§5 – <u>Thermal Properties</u>

5.1 Thermal Excitation of Phonons

Phonons are created and destroyed by thermal excitation and make a significant contribution to the heat capacity:

$$C = \underbrace{C_{\text{phonon}}}_{\text{all solids}} + \underbrace{C_{\text{electrons}}}_{\text{metals only}} + \underbrace{C_{\text{magnetic}}}_{\text{magnets only}}$$

Thus, a non-magnetic insulator has only the phonons contributing to its thermal properties.

We define the ***heat capacity at constant volume*** as $C_V \equiv \left(\dfrac{\partial U}{\partial T}\right)_V$, where U is the internal energy.

For a solid, this is almost the same as C_p: the heat capacity at constant pressure.

The total energy of photons at a temperature T can be written as a sum over all phonon modes, which is specified by a wavenumber K and polarisation p:

$$U = U_{\text{lattice}} = \sum_K \sum_p \langle n_{K,p} \rangle \hbar \omega_p(K) \qquad (5.1)$$

Where: $n_{K,p}$ is the number of phonons in the branch p with wavenumber K.

Here, $\omega_p(K)$ is the frequency from the dispersion relation.

In thermal equilibrium, since phonons are bosons, $\langle n \rangle$ is given by the Planck distribution, as for black body radiation:

$$\langle n \rangle = \frac{1}{\exp(\hbar \omega / k_B T) - 1} \qquad (5.2)$$

We now need to count up the phonons in the crystal.

A large crystal has many modes, so we can replace the sum by an integral:

$$U = \sum_{p \text{ all bands}} \int D_p(\omega) \frac{\hbar \omega}{\exp(\hbar \omega / k_B T) - 1} d\omega \qquad (5.3)$$

Where: $D_p(\omega)$ is a weighting factor known as the ***density of (frequency) states***, which is derived from the dispersion relation.

Last Modified: 28/12/2006

Since, $D(\omega)$ does **not** depend on T, we can perform the T-differentiation first, so C_V is simply:

$$C_V = \frac{\partial U}{\partial T} = \sum_{\text{p all bands}} \int D_p(\omega) \frac{\hbar\omega \exp(\hbar\omega/k_B T)}{\left(\exp(\hbar\omega/k_B T)-1\right)^2} \frac{\hbar\omega}{k_B T^2} d\omega$$

$$C_V = k_B \sum_p \int D_p(\omega) \frac{x^2 e^x}{\left(e^x-1\right)^2} d\omega \qquad (5.4)$$

Where: $x \equiv \dfrac{\hbar\omega}{k_B T}$.

5.2 Einstein Model

This is the earliest model of the heat capacity of the lattice. It bypasses the specific details of the density of states.

The Einstein model is a reasonable approximation for a molecular crystal with numerous optical modes.

If there are *N* atoms in a crystal, then for a crystal with 3 unconstrained dimensions, there are 3*N* degrees of freedom. We will assume that all vibrations have the same frequency ω_E .

This Einstein frequency is typically an optical frequency of the order 10^{12} Hz.

The Einstein model assumes that the density of frequency states is simply a ***Dirac delta function*** $\delta(\omega_E)$, which is zero everywhere, except at $\omega = \omega_E$, where it is infinite.
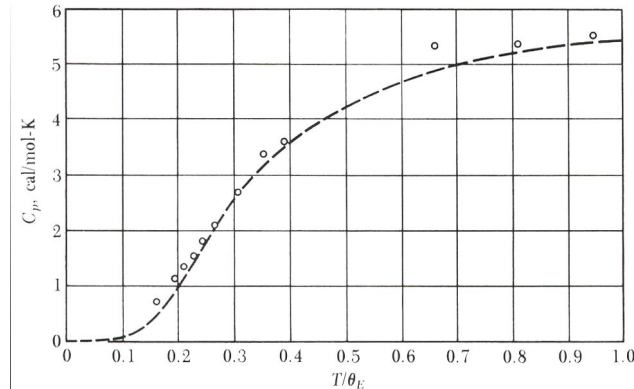
Thus, the heat capacity becomes:

$$C_V = k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{\exp(\hbar\omega_E/k_B T)}{\left(\exp(\hbar\omega_E/k_B T)-1\right)^2} \cdot \underbrace{3N}_{\text{from summation}} \qquad (5.5)$$

We can take the high-temperature limit ($T \to \infty$). This means that $x \to 0$, $e^x \to 1+x$ and $\left(e^x-1\right)^2 \to x^2$.

Finally, this gives a high-temperature heat capacity as:

$$C_V = 3N k_B \qquad (5.6)$$

Last Modified: 28/12/2006

This agrees with the Dulong and Petit law, which states that all substances have the same specific heat per mole.

Figure 5.1: Comparison of experimental values for diamond with those predicted by the Einstein model, using the characteristic temperature $\Theta_E = x\,T = \hbar\omega/k_B\,T = 1320\,\mathrm{K}.$. At low temperatures the model predicts an exponential decay, whereas experiment shows a T^3 relation.

5.3 Density of States in 1-Dimension

As illustrated in Fig. 5.1, the Einstein model fails at low temperatures, although it works relatively well at large temperatures. So, we need a better method for counting the 3N vibrational modes and determining their frequencies.

This is a two-stage process:

1. Find the allowed K values;

2. Look up the frequencies $\omega(K)$.

We said that the Einstein frequency is usually in the optical part of the phonon spectrum.

Thus, the main failings of the Einstein model come mainly from its not accounting for the acoustic modes.

Let us consider the following a boundary-value problem: a finite crystal with fixed ends, comprising *N* identical atoms with spacing *a*.

The length *L* of the crystal is therefore, $L = N\,a$.

Alternatively, we could consider an open-ended string, or a periodic boundary condition. These all yield the same result.

As in section 4, we will have a wave solution of the form: $u_s = u\,e^{i(K\,s\,a - \omega\,t)}$.

– 3 –

To satisfy the boundary conditions, we can either use a superposition of positive and negative wavenumber states, or we can write the solution of the wave equation as:

$$u_s' = \frac{1}{2i}\left(u_s(K) - u_s(-K)\right) = u\, e^{-i\omega t}\sin(K\,s\,a)$$

This will be zero at $s=0$, by construction. We also need to define that value at $s=N$, which must be equal to zero.

This gives the boundary condition:

$$\sin(K\,N\,a) = 0$$

$$\Rightarrow\ K\,N\,a = m\pi\ \ \text{where:}\ \ m \in \mathbb{Z}$$

Thus, the allowed values of *K* are:

$$K = \frac{m}{N}\frac{\pi}{a} = \frac{m\pi}{L}$$

(5.7)

Since *N* is generally large, these discrete wavenumbers are closely spaced.

Recall that the solutions are periodic, with repetition outside $-\frac{\pi}{a} < K < \frac{\pi}{a}$, indistinguishable from the first Brillouin zone.

The eigenvectors are all ***orthogonal*** to each other, so they are are independent modes of oscillation.

In this case, the $+$ and $-\,K$ values give the same solutions. Thus, the total number of solutions is *N*.

For atoms free to move in 3-dimensions, there will be three modes for each atom, which gives 3*N* solutions.

If instead we had used a periodic boundary condition, $u_s = u_{s+N}$, we would find that the allowed values of K would be $K = \frac{\pm 2m\pi}{L}$. This time, the $+$ and $-\,K$ solutions are different, however, the spacing has doubled, so we still have *N* solutions.

Consider the density of wavenumber states, the number of states in the range $K \to K + dK$, a single state occupies $\Delta K = \frac{\pi}{L}$.

It is clear that for a single state, the density of K states will satisfy $D(K)\Delta K = 1$. So, the density of K states is given by:

$$D(K) = \frac{1}{\Delta K} = \frac{L}{\pi}$$

(5.8)

And since $\omega \propto K$, the density of angular frequency states is given by:

$$D(\omega) = \frac{dk}{d\omega} D(K) = \frac{L}{\pi} \frac{1}{(d\omega/dk)} = \frac{L}{\pi} \frac{1}{v_g}$$

(5.9)

5.4   Density of States in 2D or 3D Cases

It is easiest to consider a square/cubic array of atoms on a square/cubic lattice. The result can be shown to generalise to any case.

Let the crystal comprise a cubic lattice with sides of length $L = Na$.

The vibrations will have discrete wavevector components K_x, K_y, K_z . We can assume a wavefunction of separable wavevector components:

$$u_{s_1, s_2, s_3} = u\, e^{-i\omega t}\, e^{iK_x s_1 a}\, e^{iK_y s_2 a}\, e^{iK_z s_3 a}$$

(5.10)

Periodic boundary conditions require that the wavefunction is periodic in **all** $s_i \to s_i + N$.

Thus, we have:

$$K_x = K_y = K_z = \frac{m}{N} \frac{2\pi}{a} = 2\frac{m\pi}{L}$$

(5.11)

Where: $m \in \mathbb{Z}$ is an integer.

So, the 3D reciprocal lattice comprises a set of points with spacing $\frac{\pi}{L}$ in K_x, K_y and K_z.

For the thermal models we are considering, we only need to consider *isotropic* cases, where $\omega(K)$ looks the same in all directions.

Last Modified: 28/12/2006

Then, $D(K)d\,k$ will be the number of states in a **shell** of width $K \to K+dK$.

A sphere of radius K will contain $N = \frac{4}{3}\pi K^3 \left(\frac{L}{2\pi}\right)^3$ states.

A shell of width dK contains $\frac{dN}{dK}d\,K$ states.

Thus, we have $D(K)d\,K = \frac{dN}{dK}d\,K$, so the density of K states in 3D is given by:

$$D(K) = \frac{dN}{dK} = 4\pi K^2 \left(\frac{L}{2\pi}\right)^3 = \frac{VK^2}{2\pi^2}$$

(5.12)

So, the density of angular frequency states in 3D is given by:

$$D(\omega) = \frac{dN}{d\omega} = D(K)\frac{dK}{d\omega} = \frac{VK^2}{2\pi^2}\left(\frac{dK}{d\omega}\right) = \frac{VK^2}{2\pi^2}\frac{1}{v_g}$$

(5.13)

5.5 Real Density of States

$D(\omega)$ has a tangible meaning in real life. We can see it as indicating the spectrum of vibrational frequencies of a solid.

If we can determine $\omega(K)$, we can can use this to determine the density of states.

Frequency "gaps" appear as gaps in the spectrum and in 1-dimension, turning points appear as divergences.

In higher dimensions (2D and 3D), the divergences are more spread out and appear as kinks and plateaux in the spectrum.

We can measure $\omega(K)$ using optical spectroscopy, neutron scattering or other processes, such as inelastic X-ray scattering.

Brillouin scattering is a process in which light in a medium (in our case a crystal) interacts with variations in density in the medium, changing its path. We can consider this to occur from photons interacting with phonons. This has strong peaks at the optical zone centre.

Last Modified: 28/12/2006

When using the neutron scattering method, we prefer to use a powder sample to average all crystal directions. This yields a similar result to Brillouin scattering.

Inelastic X-ray scattering has a much lower resolution than the above two approaches. However, it is a viable approach for small volumes (e.g. under high pressure).

5.6 Debye Model

Now we have a general equation for the density of states, we can improve on the Einstein model by incorporating the long-wavelength acoustic phonons, ignoring any zone boundary effects.

Let us assume that:

$$\omega = v_s K \tag{5.14}$$

Where: $v_s \equiv$ speed of sound .

The density of states is then given by:

$$D(\omega) = \frac{V K^2}{2\pi^2 v_s} = \frac{V \omega^2}{2\pi^2 v_s^3} \tag{5.15}$$

This is the first assumption that Debye made.

The second assumption is that there is **no** dispersion up to a ***cut-off frequency***, set by the total number of allowed modes, N_{cells} ,the number of primitive cells, which is equal to the number of atoms in the crystal.

This approximation turns out to be a good one, as the thermal properties are dominated by low frequency contributions.

Now, let us consider this cut-off point:

$$\underbrace{\frac{4}{3}\pi K_D^3}_{V_{k-\text{sphere}}} \underbrace{\left(\frac{L}{2\pi}\right)^3}_{1/V_{\text{state}}} = N_{\text{cells}} = N_{DOF} \tag{5.16}$$

Where: K_D is the ***Debye wavenumber***.

Last Modified: 28/12/2006

Now, set $L^3 = V \equiv V_{sample}$. This gives the cube of the Debye wavenumber:

$$K_D^3 = 3 \frac{(2\pi)^3}{4\pi} \frac{N}{V} = 6\pi^2 n_V \qquad (5.17)$$

Where: n_V is the number density (N / V).

Substituting equation (5.17) into equation (5.14) gives the cube of the **Debye angular frequency**:

$$\omega_D^3 = 6\pi^2 v_s^3 n_V \qquad (5.18)$$

We can determine the total energy of the system by integrating the density of states over ω, including a factor of 3 for the polarisation:

$$U = 3 \int D(\omega) \langle n(\omega) \rangle \hbar \omega \, d\omega \qquad (5.19)$$

Where: $\langle n(\omega) \rangle$ is the expectation value of the **occupation number** of an energy state as a function of ω, given by $\langle n(\omega) \rangle = \dfrac{1}{e^{\hbar\omega/k_b T} - 1}$. Thus, substituting equation (5.15) into equation (5.19) gives:

$$U = 3 \int_0^{\omega_D} \left(\frac{V\omega^2}{2\pi^2 v_s^3} \right) \left(\frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} \right) d\omega \qquad (5.20)$$

We can define a unitless quantity $x \equiv \dfrac{\hbar\omega}{k_B T}$. This allows us to simplify equation (5.20):

$$U = 3 \frac{V\hbar}{2\pi^2 v_s^3} \left(\frac{k_B T}{\hbar} \right)^4 \int_0^{x_D} \frac{x^3}{e^x - 1} \, dx \qquad (5.21)$$

Where: $x_D \equiv \dfrac{\hbar\omega_D}{k_B T}$.

Last Modified: 28/12/2006

We can also write this as a ratio of temperatures $x_D = \dfrac{\Theta_D}{T}$, where Θ_D is the **Debye (characteristic) temperature**, given by:

$$\Theta_D = \frac{\hbar \omega_D}{k_B} = \frac{\hbar v_s}{k_B} \left(6 \pi^2 n_V \right)^{\frac{1}{3}}$$

We can use the Debye temperature to significantly tidy up equation (5.21).

Note:

Θ_D is an **intrinsic** property of the solid, meaning that it is only dependant on the chemical structure of a medium, not on any physical properties such as temperature, pressure etc.

Finally, we can write the total energy as:

$$U = 9 N k_B T \left(\frac{T}{\Theta_D} \right)^3 \int_0^{x_D} \frac{x^3}{e^x - 1} \, dx \tag{5.22}$$

From equation (5.22), we immediately find the heat capacity according to the Debye model:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 9 N k_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} \, dx \tag{5.23}$$

We can consider the two extremes:

a) High-Temperature Limit

In the high-temperature limit, $x \to 0$. Expanding e^x as a Maclaurin series, and ignoring order greater than the linear term, $e^x \to 1 + x + O(x^2)$. Thus, we can write the high-temperature specific heat as:

$$C_V \approx 9 N k_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{x_D} \frac{x^4 (1+x)}{x^2} \, dx = 9 N k_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{x_D} x^2 (1+x) \, dx$$

Now, taking $x^2(1+x) \to x^2$ gives:

$$C_V \approx 9 N k_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{x_D} x^2 \, dx = 9 N k_B \left(\frac{T}{\Theta_D} \right)^3 \left(\frac{x_D^3}{3} \right)$$

Finally, replacing x_D by $\dfrac{\Theta_D}{T}$ gives:

$$C_V \approx 9 N k_B \left(\frac{T}{\Theta_D}\right)^3 \left[\frac{1}{3}\left(\frac{\Theta_D}{T}\right)^3\right] = 3 N k_B \tag{5.24}$$

So, in the high-temperature limit, we get the Dulong-Petit value, as before.

b) Low-Temperature Limit

Important:

Make sure to take the limit for U **before** evaluating C_V, as this make the integrals MUCH easier.

In the limit $T \to 0$, $x_D \to \dfrac{\Theta_D}{T} \to \infty$, so we can approximate to the standard integral:

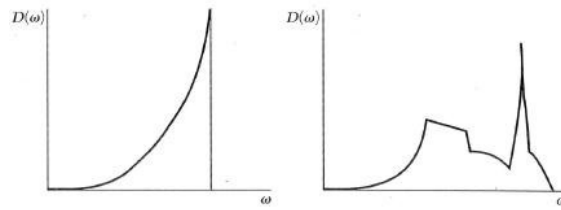$$\int_0^{x_D} \frac{x^3}{e^x - 1} dx \to \int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15} \tag{5.25}$$

Substituting into equation (5.22) gives:

$$U = 9 N k_B T \left(\frac{T}{\Theta_D}\right)^3 \frac{\pi^4}{15} \tag{5.26}$$

This gives the heat capacity in the low-temperature limit:

$$C_V = 4\mathrm{T}^3 \left(9 N k_B \left(\frac{1}{\Theta_D}\right)^3 \frac{\pi^4}{15}\right) = 12 \frac{\pi^4}{5} N k_B \left(\frac{T}{\Theta_D}\right)^3 \tag{5.27}$$

This is known as the ***Debye T³ law***.

Last Modified: 28/12/2006

Figure 5.2: Density of states as a function of frequency for a) Debye solid b) real crystal structure. For small ω the density of states increases as ω^2 in both but discontinuities appear in the real crystal due to singularities.

5.7 Anharmonic Crystal Interactions

So far, we have considered "harmonic" models: a spring compressed by a displacement *x* exerts the same force as a spring expanded by a displacement *x*.

However, cohesive forces are inherently anharmonic:
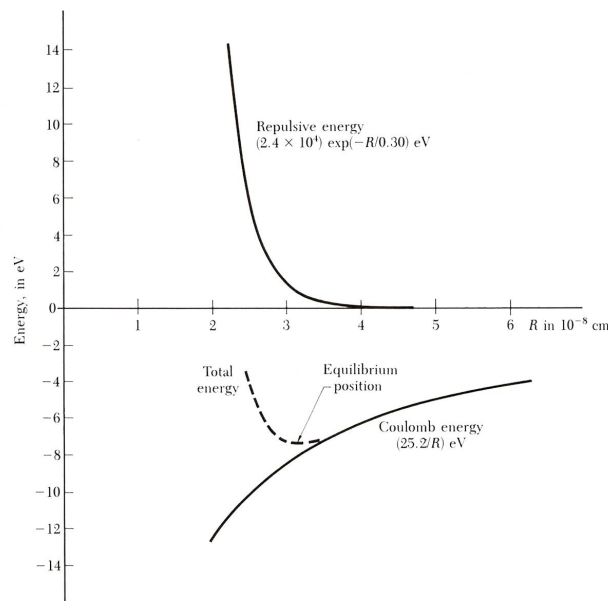
Figure 5.3: Graph of cohesive forces showing core repulsion and Coulomb forces. The dashed line represents the harmonic solution.

For small deviations, a harmonic approximation works relatively well. However, at large deviations (high *T*), such an approximation is insufficient.

There are two main consequences of anharmonicity:

1. Thermal expansion exists in crystals. The average position is generally $\neq r_{min}$ when neighbours travel far from equilibrium separation;

2. Phonons can interact with each other. This is not true in a purely harmonic crystal, where

Last Modified: 28/12/2006

the modes are independent.

Instead, one phonon causes a momentary deviation of r_{min} on one side or the other. The second phonon then "sees" a **different** spring constant (larger to the left of graph). So, they are **not** independent.

According to anharmonic models, phonon-phonon interactions follow the energy and momentum-conservation laws:

Conservation of momentum: $\Rightarrow K_1 + K_2 = K_3$

Conservation of energy: $\Rightarrow \omega_1 + \omega_2 = \omega_3$

5.8 Thermal Conductivity

From the kinetic theory of gases, we can express the thermal conductivity, κ as:

$$\kappa = \frac{1}{3} C_V v_s l \qquad\qquad (5.28)$$

Where: C_V is the specific heat, v_s is the speed of sound and l is the ***mean free path*** (between collisions).

To define thermal conductivity, there must be a mechanism in the crystal whereby the phonons may be brought into thermal equilibrium. Anharmonicity alone is insufficient.

Outside the first Brillouin zone, real momentum is not conserved for $\vec{K}_3 = \vec{K}_1 + \vec{K}_2$ because the total momentum of the phonon gas is unchanged by this process.

In order to establish equilibrium, we need to introduce the ***umklapp process***, in which a three-phonon process is of the form:

$$\vec{K}_1 + \vec{K}_2 = \vec{K}_3 + \vec{G} \qquad\qquad (5.29)$$

This has the effect of translating phonons produced in a collision into the first Brillouin zone.
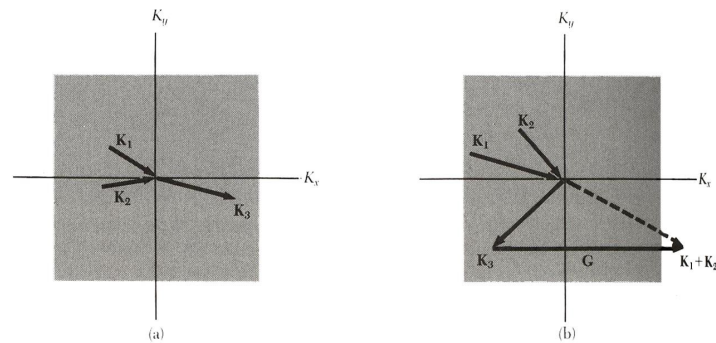
Last Modified: 28/12/2006

Figure 5.4: Diagram showing a) normal and b) Umklapp phonon process. A phonon at $\vec{K}_1 + \vec{K}_2$ can be translated into the first Brillouin zone by displacement by $\vec{G}$.

The mean free path in equation (5.28), is the mean free path for umklapp collisions **only** because other processes do **not** cause thermal resistivity.

The variables in equation (5.28) have the following temperature depenence:

Specific heat – $C_V \propto T^3$ at low temperatures, and approximately constant at higher temperatures

Speed of sound – v_s has no temperature dependence,since it is an intrinsic property of the crystal

Mean free path – $l \propto \dfrac{1}{T}$ at high temperatures. It has a strong activation at high T, where umklapp process are predominant.

Note:

Thermal resistivity is **not** always an intrinsic property of a crystal because it can depend on the size of the sample.