Glazer & Wark

3.3. Show that the zero-point motion of an assembly of simple harmonic oscillators does not contribute to its entropy or heat capacity.

For simple harmonic oscillator, we have

$$Z_{sp} = \exp\left(-\frac{h\nu}{2k_BT}\right) \times \sum_0^\infty \exp\left(-\frac{nh\nu}{k_BT}\right) = \frac{\exp\left(-\frac{h\nu}{2k_BT}\right)}{1-\exp\left(-\frac{h\nu}{k_BT}\right)}$$

define Z_ϕ by removing the $n=0$ mode:

$$Z_\phi = \exp\left(-\frac{h\nu}{2k_BT}\right) \times \sum_1^\infty \exp\left(-\frac{nh\nu}{k_BT}\right) = \frac{-\exp\left(-\frac{3}{2}\frac{h\nu}{k_BT}\right)}{1-\exp\left(-\frac{h\nu}{k_BT}\right)}.$$

$$\Rightarrow \ln Z_\phi = \ln Z_{sp} - \frac{h\nu}{k_BT}.$$

$$\rightarrow \frac{d}{dT}\ln Z_\phi = \frac{d}{dT}\ln Z_{sp} + \frac{h\nu}{k_BT^2}.$$

$$S_\phi = k_B \ln Z_\phi + k_B T \frac{d}{dT}\ln Z_\phi \sim \ln Z_\phi + T\frac{d}{dT}\ln Z_\phi.$$

$$= \ln Z_{sp} \cancel{- \frac{h\nu}{k_BT}} + T\frac{d}{dT}\ln Z_{sp} \cancel{+ \frac{h\nu}{k_BT}}$$

$$= \ln Z_{sp} + T\frac{d}{dT}\ln Z_{sp} = S_{sp}. \checkmark$$

For heap capacity, we use

$$C_\phi = \frac{dU}{dT} \sim 2T\frac{\partial \ln Z_\phi}{\partial T} + T^2\frac{\partial^2}{\partial T^2}\ln Z_\phi.$$

$$= 2T\left[\frac{\partial}{\partial T}\ln Z_{sp} + \frac{h\nu}{k_B T^2}\right] + T^2\left[\frac{d^2}{dT^2}\ln Z_{sp} - 2\frac{h\nu}{k_B T^3}\right]$$

$$= 2T\frac{\partial}{\partial T}\ln Z_{sp} + \cancel{\frac{2h\nu}{k_B T}} + T^2\frac{\partial}{\partial T}\ln Z_{sp} \cancel{- \frac{2h\nu}{k_B T}}$$

$= C_{sp}$ by a constant coefficient that is equal to that of C_ϕ. ✓.