3.3

a) $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

$K_T = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

$$\left.\begin{aligned} dS &= \frac{\delta Q}{T} \\ \delta Q &= c\, dT \end{aligned}\right\} \Rightarrow \begin{aligned} c_P &= T\left(\frac{\partial S}{\partial T}\right)_P \\ c_V &= T \cdot \left(\frac{\partial S}{\partial T}\right)_V \end{aligned}$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP =$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Maxwell relations

$$= \frac{c_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP =$$

$$= \frac{c_P}{T} dT - \alpha V dP$$

$$\Rightarrow c_P - c_V = \alpha V T \left(\frac{\partial P}{\partial T}\right)_V =$$

$$= \alpha V T \frac{\partial(P,V)}{\partial(T,V)} \frac{\partial(T,P)}{\partial(T,P)} =$$

$$= -\alpha V T \frac{\partial(V,P)}{\partial(T,P)} \frac{\partial(P,T)}{\partial(V,T)} =$$

$$= -\alpha V T \left(\frac{\partial V}{\partial T}\right)_P \Big/ \left(\frac{\partial V}{\partial P}\right)_T = V T \frac{\alpha^2}{K_T}$$

b) Ideal gas $\Rightarrow$ $PV = nRT$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{nRT}{P^2}$$

$$\Rightarrow \alpha = \frac{1}{V}\frac{nR}{P}$$

$$\Rightarrow c_p - c_v = -\frac{1}{V}\frac{nR}{P} V \frac{nR}{P} \cdot T \Big/ \left(-\frac{nRT}{P^2}\right) =$$

$$= nR$$

c)

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

for solids at room temperature

$$\left(\frac{\partial V}{\partial T}\right)_P \approx 0 \quad \Rightarrow \alpha \approx 0$$

$$\Rightarrow \quad c_p \approx c_v$$

3.5 $\quad E = \hbar\omega\left(n + \frac{1}{2}\right) \quad , \beta = \frac{1}{k_B T}$

$$Z = \sum_{n=0} e^{-\beta E} =$$

$$= \left[\sum_{n=0} e^{-n\beta\hbar\omega}\right] \cdot e^{\hbar\omega/2} =$$

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

$$E = -\frac{\partial}{\partial\beta} \ln Z = \frac{\partial}{\partial\beta} \ln\left(1 - e^{-\beta\hbar\omega}\right) + \underbrace{\frac{\hbar\omega}{2}}_{\to 0} =$$

$$= \frac{\hbar\omega \, e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} = \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1}$$

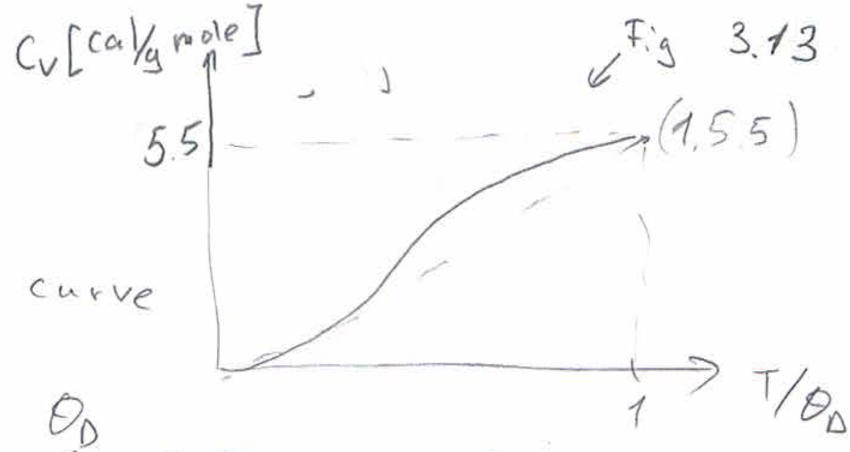
3.6 a) $\Theta_D^{Cu} = 340\ K$

$C_V = 3R$ (eq 3.24)

$E = C_V T = 3RT = 3 \cdot 8.3\ J/mol\,K\ (340K) =$

$= 8480\ J/mol$

b)



E - area under the curve

$$E = \int_0^{\Theta_D} C_V\, dT = \int_0^{\Theta_D} \frac{5.5}{\Theta_D} \cdot T = \frac{5.5}{2\Theta_D} \Theta_D^2 =$$

$$= \frac{5.5}{2} \Theta_D = \frac{5.5}{2} 340 = 935\ cal/mol =$$

$$= 3912\ J/mol$$

$\Rightarrow$ classical approach overestimates more than twice

c) Average energy per atom:

$$\langle E/_{atom} \rangle = 3912/_{6 \cdot 10^{23}} \quad J$$

$$\langle E/_{atom}/_{spring} \rangle = \frac{3912 \ J/mole}{6 \cdot 10^{23} \ mole^{-1} \cdot 3} = 4.6 \cdot 10^{-20} \ J$$

$$= \frac{1}{2} \omega_D^2 \ m \ x_{max}^2 = \frac{1}{2} \left(\frac{k_b \Theta_D}{\hbar} \right)^2 m \ x^2$$

$$\Rightarrow x_{max} = \sqrt{\frac{4.6 \cdot 10^{-20} \cdot 2 \cdot 1 \cdot (10^{-34})^2 \ 6 \cdot 10^{+23}}{(1.38 \cdot 10^{-23})^2 \cdot 340K \cdot 63.55}} =$$

$$= 7 \cdot 10^{-11} \ m$$

$$a_{copper} = 3.61 \ A^{\circ} = 3.61 \cdot 10^{-10} \ m$$

$\Rightarrow$ displacement is ~~much~~ smaller than interatomic distance.

$$\frac{X_{max}}{a_{copper}} \simeq 0.2$$

3.9

a) 1D $\Rightarrow$

$$\Rightarrow g(\omega) = \frac{L}{\pi} \frac{1}{v_s} \qquad (\text{eq } 3.14)$$

$$\int_0^{\omega_D} g(\omega)\, d\omega = N_A = \frac{L}{\pi} \omega_D \frac{1}{v_s}$$

$$\Rightarrow \omega_D = \frac{v_s \pi \cdot N_A}{L}$$

$$(\text{eq } 3.26)$$

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

$$\Rightarrow E = \int \bar{\epsilon}(\omega)\, g(\omega)\, d\omega =$$

$$= \frac{L}{\pi v_s} \int_0^{\omega_D} \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1}\, d\omega$$

$$C_e = \left(\frac{\partial E}{\partial T}\right) = \frac{L}{\pi v_s} \int_0^{\omega D} \frac{+\hbar\omega \frac{1}{T^2} \hbar\omega/k\, e^{\frac{\hbar\omega}{kT}}}{\left(e^{\hbar\omega/kT} - 1\right)^2}\, d\omega =$$

$$= \frac{+L\, \hbar^2}{\pi v_s\, kT^2} \int_0^{\omega_D} \frac{\omega^2 e^{\hbar\omega/kT}}{\left(e^{\hbar\omega/kT} - 1\right)^2}\, d\omega$$

$$T \to 0 \Rightarrow e^{\hbar\omega/kT} \gg 1$$

$$\Rightarrow c_V = \frac{+L\hbar^2}{\pi v_s T^2 k}\int_0^{\omega_D} \omega^2 e^{-\hbar\omega/kT}\, d\omega =$$

$$= \frac{+L\hbar^2}{\pi v_s T^2 k}\, \frac{e^{-\hbar\omega/kT}\left(-\cancel{\frac{\hbar}{kT}}\,\omega_D\left(\frac{\hbar\omega_D}{kT}+2\right)-2\right)+2}{\left(\hbar/kT\right)^3} \Rightarrow$$

$$\to \frac{+L\hbar^2\; k^3T^3\cdot 2}{\pi v_s T^2\, k\, \hbar^3} = \frac{+2L\; k^2 \cdot T}{\pi v_s}$$

$$T \to \infty \Rightarrow e^{\hbar\omega/kT} \approx 1 + \frac{\hbar\omega}{kT}$$

$$\Rightarrow c_V = \frac{L\hbar^2}{k\pi v_s T^2}\int_0^{\omega_D} \frac{\omega^2}{\left(\frac{\hbar\omega}{kT}\right)^2}\, d\omega =$$

$$= \frac{\cancel{L}\hbar^2\; k^2 \cancel{T^2}}{\pi v_s \cancel{T^2}\, k\, \cancel{\hbar^2}}\; \frac{v_s\pi \cdot N_A}{\cancel{L}} =$$

$$= R$$

b) $2\left(\frac{L}{\pi}\right)^2 \pi q\,dq = g(\omega)\,d\omega$

$\omega = q v_s \qquad d\omega = v_s\,dq$

$\Rightarrow g(\omega) = \frac{2L^2 \omega}{\pi v_s^2}$

$\bar{\epsilon} = \frac{\hbar\omega}{e^{\hbar\omega/kT}-1}$ (eq 3.26)

$E = \int \bar{\epsilon}\, g(\omega)\, d\omega =$

$= \frac{2L^2}{\pi v_s^2} \int_0^{\omega_D} \frac{\hbar\omega^2}{e^{\hbar\omega/kT}-1}\, d\omega$

$\Rightarrow c_v = \frac{2L^2\hbar}{\pi v_s^2} \int_0^{\omega_D} \frac{\omega^2 \frac{1}{T^2}\, \hbar\omega/k\; e^{\hbar\omega/kT}}{\left(e^{\hbar\omega/kT}-1\right)^2}\, d\omega$

$= \frac{2L^2\hbar^2}{\pi v_s^2 T^2 k} \int_0^{\omega_D} \frac{\omega^3\, e^{\hbar\omega/kT}\, d\omega}{\left(e^{\hbar\omega/kT}-1\right)^2}$

$$T \to 0 \Rightarrow e^{\hbar\omega/kT} \gg 1$$

$$\int_0^{\omega_D} g(\omega)\, d\omega = 2N_A$$

$$\frac{2L^2}{\pi v_s^2}\, \omega_D^2 \cdot \frac{1}{2} = 2N_A$$

$$\Rightarrow \omega_D = \sqrt{\frac{2N_A\, \pi v_s^2}{L^2}}$$

$$c_v = \frac{2L^2\hbar^2}{\pi v_s^2 T^2 k} \int_0^{\omega_D} \omega^3\, e^{-\hbar\omega/kT}\, d\omega \rightarrow$$

$$\rightarrow \frac{2L^2\hbar^2}{\pi v_s^2 T^2 k} \cdot \frac{3}{(\hbar/kT)^4} = \frac{6L^2T^2k^3}{\pi v_s^2 \hbar^2}$$

$$T \to \infty \quad e^{\hbar\omega/kT} \approx 1 + \frac{\hbar\omega}{kT}$$

$$\Rightarrow c_v = \frac{2L^2\hbar^2}{\pi v_s^2 T^2 k} \int_0^{\omega_D} \frac{\omega^3}{\left(\frac{\hbar\omega}{kT}\right)^2}\, d\omega =$$

$$= \frac{\cancel{2}\cancel{L^2}\cancel{\hbar^2}}{\cancel{\pi}\cancel{v_s^2}\cancel{T^2}\cancel{k} \cdot \cancel{\hbar^2}} \frac{\cancel{T^2}}{\cancel{2}} \frac{\cancel{2} \cdot N_A\, \cancel{\pi}\cancel{v_s^2}\, k^{\cancel{2}}}{\cancel{L^2}} = 2R$$

3.10

$$v_p = \frac{\omega}{q}$$

$$v_g = \frac{\partial \omega}{\partial q}$$

$$\omega = \omega_m \left|\sin\left(qa/2\right)\right|$$

$$v_p = \frac{\omega_m \left|\sin\left(qa/2\right)\right|}{q}$$

$$v_g = \frac{\omega_m \cos\left(\frac{qa}{2}\right) \cdot a}{2}$$

$q = 0 \iff \lambda$ big $\quad v_p = v_g$

$q = \frac{\pi}{a}$ edge of the Brillouin zone

$v_g = 0 \Rightarrow$ reflection $\Rightarrow$ standing wave.

$\omega_m = 1 \qquad a = 1$