SCIENCE - I

PURU GUPTA
20171187

CLASS ASSIGNMENT

1) $Z = \left(\sum_j e^{-\beta E_j}\right)^N$ for N particles

$E = \{ \epsilon_0, -\epsilon_0 \}$

$Z = \left(e^{-\beta\epsilon_0} + e^{\beta\epsilon_0}\right)^N$

(a) Internal Energy $= \langle E \rangle = -\dfrac{\partial \ln z}{\partial \beta}$

$\Rightarrow -N \dfrac{\partial \ln\left(e^{-\beta\epsilon_0} + e^{\beta\epsilon_0}\right)}{\partial \beta} = \dfrac{-N\epsilon_0\left(e^{\beta\epsilon_0} - e^{-\beta\epsilon_0}\right)}{\left(e^{\beta\epsilon_0} + e^{-\beta\epsilon_0}\right)}$

(b) $C_V = \dfrac{\partial \langle E \rangle}{\partial T} = \dfrac{-1}{k_B T^2} \dfrac{\partial \langle E \rangle}{\partial \beta}$

$$\Rightarrow \frac{N\epsilon_0}{k_B T^2}\left[\frac{\left(e^{\beta\epsilon_0} + e^{-\beta\epsilon_0}\right)\left(\epsilon_0 e^{\beta\epsilon_0} + \epsilon_0 e^{-\beta\epsilon_0}\right) - \left(e^{\beta\epsilon_0} - e^{-\beta\epsilon_0}\right)\left(\epsilon_0 e^{\beta\epsilon_0} - \epsilon_0 e^{-\beta\epsilon_0}\right)}{\left(e^{\beta\epsilon_0} + e^{-\beta\epsilon_0}\right)^2}\right]$$

$$\Rightarrow \frac{N\epsilon_0^2}{k_B T^2}\left[\frac{\left(e^{\beta\epsilon_0} + e^{-\beta\epsilon_0}\right)^2 - \left(e^{\beta\epsilon_0} - e^{-\beta\epsilon_0}\right)^2}{\left(e^{\beta\epsilon_0} + e^{-\beta\epsilon_0}\right)^2}\right]$$

$$\Rightarrow \frac{4N\epsilon_0^2}{k_B T^2\left(e^{\beta\epsilon_0} + e^{-\beta\epsilon_0}\right)^2}$$

(c) Helmholtz free Energy $= -k_B T \ln Z$

$$\Rightarrow \quad -Nk_BT \ln \left(e^{\beta\epsilon_0} + e^{-\beta\epsilon_0}\right)$$

(d) Entropy of system $= k_B[\ln Z + \beta\langle E\rangle]$

$$\Rightarrow \quad k_B\left[N \ln\left(e^{\beta\epsilon_0} + e^{-\beta\epsilon_0}\right) - \beta N\epsilon_0 \frac{\left(e^{\beta\epsilon_0} - e^{-\beta\epsilon_0}\right)}{\left(e^{\beta\epsilon_0} + e^{-\beta\epsilon_0}\right)}\right]$$

2) Let us use n for number of monomer units in state α and $(N-n)$ for state β.
To get relation between f and L, we shall define the Hamiltonian.

$$H = KE + U \Rightarrow H = nE_a + (N-n)E_b + fL \quad \text{-(i)}$$

Also,

$$L = na + (N-n)b \quad \text{-(ii)}$$

from (i) and (ii),

$$H = nE_a + (N-n)E_b + naf + (N-n)bf$$

We know,

$$Z = \sum_j e^{-\beta E_j} = \sum \frac{N!}{n!(N-n)!} e^{-\beta E_j}$$

$$= \sum_N \frac{N!}{n!(N-n)!} e^{-\beta(NE_b + Nbf + n(E_a-E_b) + nf(a-b))}$$

Using $\sum_N {}^N C_r x^r = (1+x)^N$

$$\Rightarrow \quad e^{-\beta N(fb+E_b)} \left(1 + e^{-\beta(E_a-E_b+f(a-b))}\right)^N$$

$$= \left[e^{-\beta(E_a+fa)} + e^{-\beta(E_b+fb)}\right]^N$$

To obtain relation between L and f, we will use free energy,

$$F = -\frac{\ln Z}{\beta} = -\frac{N}{\beta} \ln\left(e^{-\beta(E_a+fa)} + e^{-\beta(E_b+fb)}\right)$$

$$L = -\frac{\partial F}{\partial f} = -\left(\frac{N}{\beta}\right)\left(\frac{-\beta a e^{-\beta(E_a+fa)} - \beta b e^{-\beta(E_b+fb)}}{e^{-\beta(E_a+fa)} + e^{-\beta(E_b+fb)}}\right)$$

$$L = N\left(\frac{a e^{-\beta(E_a+fa)} + b e^{-\beta(E_b+fb)}}{e^{-\beta(E_a+fa)} + e^{-\beta(E_b+fb)}}\right)$$

<u>Internal Energy</u> $= \langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$

$$\langle E \rangle = -\frac{\partial\left(N \ln\left(e^{-\beta(E_a+fa)} + e^{-\beta(E_b+fb)}\right)\right)}{\partial \beta}$$

$$= -N \times \left[\frac{-(E_a+fa)e^{-\beta(E_a+fa)} - (E_b+fb)e^{-\beta(E_b+fb)}}{e^{-\beta(E_a+fa)} + e^{-\beta(E_b+fb)}}\right]$$

$$= N\left[\frac{(E_a+fa)e^{-\beta(E_a+fa)} + (E_b+fb)e^{-\beta(E_b+fb)}}{e^{-\beta(E_a+fa)} + e^{-\beta(E_b+fb)}}\right]$$

<u>Entropy</u> $= k_B\left[\ln Z + \beta\langle E \rangle\right]$

$$\Rightarrow k_B\left[N \ln\left(e^{-\beta(E_a+fa)} + e^{-\beta(E_b+fb)}\right) + N\beta\left[\frac{(E_a+fa)e^{-\beta(E_a+fa)} + (E_b+fb)e^{-\beta(E_b+fb)}}{e^{-\beta(E_a+fa)} + e^{-\beta(E_b+fb)}}\right]\right]$$

Helmholtz Free Energy $= -k_B T \ln Z$

$$\Rightarrow -k_B T N \ln\left(e^{-\beta(E_a+f_a)} + e^{-\beta(E_b+f_b)}\right)$$

Heat Capacity $= C_v = \dfrac{\partial \langle E \rangle}{\partial T}$

$$\frac{\partial \beta}{\partial T} = \frac{-1}{k_B T^2} \Rightarrow C_v = \frac{-1}{k_B T^2} \frac{\partial \langle E \rangle}{\partial \beta}$$

$$\Rightarrow -\frac{N}{k_B T^2}\left[\left(e^{-\beta(E_a+f_a)} + e^{-\beta(E_b+f_b)}\right)\left(-(E_a+f_a)^2 e^{-\beta(E_a+f_a)} - (E_b+f_b)^2 e^{-\beta(E_b+f_b)}\right) + \left[\left((E_a+f_a)e^{-\beta(E_a+f_a)} + (E_b+f_b)e^{-\beta(E_b+f_b)}\right) \cdot \frac{\left(+(E_a+f_a)e^{-\beta(E_a+f_a)} + (E_b+f_b)e^{-\beta(E_b+f_b)}\right)}{\left(e^{-\beta(E_a+f_a)} + e^{-\beta(E_b+f_b)}\right)^2}\right]\right]$$

$$\Rightarrow \frac{N}{k_B T^2}\left[\left(e^{-\beta(E_a+f_a)} + e^{-\beta(E_b+f_b)}\right)\left((E_a+f_a)^2 e^{-\beta(E_a+f_a)} + (E_b+f_b)^2 e^{-\beta(E_b+f_b)}\right) - \frac{\left((E_a+f_a)e^{-\beta(E_a+f_a)} + (E_b+f_b)e^{-\beta(E_b+f_b)}\right)^2}{\left(e^{-\beta(E_a+f_a)} + e^{-\beta(E_b+f_b)}\right)^2}\right]$$

3) $Z = \sum_j \left(e^{-\beta E_j}\right)^N$ for N particles

$E = \{\mu H, -\mu H\}$

$$Z = \left(e^{-\beta \mu H} + e^{\beta \mu H}\right)^N$$

(a) $$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$$

$$\Rightarrow -N \frac{\partial \ln (e^{-\beta \mu H} + e^{\beta \mu H})}{\partial \beta} = \frac{-N\mu H (e^{\beta \mu H} - e^{-\beta \mu H})}{(e^{\beta \mu H} + e^{-\beta \mu H})}$$

(b) $$C_v = \frac{\partial \langle E \rangle}{\partial T} = -\frac{1}{k_B T^2} \frac{\partial \langle E \rangle}{\partial \beta}$$

$$\Rightarrow \frac{N(\mu H)^2}{k_B T^2} \left[\frac{(e^{\beta \mu H} + e^{-\beta \mu H})^2 - (e^{\beta \mu H} - e^{-\beta \mu H})^2}{(e^{\beta \mu H} + e^{-\beta \mu H})^2} \right]$$

$$\Rightarrow \frac{4N\mu^2 H^2}{k_B T^2 (e^{\beta \mu H} + e^{-\beta \mu H})^2}$$

(c) Helmholtz free Energy $= -k_B T \ln Z$

$$\Rightarrow -N k_B T \ln (e^{\beta \mu H} + e^{-\beta \mu H})$$

(d) Entropy of System $= k_B (\ln Z + \beta \langle E \rangle)$

$$\Rightarrow k_B N \left[\ln (e^{\beta \mu H} + e^{-\beta \mu H}) - \beta \mu H \frac{(e^{\beta \mu H} - e^{-\beta \mu H})}{(e^{\beta \mu H} + e^{-\beta \mu H})} \right]$$