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On statistical mechanics:

what happens when there are too many particles?

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Theoretical Physics

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Part I

Thermodynamics

Chapter 1

Equilibrium and the laws of Thermodynamics

In this chapter, we will recall some notions of thermodynamics.

1.1 Equilibrium

Thermodynamics studies large systems that reach equilbrium configurations. But, what is equilibrium?

Suppose we have a system immersed in its surroundings. It can be isolated or it can exchange matter and/or energy (mechanical, electric, magnetic, chemical work). The configuration it reaches and its stability can be selected by the boundary conditions, i.e. the specification on how the system is in contact and how it interacts with its surroundings. In other words, there is only one and only one final equilibrium configuration towards the system evolves, once the boundary conditions have beeen given. However, the way the system reaches the equilibrium configuration is irreversible. Equilibrium therefore means that once the system has reached its final configuration, it will stay there forever.

1.2 States

In thermodynamics, a state is a macroscopic configuration. It is defined by a set of macroscopic quantities, called thermodynamical variables. They can be divided into two groups, one conjugate to the other, according to their behaviour when the physical system is rescaled, i.e. when the volume and the number of particles change: extensive variables do scale with it whereas intensive ones do not. See Table 1.1.

However, we have to be careful, since only volume is by definition extensive and all the others quantities can be considered extensive only if the surfaces terms are neglectible when we take the thermodynamic limit. An equation of state is a

Extensive	Intensive
Energy E	-
Entropy S	Temperature T
Volume V	Pression p
Number of particles E	Chemical potential μ
Polarization $\mathbf{P}$	Electric field $\mathbf{E}$
Magnetization $\mathbf{M}$	Magnetic field $\mathbf{B}$

Table 1.1: Extensive and intensive thermodynamical variables.

functional relation among them, which restrict the number of independent variables. Geometrically, it means that the only admissible states are a submanifold of the entire manifold of states.

Example 1.1 (Perfect gas)**.** A perfect gas is described by 3 state variables (p, V, T) and an equation of state $PV = Nk_BT$. This means that the allowed states are in a 2-dimensional manifold embedd in $\mathbb{R}^3$.

1.3 The laws of thermodynamics

Thermodynamics is governed by a set of laws that every system must obey. However, they are limitation laws, since they tell us only which processes cannot happen.

Law 1.1 (0th)
Let A and B be 2 thermodynamic systems in thermal contact. At equilibrium, only a subset of states $\mathcal{M}_A \times \mathcal{M}_B$ is accessible. Mathematically, it means that there exists a functional relation

$$F_{AB}(a, b) = 0 \ , \tag{1.1}$$

with $a \in \mathcal{M}_A$ and $b \in \mathcal{M}_B$. Moreover, thermal equilibrium is an equivalence class. It can be proved that the latter means that

$$F_{AB}(a, b) = f_A(a) - f_B(b) \ . \tag{1.2}$$

Putting together (1.1) *and* (1.2)*, we define the empirical temperature*

$$t_A = f_A(a) = t_B = f_B(b) \ .$$

It is a limitation law because it limit the configuration that a system can reach in thermal contact with a second one.

Law 1.2 (1st)

Let δQ be the infinitesimal heat and δL the infinitesimal work exchanged in a quasi-static process ($\delta Q > 0$ means absorbed by the system, $\delta L > 0$ means performed by the system). For any cyclic process

$$\oint (\delta Q - \delta L) = 0 \ .$$

This means that $\delta Q - \delta L$ is a one-form, which vanishes line-integrated along a closed curve in $\mathcal{M}$. This implies, by the Poincaré lemma, that it is an exact differential

$$dE = \delta Q - \delta L \ ,$$

called the internal energy. However, notice that heat and word are not exact differential, since $\oint \delta Q \neq 0$ and $\oint \delta H \neq 0$. We can generalised to a system that can exchange matter with

$$\oint (\delta Q - \delta L + \mu dN) = 0 \ , \quad dE = \delta Q - \delta L + \mu dN \ , \tag{1.3}$$

where μ is the chemical potential (the necessary energy to add or remove a particle). Furthermore, we can expressed both δQ and δL as a linear combination of infinitesimal change of independent coordinates. We assume that the internal energy is extensive. Therefore, the chemical potential is intensive.

It is a limitation law because it limits the configuration that a system can reach in isolation to whose with $E = const$.

Law 1.3 (2nd)

For any cyclic process

$$\oint \frac{\delta Q}{T} \begin{cases} = 0 & \text{reversible process} \\ < 0 & \text{irreversible process} \end{cases} .$$

For reversible processes, $\frac{\partial \delta Q}{\partial T} = 0$ is an exact differential. This implies that we can define

$$S(a) - S(b) = \int_a^b \frac{\delta S}{T} \ ,$$

called the entropy. The integral is along any reversible path. Therefore, we have

$$dS \begin{cases} = 0 & \text{reversible process} \\ < 0 & \text{irreversible process} \end{cases} . \tag{1.4}$$

It is a limitation law because it limits the configuration that a system can reach in isolation to whose in which entropy cannot decrease.

Law 1.4 (3rd)

Isothermal and adiabatic processes coincides whet $T = 0$, or, equivalently, it is impossible to reach $T = 0$ with a finite number of processes. Mathematically

$$\Delta S \to 0 \text{ as } T \to 0 \ .$$

Therefore, $T = 0$ is a singular point. Furthermore, if it were possible to reach $T = 0$, the second law $\delta Q \leq 0$ implies that it is impossible to raise the temperature. It is a thermodynamic features, since it can be proved that it is impossible to realize an engine with efficency $\eta = 1$

It is a limitation law because it limits the configuration that a system can reach in isolation to whose in which $T \neq 0$.

1.4 The fundamental equation of thermodynamics

Combining (1.3) and (1.4), we obtain

$$dE \begin{cases} = TdS - pdV + \mu dN & \text{reversible process} \\ < TdS - pdV + \mu dN & \text{irreversible process} \end{cases} . \tag{1.5}$$

Proof. In fact, we invert (1.3)

$$\delta Q = dE + \delta L - \mu dN \ ,$$

we use $\delta L = pdV$

$$\delta Q = dE + pdV - \mu dN \ ,$$

and we put it into (1.4)

$$dS \leq \frac{\delta Q}{T} = \frac{dE + pdV - \mu dN}{T} \ , \tag{1.6}$$

$$dE \leq TdS - pdV + \mu dN \ . \tag{1.7}$$

q.e.d.

Notice that the non-differential variables are intensive and the differential variables are extensive. This tells us that $E(S, V, N)$ is a function of the extensive variables S, V and N. The intensive variables T, p and μ can be derived from E by the following relations

$$T = \left.\frac{\partial E}{\partial S}\right|_{V,N} \ , \quad p = -\left.\frac{\partial E}{\partial V}\right|_{S,N} \ , \quad \mu = \left.\frac{\partial E}{\partial N}\right|_{S,V} \ . \tag{1.8}$$

This are called the equation of state of the system, since we can calculate one variable from it, e.g. $T = T(S, V, N)$, $p = p(S, V, N)$ or $\mu = \mu(S, V, N)$. It is important to say that this is all thermodynamics can tell us, thus in order to find the explicit expression of E, we must go into statistical mechanics.

Proof. At constant V and N, (1.5) becomes

$$dE = TdS - p\underbrace{dV}_{0} + \mu\underbrace{dN}_{0} = TdS \ ,$$

hence

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

At constant S and N, (1.5) becomes

$$dE = T\underbrace{dS}_{0} - pdV + \mu\underbrace{dN}_{0} = -pdV \ ,$$

hence

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

At constant S and V, (1.5) becomes

$$dE = T\underbrace{dS}_{0} - p\underbrace{dV}_{0} + \mu dN = \mu dN \ ,$$

hence

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

<div align="right">q.e.d.</div>

E is an extensive variable, i.e. an homogeneous function of degree one of the extensive variables

$$E(\lambda S, \lambda V, \lambda N) = \lambda E(S, V, N) \ , \quad \forall \lambda > 0 \ .$$

The physical meaning is that if we rescale the volume, the energy is rescaled bu the same amount.

Moreover, the intensive variable are homogeneous function of degree zero of the extensive variables

$$T(S, V, N) = T(\frac{S}{N}, \frac{V}{N}) \ , \quad p(S, V, N) = p(\frac{S}{N}, \frac{V}{N}) \ , \quad \mu(S, V, N) = \mu(\frac{S}{N}, \frac{V}{N}) \ . \tag{1.9}$$

By homogeneity properties

$$E = NE(\frac{S}{N}, \frac{V}{N}, 1) = Ne \ , \quad S = NS(\frac{E}{N}, \frac{V}{N}, 1) = Ns \ ,$$

we can define specific energy and entropy

$$e = \frac{E}{N} = e(s, v) \ , \quad s = \frac{S}{N} = s(e, v) \ ,$$

where $v = \frac{V}{N}$ is the specific volume.

The Euler's theorem allows us to state that, if E is smooth, it can be written as

$$E = S\frac{\partial E}{\partial S} + V\frac{\partial E}{\partial V} + N\frac{\partial E}{\partial N} \ ,$$

or, using (1.5) and (1.8),

$$E = TS - pV + \mu N \ . \tag{1.10}$$

The Gibbs-Duhem relation expresses μ in terms of p and T

$$SdT - Vdp + Nd\mu = 0 \ , \quad \mu = vdp - sdT \ .$$

Proof. Computing the differential of (1.10)

$$dE = TdS + SdT - pdV + \mu dN + Nd\mu$$

and comparing it with (1.5)

$$dE = \cancel{TdS} + SdT - \cancel{pdV} + -Vdp + \cancel{\mu dN} + Nd\mu = \cancel{TdS} - \cancel{pdV} + \cancel{\mu dN} \ ,$$

we obtain

$$SdT - Vdp + Nd\mu = 0 \ .$$

which can be written as

$$d\mu = \frac{V}{N}dp - \frac{S}{N}dT = vdp - sdT \ .$$

q.e.d.

1.5 Integrability condition

In order to be an exact differential, the exterior derivative of the right handed side of (1.5) must have vanishing exterior derivative

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

Proof. By the means of the exterior derivative, we have

$$d(dE) = d(TdS) - d(pdV) + d(\mu dN)$$

$$= \frac{\partial T}{\partial S} \underbrace{dS \wedge dS}_{0} + \frac{\partial T}{\partial V} dV \wedge dS + \frac{\partial T}{\partial N} dN \wedge dS - \frac{\partial p}{\partial S} dS \wedge dV - \frac{\partial p}{\partial V} \underbrace{dV \wedge dV}_{0}$$

$$- \frac{\partial p}{\partial N} dN \wedge dV + \frac{\partial \mu}{\partial S} dS \wedge dN + \frac{\partial \mu}{\partial V} dV \wedge dN + \frac{\partial \mu}{\partial N} \underbrace{dN \wedge dN}_{0}$$

$$= \frac{\partial T}{\partial V} dV \wedge dS + \frac{\partial T}{\partial N} dN \wedge dS - \frac{\partial p}{\partial S} dS \wedge dV$$

$$- \frac{\partial p}{\partial N} dN \wedge dV + \frac{\partial \mu}{\partial S} dS \wedge dN + \frac{\partial \mu}{\partial V} dV \wedge dN \ .$$

At constant N

$$0 = d^2 E = \frac{\partial T}{\partial V} dV \wedge dS + \frac{\partial T}{\partial N} \underbrace{dN}_{0} \wedge dS - \frac{\partial p}{\partial S} dS \wedge dV$$

$$- \frac{\partial p}{\partial N} \underbrace{dN}_{0} \wedge dV + \frac{\partial \mu}{\partial S} dS \wedge \underbrace{dN}_{0} + \frac{\partial \mu}{\partial V} dV \wedge \underbrace{dN}_{0}$$

$$= \frac{\partial T}{\partial V} dV \wedge dS - \frac{\partial p}{\partial S} dS \wedge dV = \frac{\partial T}{\partial V} dV \wedge dS + \frac{\partial p}{\partial S} dV \wedge dS \ ,$$

hence

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

At constant V

$$0 = d^2 E = \frac{\partial T}{\partial V} \underbrace{dV}_{0} \wedge dS + \frac{\partial T}{\partial N} dN \wedge dS - \frac{\partial p}{\partial S} dS \wedge \underbrace{dV}_{0}$$

$$- \frac{\partial p}{\partial N} dN \wedge \underbrace{dV}_{0} + \frac{\partial \mu}{\partial S} dS \wedge dN + \frac{\partial \mu}{\partial V} \underbrace{dV}_{0} \wedge dN$$

$$= \frac{\partial T}{\partial N} dN \wedge dS + \frac{\partial \mu}{\partial S} dS \wedge dN = \frac{\partial T}{\partial N} dN \wedge dS - \frac{\partial \mu}{\partial S} dN \wedge dS \ ,$$

hence

$$\frac{\partial T}{\partial N}\bigg|_{S,V} = \frac{\partial \mu}{\partial S}\bigg|_{N,V} \ .$$

At constant S

$$0 = d^2 E = \frac{\partial T}{\partial V} dV \wedge \underbrace{dS}_{0} + \frac{\partial T}{\partial N} dN \wedge \underbrace{dS}_{0} - \frac{\partial p}{\partial S} \underbrace{dS}_{0} \wedge dV$$

$$- \frac{\partial p}{\partial N} dN \wedge dV + \frac{\partial \mu}{\partial S} \underbrace{dS}_{0} \wedge dN + \frac{\partial \mu}{\partial V} dV \wedge dN$$

$$= -\frac{\partial p}{\partial N} dN \wedge dV + \frac{\partial \mu}{\partial V} dV \wedge dN = -\frac{\partial p}{\partial N} dN \wedge dV - \frac{\partial \mu}{\partial V} dN \wedge dV \ ,$$

hence

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

q.e.d.

1.6   Thermodynamic states as a manifold

S, V and N as independent (local) coordinates, i.e. a chart for $\mathcal{M}$. In our case, it can be thought as an open subset of $\mathbb{R}^3$. A reversible process is a path. An irreversible process is an oriented path. Different thermodynamic systems are not connected by any process. Therefore, the manifold is path-connected and simply connected. Solving thermodynamics means find the fundamental equation

$$E = E(S, V, N) .$$

However, we could have chosen as fundamental equation

$$S = S(E, V, N)$$

and a chart would have had E, V and N as coordinates. At least one of the local coordinates in any chart for $\mathcal{M}$ must be extensive.

Proof. By the $0th$ law and (1.9), there must exist a functional relation between intensive variables. This means that one of the three is already fixed once the other two are given and they cannot be used all three as independent coordinates.   q.e.d.

There are different thermodynamic potentials, which are functions of 3 independent variables that can be used to define a different chart for $\mathcal{M}$. Therefore, there are different aproaches to thermodynamics.

Chapter 2

Thermodynamic potentials

Thermodynamic potentials can be obtained by various kind of Legendre transforms of (1.5), which exchange the role of an extensive variable to its conjugate intensive variable as independent variable. We require that the hypothesis of the inverse function theorem are satisfied, e.g.

$$\frac{\partial^2 E}{\partial S^2}\Big|_{V,N} \neq 0 \ , \quad \frac{\partial^2 E}{\partial V^2}\Big|_{S,N} \neq 0 \ , \quad \frac{\partial^2 E}{\partial N^2}\Big|_{S,V} \neq 0 \ .$$

The thermodynamic potentials are the Helmoltz free energy F, the entalpy H, the Gibbs free energy G and the granpotential Ω.

2.1   Helmoltz free energy F

The Helmoltz free energy is defined as

$$F = E - TS \ .$$

Its differential is

$$dF \leq -SdT - pdV + \mu dN \ .$$

Therefore

$$F = F(T, V, N) \ .$$

Proof. By a Legendre transform, which means to complete a differential

$$dE \leq TdS - pdV + \mu dN = d(TS) - SdT - pdV + \mu dN \ ,$$

hence

$$dF = d(E - TS) \leq -SdT - pdV + \mu dN \ .$$

q.e.d.

The equations of state are

$$S = -\frac{\partial F}{\partial T}\Big|_{V,N} , \quad p = -\frac{\partial F}{\partial V}\Big|_{T,N} , \quad \mu = \frac{\partial F}{\partial N}\Big|_{T,V} . \tag{2.1}$$

Proof. At constant V and N

$$dF = -SdT - p\underbrace{dV}_{0} + \mu\underbrace{dN}_{0} = -SdT ,$$

hence

$$S = -\frac{\partial F}{\partial T}\Big|_{V,N} .$$

At constant T and N

$$dF = -S\underbrace{dT}_{0} - pdV + \mu\underbrace{dN}_{0} = -pdV ,$$

hence

$$p = -\frac{\partial F}{\partial V}\Big|_{T,N} .$$

At constant T and V

$$dF = -S\underbrace{dT}_{0} - p\underbrace{dV}_{0} + \mu dN = \mu dN ,$$

hence

$$\mu = \frac{\partial F}{\partial N}\Big|_{T,V} .$$

q.e.d.

2.2 Enthalpy H

The enthalpy is defined as
$$H = E + pV .$$
Its differential is
$$dH \leq TdS + Vdp + \mu dN .$$
Therefore
$$H = H(p, S, N) .$$

Proof. By a Legendre transform, which means to complete a differential

$$dE \leq TdS - pdV + \mu dN = TdS - d(pV) + Vdp + \mu dN \ ,$$

hence

$$dH = d(E + pV) \leq TdS + Vdp + \mu dN \ .$$

<div align="right">q.e.d.</div>

The equations of state are

$$T = \frac{\partial H}{\partial S}\Big|_{p,N} \ , \quad V = -\frac{\partial H}{\partial p}\Big|_{S,N} \ , \quad \mu = \frac{\partial H}{\partial N}\Big|_{S,p} \ . \qquad (2.2)$$

Proof. At constant p and N

$$dH = TdS + V \underbrace{dp}_{0} + \mu \underbrace{dN}_{0} \ ,$$

hence

$$T = \frac{\partial H}{\partial S}\Big|_{p,N} \ .$$

At constant S and N

$$dH = T \underbrace{dS}_{0} + Vdp + \mu \underbrace{dN}_{0} \ ,$$

hence

$$V = -\frac{\partial H}{\partial p}\Big|_{S,N} \ .$$

At constant S and p

$$dH = T \underbrace{dS}_{0} + V \underbrace{dp}_{0} + \mu dN \ ,$$

hence

$$\mu = \frac{\partial H}{\partial N}\Big|_{S,p} \ .$$

<div align="right">q.e.d.</div>

2.3   Gibbs free energy G

The Gibbs free energy is defined as

$$G = E - TS + pV = F + pV = H - TS .$$

Its differential is

$$dG \leq -SdT + Vdp + \mu dN .$$

Therefore

$$G = G(p, T, N) .$$

Proof. By a Legendre transform, which means to complete a differential

$$dE \leq TdS - pdV + \mu dN = d(TS) - SdT - d(pV) + Vdp + \mu dN ,$$

hence

$$dG = d(E - TS + pV) \leq -SdT + Vdp + \mu dN .$$

<div align="right">q.e.d.</div>

The equations of state are

$$S = -\left.\frac{\partial G}{\partial T}\right|_{p,N} , \quad V = \left.\frac{\partial G}{\partial p}\right|_{T,N} , \quad \mu = \left.\frac{\partial G}{\partial N}\right|_{p,T} . \tag{2.3}$$

Proof. At constant p and N

$$dG = -SdT + V \underbrace{dp}_{0} + \mu \underbrace{dN}_{0} ,$$

hence

$$S = -\left.\frac{\partial G}{\partial T}\right|_{p,N} .$$

At constant T and N

$$dG = -S \underbrace{dT}_{0} + Vdp + \mu \underbrace{dN}_{0} ,$$

hence

$$V = \left.\frac{\partial G}{\partial p}\right|_{T,N} .$$

At constant p and T

$$dG = -S \underbrace{dT}_{0} + V \underbrace{dp}_{0} + \mu dN ,$$

hence

$$\mu = \left.\frac{\partial G}{\partial N}\right|_{p,T} .$$

<div align="right">q.e.d.</div>

2.4   Granpotential Ω

The granpotential is defined as
$$\Omega = E - TS - \mu N = F - \mu N \; .$$
Its differential is
$$d\Omega \leq -SdT - pdV - Nd\mu \; .$$
Therefore
$$\Omega = \Omega(T, V, \mu) \; .$$

Proof. By a Legendre transform, which means to complete a differential
$$dE \leq TdS - pdV + \mu dN = d(TS) - SdT - pdV + (\mu N) - Nd\mu \; ,$$
hence
$$d\Omega = d(E - TS - \mu N) \leq -SdT - pdV - Nd\mu \; .$$
$$\text{q.e.d.}$$

The equations of state are
$$S = -\left.\frac{\partial \Omega}{\partial T}\right|_{\mu, V} \; , \quad p = -\left.\frac{\partial \Omega}{\partial V}\right|_{T, \mu} \; , \quad \mu = -\left.\frac{\partial \Omega}{\partial N}\right|_{T, V} \; . \tag{2.4}$$

Proof. At constant μ and V
$$d\Omega = -SdT - p\underbrace{dV}_{0} - N\underbrace{d\mu}_{0} = -SdT \; ,$$
hence
$$S = -\left.\frac{\partial \Omega}{\partial T}\right|_{\mu, V} \; .$$
At constant T and μ
$$d\Omega = -S\underbrace{dT}_{0} - pdV - N\underbrace{d\mu}_{0} = -pdV \; ,$$
hence
$$p = -\left.\frac{\partial \Omega}{\partial V}\right|_{T, \mu} \; .$$
At constant T and V
$$d\Omega = -S\underbrace{dT}_{0} - p\underbrace{dV}_{0} - Nd\mu = -Nd\mu \; ,$$
hence
$$\mu = -\left.\frac{\partial \Omega}{\partial N}\right|_{T, V} \; .$$
$$\text{q.e.d.}$$

2.5 Integrability condition and equilibrium condition

Chapter 3

Boh

3.1 Thermodynamical potentials

Similar expression can be found for other thermodynamical quantities, simply exchanging the role of conjugate functions. See Table 3.1.

Potentials	Differential
Internal energy $E(S,\ V,\ N) = TS - pV + \mu N$	$dE = TdS - pdV + \mu dN$
Helmotz free energy $F(T,\ V,\ N) = E - TS = -pV + \mu N$	$dF = -SdT - pdV + \mu dN$
Entalpy $H(S,\ p,\ N) = E + pV = St + \mu N$	$dH = TdS + Vdp + \mu dN$
Gibbs free energy $G(T,\ p,\ N) = E - TS + pV = \mu N$	$dG = -SdT + Vdp + \mu dN$
Granpotential $\Omega(T,\ V,\ \mu) = E - TS - \mu N = -pV$	$d\Omega = -SdT - pdV - Nd\mu$

Table 3.1: Thermodynamical potentials.

Proof. Maybe in the future. q.e.d.

Fixing three of the thermodynamical variables to be constant, a system evolves in order to minimises the corresponding thermodynamical potential until it reaches its minimum, i.e the equilibrium state. Mathematically, it means that the first derivative must be vaninshing and the hessian must be positive defined. See Table 3.2.

Inequality	Constant quantities
$dE \leq 0$	S, V, N
$dF \leq 0$	T, V, N
$dH \leq 0$	S, p, N
$dG \leq 0$	T, p, N
$d\Omega \leq 0$	T, V, μ

Table 3.2: Thermodynamical variation principles.

Proof. Maybe in the future. q.e.d.

Part II

Classical statistical mechanics

Chapter 4

Classical mechanics

A state constitued by a system of N particles is described by a point in a $2N$-dimensional manifold $\mathcal{M}^N$, called the phase space, which is the Cartesian product of N single particle manifolds

$$\{(q^i,\ p_i)\} \in \mathcal{M}^N$$

where $i = 1, \ldots N$.

An observable is a smooth real function

$$f\ :\ \mathcal{M}^N \to \mathbb{R}$$

and its measurement in a fixed point $(\tilde{q}^i,\ \tilde{p}_i)$ is its value in it

$$f = f(\tilde{q}^i,\ \tilde{p}_i)$$

The time evolution is governed by a real function, called the hamiltonian $H(q^i,\ p_i,\ t)$, which is the solution of the equations of motion, called the Hamilton's equations

$$\dot{q}^i = \frac{\partial H}{\partial p_i} \quad \dot{p}_i = -\frac{\partial H}{\partial q^i}$$

Theorem 4.1 (Conservation of energy)
If the hamiltonian does not depend explicitly on time, it can be intepreted physically as the energy of the system, which is constants

$$H(q^i(t),\ p_i(t)) = H(q^i(0),\ p_i(0)) = E = const$$

Since they are deterministic, once the initial conditions are given, the trajectory in phase space is completely determined

4.1 Probability density distribution

A macrostate is defined by setting the macroscopic thermodynamical quantities. A microstate is the knowledge of the phase space behaviour $(q^i,\ p_i)$.

In general, there are more microstates associated to the same macrostates, raising the concept of ensemble: fixing a macrostate, it is created a large number of copies of the same physical system but with different microstates. It can be studied with the introduction of a probability density distribution

$$\rho(q_i(t),\ p_i(t),\ t)$$

such that it satisfies the following properties

1. positivity, i.e.
$$\rho(q_i,\ p_i,\ t) \geq 0$$

2. normalisation, i.e.
$$\int_{\mathcal{M}^n} \underbrace{\prod_{i=1}^{N} d^d q^i d^d p^i}_{d\Gamma}\ \rho(q_i,\ p_i,\ t) = \int_{\mathcal{M}^n} d\Gamma\ \rho(q_i,\ p_i,\ t) = 1$$

To solve the dimensional problem of the volume element $d\Gamma$, which must be adimensional but it has the dimension of an action to the power of d, it can be introduced the adimensional volume element

$$d\Omega = \frac{d\Gamma}{h^d} = \frac{\prod_{i=1}^{N} d^d q^i d^d p^i}{h^d}$$

where the scale factor h has the dimension of an action.

The probability to find the system in a finite portion of the phase space $\mathcal{U} \subset \mathcal{M}^N$ is

$$\int_{\mathcal{U}} d\Gamma\ \rho(q_i,\ p_i,\ t)$$

4.2 Liouville's theorem

The flow of a system of particles keeps trasf of all their motions. See Figure.

Theorem 4.2 (Liouville)
The volume through the flow generated by the hamilton's equations is constant. See Figure. Mathematically

$$vol\Omega(t=0) = vol\Omega(t) \ \Rightarrow\ \frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + [\rho,\ H] = 0$$

Proof. Maybe in the future. q.e.d.

The physical intepretation of this theorem is that particles do not appear nor disappear due to conservation of charge, mass, etc...

For stationary systemas, i.e. when $\frac{\partial \rho}{\partial t} = 0$, the necessary condition for equilibrium is $[\rho, \ H] = 0$, which is satisfied only if

$$\rho = const$$

like in the microcanonical ensemble, and

$$\rho = \rho(H)$$

like in the canonical or the grancanonical ensembles.

Proof. Maybe in the future. q.e.d.

The average value of an observable is weighted by the probability density distribution

$$\langle f \rangle = \int_{\mathcal{M}^N} d\Gamma \ \rho(q^i, \ p_i) f(q^i, \ p_i) \tag{4.1}$$

and the standard deviation is

$$(\Delta f)^2 = \langle f^2 \rangle - \langle f \rangle^2$$

4.3   Time-independent Hamiltonian

Consider a time-independent hamiltonian. Since the energy is constant for the theorem 4.1.

$$\int_{\mathcal{M}^N} \rho = 1 \tag{4.2}$$

$$\frac{\partial S}{\partial E} = \frac{1}{T} \tag{4.3}$$

$$\frac{\partial F}{\partial T} = -S \tag{4.4}$$

$$\Omega = -pV = E - TS - \mu N \tag{4.5}$$

Chapter 5

Microcanonical ensemble

A microcanonical ensemble is a system which is isolated from the environment, i.e. it cannot exchange neither energy nor matter, so E, N and V are fixed. Since energy is conserved and the hamiltonian is time-independent, the trajectory of motion is restricted on the surface S_E and not on all the phase space.

Assume an a-priory uniform probability

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

where C is a normalisation constant, which can be evaluated by (4.2)

$$1 = \int_{\mathcal{M}^N} d\Omega \rho_{mc} = \int_{\mathcal{M}^N} d\Omega C\delta(\mathcal{H} - E) = C \int_{\mathcal{M}^N} d\Omega \delta(\mathcal{H} - E) = C\omega(E)$$

Hence

$$\rho_{mc}(q^i, \ p_i) = \frac{1}{\omega(E)}\delta(\mathcal{H}(q^i, p_i) - E)$$

Consider a displacement on an infinitesimal displacement of energy $\Delta E \ll 1$, then

$$\Gamma(E) = \int_E^{E+dE} dE' \ \omega(E') \simeq \omega(E)\Delta E$$

and the distribution is

$$\rho_{mc}(q^i, p_i) = \begin{cases} \frac{1}{\Gamma(E)} & \mathcal{H} \in [E, E + \Delta E] \\ 0 & otherwise \end{cases}$$

Let $f(q^i, p_i)$ be an observable, then its microcanonical average is

$$\langle f(q^i, p_i) \rangle_{mc} = \int_{\mathcal{M}} d\Omega \ \rho_{mc} f = \int_{\mathcal{M}} d\Omega \ \frac{1}{\omega(E)}\delta(\mathcal{H} - E)f = \frac{1}{\omega(E)} \int_{S_E} dS_E \ f = \langle f \rangle_E \tag{5.1}$$

5.1 Thermodynamics potentials

The microcanonical entropy S_{mc} is defined by

$$S_{mc}(E, V, N) = k_B \ln \omega(E) \tag{5.2}$$

The logarithm is justified by the fact that the volume of a N-particle phase space is $(W_1)^N$, where W_1 is the volume of a single particle phase space. According to the properties of the logarithm, entropy becomes extensive.

In the thermodynamic limit, the following equations hold

$$s_{mc} = \lim_{td} \frac{S_{mc}}{N} = k_B \lim_{td} \frac{\log \omega(E)}{N} = \underbrace{k_B \lim_{td} \frac{\log \Sigma(E)}{N}}_{\mathcal{H} \in [0, E]} = \underbrace{k_B \lim_{td} \frac{\log \Gamma(E)}{N}}_{\mathcal{H} \in [E, E + \Delta E]}$$

Entropy is additive, so given two sistems 1 and 2

$$s_{mc}^{tot} = s_{mc}^{(1)} + s_{mc}^{(2)}$$

Proof. Consider two isolated systems in contact at equilibrium with the same temperature $T = T_1 = T_2$. The total energy is $E = E_1 + E_2 + E_{surface}$ but, in the thermodynamic limit, the energy exchanged by the surface is a subleading term (E_1 and E_2 go as L^3 whereas $E_{surface}$ goes as L^2) and can be neglected. The energy density is

$$\omega(E) = \int_{\mathcal{M}^N} d\Gamma_1 d\Gamma_2 \delta(\mathcal{H} - E)$$

$$= \int dE_1 \int dS_{E_1} \int dE_2 \int dS_{E_2} \delta(E - E_1 - E_2)$$

$$= \int dE_1 \int dE_2 \omega_1(E_1) \omega_2(E_2) \delta(E - E_1 - E_2)$$

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

Since the integrand is a positive function with a maximum in $_1 \in [0, E]$

$$\int_0^E dE_1 \, \omega_1(E_1) \omega_2(E_2 = E - E_1) \leq \omega_1(E_1^*) \omega_2(E_2^* = E - E_1^*) \int_0^E dE_1 \tag{5.3}$$

$$= \omega_1(E_1^*) \omega_2(E_2^* = E - E_1^*) E$$

On the other hand, it is always possible to find a value for ΔE in order to have

$$\Delta E \omega_1(E_1^*) \omega_2(E_2^*) \leq \omega(E) \tag{5.4}$$

Putting together (5.3) and (5.4)

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

$$\omega_1(E_1^*)\Delta E \omega_2(E_2^*)\Delta E \le \omega(E)\Delta E \le \frac{E}{\Delta E}\omega_1(E_1^*)\Delta E \omega_2(E_2^*)\Delta E$$

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

Since the logarithm is a monotomic function

$$\log\left(\Gamma_1(E_1^*)\Gamma(E_2^*)\right) \le \log\Gamma(E) \le \log\left(\frac{E}{\Delta E}\Gamma(E_1^*)\Gamma(E_2^*)\right)$$

$$k_B\log\left(\Gamma_1(E_1^*)\Gamma(E_2^*)\right) \le k_B\log\Gamma(E) \le k_B\log\left(\frac{E}{\Delta E}\Gamma(E_1^*)\Gamma(E_2^*)\right)$$

$$k_B\log\Gamma_1(E_1^*)+k_B\log\Gamma(E_2^*) \le k_B\log\Gamma(E) \le k_B\log\frac{E}{\Delta E}+k_B\log\Gamma(E_1^*)+k_B\log\Gamma(E_2^*)$$

$$\frac{k_B\log\Gamma_1(E_1^*)+k_B\log\Gamma(E_2^*)}{N} \le \frac{k_B\log\Gamma(E)}{N} \le \frac{k_B\log\frac{E}{\Delta E}+k_B\log\Gamma(E_1^*)+k_B\log\Gamma(E_2^*)}{N}$$

In the thermodynamic limit, the last term vanishes, since $\lim_{td}\frac{1}{N}\log\frac{N}{\Delta N} = 0$. Hence

$$s_{mc}(E) = s_{mc}^{(1)} + s_{mc}^{(2)}$$

q.e.d.

The last result tells also that at equilibrium entropy is maximum.

In the thermodynamic limit, microcanonical entropy coincides with the thermodynamical one

$$s_{mc} = s_{td}$$

Proof. Since entropy is maximum at equilibrium, also $\Gamma_1(E_1)\Gamma_2(E_2)$ is so and

$$\begin{aligned}
0 &= \delta(\Gamma_1(E_1^*)\Gamma_2(E_2^* = E - E_1^*)) \\
&= \delta\Gamma_1(E_1^*)\Gamma_2(E_2^*) + \Gamma_1(E_1^*)\delta\Gamma_2(E_2^*) \\
&= \left.\frac{\partial\Gamma_1}{\partial E_1}\right|_{E_1^*}\delta E_1\Gamma_2(E_2^*) + \Gamma_1(E_1^*)\left.\frac{\partial\Gamma_2}{\partial E_2}\right|_{E_2^*}\delta E_2
\end{aligned}$$

Since $E = const$, $0 = \delta E = \delta E_1 + \delta E_2$, $\delta E_2 = \delta E_1$ and

$$0 = \left.\frac{\partial\Gamma_1}{\partial E_1}\right|_{E_1^*}\delta E_1\Gamma_2(E_2^*) - \Gamma_1(E_1^*)\left.\frac{\partial\Gamma_2}{\partial E_2}\right|_{E_2^*}\delta E_1$$

$$0 = \left.\frac{\partial\Gamma_1}{\partial E_1}\right|_{E_1^*}\Gamma_2(E_2^*) - \Gamma_1(E_1^*)\left.\frac{\partial\Gamma_2}{\partial E_2}\right|_{E_2^*}$$

$$\left.\frac{\partial\Gamma_1}{\partial E_1}\right|_{E_1^*}\Gamma_2(E_2^*) = \Gamma_1(E_1^*)\left.\frac{\partial\Gamma_2}{\partial E_2}\right|_{E_2^*}$$

$$\frac{1}{\Gamma_1(E_1^*)}\left.\frac{\partial\Gamma_1}{\partial E_1}\right|_{E_1^*} = \frac{1}{\Gamma_2(E_2^*)}\left.\frac{\partial\Gamma_2}{\partial E_2}\right|_{E_2^*}$$

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

Using the thermodynamical relation (4.3)

$$S_{mc}(E) = S_{td}(E) \times const$$

where the constant can be chosen in order to have k_B in the same unit.   q.e.d.

The universal Boltzmann's formula is

$$s_{mc} = s_{td} = k_B \log \omega(E) = -k_B \langle \log \rho_{mc} \rangle_{mc} \, . \qquad (5.5)$$

Proof. Using (5.1),

$$
\begin{aligned}
\langle \log \rho_{mc} \rangle_{mc} &= \int d\Gamma \, \rho_{mc} \log \rho_{mc} \\
&= \int d\Gamma \frac{1}{\omega(E)} \delta(\mathcal{H} - E) \log \left(\frac{1}{\omega(E)} \delta(\mathcal{H} - E) \right) \\
&= \int dS_E \frac{1}{\omega(E)} \log \frac{1}{\omega(E)} \\
&= -\frac{1}{\omega(E)} \log \omega(E) \int dS_E \\
&= -\log \omega(E)
\end{aligned}
$$

q.e.d.

Chapter 6

Canonical ensemble

A canonical ensemble is a system which is immersed in a bigger environment or reservoir, which can exchange energy but not matter, so T, N and V are fixed. Globally, energy is conserved, since the universe composed by the union of the system and the environment can be considered as a microcanonical ensemble.

The canonical probability density distribution is

$$\rho_c(q^i, p_i) = \frac{1}{Z_N} \exp(-\beta \mathcal{H}(q^i, p_i))$$

where β is

$$\beta = \frac{1}{k_B T}$$

and Z_N is the partition function

$$Z_N[V, T] = \int_{\mathcal{M}^N} d\Omega \ \exp(-\beta \mathcal{H}(q^i, p_i)) \tag{6.1}$$

which depends on the temperature through β and volume and temperature due to the integration domain $\mathcal{M}^N = V \otimes \mathbb{R}^d$.

Notice that the probability is a function of the hamiltonian, like Liouville's theorem said.

Proof. Consider the universe as a microcanonical ensemble. Its probability density distribution is

$$\rho_{mc}(q_i^{(1)}, p_i^{(1)}, q_i^{(2)}, p_i^{(2)}) = \frac{1}{\omega(E)} \delta(\mathcal{H}(q_i^{(1)}, p_i^{(1)}, q_i^{(2)}, p_i^{(2)}) - E)$$

where the total hamiltonian is

$$\mathcal{H}(q_i^{(1)}, p_i^{(1)}, q_i^{(2)}, p_i^{(2)}) = \mathcal{H}_1(q_i^{(1)}, p_i^{(1)}) + \mathcal{H}_2(q_i^{(2)}, p_i^{(2)})$$

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Integrating it to all the possible state in the environment

$$\rho^{(1)} = \int d\Omega_2 \rho_{mc} = \int d\Omega_2 \frac{1}{\omega(E)} \delta(\mathcal{H} - E) = \frac{1}{\omega(E)} \int dS_{E_2} = \frac{1}{\omega(E)} \omega(E_2 = E - E_1)$$

and the corresponding entropy is

$$S_2(E_2) = k_B \ln \omega_2(E_2)$$

Applying small variation δE_1 to E_1 to preserve equilibrium, the entropy trasforms, using (4.3)

$$k_B \ln \omega_2(E_2) = S_{mc}(E) - E_1 \frac{\partial S_{mc}}{\partial E}\Big|_{E_2} = S_{mc}(E) - E_1 \frac{1}{T}$$

$$\ln \omega_2(E_2) = \frac{S_{mc}(E)}{k_B} - E_1 \frac{1}{k_B T}$$

$$\omega_2(E_2) = \exp(\frac{S_{mc}(E)}{k_B} - E_1 \frac{1}{k_B T}) = \exp(\frac{S_{mc}(E)}{k_B}) \exp(-\frac{E_1}{k_B T})$$

Putting together, dropping the indices

$$\rho_c = \frac{\omega(2)(E_2)}{\omega(E)} = \frac{1}{\omega(E)} \exp(\frac{S_{mc}(E)}{k_B}) \exp(-\frac{E_1}{k_B T}) = C \exp(-\frac{E_1}{k_B T}) \qquad (6.2)$$

where C is a normalisation constant, which can be evaluated by (4.2)

$$1 = \int_{\mathcal{M}^N} d\Omega \rho = \int_{\mathcal{M}^N} d\Omega C \exp(-\frac{E_1}{k_B T}) = C \int_{\mathcal{M}^N} d\Omega \exp(-\frac{E_1}{k_B T})$$

q.e.d.

The partition function can also be written as

$$Z_N[T, V] = \int_0^\infty dE \, \omega(E) \exp(-\beta E)$$

Proof. Foliating the phase space in energy hyper-surfaces

$$Z_N = \int_{\mathcal{M}^N} d\Omega \exp(-\beta\mathcal{H}) = \int_0^\infty dE \int dS_E \, \exp(-\beta\mathcal{H}) = \int_0^\infty dE \, \omega(E) \exp(-\beta E)$$

q.e.d.

Taking also in consideration indistinguishable particles, the partition function

$$Z_N = \int \frac{\prod_{i=1}^N d^d q^i d^d p^i}{h^{dN} \zeta_N} \exp(-\beta \mathcal{H})$$

where ζ_N is

$$\zeta_N = \begin{cases} 1 & \text{distinguishable} \\ N! & \text{indistinguishable} \end{cases}$$

The partition function of two systems is the multiplication of the single system ones

$$Z_N = Z_{N_1} Z_{N_2} \tag{6.3}$$

Proof. Since $\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2$,

<div align="right">q.e.d.</div>

If the hamiltonian is the sum of N identical ones, like N non-interacting particles

$$\mathcal{H} = \sum_{i=1}^N \mathcal{H}_i$$

the partition function becomes

$$Z_N = \frac{(Z_1)^N}{\zeta_N}$$

Proof. Denominating Z_1 the single-particle partition function

$$\begin{aligned}
Z_N &= \int_{\mathcal{M}^N = \mathcal{M}^{(1)} \otimes \ldots \otimes \mathcal{M}^{(1)}} \prod_{i=1}^N \frac{d^d q^i d^d p^i}{h^{dN} \zeta_N} \exp(-\beta \mathcal{H}) \\
&= \int_{\mathcal{M}^N = \mathcal{M}^{(1)} \otimes \ldots \otimes \mathcal{M}^{(1)}} \prod_{i=1}^N \frac{d^d q^i d^d p^i}{h^{dN} \zeta_N} \exp(-\beta \sum_{i=1}^N \mathcal{H}_i) \\
&= \int_{\mathcal{M}^N = \mathcal{M}^{(1)} \otimes \ldots \otimes \mathcal{M}^{(1)}} \prod_{i=1}^N \frac{d^d q^i d^d p^i}{h^{dN} \zeta_N} \prod_{i=1}^N \exp(-\beta \mathcal{H}_i) \\
&= \int_{\mathcal{M}^N = \mathcal{M}^{(1)} \otimes \ldots \otimes \mathcal{M}^{(1)}} \prod_{i=1}^N \frac{d^d q^i d^d p^i}{h^{dN} \zeta_N} \exp(-\beta \mathcal{H}_i) \\
&= \frac{Z_1 Z_1 \ldots Z_1}{\zeta_N} = \frac{(Z_1)^N}{\zeta_N}
\end{aligned}$$

<div align="right">q.e.d.</div>

Let $f(q^i, p_i)$ be an observable, then its canonical average is

$$\langle f(q^i, p_i) \rangle_c = \int_{\mathcal{M}} d\Omega \, \rho_c f = \int_{\mathcal{M}} d\Omega \, \frac{\exp(-\beta \mathcal{H})}{Z_N} f$$

6.1 Thermodynamics variable

The canonical Helmotz free energy F is defined by

$$Z_{[}V,T] = \exp(-\beta F[N,V,T]) \tag{6.4}$$

or, equivalently,

$$F[V,N,T] = -\frac{1}{\beta}\ln Z_N \tag{6.5}$$

Furthermore, the canonical internal energy is

$$E = \langle \mathcal{H} \rangle_c = \int d\Omega \frac{\exp(-\beta(\mathcal{H}))}{Z_N}\mathcal{H} \tag{6.6}$$

Proof. By normalisation condition

$$1 = \int d\Omega \frac{\exp(-\beta\mathcal{H})}{Z_N} = \int d\Omega \frac{\exp(-\beta\mathcal{H})}{\exp(-\beta F)} = \int d\Omega \exp(-\beta(\mathcal{H}-F))$$

Since F depends on the temperature, it is possible to derive with respect to β

$$0 = \frac{\partial}{\partial\beta}\left(\int d\Omega \exp(-\beta(\mathcal{H}-F))\right)$$

$$= \int d\Omega \exp(-\beta(\mathcal{H}-F))\left(-(\mathcal{H}-F)+\beta\frac{\partial F}{\partial\beta}\right)$$

$$= -\underbrace{\int d\Omega \frac{\exp(-\beta\mathcal{H})}{Z_N}\mathcal{H}}_{E} + F\underbrace{\int d\Omega \frac{\exp(-\beta\mathcal{H})}{Z_N}}_{1} + \beta\frac{\partial F}{\partial\beta}\underbrace{\int d\Omega \frac{\exp(-\beta\mathcal{H})}{Z_N}}_{1}$$

$$= -E + F + \beta\frac{\partial F}{\partial\beta}$$

Hence, using (4.4)

$$F = E + \beta\frac{\partial F}{\partial\beta} = E + T\frac{\partial F}{\partial T} = E - TS$$

showing that is indeed the Helmotz free energy. q.e.d.

Notice that in the last result, the entropy can be also written as

$$S_c = \frac{E-F}{T} \tag{6.7}$$

The internal energy can also be written as

$$E = -\frac{\partial}{\partial\beta}\ln Z_N$$

Proof. Using (6.6),

$$-\frac{\partial}{\partial \beta} \ln Z_N = -\frac{1}{Z_N}\frac{\partial Z_N}{\partial \beta} = -\frac{1}{Z_N}\frac{\partial}{\partial \beta}\int d\Omega \exp(-\beta\mathcal{H}) = \int d\Omega \frac{\exp(-\beta\mathcal{H})}{Z_N}\mathcal{H} = \langle \mathcal{H} \rangle_c = E$$

q.e.d.

The universal Boltzmann's formula is still valid

$$S_c = -k_B \langle \ln \rho_c \rangle_c$$

Proof. Using (6.6) and (6.5)

$$-k_B \langle \ln \rho_c \rangle_c = -k_B \int d\Omega \rho_c \ln \rho_c$$

$$= -k_B \int d\Omega \rho_c \ln \frac{\exp(-\beta\mathcal{H})}{Z_N}$$

$$= -k_B \int d\Omega \rho_c \ln \exp(-\beta\mathcal{H}) - k_B \int d\Omega \rho_c \ln Z_N$$

$$= k_B \int d\Omega \beta\mathcal{H} - k_B \underbrace{\ln Z_N}_{\beta F} \underbrace{\int d\Omega \rho_c}_{1}$$

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

q.e.d.

6.2   Equipartition theorem

Theorem 6.1 (Generalised equipartition theorem)
Let $\xi \in [a, b]$ and ξ_j with $j \neq 1$ all the other coordinates or momenta. Suppose also

$$\int \prod_{j\neq 1} d\xi_j [\xi_1 \exp(-\beta\mathcal{H})]_a^b = 0 \tag{6.8}$$

Then

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

Proof. By normalisation condition

$$1 = \int d\Omega \frac{\exp(-\beta\mathcal{H})}{Z_N} = \frac{1}{Z_N}\int \prod_{j\neq 1} d\xi_j \exp(-\beta\mathcal{H})$$

Using

$$d\xi_1(\xi_1 \exp(-\beta\mathcal{H})) = d\xi_1 \exp(-\beta\mathcal{H}) + \xi \exp(-\beta\mathcal{H})(-\beta)\frac{\partial\mathcal{H}}{\partial\xi_1}d\xi_1$$

and integrating per parts

$$1 = \frac{1}{Z_N}\int\prod_{j\neq 1}d\xi_j\underbrace{[\xi_1\exp(-\beta\mathcal{H})]_a^b}_{0} + \frac{\beta}{Z_N}\int\prod_{j\neq 1}d\xi_j d\xi_1\xi_1\frac{\partial\mathcal{H}}{\partial\xi_1}\exp(-\beta\mathcal{H})$$

$$= \beta\int d\Omega\xi_1\frac{\partial\mathcal{H}}{\partial\xi_1}\frac{\exp(-\beta\mathcal{H})}{Z_N}$$

$$= \beta\langle\xi_1\frac{\partial\mathcal{H}}{\partial\xi_1}\rangle_c$$

Hence

$$\langle\xi_1\frac{\partial\mathcal{H}}{\partial\xi_1}\rangle_c = \frac{1}{\beta} = k_B T$$

q.e.d.

Examples of system that satisfies the condition (6.8) are hamiltonians which depend on the square of momentum or confining potentials which go to infinity on the extremes a and b.

Corollary 6.1 (Equipartition theorem)
If ξ_1 appears quadratically in $\mathcal{H}$, then its contribution to E is $\frac{1}{2}k_B T$

Proof. Consider $\mathcal{H} = A\xi_1^2 + B\xi_j^2$ with $j \neq 1$, then by the previous theorem

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

and

$$\langle A\xi_1^2\rangle_c = \frac{1}{2}k_B T$$

q.e.d.

Chapter 7

Grancanonical ensemble

A grancanonical ensemble is a system which is immersed in a bigger environment or reservoir, which can exchange both energy and matter, so T, and V are fixed. Globally, both energy and number of particles are conserved, since the universe composed by the union of the system and the environment can be considered as a microcanonical ensemble. First, with the same method used in the previous chapter, microcanonical can be transformed into canonical. Now, the universe is canonical and, globally, the number of particles is conserved.

The grancanonical probability density distribution is

$$\rho_{gc}(q^i, p_i) = \frac{\exp(-\beta \mathcal{H}_1)}{N_1! h^{dN_1}} \frac{Z_{N_2}[T, V_2]}{Z_N[T, V]}$$

Proof. Consider the universe as a canonical ensemble. Its probability density distribution is

$$\rho_c(q_i^{(1)}, p_i^{(1)}, q_i^{(2)}, p_i^{(2)}) = \frac{\exp(-\beta \mathcal{H}(q_i^{(1)}, p_i^{(1)}, q_i^{(2)}, p_i^{(2)}))}{Z_N[T, V]}$$

where the total hamiltonian is

$$\mathcal{H}(q_i^{(1)}, p_i^{(1)}, q_i^{(2)}, p_i^{(2)}) = \mathcal{H}_1(q_i^{(1)}, p_i^{(1)}) + \mathcal{H}_2(q_i^{(2)}, p_i^{(2)})$$

Integrating it to all the possible state in the environment

$$\begin{aligned}
\rho^{(1)} &= \int d\Omega_2 \; \rho_c \\
&= \int \prod_{i=1}^{N} \frac{d^d q_i^{(2)} d^d p_i^{(2)}}{N! h^{dN}} \frac{\exp(-\beta(\mathcal{H}_1 + \mathcal{H}_2))}{Z_N} \\
&= \frac{\exp(-\beta \mathcal{H}_1)}{N_1! h^{dN_1}} \frac{1}{Z_N} \int \prod_{i=1}^{N} \frac{d^d q_i^{(2)} d^d p_i^{(2)}}{N_2! h^{dN_2}} \exp(-\beta \mathcal{H}_2) \\
&= \frac{\exp(-\beta \mathcal{H}_1)}{N_1! h^{dN_1}} \frac{Z_{N_2}[T, V_2]}{Z_N[T, V]}
\end{aligned}$$

The normalisation condition becomes

$$\sum_{N_1=0}^{N} \int_{\mathcal{M}^{N_1}} d\Omega_1 \rho_{gc} = 1$$

Proof. Using the expression to evaluate the power of a sum

$$(a+b)^n = \sum_{i=1}^{n} \binom{n}{i} a^i b^{n-i}$$

and

$$
\begin{aligned}
\int_{\mathcal{M}^{N_1}} d\Omega_1 \ \rho_{gc} &= \int_{\mathcal{M}^{N_1}} d\Omega_1 \frac{\exp(-\beta\mathcal{H}_1)}{N_1! h^{dN_1}} \frac{Z_{N_2}[T,V_2]}{Z_N[T,V]} \\
&= \frac{N!}{N_1! N_2} \frac{\int_{\mathcal{M}^{N_1}} d\Omega_1 \ \exp(-\beta\mathcal{H}_1) \int_{\mathcal{M}^{N_2}} d\Omega_2 \ \exp(-\beta\mathcal{H}_2)}{\int_{\mathcal{M}^N} d\Omega \ \exp(-\beta\mathcal{H})} \\
&= \frac{N!}{N_1! N_2} \frac{\frac{\int_{\mathcal{M}^{N_1}} d\Omega_1 \ \exp(-\beta\mathcal{H}_1)}{(V_1)^{N_1}} \frac{\int_{\mathcal{M}^{N_2}} d\Omega_2 \ \exp(-\beta\mathcal{H}_2)}{(V_2)^{N_2}}}{\frac{\int_{\mathcal{M}^N} d\Omega \ \exp(-\beta\mathcal{H})}{V^N}} \frac{(V_1)^{N_1}(V_2)^{N_2}}{V^N}
\end{aligned}
$$

which in the thermodynamical limit

$$\lim_{td} \frac{\frac{\int_{\mathcal{M}^{N_1}} d\Omega_1 \ \exp(-\beta\mathcal{H}_1)}{(V_1)^{N_1}} \frac{\int_{\mathcal{M}^{N_2}} d\Omega_2 \ \exp(-\beta\mathcal{H}_2)}{(V_2)^{N_2}}}{\frac{\int_{\mathcal{M}^N} d\Omega \ \exp(-\beta\mathcal{H})}{V^N}} = 1$$

Hence

$$\int_{\mathcal{M}^{N_1}} d\Omega_1 \ \rho_{gc} = \frac{N!}{N_1! N_2} \frac{(V_1)^{N_1}(V_2)^{N_2}}{V^N}$$

and the normalisation condition becomes, using $N = N_1 + N_2$,

$$\sum_{N_1=0}^{N} \int_{\mathcal{M}^{N_1}} d\Omega_1 \rho_{gc} = \sum_{N_1=0}^{N} \frac{N!}{N_1! N_2!} \frac{(V_1)^{N_1}(V_2)^{N_2}}{V^N} = \sum_{N_1=0}^{N} \binom{N}{N_1} \left(\frac{V}{V}\right)^{N_1} \left(\frac{V_2}{V}\right)^{N-N_1} = \left(\frac{V_1 + V_2}{V}\right)^N$$

which in the thermodynamical limit is

$$\lim_{td} \left(\frac{V_1 + V_2}{V}\right)^N = 1$$

7.1   Thermodynamical potentials

The grancanonical probability density distribution can be also written as

$$\rho_{gc}(q_i, p_i) = \frac{\exp(-\beta(\mathcal{H}(q_i, p_i) - \mu N))}{\mathcal{Z}}$$

where μ is the chemical potential and $\mathcal{Z}$ is the grancanonical partition function

$$\mathcal{Z} = \sum_{N=0}^{\infty} z^N Z_N = \exp(-\beta\Omega)$$

where $z = \exp(\beta\mu)$ is the fugacity and Ω is the granpotential.

Proof. Using (6.4) and Taylor expanding to first order in $N_1 \ll N$ and $V_1 \ll V$,

$$\begin{aligned}
\frac{Z_{N_2}[T, V]}{Z_N[T, V]} &= \frac{\exp(-\beta F(T, N_2, V_2))}{\exp(-\beta F(T, N, V))} \\
&= \exp(-\beta(F(T, N - N_1, V - V_1) - F(T, N, V))) \\
&\simeq \exp(-\beta(\underbrace{\frac{\partial F}{\partial N}\Big|_{T,V}}_{\mu}(-N_1) + \underbrace{\frac{\partial F}{\partial V}\Big|_{T,N}}_{-p}(-V_1))) \\
&= \exp(-\beta(-\mu N_1 + p V_1))
\end{aligned}$$

Hence, now all the degrees of freedom of the environment has been removed

$$\begin{aligned}
\rho_{gc} &= \frac{\exp(\beta\mathcal{H})}{N! h^{dN}} \exp(-\beta(-\mu N + pV)) \\
&= \frac{\exp(\beta\mathcal{H})}{N! h^{dN}} \underbrace{\exp(\beta\mu)^N}_{z^N} \exp(-\beta pV) \\
&= \frac{z^N \exp(\beta\mathcal{H})}{N! h^{dN}} \exp(-\beta pV)
\end{aligned}$$

where we introduced the fugacity.

Recall (4.5), the normalisation condition becomes

$$
\begin{aligned}
1 &= \sum_{N=0}^{\infty} \int_{\mathcal{M}^N} d\Omega \, \rho_{gc} \\
&= \sum_{N=0}^{\infty} \int_{\mathcal{M}^N} d\Omega \frac{z^N \exp(\beta \mathcal{H})}{N! h^{dN}} \exp(-\beta p V) \\
&= \exp(-\beta p V) \sum_{N=0}^{\infty} z^N \frac{\int_{\mathcal{M}^N} d\Omega}{h^{dN} N!} \\
&= \exp(-\beta p V) \underbrace{\sum_{N=0}^{\infty} z^N Z_N}_{\mathcal{Z}} \\
&= \exp(-\beta p V) \mathcal{Z}
\end{aligned}
$$

Hence

$$
\mathcal{Z} = sum_{N=0}^{\infty} z^N Z_N = \exp(\beta p V)
$$

and

$$
\rho_{gc}(q_i, p_i) = \frac{\exp(-\beta(\mathcal{H}(q_i, p_i) - \mu N))}{\mathcal{Z}} = \frac{\exp(-\beta \mathfrak{H}(q_i, p_i))}{\mathcal{Z}}
$$

where $\mathfrak{H} = \mathcal{H} - \mu N$ is the grancanonical hamiltonian. q.e.d.

Let $f(q^i, p_i)$ be an observable, then its grancanonical average is

$$
\begin{aligned}
\langle f(q^i, p_i) \rangle_{gc} &= \sum_{N=0}^{\infty} \int_{\mathcal{M}} d\Omega \, \rho_{gc} f_N \\
&= \sum_{N=0}^{\infty} \int_{\mathcal{M}} d\Omega \, \frac{\exp(-\beta(\mathcal{H} - \mu N))}{\mathcal{Z}} f_N \\
&= \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} z^N Z_N \int_{\mathcal{M}} d\Omega \frac{\exp(-\beta \mathcal{H})}{Z_N} f_N \\
&= \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} z^N Z_N \langle f_N \rangle_c
\end{aligned}
$$

The grancanonical internal energy is

$$
E = -\frac{\partial}{\partial \beta} \ln \mathcal{Z} \Big|_z
$$

Proof.

$$-\frac{\partial}{\partial\beta}\ln\mathcal{Z}\bigg|_{z} = -\frac{1}{\mathcal{Z}}\frac{\partial}{\partial\beta}\mathcal{Z}\bigg|_{z}$$

$$= -\frac{1}{\mathcal{Z}}\frac{\partial}{\partial\beta}\sum_{N=0}^{\infty}z^{N}Z_{N}\bigg|_{z}$$

$$= -\sum_{N=0}^{\infty}\frac{z^{N}}{\mathcal{Z}}\frac{\partial}{\partial\beta}\int d\Omega\exp(-\beta\mathcal{H})$$

$$= \sum_{N=0}^{\infty}\int d\Omega\,\frac{\exp(-\beta(\mathcal{H}+\mu N))}{\mathcal{Z}}\mathcal{H}$$

$$= \langle\mathcal{H}\rangle_{gc} = E$$

<div align="right">q.e.d.</div>

The grancanonical number of particles is

$$\langle N\rangle_{gc} = z\frac{\partial}{\partial z}\ln\mathcal{Z}\bigg|_{T}$$

Proof.

$$z\frac{\partial}{\partial z}\ln\mathcal{Z}\bigg|_{T} = \frac{z}{\mathcal{Z}}\frac{\partial}{\partial z}\mathcal{Z}\bigg|_{T}$$

$$= \frac{z}{\mathcal{Z}}\frac{\partial}{\partial z}\sum_{N=0}^{\infty}z^{N}Z_{N}$$

$$= fracz\mathcal{Z}\sum_{N=0}^{\infty}Nz^{N-1}Z_{N}$$

$$= \sum_{N=0}^{\infty}z^{N}Z_{N}N = \langle N\rangle_{gc}$$

<div align="right">q.e.d.</div>

The grancanonical potential is

$$\Omega = -\frac{1}{\beta}\ln\mathcal{Z} \tag{7.1}$$

The universal Boltzmann's formula is still valid

$$S_{gc} = -k_{B}\langle\ln\rho_{gc}\rangle_{gc}$$

Proof. Using (7.1),

$$-k_B \langle \ln \rho_{gc} \rangle_{gc} = -k_B \int d\Omega \ \rho_{gc} \ln \rho_{gc}$$

$$= -k_B \sum_{N=0}^{\infty} \frac{z^N}{\mathcal{Z}} \int d\Omega \ \exp(-\beta\mathcal{H}) \ln \rho_{gc}$$

$$= = -k_B \sum_{N=0}^{\infty} \frac{z^N}{\mathcal{Z}} \int d\Omega \ \exp(-\beta\mathcal{H})(-\beta\mathcal{H} + \beta\mu N + \ln \mathcal{Z})$$

$$= k_B \beta \underbrace{\sum_{N=0}^{\infty} \frac{z^N}{\mathcal{Z}} \int d\Omega \ \exp(-\beta\mathcal{H})\mathcal{H}}_{E} - k_B \beta \mu \underbrace{\sum_{N=0}^{\infty} \frac{z^N}{\mathcal{Z}} \int d\Omega \ \exp(-\beta\mathcal{H})N}_{N}$$

$$+ k_B \ln \mathcal{Z} \underbrace{\sum_{N=0}^{\infty} \frac{z^N}{\mathcal{Z}} \int d\Omega \ \exp(-\beta\mathcal{H})}_{1}$$

$$= \frac{E - \mu N - \Omega}{T} = S$$

q.e.d.

Chapter 8

Entropy

The Boltzmann's universal law allows us to define entropy in terms of number of states

$$S = -k_B \langle \ln \rho \rangle = k_B \ln \Sigma = \lim_{TD} S_{TD}$$

Thermodynamics tells us that equilibrium corresponds to maximum entropy.

We consider a canonical ensemble with a discrete set of energy values, but it can be generalised for grancanonical and continuous energy levels. Therefore, the probability density distribution is (**??**)

$$\rho_c(E_r) = \frac{\exp(-\beta E_r)}{Z_N}$$

where the canonical partition function (**??**) becomes

$$Z_N = \int_{\mathcal{M}^N} d\Omega \ \exp(-\beta \mathcal{H}(q^i, p_i)) = int_0^\infty dE \int_{S_E} dS_E \ \exp(-\beta E) \simeq \sum_{r=1}^{p} g_r \exp(-\beta E_r)$$

where we foliated $\mathcal{M}^N$ in energy surfaces S_E and g_r is the multiplicity or degeneracy, i.e. how many levels have the same energy.

So far, we have started from an a-priori probability density distribution and from it derive the entropy. From now on, we will change the picture and do the converse: the probability distibution is the one corresponding to maximum entropy, given the macroscopic constains. To do so, we introduce the Shannon's information entropy

$$H = -\sum_{i=1}^{N} p_i \ln p_i$$

which is the only function with the following properties for a random variable x such that it has N possible outcomes x_i with probability p_i

1. it is continuous with p_i,

2. is monotonically increasing with N,

3. it is invariant under compositions of subsystems, i.e. change how we collect in group.

Inference problem

Given a certain constraint for a function $\langle f \rangle$, what is the expectation value for another function g? The answer can be found with the principle of maximum entropy, subjected to Lagrange multipliers given by the constraints

$$\sum_{i=1}^{N} p_i = 1 \quad \sum_{i=1}^{N} p_i f(x_i) = \langle f(x) \rangle$$

Hence, the problem reduces to maximise the function

$$H = -\sum_{i=1}^{N} p_i \ln p_i + \alpha \left(\sum_{i=1}^{N} p_i - 1 \right) + \beta \left(\sum_{i=1}^{N} p_i f(x_i) - \langle f \rangle \right) \tag{8.1}$$

In particular, we need to count the number of ways $W_{\{n_r\}}$ we can find n_r systems with energy E_r, given a set of discrete energy levels E_r, each of degeneracy g_r on which we distribute n_r particles. Hence, the probability density distribution n_r^* is the one which maximises (8.1), with entropy

$$S = \ln W_{\{n_r\}}$$

and the constrains

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

In order to count $W_{\{n_r\}}$, we need to take into account distinguishablility or not of particles. Therefore, we decomposed it into

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

where $W_{\{n_r\}}^{(1)}$ countsin how many we can put n_r particles in the energy level E_r and $W_{\{n_r\}}^{(1)}$ consider the degeneracy of these levels.

Boltzmann distribution

Bose-Einstein distribution

Fermi-Dirac distribution

Part III

Applications of classical statistical mechanics

Chapter 9

Microcanonical ensemble

9.1 Non-relativistic ideal gas

The hamiltonian of a non-relativistic ideal (non-interacting) gas is

$$H = \sum_i \frac{p_i^2}{2m} \ .$$

The number of states $\Sigma(E)$ is

$$\Sigma(E) = \frac{2V^N}{\xi_N dN \Gamma(\frac{dN}{2})} \left(\frac{2\pi m E}{h^2}\right)^{\frac{dN}{2}} \ .$$

The density state $\omega(E)$ is

$$\omega(E) = \frac{V^N}{\xi_N \Gamma(\frac{dN}{2})} \left(\frac{2\pi m}{h^2}\right)^{\frac{dN}{2}} E^{\frac{dN}{2}-1} \ .$$

Proof. Maybe in the future. q.e.d.

Now, consider a 3-dimensional ideal gas. The entropy is

$$\frac{S}{k_B} = \ln \Gamma(E) = \ln \omega(E) + \ln \Delta E = \ln \Sigma(E) = \ln \Sigma(E) + \ln \frac{3N}{2E} + \ln \Delta E \ ,$$

or, in the thermodynamic limit,

$$S = k_B \begin{cases} \frac{3}{2}N + N \ln \left(V(\frac{4\pi m E}{3Nh^2})^{\frac{3}{2}}\right) & \text{for distinguishable particles} \\ \frac{5}{2}N + N \ln \left(V(\frac{4\pi m E}{3Nh^2})^{\frac{3}{2}}\right) & \text{for indistinguishable particles} \end{cases} \ .$$

Proof. Maybe in the future.   q.e.d.

The internal energy is
$$E = \frac{3}{2} N k_B T \ .$$

Proof. Maybe in the future.   q.e.d.

The pressure is
$$P = \frac{N k_B T}{V} \ .$$

Proof. Maybe in the future.   q.e.d.

9.2   Gas of harmonic oscillators

The hamiltonian of a non-relativistic ideal (non-interacting) gas is
$$H = \sum_i \left(\frac{p_i^2}{2m} + \frac{m\omega^2}{2} q_i^2 \right) \ .$$

The number of states $\Sigma(E)$ is
$$\Sigma(E) = \frac{1}{\xi_N \Gamma(dN + 1)} \left(\frac{2\pi E}{h\omega} \right)^{dN} \ .$$

The density state $\omega(E)$ is
$$\omega(E) = \frac{1}{\xi_N \Gamma(dN)} \left(\frac{1}{h\omega} \right)^{dN} E^{dN-1} \ .$$

Proof. Maybe in the future.   q.e.d.

Chapter 10

Canonical ensemble

10.1 Non-relativistic ideal gas

The canonical partition function is

$$Z = \frac{V^N}{N!\lambda_T^{3N}} = \frac{V^N}{N!} \sqrt{\frac{2\pi m k_B T}{h^2}} \ .$$

Proof. Maybe in the future. q.e.d.

The internal energy is

$$E = \frac{3}{2} N k_B T \ .$$

Proof. Maybe in the future. q.e.d.

The Helmoltz free energy is

$$F = \frac{N}{\beta} (\ln(n\lambda_T^3) - 1) \ .$$

Proof. Maybe in the future. q.e.d.

The entropy is

$$S = N k_B \left(\frac{5}{2} - \ln(n\lambda_t^3)\right) \ .$$

Proof. Maybe in the future. q.e.d.

The pression is

$$p = \frac{N}{Vk_B} \ .$$

Proof. Maybe in the future.   q.e.d.

The chemical potential is

$$\mu = \frac{1}{\beta} \ln(n\lambda_T^3) \ .$$

Proof. Maybe in the future.   q.e.d.

The specific heats per particle are

$$c_V = \frac{3}{2}k_B \ , \quad c_p = \frac{5}{2}k_B \ .$$

Proof. Maybe in the future.   q.e.d.

10.2   Gas of harmonic oscillators

The canonical partition function is

$$Z = \left(\frac{k_BT}{\hbar\omega}\right)^N \ .$$

Proof. Maybe in the future.   q.e.d.

The internal energy is

$$E = Nk_BT \ .$$

Proof. Maybe in the future.   q.e.d.

The Helmoltz free energy is

$$F = Nk_BT \ln \frac{\hbar\omega}{k_BT} \ .$$

Proof. Maybe in the future.   q.e.d.

The entropy is

$$S = N k_B \left(1 - \ln \frac{\hbar \omega}{k_B T} \right) .$$

Proof. Maybe in the future.   q.e.d.

The pression is

$$p = 0 .$$

Proof. Maybe in the future.   q.e.d.

The chemical potential is

$$\mu = k_B T \ln \frac{\hbar \omega}{k_B T} .$$

Proof. Maybe in the future.   q.e.d.

The specific heats per particle are

$$c_V = k_B , \quad c_p = k_B .$$

Proof. Maybe in the future.   q.e.d.

10.3   Ultra-relativistic ideal gas

The hamiltonian of an ultra-relativistic ideal (non-interacting) gas is

$$H = \sum_i c |p_i|$$

The canonical partition function is

$$Z = \frac{1}{N!} \left(\frac{8 \pi V}{(\beta h c)^3} \right)^N .$$

Proof. Maybe in the future.   q.e.d.

The internal energy is

$$E = 3Nk_BT \ .$$

Proof. Maybe in the future.   q.e.d.

The Helmoltz free energy is

$$F = Nk_BT \left(\ln \frac{n(\beta hc)^3}{8\pi} - 1 \right) \ .$$

Proof. Maybe in the future.   q.e.d.

The entropy is

$$S = Nk_B \left(4 - \ln \frac{n(\beta hc)^3}{8\pi} \right) \ .$$

Proof. Maybe in the future.   q.e.d.

The pression is

$$p = \frac{N}{V\beta} \ .$$

Proof. Maybe in the future.   q.e.d.

The chemical potential is

$$\mu = -k_BT \ln \frac{8\pi(k_BT)^3}{n(hc)^3} \ .$$

Proof. Maybe in the future.   q.e.d.

The specific heats per particle are

$$c_V = 3k_B \ , \quad c_p = 4k_B \ .$$

Proof. Maybe in the future.   q.e.d.

10.4 Maxwell-Boltzmann velocity distribution

10.5 Magnetic solid

The hamiltonian of a magnetic solid is

$$H = \sum_i \boldsymbol{\mu}_i \cdot \mathbf{H} = -\mu H \sum_i \cos \theta_i$$

The canonical partition function is

$$Z = \left(4\pi \frac{\sinh(\beta \mu H)}{\beta \mu H} \right)^N .$$

Proof. Maybe in the future. q.e.d.

The internal energy is

$$E = -N\mu H \left(\coth(\beta \mu H) - \frac{1}{\beta \mu H} \right) .$$

Proof. Maybe in the future. q.e.d.

The Helmoltz free energy is

$$F = -\frac{N}{\beta} \ln \frac{4\pi \sinh(\beta \mu H)}{\beta \mu H} .$$

Proof. Maybe in the future. q.e.d.

The entropy is

$$S = .$$

Proof. Maybe in the future. q.e.d.

Chapter 11

Grancanonical ensemble

Chapter 12

Entropy

Part IV

Quantum mechanics

Chapter 13

Quantum Mechanics

In this chapter, we will study the mathematical framework necessary to study quantum statistical mechanics.

13.1 States

In quantum mechanics, a pure state of a quantum particle is represented by a normalised vector in a Hilbert space $|\psi\rangle \in \mathcal{H}$. An Hilbert space $\mathcal{H}$ is a vector space on $\mathbb{C}$, i.e. in which a linear superposition of is still in the space

$$\lambda|\psi\rangle + \mu|\phi\rangle \in \mathcal{H} , \quad \forall|\psi\rangle, |\phi\rangle \in \mathcal{H} , \forall \lambda, \mu \in \mathbb{C} ,$$

endowed with a scalar product $\langle\psi|\phi\rangle$. In particular, via the scalar product, it is possible to associate a norm to the state, which is set to zero by the probability intepretation $||\psi||^2 = \langle\psi|\psi\rangle = 1$. In the Schoredinger representation, this means that the wave function is a square-integrable function $\psi(t, \mathbf{x}) \in L^2(\mathbb{R}^d)$, the probability intepretation tells us that $|\psi(t, \mathbf{x})|$ is the probability density to find the particle in a volume element $d^d x$ at time t and the normalisation condition that the total probability to find the particle in the whole $\mathbb{R}^d$ is 1

$$\int_{\mathbb{R}^d} d^d x \, |\psi(t, x)|^2 = 1 .$$

However, by the normalisation condition, a state is not associated to a single vector, but a class of equivalence of them, called a ray in the Hilbert space, since two states are physically equivalent if $|\psi'\rangle = \exp(i\varphi)|\psi\rangle$, because their norms are the same.

Projectors

To remove this ambiguity, we introduce the notion of projection operators or projectors, which uniquely determine a state

$$P_\psi = \frac{|\psi\rangle\langle\psi|}{\langle\psi|\psi\rangle} ,$$

which for normalisation states becomes

$$P_\psi = |\psi\rangle\langle\psi| . \tag{13.1}$$

Proof. If $|\psi'\rangle = \exp(i\varphi)|\psi\rangle$ and $\langle\psi'| = \exp(-i\varphi)\langle\psi|$, we have

$$P_{\psi'} = |\psi'\rangle\langle\psi'| = \underline{\exp(i\varphi)}|\psi\rangle\underline{\exp(-i\varphi)}\langle\psi| = |\psi\rangle\langle\psi| = P_\psi .$$

q.e.d.

It projects onto the 1-dimensional subspace $\mathcal{H}_\psi = \{\lambda|\psi\rangle \colon \lambda \in \mathbb{C}\}$ generated by the state $|\psi\rangle$

$$P_\psi \colon \mathcal{H} \to \mathcal{H}_\psi .$$

Proof. In fact, $\forall|\phi\rangle \in \mathcal{H}$, we decomposed the Hilbert space into the direct orthogonal sum of the subspace spanned by $\mathcal{H}_\psi$ and its orthogonal complement $\mathcal{H}^\perp$:

$$|\phi\rangle = \alpha|\psi\rangle + \beta|\psi^\perp\rangle ,$$

where $|\psi\rangle \in \mathcal{H}_\psi$, $|\psi^\perp\rangle \in \mathcal{H}^\perp$ and $\langle\psi|\psi^\perp\rangle = 0$. Therefore, the action of the projector is

$$P_\psi|\phi\rangle = \alpha P_\psi|\psi\rangle + \beta P_\psi|\psi^\perp\rangle = \alpha|\psi\rangle \underbrace{\langle\psi|\psi\rangle}_{1} + \beta|\psi\rangle \underbrace{\langle\psi|\psi^\perp\rangle}_{0} = \alpha|\psi\rangle \in \mathcal{H}_\psi .$$

q.e.d.

Moreover, since the projectors is orthogonal, we can define the projector onto the orthogonal subspace as $P_\psi^\perp = \mathbb{I} - P_\psi$ such that it satisfies $P_\psi P_\psi^\perp = P_\psi^\perp P_\psi = 0$. This can be generalised for a generic set of orthogonal subspaces. In fact, given an orthonormal basis $\{|e_n\rangle\}$, a projector onto an element of this basis is $P_n = |e_n\rangle\langle e_n|$ and the orthonormality condition reads as $P_n P_m = P_m P_n = 0$ for $n \neq m$.

It satisfies the following properties

1. boundness, i.e.
$$||P_\psi|| < \infty ,$$

2. hermiticity, i.e.
$$P_\psi^\dagger = P_\psi ,$$

3. idempotence, i.e.
$$P_\psi^2 = P_\psi , \tag{13.2}$$

4. positive defined, i.e. $\forall|\phi\rangle \in \mathcal{H}$
$$\langle\phi|P_\psi|\phi\rangle \geq 0 ,$$

5. trace equals to 1, i.e.
$$\text{tr}\, P_\psi = 1 \ .$$

Actually, there is a theorem that ensures that an operators such that it satifies these 5 conditions is indeed a projector.

Proof. For the boundness, $\forall |\phi\rangle \in \mathcal{H}$

$$||P_\psi|\phi\rangle||^2 = \langle\phi|P_\psi^\dagger P_\psi|\phi\rangle = \langle\phi|\psi\rangle \underbrace{\langle\psi|\psi\rangle}_{1}\langle\psi|\phi\rangle = |\langle\psi|\phi\rangle|^2 \leq ||\phi||^1 \ ,$$

hence
$$||P_\psi|| = \frac{||P_\psi|\phi\rangle||}{||\phi||} \leq 1 \ .$$

For the hermiticity
$$P_\psi^\dagger = (|\psi\rangle\langle\psi|)^\dagger = \langle\psi|^\dagger|\psi\rangle^\dagger = |\psi\rangle\langle\psi| = P_\psi \ .$$

For the idempotence
$$P_\psi^2 = (|\psi\rangle\langle\psi|)^2 = |\psi\rangle \underbrace{\langle\psi|\psi\rangle}_{1}\langle\psi| = |\psi\rangle\langle\psi| = P_\psi \ .$$

For the positive definedness
$$\langle\phi|P_\psi|\phi\rangle = \langle\phi|\psi\rangle\langle\psi|\phi\rangle = |\langle\psi|\phi\rangle|^2 \geq 0 \ .$$

For the trace, since it is independent from the choice of the basis, we choose $|\psi\rangle = |\psi_1\rangle$ such that $\langle\psi|\psi_n\rangle = \delta_{n,1}$ and

$$\text{tr}\, P_\psi = \sum_{n=0}^{\infty}\langle\psi_n|P_\psi|\psi_n\rangle = \sum_{n=0}^{\infty}\underbrace{\langle\psi_n|\psi\rangle}_{\delta_{n,1}}\langle\psi|\psi_n\rangle = \sum_{n=0}^{\infty}\underbrace{\delta_{n,1}}_{n=1}\langle\psi|\psi_n\rangle = \langle\psi|\psi_1\rangle = \langle\psi_1|\psi_1\rangle = 1 \ .$$

q.e.d.

Trace

Given an orthonormal basis $\{|e_n\rangle\}_{n=1}^{\infty}$ of a separable Hilbert space, the trace is defined as
$$\text{tr}\, A = \sum_{n=1}^{\infty} A_{nn} = \sum_{n=1}^{\infty}\langle e_n|A|e_n\rangle \ .$$

It may happen that this series is not convergent. If it is convergent, the operator A is called a trace-class operator. Furthermore, if it is absolute convergent, the trace is independent on the choice of the basis. Recall that in the finite-dimensional case, the trace of a matrix is always convergent and independent on the choice of the basis.

13.2　Observables

An observable is a linear hermitian operator $\hat{A}$ acting on the Hilbert space. We require the self-adjointness because, by the spectral theorem, they are always diagonalisable with a positive spectrum. This means that its eigenvalues are real and it always admit an orthonormal eigenbasis $\{|\psi_n\rangle\}$

$$A|\psi_n\rangle = \lambda_n|\psi_n\rangle \ , \tag{13.3}$$

where $\lambda_n \in \mathbb{R}$. In this way, $\forall |\phi\rangle \in \mathcal{H}$, we can expand it into the eigenbasis

$$|\phi\rangle = \sum_{n=1}^{\infty} c_n|\psi_n\rangle \ , \tag{13.4}$$

where $c_n \in \mathbb{C}$.

The eigenprojectors, defined as

$$P_n = |\psi_n\rangle\langle\psi_n| \ ,$$

satisfy the following properties

1. self-adjointness, i.e.

$$P_n^\dagger = P_n \ ,$$

2. orthonormality, i.e.

$$P_n P_m = \delta_{nm} P_n \ ,$$

3. completeness relation, i.e.

$$\sum_{n=0}^{\infty} P_n = \mathbb{I} \ , \tag{13.5}$$

4. spectral decomposition, i.e.

$$\hat{A} = \sum_{n=0}^{\infty} \lambda_n P_n \ . \tag{13.6}$$

Measure

Prepare a quantum system in a state $|\psi\rangle$. A measurement of an observable $\hat{A}$ has outcomes corresponding to its eigenvalues λ_n with probability $p_n = |c_n|^2$. Recall that λ_n are the coefficients in (13.3) and c_n in (13.4). Its average value is

$$\langle A \rangle = \langle\psi|\hat{A}|\psi\rangle = \sum_n \lambda_n|c_n|^2 = \sum_n \lambda_n p_n \ , \tag{13.7}$$

whereas its standard deviation is

$$(\Delta A)^2 = \langle A^2 \rangle - \langle A \rangle^2 .$$

Proof. In fact, using (13.3) and (13.4)

$$\langle A \rangle = \langle \psi | \hat{A} | \psi \rangle$$

$$= \sum_{m=0}^{\infty} c_m^* \langle \psi_m | \sum_{n=0}^{\infty} c_n \underbrace{\hat{A} | \psi_n \rangle}_{\lambda_n | \psi_n \rangle}$$

$$= \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \lambda_n c_m^* c^n \underbrace{\langle \psi_m | \psi_n \rangle}_{\delta_{nm}}$$

$$= \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \lambda_n c_m^* c^n \underbrace{\delta_{nm}}_{n=m}$$

$$= \sum_{n=0}^{\infty} \lambda_n \underbrace{c_n^* c_n}_{|c_n|^2}$$

$$= \sum_n \lambda_n |c_n|^2 .$$

q.e.d.

Notice that measurement in quantum mechanics is a destructive process, since the wave function collapses into one of the eigenstates.

Time evolution

Time evolution of a quantum system is governed by a special observable, the hamiltonian $\hat{H}$, through the Schroedinger equation

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

Notice that this equation is linear, consistent with the superposition principle. It is also at first-order in time, meaning that once the initial condition is fixed, $|\psi(t)\rangle$ is completely determined.

Moreover, for a time-independent hamiltonian, time evolution can be equivalently expressed by a unitary operator $\hat{U}(t)$

$$| \psi(t) \rangle = \hat{U}(t) | \psi(0) \rangle , \tag{13.8}$$

where $\hat{U}(t) = \exp(\frac{i}{\hbar}\hat{H}t)$. Since it is unitary

$$\hat{U}^\dagger(t) = \exp(-\frac{i}{\hbar}\hat{H}t) = \hat{U}(-t) = U^{-1}(t) \ ,$$

it preserves the probability.

13.3   Density matrices and mixed states

The projector (15.1) is also called a density matrix ρ_ψ. In terms of the density matrix, the average value (13.7) of an operator $\hat{A}$ is

$$\langle A \rangle = \langle \psi | \hat{A} | \psi \rangle = \mathrm{tr}(\hat{A}\rho_\psi) \ .$$

Proof. In fact, using (13.5)

$$\begin{aligned}
\langle A \rangle &= \langle \psi | \hat{A} | \psi \rangle \\
&= \langle \psi | \mathbb{I}\hat{A} | \psi \rangle \\
&= \sum_{n=0}^{\infty} \langle \psi | P_n \hat{A} | \psi \rangle \\
&= \sum_{n=0}^{\infty} \langle \psi | \psi_n \rangle \langle \psi_n | \hat{A} | \psi \rangle \\
&= \sum_{n=0}^{\infty} \langle \psi_n | \hat{A} \underbrace{| \psi \rangle \langle \psi |}_{\rho_\psi} | \psi_n \rangle \\
&= \sum_{n=0}^{\infty} \langle \psi_n | \hat{A}\rho_\psi | \psi_n \rangle \\
&= \mathrm{tr}(\hat{A}\rho_\psi) \ ,
\end{aligned}$$

where we have exchanged brakets because they are only numbers.   q.e.d.

The time evolution of the density matrix is

$$\rho_\psi(t) = \exp(-\frac{i}{\hbar}\hat{H}t)\rho_\psi(0)\exp(\frac{i}{\hbar}\hat{H}t) \ .$$

Proof. In fact, using (13.8)

$$\rho_\psi(t) = |\psi(t)\rangle\langle\psi(t)| = \exp(-\frac{i}{\hbar}\hat{H}t)\underbrace{|\psi(0)\rangle\langle\psi(0)|}_{\rho_\psi(0)}\exp(\frac{i}{\hbar}\hat{H}t) = \exp(-\frac{i}{\hbar}\hat{H}t)\rho_\psi(0)\exp(\frac{i}{\hbar}\hat{H}t) \ .$$

q.e.d.

Mixed states

A mixed state belonging to a classical mixture is a system which can be found in a state $|\psi_n\rangle$ with a probability p_n

$$\{|\psi_n\rangle, p_n\} ,$$

where $p_n \geq 0$ and $\sum_{n=0}^{\infty} p_n = 1$. The difference from a pure state is that, in a mixed state, the system is in a classical fixed state before the measurement whereas in a pure state, the state is in a quantum superposition. The density matrix of a mixed state is

$$\rho = \sum_n p_k |\psi_n\rangle \langle \psi_n| = \sum_n p_n \rho_n , \tag{13.9}$$

It defines a statistical ensemble.

Similarly to the pure state case, it satisfies the following properties

1. boundness, i.e.
$$||\rho|| < \infty ,$$

2. hermiticity, i.e.
$$\rho^\dagger = \rho ,$$

3. positive defined, i.e. $\forall |\phi\rangle \in \mathcal{H}$
$$\langle \phi|\rho|\phi\rangle \geq 0 ,$$

4. trace equals to 1, i.e.
$$\text{tr}\,\rho = 1 .$$

However, the idempotence property (13.2) is a particular property of only pure states. There is a theorem that states that a state is pure if and only if $\rho^2 = \rho$.

Proof. In the simple case of orthogonal states $|\psi_n\rangle$, i.e. $\langle \psi_n|\psi_m\rangle = \delta_{nm}$, we have

$$\begin{aligned}
\rho^2 &= \sum_n p_n |\psi_n\rangle \langle \psi_n| \sum_m p_m |\psi_m\rangle \langle \psi_m| \\
&= \sum_n \sum_m p_n p_m |\psi_n\rangle \underbrace{\langle \psi_n|\psi_m\rangle}_{\delta_{nm}} \langle \psi_m| \\
&= \sum_n \sum_m p_n p_m |\psi_n\rangle \underbrace{\delta_{nm}}_{n=m} \langle \psi_m| \\
&= \sum_n p_n^2 |\psi_n\rangle \langle \psi_n| \\
&= \sum_n p_n^n \rho_n .
\end{aligned}$$

This means that if $\rho^2 = \rho$, we obtain

$$p_n^2 = p_n \ ,$$

which means that $p_{\bar{n}} = 1$ for a single $\bar{n}$ and for all the others $p_n = 0$ for $n \neq \bar{n}$, but this is indeed a pure state $\rho = |\psi_{\bar{n}}\rangle\langle\psi_{\bar{n}}|$.   q.e.d.

However, the average value of an observable is the same as the pure states

$$\langle \hat{A} \rangle = \langle \psi | \hat{A} | \psi \rangle = \mathrm{tr}(\rho \hat{A}) \ . \tag{13.10}$$

Proof. In fact,

$$\langle \hat{A} \rangle = \sum_n p_n \langle \hat{A} \rangle_n = \sum_n p_n \, \mathrm{tr}(\hat{A}\rho_n) = \mathrm{tr}(\hat{A} \underbrace{\sum_n p_n\rho_n}_{\rho}) = \mathrm{tr}(\hat{\rho}) \ ,$$

where we have used the linearity of the trace.   q.e.d.

Notice that in the classical case, the average value of an observable is (4.1)

$$\langle f \rangle = \int_{\mathcal{M}} d^d x \ f(x)\rho(x) \ ,$$

which shows that, in the quantum case, we have substituted the integral with the trace, the function with the observable operator and the density distribution with the density matrix.

13.4   Composite systems

Consider a quantum system composed by 2 particles. The total Hilbert space is the tensor product between the 2 single particle Hilbert spaces

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

Given an orthonormal basis for each Hilbert space $\{|\psi_n\rangle\} \in \mathcal{H}_1$ and $\{|\phi_m\rangle\} \in \mathcal{H}_2$, the orthonormal basis for the total Hilbert space is

$$\{|\psi_n\rangle_1 |\phi_m\rangle_2 = |\psi_n\phi_m\rangle\} \ ,$$

such that a generic state can be expanded into this basis, $\forall |\phi\rangle \in \mathcal{H}_{tot}$

$$|\phi\rangle = \sum_n \sum_m \alpha_{nm} |\psi_n\phi_m\rangle \ ,$$

where $\alpha_{nm} \in \mathbb{C}$ and the normalisation condition reads $\sum_{nm} |\alpha_{nm}|^2 = 1$.

If the 2 particle are identical, we have $\mathcal{H}_1 = \mathcal{H}_2 = \mathcal{H}$. Therefore $\mathcal{H}_{tot} = \mathcal{H}^{\otimes 2}$. The scalar product between two sparable is

$$\langle \psi_n \phi_m | \psi_{n'} \phi_{m'} \rangle = \langle \psi_n | \psi_{n'} \rangle_1 \langle \phi_m | \phi_{m'} \rangle_2 \ ,$$

such that if the two states are orthonormal we have

$$\langle \psi_n \phi_m | \psi_{n'} \phi_{m'} \rangle = \langle \psi_n | \psi_{n'} \rangle_1 \langle \phi_m | \phi_{m'} \rangle_2 = \delta_{nn'} \delta_{mm'} \ .$$

By linerity, we can generalised this construction for N particles. However, for infinite dimensional Hilbert spaces, we need the convergence of $\sum_{nm} |\alpha_{nm}|^2$ in order to remain in a Hilbert space. The total Hilbert space is

$$\mathcal{H}_{tot} = \mathcal{H}_1 \otimes \ldots \otimes \mathcal{H}_N \ ,$$

its orthonormal basis is

$$|e_{n_1}\rangle \ldots |e_{n_N}\rangle$$

and its scalar product is

$$\langle \cdot | \cdot \rangle = \prod_k \langle \cdot | \cdot \rangle_k \ .$$

A generic state can be expanded into the orthonormal basis, $\forall |\phi\rangle \in \mathcal{H}_{tot}$

$$|\phi\rangle = \sum_{n_1,\ldots n_N} \alpha_{n_1,\ldots n_N} |e_{n_1}\rangle \ldots |e_{n_N}\rangle \ .$$

If all the particles are identical, we have $\mathcal{H}_1 = \ldots = \mathcal{H}_N = \mathcal{H}$. Therefore $\mathcal{H}_{tot} = \mathcal{H}^{\otimes N}$.

N particles

Explicitly, a single particle lives in $\mathbb{R}^3$ and its Hilbert space is $\mathcal{H} = L^2(\mathbb{R}^3) \ni \psi(x)$. The scalar product is

$$\langle \psi | \phi \rangle = \int d^3 x \ \psi^*(x) \phi(x) \ ,$$

where the normalisation condition is

$$||\psi||^2 = \langle \psi | \psi \rangle = \int_{\mathbb{R}^3} d^3 x \ |\psi(x)|^2 < \infty \ .$$

For N distinguishable particles, the total Hilbert space is $\mathcal{H}_{tot} = \mathcal{H} \otimes \ldots \otimes \mathcal{H}$ and a generic state is $|\psi_{n_1} \ldots \psi_{n_N}\rangle$ where $|\psi_{n_j}\rangle$ is a single particle state. Explicitly, N distinguishable particle live in $\mathbb{R}^{3N}$ and their Hilbert space is $\mathcal{H}_N = L^2(\mathbb{R}^3) \otimes \ldots \otimes L^2(\mathbb{R}^3) = L^2(\mathbb{R}^{3N}) \ni \psi(x_1, \ldots x_N)$. Therefore, an orthonormal basis is $\{u_{\alpha_1(x_1)} \ldots u_{\alpha_N(x_N)} = u_{\alpha_1 \ldots \alpha_N}(x_1, \ldots x_N)\}$ where $\{u_\alpha(x)\}$ is the single particle orthonormal basis. A generic state can be expanded in this basis as

$$\psi(x_1, \ldots x_N) = \sum_{\alpha_1 \ldots \alpha_N} c_{\alpha_1 \ldots \alpha_N} u_{\alpha_1 \ldots \alpha_N}(x_1, \ldots x_N) \ .$$

Distinguishable and indistinguishable particles

Choosing $\alpha_1 = a$ and $\alpha_2 = b$ or viceversa, we obtain

$$u_{\alpha_1=a}(x_1)u_{\alpha_2=b}(x_2) \neq u_{\alpha_1=b}(x_1)u_{\alpha_2=a}(x_2) \ ,$$

but if the particle are indistinguishable, we have

$$u_{\alpha_1=a}(x_1)u_{\alpha_2=b}(x_2) \propto u_{\alpha_1=b}(x_1)u_{\alpha_2=a}(x_2) \ ,$$

where the proportionality factor is due to the fact that states are the same up to a global phase factor. This means that they are invariant under permutations

$$\psi(P(x_1, \ldots x_N)) = \exp(i\alpha_P)\psi(x_1, \ldots x_N) \ ,$$

since in this way

$$|\psi(P(x_1, \ldots x_N))|^2 = |\psi(x_1, \ldots x_N)|^2 \ ,$$

where P belongs to the permutation group. In the next chapter, we will evaluate the phase factor α_P.

Chapter 14

Permutation group

14.1 Permutation as consecutive transpositions

The premutation of N elements form a group P_N. The composition of 2 permutations PP' is defined as the permutation obtained by applying first P and then P'. The identity permutation $\mathbb{I}$ does not change anything and the inverse is the permutation such that $PP^{-1} = \mathbb{I}$.

Example 14.1. Given 4 numbers $(1, 2, 3, 4)$,

1. the identity is
$$(1, 2, 3, 4) \overset{\mathbb{I}}{\mapsto} (1, 2, 3, 4) ,$$

2. the inverse of
$$(1, 2, 3, 4) \overset{P}{\mapsto} (4, 2, 1, 3) ,$$

   is
$$(1, 2, 3, 4) \overset{P^{-1}}{\longmapsto} (3, 2, 4, 1) ,$$

   since
$$(1, 2, 3, 4) \overset{P}{\mapsto} (4, 3, 1, 3) \overset{P^{-1}}{\longmapsto} (1, 2, 3, 4) ,$$

This group is generated by transposition, since any permutation $P \in P_N$ can be decomposed and written as a consecutive swap of two near elements

$$\sigma_i \colon (1, 2, \ldots, i, i+1, \ldots N) \mapsto (1, 2, \ldots, i+1, i, \ldots N) ,$$

in the following way

$$P = \sigma_{\alpha_1} \ldots \sigma_{\alpha_k} . \tag{14.1}$$

However, this decomposition is not unique but the number of transposition in its decomposition is always even or odd. Therefore, we can define the sign of a permutation $\forall P \in P_N$

$$\text{sgn}(P) = \begin{cases} +1 & \text{even number of transposition in its decomposition} \\ -1 & \text{odd number of transposition in its decomposition} \end{cases} .$$

Transpositions follow the properties

1. if $|i - j| > 2$, which means that they are not next to each other,

$$\sigma_i \sigma_j = \sigma_j \sigma_i , \tag{14.2}$$

2.

$$\sigma_i \sigma_{i+1} \sigma_i = \sigma_{i+1} \sigma_i \sigma_{i+1} , \tag{14.3}$$

3.

$$(\sigma_i)^2 = \mathbb{I} . \tag{14.4}$$

Proof. A transposition can be pictorially seen in Figure 14.1. The proofs can be seen in Figure 14.2, Figure 14.4 and Figure 14.3.   q.e.d.
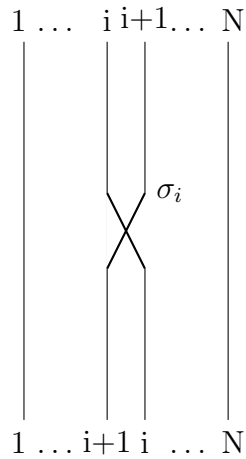

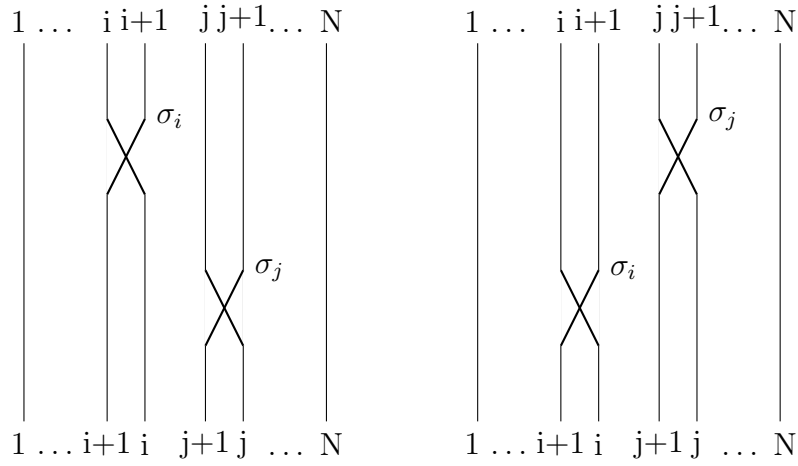Figure 14.1: A pictorial diagram of a transposition σ_i

Figure 14.2: A pictorial diagram of a transposition $\sigma_i \sigma_j$ on the left and $\sigma_j \sigma_i$ on the right, where $|i - j| > 2$
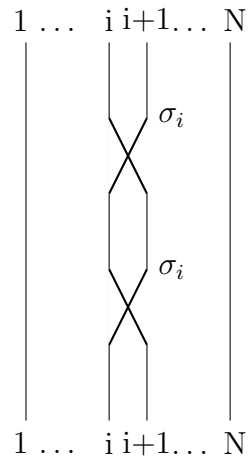
Figure 14.3: A pictorial diagram of a transposition $(\sigma_i)^2$
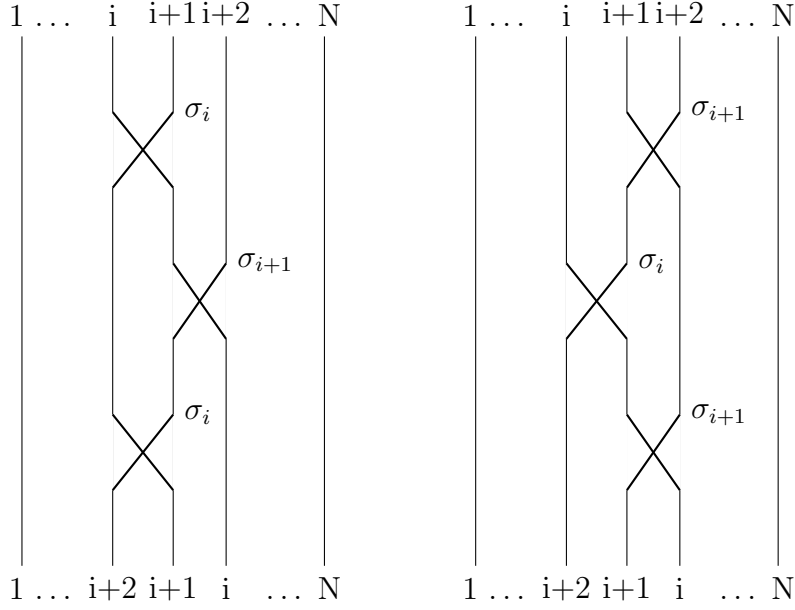
Figure 14.4: A pictorial diagram of a transposition $\sigma_i \sigma_{i+1} \sigma_i$ on the left and $\sigma_{i+1} \sigma_i \sigma_{i+1}$ on the right

14.2   Bosons and fermions

Hence, we can calculate explicitly (13.4), which is

$$\alpha_P = \alpha_1 + \ldots \alpha_N \ , \tag{14.5}$$

where α_i is the phase factor of a transposition σ_{α_i}

$$\psi(\sigma_{\alpha_i}(x_1, \ldots x_N)) = \exp(i\alpha_i)\psi(x_1, \ldots x_N) \ .$$

Proof. In fact, using (14.1)

$$\begin{aligned}
\psi(P(x_1, \ldots x_N)) &= \psi((\sigma_{\alpha_1} \ldots \sigma_{\alpha_N})(x_1, \ldots x_N)) \\
&= \exp(i\alpha_1)\psi((\sigma_{\alpha_2} \ldots \sigma_{\alpha_N})) \\
&\ \ \vdots \\
&= \exp(i\alpha_1) \ldots \exp(i\alpha_N)\psi(x_1, \ldots x_N) \\
&= \exp(i(\alpha_1 + \ldots \alpha_N))\psi(x_1, \ldots x_N) \\
&= \exp(i\alpha_P)\psi(x_1, \ldots x_N) \ .
\end{aligned}$$

q.e.d.

Furthermore, there are only two possibilities for α_P

1. $\alpha_P = 0$ and $\exp(i\alpha_P) = 1$, which correspond respectively to a bosonic totally symmetric wavefunction, i.e. under P

$$\psi(x_1, \ldots x_N) \overset{P}{\mapsto} (+1)\psi(x_1, \ldots x_N) \ ,$$

2. $\alpha_P = \pi$ and $\exp(i\alpha_P) = \text{sgn}(P)$, which correspond respectively to a fermionic totally antisymmetric wavefunction, i.e. under P

$$\psi(x_1, \ldots x_N) \overset{P}{\mapsto} \text{sgn}(P)\psi(x_1, \ldots x_N) = \begin{cases} +\psi(x_1, \ldots x_N) & \text{sign(P)} = +1 \\ -\psi(x_1, \ldots x_N) & \text{sign(P)} = \text{-} 1 \end{cases} .$$

By the spin-statistic theorem, bosons, which have symmetric wavefunctions, are associated to integer spin particles and fermions, which have antisymmetric wavefunctions, are associated to half-integer spin particles.

Proof. Using (14.2)

$$\psi(x_1, \ldots x_N) \overset{\sigma_i}{\mapsto} \exp(i\alpha_i)\psi(x_1, \ldots x_N) \overset{\sigma_i\sigma_j}{\mapsto} \exp(i\alpha_i)\exp(i\alpha_j)\psi(x_1, \ldots x_N) \ ,$$

$$\psi(x_1, \ldots x_N) \overset{\sigma_j}{\mapsto} \exp(i\alpha_j)\psi(x_1, \ldots x_N) \overset{\sigma_j\sigma_i}{\mapsto} \exp(i\alpha_j)\exp(i\alpha_i)\psi(x_1, \ldots x_N) \ ,$$

hence

$$\exp(i\alpha_i)\exp(i\alpha_j) = \exp(i\alpha_j)\exp(i\alpha_i) \ ,$$

which means that they commute

$$\alpha_i + \alpha_j = \alpha_j + \alpha_i \ . \tag{14.6}$$

Using (14.3)

$$\psi(x_1, \ldots x_N) \overset{\sigma_i}{\mapsto} \exp(i\alpha_i)\psi(x_1, \ldots x_N)$$
$$\overset{\sigma_i\sigma_{i+1}}{\mapsto} \exp(i\alpha_i)\exp(i\alpha_{i+1})\psi(x_1, \ldots x_N)$$
$$\overset{\sigma_i\sigma_{i+1}\sigma_i}{\mapsto} \exp(i\alpha_i)\exp(i\alpha_{i+1})\exp(i\alpha_i)\psi(x_1, \ldots x_N) \ ,$$

$$\psi(x_1, \ldots x_N) \overset{\sigma_{i+1}}{\mapsto} \exp(i\alpha_{i+1})\psi(x_1, \ldots x_N)$$
$$\overset{\sigma_{i+1}\sigma_i}{\mapsto} \exp(i\alpha_{i+1})\exp(i\alpha_i)\psi(x_1, \ldots x_N)$$
$$\overset{\sigma_{i+1}\sigma_i\sigma_{i+1}}{\mapsto} \exp(i\alpha_{i+1})\exp(i\alpha_i)\exp(i\alpha_{i+1})\psi(x_1, \ldots x_N) \ ,$$

hence

$$\exp(i\alpha_i)\exp(i\alpha_{i+1})\exp(i\alpha_i) = \exp(i\alpha_{i+1})\exp(i\alpha_i)\exp(i\alpha_{i+1}) \ ,$$

which means that

$$\alpha_i + \alpha_{i+1} + \alpha_i = \alpha_{i+1} + \alpha_i + \alpha_{i+1} \ . \tag{14.7}$$

Putting together this two properties (14.6) and (14.7), we have

$$\alpha_i + \alpha_{i+1} + \alpha_i = \alpha_{i+1} + \alpha_i + \alpha_{i+1} \ ,$$

$$\cancel{\alpha_{i+1}} + \cancel{\alpha_i} + \alpha_i = \cancel{\alpha_{i+1}} + \cancel{\alpha_i} + \alpha_{i+1} \ ,$$

$$\alpha_i = \alpha_{i+1} \ .$$

Therefore, $\forall i = 1, \ldots N - 1$ and $\alpha_i \in [0, 2\pi[$ we have $\alpha_i = \alpha_{i+1} = \alpha$.
Using (14.4)

$$\exp(i\alpha)^2 = \exp(2i\alpha) = \mathbb{I} = \exp(0) \ ,$$

which means that

$$\alpha = 0, \pi \ .$$

Finally, there are only two possibilities

$$\psi(x_1, \ldots x_N) \xrightarrow{\sigma_i} \underbrace{\exp(i0)}_{+1} \psi(x_1, \ldots x_N) = \psi(x_1, \ldots x_N)$$

and

$$\psi(x_1, \ldots x_N) \xrightarrow{\sigma_i} \underbrace{\exp(i\pi)}_{-1} \psi(x_1, \ldots x_N) = -\psi(x_1, \ldots x_N) \ .$$

$$\text{q.e.d.}$$

The Hilbert space of indistinguishable particle is smaller than the distinguishable one, because we have seen that the phase factor can only have two possible values. In the next chapters, we will see how we can describe such spaces, in terms of the symmetrised or antisymmetrised Hilbert space $\mathcal{H}_{S/A}$ in the language of first quantisation and in terms of the Fock space $\mathcal{F}_{B/F}$ in the language of second quantisation.

Chapter 15

First quantisation

15.1 Symmetric/antisymmetric Hilbert space

2 particles

Consider 2 particles. If they are distinguishable, the total Hilbert space is

$$\mathcal{H}_{tot} = \mathcal{H} \otimes \mathcal{H} \ ,$$

whereas if the particles are indistinguishable, we can decomposed the Hilbert space into

$$\mathcal{H}_{tot} = \mathcal{H}_S \oplus_\perp \mathcal{H}_A \ .$$

Proof. In fact, given two states $|a\rangle_1 \in \mathcal{H}_1$ and $|b\rangle_2 \in \mathcal{H}_2$, we have

$$
\begin{aligned}
|a\rangle_1 |b\rangle_2 &= \frac{2}{2}|a\rangle_1 |b\rangle_2 + \frac{1}{2}|b\rangle_1 |a\rangle_2 - \frac{1}{2}|b\rangle_1 |a\rangle_2 \\
&= \underbrace{\frac{|a\rangle_1 |b\rangle_2 + |b\rangle_1 |a\rangle_2}{2}}_{|\psi_S\rangle} + \underbrace{\frac{|a\rangle_1 |b\rangle_2 - |b\rangle_1 |a\rangle_2}{2}}_{|\psi_A\rangle} \\
&= |\psi_S\rangle + |\psi_A\rangle \ .
\end{aligned}
$$

Furthermore, the permutation group for 2 particles is $P_2 = \{\mathbb{I}, \sigma\}$. The symmetric part $|\psi_S\rangle \in \mathcal{H}_S$, since

$$\sigma|\psi_S\rangle = \sigma\frac{|a\rangle_1 |b\rangle_2 + |b\rangle_1 |a\rangle_2}{2} = \frac{|b\rangle_1 |a\rangle_2 + |a\rangle_1 |b\rangle_2}{2} = \frac{|a\rangle_1 |b\rangle_2 + |b\rangle_1 |a\rangle_2}{2} = |\psi_S\rangle \ ,$$

where we used the commutativity property. The antysymmetric part is $|\psi_A\rangle \in \mathcal{H}_A$, since

$$\sigma|\psi_A\rangle = \sigma\frac{|a\rangle_1 |b\rangle_2 - |b\rangle_1 |a\rangle_2}{2} = \frac{|b\rangle_1 |a\rangle_2 - |a\rangle_1 |b\rangle_2}{2} = -\frac{|a\rangle_1 |b\rangle_2 - |b\rangle_1 |a\rangle_2}{2} = -|\psi_A\rangle \ ,$$

where we used the commutativity property. Finally, the decomposition is orthogonal, since

$$\langle\psi_S|\psi_A\rangle = \frac{\langle a|_1\langle b|_2 + \langle b|_1\langle a|_2}{2}\frac{|a\rangle_1|b\rangle_2 - |b\rangle_1|a\rangle_2}{2}$$

$$= \frac{1}{4}(\underbrace{\langle a|a\rangle_1}_{1}\underbrace{\langle b|b\rangle_2}_{1} - \langle a|b\rangle_1\langle b|a\rangle_2 + \langle b|a\rangle_1\langle a|b\rangle_2 - \underbrace{\langle b|b\rangle_1}_{1}\underbrace{\langle a|a\rangle_2}_{1})$$

$$= \frac{1}{4}(-\langle a|b\rangle_1\langle b|a\rangle_2 + \langle b|a\rangle_1\langle a|b\rangle_2)$$

and

$$-\langle\psi_S|\psi_A\rangle = -\frac{\langle a|_1\langle b|_2 + \langle b|_1\langle a|_2}{2}\frac{|a\rangle_1|b\rangle_2 - |b\rangle_1|a\rangle_2}{2}$$

$$= -\frac{1}{4}(\underbrace{\langle a|a\rangle_1}_{1}\underbrace{\langle b|b\rangle_2}_{1} - \langle a|b\rangle_1\langle b|a\rangle_2 + \langle b|a\rangle_1\langle a|b\rangle_2 - \underbrace{\langle b|b\rangle_1}_{1}\underbrace{\langle a|a\rangle_2}_{1})$$

$$= -\frac{1}{4}(-\langle a|b\rangle_1\langle b|a\rangle_2 + \langle b|a\rangle_1\langle a|b\rangle_2)$$

$$= \frac{1}{4}(-\langle a|b\rangle_2\langle b|a\rangle_1 + \langle b|a\rangle_2\langle a|b\rangle_1)\ ,$$

which means that $\langle\psi_S|\psi_A\rangle = -\langle\psi_S|\psi_A\rangle$. Therefore, the only solution is $\langle\psi_S|\psi_A\rangle = 0$.
                                                                                          q.e.d.

Notice that Pauli's exclusion principle is encoded into the antysymmetric part, because if $a = b$ we have $|\psi_A\rangle = 0$.

The decomposition is equivalent to define two orthogonal projectors: the symmetriser

$$\hat{S}\colon \mathcal{H} \to \mathcal{H}_S$$

and the antisymmetriser

$$\hat{A}\colon \mathcal{H} \to \mathcal{H}_A\ ,$$

such that they satisfy the properties

$$\hat{S}^\dagger = \hat{S}\ ,\quad \hat{A}^\dagger = \hat{A}\ ,\quad \hat{S}^2 = \hat{S}\ ,\quad \hat{A}^2 = \hat{A}\ ,\quad \hat{S}\hat{A} = \hat{A}\hat{S} = 0\ . \tag{15.1}$$

N particles

Generalising for N particles, if they are distinguishable, the total Hilbert space is

$$\mathcal{H}_{tot} = \mathcal{H} \otimes \ldots \mathcal{H}$$

and a state is $|\psi\rangle = |a_1\rangle_1 \ldots |a_N\rangle_N = |1,\ldots N\rangle$ where $|a_j\rangle \in \mathcal{H}$.

However, if the particle are indistinguishable, similarly to the 2 particles case, we can define the symmetriser

$$\hat{S} \colon |\psi\rangle \mapsto \frac{1}{N!} \sum_{P \in P_N} |P(1), \dots P(N)\rangle$$

and the antisymmetriser

$$\hat{A} \colon |\psi\rangle \mapsto \frac{1}{N!} \sum_{P \in P_N} sgn(P)|P(1), \dots P(N)\rangle \ ,$$

where $P(1, \dots N) \mapsto (P(1), \dots P(N))$. They satisfy the orthogonal projector properties (15.1). Notice that for $N > 2$ particles, the total Hilbert space is $\mathcal{H}_{tot} = \mathcal{H}_S \otimes \mathcal{H}_A \otimes \mathcal{H}'$, where bosons work only in $\mathcal{H}_S$, fermions work only in $\mathcal{H}_A$ and $\mathcal{H}'$ is not physical.

Example 15.1. For $N = 3$, we can have $\psi_S \in mathcalH_S$

$$\psi_S = \hat{S}\psi = \psi(1,2,3) + \psi(1,3,2) + \psi(2,1,3) + \psi(2,3,1) + \psi(3,1,2) + \psi(3,2,1)$$

and $\psi_A \in mathcalH_A$

$$\psi_A = \hat{A}\psi = \psi(1,2,3) - \psi(1,3,2) - \psi(2,1,3) + \psi(2,3,1) + \psi(3,1,2) - \psi(3,2,1) \ .$$

However, we can also have $\psi' \in \mathcal{H}'$ such that

$$\psi' = \psi(1,2,3) + \psi(1,3,2) - \psi(2,1,3) - \psi(2,3,1) + \psi(3,1,2) + \psi(3,2,1) \ .$$

For N distinguishable particle, consider an orthonormal basis for the total Hilbert space

$$\{u_{\alpha_1}(x_1) \dots u_{\alpha_N}(x_N)\}_{\alpha_1, \dots \alpha_N = 0}^{\infty} \ ,$$

where $\{u_{\alpha_K}(x_k)\}_{\alpha_k = 1}^{\infty}$ is an orthonormal basis for a single Hilbert space $\mathcal{H}_1$. Notice that they are labelled by the ordered set $(\alpha_1, \dots \alpha_N)$ and we are specifying which particle is in which states.

In order to construct an orthonormal basis for $\mathcal{H}_A$ and $\mathcal{H}_S$ for N indistinguishable particles, we project the distinguishable orthonormal basis respectively with the antisymmetriser and the symmetriser

$$|n_1, \dots n_j, \dots\rangle = C \begin{cases} \hat{S} \\ \hat{A} \end{cases} u_{\alpha_1}(x_1) \dots u_{\alpha_N}(x_N) \ .$$

By the properties of the projectors, they are orthonormal but they are not normalised. Therefore, we need to choose a normalisation constant

$$C = \begin{cases} \sqrt{\frac{N!}{n_1! \dots n_k! \dots}} & \mathcal{H}_S \\ \sqrt{N!} & \mathcal{H}_A \end{cases} \ .$$

On the contrary for the distinguishable case, now we lose information, because we know only how many particle are in each state and not anymore which is in which state. We label the states with $n_1, \ldots n_k, \ldots$ with $j = 1, \ldots \infty$, which are the occupation number. For bosons, we have $n_k = 0, 1, \ldots, \infty$, whereas for fermions, we have $n_k = 0, 1$. For both cases, there is the constrain $N = \sum_k n_k$, which is an infinite sum but mostly are zero occupied. Moreover, given the set α_k, we uniquely determine the occupation number n_k, but given the occupation number n_k, we use the symmetric or antisymmetric property to uniquely determine the state, because it is in $1 - 1$ correspondence to the set n_k.

Nonetheless, there is another way to describe fermionic or bosonic quantum space in a intrinsic way, called the second quantisation because we make a further quantisation, promoting fields to operators.

Chapter 16

Second quantisation

16.1 Bosonic case

We define bosonic creation and annihilation operators such that they satisfies the properties

$$[\hat{a}, \hat{a}^\dagger]_- = \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a} = \mathbb{I} \ . \tag{16.1}$$

Furthermore, the number operator $\hat{N} = \hat{a}^\dagger\hat{a}$ such that

$$[\hat{N}, \hat{a}] = -\hat{a} \ , \quad [\hat{N}, \hat{a}^\dagger] = \hat{a}^\dagger \ .$$

By analogy with the harmonic oscillator, the ground state is the vacuum

$$\hat{a}|0\rangle = 0 \ ,$$

and a generic state is defined by the ladder operators

$$|\psi\rangle = \frac{1}{\sqrt{n!}}(\hat{a}^\dagger)^N|0\rangle \ .$$

16.2 Fermionic case

We define fermionic creation and annihilation operators such that they satisfies the properties

$$[\hat{a}, \hat{a}^\dagger]_+ = \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a} = \mathbb{I} \ . \tag{16.2}$$

Furthermore, the number operator $\hat{N} = \hat{a}^\dagger\hat{a}$ such that

$$[\hat{N}, \hat{a}] = -\hat{a} \ , \quad [\hat{N}, \hat{a}^\dagger] = \hat{a}^\dagger \ .$$

The properties can be obtained from the Pauli matrices

$$\sigma_\pm = \sigma_1 \pm i\sigma_2 \ ,$$

such that

$$(\sigma_+)^\dagger = \sigma_- \ , \quad (\sigma_-)^\dagger = \sigma_+ \ , \quad (\sigma_+)^2 = (\sigma_-)^2 = 0 \ , \quad [\sigma_-, \sigma_+]_+ = \mathbb{I} \ .$$

By analogy with the harmonic oscillator, the ground state is the vacuum

$$\hat{a}|0\rangle = 0 \ ,$$

and a generic state is defined by the ladder operators

$$|\psi\rangle = \frac{1}{\sqrt{n!}}(\hat{a}^\dagger)^N|0\rangle \ .$$

However, the anticommutator relation ensures the validity of the Pauli's exclusion principle. In fact, we have

$$a^2 = (\hat{a}^\dagger)^2 = 0 \ .$$

16.3   Fock space

Consider a single particle Hilbert space $\mathcal{H}$ with an orthonormal basis $\{|e_n\rangle\}_{n=1}^\infty$. To each $|e_n\rangle$, we associate an annihilation and a creation operators

$$|e_n\rangle \mapsto \{\hat{a}_n, \hat{a}_n^\dagger\}_{n=1}^\infty \ ,$$

such that they satisfy

$$[\hat{a}_n, \hat{a}_m]_\pm = [\hat{a}_n^\dagger, \hat{a}_m^\dagger]_\pm = 0 \ , \quad [\hat{a}_n, \hat{a}_m^\dagger]_\pm = \delta_{nm} \ ,$$

where the minus sign correponds to the commutator (bosons) (16.1) and the plus sign to the anticommutator (fermions) (**??**).

The normalised vacuum state, which describes a no particle state, is defined by the annihilation of every annihilation operator

$$\hat{a}_n|0\rangle = 0 \quad \forall n \ .$$

It generates a subspace of dimension 1

$$\mathcal{H}_{S/A}^{(0)} = \{\lambda|0\rangle : \lambda \in \mathbb{C}\} \ . \tag{16.3}$$

Now, we define the one-particle state. For each $|e_n\rangle$, we associate a number operator $\hat{n}_k = \hat{a}_k^\dagger \hat{a}_k$ such that

$$\hat{n}_k \hat{a}_k^\dagger|0\rangle = 1\hat{a}_k^\dagger|0\rangle \ , \quad \hat{n}_{k'} \hat{a}_k^\dagger|0\rangle = 0 \quad k' \neq k \ .$$

For a n particle state, we have

$$\hat{a}_k^\dagger|0\rangle = |n_1 = 0, \ldots n_k = 1, \ldots n_N = 0\rangle = |e_k\rangle \ .$$

However, for

$$\hat{a}_{k_1}^\dagger \hat{a}_{k_2}^\dagger|0\rangle = |e_{k_1}\rangle|e_{k_2}\rangle$$

we have for fermions, if $k_1 = k_2 = k$

$$(\hat{a}_k^\dagger)^2|0\rangle = 0 \ ,$$

whereas for bosons

$$(\hat{a}_k^\dagger)^2|0\rangle \neq 0 \ .$$

Furthermore, if $k_1 \neq k_2$, we have for fermions

$$\hat{a}_{k_1}^\dagger \hat{a}_{k_2}^\dagger|0\rangle = -\hat{a}_{k_2}^\dagger \hat{a}_{k_1}^\dagger|0\rangle \ ,$$

whereas for bosons

$$\hat{a}_{k_1}^\dagger \hat{a}_{k_2}^\dagger|0\rangle = \hat{a}_{k_2}^\dagger \hat{a}_{k_1}^\dagger|0\rangle \ .$$

There is a $1-1$ correspondence between the orthonormal basis $\{|e_n\rangle\}_{n=1}^\infty$ of $\mathcal{H}$ and the orthonormal basis $\{\hat{a}_k|0\rangle\}_{k=1}^\infty$ of $\mathcal{H}_{S/A}$. Hence for N particles, we have

$$\mathcal{H}_{S/A}^{(N)} = \{|n_1, \ldots n_k, \ldots\rangle = \frac{1}{\sqrt{\prod_j n_j}}(\hat{a}_1^\dagger)^{n_1} \ldots (\hat{a}_k^\dagger)^{n_k} \ldots |0\rangle\} \ .$$

If N is not fixed, like the passage from canonical to grancanonicl ensemble, the total Fock space is

$$\mathcal{F} = \bigoplus_{N=0}^\infty \mathcal{H}_{S/A}^{(N)} \ .$$

It satisfies the following properties

1. orthonormality, i.e.

$$\langle n'_1, \ldots n'_k, \ldots |n_1, \ldots n_k, \ldots\rangle = \delta_{n'_1, n_1} \ldots \delta_{n'_k, n_k} \ldots \ ,$$

2. annihilation $\hat{a}_k \colon \mathcal{H}_{S/A}^{(N)} \to \mathcal{H}_{S/A}^{(N-1)}$, i.e.

$$\hat{a}_k|n_1, \ldots n_k, \ldots\rangle = \eta_k \sqrt{n_k}|n_1, \ldots (n_k - 1), \ldots\rangle \ ,$$

where for bosons $\eta_k = 1$ and for fermions $\eta_k = (-1)^{\sum_{j<k} n_j}$,

3. creation $\hat{a}_k^\dagger \colon \mathcal{H}_{S/A}^{(N)} \to \mathcal{H}_{S/A}^{(N+1)}$, i.e. for bosons

$$\hat{a}_k^\dagger|n_1, \ldots n_k, \ldots\rangle = \sqrt{n_k + 1}|n_1, \ldots (n_k + 1), \ldots\rangle \ ,$$

and for fermions

$$\hat{a}_k^\dagger|n_1, \ldots n_k, \ldots\rangle = \eta_k \sqrt{1 - n_k}|n_1, \ldots (n_k + 1), \ldots\rangle \ ,$$

4. number operator $\hat{n}_k = \hat{a}_k^\dagger \hat{a}_k$ such that

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

and the total number operator $\hat{N} = \sum_k \hat{n}_k \sum_k \hat{a}_k^\dagger \hat{a}_k$ such that

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

16.4   Field operators

In the first quantisation, we quantise observables to operators, while, in the second quantisation, we quantise fields to operators. Now, a generic particle state is represented by $|f\rangle = \sum_k f_k |e_k\rangle \in \mathcal{H}$, which is equivalent to $sum_k f_k \hat{a}_k^\dagger |0\rangle$. Hence, we define the field operators

$$\hat{\psi}^\dagger(f) = \sum_k f_k \hat{a}_k^\dagger \ , \quad \hat{\psi}(f) = \sum_k f_k^* \hat{a}_k \ ,$$

in order to get a state $\hat{\psi}(f)|0\rangle$. The related commutator relations become

$$[\hat{\psi}(f), \hat{\psi}^\dagger(g)]_\pm = \langle f|g \rangle \mathbb{I} \ .$$

Proof. In fact,

$$[\hat{\psi}(f), \hat{\psi}^\dagger(g)]_\pm = [\sum_k f_k^* \hat{a}_k, \sum_m g_m \hat{a}^\dagger]_\pm = \sum_k \sum_m f_k^* g_m \underbrace{[\hat{a}_k, \hat{a}_m^\dagger]}_{\delta_{km}\mathbb{I}} = \sum_k \sum_m f_k^* g_m \underbrace{\delta_{km}}_{k=m} \mathbb{I} = \sum_k f_k^* g_k \mathbb{I} = \langle f|$$

where we have used $|f\rangle \sum_k f_k |e_k\rangle$, $|g\rangle = \sum_m g_m |e_m\rangle$ and $\langle f|g \rangle = \sum_k \sum_m f_k^* g_m \underbrace{\langle e_k|e_m \rangle}_{\delta_{km}} =$

$\sum_k f_k^* g_k$.   q.e.d.

Consider a single particle state in $\mathcal{H} = L^2(\mathbb{R}^d) \ni \psi(x)$ with an orthonormal basis $u_k(x)$ such that to each ket there are ladder operators $\hat{a}_k$ and $\hat{a}_k^\dagger$. Hence $L^2(\mathbb{R}^d) \ni f(x) = \sum_k f_k u_k(x)$ and we define field operators

$$\hat{\psi}(x) = \sum_k u_k^*(x) \hat{a}_k \ , \quad \hat{\psi}^\dagger(x) = \sum_k u_k(x) \hat{a}_k^\dagger \ ,$$

which is alinear superposition of annihilation and creation operators. Actually, it is called an operator-valued function because its output is an operator. In fact

$$\int_{\mathbb{R}^d} d^d x \ \psi^\dagger(x) \sum_k u_k^*(x) \hat{a}_k^\dagger = \sum_k \hat{a}_k^\dagger \int_{\mathbb{R}^d} d^d x \ u_k^*(x) f(x) = \sum_k \hat{a}_k^\dagger f_k \ ,$$

where we have exchanged sum and integral because they are convergent.

The commutation relations are

$$[\psi(x), \psi^\dagger(y)] = \mathbb{I}\delta(x - y) \ .$$

Proof. In fact,

$$[\hat{\psi}(f), \hat{\psi}^\dagger(g)]_\pm = [\int d^d x \ f^*(x)\hat{\psi}(x), \int d^d y \ g(y)\hat{\psi}^\dagger(y)]_\pm = \int d^d x \int d^d y \ f^*(x)g(y)[\psi(x), \psi^\dagger(y)] \ ,$$

which must be equal to

$$\langle f|g \rangle = \int d^d x \ f^*(x)g(x) \ .$$

Hence

$$[\psi(x), \psi^\dagger(y)] = \mathbb{I}\delta(x - y) \ .$$

q.e.d.

For instance, a plane wave $u(x) = \exp(i\mathbf{k} \cdot \mathbf{x})$ and $\hat{\psi}(x) = \sum_k \hat{a}_k^\dagger \exp(i\mathbf{k} \cdot \mathbf{x})$. Notice that field operators are basis independent

16.5   Operators

Consider a Fock space $\mathcal{F} = \bigoplus_{N=0}^\infty \mathcal{H}_{B/F}^{(N)}$ with orthonormal basis $|n_1, \ldots n_k, \ldots\rangle = \frac{1}{\sqrt{\Pi_j n_j!}}(\hat{a}_1^\dagger)^{n_1} \ldots (\hat{a}_k^\dagger)^{n_k} \ldots |0\rangle$, which is in $1 - 1$ correspondence to the orthonormal basis $\psi_{n_1 \ldots n_k \ldots}(x_1, \ldots x_k, \ldots) = c_N \begin{bmatrix} \hat{S} \\ \hat{A} \end{bmatrix} u_{\alpha_1}(x_1) \ldots u_{\alpha_k}(x_k) \ldots$, where $hatS$ is the symmetriser and $\hat{A}$ is the antisymmetriser.

We define a one-body operator, associated to a system in which all the particles are the same, as

$$\hat{O}^{(1)} = \sum_{j=1}^N \hat{O}(\hat{p}_j, \hat{x}_j) \ .$$

Since it is self-adjoint, it exists an orthonormal basis of eigenvalues $\{u_\alpha(x)\}$, such that

$$\hat{O}(\hat{p}, \hat{x})u_\alpha(x) = \epsilon_\alpha u_\alpha(x) \ .$$

Since

$$\hat{O}^{(1)}\psi_{n_1\ldots n_k\ldots}(x_1,\ldots x_k,\ldots) = \Big(\sum_{j=1}^{\infty}\hat{O}(\hat{p}_j,\hat{x}_j)\Big)\psi_{n_1\ldots n_k\ldots}(x_1,\ldots x_k,\ldots)$$

$$= \Big(\sum_{j=1}^{\infty}\hat{O}(\hat{p}_j,\hat{x}_j)\Big)c_N\begin{bmatrix}\hat{S}\\\hat{A}\end{bmatrix}u_{\alpha_1}(x_1)\ldots u_{\alpha_k}(x_k)\ldots$$

$$= c_N\begin{bmatrix}\hat{S}\\\hat{A}\end{bmatrix}\Big(\sum_{j=1}^{\infty}\hat{O}(\hat{p}_j,\hat{x}_j)u_{\alpha_1}(x_1)\ldots u_{\alpha_k}(x_k)\ldots\Big)$$

$$= c_N\begin{bmatrix}\hat{S}\\\hat{A}\end{bmatrix}\Big(\sum_{j=1}^{\infty}u_{\alpha_1}(x_1)\ldots\underbrace{\hat{O}(\hat{p}_j,\hat{x}_j)u_{\alpha_j}(x_j)}_{\epsilon_{\alpha_j}u_{\alpha_j}(x_j)}\ldots\Big)$$

$$= \Big(\sum_{j=1}^{\infty}\epsilon_j n_j\Big)\psi_{n_1\ldots n_k\ldots}(x_1,\ldots x_k,\ldots)\ .$$

For the Fock space, we have

$$\hat{O}_F^{(1)} = \sum_{j=1}^{\infty}\epsilon_j\hat{n}_j = \sum_{j=1}^{\infty}\epsilon_j\hat{a}_j^{\dagger}\hat{a}_j\ ,$$

where

$$\epsilon_j = \langle u_j(x)|\hat{O}(\hat{p}_j,\hat{x}_j)|u_j(x)\rangle\ .$$

Hence

$$\hat{O}_F^{(1)} = \sum_{j=1}^{\infty}\langle u_j(x)|\hat{O}(\hat{p}_j,\hat{x}_j)|u_j(x)\rangle\hat{a}_j^{\dagger}\hat{a}_j\ .$$

Since it is dependent of the basis, because we choose the eigenbasis, we choose a different arbitrary basis

$$\psi^{\dagger}(x) = \sum_k u_k(x)\hat{a}_k^{\dagger} = \sum_m v_m(x)b_m^{\dagger}\ ,$$

and we define the one-body operator

$$\hat{O}_F^{(1)} = \int d^dx\ \hat{\varphi}^{\dagger}(x)\hat{O}(\hat{p},\hat{x})\hat{\varphi}(x)\ , \tag{16.4}$$

which this time is basis independent.

Proof. In fact

$$\int d^d x \; \hat{\varphi}^\dagger(x)\hat{O}(\hat{p},\hat{x})\hat{\varphi}(x) = \int d^d x \; \Big(\sum_k u_k(x)\hat{a}^\dagger(x)\Big)\hat{O}(\hat{p},\hat{x})\Big(\sum_m u_m^*(x)\hat{a}_m(x)\Big)$$

$$= \sum_k \sum_m \hat{a}_k^\dagger \hat{a}_m \int d^d x \; u_k(x)\underbrace{\hat{O}(\hat{p},\hat{x})u_m^*(x)}_{\epsilon_m u_m^*(x)}$$

$$= \sum_k \sum_m \hat{a}_k^\dagger \hat{a}_m \epsilon_m \underbrace{\int d^d x \; u_k(x)u_m^*(x)}_{\delta_{km}}$$

$$= \sum_k \sum_m \hat{a}_k^\dagger \hat{a}_m \epsilon_m \underbrace{\delta_{km}}_{k=m}$$

$$= \sum_k \hat{a}_k^\dagger \hat{a}_k \epsilon_k = \hat{O}_F^{(1)} \; .$$

q.e.d.

It can be written as

$$\hat{O}_F^{(1)} = \sum_k \sum_m t_{km}\hat{b}_k^\dagger \hat{h}_m \; ,$$

where the transition amplitude is

$$t_{km} = \langle v_k|\hat{O}(\hat{p},\hat{x})|v_m\rangle \; .$$

To summarise, the onebody operator is

$$\hat{O}_F^{(1)} = \begin{cases} \sum_{mm'} t_{mm'}\hat{b}_m^\dagger \hat{b}_m & \text{arbitrary basis} \\ \sum_k \epsilon_k \hat{a}_k^\dagger \hat{a}_k & \text{eigenbasis} \end{cases} \; .$$

16.6   Examples

The density operator of a single particle j is

$$\hat{\rho}_j = \delta(x - x_j)$$

and the corresponding field operator is

$$\hat{\varphi}(x_j) = \int d^d x \psi(x)\delta(x - x_j) \; .$$

The onebody operator is

$$\hat{\rho}^{(1)} = \sum_{j=1}^N \delta(x - x_j) \; ,$$

which in the basis independent definition (16.4) on the Fock space

$$\hat{\rho}_F = \int d^d y \hat{\psi}^\dagger(y)\delta(x-y)\hat{\psi}(y) = \hat{\psi}^\dagger \hat{\psi} = \sum_{kk'} u_k^*(x)u_{k'}(x)\hat{a}_k^\dagger \hat{a}_{k'} \ .$$

The number of particle operator is

$$\hat{N} = \int d^d x \hat{\rho}_F^{(1)}(x) = \int d^d x \sum_{kk'} u_k^*(x)u_{k'}(x)\hat{a}_k^\dagger \hat{a}_{k'} = \sum_{kk'} \hat{a}_k^\dagger \hat{a}_{k'} \underbrace{\int d^d x u_k^*(x)u_{k'}(x)}_{\delta_{kk'}} = \sum_{kk'} \hat{a}_k^\dagger \hat{a}_{k'} \underbrace{\delta_{kk'}}_{k=k'} = \sum_k$$

which is consistent with the definition of ρ since it can be seen as a density of particle whose intergral is indeed the number of particles.

Free non-relativistic 3-dimensional particles

Consider the hamiltonian of a single particle described by the wave function $\psi(x) \in L^2(\mathbb{R}^d)$

$$\hat{H}_1 = \frac{\hbar^2 \hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\nabla_x^2 \ .$$

The onebody operator for N particles is

$$\hat{H} = \sum_{j=1}^N \frac{\hbar^2 hatp_j^2}{2m} = -\sum_{j=1}^N \frac{\hbar^2}{2m}\nabla_{x_j}^2 \ .$$

On the Fock space, it becomes

$$H = \sum_k \epsilon_k \hat{a}_k^\dagger \hat{a}_k \ ,$$

where

$$\hat{H}_1 u_k(x) = -\frac{\hbar^2}{2m}u_k(x) = \epsilon_k u_k(x) \ .$$

However, wave plane solutions do not belong in $u_k(x) \sim \exp(i\mathbf{k}\cdot\mathbf{x}) \notin L^2(\mathbb{R}^d)$, because they are not normalisable. The trick is to go into a finite volume V and consider the space $L^2(V)$. The simple example is the particle in a cube of length L describer by the coordinates $(x,y,z) \in [0,L]$. The Schoredinger's equation becomes

$$-\frac{\hbar^2}{2m}\nabla_x^2 u_k(x,y,z) = \epsilon_k u_k(x,y,z) \ .$$

Now, we do not choose the Dirichlet or the Neumann boundary condition, but we choose the periodic boundary conditions

$$\begin{cases} u(x=0,y,z) = u(x=L,y,z) \\ u(x,y=0,z) = u(x,y=L,z) \\ u(x,y,z=0) = u(x,y,z=L) \end{cases} \ ,$$

which trasforms the cube into a 3-torus.

The ansatz solution is
$$u_\alpha(\mathbf{x}) = c \exp(i\mathbf{k} \cdot \mathbf{x}) \ ,$$
where c is a normalisation constant and
$$\nabla_2 u_\alpha(\mathbf{x}) = -(k_x^2 + k_y^2 + k_z^2)u_\alpha(\mathbf{x}) = \epsilon_\mathbf{k} = -k^2 \ .$$
Imposing the periodic boundary conditions, we obtain
$$u_\mathbf{k}(0, y, z) = \cancel{c}\exp(i(\cancel{k_y y} + \cancel{k_z z})) = u_\mathbf{k}(L, y, z) = \cancel{c}\exp(i(k_x L + \cancel{k_y y} + \cancel{k_z z})) \ ,$$
hence
$$\exp(ik_x L) = 0$$
and
$$k_x = \frac{2\pi}{L}n_x \ ,$$
where $n \in \mathbb{Z}$ is an integer number. Simiarly for y and z, we have
$$\mathbf{k} = (k_x, k_y, k_z) = \frac{2\pi}{L}\mathbf{n} = \frac{2\pi}{L}(n_x, n_y, n_z)$$
where $n_x, n_y, n_z \in \mathbb{Z}$. Finally, the energy eigenvalues are
$$\epsilon_{n_x, n_y, n_z} = -\frac{4\pi^2}{L^2}(n_x^2 + n_y^2 + n_z^2)$$
and the eigenstates are
$$u_{n_x, n_y, n_z} = c \exp(i\frac{2\pi}{L}(n_x x + n_y y + n_z z)) \in L^2(V) \ .$$
The normalisation constant is
$$C = \frac{1}{\sqrt{V}} \ .$$
In fact
$$1 = ||u_{n_x, n_y, n_z}||^2 = \int_V dx \ dy \ dz \ |c|^2 |\exp(i\mathbf{k} \cdot \mathbf{x})|^2 = |c|^2 V \ .$$
Hence, the onebody operator is
$$\hat{O}^{(1)} = \sum_{j=1}^N \frac{\hat{p}_j^2}{2m} = -\sum_{j=1}^N \frac{\hbar^2}{2m}\nabla_{\mathbf{x}_j}^2 \ ,$$
and choosing the orthonormal basis of wavefunctions, we have in the Fock space
$$\hat{O}_F = \sum_\mathbf{k} \epsilon_\mathbf{k}\hat{a}_\mathbf{k}^\dagger\hat{a}_\mathbf{k} \ ,$$
where $\mathbf{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$ and $\epsilon_\mathbf{k} = \frac{\hbar^2}{2m}k^2$.

Interaction potential

Now, consider a different operator than the onebody one: the two particles operatior, used to describe interaction potential

$$\hat{O}^{(2)} = \sum_{i<j} V(x_i, x_j) = \frac{1}{2} \int dx \int dy V(x,y) \hat{\psi}^\dagger(x) \hat{\psi}^\dagger(y) \psi(y) \psi(x) \ ,$$

or

$$\hat{O}^{(2)} = \frac{1}{2} \sum_{ijkl} V_{ijkl} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k \hat{a}_l \ ,$$

where the first expression is basis-independent, while in the last one it is in the eigenbasis.

Proof. Maybe in the future.   q.e.d.

Part V

Quantum statistical mechanics

Chapter 17

Microcanonical ensemble

The microcanonical ensemble is characterised by constant volume, energy and number of particle. Since N is fixed, we can work in the Hilbert space $\mathcal{H}_{tot}$. Given a time-independent hamiltonian operator $\hat{H}$, we find the energy eigenbasis $|\psi_j\rangle \in \mathcal{H}_{tot}$

$$\hat{H}|\psi_j\rangle = E_j|\psi_j\rangle \ .$$

However, there could be some degeneracy we want to consider, i.e. $E_{j,\alpha} = E_{j,\beta}$ for $|\psi_{j,\alpha}\rangle \neq |\psi_{j,\beta}\rangle$. Therefore, we have

$$\hat{H}|\psi_{j,\alpha}\rangle = E_j|\psi_{j,\alpha}\rangle \ , \tag{17.1}$$

where $\alpha = 1, \ldots n_j$.

The density operator for mixed states is (13.9)

$$\rho_{mc} = \sum_{\alpha=1}^{n_j} p_\alpha |\psi_{j,\beta}\rangle\langle\psi_{j,\beta}| \ ,$$

where p_α is the probability for the eigenstate $|\psi_{j,\beta}\rangle$. Since $E = E_j$ is fixed, all the eigenstates have the same probability to occur. Therefore $p_\alpha = \frac{1}{n_j}$ and

$$\rho_{mc} = \frac{1}{n_j}\sum_{\alpha=1}^{n_j} |\psi_{j,\alpha}\rangle\langle\psi_{j,\alpha}| = \frac{1}{n_j}\hat{P}_j \ ,$$

where

$$P_j = \sum_{\alpha=1}^{n_j} |\psi_{j,\alpha}\rangle\langle\psi_{j,\alpha}|$$

is the projector onto the energy eigenspace. Notice that we can expand the hamiltonian using (13.6)

$$\hat{H} = \sum_j E_j\hat{P}_j \ . \tag{17.2}$$

The average of an observable $\hat{A}$ in the microcanonical ensemble is

$$\langle A \rangle_{mc} = \frac{1}{n_j} \sum_{\alpha=1}^{n_j} \langle \psi_{n,\alpha} | \hat{A} | \psi_{n,\alpha} \rangle \ .$$

Proof. In fact, choosing an orthonormal basis $|e_j\rangle$, the trace is

$$\text{tr}_{\mathcal{H}_{tot}} \hat{A} = \sum_j \langle e_j | \hat{A} | e_j \rangle \ .$$

Therefore, using (13.10)

$$\begin{aligned}
\langle A \rangle_{mc} &= \text{tr}_{\mathcal{H}_{tot}} (\hat{A} \rho_{mc}) \\
&= \text{tr}_{\mathcal{H}_{tot}} \left(\hat{A} \frac{1}{n_j} \sum_{\alpha=1}^{n_j} |\psi_{j,\alpha}\rangle\langle\psi_{j,\alpha}| \right) \\
&= \frac{1}{n_j} \sum_{\alpha=1}^{n_j} \text{tr}_{\mathcal{H}_{tot}} \left(\hat{A} |\psi_{j,\alpha}\rangle\langle\psi_{j,\alpha}| \right) \\
&= \frac{1}{n_j} \sum_{\alpha=1}^{n_j} \langle \psi_{j,\alpha} | \hat{A} | \psi_{j,\alpha} \rangle \ .
\end{aligned}$$

q.e.d.

The entropy in the microcanonical ensemble is

$$S_{mc} = k_B \log n_j \ ,$$

where n_j is the number of states with $E = E_j$. Notice that it is similar to the classical case (5.2).

Proof. In fact, using (5.5)

$$S_{mc} = -k_B \langle \log \rho_{mc} \rangle_{mc} = -k_B \, \text{tr}_{\mathcal{H}_{tot}} (\rho_{mc} \log \rho_{mc}) \ .$$

In matrix notation, the density operator is

$$
\rho_{mc} = \begin{bmatrix}
\begin{bmatrix} \frac{1}{n_1} & 0 & \dots & 0 \\ 0 & \frac{1}{n_1} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \frac{1}{n_1} \end{bmatrix} & 0 & \dots & 0 & \dots & \dots \\
0 & \begin{bmatrix} \frac{1}{n_2} & 0 & \dots & 0 \\ 0 & \frac{1}{n_2} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \frac{1}{n_2} \end{bmatrix} & \dots & 0 & \dots & \dots \\
\dots & \dots & \dots & \dots & \dots & \dots \\
0 & 0 & \dots & \begin{bmatrix} \frac{1}{n_j} & 0 & \dots & 0 \\ 0 & \frac{1}{n_j} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \frac{1}{n_j} \end{bmatrix} & \dots & \dots \\
\dots & \dots & \dots & \dots & \dots & \dots \\
\dots & \dots & \dots & \dots & \dots & \dots
\end{bmatrix}
$$

$$
= \sum_j \begin{bmatrix}
0 & 0 & \dots & 0 & \dots & \dots \\
0 & 0 & \dots & 0 & \dots & \dots \\
\dots & \dots & \dots & \dots & \dots & \dots \\
0 & 0 & \dots & \begin{bmatrix} \frac{1}{n_j} & 0 & \dots & 0 \\ 0 & \frac{1}{n_j} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \frac{1}{n_j} \end{bmatrix} & \dots & \dots \\
\dots & \dots & \dots & \dots & \dots & \dots
\end{bmatrix}
$$

In order to compute the logarithm of 0, we use a trick: we define a small parameter ϵ and we make it go to zero. In this way, the limit becomes $\epsilon \log \epsilon \xrightarrow{\epsilon \to 0} = 0$. Finally, we compute the trace

$$
\mathrm{tr}_{\mathcal{H}_{tot}}(\rho_{mc} \log \rho_{mc}) = \mathrm{tr} \begin{bmatrix}
0 & 0 & \dots & 0 & \dots & \dots \\
0 & 0 & \dots & 0 & \dots & \dots \\
\dots & \dots & \dots & \dots & \dots & \dots \\
0 & 0 & \dots & \begin{bmatrix} \frac{1}{n_j} \log \frac{1}{n_j} & 0 & \dots & 0 \\ 0 & \frac{1}{n_j} \log \frac{1}{n_j} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \frac{1}{n_j} \log \frac{1}{n_j} \end{bmatrix} & \dots & \dots \\
\dots & \dots & \dots & \dots & \dots & \dots
\end{bmatrix}
$$

$$
= \sum_j \frac{1}{n_j} \log \frac{1}{n_j} = n_j \frac{1}{n_j} \log \frac{1}{n_j} = -\log n_j \ .
$$

Hence,

$$S_{mc} = -k_B \, \text{tr}_{\mathcal{H}_{tot}}(\rho_{mc} \log \rho_{mc}) = k_B \log n_j \; .$$

<div align="right">q.e.d.</div>

Notice that entropy is always a positive function, since there is at least one state occupied $n_j \geq 1$, which implies $S \geq 0$.

Chapter 18

Canonical ensemble

The canonical ensemble is characterised by constant volume, temperature and number of particle. Energy, which can be exchange in an external reservoir, can be in one of the eigenstates (17.1) with probability

$$p_j \propto \exp(-\beta E_j) \ . \tag{18.1}$$

Consider a family of projectors $\{\hat{P}_j\}$, the density matrix of a mixed states is

$$\rho_c = \frac{1}{Z_N} \sum_j \exp(-\beta E_j) \hat{P}_j = \frac{\exp(-\beta \hat{H})}{Z_N} \ ,$$

where the quantum canonical partition function is

$$Z_N(T, V) = \mathrm{tr}_{\mathcal{H}_{tot}} \left(\frac{\exp(-\beta \hat{H})}{Z_N} \right) \ .$$

Proof. For a mixed state, the density matrix is (13.9)

$$\rho_c = \sum_j p_j \hat{P}_j = C \sum_j \exp(-\beta E_j) \hat{P}_J \ ,$$

where the probability is given by (18.1) and C is a normalisation function.

Moreover, using (17.2)

$$\rho_c = C \sum_j \exp(-\beta E_j) \hat{P}_J$$

$$= C \sum_j \sum_k \frac{1}{k!} (-\beta E_j)^k \underbrace{\hat{P}_j}_{(P_j)^k}$$

$$= C \sum_j \sum_k \frac{1}{k!} (-\beta E_j \hat{P}_j)^k$$

$$= C \sum_k \frac{1}{k!} (-\beta \sum_j E_j \hat{P}_j)^k$$

$$= C \exp(-\beta \underbrace{\sum_j E_j \hat{P}_j}_{\hat{H}})$$

$$= C \exp(-\beta \hat{H}) \ ,$$

where we have used the Taylor expansion of the exponential, one of the properties of the projectors (13.2) and we have exchanged the two series.

Finally, We set $C = \frac{1}{Z_N}$, where Z_N is the quantum canonical partition function, and by the normalisation condition

$$1 = \text{tr}_{\mathcal{H}_{tot}} \rho_c = \frac{1}{Z_N} \text{tr}_{\mathcal{H}_{tot}} \exp(-\beta \hat{H}) \ ,$$

hence

$$Z_N = \text{tr}_{\mathcal{H}_{tot}} \exp(-\beta \hat{H}) \ .$$

<div align="right">q.e.d.</div>

We define the Helmoltz free energy

$$Z_N = \exp(-\beta F) \ ,$$

or equivalently

$$F = -\frac{1}{\beta} \log Z_N \ .$$

The average energy is

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

Proof. In fact,

$$
\begin{aligned}
E &= \langle \hat{H} \rangle_c \\
&= \mathrm{tr}_{\mathcal{H}_{tot}}(\hat{H} \rho_c) \\
&= \mathrm{tr}_{\mathcal{H}_{tot}} \left(\hat{H} \frac{\exp(-\beta \hat{H})}{Z_N} \right) \\
&= \frac{1}{Z_N} \mathrm{tr}_{\mathcal{H}_{tot}} \left(-\frac{\partial}{\partial \beta} \exp(-\beta \hat{H}) \right) \\
&= -\frac{1}{Z_N} \frac{\partial}{\partial \beta} \underbrace{\mathrm{tr}_{\mathcal{H}_{tot}} \exp(-\beta \hat{H})}_{Z_N} \\
&= -\frac{1}{Z_N} \frac{\partial}{\partial \beta} Z_N \\
&= -\frac{\partial}{\partial \beta} \log Z_N \ .
\end{aligned}
$$

<div align="right">q.e.d.</div>

The entropy is

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

Proof. In fact, using (5.5)

$$
\begin{aligned}
S_c &= -k_B \langle \log \rho_c \rangle_c \\
&= -k_B \, \mathrm{tr}_{\mathcal{H}_{tot}}(\rho_c \log \rho_c) \\
&= -k_B \, \mathrm{tr}_{\mathcal{H}_{tot}} \left(\frac{\exp(-\beta \hat{H})}{Z_N} \log \frac{\exp(-\beta \hat{H})}{Z_N} \right) \\
&= -k_B \, \mathrm{tr}_{\mathcal{H}_{tot}} \left(\frac{\exp(-\beta \hat{H})}{Z_N} (\log \exp(-\beta \hat{H}) - \log Z_N) \right) \\
&= -k_B \, \mathrm{tr}_{\mathcal{H}_{tot}} \left(\frac{\exp(-\beta \hat{H})}{Z_N} (-\beta \hat{H} - \log Z_N) \right) \\
&= k_B \beta \, \underbrace{\mathrm{tr}_{\mathcal{H}_{tot}} \left(\frac{\exp(-\beta \hat{H})}{Z_N} \hat{H} \right)}_{E} + k_B \, \mathrm{tr}_{\mathcal{H}_{tot}} \left(\frac{\exp(-\beta \hat{H})}{Z_N} \underbrace{\log Z_N}_{-\beta F} \right) \\
&= \frac{E}{T} - k_B \beta F \, \frac{1}{Z_N} \underbrace{\mathrm{tr}_{\mathcal{H}_{tot}}(\exp(-\beta \hat{H}))}_{Z_N} \\
&= \frac{E - F}{T} \ .
\end{aligned}
$$

<div align="right">q.e.d.</div>

Notice that the entropy is well defined because the trace of the exponential of the energy eigenvalues diverges only if they are negative. Thus, we assume that $E_j \geq \min E_j = 0$.

Chapter 19

Grancanonical ensemble

The grancanonical ensemble is characterised by constant volume, temperature and chemical potential. Since N is not fixed, we work in the full Fock space $\mathcal{F}_N$. However, we restrict the hamiltonian operator in the Fock space to the condition that it conserves the number of particles, i.e. $[\hat{H}, \hat{N}] = 0$

$$\hat{H}\Big|_{\mathcal{F}_N} = \hat{H}_N \ .$$

An example of physical system which does not satisfy this condition is a photons absorbed by an electron. Energy can be in one of the eigenstates, each for a fixed N

$$\hat{H}^{(N)}|\psi_{j,\alpha}^{(N)}\rangle = E_j^{(N)}|\psi_{j,\alpha}^{(N)}\rangle \ ,$$

with probability

$$p_j^{(N)} \propto \exp(-\beta(E_j - \mu N)) \ . \tag{19.1}$$

Consider a family of projectors $\{\hat{P}_j^{(N)}\}$

$$\hat{P}_j^N = \sum_\alpha |\psi_{j,\alpha}^{(N)}\rangle\langle\psi_{j,\alpha}^{(N)}| \ ,$$

the density matrix of a mixed states is

$$\rho_{gc} = \frac{1}{\mathcal{Z}} \sum_N \sum_j \exp(-\beta(E_j - \mu N))\hat{P}_j^{(N)} = \frac{\exp(-\beta(\hat{H} - \mu\hat{N}))}{\mathcal{Z}} \ ,$$

where $z = \exp(\beta\mu)$ is the fugacity and the quantum grancanonical partition function is

$$\mathcal{Z} = \sum_{N=0}^{\infty} \text{tr}_{\mathcal{H}_{tot}}\left(\exp(-\beta(\hat{H} - \mu\hat{N}))\right) = \sum_{N=0}^{\infty} z^N Z_N \ .$$

Proof. For a mixed state, the density matrix is (13.9)

$$\rho_{gc} = \sum_N \sum_j p_j \hat{P}_j^{(N)} = C \sum_N \sum_j \exp(-\beta(E_j^{(N)} - \mu N)) \hat{P}_j^{(N)} \ ,$$

where the probability is given by (19.1) and C is a normalisation function.

Moreover, using (17.2) and (**??**)

$$\rho_{gc} = C \sum_N \sum_j \exp(-\beta(E_j - \mu N)) \hat{P}_j^{(N)}$$

$$= C \sum_N \sum_j \sum_k \frac{1}{k!} (-\beta(E_j^{(N)} - \mu N))^k \underbrace{\hat{P}_j^{(N)}}_{(P_j^{(N)})^k}$$

$$= C \sum_j \sum_k \frac{1}{k!} (-\beta(E_j^{(N)} \hat{P}_j^{(N)} - \nu N P_j^{(N)}))^k$$

$$= C \sum_k \frac{1}{k!} (-\beta \sum_N \sum_j (E_j^{(N)} \hat{P}_j^{(N)} - \mu N P_j^{(N)}))^k$$

$$= C \exp(-\beta(\underbrace{\sum_j \sum_N E_j^{(N)} \hat{P}_j^{(N)}}_{\hat{H}}) - \mu \underbrace{\sum_j \sum_N N \hat{P}_j^{(N)}}_{\hat{N}})$$

$$= C \exp(-\beta(\hat{H} - \mu \hat{N})) \ ,$$

where we have used the Taylor expansion of the exponential, one of the properties of the projectors (13.2) and we have exchanged the two series.

Finally, We set $C = \frac{1}{\mathcal{Z}}$, where $\mathcal{Z}$ is the quantum canonical partition function, and by the normalisation condition

$$1 = \mathrm{tr}_{\mathcal{F}} \rho_{gc} = \sum_N \frac{1}{\mathcal{H}_{tot}} \mathrm{tr}_{\mathcal{F}} \exp(-\beta(\hat{H} - \mu \hat{N})) \ ,$$

hence

$$\mathcal{Z} = \mathrm{tr}_{\mathcal{F}} \exp(-\beta(\hat{H} - \mu \hat{N})) = \sum_{N=0}^{\infty} \mathrm{tr}_{\mathcal{H}_{tot}} \exp(-\beta(\hat{H} - \mu \hat{N})) = \sum_{N=0}^{\infty} z^N \underbrace{\mathrm{tr}_{\mathcal{H}_{tot}} \exp(-\beta \hat{H})}_{Z_N} = \sum_N z^N Z_N \ .$$

q.e.d.

Consider an observable $\hat{A}$ such that it conserves the number of particles, i.e. $[\hat{A}, \hat{N}]$, the average value is

$$\langle \hat{A} \rangle_{gc} = \mathrm{tr}_{\mathcal{F}}(\hat{A} \rho_{gc}) = \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} z^N Z_N \langle \hat{A} \rangle_c \ .$$

Proof. In fact,

$$
\begin{aligned}
\langle \hat{A} \rangle_{gc} &= \text{tr}_{\mathcal{F}}(\hat{A} \rho_{gc}) \\
&= \sum_{N=0}^{\infty} \text{tr}_{\mathcal{H}_{tot}} \left(\hat{A} \frac{z^N \exp(-\beta \hat{H})}{\mathcal{Z}} \right) = \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} z^N \, \text{tr}_{\mathcal{H}_{tot}}(\hat{A} \exp(-\beta \hat{H})) \\
&= \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} z^N Z_N \underbrace{\frac{\text{tr}_{\mathcal{H}_{tot}}(\hat{A} \exp(-\beta \hat{H}))}{Z_N}}_{\langle \hat{A} \rangle_c} \\
&= \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} z^N Z_N \langle \hat{A} \rangle_c \; .
\end{aligned}
$$

q.e.d.

We define the granpotential

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

the energy in the grancanonical is

$$
E - \mu N = \langle \hat{H} - \mu \hat{N} \rangle = -\frac{\partial}{\partial \beta} \log \mathcal{Z} \; .
$$

Proof. In fact

$$
\begin{aligned}
E - \mu N &= \langle \hat{H} - \mu \hat{N} \rangle \\
&= \text{tr}_{\mathcal{F}} \left((\hat{H} - \mu \hat{N}) \frac{\exp(-\beta(\hat{H} - \mu \hat{N}))}{\mathcal{Z}} \right) \\
&= -\frac{1}{\mathcal{Z}} \frac{\partial}{\partial \beta} \underbrace{\text{tr}_{\mathcal{F}}(\exp(-\beta(\hat{H} - \mu \hat{N})))}_{\mathcal{Z}} \\
&= -\frac{1}{\mathcal{Z}} \frac{\partial}{\partial \beta} \mathcal{Z} \\
&= -\frac{\partial}{\partial \beta} \log \mathcal{Z} \; .
\end{aligned}
$$

q.e.d.

The entropy in the grancanonical ensemble is

$$
S = \frac{E - \mu N - \Omega}{T} \; .
$$

Proof. In fact

$$
\begin{aligned}
S &= -k_B \langle \log \rho_{gc} \rangle_{gc} \\
&= -k_B \operatorname{tr}_{\mathcal{F}}(\rho_{gc} \log \rho_{gc}) \\
&= -k_B \operatorname{tr}_{\mathcal{F}} \left(\frac{\exp(-\beta(\hat{H} - \mu \hat{N}))}{\mathcal{Z}} \log \frac{\exp(-\beta(\hat{H} - \mu \hat{N}))}{\mathcal{Z}} \right) \\
&= -k_B \operatorname{tr}_{\mathcal{F}} \left(\frac{\exp(-\beta(\hat{H} - \mu \hat{N}))}{\mathcal{Z}} \left(\log \exp(-\beta(\hat{H} - \mu \hat{N})) - \log \mathcal{Z} \right) \right) \\
&= k_B \beta \underbrace{\operatorname{tr}_{\mathcal{F}} \frac{\exp(-\beta(\hat{H} - \mu \hat{N}))}{\mathcal{Z}} (\hat{H} - \mu \hat{N})}_{E - \mu N} + k_B \underbrace{\operatorname{tr}_{\mathcal{F}} \log \mathcal{Z}}_{-\beta \Omega} \\
&= \frac{E - \mu N - \Omega}{T} \ .
\end{aligned}
$$

<div align="right">q.e.d.</div>

Chapter 20

Quantum gas

20.1 Generic quantum gas

Consider a quantum gas. The hamiltonian operator of one particle, labelled by k is

$$\hat{H}_k = \epsilon_k \hat{n}_k = \epsilon_k \hat{a}_k^\dagger \hat{a}_k \ ,$$

where $\hat{n}_k = \hat{a}_k^\dagger \hat{a}_k$ is the number operator and ϵ_k is the energy eigenvalue associated to the eigenbasis $|u_k(x)\rangle$ by the eigenvalue relation

$$\hat{H}_k |u_k(x)\rangle = \epsilon_k |u_k(x)\rangle \ .$$

Therefore, the hamiltonian one-body operator in the Fock space $\mathcal{F}$, created by the ladder operators $\hat{a}_k^\dagger$ each associated to the element of the eigenbasis $|u_k(x)\rangle$, is

$$\hat{H} = \sum_k \hat{H}_k = \sum_k \epsilon_k \hat{n}_k = \sum_k \epsilon_k \hat{a}_k^\dagger \hat{a}_k \ .$$

In $\mathcal{F}$, the total number onebody operator is

$$\hat{N} = \sum_k \hat{n}_k \ ,$$

where their eignevalues are given with respect to an orthonormal basis $|n_1, \ldots n_k, \ldots\rangle$ by the eigenvalue relation

$$\hat{n}_k |n_1, \ldots n_k, \ldots\rangle = n_k |n_1, \ldots n_k, \ldots\rangle \ .$$

In particular, we distinguish the bosonic and the fermionic case

$$n_k = \begin{cases} 0, 1, 2, \ldots & \text{bosons} \\ 0, 1 & \text{fermions} \end{cases} \ .$$

We exploit the grancanonical ensemble. The grancanonical partition function is

$$\mathcal{Z} = \text{tr}_{\mathcal{F}} \exp(-\beta(\hat{H} - \mu\hat{N})) = \prod_k \sum_{n_1,\dots n_k,\dots} \exp(-\beta(\epsilon_k - \mu)n_k) \ .$$

Proof. In fact,

$$\begin{aligned}
\mathcal{Z} &= \text{tr}_{\mathcal{F}} \exp(-\beta(\hat{H} - \mu\hat{N})) \\
&= \sum_{n_1,\dots n_k,\dots} \langle n_1,\dots n_k,\dots | \exp(-\beta \sum_k (\epsilon - \mu) \underbrace{\hat{n}_k)|n_1,\dots n_k,\dots\rangle}_{n_k|n_1,\dots n_k,\dots\rangle} \\
&= \sum_{n_1,\dots n_k,\dots} \langle n_1,\dots n_k,\dots | \underbrace{\exp(-\beta \sum_k (\epsilon - \mu)n_k)}_{\prod_k \exp} |n_1,\dots n_k,\dots\rangle \\
&= \sum_{n_1,\dots n_k,\dots} \prod_k \exp(\beta(\epsilon - \mu)n_k)\langle n_1,\dots n_k,\dots |n_1,\dots n_k,\dots\rangle \\
&= \prod_k \sum_{n_1,\dots n_k,\dots} \exp(-\beta(\epsilon_k - \mu)n_k) \ ,
\end{aligned}$$

where in the last passage, we have switched the product with the sum because $n_1,\dots,n_k,\dots$ are independent. q.e.d.

Furthermore, for bosons and fermions, it becomes

$$\mathcal{Z} = \begin{cases} \prod_k \frac{1}{1-\exp(-\beta(\epsilon_k-\mu))} & \text{bosons} \\ \prod_k \left(1 + \exp(-\beta(\epsilon_k - \mu))\right) & \text{fermions} \end{cases} \ ,$$

or, in compact notation,

$$\mathcal{Z}_{\mp} = \prod_k \left(1 \mp \exp(-\beta(\epsilon_k - \mu))\right)^{\mp} \ ,$$

where the minus is associated to bosons and the plus to fermions.

Proof. For fermions, $n_k = 0, 1$

$$\mathcal{Z}_+ = \prod_k \sum_{n_1,\dots n_k,\dots=0}^1 \exp(-\beta(\epsilon_k - \mu)n_k) = \prod_k \left(1 + \exp(-\beta(\epsilon_k - \mu))\right) \ .$$

For bosons, $n_k = 0, 1, 2, \ldots$

$$\mathcal{Z}_- = \prod_k \sum_{n_1, \ldots n_k, \ldots = 0}^{\infty} \exp(-\beta(\epsilon_k - \mu)n_k)$$

$$= \prod_k \underbrace{\sum_{n_1, \ldots n_k, \ldots = 0}^{\infty} \exp(-\beta(\epsilon_k - \mu))^{n_k}}_{\text{geometrical series}}$$

$$= \prod_k \frac{1}{1 - \exp(-\beta(\epsilon_k - \mu))} \ .$$

Notice that the condition of convergence of the geometrical series is $\mu < \min \epsilon_k = 0$, which we have set to zero for convenience.   q.e.d.

The grancanonical potential is

$$\Omega_\mp = -\frac{1}{\beta} \log \mathcal{Z}_\mp = \pm \frac{1}{\beta} \sum_k \log \left(1 \mp \exp(-\beta(\epsilon_k - \mu)) \right) \ .$$

Proof. In fact

$$\Omega_\mp = -\frac{1}{\beta} \log \mathcal{Z}_\mp$$

$$= -\frac{1}{\beta} \log \left(\underbrace{\prod_k (1 \mp \exp(-\beta(\epsilon_k - \mu)))^\mp}_{\sum_k \log} \right)$$

$$= -(\mp) \sum_k \log \left(1 \mp \exp(-\beta(\epsilon_k - \mu)) \right)$$

$$= \pm \frac{1}{\beta} \sum_k \log \left(1 \mp \exp(-\beta(\epsilon_k - \mu)) \right) \ .$$

q.e.d.

The grancanonical average number of particle in an energy level state $\overline{k}$ is

$$\langle \hat{n}_{\overline{k}} \rangle_{gc} = \text{tr}_{\mathcal{F}} \left(\hat{n}_{\overline{k}} \frac{\exp(-\beta \sum_k (\epsilon_k - \mu)\hat{n}_k)}{\mathcal{Z}} \right) = \frac{\partial \Omega}{\partial \epsilon_{\overline{k}}} = \frac{1}{\exp(\beta(\epsilon_{\overline{k}} \mp 1))} \ .$$

Proof. In fact

$$\langle \hat{n}_{\overline{k}} \rangle_{gc} = \text{tr}_{\mathcal{F}} \left(\hat{n}_{\overline{k}} \frac{\exp(-\beta \sum_k (\epsilon_k - \mu) \hat{n}_k)}{\mathcal{Z}} \right)$$

$$= \frac{1}{\mathcal{Z}} \text{tr}_{\mathcal{F}} \left(-\frac{1}{\beta} \frac{\partial}{\partial \epsilon_{\overline{k}}} \exp(-\beta \sum_k (\epsilon_k - \mu) \hat{n}_k) \right)$$

$$= -\frac{1}{\beta \mathcal{Z}} \frac{\partial}{\partial \epsilon_{\overline{k}}} \underbrace{\text{tr}_{\mathcal{F}} \left(\exp(-\beta \sum_k (\epsilon_k - \mu) \hat{n}_k) \right)}_{\mathcal{Z}}$$

$$= -\frac{1}{\beta \mathcal{Z}} \frac{\partial}{\partial \epsilon_{\overline{k}}} \mathcal{Z} =$$

$$= \frac{\partial}{\partial \epsilon_{\overline{k}}} \underbrace{\left(-\frac{\log \mathcal{Z}}{\beta} \right)}_{\Omega}$$

$$= \frac{\partial}{\partial \epsilon_{\overline{k}}} \Omega \ .$$

Therefore,

$$\frac{\partial}{\partial \epsilon_{\overline{k}}} \Omega = \frac{\partial}{\partial \epsilon_{\overline{k}}} \left(\pm \frac{1}{\beta} \sum_k \log(1 \mp \exp(-\beta(\epsilon_k - \mu))) \right)$$

$$= \pm \frac{1}{\beta} (-\beta) \frac{\exp(-\beta(\epsilon_k - \mu))}{1 \mp \exp(-\beta(\epsilon_k - \mu))}$$

$$= \mp \frac{1}{1 \mp \exp(\beta(\epsilon_k - \mu))}$$

$$= \frac{1}{\exp(\beta(\epsilon_k - \mu)) \mp 1} \ .$$

q.e.d.

The average total number of particle is

$$N = \langle \hat{N} \rangle_{gc} = \left\langle \sum_k \hat{n}_k \right\rangle_{gc} = \sum_k \frac{1}{\exp(\beta(\epsilon_k - \mu)) \mp 1} \ .$$

The average energy is

$$E = \langle \hat{H} \rangle_{gc} = \text{tr}_{\mathcal{F}} \left(\hat{H} \frac{\exp(-\beta(\hat{H} - \mu \hat{N}))}{\mathcal{Z}} \right) = \sum_k \epsilon_k \langle \hat{n}_k \rangle$$

Proof. In fact

$$E = \langle \hat{H} \rangle_{gc}$$

$$= \text{tr}_{\mathcal{F}} \left(\hat{H} \frac{\exp(-\beta(\hat{H} - \mu \hat{N}))}{\mathcal{Z}} \right)$$

$$= \frac{1}{\mathcal{Z}} \text{tr}_{\mathcal{F}} \left(-\frac{\partial}{\partial \beta} \exp(-\beta(\hat{H} - \mu \hat{N})) \right)$$

$$= -\frac{1}{\mathcal{Z}} \frac{\partial}{\partial \beta} \underbrace{\text{tr}_{\mathcal{F}} \left(\exp(-\beta(\hat{H} - \mu \hat{N})) \right)}_{\mathcal{Z}}$$

$$= -\frac{\partial}{\partial \beta} \Big|_z \log \mathcal{Z}$$

$$= -\frac{\partial}{\partial \beta} \Big|_z \left(\mp \sum_k \log \left(1 \mp \exp(-\beta(\epsilon_k - \mu)) \right) \right)$$

$$= \mp \sum_k \frac{\epsilon_k \exp(-\beta(\epsilon_k - \mu))}{1 \mp \exp(-\beta(\epsilon_k - \mu))}$$

$$= \sum_k \frac{\epsilon_k}{\exp(\beta(\epsilon_k - \mu)) \mp 1}$$

$$= \sum_k \epsilon_l \langle \hat{n}_k \rangle$$

where we have kept the fugacity z constant.   q.e.d.

20.2   Non-relativistic non-interacting quantum gas

So far, we have made computations for a generic quantum gas. From now on, we will deal with non-relativistic non-interacting quantum gas. The finite-volume energy eigenvalues are

$$\epsilon_k = \frac{\hbar^2 k^2}{2m} \qquad \mathbf{k} = \frac{2\pi}{L} \mathbf{n} ,$$

where $\mathbf{n} = (n_1, n_2, n_3) \in \mathbb{Z}^3$. In the thermodynamic limit, the spectrum $\mathbf{k}$ becomes continuous, but $\mathbf{n}$ not, because

$$\Delta K_i = \frac{2\pi}{L}(n_i + 1 - n_i) = \frac{2\pi}{L} .$$

Therefore, sums in k becomes integrals in dk

$$\sum_k = \sum_{n_1, n_2, n_2 = -\infty}^{\infty} \to \frac{V}{2\pi^2} \int dk \ k^2 .$$

Proof. In fact, in 1-dimensional

$$\sum_{n_1} \underbrace{\Delta n_1}_{1} = \sum_{k_1} \frac{L}{2\pi} \Delta k_1 \rightarrow \frac{L}{2\pi} \int dk_1 \ .$$

Similarly, in the 3-dimensional case

$$\sum_{n_1,n_2,n_3=-\infty}^{\infty} \underbrace{\Delta n_1 \Delta n_2 \Delta n_3}_{1} \rightarrow \left(\frac{L}{2\pi}\right)^3 \int dk_1 dk_2 dk_3 = \left(\frac{L}{2\pi}\right)^3 \int dk_1 dk_2 dk_3 = \left(\frac{L}{2\pi}\right)^3 \int dk^3 = \left(\frac{L}{2\pi}\right)^3 4\pi \int$$

q.e.d.

The grandcanonical potential is

$$\Omega_{\mp} = \mp \frac{2}{3} AV \int_0^{\infty} d\epsilon^{\frac{3}{2}} \frac{1}{\exp(\beta(\epsilon - \mu)) \mp 1} \ .$$

Proof. In fact

$$\Omega_{\mp} = \pm \frac{1}{\beta} \sum_k \log\left(1 \mp \exp(-\beta(\epsilon_k - \mu))\right)$$

$$\rightarrow \pm \frac{1}{\beta} \frac{V}{2\pi^2} \int_{-\infty}^{\infty} dk \ k^2 \log\left(1 \mp \exp(-\beta(\epsilon_k - \mu))\right) \ .$$

Under a change of variable

$$\epsilon = \frac{\hbar^2 k^2}{2m} \ , \quad k^2 dk = \frac{1}{2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \sqrt{\epsilon} d\epsilon \ ,$$

we obtain

$$\Omega_{\mp} = \pm \frac{AV}{\beta} \int_0^{\infty} \underbrace{d\epsilon \sqrt{\epsilon}}_{\frac{2}{3} d\epsilon^{\frac{3}{2}}} \log(1 \mp \exp(-\beta(\epsilon_k - \mu)))$$

$$= \pm \frac{2}{3} \frac{AV}{\beta} \int_0^{\infty} d\epsilon^{\frac{3}{2}} \log(1 \mp \exp(-\beta(\epsilon_k - \mu)))$$

$$= \pm \frac{2}{3} \frac{AV}{\beta} \underbrace{\epsilon^{\frac{3}{2}}}_{0 \text{ for } \epsilon=0} \underbrace{\log(1 \mp \exp(-\beta(\epsilon_k - \mu)))}_{0 \text{ for } \epsilon=\infty} \Big|_0^{\infty} \mp \frac{2}{3} \frac{AV}{\beta} \beta \int_0^{\infty} d\epsilon^{\frac{3}{2}} \frac{1}{\exp(\beta(\epsilon - \mu)) \mp 1}$$

$$= \mp \frac{2}{3} AV \int_0^{\infty} d\epsilon^{\frac{3}{2}} \frac{1}{\exp(\beta(\epsilon - \mu)) \mp 1}$$

$$= \mp \frac{2}{3} AV \int_0^{\infty} d\epsilon^{\frac{3}{2}} \frac{1}{\exp(\beta(\epsilon - \mu)) \mp 1} \ .$$

where we have integrated by parts and, introducing the degeneracy ($g = 2s + 1$ for spin particles), we have called

$$A = \frac{g}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} .$$

q.e.d.

The equation of state reads as

$$\Omega = -pV = -\frac{2}{3}E .$$

Furthermore, we have the formulas

$$N = AV \int_0^\infty d\epsilon\, \epsilon^{\frac{1}{2}} n(\epsilon) ,$$

$$P = \frac{2}{3}\frac{E}{V} = \frac{2}{3}A \int_0^\infty d\epsilon\, \epsilon^{\frac{3}{2}} n(\epsilon) .$$

20.3   Expanding with respect to fugacity z

We can expand the density with respect to the fugacity $z = \exp(\beta\mu) \geq 0$

$$n = \frac{g}{\lambda_T^3} f_{\frac{3}{2}}^{\mp} ,$$

where

$$f_l^{\mp} = \begin{cases} \sum_{n=0}^\infty \frac{2^{n+1}}{(n+1)^l} & f^- \text{ for bosons} \\ \sum_{n=0}^\infty \frac{(-1)^n 2^{n+1}}{(n+1)^l} & f^+ \text{ for fermions} \end{cases} .$$

Proof. Under a change of variable

$$x^2 = \beta\epsilon , \quad \beta d\epsilon = 2x dx ,$$

we obtain

$$n = A \int_0^\infty dx \, \frac{2x}{\beta} \frac{x}{\sqrt{(\beta)}(\exp(x^2)z^{-1}) \mp 1}$$

$$= \frac{4g}{\sqrt{\pi}\lambda_T^3} \int_0^\infty dx \, \frac{x^2 z}{\exp(x^2) \mp 2}$$

$$= \frac{4g}{\sqrt{\pi}\lambda_T^3} \int_0^\infty dx \, x^2 z \exp(-x^2) \sum_{n=0}^\infty (\pm 1) z^n \exp(-nx^2)$$

$$= \frac{4g}{\sqrt{\pi}\lambda_T^3} \sum_{n=0}^\infty (\pm 1)^n z^{n+1} \underbrace{\int_0^\infty dx \, x^2 \exp(-x^2(n+1))}_{\frac{\sqrt{\pi}}{4(n+1)^{\frac{3}{2}}}}$$

$$= \frac{g}{\lambda_T^3} \sum_{n=0}^\infty (\pm 1)^n \frac{z^{n+1}}{(n+1)^{\frac{3}{2}}}$$

$$= \frac{g}{\lambda_T^3} f_{\frac{3}{2}}^{\mp} \, .$$

q.e.d.

Notice that for bosons, the convergence of the series implies $z < 1$, which means $\mu > 0$.

20.4 Classical limit

20.5 Semiclassical limit

Chapter 21

Fermions

In this chapter, we restrict ourselves with the fermionic case. The equations of state are

$$n = \frac{g}{\lambda_T^3} f_{\frac{3}{2}}^+(z) , \quad \beta p = \frac{g}{\lambda_T^3} f_{\frac{5}{2}}^+(z) ,$$

where

$$f_l^+(z) = \sum_{n=0}^{\infty} \frac{(-1)^n z^{n+1}}{(n+1)^l}$$

which is an alternate-sign power series in $z = \exp(\beta\mu) > 0$, always positive. It absolutely converges for $z < 1$ and pointwisely converges for $z > 1$. Moreover, it is a monotonic function in z.

It is interesting to study its behaviour for $z \ll 1$. In fact, in the classical limit

$$f_{\frac{3}{2}}(z) \sim f_{\frac{5}{2}}(z) \sim z ,$$

and in the semiclassical limit

$$f_{\frac{3}{2}}(z) \sim z - \frac{z^2}{2^{\frac{3}{2}}} , \quad f_{\frac{5}{2}}(z) \sim z - \frac{z^2}{2^{\frac{5}{2}}} .$$

21.1   Low temperature limit

For the zero temperature limit $T = 0$, the Fermi-Dirac distribution becomes

$$n(\epsilon) = \frac{1}{\exp(\beta(\epsilon - \mu)) + 1} \xrightarrow{T \to 0} \begin{cases} 0 & \epsilon > \mu \\ \frac{1}{2} & \epsilon = \mu \\ 1 & \epsilon < \mu \end{cases} .$$

It is a step function in $\epsilon = \mu$. This energy value is called Fermi energy ϵ_F. Physically, it means that all the states below this energy level are occupied. Hence, for $\epsilon < \epsilon_F$,

we have as many states as particles. If we add a particle, we increase ϵ_F, whereas if we remove a particle, we decrease ϵ_F. This is the procedure to dope a material.

For small T, it is no longer a step function, but it can be accurately approximate to it for a certain range $\Delta\epsilon$. Physically, more energetic particle are transfered over ϵ_F. We define Fermi temperature T_F

$$\epsilon_F = \lim_{T\to 0} \mu(T) = k_B T_F \ .$$

In fact, if $\Delta\epsilon \ll \epsilon_F$, which means $T \ll T_F$, we can approximate $n(\epsilon)$ with a step function without making a big error.

21.2 Fermi Energy for a non-relativistic non-interacting quantum gas

In the 3-dimensional case, the density is

$$n = A\frac{2}{3}\epsilon_F^{\frac{3}{2}} \ .$$

Proof. In fact, using $n(\epsilon) = \theta(-\epsilon_F)$

$$\begin{aligned}
n &= A\int_0^\infty d\epsilon\,\epsilon^{\frac{1}{2}}n(\epsilon) \\
&= A\int_0^{\epsilon_F} d\epsilon\,\epsilon^{\frac{1}{2}} \\
&= A\frac{2}{3}\epsilon_F^{\frac{3}{2}} \ .
\end{aligned}$$

q.e.d.

The energy is

$$E = AV\frac{2}{5}\epsilon_F^{\frac{5}{2}} \ .$$

Proof. In fact, using $n(\epsilon) = \theta(-\epsilon_F)$

$$\begin{aligned}
n &= A\int_0^\infty d\epsilon\,\epsilon^{\frac{3}{2}}n(\epsilon) \\
&= A\int_0^{\epsilon_F} d\epsilon\,\epsilon^{\frac{3}{2}} \\
&= A\frac{2}{5}\epsilon_F^{\frac{5}{2}} \ .
\end{aligned}$$

q.e.d.

Notice that at $T = 0$, there is a positive pressure

$$p = \frac{2}{5}n\epsilon_F > 0 \ .$$

This can be seen visually, because at $T = 0$, there are particle with energy $\epsilon \neq 0$, unlikely the classical case, in which $p = 0$.

Proof. In fact

$$p = \frac{2}{3}\frac{E}{V} = \frac{2}{3}\frac{E}{N}\frac{N}{V} = \frac{2}{5}n\epsilon_F \ .$$

q.e.d.

Chapter 22

Bosons

In this chapter, we restrict ourselves with the bosonic case. The equations of state are

$$n = \frac{g}{\lambda_T^3} f_{\frac{3}{2}}^-(z) \ , \quad \beta p = \frac{g}{\lambda_T^3} f_{\frac{5}{2}}^-(z)$$

where

$$f_l^-(z) = \sum_{n=0}^{\infty} \frac{z^{n+1}}{(n+1)^l}$$

which is a positive-terms power series in $z = \exp(\beta\mu) > 0$, always positive. It absolutely converges for $z < 1$ and converges for $z > 1$ only if $l < 2$. Moreover, it is a monotonic function in z. At $z = 1$, it becomes the Riemann zeta

$$g_{\frac{3}{2}}(z = 1) = \sum_{n=0}^{\infty} \frac{1}{n+1}^{\frac{3}{2}} = \zeta(\frac{3}{2}) \ .$$

Notice that in $z = 1$, it has a vertical derivative, and for $z > 1$, it is not defined according to the physical $\mu > 0$ in the grandcanonical ensemble.

We can study the behaviour of the chemical potential μ. It goes to $-\infty$ for $T \to \infty$ but the equilibrium condition implies that $\frac{\partial \mu}{\partial T} < 0$, therefore, it cannot increase.

22.1 Low temperature limit

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Part VI

Application of quantum statistical mechanics