Statistical Physics

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1 Revisit Thermodynamical Relations : Group A : Page 4-5 of Lecture note-1

Here, we will quickly revisit our old Thermodynamical understanding. Let us start with Euler thermodynamical relation:

$$TS = U + PV - \mu N$$
$$\implies U = TS - PV + \mu N \tag{1}$$

The various quantities used in the above equation are as follows :

$U =$ Internal energy
$T =$ Temperature
$S =$ Entropy
$P =$ Pressure
$V =$ Volume
$\mu =$ Chemical potential
$N =$ Number of particles

Taking total differential on both sides, we get :

$$dU = TdS + SdT - PdV - VdP + \mu dN + Nd\mu \tag{2}$$

From the 2nd law of thermodynamics, we get :

$$TdS = dU + PdV - \mu dN \tag{3}$$

Substituting $TdS = dU + PdV - \mu dN$ in (2), we obtain :

$$dU = dU + PdV - \mu dN + SdT - PdV - VdP + \mu dN + Nd\mu$$
$$\implies SdT - VdP + Nd\mu = 0$$

The above relation is called the **Gibb's Duhem** relation.

In thermodynamics, the Gibbs–Duhem equation describes the relationship between <mark>changes in chemical potential</mark> for components in a thermodynamic system. However, it cannot be used for small thermodynamic systems due to the influence of surface effects and other microscopic phenomena.

From eqn.(1), we get :

$$S = \frac{U}{T} + V\frac{P}{T} - N\frac{\mu}{T}$$

$$\implies dS = Ud(\frac{1}{T}) + Vd(\frac{P}{T}) - Nd(\frac{\mu}{T}) + (\frac{1}{T})dU + (\frac{P}{T})dV - (\frac{\mu}{T})dN \quad (\text{\colorbox{yellow}{Product Rule}})$$

$$\implies dS = Ud(\frac{1}{T}) + Vd(\frac{P}{T}) - Nd(\frac{\mu}{T}) + dS \qquad (\text{Using } dS = (\frac{1}{T})dU + (\frac{P}{T})dV - (\frac{\mu}{T})dN \text{ from (3)})$$

$$\implies Ud(\frac{1}{T}) + Vd(\frac{P}{T}) - Nd(\frac{\mu}{T}) = 0$$

$$(4)$$

We know that <mark>$U = \frac{3}{2}NK_BT$</mark> (Internal energy of ideal gas) i.e. $\frac{1}{T} = \frac{3NK_B}{2U}$ and $\frac{P}{T} = \frac{NK_B}{V}$ (from Ideal Gas equation).

Substituting these values in eqn.(4), we get :

$$Ud(\frac{3NK_B}{2U}) + Vd(\frac{NK_B}{V}) - Nd(\frac{\mu}{T}) = 0$$

$$\implies Nd(\frac{\mu}{T}) = \frac{3}{2}K_BUd(\frac{N}{U}) + K_BVd(\frac{N}{V})$$

$$\implies Nd(\frac{\mu}{K_BT}) = \frac{3}{2}Ud(\frac{N}{U}) + Vd(\frac{N}{V})$$

$$\implies d(\frac{\mu}{K_BT}) = \frac{3U}{2N}d(\frac{N}{U}) + \frac{V}{N}d(\frac{N}{V})$$

$$\implies d(\frac{\mu}{K_BT}) = \frac{3U}{2N}[\frac{dN}{U} - \frac{NdU}{U^2}] + \frac{V}{N}[\frac{dN}{V} - \frac{NdV}{V^2}]$$

$$\implies d(\frac{\mu}{K_BT}) = \frac{3U}{2N}[\frac{dN}{U} - \frac{NdU}{U^2}] + \frac{V}{N}[\frac{dN}{V} - \frac{NdV}{V^2}]$$

$$\implies d(\frac{\mu}{K_BT}) = \frac{3}{2}\frac{dN}{N} - \frac{3}{2}\frac{dU}{U} + \frac{dN}{N} - \frac{dV}{V}$$

$$\implies d(\frac{\mu}{K_BT}) = \frac{5}{2}\frac{dN}{N} - \frac{3}{2}\frac{dU}{U} - \frac{dV}{V}$$

After integrating both sides we get :

$$\frac{\mu}{K_B T} = \frac{5}{2}\ln N - \frac{3}{2}\ln U - \ln V - \ln C$$

$$\implies \frac{\mu}{K_B T} = \ln\left[\frac{N^{\frac{5}{2}}}{U^{\frac{3}{2}}VC}\right] \tag{5}$$

$$\implies \boxed{\frac{\mu}{T} = K_B \ln\left[\frac{N^{\frac{5}{2}}}{U^{\frac{3}{2}}VC}\right]}$$

Again, from eqn.(1), we obtain :

$$S = \frac{U}{T} + V\frac{P}{T} - N\frac{\mu}{T}$$

$$\implies S = \frac{\frac{3}{2}NK_B T}{T} + NK_B - N(\frac{\mu}{T})(\text{Using Ideal Gas Equation})$$

$$\implies S = \frac{5}{2}NK_B - NK_B\ln\left[\frac{N^{\frac{5}{2}}}{U^{\frac{3}{2}}VC}\right] \qquad (\text{Using eq.(5)})$$

$$\implies \boxed{S = NK_B\left[\ln\left(\frac{U^{\frac{3}{2}}VC}{N^{\frac{5}{2}}}\right) + \frac{5}{2}\right]}$$

Thus, we have obtained an expression for entropy in terms of other macroscopic quantities like internal energy, volume and number of particles.

2 MCE calculation for ideal Gas : Group F : Page 6-7 of Lecture note-1

Hamiltonian of a system comprising of N-ideal gas molecules is given by,

$$H = T + V$$

$$H(q_i, p_i) = \sum_{i=1}^{3N}\frac{p_i^2}{2m} + \sum_{i=1}^{N}\phi(x_i) \tag{6}$$

where H represents the Hamiltonian, T represents the kinetic energy and V represents the potential energy of the particle. The above expression is obtained from the Hamiltonian formalism in classical mechanics. Another important assumption that we are making here is as this is an ideal gas, there will be no interaction between the molecules of the gas. As a result we can replace ϕ with zero. However with the application of the boundary condition for the box we get the following revised equation of the potential,

$$\phi(x) = \begin{cases} 0 & \text{for x inside box} \\ \infty & \text{for x outside box} \end{cases} \tag{7}$$

Thus the expression for Hamiltonian inside the volume of the container is given by,

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m} \tag{8}$$

But for our system of particles we know,

$$H(q_i, p_i) = E \tag{9}$$

$$\sum_{i=1}^{3N} \frac{p_i^2}{2m} = E$$

$$\boxed{\sum_{i=1}^{3N} p_i^2 = 2mE = R} \tag{10}$$

Eqn.(9) is the constant energy equation which imposes constraint on the system limiting the available the momentum space to the surface of sphere. This geometric symmetry is evident from the close resemblance of the eqn.(10) with the equation of sphere.

$$p_1^2 + p_2^2 + p_3^2 + \ldots\ldots = 2mE \tag{11}$$

$$x^2 + y^2 + z^2 = R^2 \tag{12}$$

On comparing the eqn.(12) and eqn.(11) we can deduce the value of the radius of the analogous sphere in the 3-N dimensional space.

$$\boxed{R = \sqrt{2mE}} \tag{13}$$

Using symmetry and applying constraints to our system we have reduced the problem from abstract integral over 3-N dimensional space to integration over a surface of 3-N dimensional hyper-sphere.

For a micro-canonical ensemble, the equilibrium density distribution represented by ρ_{eq} is assumed to be constant in between two constant energy surfaces separated by a very small distance in the phase space.The equilibrium density distribution is analogous to to the probability distribution function from the quantum mechanics. In order to understand how ρ_{eq} evolves with time we need to first revisit a few properties of the phase space. A given space is represented by a trajectory in the phase space. Some of the important properties of the trajectories in the phase space are as follows,

- Flow lines are deterministic, i.e. there is no intersections between the trajectories which may give rise to the uncertainty in the sate of the system in phase space.

- Liouvilles' theorem states that there can be no points of convergence in the phase space,i.e.

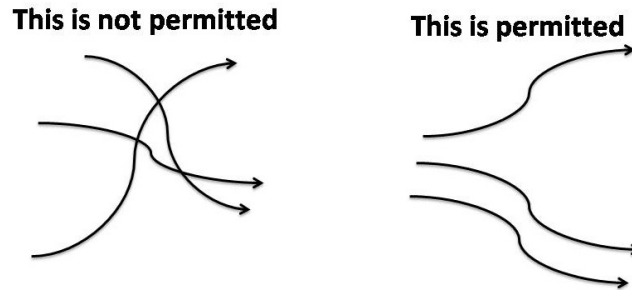$$\boxed{\frac{d\rho}{dt} = 0} \tag{14}$$

Figure 1: Intersection of flow lines is strictly not permitted and it gives rise to uncertainty in the state of the system
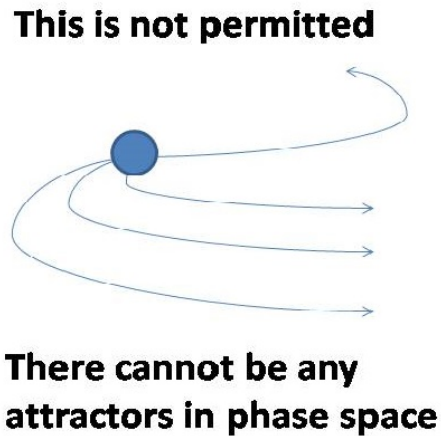

Figure 2: Such points where phase space trajectories converge are not permitted according to Liouvilles' theorem implying absence of source or sink

If a small volume with constant density is allowed to evolve with time every point in the system will have moved a certain distance. However from liouville's theorem we van say that the density of the system will stay constant, but the new topology of the system will be quite complicated due to the constraint on the system. Thus for our micro-canonical ensemble density will be constant between two constant energy surfaces. The equilibrium density distribution can be used to obtain the following properties of the system,

- Ensemble Averages- These are the macroscopically measure quantities which we actually measure.

- Statistical distributions of parameters such as momentum, etc.

- Other thermodynamic properties.

$$\rho_{eq}(\mu) = \begin{cases} C' & E \leq H(\mu) \leq E + \delta E \\ 0 & otherwise \end{cases} \qquad (15)$$
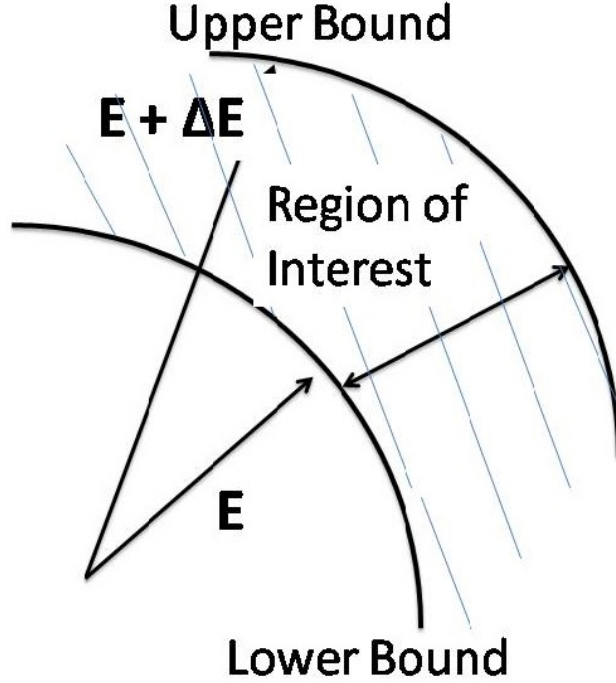

Figure 3: Figure depicting the area of interest between two constant energy surfaces bounded by E and $E + \delta E$

In order to determine the value of the equilibrium density distribution we first need to figure out the value of the constant in the eqn.(15). To obtain the value of C' we use the following normalisation condition,

$$\int \rho_{eq}(\mu)d^{6N}\mu = 1 \qquad (16)$$

Thus we have a integral of a function dependent on the variable μ where μ represents a generalised coordinate in a phase space, in a $6N$ dimensional space.

Substituting the value of eqn.(15) in eqn.(16)

$$\int \rho_{eq}(\mu)d^{6N}\mu = 1$$

$$\int_{E \leq H(\mu) \leq E+\delta} C'd^{6N}\mu = 1$$

$$C'\int_{E \leq H(\mu) \leq E+\delta E} d^{6N}\mu = 1$$

$$\left[\tilde{\Omega}(E+\delta E) - \tilde{\Omega}(E)\right] \times C' = 1$$

$$C' = \frac{1}{\tilde{\Omega}(E+\delta E) - \tilde{\Omega}(E)} \tag{17}$$

As equilibrium density distribution function is zero everywhere except in the regions between the two constant energy surfaces represented by E and $E+\delta E$. According to Noether's theorem time invariant or symmetric systems have their energy conserved. So for a system varying with time, we can understand its evolution with time by understanding how it responds to change in the energy of the system.Thus to understand the time dependence of ρ_{eq} we try to observe the effects of change in energy on the value of ρ_{eq}. The $\tilde{\Omega}(E)$ term used in the above expression is the integration term written in a more compact form.

Eq.(18) represents the generalised expression for finding the ensemble average. The macroscopic quantity to be measured is represented by the $A(\mu)$and multiplied by the equilibrium density distribution to obtain the ensemble average. The procedure followed is analogous to the method of finding expectation values in the quantum mechanics using the probability distribution function.

$$\langle A \rangle_{eq} = \int A(\mu)\rho_{eq}(\mu)d^{6N}\mu \tag{18}$$

$\tilde{\Omega}(E)$ represents the volume enclosed by the boundary condition $H(\mu) \leq E$ in the integral eqn.19. We will try to further evaluate the integral in detail what each term in the eqn.19 represents.

$$\tilde{\Omega}(E) = \int_{H(\mu) \leq E} d^{6N}\mu \tag{19}$$

μ is the generalised coordinate in the phase space as mentioned previously. It can be written in the expanded form as shown below, by splitting it into it's constituents i.e. momentum and position. In d^3x_N the 3 represents the three coordinates required to uniquely determine the position of the particle. N represents the no. of particles. In quantum mechanics each particle is defined using its own set of coordinates , as result for N particles we need $3N$ coordinates. Similarly for momentum to we need another $3N$ coordinates to define the particle in phase space. As a result the total number of coordinates end up

being 6N which represents the 6N dimensional phase space through which our system of N-particles is defined.

$$d^{6N}\mu \Rightarrow d^3x_1 d^3x_2 d^3x_3....d^3x_N d^3p_1 d^3p_2 d^3p_3....d^3p_N \qquad (20)$$

Integration of position coordinates gives us the volume of the closed system. For a single particle integral over a volume is represented by V. As all the particles are identical, using symmetry the value of the integral over position will give same results for all the other particles. Thus the total value of the integral is V^N.

$$\int dx_1 dx_2 dx_3...dx_{3N} = V^N \qquad (21)$$

As energy is not dependent on the value of the position of the particle, hence the integral of the position dependent terms can be treated separately. The value of this separated integral was already obtained above in the eq.(21). Thus to obtain the value of the integral we need to obtain the value of the momentum integral.

$$\tilde{\Omega}(E) = V^N \int_{\sum_{i=1}^{3N} p_i^2 \leq 2mE} dp_1 dp_2 dp_3....dp_{3N} \qquad (22)$$

As discussed previously, due to the boundary conditions applied on our system it is spherically symmetric in the momentum space. Thus in order to find out the value of the value of the integral in the eqn.(22) we need to find out the value of the hyper-sphere. The equation for the value of the hyper-sphere is given by-

$$\boxed{V_{sp}(R,d) = \frac{\pi^{\frac{d}{2}} R^d}{\Gamma(\frac{d}{2}+1)}} \qquad (23)$$

where R denotes the radius of the hyper-sphere and d denotes the dimensions.

$$\int_{\sum_{i=1}^{3N} p_i^2 \leq 2mE} dp_1 dp_2 dp_3....dp_{3N} \qquad (24)$$

From eqn.(24) and eqn.(23) we get the following simplified expression for the value of integral in the momentum space.

$$V_{sp}(R,3N) = \frac{\pi^{\frac{3N}{2}} R^{3N}}{\Gamma(\frac{3N}{2}+1)} \qquad \text{where R}=\sqrt{2mE} \qquad (25)$$

Replacing the volume of momentum integral from eqn.(25) in eqn.(22) we get the following final expression for the value of $\tilde{\Omega}(E)$.

$$\boxed{\tilde{\Omega}(E) = V^N \frac{\pi^{\frac{3N}{2}} R^{3N}}{\Gamma(\frac{3N}{2}+1)}} \qquad \text{where R}=\sqrt{2mE} \qquad (26)$$

In the phase space the momentum and position cannot take up any small value indiscriminately. The uncertainty principle puts a limiting condition on the minimum values of the momentum and position of the molecules in the phase

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space. This is obtained by dividing our final expression for the <mark>no. of micro-states by h^{3N}</mark> as shown below.

$$\Omega = \frac{1}{h^{3N}} \times \frac{\partial \tilde{\Omega}(E)}{\partial E} \times \delta E \tag{27}$$

Thus eqn.(27) represents the final form for obtaining the number of micro-states in the micros-canonical ensemble. The value of the entropy can be obtained using the following procedure. From eqn.(27) and eqn.(26) we get,

$$\frac{d\tilde{\Omega}}{dE} = V^N \frac{(2\pi m)^{\frac{3N}{2}} E^{\frac{3N}{2} - 1}}{\left(\frac{3N}{2} - 1\right)!} \tag{28}$$

From eqn.(28) and eqn.(26) we get the value of number of micro-states in an ensemble given by,

$$\Omega = \frac{V^N}{h^{3N}} \times \frac{(2\pi m)^{\frac{3N}{2}} E^{\frac{3N}{2} - 1}}{\left(\frac{3N}{2} - 1\right)!} \times \delta E \tag{29}$$

Using logarithm operator on both sides of the above equation,

$$\log(\Omega) = -3N\log(h) + \frac{3N}{2}\log(2\pi m) + \left(\frac{3N}{2} - 1\right)\log(E)$$
$$- \log\left(\frac{3N}{2} - 1\right)! + N\log(V) + \log(\delta E) \tag{30}$$

Applying Stirling's approximation on the above equation, and keeping only the lower order terms of N,

$$\log(\Omega) \approx -N\log(h^3) + N\log(2\pi mE)^{\frac{3}{2}} - \left(\frac{3N}{2}\right)\log\left(\frac{3N}{2}\right)$$
$$+ N\log(V) + \left(\frac{3N}{2}\right) \tag{31}$$

Replacing the constants like <mark>π, m, E w</mark>ith another single <mark>constant C</mark>. Therefore above equations transforms to,

$$\boxed{\log(\Omega) = N\left[\log\left(\frac{E^{\frac{3}{2}} V C}{N^{\frac{3}{2}}}\right) + \frac{3}{2}\right]} \tag{32}$$

Using Boltzmann expression for entropy we get,

$$\boxed{S = NK_B\left[\log\left(\frac{E^{\frac{3}{2}} V C}{N^{\frac{3}{2}}}\right) + \frac{3}{2}\right]} \tag{33}$$

where <mark>K_B is known as Boltzmann's constant</mark>.

3 Gibb's paradox : Group B : Page 8-9 of Lecture note-1

There are two identical boxes of volume V_1 and V_2 and the number of molecules in it are N_1 and N_2 respectively.

After mixing two system at same temperature(T),

$$\boxed{V_1 + V_2 = V_f \text{ and } N_1 + N_2 = N_f}$$

Entropy Change:-

$S_f - (S_1 + S_2) = KN_f(ln[V_1(\frac{3}{2}KT)^{\frac{3}{2}}] + \frac{3}{2}) + \frac{3}{2}N_f K ln(\frac{4\pi m}{3h^2}) - KN_1(ln[V_1(\frac{3}{2}KT)^{\frac{3}{2}}] + \frac{3}{2} + \frac{3}{2}ln(\frac{4\pi m}{3h^2})) - KN_2(ln[V_2(\frac{3}{2}KT)^{\frac{3}{2}}] + \frac{3}{2} + \frac{3}{2}ln(\frac{4\pi m}{3h^2}))$

$\implies \Delta S = KN_f ln[V_1] - KN_1 ln[V_1] - KN_2 ln[V_2] + K(\frac{3}{2}ln[\frac{3}{2}KT] + \frac{3}{2} + \frac{3}{2}ln[\frac{4\pi m}{3h^2}])(N_f - N_1 - N_2)$

We know that, $N_f - N_1 - N_3 = 0$
Therefore,
$\Delta S = KN_1 ln[\frac{V_f}{V_1}] + KN_2 ln[\frac{V_f}{V_2}]$ ——— eqn.[A]

For $V_1 = V_2$ and $V_f = 2V$, $N_1 = N_2 = N$ and $N_f = 2N$
from eqn.[A],
$\Delta S = KN_1 ln[\frac{V_f}{V_1}] + KN_2 ln[\frac{V_f}{V_2}]$
Now the equation becomes,
$\Delta S = KN_1 ln[\frac{2V}{V}] + KN_2 ln[\frac{2V}{V}]$
$\Delta S = KN_1 ln[2] + KN_2 ln[2]$
Since $N_1 = N_2$,
$\boxed{\Delta S = 2KN ln 2}$ ——— from eqn.[A]

$$\boxed{\Delta S = 0 \text{ (expected)}}$$

But [A] shows that,

$$\Delta S = 2KN ln 2 > 0 \tag{34}$$

Since for Carnot Entropy,

$S_f - (S_1 + S_2) = KN_f(ln[\frac{V_f}{N_f} (\frac{3}{2}KT)^{\frac{3}{2}}] + \frac{5}{2} + \frac{3}{2}ln[\frac{4\pi m}{3h^2}]) - KN_1(ln[\frac{V_1}{N_1}(\frac{3}{2}KT)^{\frac{3}{2}}] + \frac{5}{2} + \frac{3}{2}ln[\frac{4\pi m}{3h^2}]) - KN_2(ln[\frac{V_2}{N_2}(\frac{3}{2}KT)^{\frac{3}{2}}] + \frac{5}{2} + \frac{3}{2}ln[\frac{4\pi m}{3h^2}])$

$\Delta S = KN_f ln[\frac{V_f}{N_f}] - KN_1 ln[\frac{V_1}{N_1}] - KN_2 ln[\frac{V_2}{N_2}] + K(\frac{3}{2}ln[\frac{3}{2}KT] + \frac{5}{2} + \frac{3}{2}ln[\frac{4\pi m}{3h^2}])(N_f - N_1 - N_2)$

We know that, $N_f - N_1 - N_3 = 0$

Therefore, $\Delta S = KN_1 ln[\frac{V_f}{V_1} \frac{N_1}{N_f}] + KN_2 ln[\frac{V_f}{V_2} \frac{N_2}{N_f}]$

Now for $V_1 = V_2 = V$ and $V_f = 2V$, $N_1 = N_2 = N$ and $N_f = 2N$

$$\boxed{\Delta S = KNln[\frac{2V}{V} \frac{N}{2N}] + KNln[\frac{2V}{V} \frac{N}{2N}] = 0} \qquad \because ln1 = 0$$

So, to get $S_{carnot} = NK[ln[\frac{V}{N}(\frac{3}{2}KT)^{\frac{3}{2}}] + \frac{5}{2}] + C$

$\frac{\Omega}{N!} = \Omega_{Gibbs} \longleftarrow \Omega = (V(\frac{2\pi mv}{h^2})^{\frac{3}{2}})^N \frac{3}{2}N \frac{\Delta}{U} \frac{1}{\Gamma \frac{3N}{2}!}$

$S_B \uparrow = NK[ln(V(\frac{3}{2}KT)^{\frac{3}{2}}) + \frac{3}{2} + \frac{3}{2}ln[\frac{4\pi m}{3h^2}]]$

Since $KlnN! = KNlnN - KN$

$S_B - KlnN! = NK[ln(\frac{V}{N}(\frac{3}{2}KT)^{\frac{3}{2}}) + \frac{5}{2} + \frac{3}{2}ln[\frac{4\pi m}{3h^2}]]$
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4 Canonical Ensemble : Group C : Page 10-11 of Lecture note-1

In the above sections, we have discussed the basic thermodynamic relations and derived an expression of entropy as a function of number of particles (N), volume (V) and total internal energy of the system (U) for a micro-canonical ensemble. In the micro-canonical ensemble, the thermodynamic properties U, V, N remain constant throughout the process. In the canonical ensemble however, the internal energy of the system ceases to be a constant parameter, as the system is allowed to exchange energy with the surroundings while keeping the number of particles and volume of the system constant.

In the canonical ensemble, the system is in thermal equilibrium with the surroundings (heat reservoir). Both the system and heat reservoir attain the same temperature at the equilibrium condition. Hence, to derive all the thermodynamic properties of this type of system configuration, we need to define a state function at the macroscopic level which is a function of T, V and N. But before that, it would be a good idea to define a function at the microscopic level, and then derive a relationship between the microscopic function and its macroscopic counterpart.

Let us consider a system immersed into a very large heat reservoir. At equilibrium, the system and the reservoir attain the same temperature T, but their energies would be variable at any instant. The energy values of system and reservoir will lie between 0 and E_0, where E_0 is the combined total energy of the system and reservoir. At any instant, the system and reservoir will have the energy values E and E_R such that

$$E + E_R = E_0$$

where E_0 is constant at any instant. Now, since the reservoir is much larger than the system, E_R is much greater than E. It also implies that

$$E \ll E_0$$

i.e., the energy of the system E is a very small fraction of the combined total energy E_0.

Now let us focus on the energy configuration of the reservoir. The probability of the reservoir assuming a particular energy value E_R is directly proportional to the number of micro states having the energy value E_R.

Mathematically, the above statement can be represented as

$$p \propto \Omega_R(E_R)$$

We can also write p in terms of E as

$$p \propto \Omega_R(E_0 - E)$$

Now, if we take the ratio of the probabilities of the reservoir assuming the energy states E_j and E_k respectively, then we can write it as follows

$$\frac{p(E_j)}{p(E_k)} = \frac{\Omega_R(E_0 - E_j)}{\Omega_R(E_0 - E_k)}$$

Using the famous Boltzmann expression for entropy, we can write the number of micro states of a reservoir having the energy value E as a function of entropy of the reservoir at that particular energy value.

$$S_R = k_B \ ln \ \Omega_R(E_0 - E)$$

$$\Rightarrow \Omega_R(E_0 - E) = \exp\left(\frac{S_R(E_0 - E)}{k_B}\right)$$

Hence we can write the probability ratios at E_j and E_k as

$$\frac{p(E_j)}{p(E_k)} = \exp\left[\frac{(S_R(E_0 - E_j) - S_R(E_0 - E_k))}{k_B}\right]$$

We have already proved above that $E \ll E_0$ for all practical purposes. In this case, we can expand the entropy term as

$$S_R(E_0 - E) = S_R(E_0) - E\left(\frac{\partial S_R}{\partial E}\right)_{V,N}$$

From the second law of thermodynamics, we can see that

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

Hence, we get the final expression of entropy of the reservoir as

$$S_R(E_0 - E) = S_R(E_0) - \frac{E}{T}$$

From the above results, we get

$$\frac{p(E_j)}{p(E_k)} = \exp\left[-\frac{E_j}{k_B T} + \frac{E_k}{k_B T}\right]$$

By the above equation, we can see that

$$p(E_j) \propto \exp\left(-\frac{E_j}{k_B T}\right) \equiv \exp\left(-\beta E_j\right)$$

where $\beta = \dfrac{1}{k_B T}$

We have discussed the relationship between probability at a particular energy

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value $p(E)$ and energy of the system E. Now, it would be great if could obtain a complete expression of $p(E)$ by normalizing it. We can write $p(E)$ at a particular energy value E as

$$p(E) = \frac{e^{-\beta E}}{Z}$$

where Z is the normalizing constant.

To compute the value of Z, we add up all the probabilities at all possible energy values. This can be represented mathematically as given below

$$\sum_j p(E_j) = 1$$

$$\Rightarrow \frac{\sum_j e^{-\beta E_j}}{Z} = 1$$

$$\Rightarrow \boxed{Z = \sum_j e^{-\beta E_j}}$$

In the above equation, Z signifies the sum of all the possible energy states in the system at equilibrium, and is also known as the "Canonical Partition Function". To avoid confusion with the Grand Canonical Partition Function Z_{GCE}, we shall represent canonical partition function by Z_{CE} hereafter.

Since we know the probability distribution of states corresponding to an energy value, we can calculate the expectation value of energy (mean energy) of the system.

$$\langle E \rangle = \sum_j E_j p(E_j)$$

$$\Rightarrow \langle E \rangle = \frac{\sum_j E_j e^{-\beta E_j}}{\sum_j e^{-\beta E_j}}$$

Now we already know that

$$Z_{CE} = \sum_j e^{-\beta E_j}$$

On differentiating Z_{CE} wrt β, we get

$$\frac{\partial Z_{CE}}{\partial \beta} = -\sum_j E_j e^{-\beta E_j}$$

Hence we can write $\langle E \rangle$ as

$$\langle E \rangle = -\frac{1}{Z_{CE}} \left(\frac{\partial Z_{CE}}{\partial \beta} \right)_{V,N}$$

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or

$$\langle E \rangle = - \left(\frac{\partial \left(ln \ Z_{CE} \right)}{\partial \beta} \right)_{V,N}$$

The calculations done above were based on the assumption that each state has its own distinct energy values, which is not true in reality. We always have a certain degeneracy in the number of states $\Omega(E)$ corresponding to an energy value. So, to account for all these degenerate states, we need to modify the expression of canonical partition function Z_{CE} by multiplying the number of states $\Omega(E)$ with the exponential term in the former expression of Z_{CE}.

Mathematically, the above statement can be represented as

$$Z_{CE} = \sum_{\nu} \Omega(E_\nu) e^{-\beta E_\nu}$$

We already know that

$$\Omega(E_\nu) = \exp \left(\frac{S(E_\nu)}{k_B} \right)$$

Substituting this value in the expression of Z_{CE}, we get

$$Z_{CE} = \sum_{\nu} \exp \left(\frac{S(E_\nu)}{k_B} - \beta E_\nu \right)$$

The above expression of canonical partition function can be approximated by taking the peak value of energy U and its corresponding entropy value $S(U)$ in place of the summation of the exponential terms for different energy values E_ν. This can be shown mathematically as

$$Z_{CE} \approx \exp \left(\frac{S(U)}{k_B} - \beta U \right)$$

Substituting the value of β in the above expression, we get

$$Z_{CE} = \exp \left(\frac{S}{k_B} - \frac{U}{k_B T} \right)$$

or

$$\boxed{Z_{CE} = \exp \left(-\frac{U - TS}{k_B T} \right)}$$

So far, we have derived the general expression for the canonical partition function Z_{CE}. We wish to develop a relationship between the above statistical (microscopic) quantity and a thermodynamic (macroscopic) quantity. Let us introduce a new thermodynamic property A, or the Helmholtz free energy. The mathematical expression of A is as given below:

$$A = U - TS$$

Now, by substituting the above relation in the expression for Z_{CE} and taking log on both sides, we get

$$A(T, V, N) = -k_B T \ ln(Z_{CE}(T, V, N))$$

We have successfully developed a relationship between the canonical partition function (microscopic quantity) and Helmholtz free energy (macroscopic quantity). Now we can derive all the thermodynamic properties as a function of Helmholtz free energy A, the details of which are discussed in the further sections.

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5 Grand-Canonical Ensemble : Group D : Page 13-14 of Lecture note-1

According to grand canonical ensemble,
$E + E_R = E_0 = $ Constant
$N + N_R = N_0 = $ Constant

The Probability of system = Probability of R
Here, $\rho(E, N) = \rho(E_0 - E, N_0 - N)$

$$\frac{\rho(E_j, N_j)}{\rho(E_k, N_k)} = \frac{\Omega_R(E_0 - E_j, N_0 - N_j)}{\Omega_R(E_0 - E_k, N_0 - N_k)} = \frac{e^{S_R(E_0 - E_j, N_0 - N_j)/K_B}}{e^{S_R(E_0 - E_k, N_0 - N_k)/K_B}}$$

Now $S_R(E_0 - E_j, N_0 - N_j) = S_R(E_0, N_0) - E_j\left(\frac{\partial S_R}{\partial E_j}\right)_N - N_j\left(\frac{\partial S_R}{\partial N_j}\right)_E$

$\because TdS = dU + PdV - \mu dN$

$\Rightarrow \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}$ and $\left(\frac{\partial S}{\partial N}\right)_{V,U} = -\frac{\mu}{T}$

$\therefore S_R(E_0 - E_j, N_0 - N_j) = S_R(E_0, N_0) - \frac{E_j}{T} + \frac{\mu N_j}{T}$

$\therefore \frac{\rho(E_j, N_j)}{\rho(E_K, N_K)} = \exp\left[\frac{S_R}{K_B} - \frac{E_j}{K_BT} + \frac{\mu N_j}{K_BT} - \left(\frac{S_R}{K_B} - \frac{E_k}{K_BT} + \frac{\mu N_k}{K_BT}\right)\right]$

$\Rightarrow \rho(E, N) \propto e^{-\frac{(E - \mu N)}{kT}}$

$$\propto e^{-\beta(E - \mu N)}$$

$\Rightarrow \rho_j = \frac{e^{-\beta(E_j - \mu N_j)}}{\sum_j e^{-\beta(E_j - \mu N_j)}} \Rightarrow \boxed{Z = \sum_j e^{-\beta(E_j - \mu N_j)}}$

Partition Function

Now,
$Z = \sum_j e^{-\beta(E_j - \mu N_j)}$
$Z = \sum_\gamma \omega(E_\gamma)e^{-\beta(E_\gamma - \mu N_\gamma)}$ (This is Density of states concept)
$Z = \sum_\gamma exp\left[\frac{S(E_\gamma)}{K} - \frac{E_\gamma}{KT} + \frac{\mu N_\gamma}{KT}\right]$
$Z \simeq exp\left[\frac{S}{K} - \frac{\gamma}{KT} + \frac{\mu N}{KT}\right]$
$\implies \boxed{TS - U + \mu N = KTlnZ = PV = \Phi}$ which is Grand Canonical potential.
....

6 Micro to Macro of CE and GCE : Group E : Page 15-16 of Lecture note-1

Canonical Ensemble :

In statistical physics, a canonical ensemble is the statistical ensemble that represents the possible states of a mechanical system in thermal equilibrium with a heat bath at a fixed temperature.The system can exchange energy with the heat bath, so that the states of the system will differ in total energy.
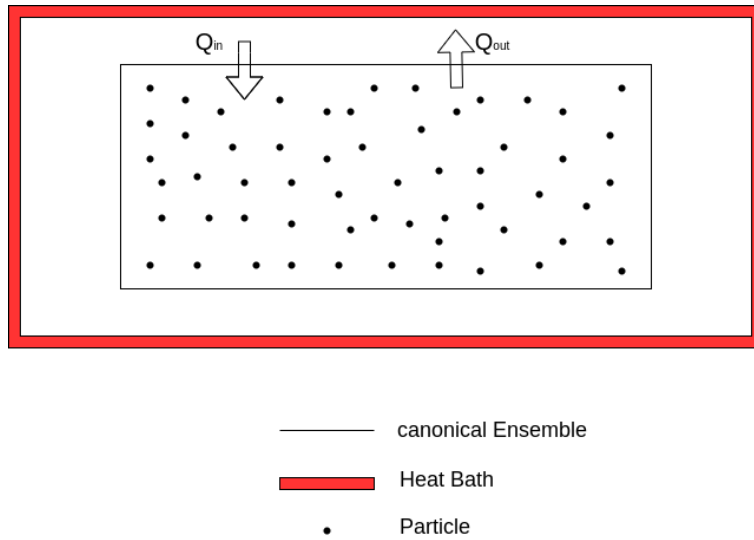

Figure 4: Canonical Ensemble

$$A = -KTlnZ \qquad (35)$$

$$A = U - TS \qquad (36)$$

$$A = -PV + \mu N \qquad (37)$$

From the second law of thermodynamics, we know that :

$$TdS = dU + PdV - \mu dN \qquad (38)$$

Now, from above

$$dA = dU - TdS - SdT$$

$$dA = -PdV + \mu dN - SdT \qquad \text{[using (38)]}$$

$$\Rightarrow S = -\left(\frac{\partial A}{\partial T}\right)_{V,N} = K_B \left[\frac{\partial(TlnZ)}{\partial T}\right]_{V,N} \tag{39}$$

$$\Rightarrow P = -\left(\frac{\partial A}{\partial V}\right)_{T,N} = K_B T \left[\frac{\partial(lnZ)}{\partial V}\right]_{N,T} \tag{40}$$

$$\Rightarrow \mu = \left(\frac{\partial A}{\partial N}\right)_{V,T} = -K_B T \left[\frac{\partial(lnZ)}{\partial N}\right]_{V,T} \tag{41}$$

Now,

$$U = A + TS$$

$$U = -K_B TlnZ + TK_B \left[\frac{\partial(TlnZ)}{\partial T}\right]_{V,N}$$

$$\boxed{U = T^2 K_B \left[\frac{\partial(lnZ)}{\partial T}\right]_{V,N}} \tag{42}$$

Grand Canonical Ensemble :

In statistical physics,a grand canonical ensemble (also known as the macro canonical ensemble) is the statistical ensemble that is used to represent the possible states of a mechanical system of particles that are in thermodynamic equilibrium (thermal and chemical) with a reservoir.The system is said to be open in the sense that the system can exchange energy and particles with a reservoir, so that various possible states of the system can differ in both their total energy and total number of particles. The system's volume, shape, and other external coordinates are kept the same in all possible states of the system.
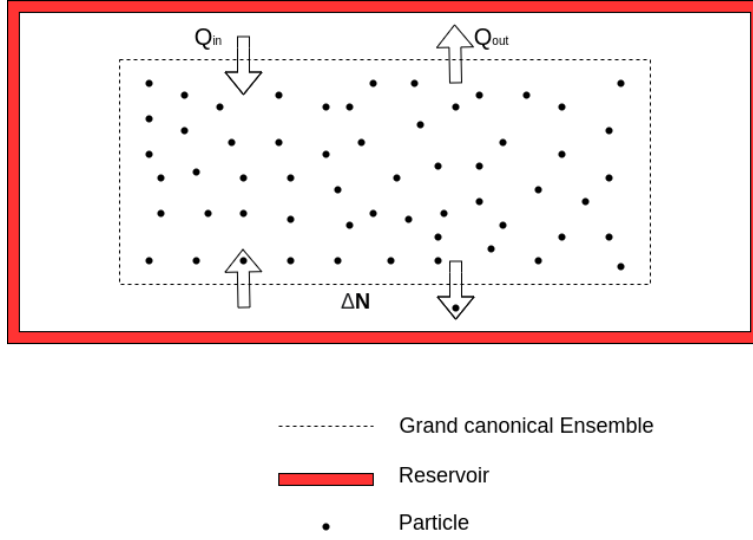
Figure 5: Grand Canonical Ensemble

$$\Phi = -KTlnZ(T, \mu, V) \tag{43}$$

$$\Phi = -PV \tag{44}$$

$$\Phi = U - TS - \mu N \tag{45}$$

From the second law of thermodynamics, we know that :

$$TdS = dU + PdV - \mu dN \tag{46}$$

From above,

$$d\Phi = dU - TdS - SdT - \mu dN - Nd\mu$$

$$d\Phi = -PdV - SdT - Nd\mu$$

$$\Rightarrow S = -\left(\frac{\partial \Phi}{\partial T}\right)_{\mu, V} = K_B \left[\frac{\partial (TlnZ)}{\partial T}\right]_{\mu, V} \tag{47}$$

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$$\Rightarrow P = -\left(\frac{\partial \Phi}{\partial V}\right)_{\mu,T} = K_B T \left[\frac{\partial (lnZ)}{\partial V}\right]_{\mu,T} \tag{48}$$

$$\Rightarrow N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{V,T} = K_B T \left[\frac{\partial (lnZ)}{\partial \mu}\right]_{V,T} \tag{49}$$

Now,

$$U = \Phi + TS + \mu N$$

$$U = -K_B T lnZ + TK_B \left[\frac{\partial (TlnZ)}{\partial T}\right]_{\mu,V} + \mu K_B T \left[\frac{\partial (lnZ)}{\partial \mu}\right]_{V,T}$$

$$U = T^2 K_B \left[\frac{\partial (lnZ)}{\partial T}\right]_{\mu,V} + \mu T K_B \left[\frac{\partial (lnZ)}{\partial \mu}\right]_{V,T}$$

Here Finally,

$$\boxed{U = K_B T \left[T\frac{\partial (lnZ)}{\partial T} + \mu\frac{\partial (lnZ)}{\partial \mu}\right]} \tag{50}$$

7 CE Partition function for non-interacting gas: Group G : Page 17-18 of Lecture note-1

Canonical Ensemble partition function for non-interacting gases :

Now we are going to calculate the partition function for the Canonical Ensemble and derive the physical macro quantities like Helmholtz free energy, Entropy,Pressure and internal energy form that partition function of canonical ensemble.

Formula for canonical partition function is:

$$Z = \sum_i e^{-\beta E_i} \tag{51}$$

$$Z = \sum_v \Omega(E_v) e^{-\beta E_v} \tag{52}$$

$$Z = \sum \left[\frac{d^{3N}x d^{3N}p}{N! h^{3N}} \right]_v e^{-\beta E_v} \tag{53}$$

$$Z = \int \left[\frac{d^{3N}x d^{3N}p}{N! h^{3N}} \right]_v e^{-\beta E_v} \qquad where E = \frac{p^2}{2m} \tag{54}$$

$$Z = \frac{V^N}{N! h^{3N}} \left[\int_0^\infty 4\pi p^2 dp e^{-\frac{\beta p^2}{2m}} \right]^N \tag{55}$$

But $\frac{\beta p^2}{2m} = z \Rightarrow$ pdp$= \frac{2m}{\beta} dz$;

$$Z = \frac{V^N}{N! h^{3N}} \left[\int_0^\infty 4\pi \left[\frac{2m}{\beta} \right]^{\frac{1}{2}} z^{\frac{1}{2}} dz \frac{m}{\beta} e^{-z} \right]^N \tag{56}$$

$$Z = \frac{V^N}{N! h^{3N}} \left[4\pi\sqrt{2} \left[\frac{m}{\beta} \right]^{\frac{3}{2}} \int_0^\infty z^{\frac{1}{2}} dz e^{-z} \right]^N \tag{57}$$

since $\int_0^\infty z^{\frac{1}{2}} dz e^{-z} = \frac{\sqrt{\pi}}{2}$

$$Z = \frac{V^N}{N! h^{3N}} \left[\left[\frac{2\pi m}{\beta} \right]^{\frac{3}{2}} \right]^N \tag{58}$$

$$Z = \frac{1}{N!} \left[\frac{V}{h^3} \left[2\pi m kT \right]^{\frac{3}{2}} \right]^N \quad as \frac{1}{\beta} = kT \tag{59}$$

$$\boxed{Z = \frac{1}{N!} \left[\frac{V}{h^3} \left[2\pi m kT \right]^{\frac{3}{2}} \right]^N} \tag{60}$$

Helmholtz free Energy:

Formula for Hamiltonian free energy is :

$$A(N, V, T) = -KT \ln Z \qquad (61)$$

$$A(N, V, T) = -NKT \left[\ln \left[\frac{V}{\lambda^3} \right] + \ln N - 1 \right] \qquad (62)$$

$$\text{AS } \ln(N!) = N \ln N - N$$

and Here $\lambda = \dfrac{h}{\sqrt{2m\pi kT}}$ which is "Thermal de-Broglie wavelength"

$$A(N, V, T) = NKT \left[\ln \left[\frac{N\lambda^3}{v} \right] - 1 \right] \qquad (63)$$

$$\boxed{A = NKT \left[\ln \left[\frac{N\lambda^3}{v} \right] - 1 \right]} \qquad (64)$$

Entropy:

Formula for Entropy :

$$S = - \left[\frac{\partial A}{\partial T} \right] \qquad (65)$$

$$S = -Nk \left[\ln[\frac{N\lambda^3}{V} - 1 \right] + NKT \left[\frac{3}{2T} \right] \qquad (66)$$

$$S = NK \left[\ln \left[\frac{V}{N\lambda^3} + \frac{5}{2} \right] \right] \qquad (67)$$

$$\boxed{S = NK \left[\ln \left[\frac{V}{N\lambda^3} + \frac{5}{2} \right] \right]} \tag{68}$$

Pressure :

Formula for pressure :

$$P = - \left[\frac{\partial A}{\partial V} \right]_{N,T} \tag{69}$$

$$P = NKT \frac{1}{V} \tag{70}$$

$$P = \frac{NKT}{V} \tag{71}$$

$$\boxed{PV = NKT} \tag{72}$$

Internal energy :

Formula for Internal energy:

$$U = A + TS \tag{73}$$

$$U = NKT \left[\ln \left[\frac{N\lambda^3}{v} \right] - 1 \right] + NKT \left[\ln \left[\frac{V}{N\lambda^3} + \frac{5}{2} \right] \right] \tag{74}$$

$$U = \frac{3NKT}{2} \tag{75}$$

$$\boxed{\mho = \frac{3}{2}NKT} \tag{76}$$

8 CE Partition function for Classical Harmonic Oscillator (CHO): Group H : Page 19-20 of Lecture note-1

Now, in the next two sections we are going to replace our system with simple harmonic oscillator (SHO), first classical and then quantum.

So, consider N non-interacting classical SHOs in equilibrium at temperature T. Each one has two degrees of freedom (x, p), and hamiltonian

$$H_1 = H_1(x,p) = \frac{1}{2}kx^2 + \frac{p^2}{2m} = \frac{1}{2}m\omega^2 x^2 + \frac{p^2}{2m} \tag{77}$$

here m is the mass and is the spring constant; in the second expression, $\omega \equiv \sqrt{k/m}$ is the natural frequency. Assume their locations are fixed so they are distinguishable, although identical.

Thus, we know that Then $Z = Z_1^N$ where Z_1 is the partition function of one of them and is given by the following equation:

$$\text{Partition function,} \quad \boxed{Z_1 = \int e^{-\beta H}\frac{dxdP}{h}} \tag{78}$$

Solving the above integral equation:

$$Z_1 = \int e^{-\beta H}\frac{dxdP}{h}$$

$$\implies Z_1 = \frac{1}{h}\left[\int_{-\infty}^{\infty} e^{-\beta m\omega^2 x^2/2}dx\right]\left[\int_{-\infty}^{\infty} e^{-\beta p^2/2m}dp\right]$$

$$\implies Z_1 = \frac{1}{h}\left[2\int_0^{\infty} e^{-Z}\left(2\beta m\omega^2\right)^{\frac{-1}{2}} z^{\frac{-1}{2}}dz\right]\left[2\int_0^{\infty} e^{-Z}\left(\frac{m}{2\beta}\right)^{\frac{1}{2}} z^{\frac{-1}{2}}dz\right]$$

This is two Gaussian integrals:

$$Z_1 = \frac{1}{h}\left[2\left(\frac{1}{2\beta m\omega^2}\right)^{\frac{1}{2}}\sqrt{\pi}\right]\left[2\left(\frac{m}{2\beta}\right)^{\frac{1}{2}}\sqrt{\pi}\right]$$

$$Z_1 = \frac{1}{h}\left[\left(\frac{2\pi KT}{m\omega^2}\right)^{\frac{1}{2}}\right]\left[\left(2\pi KTm\right)^{\frac{1}{2}}\right]$$

Thus, we get:

$$\boxed{Z_1 = \frac{2\pi KT}{h\omega} = \left(\frac{K_B T}{\hbar\omega}\right)}$$

Note that in the last step, we re-wrote the answer in terms of the natural frequency of the oscillator.(Note that this is a ratio of energies.)

Now consider many oscillators (like positions of atoms in a crystal), and let's extract the thermodynamics:

$$Z = Z_1^N = \left(\frac{K_B T}{\hbar \omega}\right)^N$$

also,

$$\therefore A = -KT ln Z_N \tag{79}$$

$$\implies \boxed{A = NKT ln\left(\frac{\hbar \omega}{KT}\right)} \tag{80}$$

Also P, S, V and U can be calculated from the above equation as follows:

$$P = -\frac{\partial A}{\partial V} = 0, \text{ Since } A(V) = \text{constant} \tag{81}$$

Above equation holds true since, $A_{(V)} = \text{constant}$.

$$S = -\frac{\partial A}{\partial V}_N \tag{82}$$

$$V = -NK[\ln(\frac{\hbar \omega}{KT})] + NKT[\frac{1}{T}] = NK[\ln(\frac{KT}{\hbar \omega})] + 1] \tag{83}$$

$$U = A + TS = NKT \tag{84}$$

Now if the system is composed of Ideal Gas, then the following calculations hold:

$$C_P = [\frac{\partial}{\partial T}(U + PV)]_P \Rightarrow C_P = [\frac{\partial}{\partial T}(\frac{3}{2}NKT + NKT)] \Rightarrow C_P = \frac{5}{2}NK$$

Similarly,

$$C_V = [\frac{\partial U}{\partial T}]_V \Rightarrow C_V = [\frac{\partial}{\partial T}(\frac{3}{2}NKT)] \Rightarrow C_V = \frac{3}{2}NK$$

This implies:

$$C_P - C_V = NK \tag{85}$$

But here,

$$\boxed{C_P = C_V = \frac{\partial U}{\partial T} = NK} \tag{86}$$

since, $A_{(V)} = \text{constant}$.

9 CE Partition function for quantum Harmonic Oscillator (QHO): Group I : Page 21-22 of Lecture note-1

Quantum harmonic oscillator:

$$\epsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega \tag{87}$$

Partition function:

$$z_1 = \sum_{n=0}^{\infty} e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega} = \frac{e^{k-\beta k\omega/2}}{1-e^{-\beta\hbar\omega}} = \left[\frac{1}{2\sinh\left(\frac{\Delta k\omega}{2}\right)}\right] \tag{88}$$

Total partition function:

$$z_n = (z_1)^N = \left[\frac{1}{2\sinh\left(\frac{\beta\hbar\omega}{2}\right)}\right]^N e^{-\left(\frac{N}{2}\beta\hbar\omega\right)}\left\{1-e^{-\beta\hbar\omega}\right\}^N \tag{89}$$

Helmholtz free energy:

$$A = -KT\ln 2 = NKT\left[\beta\frac{\hbar\omega}{2} + \ln\left\{1-e^{-\beta\hbar\omega}\right\}\right] \tag{90}$$

Therefore, using above formula we get,

$$\dot{P} = -\left(\frac{\partial A}{\partial V}\right)_{N,T} = 0 \tag{91}$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{\nu,N} = -NK\left[\ln\left\{1-e^{-\beta\hbar\omega}\right\}\right] + \frac{NKTe^{-\beta\hbar\omega}(t\hbar\omega/kT^2)}{1-e^{-\beta\hbar\omega}}$$

$$S = NK\left[\frac{\left(\frac{\hbar\omega}{KT}\right)}{e^{\beta\hbar\omega}-1} - \ln\left\{1-e^{-\beta\hbar\omega}\right\}\right] \tag{92}$$

$$\boxed{V = TS + A = N\left[\frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right]} \tag{93}$$

$$\left(\frac{N}{V}\right) \hbar\omega \left[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right]$$
$$= \frac{U}{V}$$

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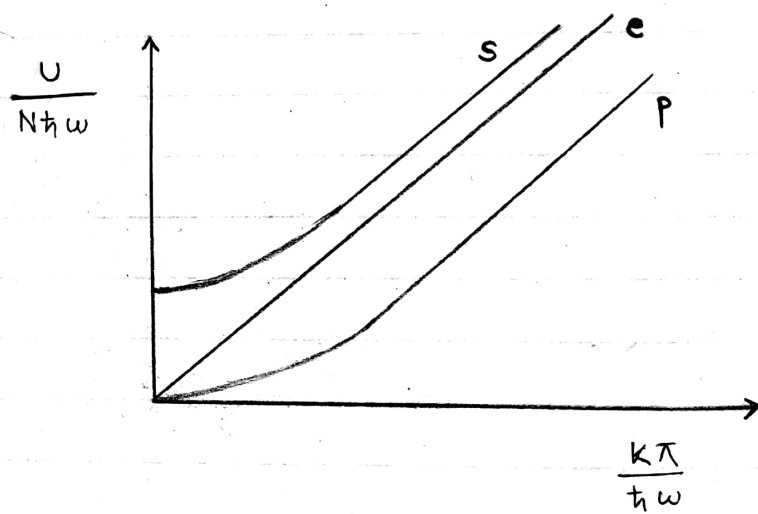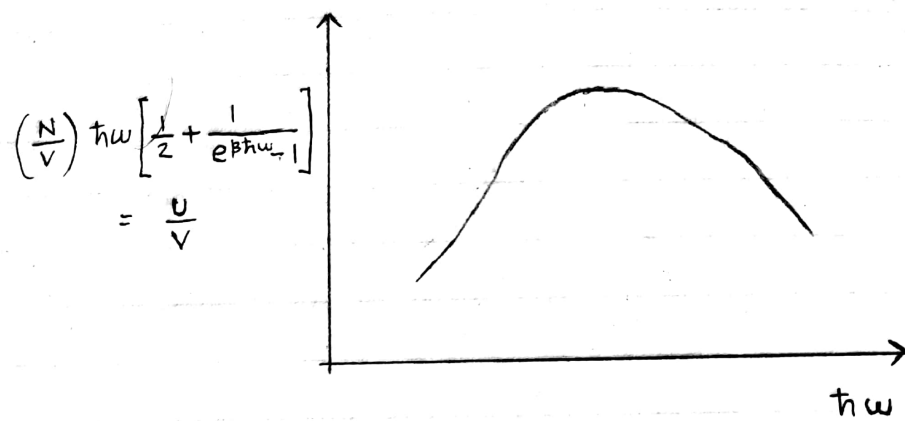
10 Group J 1st Assignment: page 1 and 3 of Note2

Partition Function : In physics, a partition function describes the statistical properties of a system in thermodynamic equilibrium. Partition functions are functions of the thermodynamic state variables, such as the temperature and volume. Most of the aggregate thermodynamic variables of the system, such as the total energy, free energy, entropy, and pressure, can be expressed in terms of the partition function or its derivatives. The partition function is dimensionless. Each partition function is constructed to represent a particular statistical ensemble (which, in turn, corresponds to a particular free energy). The most common statistical ensembles have named partition functions.

For Canonical Ensemble :
The canonical partition function applies to a canonical ensemble, in which the system is allowed to exchange heat with the environment at fixed temperature, volume, and number of particles.

$$Z_N^{CE} \;=\; \sum_{i=0} e^{-(\beta E_i)} \tag{94}$$

$$=\; \sum_{\mu} \frac{d^{3N}x d^{3N}P}{N! h^{3N}} e^{(-\beta E_\mu)} \qquad (E_\mu = N\epsilon) \tag{95}$$

$$=\; \frac{V^N}{N! h^{3N}} [\int d^3 P e^{-\beta\epsilon}]^N \tag{96}$$

$$=\; \frac{Z_N^{CE}}{N!} \tag{97}$$

For Grand Canonical Ensemble :
The grand canonical partition function applies to a grand canonical ensemble, in which the system can exchange both heat and particles with the environment, at fixed temperature, volume, and chemical potential.

$$Z^{GCE} \;=\; \sum_{i=0} e^{-\beta(E-\mu)} \tag{98}$$

$$=\; \sum_{\nu,\alpha} (\frac{d^{3N}x d^{3N}P}{N_\alpha! h^{3N}})_{E_\nu, N_\alpha} e^{-\beta(E_\nu - \mu_\alpha)} \tag{99}$$

$$=\; \sum_{\alpha} \frac{V^N}{N! h^{3N}} [\int d^3 P e^{-\beta(E-\mu)}]^N \qquad (\because \mu_\alpha = N\mu) \tag{100}$$

$$=\; \sum_{\alpha} \frac{(e^{\beta\mu} Z_{CE})^{N_\alpha}}{N_\alpha!} \tag{101}$$

$$\text{where} \quad Z \;=\; \frac{V}{h^3} \int d^3 P e^{-\beta\epsilon} = \frac{V}{\lambda^3} \quad \text{for } \epsilon = \frac{p^2}{2m} \tag{102}$$

is one particle partition function of CE system with

$$\lambda = \frac{h}{\sqrt{2\pi mKT}} \quad \text{(thermal de-Broglie wavelength)} \tag{103}$$

So if we take all N_α from 0 to α

$$Z^{GCE}(\mu, T, V) = \sum_{N_\alpha = 0}^{\infty} \frac{(e^{\beta\mu}Z_{CE})^{N_\alpha}}{N_\alpha!} \tag{104}$$

$$= exp\{e^{\beta\mu}Z_{CE}\} \tag{105}$$

$$\Rightarrow \quad -PV = \Phi = -KTlnZ^{GCE} = -KT\{e^{\beta\mu}Z_{CE}\} \tag{106}$$

$$= -KT \int \frac{Vd^3P}{h^3} e^{-\beta(\epsilon - \mu)} \tag{107}$$

$$\text{where} \quad N = \int \frac{Vd^3P}{h^3} e^{-\beta(\epsilon - \mu)} \tag{108}$$

GCE (Classical Ideal Gas) :

1. **For one-particle:** Partition function

$$Z_1 = \sum e^{-\beta(\epsilon - \mu)} \tag{109}$$

$$= \int \frac{d^3x d^3P}{h^3} e^{-\beta(\epsilon - \mu)} \tag{110}$$

$$\tag{111}$$

Remember, $\boxed{\sum = \int \frac{d^3x d^3P}{h^3}}$

2. **For many or N particle:** Partition function

$$Z_N = Z_1 \times Z_2 \times Z_3... \tag{112}$$

$$= \prod_i Z_i \tag{113}$$

$$= \prod_i e^{-\beta(\epsilon_i - \mu_i)} \tag{114}$$

$$\Phi = -PV = -KTlnZ_N \tag{115}$$

$$= -KTln\{\prod_i Z_i\} \tag{116}$$

$$= -KT\sum_i lnZ_i \tag{117}$$

$$= -KT \int \frac{d^3x d^3P}{h^3} ln(Z) \tag{118}$$

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where,

$$Z = exp\{e^{-\beta(\epsilon-\mu)}\} \tag{119}$$

$$= \sum_{N_\alpha}^{\alpha} \frac{\{e^{-\beta(\epsilon-\mu)}\}^{N_\alpha}}{N_\alpha!} \tag{120}$$

This imples,

$$\boxed{P = KT \int \frac{d^3P}{h^3} e^{-\beta(\epsilon-\mu)} = \frac{KTN}{V}} \tag{121}$$

$$\Phi = -PV = -KT \int \frac{Vd^3P}{h^3} e^{-\beta(\epsilon-\mu)} \tag{122}$$

$$\Rightarrow P = \frac{KT}{V} N, where \quad N = \frac{V}{h^3} \int d^3P e^{-\beta(\epsilon-\mu)} \tag{123}$$

$$= \frac{V}{h^3} \int d^3P f_o(\epsilon) \quad \text{(MB distribution function)} \tag{124}$$

Now,

$$N = -(\frac{d\Phi}{d\mu})_{V,T} \tag{125}$$

$$= -(-KT)\beta \int \frac{Vd^3P}{h^3} e^{-\beta(\epsilon-\mu)} \tag{126}$$

$$\boxed{N = \frac{V}{h^3} \int d^3P f_o(\epsilon)} = V\frac{1}{\lambda^3(T)} \quad \text{for} \quad \epsilon = \frac{p^2}{2m} \tag{127}$$

(Thermal distribution of function of particle with energy ϵ)

Since,

$$S = -\left(\frac{d\Phi}{dT}\right)_{\mu,V} \tag{128}$$

$$= K \underbrace{\int \frac{Vd^3P}{h^3} e^{-\beta(\epsilon-\mu)}}_{N} + KT\frac{(\mu-\epsilon)}{-KT^2} \underbrace{\int \frac{Vd^3P}{h^3} e^{-\beta(\epsilon-\mu)}}_{N} \tag{129}$$

$$\tag{130}$$

when the above equation is multiplied with T, we get

$$TS = KTN - \mu N + \underbrace{\int \frac{Vd^3P}{h^3} \epsilon f_o(\epsilon)}_{U} \tag{131}$$

$$\implies TS = PV - \mu N + U \tag{132}$$

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Internal Energy:

$$\mho \quad = \quad \frac{V d^3 P}{h^3} [\epsilon] f_o \tag{133}$$

$$= \quad \frac{3}{2} NKT \tag{134}$$

$$= \quad \frac{3}{2} KT \left\{ \frac{V}{\lambda^3(T)} \right\} \quad for \quad \epsilon = \frac{p^2}{2m} \tag{135}$$

$$\tag{136}$$

After knowing N, U, we get:

$$S \quad = \quad \frac{U + PV - \mu N}{T} \tag{137}$$

$$= \quad \frac{5}{2} NK - \frac{\mu N}{T} \tag{138}$$

11   Group A 2nd Assignment: page 4 of Note2

According to classical physics, the partition function for a single particle is defined mathematically as :

$$Z = e^{-\beta(\epsilon - \mu)} \tag{139}$$

In quantum mechanics, an energy level is degenerate if it corresponds to two or more different measurable states of a quantum system. Conversely, two or more different states of a quantum mechanical system are said to be degenerate if they give the same value of energy upon measurement.

If quantum degeneracy is n for energy state ϵ, then its partition function is:

$$Z = \sum_n e^{-\beta n(\epsilon - \mu)} \tag{140}$$

Pauli exclusion principle states that no two electrons in an atom can be at the same time in the same state or configuration.The exclusion principle subsequently has been generalized to include a whole class of particles.

Subatomic particles fall into two classes, based on their statistical behaviour. Those particles which follow the Pauli exclusion principle are called fermions while those that do not obey this principle are called bosons.

According to Pauli Exclusion Principle, $n = 1$ for fermion i.e only one state is allowed in a particular energy level. But, for Boson, the quantum degeneracy of energy levels,n can take any value from $1, 2, 3, ...\infty$. The classical definition also misses the possibility of $n = 0$. But this is a valid quantum degeneracy value for both boson and fermion. Hence, the partition function for each energy

level for fermions and bosons is given by :

(i) Fermion -

$$Z = \sum_{n=0}^{1} e^{-\beta n(\epsilon - \mu)} = [1 + e^{-\beta(\epsilon - \mu)}] \tag{141}$$

(ii) Boson -

$$Z = \sum_{n=0}^{\infty} e^{-\beta n(\epsilon - \mu)} = \frac{1}{1 - e^{-\beta(\epsilon - \mu)}} \tag{142}$$

(Using the formula for sum of infinite G.P.)

The total partition function, Z_t for all particles is given by the expression below :

$$Z_t = \prod_i Z_i = Z_1 \times Z_2 \times Z_3 \times ... \implies \ln Z_t = \ln \{\prod_i Z_i\} = \sum_i \ln Z_i \tag{143}$$

The above calculation of $\ln Z_t$ will be useful for the calculation of Grand Canonical Potential i.e Φ since we know that $\Phi = -KT \ln Z_t$

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Bosons are particles which have integer spin and which therefore are not constrained by the Pauli exclusion principle like the half-integer spin fermions.

Boson $\rightarrow$ spin is integer $\hbar \implies$ s = $(0,1,2,3,...)\hbar$

Fermions are particles which have half-integer spin and therefore are constrained by the Pauli exclusion principle.

Fermion $\rightarrow$ spin is half integer of $\hbar \implies$ s= $(1,3,5,7,...)\frac{\hbar}{2}$

So now we can calculate -PV:

$$-PV = \Phi = -KT \ln Z_t = -KT \sum \ln Z \tag{144}$$

For Fermion :

$$\phi_{fermion} = -KT \sum \ln [1 + e^{-\beta(\epsilon - \mu)}] \tag{145}$$

For Boson :

$$\phi_{boson} = -KT \sum \ln [1 - e^{-\beta(\epsilon - \mu)}]^{-1} \tag{146}$$

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In general, we can write:

$$-PV = \Phi = \frac{-KT}{\eta} \sum \ln\left[1 + \eta e^{-\beta(\epsilon-\mu)}\right] \tag{147}$$

$$= \frac{-KT}{\eta} V \int \frac{d^3p}{h^3} \ln\left[1 + \eta e^{-\beta(\epsilon-\mu)}\right] \tag{148}$$

where $\eta = +1$ for Fermion and -1 for Boson

Now we know that:

$$N = -\left(\frac{\partial\Phi}{\partial\mu}\right)_{T,V} = \frac{1}{\eta}\sum \frac{\eta e^{-\beta(\epsilon-\mu)}}{1 + \eta e^{-\beta(\epsilon-\mu)}} = \sum \frac{1}{e^{\beta(\epsilon-\mu)} + \eta} = \int \frac{V d^3p}{h^3}\frac{1}{e^{\beta(\epsilon-\mu)} + \eta} \tag{149}$$

The **Fermi-Dirac distribution** applies to fermions, particles with half-integer spin which must obey the Pauli exclusion principle. It is a type of quantum statistics that applies to the physics of a system consisting of many identical particles.

Number of molecules (using Fermi-Dirac distribution) where $\eta = +1$:

$$N_{FD} = V \int \frac{d^3p}{h^3} f_o = V \int \frac{d^3p}{h^3}\frac{1}{e^{\beta(\epsilon-\mu)} + 1} \tag{150}$$

The **Bose-Einstein distribution** describes the statistical behavior of integer spin particles (bosons). At low temperatures, bosons can behave very differently than fermions because an unlimited number of them can collect into the same energy state, a phenomenon called "condensation".

Number of molecules (using Bose-Einstein distribution) where $\eta = -1$:

$$N_{BE} = V \int \frac{d^3p}{h^3} f_o = V \int \frac{d^3p}{h^3}\frac{1}{e^{\beta(\epsilon-\mu)} - 1} \tag{151}$$

The **Maxwell–Boltzmann distribution** describes the distribution of speeds among the particles in a sample of gas at a given temperature. The distribution is often represented graphically, with particle speed on the x-axis and relative number of particles on the y-axis. The distribution function implies that the probability dp that any individual molecule has an energy between ϵ and ϵ + dϵ. The total energy (ϵ) usually is composed of several individual parts, each corresponding to a different degree of freedom of the system.

Number of molecules (using Maxwell-Boltzmann distribution) where $\eta = 0$:

$$N_{MB} = V \int \frac{d^3p}{h^3} f_o = V \int \frac{d^3p}{h^3} e^{-\beta(\epsilon-\mu)} \tag{152}$$

We discussed indistinguishability before in the context of the second law of thermodynamics and the Gibbs paradox. In that, we found that we could decide if we want to treat particles as distinguishable or indistinguishable. If we want to treat the particles as distinguishable, then we must include the entropy increase from measuring the identity of all the particles to avoid a conflict with the second law of thermodynamics. We do this by adding a factor of $\frac{1}{N!}$ to the number of states Ω, i.e. instead of $\Omega \sim V^N$ we take $\Omega \sim \frac{1}{N!}V^N$; then there is automatically no conflict with the second law of thermodynamics. This kind of classical indistinguishable-particle statistics, with the N! included, is known as Maxwell-Boltzmann statistics. Quantum identical particles is a stronger requirement, since it means the multiparticle wavefunction must be totally symmetric or totally antisymmetric. In a classical system, the states are continuous, so there is exactly zero chance of two particles being in the same state. Thus, the difference among Fermi-Dirac, Bose-Einstein and Maxwell-Boltzmann statistics arises entirely from situations were a single state has a nonzero change of being multiply occupied.

Classical distribution $\rightarrow$ Quantum distribution

$$f_0 = e^{-\beta(\epsilon-\mu)} \quad [for \ MB \ distribution] \tag{153}$$

For Fermi-Dirac distribution,

$$f_0 = \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \tag{154}$$

For Bose-Einstein distribution,

$$f_0 = \frac{1}{e^{\beta(\epsilon-\mu)} - 1} \tag{155}$$

Now, we formulate a general equation for the number of molecules N for different types of distribution as follows:

$$\sum f_0 = N = \frac{V}{h^3} \int d^3p f_0(\epsilon) \tag{156}$$

Now we substitute the value of f_0 where the value of η can be varied to get the value of N for different quantum distributions.
the equation (107) becomes,

$$N = \frac{V}{h^3} \int d^3p \left(\frac{1}{e^{\beta(\epsilon-\mu)} + \eta}\right) \tag{157}$$

for MB distribution, the value of η is 0
for FD distribution, the value of η is 1
for BE distribution, the value of η is -1

Now we can calculate the internal energy

$$\sum \epsilon f_0 = U = \frac{V}{h^3} \int d^3 p[\epsilon] f_0(\epsilon) = \frac{V}{h^3} \int d^3 p[\epsilon] \frac{1}{e^{\beta(\epsilon-\mu)} + \eta} \qquad (158)$$

Calculating the value of PV:

$$PV = -\Phi = \frac{KT}{\eta} \sum \ln\{1 + \eta e^{\beta(\mu-\epsilon)}\} \qquad (159)$$

$$PV = \frac{KT}{\eta} \int \frac{V d^p}{h^3} \ln\{1 + \eta e^{\beta(\mu-\epsilon)}\} = \frac{V}{h^3} \int d^3 p[?] \frac{1}{e^{\beta(\epsilon-\mu)+\eta}} \qquad (160)$$

Now we can cross check through the value of PV deduced above if it is same as that of -KTln z and calculate pressure for fermi-dirac, bose-einstein and maxwell-boltzmann accordingly:

$$\ln z = \frac{-1}{\eta} \sum_i \ln[1 + \eta e^{\beta(\mu-\epsilon)}] = \lim_{\eta \to 0} \frac{-\sum_i \frac{\partial}{\partial \eta} \ln[1 + \eta e^{\beta(\mu-\epsilon)}]}{\frac{\partial \eta}{\partial \eta}} \qquad (161)$$

It will give us

$$\ln z = -\sum_i \lim_{\eta \to 0} \frac{e^{\beta(\mu-\epsilon)}}{1 + \eta e^{\beta(\mu-\epsilon)}} = -\sum_i e^{\beta(\mu-\epsilon)} \qquad (162)$$

Hence:

$$PV = \Phi = -KT \ln z = KT \sum_i e^{-\beta(\epsilon-\mu)} = KT \int \frac{d^3 x d^3 p}{h^3} e^{-\beta(\epsilon-\mu)} \qquad (163)$$

where N = $\int \frac{d^3 x d^3 P}{h^3} e^{-\beta(\epsilon-\mu)}$

Now we know that:

$$N = (\frac{\partial \Phi}{\partial \mu})_{T,V} = KT * \beta \sum e^{-\beta(\epsilon-\mu)} = \int \frac{d^3 x d^3 p}{h^3} e^{-\beta(\epsilon-\mu)} \qquad (164)$$

Now, similarly we apply the three distributions individually and find the Pressure for respective distributions.

Pressure for Fermi-Dirac(P_{FD}):

$$P_{FD} = KTV \int \frac{d^3p}{h^3} \left(-\ln\{1 + e^{-\beta(\epsilon-\mu)}\}\right) \tag{165}$$

Pressure for Bose-Einstein(P_{BE}):

$$P_{BE} = KTV \int \frac{d^3p}{h^3} \ln\{1 - e^{-\beta(\epsilon-\mu)}\} \tag{166}$$

Pressure for Maxwell-Boltzmann(P_{MB}):

$$P_{MB} = KTV \int \frac{d^3p}{h^3} e^{-\beta(\epsilon-\mu)} \tag{167}$$

13 Group C 2nd Assignment: page 1-2 of Note3: Photon Energy Momentum

In the previous sections, we have explored the realms of the Grand Canonical Ensemble, and have ventured into the quantum mechanical aspects of statistical mechanics. We are also familiar with some of the statistical distributions used to calculate the macroscopic variables from microscopic variables.

Before proceeding to the next topic, it would be great if we go through the statistical distributions part once again as a primer to the next topic. In the Grand Canonical Ensemble, Maxwell-Boltzmann distribution is used for classical systems (systems under the domain of classical mechanics), while Fermi-Dirac and Bose-Einstein distributions are used for quantum systems. In addition, Fermi-Dirac distribution is applicable on Fermions (electrons, protons, muons etc.), while Bose-Einstein distribution is applicable on Bosons (photons, gluons etc.)

The statistical distributions can be written as

$$f = \frac{1}{e^{\beta(\epsilon-\mu)} + \eta} \tag{168}$$

If $\eta = 1$, eqn.(168) becomes Fermi-Dirac distribution
If $\eta = 0$, eqn.(168) becomes Maxwell-Boltzmann distribution
If $\eta = -1$, eqn.(168) becomes Bose-Einstein distribution

Now that we have gone through the statistical distributions used in the Grand Canonical Ensemble, let us proceed to the application of the theories that we have studied above. One of the most prominent applications of the Bose-Einstein statistical distribution is the study of photon gas and calculation of macroscopic variables for the same. As it is already known, light constitutes of energy packets known as photons, which are basically Bosons with spin 1. Hence we can consider light to be a gas of photons, with each photon having energy-momentum relation as

$$\epsilon = pc$$

We can use the above energy-momentum relation to calculate the macroscopic parameters such as number of particles (N), total internal energy (U) and pressure (P). Let us start with the calculation of the number of particles in the system.

$$N = 2 \int \frac{d^3x d^3p}{h^3} \frac{1}{e^{\beta\epsilon} - 1} \tag{169}$$

In eqn.(169), the general expression for number of particles is multiplied by 2 to account for two spin states $(+1$ and $-1)$ of the photons. We already know that

$$\int d^3x = V$$

Plugging this value in eqn.(169), we get

$$N = \frac{2V}{h^3} \int 4\pi p^3 dp \frac{1}{e^{\beta px} - 1} \tag{170}$$

$$\text{Let } \beta pc = x$$

$$\implies dp = \frac{kT}{c} dx$$

On substituting these values in eqn.(170), we get

$$N = \frac{8\pi V (KT)^3}{h^3 c^3} \int_0^\infty \frac{x^2}{e^x - 1} dx \tag{171}$$

In the above equation, the integral term is a special integral also known as <mark>Riemann Zeta function</mark>, and it is denoted by <mark>$\zeta(n)$.</mark> The Riemann Zeta-function is defined as

$$\zeta(n) = \frac{1}{\Gamma(n)} \int_0^\infty \frac{x^{n-1}}{e^x - 1} dx$$

On comparing the above equation with the integral term in eqn.(171), we can clearly see that n=3.

On dividing both sides of eqn.(171) by V and substituting the value of Riemann Zeta function in place of the integral term, we get

$$\boxed{\frac{N}{V} = 8\pi \left(\frac{kT}{hc}\right)^3 \zeta(3) \Gamma(3)}$$

$$= 16\pi \left(\frac{kT}{hc}\right)^3 \zeta(3) \propto T^3$$

Hence from the above equation, we can see that the number density of a photon gas system is directly proportional to the third <mark>power of Temperature (T).</mark>

Let us now proceed to the calculation of internal energy of the photon gas. The microscopic variable in this case is the energy of a single photon. The total internal energy of the photon gas system is defined as

$$U = 2 \int \frac{d^3x d^3p}{h^3} \frac{\epsilon}{e^{\beta\epsilon} - 1}$$

$$\implies U = \frac{2V}{h^3} \int 4\pi p^3 dp \frac{\epsilon}{e^{\beta\epsilon} - 1}$$

Dividing both sides by V, we get

$$\frac{U}{V} = \frac{8\pi c}{h^3} \int \frac{p^3}{e^{\beta pc} - 1} dp = \int u_V d\nu \tag{172}$$

where

$$u_\nu d\nu = \frac{8\pi c}{h^3}\frac{p^3}{e^{\beta pc}-1}dp$$

Substituting $p = \frac{h\nu}{c}$ and $dp = \frac{hd\nu}{c}$ in the above equation, we get

$$u_\nu d\nu = \left(\frac{8\pi h}{c^3}\right)\frac{d\nu}{e^{\beta h\nu}-1} \tag{173}$$

In eqn.(173), the term u_ν represents the spectral distribution of energy in the black body radiation. It is now very clear that we can easily calculate the total energy density by integrating the spectral distribution from 0 to infinity.

Let us now solve eqn.(172)

$$\begin{aligned}
\frac{U}{V} &= \int u_\nu d\nu \\
&= \frac{8\pi c}{h^3}\int \frac{p^3 dp}{e^{\beta pc}-1}
\end{aligned} \tag{174}$$

$$\text{Let } \beta pc = x$$

$$\implies dp = \frac{kT}{c}dx$$

On substituting the above values in eqn.(174), we get

$$\begin{aligned}
\frac{U}{V} &= \frac{8\pi c}{h^3}\left(\frac{kT}{c}\right)^4 \int_0^\alpha \frac{x^{4-1}}{e^x-1}dx \\
&= \frac{8\pi}{h^3 c^3}(kT)^4 \zeta(4) \propto T^4 \\
&= \frac{8\pi}{h^3 c^3}(kT)^4 \zeta(4)
\end{aligned} \tag{175}$$

Here

$$\boxed{\zeta(4) = \frac{\pi^4}{90}}$$

Hence

$$\begin{aligned}
\frac{U}{V} &= \frac{8(\pi)^5}{15h^3 c^3}(kT)^4 \\
&= \frac{\pi^2}{15(\hbar c)^3}(kT)^4 \propto T^4
\end{aligned} \tag{176}$$

Hence we are able to get a relationship between energy density and temperature in the above equation. We can clearly see from eqn.(176) that the energy density is directly proportional to the fourth power of temperature. This relation goes a long way in deriving the Stefan-Boltzmann law of radiation.

Now that we have already ventured into the total internal energy of the photon gas, let us try to calculate the value of Stefan constant. For a blackbody, the intensity is given by

$$I = \frac{c}{4}\frac{U}{V} \tag{177}$$

By Stefan-Boltzmann's law, we already know that the intensity of a blackbody can be written as

$$I(T) = \sigma T^4 \tag{178}$$

On comparing eqns. (177) and (178), we get

$$\boxed{\sigma = \frac{\pi^2 k^4}{60h^3 c^2}} \tag{179}$$

14 Group D 2nd Assignment: page 3 of Note3

Now, let us try to calculate the pressure of the system.

$$\text{Pressure} \quad \boxed{P = -\frac{\Phi}{V}}$$

$$= -\frac{1}{V}\left[\frac{-KT}{-1}\int \frac{2d^3p\,d^3x}{h^3}\ln\left\{1 - e^{-\beta\epsilon}\right\}\right]$$

$$= -\frac{2KT}{h^3}\int d^3p \ln\left\{1 - e^{-\beta\epsilon}\right\}$$

Here, $\phi = -PV$, is the $\boxed{\text{grand chemical potential}}$ ϵ, is the single particle energy. Now, we substitute $\epsilon = pc$(relativistic value) where p is momentum and c is the speed of light. We also know that, $\beta = \frac{1}{KT}$.

$$\frac{P}{KT} = -\frac{8\pi}{h^3}\int_0^\infty P^2 dP \ln\left\{1 - e^{-\beta pc}\right\}, \qquad \epsilon = \text{pc}$$

$$= -\frac{8\pi}{h^3}\left[\left|\frac{p^3}{3}\ln\left\{1 - e^{-\beta pc}\right\}\right|_0^\infty - \int_0^\infty \frac{p^3}{3}\frac{\beta c e^{-\beta pc}}{1 - e^{-\beta pc}}dp\right]$$

$$\text{Here,}\left|\frac{p^3}{3}\ln\left\{1 - e^{-\beta pc}\right\}\right|_0^\infty = 0$$

$$= \frac{8\pi}{h^3}\int_0^\infty \frac{\beta p^3}{3}\frac{c}{e^{\beta pc} - 1}dp, \qquad \beta\text{pc} = \text{x and } dp = \frac{KT}{c}dx$$

$$= \frac{8\pi}{h^3}\left(\frac{\beta c}{3}\right)\left(\frac{KT}{c}\right)^4 \int_0^\infty \frac{x^{4-1}}{e^x - 1}dx$$

Here, we brought βc outside of integral as they are constants.
Then, we multiplied and divided by $\beta^3 c^3$ to convert the integral into $\Gamma(4)\zeta(4)$.

$$P = \frac{8\pi}{3}\frac{1}{h^3c^3}(KT)^4\Gamma(4)\zeta(4) = \frac{1}{3}\frac{U}{V}, \qquad PV = \frac{1}{3}U$$

Now, lets substitue the value of $\Gamma(4)\zeta(4)$ in the above equation

$$= \frac{16\pi}{h^3c^3}K^4T^4\left(\frac{\pi^4}{90}\right)$$

$$= \left(\frac{8\pi^5 K^4}{45h^3c^3}\right)T^4$$

15 Calculation of average temperature inside Sun: Group E 2nd Assignment: page 1-2 of Note STAR

From photon gas calculation, either from Stefan-Boltzmann's law or Wein's displacement law, one can easily able to calculate surface temperature of Sun ($\sim 5 \times 10^3 \ ^0$K) or any stars. However, as we go towards the core of the Sun or star, the temperature will increase gradually. Here we will calculate average temperature of Sun or any (young) star. ....

16 Degenerate density, pressure, internal energy for non-relativistic (NR) case: Group G 2nd Assignment: page 3-4 of Note STAR

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17 Degenerate density, pressure, internal energy for ultra-relativistic (UR) and relativistic (R) cases: Group H 2nd Assignment: page 21-23 of Note Degenerategas.pdf

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18 White Dwarf: Group I 2nd Assignment: page 42-49 of Note Degenerategas.pdf

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19 Neutron Star: Group J 2nd Assignment: page 50-54 of Note Degenerategas.pdf

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