Phys 114 2018
Seminar 6
Warmup problem Solutions

1) High T limit of partition functions:
B+B 20.1

WTS: If $kT \gg \hbar\omega$, for SHO it's the case that $Z \approx (\beta\hbar\omega)^{-1}$
Thence we find U, C, F & S in this limit.

Also, WTS that in high T limit, for diatomic rotor, $Z \approx (\beta\hbar^2/2I)^{-1}$.
Note that this is shown in Eqn's leading up to Eq. (20.35)

From other problems we have done and/or SHO example on pp. 220 and 226,

$$Z = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$$

For $T \to \infty$, thus $\beta \to 0$, this becomes

$$\frac{(1 - \underbrace{\beta\hbar\omega/2}_{\text{ignore cf. 1}})}{(1 - (1 - \beta\hbar\omega))} \approx \frac{1}{\beta\hbar\omega} \checkmark \quad \text{QED}$$

Then $\bar{E} = -\frac{\partial}{\partial\beta}\ln Z = -\frac{1}{Z}\frac{\partial Z}{\partial\beta} = -\beta\hbar\omega\left(-\frac{1}{\beta^2\hbar\omega}\right)$

$\Rightarrow \bar{E} = \frac{1}{\beta} = \underline{kT}$ (or for N particles NkT)

$$C = \frac{\partial \bar{E}}{\partial T} = \underline{k} \quad \text{(per particle)}$$

$$F = -kT\ln\left(\frac{1}{\beta\hbar\omega}\right) = \underline{kT\ln\frac{\hbar\omega}{kT}}$$

$$S = -\frac{\partial F}{\partial T} \quad \text{or} \quad \frac{\bar{E}}{T} + k\ln Z = \frac{\bar{E} - F}{T}$$

W2

Either way,

$$S = k\left(1 - \ln\left(\frac{\hbar\omega}{kT}\right)\right)$$

Now for rotor, following along with B+B p.227,

$$Z = \sum_{j=0}^{\infty} (2J+1) e^{-\beta \Delta J(J+1)} \qquad \text{where } \Delta = \frac{\hbar^2}{2I}$$

$\beta \to 0$ $$\simeq \int_0^{\infty} (2J+1) e^{-\beta \Delta J(J+1)} \, dJ$$

(perfect differential ☺)

$$= \int_0^{\infty} e^{-\beta \Delta u} \, du = \frac{1}{\beta \Delta} = \left(\beta \hbar^2/2I\right)^{-1} \quad \text{QED}$$

Then $$F = -kT \ln\left(\frac{kT}{\Delta}\right) = +kT \ln\left(\frac{\hbar^2}{2IkT}\right)$$

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

$$C = k$$

$$S = -\frac{\partial F}{\partial T} = \frac{\bar{E} - F}{T}, \cancel{= k\left(1 - \frac{\hbar^2}{2IkT}\right)}$$

$$\cancel{S = kT(}$$

$$S = k\left(1 - \ln\left(\frac{\hbar^2}{2IkT}\right)\right)$$