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**The specific heat of solids**

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The temperature-dependence of the specific heat of a crystalline solid was one of the most important physical problems that contributed to the development of quantum theory in the early days. It turns out that this  $T$ -dependence is quite striking, especially at very low temperatures. We know now that there are in fact two distinct contributions to the specific heat of (metallic) crystalline solids at very low  $T$  – one due to the electron ‘gas’ in the metal, and the other due to collective vibrations of the lattice. The first is dominant at very low temperatures, and is **linear** in  $T$ ; the second is proportional to  $T^3$  at low temperatures (the “Debye  $T^3$  law”), and rises thereafter to a saturation value. The electronic contribution requires treatment of the electron gas in terms of Fermi-Dirac (quantum) statistics, and will be taken up later. The lattice contribution can be computed – at least in the framework of a simplified model – using what we have learnt so far. The simplified model, called the **Einstein model**, turns out to have problems at very low  $T$ , and does not in fact yield the correct ( $T^3$ ) behaviour. We shall see where the problem lies and then see how Debye set matters right.

**The Einstein Model**

Consider a crystal consists of  $N$  atoms located at the points on a lattice. From our classical mechanics course, we know that the positions of these  $N$  corresponds to  $3N$  degrees of freedom with the points on the lattice corresponding to equilibrium positions. When the crystal is in contact with an heat bath at temperature  $T$ , the atoms oscillate about the equilibrium positions. Assuming that the oscillations are **small**, we know that the oscillations are characterised by  $3N$  **normal** modes – these modes are called **phonons** – with a spectrum of normal frequencies. As a first approximation, let us assume that there is just one natural frequency,  $\omega_E$ . From quantum mechanics, we know that the **linear** harmonic oscillator has discrete non-degenerate energy levels given by

$$\left(n + \frac{1}{2}\right) \hbar\omega_E, \quad n = 0, 1, 2, \dots \text{ ad inf.}$$

The quantum canonical partition function of the solid is then given by

$$Z = \mathfrak{z}^{3N}, \quad \text{where } \mathfrak{z} = (2 \sinh(\beta\hbar\omega_E/2))^{-1}, \quad (1)$$

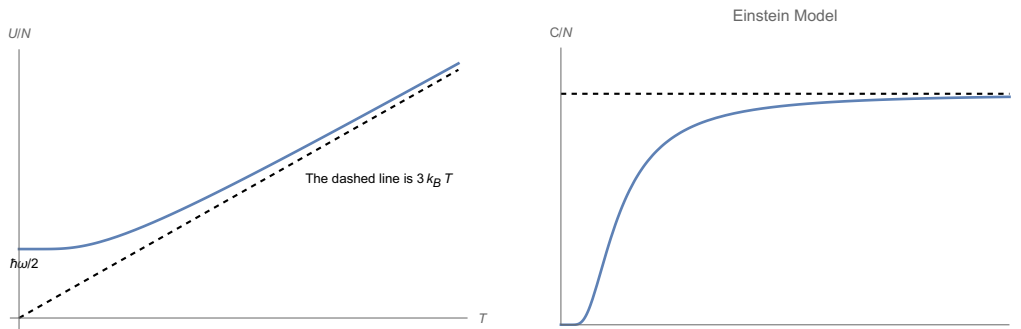


Figure 1: We plot  $U/N$  vs  $T$  and  $C/N$  vs  $T$  for the Einstein model

where  $\mathfrak{z}$  is the canonical partition function of a single harmonic oscillator with angular frequency  $\omega$ . Computing the internal energy of the system from the above partition functions gives

$$U = \left( \frac{3N\hbar\omega_E}{2} \right) \coth \left( \frac{\hbar\omega_E}{2k_B T} \right). \quad (2)$$

In Figure 1, we sketch the variation of  $U/N$  with  $T$ . What should one call ‘high’ and ‘low’ temperature limits in this problem? The dimensionless constant ( $\hbar\omega/k_B T$ ) determines these limits.

It is easy to see that the specific heat  $C$ , the quantity that we want to compute, is given by

$$C = 3Nk_B \left( \frac{\xi}{\sinh \xi} \right)^2, \quad \text{where } \xi = \hbar\omega_E/(2k_B T).$$

Figure 1 show the variation of  $C$  as a function of  $T$ . The above expression tends, as  $T \rightarrow \infty$  (or  $\xi \rightarrow 0$ ), to the constant value,  $3k_B$ , as expected from the classical equipartition theorem for a collection of oscillators (the ‘Dulong and Petit law’ for this particular system).

**How** does  $C$  tend to zero as  $T \rightarrow 0$ ? (Why should it tend to zero at all as  $T \rightarrow 0$ ?) We see that

$$C \sim 2Nk_B \xi^2 e^{-2\xi} \rightarrow 0 \quad \text{as } \xi \rightarrow \infty \text{ or } T \rightarrow 0.$$

This model thus fails to yield the experimentally correct  $T^3$  variation of  $C$  as  $T \rightarrow 0$ . We will next see another model that reproduces the required behaviour.

The Helmholtz free energy  $F = -k_B T \ln Z$  of the system can be determined from the canonical partition function given in Eqn. (1). Then the entropy of the solid is obtained using  $S = -(\partial F/\partial T)$ . (You could also use  $S = (U - F)/T$ , of course!). The answer is

$$S = 3Nk_B \left[ \xi \coth \xi - \ln(2 \sinh \xi) \right]$$

where  $\xi = \hbar\omega/(2k_B T)$  as defined earlier. **Verify that  $S \rightarrow 0$  as  $T \rightarrow 0$ , in accordance with the Nernst heat theorem.**

## The Debye Model

In the Einstein model, we assumed that all  $3N$  modes had the same frequency  $\omega$ . However, in any crystalline solid, the normal modes of vibrations have a range of frequencies in the harmonic approximation – the quanta associated with these modes are called *phonons*. In the Debye model, the phonons are assumed to have frequencies in the range  $(0, \omega_D)$  where  $\omega_D$  is called the Debye frequency. Further, the *dispersion relation* i.e., the relation between frequency and momentum is taken to be linear:  $\omega = c_s k$ , where  $c_s$  is the speed of sound in the medium and  $\mathbf{p} = \hbar \mathbf{k}$ .

Define the density of states  $\rho(\omega)$  in the usual fashion:  $\rho(\omega) \delta\omega$  is the number of normal frequencies in the range  $(\omega, \omega + \delta\omega)$ . In the Einstein model, one has

$$\rho(\omega) = 3N\delta(\omega - \omega_E) ,$$

where  $\omega_E$  is the frequency assigned to all  $3N$  oscillators. In the discrete model, let  $(\omega_1, \omega_2, \dots, \omega_{3N})$  denote the angular frequencies of the normal modes. Then, one has

$$\rho(\omega) = \sum_{i=1}^{3N} \delta(\omega - \omega_i) ,$$

In general, it is hard to determine the normal frequencies. We will instead estimate the continuum limit using a semi-classical computation. The second-quantized description in terms of phonons is useful here. A particle with energy  $\hbar\omega$  and momentum  $\hbar\mathbf{k}$  will have density of states given by

$$\begin{aligned} \rho(\omega)\delta\omega &= \int_{\text{accessible states}} \frac{d^3x d^3p}{h^3} \\ &= \frac{V}{(2\pi)^3} 4\pi \int_{\text{accessible states}} k^2 dk \\ &= \frac{V}{2\pi^2} \int_{\text{accessible states}} k^2 dk \\ &= \frac{V}{2\pi^2 c_s^3} \omega^2 \delta\omega , \end{aligned}$$

where we used the dispersion relation  $\omega = c_s k$  in the last line. the density of states is given by

$$\rho(\omega) = \frac{V\omega^2}{2\pi^2 c_s^3} . \quad (3)$$

However, this formula cannot hold for all values of  $\omega$ . Debye cutoff this formula at an angular frequency,  $\omega_D$ , that we shall refer to as the Debye frequency. This takes into account that the normal modes of crystal have a maximum frequency. The frequency is fixed by the condition

$$\int_0^{\omega_D} \rho(\omega) d\omega = 3N .$$

This sets

$$\omega_D = \left( \frac{18\pi^2 c_s^3 N}{V} \right)^{1/3} . \quad (4)$$

We can then rewrite the density of states in terms of  $\omega_D$ .

$$\rho(\omega) = \frac{9N\omega^2}{\omega_D^3} . \quad (5)$$

The (vibrational) internal energy of the solid is then given by

$$U = \int_0^{\omega_D} \rho(\omega) n(\omega) d\omega , \quad (6)$$

where  $n(\omega)$  is the average number of phonons with energy  $\omega$ . Let us compute  $n(\omega)$ .

$$n(\omega) := \langle n \rangle = \frac{\sum_{n=0}^{\infty} n e^{-\beta n \hbar \omega}}{\sum_{n=0}^{\infty} e^{-\beta n \hbar \omega}} = \frac{1}{e^{\beta \hbar \omega} - 1} .$$

Using the above expression for  $n(\omega)$  and well as the expression for the density of states we obtain (with  $x_D = \hbar \omega_D / (k_B T)$ )

$$U = 3Nk_B T \left[ \frac{3}{x_D^3} \int_0^{x_D} \frac{x^3 dx}{e^x - 1} \right] =: 3Nk_B T D(x_D) . \quad (7)$$

We have defined the Debye function  $D(y)$  as follows;

$$D(y) := \left[ \frac{3}{y^3} \int_0^y \frac{x^3 dx}{e^x - 1} \right] . \quad (8)$$

In figure 2, we plot the internal energy of the two models. At low temperatures, the Einstein model has a non-zero value corresponding to the zero-point energy. We have not included that in the discussion of the Debye model. Thus the internal energy is off by an additive constant. In the figure, we have shifted the curve (visually) for the Einstein model so that both curves agree at high temperatures. The zero-point energy is not computable in the Debye model.

Using the definition of the Debye function, one can show that

$$D(y) = \begin{cases} 1 - \frac{3y}{8} + \frac{y^2}{20} + O(x^3) , & y < 1 , \\ \frac{\pi^4}{5y^3} + O(e^{-y}) , & y > 1 . \end{cases}$$

Thus at high temperatures, one has

$$U = 3Nk_B T - 9\hbar\omega + O(1/T) .$$

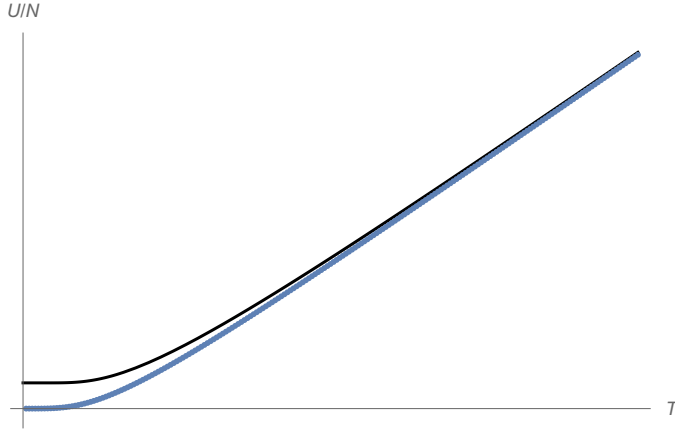


Figure 2: We plot  $U/N$  for both models after adding a constant to internal energy of the Einstein model so that both curves agree at large  $T$ . The black curve is for the Einstein model and the blue curve is for the Debye model. We assume that  $\omega_E \sim \omega_D$  for this plot.

which gives  $C/N = 3k_B + O(1/T^2)$  at high temperatures. Similarly, at low temperatures, one has

$$U/N = \frac{3\pi^4}{5\hbar\omega_D^3} (k_B T)^4 + \text{exponentially suppressed terms} .$$

Thus, we obtain

$$C/N = \frac{12\pi^4 k_B^4}{5\hbar\omega_D^3} T^3 + \text{exponentially suppressed terms} .$$

which has the correct low-temperature behaviour. An exact formula for the specific heat in the Debye model is

$$C = 3Nk_B \left[ \frac{3}{x_D^3} \int_0^{x_D} \frac{x^4 e^x dx}{(e^x - 1)^2} \right] , \quad (9)$$

$$= 3Nk_B \left[ -\frac{3x_D}{e^{x_D} - 1} + 4D(x_D) \right] . \quad (10)$$

In Figure 3, we plot the specific heat for the two models alongside the low temperature behaviour of the Debye model.

**Further Reading:** An introduction to the Debye model can be obtained from any one of the following books:

1. *Statistical Mechanics* by R.K. Pathria
2. See the chapter on “Quantum theory of the harmonic crystal” in the book by Ashcroft and Mermin titled *Solid State Physics*.

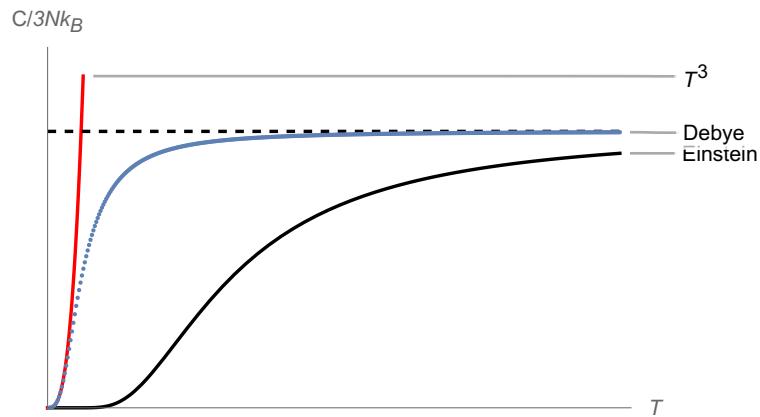


Figure 3: The specific heat for the Einstein and Debye models. The dashed line is the limiting value at high temperature. The red curve is proportional to  $T^3$ .

3. See the chapter on “Thermal properties of Phonons” in the book by C. Kittel titled *Introduction to Solid State Physics*.