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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

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	Pressure p
Number of particles N	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

$$dE = \delta Q - \delta L + \mu dN \quad (1.1)$$

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 work are not, i.e $\oint \delta Q \neq 0$ and $\oint \delta L \neq 0$.

Law 1.3 (2nd)

A system naturally evolves in order to maximize its entropy S . For reversible processes

$$dS = \frac{\delta Q}{T} \quad (1.2)$$

whereas for irreversible processes

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

Law 1.4 (3rd)

For any reversible isothermal process

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

1.2 Thermodynamical potentials

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

$$dE = TdS - pdV + \mu dN \quad (1.3)$$

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 $E(S, V, N) = TS - pV + \mu N$	$dE = TdS - pdV + \mu dN$
Helmoltz 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 minimise the corresponding thermodynamical potential until it reaches its minimum, i.e the equilibrium state. Mathematically, it means that the first derivative must be vanishing 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 constituted 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 $i = 1, \dots, N$.

An observable is a smooth real function

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

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 interpreted physically as the energy of the system, which is constants

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

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

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

$$\rho = \text{const}$$

like in the microcanonical ensemble, and

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

like in the canonical or the grandcanonical ensembles.

Proof. Maybe in the future.

q.e.d.

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

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

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.

$$\int_{\mathcal{M}^N} \rho = 1 \tag{2.1}$$

$$\frac{\partial S}{\partial E} = \frac{1}{T} \tag{2.2}$$

$$\frac{\partial F}{\partial T} = -S \tag{2.3}$$

$$\Omega = -pV = E - TS - \mu N \tag{2.4}$$

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 (2.1)

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

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

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

and the distribution is

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

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

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

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

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

Entropy is additive, so given two systems 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

$$\begin{aligned} \omega(E) &= \int_{\mathcal{M}^N} d\Gamma_1 d\Gamma_2 \delta(\mathcal{H} - E) \\ &= \int dE_1 \int dS_{E_1} \int dE_2 \int dS_{E_2} \delta(E - E_1 - E_2) \\ &= \int dE_1 \int dE_2 \omega_1(E_1) \omega_2(E_2) \delta(E - E_1 - E_2) \\ &= \int_0^E dE_1 \omega_1(E_1) \omega_2(E_2 = E - E_1) \end{aligned}$$

Since the integrand is a positive function with a maximum in $E_1 \in [0, E]$

$$\begin{aligned} \int_0^E dE_1 \omega_1(E_1) \omega_2(E_2 = E - E_1) &\leq \omega_1(E_1^*) \omega_2(E_2^* = E - E_1^*) \int_0^E dE_1 \\ &= \omega_1(E_1^*) \omega_2(E_2^* = E - E_1^*) E \end{aligned} \quad (3.2)$$

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

$$\Delta E \omega_1(E_1^*) \omega_2(E_2^*) \leq \omega(E) \quad (3.3)$$

Putting together (3.2) and (3.3)

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

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

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

Since the logarithm is a monotomic function

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

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

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

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

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

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

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

$$\begin{aligned} 0 &= \frac{\partial\Gamma_1}{\partial E_1}\Big|_{E_1^*} \delta E_1 \Gamma_2(E_2^*) - \Gamma_1(E_1^*) \frac{\partial\Gamma_2}{\partial E_2}\Big|_{E_2^*} \delta E_1 \\ 0 &= \frac{\partial\Gamma_1}{\partial E_1}\Big|_{E_1^*} \Gamma_2(E_2^*) - \Gamma_1(E_1^*) \frac{\partial\Gamma_2}{\partial E_2}\Big|_{E_2^*} \\ \frac{\partial\Gamma_1}{\partial E_1}\Big|_{E_1^*} \Gamma_2(E_2^*) &= \Gamma_1(E_1^*) \frac{\partial\Gamma_2}{\partial E_2}\Big|_{E_2^*} \\ \frac{1}{\Gamma_1(E_1^*)} \frac{\partial\Gamma_1}{\partial E_1}\Big|_{E_1^*} &= \frac{1}{\Gamma_2(E_2^*)} \frac{\partial\Gamma_2}{\partial E_2}\Big|_{E_2^*} \end{aligned}$$

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

Using the thermodynamical relation (2.2)

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

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

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

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 transforms, using (2.2)

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

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

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

Putting together, dropping the indices

$$\rho_c = \frac{\omega_2(E_2)}{\omega(E)} = \frac{1}{\omega(E)} \exp\left(\frac{S_{mc}(E)}{k_B}\right) \exp\left(-\frac{E_1}{k_B T}\right) = C \exp\left(-\frac{E_1}{k_B T}\right) \quad (4.2)$$

where C is a normalisation constant, which can be evaluated by (2.1)

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

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

$$Z_N = Z_{N_1} Z_{N_2} \quad (4.3)$$

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

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

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

$$Z[V, T] = \exp(-\beta F[N, V, T]) \quad (4.4)$$

or, equivalently,

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

Furthermore, the canonical internal energy is

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

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

$$\begin{aligned} 0 &= \frac{\partial}{\partial \beta} \left(\int d\Omega \exp(-\beta(\mathcal{H} - F)) \right) \\ &= \int d\Omega \exp(-\beta(\mathcal{H} - F)) \left(-(\mathcal{H} - F) + \beta \frac{\partial F}{\partial \beta} \right) \\ &= - \underbrace{\int d\Omega \frac{\exp(-\beta\mathcal{H})}{Z_N} \mathcal{H}}_E + F \underbrace{\int d\Omega \frac{\exp(-\beta\mathcal{H})}{Z_N}}_1 + \beta \frac{\partial F}{\partial \beta} \underbrace{\int d\Omega \frac{\exp(-\beta\mathcal{H})}{Z_N}}_1 \\ &= -E + F + \beta \frac{\partial F}{\partial \beta} \end{aligned}$$

Hence, using (2.3)

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

showing that is indeed the Helmotz free energy.

q.e.d.

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

$$S_c = \frac{E - F}{T} \quad (4.7)$$

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

$$\int \prod_{j \neq 1} d\xi_j [\xi_1 \exp(-\beta \mathcal{H})]_a^b = 0 \quad (4.8)$$

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

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

and integrating per parts

$$\begin{aligned} 1 &= \frac{1}{Z_N} \int \underbrace{\prod_{j \neq 1} d\xi_j [\xi_1 \exp(-\beta\mathcal{H})]_a^b}_0 + \frac{\beta}{Z_N} \int \prod_{j \neq 1} d\xi_j d\xi_1 \xi_1 \frac{\partial \mathcal{H}}{\partial \xi_1} \exp(-\beta\mathcal{H}) \\ &= \beta \int d\Omega_{\xi_1} \frac{\partial \mathcal{H}}{\partial \xi_1} \frac{\exp(-\beta\mathcal{H})}{Z_N} \\ &= \beta \langle \xi_1 \frac{\partial \mathcal{H}}{\partial \xi_1} \rangle_c \end{aligned}$$

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 (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 $\frac{1}{2}k_B T$

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

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

and

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

q.e.d.

Chapter 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 $N = N_1 + N_2$,

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

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 $V_1 \ll V$,

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

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 (2.4), the normalisation condition becomes

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

Hence

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

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

$$\Omega = -\frac{1}{\beta} \ln \mathcal{Z} \quad (5.1)$$

The universal Boltzmann's formula is still valid

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

Proof. Using (5.1),

$$\begin{aligned}
-k_B \langle \ln \rho_{gc} \rangle_{gc} &= -k_B \int d\Omega \rho_{gc} \ln \rho_{gc} \\
&= -k_B \sum_{N=0}^{\infty} \frac{z^N}{\mathcal{Z}} \int d\Omega \exp(-\beta \mathcal{H}) \ln \rho_{gc} \\
&== -k_B \sum_{N=0}^{\infty} \frac{z^N}{\mathcal{Z}} \int d\Omega \exp(-\beta \mathcal{H}) (-\beta \mathcal{H} + \beta \mu N + \ln \mathcal{Z}) \\
&= k_B \beta \underbrace{\sum_{N=0}^{\infty} \frac{z^N}{\mathcal{Z}} \int d\Omega \exp(-\beta \mathcal{H}) \mathcal{H}}_E - k_B \beta \mu \underbrace{\sum_{N=0}^{\infty} \frac{z^N}{\mathcal{Z}} \int d\Omega \exp(-\beta \mathcal{H}) N}_N \\
&\quad + k_B \ln \mathcal{Z} \underbrace{\sum_{N=0}^{\infty} \frac{z^N}{\mathcal{Z}} \int d\Omega \exp(-\beta \mathcal{H})}_1 \\
&= \frac{E - \mu N - \Omega}{T} = S
\end{aligned}$$

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 grandcanonical 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 distribution is the one corresponding to maximum entropy, given the macroscopic constraints. 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

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

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 distinguishability or not of particles. Therefore, we decomposed it into

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

where $W_{\{n_r\}}^{(1)}$ counts in how many we can put n_r particles in the energy level E_r and $W_{\{n_r\}}^{(2)}$ 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,

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

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

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

Proof. Maybe in the future.

q.e.d.

The Helmholtz 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

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

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 Helmolzt 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

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

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.

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

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

Proof. Maybe in the future.

q.e.d.

The internal energy is

$$E = 3Nk_B T .$$

Proof. Maybe in the future.

q.e.d.

The Helmholtz free energy is

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

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

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

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 Helmholtz 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

9.1 Non-relativistic ideal gas

9.2 Gas of harmonic oscillators

9.3 Solid-vapor equilibrium phase

Chapter 10

Entropy

10.1 Maxwell-Boltzmann distribution

10.2 Fermi-Dirac distribution

10.3 Bose-Einstein distribution

Part IV

Quantum statistical mechanics

Chapter 11

Quantum mechanics

In quantum mechanics, a pure state is described by a normalised vector in a Hilbert space $|\psi\rangle \in \mathcal{H}$, which is a vector space on \mathbb{C} , i.e. in which a linear superposition is still in the space $\lambda_1|\psi_1\rangle + \lambda_2|\psi_2\rangle$, endowed with a scalar product $\langle\psi|\phi\rangle$ through which it is possible to associate a probability and the normalisation condition $||\psi||^2 = \langle\psi|\psi\rangle = 1$. Furthermore, the normalisation condition ensures that a state is not only a vector, but a ray in a Hilbert space, since two states are physically equivalent if $|\psi\rangle \sim \exp(i\phi)|\psi\rangle$. It can be seen as an equivalence class of states.

11.1 Projectors

It is possible to uniquely determine the state via a projection operator or projector

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

which for normalisation states becomes

$$P_\psi = |\psi\rangle\langle\psi| .$$

Proof. If $|\psi\rangle \mapsto \exp(i\phi)|\psi\rangle$ and $\langle\psi| \mapsto \exp(-i\phi)\langle\psi|$, we have

$$P_\psi \mapsto \exp(i\phi)|\psi\rangle\exp(-i\phi)\langle\psi| = |\psi\rangle\langle\psi| = P_\psi .$$

q.e.d.

It projects onto the 1-dimensional subspace generated by the state $|\psi\rangle$

$$P_\psi: \mathcal{H} \rightarrow \mathcal{H}_\psi ,$$

where $\mathcal{H}_\psi = \{\lambda|\psi\rangle: \lambda \in \mathbb{C}\}$.

Proof. In fact, $\forall |\psi\rangle \in \mathcal{H}$, we decomposed it into

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

and the action of the projector

$$P_\psi|\psi\rangle = \alpha \underbrace{P_\psi}_{|\psi\rangle\langle\psi|} |\psi\rangle + \beta \underbrace{P_\psi}_{0} |\psi^\perp\rangle = \alpha|\psi\rangle \underbrace{\langle\psi|\psi\rangle}_1 = \alpha|\psi\rangle .$$

q.e.d.

The projector is also called density matrix ρ_ψ . It satisfies the following properties

1. boundness, i.e.

$$||\rho_\psi|| < C ,$$

2. hermiticity, i.e.

$$\rho_\psi^\dagger = \rho_\psi ,$$

3. idempotence, i.e.

$$\rho_\psi^2 = \rho_\psi ,$$

4. positive defined, i.e. $\forall |\phi\rangle \in \mathcal{H}$

$$\langle\phi|\rho_\psi|\phi\rangle \geq 0 ,$$

5. unit trace, i.e.

$$\text{tr } \rho_\psi = 1 .$$

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

Proof. For the hermiticity

$$\rho_\psi^\dagger = (|\psi\rangle\langle\psi|)^\dagger = \langle\psi|^\dagger|\psi\rangle^\dagger = |\psi\rangle\langle\psi| = \rho_\psi .$$

For the idempotence

$$\rho_\psi^2 = (|\psi\rangle\langle\psi|)^2 = |\psi\rangle \underbrace{\langle\psi|\psi\rangle}_1 \langle\psi| = |\psi\rangle\langle\psi| = \rho_\psi .$$

q.e.d.

Given an orthonormal basis $\{|e_n\rangle\}_{n=1}^\infty$ of a separable Hilbert space, the trace is defined as

$$\text{tr } A = \sum_{n=1}^\infty A_{nn} = \sum_{n=1}^\infty \langle e_n | A | e_n \rangle .$$

If it convergent, it is called a trace-class operator. Furthermore, if it is absolute convergent, the trace is independent on the choice of the basis.

11.2 Observable

An observable is a linear hermitian operator acting on the Hilbert space. We require the self-adjointness because its eigenvalues are real and it always admit an eigenbasis, such that every state can be expanded in this basis

$$A|\psi_n\rangle = \lambda_n|\psi_n\rangle ,$$

such that

$$\lambda_n \in \mathbb{R}$$

and $\forall |\phi\rangle \in \mathcal{H}$

$$|\phi\rangle = \sum_{n=1}^{\infty} c_n |\psi_n\rangle .$$

The projectors on the eigenstates are orthogonal

$$P_n P_m = P_n P_m = 0 .$$

If we prepare the system in a state $|\psi\rangle$, a measurement of an observable A can have outcomes λ_n with probability $P_n = |c_n|^2$ where we have defined

$$|\phi\rangle = \sum_n c_n |\psi_n\rangle , \quad A|\psi_n\rangle = \lambda_n |\psi_n\rangle .$$

Its average value is

$$\langle A \rangle = \sum_n \lambda_n P_n = \sum_n \lambda_n |c_n|^2 = \text{tr}(A \rho_\psi) .$$

11.3 Composite system

For 2 particles, the total Hilbert space is the tensor product between the 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 total orthonormal basis 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, $\forall |\phi\rangle \in \mathcal{H}_{tot}$

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

where the normalisation condition is $\sum_{nm} |a_{nm}|^2 = 1$.

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 is

$$\langle \psi_n \phi_m | \psi_{n'} \phi_{m'} \rangle = \langle \psi_n | \psi_{n'} \rangle \langle \phi_m | \phi_{m'} \rangle .$$

11.4 *N* distinguishable particles

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

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

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

A generic state can be expanded in this basis as

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

For instance, choosing $\alpha_1 = a$ and $\alpha_2 = b$ or viceversa

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

If the particles are indistinguishable, they are invariant under permutations

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

where P belongs to the permutation group.

Chapter 12

Permutation group

The permutation of N elements form a group P_N . This group is generated by transposition $\{\sigma_i\}_{i=1}^N$. In fact, any permutation can be defined by consecutive transposition, where a transposition is defined as

$$\sigma_i: (1, 2, \dots, i, i+1, \dots, N) \mapsto (1, 2, \dots, i+1, i, \dots, N) .$$

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 permutation $\forall P \in P_N$

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

Transpositions follow the properties

1. if $|i - j| > 2$

$$\sigma_i \sigma_j = \sigma_j \sigma_i , \tag{12.1}$$

2.

$$\sigma_i \sigma_{i+1} \sigma_i = \sigma_{i+1} \sigma_i \sigma_{i+1} , \tag{12.2}$$

3.

$$(\sigma_i)^2 = \mathbb{I} . \tag{12.3}$$

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

$$\alpha_P = \alpha_1 + \dots \alpha_N . \tag{12.4}$$

Proof. In fact

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

where $P = \sigma_{\alpha_1} \dots \sigma_{\alpha_N}$.

q.e.d.

Furthermore, $\alpha_P = 0, m\pi$, which correspond respectively to a bosonic totally symmetric wavefunction, i.e. under P

$$\psi(x_1, \dots, x_N) \xrightarrow{P} +1 \psi(x_1, \dots, x_N) ,$$

or to a fermionic totally antisymmetric wavefunction, i.e. under P

$$\psi(x_1, \dots, x_N) \xrightarrow{P} (-1)^m \psi(x_1, \dots, x_N) = \begin{cases} + & \text{sign}(P) = +1 \\ - & \text{sign}(P) = -1 \end{cases} .$$

Proof. For (12.1)

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

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

which means that

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

For (12.2)

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

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

which means that

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

where we have used the fact that $\exp(i\alpha_i) \exp(i\alpha_j)$ commutes. Therefore, $\forall i = 1, \dots, N-1$ and $\alpha_i \in [0, 2\pi[$ we have $\alpha_i = \alpha_{i+1} = \alpha$.

For (12.3)

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

which means that

$$\alpha = 0, 2\pi .$$

Finally, there are only two possibilities

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

and

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

q.e.d.

12.1 Symmetric/antisymmetric Hilbert space

Consider 2 distinguishable particles. In general, the Hilbert space is $\mathcal{H}_{tot} = \mathcal{H} \otimes \mathcal{H}$. If the particles are indistinguishable, we can decompose the Hilbert space into $\mathcal{H}_{tot} = \mathcal{H}_S \oplus \mathcal{H}_A$. 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 antisymmetric part, because if $a = b$ we have $|\psi_A\rangle = 0$. It is also an orthogonal decomposition. In fact

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

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

$$\hat{S}: \mathcal{H} \rightarrow \mathcal{H}_S$$

and the antisymmetriser

$$\hat{A}: \mathcal{H} \rightarrow \mathcal{H}_A ,$$

such that they satisfy the properties

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

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

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

and the antisymmetriser is

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

where $P(1, \dots, N) \mapsto (P(1), \dots, P(N))$. 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 $\{u_{\alpha_1}(x_1) \dots u_{\alpha_N}(x_N)\}_{\alpha_1, \dots, \alpha_N=0}^{\infty}$ labelled by the ordered set $(\alpha_1, \dots, \alpha_N)$. 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 particles are in each state. We label the states with n_1, \dots, n_j with $j = 1, \dots, \infty$, which are the occupation numbers. For bosons, we have $n_k = 0, 1, \dots, \infty$, whereas for fermions, we have $n_k = 0, 1$. For both cases, there is the constraint $N = \sum_k n_k$, which is an infinite sum but mostly are zero occupied.

Chapter 13

Second quantisation

13.1 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

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

13.2 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

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

13.3 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 corresponds 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

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

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

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

13.4 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 grandcanonical 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 $\hat{a}_k: \mathcal{H}_{S/A}^{(N)} \rightarrow \mathcal{H}_{S/A}^{(N-1)}$, 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 $\hat{a}_k^\dagger: \mathcal{H}_{S/A}^{(N)} \rightarrow \mathcal{H}_{S/A}^{(N+1)}$, 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

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

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

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

13.5 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,

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

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

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

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,

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

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

13.6 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 $\psi_{n_1 \dots n_k \dots}(x_1, \dots, x_k, \dots) = c_N \left[\begin{smallmatrix} \hat{S} \\ \hat{A} \end{smallmatrix} \right] u_{\alpha_1}(x_1) \dots u_{\alpha_k}(x_k) \dots$, where \hat{S} 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

$$\begin{aligned}
\hat{O}^{(1)}\psi_{n_1\dots n_k\dots}(x_1,\dots x_k,\dots) &= \left(\sum_{j=1}^{\infty}\hat{O}(\hat{p}_j,\hat{x}_j)\right)\psi_{n_1\dots n_k\dots}(x_1,\dots x_k,\dots) \\
&= \left(\sum_{j=1}^{\infty}\hat{O}(\hat{p}_j,\hat{x}_j)\right)c_N\left[\begin{smallmatrix}\hat{S}\\\hat{A}\end{smallmatrix}\right]u_{\alpha_1}(x_1)\dots u_{\alpha_k}(x_k)\dots \\
&= c_N\left[\begin{smallmatrix}\hat{S}\\\hat{A}\end{smallmatrix}\right]\left(\sum_{j=1}^{\infty}\hat{O}(\hat{p}_j,\hat{x}_j)u_{\alpha_1}(x_1)\dots u_{\alpha_k}(x_k)\dots\right) \\
&= c_N\left[\begin{smallmatrix}\hat{S}\\\hat{A}\end{smallmatrix}\right]\left(\sum_{j=1}^{\infty}u_{\alpha_1}(x_1)\dots\underbrace{\hat{O}(\hat{p}_j,\hat{x}_j)u_{\alpha_j}(x_j)}_{\epsilon_{\alpha_j}u_{\alpha_j}(x_j)}\dots\right) \\
&= \left(\sum_{j=1}^{\infty}\epsilon_j n_j\right)\psi_{n_1\dots n_k\dots}(x_1,\dots x_k,\dots) .
\end{aligned}$$

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

$$\hat{O}_F^{(1)} = \int d^d x \ \hat{\varphi}^\dagger(x)\hat{O}(\hat{p},\hat{x})\hat{\varphi}(x) , \quad (13.1)$$

which this time is basis independent.

Proof. In fact

$$\begin{aligned}
\int d^d x \hat{\varphi}^\dagger(x) \hat{O}(\hat{p}, \hat{x}) \hat{\varphi}(x) &= \int d^d x \left(\sum_k u_k(x) \hat{a}_k^\dagger(x) \right) \hat{O}(\hat{p}, \hat{x}) \left(\sum_m u_m^*(x) \hat{a}_m(x) \right) \\
&= \sum_k \sum_m \hat{a}_k^\dagger \hat{a}_m \int d^d x u_k(x) \underbrace{\hat{O}(\hat{p}, \hat{x}) u_m^*(x)}_{\epsilon_m u_m^*(x)} \\
&= \sum_k \sum_m \hat{a}_k^\dagger \hat{a}_m \epsilon_m \underbrace{\int d^d x u_k(x) u_m^*(x)}_{\delta_{km}} \\
&= \sum_k \sum_m \hat{a}_k^\dagger \hat{a}_m \epsilon_m \underbrace{\delta_{km}}_{k=m} \\
&= \sum_k \hat{a}_k^\dagger \hat{a}_k \epsilon_k = \hat{O}_F^{(1)} .
\end{aligned}$$

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

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

13.7 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 (13.1) 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

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

which is consistent with the definition of ρ since it can be seen as a density of particle whose integral 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

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

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 transforms 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

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

hence

$$\exp(ik_x L) = 1$$

and

$$k_x = \frac{2\pi}{L} n_x ,$$

where $n \in \mathbb{Z}$ is an integer number. Similarly 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 operator, 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.

Chapter 14

Ensemble theory

Part V

Application of quantum statistical mechanics

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