11. ***Heat capacity of solids in high temperature limit*.** Show that in the limit of $T >> \theta$ the heat capacity of a solid goes towards the limit of $C_V \rightarrow 3Nk$, in conventional units. To obtain higher accuracy when T is only moderately larger than θ, the heat capacity can be expanded as a power series in $1/T$, of the form

$$C_V = 3Nk_B \times \left[1 - \sum_n \frac{a_n}{T^n}\right] \quad (56)$$

Determine the first nonvanishing term in the sum. Check your result by inserting $T = \theta$ and comparing with Table 4.2.

Solution:

We know that the heat capacity is defined as

$$C_V = \left(\frac{\partial U}{\partial \tau}\right)_V$$

And from equation (38) the thermal energy of the phonons is

$$U = \frac{3\pi}{2}\int_0^{n_D} dn\, n^2 \frac{\hbar\omega_n}{\exp(\hbar\omega_n/\tau) - 1}$$

With the following identities

$$\omega_n = \frac{n\pi v}{L}$$

$$n_D = \left(\frac{6N}{\pi}\right)^{1/3}$$

$$\tau = k_B T$$

$$\theta = \frac{\hbar v}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{1/3}$$

The only place τ appears is in the integrand and we can differentiated before integration yielding

$$C_V = \frac{3\pi}{2}\int_0^{n_D} dn\, n^2 \frac{\hbar\omega_n}{[\exp(\hbar\omega_n/\tau) - 1]^2}\exp(\hbar\omega_n/\tau)\frac{\hbar\omega_n}{\tau^2}$$

$$= \frac{3\pi}{2}\int_0^{n_D} dn\, n^2 \left(\frac{\hbar\omega_n}{\tau}\right)^2 \frac{\exp(\hbar\omega_n/\tau)}{[\exp(\hbar\omega_n/\tau) - 1]^2}$$

Using the substitution

$$x = \frac{\hbar\omega_n}{\tau} = \frac{\hbar n\pi v}{\tau L}$$

$$dx = \frac{\hbar\pi v}{\tau L} dn$$

Yields

$$C_V = \frac{3\pi}{2} V \left(\frac{\tau}{\hbar\pi v}\right)^3 \int_0^{x_D} dx\, x^4 \frac{\exp(x)}{[\exp(x)-1]^2}$$

Where we have substituted V for L^3

To integrate the function we make use of the expansion

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots$$

Which gives for the integral

$$I = \int_0^{x_D} dx\, x^4 \frac{\exp(x)}{[\exp(x)-1]^2}$$

$$= \int_0^{x_D} dx\, x^4 \frac{1 + x + \frac{x^2}{2}}{[x + \frac{x^2}{2} + \frac{x^3}{6}]^2}$$

$$= \int_0^{x_D} dx\, x^2 \frac{1 + x + \frac{x^2}{2}}{[1 + \frac{x}{2} + \frac{x^2}{6}]^2}$$

Where only the first few terms in the expansions are retained. Squaring the denominator and again retaining on the first few terms gives

$$I = \int_0^{x_D} dx\, x^2 \frac{1 + x + \frac{x^2}{2}}{\left[1 + x + \frac{7x^2}{12}\right]}$$

Expanding the denominator in a Taylor series of the form

$$\frac{1}{1+y} = 1 + y\left(\frac{d}{dy}\frac{1}{1+y}\right)\Bigg|_{y=0} + \frac{1}{2!} y^2 \left(\frac{d^2}{dy^2}\frac{1}{1+y}\right)\Bigg|_{y=0} + \ldots$$

Where

$$y = x + \frac{7x^2}{12}$$

Gives

$$I = \int_0^{x_D} dx\, x^2 \left(1 + x + \frac{x^2}{2}\right)\left[1 - \left(x + \frac{7x^2}{12}\right) + \left(x + \frac{7x^2}{12}\right)^2\right]$$

$$= \int_0^{x_D} dx\, x^2 \left(1 + x + \frac{x^2}{2} - x - \frac{7x^2}{12} - x^2 + x^2\right)$$

$$= \int_0^{x_D} dx\, x^2 \left(1 - \frac{x^2}{12}\right)$$

Again retaining only the first few terms. The resulting integral is easily evaluated

$$I = \frac{1}{3} x_D^{\ 3} - \frac{1}{60} x_D^{\ 5}$$

Using the substitution of x and the definition of θ we see that

$$x_D = \frac{\hbar n_D \pi v}{\tau L} = \frac{\hbar \pi v}{\tau L}\left(\frac{6N}{\pi}\right)^{1/3} = \frac{\hbar v}{k_B T}\left(\frac{6N\pi^2}{V}\right)^{1/3} = \frac{\theta}{T}$$

And the heat capacity is

$$C_V = \frac{3\pi}{2} V \left(\frac{\tau}{\hbar \pi v}\right)^3 \left[\frac{1}{3}\left(\frac{\theta}{T}\right)^3 - \frac{1}{60}\left(\frac{\theta}{T}\right)^5\right]$$

Further simplification yields

$$C_V = \frac{3}{2\pi^2} V \left(\frac{k_B T}{\hbar v}\right)^3 \left[\frac{1}{3}\left(\frac{\theta}{T}\right)^3 - \frac{1}{60}\left(\frac{\theta}{T}\right)^5\right]$$

$$C_V = \frac{3}{6\pi^2} V \left(\frac{k_B T}{\hbar v}\right)^3 \left[\left(\frac{\theta}{T}\right)^3 - \frac{1}{20}\left(\frac{\theta}{T}\right)^5\right]$$

$$C_V = \frac{3Nk_B}{\theta^3} T^3 \left[\left(\frac{\theta}{T}\right)^3 - \frac{1}{20}\left(\frac{\theta}{T}\right)^5\right]$$

$$C_V = 3Nk_B \left[1 - \frac{1}{20}\left(\frac{\theta}{T}\right)^2\right]$$

In the limit of large T the heat capacity becomes

$$C_V = 3Nk_B$$

For smaller values of T using the power series expansion we can identify the coefficients as

$$C_V = 3Nk_B\left[1-\frac{1}{20}\left(\frac{\theta}{T}\right)^2\right] = 3Nk_B\times\left[1-\frac{a_1}{T}-\frac{a_2}{T^2}\right]$$

$$a_1 = 0$$

$$a_2 = \frac{\theta^2}{20}$$

When $T = \theta$

$$C_V = 3Nk_B\left[1-\frac{1}{20}\right]$$

Or:

$$C_V = 3\times 6.02205\times 10^{23}\,\text{mol}^{-1}\times 1.38066\times 10^{-23}\,\text{J K}^{-1}\times\left[1-\frac{1}{20}\right]$$

$$= 23.70\ \text{J K}^{-1}\text{mol}^{-1}$$

Which compares favorably with the value listed in Table 4.2 of 23.74 J K^{-1} mol^{-1}

12 . *Heat capacity of photons and phonons*. Consider a dielectric solid with a Debye temperature equal to 100 K and with 10^{22} atoms cm^3. Estimate the temperature at which the photon contribution to the heat capacity would equal to the phonon contribution at 1 K.

Solution:

From equation 47a the heat capacity of a low temperature dielectric is

$$C_V = \frac{12\pi^4 N k_B}{5}\left(\frac{T}{\theta}\right)^3$$

And from equation 20 the energy of a photon gas is

$$U = \frac{\pi^2}{15\hbar^3 c^3} V k_B{}^4 T^4$$

Which gives for the heat capacity

$$U = \frac{\pi^2}{15\hbar^3 c^3} V \tau^4$$

Since the heat capacity is defined as

$$C_V = \left(\frac{\partial U}{\partial \tau}\right)_V$$

The heat capacity for the photon gas is

$$C_V = \frac{4\pi^2}{15\hbar^3 c^3} V \tau^3$$

Setting the two heat capacity equal to each other we can solve for the temperature

$$C_V^{photons} = C_V^{phonons}$$

$$\frac{4\pi^2 k_B}{15\hbar^3 c^3} V \left(k_B T_{photon}\right)^3 = \frac{12\pi^4 N k_B}{5}\left(\frac{T_{phonon}}{\theta}\right)^3$$

Substituting values

$$\frac{V\left(1.38066\times10^{-16}\,\text{erg K}^{-1}\,T_{photon}\right)^3}{3(1.05459\times10^{-27}\text{ erg s})^3(2.997925\times10^{10}\text{cm s}^{-1})^3}=3\pi^2 10^{22}\,\text{atoms cm}^{-3}V\left(\frac{1\text{ K}}{100\text{ K}}\right)^3$$

$$\left(T_{photon}\right)^3=1.067\times10^{16}\,\text{K}^3$$

$$T_{photon}\approx 220{,}000\text{ K}$$

13. ***Energy fluctuations in a solid at low temperatures.*** Consider a solid of N atoms in the temperature region in which the Debye T^3 law is valid. The solid is in thermal contact with a heat reservoir. Use the results on energy fluctuations from Chapter 3 to show that the root mean square fractional energy fluctuation $\mathscr{F}$ is given by

$$\mathscr{F}^2 = \left\langle \left(\varepsilon - \langle\varepsilon\rangle\right)^2 \right\rangle / \langle\varepsilon\rangle^2 \approx \frac{0.07}{N}\left(\frac{\theta}{T}\right)^3$$

Suppose that $T = 10^{-2}$ K; $\theta - 200$ K; and $N \approx 10^{15}$ for a particle 0.01 cm on a side; then $\mathscr{F} \sim 0.02$. At 10^{-5} K the fractional fluctuation in energy is of the order unity for a dielectric particle of volume 1 cm^3.

From Chapter 3 equation 89 we learn that

$$\left\langle \left(\varepsilon - \langle\varepsilon\rangle\right)^2 \right\rangle = \tau^2 \left(\frac{\partial U}{\partial \tau}\right)_V$$

And from Chapter 3 equation 14

$$\langle\varepsilon\rangle \equiv U$$

Which yields for root mean square fractional energy fluctuation

$$\mathscr{F}^2 = \frac{\tau^2 \left(\frac{\partial U}{\partial \tau}\right)_V}{U^2}$$

The Debye T3 law is the low temperature limit and gives from Chapter 4 equations 46 and 47a the energy

$$U \approx \frac{3\pi^4 N \tau^4}{5 k_B^3 \theta^3}$$

And heat capacity

$$C_V = \frac{12\pi^4 N k_B}{5}\left(\frac{T}{\theta}\right)^3$$

Which allows us to calculate

$$\mathscr{F}^2 = \frac{\tau^2 \left(\frac{\partial U}{\partial \tau} \right)_V}{U^2} = \frac{\tau^2 \frac{3\pi^4 N}{5k_B^3\theta^3} 4\tau^3 k_B}{\left(\frac{3\pi^4 N k_B T^4}{5\theta^3} \right)^2} = \frac{\left(k_B T\right)^2 \frac{12\pi^4 N k_B^2}{5} \left(\frac{T}{\theta} \right)^3}{\left(\frac{3\pi^4 N k_B T^4}{5\theta^3} \right)^2}$$

Simplifying yields

$$\mathscr{F}^2 \approx \frac{20}{3\pi^4} \frac{1}{N} \left(\frac{\theta}{T} \right)^3$$

Or

$$\mathscr{F}^2 \approx \frac{0.07}{N} \left(\frac{\theta}{T} \right)^3$$

14, ***Heat capacity of liquid ^{4}He at low temperature***. The velocity of longitudinal sound waves in liquid ^{4}He at temperatures below 0.6K is 2.383×10^4 cm s^{-1}. There are no transverse sound waves in the liquid. The density is 0.145 g cm^{-3}. (a) Calculate the Debye temperature. (b) Calculate the heat capacity per gram on the Debye theory and compare with the experimental value $C_V = 0.0204\times T^3$, in J g^{-1} K^{-1}. The T^3 dependence of the experimental value suggests that phonons are the most important excitations in liquid ^{4}He below 0.6K. Note that the experimental value has been expressed per gram of liquid. The experiments are due to J. Wiebes, C. G. Niels-Hakkenberg, and H. C. Krammers, Physca **23**, 625 (1957).

Solution:

The Debye temperature is defined in equation 44

$$\theta = \frac{\hbar v}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{1/3}$$

Substituting values

$$\theta = \frac{(1.05459\times10^{-27}\,\text{erg s})(2.383\times10^{4}\,\text{cm s}^{-1})}{1.38066\times10^{-16}\,\text{erg K}^{-1}}\left(6\pi^2\frac{0.145\text{ g cm}^{-3}}{4\text{ g mol}^{-1}}6.02205\times10^{23}\,\text{mol}^{-1}\right)^{1/3}$$

$$\theta = 19.8\text{ K}$$

The heat capacity is from equation 47b

$$C_V = \frac{12\pi^4 N k_B}{5}\left(\frac{T}{\theta}\right)^3$$

Substituting values

$$C_V = \frac{12\pi^4 6.02205\times10^{23}\,\text{mol}^{-1}}{5}1.38066\times10^{-23}\,\text{J K}^{-1}\left(\frac{T}{19.8\text{ K}}\right)^3$$

$$C_V = 0.249\times T^3\text{ J mol}^{-1}\text{ K}^{-1}$$

Converting to grams using the atomic weight

$$C_V = 0.249\times T^3\text{ J mol}^{-1}\text{ K}^{-1}/4\text{ g mol}^{-1}$$

$$C_V = 0.062\times T^3\text{ J g}^{-1}\text{ K}^{-1}$$

Compare this value to the value calculated in the Wiebes et al. article

$$C_V = \frac{16}{15}\pi^5\frac{k_B^4}{\hbar^3}\frac{1}{\rho}\frac{T^3}{v^3}$$

Which arrived at considering that only the longitudinal waves are present and the transverse waves are absent. Substituting values gives

$$C_V = \frac{16}{15}\pi^5 \frac{(1.38066\times10^{-23}\,\mathrm{J\,K^{-1}})^4}{(6.62618\times10^{-34}\,\mathrm{J\,s})^3} \frac{1}{0.145\ \mathrm{g\ cm^{-3}}} \frac{T^3}{(2.383\times10^4\,\mathrm{cm\ s^{-1}})^3}$$

$$C_V = 0.0224\times T^3\ \mathrm{J\ g^{-1}\ K^{-1}}$$