Ensemble Theory

In statistical mechanics, a system is represented by a particle and collection of such particles (systems) is represented as "metal copies" of single particle or system.

Then Ensemble is nothing but collection of systems. Based on different conditions ensembles can be categorized as Micro-Canonical, Canonical & Grand-Canonical.

Here, the obvious meaning of the term Canonical is "set of rules".

Thus ensembles characterized by different set of rules governs three different types of ensemble.

These three ensembles are analogous to our understanding of isolated, closed & open systems in contact with a reservoir.

Ensemble :- An ensemble is defined as an aggregation of large no. of macroscopic identical systems which are essentially independent.

Microcanonical Ensemble : It is an aggregation of essentially independent system with same value of energy (E), volume V & no. of particles N.
(walls are rigid, impermiable & insulated)

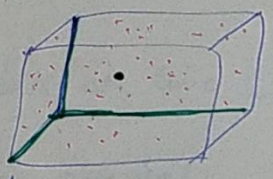
Canonical Ensemble :- It is an aggregation of essentially independent system with same value of Temperature (T), volume (V) & no. of particles N. (walls are conducting, rigid & impermiable)

Grand Canonical Ensemble :- It is an aggregation of essentially independent system with same value of Temperature (T), volume (V) & chemical potential (μ) (walls are conducting, rigid, permeable)

(Chemical potential :- Capability of an entity (atom, molecule) to do work.)

PHASE SPACE

Consider a classical system (dynamic), with collection of particles moving inside some space (3D) as shown



then at any instant of time, the system can be defined by instantaneous position & momentum (dynamic) co-ordinates.

i.e for N particles we need 3N position ($q_1, q_2 \cdots q_{3N}$) & 3N momentum coordinates ($p_1, p_2 \cdots p_{3N}$).

Hence, set of co-ordinates (q_i, p_i) $i = 1, 2 \cdots 3N$ may be considered as point in 6N dimentional space called phase space.

Phase Space = Position space + Momentum space.

Now we know time evolution of q_i & p_i can be represented as

$$\dot{q}_i = \frac{\partial H(q_i,p_i)}{\partial p_i}$$
$$\dot{p}_i = \frac{\partial H(q_i,p_i)}{\partial q_i}$$
— (1)

$i = 1, 2, \ldots 3N$

$H(q_i, p_i)$ = Hamiltonian

Now for a system with finite volume V & Energy E, we may write $H(q_i,p_i) = E$

Now, analogous to Ensemble picture, in phase space the member of ensemble is represented by collection of $(q_i\ p_i)$ at any given instant of time.

At any time, the no. of representative points in the volume element $(d^{3N}q\ d^{3N}p)$ around the point (q,p) of the phase space can be represented as

$$\rho(q,p,t)\, d^{3N}q\, d^{3N}p$$

where $\rho(q,p,t)$ gives arrangement of points at time t

$\Rightarrow$ Ensemble average $\langle f \rangle$ of a given physical quantity $f(q,p)$ is given by

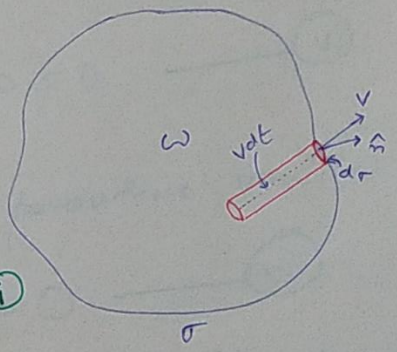
$$\langle f \rangle = \frac{\int f(q,p)\, \rho(q,p,t)\, d^{3N}q\, d^{3N}p}{\rho(q,p,t)\, d^{3N}q\, d^{3N}p} \quad \text{— (3)}$$

An ensemble is said to be stationary if ρ does not depend explicitly on time

i.e then $$\frac{\partial \rho}{\partial t} = 0 \quad \text{---(4)}$$

for such a system ensemble average $\langle f \rangle$ of any physical quantity $f(q,p)$ will be independent of time (representing a system in equilibrium)

Liouville's Thm :- Consider an arbitrary volume ω in phase space enclosed by a surface denoted by σ.



Then the rate at which the no. of representation points in this volume increases with time is given by $$\frac{\partial}{\partial t}\int_{\omega} \rho \, d\omega \quad \text{---(i)}$$

Also, the rate at which the representation points flows out of ω is given by

$$\int_{\sigma} \rho \mathbf{v} \cdot \hat{n} \, d\sigma \quad \text{---(ii)}$$

$\mathbf{v}$ is velocity vector of representation points

Using divergence thm eq. (ii) can be written as

$$\int_\omega \operatorname{div}(\rho V)\, d\omega \qquad \text{(iii)}$$

where $$\operatorname{div}(\rho V) = \sum_{i=1}^{3N} \left[\frac{\partial}{\partial q_i}(\rho \dot{q}_i) + \frac{\partial}{\partial p_i}(\rho \dot{p}_i) \right] \qquad \text{(iv)}$$

For no source or sinks in phase space, i.e total no. of representative points remains conserved from eq. (i) & (iii) we can write

$$\frac{\partial}{\partial t}\int_\omega \rho\, d\omega = -\int_\omega \operatorname{div}(\rho V)\, d\omega \qquad \text{(v)}$$

i.e $$\int_\omega \left(\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho V) \right) d\omega = 0 \qquad \text{(vi)}$$

Above eq. holds if terms in parantheses vanishes.

i.e $$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho V) = 0 \qquad \text{(vii)}$$

which is equation of continuity for the swarm of the representation points.

Q: what eq. (vii) represents? Explain its significance.

using value of $\text{div}(\rho v)$ from eq. (iv) in eq. (vii)

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N}\left(\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i\right) + \rho \sum_{i=1}^{3N}\left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right) = 0 \quad \text{(viii)}$$

Now we know that

$$\frac{\partial \dot{q}_i}{\partial q_i} = \frac{\partial^2 H(q_i p_i)}{\partial q_i \partial p_i} \equiv \frac{\partial^2 H(q_i p_i)}{\partial p_i \partial q_i} = -\frac{\partial \dot{p}_i}{\partial p_i} \quad \text{(ix)}$$

the underline term in eq (viii) vanishes as per eq. (ix)

$$\therefore \quad \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N}\left(\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i\right) = 0$$

using eq. (1) page (51) above eq. can be written as

$$\boxed{\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, H] = 0} \quad \text{(x)}$$

where $[\rho, H] = \frac{\partial \rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i}\frac{\partial H}{\partial q_i}$

Eq. (x) represents Liouville's thm, the thm states that local density of the representative points, as viewed by an observer moving with a representative point, stays constant in time.

Now, earlier we have seen that $\frac{\partial \rho}{\partial t} = 0$ (page 52 eq. (4))

and now $\frac{d\rho}{dt} = 0$. what does it signify ?

$\frac{dP}{dt} = 0$ shows basic mechanism of representation points or particles and is quite general

$\frac{\partial P}{\partial t} = 0$ is a special case representing equilibrium condition.

we can achieve $\frac{\partial P}{\partial t} = 0$ from eq. (x) if

$$[P, H] = \sum_{i=1}^{3N} \left(\frac{\partial P}{\partial q_i} \dot{q}_i + \frac{\partial P}{\partial p_i} \dot{p}_i \right) = 0 \quad \text{(xi)}$$

which is only possible if P is independent of time & q_i, p_i are well.

i.e $P(q,p) = \text{constant}$ (xii)

Above eq. means that representation points are uniformly distributed over all possible microstates at all times

$\Rightarrow$ Ensemble average $\langle f \rangle$ (eq. 3, page 51) becomes.

$$\langle f \rangle = \frac{1}{\omega} \int f(q,p)\, d\omega \quad \text{(xiii)}$$

ω = total vol. of relevant region in phase space.

Eq. (xiii) says that any member of ensemble is equally likely to be in any one of the various possible microstates

OR

Any representative points in the swarm is equally likely to be in the neighbourhood of any phase point-

in the allowed region of the phase space. Which is refered to as the postulate of "equal a priori probabilities" for various possible microstates. (or for the various volume elements in the allowed region of the phase space). The resulting ensemble is refered to as "micro-canonical ensemble"

Microchanonical Ensemble (MCE)

In MCE, the macrostate of a system is defined by a no. of molecule N, vol. V & the energy E. However, in MCE which is considered to be isolated by definition, it is hard to consider energy to be exactly equal to a value E. (Why?) And it is rather more practical to consider range of energy value say $\left(E - \frac{1}{2}\Delta \text{ to } E + \frac{1}{2}\Delta\right)$

Now, as the system could be in any microstate of the ensemble.
i.e representative points of the ensemble have a choice to lie anywhere within "hypershell"

defined by the condition

$$\left(E - \frac{1}{2}\Delta\right) \leq H(q,p) \leq \left(E + \frac{1}{2}\Delta\right) \qquad \text{(xi)}$$

the volume of the phase space enclosed within this shell

$$\omega = \int' w \equiv \int' \left(d^{3N}q\, d^{3N}p\right) \qquad \text{(xii)}$$

where primed integration extends only over that part of the phase space defined by eq. (xi)

Now, the microcanonical ensemble is a collection of systems for which the density ρ is

$$\rho(q,p) = \begin{cases} \text{constant} & \text{if } E - \frac{1}{2}\Delta \leq H(q,p) \leq E + \frac{1}{2}\Delta \\ 0 & \text{otherwise} \end{cases}$$

Now, following a priori probability condition, finding a representative point in an eq. given volume element $d\omega$ is the same as that of finding a representative point in an equivalent volume element $d\omega$ located anywhere in the hypershell.

$\Rightarrow$ An equal a priori probability for a given member of the ensemble to be in any one of the various possible microstates

Since, the ensemble under study is a stationary one, the ensemble average of any physical quantity f will be independent of time.
$\Rightarrow$ taking time average will not produce any new result.

$\Rightarrow \langle f \rangle \equiv$ the ensemble average of f
$=$ time average of (the ensemble average of f)

the reverse of this can also be true

i.e $\langle f \rangle =$ the ensemble av. of f (the time average of f)

now the time average of any physical quantity, taken over a sufficiently long interval of time, must be same for every member of the ensemble.

i.e $\langle f \rangle =$ the long-time average of f

this can only be achieved by making a measurement of that quantity on the given system. Which may be identified with the value one expect-to obtain through experiment

i.e $\langle f \rangle = f_{exp.}$

i.e the ensemble average of any physical quantity f is identical to the value one expect to obtain on making an appropriate measurement on the given system.

For a volume ω (of the allowed region of the phase space) we can write

$$\Gamma = \frac{\omega}{\omega_0}$$

Γ = multiplicity of the microstate

ω_0 = vol. of one microstate

we know that $S = k \ln(\Gamma)$

or $S = k \ln\left(\frac{\omega}{\omega_0}\right)$

Now $\omega_0 = h^N$ for classical ideal gas

$= h$ for 1D harmonic oscillator

Canonical Ensemble (CE)

Consider a system in contact with reservoir. such that macroscopic properties of reservoir are huge ex(in magnitude) as compare to system.

If the system is in contact with reservoir through conducting walls then they can exchange energy b/w them & both of them progress towards achieving equilibrium temp.

Now consider "independent" mental copies of this system defined by (T, V, N) in contact with reservoir (T', V', N') such that $(T' >> T,\ V' >> V,\ N' >> N)$ then collection of these "mental copies" forms an ensemble known as Canonical Ensemble.

Q Why we need CE when we have MCE ? Explain in detail.

In canonical ensemble, E is variable as walls are conducting, so at any time t, a system of ensemble can have energy E_r with proper probability P_r.

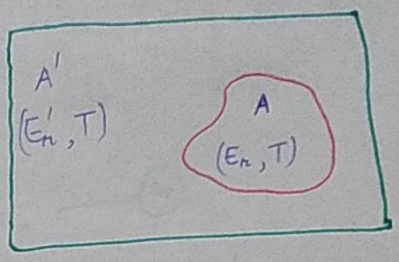
How to determine dependence of E_r on P_r ?

One is by considering system and reservoir is at equilibrium temp & studing the statistics of energy exchange b/w the two.

Lets explore this

Equilibrium b/w a system & reservoir.

Here A' = reservoir
A = system



At any time, the system happens to be in a state characterized by the energy E_r,

E_r' = reservoir energy

then $E_r + E_r' = E^{(0)} = \text{constant}$ —— (1)

Since reservoir is huge as compare to system we can say

$$\frac{E_r}{E^\circ} = 1 - \frac{E_r'}{E^\circ} \leq 1 \quad \text{—— (2)}$$

Now, E_r' is the energy of reservoir. A reservoir can also have different states in which it can exist at time for given. Let the no. of these states of reservoir be denoted by $\Omega'[E_r']$.

Now, Larger the no. of states available to reservoir, larger the probability of the reservoir assuming that particular energy E_r' (& hence of the system A assuming corresponding energy value E_r)

~~Also~~, so we can write

$$P_r \propto \Omega'(E_r') \equiv \Omega'(E^\circ - E_r) \quad \text{—— (3)}$$

∵ the various possible states are equally likely to occur.

Taking log & expanding Taylor's series

we can write

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

$$\simeq \text{constant} - \beta' E_r \quad \text{— (4)}$$

$$\because \left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V} \equiv \beta \quad \text{(5)}$$

from eq. (3) & (4)

$$P_r \propto \exp(-\beta E_r) \quad \text{— (6)}$$

Normalizing above eq., we get

$$P_r = \frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)} \quad \text{— (7)}$$

where the summation goes over all states accessible to the system A.

In the second way, we can explore dependence of P_r on E_r i.e when energy E is being shared by N identical systems of ensemble. (Canonical). Then we can explore the statistics of sharing.

A System in the Canonical ensemble

Consider an ensemble of N identical systems $(1, 2, \ldots N)$ sharing total energy E.

Let ε_λ $(\lambda = 0, 1, 2 \ldots)$ denote the energy eigenvalues of the system.

Now it can say

$$\left.\begin{aligned} \sum_\lambda n_\lambda &= N \\ \sum_\lambda n_\lambda \varepsilon_\lambda &= E = NU \end{aligned}\right\} \quad \text{——— (1)}$$

where $U = \frac{E}{N}$ denote energy of a system in the ensemble.

Now the ways in which n_λ can be arranged is represented by

$$W(n_\lambda) = \frac{N!}{n_0! n_1! n_2! \ldots} \quad \text{——— (2)}$$

Now, since each system of the ensemble is equally likely to occur, the frequency of appearance of n_λ will be directly proportional of $W(n_\lambda)$.

$\Rightarrow$ the most probable rearrangement of n_λ will be those for which $W(n_\lambda)$ is maximum, we denote that rearrangement by n_λ^*. (n_λ^* also must satisfy eq. (1))

Now the expectation value of n_λ

$$\langle n_\lambda \rangle = \frac{\sum_{n_\lambda}{}' n_\lambda W(n_\lambda)}{\sum_{n_\lambda}{}' W(n_\lambda)} \quad \text{——— (3)}$$

where the primed summation go over all the rearrangements satisfying eq. (1)

the mean value $\langle n_k \rangle$, which is fraction of total no. N, should be a natural analog of probability P_k

Now, in the limit $N \to \infty$, let try to solve expression for n_k^* & $\langle n_k \rangle$ or n_k

For simplicity, take log on b/s of eq. (2)

$$\ln W = \ln N! - \sum_k \ln n_k! \quad \text{—— (4)}$$

using stirling's relation $\ln n! \simeq n \ln n - n$

$$\ln W = N \ln N - \sum_k n_k \ln n_k \quad \text{—— (5)}$$

or $$\delta \ln W = - \sum_k (\ln n_k + 1) \delta n_k \quad \text{—— (6)}$$ (taking partial derivation)

Now for n_k to be maximum $\delta \ln W$ should vanish

$$\Rightarrow \quad - \sum_k (\ln n_k + 1) \delta n_k = 0$$

Now eq. (6) must satisfy $\sum_k \delta n_k = 0$, $\sum_k E_k \delta n_k = 0$ —— (7)

Now, the maximum probable arrangement n_k^* can be determined by the method of "Lagrange multiplies" by which the condition determining n_k^* becomes

$$\sum_k \{ -(\ln n_k^* + 1) - \alpha - \beta E_k \} \delta n_k = 0 \quad \text{—— (8)}$$

where α & β are the Lagrangian undetermined multipliers that take care of the conditions expressed in (7)

Now, eq. (8) holds if terms in parenthesis vanishes

i.e $\ln n_n^* = -(\alpha+1) - \beta E_n$

or $n_n^* = C e^{-\beta E_n}$ ——— (9) C = undetermined parameters.

from eq. (9) & (1) we find

$$\frac{n_n^*}{N} = \frac{\exp(-\beta E_n)}{\sum_n \exp(-\beta E_n)} \quad \text{——— (10)} \qquad n_n$$

And $$\frac{\mathcal{E}}{N} = U = \frac{\sum_n E_n \exp(-\beta E_n)}{\sum_n \exp(-\beta E_n)} \quad \text{——— (11)}$$

PHYSICAL SIGNIFICANCE OF STATISTICAL QUANTITIES IN CANONICAL ENSEMBLE

$$P_n \equiv \frac{\langle n_n^* \rangle}{N} = \frac{\exp(-\beta E_n)}{\sum_n \exp(-\beta E_n)} \quad \text{——— (1)}$$

Now, rewrite eq. (11) as

$$U = \frac{\sum_n E_n \exp(-\beta E_n)}{\sum_n \exp(-\beta E_n)} = -\frac{\partial}{\partial \beta} \ln\left\{\sum_r \exp(-\beta E_n)\right\} \quad \text{——— (2)}$$

We know the term Helmholtz free energy, F (or A)

i.e $A = U - TS$

i.e $dA = dU - TdS - SdT$ ——— (3)

or $dA = -SdT - PdV + \mu dN$

$$\Rightarrow \quad S = -\left(\frac{\partial A}{\partial T}\right)_{N,V}, \quad P = -\left(\frac{\partial A}{\partial V}\right)_{N,T}, \quad \mu = \left(\frac{\partial A}{\partial N}\right)_{V,T} \quad \text{——— (4)}$$

Also $U = A + TS = A - T\left(\frac{\partial A}{\partial T}\right)_{N,V}$

$$= -T^2\left[\frac{\partial}{\partial T}\left(\frac{A}{T}\right)\right]_{N,V} = \left[\frac{\partial (A/T)}{\partial (1/T)}\right]_{N,V} \quad \text{——— (5)}$$

Comparing (5) or (2) we find that

$$\beta = \frac{1}{kT}, \quad \ln\left\{\sum_r \exp(-\beta E_r)\right\} = \frac{-A}{kT} \quad \text{——— (6)}$$

where k is a constant.

From eq. (6) we can write that

$$A = -kT \ln\left\{\sum_r \exp(-\beta E_r)\right\}$$

or $$A_{(N,V,T)} = -kT \ln Q_N(V,T) \quad \text{——— (7)}$$

where $$Q_N(V,T) = \sum_r \exp(-\beta E_r) \quad \text{——— (8)}$$

$Q_N(V,T)$ is called Partition function of the system

Q = Is $Q_N(V,T)$ extensive or intensive or None ?

Explain

we also know $C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_{N,V}$ ——— (9)

we know Gibbs free Energy

$$G = A + PV = A - V\left(\frac{\partial A}{\partial V}\right)_{N,T} = N\left(\frac{\partial A}{\partial N}\right)_{V,T} = N\mu$$

——— (10)

from eq. (4) & (6) we can write

$$P = -\frac{\sum_n \frac{\partial E_n}{\partial V} \exp(-\beta E_n)}{\sum_n \exp(-\beta E_n)} \quad \text{——— (11)}$$

(pressure)

or $$P dV = -\sum_r P_n dE_n = -dU \quad \text{——— (12)}$$

now we know, probability $P_n = \frac{\exp(-\beta E_n)}{\sum_r \exp(-\beta E_r)}$ from eq. (1) page (65)

or $P_n = Q^{-1} \exp(-\beta E_n)$ from eq. (8)

or $\langle \ln P_n \rangle = -\ln Q - \beta \langle E_n \rangle = \beta(A - U) = -\frac{S}{k}$

$$\Rightarrow \quad S = -k\langle \ln P_n \rangle = -k \sum_n P_n \ln P_n \quad \text{——— (13)}$$

$$\boxed{S = -k \sum_n P_n \ln P_n}$$

$\Rightarrow$ Entropy of the physical system is completely determined by P_n

If (at T=0K) system occupies the ground state, this means $P_n = 1$ which means entropy is zero, which is true as all the entities move to the ground state. i.e Vanishing entropy & perfect statistical order go together.

As the no. of accesible states increases, more and more of the P_n become non-zero, thereby increasing the entropy. As the no. of states becomes huge, most of the P-values becomes exceedingly small, the net result is that the entropy becomes exceedingly large.
That means, the largeness of entropy and the high degree of statistical disorder (or unpredictability) in the system also go hand in hand.

ALTERNATIVE EXPRESSIONS FOR PARTITION FUNCTION

For a system with degenerate energy levels, i.e group of states g_i (in number) having same energy E_i,
then we can write, partition fn as

$$Q_N(V,T) = \sum_i g_i \exp(-\beta E_i) \qquad \text{---------- (1)}$$

then, corresponding eq. for probability P_i, i.e probability that the system is in a system state with energy E_i

$$P_i = \frac{g_i \exp(-\beta E_i)}{\sum_i g_i \exp(-\beta E_i)} \qquad \text{---------- (2)}$$

Here g_i is the "weight factor" for the level E_i, the actual probability is then determined by g_i as well as $e^{-\beta E_i}$.

Now, for a given system (which is a member of ensemble), may have energy in the range $E+dE$, the corresponding probability will be $P(E)dE$

Now this probability $P(E)dE$ can be expressed as product of single-state probability & no. of energy states lying in the specified range.

i.e $P(E)dE \propto \exp(-\beta E)\, g(E)dE$ — (3)

where $g(E)dE$ = density of states around energy value E

by normalizing we get

$$P(E)dE = \frac{\exp(-\beta E)\, g(E)dE}{\int_0^\infty \exp(-\beta E)\, g(E)dE} \quad \text{— (4)}$$

where $Q_N(V,T) = \int_0^\infty e^{-\beta E}\, g(E)dE$ — (5)

is another expression for partition function

Ally, expectation value of some physical quantity f,

$$\langle f \rangle \equiv \sum_i f_i P_i = \frac{\sum_i f(E_i)\, g_i e^{-\beta E_i}}{\sum_i g_i e^{-\beta E_i}} \longrightarrow \frac{\int_0^\infty f(E)\, e^{-\beta E}\, g(E)dE}{\int_0^\infty e^{-\beta E}\, g(E)dE} \quad \text{— (6)}$$

Energy Fluctuations in CE

Despite variation of energy in MCE & CE is very different how the two ensembles have same results of thermodynamic properties

To answer this question, we have to obtain range of energy of the system (in CE) over which the probability of the system to exist is significant.

This will tell us, how CE & MCE really differ from each other.

If this energy range comes out to be of similar to energy in MCE or if energy fluctuation in CE is negligible then we can answer our question.

Now we know

$$U \equiv \langle E \rangle = \frac{\sum_r E_r \exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)} \quad \text{(1)}$$

differentiating w.r.t β

$$\frac{\partial U}{\partial \beta} = -\frac{\sum_r E_r^2 \exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)} + \left(\frac{\sum_r E_r \exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}\right)^2 \quad \text{(2)}$$

$$= -\langle E^2 \rangle + \langle E \rangle^2$$

We can also write,

$$\langle (\Delta E)^2 \rangle \equiv \langle E^2 \rangle - \langle E \rangle^2$$

$$= -\left(\frac{\partial U}{\partial \beta}\right)$$

$$= kT^2 \left(\frac{\partial U}{\partial kT}\right)$$

$$\langle (\Delta E)^2 \rangle = kT^2 C_v \quad \text{---} (3)$$

$\because C_v = \frac{\partial U}{\partial T}$

$$\Delta E = \sqrt{kT^2 C_v}$$

$$\Delta E = \sqrt{\langle (E - \langle E \rangle)^2 \rangle}$$

$$\Delta E^2 = (E - \langle E \rangle)^2$$

$$= E^2 + \langle E \rangle^2 - 2E\langle E \rangle$$

$$\langle (\Delta E)^2 \rangle = \langle E^2 \rangle + \langle E \rangle^2 - 2\langle E \rangle^2$$

$$\langle (\Delta E)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2$$

Now, the relative root-mean square fluctuation in E

$$\frac{\sqrt{\langle (\Delta E)^2 \rangle}}{\langle E \rangle} = \frac{\sqrt{kT^2 C_v}}{U} \quad \text{---} (4)$$

Now $C_v = \frac{3}{2} N k$ or $C_v \propto N$ i.e C_v is of the order of N or we can say ΔE is of the order of $N^{1/2}$ i.e $O(N^{1/2})$

$\because \Delta E = \sqrt{kT^2 C_v}$ (Root mean sq. fluctuation in energy $\propto N^{1/2}$

Also, $U \propto N$

$\Rightarrow$ the relative R.M.S deviation in energy

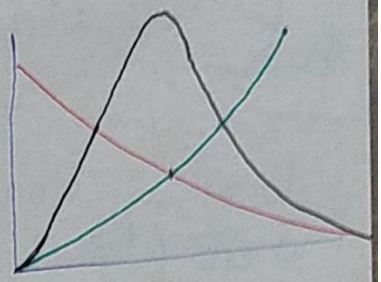
i.e $\frac{\sqrt{\langle (\Delta E)^2 \rangle}}{\langle E \rangle} = \frac{\sqrt{kT^2 C_v}}{U}$ is of the order of $N^{-1/2}$

i.e $O(N^{-1/2})$

Now, we know in thermodynamic limit as $N \to \infty$, the relative R.M.S fluctuation in energy is negligible. $\left(\frac{\Delta E}{U} \ll 1\right)$
i.e a system in the canonical ensemble has energy $\simeq$ the mean energy U.
i.e the situation in this ensemble is practically same as in the microcanonical ensemble.

Now, we know that

$$P(E)\,dE \propto \exp(-\beta E)\, g(E)\,dE$$



Now $P(E)$ has an extremum at some value of E, say E^* which can be determined by

$$\left.\frac{\partial}{\partial E}\left(e^{-\beta E} g(E)\right)\right|_{E=E^*} = 0 \quad \text{—— (5)}$$

i.e $g(E)(-\beta)e^{-\beta E} + \frac{\partial}{\partial E} g(E) \cdot e^{-\beta E} = 0$

i.e $-\beta e^{-\beta E} g(E) + e^{-\beta E} \frac{\partial}{\partial E} g(E) = 0$

Above eq. satisfies only if $\left.\frac{\partial}{\partial E} \ln g(E)\right|_{E=E^*} = \beta$ —— (5)

i.e $\frac{1}{g(E)} \frac{\partial g(E)}{\partial E} = \beta$ at $E = E^*$

Now, we also know

$$S = k \ln g \quad \& \quad \left(\frac{\partial S(E)}{\partial E}\right)_{E=U} = \frac{1}{T} = k\beta$$

$$\Rightarrow \qquad E^* = U \qquad \text{——— (6)}$$

i.e the most probable energy is the mean value of same energy.

Now, expanding the logarithm of $P(E)$ at $E=E^*$ or $E^* \simeq U$, we get

$$\ln\left(e^{-\beta E} g(E)\right) = \left(-\beta U + \frac{S}{k}\right) + \frac{1}{2}\frac{\partial^2}{\partial E^2} \ln\left\{e^{-\beta E} g(E)\right\}\Big|_{E=U} (E-U)^2 + \ldots\ldots$$

$$= -\beta(U-TS) - \frac{1}{2kT^2C_V}(E-U)^2 + \ldots\ldots \quad \text{— (7)}$$

we can write

$$P(E) \propto e^{-\beta E} g(E) \simeq e^{-\beta(U-TS)} \exp\left\{-\frac{(E-U)^2}{2kT^2C_V}\right\}. \quad \text{— (8)}$$

Above, eq. represents the distribution of $P(E)$ which is gaussian with dispersion $\sqrt{kT^2C_V}$ and mean value U.

In terms of reduced variable E/U, the distribution is gaussian again with mean value unity & dispersion $\frac{\sqrt{kT^2C_V}}{U}$ which is $O(N^{-1/2})$.

As $N \gg 1$, the distribution is extremely sharp

for $N \to \infty$, " becomes delta-function.

Now again we can write

$$Q_N(V,T) \simeq e^{-\beta(U-TS)} \int_0^\infty e^{-(E-U)^2/2kT^2C_V}\, dE$$

$$\simeq e^{-\beta(U-TS)} \sqrt{2kT^2C_V} \int_{-\infty}^{\infty} e^{-x^2}\, dx$$

$$= e^{-\beta(U-TS)} \sqrt{2\pi kT^2C_V}$$

$$\Rightarrow \quad -kT \ln Q_N(V,T) \equiv A \simeq (U-TS) - \frac{1}{2} kT \ln(2\pi kT^2C_V) \quad (7)$$

$(U-TS)$: $O(N)$

$\frac{1}{2} kT \ln(2\pi kT^2C_V)$: $O(\ln N)$

Neglecting last term, we can write

$$A \simeq U - TS \quad (10)$$

U comes from CE

TS comes from MCE

The validity of above relation confirms that two approaches (CE or MCE) are identical for all practical purposes.

CLASSICAL IDEAL GAS (MONOATOMIC)

We know $U = \frac{3}{2} NKT$

$C_V = \frac{3}{2} NK$

then R.M.S (relative) i.e $\frac{\Delta E}{U}$ =

$$= \frac{\sqrt{kT^2C_V}}{U} = \frac{\sqrt{kT^2 \frac{3}{2} NK}}{\frac{3}{2} NKT} = \sqrt{\frac{2}{3N}}$$

⇒ Relative R.M.S fluctuations in energy (for classical monoatomic ideal gas) is $\boxed{\frac{\Delta E}{U} = \sqrt{\frac{2}{3N}}}$

For CLASSICAL HARMONIC OSCILLATOR :-

$C_v = Nk \quad U = NkT$

$$\frac{\Delta E}{U} = \frac{\sqrt{kT^2 Nk}}{NkT} = \frac{1}{\sqrt{N}} \qquad \boxed{\frac{\Delta E}{U} = \frac{1}{\sqrt{N}}}$$

Grand Canonical Ensemble (GCE)

Here, ensemble is defined by macroscopic variable N, V, E.

Again the statistics in GCE can be observed by two ways.

1) A system immersed in large reservoir and exchange of both energy & N can occur. (eventually reach equilibrium)

2) System is a member of GCE, where no. of particle is shared by members of ensemble ☆.

1) Equilibrium b/w System & particle-energy Reservoir

Consider a system A in reservoir A' with which it can exchange both energy & particles. After some time,

both attains state of mutual equilibrium.
i.e Both have same temp. T & chemical potential μ.

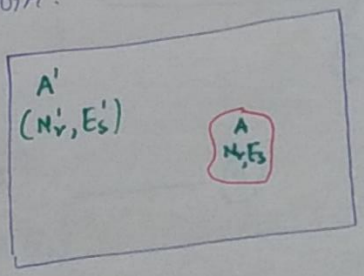
At any time, the system can have no. of particles & energy (whose value can lie b/w 0 to ∞) equal to fraction of N° & E°. where N°, E° are variables of total system (system + reservoir).

Now, consider at any time, system is in state characterized by N_r & energy E_s, then

$$N_r + N_r' = N^\circ = \text{constant} \quad \text{——— (1)}$$

$$E_s + E_s' = E^\circ = \text{constant} \quad \text{——— (2)}$$

where N_r' & E_s' are variables of reservoir.



Again, we can write

$$\frac{N_r}{N^\circ} = 1 - \frac{N_r'}{N^\circ} << 1 \quad \text{——— (3)}$$

& $$\frac{E_s}{E^\circ} = 1 - \frac{E_s'}{E^\circ} << 1 \quad \text{——— (4)}$$

Now, the probability $P_{r,s}$, that at any time t, the system to be in state (N_r, E_s) is given by

$$P_{r,s} \propto \Omega'(N^\circ - N_r, E^\circ - E_s) \quad \text{——— (5)}$$

Now we can write

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

$$\simeq \ln \Omega'(N^\circ, E^\circ) + \left(\frac{+\mu'}{kT'}\right)N_r - \frac{1}{kT'}E_s \quad \text{——— (6)}$$

Here, μ' & T' are the chemical potential & temperature of reservoir.

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

$$P_{r,s} \propto \exp(-\alpha N_r - \beta E_s) \quad \text{——— (7)}$$

where $\alpha = \frac{-\mu}{kT}$, $\beta = \frac{1}{kT}$ (8)

By Normalizing

$$P_{r,s} = \frac{\exp(-\alpha N_r - \beta E_s)}{\sum_{r,s}\exp(-\alpha N_r - \beta E_s)} \quad \text{——— (9)}$$

where $\sum_{r,s}$ is sum all (N_r, E_s) state accessible to the system.

2) A System in GCE

We know visualize ensemble of N identical system mutually sharing total no. of particle $N\bar{N}$ & total energy $N\bar{E}$.

Let $n_{r,s}$ denote no. of system that have, at any time t, the no. of particle N_r & energy E_s $(r,s = 0,1,2\cdots)$

then
$$\sum_{r,s} n_{r,s} = N \quad \text{——} (1a)$$

$$\sum_{r,s} n_{r,s} N_r = N\bar{N} \quad \text{——} (1b)$$

$$\sum_{r,s} n_{r,s} E_s = N\bar{E} \quad \text{——} (1c)$$

No. of mode (rearrangement) to obtain $n_{r,s}$ can be represented as
$$W(n_{r,s}) = \frac{N!}{\prod_{r,s} (n_{r,s}!)} \quad \text{——} (2)$$

Now, if $n^*_{r,s}$ $n^*_{r,s}$ is the most probable mode (satisfying eq. (1)) we can write
$$\frac{n^*_{r,s}}{N} = \frac{\exp(-\alpha N_r - \beta E_s)}{\sum_{r,s} \exp(-\alpha N_r - \beta E_s)} \quad \text{——} (3)$$

Now we can write, expectation value of $n_{r,s}$
$$\langle n_{r,s} \rangle = \frac{\sum'_{n_{r,s}} n_{r,s} W(n_{r,s})}{\sum'_{n_{r,s}} W(n_{r,s})} \quad \text{——} (4)$$

the $\sum'_{n_{r,s}}$ is over all distribution sets obeying eq. (1)

Now in thermodynamic limit

$$\lim_{N\to\infty} \frac{\langle n_{r,s}\rangle}{N} \simeq \frac{n^*_{r,s}}{N} = \frac{\exp(-\alpha N_r - \beta E_s)}{\sum_{r,s} \exp(-\alpha N_r - \beta E_s)} \quad \text{—— (5)}$$

And α, β can be obtain from

$$\bar{N} = \frac{\sum_{r,s} N_r \exp(-\alpha N_r - \beta E_s)}{\sum_{r,s} \exp(-\alpha N_r - \beta E_s)} \equiv -\frac{\partial}{\partial \alpha}\left\{\ln \sum_{r,s} \exp(-\alpha N_r - \beta E_s)\right\} \quad \text{(6)}$$

& $$\bar{E} = \frac{\sum_{r,s} E_s \exp(-\alpha N_r - \beta E_s)}{\sum_{r,s} \exp(-\alpha N_r - \beta E_s)} \equiv -\frac{\partial}{\partial \beta}\left\{\ln \sum_{r,s} \exp(-\alpha N_r - \beta E_s)\right\} \quad \text{(7)}$$

Physical Significance Of the Various Statistical Quantities

To connect statistics with grand canonical ensemble with thermodynamics, let us define a quantity

$$q \equiv \ln\left\{\sum_{r,s} \exp(-\alpha N_r - \beta E_s)\right\} \quad \text{—— (1)}$$

(q-potential)

q-potential is a f^n of α, β & E_s.

Differentiating eq. (1)

$$dq = -\bar{N}\,d\alpha - \bar{E}\,d\beta - \frac{\beta}{N}\sum_{r,s}\langle n_{r,s}\rangle\, dE_s \quad \text{—— (2)}$$

(using eq. (5), (6) & (7), page 79)

Eq. (2) can be written as

$$d(q+\alpha\bar{N}+\beta\bar{E}) = \beta\left(\frac{\alpha}{\beta}d\bar{N} + d\bar{E} - \frac{1}{N}\sum_{r,s}\langle n_{r,s}\rangle dE_s\right) \quad \text{——— (3)}$$

Comparing the underlined terms with I^{st} Law of thermodynamics i.e $\delta Q = d\bar{E} + \delta W - \mu d\bar{N}$ ——— (4)

i.e Comparing eq. (4) & underlined terms of eq (3)

$$\delta W = -\frac{1}{N}\sum_{r,s}\langle n_{r,s}\rangle dE_s \qquad \mu = -\frac{\alpha}{\beta} \quad \text{——— (5)}$$

$\Rightarrow$ eq. (3) becomes.

$$d(q+\alpha\bar{N}+\beta\bar{E}) = \beta\,\delta Q \quad \text{— (6)}$$ δQ as Heat

Here $\beta = \frac{1}{kT}$ ——— (7)

$\Rightarrow$ from eq. (5) $\mu = -kT\alpha$

or $\boxed{\alpha = -\frac{\mu}{kT}}$ ——— (8)

Now, the quantity $(q+\alpha\bar{N}+\beta\bar{E}) = \frac{S}{k}$

$$q+\alpha\bar{N} = \frac{S}{k} - \beta\bar{E}$$

$$q = \frac{S}{k} - \beta\bar{E} - \alpha\bar{N} = \frac{S}{k} - \frac{\bar{E}}{kT} + \frac{\mu\bar{N}}{kT}$$

$$q = \frac{TS - \bar{E} + \mu\bar{N}}{kT} \quad \text{——— (9)}$$

Here $\mu\bar{N}$ is Gibbs free energy $G = \bar{E} - TS + PV$

$$\Rightarrow q = \frac{TS - \bar{E} + \bar{E} - TS + PV}{KT} = \frac{PV}{KT}$$

$$\Rightarrow q \equiv \ln\left\{ \sum_{r,s} \exp\left[-\alpha N_r - \beta E_s\right) \right\} = \frac{PV}{KT} \quad \text{---(10)}$$

Statistic of GCE ; Thermodynamic

Now Let us define a quantity z, such that

$$z \equiv e^{-\alpha} = e^{\frac{\mu}{KT}} \quad \text{---(11)}$$

β is called fugacity.

we can write eq. (1) as

$$q \equiv \ln\left\{ \sum_{r,s} z^{N_r} e^{-\beta E_s} \right\} \quad \text{---(12)}$$

$$q = \ln\left\{ \sum_{N_r=0}^{\infty} z^{N_r} Q_{N_r}(V,T) \right\} \quad \text{---(13)} \quad \text{with } Q_0 \equiv 1$$

And $$q \equiv \ln Q(z,V,T) \quad \text{---(14)}$$

(z,V,T)

where $$Q(z,V,T) \equiv \sum_{N_r=0}^{\infty} z^{N_r} Q_{N_r}(V,T) \quad \text{with } Q_0 = 1$$

Q ↑ Grand Partition function

Thus q is logarithm of Grand Partition function

Now, from eq. (10) we can write

$$q(z,V,T) = \frac{PV}{kT}$$

$$P(z,V,T) = \frac{kT}{V} q(z,V,T) \equiv \frac{kT}{V} \ln \underline{Q}(z,V,T)$$

$N \to \bar{N}$ & $U \to \bar{E}$ can be obtained by using (6) & (7) from page-79 & eq. (11) page (81)

$$\bar{N}(z,V,T) = z\left[\frac{\partial}{\partial z} q(z,V,T)\right]_{V,T} = kT\left[\frac{\partial}{\partial \mu} q(\mu,V,T)\right]_{V,T} \quad (17)$$

& $$\bar{U}(z,V,T) = -\left[\frac{\partial}{\partial \beta} q(z,V,T)\right]_{V,T} = kT^2\left[\frac{\partial}{\partial T} q(z,V,T)\right]_{z,V} \quad (18)$$

Now, Helmholtz energy is given by

$$A = N\mu - PV$$

$$= NkT \ln z - kT \ln \underline{Q}(z,V,T)$$

$$A = -kT \ln \frac{\underline{Q}(z,V,T)}{z^N} \quad \text{——— (19)}$$

Helmholtz free energy for GCE

& $$S = \frac{U-A}{T} = kT\left(\frac{\partial q}{\partial T}\right)_{z,V} - Nk \ln z + kq \quad \text{——— (20)}$$

Entropy for GCE

Density And Energy Fluctuations in GCE

We know in GCE, exchange of No. of particles (N) & Energy E b/w system & reservoir is allowed. These variables N & E have value b/w $(zero)^0$ & infinity for any member (system) of ensemble.

Illy, in case of CE, we have seen that since energy can have value b/w zero & infinity, there are fluctuations in energy. These fluctuations are found to be negligible. And hence statistics of MCE & CE gave same (almost) result for thermodynamical quantities. And can be considered identical for all practical purposes.

Similar results are exported from GCE. i.e if the fluctuations in density of particles & fluctuations in energy come out to be negligible (which it should be, because thermodynamic results are identical), we can say that MCE, CE & GCE can be considered identical for all practical purposes. (But it founds out that is not the case always.)

Now, we know that

$$\bar{N} = \frac{\sum_{r,s} N_r e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}} \qquad \text{——— (1)}$$

$$\left(\frac{\partial N}{\partial \alpha}\right)_{\beta, E_s} = \frac{-\sum_{r,s} N_r^2 e^{-\alpha N_r - \beta E_s} \sum_{r,s} e^{-\alpha N_r - \beta E_s}}{\left(\sum_{r,s} e^{-\alpha N_r - \beta E_s}\right)^2} + \left(\frac{\sum_{r,s} N_r e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}}\right)^2$$

$$\Rightarrow \left(\frac{\partial \bar{N}}{\partial \alpha}\right)_{\beta,G} = -\bar{N}^2 + \bar{N}^2 \quad \text{——— (2)}$$

$$\Delta N = \sqrt{\langle (N - \langle N \rangle)^2 \rangle}$$

or

$$\langle (\Delta N)^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2$$

or

$$\overline{(\Delta N)^2} = \bar{N}^2 - \bar{N}^2$$

$$\Rightarrow \left(\frac{\partial \bar{N}}{\partial \alpha}\right)_{T,V} = -\bar{N}^2 + \bar{N}^2 \equiv \overline{(\Delta N)^2}$$

$$\left(\frac{\partial \bar{N}}{\partial \alpha}\right)_{T,V} = \left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V}^{kT} \equiv \overline{(\Delta N)^2} \quad \text{——— (3)}$$

Now, relative root-mean square fluctuations in particle can be represented as.

$$\frac{\sqrt{\overline{(\Delta N)^2}}}{\bar{N}} = \frac{\sqrt{kT\left(\frac{\partial N}{\partial \mu}\right)_{T,V}}}{\bar{N}} \sim O(N^{-1/2}) \quad \text{——— (4)}$$

$\Rightarrow$ The RMS fluctuations in no. of particles is of the $O(N^{-1/2})$

The RMS ~~fluctions~~ fluctuations in no. of particles can be represented in terms of Isothermal compressibility (k_T)

$$k_T = -\frac{1}{\underline{v}}\left(\frac{\partial \underline{v}}{\partial P}\right)_T \quad \text{——— (5)} \quad \text{where } \underline{v} = \frac{V}{N}$$

Now we can write

$$d\mu = \underline{v}\,dP - \underline{s}\,dT \quad \text{——— (6)}$$

at constant temp

$$d\mu = \underline{v}\,dP$$

or

$$\frac{\partial \mu}{\partial N} = \underline{v}\frac{\partial P}{\partial N}$$

$$G = A + PV = \mu N$$

$$G = U - TS + PV$$

$$dG = dU - T\,ds - s\,dT + P\,dV + V\,dP$$

$$dG = \cancel{T\,ds} - \cancel{P\,dV} - \cancel{T\,ds} - s\,dT + \cancel{P\,dV} + V\,dP$$

$$dG = -s\,dT + V\,dP = d\mu$$

$$\frac{\partial}{\partial N}$$

or $\left(\frac{\partial \mu}{\partial N}\right)_{T,V} = \frac{V}{N}\left(\frac{\partial P}{\partial N}\right)_{T,V}$ Why $\left(\frac{\partial \mu}{\partial V}\right)_{T,N} = \frac{V}{N}\left(\frac{\partial P}{\partial V}\right)_{T,N}$

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

$A = U - TS$

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

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

or

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

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

Now R.M.S fluctuations in particles can be written as

$$\frac{\sqrt{\overline{\Delta N^2}}}{\overline{N}} = \frac{\sqrt{kT\left(\frac{\partial N}{\partial \mu}\right)}}{\overline{N}} \simeq \frac{\sqrt{kT\left(\frac{\partial N}{\partial \mu}\right)}}{N} = \frac{\sqrt{kT \cdot \frac{N^2}{V^2}\left(-\frac{\partial V}{\partial P}\right)}}{N}$$

$$= \frac{\sqrt{kT \cdot \frac{N^2}{V^2}\left(-\frac{\partial V}{\partial P}\right)}}{N} \simeq \sqrt{\frac{kT}{V} \cdot \left(-\frac{1}{V}\frac{\partial V}{\partial P}\right)}$$

$$\simeq \sqrt{\frac{kT}{V}\left(-\frac{1}{V}\frac{\partial V}{\partial P}\right)} \simeq \sqrt{\frac{kT}{V}(k_T)} \quad \text{—— (7)}$$

Order of fluctuation depend on $\left(\frac{k_T}{V}\right)$.

Now $k_T(T_c) \sim N^{\gamma/d\nu}$

For system, near phase transition, compressibility becomes of the order of $O(N)$ i.e fluctuation in no. of particles

become significant.

So, in GCE, for system exhibiting phase transition, near the phase transition, the fluctuations in no. of particles become significant.

We shall now examine fluctuations in energy.

we can straightforward write the expression for energy

$$\overline{(\Delta E)^2} \equiv \overline{E^2} - \bar{E}^2 = -\left(\frac{\partial \bar{E}}{\partial \beta}\right)_{z,V} = kT^2\left(\frac{\partial U}{\partial T}\right)_{z,V} \quad \text{——— (8)}$$

$\bar{E}$ = eq. 7 Page-79

Now $$\left(\frac{\partial U}{\partial T}\right)_{z,V} = \left(\frac{\partial U}{\partial T}\right)_{N,V} + \left(\frac{\partial U}{\partial N}\right)_{T,V}\left(\frac{\partial N}{\partial T}\right)_{z,V} \quad \text{——— (9)}$$

Now $$N = -\left(\frac{\partial}{\partial \alpha} \ln \underline{Q}\right)_{\beta,V}, \quad U = -\left(\frac{\partial}{\partial \beta} \ln \underline{Q}\right)_{\alpha,V} \quad \text{——— (10)}$$

$\underline{Q}$ = Grand Partition fn.

or we can write $$\left(\frac{\partial N}{\partial \beta}\right)_{\alpha,V} = \left(\frac{\partial U}{\partial \alpha}\right)_{\beta,V} \quad \text{——— (11)}$$

& $$\left(\frac{\partial N}{\partial T}\right)_{z,V} = \frac{1}{T}\left(\frac{\partial U}{\partial \mu}\right)_{T,V} \quad \text{——— (12)}$$

from eq. (8) & (9)

$$\overline{(\Delta E)^2} = kT^2\left[\left(\frac{\partial U}{\partial T}\right)_{N,V} + \left(\frac{\partial U}{\partial N}\right)_{T,V}\left(\frac{\partial N}{\partial T}\right)_{z,V}\right]$$

$$= kT^2 C_V + kT^2 \cdot \left(\frac{\partial U}{\partial N}\right)_{T,V} \cdot \frac{1}{T}\left(\frac{\partial U}{\partial \mu}\right)_{T,V}$$

$$\overline{(\Delta E)^2} = kT^2 C_v + kT\left(\frac{\partial U}{\partial N}\right)_{T,V}\left(\frac{\partial U}{\partial \mu}\right)_{T,V} \quad (13)$$

$$= kT^2 C_v + kT\left(\frac{\partial U}{\partial N}\right)_{T,V} \cdot \frac{\partial U}{\partial N}\cdot\left(\frac{\partial N}{\partial \mu}\right)_{T,V}$$

$$= kT^2 C_v + \left(\frac{\partial U}{\partial N}\right)^2_{T,V} \cdot kT\left(\frac{\partial N}{\partial \mu}\right)_{T,V}$$

$$\overline{(\Delta E)^2} = kT^2 C_v + \left[\left(\frac{\partial U}{\partial N}\right)_{T,V}\right]^2 \cdot \overline{(\Delta N)^2} \quad \text{(from eq (3))}$$

$$\overline{(\Delta E)^2} = \langle (\Delta E)^2 \rangle_{Can} + \left[\left(\frac{\partial U}{\partial N}\right)_{T,V}\right]^2 \cdot \overline{(\Delta N)^2} \quad (14)$$

This means that the ~~too~~ mean-square fluctuation in the energy of a system in GCE is equal to fluctuation in energy in case of canonical ensemble and a contribution from fluctuation in no. of particles.

Now, we know that in normal case the fluctuation in no. of particle is negligible. So the fluctuation in energy for GCE & CE would be same.

However, in a region close to phase transition, no. of particle fluctuations becomes significant, leading to ~~for~~ significant fluctuations in energy as well.

Q Discuss in your own words thermodynamic phase diagrams.