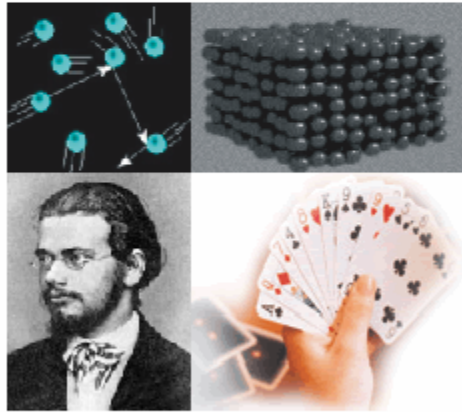


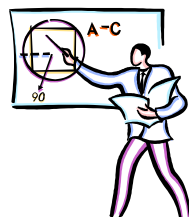
Introduction to Thermodynamics and Kinetics

F31ST1



School of Physics & Astronomy
Spring Semester 02-03

Lecture Notes *Set 5: Introduction to the* *Thermal properties of Solids*



5.1 The Einstein Model of a Solid revisited

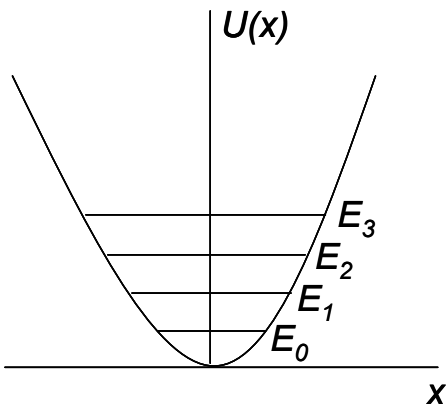


Fig. 5.1 Quantised energy levels for a simple harmonic oscillator

In Section 3 of the notes a simplified model of a solid as put forward by Einstein was introduced. Each atom is considered as moving independently of its neighbours and, moreover, the three dimensional motion of the atom is broken down into three independent one dimensional oscillators (oscillating in the x, y, and z directions respectively). The energies of these oscillators are quantised and given by:

$E_n = (n + \frac{1}{2})\hbar\omega_0$ (where ω_0 is the resonant frequency of the oscillator). Thus, the energy difference between consecutive levels (eg levels E_0 and E_1 in Fig. 5.1) is $\hbar\omega_0$.

5.2 Specific heats and equipartition of energy: revision

? *According to the equipartition of energy theorem what is the average thermal energy per degree of freedom?*

? *Which means that the average thermal energy of a gas molecule is.....?*

? *Which in turn means that the average thermal energy of 1 mole of an ideal gas is...?*

NOTES

In a solid there are no translational or vibrational degrees of freedom – only vibrational degrees of freedom remain.

? *What is the average thermal energy of 1 mole of a solid according to the equipartition theorem?*

NOTES

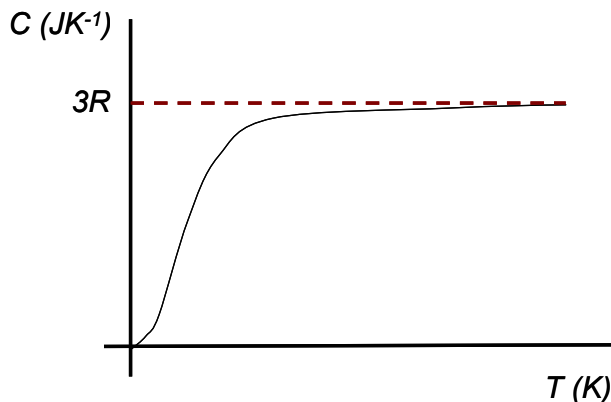


Fig. 5.2 Variation of specific heat with temperature for a solid

The specific heat capacity at constant volume is given by $C_v = \left(\frac{\partial U}{\partial T}\right)_v$ and is thus $3R$ for a solid according to classical equipartition theory. Note that this value is independent of temperature. We now ask how this value compares to the experimental results and we find, as shown in Fig. 5.2, that only at high temperatures is a value of $3R$ observed.

? *Why is a value of $3R$ for the heat capacity of a solid found only at high temperatures?*

NOTES

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5.3 Modes of vibration in solids

The quantised vibrational energy levels in a solid arise not from the vibrations of individual atoms but from *collective* oscillations of the atoms: *normal* modes of vibration where all the atoms oscillate at the same frequency (see your Vibration & Waves notes and/ or Grant & Phillips Chapter 7 for a discussion of normal modes). Each vibrational mode can only have certain discrete energy values which are given by the formula: $E_n = (n + \frac{1}{2})\hbar\omega_0$ where ω_0 is now the (angular) frequency of a particular *mode* of vibration (and not the resonant frequency of a single oscillator). As the temperature is lowered, the probability of exciting a vibrational mode of frequency ω_0 is reduced by the Boltzmann factor $\exp(-\frac{\hbar\omega_0}{kT})$. So, just as we found for the specific heats of gases, the specific heat of a solid has a temperature dependence not predicted by classical equipartition theory that originates from the quantised nature of the energy levels.

5.4 Thermal Conductivity in Solids: Phonons and Electrons

In insulating solids heat is transferred through the solid via lattice vibrations. However, the picture of lattice vibrations given above is somewhat oversimplified. It is not quite correct to think of the vibrational modes as extending unimpeded across the entire length of a solid.

There are fluctuations in thermal energy in a solid. These set up vibrational waves of slightly different frequency and the superposition of these waves produces a **wavepacket** (Fig. 5.3 - again, see your Vibrations & Waves notes and/or Grant & Phillips Chapter 7). A vibrational wavepacket in a solid is termed a *phonon*.

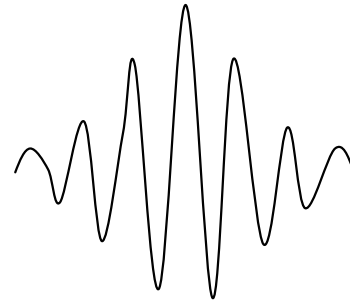


Fig. 5.3 Simple schematic illustration of a wavepacket

Just as we can discuss electrons in terms of wave-like or particle-like behaviour, we can think of phonons (groups of waves) as particles that travel through the lattice carrying thermal energy. The movement of phonons from hot to cold regions of the solid is analogous to the motion of molecules causing heat transfer in gases (Section 2c of the notes). Solids are not perfect – they contain many defects. These act to scatter the phonons as they travel through the lattice, giving rise to a *mean free path* for a phonon (which is again analogous to the mean free path of a molecule in a gas that was discussed in Section 2c).

While heat transfer in insulators (for example, glass) is driven entirely by phonons, the thermal conductivity of a metal is very much higher than that of an insulator. This is because the free electrons in the metal can transfer heat and as the speed of electrons in the solid is very much greater than the speed of phonons the electronic contribution to thermal conductivity dominates.

NOTES

Note that the following equation, which we defined in Lecture 9 (Lecture Notes Set 2c) for gases, also holds for solids:

$$\frac{dQ}{dt} = -\kappa A \frac{dT}{dx}$$

where Q is the heat current, κ is the thermal conductivity, A is the cross sectional area, and dT/dx is the temperature gradient.

5.5 Thermal Expansion of Solids

The final topic we'll consider in the Thermal & Kinetic module was introduced at the very start of the course (Lecture 1, Set 1 of the notes). As the thermal energy in a solid increases, the mean separation of the atoms increases because the force curve is *anharmonic* (see Fig. 5.4). This cause the solid to expand. For a small temperature change ΔT , the change in length, Δl , of a sample is given by:

$$\Delta l = \alpha \Delta T l$$

where l is the original length of the sample and α is the *linear expansion coefficient*.

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