Matteo Zandi

On statistical mechanics:

what happens when there are too many particles?

November 24, 2023

Theoretical Physics

Contents

$$\text{Page}$$

V Quantum statistical mechanics   66

15 Microcanonical ensemble   67

16 Canonical ensemble   68

17 Grancanonical ensemble   69

VI Application of quantum statistical mechanics   70

Part I

Thermodynamics

Chapter 1

Laws of Thermodynamics

1.1 The laws of Thermodynamics

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

In Thermodynamics, a state 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. An equation of state is a functional relation among them.

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.

Thermodynamics is described by four laws.

Law 1.1 (0th)
Two systems in thermal contact have the same empirical temperature T at equilibrium

$$T_1 = T_2$$

.

Law 1.2 (1st)
The (generalised) principle of conservation of energy states that

$$dE = \delta Q - \delta L + \mu dN \tag{1.1}$$

where E is the internal energy, Q is the heat, L is the work, μ is the chemical potential (the necessary energy to add or remove a particle) and N is the number of particles.

Recall that E is a exact differential, i.e $\oint dE = 0$, whereas heat and word are not, i.e $\oint \delta Q \neq 0$ and $\oint \delta H \neq 0$.

Law 1.3 (2nd)
A system naturally evolves in order to maximize its entropy S. For reversible processes

$$dS = \frac{\delta Q}{T} \tag{1.2}$$

whereas for irreversible processes

$$dS \geq \frac{\delta Q}{T}$$

Law 1.4 (3rd)
For any reversible isothermal process

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

1.2 Thermodynamical potentials

For reversible processes, using (1.2) and $\delta L = pdV$, (1.1) can be expressed as

$$dE = TdS - pdV + \mu dN \tag{1.3}$$

Notice that the left variables are intensive and the right variables (those with the differential) are extensive.

E is a function of S, V, N, hence it must be extensive and a homogeneous function of degree one, satisfying the property

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

where $\lambda > 0$ is the scale factor. It can be proved that the only function is

$$E(S, \ V, \ N) = TS - pV + \mu N$$

Similar expression can be found for other thermodynamical quantities, simply exchanging the role of conjugate functions. See Table 1.2.

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 1.2: 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 1.3.

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 1.3: Thermodynamical variation principles.

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

Part II

Classical statistical mechanics

Chapter 2

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 2.1 (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

2.1 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

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

2.2 Liouville's theorem

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

Theorem 2.2 (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

$$\langle f \rangle = \int_{\mathcal{M}^N} d\Gamma \ \rho(q^i, \ p_i) f(q^i, \ p_i) \tag{2.1}$$

and the standard deviation is

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

2.3   Time-independent Hamiltonian

Consider a time-independent hamiltonian. Since the energy is constant for the theorem 2.1.

$$\int_{\mathcal{M}^N} \rho = 1 \tag{2.2}$$

$$\frac{\partial S}{\partial E} = \frac{1}{T} \tag{2.3}$$

$$\frac{\partial F}{\partial T} = -S \tag{2.4}$$

$$\Omega = -pV = E - TS - \mu N \tag{2.5}$$

Chapter 3

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 (2.2)

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

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

$$\langle f(q^i,p_i)\rangle_{mc} = \int_{\mathcal{M}} d\Omega\ \rho_{mc}f = \int_{\mathcal{M}} d\Omega\ \frac{1}{\omega(E)}\delta(\mathcal{H} - E)f = \frac{1}{\omega(E)}\int_{S_E} dS_E\ f = \langle f\rangle_E \tag{3.1}$$

9

3.1   Thermodynamics potentials

The microcanonical entropy S_{mc} is defined by

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

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 $_1 \in [0, E]$

$$\int_0^E dE_1 \, \omega_1(E_1) \omega_2(E_2 = E - E_1) \leq \omega_1(E_1^*) \omega_2(E_2^* = E - E_1^*) \int_0^E dE_1 \tag{3.2}$$
$$= \omega_1(E_1^*) \omega_2(E_2^* = E - E_1^*) E$$

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

$$\Delta E \omega_1(E_1^*) \omega_2(E_2^*) \leq \omega(E) \tag{3.3}$$

Putting together (3.2) and (3.3)

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

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

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

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

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

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

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

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

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

Using the thermodynamical relation (2.3)

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

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

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

Proof. Using (3.1),

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

q.e.d.

Chapter 4

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

$$Z_N[V, T] = \int_{\mathcal{M}^N} d\Omega \ \exp(-\beta \mathcal{H}(q^i, p_i)) \tag{4.1}$$

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

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

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 (2.3)

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

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

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

Putting together, dropping the indices

$$\rho_c = \frac{\omega(2)(E_2)}{\omega(E)} = \frac{1}{\omega(E)} \exp(\frac{S_{mc}(E)}{k_B}) \exp(-\frac{E_1}{k_B T}) = C \exp(-\frac{E_1}{k_B T}) \qquad (4.2)$$

where C is a normalisation constant, which can be evaluated by (2.2)

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

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

$$Z_N = Z_{N_1} Z_{N_2} \tag{4.3}$$

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

q.e.d.

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

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

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

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

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

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

q.e.d.

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

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

4.1 Thermodynamics variable

The canonical Helmotz free energy F is defined by

$$Z_{[}V,T] = \exp(-\beta F[N,V,T]) \tag{4.4}$$

or, equivalently,

$$F[V,N,T] = -\frac{1}{\beta}\ln Z_N \tag{4.5}$$

Furthermore, the canonical internal energy is

$$E = \langle \mathcal{H} \rangle_c = \int d\Omega \frac{\exp(-\beta(\mathcal{H}))}{Z_N}\mathcal{H} \tag{4.6}$$

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

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

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

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

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

Hence, using (2.4)

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

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

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

$$S_c = \frac{E-F}{T} \tag{4.7}$$

The internal energy can also be written as

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

Proof. Using (4.6),

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

q.e.d.

The universal Boltzmann's formula is still valid

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

Proof. Using (4.6) and (4.5)

$$\begin{aligned}
-k_B\langle\ln\rho_c\rangle_c &= -k_B\int d\Omega\rho_c\ln\rho_c \\
&= -k_B\int d\Omega\rho_c\ln\frac{\exp(-\beta\mathcal{H})}{Z_N} \\
&= -k_B\int d\Omega\rho_c\ln\exp(-\beta\mathcal{H}) - k_B\int d\Omega\rho_c\ln Z_N \\
&= k_B\int d\Omega\beta\mathcal{H} - k_B\underbrace{\ln Z_N}_{\beta F}\underbrace{\int d\Omega\rho_c}_{1} \\
&= \frac{E-F}{T} = S_c
\end{aligned}$$

q.e.d.

4.2 Equipartition theorem

Theorem 4.1 (Generalised equipartition theorem)
Let $\xi \in [a, b]$ and ξ_j with $j \neq 1$ all the other coordinates or momenta. Suppose also

$$\int\prod_{j\neq1}d\xi_j[\xi_1\exp(-\beta\mathcal{H})]_a^b = 0 \tag{4.8}$$

Then

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

Proof. By normalisation condition

$$1 = \int d\Omega\frac{\exp(-\beta\mathcal{H})}{Z_N} = \frac{1}{Z_N}\int\prod_{j\neq1}d\xi_j\exp(-\beta\mathcal{H})$$

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

$$1 = \frac{1}{Z_N}\int \underbrace{\prod_{j\neq1}d\xi_j[\xi_1\exp(-\beta\mathcal{H})]_a^b}_{0} + \frac{\beta}{Z_N}\int\prod_{j\neq1}d\xi_j d\xi_1 \xi_1\frac{\partial\mathcal{H}}{\partial\xi_1}\exp(-\beta\mathcal{H})$$

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

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

Hence

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

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

Examples of system that satisfies the condition (4.8) are hamiltonians which depend on the square of momentum or confining potentials which go to infinity on the extremes a and b.

Corollary 4.1 (Equipartition theorem)
If ξ_1 appears quadratically in $\mathcal{H}$, then its contribution to E is $\frac{1}{2}k_BT$

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

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

and

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

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

Chapter 5

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

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

q.e.d.

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

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

q.e.d.

5.1 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 (4.4) and Taylor expanding to first order in $N_1 \ll N$ and $V_1 \ll V$,

$$
\begin{aligned}
\frac{Z_{N_2}[T,V]}{Z_N[T,V]} &= \frac{\exp(-\beta F(T, N_2, V_2))}{\exp(-\beta F(T, N, V))} \\
&= \exp(-\beta(F(T, N - N_1, V - V_1) - F(T, N, V))) \\
&\simeq \exp(-\beta(\underbrace{\frac{\partial F}{\partial N}\Big|_{T,V}}_{\mu}(-N_1) + \underbrace{\frac{\partial F}{\partial V}\Big|_{T,N}}_{-p}(-V_1))) \\
&= \exp(-\beta(-\mu N_1 + pV_1))
\end{aligned}
$$

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 (2.5), 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.

$$
\begin{aligned}
-\frac{\partial}{\partial \beta} \ln \mathcal{Z}\Big|_{z} &= -\frac{1}{\mathcal{Z}} \frac{\partial}{\partial \beta} \mathcal{Z}\Big|_{z} \\
&= -\frac{1}{\mathcal{Z}} \frac{\partial}{\partial \beta} \sum_{N=0}^{\infty} z^{N} Z_{N}\Big|_{z} \\
&= -\sum_{N=0}^{\infty} \frac{z^{N}}{\mathcal{Z}} \frac{\partial}{\partial \beta} \int d\Omega \exp(-\beta \mathcal{H}) \\
&= \sum_{N=0}^{\infty} \int d\Omega \, \frac{\exp(-\beta(\mathcal{H} + \mu N))}{\mathcal{Z}} \mathcal{H} \\
&= \langle \mathcal{H} \rangle_{gc} = E
\end{aligned}
$$

q.e.d.

The grancanonical number of particles is

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

Proof.

$$
\begin{aligned}
z \frac{\partial}{\partial z} \ln \mathcal{Z}\Big|_{T} &= \frac{z}{\mathcal{Z}} \frac{\partial}{\partial z} \mathcal{Z}\Big|_{T} \\
&= \frac{z}{\mathcal{Z}} \frac{\partial}{\partial z} \sum_{N=0}^{\infty} z^{N} Z_{N} \\
&= frac z \mathcal{Z} \sum_{N=0}^{\infty} N z^{N-1} Z_{N} \\
&= \sum_{N=0}^{\infty} z^{N} Z_{N} N = \langle N \rangle_{gc}
\end{aligned}
$$

q.e.d.

The grancanonical potential is

$$
\Omega = -\frac{1}{\beta} \ln \mathcal{Z} \tag{5.1}
$$

The universal Boltzmann's formula is still valid

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

Proof. Using (5.1),

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

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

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

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

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

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

q.e.d.

Chapter 6

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

$$H = -\sum_{i=1}^{N} p_i \ln p_i + \alpha \left(\sum_{i=1}^{N} p_i - 1 \right) + \beta \left(\sum_{i=1}^{N} p_i f(x_i) - \langle f \rangle \right) \qquad (6.1)$$

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 (6.1), 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 7

Microcanonical ensemble

7.1   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.

7.2   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 8

Canonical ensemble

8.1 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

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

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

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

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

The pression is

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

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.

8.2   Gas of harmonic oscillators

The canonical partition function is

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

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

The internal energy is

$$E = N k_B T \ .$$

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

The Helmoltz free energy is

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

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

The entropy is

$$S = Nk_B\left(1 - \ln\frac{\hbar\omega}{k_BT}\right) .$$

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

$$\mu = k_BT\ln\frac{\hbar\omega}{k_BT} .$$

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.

8.3   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

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

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.

8.4   Maxwell-Boltzmann velocity distribution

8.5   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 9

Grancanonical ensemble

Chapter 10

Entropy

Part IV

Quantum mechanics

Chapter 11

Quantum Mechanics

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

11.1   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

$$P_\psi = |\psi\rangle\langle\psi| \ . \tag{11.1}$$

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

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

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.
$$P_\psi^2 = P_\psi \ , \tag{11.2}$$

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.
$$\operatorname{tr} P_\psi = 1 \ .$$

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, $\forall |\phi\rangle \in \mathcal{H}$
$$||P_\psi|\phi\rangle||^2 = \langle\phi|P_\psi^\dagger P_\psi|\phi\rangle = \langle\phi|\psi\rangle \underbrace{\langle\psi|\psi\rangle}_{1}\langle\psi|\phi\rangle = |\langle\psi|\phi\rangle|^2 \le ||\phi||^1 \ ,$$

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

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
$$\langle\phi|P_\psi|\phi\rangle = \langle\phi|\psi\rangle\langle\psi|\phi\rangle = |\langle\psi|\phi\rangle|^2 \ge 0 \ .$$

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

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

Trace

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

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.

11.2 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 $\{|\psi_n\rangle\}$

$$A|\psi_n\rangle = \lambda_n|\psi_n\rangle \ , \tag{11.3}$$

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

$$|\phi\rangle = \sum_{n=1}^{\infty} c_n|\psi_n\rangle \ , \tag{11.4}$$

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.
$$\sum_{n=0}^{\infty} P_n = \mathbb{I} \ , \tag{11.5}$$

4. spectral decomposition, i.e.
$$\hat{A} = \sum_{n=0}^{\infty} \lambda_n P_n \ .$$

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 (11.3) and c_n in (11.4). Its average value is

$$\langle A\rangle = \langle\psi|\hat{A}|\psi\rangle = \sum_n \lambda_n|c_n|^2 = \sum_n \lambda_n p_n \ , \tag{11.6}$$

whereas its standard deviation is

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

Proof. In fact, using (11.3) and (11.4)

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

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

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

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

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

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

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 $\hat{U}(t)$

$$|\psi(t)\rangle = \hat{U}(t) |\psi(0)\rangle \ , \tag{11.7}$$

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.

11.3 Density matrices and mixed states

The projector (11.1) is also called a density matrix ρ_{ψ}. In terms of the density matrix, the average value (11.6) of an operator $\hat{A}$ is

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

Proof. In fact, using (11.5)

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

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 (11.7)

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

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

$$\rho = \sum_n p_k |\psi_n\rangle\langle\psi_n| = \sum_n p_n \rho_n \ ,$$

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.
$$\operatorname{tr}\rho = 1 \ .$$

However, the idempotence property (11.2) 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

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

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 (2.1)

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

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.

11.4   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

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

where the normalisation condition is

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

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 12

Permutation group

12.1 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 12.1. 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
$$P = \sigma_{\alpha_1} \ldots \sigma_{\alpha_k} \;. \tag{12.1}$$

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,

$$\sigma_i \sigma_j = \sigma_j \sigma_i , \tag{12.2}$$

2.

$$\sigma_i \sigma_{i+1} \sigma_i = \sigma_{i+1} \sigma_i \sigma_{i+1} , \tag{12.3}$$

3.

$$(\sigma_i)^2 = \mathbb{I} . \tag{12.4}$$

Proof. A transposition can be pictorially seen in Figure 12.1. The proofs can be seen in Figure 12.2, Figure 12.4 and Figure 12.3. q.e.d.
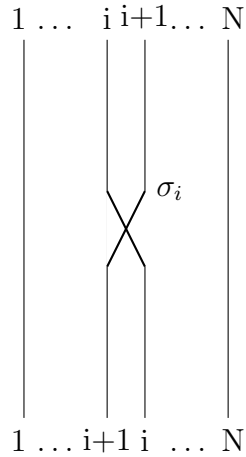

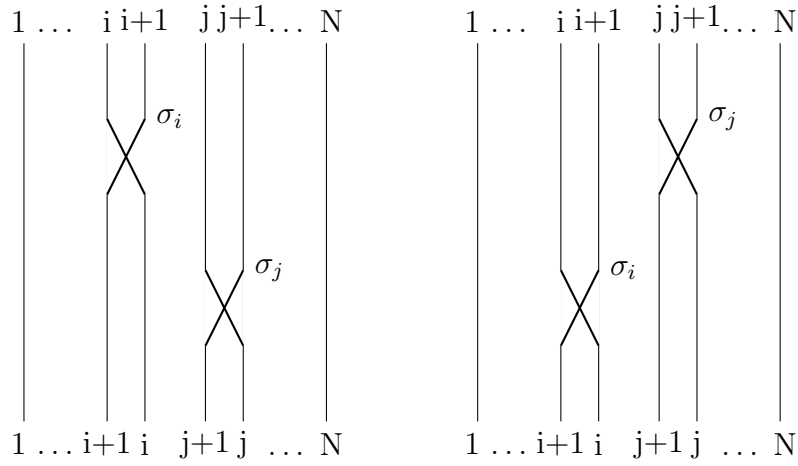Figure 12.1: A pictorial diagram of a transposition σ_i

Figure 12.2: A pictorial diagram of a transposition $\sigma_i \sigma_j$ on the left and $\sigma_j \sigma_i$ on the right, where $|i - j| > 2$
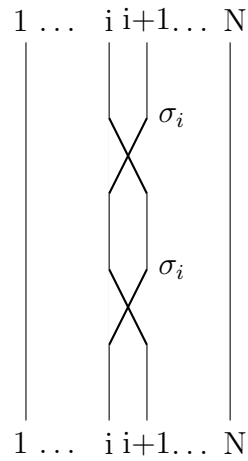

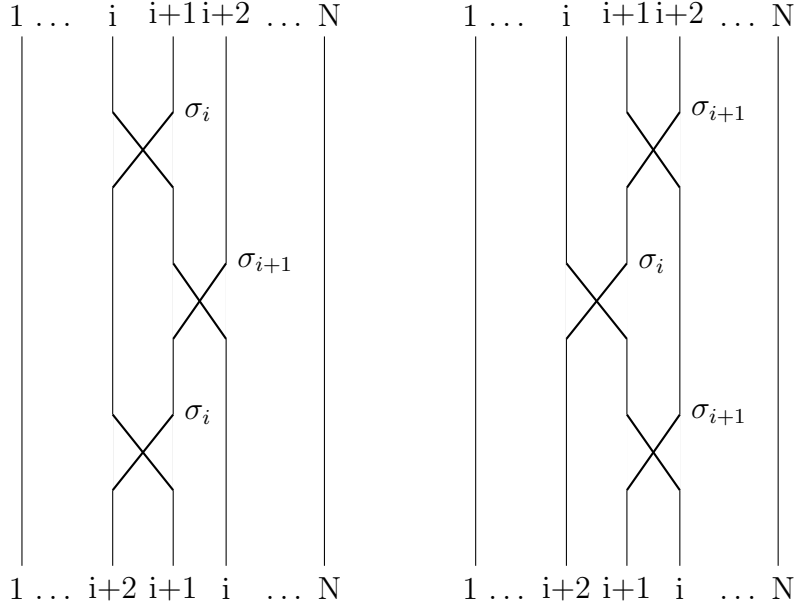Figure 12.3: A pictorial diagram of a transposition $(\sigma_i)^2$

Figure 12.4: 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

12.2 Bosons and fermions

Hence, we can calculate explicitly (11.4), which is

$$\alpha_P = \alpha_1 + \ldots \alpha_N \ , \tag{12.5}$$

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 (12.1)

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

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

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

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

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

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 (12.2)

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

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

hence

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

which means that they commute

$$\alpha_i + \alpha_j = \alpha_j + \alpha_i \ . \tag{12.6}$$

Using (12.3)

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

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

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

$$\alpha_i + \alpha_{i+1} + \alpha_i = \alpha_{i+1} + \alpha_i + \alpha_{i+1} \ . \tag{12.7}$$

Putting together this two properties (12.6) and (12.7), 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, $\forall i = 1, \dots N - 1$ and $\alpha_i \in [0, 2\pi[$ we have $\alpha_i = \alpha_{i+1} = \alpha$.

Using (12.4)

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

which means that

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

Finally, there are only two possibilities

$$\psi(x_1, \dots x_N) \overset{\sigma_i}{\mapsto} \underbrace{\exp(i0)}_{+1} \psi(x_1, \dots x_N) = \psi(x_1, \dots x_N)$$

and

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

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 13

First quantisation

13.1 Symmetric/antisymmetric Hilbert space

Consider 2 distinguishable particles. In general, the Hilbert space is $\mathcal{H}_{tot} = \mathcal{H} \otimes \mathcal{H}$. If the particle are indistinguishable, we can decomposed the Hilbert space into $\mathcal{H}_{tot} = \mathcal{H}_S \otimes_\perp \mathcal{H}_A$. In fact, given two states $|a\rangle_1 \in \mathcal{H}_1$ and $|b\rangle_2 \in \mathcal{H}_2$, we have

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

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

$$
\begin{aligned}
\langle\psi_S|\psi_A\rangle &= \frac{\langle a|_1\langle b|_2 + \langle b|_1\langle a|_2}{2} \frac{|a\rangle_1|b\rangle_2 - |b\rangle_1|a\rangle_2}{2} \\
&= \frac{1}{4}(\underbrace{\langle a|a\rangle_1}_{1}\underbrace{\langle b|b\rangle_2}_{1} - \cancel{\langle a|b\rangle_1}\cancel{\langle b|a\rangle_2} + \cancel{\langle b|a\rangle_1}\cancel{\langle a|b\rangle_2} - \underbrace{\langle b|b\rangle_1}_{1}\underbrace{\langle a|a\rangle_2}_{1}) = 0 \ .
\end{aligned}
$$

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

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

and the antisymmetriser

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

such that they satisfy the properties

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

Generalising for N particles, we have $\mathcal{H}_{tot} = \mathcal{H} \otimes \ldots \mathcal{H}$ and a state is $|a_1\rangle_1 \ldots |a_N\rangle_N$ where $|a_j\rangle \in \mathcal{H}$. The symmetriser is

$$\hat{S} \colon |\psi\rangle \mapsto \frac{1}{N!} \sum_{P \in P_N} |a_{P(1)}\rangle_1 \ldots |a_P(N)\rangle_N$$

and the antisymmetriser is

$$\hat{A} \colon |\psi\rangle \mapsto \frac{1}{N!} \sum_{P \in P_N} sgn(P)|a_{P(1)}\rangle_1 \ldots |a_P(N)\rangle_N$$

where $P(1, \ldots N) \mapsto (P(1), \ldots P(N))$. They satisfy the orthogonal projector properties. 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.

For distinguishable particles, we have $\mathcal{H}_{tot} = \mathcal{H}^{\otimes N}$ with orthonormal basis $\{u_{\alpha_1}(x_1) \ldots u_{\alpha_N}(x_N)\}_{\alpha_1, \ldots \alpha_N = 0}^{\infty}$ labelled by the ordered set $(\alpha_1, \ldots \alpha_N)$. In this case, we are specifying which particle is in which states. However, for indistinguishable particles, we lose information because we know only how many particle are in each state. We label the states with $n_1, \ldots n_j$ 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.

Chapter 14

Second quantisation

14.1 Bosonic case

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

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

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

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

14.2 Fermionic case

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

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

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

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

14.3 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) and the plus sign to the anticommutator (fermions).

The vacuum state is defined as

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

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

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

14.4   Alternative way

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

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

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.

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

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

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

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

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

and for fermions

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

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

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

14.5   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

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

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

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

14.6   Operators

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

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

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

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

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

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

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

$$\hat{O}_F^{(1)} = \int d^d x\ \hat{\varphi}^{\dagger}(x)\hat{O}(\hat{p},\hat{x})\hat{\varphi}(x)\ , \tag{14.1}$$

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

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

14.7   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 (14.1) 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

$$u_\mathbf{k}(0, y, z) = \cancel{c} \exp(i(\cancel{k_y y + k_z z})) = u_\mathbf{k}(L, y, z) = \cancel{c} \exp(i(k_x L + \cancel{k_y y + k_z z})) \ ,$$

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 15

Microcanonical ensemble

Chapter 16

Canonical ensemble

Chapter 17

Grancanonical ensemble

Part VI

Application of quantum statistical mechanics