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## C12T (Solid State Physics)

### Topic – Elementary Lattice Dynamics (Part – 2)

We have already discussed part 1 of this e-report.

Now let us continue part 2 of it.

#### Classical Theory of Lattice Specific Heat:

The major contribution to the specific heat (or heat capacity) of solids comes from lattice vibrations. In non-magnetic insulators, lattice vibrations are the only contributors. Other contributions come from conduction electrons in metals and the ordering in magnetic materials. In this e-report, we deal with lattice vibrations only. In classical theory, the internal energy ( $U$ ) of a solid can be expressed as

$$U = \varepsilon_s + \varepsilon_v$$

where  $\varepsilon_s$  is the energy of the static lattice and  $\varepsilon_v$  is the vibration energy of the solid. The classical equi-partition theory says that the energy of vibration of an atom is  $k_B T$  at temperature  $T$ ,  $k_B$  being the Boltzmann constant. This gives the total vibrational energy  $3Nk_B T$  if there are  $N$  atoms in the solid.

Substituting this we get  $U = \varepsilon_s + 3Nk_B T$ . At  $T = 0$  K, we obtain  $U = \varepsilon_s$  which does not include zero point energy, as in classical mechanics there is no concept of zero point motion.

**Dulong-Petit Law.** Using the expression of internal energy derived from classical equi-partition theory, the specific heat (at constant volume) is defined as

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V$$

Using the previous expression we obtain  $C_V = 3Nk_B$ . This is known as the *Dulong-Petit Law*. According to this law, specific heat capacity is constant

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$= 3Nk_B$  for a solid and independent of temperature. The experimentally measured value of specific heat approaches this value at high temperatures and remains almost constant thereafter in the solid state (as shown in Fig. 1). This is how Dulong and Petit explained the behaviour of solids at high temperatures. This law, however, fails to explain the variation of specific heat with temperature. Most significantly, experiments reveal that the specific heat drops to zero as the temperature approaches 0 K. But by no means the limited success of the Dulong-Petit law will be considered as a mean achievement because the behaviour which it fails to account for is explained only by the use of quantum theory which came much later.

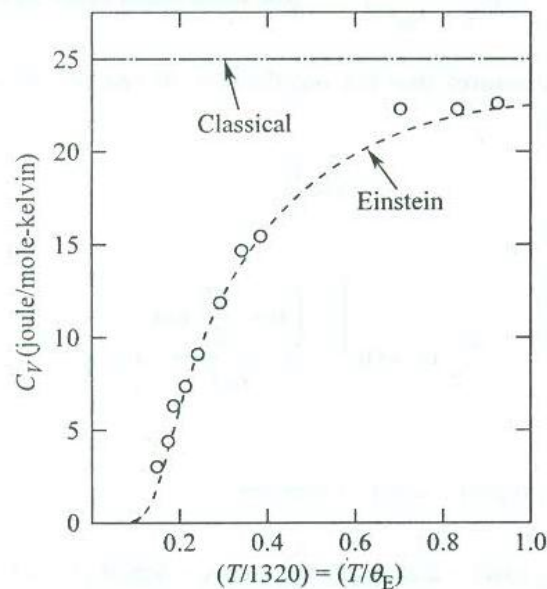


Fig. 1

### **Quantum Theory of Lattice Specific Heat:**

Now we build up the structure for calculating lattice specific heat capitalizing on the principles of quantum theory. Since lattice vibrations are pictured as quantized in this theory, the term *phonon specific heat* sounds more appropriate than the conventional term. The calculation of phonon specific heat is concerned mainly with the evaluation of the average thermal energy, which in turn requires the knowledge of the vibration spectrum of the solid under study. Since we have decided to work within the harmonic approximation, our first

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attempt would be to calculate the average thermal energy of a harmonic oscillator.

**Average Thermal Energy of a Harmonic Oscillator.** The energy levels of a quantum harmonic oscillator is defined as

$$\varepsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

where  $\omega$  is the angular frequency of the oscillator. The average thermal energy of the oscillator  $\langle\varepsilon\rangle$  in thermal equilibrium with temperature  $T$  is given by  $\langle\varepsilon\rangle = \sum_n \varepsilon_n p_n$  where  $p_n$  is the probability of finding the oscillator in the energy level  $\varepsilon_n$ . Using the expression of  $\varepsilon_n$  and the Boltzmann distribution function  $p_n$  is obtained as

$$p_n = e^{-\frac{n\hbar\omega}{k_B T}} (1 - e^{-\frac{\hbar\omega}{k_B T}})$$

Substituting the expression of  $p_n$  in the formula of  $\langle\varepsilon\rangle$ , we write

$$\langle\varepsilon\rangle = (1 - e^{-\frac{\hbar\omega}{k_B T}})\hbar\omega \sum_{n=0}^{\infty} \left[\left(n + \frac{1}{2}\right) e^{-\frac{n\hbar\omega}{k_B T}}\right]$$

Putting  $e^{-\frac{\hbar\omega}{k_B T}} = x$  we get  $\langle\varepsilon\rangle = (1 - x)\hbar\omega \sum_{n=0}^{\infty} \left[\left(n + \frac{1}{2}\right) x^n\right]$

$$\text{or } \langle\varepsilon\rangle = (1 - x)\hbar\omega \sum_{n=0}^{\infty} \left(nx^n + \frac{1}{2}x^n\right)$$

Since  $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$  and  $\sum_{n=0}^{\infty} nx^n = \frac{x}{(1-x)^2}$ , we obtain

$$\langle\varepsilon\rangle = (1 - x)\hbar\omega \left[\frac{x}{(1-x)^2} + \frac{1}{2(1-x)}\right]$$

$$\text{or } \langle\varepsilon\rangle = \left(\frac{x}{1-x} + \frac{1}{2}\right)\hbar\omega = \left(\frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} + \frac{1}{2}\right)\hbar\omega$$

Also from  $\varepsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega$  we see that  $\langle\varepsilon\rangle = \left(\langle n \rangle + \frac{1}{2}\right)\hbar\omega$ . This comparison with the previous result gives us  $\langle n \rangle = \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}$ .

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We see that  $\langle n \rangle$  must denote the phonon occupancy, which is also known as the Planck's distribution function obtained by Planck for the radiation oscillators. The above exercise is a simple demonstration of the fact that lattice vibrations are quantized the same way as the radiation oscillators.  $\langle n \rangle$  stands for the occupancy of phonons in the energy level  $\varepsilon_n$  which is also interpreted as the expected number of phonons in the energy state  $\varepsilon_n$  of an oscillator in thermal equilibrium at temperature  $T$ .

**Phonon Density of States.** Density of states for phonons ( $D(\omega)$ ) is defined as the number of available phonon states per unit frequency window. So, we can write  $D(\omega) = \frac{dN}{d\omega}$ . In three dimension, let us consider a cube of side  $L$ , whose each side contains  $N$  primitive cells. That means the whole cube will have  $N^3$  primitive cells within it. In order to calculate the density of states for phonons, we apply *periodic boundary conditions* over the trial solutions. If we assume a running wave like solution

$$u_s = u_0 e^{i(\vec{k} \cdot \vec{r} - \omega t)}$$

then according to the periodic boundary condition  $e^{i\vec{k} \cdot \vec{r}} = e^{i(k_x x + k_y y + k_z z)}$  must be equal to  $e^{i\{k_x(x+L) + k_y(y+L) + k_z(z+L)\}}$ . This method does not change the physics of the problem in any essential respect for a large system. Therefore we must have

$$e^{i(k_x L + k_y L + k_z L)} = 1$$

It sets a restriction on the allowed values of all three components of  $\vec{k}$  as

$$k_x, k_y, k_z = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \pm \frac{6\pi}{L}, \dots, \pm \frac{N\pi}{L}.$$

Therefore in three dimensional reciprocal space, one allowed  $\vec{k}$ -state requires a volume of  $\left(\frac{2\pi}{L}\right)^3 = \frac{8\pi^3}{V}$ , where  $V = L^3$  is the volume of the cubic specimen. Again the total volume consumed by all  $N$  modes or states (with a wave vector  $k$ ) will be equal to the volume of the sphere (as shown in Fig. 2) with a radius  $k$ , which is  $\frac{4}{3}\pi k^3$ . Therefore, we can write

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$$N \frac{8\pi^3}{V} = \frac{4}{3} \pi k^3$$

$$\text{or } N = \frac{Vk^3}{6\pi^2}$$

for each type of polarization (longitudinal or transverse).

Therefore the phonon density of states  $D(\omega)$  can be written as

$$D(\omega) = \frac{dN}{d\omega} = \frac{dN}{dk} \frac{dk}{d\omega}$$

$$\text{or } D(\omega) = \frac{Vk^2}{2\pi^2} \frac{dk}{d\omega} = \frac{Vk^2}{2\pi^2} \frac{d\omega}{dk}$$

Here  $\frac{d\omega}{dk}$  is nothing but the group velocity ( $v_g$ ) which can be obtained from the specific phonon dispersion relation.

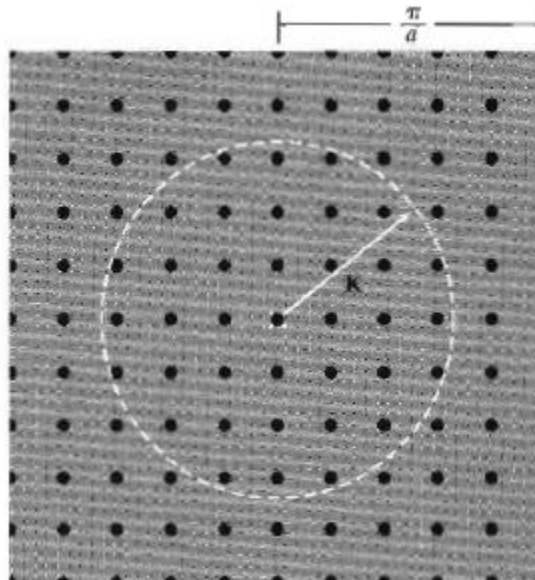


Fig. 2

### **Einstein Model of Lattice Specific Heat:**

Einstein assumed that all the atoms in a solid (say  $N$ ) vibrate with the same frequency *independently*. In other words, the frequency of vibration for all the  $3N$  normal modes is common and all the atoms oscillate independent of each

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other. Einstein treated the atomic harmonic oscillators as similar to the radiation oscillators of the Planck's theory of blackbody radiation and carried out the quantization of energy levels on parallel lines as  $\varepsilon_n = n\hbar\omega$ . Therefore in Einstein's model, the average thermal energy or equivalently the internal energy of a solid containing  $N$  atoms is expressed as

$$U = 3N\hbar\omega\langle n \rangle$$

Here  $\langle n \rangle$  is the average phonon occupancy as discussed before. The phonon specific heat is therefore expressed as

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = 3N\hbar\omega \left( \frac{\partial \langle n \rangle}{\partial T} \right)_V$$
$$\text{or } C_V = 3Nk_B \left( \frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{-\frac{\hbar\omega}{k_B T}}}{\left( e^{\frac{\hbar\omega}{k_B T}} - 1 \right)^2}$$

The plot of the above equation for diamond is shown in Fig. 1 which also shows the experimentally measured values at different temperatures. It shows a good agreement between the theoretical and experimental curves at high temperatures, and the value of specific heat approaches its value in the classical limit. The two curves tend to be separated at low temperatures. An overall view indicates that there is an agreement between the theory and the experiment for most of the temperature range excepting the low temperatures. The value of  $C_V$  in the limit of high temperatures as evaluated by the Dulong-Petit law is  $3Nk_B$ , the classical value. In the low temperatures limit, it is found to decrease as  $e^{-\frac{\hbar\omega}{k_B T}}$  and drops to zero at  $T = 0$  K. The experimental value also approaches zero as  $T \rightarrow 0$  K. Therefore, the biggest achievement of the Einstein model lies in its ability to demonstrate quickly that the phonon specific heat drops to zero at  $T = 0$  K. However, the experimental curve (shown in Fig. 1) shows that the drop is faster than that of the exponential function. The curve fits best with a  $T^3$  dependence in the low temperature region. For every solid there is a characteristic temperature above which the Einstein model works and well below this temperature the model fails. This temperature is known as *Einstein temperature*  $\theta_E$  and is defined by

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$$\theta_E = \frac{\hbar\omega_E}{k_B}$$

Here  $\omega_E$  is called as the *Einstein frequency* for the given solid.

The failure of the Einstein model at low temperatures exposes its inadequacy. The model is physically unrealistic because all vibrational modes cannot have a common frequency unless all the atoms in the solid vibrate in a manner independent of each other. The movements of adjacent atoms always tend to be correlated because of the coupling forces within the solid. Therefore, the drawback lies with the basic assumption on which the model is based. In an effort to explain the low temperature behaviour of phonon specific heat capacity, Debye put forward another approach in which he used an interpolation scheme to calculate the effective contribution from the frequency spectrum of a solid. The Debye model enjoys an overall success with its special achievement in the form of the Debye  $T^3$  Law that fits the specific heat data at low temperature reasonably well.

### **Debye Model of Lattice Specific Heat:**

In the Debye model a crystal is treated as an isotropic elastic continuum in which the velocity of sound ( $v = \frac{\omega}{k}$ ) is constant. It can take into consideration only the three acoustical branches with different sound velocities for longitudinal and transverse waves. In this case the surface  $\omega(\vec{k}) = \text{constant}$  is spherical and the group velocity  $\frac{d\omega}{dk}$  is equal to the sound velocity  $\frac{\omega}{k}$ . Therefore the phonon density of states becomes  $D(\omega) = \frac{Vk^2}{2\pi^2 \frac{d\omega}{dk}} = \frac{V\omega^2}{2\pi^2 v^3}$ . If there are  $N$  primitive cells in the specimen, the total number of acoustic phonon mode is  $N$ . Debye put a cut-off at the upper limit of frequency to ensure that the waves are long enough to have a smooth passage through the crystal which could then be justifiably treated as an elastic continuum. The cut-off frequency is known as *Debye frequency* (denoted by  $\omega_D$ ), which can be calculated by  $\omega_D^3 = \frac{6\pi^2 v^3 N}{V}$ . The density of states function sharply drops to zero at  $\omega_D$ .

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For brevity we assume that the phonon velocity independent of the polarization (longitudinal or transverse). So the average thermal energy or the internal energy is given by

$$U = 3 \int \langle n(\omega) \rangle \hbar \omega D(\omega) d\omega = 3 \int_0^{\omega_D} \frac{\hbar \omega}{e^{\frac{\hbar \omega}{k_B T}} - 1} \frac{V \omega^2}{2\pi^2 v^3} d\omega$$

$$\text{or } U = \frac{3V\hbar}{2\pi^2 v^3} \int_0^{\omega_D} \frac{\omega^3}{e^{\frac{\hbar \omega}{k_B T}} - 1} d\omega = \frac{3V k_B^4 T^4}{2\pi^2 v^3 \hbar^3} \int_0^{y_D} \frac{y^3}{e^y - 1} dy$$

Here  $y = \frac{\hbar \omega}{k_B T}$  and  $y_D = \frac{\hbar \omega_D}{k_B T} = \frac{\theta_D}{T}$ . This defines the Debye temperature  $\theta_D$  in terms of  $\omega_D$ , as  $\theta_D = \frac{\hbar \omega_D}{k_B}$ .

Using all these expressions, the internal energy becomes

$$U = 9Nk_B T \left( \frac{T}{\theta_D} \right)^3 \int_0^{y_D} \frac{y^3}{e^y - 1} dy$$

Therefore the lattice specific heat is obtained by

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V$$

$$\text{or } C_V = \frac{3V\hbar^2}{2\pi^2 v^3 k_B T^2} \int_0^{\omega_D} \frac{\omega^4 e^{\frac{\hbar \omega}{k_B T}}}{\left( e^{\frac{\hbar \omega}{k_B T}} - 1 \right)^2} d\omega$$

$$\text{or } C_V = 9Nk_B \left( \frac{T}{\theta_D} \right)^3 \int_0^{y_D} \frac{y^4 e^y}{(e^y - 1)^2} dy$$

**Debye  $T^3$  Law.** At very high temperature ( $T \gg \theta_D$ ), the lattice specific heat capacity approaches the classical value of  $3Nk_B$ , as obtained from the Dulong-Petit Law. At very low temperature ( $T \ll \theta_D$ ),  $y_D = \frac{\theta_D}{T} \rightarrow \infty$ . Using the upper limit as infinity, the value of the integral  $\int_0^{\infty} \frac{y^4 e^y}{(e^y - 1)^2} dy$  can be evaluated as  $\frac{4\pi^4}{15}$ .

This gives

$$C_V = \frac{12\pi^4}{5} Nk_B \left( \frac{T}{\theta_D} \right)^3$$

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This relation expresses Debye  $T^3$  Law. Experimental results for solid argon are plotted in Fig. 3. At sufficiently low temperature the  $T^3$  approximation is quite good, that when only long wavelength acoustic modes are thermally excited. These are just the modes that may be treated as an elastic continuum with macroscopic elastic constants. The energy of the short wavelength modes (for which this dependence fails) is too high for them to be populated significantly at low temperatures.

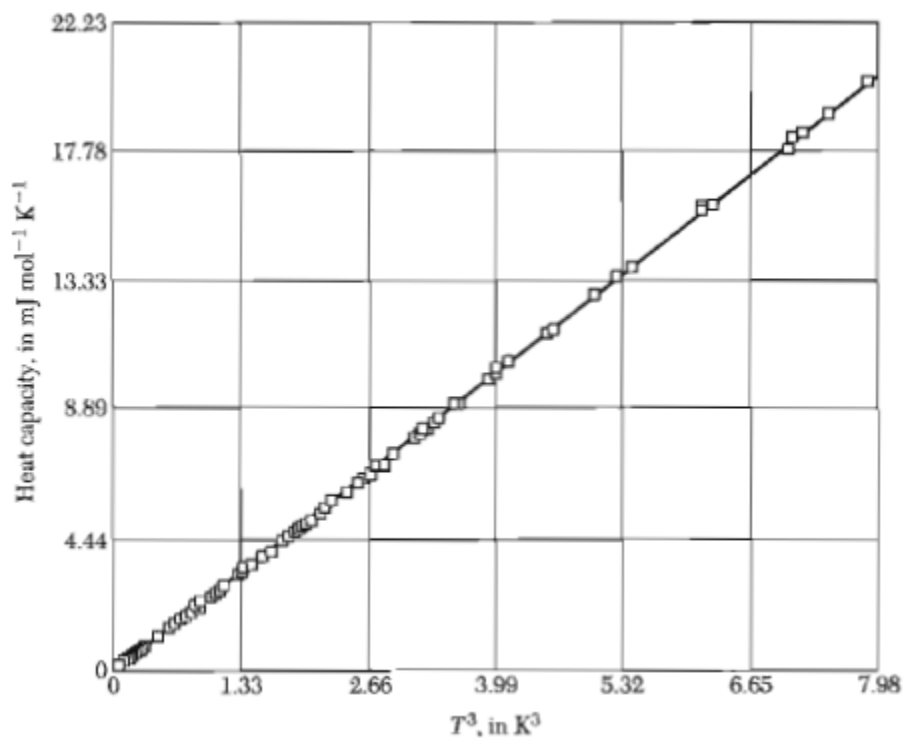


Fig. 3

For actual crystals the temperatures at which the  $T^3$  dependence holds are quite low. It may be necessary to be below  $T \approx \frac{\theta_D}{50}$  to get reasonably pure  $T^3$  behaviour.

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(All the figures have been collected from the above mentioned reference)

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