WS14/15 Condensed Matter Physics I
Exercise 2. Phonons

Date: 23/10/2014   Handover: 28/10/2014

Notice*: In solving the proposed exercises clearly motivate the passages to reach the result. The use of clear and compact notation is greatly encouraged, as well as the systematic use of dimensional checks of the expressions and results. When you are asked to "evaluate" something this means to provide a numerical evaluation of the expression. In this case, at times, it might be necessary to indicate a parameter whose explicit numerical value is not provided, i.e. $\omega_c = 1.76\,H$ (Gauss) Hertz. Otherwise specified, all the evaluations are to be given with 3 significant figures.*

2.1   Specific heat of an element   (6 pts)

In figure 1 the specific heat of a unknown element is shown.

1. Explain why this data can be described satisfactorily by the Debye approximation.

    [The specific heat reaches a plateau at high temperature, while at low temperature it behaves like T^3. This can be readily verified in the logarithmic plot, by extending with a ruler the power law (i.e. straight line in the logplot) behavior at low T and noticing that, as the temperature spans a decade (10-100 K) the specific heat spans three (1-1000 J $\mathrm{Kg}^{-1}\mathrm{K}^{-1}$).]

2. Using the Debye model and knowing that at high temperature the specific heat is 234.4 J $\mathrm{Kg}^{-1}\mathrm{K}^{-1}$ identify the element.

    [Let us consider 1 Kg of substance. Therefore the heat capacity is C=234.4 J K^{-1}. According to the high temperature limit (Dulong-Petit Law) this is equal to 3NR, where N is the number of moles in 1 Kg of substance and R=8.3145 J $\mathrm{K}^{-1}\,\mathrm{mol}^{-1}$. Therefore we obtain
    $N = \frac{C}{3R} = 9.397$ mol. This corresponds to a molar weight of $M_{mol} = \frac{1000}{9.937} = 100{,}63\ \mathrm{g\ mol}^{-1}$. With a quick check on a periodic table we find that the nearest molar weight is that of silver.]

3. Using the plots evaluate the Debye temperature, the sound velocity, its number density (number of atoms per unit volume) and, from the result of point 1, its mass density.
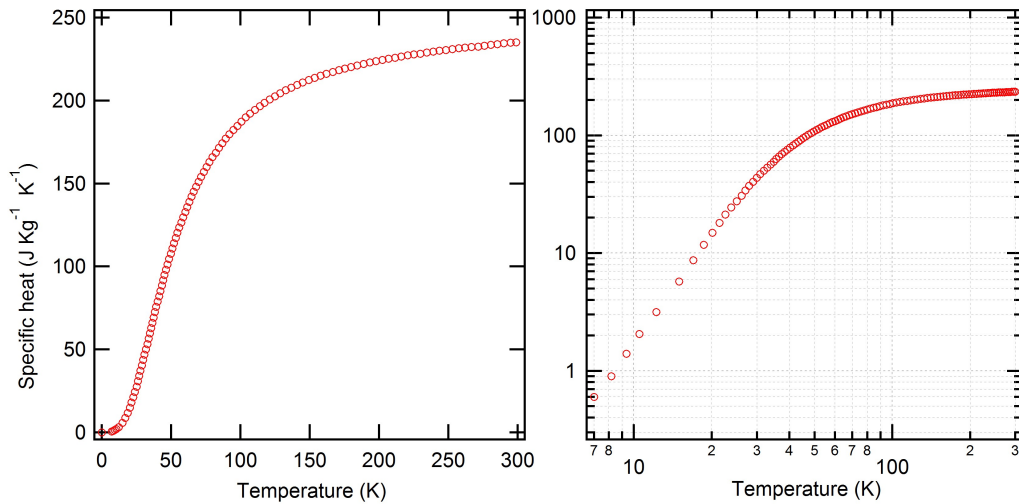
Figure 1: Specific heat of an uncknown element in linear (left) and logaritmic (right) scale.

2.2   Stability of D-dimensional crystal at T>0   (20 pts)

Consider a harmonic crystal with a single atom per cell in D dimensions. (of course we are interested in the cases D=1,2,3).

1. Show that the low-frequency phononic density of states behaves like $g(\omega) = A\omega^{D-1}$. Assume $\omega_s(\mathbf{k}) = c_s(\hat{\mathbf{k}})k$ for $\omega < \omega_c$. You should get $A = c^{-D}D\Omega_D/(2\pi)^D$ with Ω_D the D-dimensional solid angle and c an appropriate angle- and polarization- average of $c_s(\hat{\boldsymbol{k}})$. Give an expression for c.

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$$g(\omega) = \frac{1}{(2\pi)^D} \sum_s \int d\Omega_D \frac{1}{[c_s(\hat{\boldsymbol{k}})]^D} \int du\, u^{D-1} \delta(\omega - u) = \frac{\omega^{D-1}}{(2\pi)^D} \sum_s \int d\Omega_D \frac{1}{[c_s(\hat{\boldsymbol{k}})]^D}$$

By multiplying and dividing by $D\Omega_D$ we obtain finally $g(\omega) = A\omega^{D-1}$, where $A = c^{-D} D\Omega_D/(2\pi)^D$, and $c^{-D} = \frac{1}{S\Omega_D} \sum_s \int d\Omega_D \frac{1}{[c_s(\hat{\boldsymbol{k}})]^D}$.

NB. A compact expression for the D- dimensional solid angle is $\Omega_D = \frac{2\pi^{D/2}}{\Gamma(D/2)}$.]

2. Let us consider now the mean square displacement from the atomic equilibrium position

$$\overline{\mathbf{u}^2} = \frac{1}{N} \sum_{\mathbf{R}} \langle \mathbf{u}^2(\mathbf{R}) \rangle,$$

with $\langle \dots \rangle$ the thermal average at a fixed temperature. Express $\overline{\mathbf{u}^2}$ as a sum over the normal modes frequency.

[Hint: (i) express the coordinates as a sum of the normal modes $\mathbf{u}(\mathbf{R}) = (1/\sqrt{N}) \sum_{\mathbf{k},s} \mathbf{u}_s(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{R}}$, with $\mathbf{u}_s(\mathbf{k})$ the normal coordinates and $\mathbf{k}$ belonging to the FBZ; (ii) $\mathbf{u}_s(\mathbf{k}) \propto \boldsymbol{\epsilon}_s(\mathbf{k})$, and $\boldsymbol{\epsilon}_s(\mathbf{k}) \propto \boldsymbol{\epsilon}_s(-\mathbf{k})$; (iii) Because of the virial theorem, at a given temperature the average value of the potential energy of a normal mode is half the value of the average of the total energy $\hbar\omega_s(\mathbf{k})(n_s(\mathbf{k}) + 1/2)$.]

[Introducing the normal modes we have

$$\overline{\mathbf{u}^2} = \frac{1}{N^2} \sum_{\mathbf{R}} \sum_{\mathbf{k}\mathbf{k}'SS'} \langle \mathbf{u}_s(\mathbf{k}) \cdot \mathbf{u}_{s'}(\mathbf{k}') \rangle e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{R}}$$

Now we remember that

$$\frac{1}{N} \sum_{\mathbf{R}} e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{R}} = \delta(\mathbf{k} + \mathbf{k}')$$

And that since $\mathbf{u}_s(\mathbf{k}) \propto \boldsymbol{\epsilon}_s(\mathbf{k})$ the polarizations are mutually orthogonal we obtain

$$\overline{\mathbf{u}^2} = \frac{1}{N} \sum_{\mathbf{k}S} \langle \mathbf{u}_s^2(\mathbf{k}) \rangle = \frac{\hbar}{2NM} \sum_{\mathbf{k}S} (n_s(\mathbf{k}) + 1/2) / \omega_s(\mathbf{k})$$

The last passage has been perfomerd using the virial theorem (hint iii) $\langle \mathbf{u}_s^2(\mathbf{k}) \rangle = \frac{\hbar}{2M\omega_s(\mathbf{k})} (n_s(\mathbf{k}) + 1/2)$]

3. Express now $\overline{\mathbf{u}^2}$ as a frequency integral, introducing the density of states.

[

$$\overline{\mathbf{u}^2} = \frac{\hbar}{2NM} \sum_{\mathbf{k}S} (n_s(\mathbf{k}) + 1/2) / \omega_s(\mathbf{k}) = \frac{\hbar}{2M} \int_0^{\omega_c} d\omega [n(\omega) + 1/2] \, g(\omega)/\omega$$

]

4. Specialize the formula found in the preceeding point to a finite system, simply by introducing a lower cutoff frequency limiting the frequency integral to $\omega > \omega_t = 2\pi c/L$. Here $L = N^{1/D}/\rho^{1/D}$, with ρ the atomic density.

5. Evaluate now for $T > 0$ the dominant contribution to $\overline{\mathbf{u}^2}$ due to the low frequency modes $(\omega_t < \omega < \omega_c)$, in the regime for which $\beta\hbar\omega \ll 1$.

[The thermal average of the phonon occupation number is the Bose distribution. Therefore:

$$\overline{\mathbf{u}^2} = \frac{\hbar}{2M} \int_{\omega_t}^{\omega_c} d\omega \left[\frac{1}{e^{\beta\hbar\omega} - 1} + 1/2 \right] g(\omega)/\omega \approx \frac{A\hbar}{2M} \int_{\omega_t}^{\omega_c} d\omega \left[1/2 + \frac{1}{\beta\hbar\omega} \right] \omega^{D-2}$$

$$= \frac{A\hbar}{2M} \left[\frac{1}{2} \int_{\omega_t}^{\omega_c} d\omega\, \omega^{D-2} + \frac{1}{\beta\hbar} \int_{\omega_t}^{\omega_c} d\omega\, \omega^{D-3} \right]$$

6. What happens to $\overline{\mathbf{u}^2}$ for $D = 2$ when $N \to \infty$? What does that mean for the stability of the system?

[For D=2 the first integrand is the unit, while the second is ω^{-1}. Therefore the result is:

$$\overline{\mathbf{u}^2} = \frac{A\hbar}{2M} \left[\frac{\omega_c - \omega_t}{2} + \frac{1}{\beta\hbar} \log\frac{\omega_c}{\omega_t} \right].$$

This means that the system is thermodynamically stable at zero temperature ONLY, where the thermal fluctuations, with their logarithmic divergence, vanish.

7. Same question as in point 6 but with $D = 1$.

[For D=1 the first integral has a logarithmic singularity, while the second integral is divergent as ω^{-1}:

$$\overline{\mathbf{u}^2} = \frac{A\hbar}{2M} \left[\log\frac{\omega_c}{\omega_t} + \frac{1}{\beta\hbar} \left(\frac{1}{\omega_t} - \frac{1}{\omega_c} \right) \right],$$

This means that the fluctuations diverge at the thermodynamic limit even at zero temperature (quantum fluctuations). This means that a one dimensional system with one atom per cell is NOT thermodynamically stable, even at zero temperature.

2.3 1D rare gas chain   (10 pts)

Consider a 1D chain of Xenon atoms. Assume a pair interaction defined by the Lennard-Jones potential $\phi(|x|) = 4\epsilon[(\sigma/x)^{12} - (\sigma/x)^6]$. Assume atoms are evenly spaced at equilibrium (spacing $x_n^0 = na$) and that they can oscillate around equilibrium position ($x_n = x_n^0 + u_n$, with $u_n \ll a$). You can find the value of Lennard-Johnes parameters for Xenon in the Ashcroft-Mermin.

1. Calculate the energy per particle $e(a)$ for a given equilibrium spacing, as a function of ϵ and σ. [*Hint: approximating each of the sums $\zeta(p) = \sum_{n=1}^{\infty} n^{-p}, p = 6,12$ with the first 3 terms of the series we obtain $\zeta(6) = 1.02$ and $\zeta(12) = 1.00$*].

[the energy per particle is found by summing the interaction potential between the particles and all its n-th neighbors in the chain:

$$u(a) = \sum_n 4\epsilon[(\sigma/na)^{12} - (\sigma/na)^6] = 4\epsilon[(\sigma/a)^{12} - 1.02(\sigma/a)^6]$$

]

2. Calculate the equilibrium spacing as a function of σ and in Angrstrom.

[the condition for equilibrium is $\frac{du}{da} = 0$, therefore

$$6.12 - 12(\sigma/a)^6 = 0 \text{ i.e. } a = \sigma(12/6.12)^{1/6} \approx 1,12\sigma = 4.46 \text{ Å}.$$

We used here the value $\sigma = 3.98$ Å (Ashcroft Table 20.1).]

3. Consider now a nearest-neighbor approximation. Calculate the sound velocity for the acoustic phonons.

[The acoustic phonon dispersion relation is $\omega(k) = \sqrt{\frac{4K}{M}} \left| \sin \frac{ka}{2} \right|$, where M is the atomic mass and K is the second derivative of the interaction potential. In this case

$$K = \phi''(a) = \frac{24\epsilon}{\sigma^2}\left[26\left(\frac{\sigma}{a}\right)^{14} - 7\left(\frac{\sigma}{a}\right)^8 \right].$$

To simplify things we use Hartree units here: $e = \hbar = m_e = 1$, measuring distances in units of the Bohr radius (0.53 Angstrom) and Energies (and frequencies) in Hartree (27.1 eV). We will convert results at the end. In these units $\epsilon = 0.014 \, eV = 5.17 \times 10^{-4}$ Hartree, and $\sigma = 3.65$ Å $= 6.89$ Bohrs. Therefore we have

$K = \phi''(a) = 2.61 \times 109.72 \times 10^{-4} = 2.86 \times 10^{-2}$ Hartree Bohr^{-2}. Now the mass of a Xe atom is $M = 2.39 \times 10^{+5} \, m_e$. The sound velocity for low k is

$$c = a\sqrt{\frac{K}{M}} = \cdots = 2.90 \times 10^{-3} = 6,35 \times 10^3 \, m \, s^{-1}$$

In Hartree units the speed is a dimensionless number and the speed of light as the value 137. Therefore we can covert the sound velocity in SI units.]

4. Evaluate the zone boundary frequency in Hertz.

[The zone boundary frequency is of course $\omega_{max} = 2\sqrt{\frac{K}{M}} = 6,91 \times 10^{-4}$ Hartree = 18,7 meV = 4.52 THz.]