## VIBRATIONS AND PHONONS
### ───────── FYS3410: PROBLEM SHEET 2 ─────────

CANDIDATE 33

### 2. DENSITY OF STATES (DOS) FOR PHONONS

The phonon density of states in a one-dimensional array of $N$ atoms is derived in the following.

2.a. **DOS as a function of wave-vector.** One can view the one-dimensional array of atoms as a ring where the first and the last atom is connected to each other. Such a boundary condition is known as a Born-von Karman boundary condition. This boundary implies that atom number $n$ is the same atom as atom number $n + N$. The displacement of this atom is

$$\delta x_n = \delta x_{n+N}.$$

Applying Bloch's theorem[1] to this relation gives

$$\delta x_1 e^{ikan} = \delta x_1 e^{ika(n+N)},$$

where $k$ is the wave-vector and $a$ is the lattice parameter. To satisfy this condition we must have

$$1 = e^{ikaN} = \cos(kaN) + i\sin(kaN),$$

which only is satisfied if

$$2\pi\nu = kaN, \quad \nu = 1, 2, \ldots, N$$

which gives

$$k = \frac{2\pi}{Na}\nu.$$

The separation between allowed solution ($k$-values) is therefore

$$(1) \qquad \Delta k = \frac{2\pi}{Na}.$$

Thus, in one dimension the density of states is

$$(2) \qquad D(k) = \frac{1}{\Delta k} = \frac{Na}{2\pi} = \frac{L}{2\pi}.$$

One can easily see that the density of states (DOS) is independent of $k$, so the density of modes in $k$-space is uniformly distributed.

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[1] $\psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{r})$

2.b. **DOS as a function of angular frequency.** A one-dimensional lattice with one atom in the basis can be modelled as a harmonic chain, where one imagines a spring connecting all the atoms. The dipsersion relation then becomes

$$(3) \qquad \omega = \omega_0 \sin \frac{ka}{2}, \quad \omega_0 = 2\sqrt{\frac{g}{m}}$$

where $\omega$ is the angular frequency, $g$ is the spring constant and $m$ is the mass of each atom.

One can change between one density of states to the other by way of the following formula

$$(4) \qquad D(\omega)d\omega = D(k)dk = \frac{Na}{2\pi}dk.$$

which can be rewritten to include the group velocity

$$(5) \qquad D(\omega)d\omega = \frac{Na}{2\pi}\frac{dk}{d\omega}d\omega = \frac{Na}{2\pi}\frac{d\omega}{v_g}.$$

The group velocity is

$$(6) \qquad v_g = \frac{dw}{dk} = \omega_0\frac{a}{2}\cos\frac{ka}{2}.$$

This equation is to be inserted in equation 5, but first we also need a function of $\omega$ instead of $k$ which is found by inverting equation 3

$$\omega = \omega_0 \sin\frac{ka}{2}$$
$$\frac{\omega}{\omega_0} = \sin\frac{ka}{2}$$
$$\frac{ka}{2} = \arcsin\frac{\omega}{\omega_0}$$
$$k = \frac{2}{a}\arcsin\frac{\omega}{\omega_0}.$$

This can now be inserted into the group velocity

$$v_g = \omega_0\frac{a}{2}\cos\left(\frac{a}{2}\frac{2}{a}\arcsin\frac{\omega}{\omega_0}\right)$$
$$= \omega_0\frac{a}{2}\sqrt{1 - \left(\frac{\omega}{\omega_0}\right)^2}.$$

inserting this expression into 5 yields

$$(7) \qquad D(\omega) = \frac{N}{\pi\omega_0}\frac{1}{\sqrt{1 - \left(\frac{\omega}{\omega_0}\right)^2}}$$

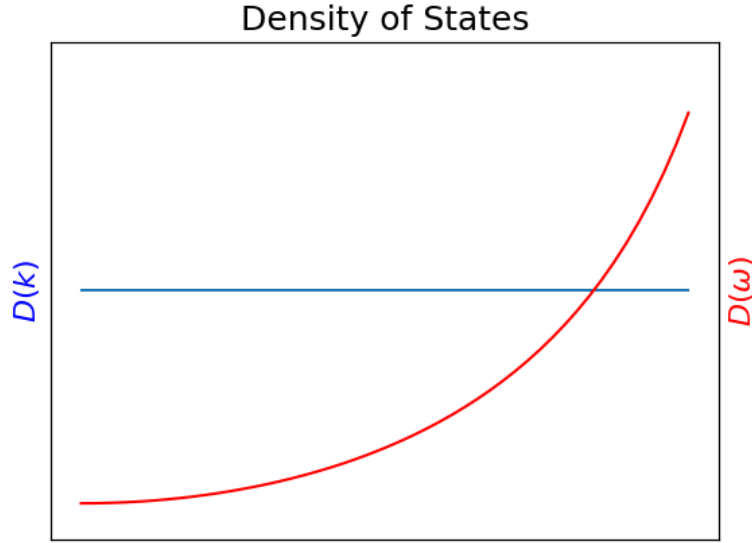which is the density of states as a function of angular frequency.

FIGURE 1. Comparison of density of states. $D(k)$ on the left axis and $D(\omega)$ on the right.

2.c. **Comparison of DOS measures.** A comparison of the two DOS measures that has been derived is shown in figure 1. The first $y$-axis is used for $D(k)$, and the second for $D(\omega)$. Because the density of states for $k$, $D(\omega)$ is constant for all $k$, this is much easier to deal with than the ever changing $D(\omega)$. The much more stable density of states i $k$-space is reason enough to use $D(\omega)$, but this one also has a closer connection with reciprocal space and diffraction patterns.

## 3. DIFFERENT MODELS FOR TEMPERATUR-HEAT CAPACITY DEPENDENCE

In the outline of the following models I will be very brief, and not fully derive the models, but rather give a more qualitative description.

3.a. **Dulong-Petit.** The Dulong-Petit law is a thermodynamic rule proposed in 1819 by French physicists Pierre Louis Dulong and Alexis Thrse Petit. They assume that every mode oscillates according to a classical harmonic oscillator, with continuous energy. In such a classical treatment, the thermal energy density is

$$(8) \qquad u = \frac{1}{V}\frac{\int dV e^{-\beta H} H}{\int dV e^{-\beta H}} = -\frac{1}{V}\frac{\partial}{\partial \beta}\ln \int dV e^{-\beta H}$$
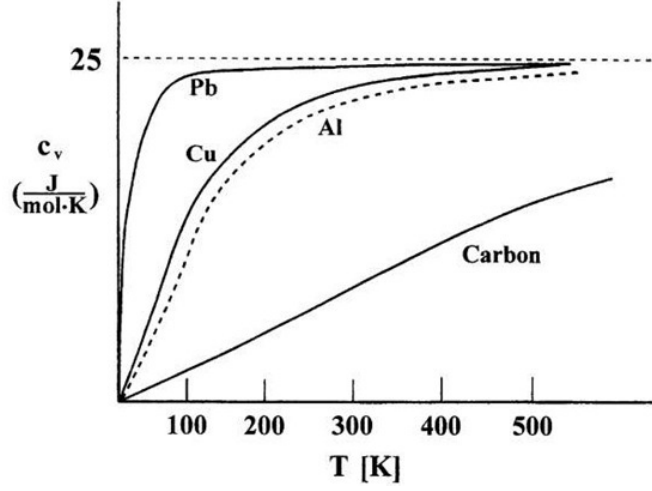
FIGURE 2. Measured heat capacities for lead, copper, aluminium and carbon. The horizontal line is the classical Dulong and Petit value.

where $\beta = 1/k_B T$ and $H$ is the enthalpy. By making a change of variables, one finds that the integral equates to

$$(9) \qquad\qquad u = u_{eq} + 3nk_B T,$$

which yields the heat capacity

$$(10) \qquad\qquad C_v = \frac{\partial u}{\partial T} = 3nk_B.$$

The heat capacity is a straight line, and measured heat capacities come quite close to the Dulong and Petit value. However, when temperature drops, the heat capacity falls well below the Dulong and Petit value. Moreover, when the temperature gets large, it seems fairly clear that the curve never quite reaches the precise value, as can be seen in figure 2. In conclusion, the law of Dulong and Petit is a reasonable approximating for higher temperatures.

3.b. **Einstein.** The Einstein model for the solid employs quantum harmonic oscillators (QHO), where the eigenvalue energies of a single oscillator is

$$(11) \qquad\qquad E_n = \hbar\omega \left( n\frac{1}{2} \right).$$

Furthermore, the model assumes that the atoms in the crystal are non-interaction.

The main difference from the Dulong and Petit model, however, is that the QHO energy levels are quantized, as $n$ in the equation above can only have integer values.

In one dimension the partition function becomes

$$(12) \qquad Z_{1D} = \sum e^{-\beta\hbar\omega(n+1/2)},$$

and from this stems the expected energy

$$(13) \qquad \langle E \rangle = -\frac{1}{Z_{1D}}\frac{\partial Z_{1D}}{\partial\beta} = \frac{\hbar\omega}{2}\coth\left(\frac{\beta\hbar\omega}{2}\right) = \hbar\omega\left(n_B(\beta\hbar\omega) + \frac{1}{2}\right),$$

where $n_B$ is the Bose occupation factor

$$n_B = \frac{1}{e^x - 1}.$$

It is easy to fathom that $\langle E_{3D} \rangle = 3\langle E_{1D} \rangle$, as each atom is oscillating in all three dimensional directions. Thus, the heat capacity becomes

$$(14) \qquad C_v(T) = \frac{\partial\langle E_{3D}\rangle}{\partial T} = 3_k B(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2},$$

where it is traditional to define the Einstein temperature as $T_{Eintstein} = \hbar\omega/k_B$. We can see that this expression *does* depend on the temperature.

The Einstein model uses quantized energy levels and as a consequence becomes dependent on temperature. The heat capacity derived from this model becomes similar to the Petit and Dulong value for hight temperatures, but will fall as the temperature get lower. This is more in accordance with the experimental data shown in figure 2. However, the heat capacity values provided by the model was found to fall too quickly for the very lowest temperatures.

3.c. **Debye.** Petrus Josephus Wilhelmus Debije[2] theorised that the oscillation modes of a solid were waves with frequencies $\omega(\mathbf{k}) = v|\mathbf{k}|$ with $v$ the sound velocity. For each $\mathbf{k}$ there are three possible oscillation modes, one for each dimension. This enables one to write an expression entirely analogous to Einstein's expression

$$(15) \qquad \langle E \rangle = 3\sum_k \hbar\omega(\mathbf{k})\left(n_b(\beta\omega(\mathbf{k})) + \frac{1}{2}\right).$$

This sum can be approximated by an integral[3] eventually finding

$$(16) \qquad C_v = \frac{\partial\langle E\rangle}{\partial T} = Nk_B\frac{(k_BT)^3}{(\hbar\omega_d)^3}\frac{12\pi^4}{4} \propto T^3.$$

The Debye frequency, $\omega_d$ in this expression is sometimes replaced by the Debye temperature, $T_{Debye} = \hbar\omega_d/k_B$.

Because the oscillations of the Debye models give slightly different results than that of the Einstein model, the Debye model yields better results than the Einstein model at low temperatures. See figure 3 for a comparison.

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[2]Yes, that is is original name. He changed the way he wrote it at some point in his life.

[3]The full derivation of this model is given in the final section of this document.
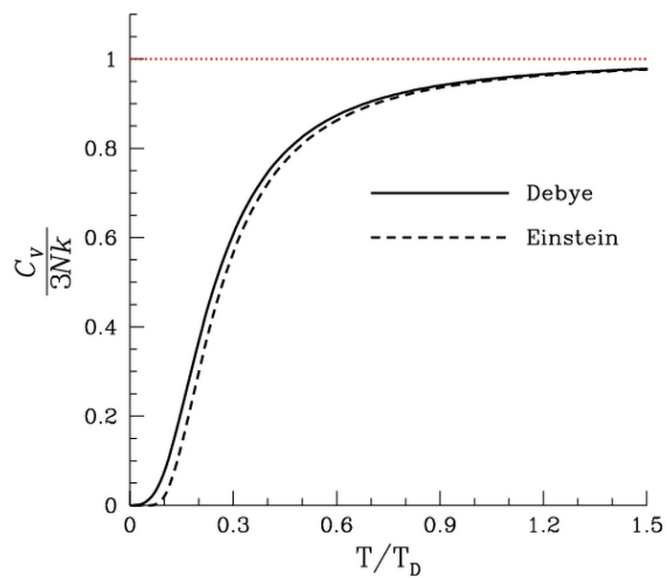
FIGURE 3. A comparison of the Einstein and Debye models for heat capacity.

6. THERMAL CONDUCTIVITY