PHYS 3014: Statistical Mechanics

Lecture Notes
Part 10

Grand Canonical Ensemble

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Grand Canonical Ensemble

In many systems it is realized that not only the energy of the system but number of particles is very hard to be measured directly. There could be estimated indirectly.

In many chemical processes the no. of particles varies. In quantum processes particles are being created and destroyed.

Therefore, we regard N and E are variables and identify their expectation values $\langle N \rangle$ and $\langle E \rangle$. Again we define new ensemble whose physical parameters could easily be controlled.

If we consider a system at constant temperature and constant chemical potential, then these could easily be measured as well as controlled by immersing the system in a large reservoir. The system exchanges both energy and particles with the reservoir so that it could atain common temperature "T" and common chemical potential "μ". These quantities associated with the reservoir could easily be measured directly.

Now we can construct a ensemble of systems. If the reservoir consists of infinitely large number of mental copies of a given system then such collection of many systems having same V, T, and μ defines an ensemble called as **Grand-Canonical Ensemble.**

In Grand Canonical Ensemble, energy and number of particles of system are variables.

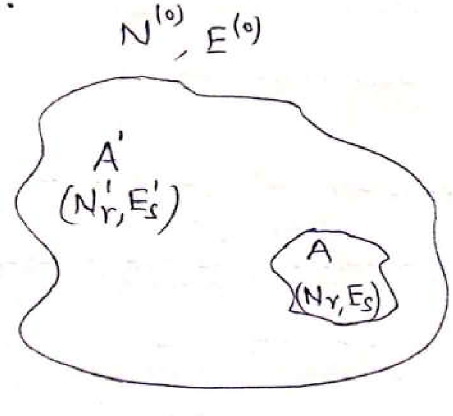
The statistics of variation of variables N and E of the system could be studied by either

(i) considering the system A to be placed in contact with a large reservoir A' with which it can exchange both energy E and particles N.

(ii) consider the system as a member of an ensemble called as grand canonical ensemble. Grand canonical ensemble consists of the given system A and a large number of mental copies of the system A. These members exchange both energy and number of particles among themselves.

Equilibrium between a system and particle-energy reservoir

Consider a system A which is immersed in a large reservoir A'. System A can exchange both energy E and number particles N with the reservoir. At equilibrium, both system A and reservoir A' will have the common temperature T and common chemical potential μ.



At any time t, the system can have any value of energy E_s and any no. of particles N_r. N_r and E_s defines a possible states possessed by the system at any time t.

Let $N^{(0)}$ and $E^{(0)}$ be the total no. of particles and total energy of the composite system (A+A'). So at any time

$$0 \leqslant \frac{N_r}{N^{(0)}} \leqslant 1 \quad \text{and} \quad 0 \leqslant \frac{E_s}{E^{(0)}} \leqslant 1 .$$

Since $N^{(0)}$ and $E^{(0)}$ are constant, then if system is in a state characterized by N_r and E_s then reservoir must have N_r' and E_s' such that

$$N_r + N_r' = N^{(0)} \quad \text{Constant} \qquad \text{---} ①$$

$$E_s + E_s' = E^{(0)} \quad \text{Constant}$$

Since the reservoir is much larger than the given system, so for practical purposes, the values of E_s and N_r will be very small fraction of the total energy $E^{(0)}$ and total no. of particles $N^{(0)}$ respectively.

$$\frac{N_r}{N^{(0)}} = 1 - \frac{N_r'}{N^{(0)}} << 1$$

and

$$\frac{E_s}{E^{(0)}} = 1 - \frac{E_s'}{E^{(0)}} << 1$$

The probability $P_{r,s}$ that the system A is found to be in a state (N_r, E_s) is proportional to the number of microstates $\Omega'(N_r', E_s')$ possessed by the reservoir for the corresponding macrostate represented by (N_r', E_s').

$$P_{r,s} \propto \Omega'(N_r', E_s') \cdot \Omega(N_r, E_s)$$

$$\propto \Omega'(N^{(0)} - N_r, E^{(0)} - E_s) \qquad \because \Omega(N_r, E_s) = 1$$

we can expand $\ln \Omega'(N^{(0)} - N_r, E^{(0)} - E_s)$ around the values $E_s' = E^{(0)}$ i.e around $E_s = 0$ and $N_r' = N^{(0)}$ i.e around $N_r = 0$

we get

$$\ln \Omega'(N^{(0)} - N_r, E^{(0)} - E_s) = \ln \Omega'(N^{(0)}, E^{(0)}) + \left(\frac{\partial \ln \Omega'}{\partial N'}\right)_{N' = N^{(0)}} (-N_r)$$

$$+ \left(\frac{\partial \ln \Omega'}{\partial E'}\right)_{E' = E^{(0)}} (-E_s) + \cdots$$

$$\simeq \ln \Omega'(N^{(0)}, E^{(0)}) + \left(\frac{\mu'}{KT'}\right) N_r - \frac{1}{KT'} E_s$$

where μ' and T' are the chemical potential and temperature of the reservoir and hence of the system as well at equilibrium.

$$-\frac{\mu'}{KT'} = \left(\frac{\partial \ln \Omega'}{\partial N'}\right)_{N' = N^{(0)}}$$

$$\frac{1}{KT'} = \left(\frac{\partial \ln \Omega'}{\partial E'}\right)_{E' = E^{(0)}}$$

$\therefore$ we can have

$$P_{r,s} \propto \exp(-\alpha N_r - \beta E_s)$$

where $\alpha = -\frac{\mu}{KT}$, $\beta = \frac{1}{KT}$

on normalization,

$$P_{r,s} = \frac{\exp(-\alpha N_r, -\beta E_s)}{\sum\limits_{r,s} \exp(-\alpha N_r, -\beta E_s)}$$

summation goes over all (N_r, E_s) states accessible to the system A.

This distribution is called as grand canonical distribution or Gibbs distribution. A ensemble of systems in which systems are distributed according to this probability distribution is called a grand canonical ensemble.

The quantity

$$Z = \sum_{r,s} e^{-\beta E_s - \alpha N_r}$$

is called as grand partition function of the grand canonical ensemble. It measures how energy and particles are 'partitioned among states of the system.

For classical system, one has to integrate over the phase space. A microstate is represented by (q_r, p_r) and summation $\sum_s \longrightarrow \frac{1}{h^{3N}} \int dq^{3N} dp^{3N}$

$$\therefore \quad Z = \sum_r \frac{1}{h^{3N_r}} \int dq^{3N_r} dp^{3N_r} \exp\cdot\left\{-\beta H(q_r, p_r) - \alpha N_r\right\}$$

the probability distribution function (grand canonical phase space density)

$$\rho_{gc}(N_r, q_\nu, p_\nu) = \frac{1}{Z} \exp\{-\beta H(q_\nu, p_\nu) - \alpha N_r\}$$

A system in a grand canonical ensemble

Consider an ensemble of $\mathcal{N}$ systems. If average no. of particles of the system be $\bar{N}$ and average energy of the system be $\bar{E}$ then total energy $\bar{E}\mathcal{N}$ and total no. of particles $\bar{N}\mathcal{N}$ are shared among the systems of ensemble. Let $n_{r,s}$ be the no. of systems at a time that have total no. of particles equal to N_r and energy E_s.

$$\therefore \quad \sum_{r,s} n_{r,s} = \mathcal{N} \quad \text{and} \quad \sum_{r,s} n_{r,s} E_s = \mathcal{N}\bar{E}$$

$$\sum_{r,s} n_{r,s} N_r = \mathcal{N}\bar{N} \qquad \text{--- ①}$$

We can find set $\{n_{r,s}\}$ of numbers $n_{r,s}$ which satisfies the condition ① will represent one of the possible modes of distribution of particles and energy among the member of ensemble.

The no. of ways for occurence of such mode of distribution is

$$W\{n_{r,s}\} = \frac{\lfloor N}{\prod_{r,s} \lfloor n_{r,s}} \quad --- ②$$

Subjected to condition ①, there are many possible states of ensemble which are equally likely to occur. The frequency with which distribution set $\{n_{r,s}\}$ may appear will be proportional to the number $W\{n_{r,s}\}$. For most probable distribution, the number $W\{n_{r,s}\}$ will be maximum. So we have to maximize $\ln W\{n_{r,s}\}$.

for most probable distribution $\{n^*_{r,s}\}$, we have

$$\delta \ln W\{n_{r,s}\} = 0$$

or $$\delta\left[\mathcal{N}\ln(\mathcal{N}) - \mathcal{N} - \sum_{r,s} n_{r,s}\ln(n_{r,s}) - n_{r,s}\right] = 0$$

or, $$\delta\left[\mathcal{N}\ln\mathcal{N} - \sum_{r,s} n_{r,s}\ln(n_{r,s})\right] = 0$$ using eqn ①

We also have $$\sum_{r,s}\delta n_{r,s} = 0 \quad \text{--③}$$ Variations in $n_{r,s}$ i.e $\delta n_{r,s}$ satisfies these conditions.

$$\sum_{r,s} E_s\,\delta n_{r,s} = 0 \quad \text{--④}$$

$$\sum_{r,s} N_r\,\delta n_{r,s} = 0 \quad \text{--⑤}$$

If we shift the set $\{n_{r,s}\}$ to a slightly different set $\{n_{r,s}+\delta n_{r,s}\}$ then change in $\ln W\{n_{r,s}\}$ will be

$$\delta \ln W\{n_{r,s}\} = -\sum_{r,s}\left(\ln(n_{r,s}) + 1\right)\delta n_{r,s} \;\; ---$$

$$= 0 \quad \text{---⑥}$$ for most probable distribution

Using Lagrange multiplier method, we have

$$\sum_{r,s}\{-(\ln n^*_{r,s}+1)+\lambda-\beta E_s-\alpha N_r\}\,\delta n_{r,s}=0$$

$\delta n_{r,s}$ are independent of eachother, so coefficient must vanish separately.

$$\ln n^*_{r,s}=(-1+\lambda)-\beta E_s-\alpha N_r$$

$$\Rightarrow \qquad n^*_{r,s}=C\exp\cdot(-\beta E_s-\alpha N_r)$$

where C is another Constant.

So the probability of finding a system with energy E_s and total no. of particles N_r is.

$$P_{r,s}=\frac{n^*_{r,s}}{\mathcal{N}}=\frac{\exp(-\beta E_s-\alpha N_r)}{\sum_{r,s}\exp(-\alpha N_r-\beta E_s)}$$

The mean particle numbers

$$\bar{N} = \frac{\sum_{r,s} N_r \exp(-\alpha N_r - \beta E_s)}{\sum_{r,s} \exp(-\alpha N_r - \beta E_s)} = -\frac{\partial}{\partial \alpha}\left\{\ln \sum_{r,s} \exp(-\alpha N_r - \beta E_s)\right\}$$

$$= -\frac{\partial}{\partial \alpha} \ln \mathcal{Z}$$

The mean value of energy

$$\bar{E} = \frac{\sum_{r,s} E_s \exp(-\alpha N_r - \beta E_s)}{\sum_{r,s} \exp(-\alpha N_r - \beta E_s)} = -\frac{\partial}{\partial \beta}\left\{\ln \sum_{r,s} \exp(-\alpha N_r - \beta E_s)\right\}$$

$$= -\frac{\partial}{\partial \beta} \ln \mathcal{Z} + \mu \bar{N}$$

$\because \alpha = -\mu\beta$

We define $$\mathcal{Z} = \sum_{r,s} \exp(-\alpha N_r - \beta E_s)$$

$\mathcal{Z}$ is called as grand canonical partition function of the ensemble. It is also called grand partition function of ensemble.

It can also be written as

$$\mathcal{Z} = \sum_{r} \frac{1}{h^{3N_r}} \int dq^{3N_r}\, dp^{3N_r} \exp\left\{-\alpha N_r - \beta H(q_\nu, p_\nu)\right\}$$

grand canonical phase space density $\rho_{gc}(N_r, q_\nu, p_\nu) = \dfrac{\exp\{-\alpha N_r - \beta H(q_\nu, p_\nu)\}}{\mathcal{Z}}$

Physical Significance of statistical quantities

Entropy S of the system can be written as an ensemble average $S = \langle -K \ln \rho_{gc} \rangle$

$$= -K \sum_{r,s} P_{r,s} \ln P_{r,s}$$

or, $$S(\beta, V, \alpha) = \sum_{r} \frac{1}{h^{3N_r}} \int d^{3N_r}q \, d^{3N_r}p \; \rho_{gc} (-K \ln \rho_{gc})$$

$$= \sum_{r} \frac{1}{h^{3N_r}} \int d^{3N_r}q \, d^{3N_r}p \; \rho_{gc} (-K) \left[-\alpha N_r - \beta E_s - \ln \mathcal{Z} \right]$$

$$= K \ln \mathcal{Z}(\beta, V, \alpha) + K\beta \bar{E} + K \alpha \bar{N}$$

$$\therefore \quad -KT \ln \mathcal{Z}(\beta, V, \alpha) = -ST + KT\beta \bar{E} + KT\alpha \bar{N}$$

$$= U - TS - \mu \bar{N} = -PV$$

We define $U - TS - \mu \bar{N} = \phi$ called as grand potential or grand canonical potential.

$$\therefore \quad \phi(T, V, \mu) = -KT \ln \mathcal{Z}(T, V, \mu) = -PV$$

Helmholtz free energy

$$F = U - TS$$
$$= \phi + \mu \bar{N}$$

Gibbs free energy

$$G = U - TS + PV$$
$$= \mu \bar{N}$$

Entropy $S = -\left(\frac{\partial \phi}{\partial T}\right)_{V,\mu} = k\left[\ln Z + T\left(\frac{\partial}{\partial T}\ln Z\right)_{V,\mu}\right]$

particle number $N = -\left(\frac{\partial \phi}{\partial \mu}\right)_{V,T} = kT\left(\frac{\partial}{\partial \mu}\ln Z\right)_{V,T}$

Pressure $P = -\left(\frac{\partial \phi}{\partial V}\right)_{T,\mu} = kT\left(\frac{\partial}{\partial V}\ln Z\right)_{T,\mu} = \frac{kT\ln Z}{V}$

Energy $U = \sum_{r,s} E_s P_{r,s} = \frac{\sum_{r,s} E_s \exp\{\beta(\mu N_r - E_s)\}}{Z}$

$$= -\left(\frac{\partial}{\partial \beta}\ln Z\right)_{V,\mu} + \frac{\mu}{\beta}\left(\frac{\partial}{\partial \mu}\ln Z\right)_{V,\beta}$$

$$= -\left(\frac{\partial}{\partial \beta}\ln Z\right)_{V,\mu} + \mu \bar{N}$$

We know that $F = \phi + \mu \bar{N}$

$$= \phi(T, V, \mu) + \bar{N}\left(\frac{\partial F}{\partial N}\right)_{V,T}$$

$$= -KT \ln \mathcal{Z}(T, V, \mu) + NKT \ln z$$

where $z = e^{-\alpha} = e^{\mu/KT}$ is a parameter called as fugacity of the system or absolute activity of the system.

$$\therefore F = -KT \ln\left(\frac{\mathcal{Z}(T,V,\mu)}{z^N}\right)$$

Again, $\mathcal{Z}(T, V, \mu) = \sum_{r,s} \exp(-\alpha N_r - \beta E_s)$

$$= \sum_r \exp(-\alpha N_r) \cdot Z(T, V, N_r) = \sum_r z^{N_r} \cdot Z(T,V,N_r)$$

$$= \sum_r e^{\beta \mu N_r} \cdot Z(T, V, N_r)$$

where $Z(T, V, N_r) = \sum_s e^{-\beta E_s}$ Canonical partition function.

For indistinguishable particles $Z(T, V, N_r) = \frac{1}{\lfloor N_r} \cdot Z(T,V,1)^{N_r}$

$$\therefore \mathcal{Z}(T, V, \mu) = \sum_r \left[\exp\left(\frac{\mu}{KT}\right)\right]^{N_r} \cdot \frac{1}{\lfloor N_r}\left[Z(T,V,1)\right]^{N_r} = \exp\left[e^{\frac{\mu}{KT}} \cdot Z(T,V,1)\right]$$

If we look at the expression for the partition function in canonical ensemble

$$Z(T, V, N) = \sum_{E_r} \exp(-\beta E_r)\, g(E_r, V, N)$$

then it is observed that canonical partition function is the sum of all microcanonical partition functions $g(E_r, N, V)$ at energy E_r, particle number N and volume V weighted by the Boltzmann factor $\exp\left(-\frac{E_r}{KT}\right)$. Here E_r is not a fixed quantity but its mean is fixed whereas temperature is fixed.

Similarly if we look at the expression for grand canonical partition function

$$\mathcal{Z}(T, V, \mu) = \sum_{N_r} \left[\exp\left(\frac{\mu}{KT}\right)\right]^{N_r} \cdot Z(T, V, N_r)$$

$$= \sum_{N_r} \exp\left(\frac{\mu N_r}{KT}\right) Z(T, V, N_r)$$

then it is observed that grand canonical partition function is the sum of all the canonical partition function z at temperature T, volume V and particle number N_r weighted by $\exp\left(\frac{\mu N_r}{KT}\right)$. N_r is not fixed, its mean value is fixed and chemical potential μ is fixed. The weight factor $\exp\left(\frac{\mu}{KT}\right) = z$ is called as absolute activity or fugacity of the system.

Ideal Gas in Grand Canonical Ensemble.

The grand canonical partition function

$$\mathcal{Z}(T,V,\mu) = \exp\left[\left\{\exp\left(\frac{\mu}{KT}\right)\right\}\cdot z(T,V,1)\right]$$

$$= \sum_{N_r} \frac{1}{\underline{|N_r}} \left[\exp\left(\frac{\mu}{KT}\right) z(T,V,1)\right]^{N_r}$$

$Z(T, V, 1) = \frac{V}{\lambda^3}$ for single particle.

where $\lambda = \frac{h}{\sqrt{2\pi m K T}}$

$\therefore \quad Z(T, V, \mu) = \exp\left\{ \exp\left(\frac{\mu}{KT}\right) \cdot V \cdot \left(\frac{2\pi m K T}{h^2}\right)^{3/2} \right\}$

$\therefore$ grand potential is

$$\phi(T, V, \mu) = -KT \ln Z(T, V, \mu)$$

$$= -KT \left[\exp\left(\frac{\mu}{KT}\right) \cdot V \left(\frac{2\pi m K T}{h^2}\right)^{3/2} \right]$$

Entropy of the system

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

$$= -\exp\left(\frac{\mu}{KT}\right) V \left(\frac{2\pi m K T}{h^2}\right)^{3/2} \cdot \left[-K - KT\left(-\frac{\mu}{KT^2}\right) - KT \frac{3}{2T} \right]$$

$$= \exp\left(\frac{\mu}{KT}\right) \cdot KV \left[\frac{2\pi m K T}{h^2}\right]^{3/2} \left[\frac{5}{2} - \frac{\mu}{KT}\right]$$

mean particle number

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

$$= \exp\left(\frac{\mu}{KT}\right) V \left(\frac{2\pi m K T}{h^2}\right)^{3/2}$$

$$\therefore \quad \mu = -KT \ln\left[\frac{V}{\bar{N}}\left(\frac{2\pi m K T}{h^2}\right)^{3/2}\right]$$

∴ entropy of the system becomes

$$S(T,V,\mu) = \bar{N}K\left[\frac{5}{2} + \ln\left\{\frac{V}{\bar{N}}\left(\frac{2\pi m K T}{h^2}\right)^{3/2}\right\}\right]$$

Pressure $P(T,V,\mu) = -\left(\frac{\partial \phi}{\partial V}\right)_{T,\mu} = KT\left\{\exp\left(\frac{\mu}{KT}\right)\right\}\cdot\left(\frac{2\pi m K T}{h^2}\right)^{3/2}$

Internal energy "U"

$$\because \quad U - TS + PV = \mu\bar{N} \Rightarrow -PV = U - TS - \mu\bar{N}$$

$$\text{or,} \quad \phi = U - TS - \mu\bar{N} \Rightarrow U = \phi + TS + \mu\bar{N}$$

$$\therefore\ U = -KT\exp\left(\frac{\mu}{KT}\right)\cdot V\left(\frac{2\pi mKT}{h^2}\right)^{3/2}$$

$$+\ \exp\left(\frac{\mu}{KT}\right) V\left(\frac{2\pi mKT}{h^2}\right)^{3/2} KT\left[\frac{5}{2}-\frac{\mu}{KT}\right]$$

$$+\ \mu\ \exp\left(\frac{\mu}{KT}\right)\cdot V\left(\frac{2\pi mKT}{h^2}\right)^{3/2}$$

$$= \exp\left(\frac{\mu}{KT}\right)\cdot V\left(\frac{2\pi mKT}{h^2}\right)^{3/2}\left[-KT+\frac{5}{2}KT-\mu+\mu\right]$$

$$= \bar{N}\ \frac{3}{2}KT.$$

$$\therefore\ U = \frac{3}{2}\bar{N}KT$$

Also $PV = \bar{N}KT$

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Thank You

For any questions/doubts/suggestions and submission of assignments

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