1) Evaluate the second virial coefficient for a hard sphere model and a square well and estimate the Boyle temperature. (Chandler 7.13)

$$B_2 = -\frac{1}{2}\int 4\pi f(r) r^2 dr$$
$$f(r) = e^{-\beta u(r)} - 1$$

For a hard sphere model,

$$u(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases} \quad (1)$$

$$B_2 = -2\pi \int_0^\sigma (e^{-\beta\infty} - 1) r^2 dr - 2\pi \int_\sigma^\infty (e^{-\beta 0} - 1) r^2 dr$$
$$B_2 = -2\pi \int_0^\sigma (0 - 1) r^2 dr - 2\pi \int_\sigma^\infty (1 - 1) r^2 dr$$
$$B_2 = 2\pi \int_0^\sigma r^2 dr - 2\pi \int_\sigma^\infty (0) r^2 dr$$
$$B_2 = 2\pi \int_0^\sigma r^2 dr$$
$$B_2 = \frac{2\pi}{3}\sigma^3$$

Since this expression does not depend on T, there is no Boyle temperature.
For a square well model,

$$u(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon & \sigma < r < \sigma' \\ 0 & r > \sigma' \end{cases} \quad (2)$$

$$B_2 = -2\pi \int_0^\sigma (e^{-\beta\infty} - 1) r^2 dr - 2\pi \int_\sigma^{\sigma'} (e^{\beta\epsilon} - 1) r^2 dr - 2\pi \int_{\sigma'}^\infty (e^{-\beta 0} - 1) r^2 dr$$
$$B_2 = -2\pi \int_0^\sigma (0 - 1) r^2 dr - 2\pi \int_\sigma^{\sigma'} (e^{\beta\epsilon} - 1) r^2 dr - 2\pi \int_{\sigma'}^\infty (1 - 1) r^2 dr$$
$$B_2 = 2\pi \int_0^\sigma (1) r^2 dr - 2\pi \int_\sigma^{\sigma'} (e^{\beta\epsilon} - 1) r^2 dr - 2\pi \int_{\sigma'}^\infty (0) r^2 dr$$
$$B_2 = 2\pi \int_0^\sigma r^2 dr - 2\pi \int_\sigma^{\sigma'} (e^{\beta\epsilon} - 1) r^2 dr$$
$$B_2 = \frac{2\pi}{3}\sigma^3 - \frac{2\pi}{3}\sigma'^3 (e^{\beta\epsilon} - 1) + \frac{2\pi}{3}\sigma^3 (e^{\beta\epsilon} - 1)$$
$$B_2 = (\frac{2\pi}{3}\sigma^3 - \frac{2\pi}{3}\sigma'^3) e^{\beta\epsilon} - \frac{2\pi}{3}\sigma'^3$$

For the Boyle temperature,

$$B_2 = 0$$

Divide by the constants,

$$(\sigma^3 - \sigma'^3) e^{\beta\epsilon} - \sigma'^3 = 0$$

$$(\sigma^3 - \sigma'^3)e^{\beta\epsilon} = \sigma'^3$$

$$e^{\beta\epsilon} = \frac{\sigma'^3}{\sigma^3 - \sigma'^3}$$

$$\beta\epsilon = ln(\frac{\sigma'^3}{\sigma^3 - \sigma'^3})$$

$$\frac{\epsilon}{kT_B} = ln(\frac{\sigma'^3}{\sigma^3 - \sigma'^3})$$

$$T_B = \frac{\epsilon}{k} \div ln(\frac{\sigma'^3}{\sigma^3 - \sigma'^3})$$

2) Find both the high and low temperature limiting forms of the heat capacity according to the Einstein model. (McQuarrie 11.2)

$$C_v = 3Nk\frac{\theta^2}{T^2}\frac{exp(-\Theta/T)}{(1 - exp(-\Theta/T))^2}$$

For low temperatures,

$$(1 - exp(-\Theta/T)) \approx 1$$

$$C_v \approx 3Nk\frac{\theta^2}{T^2}exp(-\Theta/T)$$

For high temperatures,

$$exp(-\Theta/T) \approx 1$$

and

$$\frac{\Theta}{T} \approx 0$$

$$C_v \approx 3Nk(0)^2\frac{1}{(1-1)^2}$$

$$C_v \approx 3Nk\frac{0^2}{0^2}$$

$$C_v \approx 3Nk$$

3) Show that the entropy of a Debye crystal at low temperature is given by:

$$S = \frac{4\pi^4 Nk}{5}\frac{T^3}{\Theta^3}$$

(McQuarrie 11-31)
The energy of a Debye crystal is given by:

$$U = 9NkT\frac{T^3}{\Theta^3}\int_0^{\Theta/T}\frac{x^3}{e^x - 1}dx$$

where

$$x = \hbar\omega\beta$$

At low temperatures,

$$\frac{\Theta}{T} \approx infty$$

$$U = 9NkT\frac{T^3}{\Theta^3}\int_0^{\infty}\frac{x^3}{e^x - 1}dx$$

$$int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}$$

$$U = \frac{9}{15} \pi^4 NkT \frac{T^3}{\Theta^3}$$

$$C_v = \frac{dU}{dT}$$

$$C_v = \frac{12}{5} \pi^4 Nk \frac{T^3}{\Theta^3}$$

$$S = \int \frac{C_v}{T} dT$$

$$S = \frac{12\pi^4 Nk}{5\Theta^3} \int T^2 dT$$

$$S = \frac{12\pi^4 Nk}{5\Theta^3} \frac{T^3}{3}$$

$$S = \frac{4\pi^4 NkT^3}{5\Theta^3}$$

4) Show that $g(\nu)$ of a 1D Debye crystal agrees with:

$$g(\nu) = \frac{2N}{\pi} (\nu_{max}^2 - \nu^2)^{-1/2}$$

as ν goes to zero. (McQuarrie 11.33)

$$\lim_{\nu \to 0} g(\nu) = \frac{2N}{\pi} (\nu_{max}^2)^{-1/2} = \frac{2N}{\pi \nu_{max}}$$

For a 1D Debye crystal,

$$g(\nu) = \frac{Na}{\pi} \frac{1}{d\nu/dk}$$

$$\nu = \nu_{max} |sin(ka/2)|$$

$$|x| = \sqrt{x^2}$$

$$\nu = \nu_{max} \sqrt{sin^2(ka/2)}$$

Since we are concerned about low ν,

$$sin(ka/2) \approx= \frac{ka}{2}$$

$$\nu \approx \frac{\nu_{max} ka}{2}$$

$$\frac{d\nu}{dk} \approx \frac{\nu_{max} a}{2}$$

This expression can be combined with $g(\nu)$ to give:

$$g(\nu) \approx \frac{2N}{\pi \nu_{max}}$$