Lecture III - grand canonical ensemble and quantum ideal gas

The microcanonical ensemble describes/states an isolated system, in which the total energy, volume and particle number are kept fixed. Conversely, the canonical ensemble deals with a system place in contact with a thermal reservoir, but there is no fluctuation of N (particle number) nor V (volume). Although the Gibbs ensembles are equivalent in the thermodynamic limit, at least for short range Hamiltonians, in certain situations the "usage of a given ensemble" is more convenient than another one. In this lecture, we shall first present the main ideas concerning the grand canonical ensemble, in which our system of interest is placed in contact with a thermal and particle reservoir, and the probability distribution will not the $e^{-\beta \mathcal{H}}/Z$.

Let us consider an (isolated) system composed of a thermal reservoir that exchanges "heat" and "particles" with our system S

The composite system (reservoir + system S) is isolated, in which the energy and particle number is held fixed

$$\overbrace{E_R}^{\text{Thermal bath}} + \overbrace{E_S}^{S} = \overbrace{E_0}^{\text{total}}$$

$$N_R + N_S = N_0$$

In similarity with the canonical ensemble, the probability of $\underline{S}$ be in the microscopic state $\underline{\underline{j}}$ in which its energy and particle number reads E_j and N_j reads

$$P_j = \frac{\Omega_S(E_j, N_j)\,\Omega_R(E_0 - E_j, N_0 - N_j)}{\Omega_T}$$

$= C\,\Omega_R(E_0 - E_j, N_0 - N_j)$ ← total number of configurations in which E_0 and N_0 are held fixed.

Since $E_j \ll E_0$ and $N_j \ll N_0$, one can expand the $\ln P_j$ in Taylor series (in analogy with previous lecture) and

$$\ln P_j = \ln c + \ln \Omega_R(E_0, N_0) +$$

$$+ \left(\frac{\partial \ln \Omega_R}{\partial E}\right)\Bigg|_{E_0, N_0} (-E_j) + \left(\frac{\partial \ln \Omega_R}{\partial N}\right)\Bigg|_{E_0, N_0} (-N_j) +$$

$$\frac{1}{2}\left[\frac{\partial^2 \ln \Omega_R}{\partial E^2}\right]\Bigg|_{E_0,N_0} (-E_\gamma)^2 + \frac{1}{2}\left[\frac{\partial^2 \ln \Omega_R}{\partial N^2}\right](-N_\gamma)^2 \quad b \quad 4 \quad (2)$$

$$+ \left[\frac{\partial^2 \ln \Omega_R}{\partial E\, \partial N}\right]\Bigg|_{E_0,N_0} (-E_\gamma)(-N_\gamma).$$

Let us identify each term:

(1) Since for an isolated system $S = K_B \ln \Omega$ and by approximating $S_R = K_B \ln \Omega_R$

$$\left(\frac{\partial}{\partial E} \ln \Omega_R\right)\Bigg|_{E_0,N_0} = \frac{1}{K_B T_R}$$

(2) $$\left(\frac{\partial \ln \Omega_R}{\partial N}\right)\Bigg|_{E_0,N_0} = \frac{-\mu_R}{K_B T_R}$$

(3), (4) and (5) Since $R >> S$, its temperature and chemical potential (of thermal bath) are constant and therefore fluxes of energy and particles does not change T_R and μ_R. Therefore the terms (3), (4) and (5) vanish.

Hence

$$\ln P_\gamma = \ln \tilde{c} - \frac{E_\gamma}{K_B T_R} + \frac{\mu_R N_\gamma}{K_B T_R} \quad \text{and}$$

$$P_\nu = e^{\tilde{c} - \frac{E_\nu}{k_B T} + \frac{\mu N_\nu}{k_B T}}$$

(From now on $T_R \equiv T$, $\mu_R \equiv \mu$)

Since $\sum_\nu P_\nu = 1$, we have that

$$e^{\tilde{c}} \sum_\nu e^{-\beta E_\nu + \beta \mu N_\nu} = 1$$ and

$$e^{\tilde{c}} = \frac{1}{\sum_\nu e^{-\beta E_\nu + \beta \mu_\nu}} \equiv \frac{1}{\underbrace{\Xi(T, V, \mu)}_{\text{grand canonical partition function}}}.$$

The grand canonical ensemble is constituted by the set of microscopic states ν in which the probability P_ν is given by

$$P_\nu = \frac{e^{-E_\nu/k_B T + \frac{\mu N_\nu}{k_B T}}}{\Xi(T, V, \mu)}.$$

For a fluid, Ξ solely depends on T, V, μ.

Conexion with Thermodynamics

The summation over all microscopic configurations can be carried out under two distinct steps.

1) Fixing $\underline{N}$ and by summing over all λ's in which $\underline{N}$ is kept fixed.

Further,

2) By summing over all N's.

Matematically, $\Xi(T, V, \mu)$ is given by

$$\Xi(T, V, \mu) = \underbrace{\sum_{N=0}^{\infty} e^{\beta\mu N} \underbrace{\sum_{\lambda} e^{-\beta E_\lambda(N)}}_{\text{step (1)}}}_{\text{step 2}}$$

The term $\sum_{\lambda} e^{-\beta E_\lambda(N)}$ is simply the canonical partition function $Z(T, V, N)$.

above equation can be rewritten as

$$\Xi(T, V, \mu) = \sum_N e^{\beta\mu N} Z(\beta, N) = \sum_N e^{\beta\mu N + \ln Z}$$

$$= \sum_N e^{-\beta(F - \mu N)}$$

As we have studied in the case of canonical ensemble, in the thermodynamic limit solely the largest term of $\sum_N e^{-\beta(F-\mu N)}$ dominates and will be relevant. Therefore

$$\Xi(T,V,\mu) \sim e^{-\beta \min_N (F-\mu N)},$$

where "$\min_N$" corresponds the minimum with respect to the particle number and corresponding to the Legendre transform of Helmholtz free energy with respect to N and is the grand canonical potential. Hence

$$\Xi = e^{-\beta \Phi(T,V,\mu)} \quad \text{and}$$

$$\Phi(T,V,\mu) = -\frac{1}{\beta} \ln \Xi(T,V,\mu).$$

The pressure is related to the grand canonical potential. This can be examined through the Euler relation

$$\mathcal{U} = TS - pV + \mu N$$

$$\text{Since } \Phi = F - \mu N$$
$$= (\mathcal{U} - TS) - \mu N$$

$$\Phi = (TS - pV + \mu N) - TS - \mu N$$
$$= -pV$$

$$\boxed{p = -\Phi/V.}$$

the pressure is directly related to the grand canonical potential

Next we shall derive expressions for appropriate averages in the grand canonical ensemble

The mean energy

$$\langle E_\gamma \rangle = \frac{1}{\Xi} \sum_\gamma E_\gamma \, e^{-\beta E_\gamma + \beta\mu N_\gamma}$$

$$= \frac{1}{\Xi}\left[-\frac{\partial}{\partial\beta} \sum_\gamma e^{-\beta E_\gamma + \beta\mu N_\gamma} \right] + \frac{\sum_\gamma \mu N_\gamma \, e^{-\beta E_\gamma + \beta\mu N_\gamma}}{\Xi}$$

$$= -\frac{1}{\Xi}\frac{\partial}{\partial\beta}\Xi + \frac{1}{\Xi}\frac{\mu}{\beta}\frac{\partial}{\partial\mu}\Xi$$

$$= -\frac{\partial}{\partial\beta}\ln\Xi + \underbrace{\frac{\mu}{\beta}\frac{\partial}{\partial\mu}\ln\Xi}_{\text{from the next average}} \qquad (1)$$

$$\langle N_\gamma \rangle = \frac{1}{\Xi}\sum_\gamma N_\gamma \, e^{-\beta E_\gamma + \beta\mu N_\gamma} = \frac{1}{\Xi}\frac{1}{\beta}\frac{\partial}{\partial\mu}\sum_\gamma e^{-\beta E_\gamma + \beta\mu N_\gamma}$$

$$= \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\Xi \qquad (2)$$

Both averages, $\langle E_\gamma\rangle$, $\langle N_\gamma\rangle$, are directly related with derivatives of the grand canonical partition function.

Eqs (1) – (2) and (3) – (4) are directly related :

Let $\bar{q} = -\ln \Xi$ $\qquad z = e^{\beta\mu}$

$$\left(\frac{\partial \bar{q}}{\partial \beta}\right)_z = \left(\frac{\partial \bar{q}}{\partial \beta}\right)_\mu + \left(\frac{\partial \bar{q}}{\partial \mu}\right)_\beta \left(\frac{\partial \mu}{\partial \beta}\right)_z$$

$$= \left(\frac{\partial \bar{q}}{\partial \beta}\right)_z + \left(\frac{\partial \bar{q}}{\partial \mu}\right)_\beta \left(-\frac{1}{\beta^2} \ln z\right)$$

Hence

$$\left(\frac{\partial \bar{q}}{\partial \beta}\right)_z = \left(\frac{\partial \bar{q}}{\partial \beta}\right)_\mu - \frac{\mu}{\beta}\left(\frac{\partial \bar{q}}{\partial \mu}\right)_\beta$$

(Please check Eqs. (1) and (3))

$$z\left(\frac{\partial \bar{q}}{\partial z}\right) = z\left(\frac{\partial \bar{q}}{\partial \mu}\right)\left(\frac{\partial \mu}{\partial z}\right) = K_B T \frac{\partial \bar{q}}{\partial \mu}$$

$$= \frac{1}{\beta} \frac{\partial \bar{q}}{\partial \mu}$$

(Please check Eqs. (2) and (4))

The variance of particle number is given by

$$\langle (N_g - \langle N_g \rangle)^2 \rangle = \langle N_g^2 \rangle - \langle N_g \rangle^2.$$

Since $\langle N_g \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \Xi$ and

$$\langle N_g^2 \rangle = \frac{1}{\Xi} \sum_g N_g^2 \, e^{-\beta E_g + \beta\mu N_g} = \frac{1}{\Xi} \frac{1}{\beta^2} \frac{\partial^2}{\partial \mu^2} \Xi .$$

Hence

$$\langle N_\gamma^2\rangle - \langle N_\gamma\rangle^2 = \frac{1}{\beta^2}\left[\frac{1}{\Xi}\frac{\partial^2 \Xi}{\partial \mu^2} - \frac{1}{\Xi^2}\left(\frac{\partial \Xi}{\partial \mu}\right)^2\right]$$

$$= \frac{1}{\beta^2}\frac{\partial^2}{\partial \mu^2}\ln \Xi = \frac{1}{\beta}\left(\frac{\partial \langle N_\gamma\rangle}{\partial \mu}\right)$$

By identifying $N \longrightarrow \langle N_\gamma\rangle$ (in the thermodynamic limit, I will prove it in the next page)

$$\langle N_\gamma^2\rangle - \langle N_\gamma\rangle^2 = \frac{1}{\beta}\left(\frac{\partial N}{\partial \mu}\right)$$

Since $\langle N_\gamma^2\rangle - \langle N_\gamma\rangle^2 > 0$, N <u>increases</u> with $\underline{\mu}$.

In order to prove that $N \longrightarrow \langle N_\gamma\rangle$ we shall appeal to the Gibbs–Duhem relation

$$+ S\,dT - V\,dp + N\,d\mu = 0.$$

and

$$\left(\frac{\partial \mu}{\partial N}\right)_{T,V} = \frac{V}{N}\left(\frac{\partial p}{\partial N}\right)_{T,V} \qquad (*1)$$

By resorting to the Maxwell relation

$$\left(\frac{\partial^2 F}{\partial V\,\partial N}\right) = \left(\frac{\partial^2 F}{\partial N\,\partial V}\right)$$

$$\left(\frac{\partial \mu}{\partial V}\right)_{N,T} = -\left(\frac{\partial p}{\partial N}\right)_{T,V} \qquad (*2)$$

Hence $(*1)$ reads

$$\left(\frac{\partial \mu}{\partial N}\right)_{T,V} = -\frac{V}{N}\left(\frac{\partial \mu}{\partial V}\right)_{T,N}.$$

From the Gibbs-Duhem relation we have that

$$V\left(\frac{\partial P}{\partial V}\right)_{T,N} = +N\left(\frac{\partial \mu}{\partial V}\right)_{T,N}$$ and therefore

$$\left(\frac{\partial \mu}{\partial N}\right)_{T,N} = -\frac{V^2}{N^2}\left(\frac{\partial P}{\partial V}\right)_{T,N} = \frac{V}{N^2}\frac{1}{K_T}$$

Since $K_T \geq 0 \rightarrow \left(\frac{\partial \mu}{\partial N}\right) \geq 0$ and hence

$\langle N_J^2\rangle - \langle N_J\rangle^2 \geq 0$ and N increases with μ.

The relative deviation is given by

$$\frac{\sqrt{\langle N_J^2\rangle - \langle N_J\rangle^2}}{\langle N_J\rangle} = \frac{\sqrt{\frac{1}{\beta}\frac{N^2}{V}k_T}}{N} = \left(\frac{K_B T\, K_T}{v}\right)^{1/2}\frac{1}{\sqrt{N}} \rightarrow 0$$

When $N \rightarrow \infty$, allowing us to identify $\langle N_J\rangle$ with N. In the case of a continuous phase transition, $\langle N_J^2\rangle - \langle N_J\rangle^2 \longrightarrow \infty$ and fluctuations of system density becomes huge since $K_T \rightarrow \infty$.

Application: Monoatomic Ideal gas

We have just obtained the canonical partition function for the monoatomic ideal gas

$$Z(T, V, N) = \frac{1}{N!}\left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3N}{2}} V^N$$

$$\Xi(T, V, z) = \sum_{N=0}^{\infty} \underbrace{Z(T, V, N)}_{\text{canonical partition function.}} \underbrace{z^N}_{\text{fugacity}}$$

$$\Xi(T, V, z) = \sum_{N=0}^{\infty} \frac{1}{N!}\left(\frac{2\pi m}{\beta h^2}\right)^{3N/2} V^N z^N$$

$$= \exp\left[\left(\frac{2\pi m}{\beta h^2}\right)^{3/2} V z\right]$$

$$u = \langle E_z \rangle = -\frac{\partial}{\partial \beta} \ln \Xi(T, V, z)$$

$$= \frac{3}{2}\left(\frac{2\pi m}{\beta h^2}\right)^{3/2} \beta^{-1} V z$$

$$N = \langle N_z \rangle = z \frac{\partial}{\partial z} \ln \Xi(T, V, z)$$

$$= z \frac{\partial}{\partial z}\left[\left(\frac{2\pi m}{\beta h^2}\right)^{3/2} V z\right]$$

$$= \left(\frac{2\pi m}{\beta h^2}\right)^{3/2} V z,$$

in such a way that $u = \frac{3}{2} N k_B T$ $\left(u = \frac{3}{2}\langle N_z \rangle k_B T\right)$

- The pressure $p(T, V) = \frac{1}{V\beta} \ln \mathcal{Z}(T, V, z)$ 7

$$= \frac{1}{V}\left(\frac{2\pi m}{\beta h^2}\right)^{3/2} V z = \frac{V}{N\beta}$$

$\boxed{pV = N K_B T}$, which is the same relation between p and N from the Canonical ensemble.