1. Later on, we will learn that the single molecule rotational partition function is given by:

$$q_{\text{rot}}(T) = \frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2 I_{\text{A}} k_{\text{B}} T}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_{\text{B}} k_{\text{B}} T}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_{\text{C}} k_{\text{B}} T}{h^2}\right)^{1/2}$$

Show that the rotational contribution to molar heat capacity is given by $\overline{C}_{v,rot} = \frac{3k_B}{2}$. Treat $Q = q_{rot}$

$$\ln Q = \ln\left[\frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2 I_A k_B T}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_B k_B T}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_C k_B T}{h^2}\right)^{1/2}\right]$$

$$= \text{const} + \frac{1}{2}\ln T + \frac{1}{2}\ln T + \frac{1}{2}\ln T$$

$$= \text{const} + \frac{3}{2}\ln T$$

Since this contains T's we use the partial wrt T instead of β:

$$\langle E_{\text{rot}}\rangle = k_B T^2 \frac{\partial}{\partial T}\ln Q$$

$$= k_B T^2 \frac{\partial}{\partial T}\left(\frac{3}{2}\ln T\right)$$

$$= \frac{3}{2}k_B T$$

$$C_{v,\text{rot}} = \frac{\partial\langle E_{\text{rot}}\rangle}{\partial T} = \frac{3}{2}k_B$$

2. A system of N harmonic oscillators is called an Einstein Solid. The partition function is:

$$Q = \left[\frac{1}{1 - e^{-\beta\hbar\omega}}\right]^N$$

(a) Show that the internal energy is:

$$U = \frac{N\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

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

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

$$U = -\frac{\partial}{\partial\beta} \ln Q$$

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

$$= N \frac{\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$$

Multiplying numerator and denominator by $e^{\beta\hbar\omega}$:

$$\boxed{U = \frac{N\hbar\omega}{e^{\beta\hbar\omega} - 1}}$$

(b) Show that the heat capacity is:

$$C_V = Nk_B(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

Using the β definition of heat capacity:

$$C_V = -\frac{1}{k_B T^2}\frac{\partial U}{\partial\beta}$$

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

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

$$C_V = Nk_B(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

Homework Problem 5

1. Consider a system of N independent, distinguishable particles that have two possible quantum states $\varepsilon_0 = 0$ and $\varepsilon_1 = \varepsilon$. The partition function for this system is given by:

$$Q = q^N = \left(1 + e^{-\beta\varepsilon}\right)^N$$

Show the molar heat capacity is given by: $\overline{C}_v = R(\beta\varepsilon)^2 \frac{e^{-\beta\varepsilon}}{\left(1+e^{-\beta\varepsilon}\right)^2}$