The variance from partition fcns

a) Note:

(1) $$Z = \sum_s e^{-\beta \varepsilon_s}$$

(2) $$-\frac{\partial Z}{\partial \beta} = \sum_s e^{-\beta \varepsilon_s} \varepsilon_s$$

(3) $$+\frac{\partial^2 Z}{\partial \beta^2} = \sum_s e^{-\beta \varepsilon_s} \varepsilon_s^2$$

So since $P_s = e^{-\beta \varepsilon_s}/Z$

$$\langle \varepsilon \rangle = \sum_s P_s \varepsilon_s = \frac{1}{Z} \frac{-\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \log Z$$

$$\langle \varepsilon^2 \rangle = \sum_s P_s \varepsilon_s^2 = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}$$

b) Now we have from (a)

$$\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)^2$$

So we have to check that

these are the same

$$\frac{\partial^2}{\partial \beta^2} \log Z = \frac{\partial}{\partial \beta} \frac{1}{Z} \frac{\partial Z}{\partial \beta} = \underbrace{-\frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2 + \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}}$$

So $$\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 = \frac{\partial^2}{\partial \beta^2} \log Z$$

Now since

$$\langle \varepsilon \rangle = -\frac{\partial}{\partial \beta} \log Z$$

$$\boxed{-\frac{\partial \langle \varepsilon \rangle}{\partial \beta} = \frac{\partial^2}{\partial \beta^2} \log Z = \langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2}$$ ✓

c) We have from last week the mean energy

$$\langle \varepsilon \rangle = \frac{\hbar\omega}{e^{+\beta\hbar\omega} - 1}$$

Differentiating:

$$\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 = -\frac{\partial}{\partial \beta}\langle \varepsilon \rangle = -\frac{\partial}{\partial \beta} \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

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

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

d) At low temperatures $e^{-\beta\hbar\omega} \ll 1$. So in this expression we may approximate

$$\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 \simeq (\hbar\omega)^2 e^{-\beta\hbar\omega}$$

$\boxed{e)}$ The probability of having n quanta is

$$P_n = \frac{e^{-n\beta\hbar\omega_0}}{Z} = e^{-\beta n\hbar\omega}(1 - e^{-\beta\hbar\omega})$$

Thus for $e^{-\beta\hbar\omega} \ll 1$ we have:

- $P_0 \simeq (1 - e^{-\beta\hbar\omega}) \simeq 1 - \text{small}$
- $P_1 \simeq e^{-\beta\hbar\omega}(1 + O(e^{-\beta\hbar\omega})) \simeq \text{small}$
- $P_2 = (e^{-\beta\hbar\omega})^2 (1 + O(e^{-\beta\hbar\omega})) \simeq 0$

this is $(\text{small})^2$ and can be dropped

Similarly, $P_3 \simeq e^{-3\beta\hbar\omega} \simeq (e^{-\beta\hbar\omega})^3 \simeq 0$

So

$$\langle \varepsilon \rangle = P_0 \cdot 0 + P_1 \hbar\omega = e^{-\beta\hbar\omega}\hbar\omega$$

$$\langle \varepsilon^2 \rangle = P_0 \cdot 0 + P_1 (\hbar\omega)^2 = e^{-\beta\hbar\omega}(\hbar\omega)^2$$

So

$$\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 = e^{-\beta\hbar\omega}(\hbar\omega)^2 + O(e^{-2\beta\hbar\omega})$$

$$\simeq e^{-\beta\hbar\omega}(\hbar\omega)^2$$

This agrees with part d)

Einstein Solid

$\boxed{a)}$ There are 3N oscillators. The Hamiltonian of the oscillator is

$$H = \underbrace{\frac{p^2}{2m}}_{} + \underbrace{\frac{1}{2} m \omega_0^2 x^2}_{}$$

two quadratic forms

So, $\bar{E} = 3N \times 2 \times \frac{1}{2} kT \simeq 3NkT$

Now $C_V = \partial E / \partial T$. So for $N = 1\,\text{mol}$ $N_A k_B = R$, and so

$$C_V^{1\,\text{mol}} = 3R$$

$\boxed{b)}$ $E = 3N \dfrac{\hbar \omega}{e^{\beta \hbar \omega} - 1}$ $\qquad \bar{n} = \dfrac{1}{e^{\beta \hbar \omega} - 1}$

$\boxed{c)}$ Solving for β from $\bar{n}$ (to make contact with later work in the next problem)

$$\frac{1}{\bar{n}} = e^{\beta \hbar \omega} - 1 \implies e^{\beta \hbar \omega} = 1 + \frac{1}{\bar{n}}$$

So

$$\beta \hbar \omega = \ln\left(\frac{1+\bar{n}}{\bar{n}}\right) \implies \frac{1}{kT} = \frac{1}{\hbar \omega} \ln\left(\frac{1+\bar{n}}{\bar{n}}\right)$$

$\boxed{d)}$ We know that

$$C_V = \left(\frac{\partial E}{\partial T}\right) \quad \text{with} \quad E = 3N \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

We use that for any quantity X

$$\frac{\partial X}{\partial T} = \frac{\partial X}{\partial \beta}\frac{\partial \beta}{\partial T} = \frac{\partial X}{\partial \beta}\frac{\partial}{\partial T}\left(\frac{1}{kT}\right)$$

$$\boxed{\frac{\partial X}{\partial T} = -k\beta^2 \frac{\partial X}{\partial \beta}}$$

So

$$C_V = -k\beta^2 \frac{\partial}{\partial \beta}\left(\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}\right)$$

Differentiating

$$C_V = 3Nk\beta^2 \frac{(\hbar\omega)^2 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

For 1 mol $N = N_A$ $\quad N_A k_B = R$

$$\boxed{C_V^{1m1} = 3R \frac{(\beta\hbar\omega)^2 \; e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}}$$

In the high temperature limit the mean # of quanta in the oscillator gets larger and larger. In this limit the dynamics should be classical.
(see previous homework)

Expanding for $\beta\hbar\omega \ll 1$ (high temperature), we approximate:

$$e^{\beta\hbar\omega} \simeq 1 + \beta\hbar\omega$$

And

$$C_V^{|m|} \simeq 3R \frac{(\beta\hbar\omega)^2 \, (1)}{(1+\beta\hbar\omega - 1)^2}$$

$$\boxed{C_V^{|m|} \simeq 3R}$$

this agrees with part (a) as it should

e) The hard materials have a larger $\omega_0 = \sqrt{k/m}$. They have, therefore, a larger spring constant, k. Because ω_0 is higher for diamond C_V will approach the classical limit $3R$ only at very high temperatures $kT \gg \hbar\omega_0$, when the number of vibrational quanta is large.

Einstein Model : Microcanonical Ensemble

e) $\Omega = \frac{(N+q-1)!}{q!\,(N-1)!} \simeq \frac{(N+q)!}{q!\,N!}$, Using Sterling

$$\ln\Omega \simeq (N+q)\ln(N+q) - \cancel{(N+q)} - q\ln q + \cancel{q} - N\ln N + \cancel{N}$$

we note that the mean occupation number is
$\bar{n} \equiv q/N$

$$\ln\Omega = N\left[(1+\bar{n})\ln N(1+\bar{n}) - \bar{n}\ln N\bar{n} - \ln N\right]$$

Looking at this carefully we collect all the ln N terms and the remaining:

cancel

$$\ln\Omega = N\left[\cancel{(1+\bar{n})\ln N} - \cancel{\bar{n}\ln N} - \cancel{\ln N}\right]$$

$$+ N\left[(1+\bar{n})\ln(1+\bar{n}) - \bar{n}\ln\bar{n}\right]$$

so

$$\Omega = e^{N\left[(1+\bar{n})\ln(1+\bar{n}) - \bar{n}\ln\bar{n}\right]}$$

$$\boxed{S = k\ln\Omega = Nk\left[(1+\bar{n})\ln(1+\bar{n}) - \bar{n}\ln\bar{n}\right]}$$

So

f) $\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial S}{\partial \bar{n}} \frac{\partial \bar{n}}{\partial E}$ $\qquad E = N \bar{n} \hbar \omega_0$

$$\frac{\partial E}{\partial \bar{n}} = N \hbar \omega_0$$

$$= \frac{1}{N \hbar \omega} \frac{\partial S}{\partial \bar{n}}$$

So

$$\frac{\partial S}{\partial \bar{n}} = Nk \left[\ln(1+\bar{n}) + (1+\bar{n}) \frac{1}{(1+\bar{n})} - \ln \bar{n} - \bar{n} \frac{1}{\bar{n}} \right]$$

$$= Nk \ln\left(\frac{1+\bar{n}}{\bar{n}}\right)$$

So

$$\frac{1}{T} = \frac{k}{\hbar \omega} \ln\left(\frac{1+\bar{n}}{\bar{n}}\right)$$

g) We can invert this

$$\frac{\hbar \omega}{kT} = \ln\left(\frac{1+\bar{n}}{\bar{n}}\right) \Rightarrow e^{\hbar \omega / kT} = 1 + \frac{1}{\bar{n}}$$

$$\boxed{\bar{n} = \frac{1}{e^{\hbar \omega / kT} - 1}}$$

← this agrees with the canonical approach discussed above.