Assignment 10

1a) $$\mathcal{Z} = \sum_s e^{-E_s \beta}$$

$$= \sum_s e^{-\left[C_s + \frac{3}{2} N \ln\left(\frac{\beta}{\beta_0}\right) - N \ln\left(\frac{V}{V_0}\right)\right]}$$

$$= \sum_s e^{-C_s} \left(\frac{\beta}{\beta_0}\right)^{-3N/2} \left(\frac{V}{V_0}\right)^N$$

$$= K \left(\frac{\beta}{\beta_0}\right)^{-3N/2} \left(\frac{V}{V_0}\right)^N \quad \text{where } K \equiv \sum_s e^{-C_s}$$

$$\ln \mathcal{Z} = \ln K - \frac{3N}{2} \ln\left(\frac{\beta}{\beta_0}\right) + N \ln\left(\frac{V}{V_0}\right)$$

b) $$\bar{E} = -\frac{\partial}{\partial \beta} \ln \mathcal{Z}$$

$$= \frac{3N}{2} \frac{1}{\beta}$$

$$\therefore \bar{E} = \frac{3}{2} N k_B T$$

c) $$\bar{P} = \frac{1}{\beta} \left(\frac{\partial \ln \mathcal{Z}}{\partial V}\right)_{T,N}$$

$$= \frac{1}{\beta} \frac{N}{V}$$

$$\therefore \bar{P} = \frac{N k_B T}{V}$$

d) $\bar{\mu} = -\frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Z}}{\partial N}\right)_{T,V}$

$$= -\frac{1}{\beta}\left[-\frac{3}{2}\ln\left(\frac{\beta}{\beta_0}\right) + \ln\left(\frac{V}{V_0}\right)\right]$$

$$\therefore \bar{\mu} = \frac{1}{\beta}\left[\frac{3}{2}\ln\left(\frac{\beta}{\beta_0}\right) - \ln\left(\frac{V}{V_0}\right)\right]$$

e) $F = -\frac{1}{\beta}\ln \mathcal{Z}$

$$= -\frac{1}{\beta}\left[\ln K - \frac{3N}{2}\ln\left(\frac{\beta}{\beta_0}\right) + N\ln\left(\frac{V}{V_0}\right)\right]$$

f) $S = k_B \ln \mathcal{Z} + \frac{\bar{E}}{T}$

$$= k_B\left[\ln K - \frac{3N}{2}\ln\left(\frac{\beta}{\beta_0}\right) + N\ln\left(\frac{V}{V_0}\right)\right]$$

$$+ \frac{3}{2}Nk_B$$

2) $$Z = Z_t \cdot Z_R \cdot Z_V$$

$$= \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} \left(\frac{2I}{\hbar^2\beta}\right) \left(\frac{1}{\hbar\omega\beta}\right)$$

$$\ln Z = \frac{3}{2} \ln\left(\frac{2\pi m}{h^2\beta}\right) + \ln\left(\frac{2I}{\hbar^2\beta}\right) + \ln\left(\frac{1}{\hbar\omega\beta}\right)$$

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta}$$

$$= +\left[\frac{3}{2}\,\frac{1}{\beta} + \frac{1}{\beta} + \frac{1}{\beta}\right]$$

$$= \frac{7}{2}\,\frac{1}{\beta}$$

$$\bar{E} = \frac{7}{2} k_B T$$

This is as expected since there are 7 degrees of freedom (3 translational, 2 rotational & 2 vibrational) & average energy of each is $\frac{1}{2} k_B T$.