

① $\langle E \rangle = \frac{3}{2} k_B T$

$$\langle E \rangle = \int_0^\infty E P(\epsilon) d\epsilon = \frac{2}{\sqrt{\pi}} \int_0^\infty (\beta E)^{\frac{3}{2}} e^{-\beta E} d(\beta E)$$

$$= \frac{2}{\sqrt{\pi}} \int_0^\infty x^{\frac{3}{2}} e^{-x} dx = \frac{2}{\sqrt{\pi}} \sqrt{\pi} \left(\frac{3}{4}\right) \left(\frac{1}{2}\right) = \frac{3}{2} \frac{1}{\beta} = \frac{3}{2} k_B T$$

② Boltzmann Distribution

$$p_j = \frac{e^{-\beta \epsilon_j}}{q} \quad q = \sum_j e^{-\beta \epsilon_j / k_B T}$$

Constants N indistinguishable particles w/ E ϵ_j

$$N = \sum_j n_j$$

$$E = \sum_j n_j \epsilon_j$$

Goal: Find conditions that would maximize ω or $\ln \omega$

$$\omega = \frac{N!}{n_0! n_1! \dots n_j!}$$

ω relates to # of ways to distribute particles in E levels. ω is reporter of S to maximize S maximize ω

$$\ln \omega = \ln N! - \sum_j \ln n_j!$$

$$= N \ln N - N - \sum_j n_j \ln n_j + \sum_j n_j$$

$$= N \ln N - \sum_j n_j \ln n_j$$

$$\frac{d \ln \omega}{d n_j} = - \sum_j (n_j \ln n_j + 1) dn_j = - \sum_j n_j \ln n_j - \sum_j 1 dn_j = 0$$

$$- \sum_j n_j \ln n_j = 0$$

constants

$$dE = \sum_j \epsilon_j dn_j = 0$$

$$dN = \sum_j dn_j = 0$$

$$- \sum_j n_j \ln n_j - \beta \sum_j \epsilon_j dn_j - \alpha \sum_j dn_j = 0 \quad \alpha, \beta \text{ constant}$$

$$\sum_j (\alpha + \beta \epsilon_j + \ln n_j) dn_j = 0$$

$$\ln n_j + \alpha + \beta \epsilon_j = 0$$

$$\ln n_j = -\alpha - \beta \epsilon_j$$

$$n_j = e^{-\alpha} e^{-\beta \epsilon_j}$$

$$\sum_j n_j = e^{-\alpha} \sum_j e^{-\beta \epsilon_j}$$

$$e^{-\alpha} = \frac{N}{\sum_j e^{-\beta \epsilon_j}}$$

$$p_j = \frac{n_j}{N} = \frac{e^{-\beta \epsilon_j}}{q}$$

normalization factor

③ Derivation of β

$$\omega = \frac{N!}{\prod n_i}$$

$$\begin{aligned} \ln \omega &= N \ln N - \sum n_i \ln n_i + \sum n_i \\ &= N \ln N - \sum N p_i \ln (p_i N) \\ &= N \ln N - \sum N p_i (\ln p_i + \ln N) \\ &= \cancel{N \ln N} - \sum N p_i \ln p_i - \cancel{N \ln N} \sum p_i \\ &= -N \sum p_i \ln p_i \end{aligned}$$

Since $S_{max} = k_B \ln(\omega)$

$$= -N k_B \sum p_i \ln p_i$$

$$S_{system} = \frac{S_{max}}{N} = -k_B \sum p_i \ln p_i$$

$$dS = -k_B \sum (\ln p_i + 1) dp_i$$

$$= -k_B \sum \ln p_i dp_i - k_B \sum dp_i$$

(sum to balancing \sum (implication of molecules)

Since $p_i = \frac{E_i \cdot g_i}{Q}$

$$dS = -k_B \sum [-\beta E_i - \ln g_i] dp_i$$

$$= k_B \sum \beta E_i dp_i + \frac{k_B \sum \ln g_i dp_i}{\text{For a fixed system w/cation } T, Q \text{ is constant}}$$

$$dS = k_B \sum \beta E_i dp_i + k_B \ln g_i \sum dp_i$$

$$dS = k_B \beta \sum E_i dp_i$$

since $\sum E_i dp_i = dQ_{rev}$

$$\& dS = \frac{dQ_{rev}}{T} = k_B \beta dQ_{rev}$$

$$\text{Thus } \beta = \frac{1}{k_B T}$$

④

$$dU = dQ_{rev} + dW_{rev} = dQ_{rev} - PdV \quad (1)$$

Based on stat. mech

$$U = \langle E \rangle = \sum p_i E_i \approx \sum E_i p_i$$

Hence $dU = \sum p_i dE_i + \sum E_i dp_i = \sum E_i dp_i + \sum p_i \left(\frac{\partial E_i}{\partial V} \right) dV \quad (2)$

comparing (1) & (2)

$$dQ_{rev} = \sum E_i dp_i \quad dW_{rev} = -\sum p_i \left(\frac{\partial E_i}{\partial V} \right) dV \quad \& \quad P = -\sum p_i \left(\frac{\partial E_i}{\partial V} \right)$$

(depends on $\sum E_i$ (2nd order))

(depends on $\sum p_i$)

Entropy only further of 1

$$(5) P = k_B T \left(\frac{\partial \ln q}{\partial V} \right)_{N, T} = - \sum_j P_j \left(\frac{\partial \epsilon_j}{\partial V} \right)_N$$

$$\left(\frac{\partial \ln q}{\partial V} \right)_{N, T} = \frac{1}{q} \left(\frac{\partial q}{\partial V} \right)_{N, T} = \frac{1}{q} \left(\frac{\partial \sum_j e^{-\beta \epsilon_j}}{\partial V} \right)_{N, T} = \frac{1}{q} \left[\sum_j e^{-\beta \epsilon_j} (-\beta) \left(\frac{\partial \epsilon_j}{\partial V} \right) \right]$$

$$= \frac{1}{q} \sum_j e^{-\beta \epsilon_j} (-\beta) \left(\frac{\partial \epsilon_j}{\partial V} \right) = -\beta \sum_j P_j \left(\frac{\partial \epsilon_j}{\partial V} \right) = \beta P$$

Since $P = k_B T \left(\frac{\partial \ln q}{\partial V} \right)_{N, T}$, thus we have proved the case above.

(6) Relationship between ensemble & system partition function

2 particles a & b occupy 2 ϵ levels of degeneracy of ω .

$$Q = e^{-\beta [\epsilon_{a1} + \epsilon_{b1}]} + e^{-\beta [\epsilon_{a1} + \epsilon_{b2}]} + e^{-\beta [\epsilon_{a2} + \epsilon_{b1}]} + e^{-\beta [\epsilon_{a2} + \epsilon_{b2}]} \\ = \left[e^{-\beta \epsilon_{a1}} + e^{-\beta \epsilon_{a2}} \right] \cdot \left[e^{-\beta \epsilon_{b1}} + e^{-\beta \epsilon_{b2}} \right]$$

$$= q_a \cdot q_b$$

Thus if particles are distinguishable

if particles are not " " " "

$$Q = q^N$$

$$Q = \frac{q^N}{N!}$$

same 2) for 12 same

(7) $PV = NR T$

$$P = k_B T \left(\frac{\partial \ln q}{\partial V} \right)_{N, T}$$

$$q_1 = \left[\frac{2\pi m k_B T}{h^2} \right]^{\frac{3}{2}} \cdot V$$

$$\ln q_1 = \ln(\alpha) + \ln(V)$$

$$\left(\frac{\partial \ln q_1}{\partial V} \right)_{N, T} = \frac{1}{V}$$

$$P = \frac{k_B T}{V}$$

$PV = k_B T$ for 1 particle

$$PV = N k_B T$$

$$= \frac{N \cdot N_A}{N_A} k_B T$$

$$PV = NR T$$

$$\textcircled{8} \quad \left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

$$q = \frac{(V - nb') e^{\frac{N a'}{k_B T V}}}{A}$$

$$\ln q = \ln(V - nb') + \frac{N a'}{k_B T V} - \ln(A)$$

$$\left(\frac{d \ln q}{d V} \right)_{N, T} = \frac{1}{V - nb'} - \frac{N a'}{k_B T V^2}$$

$$P = k_B T \left[\frac{\partial \ln q}{\partial V} \right]_{N, T} = k_B T \left[\frac{1}{V - nb'} - \frac{N a'}{k_B T V^2} \right]$$

$$P = \frac{k_B T}{V - nb'} - \frac{N a'}{V^2}$$

$$\left(P + \frac{N^2 a'}{V^2} \right) (V - nb') = N k_B T$$

$$N^2 a' = n^2 a$$

$$N b' = n b$$

$$N k_B = n R$$

$$\boxed{\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT}$$