Statistic Physics

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1 The fundamental postulation and Liouville's theorem

1.1 The Fundamental postulate

An isolated system in equilibrium is equally likely to be found in any of the microstates accessible to it.

- **System** an part of universe that is only weakly coupled to the rest of the universe so that its dynamic is dominated by internal interactions.

- **Equilibrium** the measurement of quantities are time independent.

- **Microstate** a complete microscope specification of coordinates of every particles (position and velocity).

- **Ensemble** a collection of the system that are macroscopically the same but microscopically different.

1.2 Motivation for the fundamental postulation

From the above fundamental postulation and use the ergodic hypothesis, we can relate the macroscopic properties of a system that we can measure to the statistic (probabilistic) description of microstate.

Ergodic hypothesis assumes that 1) the system's internal dynamics are such that the microstates of the system are constantly changing and 2) the system will visit all possible microstate and spend an equal time in each of them. As a result, as we carry out measurement, the system will likely to be found in a configuration (macroscopic properties) that is represented by the most microstates[1].

The following example illustrate this notation: consider a box of 100 identical coins, shaked hard and we measure the number of the coins facing up as we open the box (macroscopic result). We do not really care the actual configuration of the outcome (coin 1 face up, $\cdots$ coin N face down) which is a microscopic property since we know each of these configurations is equally possible. It's easy to see that the most probable result is 50 up and 50 down, but let's see the possibility of outcome that deviate from this average value:

$$
\begin{aligned}
50 \text{ up and } 50 \text{ down } &= \frac{100!}{(50!)^2} \approx 4 \times 10^{27} \\
53 \text{ up and } 47 \text{ down } &= \frac{100!}{53!47!} \approx 3 \times 10^{27} \\
90 \text{ up and } 10 \text{ down } &= \frac{100!}{90!10!} \approx 10^{13} \\
100 \text{ up and } 0 \text{ down } &= 1
\end{aligned}
\tag{1}
$$

where each result is determined by counting their configurations. We see that the probability that result deviate far from the average decay exponentially. For actual physic system, the number of particles are $\propto 10^{23}$, which essentially mean that the possibility of deviation is ignorable and when we measure the macroscopic properties of physical system, we almostly certainly obtain the value given from probabilistic calculation.

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[1] Blundell, p35-37

The macroscopic propertie of the system can thus be calculated as following: For N particles we have in total $6N$ coordinates $(q_1, q_2, \cdots, q_{3N}, p_1, p_2, \cdots, p_{3N})$ which completely define a microscope state. We define the "phase density" as:

$$\rho(q_1, q_2, \cdots, q_{3N}, p_1, p_2, \cdots, p_{3N}, t) \tag{2}$$
$$\rightarrow \text{Probability of finding a system near } (q_1, q_2, \cdots, q_{3N}, p_1, p_2, \cdots, p_{3N}) \text{at time } t \tag{3}$$

If property of this system is given by a function $f(q, p)$, then the ensemble average of f at time t will be given as:

$$\langle f(t) \rangle = \frac{\int \int \cdots \int f(q, p)\rho(q, p, t)dq^{3N}dp^{3N}}{\int \int \cdots \int \rho(q, p, t)dq^{3N}dp^{3N}} \tag{4}$$

With the above definition, $\rho(q, p, t)dq^{3N}dp^{3N}$ gives the number of states (points) that are included in the phase space volume $dq^{3N}dp^{3N}$ near (q, p).

1.3   Liouville's theorem

Liouville's theorem states that the evolution of ρ is given by:

$$\frac{d\rho}{dt} = 0 \tag{5}$$

which is to say that if we follow the trajectory of a state (q, p) as it evolve over time, its phase space density will not change (total derivative): $\rho(q(0), p(0), t = 0) = \rho(q(t'), p(t'), t = t')$.

Proof 1 In this proof, we consider the phase space points inclosed by a volume at $t = 0$ at (q_1, p_1), at a later time δt, we locate those phase space points agian and we show that the volume of phase space that enclose these points are the same. This will thus mean the phase (point) density do not change following the trajectory.

let's consider an area in a two dimensional phase space that is a rectangle specified by its 2 diagonal points $(q_1, p_1), (q_2, p_2)$ at some initial time t, then at time $t + \delta t$, the points changed to $(q_1 + \dot{q}_1\delta t, p_1 + \dot{p}_1\delta t)$ and $(q_2 + \dot{q}_2\delta t, p_2 + \dot{p}_2\delta t)$. The volume difference, to first order in δt is:

$$\begin{aligned}
\Delta V &= (q_2 + \dot{q}_2\delta t - q_1 - \dot{q}_1\delta t)(p_2 + \dot{p}_2\delta t - p_1 - \dot{p}_1\delta t) - (q_2 - q_1)(p_2 - p_1) \\
&= (\dot{q}_2 - \dot{q}_1)(p_2 - p_1) + (\dot{p}_2 - \dot{p}_1)(q_2 - q_1) \\
&= \frac{1}{V}\left(\frac{\dot{q}_2 - \dot{q}_1}{q_2 - q_1} + \frac{\dot{p}_2 - \dot{p}_1}{p_2 - p_1}\right) \\
&= \frac{1}{V}\left(\frac{\partial \dot{q}}{\partial q} + \frac{\partial \dot{p}}{\partial p}\right)\delta t
\end{aligned} \tag{6}$$

If a system envolve under Hamiltonian dynamics:

$$\dot{q}_i = \frac{\partial H}{\partial p_i}; \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \tag{7}$$

then

$$\frac{\partial \dot{q}}{\partial q} + \frac{\partial \dot{p}}{\partial p} = \frac{\partial^2 H}{\partial p \partial q} - \frac{\partial^2 H}{\partial q \partial p} = 0 \tag{8}$$

which shows that the enclosing volume of those phase space points do not change as the system evolve, and therefore, the phase space density in this volume do not change over time, giving the result:

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_i \left(\frac{\partial \rho}{\partial q_i}\frac{\partial q_i}{\partial t} + \frac{\partial \rho}{\partial p_i}\frac{\partial p_i}{\partial t}\right) = 0 \tag{9}$$

Where the first equality is given merely by the definition of total derivative.

Proof 2 In this proof, we compute the partial derivatives first and show that they result in the result of Liouville's theorem [2].

We first compute $\partial\rho/\partial t$. Consider the flow the phase space points in and out of a cubic volume element in the phase space arount (q, p), The net flow of phase space points is given by:

$$\frac{\partial N}{\partial t} = -\sum_i \left(\frac{\partial(\rho\dot{q}_i)}{\partial q_i} + \frac{\partial(\rho\dot{p}_i)}{\partial p_i} \right) dq \cdots dp$$

$$\frac{\partial \rho}{\partial t} = -\sum_i \left(\frac{\partial(\rho\dot{q}_i)}{\partial q_i} + \frac{\partial(\rho\dot{p}_i)}{\partial p_i} \right) \tag{10}$$

the total derivatve is then:

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_i \left(\frac{\partial \rho}{\partial q_i}\frac{\partial q_i}{\partial t} + \frac{\partial \rho}{\partial p_i}\frac{\partial p_i}{\partial t} \right)$$

$$= -\sum_i \left(\frac{\partial(\rho\dot{q}_i)}{\partial q_i} + \frac{\partial(\rho\dot{p}_i)}{\partial p_i} \right) + \sum_i \left(\frac{\partial \rho}{\partial q_i}\frac{\partial q_i}{\partial t} + \frac{\partial \rho}{\partial p_i}\frac{\partial p_i}{\partial t} \right)$$

$$= -\sum_i \left(\rho\frac{\partial \dot{q}_i}{\partial q_i} + \rho\frac{\partial \dot{p}_i}{\partial p_i} \right) = 0 \tag{11}$$

thus proving the Liouville's theorem.

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[2]Taken from `https://hepweb.ucsd.edu/ph110b/110b_notes/node93.html`

2 Intensive and extensive properties

2.1 Heat

We provide a definition of heat as *The thermal energy in transit*, denoted as Q[3]. We define the heat capacity C of an object as the amount of heat that is needed to increase its temperature:

$$C = \frac{dQ}{dT} \tag{12}$$

thus C has the unit J/K. The specific heat is defined to be the heat capacity per unit mass, having the unit $J/(kg \cdot K)$

2.2 Entropy

We define entropy S for an isolated macroscopic system of N particles in volume V and energy E to be:

$$S(E, N, V, x) = k_B \ln \Omega(E, N, V, x) \tag{13}$$

where $\Omega(E, N, V, x)$ is the number of accessible states at a given value of E, N, V, and x is some constraints which influence the number of accessible states. As a non-equilibrium isolated system allow to relax to equilibrium, entropy will increase monotonically and eventually maximize at equilibrium.

Temperature consider an isolated system with two subsystem in weak contact but heat is allowed to follw between the two subsystem. The total number of accessible states (configurations) are given by the product of the number of configurations of the two subsystem. Entropy will be additive. Consider the energy of one of the subsystem E_1 as the constrain for the configurations.

$$\Omega(E, E_1) = \Omega_1(E_1)\Omega_2(E_2) \tag{14}$$
$$S(E, E_1) = S_1(E_1)S_2(E_2) \tag{15}$$

Relaxation process will increase entropy by changing E_1, towards a macroscopic that correspond to more configurations. At equilibrium (heat no longer exchange), we have:

$$\frac{\partial S}{\partial E_1} = 0 \;\Rightarrow\; \left.\frac{\partial S_1(E_1)}{\partial E_1}\right|_{N_1, V_1} = \left.\frac{\partial S_2(E_2)}{\partial E_2}\right|_{N_2, V_2} = \frac{1}{T} \tag{16}$$

where the final equality gives the definition of temperature, thus if two subsystem reaches equilibrium in terms of energy flow, their temperature will be equal. This process is irreversible and thus define a arrow of time.

Chemical potential now, we fix only volume V of each subsystem and allow both energy and particles to exchange, then:

$$\left.\frac{\partial S_1(N_1)}{\partial N_1}\right|_{E_1, V_1} = \left.\frac{\partial S_2(N_2)}{\partial N_2}\right|_{E_2, V_2} = -\frac{\mu}{T} \tag{17}$$

the last equality defines the chemical potential μ.

Pressure finally, we allow the volume of the system to exchange, and we can similar define pressure:

$$\left.\frac{\partial S_1(V_1)}{\partial V_1}\right|_{E_1, N_1} = \left.\frac{\partial S_2(V_2)}{\partial V_2}\right|_{E_2, N_2} = \frac{P}{T} \tag{18}$$

Thus, we can see that if we set an initial system not in equilibrium, the two subsystem will start to exchange energy, particles and volume until T, P and μ become the same for the two subsystem.

We can separate the macroscopic properties of a system into two different catagory:

- **Extensive properties** that will increase proportional to the system size, such as N, E, V

- **Intensive properties** that will be same for any of the subsystem, such as P, μ, T

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[3]Blundell, p14

3 Ensembles

We can define an ensemble as a collection of possible configurations that satisfy a given macroscopic property[4]. We have already seem an ensemble containing possible configurations of an isolated system where energy is known and all configurations are of equal probability. This ensemble is known as the **Microcanonical ensemble**. For a microcanonical ensemble, particle number, volume and energy are specified at the same time, thus it is also called **NVE ensemble**.

Now consider a system that can exchange energy through a contact with a temperature bath and eventually come to an equilibrium. This ensemble is called **Canonical ensemble**. For canonical ensemble, it's dynamic is still governed by its internal interaction but now its energy may vary. Since now the energy of this system can change, it is more appropriate to describe it in terms of temperature T, from which we can find its energy.

Now we want to find the probability distribution of its microstate (probability of finding the system to be in a specific microstate), The system and reservoir together is described by a microcanonical ensemble, in which each state is described by $(q_1, \cdots, q_n, q_{n+1}, \cdots q_N, p_1, \cdots, p_n, p_{n+1}, \cdots p_N)$ where the first n coordinates describe the system, and the rest coordinates describe the microstate of the reservoir. Every microstates of the combined system are equal likely, therefore, the probability to find the microstate of the canonical ensemble $(q'_1, \cdots, q'_n, p'_1, \cdots, p'_n)$ depend on the number of possible configurations of the coordinates in the reservoir, i.e. the number of the microstate of the combined system in which $(q_1, \cdots, q_n, p_1, \cdots, p_n) = (q'_1, \cdots, q'_n, p'_1, \cdots, p'_n)$.

We have, with E_i^r denote the energy of the reservior for the microstate i of system, and $\Delta E = E_j - E_i$

$$\frac{P_j}{P_i} = \frac{\Omega_r(E_i^r - \Delta E)}{\Omega_r(E_i^r)} = \exp\left(\frac{S_r(E_i^r - \Delta E) - S_r(E_i^r)}{k_B}\right) \approx \exp\left(-\frac{E_j - E_i}{k_B T}\right) \tag{19}$$

This give the result, with $\beta = 1/k_B T$

$$P_i \propto e^{-\beta E_i} \tag{20}$$

Define the canonical partition function Q_N

$$Q_N(T, V, N) = \sum_j e^{-\beta E_j} \tag{21}$$

The free energy is defined by:

$$A(T, V, N) = -k_B T \ln Q_N \tag{22}$$

The probability of finding a given microstate of the system is then

$$P_i = \frac{1}{Q_N} e^{-\beta E_i} = e^{\beta(A - E_i)} \tag{23}$$

To specific a canconical potential, we need to specify V, N, T, therefore, canonical potential is also known as the **NVT ensemble**

Finally, let's consider a system that can exchange both energy and particle with a reservoir. The equilibrium will be given by equal T and μ between the two part. This ensemble is named **Grand Canonical Ensemble**. We can derive the probability of the microstate of the system similar to the case of the canconical ensemble, but now we need to consider the microstates with different number of particles.

$$\frac{P_j}{P_i} = \frac{\Omega_r(E_i^r - \Delta E, N_i^r - \Delta N)}{\Omega_r(E_i^r, N_i^r)} = \exp\left(\frac{S_r(E_i^r - \Delta E, N_i^r - \Delta N) - S_r(E_i^r, N_i^r)}{k_B}\right) \tag{24}$$

with $\Delta E = E_j - E_i, \Delta N = N_j - N_i$, to linear in $\Delta N, \Delta E$, we have:

$$\frac{P_j}{P_i} = \exp\left(-\frac{1}{k_B}\frac{\partial S}{\partial E}\Delta E - \frac{1}{k_B}\frac{\partial S}{\partial N}\Delta N\right) = \exp\left(-\frac{1}{k_B T}(E_j - E_i) + \frac{\mu}{k_B T}(N_j - N_i)\right) \tag{25}$$

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[4]Blundell, p38

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giving
$$P_i \propto e^{-\beta(E_i - \mu N)} \tag{26}$$

Define the grand canonical partition function
$$Q(\mu, T, V) = \sum_N \sum_j e^{-\beta(E_j - \mu N)} \tag{27}$$

and the grand potential
$$\Omega(\mu, T, V) = -k_B T \ln Q \tag{28}$$

we have the probability to find a microstate:
$$P_{i,N} = \frac{1}{Q} e^{-\beta(E_i - \mu N)} = e^{\beta(\Omega - E_i + \mu N)} \tag{29}$$

The grand canonical ensemble is known as the μ**VT ensemble**

4   Thermodynamic potentials

It follows from the definition of T, P and μ that

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V} \ ; \ \frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{E,V} \ ; \ \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} \tag{30}$$

we can organize:

$$dS = \frac{1}{T}dE - \frac{\mu}{T}dN + \frac{P}{T}dV \tag{31}$$

$$dE = TdS + \mu dN - PdV \tag{32}$$

leading to:

$$T = \left(\frac{\partial E}{\partial S}\right)_{N,V} \ ; \ \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V} \ ; \ P = -\left(\frac{\partial E}{\partial V}\right)_{S,N} \tag{33}$$

For the Eq.32, we can integrate the subsystems parts by parts into the whole system (S, N and V are extensive parts), since T, μ and P will be the same for all subsystems, the integration gives:

$$E = TS + \mu N - PV \tag{34}$$

Now, let's consider the canonical ensemble. The energy of the system is no longer fixed, as opposed to microcanonical ensemble in which all the microstates in the ensemble have fixed energy. However, for each energy, it is associated with a probability and thus we only consider the average energy, which we define as **internal energy**:

$$U \equiv \langle E \rangle = \sum_j P_j E_j = \frac{\sum_j E_j e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} = -\frac{1}{Q_N}\frac{\partial Q_N}{\partial \beta} \tag{35}$$

The internal energy is now the macroscopic observable instead of energy, as in the microcanonical case. We wish to establish an relationship between the internal energy and the free energy $Q_N = \exp(-\beta A)$

Let's write

$$Q_N = \sum_j e^{-\beta E_j} = \sum_{E_j} \Omega(E_j) e^{-\beta E_j} \tag{36}$$

with $\Omega(E_j)$ gives the number of microstates that have energy E_j. With the definition of entropy $S(E) = k_B \ln \Omega(E)$, we have:

$$Q_N = \sum_{E_j} e^{-\beta(E_j - S(E_j)T)} \simeq e^{-\beta(E' - S(E')T)} \tag{37}$$

with E' be the value that minimize the function $E - S(E)T$. If the fluctuation is small, we can consider only the term $e^{-\beta(E' - S(E')T)}$ in the summation is not ignorable, which gives the approximation. The requirement that E' minimize function $E - S(E)T$ is:

$$\left.\frac{\partial(E - S(E)T)}{\partial E}\right|_{E'} = 1 - T\left.\frac{\partial S(E)}{\partial E}\right|_{E'} = 0 \tag{38}$$

therefore, E' is the energy in which:

$$\left.\frac{\partial S(E)}{\partial E}\right|_{E'} = \frac{1}{T} \tag{39}$$

that is to say, E' is the energy where the system's temperature defined by Eq.16 is equal to the temperature of the heat bath, which is the equilibrium condition. This motivate us to equal $E' = \langle E \rangle = U$ leading to the result that

$$A = U - TS(U) \tag{40}$$

U minimize $U - TS(U)$ at equilibrium, therefore, the equilibrium condition of a canonical potential is the minimization of free energy A.

With Eq.40, Eq.32 and $U = \langle E \rangle$, we have

$$dA(N, V, T) = dU - TdS - SdT = -SdT - pdV + \mu dN \tag{41}$$

and

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V} \; ; \; \mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} \; ; \; P = -\left(\frac{\partial A}{\partial V}\right)_{T,N} \tag{42}$$

For Grand canonical ensemble, we can apply similar method as in the canonical ensemble, but this time adding the particle number as a summation variable in the calculation of partition function, we can obtain:

$$\Omega(\mu, T, V) = U - TS - \mu \bar{N} \tag{43}$$

with $\bar{N}$ being the average particle number. The equilibrium condition of a grand canonical ensemble is then the minimization of Ω. We also have the following relationship:

$$d\Omega(\mu, T, V) = -SdT - Nd\mu - PdV \tag{44}$$

and

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{\mu,V} \; ; \; N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} \; ; \; P = -\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu} \tag{45}$$

Legendre transformation

In general, Legendre transformation is a transformation on the real valued convex functions of one of the variable and is usually used to convert functions of one quantity (position, pressure) into function of the conjugate quantity (momentum, volume) Consider function $F(x)$ with $dF/dx = s(x)$, we can write a function $G(s)$ with property $dG/ds = x(s)$. They are related by:

$$d(F + G) = sdx + xds = d(xs) \tag{46}$$

so that $F(x) + G(s) = xs$. One property of Legendre transformation that the result of the transformation is also convex function. For details of the geometry meaning and convex requirement, see Morin's chapter.

For thermodynamic potentials, we use a *non-standard definition* $dG/ds = -x(s)$, so that the transformation agree with the thermal dynamic variables. leading to

$$d(F - G) = sdx + xds = d(xs) \tag{47}$$

and therefore $F - G = xs$ [5].

We have seem that intensity and extensity properties would come in pairs, such as (T, S), (μ, N) and (P, V) due to their definition. We have also see that by defining different ensemble, we can write down different potential function for each ensemble:

$$\text{NVT ensemble} \Rightarrow dA(N, V, T) = -SdT - pdV + \mu dN$$
$$\mu \text{VT ensemble} \Rightarrow d\Omega(\mu, V, T) = -SdT - pdV - Nd\mu$$
$$(Gibbs) \text{ NPT ensemble} \Rightarrow dG(N, p, T) = -SdT + Vdp + \mu dN$$
$$\cdots$$

The relationship between different potential function can be expressed with **Legendre transformation**.

Writting x for an intensive property and S as the conjugating extensive property. For a potential $F(x)$ with the thermodynamic relationship $dF = Sdx$, if another potential G is related to $F(x)$ by $F(x) - G(S) = xS$, then, we can find $dG(S) = -xdS$.

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[5] Both is obviously correct. An example of the standard usage is Legendre transformation for Lagrangian and Hamiltonian is given by $F + G = xs$. see "Understanding the transformation in terms of derivatives" section in `https://en.wikipedia.org/wiki/Legendre_transformation`.

As an example, to find the Legendre transformation of the free energy in canonical ensemble $A(N, V, T)$ in terms of variable V, we have:

$$dA = -p\,dV$$

The transformed potential is thus:

$$dG(N, p, T) = V\,dp$$

corresponding to the Gibbs potential.

4.1   Gibbs expression of entropy

For the canonical ensemble, we have:

$$P_i = \frac{1}{Q}e^{-\beta E_i}$$

$$A = -k_B T \ln Q = U - TS$$

This lead to the relationship:

$$S = -k_B \sum_i P_i \ln P_i \tag{48}$$

This is the Gibbs' form of entropy in terms of probability.

5 Quantum Statistical Mechanics

For a quantum **ensemble** $|\Psi\rangle$ expressed in a complete set of basis $|\phi_i\rangle$ (state of system)as

$$|\Psi\rangle = \sum_i c_i |\phi_i\rangle \tag{49}$$

we define the density matrix

$$\rho = |\Psi\rangle\langle\Psi| = \sum_{ij} |\phi_i\rangle\langle\phi_i|\Psi\rangle\langle\Psi|\phi_j\rangle\langle\phi_j| = \sum_{ij} c_i c_j^* |\phi_i\rangle\langle\phi_j| \tag{50}$$

and therefore

$$\langle\phi_i|\rho|\phi_j\rangle = c_i c_j^* \tag{51}$$

So that the expectation value of observables A is then:

$$\langle A\rangle = \langle\Psi|A|\Psi\rangle = \sum_{ij}\langle\Psi|\phi_i\rangle\langle\phi_i|A|\phi_j\rangle\langle\phi_j|\Psi\rangle = \sum_{ij} c_i^* c_j \langle\phi_i|A|\phi_j\rangle \tag{52}$$

while we also have:

$$\mathrm{Tr}[\rho A] = \sum_i \langle\phi_i|\rho A|\phi_i\rangle = \sum_{ij}\langle\phi_i|\rho|\phi_j\rangle\langle\phi_j|A|\phi_i\rangle = \sum_{ij} c_i c_j^*\langle\phi_j|A|\phi_i\rangle = \langle A\rangle \tag{53}$$

So that we find the relationship

$$\langle A\rangle = \mathrm{Tr}[\rho A] \tag{54}$$

Now, we consider the time dependence of the trace operator, using the time evolution operator:

$$
\begin{aligned}
-ih\frac{\partial}{\partial t}\rho &= -ih\frac{\partial}{\partial t}\sum_{ij} c_i c_j^* |\phi_i\rangle\langle\phi_j| \\
&= \sum_{ij} c_i c_j^* \left(-ih\frac{\partial}{\partial t}|\phi_i\rangle\langle\phi_j| - |\phi_i\rangle ih\frac{\partial}{\partial t}\langle\phi_j|\right) \\
&= \sum_{ij} c_i c_j^* \left(H|\phi_i\rangle\langle\phi_j| - |\phi_i\rangle\langle\phi_j|H\right) \\
&= [H\rho - \rho H] = [H,\rho]
\end{aligned}
\tag{55}
$$

In an equilibrium, the density operator will be time dependent: $\partial\rho/\partial t = 0$, suggesting that H and ρ commute: $[H,\rho] = 0$. The eigenstates of the Hamiltonian thus are also the eigenstates of the density operator. Therefore, the density operator in Eq.50 can be written in this form:

$$\rho = \sum_n w_n |n\rangle\langle n| \tag{56}$$

where $|n\rangle$ are the eigenstates of the Hamiltonian, and $w_n = c_n^* c_n = |c_n|^2$ is the probability for the system $|\Psi\rangle$ to be in the energy eigenstate $|n\rangle$ For Microcanonical ensemble with Ω accessible states, we simply have:

$$w_n = \frac{1}{\Omega} \tag{57}$$

For Canonical ensemble, we have:

$$w_n = \frac{e^{-\beta E_n}}{\sum_{n'} e^{-\beta E_{n'}}} \tag{58}$$

and the partition function $Q = \mathrm{Tr}e^{-\beta H}$ (an observables). For Grand Canonical ensemble, taking account of the particle number in an system state $|n\rangle$, we have:

$$w_n = \frac{e^{-\beta(E_n - \mu N_n)}}{\sum_{n'} e^{-\beta(E_{n'} - \mu N_{n'})}} \tag{59}$$

and partition function $Q = \mathrm{Tr}e^{-\beta(H - \mu N)}$, where N is the operator for particle density.

Distribution function

Suppose the Hamiltonian can be written as a function of particle number $H = \sum_p \varepsilon_p n_p$ with ε_p, n_p denoting the energy and occupation number of a single particle state p. We start by calculating the partition function of a quantum ensemble, since we wish to study the probability of system containing different particle number, we use the grand canonical potential:

$$Q(\mu, V, T) = \sum_{N=0}^{\infty} \sum_{\{n_p\}_N} e^{-\beta \sum_p (\varepsilon_p - \mu) n_p} = \sum_{\{n_p\}} e^{-\beta \sum_p (\varepsilon_p - \mu) n_p} \tag{60}$$

where in the first expression, $\{n_p\}_N$ denotes a many body state with occupation $\{n_{p_1}, n_{p_2}, \cdots, n_{p_i}\}$ in each of the single particle with the constraint that the total number of particles sum up to N. In the second expression, the two summation in the first expression are combined. We now take the summation p in the exponential out:

$$Q(\mu, V, T) = \sum_{\{n_p\}} e^{-\beta \sum_p (\varepsilon_p - \mu) n_p} = \prod_p \sum_{n_p} e^{-\beta (\varepsilon_p - \mu) n_p} = \prod_p Q_p \tag{61}$$

We can now study the sum of $e^{-\beta(\varepsilon_p - \mu) n_p}$ over all possible occupation number: **Fermion** we can only take $n_p = 0$ or 1, so that

$$Q_p = 1 + e^{-\beta(\varepsilon_p - \mu)} \tag{62}$$

$$\Omega_p = -k_B T \ln Q_p \tag{63}$$

and

$$N_p = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} = \frac{1}{e^{\beta(\varepsilon_p - \mu)} + 1} \tag{64}$$

Boson the sum of n_p is from 0 to ∞, thus:

$$\sum_{n_p = 0}^{\infty} e^{-\beta(\varepsilon_p - \mu) n_p} = \frac{1}{1 - e^{-\beta(\varepsilon_p - \mu)}} \tag{65}$$

giving

$$N_p = \frac{1}{e^{\beta(\varepsilon_p - \mu)} - 1} \tag{66}$$

The partition function and total particle number can be summarized by given by:

$$\Omega = -a k_B T \sum_p \ln(1 + a e^{-\beta(\varepsilon_p - \mu)}) \tag{67}$$

$$N = \sum_p \frac{1}{e^{\beta(\varepsilon_p - \mu)} + a} \tag{68}$$

with $a = 1$ for fermion and -1 for boson.

Boson gas

For an ideal gas of spinless bosons [6], the single particle state will be the momentum eigenstate given by k and kinetic energy $\varepsilon_k = \frac{\hbar^2 k^2}{2m}$. The chemical potential μ will be negative otherwise the state with energy

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[6]for spin S, each momentum eigenstate k will have $(2S + 1)$ fold degeneracy

smaller than μ will have negative occupation. We calculate the grand potential:

$$\Omega = k_B T \sum_k \ln(1 - e^{-\beta(\varepsilon_p - \mu)})$$

$$= k_B T \int_0^\infty \ln(1 - e^{-\beta(\varepsilon_p - \mu)}) g(\varepsilon) d\varepsilon$$

$$= k_B T \int_0^\infty \ln(1 - e^{-\beta(\varepsilon_p - \mu)}) \frac{V \varepsilon^{1/2}}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} d\varepsilon$$

$$= -\frac{2}{3} \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{e^{\beta(\varepsilon_p - \mu)} - 1} \tag{69}$$

define $z = e^{\beta\mu}$, the particle number and internal energy can be written as:

$$N = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{\varepsilon^{1/2} d\varepsilon}{e^{\beta\varepsilon_p}/z - 1} \tag{70}$$

$$U = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{e^{\beta\varepsilon_p}/z - 1} \tag{71}$$

The integral we can write in terms of **polylogarithm** function:

$$\int_0^\infty \frac{\varepsilon^{n-1} d\varepsilon}{e^{\beta\varepsilon_p}/z - 1} = (k_B T)^n (n-1)! L_n(z) \tag{72}$$

with $n/2! = n/2 \times (n-2)/2 \times \cdots \times 1/2$ with n an odd number. So that

$$N = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} (k_B T)^{3/2} (1/2)! L_{3/2}(z) = \frac{V}{\lambda^3} L_{3/2}(z) \tag{73}$$

$$U = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} (k_B T)^{5/2} (3/2)! L_{5/2}(z) = \frac{3}{2} \frac{V k_B T}{\lambda^3} L_{5/2}(z) \tag{74}$$

λ is defined to absorbed all the numerical factor in Eq.73 and $\lambda \propto T^{-1/2}$. Let's now consider Eq.73

$$n\lambda^3 = L_{3/2}(z) \tag{75}$$

since μ need to be negative, the value of z is bound to $(0, 1)$, the function $L_{3/2}$ is monoclinically increaing with z and bound between $(0, L_{3/2}(1)) \approx (0, 2.612)$, however, as we decrease temperature and $z \to 1$, λ will increase without bound, which conflict with Eq.75.

This inconsistency come from the fact that when we convert the summation of k into integral of energy ε, we essentially omitted a single state ($k = 0, \varepsilon = 0$) since $g(\varepsilon = 0) = 0$. Its density of state $g(\varepsilon)$ is ignorable compared to other states but at low temperature, it's occupation maybe very large. Including the occupation of this ground state explicitly in Eq.73:

$$N = N_0 + N_1 = \frac{1}{1/z - 1} + \frac{V}{\lambda^3} L_{3/2}(z) \tag{76}$$

if we define

$$n\lambda(T_c)^3 = L_{3/2}(z = 1) \tag{77}$$

then

$$\frac{N_0}{N} = \frac{N - N_1}{N} = 1 - \left(\frac{T}{T_c}\right)^{3/2} \tag{78}$$

if the temperature is low enough so that $N_0/N \approx 1$, then almost all particles are condensed in the ground state. T_c for an ideal boson gas can be calculated:

$$k_B T_c \approx 0.061 \frac{\hbar^2}{m} n^{2/3} \tag{79}$$

For example, liquid Helium^4 with a density of $1.5e22 cm^{-3}$ gives a $T_c \approx 3K$. Expreiment observed a phase transition to a new phase with superfluid properties around this temperature, associated with the condensation.