\xi_1}\left[\xi_1 \frac{e^{-\beta\mathcal{H}}}{Z} \right] + \int \left(d\xi_1 \prod_{j\neq 1} d\xi_j \right) \frac{1}{k_B T}\frac{e^{-\beta\mathcal{H}}}{Z}\frac{\partial\mathcal{H}}{\partial\xi_1}\xi_1$$

And from the hypothesis, the first term is zero. So:

$$k_B T = \int d\Omega \rho_c \left(\xi_1 \frac{\partial\mathcal{H}}{\partial\xi_1} \right) = \left\langle \xi_1 \frac{\partial\mathcal{H}}{\partial\xi_1} \right\rangle_c$$

$$\implies \left\langle \xi_1 \frac{\partial\mathcal{H}}{\partial\xi_1} \right\rangle_c = k_B T$$

We can now see that the standard equipartition theorem is a corollary of this:
If the coordinate ξ_1 appears quadratically in the Hamiltonian, then it contributes to the internal energy with an addend of $k_B T/2$.

Indeed, if: $\mathcal{H} = A\xi_1^2 + \tilde{\mathcal{H}}(\xi_j)$:

$$\xi_1 \frac{\partial \mathcal{H}}{\partial \xi_1} = 2A\xi_1^2 = 2\mathcal{H}_1 \implies 2\langle \mathcal{H}_1 \rangle_c = k_B T \implies \langle \mathcal{H}_1 \rangle_c = \frac{k_B T}{2}$$

Let's analyze better the condition of the theorem:

$$\xi_1 \in [a, b] \qquad \left[\xi_1 e^{-\beta \mathcal{H}(\xi_1, \xi_j)}\right]_a^b = 0$$

- Suppose $\xi_1 = q$, then: $\mathcal{H} = \mathcal{H}_{KIN} + V(q)$. The requirement becomes:

$$q \in [a, b] \qquad e^{-\beta V(q)}\Big|_a^b = 0 \implies V(q \to a, b) = \infty$$

which is not a strange condition in physics, where usually the particle is confined.

- Suppose $\xi_1 = p$, then: $\mathcal{H}_{KIN} = \frac{p^2}{2m}$ and the requirements becomes:

$$p \in [-\infty, +\infty] \qquad \left[e^{-\beta \frac{p^2}{2m}}\right]_{-\infty}^{+\infty}$$

There are some magnetic systems which don't satisfy this condition, but in general it is satisfied.
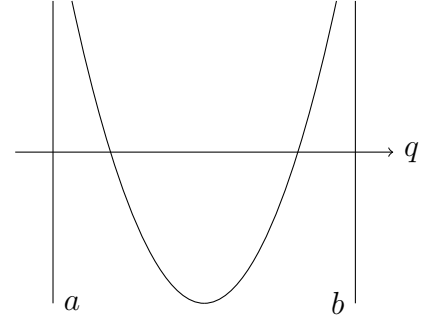
2.2.3 Exercise (2.1): Find the partition function of a (classical) perfect gas in 3D

$$\mathcal{M}_N = V^N \times \mathbb{R}^{3N} \qquad \vec{q} \in V \quad \vec{p} \in \mathbb{R}^3 \qquad \mathcal{H}(q_i, p_i) = \sum_{i=1}^{N} \frac{\vec{p_i^2}}{2m}$$

$$\rho_c(q_i, p_i) = \frac{e^{-\beta \mathcal{H}}}{Z_N}$$

$$Z_N = \frac{1}{N! \left(h^3\right)^N} \int_V \prod_{i=1}^{N} d^3 q_i \int_{\mathbb{R}^3} \left(\prod_{i=1}^{N} d^3 p_i\right) e^{-\beta \sum_{i=1}^{N} \frac{\vec{p_i^2}}{2m}}$$

$$= \frac{V^N}{N! h^{3N}} \left(\int_{\mathbb{R}^3} d^3 p \, e^{-\beta \frac{\vec{p}^2}{2m}}\right)^N \qquad (p^2 = p_x^2 + p_y^2 + p_z^2)$$

$$= \frac{V^N}{N! h^{3N}} \left(\int_{-\infty}^{+\infty} dp_\alpha e^{-\beta \frac{p_\alpha^2}{2m}}\right)^{3N} \qquad \text{Gaussian integral}$$

$$Z_N = \frac{V^N}{N!} \left(\frac{\sqrt{2mk_BT}}{h} \right)^{3N} = \frac{V^N}{N!} \frac{1}{\lambda_T^{3N}}$$

Generalizing in d-dimension: $Z_N = \dfrac{V^N}{N!} \dfrac{1}{\lambda_T^{dN}}$

From that partition function we can get:

-
$$E = -\frac{\partial}{\partial \beta} \log Z_N = \frac{3}{2} N k_B T$$

  which agrees with the equipartition theorem: $\mathcal{H} = \frac{1}{2}(p_x^2 + p_y^2 + p_z^2)$:
  3 quadratic variables $\implies 3\frac{k_BT}{2}$

-
$$F = -\frac{1}{\beta} \log Z_N = -k_B T \left[N \log V \lambda_T^3 - \log N! \right] \qquad (Stirling)$$

$$= k_B T N \left[\log \frac{\lambda_T N}{V} - 1 \right]$$

$$\frac{F}{N} = f = k_B T \left(\log \frac{\lambda_T N}{V} - 1 \right)$$

- $S = \frac{E-F}{T}$ (as an exercise) or:

$$S = -\left. \frac{\partial F}{\partial T} \right|_{V_N} = k_B N \left[\frac{5}{2} - \log(n\lambda_T^3) \right]$$

  Notice that in both cases the result is the same and implies $S = 0$, for $T < \frac{n^{2/3}h^2}{2\pi m k_B e^{5/3}}$. This is of course absurd, signalling that this model is not suited to describe the low temperature limit.
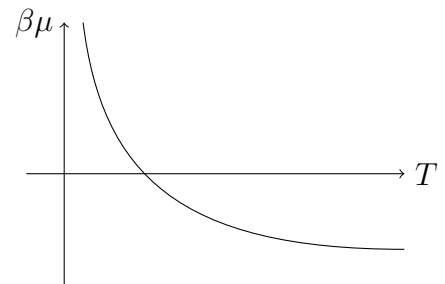
-
$$p = -\left. \frac{\partial F}{\partial V} \right|_{T,V} = \frac{k_B T N}{V} \iff pV = N k_B T$$

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-
$$\boxed{\mu = \left. \frac{\partial F}{\partial N} \right|_{T,V} = k_B T \log n\lambda_T^3}$$

  Relation between $\mu \leftrightarrow n$ at fixed T

Or, choosing the density: $\mu = \mu(T)$ (in graph). We
can see that: $\mu(T) \xrightarrow[T \to \infty]{} \infty$ and $\boxed{\dfrac{\partial \mu}{\partial T} < 0}$

This condition will play an important role in a Bose-
Einstein gas

- Specific heat:

$$\mathcal{C}_V = T \left.\frac{\partial S}{\partial T}\right|_{V,N} = \left.\frac{\partial E}{\partial T}\right|_{V,N} = \frac{3}{2} N K_B \qquad c_V = \frac{\mathcal{C}_V}{N} = \frac{3}{2} k_B \qquad \text{Dulong-Petit law}$$

$$\mathcal{C}_p = T \left.\frac{\partial S}{\partial T}\right|_{p,N} = \left.\frac{\partial E}{\partial T}\right|_{p,N} + p \left.\frac{\partial V}{\partial T}\right|_{p,N} = \frac{3}{2} N K_B + N k_B = \frac{5}{2} k_B N \qquad c_p = \frac{\mathcal{C}_p}{N} = \frac{5}{2} k_B$$

Notice that c_V comes out to be constant: this is in contradiction with thermodynamic
identities that require $cV \to 0$ as $T \to 0$. Again this shows that this model is not suited
to describe the low temperature limit.

2.2.4   Magnetic systems

Another way to make work is through magnetic interaction.
So: $dE = \delta Q - \delta \mathcal{L} + \mu dN = TdS - pdV + dE_{mag}$

If $\vec{E}, \vec{\mathcal{P}}$ are the external field and the reaction of the matter to the external field
respectively, we can define $\vec{D}$ as the Total magnetic field: $\vec{D} = \epsilon_0 \vec{E} + \vec{\mathcal{P}}$
For historical reasons, $\vec{\mathcal{P}}$ contains in its definition the factor ϵ_0 already.

The Maxwell equations in matter becomes:

$$\nabla \cdot \vec{D} = \rho \qquad \nabla \cdot \vec{B} = 0 \qquad \nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \qquad \nabla \times \vec{H} = \vec{j} + \frac{\partial \vec{D}}{\partial t}$$

where: $\vec{H} = \vec{B}/\mu_0 - \vec{\mathcal{M}}$

A charged particle is described by $\vec{F}_{el} = q\vec{E} \qquad \vec{E} = \vec{\nabla} V$ And we have:

$$\mathcal{H}_0 = \frac{\vec{p}^2}{2m} + QV(q)$$

where $V(q)$ is the elastic potential energy.

There could be some other effects, like some atoms or molecules could have a dipole
moment $\vec{d}$ (e.g. water molecule). This dipole can be seen by an external field, because
of the interaction $\vec{d} \cdot \vec{E}$. However this effect is usually not very strong ($\vec{\mathcal{P}}$ is weak), with
the exception of the ferromagnetic materials.

We have different materials with different effects: diamagnetism, paramagnetism,
ferromagnetism.

Paramagnetism The assumptions for paramagnetism are that:

- There are no macroscopic charge or net current flow

- As we said, $\vec{\mathcal{P}}$ is negligible with respect to magnetisation.

- We assume $\rho = 0$, from which the Maxwell equations become:

$$\vec{\nabla} \cdot \vec{D} = \epsilon_0 \vec{\nabla} \cdot \vec{E} = 0 \qquad \vec{\nabla} \cdot \vec{B} = 0 \qquad \vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \qquad \vec{\nabla} \times \vec{H} = \vec{j}$$

We can define the total magnetization (an extensive quantity) as:

$$\vec{M} = \int_V d^3q \vec{\mathcal{M}}(q) = V \vec{\mathcal{M}}$$

And we have: $\vec{B} = \mu_0 \vec{H} + \mu_0 \vec{\mathcal{M}}(q)$, so:

$$
\begin{aligned}
\delta \mathcal{L} &= dt \int_V d^3q \vec{j} \cdot \vec{E} \\
&= dt \int_V d^3q \left(\vec{\nabla} \times \vec{H} \right) \cdot \vec{E} \\
&= dt \int_V d^3q \left[\vec{\nabla} \cdot \left(\vec{H} \times \vec{E} \right) + \vec{H} \cdot \left(\vec{\nabla} \times \vec{E} \right) \right] \\
&= dt \left[\vec{H} \times \vec{E} \right]_{\partial V} + dt \int_V d^3q \vec{H} + \frac{\partial \vec{B}}{\partial t} \qquad \text{the first is a boundary term} \\
&= \int_V d^3q \vec{H} \cdot \left(d\vec{B} \right) = dE_{mag} \\
&= \mu_0 \int_V d^3q \vec{H} \cdot d \left(\vec{H} + \vec{\mathcal{M}} \right)
\end{aligned}
$$

If we suppose an homogeneous material, $\vec{H}$ is uniform, so $\vec{\mathcal{M}}$ is uniform too. We obtain:

$$\delta \mathcal{L} = \mu_0 V \vec{H} \cdot d\vec{G} + \mu_0 V \vec{H} \cdot d\vec{\mathcal{M}} = V \mu_0 d \left(\frac{H^2}{2} \right) + \mu_0 \vec{H} \cdot d\vec{M}$$

The first term is not relevant, since it's the same we have in vacuum.

The total energy can thus change for more reasons:

$$d\vec{E} = TdS - pdV + \mu dH + \mu_0 \vec{H} \cdot d\vec{M}$$

and $\vec{H}, \vec{M}$ are a couple of conjugated variables, just like $(T, S), (p, V), (\mu, N)$.

If we apply this to a solid $(dV = 0)$ in the canonical ensemble $(dN = 0)$:

- internal energy: $dE = TdS + \mu_0 \vec{H} \cdot d\vec{M} \implies E = E(S, \vec{M})$
  from which: $T = \frac{\partial E}{\partial S}\big|_M \qquad \vec{H} = \frac{\partial E}{\partial \vec{M}}\big|_S \qquad$ (not so useful)

- Helmotz free energy: $F = E - TS \qquad dF = SdT + \mu_0 \vec{H} \cdot d\vec{M}$

- Gibbs free energy: $G = E - TS - \mu_0 \vec{H} \cdot \vec{M} \qquad dG = -SdT - \mu_0 \vec{M} \cdot d\vec{H}$
  from which: $\vec{M} = \left.\frac{\partial G}{\partial \vec{H}}\right|_T$ (more useful, since we want the internal $\vec{M}$, given the external magnetisation $\vec{H}$)

Microscopically, paramagnetism is correlated to dipole molecules: the intrinsic magnetic moments $\vec{\mu}$ (which is due to electrons orbiting around nuclei (microscopical current) or due to spin) can interact with an external field ($\vec{\mu} \cdot \vec{B}$) originating paramagnetism.

Diamagnetism The magnetic forces are more difficult than the electric ones:

$$\vec{F}_{Lorentz} = q\vec{v} \times \vec{B} \qquad \vec{B} = \vec{\nabla} \times \vec{A} \qquad \text{(with } \vec{A}\text{: vector potential)}$$

However, we can write: $\vec{p} \to \vec{p} - \frac{Q}{c}\vec{A} = \widetilde{\vec{p}}_j$ (minimal coupling), from which:

$$\mathcal{H} = \frac{1}{2m}\left(\vec{p} - \frac{Q}{c}\vec{A}\right)^2 \xrightarrow{for \ N \ particles} \mathcal{H} = \sum_{j=1}^{N} \frac{1}{2m}\left(\vec{p}_j - \frac{Q}{c}\vec{A}(q_j)\right)^2$$

The canonical partition function is:

$$Z_N[T, V, N, \vec{H}] = \frac{1}{h^3 N!} \int \left(\prod_{j=1}^{N} d^3q_j d^3p_j\right) e^{-\beta \sum_{j=1}^{N}\left(\vec{p}_j - \frac{Q}{c}\vec{A}(q_j)\right)^2/2m}$$

$$= \frac{1}{h^3 N!} \int \prod_{j=1}^{N} d^3q_j d^3\widetilde{p}_j \ e^{-\beta \sum_{j=1}^{N} \widetilde{p}_j/2m}$$

We removed the dependency on $\vec{H}$ ($Z_N = Z_N[T, V, N]$), so any thermodynamic potential that we can get does not depend on $\vec{H}$. We have obtained the following

THEOREM: (Bohr-van Leeuwen) In classical theory there is no diamagnetism:

$$\vec{M} = -\frac{\partial G}{\partial \vec{H}} = 0$$

In quantum mechanics, we can get diamagnetism through the Langevin Theory, due to Larmor procession

Ferromagnetism In some materials, the vector $\vec{\mathcal{M}}$ is very strong and there are interactions between different magnetic moments: $\vec{\mu}_i \cdot \vec{\mu}_j$.

2.2.5   Exercise (2.5): Thermodynamics of a magnetic solid

We consider a solid of N atoms/molecules (V fixed) in a canonical setting, which have an intrinsic magnetic moment μ in a external magnetic (uniform) field $\vec{H} = H\hat{z}$. We assume that the field is not too intense, so $|\mu_i| = \mu$ does not change (the only effect the field has on μ is to make it rotate.

We assume the particle to be distinguishable (because they are fixed at their equilibrium positions) and consider the Hamiltonian: $\mathcal{H} = -\sum_{i=1}^{N} \vec{\mu}_j \cdot \vec{H}$.

Since there is no motion degree of freedom, for each particle there are only the ones due to magnetic moment: $\vec{\mu} = (\mu_x, \mu_y, \mu_z)$ with $|\vec{\mu}|^2$ fixed. The phase space (of a single particle) is a 2D sphere of radius $|\vec{\mu}| = \mu$.

So it's better to use spherical coordinates:

$$\mu_x = \mu \sin\theta \cos\phi \qquad \mu_y = \mu \sin\theta \sin\phi \qquad \mu_z = \mu \cos\theta$$

and the volume is: $dqdp = \mu^2 \sin\theta d\theta d\phi$

Indeed, if we use $q = \phi$, the conjugate variable to an angle is a momentum $p = \cos\theta$, so $dq = d\phi$, $dp = \sin\theta d\theta$.

We now have everything we need to write the partition function:

$$Z_{TOT} = (Z_1)^N \qquad \left(\mathcal{H} = -\sum \vec{\mu} \cdot \vec{H} = -\sum \mu_z H \right)$$

$$Z_1 = \int_0^\pi \int_0^{2\pi} (\sin\theta d\theta d\phi)\ e^{\beta\mu H \cos\theta}$$

And we can also calculate the total magnetization: $\vec{M}^z = \left\langle \sum_{j=1}^N \mu_j^z \right\rangle_c = \sum_{j=1}^N \mu_j^z Z$

$$\langle \mu_j^z \rangle_c \equiv \int (\sin\theta d\theta d\phi)\, \rho_c \mu_j^z = \frac{\int (\sin\theta d\theta d\phi)\, e^{\beta\mu_j^z H} \mu_j^z}{\int (\sin\theta d\theta d\phi)\, e^{\beta\mu_j^z H}}$$

$$= \frac{1}{Z_1} \frac{1}{\beta} \frac{\partial Z_1}{\partial H} = \frac{1}{\beta} \frac{\partial}{\partial H} \log Z_1 = \frac{\partial}{\partial H} \left(\frac{1}{\beta} \log Z \right)$$

Since all particles are the same: $M^z = N \langle \mu_j^z \rangle_c = N \left(-\frac{\partial F}{\partial H} \right)$

2.3 Grancanonical Ensemble

We consider a system $S = \{(q_i^{(1)}, p_i^{(1)}\}$ and an environment $\varepsilon = \{(q_j^{(2)}, p_j^{(2)}\}$ at equilibrium (thermal ($T_1 = T_2 = T$), mechanical ($p_1 = p_2 = p$) and a chemical ($\mu_1 = \mu_2 = \mu$). These two can exchange both energy and particles, but the the total energy and the total number of particles are conserved ($N = N_1 + N_2 = const$), so that the whole universe $\mathcal{U} = S \cup \varepsilon$ is canonical.

The (grancanonical) partition distribution of the system only is obtained by integrating out the environment d.o.f. So:

$$
\rho_{gc}^{(S)}\left(q_i^{(1)} p_i^{(1)}\right) = \mathcal{A} \int_\epsilon \left(\prod_j dq_j^{(2)}, dp_j^{(2)}\right) \rho_c^{(\mathcal{U})}\left(q_i^{(1)}, p_i^{(1)}; q_j^{(2)}, p_j^{(2)}\right)
$$

$$
= \frac{\mathcal{A} \int \left(\prod_j dq_j^{(2)} dp_j^{(2)}\right) e^{-\beta \mathcal{H}_1} e^{-\beta \mathcal{H}_2}}{\int \left(\prod_i^{N_1} dq_i^{(1)} dp_i^{(1)}\right) \left(\prod_j^{N_2} dq_j^{(2)} dp_j^{(2)}\right) e^{-\beta(\mathcal{H}_1 + \mathcal{H}_2)}}
$$

(the integrand term in the denominator is the total $\delta + \varepsilon$, the total volume $V = (V_1, V_2)$)

We will choose the constant $\mathcal{A} = \frac{N!}{N_1! N_2!}$, then we will prove later that it is the correct one (the one that satisfies the normalization). So we have:

$$
\rho_{gc} = \frac{\dfrac{e^{-\beta \mathcal{H}_1}}{N_1! N_2!} \int \prod_j dq_j^{(2)} dp_j^{(2)} \, e^{-\beta \mathcal{H}_2}}{\dfrac{1}{N!} \int \prod_i^{N_1} dq_i^{(1)} dp_i^{(1)} \prod_j^{N_2} dq_j^{(2)} dp_j^{(2)} e^{-\beta(\mathcal{H}_1 + \mathcal{H}_2)}}
\tag{2.4}
$$

PROOF: Let's now see that the normalization holds:

$$
\int \prod_i dq_i^{(1)}, dp_i^{(1)} \rho_{gc} = \frac{N!}{N_1! N_2!} \frac{\displaystyle\int_{V_1} \prod_i dq_i^{(1)} dp_i^{(1)} e^{-\beta \mathcal{H}_1} \int_{V_2} \prod_j dq_j^{(2)} dp_j^{(2)} e^{-\beta \mathcal{H}_2}}{\displaystyle\int_V \prod_i dq_i^{(1)} dp_i^{(1)} \prod_j dq_j^{(2)} dp_j^{(2)} e^{-\beta(\mathcal{H}_1 + \mathcal{H}_2)}}
$$

We can multiply the first integral at the numerator by $(V_1/V_1)^{N_1}$, the second by

$(V_2/V_2)^{N_2}$ and the denominator by $(V/V)^N$, obtaining:

$$= \frac{N!}{N_1! N_2!} \frac{V_1^{N_1} V_2^{N_2} \left(\frac{\int_{V_1} dq_i^{(1)} dp_i^{(1)} e^{-\beta \mathcal{H}_1}}{V_1^{N_1}} \right) \left(\frac{\int_{V_2} dq_j^{(2)} dp_j^{(2)} e^{-\beta \mathcal{H}_2}}{V_2^{N_N}} \right)}{V^N \left(\frac{\int_V \prod_i dq_i^{(1)} dp_i^{(1)} dq_j^{(2)} dp_j^{(2)} \ e^{-\beta(\mathcal{H}_1 + \mathcal{H}2)}}{V^N} \right)}$$

If V_1, V_2, V are finite, the integrals are different, but in the thermodynamic limit, $V_1, V_2, V \to \mathbb{R}^d$, so the overall ratio is 1.

$$\int \rho_{gc} = \frac{N!}{N_1! N_2!} \left(\frac{V_1}{V} \right)^{N_1} \left(\frac{V_2}{V} \right)^{N_2} = 1$$

However, N_1, N_2 are not fixed (only N is), so we have a different integral for each value of N_1. So actually what we want to calculate is:

$$\sum_{N_1=0}^{N} \int \prod_{i=1}^{N} dq_i^{(1)} dp_1^{(1)} \rho_{gc} \left(q_i^{(1)}, p_i^{(1)} \right)$$

$$= \sum_{N_1=0}^{N} \frac{N!}{N_1!(N - N_1)!} \left(\frac{V_1}{V} \right)^{N_1} \left(\frac{V_2}{V} \right)^{N-N_1} \qquad \text{expansion of the binomial}$$

$$= \left(\frac{V_1}{V} + \frac{V_2}{V} \right)^{N} = 1^N \xrightarrow[N \to \infty]{} 1$$

So what we have proved is that the sum over all the possible number of particle $\left(\sum_{N_1=0}^{\infty} \right)$ integrated over all the phase space is 1:

$$\boxed{ \sum_{N_1=0}^{\infty} \int \prod_{i=1}^{N_1} dq_i^{(1)} dp_i^{(1)} \rho_{gc} \left(q_i^{(1)}, p_i^{(1)} \right) = 1 }$$

We can re-write the (2.4):

$$\rho_{gc} = \frac{e^{-\beta \mathcal{H}_1}}{h^{dN_1} N_1!} \frac{Z_{N_2}[V_2, T]}{Z_N[V, T]}$$

$$= \frac{e^{-\beta \mathcal{H}_1}}{h^{dN_1} N_1!} \frac{e^{-\beta F[N_2, V_2, T]}}{e^{-\beta F[N, V, T]}}$$

$$= \frac{e^{-\beta \mathcal{H}_1}}{h^{dN_1} N_1!} e^{\beta(F[N,V,T] - F[N_2, V_2, T])}$$

$$F[N, V, T] - F[N_2, V_2, T] = F(N, V, T) - F(N - N_1, V - V_1, T) \qquad (N_1 \ll N, \quad V_1 \ll V)$$

$$\text{(Taylor expansion)} \quad = \left. \frac{\partial F}{\partial N} \right|_{V,T} \Delta N + \left. \frac{\partial F}{\partial V} \right|_{N,T} \Delta V + \dots$$

$$= \mu_1(N_1) + (-p_1)(V_1) + \dots$$

So we have:

$$\rho_{gc}\left(q_i^{(1)}, p_i^{(1)}\right) = \frac{1}{h^{dN_1} N_1!} e^{-\beta \mathcal{H}_1\left(q_i^{(1)}, p_i^{(1)}\right)} e^{+\beta N_1 \mu} e^{-\beta V_1 p}$$

The constant can be absorbed in the measure:

$$1 = \sum_{N_1} \left[\int \underbrace{\left(\frac{\prod_i dq_i^{(1)} dp_i^{(1)}}{h^{dN_1} N_1!} \right)}_{d\Omega} e^{-\beta \mathcal{H}_1\left(q^{(1)}, p^{(1)}\right)} e^{+\beta \mu N_1} e^{-\beta p V_1} \right] \qquad (2.5)$$

So usually we don't write the constant $\frac{1}{h^{dN_1} N_1!}$.

Now that we have integrated out all the quantities related to the environment, we will drop the superscript $^{(1)}$ from everywhere:

$$\rho_{gc}(q_i, p_i) = e^{-\beta \mathcal{H}(q_i, p_i)} e^{+\beta N \mu} e^{-\beta V p}$$

using the granpotential $\Omega = -pV$ and defining the *fugacity* $z \equiv e^{+\beta\mu}$:

$$\rho_{gc} = e^{-\beta \mathcal{H}} z^N e^{\beta \Omega}$$

From the normalization (2.5) we obtain the grancanonical partition function:

$$e^{-\beta \Omega} = \sum_N Z_N z^N \equiv \mathcal{Z} \qquad \text{(grancanonical partition function)}$$

so the grancanonical probability distribution becomes:

$$\rho_{gc} = \frac{1}{\mathcal{Z}} z^N e^{-\beta \mathcal{H}} = \frac{1}{\mathcal{Z}} e^{-\beta(\mathcal{H} - \mu N)}$$

where $\mathcal{H} - \mu N$ is sometimes denoted with $\mathcal{K}$: grancanonical hamiltonian.
Simple application of this formulas: perfect gas (exercise 3.1):

$$Z_N = \frac{V^N}{N! \lambda_T^{3N}}$$

$$\mathcal{Z} = \sum_{N=0}^{\infty} z^N \frac{V^N}{N!\lambda_T^{3N}} = \exp\left(\frac{zV}{\lambda_T^{3N}}\right)$$

$$\Omega = -\frac{1}{\beta} \log \mathcal{Z} = -\frac{1}{k_B T} \log \mathcal{Z}$$

DEFINITION: Grancanonical average
Given an observable $f_N(q_i, p_i)$ (the subscript N is because the expression of the observable can be different according to the number of particle), the grancanonical average of that observable is:

$$\langle f \rangle_{gc} = \sum_{N=0}^{\infty} \int \frac{\prod_{i=1}^{N} dq_i dp_i}{N! h^{dN}} \frac{e^{-\beta(\mathcal{H}-\mu N)}}{\mathcal{Z}} f_N(q_i, p_i)$$

$$= \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} z^N Z_N \frac{\int e^{-\beta \mathcal{H}} f}{Z_N} = \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} z^N Z_N \langle f_N \rangle_c$$

2.3.1   Thermodynamical quantities

- $-pV = \Omega = -\frac{1}{\beta} \log \mathcal{Z}$

-

$$E = \langle \mathcal{H} \rangle_{gc} = \sum_{N=0}^{\infty} \frac{z^N \int \mathcal{H} e^{-\beta \mathcal{H}}}{\mathcal{Z}}$$

$$= -\frac{1}{\mathcal{Z}} \sum_N z^N \frac{\partial}{\partial \beta} \int e^{-\beta \mathcal{H}}$$

$$= -\frac{1}{\mathcal{Z}} \frac{\partial}{\partial \beta} \underbrace{\left[\sum_{N=0}^{\infty} z^N \int e^{-\beta \mathcal{H}}\right]}_{\mathcal{Z}} {}_{z=const}$$

$$= -\left.\frac{\partial}{\partial \beta} \log \mathcal{Z}\right|_{z \ const}$$

-

$$N = \langle N \rangle_{gc} = \sum_{N=0}^{\infty} z^N \int \frac{e^{-\beta \mu} N}{\mathcal{Z}} \overset{(ex.)}{=} \left. z\frac{\partial}{\partial z} \log \mathcal{Z}\right|_{z}$$

- The entropy can be obtained from the universal Boltzmann formula:

$$S = -k_B \langle \log \rho_{gc} \rangle_{gc} = -k_B \sum_{N=0}^{\infty} \int \rho_{gc} \log \rho_{gc} = -k_B \sum_N z^N \int \frac{e^{-\beta\mu}}{\mathcal{Z}} \log \rho_{gc}$$

$$\rho_{gc} = \frac{e^{-\beta(\mathcal{H}-\mu N)}}{\mathcal{Z}} \implies \log \rho_{gc} = -\beta\mathcal{H} + \beta\mu N - \log \mathcal{Z}$$

$$S_{gc} = \sum_N z^N \left(\int \frac{\beta\mathcal{H}e^{-\beta\mathcal{H}}}{\mathcal{Z}} - \int \frac{\beta\mu N e^{-\beta\mathcal{H}}}{\mathcal{Z}} + \int e^{-\beta\mathcal{H}} \mathcal{Z} \log Z \right)$$

The last term can be re-written as:

$$\int e^{-\beta\mathcal{H}} \mathcal{Z} \log Z = \frac{\log \mathcal{Z}}{\mathcal{Z}} \sum_N z^N \int e^{-\beta\mathcal{H}} = \frac{\log \mathcal{Z}}{\mathcal{Z}} \mathcal{Z} = \log \mathcal{Z}$$

$$\implies S_{gc} = \beta \langle \mathcal{H} \rangle_{gc} - \beta\mu \langle N \rangle_{gc} + \log \mathcal{Z}$$

so:

$$S_{gc} = k_B \beta (E - \mu N - \Omega) = \frac{1}{T}(E - \mu N - \Omega)$$

and since $\Omega = E - TS - \mu N, \quad S_{th} = \frac{1}{T}(E - \mu N - \Omega) = S_{gc}$

2.3.2 Virial expansion (van der Waals gases)

A real gas is a 3D gas where

$$\mathcal{H}_N = \sum_{j=1}^N \frac{\vec{p}_j^2}{2m} + \sum_{i<j} U(\vec{r}_i, \vec{r}_j)$$

We assume that the potential is a van der Waals potential: $U(r = |\vec{r}_i - \vec{r}_j|)$, so there is interactions only between two particles.
Since this is a gas, we also assume that the interactions are weak, otherwise the system could become liquid or solid.

Starting from the grancanonical partition function, if $z = e^{\beta\mu} > 0$ is small, we can expand the expression up to the second order (Virial expansion):

$$\mathcal{Z} = \sum_{N=0}^\infty z^N Z_N \simeq 1 + z Z_1 + z^2 Z_2 + \dots$$

where Z_1 is the partition function where there is only 1 particle, Z_2 considers 2 particle, etc.. So:

$$Z_1 = \int \frac{d^3r \, d^3p}{h^3} e^{-\beta(\vec{p}^{\,2}/2m)} = \frac{V}{\lambda_T^3}$$

$$Z_2 = \frac{1}{2!} \int \frac{d^3r_1 \, d^3p_1}{h^3} \frac{d^3r_2 \, d^3p_2}{h^3} e^{-\beta(\vec{p_1}^2 + \vec{p_2}^2)} e^{-\beta U(r)}$$

Changing coordinates: $\vec{R}_{CM} = \frac{1}{2}(\vec{r}_1 + \vec{r}_2) \qquad \vec{r} = \vec{r}_1 - \vec{r}_2$

$$Z_2 = \frac{1}{2\lambda_T^6} \int d^3 R_{CM} \int_V d^3r \, e^{-\beta U(r)} = \frac{V}{2\lambda_T^6} \int d^3r \, e^{-\beta U(r)}$$

So:

$$\mathcal{Z} = 1 + \frac{Vz}{\lambda_T^3} + \frac{V}{2}\frac{z^2}{\lambda_T^6}\int d^3r\ e^{-\beta U(r)} + o(z^2)$$

And we can obtain Ω, n and p:

$$-pV = \Omega = -\frac{1}{\beta}\log\mathcal{Z} \implies \beta p = \frac{p}{k_BT} = \frac{1}{V}\log\mathcal{Z}$$

$$N = z\ \frac{\partial}{\partial z}\log\mathcal{Z}\bigg|_{\beta,V}$$

To compute the $\log\mathcal{Z}$, we remind that $\log(1+x) \simeq x - \frac{1}{2}x^2 + \ldots$ if x is small:

$$\begin{aligned}
\log\mathcal{Z} &= \frac{Vz}{\lambda_T^3} + \frac{Vz^2}{\lambda_T^6}\left(\int e^{-\beta U}\right) - \frac{1}{2}\frac{V^2z^2}{\lambda_T^6} + o\left(\frac{z^3}{\lambda_T^9}\right) \\
&= \frac{Vz}{\lambda_T^3} + \frac{Vz^2}{2\lambda_T^6}\left(\int_V d^3r\, e^{-\beta U(r)} - \int_V d^3r\right) \\
&= \frac{Vz}{\lambda_T^3} + \frac{Vz^2}{2\lambda_T^6}\ J_2(\beta)
\end{aligned}$$

where $J_2(\beta) \equiv \int_V d^3r\left[e^{-\beta U(r)} - 1\right]$ is the second Virial exponent.
From that we can obtain:

- Density:

$$n = \frac{N}{V} = \frac{1}{V}z\frac{\partial}{\partial z}\log\mathcal{Z} = \frac{z}{\lambda_T^3} + \frac{2z^2}{\lambda_T^6}J_2(\beta) + \ldots \tag{2.6}$$

- Pressure:

$$p = \frac{k_BT}{V}\log\mathcal{Z} = k_BT\left[\frac{z}{\lambda_T^3} + \frac{z^2}{2\lambda_T^6}J_2(\beta) + \ldots\right] \tag{2.7}$$

For a perfect gas, particles are non-interacting, so $J_2 = 0$. Thus:

$$n = \frac{z}{\lambda_T^3} \qquad p = k_BT\frac{z}{\lambda_T^3} = k_BTn$$

So, since we have done an expansion in $\frac{z}{\lambda_T^3}$, we can make an expansion in density n. Assuming n small means considering a diluted gas.

From the density expansion (2.6) we can obtain:

$$z = \frac{-\frac{1}{\lambda_T^3} \pm \frac{1}{\lambda_T^3}\sqrt{1 + 4nJ_2}}{\frac{2J_2}{\lambda_T^6}}$$

In the case of no interaction (perfect gas), $J_2 = 0$, and for the diluted limit, $N = \frac{z}{\lambda_T^3} \ll 1$. Reminding that $\sqrt{1+x} \simeq 1 + \frac{x}{2} - \frac{1}{8}x^2 + \dots$ for $x \ll 1$:

$$z \simeq \frac{\lambda_T^3}{2J_2}\left[-1 \pm \left(1 + \frac{1}{2}(4mJ_2) - \frac{1}{8}(4mJ_2)^2 + \dots\right)\right]$$

Now we need to decide which solution to take. Since if we stop to the first order we should obtain $z \propto n \quad (z = \lambda_T^3 n)$, then we have to take the positive solution, so:

$$z = \underbrace{n\lambda_T^3}_{\text{perfect gas}} \underbrace{-n^2 J_2 \lambda_T^3}_{\text{correction}}$$

From the expansion of the pressure (2.7), one can obtain:

$$\frac{p}{k_B T} = \frac{z}{\lambda_T^3} + \frac{z^2}{2\lambda_T^3}J_2(\beta) + \cdots \implies p = \underbrace{k_B T n\left[1 - \frac{J_2}{2}n\right]}_{\substack{\text{perfect gas} \\ \text{van der Waals}}} + O(n^3)$$

Now, if we assume that particles are spheres and the potential is the one in the Fig. 2.1, we can find the van der Waals equation of a real gas by expanding the term J_2:

$$J_2(\beta) = 4\pi \int_0^\infty dr \; r^2 \left[e^{-\beta U(r)} - 1\right]$$
$$= 4\pi \int_0^{2r_0} dr \; r^2 \left[e^{-\beta U(r)} - 1\right] + 4\pi \int_{2r_0}^\infty dr \; r^2 \left[e^{-\beta U(r)} - 1\right]$$

In the limit $e^{-\beta U(r)} \ll 1$, we can use the 1° order Taylor expansion: $e^{-\beta U(r)} - 1 \simeq |-\beta U(r)|$

$$\simeq -4\pi \int_0^{2r_0} dr \; r^2 + 4\pi \int_{2r_0}^\infty dr \; r^2 \left|-\beta U(r)\right|$$
$$= -8\frac{4\pi}{3}r_0^3 + \frac{4\pi}{k_B T}\int_{2r_0}^\infty dr \; r^2 \left|U(r)\right|$$
$$= \underbrace{-2b}_{<0} + \underbrace{\frac{2a}{k_B T}}_{>0}$$

where b is the volume of 2 particles, and a is the average measure of the potential.
So we obtain: $\frac{-J_2(\beta)}{2} = b - \frac{a}{k_B T}$ and from the expression of the pressure:

$$\boxed{p = k_B T n\left[1 + \left(b - \frac{a}{k_B T}\right)n\right] + O(n^3)}$$
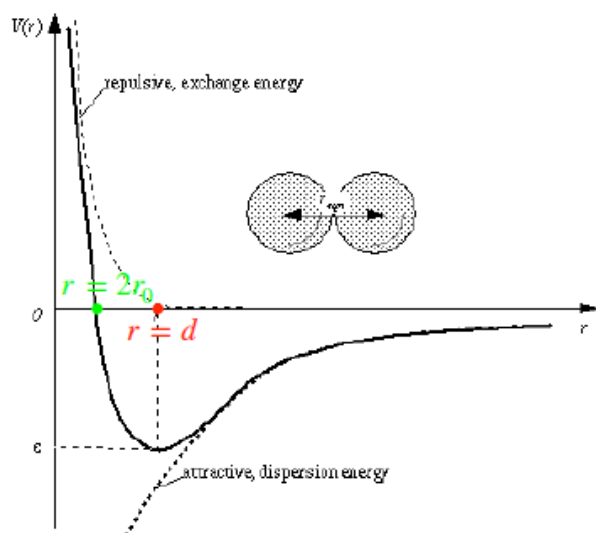
Figure 2.1: Van der Waals potential. It is repulsive when $U(r) > 0$ (in the image indicated as $V(r)$

and defining $n = N/V = 1/v$, we obtain the **van der Waals equation of a real gas**:

$$\left(p - \frac{a}{v^2}\right)(v - b) = k_B T$$

RECAP:

Microcanonical	Canonical	Grancanonical
$\rho_{mc} = \frac{1}{\omega(E)}\delta(\mathcal{H} - E)$	$\rho_c = \frac{e^{-\beta\mathcal{H}}}{Z_N}$	$\rho_{gc} = \frac{e^{-\beta(\mathcal{H} - \mu N)}}{\mathcal{Z}}$

$$S = -k_B \langle \log \rho \rangle \overset{TD\_lim}{=} S_{Th} = k_B \log \underbrace{\sum(E)}_{\#\text{states}}$$

2.4   State counting and Entropy

We have seen that the Boltzmann's universal law give a value for the entropy which (in the thermodynamic limit) is the same of the thermodynamic entropy. We also know from the variational principle of thermodynamics that the equilibrium corresponds to maximum entropy.

In this brief discussion, we fix our attention to the canonical ensemble, but similar considerations hold for the grancanonical one.

In some case, the energy is discretized and we use E (instead of $\mathcal{H}$) to indicate the energy level. Also, each energy level can be degenerate, meaning that more than one state have that energy. We indicate the degeneracy with $g_i = g(E_i)$.

We define the Boltzmann's weight as the probability to have energy E:

$$\rho_E = \frac{e^{-\beta E}}{Z_N} \quad Z_N = \sum_E g_E e^{-\beta E} \implies S = -k_B \sum_E \rho_E \log \rho_E \tag{2.8}$$

In some cases, we can measure the energy of a system, but we can't look for its microstate. However this is a general formula and we can use it even when we don't know the microstate.

Let's look back at the ensemble description:

- We have a very large number N of copies of the system, all described by the same values of macroscopic variables (macrostate), but corresponding to different values of microscopic variables (microstate)

- the probability that a given microstate occurs is the N-infinity limit of the frequency with which it appears (objective interpretation)

- all physics can be derived from knowing such probability distribution

Is there a principle to derive the probability distribution describing equilibrium?
The probability distribution describing equilibrium is the one corresponding to maximum entropy, given the macroscopic constraints.

Remark. This set-up (Boltzmann, Gibbs) is grounded on the idea that
i) we have a clear identification of what a micro/macrostate is
ii) probability are defined a-priori quantities.

> Previously, one constructed a theory based on the equations of motion, supplemented by additional hypotheses of ergodicity, metric transitivity, or equal a priori probabilities, and the identification of entropy was made only at the end, by comparison of the resulting equations with the laws of phenomenological thermodynamics. Now, however, we can take entropy as our starting concept, and the fact that a probability distribution maximizes the entropy subject to certain constraints becomes the essential fact which

justifies use of that distribution for inference.

E.T Jaynes, Information theory and Statistical Mechanics, Phys. Rev. 106 (1957) 620

Inference problem

The "objective" school of thoughts regards the probability of an event as an objective property of that event, always capable in principle of empirical measurement by observation of frequency ratios in a random experiment.
On the other hand, the "subjective" school of thought regards probabilities as expressions of human ignorance; the probability of an event is merely formal expression of our expectation that the event will or did occur, based on whatever information is available.

The inference problem is the following:
If the only info we have is that a certain function of x has a given mean value $\langle f \rangle = \sum_{j=1}^{N} p_j f(x_j)$, what is the expectation value of another function $g(x)$? We must use the probability distribution which has a maximum entropy subject to the constraints:

$$\sum_{j=1}^{N} p_j = 1 \qquad \sum_{j=1}^{N} p_j f(x_j) = \langle f(x) \rangle$$

which is obtained by maximizing (Lagrange multipliers) the function:

$$A = -\sum_{j=1}^{N} p_j \log p_j + \alpha \left(\sum_{j=1}^{N} p_j - 1 \right) + \gamma \left(\sum_{j=1}^{N} p_j(x_j) - \langle f \rangle \right)$$

Remark: It can be easily generalized to more observables and/or higher moments of the distribution

2.4.1   Probability distribution from maximum entropy principle

We have a finite set of energy levels E_r, each with degeneracy g_r, on which we distribute a number n_r of ensembles with total energy E to distribute among N copies of the system. The number of ways to do that is $W_{\{n_r\}} = W_{\{n_r\}}^{(1)} W_{\{n_r\}}^{(2)}$.
where $W^{(1)}$ does not consider degeneracy so it counts how many ways we can put n_r with E_r; while $W^{(2)}$: the n_r particles can be distributed in g_r state.

We first consider classical particles, so they are distinguishable if they have different energy. So:

$$W_{\{n_r\}}^{(1)} = \frac{N!}{n_1! n_2! \dots n_p!} \qquad N \text{ fixed} \quad n_1 \quad n_2 \quad \dots \quad n_r \quad \dots \quad n_p$$

$$W^{(1)}_{\{n_r\}} = \prod_r g_r^{n_r} \qquad E_r \text{ fixed} \qquad \underbrace{- \;\; - \;\; - \;\; - \;\; -}_{n_r} \, g_r$$

From the maximum entropy principle, the equilibrium distribution corresponds to max entropy $S = \log W_{\{n_r\}}$
with the constraints

$$N = \sum_r n_r \qquad E = \sum_r n_r E_r$$

So, in the classical case:

$$W_{\{n_r\}} = N! \prod_{r=1}^{p} \frac{g_r^{n_r}}{n_r!} \qquad S = k_B \log W_{\{n_r\}}$$

$$A = k_B \log W_{\{n_r\}} + \alpha \left(N - \sum_r n_r \right) + \beta \left(E - \sum_r n_r E_r \right)$$

$$= k_B \left[\log N! + \sum_r \log g_r^{n_r} - \sum_r \log n_r! \right] + \alpha \left(N - \sum_r n_r \right) + \beta \left(E - \sum_r n_r E_r \right)$$

$$= k_B \left[N \log N \cancel{- N} + \sum_r n_r \log g_r - \sum_r (n_r \log n_r \cancel{- n_r}) \right] + \alpha \left(N - \sum_r n_r \right) + \beta \left(E - \sum_r n_r E_r \right)$$

$$= k_B \left[N \log N + \sum_r n_r \log g_r - \sum_r n_r \log n_r \right] + \alpha \left(N - \sum_r n_r \right) + \beta \left(E - \sum_r n_r E_r \right)$$

To maximize this we derive:

$$0 = \left. \frac{\partial A}{\partial n_r} \right|_{n_r = n_r^*} = \log g_r - \log n_r^* - 1 - \alpha - \beta E_r$$

and we find the number of particle that maximizes the entropy:

$$\implies n_r^* = e^{-(1+\alpha)} g_r e^{-\beta E_r}$$

$$N = \sum_r n_r^* = e^{-(1-\alpha)} \sum_r g_r e^{-\beta E_r}$$

And we can get the probability to get a particle in the energy level r:

$$p_r = \frac{n_r^*}{N} = \frac{g_r e^{-\beta E_r}}{\sum_{r=1}^{p} g_r e^{-\beta E_r}} = \frac{g_r e^{-\beta E_r}}{Z}$$

So we get the same expression as in 2.8. Also, we obtain the Lagrange multiplier $\beta = \frac{1}{k_B T}$

Quantum particle instead are always indistinguishable, not only when they have the same energy. Thus there is only one way to have n_1 particles with energy E_1, n_2 particles with energy E_2, etc... So: $W^{(1)}_{\{n_r\}} = 1$ and

$$W_{\{n_r\}} = W^{(1)}_{\{n_r\}} W^{(2)}_{\{n_r\}} = W^{(2)}_{\{n_r\}}$$

For bosons, we can imagine of putting the particles in a line and draw boundaries to select in which energy level they are. So we have n_r indistinguishable particles and $g_r - 1$ indistinguishable boundaries. In total we have $n_r + g_r - 1$ objects:

$$W_{\{n_r\}} = W^{(2)}_{\{n_r\}} = \frac{(n_r + g_r - 1)!}{n_r!(g_r - 1)!}$$

For fermions, we can put at most 1 particle for each "box", which is like saying that each box can be empty or with a ball ($n_r < g_r$). So it's like selecting n_r objects out of g_r possibilities:

$$W_{\{n_r\}} = W^{(2)}_{\{n_r\}} = \frac{g_r!}{n_r!(g_r - n_r)!}$$

We will derive again this distributions in the next chapter.

Chapter 3

Quantum Statistical Mechanics

3.1   Review on Quantum Mechanics and Statistics

3.1.1   Quantum System

The degree of freedom of quantum particle are described in terms of a vector of the Hilbert space. With Dirac's notation, vectors are denoted like: $|\psi\rangle \in \mathcal{H}$. We can have a linear superposition: $\lambda |\psi_1\rangle + \mu |\psi_2\rangle \in \mathcal{H}$.
The scalar product of two vector is called a *braket*.

A (pure) **quantum state** is a ray (an equivalence class):

$$|\psi\rangle \sim e^{i\theta} |\psi\rangle \qquad \langle\psi| \sim e^{-i\theta} \langle\psi| \qquad \langle\psi|\psi\rangle = 1$$

So $|\psi\rangle \sim \lambda |\psi\rangle \qquad \lambda = |\lambda|e^{i\alpha} \neq 0$
The projection operator $\mathbb{P}$ represents uniquely a quantum state:

$$\mathbb{P}_\psi = \frac{|\psi\rangle \langle\psi|}{\langle\psi|\psi\rangle}$$

$\mathbb{P}$ is a projection operator if

- $\mathbb{P}$ is bounded

- $\mathbb{P}^\dagger = \mathbb{P}$ (self adjoint)

- $\mathbb{P}^2 = \mathbb{P}$ (idempotent)

PROOF:

$$\mathbb{P}_\psi^\dagger = \frac{(|\psi\rangle \langle\psi|)^\dagger = ((\langle\psi|)^\dagger(|\psi\rangle))^\dagger}{\langle\psi|\psi\rangle} = \frac{|\psi\rangle \langle\psi|}{\langle\psi|\psi\rangle} = \mathbb{P}_\psi$$

$$(\mathbb{P}_\psi)^2 = \frac{|\psi\rangle \langle\psi|\psi\rangle \langle\psi|}{\langle\psi|\psi\rangle^2} = \mathbb{P}_\psi$$

This operator projects on the linear subspace generated by $|\psi\rangle$:

$$\mathcal{H}_\psi = \{\lambda |\psi\rangle, \quad \lambda \in \mathbb{C}\} \qquad \mathbb{P}_\psi(\lambda |\psi\rangle) = \lambda |\psi\rangle$$

$$|\phi\rangle \in \mathcal{H}_\psi^\perp = \{|\phi\rangle \leq 1 \quad \langle\psi|\phi\rangle = 0\} \qquad \mathbb{P}_\psi |\phi\rangle = 0$$

An **observable** is given by a self-adjoint operator: $A : \mathcal{H} \to \mathcal{H} \qquad A^\dagger = A$
for which the spectral theorem holds: $A |\psi_j\rangle = \lambda_j |\psi_j\rangle$:

- The eigenvalues are real: $\lambda_j \in \mathbb{R}$

- The eigenvectors (normalized) are orthogonal: $\langle\psi_n|\psi_m\rangle = 0 \quad n \neq 0$

- $\{|\psi_n\rangle\}_n$ is an orthonormal (o.n) complete set, thus it's an orthonormal basis of $\mathcal{H}$.

Since we're only referring to bounded operators, the words *hermitian* and *self-adjoint* are equivalent.

So each vector of the Hilbert space can be expressed as a linear combination of the basis vectors:

$$\mathcal{H} \ni |\psi\rangle = \sum_n \epsilon_n |\psi\rangle_n$$

$$\text{if} \qquad n \neq m, \mathbb{P}_n \mathbb{P}_m = |\psi_n\rangle \underbrace{\langle \psi_n | \psi_m \rangle}_{\text{orthogonal}} \langle \psi_m | = 0 \implies \boxed{\mathbb{P}_n \mathbb{P}_m = \delta_{nm} \mathbb{P}_n}$$

Also, the sum $\mathbb{P}_1 + \mathbb{P}_2$ is the projection over the span (linear combination) of ψ_1, ψ_2, so:

$$\boxed{\sum_n \mathbb{P}_n = \mathbb{I}} \qquad \text{Completeness}$$

Let's recap better the spectral theorem: if an operator A is self-adjoint, there exists a set of projection operators that diagonalize the operator:

$$\boxed{A = \sum_n \lambda_n \mathbb{P}_n} \qquad \mathbb{P}_n = |\psi_n\rangle \langle \psi_n| \tag{3.1}$$

with: $\mathbb{P}_n^\dagger = \mathbb{P}_n \quad \mathbb{P}_n \mathbb{P}_m = \delta_{nm} \mathbb{P}_n \quad \sum_n \mathbb{P}_n = \mathbb{I} \qquad \forall n \in \mathbb{R}$

The **Evolution** of a system is fixed by a special observable, called *hamiltonian* H, through the Schrodinger equation:

$$i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} = H |\psi(t)\rangle$$

We will consider only cases where the hamiltonian is time-independent. In this case the evolution is fixed by a unitary operator U:

$$|\psi(t)\rangle = U(t) |\psi(t = 0)\rangle \qquad U(t) = e^{-itH/\hbar}$$

Unitary means: $U(t)^\dagger = U(t)^{-1} = U(-t)$.
That means that: $\langle \psi(t)|\psi(t)\rangle = \langle \psi(t = 0)|\psi(t = 0)\rangle$, so normalization is preserved (thus probability is conserved).

The dynamic of a quantum system is perfectly deterministic: if we know $|\psi(t = 0)\rangle$ and apply the equation above, we have the evolution. The probabilistic aspect arises in the measurement.

A **measure** of an observable A on a state $|\psi\rangle$ yields a set of possible outcomes $\{\lambda_n\}$ corresponding to its eigenvalues, with probabilities p_n given by:

$$p_n = |c_n|^2 \qquad \text{where } |\psi\rangle = \sum_n c_n |\psi_n\rangle \qquad \left(\sum_n |c_n|^2 = 1 \iff \langle\psi_i|\psi_j\rangle = \delta_{ij} \right)$$

$$p_n = \langle\psi|\mathbb{P}_n|\psi\rangle = \langle\psi|\psi_n\rangle \langle\psi_n|\psi\rangle = |\langle\psi_n|\psi\rangle|^2$$

$$\langle\psi_n|\psi\rangle = \left\langle \psi_n \middle| \sum_n c_n \psi_n \right\rangle = \dots$$

So: $p_n = |c_n|^2 = \langle\psi|\mathbb{P}_n|\psi\rangle$

Remark: after the measurement, the state $|\psi\rangle$ collapses into $|\psi_n\rangle$

Also, we can note that, using the spectral decomposition of the operator A (eq. 3.1) we can write:

$$\langle A\rangle = \langle\psi|A|\psi\rangle = \left\langle \psi \middle| \sum_n \lambda_n \mathbb{P}_n \middle| \psi \right\rangle = \sum_n \lambda_n \langle\psi|\mathbb{P}_n|\psi\rangle = \sum_n \lambda_n p_n$$

which is the statistical average.

This kind of measure is called projective measure, because one can also generalize the notion of measure by not starting with A decomposed using the projection operators.

3.1.2 Density matrix

Suppose we have two particles described by $\mathcal{H}_1, \mathcal{H}_2$. Then $\mathcal{H}_{TOT} = \mathcal{H}_1 \otimes \mathcal{H}_2$ and $\dim(\mathcal{H}_1 \otimes \mathcal{H}_2) = n \cdot m$. This is different from classical mechanics, where the total space is the Cartesian product between two spaces: $\mathcal{M}_1 \times \mathcal{M}_2$ and $\dim(\mathcal{M}_1 \times \mathcal{M}_2) = n + m$.

Let $\{|\psi_n\rangle\}_n, \{|\phi_m\rangle\}_m$ be the o.n basis of $\mathcal{H}_1, \mathcal{H}_2$ respectively. Then $\mathcal{H}_1 \otimes \mathcal{H}_2$ is generated by $|\psi_n\rangle |\phi_m\rangle = |\psi_n\phi_m\rangle$ o.n basis.

That means that every object of this space can be written as a linear composition of this following object:

$$\mathcal{H}_1 \otimes \mathcal{H}_2 \ni |\psi\rangle = \sum_{n,m} \alpha_{n,m} |\psi_n\phi_m\rangle$$

$$\langle\psi_n|\phi_m|\psi'_n\phi'_m\rangle = \langle\psi_n|\psi'_n\rangle_{\mathcal{H}_1} \langle\phi_m|\phi'_m\rangle_{\mathcal{H}_2} = \delta_{nn'}\delta_{mm'}$$

If we take a vector of the Hilbert space: $|\psi\rangle \in \mathcal{H}$, its projection is

$$\mathbb{P}_\psi = |\psi\rangle \langle\psi|$$

THEOREM: If $\rho_\psi = \mathbb{P}_\psi = |\psi\rangle \langle\psi|$, then ρ_ψ is:

i. A bounded operator: $\|\rho_\psi\| \leq 1$

ii. Self-adjoint: $\rho_\psi^\dagger = \rho_\psi$

iii. Positive: $\langle\alpha|\rho_\psi|\alpha\rangle \geq 0, \quad \forall\,|\alpha\rangle$

iv. Unit-trace: $Tr[\rho_\psi] = 1$

v. Idempotent: $\rho_\psi^2 = \rho_\psi$

PROOF: Let's prove the new ones (iii and iv):

iii. $\rho_\psi = |\psi\rangle\langle\psi|$

$$\langle\alpha|\rho_\psi|\alpha\rangle = \langle\alpha|\psi\rangle\langle\psi|\alpha\rangle = |\langle\alpha|\psi\rangle|^2 \geq 0$$

iv. $[\mathbb{M}]_{\min} = \langle e_n|\mathbb{M}|e_m\rangle$ $\{e_n\}$ o.n. basis

$$Tr[\mathbb{M}] = \sum_{n=1}^{N} \langle e_n|\mathbb{M}|e_n\rangle \qquad \text{finite-dim}$$

This is:

(1) linear $Tr[\mathbb{M}_1 + \mathbb{M}_2] = Tr[\mathbb{M}_1] + Tr[\mathbb{M}_2]$

(2) cyclic $Tr[\mathbb{M}_1\mathbb{M}_2\ldots\mathbb{M}_k] = Tr[\mathbb{M}_k\mathbb{M}_1\ldots\mathbb{M}_{k-1}]$

So it's independent on the chosen o.n. basis. If U is the matrix of basis change:

$$\mathbb{M} \to U^{-1}\mathbb{M}U \implies Tr[U^{-1}\mathbb{M}U] = Tr[\underbrace{UU^{-1}}_{\mathbb{I}}\mathbb{M}^{-1}] = Tr[\mathbb{M}^{-1}]$$

So we have a trace-class operator A such that:

$$TrA \equiv \sum_{n=1}^{\infty} \langle e_n|A|e_n\rangle < +\infty$$

We want to prove that $\rho_\psi = |\psi\rangle\langle\psi|$ is a trace-class operator with $Tr[\rho_\psi] = 1$.
We can choose this o.n. basis: $\{|e_1\rangle = |\psi\rangle, |e_2\rangle, |e_3\rangle\}$ such that:

$$\langle\psi|e_1\rangle = \langle\psi|\psi\rangle = 1 \qquad \langle\psi|e_j\rangle = 0 \quad j = 2,3$$

$$Tr[\rho_\psi] = \sum_n \langle e_n|\rho_\psi|e_n\rangle = \sum_n \underbrace{\langle e_n|\psi\rangle}_{\delta_{n1}}\underbrace{\langle\psi|e_n\rangle}_{\delta_{n1}} = 1$$

Let's now prove the other way:

THEOREM: If ρ is such that (i) $\leftrightarrow$ (v) are satisfied, then exists $|\psi\rangle \in \mathcal{H}$ such that $\rho = |\psi\rangle \langle\psi|$

PROOF: From (i) and (ii) follows that ρ is bounded and self-adjoint. So we can write it using the spectral decomposition: $\rho = \sum \lambda_n \mathbb{P}_n$ and states that:

$$\mathbb{P}_n = |e_n\rangle \langle e_n| \qquad \{|e_n\rangle\} \text{o.n. basis} \quad \rho |e_n\rangle = \lambda_n |e_n\rangle$$

From (iii): $\lambda_n \geq 0$
From (v):

$$\rho^2 = \left(\sum_n \lambda_n \mathbb{P}_n\right)^2 = \sum_{nm} \lambda_n \lambda_m \underbrace{\mathbb{P}_n \mathbb{P}_m}_{\delta_{nm}\mathbb{P}_n} = \sum_n \lambda_n^2 \mathbb{P}_n \stackrel{(v)}{=} \sum_n \lambda_n \mathbb{P}_n \iff \lambda_n^2 = \lambda_n$$

and since λ is positive $\iff \lambda_n = 0, \quad \lambda_n = 1 \quad \forall n$
From (iv): $Tr[\rho] = \sum_n \lambda_n = 1$. So that means that all the λ are 0 apart from one of them which is 1.

If we suppose $\lambda_1 = 1, \quad \lambda_2 = \lambda_3 = \cdots = 0 \qquad \rho = \lambda_1 \mathbb{P}_1 = \mathbb{P}_1 = |e_1\rangle \langle e_1|$

This allow us to give the following:

DEFINITION: A **pure state** of a quantum system is described by ρ such that $\rho = |\psi\rangle \langle\psi| \iff (i) \leftrightarrow (v)$
ρ is called **density operator (matrix)**.

So we've seen that a pure state is defined by a ray $[|\psi\rangle]$ or equivalently by its associated (rank-1) projector:
$\mathcal{H} \ni |\psi\rangle$ normalized $|\psi\rangle \sim e^{i\phi} |\psi\rangle \iff$ density op. $\rho_\psi = |\psi\rangle \langle\psi|$ iff $(i) \leftrightarrow (v)$

We can also have a **mixed state**, for instance an electron produced in a lab which is neither spin up nor spin down.
A mixed state is defined by a statistical ensemble of pure states:

$$\{|\psi_k\rangle, p_k\}_k \quad k = 1, \ldots, M$$

and it's represented by means of the density operator

$$\rho \equiv \sum_{k=1}^{M} \rho_k p_k$$

A mixed state satisfies (i) $\leftrightarrow$ (iv):
(i),(ii) is trivial because it's sum of (i) and (ii)

(iii) $\rho \geq 0$ because $0 \leq \rho_k \leq 1$

(iv) $Tr[\rho] = Tr[\sum_k \rho_k p_k] = \sum_k p_k Tr[\rho_k] = \sum_k p_k = 1$

However, (v) does not hold ($\rho^2 \neq \rho$).

In fact: $\{|\psi_k\rangle\}$ orthogonal $\implies \langle \psi_k|\psi_{k'}\rangle = 0$ if $k \neq k'$.

$$\rho_k \rho_{k'} = |\psi_k\rangle \underbrace{\langle \psi_k|\psi_{k'}\rangle}_{0} \langle \psi_k| = 0$$

$$\rho^2 = \left(\sum_{k=0}^{M} p_k \rho_k\right)^2 = \sum_{k=0}^{M} p_k^2 \rho_k^2 = \sum_{k=0}^{M} p_k^2 \rho_k^2$$

which is equal to $\rho = \sum_{k=0}^{M} p_k \rho_k$,   only if:

$\exists \bar{k} : p_{\bar{k}} \neq 0,$ $p_{\bar{k}} = 1$ with $p_k = 0 \; \forall k \neq \bar{k}$

So (v) is true only if $\rho = |\psi_k\rangle \langle \psi_k|$ is a pure state.

So we can say that a (generic) **state** is described by a density operator ρ that satisfies (i) $\leftrightarrow$ (iv) and:

THEOREM: A density matrix is pure ($\exists |\psi\rangle$, $\rho = |\psi\rangle \langle \psi|$) $\iff \rho^2 = \rho$

Expectation value:

The expectation value of an observable A in the case of $\rho_\psi = |\psi\rangle \langle \psi|$ can be written as:

$$\langle A\rangle_\psi = \langle \psi|A|\psi\rangle = Tr[\rho_\psi A]$$

We can generalize this to a mixed case $\rho = \sum_{k=0}^{M} p_k \rho_k$:

$$\langle A\rangle_\rho = \sum_{k=0}^{M} p_k \frac{Tr[\rho_k A]}{\langle A\rangle_{\psi_k}} = Tr\left[\left(\sum_{k=0}^{M} p_k \rho_k\right) A\right] = Tr[\rho A]$$

So in general, $\forall \rho$: $\langle A\rangle_\rho = Tr[\rho A]$

An example: the Qubit

A classic bit is just a number that can be 0 or 1, while the quantum bit is a 2-level system for which:

$$\mathcal{H} = \mathbb{C}^2 = \left\{\begin{pmatrix}\alpha\\\beta\end{pmatrix} \quad \alpha, \beta \in \mathbb{C}\right\} \qquad |\psi\rangle = \begin{pmatrix}\alpha\\\beta\end{pmatrix} \quad |\alpha|^2 + |\beta|^2 = 1$$

An equivalent way to describe it is to chose an o.n basis $\{|0\rangle, |1\rangle\}$

where: $|0\rangle = \begin{pmatrix}1\\0\end{pmatrix}$, $|1\rangle = \begin{pmatrix}0\\1\end{pmatrix}$

A qubit is a generic state of this space, which is a linear superposition of the 0 and 1 state: $\boxed{|\psi\rangle = \alpha |0\rangle + \beta |1\rangle}$ with $|\alpha|^2 + |\beta|^2 = 1$

We can describe the evolution on this system:

$$|\psi\rangle = \alpha |0\rangle + \beta |1\rangle \quad |\alpha|^2 + |\beta|^2 = 1 \quad \rightarrow \quad \alpha' |0\rangle + \beta' |1\rangle \quad |\alpha'|^2 + |\beta'|^2 = 1$$

trough a unitary operator U, which in this case represents rotations on the Bloch sphere. We can also define:

1. $\mathbb{I} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \mathbb{I} |\psi\rangle = |\psi\rangle$

2. $\text{NOT} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = X$ Pauli matrix $\qquad |0\rangle \rightarrow |1\rangle \quad |1\rangle \rightarrow |0\rangle$

3. $Z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad |0\rangle \rightarrow |0\rangle \quad |1\rangle \rightarrow -|1\rangle$

which construct a quantum gate on a single qubit.

With 2 qubits we have:

$$\mathcal{H}_1 = \{|0\rangle_1, |1\rangle_1\} \qquad \mathcal{H}_2 = \{|0\rangle_2, |1\rangle_2\} \qquad \mathcal{H}_{TOT} = \mathcal{H}_1 \otimes \mathcal{H}_2$$

and the o.n basis of $\mathcal{H}_{TOT}$ is 4 dimensional, made from:

$$|0\rangle_1 |0\rangle_2 = |00\rangle \qquad |0\rangle_1 |1\rangle_2 = |01\rangle \qquad |1\rangle_1 |0\rangle_2 = |10\rangle \qquad |1\rangle_1 |1\rangle_2 = |11\rangle$$

A generic state of 2 qubits is described by:

$$|\psi\rangle = \alpha_{00} |00\rangle + \alpha_{01} |01\rangle + \alpha_{10} |10\rangle + \alpha_{11} |11\rangle \qquad \text{with } |\alpha_{00}|^2 + |\alpha_{01}|^2 + |\alpha_{10}|^2 + |\alpha_{11}|^2 = 1$$

We can also have separable or entangled states:

1. $\alpha_{10} = \alpha_{11} = 0$
   $|\psi\rangle = \alpha_{00} |00\rangle + \alpha_{01} |01\rangle = |0\rangle_1 (\alpha_{00} |0\rangle_2 + \alpha_{01} |1\rangle_2) = |\psi\rangle_1 |\phi\rangle_2$
   In this case, the state is called separable, because it can be separated into a multiplication of a state of particle 1 · a state of particle 2.

2. $\alpha_{01} = \alpha_{10} = 0 \implies |\psi\rangle = \alpha_{00} |00\rangle + \alpha_{11} |11\rangle$
   This state is not separable, so we say it's *entangled*. An example of an entangled state is a Bell state: $|\psi\rangle = \frac{|00\rangle + |11\rangle}{\sqrt{2}}$

   Suppose these are spin $\uparrow(0)$ or $\downarrow(1)$. Alice and Bob can measure it and the output will be unpredictably $\uparrow$ or $\downarrow$ with 50% of probability. However, if Alice measure $\uparrow$, she knows for sure that Bob will measure $\uparrow$ too.

A qubit is a pure state. In fact (i)↔(v) are satisfied. In particular, (v) follows from the condition $|\alpha|^2 + |\beta|^2 = 1$.

Note that being a pure state, it means that all the particles are in the state $|\psi\rangle = \alpha|0\rangle + \beta|1\rangle$, then it's the measure procedure that makes it collapse to $|0\rangle$ or $|1\rangle$ - ↑ or ↓.

- Pure density matrix

$$\rho_\psi = |\psi\rangle\langle\psi| = \begin{pmatrix} \alpha \\ \beta \end{pmatrix} (\alpha^* \beta^*) = \begin{pmatrix} |\alpha|^2 & \alpha\beta^* \\ \alpha^*\beta & |\beta|^2 \end{pmatrix}$$

  The diagonal pieces $(p_\alpha = |\alpha|^2, p_\beta = |\beta|^2$ represents the probability of a measure. The non-diagonal pieces are instead responsible for the quantum interference phenomena.

- Mixed density matrix
  A mixed state would be a state where some particles are prepared as ↑, some others as ↓ (a so-called *classical mixture*):

$$\begin{cases} |0\rangle & \text{with } p_0 = |\alpha|^2 \quad \rho_0 = |0\rangle\langle0| \\ |1\rangle & \text{with } p_1 = |\beta|^2 \quad \rho_1 = |1\rangle\langle1| \end{cases} \qquad \text{Mixed state: } \rho = p_0\rho_0 + p_1\rho_1$$

$$\rho_0 = |0\rangle\langle0| = \begin{pmatrix} 1 \\ 0 \end{pmatrix}(1 \quad 0) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \qquad \rho_1 = |1\rangle\langle1| = \begin{pmatrix} 0 \\ 1 \end{pmatrix}(0 \quad 1) = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\rho = |\alpha|^2 \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + |\beta|^2 \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} |\alpha|^2 & 0 \\ 0 & |\beta|^2 \end{pmatrix}$$

We can notice that if we do a measure, the probabilities of the outcome are the same as before, even if the matrices are different.

Exercise: Design an experiment which is able to determine if the system is in a pure on in a mixed state.

3.1.3 Identical particles - Permutation group

Let's consider a system composed by N subsystems (N particles), each described by $\mathcal{H}_j \quad j = 1, \ldots, N$. The system will be described by the Hilbert space:

$$\mathcal{H}_{tot} = \mathcal{H}_1 \otimes \mathcal{H}_2 \otimes \cdots \otimes \mathcal{H}_N$$

If the subsystems are identical: $\mathcal{H}_j \equiv \mathcal{H} \implies \mathcal{H}_{tot} = \mathcal{H}^{\otimes N}$
If they are also indistinguishable, the states span only a subspace of $\mathcal{H}_{tot}$, whose vector

have special properties under the action of the permutation group: under the action of
a permutation (i.e. swapping particles around), the state should be invariant, up to a
phase. In the following we will see why and also that there are two way to achieve this
result: this will lead to the definition of bosons and fermions.

We need to see the properties of a quantum system under the effect of permutation
group. Let's see the permutations of the N objects we have:

$$(1, 2, 3, \ldots N) \xrightarrow{\sigma} (\sigma(1), \sigma(2), \ldots, \sigma(N))$$

The set of all possible permutations of N elements is a group. Let's call it $\mathbb{P}_N$: the
permutation group on N elements. This is a group because:

- it's closed under composition (a composition of permutation is a permutation)

- has an identity $\mathbb{I} : (1, 2, \ldots, N) \to (1, 2, \ldots, N)$

- $\forall \sigma, \exists \sigma^{-1}$(inverse) $s.t.$ $\sigma^{-1} \circ \sigma = \mathbb{I}$

We can notice that $\mathbb{P}_N$ has a finite number of elements $(= N!)$.

A transposition (or elementary permutation) σ_j $j = 1, \ldots, N-1$ is a swap between
the j and the $j+1$ elements. Then a permutation can be decomposed into transpositions.
In other words, the $N - 1$ transpositions are the generator of the group:
  THEOREM: $\forall \sigma \in \mathbb{P}_N :$ $\sigma = \sigma_{\alpha_1} \sigma_{\alpha_2} \ldots \sigma_{\alpha_k}$ k finite
This decomposition is not unique and also k is not an unique value. However, all de-
composition of the same element has always an even/odd number of transposition (k
is always even or odd)

This allows us to divide the permutations into even and odd permutations.
  DEFINITION: $sgn(\sigma) = \begin{cases} +1 & k \text{ is even} \\ -1 & k \text{ is odd} \end{cases}$
  The transpositions are not all independent, but there are relations between them.
In fact, they satisfy the identities:

  i. $\sigma_i \sigma_j = \sigma_j \sigma_i$ if $|i - j| \geq 2$ (visual proof in figure 3.1a)

  ii. $\sigma_i \sigma_{i+1} \sigma_i = \sigma_{i+1} \sigma_i \sigma_{i+1}$ (visual proof in figure 3.1b)

  iii. $(\sigma_i)^2 = \mathbb{I}$ (trivial)

$\mathbb{P}_N$, the group generated by the $N - 1$ transpositions σ_j, satisfies as well the prop-
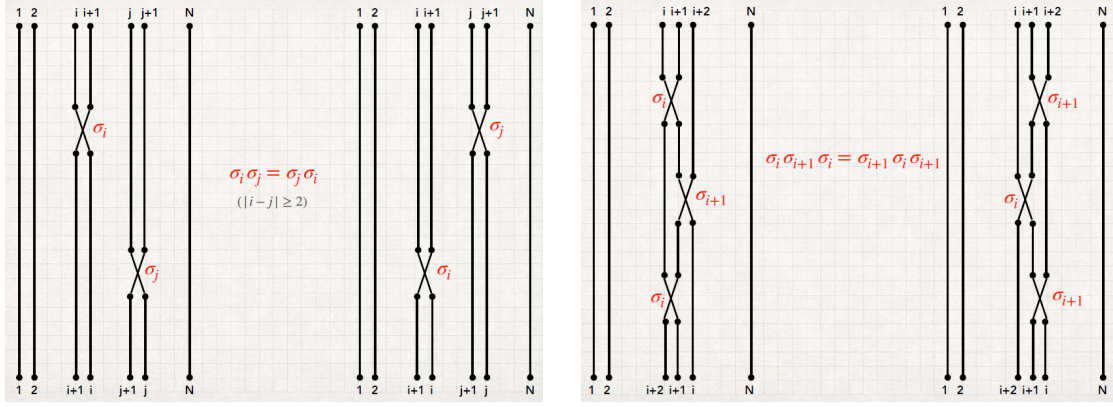erties (i) (ii) (iii).

Figure 3.1: Visual proofs of identities between the transpositions

3.1.4 Quantum statistic

If some objects are indistinguishable, it means that a permutation among those

$$\psi(1, 2, \ldots, N) \overset{\sigma}{\mapsto} \psi(\sigma(1), \sigma(2), \sigma(N))$$

doesn't affect the physical content of a wave function, which is $|\psi(x_1, x_2, \ldots, x_N)|^2$. That means that the wave function should be the same up to a global phase:

$$\psi(\sigma(1), \sigma(2), \ldots, \sigma(N)) = e^{i\phi_\sigma} \psi(1, 2, \ldots, N)$$

Remark: this is a physical property, not a mathematical one.

If we then decompose a permutation into transpositions that generate it:

$$\sigma = \sigma_{\alpha_1}, \sigma_{\alpha_2}, \ldots, \sigma_{\alpha_k}$$

$$
\begin{aligned}
\psi(1, 2, \ldots, N) &\overset{\sigma_{\alpha_1}}{\longmapsto} \psi(\sigma_{\alpha_1}(1, \ldots N)) = e^{i\phi_{\alpha_1}} \psi(1, \ldots, N) \\
&\overset{\sigma_{\alpha_2}}{\longmapsto} e^{i\phi_{\alpha_2}} \left(e^{i\phi_{\alpha_1}} \psi(1, \ldots, N) \right) \\
&\overset{\cdots}{\longmapsto} e^{i(\phi_{\alpha_1} + \phi_{\alpha_2} + \cdots + \phi_{\alpha_N})} \psi(1, \ldots, N) = e^{\phi_\sigma} \psi(1, \ldots, N)
\end{aligned}
$$

with: $\phi_\sigma = \phi_{\alpha_1} + \phi_{\alpha_2} + \cdots + \phi_{\alpha_k}$

Let's now analyze a single transposition: $\sigma_j : \psi(1, \ldots, N) \mapsto e^{i\phi_j} \psi(1, \ldots, N)$, which we will simply write as $\sigma_j \mapsto e^{i\phi_j}$.

This must satisfy the (i),(ii),(iii) relations of a transposition and this leads to some considerations on the phase:

i if $|i - j| \geq 2$, then $\sigma_i \sigma_j = \sigma_j \sigma_i$, so:

$$\left. \begin{aligned} \sigma_i \sigma_j &\mapsto e^{i(\phi_i + \phi_j)} \\ \sigma_j \sigma_i &\mapsto e^{i(\phi_j + \phi_i)} \end{aligned} \right\} \iff \phi_i + \phi_j = \phi_j + \phi_i \qquad \text{Trivially satisfied}$$

ii $\sigma_i\sigma_{i+1}\sigma_i = \sigma_{i+1}\sigma_i\sigma_{i+1}$, so:

$$\left.\begin{array}{ll}\sigma_i\sigma_{i+1}\sigma_i & \mapsto e^{i(\phi_i+\phi_{i+1}+\phi_i)} \\[6pt] \sigma_{i+1}\sigma_i\sigma_{i+1} & \mapsto e^{i(\phi_{i+1}+\phi_i+\phi_{i+1})}\end{array}\right\} \iff \phi_i+\phi_{i+1}+\phi_i = \phi_{i+1}+\phi_i+\phi_{i+1} \iff \boxed{\phi_i = \phi_{i+1}}\ \forall i$$

So $\phi_j = \phi\ \forall j$ and the single transposition $\sigma_j \mapsto e^{i\phi_j}$ becomes simply: $\sigma_j \mapsto e^{i\phi}$

iii $(\sigma_j)^2 = \mathbb{I}$, so:

$$\left.\begin{array}{ll}(\sigma_j)^2 & \mapsto e^{i(\phi+\phi)} = e^{i2\phi} \\[6pt] \mathbb{I} & \mapsto e^{i2\pi n}\end{array}\right\} \iff 2\phi = 2\pi n \quad n \in \mathbb{Z}$$

So there are only 2 possibilities (since $\phi \in [0, 2\pi[$):

1. $\phi = 0$ $\psi(1, \ldots, N) \xmapsto{\sigma_j} \psi(1, \ldots, N)$

2. $\phi = \pi$ $\psi(1, \ldots, N) \xmapsto{\sigma_j} -\psi(1, \ldots, N)$ $(e^{i\pi} = -1)$

This applies for a single transposition. For the whole permutation $\sigma = \sigma_{\alpha_1}\sigma_{\alpha_2}\ldots\sigma_{\alpha_k}$ and $\phi_\sigma = \phi_{\alpha_1} + \phi_{\alpha_2} + \cdots + \phi_{\alpha_k}$. So we have:

1. $\phi_{\alpha_j} = 0$ $\phi_\sigma = 0$ $\psi(1, \ldots, N) \xmapsto{\forall \sigma \in \mathbb{P}_N} \psi(1, \ldots, N)$ (Bosons)

2. $\phi_{\alpha_j} = \pi$ $\phi_\sigma = k\pi$ $e^{i\phi_\sigma} = e^{ik\pi} = (-1)^k$ $\begin{array}{l}k \text{ even } \psi \mapsto \psi \\ k \text{ odd } \psi \mapsto -\psi\end{array}$ (Fermions)

For bosons, the way function is completely symmetric. For fermions it is completely anti-symmetric. Remark: what we call *bosons* and *fermions* are just due to the statistic and has nothing to do with spin. Only in relativistic quantum mechanics one can prove the spin-statistic theorem.

(VIII) MON 14/11/2022

An example: System of N=2 particles in $\mathbb{R}^3$

We can describe two particles in $\mathbb{R}^3$ with two vectors: $\vec{x}_1, \vec{x}_2 \in \mathbb{R}^3$.
The Hilbert spaces respectively for a single particle and for two particles are

$$\mathcal{H}_{N=1} = L^2(\mathbb{R}^3) = \{\psi(\vec{x}_1) \quad \text{square integral}\}$$
$$\mathcal{H}_{N=2} = L^2(\mathbb{R}^6) = \{\psi(\vec{x}_1, \vec{x}_2), \quad \text{square integral}\}$$

where $L^2(\mathbb{R}^6) = L^2(\mathbb{R}^3) \circ L^2(\mathbb{R}^3)$.
Permutations are described by the permutation group: $\mathbb{P}_2 = \{\mathbb{I}, \sigma\}$ with $\sigma : x_1 \leftrightarrow x_2$
According to our rules, the wave function should be symmetric in the bosonic case and anti-symmetric in the fermionic case. So we define two operators:

- Symmetrizer: $\widehat{S} : \psi(x_1, x_2) \mapsto \frac{\psi(x_1, x_2) + \psi(x_2, x_1)}{2} = \psi_+(x_1, x_2)$ (symmetric by construction)

- Antisymmetrizer: $\widehat{A} : \psi(x_1, x_2) \mapsto \frac{\psi(x_1, x_2) - \psi(x_2, x_1)}{2} = \psi_-(x_1, x_2)$ (antysimmetric)

It is easy to show (as an exercises), that $\widehat{S}$ and $\widehat{A}$ are projection operators. In fact
$$\widehat{S}^\dagger = \widehat{S} \qquad \widehat{S}^2 = \widehat{S} \qquad \widehat{A}^\dagger = \widehat{A} \qquad \widehat{A}^2 = \widehat{A}$$
If we call $\mathcal{H}_S$ and $\mathcal{H}_A$ respectively the spaces of symmetric and anti-symmetric wave functions: $\widehat{S} : \mathcal{H} \mapsto \mathcal{H}_S \qquad \widehat{A} : \mathcal{H} \mapsto \mathcal{H}_A \qquad \mathcal{H}_S, \mathcal{H}_A \subset \mathcal{H} = L^2(\mathbb{R}^6)$
Also: $\widehat{S}\widehat{A} = \widehat{A}\widehat{S} = 0 \rightarrow \mathcal{H}_S \perp \mathcal{H}_A$
In fact:

$$\langle \psi_+ | \phi_- \rangle \overset{\text{def. of scalar prod.}}{=\!=\!=} \int d^3\vec{x}_1 d^3\vec{x}_2 \; \psi_+^*(x_1, x_2)\phi_-(x_1, x_2)$$

$$= \int symm \cdot antisymm = \int \text{anti-symmetric function} = 0$$

So we can write $\mathcal{H} = \mathcal{H}_S \oplus_\perp \mathcal{H}_A$. In fact every function can be written as the sum of a symmetric and an anti-symmetric function:

$$\psi(x_1, x_2) = \frac{\psi_+(x_1, x_2) + \psi_-(x_1, x_2)}{2}$$

Notice that since fermions are described by an anti-symmetric wave function, they can't occupy the same state (Pauli exclusion principle is automatically included in this construction):

$$u_\alpha(x_1)u_\beta(x_2) \mapsto \frac{u_\alpha(x_1)u_\beta(x_2) - u_\alpha(x_1)u_\beta(x_2)}{2} = 0 \quad \text{if } \alpha = \beta$$

Generic $N > 2$ particles in $\mathbb{R}^3$
With N particles, we can have more transpositions. Let's indicate with $P \in \mathbb{P}_N$ a permutation: $\widehat{P} : \psi(x_1, x_2, \dots, x_n) \mapsto \psi\left(x_{P^{-1}_{(1)}}, x_{P^{-1}_{(2)}}, \dots, x_{P^{-1}_{(N)}}\right)$. This just re-shuffle the order of particles.
We define:

$$\widehat{S} = \frac{1}{N!} \sum_{P \in \mathbb{P}_N} \widehat{P} \qquad \widehat{S} : \psi(x_1, x_2, \dots, x_N) \mapsto \frac{1}{N!} \sum_P \widehat{P}_\psi$$

$$\widehat{A} = \frac{1}{N!} \sum_{P \in \mathbb{P}_N} sgn(P)\widehat{P} \qquad sgn(P) = \begin{cases} +1 & P \text{ is an even permutation} \\ -1 & P \text{ is an odd permutation} \end{cases}$$

As before, $\widehat{S}$ and $\widehat{A}$ are orthogonal projector operators:
$$\widehat{S}^\dagger = \widehat{S} \qquad \widehat{S}^2 = \widehat{S} \qquad \widehat{A}^\dagger = \widehat{A} \qquad \widehat{A}^2 = \widehat{A}. \qquad \text{and: } \widehat{S}\widehat{A} = \widehat{A}\widehat{S} = 0$$
Also: $\widehat{S} : \mathcal{H}_N \rightarrow \mathcal{H}_S \qquad \widehat{A} : \mathcal{H}_N \rightarrow \mathcal{H}_A \qquad \mathcal{H}_S \perp \mathcal{H}A$

$$\implies \mathcal{H}_N = \underbrace{\mathcal{H}_S}_{\text{bosons}} \oplus_\perp \underbrace{\mathcal{H}_A}_{\text{fermions}} \oplus_\perp \underbrace{\mathcal{H}'}_{\text{non-physical}}$$

with 3 or more particles there are function that ar neither symmetric nor anti-symmetric.

We can have an example of $\mathcal{H}'$ in a system of N particles in $\mathbb{R}^d$. A single particle is described by $\mathcal{H}_1 = L^2(\mathbb{R}^d)$ with the orthonormal basis: $\{u_\alpha(x)\}_{\alpha=1}^\infty$.
N particles are described by $\mathcal{H}_N = \underbrace{L^2(\mathbb{R}^d) \otimes \cdots \otimes L^2(\mathbb{R}^d)}_{N \text{ times}}$ with the o.n basis

$\{\psi_{\alpha_1\alpha_2\ldots\alpha_N}(x_1, x_2, \ldots, x_N) = u_{\alpha_1}(x_1)u_{\alpha_2}(x_2)\ldots u_{\alpha_N}(x_N)\}_{\alpha_1\alpha_2\ldots\alpha_N}$
Notice that the order is important, because it indicates that there is particle 1 in α, particle 2 in β etc..

We aim at describing in an intrinsic way each $\mathcal{H}_N^{(\widehat{S})}, \mathcal{H}_N^{(\widehat{A})}$. We can define the symmetrizer and antisymmetrizer as:

$$\widehat{S} : \psi_{\alpha_1\alpha_2\ldots\alpha_N}(x_1, x_2, \ldots, x_N) = \psi_{n_1,n_2,\ldots,n_k\ldots}^{\widehat{S}}(x_1, x_2, \ldots, x_N)$$
$$\widehat{A} : \psi_{\alpha_1\alpha_2\ldots\alpha_N}(x_1, x_2, \ldots, x_N) = \psi_{n_1,n_2,\ldots,n_k\ldots}^{\widehat{A}}(x_1, x_2, \ldots, x_N)$$

Here we can see that the order is no longer important and what matters is just how many particle are in each state. n_k is called *occupation number* and counts just that: how many particles are in the k state. Notice that for bosons there are no constraints ($n_k = 0, 1, 2, \ldots$), while for fermions there can only be 1 particle at maximum for each state ($n_k = 0, 1$).

Also, the total number of particles should be constant, so $\boxed{\sum_{k=1}^\infty n_k = N}$

For example, with $N = 3$ we have: $u_\alpha(x_1)u_\beta(x_2)u_\gamma(x_3)$ as the o.n basis and the possible permutations are:

$$
\begin{array}{lll}
1\ 2\ 3 & + & \\
1\ 3\ 2 & - & \\
2\ 1\ 3 & - & \\
2\ 3\ 1 & + & \text{(the sign indicate if it's an even or odd permutation)} \\
3\ 1\ 2 & + & \\
3\ 2\ 1 & - &
\end{array}
$$

So we have:

$$
\begin{aligned}
\widehat{S}\left(u_\alpha(x_1)u_\beta(x_2)u_\gamma(x_3)\right) = \frac{1}{3!}\Big\{ & u_\alpha(x_1)u_\beta(x_2)u_\gamma(x_3) \\
\pm\ & u_\alpha(x_1)u_\beta(x_3)u_\gamma(x_2) \\
\pm\ & u_\alpha(x_2)u_\beta(x_1)u_\gamma(x_3) \\
+\ & u_\alpha(x_2)u_\beta(x_3)u_\gamma(x_1) \\
+\ & u_\alpha(x_3)u_\beta(x_1)u_\gamma(x_2) \\
\pm\ & u_\alpha(x_3)u_\beta(x_2)u_\gamma(x_1) \Big\}
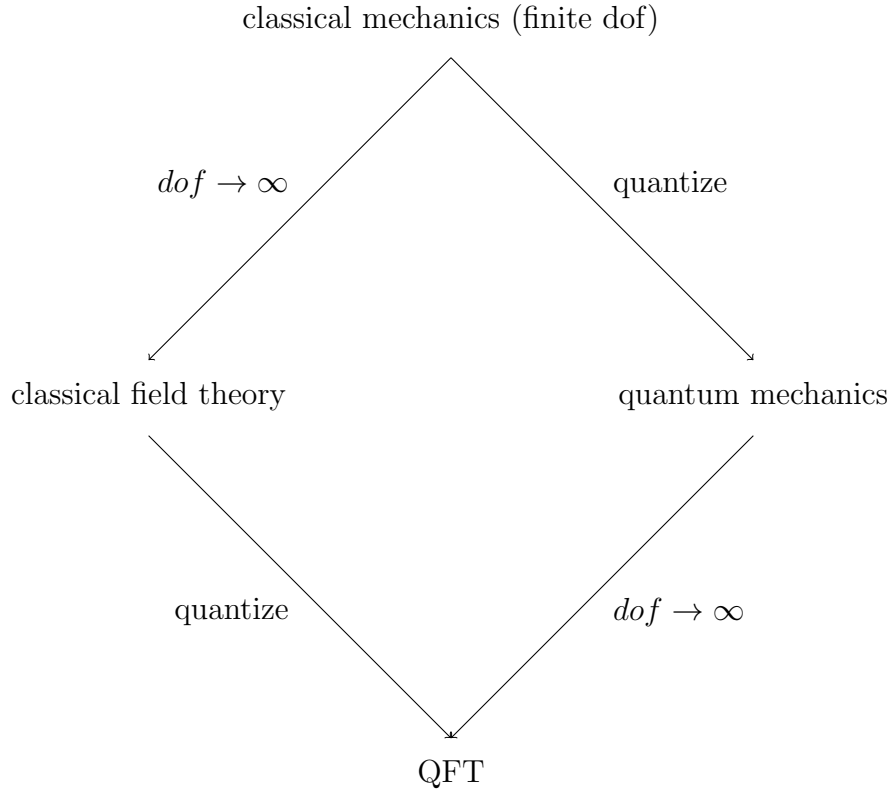\end{aligned}
$$

(and similar for $\widehat{A}$)

Bosons are described by taking all the signs above (all +), fermions are described by the bottom one (so + - - + + -). However, one could take another combination of plus an minus, obtaining something non-physical ($\in \mathcal{H}'$)

3.2 Second quantization

We can't work with a wave function spit in $N!$ peaces (in a gas $N \sim 10^{23}$). So, we see the *second quantization*, an algebraic and abstract approach that will lead to very powerful results.

The approach is different from what it is followed in QFT

classical mechanics (finite dof)

$dof \to \infty$ quantize

classical field theory   quantum mechanics

quantize $dof \to \infty$

QFT

We follow the right path. Also, we are not interested on time: time is fixed and independent.

3.2.1 Creation/Annihilation operators

There are two kinds of these operators: bosonic and fermionic

- **Bosonic creation/annihilation operators**

  We define $a, a^\dagger$ such that $\left[a, a^\dagger\right] = aa^\dagger - a^\dagger a = \mathbb{I}$ on some $\mathcal{H}$ whose dim$=\infty$
  If that wasn't the case (and $\dim \mathcal{H} = n$) then $Tr\left[\left[a, a^\dagger\right]\right] = Tr\left[\mathbb{I}\right] = n$ But also:
  $Tr\left[aa^\dagger - a^\dagger a\right] = Tr\left[aa^\dagger\right] - Tr\left[a^\dagger a\right] \overset{\text{Tr is circular}}{=} Tr\left[aa^\dagger\right] - Tr\left[aa^\dagger\right] = 0$
  So $\dim \mathcal{H} = \infty$.
  Notice that they are not self-adjoint operators, so they aren't observables.

  We also define $\widehat{N} = a^\dagger a$ $\left[\widehat{N}, a\right] = -a$ $\left[\widehat{N}, a^\dagger\right] = a^\dagger$

For instance, this is the operator used in the 1D harmonic oscillator problem:

$$\widehat{H} = \frac{\hbar\omega}{2}\left(\hat{x}^2 + \hat{p}^2\right) \qquad\qquad a = \frac{\hat{x} + i\hat{p}}{\sqrt{2}} \quad a^\dagger = \frac{\hat{x} - i\hat{p}}{\sqrt{2}}$$

$$= \hbar\omega\left(a^\dagger a + \frac{1}{2}\right) \qquad\qquad \hat{x} = \frac{a + a^\dagger}{\sqrt{2}} \quad i\hat{p} = \frac{a - a^\dagger}{\sqrt{2}}$$

$$= \hbar\omega\left(\widehat{N} + \frac{1}{2}\right)$$

The o.n basis is given by:

$$\widehat{H}\left|n\right\rangle = \hbar\omega\left(n + \frac{1}{2}\right)\left|n\right\rangle$$

We won't prove it (it's just algebra), but

$$\widehat{N}\left|n\right\rangle = n\left|n\right\rangle \qquad \text{when} \quad \left|n\right\rangle = \frac{1}{\sqrt{n!}}\left(a^\dagger\right)^n\left|0\right\rangle \qquad \widehat{N}\left|0\right\rangle = 0 \quad \text{(g.s. or vacuum state)}$$

$\widehat{N}$ is called number operator, because the eigenvalue is just the number of quanta. The base $\{|n\rangle\}_{n=0}^\infty$ is called **Fock basis** and it is an o.n. basis on $\mathcal{H}$.
Of course, one can chose another base, but we know very well how this base here behaves.
Applying the creation/annihilation operators just consists in going up or down in the ladder in Fig. 3.2:

$$a\left|n\right\rangle = \sqrt{n-1}\left|n-1\right\rangle \qquad \text{Going down the ladder (destroying a particle)}$$
$$a^\dagger\left|n\right\rangle = \sqrt{n}\left|n+1\right\rangle \qquad\qquad \text{Going up the ladder(creating a particle)}$$

Also, the fact that we can apply $a^\dagger$ many times is another reason why the Hilbert space should have dim $= \infty$.

- **Fermionic creation/annihilation operators**

  We define $c, c^\dagger$ such that $\left\{c, c^\dagger\right\} = cc^\dagger + c^\dagger c = \mathbb{I}$ and $c^2 = \left(c^\dagger\right)^2 = 0$.
  As before we also define the number operator
  $$\widehat{N} = c^\dagger c \qquad \left[\widehat{N}, c\right] = -c \qquad \left[\widehat{N}, c^\dagger\right] = c^\dagger$$

  For instance, this is the operator used in a spin $1/2$ particle system. Given the Pauli matrices:

  $$\sigma^x = \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad \sigma^y = \frac{1}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \qquad \sigma^z = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$
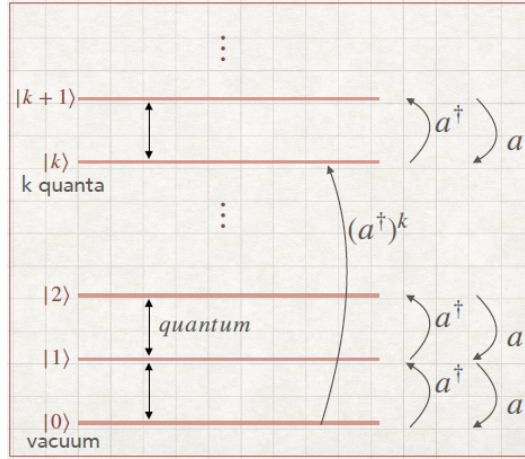
Figure 3.2: Creation/annihilation "ladder" for bosons.

satisfying $\left[\sigma^\alpha, \sigma^\beta\right] = \epsilon_{\alpha\beta\gamma}\sigma^\gamma$,   one can construct:

$$\sigma^\pm \equiv \sigma^x \pm i\sigma^y \implies \sigma^+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad \sigma^- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

such that $\{\sigma^-, \sigma^+\} = \mathbb{I}_{2\times 2}$ $(\sigma^-)^\dagger = \sigma^+$ $(\sigma^-)^2 = (\sigma^+)^2 = 0$

The Fock basis is the o.n. basis given by:
$|0\rangle$ vacuum $|1\rangle = c^\dagger |0\rangle$ $|2\rangle = c^\dagger c^\dagger |0\rangle = 0$ (since $(c^\dagger)^2 = 0$)

So we have only two possible states: $\widehat{N} |0\rangle = 0$ $\widehat{N} |1\rangle = 1 \cdot |1\rangle$
as shown in Fig. 3.3.
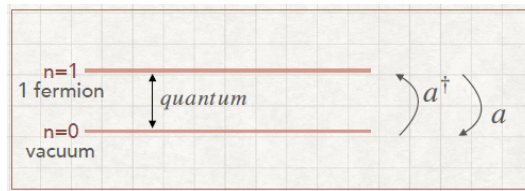
Figure 3.3: Creation/annihilation "ladder" for fermions.

As before $\widehat{N} |n\rangle = n |n\rangle$ is called number operator, but this time $n = 0, 1$

In both cases the vacuum $|0\rangle$ $(n = 0)$ is the lowest level and it's defined by $a |0\rangle = 0$ $c |0\rangle = 0$

17/11/2022

From now on we will indicate with $a, a^\dagger$ both the fermionic and bosonic operators and we will write: $\left[a, a^\dagger\right]_\mp = aa^\dagger \mp a^\dagger a\Big|_F^B$

3.2.2 Fock Space

We will give now a rather simple algebraic construction of the Fock space $\mathbb{H}_F$, showing that it has all the required properties.

We want to construct $\mathcal{H}^{(S/A)} \equiv \bigoplus_{N=0}^{\infty} \mathcal{H}_N^{(S/A)}$ in an intrinsic way.

For each element of an (arbitrary) o.n. basis $\{u_\alpha(x)\} \in L^2(\mathbb{R}^3)$ in a single particle $\mathcal{H}$, we can consider a couple of creation/annihilation operators $a_\alpha^\dagger, a_\alpha$ such that:

$$[a_\alpha, a_\beta]_\mp = \left[a_\alpha^\dagger, a_\beta^\dagger\right]_\mp = 0 \quad \forall \alpha, \beta \qquad \left[a_\alpha, a_\beta^\dagger\right]_\mp = \delta_{\alpha\beta}$$

The α's are the quantum number labeling the one-particle basis $\{u_\alpha\}$.

These are called *canonical commutation relations (CRR)*. Note that this relations imply automatically that $(a_\alpha)^2 = (a_\alpha^\dagger)^2 = 0$. In this case:

i. We can define the vacuum state $|0\rangle$ by requiring that the a_α's annihilate it:

$$|0\rangle : \quad a_\alpha |0\rangle = 0 \quad \forall \alpha$$

We will see immediately that this single requirement allows for a complete construction of the Fock space. In fact we can construct
$$\mathcal{H}_0^{B/F} = \{\lambda |0\rangle, \ \lambda \in \mathbb{C}\} \overset{\text{isomorphic to}}{\simeq} \mathbb{C}$$

ii. What happens if the creation operator is applied to $|0\rangle$?
$a_\alpha^\dagger |0\rangle \iff u_\alpha(x)$ creates one particle in the state α. The one-particle state will be defined as:
$$a_\alpha^\dagger |0\rangle = |0, \ldots, 0, 1_\alpha, 0, \ldots\rangle$$

For example:
$$\mathcal{H}_1^{B/F} = \left\{\left\{a_\alpha^\dagger |0\rangle\right\}_{\alpha=1}^{\infty} \text{ o.n basis}\right\} \simeq L^2(\mathbb{R}^3)$$

$$\sum_{\alpha=1}^{\infty} f_\alpha a_\alpha^\dagger |0\rangle \iff |f(x)\rangle = \sum_\alpha f_\alpha u_\alpha(x)$$

iii. Then, recursively, what about $N = 2$?
We'll start with one particle in the state α ($a_\alpha^\dagger |0\rangle$), then we'll add the second one:

- First case: second particle in α
  For Bosons: $\left(a^\dagger\right)^2 |0\rangle$ (2 particles in α)
  For Fermions: $\left(a^\dagger\right)^2 |0\rangle = 0$ (The rules of our creation/annihilation algebra implicitly define Pauli exclusion principle)
- Second case: second particle in $\beta \neq \alpha$
  Both for bosons and fermions we have: $a_\beta^\dagger a_\alpha^\dagger |0\rangle$
  What if instead $a_\alpha^\dagger a_\beta^\dagger |0\rangle$ (we add first the particle in β and the the one in α) ? From the condition on the (anti)commutator, we have that $a_\alpha^\dagger a_\beta^\dagger |0\rangle = \pm a_\beta^\dagger a_\alpha^\dagger |0\rangle$.

iv. We can now generalize to N particles:

$$|n_1, n_2, \ldots, n_k, \ldots\rangle \equiv \eta \sqrt{\frac{1}{\prod_j n_j!}} \left(a_1^\dagger\right)^{n_1} \left(a_2^\dagger\right)^{n_2} \ldots \left(a_k^\dagger\right)^{n_k} \ldots |0\rangle \iff \qquad (3.2)$$

$$\xleftrightarrow{\text{1-1 corresp.}} \psi_{\{k\}} = \hat{S}_{\hat{A}}\left(u_{\alpha_1}(x_1), \ldots, u_{\alpha_k}(x_k)\right) \quad \text{o.n. basis for } \mathcal{H}_S, \mathcal{H}_A$$

where $\eta = \begin{cases} 1 & \text{for bosons} \\ (-1)^{\sum_{j=1}^{k-1} n_j} & \text{for fermions} \end{cases}$

since we pick up a -sign every time we commute to bring $a_k^\dagger$ to $|n_k\rangle$.
Remember also that n_j indicate the number of particles in the state j.

Then if we chose $|n_1, \ldots, n_k \ldots\rangle$ as an o.n basis, we can define $\mathcal{H}^{B/F}$ "automatically" from $a^\dagger$:

$$\mathcal{H}^{S/A} = \mathcal{H}^{B/F} = \{\{|n_1, \ldots, n_k \ldots\rangle\} \text{ o.n. basis}\}$$

- For example, let's analyze two 1-particle states $\alpha \neq \beta$.

$a_\alpha^\dagger |0\rangle \leftrightarrow u_\alpha \qquad a_\beta^\dagger |0\rangle \leftrightarrow u_\beta \qquad \left(a_\beta^\dagger |0\rangle\right)^\dagger = \langle 0| a_\beta \qquad\qquad \text{Then:}$

$$\langle u_\beta | u_\alpha \rangle \iff \langle 0| a_\beta a_\alpha^\dagger |0\rangle = 0 \qquad\qquad \text{since } a_\alpha a_\beta^\dagger \mp a_\beta^\dagger a_\alpha = 0$$

$$\langle 0| \pm a_\alpha^\dagger a_\beta |0\rangle = 0 \qquad\qquad \text{since } a_\beta |0\rangle = 0$$

The trick is to put all the annihilation operators to the right (not only in this case, but always).

Now let's analyze better for N particles: we expect $a_k^\dagger |n_1 \ldots n_k \ldots\rangle$ to be proportional to $|n_1 \ldots (n_k + 1) \ldots\rangle$

$$|n_1 \ldots (n_k + 1) \ldots\rangle \overset{(3.2)}{=} \frac{\eta}{\sqrt{\prod_{i \neq k} n_i!(n_k+1)!}} \left(a_1^\dagger\right)^{n_1} \ldots \left(a_k^\dagger\right)^{n_k+1} \ldots |0\rangle$$

If we compute:

$$a_k^\dagger \frac{1}{\sqrt{\prod_i n_i!}} \left(a_1^\dagger\right)^{n_1} \left(a_2^\dagger\right)^{n_2} \ldots \left(a_k^\dagger\right)^{n_k} \ldots |0\rangle = \sqrt{n_k + 1}\, \eta\, |n_1, n_2, \ldots, (n_k+1), \ldots\rangle$$

Therefore $\qquad a_k^\dagger : \mathcal{H}_N^{B/F} \to \mathcal{H}_{N+1}^{B/F}$

One can prove (as an exercise) that $a_k |n_1 \ldots n_k\rangle = \eta \sqrt{n_k} |n_1, \ldots, (n_k - 1), \ldots\rangle$
and if $n_k = 0 \implies a_k |n_i \ldots n_k\rangle = 0$ so that $\qquad a_k : \mathcal{H}_N^{B/F} \to \mathcal{H}_{N-1}^{B/F}$

We can thus construct the **Fock space** (useful in the grancanonical):

$$\mathcal{H}_F^{B/F} = \bigoplus_{N=0}^{\infty} \mathcal{H}_N^{B/F}$$

It is also useful to define the operator $\hat{n}_k$ which counts how many particles occupy the k-th state: $\hat{n}_k \equiv a_k^\dagger a_k$

$$\hat{n}_k : \mathcal{H}_N^{B/F} \to \mathcal{H}_N^{B/F} \qquad \hat{n}_k \left| n_1 \ldots n_k \ldots \right\rangle = n_k \left| n_1 \ldots n_k \ldots \right\rangle$$

the so-called *Fock basis*: $\{\left| n_1 \ldots n_k \ldots \right\rangle\}_{\{n_1, n_2 \ldots\}}$ is a basis of eigenstates for $\hat{n}_k$ and we can build the number operator $\widehat{N}$, that counts the total number of particles $\widehat{N} = \sum_{k=1}^{\infty} \hat{n}_k$.

What we have seen is the following:

THEOREM:

1. The multi-particle states are an o.n basis for $\mathcal{H}_N^{S/A}$ (in both cases):

    $$\left\langle n_1', n_2', \ldots, n_k' \ldots | n_1, n_2, \ldots, n_k \ldots \right\rangle = \delta_{n_1' n_1} \delta_{n_2' n_2} \ldots \delta_{n_k' n_k} \ldots$$

2. annihilation: $\qquad a_k : \mathcal{H}_N^{S/A} \to \mathcal{H}_{N-1}^{S/A}$

    $$a_k \left| n_1, n_2, \ldots n_k \ldots \right\rangle = \eta \, \sqrt{n_k} \left| n_1, n_2, \ldots, (n_k - 1) \ldots \right\rangle$$

    where $\eta = \begin{cases} 1 & \text{for bosons} \\ (-1)^{\sum_{j=1}^{k-1} n_j} & \text{for fermions} \end{cases}$

3. creation: $\qquad a_k^\dagger : \mathcal{H}_N^{S/A} \to \mathcal{H}_{N+1}^{S/A}$

    $$a_k^\dagger \left| n_1, n_2, \ldots n_k \ldots \right\rangle = \sqrt{n_k + 1} \left| n_1, n_2, \ldots, (n_k + 1) \ldots \right\rangle$$

    Note that in the fermionic case we have $a_k^\dagger \left| n_1, n_2, \ldots, n_k, \ldots \right\rangle = 0$ if $n_k = 1$. This is again the expression of Pauli exclusion principle.

4. the operator $\hat{n}_k = a_k^\dagger a_k$ counts how many particles occupy the k-th state:

    $$\hat{n}_k \left| n_1, n_2, \ldots, n_k, \ldots \right\rangle = n_k \left| n_1, n_2, \ldots, n_k, \ldots \right\rangle$$

    and the operator $\widehat{N} = \sum_k \hat{n}_k = \sum_k a_k^\dagger a_k$ counts the total number of particles:

    $$\widehat{N} \left| n_1, n_2, \ldots n_k \ldots \right\rangle = \left(\sum_k n_k = N \right) \left| n_1, n_2, \ldots n_k \ldots \right\rangle$$

Remarks:

- The states $|n_1, n_2, \ldots, n_k\rangle$, hence any state in $\mathcal{H}_N^{(S/A)}$, are symmetric/antisymmetric by construction, thanks to the commutation/anticommutation relations among the creation/annihilation operators.

- As we've seen, in the fermionic case Pauli exclusion principle is automatically encoded.

- States are written in terms of creation/annihilation operators: in particular, single particle states $|e_n\rangle$ are in 1-1 correspondence with $a_n^\dagger |0\rangle$. In general, a generic single-particle state $|f\rangle = \sum_n f_n |e\rangle_n$ with $f_n = \langle e_n | f \rangle$ is represented by the vector in the Fock space: $\sum_n f_n a_n^\dagger |0\rangle \equiv \psi^\dagger(f) |0\rangle$.
  So we say that a state $|f\rangle$ is represented by/becomes the operator $\psi^\dagger(f)$
  This is called the *second quantization procedure*.

3.2.3   Field operator

The creation and annihilation operators introduced so far are tied to the (arbitrary, of course) choice of a basis of one-particle states. The state $a_\alpha^\dagger |0\rangle$ corresponds then to the creation of one particle in the state u_α out of the vacuum or, more generally, $a_\alpha^\dagger |n_1, \ldots, n_i, \ldots\rangle$ will correspond to the addition of a particle in the same state. What if we want to "create" an additional particle in an arbitrary state represented by the wavefunction $f(\vec{x}) = \sum_\alpha u_\alpha(\vec{x}) \langle u_\alpha | f \rangle$?
A little thought suffices to conclude that, if $a_\alpha^\dagger$ creates a particle in the basis state u_α, then a particle in a generic state $f \in L^2(\mathbb{R}^d)$ will be created by the operator:

$$\psi^\dagger(f) = \sum_\alpha \langle u_\alpha | f \rangle a_\alpha^\dagger \tag{3.3}$$

And the adjoint of $\psi^\dagger(f)$:

$$\psi(f) = \sum_\alpha \langle f | u_\alpha \rangle a_\alpha \tag{3.4}$$

will act as the corresponding annihilation operator.
   Let's make things a little more formally: firstly, we chose to work within the coordinate representation:

$$\mathcal{H} = L^2(\mathbb{R}^d) \qquad \{|e_\alpha\rangle = u_\alpha\}_\alpha \qquad f(x) = \sum_\alpha u_\alpha(x) f_\alpha \quad f_\alpha = \int_{\mathbb{R}^d} u_\alpha^*(x) f(x) = \langle u_\alpha | f \rangle$$

Then, if the associated creation/annihilation operators are denoted with $a_\alpha, a_\alpha^\dagger$, we define the creation/annihilation **field operators** as:

$$\psi^\dagger(x) = \sum_\alpha u_\alpha^*(x) a_\alpha^\dagger \qquad \psi(x) = \sum_\alpha u_\alpha(x) a_\alpha$$

and the (3.3) and (3.4) can be written as integrals of those (see the following theorem).

It is pretty obvious that $\psi^\dagger(\vec{x})$ is a rather ill-defined operator on Fock space. Indeed, it is easily checked that, say, $\|\psi^\dagger(\vec{x})\,|0\rangle\|^2 = \delta(\vec{0})$, a diverging quantity, and hence that $\psi^\dagger(\vec{x})\,|0\rangle$ cannot be considered as a vector in Fock space. $\psi^\dagger(\vec{x})$ has rather to be considered as a "distribution-valued" operator, i.e. it acquires a reasonable mathematical meaning only when it operates on functions in $L^2(\mathbb{R}^d)$ like in the definition of $\psi^\dagger(f)$ below.

THEOREM:

i) (3.3) can be expressed by the field operator:

$$\psi^\dagger(f) = \int_{\mathbb{R}^d} \psi^\dagger(x) f(x) \qquad \text{in particular: } \psi^\dagger(u_\alpha) = \int_{\mathbb{R}^d} \psi^\dagger(x) u_\alpha(x) = a_\alpha^\dagger$$

ii) Some nice commutation relations holds:

$$[\psi(f)\psi(g)]_\mp = \left[\psi^\dagger(f)\psi^\dagger(g)\right]_\mp = 0 \qquad \left[\psi(f)\psi^\dagger(g)\right]_\mp = \langle f, g\rangle$$
$$[\psi(x)\psi(y)]_\mp = \left[\psi^\dagger(x)\psi^\dagger(y)\right]_\mp = 0 \qquad \left[\psi(x)\psi^\dagger(y)\right]_\mp = \delta(x-y)$$

iii) The field operators are independent on the chosen basis:

$$\psi^\dagger(x) = \sum_\alpha u_\alpha^*(x) a_\alpha^\dagger = \sum_\beta v_\beta^*(x) b_\beta^\dagger$$

PROOF:

(i)

$$\int_{\mathbb{R}^d} \psi^\dagger(x) f(x) = \int f(x) \sum_\alpha u_\alpha^* a_\alpha^\dagger = \sum_\alpha \int \underbrace{f(x) u_\alpha^*}_{\langle f|u\rangle} a_\alpha^\dagger = \sum_\alpha f_\alpha a_\alpha^\dagger = \psi^\dagger(f)$$

(ii) •

$$[\psi(f), \psi(g)]_\mp = \left[\sum_\alpha u_\alpha(x) a_\alpha \, , \, \sum_\beta v_\beta(y) a_\beta\right]_\mp = \sum_{\alpha\beta} u_\alpha v_\beta \, [a_\alpha, a_\beta]_\mp = 0$$

• $\left[\psi^\dagger(x), \psi^\dagger(y)\right] = 0$ is proven similarly.

•

$$[\psi(f), \psi^\dagger(g)]_\mp = \left[\sum_\alpha f_\alpha a_\alpha \, , \, \sum_\beta g_\beta^* a_\beta^\dagger\right]_\mp = \sum_{\alpha\beta} f_\alpha g_\beta^* \underbrace{\left[a_\alpha, a_\beta^\dagger\right]}_{\delta_{\alpha\beta}}$$
$$= \sum_\alpha f_\alpha g_\alpha^* = \langle f, g\rangle \, \mathbb{1}$$

- From (i): $\psi^\dagger(f) = \int f(x)\psi^\dagger(x) \qquad \psi(g) = \int g^*(y)\psi(y)$

$$\langle f, g \rangle = \int d^d x \int d^d y \ f(x)g^*(y) \left[\psi(y), \psi^\dagger(x)\right]_\mp \implies \left[\psi(y), \psi^\dagger(x)\right] = \delta_{(x-y)} \mathbb{1}$$

(iii) Let's have another base $\{v_\beta(x)\}$ from which we can get different creation annihilation operators $b_\beta, b_\beta^\dagger$.

$$\{u_\alpha(x)\} \to a_\alpha, a_\alpha^\dagger \implies |n_1, n_2, \ldots, n_k \ldots\rangle = C \left(a_1^\dagger\right)^{n_1} \left(a_2^\dagger\right)^{n_2} \ldots |0\rangle$$

$$\{v_\beta(x)\} \to b_\beta, b_\beta^\dagger \implies |m_1, m_2, \ldots, m_k \ldots\rangle = C \left(b_1^\dagger\right)^{m_1} \left(b_2^\dagger\right)^{m_2} \ldots |0\rangle$$

$$f(x) = \sum_\alpha f_\alpha u_\alpha(x) \qquad \psi^\dagger(f) = \sum_\alpha f_\alpha a_\alpha^\dagger$$

$$f(x) = \sum_\beta \tilde{f}_\beta v_\beta(x) \qquad \psi^\dagger(f) = \sum_\beta f_\beta b_\beta^\dagger$$

We won't prove it, but the expressions on the right are equal. That means that they are independent on the chosen basis.

This is also true for the field operators:

$$\psi^\dagger(x) = \sum_\alpha u_\alpha^*(x) a_\alpha^\dagger = \psi^\dagger(x) = \sum_\beta v_\beta^*(x) b_\beta^\dagger$$

The two expressions are the field operator expressed in two different basis. Since they are equal, it means it is basis independent.

3.2.4   Observable operators

We want now to characterize how observables act in Fock space.

Single particles observables

In first quantization, single particles observables are written in $\mathcal{H}_N^{S/A}$ as:

$$\widehat{A} : \sum_{j=1}^N A^{(1)}(\vec{p}_j, \vec{x}_j)$$

where $A^{(1)}$ is an operator on the single particle $\mathcal{H}$, and let $\{u_\alpha\}$ be the basis of the eigenfunctions of $A^{(1)}$, i.e.: $A^{(1)}(\vec{p}, \vec{x})u_\alpha(x) = \epsilon_\alpha u_\alpha(x)$

A trivial example could be the harmonic oscillator: $\widehat{A} = \sum_{j=1}^N \underbrace{\left(\dfrac{\widehat{\vec{p}}_j^{\,2}}{2m} + \dfrac{\omega^2 m}{2}\hat{x}_j^2\right)}_{A^{(1)}(p_j, x_j)}$

So (in the following, C is a constant that we don't care about):

$$\psi_{n_1,n_2,\ldots,n_k\ldots}(x_1, x_2, \ldots, x_N) = C \, \hat{S}_{\hat{A}} \left(u_{\alpha_1}(x_1) \ldots u_{\alpha_N}(x_N) \right)$$

Multiplying both sides by $\widehat{A} = \sum_{j=1}^{N} A^{(1)}(\vec{p}_j, \vec{x}_j)$:

$$\widehat{A} \, \psi_{n_1,n_2,\ldots,n_k\ldots}(x_1, x_2, \ldots, x_N) = C \, \hat{S}_{\hat{A}} \left(\sum_{j=1}^{N} A^{(1)}(\vec{p}_j, \vec{x}_j) \left(u_{\alpha_1}(x_1) \ldots u_{\alpha_N}(x_N) \right) \right)$$

$$= C \, \hat{S}_{\hat{A}} \left(\sum_{j=1}^{N} \epsilon_{\alpha_j} \right) \left(u_{\alpha_1}(x_1) \ldots u_{\alpha_N}(x_N) \right)$$

using linearity of all the operators:

$$= \left(\sum_{j=1}^{N} \epsilon_{\alpha_j} \right) \psi_{n_1,n_2,\ldots}(x_1, x_2, \ldots, x_N)$$

Another way to write it could be:

$$= \left(\epsilon_{\alpha_1} + \epsilon_{\alpha_2} + \cdots + \epsilon_{\alpha_N} \right) \psi_{n_1,\ldots,n_k,\ldots}$$

and another one:

$$= \left(\sum_{\alpha=1}^{\infty} \epsilon_\alpha n_\alpha \right) \psi_{n_1,n_2,\ldots}$$

What we have shown is that: $\widehat{A}\psi_{n_1,n_2,\ldots}(x_1, \ldots, x_N) = \left(\sum_{\alpha=1}^{\infty} \epsilon_\alpha n_\alpha \right) \psi_{n_1,n_2,\ldots}(x_1, \ldots, x_N)$
We now want to define in the Fock space an operator that acts the same as our original operator, so such that:

$$\widehat{A} \, |n_1, n_2 \ldots, n_k, \ldots\rangle = \left(\sum_{\alpha} \epsilon_{\alpha_n} n_\alpha \right) |n_1, n_2 \ldots, n_k, \ldots\rangle$$

It follows that, in Fock space $\mathbb{H}_N^{\text{B/F}}$, the "second-quantized" version of $\widehat{A}$ is:

$$\boxed{\widehat{A}_F = \sum_{\alpha=1}^{\infty} \epsilon_\alpha \hat{n}_\alpha = \sum_{\alpha=1}^{\infty} \epsilon_\alpha a_\alpha^\dagger a_\alpha} \tag{3.5}$$

with $\epsilon_\alpha = \langle u_\alpha | A^{(1)} | u_\alpha \rangle$ \qquad or equivalently: $A^{(1)}(\vec{p}, \vec{x}) u_\alpha(x) = \epsilon_\alpha u_\alpha(x)$
Notice that $\hat{n}_\alpha = a_\alpha^\dagger a_\alpha$, so this operator destroy then create a particle, thus the total number of particle is conserved.

We have shown that both the creation operators and the field operator are base-independent. However this is not the case for the single particles observables in Fock space $\widehat{A}_F$ in eq. (3.5). In fact, if $\{u_\alpha\}$ is a generic basis and not the basis of eigenfunctions of $A^{(1)}$, we have:

$$\left\langle u_\beta \left| \hat{A}^{(1)}(\vec{p}, \vec{x}) \right| u_\alpha \right\rangle = \epsilon_\alpha \langle u_\beta | u_\alpha \rangle = \epsilon_\alpha \delta_{\alpha\beta}$$

$$\widehat{A}_F = \sum_{\alpha\beta} \left\langle u_\beta \left| \hat{A}^{(1)} \right| u_\alpha \right\rangle a_\alpha^\dagger a_\beta$$

Which is equal to eq. (3.5) only if we add $\delta_{\alpha\beta}$.

Choosing a different basis v_j with the corresponding creation/annihilation operators $b_j, b_j^\dagger$:

$$\widehat{A}_F = \sum_{jk} \underbrace{\left\langle v_j \left| \hat{A}^{(1)} \right| v_k \right\rangle}_{t_{jk}} b_j^\dagger b_k = \sum_{jk} t_{jk} b_j^\dagger b_k$$

This operator is no longer diagonal (indexes are different). It destroys a particle in the state k and create another one in the state j.

Using the definition of the field operators $\psi(\vec{x}), \psi^\dagger(\vec{x})$, there also exists a way to write everything without referring to a basis:

$$\widehat{A} = \sum_{j=1}^N A^{(1)}(\vec{p}_j, \vec{x}_j) \xrightarrow{\text{in Fock space}} \widehat{A}_F = \int d^3x \; \psi^\dagger(x) A^{(1)}(\vec{p}, \vec{x}) \psi(x)$$

In fact: $\psi^\dagger(x) \equiv \sum_\alpha u_\alpha^*(x) a_\alpha^\dagger \qquad \psi(x) \equiv \sum_\beta u_\beta(x) a_\beta$:

$$A = \int d^3x \left(\sum_\alpha u_\alpha^*(x) a_\alpha^\dagger \right) A^{(1)} \left(\sum_\beta u_\beta(x) a_\beta \right)$$

$$= \sum_{\alpha\beta} \underbrace{\int d^3x \; u_\alpha^*(x) A^{(1)}(\vec{p}, \vec{x}) u_\beta(x)}_{\left\langle u_\alpha \left| A^{(1)} \right| u_\beta \right\rangle} a_\alpha^\dagger a_\beta$$

$$= \sum_{\alpha\beta} t_{\alpha\beta} a_\alpha^\dagger a_\beta$$

Now let's see some examples:

i) Density operator

On a single particle $u(x) \in L^2\left(\mathbb{R}^3\right)$, we have:

$$\hat{\rho}^{(1)} = \delta(x - x_0) \qquad \hat{\rho}^{(1)} : u(x) \mapsto \int_{\mathbb{R}^3} d^3x u(x) \delta(x - x_0) = u(x_o)$$

For N particles, we have N coordinates:

$$x_1, x_2, \ldots x_N \qquad \hat{\rho}(y) = \sum_{j=1}^{N} \delta(y - x_j)$$

In Fock space it becomes:

$$\hat{\rho}_F = \int d^3y \; \psi^\dagger(y)\rho^{(1)}\psi(y) = \int d^3y \; \psi^\dagger(y)\delta(y-x)\psi(y) = \psi^\dagger(x)\psi(x)$$

ii) Number operator

The previous operator is called density operator because the number operator is expressed by: $\hat{N} = \int_{\mathbb{R}^3} d^3x \hat{\rho}(x)$. In fact, in Fock space the number operator is:

$$\hat{N}_F = \int d^3x \; \psi^\dagger(x)\psi(x) \qquad\qquad \text{using definition of } \psi^\dagger, \psi$$

$$= \int d^3x \left(\sum_\alpha u_\alpha^*(x)a_\alpha^\dagger \right) \left(\sum_\beta u_\beta(x)a_\beta \right)$$

$$= \sum_{\alpha\beta} \underbrace{\left(\int d^3x u_\alpha^*(x)u_\beta(x) \right)}_{\langle u\alpha | u_\beta \rangle = \delta_{\alpha\beta}} a_\alpha^\dagger a_\beta = \sum_\alpha a_\alpha^\dagger a_\alpha = \sum_\alpha \hat{n}_\alpha$$

which is just the total number of particle.

iii) Free hamiltonian

With N particles the hamiltonian is

$$H = \sum_{j=1}^{N} \underbrace{\frac{\vec{p_j}^2}{2m}}_{A^{(1)}(\vec{p}_j, x_j)}$$

acting in $L^2(\mathbb{R}^3) = \phi(x_1, x_2 \ldots, x_N)$

Using the substitution: $\vec{p} \mapsto -i\hbar\nabla$

$$\frac{\vec{p_j}^2}{2m}\phi(x_1, \ldots, x_N) = \frac{\left(-i\hbar\nabla_{x_j}\right)^2}{2m}\phi(x_1, \ldots, x_j \ldots x_N)$$

with $A^{(1)}(\vec{p}_j, x_j) = \frac{\hbar^2}{2m}\nabla_x^2$.

In Fock space the hamiltonian becomes:

$$H_F = \int d^3x \; \psi^\dagger(x)A^{(1)}(\vec{p}_j, x_j)\psi(x) = \int d^3x \; \psi^\dagger(x)\left[\frac{\hbar^2}{2m}\nabla_x^2\right]\psi(x) \qquad (3.6)$$

$$\nabla_x^2 \psi(x) = \nabla_x^2 \left(\sum_\alpha u_\alpha(x) a_\alpha \right) = \sum_\alpha \left(\nabla_x^2 u_\alpha(x) \right) a_\alpha \qquad (3.7)$$

We want to choose $u_\alpha(x)$ such that $\nabla_x^2 u_\alpha(x) = \epsilon_\alpha u_\alpha(x)$
where $\alpha = \vec{k}$ (α is the momentum).
The solution is to choose the single particle o.n. basis: $u_{\vec{k}} = e^{i\vec{k}\cdot\vec{x}}/\sqrt{V}$. We will comment later about the normalization factor $1/\sqrt{V}$
In fact:

$$\nabla_x^2 u_{\vec{k}}(x) = \underbrace{-\vec{k}^2}_{\epsilon_{\vec{k}}} u_\alpha(x) \implies (3.7) = \sum_{\vec{k}} (-k)^2 u_{\vec{k}}(x) a_{\vec{k}}$$

And the hamiltonian in Fock space (3.6) becomes:

$$H_F = \int d^3x \ \psi^\dagger(x) \left(-\frac{\hbar^2}{2m} \nabla_x^2 \right) \psi(x)$$

$$= \int d^3x \left(\sum_{\vec{k}'} u_{\vec{k}'}^*(x) a_{\vec{k}'}^\dagger \right) \left(-\frac{\hbar^2}{2m} \right) \sum_{\vec{k}} a_{\vec{k}} \left(-\vec{k}^2 \right) u_{\vec{k}}(x)$$

$$= \sum_{\vec{k}\vec{k}'} a_{\vec{k}'}^\dagger a_{\vec{k}} \left(\frac{\hbar^2 k^2}{2m} \underbrace{\int d^3x \ u_{\vec{k}'}^*(x) u_{\vec{k}}(x)}_{\langle u_{k'} | u_k \rangle = \delta_{kk'}} \right)$$

$$= \sum_k \frac{\hbar^2 k^2}{2m} a_k^\dagger a_k = \sum_k \epsilon_n a_k^\dagger a_k$$

This describes free particles in Fock space.

<u>About the normalization factor</u>
However, there's actually a problem (we've cheated a bit): the solution $u_{\vec{k}}(x) = e^{i\vec{k}\cdot x}$ is not normalizable:

$$\| u_{\vec{k}}(x) \|^2 = \int_{\mathbb{R}^3} d^3x \underbrace{|u_{\vec{k}}(x)|}_{1} = \infty$$

To fix this problem we don't work in all $\mathbb{R}^3$, but with a finite volume. We choose a cube of size L. So we also have to specify the boundary conditions. Those can be (in 1D):

$$x \in [0, L] \qquad -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} u_\alpha(x) = \epsilon_\alpha u_\alpha(x)$$

but we can also have periodic boundary conditions, where $\psi(L) = \psi(0)$.

$$\text{in 3D:} \begin{cases} \psi(x = L, y, z) = \psi(x = 0, y, z) \\ \psi(x, y = L, z) = \psi(x, y = 0, z) \\ \psi(x, y, z = L) = \psi(x, y, z = 0) \end{cases}$$

So now we have:

$$u_{\vec{k}} = e^{i\vec{k}\cdot x} \qquad e^{i(k_x L + k_y y + k_z z)} = e^{i(k_x 0 + k_y y + k_z z)}$$

$$\implies e^{ik_x L} = 1 \implies k_x L = 2\pi n_x \quad (n_x \in \mathbb{Z}) \implies k_x = \frac{2\pi}{L} n_x$$

(and similarly for k_y, k_z) which means that k is quantized.

Now we can also normalize the wave function:

$$u_\alpha(\vec{x}) = C e^{i\vec{k}\cdot x} \qquad \int_{\mathbb{R}^3} d^3 x \underbrace{|u_\alpha(x)|^2}_{C} = C^2 L^3 = 1 \quad \text{if } C = \frac{1}{\sqrt{L^3}} = \frac{1}{\sqrt{V}}$$

So:

$$H = \sum_{\vec{k}} \epsilon_{\vec{k}} a_{\vec{k}}^\dagger a_{\vec{k}} \qquad \epsilon_{\vec{k}'} = -\frac{\hbar^2 \vec{k}^2}{2m} = -\frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 \left(n_x^2 + n_y^2 + n_z^2\right)$$

So $\sum_{\vec{k}}$ is replaced by $\sum_{n_x, n_y, n_z}$.

iv) For completeness we can also show that in the case where we include a potential to the hamiltonian:

$$H = \sum_{j=1}^{N} \left(\frac{\vec{p_j}^2}{2m} + V(x_j)\right) + \sum_{i<j} V(x_i, x_j) \qquad \text{in } L^2\left(\mathbb{R}^{3N}\right)$$

how is the potential written in Fock space? The idea is the following:

$$V = \sum_{i<j} V(x_i, x_j) = \frac{1}{2}\sum_{i\neq j} V(x_i x_j) = \frac{1}{2}\sum_{i,j} V(x_i, x_j) - \frac{1}{2}\sum_i V(x_i, x_i)$$

$$= \frac{1}{2}\sum_{i,j} \int d^3 x \int d^3 y\, V(x, y)\delta(x - x_i)\delta(y - y_j) - \frac{1}{2}\sum_i \int d^3 x\, V(x, x)\delta(x - x_i)$$

$$= \frac{1}{2}\int d^3 x \int d^3 y\, V(x, y)\underbrace{\left(\sum_i \delta(x - x_i)\right)}_{\rho}\underbrace{\left(\sum_j \delta(y - y_j)\right)}_{\rho} - \frac{1}{2}\int d^3 x\, V(x, x)\underbrace{\left(\sum_i \delta(x - x_i)\right)}_{\rho}$$

where $\rho = \sum_i \delta(x - xi)$ in Fock space becomes $\rho_F = \psi^\dagger(x)\psi(x)$, so:

$$V_F = \frac{1}{2}\int d^3 x \int d^3 y V(x, y)\left[\psi^\dagger(x)\underbrace{\psi(x)}_{(*)}\right]\left[\psi^\dagger(y)\,\psi(y)\right] - \frac{1}{2}\int d^3 x\, V(x, x)\left[\psi^\dagger(x)\psi(x)\right]$$

and we have already proved that

$$\psi(x)\psi^\dagger(y) \mp \psi^\dagger(x)\psi(y) = \left[\psi(x)\psi^\dagger(y)\right]_\mp = \delta(x-y),$$
$$\implies \quad (*) = \psi(x)\psi^\dagger(y) = \delta(x-y) \pm \psi^\dagger(y)\psi(x)$$

$$V_F = \pm\frac{1}{2}\int d^3x \int d^3y\ V(x,y)\psi^\dagger(x)\psi^\dagger(y)\underbrace{\psi(x)\psi(y)}_{\pm\psi(y)\psi(x)}$$

$$= \frac{1}{2}\int d^3x \int d^3y\ V(x,y)\psi^\dagger(x)\psi^\dagger(y)\psi(y)\psi(x)$$

Using the definition of $\psi^\dagger, \psi$, we get

$$= \sum_{\alpha\beta\gamma\delta} V_{\alpha\beta\gamma\delta}\, a_\alpha^\dagger a_\beta^\dagger a_\gamma a_\delta$$

$$\text{with } V_{\alpha\beta\gamma\delta} = \frac{1}{2}\int d^3x \int d^3y\ V(x,y)u_\alpha^*(x)u_\beta^*(y)u_\gamma(y)u_\delta(x)$$

3.3 Quantum ensembles

In the following we work with systems with finite volume. As usual the thermodynamic limit is taken only at the end of the calculations.

N denotes the number of particles and, depending on whether particles are distinguishable or not, we will work in the Hilbert space $\mathcal{H}_N^{tot} = \mathcal{H} \otimes \cdots \otimes \mathcal{H} = \mathcal{H}^{\otimes N}$ or $\mathcal{H}_N^{tot} = \mathcal{H}_N^{S/A}$.

Also, the system will be described by a Hamiltonian H_N

If we allow N to change, we have to work on the Hilbert space $\mathcal{H} \equiv \bigoplus_{N=0}^{\infty} \mathcal{H}_N$, and the system will be described by a Hamiltonian H that conserve the number of particles (commuting with the number operator), so that: $H|_{\mathcal{H}_N} = H_N$

3.3.1 Microcanonical ensembles

In the microcanonical ensemble, V, N, E are fixed. Since the hamiltonian is an observable, we can write it as its spectral decomposition:

$$H = \sum_j E_j \mathbb{P}_j \qquad \mathbb{P}_j = \sum_{\alpha=1}^{n_j} \underbrace{|\psi_{j,\alpha}\rangle \langle \psi_{j,\alpha}|}_{\mathbb{P}_{j,\alpha}} \qquad H|\psi_{j,\alpha}\rangle = E_j |\psi_{j,\alpha}\rangle$$

where j is the index that represents the energy level, while $\alpha = 0, 1 \ldots, n_j$ indicate the degeneracy of level ϵ_j. Note that we assume that n_j is a finite number, so there is not infinite degeneracy. $\mathbb{P}_j$ is the projection on the eigenspace $E = E_j$, which is equivalent to the selection of an energy sheet in the phase space.

Now we do the same thing that we did classically: once the system is fixed with an energy level, it can be in every point of the hypersurface with the same probability. The only different is that in quantum mechanics a probability distribution becomes an operator, so we'll indicate it with $\hat{}$.

Also the normalization requirement (which in the classical case is that the integral over the phase space needs to equal 1) becomes that the trace over the Hilbert space needs to equal 1.

Energy is conserved, so $E \equiv E_j$ is fixed and the n_j states $\{|\psi_{j,\alpha}\rangle\}_{\alpha=1,\ldots,n_j}$ have the same probability. The mixed density matrix is:

$$\hat{\rho}_{mc} = \sum_{\alpha=1}^{n_j} p |\psi_{j,\alpha}\rangle \langle \psi_{j,\alpha}|$$

since $Tr\,[\rho_{mc}] = 1 \implies \sum_{\alpha=1}^{n_j} p = 1 \implies p = 1/n_j$, so:

$$\hat{\rho}_{mc} = \frac{1}{n_j} \sum_{\alpha=1}^{n_j} |\psi_{j,\alpha}\rangle \langle \psi_{j,\alpha}|$$

If we have an observable A ($A^\dagger = A$), then: $\langle A \rangle = Tr\,[\rho_{mc}A]$ (this is simply the definition of mean of an operator).

We can also define entropy using the Universal Boltzmann formula:

$$S_{mc}^{(q)} = -k_B \langle \log \rho_{mc} \rangle_{mc} = -k_B Tr \left[\rho_{mc} \log \rho_{mc} \right]$$

Using the o.n. basis of the Hilbert space $\{|\phi_\lambda\rangle\}_\lambda$, the trace of an operator is $Tr[A] = \sum_\lambda \langle \phi_\lambda | A | \phi_\lambda \rangle$, then :

$$S_{mc}^{(q)} = -k_B \sum_{\alpha=1}^{n_j} \frac{1}{n_j} \log \frac{1}{n_j} = -k_B n_j \left(\frac{1}{n_j} (-\log n_j) \right) = k_B \log n_j$$

3.3.2   Canonical ensemble

In the canonical ensemble, V, N, T are fixed, while E can be exchanged with a big reservoir. We can write the Hamiltonian as:

$$H = \sum_j E_j \mathbb{P}_j \qquad \mathbb{P}_j = |\psi_{j,\alpha}\rangle \langle \psi_{j,\alpha}|$$

This time the probability is not the same for all the state, but we assume that:

$$p_j \propto e^{-\beta E_j} \qquad \beta = \frac{1}{k_B T}$$

We also recall that $\mathbb{P}_k^\dagger = \mathbb{P}_j \quad \mathbb{P}_j^2 = \mathbb{P}_j \quad \mathbb{P}_j \mathbb{P}_k = \delta_{jk}$ And

$$\rho_c \propto \sum_j e^{-\beta E_j} \mathbb{P}_j \overset{(*)}{=} e^{-\beta \sum_j E_j \mathbb{P}_j} \implies \hat{\rho}_c \propto e^{-\beta \hat{H}}$$

$(*)$ is justified by the following: PROOF:

$$e^{-\beta \hat{H}_N} = e^{\beta \sum_{j=1}^\infty E_j \mathbb{P}_j} = \sum_{n=0}^\infty \frac{1}{n!} \left(-\beta \sum_j E_j \mathbb{P}_j \right)^n \overset{(\mathbb{P}_j)^n = \mathbb{P}_j}{=} \sum_j \left[\sum_{n=0}^\infty \frac{1}{n!} (-\beta E_j)^n \right] \mathbb{P}_j = \sum_j e^{-\beta E_j} \mathbb{P}_j$$

Now we should fix the normalization constant in front, imposing $Tr_\mathcal{H}[\rho_c] = 1$:

$$1 = Tr \left[\frac{1}{Z_N} e^{-\beta H} \right] = \frac{1}{Z_N} Tr_\mathcal{H} \left[e^{-\beta \hat{H}} \right]$$

where $Z_N \equiv Tr_\mathcal{H} \left[e^{-\beta \hat{H}} \right]$ is the quantum canonical partition function.

So we get:

$$\rho = \frac{1}{Z_N} e^{-\beta H}$$

We can also compute:

$$\langle A \rangle_c = Tr_\mathcal{H} \left[\rho_c A \right] = \frac{1}{Z_N} Tr \left[e^{-\beta H} A \right]$$

$$S_c = k_B \langle \log \rho_c \rangle_c = -k_B Tr \left[\rho_c \log \rho_c \right]$$

Let's now define all the thermodynamic quantities and then see that the relation $S = \frac{E-F}{T}$ holds:

- Free energy (F) $\qquad Z_N = e^{-\beta F} \implies F = -\frac{1}{\beta} \log Z_N$

- Internal energy(E) $\qquad$ By definition:

$$E = \langle H \rangle_c = Tr\left[\rho_c H\right]$$

$$= Tr\left[\frac{e^{\beta H}}{Z_N} H\right] = \frac{1}{Z_N}\left(-\frac{\partial}{\partial \beta} \underbrace{Tr\left[e^{-\beta H}\right]}_{Z_N}\right)$$

$$= -\frac{1}{Z_N}\frac{\partial}{\partial \beta} Z_N$$

$$= -\frac{\partial \log Z_N}{\partial \beta} \qquad \text{(same result as classical)}$$

- Entropy (S) $\qquad S = -\frac{\partial F}{\partial T}$ and it is more convenient to write:

$$\frac{\partial}{\partial T} = \frac{\partial \beta}{\partial T}\frac{\partial}{\partial \beta} = -k_B \beta^2 \frac{\partial}{\partial \beta}$$

So:

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

$$= k_B \beta^2 \frac{\partial}{\partial \beta}\left(-\frac{1}{\beta} \log Z_N\right)$$

$$= -k_B \beta^2 \left[-\frac{1}{\beta^2} \log Z_N + \frac{1}{\beta}\frac{1}{Z_N}\frac{\partial Z_N}{\partial \beta}\right] \qquad Z_N = Tr\left[e^{-\beta H}\right]$$

$$= \frac{-k_B}{Z_N}\left[-Tr\left[e^{-\beta H} \log Z_N\right] + Tr\left[-\beta H e^{-\beta H}\right]\right] \qquad \beta H = -\log e^{-\beta H}$$

$$= \frac{+k}{Z_N}Tr\left[e^{-\beta H}\left(-\log \underbrace{\frac{e^{-\beta H}}{Z_N}}_{\rho_c}\right)\right]$$

putting the term $1/Z_N$ inside the trace:

$$= -k_B Tr\left[\rho_c \log \rho_c\right] = \langle \log \rho_c \rangle_c$$

$$= S = \frac{E - F}{T} \qquad \text{(same result as classical)}$$

3.3.3 Grancanonical ensemble

In the canonical ensemble, V and T are fixed, while E and N can be exchanged with a big reservoir. We will work on the Hilbert state $\mathcal{H} = \bigoplus_{N=0}^{\infty} \mathcal{H}_N$ or equivalently with

an hamiltonian that conserve the number of particles (commutes with the number operator): $H = \bigoplus_{N=0}^{\infty} H_N \iff \left[\hat{H}, \hat{N}\right] = 0.$

$$H \left|\psi_{n\alpha}\right\rangle = E_n \left|\psi_{n\alpha}\right\rangle \qquad \alpha = 1, \dots n_N$$

n labels the possible states/eigenvalues, but it's actually a double label. In fact before the number of particle N is fixed, $\tilde{n}$ expresses the set of eigenvalues and it can happen that the same energy comes from two different N.

So we have: $\hat{H} = \sum_n E_n \mathbb{P}_n \qquad \left[\hat{H}, \hat{N}\right] = 0 \qquad \hat{N} = \sum_{n(=N,\tilde{n})} N \mathbb{P}_n$

The energy can be any of the eigenvalues $E_j^{(N)}$ of H_N, with probability $p_j \propto e^{-\beta(E_j - \mu N)}$ as in the classical case (this is an assumption).

The system is in a mixed state whose density matrix is given by:

$$\rho_{gc} \propto \sum_{N=0}^{\infty} \sum_j e^{-\beta(E_j - \mu N)} \mathbb{P}_j = e^{-\beta(\hat{H} - \mu \hat{N})} = e^{-\beta \hat{K}}$$

where $\hat{K}$ is the grancanonical hamiltonian: $\hat{K} = \hat{H} - \mu\hat{N}$.

We can also write: $\rho_c = \frac{1}{\mathcal{Z}} e^{-\beta(\hat{H} - \mu\hat{N})}$, and from $Tr_{\mathbb{H}_F}[\rho_c] = 1$ we get the **grancanonical partition function**:

$$\mathcal{Z} = Tr_{\mathcal{H}}\left[e^{-\beta(\hat{H} - \mu\hat{N})}\right] \qquad\qquad \mathcal{H} = \bigoplus_{N=0}^{\infty} \mathcal{H}_N$$

$$= \sum_{N=0}^{\infty} Tr_{\mathcal{H}_N}\left[e^{-\beta(\hat{H} - \mu\hat{N})}\right] \qquad\qquad \text{now } \hat{N} = N$$

$$= \sum_{N=0}^{\infty} \underbrace{e^{\beta\mu N}}_{z^N} \underbrace{Tr_{\mathcal{H}_N}\left[e^{-\beta\hat{H}}\right]}_{Z_N}$$

$$= \sum_{N=0}^{\infty} z^N Z_N \qquad \text{as in the classical case.}$$

where z is the fugacity and $z^N = e^{\beta\mu N}$

We can also define the grancanonical average of an observable:

$$\langle A \rangle_{gc} = Tr_{\mathcal{H}}[\rho_{gc} A] = \sum_{N=0}^{\infty} Tr_{\mathcal{H}_N}[\rho_{gc} A] = \sum_{N=0}^{\infty} z^N Tr_{\mathcal{H}_N}\left[\frac{e^{-\beta H_N}}{\mathcal{Z}} A\right]$$

Doing this calculation we are assuming that $\left[\hat{A}, \hat{N}\right] = 0$, so this is true only for operators that conserves the number of particles.

Now we can define the thermodynamic functions as:

- The grancanonical potential: $\Omega = -\frac{1}{\beta} \log \mathcal{Z} \implies \mathcal{Z} = e^{-\beta\Omega}$

- Internal energy:

$$E - \mu N = \left\langle \hat{H} - \mu\hat{N} \right\rangle_{gc} \overset{\text{as exercise}}{=} -\frac{\partial \log \mathcal{Z}}{\partial \beta}$$

$$\implies E = \left\langle \hat{H} \right\rangle_{gc} = -\left.\frac{\partial \log \mathcal{Z}}{\partial \beta}\right|_z$$

- Entropy. Using universal Boltzmann formula:

$$S_{gc} = -k_B \left\langle \rho_c \right\rangle_{gc} = -k_B Tr_{\mathcal{H}} \left[\hat{\rho}_{gc} \log \hat{\rho}_{gc} \right] \overset{\text{as exercise}}{=} \frac{E - \mu N - \Omega}{T}$$

15/12/2022

3.3.4 Exercise (1.1): Quantum magnetic dipoles

3.3.5 Exercise (1.2): Quantum harmonic oscillators

3.4   Quantum gases

Here we'll talk about bosonic/fermionic indistinguishable particles in an external magnetic field. We are neglecting any relativistic effect and any particle-particle interactions.

If we have N particles, we can write the hamiltonian operator in first quantization as:

$$\hat{H} = \sum_{j=1}^{N} \frac{\widehat{\vec{p}}_j^{\,2}}{2m} + \sum_{j=1}^{N} V(\hat{x}_j)$$

The o.n Fock basis $\mathbb{H}_F$ is obtained starting from the base of a single particle hamiltonian:

$$\mathcal{H}_1\{u_\alpha(x)\} \to a_\alpha, a_\alpha^\dagger \qquad \hat{n}_\alpha = a_\alpha^\dagger a_\alpha \quad n_j = \begin{cases} 0, 1, \dots & \text{B} \\ 0, 1 & \text{F} \end{cases}$$

$$\mathbb{H}_F = \bigoplus_{N=0}^{\infty} \mathbb{H}_N^{B/F} \to |n_1, n_2 \dots, n_k, \dots\rangle = C \left(a_1^\dagger\right)^{n_1} \left(a_2^\dagger\right)^{n_2} \dots |0\rangle$$

That's why (as we'll see), it is easier to work with the grancanonical ensemble, because we don't have to keep track of the conditions. We will come back on this.

The Hamiltonian operator can be written, in second quantization, as:

$$\boxed{\hat{H} = \sum_\alpha \epsilon_\alpha a_\alpha^\dagger a_\alpha = \sum_\alpha \epsilon_\alpha \hat{n}_\alpha} \qquad H^{(1)}|u_\alpha(x)\rangle = \epsilon_\alpha |u_\alpha(x)\rangle \qquad \epsilon_\alpha = \frac{p_\alpha^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

where α labels single particle states and $\hat{a}_\alpha^\dagger, \hat{a}_\alpha$ are the creation/annihilation operators that create/destroy a particle in the state indexed by α.

The grancanonical partition function is easily obtained using the Fock basis:

$$\mathcal{Z} = Tr_{\mathbb{H}_F}\left[e^{-\beta(\hat{H} - \mu\hat{N})}\right]$$

$$= \sum_{n_1, n_2, \dots} \left\langle n_1, n_2, n_3, \dots \middle| e^{-\beta \sum_\alpha (\epsilon_\alpha - \mu)\hat{n}_\alpha} \middle| n_1, n_2, n_3, \dots \right\rangle$$

$$(\hat{n}_\alpha |n_1, n_2, \dots, n_\alpha, \dots\rangle = n_\alpha |n_1, n_2, \dots, n_\alpha, \dots\rangle)$$

$$= \sum_{n_1, n_2, \dots} e^{-\beta \sum_\alpha (\epsilon_\alpha - \mu)n_\alpha} \underbrace{\langle n_1, n_2, \dots | n_1, n_2, \dots \rangle}_{1}$$

$$= \sum_{n_1, n_2, \dots} \prod_\alpha e^{-\beta(\epsilon_\alpha - \mu)n_\alpha} \qquad\qquad \text{I can switch } \sum \text{ with } \prod$$

$$= \prod_\alpha \left[\sum_{n_\alpha} e^{-\beta(\epsilon_\alpha - \mu)n_\alpha}\right] \qquad\qquad n_\alpha = \begin{cases} 0, 1, 2 \dots & (B) \\ 0, 1 & (F) \end{cases}$$

So, recalling the geometric series $\sum_{N=0}^{\infty} x^n = \frac{1}{1-x}$ if $x < 1$, we get:

$$\mathcal{Z}_F = \prod_{\alpha} \sum_{n_\alpha=0,1} e^{-\beta(\epsilon_\alpha-\mu)n_\alpha} = \prod_{\alpha} \left[1 + e^{-\beta(\epsilon_\alpha-\mu)}\right]$$

$$\mathcal{Z}_B = \prod_{\alpha} \sum_{n_\alpha=0}^{\infty} e^{-\beta(\epsilon_\alpha-\mu)n_\alpha} = \prod_{\alpha} \left[\frac{1}{1 - e^{-\beta(\epsilon_\alpha-\mu)}}\right]$$

The geometric series apply if:

$$e^{-\beta(\epsilon_\alpha-\mu)} < 1 \iff \beta(\epsilon_\alpha - \mu) > 0 \implies \mu < \epsilon_\alpha \; \forall \alpha \implies \mu < \epsilon_0 = 0$$

so for bosons we re-scale the energy levels to have $\epsilon_0 = 0$

(X) MON 28/11/2022

We can re-write the grancanonical partition function as:

$$\mathcal{Z}_{B/F} = \prod_{\alpha} \left[1 \mp e^{-\beta(\epsilon_\alpha-\mu)}\right]^{\mp 1} = e^{\beta\Omega_{B/F}} \tag{3.8}$$

where $\Omega_{B/F}$ is the grancanonical potential:

$$\Omega_{B/F} = -\frac{1}{\beta}\log\mathcal{Z}_{B/F} = \pm\frac{1}{\beta}\sum_{\alpha}\log\left[1 \mp e^{-\beta(\epsilon_\alpha-\mu)}\right]$$

We can also calculate the average number of particle for the k-th state:

$$\begin{aligned}
n_k = \langle\hat{n}_k\rangle_{gc} &= Tr_{\mathbb{H}_F}\left[\rho\hat{n}_k\right] \\
&= Tr\left[\frac{e^{-\beta\sum_\alpha(\epsilon_\alpha-\mu)\hat{n}_\alpha}}{\mathcal{Z}}\hat{n}_k\right] \\
&= \frac{1}{\mathcal{Z}}Tr\left[-\frac{1}{\beta}\frac{\partial}{\partial\epsilon_k}e^{-\beta\sum_\alpha(\epsilon_\alpha-\mu)\hat{n}_\alpha}\right] \\
&= -\frac{1}{\beta}\frac{1}{\mathcal{Z}}\frac{\partial\mathcal{Z}}{\partial\epsilon_k} \\
&= \frac{\partial}{\partial\epsilon_k}\left(-\frac{1}{\beta}\log\mathcal{Z}\right) \\
&= \frac{\partial}{\partial\epsilon_k}\Omega_{B/F} \\
&= \frac{1}{e^{\beta(\epsilon_k-\mu)} \mp 1}
\end{aligned}$$

Using the (-) we get the **Bose-Einstein** distribution, while using the (+) we get the **Fermi-Dirac** distribution. Comparing this with the classical distribution (the Maxwell Boltzmann distribution $n_{MB} = e^{-\beta(\epsilon-\mu)}$), we can see in Fig. 3.4 that in the limit of high temperatures, the distributions converges.
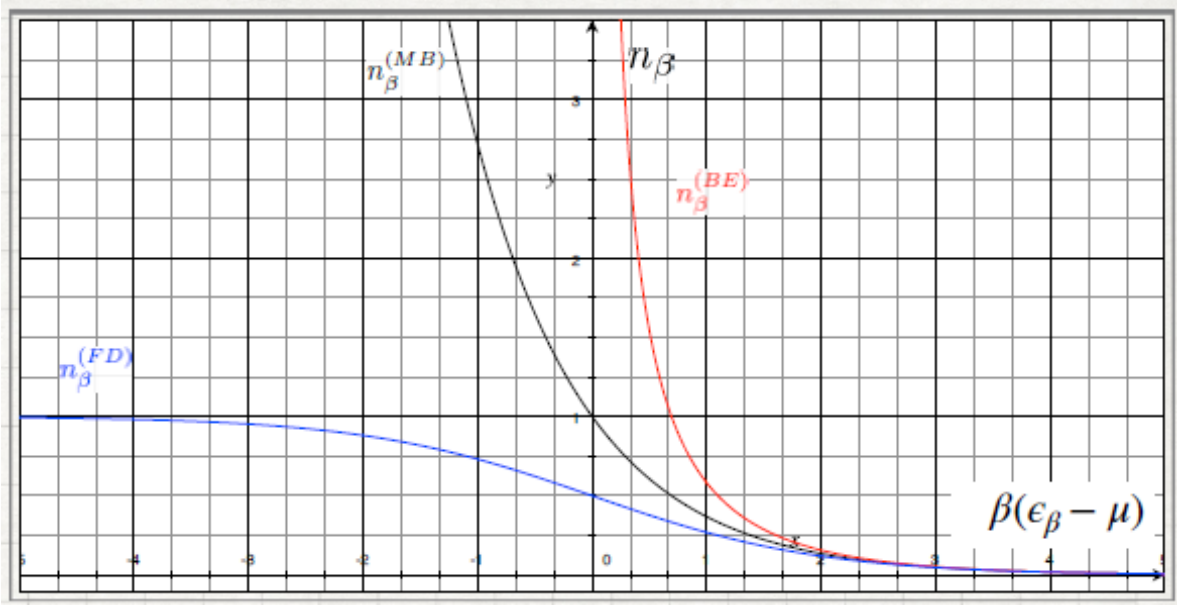
Figure 3.4: Maxwell-Boltzmann, Fermi-Dirac and Bose-Einstein distributions. We can see that for high temperature (on the right of the graph), the distributions converges. (in the figure the subscript $_k$ is instead denoted with $_\beta$)

Now that we got n_k, we can also get the number of particles N, simply by evaluating:

$$N = \sum_k \langle \hat{n}_k \rangle = \sum_k \frac{1}{e^{\beta(\epsilon_k - \mu)} \mp 1} \tag{3.9}$$

Or also, N can also be obtained from:

$$N = -\frac{\partial \Omega_{B/F}}{\partial \mu} = (3.9) \text{ as exercise}$$

We can also evaluate the energy as:

$$E = \sum_k \epsilon_k n_k = \sum_k \frac{\epsilon_k}{e^{\beta(\epsilon_k - \mu)} \mp 1}$$

Thermodynamic limit

What we've done up to now works within a finite volume and in a discrete case:

$$\epsilon_\alpha = \frac{\hbar^2 \vec{k}^2}{2m} \qquad \text{periodic BCs} \rightarrow \vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z) \qquad n_j \in \mathbb{Z} \qquad \alpha = (n_x, n_y, n_z)$$

In the thermodynamic limit $V, L \rightarrow \infty$, $\frac{2\pi}{L} \rightarrow 0$, so the space between different levels becomes smaller and smaller and k becomes continuous. All the sum expressions

become integrals. Let's see how. For a single component $n_j = n_x, n_y, n_z$:

$$\sum_{n_j}() = \sum_{n_j}()\underbrace{\Delta n_j}_{=1} \qquad\qquad k_j = \frac{2\pi}{L}n_j \iff \Delta k_j = \frac{2\pi}{L}\Delta n_j$$

$$= \sum_{k_j}()\frac{L}{2\pi}\Delta k_j \qquad\qquad \Delta k_j \to dk_j \text{ in the limit}$$

$$= \frac{L}{2\pi}\int_{-\infty}^{\infty} dk_j()$$

Repeating this procedure for all the components give us:

$$\sum_{\alpha}() = \sum_{n_x,n_y,n_z}() \to \left(\frac{L}{2\pi}\right)^3 \int d^3k\ () = \frac{V}{(2\pi)^3}\int d^3k\ ()$$

Since sometimes we have $|\vec{k}|$, it is convenient to use spherical coordinates:

$$= \frac{V4\pi}{(2\pi)^3}\int_0^{\infty} k^2 dk\ f(|\vec{k}| = k)$$

since $\epsilon_\alpha = \epsilon_\alpha(k) = \frac{\hbar^2 k^2}{2m}$, we can change variable: $d\epsilon = \frac{\hbar^2 k}{m}dk$

$$\stackrel{\text{as exercise}}{=} \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^{\infty} \epsilon^{1/2}d\epsilon$$

So:

$$\sum_{\alpha} \to VA\int_0^{\infty} \epsilon^{1/2}d\epsilon \qquad \text{with } A = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}$$

we call $g(\epsilon) = A\epsilon^{\frac{1}{2}}$ **density of states**.

Since we are using $\epsilon_\alpha = \frac{\hbar^2 k^2}{2m}$, this only works for non-interacting (free) non-relativistic particles. Also, we are assuming that we are in a three-dimensional space, otherwise the change of variable would be different.

Also notice something: in writing the grancanonical partition function (3.8), we didn't consider the fact that an energy level can be degenerate. If we want to take that into account, we would have:

$$\mathcal{Z}_{B/F} = \prod_{\alpha}\left[1 \mp e^{-\beta(\epsilon_\alpha - \mu)}\right]^{\mp g}$$

$$\Omega = \frac{1}{\beta}\log\mathcal{Z} = \mp g\sum_{\alpha}\log\left[1 \mp e^{-\beta(\epsilon_\alpha - \mu)}\right]$$

and: $\qquad N = g\sum_{\alpha}\alpha\langle\hat{n}_\alpha\rangle \qquad E = g\sum_{\alpha}\epsilon_\alpha n_\alpha \qquad$ etc

Now that we are in the continuous case, we can evaluate Ω, N, E as integrals.

$$\Omega = \pm V \frac{A}{\beta} \int_0^\infty \epsilon^{1/2} \log\left[1 \mp e^{-\beta(\epsilon_\alpha - \mu)}\right] d\epsilon$$

$$N = AV \int_0^\infty \epsilon^{1/2} \frac{1}{e^{\beta(\epsilon-\mu)} \mp 1} d\epsilon \qquad (3.10)$$

$$E = AV \int_0^\infty \epsilon^{3/2} \frac{1}{e^{\beta(\epsilon-\mu)} \mp 1} d\epsilon \qquad (3.11)$$

Notice that their expressions scale with V (as it should be, since they are extensive quantities)

Integrating by parts:

$$\frac{\Omega}{V} = \frac{A}{\beta} \left\{ \left[\pm \frac{2}{3} \epsilon^{3/2} \cancel{\log(\dots)}\right]_0^\infty \mp \int_0^\infty \frac{2}{3} \epsilon^{3/2} \frac{\pm\beta}{e^{\beta(\epsilon-\mu)} \mp 1} d\epsilon \right\}$$

$$= \frac{2}{3} A \int_0^\infty \epsilon^{3/2} \frac{1}{e^{\beta(\epsilon-\mu)} \mp 1} d\epsilon$$

$$\implies \underbrace{\frac{\Omega}{V}}_{-pV} = -\frac{2}{3} E \implies \boxed{pV = \frac{2}{3} E} \quad \text{Equation of state}$$

This is the equation of state of a perfect (quantum) gas. In the classical case, $E = \frac{3}{2} N k_B T \implies pV = N k_B T$

3.4.1 Fundamental equations

We can also calculate (remind that (-)Bosonic gas (+)Fermionic gas):

$$n = \frac{N}{V} = A \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{e^{\beta(\epsilon-\mu)} \mp 1} \qquad p = \frac{2}{3} \frac{E}{V} = \frac{2}{3} A \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{e^{\beta(\epsilon-\mu)} \mp 1}$$

By solving these equation, we would know the state of the gas (bosonic or fermionic). The problem is that they don't have a solution/primitive in 3D. We'll see the solution for low and high temperatures.

Using the fugacity $z = e^{\beta\epsilon}$:

$$n = A \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{e^{\beta\epsilon} z^{-1} \mp 1}$$

$$= A \int_0^\infty \frac{z\epsilon^{1/2} d\epsilon}{e^{\beta\epsilon} \mp z} = \qquad \text{change of variable: } \beta\epsilon = x^2 \quad \beta d\epsilon = 2x dx$$

$$= \frac{4g}{\sqrt{\pi}} \frac{1}{\lambda_T^3} \int_0^\infty \frac{zx^2 dx}{e^{x^2} \mp z}$$

with $\lambda_T = \frac{\hbar}{\sqrt{2\pi m k_B T}}$

Clearly, since we are not able to do the first integral, we can't do the last either, but:

$$\frac{z}{e^{x^2} \mp z} = \frac{ze^{-x^2}}{1 \pm ze^{-x^2}} = ze^{-x^2} \sum_{n=0}^{\infty} (\mp 1)^n \left(ze^{-x^2}\right)^n \quad \text{if the series is convergent}$$

For fermions(-), it converges $\forall z \notin [-\infty, -1]$
For bosons(+), it converges only for $z < 1 \implies \mu < 0$, but this is only what we needed to suppose from the beginning. So n becomes:

$$n = \frac{4g}{\sqrt{\pi}} \frac{1}{\lambda_T^3} \int_0^\infty dx \, x^2 e^{-x^2} z \sum_{n=0}^{\infty} (\pm 1)^n \left(ze^{-x^2}\right)^n$$

and if the series is convergent I can swap the sum with the integral.

$$= \frac{4g}{\sqrt{\pi}} \frac{1}{\lambda_T^3} \sum_{n=0}^{\infty} (\pm 1)^n z^{n+1} \int_0^\infty dx \, x^2 e^{-(n+1)x^2}$$

Now the integral can be evaluated, because it is the second moment of the Gaussian integral: $\frac{\sqrt{\pi}}{4} \frac{1}{(n+1)^{3/2}}$

$$n = \frac{g}{\lambda_T^3} \sum_{n=0}^{\infty} \frac{z^{n+1}(\pm 1)^n}{(n+1)^{3/2}}$$

Similar calculations can be done for p, with the only difference being a x^4 instead of x^2 inside the integral. Thus obtaining:

$$p = k_B T \frac{g}{\lambda_T^3} \sum_{n=0}^{\infty} \frac{z^{n+1}(\pm 1)^n}{(n+1)^{5/2}}$$

If we define

$$\text{Bosons} \qquad b_l(z) \equiv \sum_{n=0}^{\infty} \frac{z^{n+1}}{(n+1)^l}$$

$$\text{Fermions} \qquad f_l(z) \equiv \sum_{n=0}^{\infty} (-1)^n \frac{z^{n+1}}{(n+1)^l}$$

then we obtain the **fundamental equations**:

$$\boxed{n = \frac{N}{V} = \frac{g}{\lambda_T^3} \begin{cases} b_{3/2}(z) \\ f_{3/2}(z) \end{cases} \qquad \frac{p}{k_B T} = \frac{g}{\lambda_T^3} \begin{cases} b_{5/2}(z) \\ f_{5/2}(z) \end{cases}} \tag{3.12}$$

In the classical limit $z \ll 1$, we can take just the first term of the f_l and g_l functions: $b_l(z) \simeq f_l(z) \simeq z$ so we get:

$$n = \frac{g}{\lambda_T^3} z \implies z = \frac{n\lambda_T^3}{g} \ll 1 \quad \text{dilute gas, } \lambda_T^3 \text{ small} \to T \text{ large}$$

$$\frac{p}{k_B T} = \frac{g}{\lambda_T^3} z = n = \frac{N}{V} \implies pV = N k_B T$$

which is the equation of a perfect classical gas, which we obtained from Bosons and Fermions statistic.

Also, in the limit of high temperatures we get the exact formulas for μ and $n(\epsilon)$ that we got for a classical gas:

$$n = \frac{g}{\lambda_T^3} e^{\beta\mu} \implies \mu(T) = -\frac{3}{2} k_B T \log\left(\frac{n k_B T}{2\pi\hbar^2 n^{3/2}}\right) \xrightarrow[T\to\infty]{} -\infty$$

$$\beta\mu \to -\infty \implies n(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)} \mp 1} \simeq e^{-\beta(\epsilon-\mu)} = n_{MB}$$

So in the limit of high temperatures, both the Bose-Einstein and the Fermi-Dirac distributions converges to the Maxwell-Boltzmann distribution.

3.4.2   Semi-classical limit (exercise 2.1)

01/12/2022

At first, we can study the semi-classical limit, by taking the expansion of the fundamental equations (3.12):

$$\begin{cases} n = \frac{g}{\lambda_T^3}\left[z \pm \frac{z^2}{2^{3/2}}\right] & \text{(I)} \\ \frac{p}{k_B T} = \frac{g}{\lambda_T^3}\left[z \pm \frac{z^2}{2^{5/2}}\right] & \text{(II)} \end{cases}$$

We will derive $z = z(n)$ from the first and plug into the second equation:

$$\text{from (I)} \quad \frac{z^2}{2\sqrt{2}} \pm z \mp \frac{n\lambda_T^3}{g} = 0$$

$$\implies z_{1,2} = \sqrt{2}\left[\begin{smallmatrix}(B)\\(F)\end{smallmatrix} \mp 1 \pm^{(z_2)}_{(z_1)} \sqrt{1 \pm \frac{2}{\sqrt{2}}\left(\frac{n\lambda_T^3}{g}\right)}\right]$$

If we expand up to second order: $\sqrt{1 \pm x} \simeq 1 \pm \frac{1}{2}x - \frac{1}{8}x^2$

$$\cong \sqrt{2}\left[\mp 1 \pm \left(1 \pm \frac{1}{\sqrt{2}}\left(\frac{n\lambda_T^3}{g}\right) - \frac{1}{4}\left(\frac{n\lambda_T^3}{g}\right)^2\right)\right]$$

Now, which one between z_1 and z_2 should we accept? The one that made the ∓ 1 cancels with ± 1, since we already know that the first order of z is $z \sim \frac{n\lambda_T^3}{g}$. So:

$$z = \frac{n\lambda_T^3}{g} \mp \frac{1}{2\sqrt{2}}\left(\frac{n\lambda_T^3}{g}\right)^2$$

Plugging this into (II) keeping only the first order of $\frac{n\lambda_T^3}{g}$, gives:

$$\frac{p}{k_B T} = \frac{g}{\lambda_T^3} \frac{n\lambda_T^3}{g} \left[1 \mp \frac{1}{4\sqrt{2}} \left(\frac{n\lambda_T^3}{g} \right) \right] = n \left[1 \mp \frac{1}{2^{5/2}} \frac{n\lambda_T^3}{g} \right]$$

The term $\frac{1}{2^{5/2}} \frac{n\lambda_T^3}{g}$ is called *quantum correction* or *semiclassical correction*.

We can notice the sign of the quantum correction: it is - for bosons and + for fermions. That means that the pressure p is reduced by bosonic gases and increased by fermionic gases, as if there is an attractive potential between bosons and a repulsive between fermions.

We also notice that the correction is quantum in nature, as it is shown by the fact that it goes to zero when $h \to 0 \implies \lambda = \frac{h}{\sqrt{2mk_B T}} \to 0$ or when $g = 2S + 1 \to \infty$, i.e. when all states have an infinite degeneracy so that quantum counting does not have anymore effect.

How much high should the temperature T be to have $z \ll 1$? It depends on n: it must be $\quad n\lambda_T^3 \ll 1$.

Now let's do the opposite limit and analyze very low temperatures:

3.4.3   Fermions at T=0

Starting from the Fermi-Dirac distribution:

$$n_\alpha = \frac{1}{e^{\beta(\epsilon_\alpha - \mu)} + 1}$$

we'll take the limit $T \to 0 \implies \beta \to \infty$, so the behaviour of n_α depends on the sign of $\epsilon - \mu$:

- if $\epsilon_\alpha - \mu < 0 \implies \epsilon_\alpha < \mu \implies n_\alpha \xrightarrow[\beta \to \infty]{} 1 \quad \forall \epsilon_\alpha$

- if $\epsilon_\alpha - \mu > 0 \implies \epsilon_\alpha > \mu \implies n_\alpha \xrightarrow[\beta \to \infty]{} 0 \quad \forall \epsilon_\alpha$

- if $\epsilon_\alpha - \mu = 0 \implies \epsilon_\alpha = \mu \implies n_\alpha = \frac{1}{2}$

We call the **Fermi energy**: $\boxed{\epsilon_F \equiv \lim_{T \to 0} \mu(T)}$

So at $T = 0$, the Fermi distribution is a step function: all states with energy $\epsilon < \epsilon_F$ are occupied (with only 1 particles, since they are fermions) and all the states with energy $\epsilon > \epsilon_F$ are empty (red in Fig. 3.5)

ϵ_F is defined by the number of particle N (since there is just one particle for every ϵ_α), so the equation $N = \sum_\alpha n_\alpha$ fixes $\mu(T)$. In other words, to change the Fermi energy we have to change the number of particles.
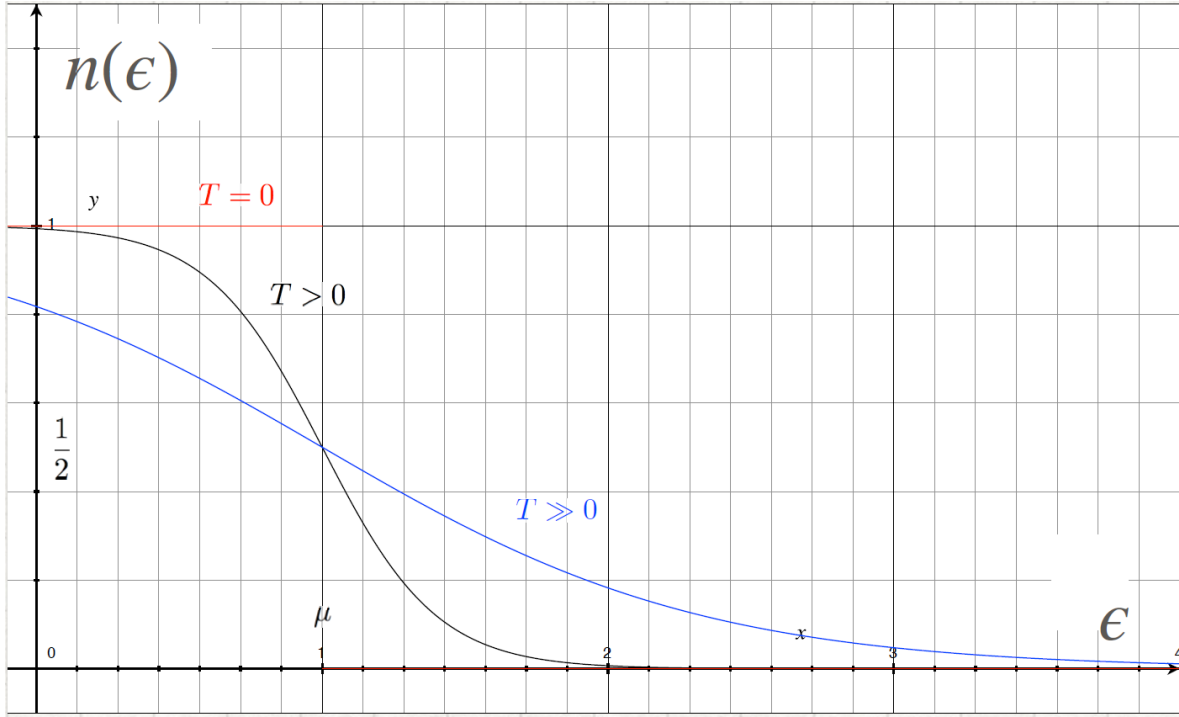
Figure 3.5: Fermions distribution at different temperatures

Now $z = e^{\beta\mu}$ is no longer small.

Also recall that any $f_l(z)$ is convergent $\forall z < 1$ and it's a smooth function.

We can also define the **Fermi temperature** as: $\epsilon_F = k_B T_F$. If a system has a temperature $T \ll T_F$, then we are in the so-called **degeneration limit** and the system behaves effectively as at $T = 0$ ($n(\epsilon)$ actually look like a step function and the calculations are easier). Examples could be:

- conduction electrons in metals, with $T \sim 100K$ and $T_F \sim 10^4 - 10^5 K$

- free electrons in white dwarfs (ionised helium), with $T \sim 10^7 K$ and $T_F \sim 10^{11}$ since the density is very high ($n \sim 10^{30}/cm^3$)
  (even if, at this temperature, speeds are relativistic –we will see later)

The initial equations (3.10) and (3.11), becomes for $T = 0$:

$$\frac{N}{V} = gA \int_0^\infty d\epsilon \frac{\epsilon^{1/2}}{e^{\beta(\epsilon-\mu)} + 1} \overset{(*)}{=} gA \int_0^{\epsilon_F} d\epsilon \ \epsilon^{1/2} = gA\frac{2}{3}\epsilon_F^{3/2}$$

$$\frac{E}{V} = gA \int_0^\infty d\epsilon \frac{\epsilon^{3/2}}{e^{\beta(\epsilon-\mu)} + 1} \overset{(*)}{=} gA \int_0^{\epsilon_F} d\epsilon \ \epsilon^{3/2} = gA\frac{2}{5}\epsilon_F^{5/2}$$

$(*)$ is justified because, when $T = 0$ $\quad \frac{1}{e^{\beta(\epsilon-\mu)}+1} = n_\alpha \neq 0 \ (= 1)$ only if $\epsilon < \epsilon_F$.

From the first expression, one gets: $\epsilon_F = \left(\frac{3}{2}\frac{n}{gA}\right)^{2/3}$ and dividing the second by the first, we can get the energy for particle: $\frac{E}{V} = \frac{3}{5}\epsilon_F$. Using this and the fact that $-pV = \Omega = -\frac{2}{3}E$ we can get:

$$p = \frac{2}{5}\frac{N}{V}\epsilon_F = \frac{2}{3}n\epsilon_F$$

So notice that at $T = 0, \quad p > 0$.

This is a consequence of the Pauli exclusion principle

Remark: it is also possible to expand the fundamental equations for small temperatures, using the Sommerfield expansion.

3.4.4 Bosons at T=0

(XI) MON 05/12/2022

We will start from the fundamental equation (3.12) for bosons, recalling that the series $b_{3/2}(z)$ it's only convergent if $|z| < 1$. At $z = 1$, $g_{3/2}(z)$ is still defined and it's called the Reimann function $\zeta(3/2)$, but it has a vertical derivative ($g'_{3/2}(1) = \infty$), so the function is no longer analytic. This is a signal that something is happening in the gas of bosons. Since, $z = e^{\beta\mu}$, let's focus on the chemical potential $\mu(T)$.

- We proved that in the classical limit, $\mu(T) \xrightarrow[T\to\infty]{} -\infty$

- From general thermodynamics it can be proved that: $\frac{\partial\mu}{\partial T} \leq 0$

- For bosons, we proved that $\mu \leq 0$ (from the definition of $\mathcal{Z}$).

So there are only two possibilities:

1. $\mu(T) \to 0$ for $T \to 0$, which is what happen for a non-relativistic Bose gas in 2D (Fig. 3.6 left).

2. $\mu(T) \to 0$ for finite $T_c > 0$, which is what we have for a non-relativistic Bose gas in 3D (Fig. 3.6 right)

Now we would like to find T_c. We can invert the first fundamental equation (3.12) to get $\mu(T)$:

$$\text{from} \quad n = \frac{g}{\lambda_T^3}g_{3/2}(z) \to \mu = \mu(T)$$

T_c will be the (critical) temperature such that: $\mu(T = T_c) = 0$ and we can find it by evaluating n with $z = 1$ (since $z = e^{\beta\mu}$):

$$n = \frac{g}{\lambda_T^3}g_{3/2}(z = 1) \xrightarrow[T\to 0]{} 0$$
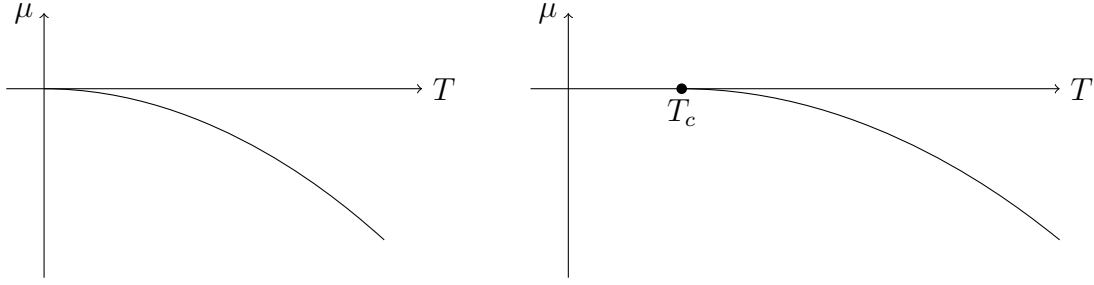
Figure 3.6: $\mu(T)$ for 2D (left) and 3D non-relativistic Bose gas

This is absurd: particles are not leaving the container! There must be something we have missed and this formula is not correct in the range $T < T_c$.

To understand why, let's go back to the Bose-Einstein distribution:

$$n_{BE}(\epsilon) = \frac{1}{e^{\beta(\epsilon - \mu)} - 1} \overset{\mu=0}{=} \frac{1}{e^{\beta\epsilon} - 1}$$

which is well defined if $\epsilon > 0$, but divergent if $\epsilon = 0$:

$$n_{BE}(\epsilon = 0) = \lim_{\epsilon \to 0} \frac{1}{e^{\beta\epsilon} - 1} \to \infty$$

So the $\epsilon = 0$ level is filled with an increasing number of particles. In other words, particles like to go in the ground state.

So the number of particles in the $\epsilon = 0$ state diverges: $N_0 \equiv N_{\epsilon=0} = \infty$. That means that, even if in the thermodynamic limit $N \to \infty$, the ratio $\frac{N_0}{N}$ stays finite, while usually $\frac{N(\epsilon \neq 0)}{N}$ is infinitesimal and such that $\int_0^\infty \frac{N(\epsilon \neq 0)}{N} d\epsilon = 1$.
This is what we call *macroscopic occupation* of the ground state.
We can also define the density of particle in the ground state (**ground state density**) as:

$$n_0 \equiv \frac{N_0}{V} = \frac{N_0}{N}\frac{N}{V} = \frac{N_0}{N}n$$

which is finite.

We can now notice something: $n = \frac{g}{\lambda_T^3}g_{3/2}$ is the TD limit of the equation:

$$N = \sum_\alpha n_{BE}(\epsilon_\alpha) = \sum_\epsilon \frac{1}{e^{\beta(\epsilon-\mu)} - 1} \xrightarrow[\text{TD limit}]{} V \int_0^\infty d\epsilon \, g(\epsilon) n_{BE}(\epsilon)$$

$\epsilon = 0$ is just an external point of the integral $\int_0 d\epsilon \ldots$, so even if $n_{BE} \xrightarrow{\epsilon \to 0} \infty$, the integral is convergent. That is the reason why we didn't see the divergence when we performed the calculations. But now, if $\mu = 0$, then the fraction of particles in $\epsilon = 0$ becomes macroscopic and, as we have seen, it gives problems if we don't consider it, so

we have to add it manually, writing:

$$N = \sum_{\epsilon} n_{BE}(\epsilon) = n_{BE}(0) + \sum_{\epsilon > 0} n_{BE}(\epsilon) = N_0 + \sum_{\epsilon > 0} n_{BE}(\epsilon)$$

$$\xrightarrow[\text{TD limit}]{} N_0 + V \int_0^{\infty} d\epsilon \, g(\epsilon) n_{BE}(\epsilon)$$

and the integral is not divergent since $n(\epsilon \neq 0)$ in 0 is infinitesimal.

Dividing by V we obtain:

$$n = n_0 + \frac{g}{\lambda_T^3} g_{3/2}(z) = n_0 + n_n(T) \qquad n_{normal} \equiv n(\epsilon \neq 0)$$

- for $T \geq T_c$ $\qquad n_0 = \frac{N_0}{V} \xrightarrow[\text{TD limit}]{} 0 \qquad n_n(T) = n = \frac{g}{\lambda_T^3} g_{3/2}(z)$

- for $T \leq T_c$ $\qquad n_0(T) = n - n_n \neq 0 \qquad n_n = \frac{g}{\lambda_T^3} g_{3/2}(1) = \frac{g}{\lambda_T^3} \frac{n \lambda_{T_c}^3}{g} = \left(\frac{T}{T_c}\right)^{3/2} n$

So:

$$n_0(T) = \begin{cases} 0 & T \geq T_c \\ n \left[1 - \left(\frac{T}{T_c}\right)^{3/2}\right] & T < T_c \end{cases} \qquad n_n(T) = \begin{cases} n & T \geq T_c \\ n \left(\frac{T}{T_c}\right)^{3/2} & T < T_c \end{cases}$$

As you can notice in Fig. 3.7, both $n_0(T)$ and $n_n(T)$ are continuous at $T = T_c$ but not differentiable. As always happen, this is the sign of a **phase transition**: in this case between a quantum gas to a Bose-Einstein condensate. This is a new state of matter, so the population of the ground state actually has a macroscopic effect.
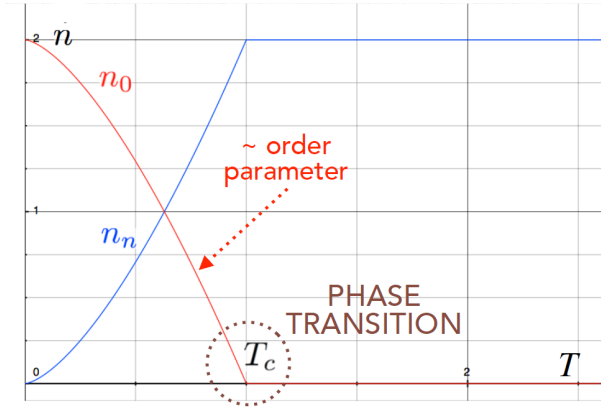

Figure 3.7: $n_n(T)$ and $n_0(T)$. For $T < T_c$ we have a Bose-Einstein condensate.

We could analyze the other fundamental equation (3.12), to see that is has no problems $\forall z$ and $\forall T$, because $g_{5/2}$ doesn't have the same divergence problem as $g_{3/2}$:

$$\frac{p}{k_B T} = \frac{g}{\lambda_T^3} g_{5/2}(z) \qquad \text{both with} \begin{cases} z = e^{\beta \mu} & T \geq T_c \\ z = 1 & T \leq T_c \end{cases}$$

Thermodynamical quantities

- Energy per particle $u(T) = \frac{E}{V}$
  Using the above equations and recalling that:

$$-pV = \Omega = -\frac{2}{3}E \quad \Longrightarrow \quad \frac{E}{V} = \frac{3}{2}p = \frac{3}{2}k_B T \frac{p}{k_B T} = \frac{3}{2}k_B T \frac{g}{\lambda_T^3} g_{5/2}(z)$$

we can calculate

$$u \equiv \frac{E}{N} = \frac{E/V}{N/V} = \frac{E/V}{n(T)}$$

$$= \frac{3 k_B T}{2} \begin{cases} \frac{g_{5/2}(z)}{g_{3/2}(z)} & T \geq T_c \\ \frac{g_{5/2}(1)}{g_{3/2}(1)} \left(\frac{T}{T_c}\right)^{3/2} & T \leq T_c \end{cases}$$

which is continuous at $T = T_c$.

- Specific heat (at constant V) per particle $c_V = \left.\frac{\partial u}{\partial T}\right|_V = \frac{1}{N}\left.\frac{\partial E}{\partial T}\right|_V = \frac{C_V}{N}$
  This is a really complex calculation for $T \geq T_c$.
  Recall that classically we had $E = N\frac{3}{2}k_B T$, so $c_V = \frac{3}{2}k_B T$, which was wrong for low temperatures ($c_V \xrightarrow[T \to 0]{} 0$ classically). Now quantum mechanics solves the problem and we can correct it. $c_V(T)$ is plotted in Fig. 3.8, where we can see that it is continuous in T_c but not differentiable (it has a cusp). This is again another signal of a phase transition.
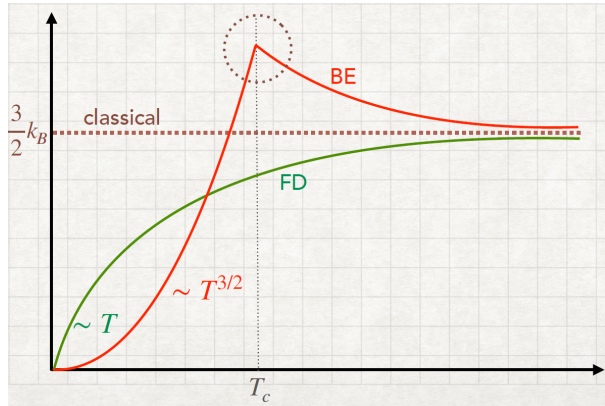

Figure 3.8: $c_V(T)$ for Bosons (red) and Fermions (green). In the Bose-Einstein distribution, the cusp at T_c indicate a phase transition.

- Entropy S

$$S = \frac{E - \Omega - \mu N}{T} = k_B \left(\frac{E + \frac{2}{3}E - N\beta^{-1}\log Z}{k_B T}\right) = k_B N \left(\frac{5}{3}\frac{1}{k_B T}\frac{E}{N} - \log Z\right)$$

Since $z = e^{\beta\mu}$ $-pV = \Omega = -\frac{2}{3}E$.

$$s = \frac{S}{N} = k_B \left[\frac{5}{3} \frac{E/N}{k_B T} - \log z \right]$$

$$= k_B \left(\frac{5}{2} \frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{g_{3/2}(z)}{g_{3/2}(z)} \log z \right)$$

$$= \frac{k_B}{g_{3/2}(z)} \left[\frac{5}{2} g_{5/2}(z) - g_{3/2}(z) \log z \right]$$

$$= \frac{k_B}{g_{3/2}} \left(\frac{T}{T_c} \right)^{3/2} \left(\frac{5}{2} g_{5/2}(z) - g_{3/2}(z) \log z \right)$$

We can check that this equation holds $\forall T$ as long as we use $g_l(z) = g_l(1)$ for $T \leq T_c$:

- $T > T_c$ $z < 1$ all good

- $T = T_c$ $s(T = T_c) = \frac{5}{2} k_B \frac{g_{5/2}(1)}{g_{3/2}(1)}$

- $T < T_c$ $s = \frac{5}{2} k_B \left(\frac{T}{T_c} \right)^{3/2} \frac{g_{5/2}(1)}{g_{3/2}(1)} \xrightarrow[T \to 0]{} 0$

  however, at $T = 0$, all the particles are in the ground state $(n_0(T) \xrightarrow[T \to 0]{} n$. This means that particles in the condensate carry no entropy $S_{cond} = 0$. So s below T_c gets smaller and smaller as T decreases, since more and more particles go to the ground state.

Consider one particle jumping from $\epsilon > 0$ to the ground state at $T = T_c$. Then:

$$\Delta s = s(T = T_c) - 0 = k_B \frac{5}{3} \frac{g_{5/2}(1)}{g_{3/2}(1)} \neq 0$$

But we also know that $0 \neq \Delta S = \Delta Q / T_c$. So the process of of decaying from $\epsilon > 0$ to $\epsilon = 0$ costs some energy, some heat. This heat $\Delta Q \neq 0$ is called latent heat.

This is a peculiar phase transition, with continuous thermodynamic potentials, but latent heat as (for instance) in evaporation.

It is the same as water boiling, which stops at $T = 100^o C$ since particles absorb latent heat.

3.4.5   Exercise (2.5): Gas of photons

Let us consider a gas of photons, confined in a volume V at equilibrium at a temperature T. Photons are ultra-relativistic bosonic particles, for which: $\epsilon_{\vec{p}} = c|\vec{p}|$. They can be absorbed/emitted so that their particle number is not conserved, providing an example of bosonic systems with zero chemical potential: $\mu(T) \equiv 0$. Recall also that photons have two independent polarizations, so that g = 2.

1. **Density of states:**
   The density of states is easily obtained from

   $$\Sigma(\epsilon) = g \int_{cp<\epsilon} \frac{d^3x \, d^3p}{h^3} = \frac{8\pi V}{h^3} \int_0^{\epsilon/c} dp \, p^2 = \frac{8\pi V}{3(hc)^3} \epsilon^3$$

   since $\omega(\epsilon) = \partial\Sigma/\partial\epsilon$.

2. **Granpotential, number of particles, internal energy**
   From the previous point it follows that:

   $$\Omega = \frac{1}{\beta} \int_0^\infty d\epsilon \, \omega(\epsilon) \log(1 - e^{\beta\epsilon}) = -\frac{8\pi V}{3(hc)^3} \int_0^\infty \frac{\epsilon^3}{e^{\beta\epsilon} - 1} d\epsilon$$

   where the last equality has been found after integration by parts.
   Similarly, one gets:

   $$N = \int_0^\infty d\epsilon \, \omega(\epsilon) n(\epsilon) = \frac{8\pi V}{(hc)^3} \int_0^\infty \frac{\epsilon^2}{e^{\beta\epsilon} - 1} d\epsilon$$

   $$E = \int_0^\infty d\epsilon \, \omega(\epsilon) \epsilon n(\epsilon) = \frac{8\pi V}{(hc)^3} \int_0^\infty \frac{\epsilon^3}{e^{\beta\epsilon} - 1} d\epsilon$$

   From the relation $\Omega = -pV$ it follows that: $p = \frac{1}{3}\frac{E}{V}$

3. **Density of energy and particles**
   Using the relation

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

   we can show that:

   $$\frac{N}{V} = \frac{8\pi\zeta(3)}{(hc)^3} (k_B T)^3$$

   $$\frac{E}{V} = \frac{8\pi\zeta(4)}{(hc)^3} (k_B T)^4$$

   Also, as a consequence of $C_V = \partial E/\partial T$, we have: $c_v = \frac{C_V}{V} \propto T^3$

4. **Spectral distribution and density** Recalling that the energy of a photon is related to the frequency through: $\epsilon = h\nu$, we can consider the number of photons $N(\nu)$ with an energy $0 \leq \epsilon \leq h\nu$, given by:

$$N(\nu) = \frac{8\pi V}{(hc)^3} \int_0^{h\nu} \frac{\epsilon^2}{e^{\beta\epsilon} - 1} d\epsilon$$

We can calculate the spectral distribution:

$$f(\nu) = \frac{dN(\nu)}{d\nu} = \frac{8\pi V}{(\beta hc)^3} \frac{(\beta h\nu)^2}{e^{\beta h\nu} - 1} \beta h = \frac{8\pi V}{c^3} \frac{\nu^2}{e^{\beta h\nu} - 1}$$

This represents the number of photons with frequency between ν and $\nu + d\nu$. We can also show that the energy spectral density (defined as the energy for unit frequency and volume) is:

$$u(\nu) = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{\beta h\nu} - 1}$$

5. **Wein's and Rayleigh-Jeans' laws**
Rayleigh-Jeans' law is obtained by expanding the exponential function in the denominator at first order, while Wien's law is got by neglecting the addend -1 in the denominator:

$$u(\nu) \simeq 8\pi h \left(\frac{v}{c}\right)^3 e^{-\beta h\nu} \qquad \beta h\nu \gg 1$$

$$u(\nu) \simeq \frac{8\pi h}{c^3} \frac{\nu^3}{\beta h\nu} = \frac{8\pi}{c^3 \beta} \nu^2 \qquad \beta h\nu \ll 1$$