Open System: Grand-canonical Ensemble

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- In microcanonical ensemble, each system contains same fixed energy as well as same number of particles. Hence, the system dealt within this ensemble is a closed isolated system.

- With microcanonical ensemble, we can not deal with the systems that are kept in contact with a heat reservoir at a given temperature.

- In canonical ensemble, the condition of constant energy is relaxed and the system is allowed to exchange energy but not the particles with the system, i.e. those systems which are not isolated but are in contact with a heat reservoir.

- This model could not be applied to those processes in which number of particle varies, i.e. chemical process, nuclear reactions (where particles are created and destroyed) and quantum process.

- So, for the method of ensemble to be applicable to such processes where number of particles as well as energy of the system changes, it is necessary to relax the condition of fixed number of particles.

- Such an ensemble where both the energy as well as number of particles can be exchanged with the heat reservoir is called Grand Canonical Ensemble.

- In canonical ensemble, T, V and N are independent variables. Whereas, in grand canonical ensemble, the system is described by its temperature (T),volume (V) and chemical potential (μ).

- Since, the system is not isolated, its microstates are not equally probable. So, for this we have to first construct an isolated system where we can apply the assumption of equi-probable microstates and then to calculate the probability of a microstate of an open system.

Let us consider a subsystem *s* in contact with a heat reservoir *r* and the subsystem can exchange energy as well as particles with the reservoir. Total energy of the system is represented by microcanonical ensemble with constant energy E and number of particles N.

If E_s, N_s refer to the energy and number of particles of subsystem; E_r, N_r refer to the energy and number of particles of reservoir and E_t, N_t refer to the energy and number of particles of the total system then,

$$E_s + E_r = E_t \quad and \quad N_s + N_r = N_t$$

Let $d\omega_s(N_s)$ denote the probability of finding a subsystem *s* in a state which contains N_s particles and is found in the element $d\Gamma_s(N_s)$ of its phase space. Therefore,

$$d\omega_s(N_s) = cd\Gamma_s(N_s)\Delta\Gamma_r(N_t - N_s)$$

$$d\omega_s(N_s) = cd\Gamma_s(N_s)\exp\left[S_r(E_t - E_s, N_t - N_s)/k\right] \quad ....(1)$$

using Taylor expansion, S_r can be expressed as -

$$S_r(E_t - E_s, N_t - N_s) = S_r(E_t, N_t) - \frac{\partial S_r(E_t, N_t)}{\partial E_t}E_s - \frac{\partial S_r(E_t, N_t)}{\partial N_t}N_s \quad ....(2)$$

From the first law of thermodynamics, we have for a reversible process

$$dE = TdS - PdV + \mu dN \quad ....(3)$$

$$dS = \frac{dE}{T} + \frac{PdV}{T} - \frac{\mu dN}{T} \quad ....(4)$$

Now,

$$S \cong S(E, V, N)$$

$$dS = \left(\frac{\partial S}{\partial E} \right)_{V,N} dE + \left(\frac{\partial S}{\partial V} \right)_{E,N} dV + \left(\frac{\partial S}{\partial N} \right)_{E,V} dN \quad ....(5)$$

From (4) and (5), we get

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T} \, , \quad \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T} \quad , \left(\frac{\partial S}{\partial N}\right)_{E,V} = \frac{-\mu}{T} \quad ....(6)$$

$$\therefore \quad S_r(E_t - E_s, N_t - N_s) = S_r(E_t, N_t) - \frac{E_s}{T} + \frac{\mu N_s}{T} \quad ....(7)$$

Now, probability of a microstate is given by

$$P_s(N_s) = \frac{w(E_t - E_s, N_t - N_s)}{w_{total}} \quad ....(8)$$

$$P_s(N_s) = \frac{1}{w_{total}} \exp\left[\frac{1}{k} S(E_t - E_s, N_t - N_s)\right]$$

$$P_s(N_s) = \frac{1}{w_{total}} \exp\left[\frac{S_r(E_t, N_t)}{k} - \frac{E_s}{kT} + \frac{\mu N_s}{kT}\right]$$

$$P_s(N_s) = \alpha \exp\left[-\beta(E_s - \mu N_s)\right] \quad ....(9)$$

where constant α can be determined by the normalization condition

$$\sum_{s} P_s(N_s) = 1$$

and the sum is over all the microstates of the system.

$$P_s(N_s) = \frac{1}{Q} \exp\left[-\beta\left(E_s - \mu N_s\right)\right] \quad ....(10)$$

where

$$Q(T,V,\mu) = \sum_s \exp\left[-\beta(E_s - \mu N_s)\right] \quad ....(11)$$

An ensemble characterized by the distribution function given by eq$^{\text{n}}$. (11) is called the ***grand partition function***. It is the sum of canonical partition function Z for ensembles with different N's, with weighting factor $\exp(\beta N\mu)$.

$$Q(T, V, \mu) = \sum_s \lambda^{N_s} \exp(-\beta E_s) \quad \ldots\ldots\ldots(12)$$

where $\lambda = \exp(\beta\mu)$ is *fugacity*.

Therefore, we can write the grand canonical partition function as

$$Q(T, V, \mu) = \sum_{N=0}^{\infty} \lambda^N Z(T, V, N) \quad \ldots\ldots\ldots(13)$$

Thermodynamic Potential

The normalization factor is expected to give the thermodynamic potential for T, V, μ which is the ***grand potential or Landau potential*** as –

$$\zeta(T,V,\mu) = E(S,V,N) - TS - \mu N \qquad ....(14)$$

Relation between ζ and Q

Since, number of particles in an open system under equilibrium is not fixed and it fluctuates from one microstate to another. However, these fluctuations are very small. So, in general eq^n. (13) is represented as -

$$Q(T,V,\mu) = \lambda^N Z(T,V,N) \quad ....(15)$$

$$\ln Q(T,V,\mu) = \beta\mu N + \ln Z(T,V,N)$$

$$\ln Q(T,V,\mu) = \frac{\mu N}{kT} + \ln Z(T,V,N) \quad ....(16)$$

$$kT \ln Q = \mu N + kT \ln Z(T,V,N) \quad ....(17)$$

In canonical ensemble,

$$F(T,V,N) = -kT \ln Z(T,V,N)$$

From eq$^{\text{n}}$. (17)

$$kT \ln Q = \mu N - F(T,V,N) \quad ....(18)$$

$$-kT \ln Q = F - \mu N = E - TS - \mu N \quad ....(19)$$

As we know that chemical potential (μ) is conjugate variable of N. Thus, we transform to a quantity that is a function of μ rather than being a function of N. Such potential are known as **grand potentials**.

Thus, we have

$$\zeta(T,V,\mu) = F\{T,V,N(\mu)\} - \frac{\partial F}{\partial N}N$$

$$d\zeta = dF - \mu dN - N d\mu = S dT - p dV - N d\mu$$

So, grand potential is the available energy for a system in contact with a heat reservoir that is required to keep the system at constant temperature and the particles necessary to maintain the constant chemical potential.

$$\zeta(T,V,\mu) = -kT \ln Q(T,V,\mu)$$

This can be used as a fundamental relation between thermodynamics and statistical mechanics for open systems.

Summary

- Find Q (T,V,µ)

- Grand Potential, $\zeta = -kT\ln Q$

- Entropy of the System, $S = -\left(\dfrac{\partial \zeta}{\partial T}\right)_{V,\mu}$

- Average number of particles, $\overline{N} = \langle N \rangle = -\left(\dfrac{\partial \zeta}{\partial \mu}\right)_{V,T}$

- $p = -\left(\dfrac{\partial \zeta}{\partial V}\right)_{T,\mu}$

$$F = \zeta + \mu N$$

$$E = F + TS = \zeta + \mu N + TS$$

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

$$H = E + pV$$

References: Further Readings

1. *Statistical Mechanics* by R.K. Pathria

2. *Elementary Statistical Mechanics* by Gupta & Kumar

3. *Statistical Mechanics* by K. Huang

4. *Statistical Mechanics* by B.K. Agrawal and M. Eisner

5. *Statistical Mechanics* by Satya Prakash

Thank You

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