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

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

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

② Boltzmann Distribution

$$\boxed{P_j = \frac{e^{-\beta E_j}}{q} \qquad q = \sum_j e^{-E_j/k_BT}}$$

Constants: N indistinguishable particles w/ E & T

$N = \sum n_j$

$E = \sum_j nE_j$

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

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

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

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

$$= N\ln N - \cancel{N} - \sum_j n_j \ln n_j + \cancel{\sum_j n_j = N}$$

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

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

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

constants

$$dE = \sum_j E_j\,dn_j = 0$$

$$dN = \sum_j dn_j = 0$$

$$-\sum_j \ln n_j dn_j - \beta\sum_j E_j\,dn_j - \alpha\sum_j dn_j = 0 \qquad \alpha, \beta \text{ constants}$$

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

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

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

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

$$\sum n_j = e^{-\alpha}\sum e^{-\beta E_j}$$

$$e^{-\alpha} = \frac{N}{\sum e^{-\beta E_j}}$$

$$\boxed{P_j = \frac{n_j}{N} = \frac{e^{-\beta E_j}}{q}}$$

normalization factor

③ Derivation of β

$$\omega = \frac{N!}{\prod_j n_j}$$

$$\ln \omega = N\ln N - \cancel{N} - \sum_j n_j \ln n_j + \sum_j n_j^{\cancel{N}}$$

$$= N\ln N - \sum_j N p_j \ln (p_j N)$$

$$= N\ln N - \sum_j N p_j (\ln p_j + \ln N)$$

$$= \cancel{N\ln N} - \sum_j N p_j \ln p_j - \cancel{N\ln N \sum_j p_j}^{\,1}$$

$$= -N \sum_j p_j \ln p_j$$

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

$$= -N k_B \sum_j p_j \ln p_j$$

$$S_{system} = \frac{S_{total}}{N} = -k_B \sum_j p_j \ln p_j$$

$$dS = -k_B \sum_j (\ln p_j + 1)\, dp_j$$

$$= -k_B \sum_j \ln p_j \, dp_j - k_B \cancel{\sum_j dp_j}^{\,0}$$ (due to balancing E / composition of molecule)

Since $p_j = \frac{e^{-\beta E_j}}{q}$

$$dS = -k_B \sum_j [-\beta E_j - \ln q]\, dp_j$$

$$= k_B \sum_j \beta E_j \, dp_j + \underbrace{k_B \sum_j \ln q \, dp_j}_{\text{For a fixed system w/ certain } T,\ q \text{ is constant}}$$

$$dS = k_B \sum_j \beta E_j \, dp_j + k_B \ln q \cancel{\sum_j dp_j}^{\,0}$$

$$dS = k_B \beta \sum_j E_j \, dp_j$$

Since $\sum_j E_j \, dp_j = dq_{rev}$

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

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

④

$$dU = dq_{rev} + dw_{rev} = dq_{rev} - PdV \quad (1)$$

Based on stat. mech

$$U = \langle E \rangle = \sum_j p_j E_j \quad \text{SEPIE JNE}$$ $\sum_j E_j \, dp_j + \sum_j p_j \left(\frac{\partial E_j}{\partial V}\right)_N dV \quad (2)$

Hence $dU = \sum_j p_j \, dE_j + \sum_j E_j \, dp_j = \sum_j E_j \, dp_j + \sum_j p_j \left(\frac{\partial E_j}{\partial V}\right)_N dV$

Comparing (1) & (2) depends on $\sum_j E_j \left(\frac{\partial p_j}{\partial S}\right) dS$ — Entropy only function of p; depends on V

$$dq_{rev} = \sum_j E_j \, dp_j \qquad dw_{rev} = \sum_j p_j \left(\frac{dE_j}{\partial V}\right)_N dV \quad \& \quad P = -\sum_j p_j \left(\frac{\partial E_j}{\partial V}\right)$$

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

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

$$= \sum_j \frac{e^{-\beta E_j}}{q}(-\beta)\left(\frac{\partial E_j}{\partial V}\right) = -\beta \sum_j p_j \left(\frac{\partial E_j}{\partial V}\right) = \beta P$$

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 E levels w/ degeneracy of 2.

$$Q = e^{-\beta[E_a^1 + E_b^1]} + e^{-\beta[E_a^1 + E_b^2]} + e^{-\beta[E_a^2 + E_b^1]} + e^{-\beta[E_a^2 + E_b^2]}$$

$$= \left[e^{-\beta E_{a_1}} + e^{-\beta E_{a_2}}\right] \cdot \left[e^{-\beta E_{b_1}} + e^{-\beta E_{b_2}}\right]$$

$$= q_a \cdot q_b$$

Thus if particles are distinguishable $\boxed{Q = q^N}$

if particles are not " _____ " $\boxed{Q = \frac{q^N}{N!}}$ since 2,1 & 1,2 are same

(7) $PV = nRT$

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

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

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

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

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

$PV = k_B T$ for 1 particle

$$PV = N k_B T$$

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

$$\boxed{PV = nRT}$$

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

$$q = \frac{(V - nb')\, e^{\frac{N\alpha'}{k_B T V}}}{\Lambda}$$

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

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

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

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

$$\left(P + \frac{N^2 \alpha'}{V^2}\right)(V - Nb') = Nk_B T$$

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

$$Nb' = nb$$

$$Nk_B = nR$$

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