Statistical Mechanics
Lecture 3

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Phase Space:

The state of gas is completely known if the position and momentum of each atom of the gas is specified. The position of an atom can be specified in terms of its rectangular coordinate (x, y, z). The momentum of an atom is completely known by (p_x, p_y, p_z). These six quantities (x, y, z, p_x, p_y, p_z) for each atom, when known the state of gas can be determined. Three position & three momentum coordinate together give the state of an atom in a six dimensional space called phase space.

The phase space can be divided into $(\Delta \mathrm{x}, \Delta \mathrm{y}, \Delta \mathrm{z}, \Delta \mathrm{p}_{\mathrm{x}}, \Delta \mathrm{p}_{\mathrm{y}}, \Delta \mathrm{p}_{\mathrm{z}})$ and volume of each state is given by

$$H = \Delta x \Delta y \Delta z \Delta p_x \Delta p_y \Delta p_z$$

According to Hisenberg uncertainty Principle

$$\Delta x \Delta p_x = h$$
$$\Delta y \Delta p_y = h$$
$$\Delta z \Delta p_z = h$$

Therefore

$$\Delta x \Delta y \Delta z \Delta p_x \Delta p_y \Delta p_z = h^3$$

Therefore

$$H = h^3$$

Therefore according to uncertainty principle in phase space the coordinate of a particle can be specified only to the extent that the particle under consideration has position and momentum laying within an element of phase space of volume h^3 .

Grand Canonical Ensemble:

Although the canonical and microcanonical ensemble give equivalent result, it may be argued that conceptually the canonical ensemble corresponds more closely to physical situation. In experiment we never deal with a completely isolated system nor do we directly measure the total energy of a macroscopic system. By the same attitude, we would only consider it unphysical to specify the number of particles of a macroscopic system for that it is never known. Actually we can found out from experiment is the average number of particles only.

This is the reason for introducing ***Grand Canonical Ensemble*** in which the system can have any number of particles, but the average is determined by the external conditions of the system. This is analogous to the situation in the canonical ensemble, where the average energy of system is determined by the temperature of the heat reservoir with which it is in contact.

In the canonical ensemble the subsystem could exchange energy , but not the particles with the reservoir. Therefore it can be considered that the grand canonical ensemble in which the subsystem can exchange energy, as well as the particles with the reservoir (r).

Here the variable *N* is replaced by the variable μ, the chemical potential per particle. The composite system (c), is again represented by microcanonical ensemble, because the total energy E_c and total number of particles N_c are fixed.

$$E_c = E_i + E_{r'} \rightarrow (i)$$

$$N_c = N_i + N_{r'} \rightarrow (ii)$$

$$\Delta\Gamma_c(E_{c'} N_{c'} E_{s'} N_r) = \Delta\Gamma_s(\mathrm{E}_{s'} \mathrm{N}_s)\, \Delta\Gamma_r(E_{r'} N_r) \rightarrow (iii)$$

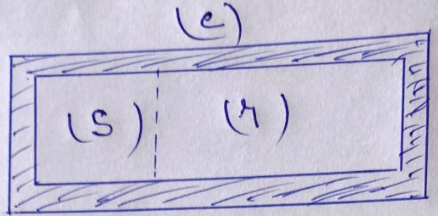

Fig ⓛ

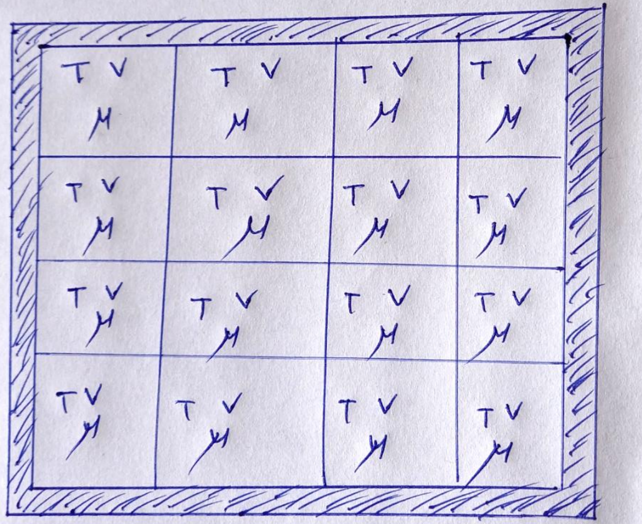

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Fig ⓜ

The phase space now depends on the number of particles N_i in the quantum sate (*i*)of the system, because it affects the number of dimensions. A particular quantum state of the system is denoted by ψ_{Ni} . Now to find P_{Ni}, the probability in the ensemble of finding the system (*s*) in a given state (*i*) When it contains $N_i = N$ particles and has an energy $E_i = E_{Ni}$. Following the same arguments similar to those leading to canonical ensemble

$$P_{Ni}(E_{Ni}\,, N) \propto \Delta\Gamma_r\,(E_c - E_{Ni}\,, N_c - N) \rightarrow (iv)$$

Since (*s*) is very small compared to (*r*), we can write

$$E_{Ni} \ll E_c \, and \, N \ll N_c$$

Therefore

$$\Delta\Gamma_r(E_c - E_{Ni}, N_c - N) = \Delta\Gamma_r(E_c, N_c)exp[-\beta(E_{N'} - N_\mu)] \to (v)$$

Where the chemical potential μ represents the Gibbs free energy per particle. Since $\Delta\Gamma_r(E_c, N_c)$ is just a constant independent of *i* and *N* , Equation (*iv*) can be written as

$$P_{Ni}(E_{Ni}, N) = C\, exp[-\beta(E_{N'} - N_\mu)] \to (vi)$$

Here

$$C = B\Delta\, \Gamma_r(E_c, N_c) \to (vii)$$

Where C and B are constants independent of *i* and *N*. This is called Grand Canonical Distribution.

The constant C is determined by the normalization condition

$$\sum P_{Ni}(E_{Ni}, N) = C \sum_{N,i} exp[-\beta(E_{Ni} - N_{\mu})] = 1 \rightarrow (viii)$$

Then

$$P_{Ni}(E_{Ni}, N) = \frac{exp[-\beta(E_{Ni} - N_{\mu})]}{Z} \rightarrow (ix)$$

Where *Z* is called the Grand Partition Function. It is the sum of the canonical partition function *Z(N)* for ensembles with different N with weighting factor (βN_{μ})

$$Z = \sum_{N,i} exp[-\beta(E_{Ni} - N_{\mu})] \rightarrow (x)$$

Again

$$z = \sum_{N=0}^{\infty} Z(N)\exp(\beta N_{\mu}) \rightarrow (xi)$$

And

$$Z(N) = \sum_{i} \exp(-\beta\, E_{Ni}) \rightarrow (xii)$$

Consider a grand canonical ensemble of M $(M \to \infty)$

The state of each element is characterized by the energy E_{Ni} and the number N of particles in it. The statistical weight Ω_{gM} of the ensemble associated with a particular microstate (m_{Ni}) is

$$\Omega_{\mathrm{gM}}(\mathrm{m}_{\mathrm{Ni}}) = \frac{M!}{\prod_N \prod_i m_{Ni}!} \to (xiii)$$

To find the most probable microstate (m_{Ni}) we maximize $\Omega_{\mathrm{gM}}(\mathrm{m}_{\mathrm{Ni}})$ subject to the constraints which are generalizations of equation (*i*) and (*ii*)

$$\sum_{N,i} m_{Ni} = M \rightarrow (xiv)$$

$$\sum_{N,i} m_{Ni} E_{ni} = E_c{}' \rightarrow (xv)$$

$$\sum_{N,i} N m_{Ni} = N_c{}' \rightarrow (xvi)$$

Where N_c is the total number of particles in the ensemble. The result is

$$\frac{m_{Ni}}{M} = P_{Ni} = \frac{exp[-\beta(E_{Ni} - N_{\mu})]}{\sum_{Ni} exp[-\beta](E_{Ni} - N_{\mu})'} \rightarrow (xvii)$$

Here $\beta = \frac{1}{KT}$ and $\alpha = \frac{\mu}{KT}$ for the Lagrange multipliers

Here α or μ is determined by the condition in equation (*xv*). The identification of β follows from the fact that we get back the canonical distribution if assume *N* to have a fixed value.

We can define entropy by

$$S = -K \sum_{N,i} P_{Ni} ln P_{N} \rightarrow (xviii)$$

From equation (*x*) and (*xviii*) we can write and taking that E_{Ni} is a function of V alone.

$$S = K\beta\bar{E} + K\ln Z - K\beta\bar{N}\mu \rightarrow (xix)$$

$$dS = K\beta\overline{dE} - K\beta\left[\sum_{N,i} P_{Ni}\left(\frac{\partial E_{Ni}}{\partial V}\right)\right]dV \rightarrow (xx)$$

Since $\beta = \frac{1}{KT}$

Therefore

$$P = -\sum_{N,i} P_{Ni}\left(\frac{dE_{Ni}}{dV}\right) \rightarrow (xxi)$$

Therefore we can write from equation (*xix*)

$$\Omega_g = U\text{-}TS\text{-}\mu N = -P(T, V, \mu) = -KT \ln Z(T, V, \mu) \rightarrow (xxii)$$

Where $\bar{E} = U$ and Ω_g is the grand canonical potential which determines the entire thermodynamics

In particular

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

Therefore

$$G \equiv U - TS + PV = \mu \rightarrow (xxiii)$$

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

So from equation (xxii) and dropping the suffixes

$$P(N) = exp\left[\frac{\Omega_g - E + N_\mu}{KT}\right] \rightarrow (xxiv)$$

$$Z = exp\left(\frac{-\Omega_g}{KT}\right)$$

$$Z = \sum_N exp\left(\frac{N_\mu}{KT}\right)\int exp\left[\frac{-E(N)}{KT}\right] d\Gamma(N) \rightarrow (xxv)$$

Postulates of Equal a Priori Probability:

When a macroscopic system is in thermodynamical equilibrium its state is equally likely to be any state satisfying the macroscopic condition of the system. This postulate implies that in thermodynamical equilibrium the system under consideration is a member of an ensemble called microcanonical ensemble whose density function is

$$\rho(p,q) = 1 \ \ if \ E < H(p,q) < E + \Delta$$

$$\rho(p,q) = 0 \ \ otherwise$$

It is clear that all members of the ensemble have the same number of particle *N* and same volume *V* .

Let $f(p, q)$ is a measurable property like energy and momentum. When system is in equilibrium the observed value of (p, q) must be result by averaging $f(p, q)$ over microcanonical ensemble in some manner. So if the postulate of equal a priori probability is to be useful, all manners of averaging must yield essentially the same answer.

Two kinds of average values are introduced. First one is most probable value and second one is ensemble average.

The most probable value of $f(p,q)$ is the value of $f(p,q)$ that is possessed by the largest member of systems in ensemble.

Again ensemble average of $f(p,q)$ is defined as

$$< f > \frac{\int d^{3N}p\, d^{3N}q\, f(p,q)\rho\,(p,q)}{\int d^{3N}p\, d^{3N}q\, \rho(p,q)}$$

The ensemble average and most probable value are nearly equal if the mean square fluctuation is small i.e. if

$$\frac{<f^2> \; - <f>^2}{<f^2>} \le 1$$

In all physical cases we find that the mean square function are of order of $\frac{1}{N}$. Thus in limit as $N \rightarrow \infty$, the ensemble average and most probable values become identical.