Microstates and Macrostates

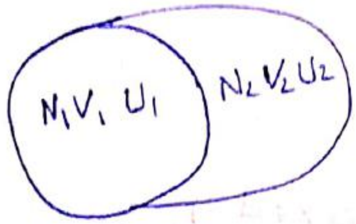
Macrostate will be characterize by macroscopic variable — (1) total internal energy U
(2) Volume V
(3) total no. of particle N.

will not bothered about properties of individual particles

Microstate, characterized state of each particle of system.

Macrostate have many different microstate

How many? → Let us say $\Omega(U, V, N)$



$$\Omega(U,V,N) = \Omega_1(U_1,V_1,N_1)\,\Omega_2(U_2,V_2,N_2)$$

$U = U_1 + U_2$

$dU_1 + dU_2 = 0$

$\Rightarrow dU_1 = -dU_2$

$$\Rightarrow \underset{0}{\underset{\parallel}{d\Omega}} = \Omega_2 \frac{\partial \Omega_1}{\partial U_1} dU_1 + \Omega_1 \frac{\partial \Omega_2}{\partial U_2} dU_2$$

$$\Rightarrow \Omega_2 \frac{\partial \Omega_1}{\partial U_1} = \Omega_1 \frac{\partial \Omega_2}{\partial U_2} \quad (\because dU_1 = -dU_2)$$

$$\Rightarrow \frac{\partial}{\partial U_1}(\ln \Omega_1) = \frac{\partial}{\partial U_2}(\ln \Omega_2) = \text{constant}$$

$$\Rightarrow \beta = \left(\frac{\partial \ln \Omega}{\partial U}\right)_{N,V} = \text{constant}$$

Now from thermodynamics

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

$$\frac{1}{K_B T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} \text{ with } \boxed{S = K_B \ln \Omega} \qquad \Rightarrow \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}$$

Boltzmann Entropy

Guess count Ω!

No of ways, each particle can stay in volume 'V'

is $\Omega(U, V, 1) \propto V$

for N particle, $\Omega(U, V, N) \propto V^N$

$$= V^N f(U, N)$$

Boltzman entropy

$$S(U, V, N) = K_B \ln \Omega$$

$$= N K_B \ln V + \underbrace{K \ln f(U, N)}_{F(U, N)} \quad \text{—— (a)}$$

Now from thermodynamics $TdS = PdV + dU - \mu dN$

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

$$(a) \Rightarrow \frac{\partial S}{\partial V} = \frac{N K_B}{V} + 0 = \frac{P}{T} \quad \text{(checked)}$$

If $V = L^3$, then momentum $p_r = \left(\frac{\pi\hbar}{L}\right) n_r$

$$r = 1, 2, \cdots 3N$$

Total energy $U = \sum_{r=1}^{3N} \frac{p_r^2}{2m} = \frac{1}{2m}\left(\frac{\pi\hbar}{L}\right)^2 \sum_{r=1}^{3N} n_r^2$

$$\Rightarrow \sum_{r=1}^{3N} n_r^2 = 2mU\left(\frac{L}{\pi\hbar}\right)^2 \qquad L^3 = V$$

$$= \frac{2m}{\pi^2\hbar^2} U V^{2/3}$$

$$\Omega(U,V,N) = \Omega(UV^{2/3}, N) \qquad (UV^{2/3})^{3/2} = U^{3/2} V$$

$$\Rightarrow \ln\Omega \sim S \Rightarrow S(U,V,N) = S(UV^{2/3}, N)$$

$$\Rightarrow UV^{2/3} = f(S,N)$$

$$\Rightarrow U = \frac{f(S,N)}{V^{2/3}}$$

Now $\overset{\text{Thermo}}{P} = -\left(\frac{\partial U}{\partial V}\right)_{S,N} = f(S,N)\frac{\partial}{\partial V}\left(\frac{1}{V^{2/3}}\right)$

$$= \frac{2}{3}\cdot\frac{f(S,N)}{V^{5/3}}$$

$$= \frac{2}{3}\frac{U}{V} \text{ (checked)} \qquad \frac{f}{V^{2/3}} = U$$

So $PV^{5/3} = \frac{2}{3} f(S,N) =$ constant for $S =$ const.

$V \to VU^{3/2} \xrightarrow{\text{Modify}} S(U,V,N) = NK\ln(VU^{3/2}) + f(N)$ — (b)

instead of $= NK\ln V + f(N,U)$

Defining $u = \frac{U}{N}$, $s = \frac{S}{N}$, $v = \frac{V}{N}$

we can write $s = s(u,v) = s(uv^{2/3})$

$$= s\left(\frac{UV^{2/3}}{N^{5/3}}\right)$$

$$\Rightarrow \frac{S}{N} = s\left(\frac{UV^{2/3}}{N^{5/3}}\right)$$

$$S = N\, s\left(\left\{\frac{UV^{2/3}}{N^{5/3}}\right\}^{3/2}\right) = NK\ln\left(VU^{3/2}\right) + \underset{?}{f(N)}$$

$$= NK\ln\left(\frac{U^{3/2}V}{N^{5/2}}\right) + B \Rightarrow f(N) = -NK\ln N^{5/2}$$

Euler thermodynamic relation

$$TS = U + PV - \mu N \quad \text{--- (1)}$$

Gibb's-Duhem relation.

$$dU = TdS + SdT - PdV - VdP + \mu dN + Nd\mu \quad \text{--- (2)}$$

derivative of Euler equation

2nd law of thermodynamics

$$TdS = dU + PdV - \mu dN \quad \text{--- (3)}$$

$$\Rightarrow SdT - VdP + Nd\mu = 0$$

$$(1) \Rightarrow \underbrace{dS =}\ \underbrace{Ud\left(\frac{1}{T}\right) + Vd\left(\frac{P}{T}\right) - Nd\left(\frac{\mu}{T}\right)}_{0}$$

when S, U, V, N are constant

$$\Rightarrow \underbrace{\frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN}_{dS}$$

$$\Rightarrow Nd\left(\frac{\mu}{T}\right) = Ud\left(\frac{3NK}{2U}\right) + Vd\left(\frac{NK}{V}\right)$$

$$d\left(\frac{\mu}{K_BT}\right) = -\frac{\cancel{U}}{N}\frac{3}{2}\frac{N}{U^2}dU + \frac{\cancel{U}}{N}\times\frac{3}{2}\frac{1}{\cancel{U}}dN - \frac{V}{\cancel{N}}\frac{\cancel{N}}{V^2}dV + \frac{\cancel{V}}{N}\frac{1}{\cancel{V}}\times dN$$

$$= -\frac{3}{2}\frac{dU}{U} + \frac{3}{2}\frac{dN}{N} + \frac{dN}{N} - \frac{dV}{V}$$

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$$d\left(\frac{\mu}{K_B T}\right) = \frac{5}{2}\frac{dN}{N} - \frac{3}{2}\frac{dU}{U} - \frac{dV}{V}$$

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

$$\Rightarrow \frac{\mu}{K_B T} = \ln\left[\frac{N^{5/2}}{U^{3/2} V C}\right]$$

Now $S = \frac{U}{T} + \frac{PV}{T} - \frac{\mu N}{T}$

$$= \left(\frac{3}{2} + 1\right)\frac{PV}{T} - \frac{\mu N}{T}$$

$$= \frac{5}{2} N K_B - N K_B \ln\left[\frac{N^{5/2}}{U^{3/2} V C}\right]$$

$$= \cancel{N K_B \left[\ln \frac{N^{5/2}}{U^{3/2} V}\right.}$$

$$\boxed{S = N K_B \left[\ln\left(\frac{U^{3/2} V C}{N^{5/2}}\right) + \frac{5}{2}\right]}$$

Micro-Canonical Ensemble

counting states

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} \qquad U - \Delta \le H \le U$$

phase space $\Gamma = \int d^{3N}q \int d^{3N}p$

$$= \left(V^N \frac{2\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)} \left[(2mU)^{\frac{1}{2}}\right]^{3N-1} = \frac{V^N \, 2(2m\pi U)^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)\sqrt{2mU}} \right)$$

Surface area 'd' dimension, $S_d = A_d r^{d-1}$

r is radius and A_d constant and $A_d = \dfrac{2\pi^{d/2}}{\Gamma\left(\frac{d}{2}\right)}$

Example $\rightarrow$ $d = 3 \Rightarrow A_3 = \dfrac{2\pi^{3/2}}{\Gamma\left(\frac{3}{2}\right)} = \dfrac{2\pi\sqrt{\pi}}{\frac{1}{2}\sqrt{\pi}} = 4\pi$

$$\Rightarrow S_3 = A_3 r^{3-1} = 4\pi r^2$$

$d = 2 \Rightarrow A_2 = \dfrac{2\pi^{2/2}}{\Gamma\left(\frac{2}{2}\right)} = 2\pi$, so $S_2 = A_2 r^{2-1} = 2\pi r$

$$I = \int_{-\infty}^{\infty} dx_1 \cdots \int_{-\infty}^{\infty} dx_n \exp\left(-\sum_{i=1}^{d} x_i^2\right) = \prod_{i=1}^{d} \int_{-\infty}^{\infty} dx_i \, e^{-x_i^2} = \left(\pi^{1/2}\right)^d = \pi^{d/2}$$

if $\sum_i x_i^2 = r^2$ then $I = \int_0^{\infty} dr \, A_d r^{d-1} e^{-r^2}$

$$\begin{array}{c|c|c} r^2 & 0 & \infty \\ \hline y & 0 & \infty \end{array} \qquad dy = 2r\,dr$$

$$= \frac{A_d}{2} \int y^{\frac{d-2}{2}} e^{-y} \, dy$$

$$= \frac{A_d}{2} \Gamma\left(\frac{d}{2}\right)$$

$$\Rightarrow \frac{A_d}{2} \Gamma\left(\frac{d}{2}\right) = \pi^{d/2} \Rightarrow \boxed{A_d = \frac{2\pi^{d/2}}{\Gamma\left(\frac{d}{2}\right)}}$$

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Volume in momentum space $= S_d \times$ thickness

Thickness $= \sqrt{2mU} - \sqrt{2m(U-\Delta)} \approx \Delta\sqrt{\frac{m}{2U}}$

$\sqrt{2mU} - \sqrt{2mU}\left[1 - \frac{\Delta}{U}\right]^{1/2} \approx \sqrt{2mU} \times \frac{1}{2}\frac{\Delta}{U} \approx \Delta\sqrt{\frac{m}{2U}}$

$$\Omega = \frac{\Gamma}{h^{3N}} = \frac{3N}{2} \times \frac{2}{\Gamma(\frac{3N}{2}+1)} \frac{V^N}{h^{3N}} \frac{(2\pi mU)^{3N/2}}{\sqrt{2mU}} \times \left(\frac{\Delta}{U}\sqrt{\frac{2m}{2U}}\right) = \frac{3N}{2}\frac{V^N}{h^{3N}}(2\pi m \times \frac{\Delta}{2U} \times \frac{2}{\Gamma(\frac{3N}{2}}$$

$$\Rightarrow S = K \ln \Omega = K\left[\ln\left\{\frac{V}{h^3}(2\pi mU)^{3/2}\right\}^N - \ln\Gamma\left(\frac{3N}{2}+1\right) + \underbrace{\ln\frac{3N\Delta}{2U}}_{\to 0}\right]$$

$$= NK\left[\ln\left\{\frac{V}{h^3}(2\pi mU)^{3/2}\right\} - \frac{3}{2}\ln\frac{3N}{2} + \frac{3}{2}\right]$$

$\because$ Stirling $\ln N! = N(\ln N - 1) = \ln\Gamma(N+1)$

$$\boxed{S = NK\left[\ln\left\{\frac{V}{h^3}\left(\frac{4\pi mU}{3N}\right)^{3/2}\right\} + \frac{3}{2}\right]}$$

$$\Rightarrow S - \frac{3}{2}NK = \ln\{\# U\}^{\frac{3NK}{2}} \qquad \# = \frac{4\pi mU}{3N}\frac{V^{2/3}}{h^2}$$

$$\Rightarrow U = \frac{3Nh^2}{4\pi m V^{2/3}} e^{(S - \frac{3}{2}NK)/3NK/2} = \frac{3h^2}{4\pi m}\frac{N}{V^{2/3}}\exp\left\{\frac{2}{3}\frac{S}{NK} - 1\right\}$$

$$\Rightarrow T = \left(\frac{\partial U}{\partial S}\right)_V = \frac{2}{3NK} \times U \Rightarrow U = \frac{3}{2}NKT \text{ — ideal}$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_S = -\left(-\frac{2}{3}V^{-\frac{2}{3}-1}\right)\# = \frac{2}{3V} \times U = \frac{NKT}{V} \text{ — ide}$$

Let us compare Carnot entropy and Boltzmann entropy

$$S_c = NK\left[\ln\left(\frac{U^{3/2}V}{N^{5/2}}\right) + \frac{5}{2}\right] + C$$

$$= NK\left\{\ln\left[\left(\frac{3}{2}KT\right)^{3/2}\left(\frac{V}{N}\right)\right] + \frac{5}{2}\right\} + C \quad \text{where } \frac{U}{N} = \frac{3}{2}KT$$

$$S_B = NK\left\{\ln\left[V\left(\frac{U}{N}\right)^{3/2}\right] + \frac{3}{2} + \ln\left(\frac{4\pi m}{h^2 3}\right)^{3/2}\right\}$$

$$= NK\left\{\ln\left[V\left(\frac{3}{2}KT\right)^{3/2}\right] + \frac{3}{2}\right\} + C$$

$$\text{where } C = \frac{3Nk}{2}\ln\left(\frac{4\pi m}{3h^2}\right)$$

Gibb's paradox: $\rightarrow$ After mixing two system at same T, $V_1 + V_2 = V_f$ and $N_1 + N_2 = N_f$

entropy change $S_f - (S_1 + S_2) = KN_f\left\{\ln\left[V_f\left(\frac{3}{2}KT\right)^{3/2}\right] + \frac{3}{2}\right\}$

$$+ \frac{3}{2}N_f K\ln\left(\frac{4\pi m}{3h^2}\right) - KN_1\left\{\ln\left[V_1\left(\frac{3}{2}KT\right)^{3/2}\right] + \frac{3}{2} + \frac{3}{2}\ln\left(\frac{4\pi m}{h^2}\right)\right\}$$

$$- KN_2\left\{\ln\left[V_2\left(\frac{3}{2}KT\right)^{3/2}\right] + \frac{3}{2} + \frac{3}{2}\ln\left(\frac{4\pi m}{h^2}\right)\right\}$$

$$\Rightarrow \Delta S = KN_f\ln[V_f] - \cancel{K(N_1+N_2)\ln(V_1+V_2)}KN_1\ln V_1 - KN_2\ln V_2$$

$$+ K\left\{\frac{3}{2}\ln\left(\frac{3}{2}KT\right) + \frac{3}{2} + \frac{3}{2}\ln\left(\frac{4\pi m}{3h^2}\right)\right\}\{\underbrace{N_f - N_1 - N_2}_{=0}\}$$

$$= KN_1\ln\left(\frac{V_f}{V_1}\right) + KN_2\ln\left(\frac{V_f}{V_2}\right) \quad \text{——— (A)}$$

For $V_1 = V_2 = V$ and $V_f = 2V$, $N_1 = N_2 = N$ and $N_f = 2N$, $\Delta S = 0$ (expect)

But (A) show $\Delta S = 2KN\ln 2 > 0 \Rightarrow$ Something wrong in S_B

Since for carnot entropy,

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

$$\Delta S = KN_f \ln\left(\frac{V_f}{N_f}\right) - KN_1 \ln\left(\frac{V_1}{N_1}\right) - KN_2 \ln\left(\frac{V_2}{N_2}\right)$$
$$+ K\left\{\frac{3}{2}\ln\left(\frac{3}{2}KT\right) + \frac{5}{2} + \frac{3}{2}\ln\left(\frac{4\pi m}{3h^2}\right)\right\} \underbrace{\{N_f - N_1 - N_2\}}_{=0}$$

$$= KN_1 \ln\left(\frac{V_f}{V_1}\cdot\frac{N_1}{N_f}\right) + KN_2 \ln\left(\frac{V_f}{V_2}\cdot\frac{N_2}{N_f}\right)$$

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

$$\Delta S = KN \ln\left(\frac{2V}{V}\cdot\frac{N}{2N}\right) + KN \ln\left(\frac{2V}{V}\cdot\frac{N}{2N}\right) = 0 \quad \because \ln 1 = 0$$

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

$$\frac{\Omega}{N!} = \Omega_{Gibb} \leftarrow \Omega = \left\{V\left(\frac{2\pi m U}{h^2}\right)^{3/2}\right\}^N \frac{3}{2}N\left(\frac{\Delta}{U}\right)\frac{1}{\Gamma\frac{3N}{2}!}$$

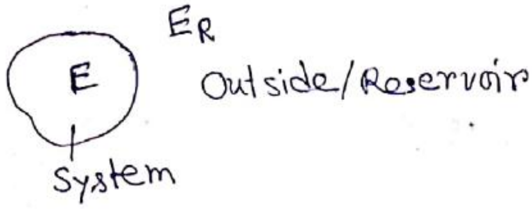
$$S_B = NK\left[\ln\left\{V\left(\frac{3}{2}KT\right)^{3/2}\right\} + \frac{3}{2} + \frac{3}{2}\ln\left(\frac{4\pi m}{3h^2}\right)\right]$$

since $K\ln N! = KN\ln N - KN$

$$\Rightarrow S_B - K\ln N! = NK\left[\ln\left\{\frac{V}{N}\left(\frac{3}{2}KT\right)^{3/2}\right\} + \frac{5}{2} + \frac{3}{2}\ln\frac{4\pi m}{3h^2}\right]$$

Canonical Ensemble :-

$UNV \rightarrow TNV$



$$E + E_R = E_0 = \text{Constant}$$

$$\rho(E) = \rho(E_R = E_0 - E)$$; Since they are equilibrium to each other

Now for $E = E_j$, and $E = E_K$, probabilities ratios

$$\frac{\rho_j}{\rho_K} = \frac{\Omega_R(E_0 - E_j)}{\Omega_R(E_0 - E_K)}$$ where $\Omega_R(E_R)$ = no. of microstate of reservoir.

Since $S_R = K_B \ln \Omega_R(E_R) \Rightarrow \Omega_R(E_R) = e^{S_R/K_B}$

$$\Rightarrow \frac{\rho_j}{\rho_K} = \exp\left[\frac{1}{K_B}\{S_R(E_0 - E_j) - S_R(E_0 - E_K)\}\right]$$

If $E_j \ll E_0 \Rightarrow S_R(E_0 - E_j) = S_R(E_0) - E_j\left(\frac{\partial S_R}{\partial E_R}\right)_{V,N}$

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

$$\Rightarrow \frac{\rho_j}{\rho_K} = \exp\left[\frac{-E_j + E_K}{K_B T}\right]$$

[$\because TdS = dU + PdV \pm \mu dN$
$\Rightarrow T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$]

$$\Rightarrow \rho_j \propto \exp(-E_j/K_B T)$$

$$= \frac{1}{Z} e^{-\beta E_j} \quad Z = ?$$

Total probability $\sum \rho_j = 1$

$Z = \sum e^{-\beta E_j} \Rightarrow$ Canonical partition function.

$$\langle E \rangle = \sum_j p_j E_j = \frac{\sum_j E_j e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} \qquad \text{Since } Z = \sum_j e^{-\beta E_j}$$

we can write

$$\langle E \rangle = -\frac{1}{Z}\left(\frac{\partial Z}{\partial \beta}\right)_{V,N} = -\frac{\partial}{\partial \beta}(\ln Z)\Big|_{V,N}$$

$$Z = \sum_{\nu} \Omega(E_\nu)\, e^{-\beta E_\nu} \qquad \Omega(E_\nu) = e^{S(E_\nu)/K_B}$$

$$Z = \sum_{\nu} \exp\left[\frac{S(E_\nu)}{K_B} - \beta E_\nu\right]$$

instead of sum
$\Downarrow$
peak value of
energy $U \Leftrightarrow S$

$$\approx \exp\left[\frac{S}{K_B} - \beta U\right]$$

$$= \exp\left[-\frac{U - TS}{K_B T}\right]$$

$$\Rightarrow A(T,V,N) = -K_B T \ln Z(T,V,N)$$

$$A = U - TS$$

Helmholtz free Energy

$$\therefore S = \frac{U}{T} + K_B \ln Z = K_B \frac{\partial}{\partial T}(T \ln Z)\Big|_{V,N}$$

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In terms of integration,

$$Z = \sum e^{-\beta E_j}$$

$$\downarrow$$

$$Z = \frac{1}{h^n} \int d\gamma \, e^{-\beta H}$$

$d\gamma \to$ differential measure of the phase-space containing n-coordinate and moments

Probability distribution function

$$\rho(\gamma) = \frac{e^{-\beta H(p,q)}}{Z \, (h)^n}$$

$$= \frac{e^{-\beta H(p,q)}}{\int d\gamma \, e^{-\beta H(p,q)}}$$

$$\langle F \rangle = \frac{\int_\Gamma d\gamma \, e^{-\beta H} F(\gamma)}{\int d\gamma \, e^{-\beta H}}$$

$$A = U - TS \Rightarrow dA = dU - TdS - SdT \quad \text{(1)} \quad \text{(2)}$$

$$= -PV + \mu N \quad \cancel{\left(\frac{\partial A}{\partial T}\right)_{V,N}} \qquad = -pdV + \mu dN - SdT$$

$$TdS = dU + pdV - \mu dN \quad \text{(2)} \qquad \Rightarrow \left(\frac{\partial A}{\partial T}\right)_{V,N} = -S$$

$$\therefore \boxed{S = -\left(\frac{\partial A}{\partial T}\right)_{V,N} = k_B \frac{\partial}{\partial T}(T \ln Z)}$$

$$\therefore U = TS + A = T k_B \frac{\partial}{\partial T}(T \ln Z) - k_B T \ln Z$$

$$\boxed{U = T^2 k_B \frac{\partial}{\partial T} \ln Z}$$

Grand cannonical ensemble :-

$$\overset{S}{E} + \overset{R}{E_R} = E_0 = \text{Constant}$$

$$N + N_R = N_0 = \text{Constant}$$

probability of system = probability of R

$$\rho(E,N) = \rho(E_0 - E, N_0 - N)$$

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

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

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

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

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

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

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

partition function

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

$$= \sum_\nu \Omega(E_\nu)\, e^{-\beta(E_\nu - \mu N_\nu)}$$ Density of states concept

$$= \sum_\nu \exp\left[\frac{S(E_\nu)}{K} - \frac{E_\nu}{KT} + \frac{\mu N_\nu}{KT}\right]$$

$\sum_\nu \cong$ Max

$$\Rightarrow Z \simeq \exp\left[\frac{S}{K} - \frac{U}{KT} + \frac{\mu N}{KT}\right]$$

$$\Rightarrow \underbrace{TS - U + \mu N}_{\begin{subarray}{c} \| \\ PV \\ \| \\ \Phi \end{subarray}} = KT \ln Z$$

$\Phi \rightarrow$ Grand canonical potential.

Cannonical Ensemble

$$A = -KT \ln Z \quad \text{——— (1)}$$

$$A = U - TS \quad \text{——— (2)} \qquad TdS = dU + PdV - \mu dN \quad \text{——— (4)}$$

$$= -PV + \mu N \quad \text{——— (3)}$$

$$dA = dU - TdS - SdT$$

$$= -PdV + \mu dN - SdT \quad [\text{using (4)}]$$

$$\Rightarrow S = -\left(\frac{\partial A}{\partial T}\right)_{V,N} = K_B\left[\frac{\partial}{\partial T}(T\ln Z)\right]_{V,N} \quad \text{——— (5)}$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,N} = K_B T\left(\frac{\partial}{\partial V}\ln Z\right)_{N,T} \quad \text{——— (6)}$$

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{V,T} = -K_B T\left(\frac{\partial}{\partial N}\ln Z\right)_{V,T} \quad \text{——— (7)}$$

Now $U = A + TS$

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

$$\boxed{U = T^2 K_B\left(\frac{\partial}{\partial T}\ln Z\right)_{V,N}} \quad \text{——— (8)}$$

Grand Canonical Ensemble

$$\Phi = -KT \ln Z(T,\mu,V) \quad \text{——} \ (1)$$

$$TdS = dU + PdV - \mu dN \quad \text{——} \ (4)$$

$$\Phi = -PV \quad \text{——} \ (2)$$

$$= U - TS - \mu N \quad \text{——} \ (3)$$

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

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

$$\Rightarrow S = -\left(\frac{\partial \Phi}{\partial T}\right)_{\mu,V} = K_B \frac{\partial}{\partial T}\left[T \ln Z\right]_{\mu,V} \quad \text{——} \ (5)$$

$$P = -\left(\frac{\partial \Phi}{\partial V}\right)_{\mu,T} = K_B T\left(\frac{\partial}{\partial V} \ln Z\right)_{\mu,T} \quad \text{——} \ (6)$$

$$N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{V,T} = K_B T\left(\frac{\partial}{\partial \mu} \ln Z\right)_{V,T} \quad \text{——} \ (7)$$

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

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

$$= T^2 K_B \left(\frac{\partial}{\partial T} \ln Z\right)_{\mu,V} + \mu T K_B \left(\frac{\partial}{\partial \mu} \ln Z\right)_{V,T}$$

$$\boxed{U = K_B T\left[T \frac{\partial}{\partial T} \ln Z + \mu \frac{\partial}{\partial \mu} \ln Z\right]} \quad \text{——} \ (8)$$

Carnot's entropy :→ $S_c = NK\left[\ln\left\{\frac{V}{N}\times\frac{1}{\lambda^3}\right\}+\frac{5}{2}\right]$ λ→unknown

Stat./Boltz. " → S_B //

$\left[\lambda = \frac{h}{\sqrt{2m(\pi KT)}}\right.$ → Thermal de Broglie wavelength]

Micro-canonical ensemble (MCE) :→ $\Omega \rightarrow S_{MCE} = K\ln\Omega$

C.E. → Partition function

$$Z = \sum_i e^{\beta E_i} = \sum_\nu \Omega(E_\nu)\, e^{-\beta E_\nu}$$

$$= \sum_\nu \left(\frac{d^{3N}x\, d^{3N}p}{N!\, h^{3N}}\right)_{E_\nu} e^{-\beta E_\nu}$$

$$= \int \frac{d^{3N}x\, d^{3N}p}{N!\, h^{3N}}\, e^{-\beta E}, \text{ where } E = \frac{p^2}{2m}$$

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

$$\frac{\beta p^2}{2m} = z \Rightarrow p\,dp = \left(\frac{m}{\beta}\right)dz$$

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

$$= \frac{V^N}{N!\, h^{3N}}\left[\left(\frac{m}{\beta}\right)^{3/2} 4\pi\sqrt{2}\underbrace{\int_0^\infty e^{-z} z^{1/2}\, dz}_{\sqrt{\pi}/2}\right]^N \qquad \because \int_0^\infty e^{-z} z^{\frac{3}{2}-1}\, dz = \Gamma\left(\frac{3}{2}\right) = \frac{1}{2}\sqrt{\pi}$$

$$= \frac{V^N}{N!\, h^{3N}}\left[\left(\frac{m}{\beta}2\pi\right)^{3/2}\right]^N = \left[\frac{V}{h^3}(2\pi m KT)^{3/2}\right]^N \frac{1}{N!}$$

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So Helmholtz free energy

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

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

$\because \ln N! = N\ln N - N$

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

$$\lambda = \frac{h}{\sqrt{2m(\pi KT)}}$$

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

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

$$S = NK\left[\ln\left(\frac{V}{N}\cdot\frac{1}{\lambda^3}\right) + \frac{5}{2}\right] \quad \text{(checked)}$$

Pressure $P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} = +NKT\left[\frac{1}{V}\right] \Rightarrow PV = NKT$ (che

Internal energy

$$U = A + TS$$

$$= NKT\left[\ln\left(\frac{N}{V}\lambda^3\right) - 1\right] + TNK\left[\ln\left(\frac{V}{N}\frac{1}{\lambda^3}\right) + \frac{5}{2}\right]$$

$$U = \frac{3}{2}NKT \quad \text{(checked)}$$

Harmonic Oscillator:-

$$H(x,p) = \frac{1}{2} m\omega^2 x^2 + \frac{p^2}{2m}$$

Partition function $Z_1 = \int e^{-\beta H} \frac{dx\,dp}{h}$

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

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

$$\beta m\omega^2 x^2/2 = z$$

$$x\,dx = \frac{1}{\beta m\omega^2}\,dz$$

$$\Rightarrow dx = \left(\frac{1}{\beta m\omega^2}\right)\left(\frac{2z}{\beta m\omega^2}\right)^{-1/2} dz$$

$$= \left(\frac{2\beta m\omega^2}{\cancel{2}}\right)^{-1/2} z^{-1/2}\,dz$$

$$\frac{\beta p^2}{2m} = z$$

$$p\,dp = \frac{m}{\beta}\,dz$$

$$dp = \left(\frac{m}{\beta}\right)\left(\frac{\beta}{2mz}\right)^{1/2} dz$$

$$= \left(\frac{m}{2\beta}\right)^{1/2} z^{-1/2}\,dz$$

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

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

$$Z_1 = \frac{2\pi KT}{h\omega^{\cancel{2}}} = \left(\frac{KT}{\hbar\omega}\right) \Rightarrow \text{total } Z_N = (Z_1)^N = \left(\frac{KT}{\hbar\omega}\right)^N$$

$$\therefore A = -KT \ln Z_N$$

$$\boxed{A = NKT \ln\left(\frac{\hbar\omega}{KT}\right)} \rightarrow \text{NO}$$

$$\Rightarrow P = -\frac{\partial A}{\partial V} = 0 \quad (\text{Since } A(V) = \text{const})$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V} = -NK\left[\ln\left(\frac{\hbar\omega}{KT}\right)\right] + NKT\left[\frac{1}{T}\right]$$

$$= NK\left[\ln\left(\frac{KT}{\hbar\omega}\right) + 1\right]$$

$$U = A + TS = NKT$$

For ideal gas:-

$$C_p = \frac{\partial}{\partial T}(U + PV)\Big]_P \qquad C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$= \frac{\partial}{\partial T}\left(\frac{3}{2}NKT + NKT\right) \qquad = \frac{\partial}{\partial T}\left(\frac{3}{2}NKT\right)$$

$$= \frac{5}{2}NK \qquad = \frac{3}{2}NK$$

$$\Rightarrow C_p - C_V = NK$$

but here $C_p = C_V = \frac{\partial U}{\partial T} = NK$ (Since $A(V) = \text{const}$)

Quantum harmonic Oscillator

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

Partition function $Z_1 = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega}$

$$= \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} = \left[\frac{1}{2\sinh\left(\frac{\beta\hbar\omega}{2}\right)}\right]$$

total partition function $Z_N = (Z_1)^N$

$$= \left[\frac{1}{2\sinh\left(\frac{\beta\hbar\omega}{2}\right)}\right]^N$$

$$= e^{-\left(\frac{N}{2}\beta\hbar\omega\right)}\left\{1 - e^{-\beta\hbar\omega}\right\}^{-N}$$

Helmholtz free energy

$$A = -KT \ln Z$$

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

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

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

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

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

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