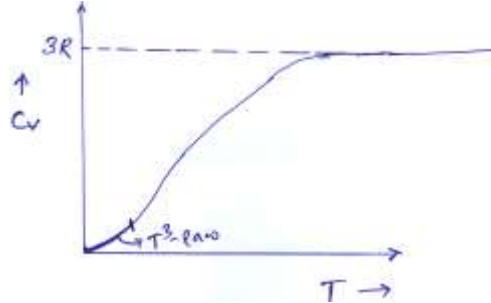


Quantum Theory of Solids

Introduction: Classical approach to specific solids predicts that C_V is constant at $3R$ (equi-partition principle). This is known as Dulong–Petit’s Law. This law works very well at high temperature region. But in early twentieth century, low temperature measurements revealed an interestingly different story.

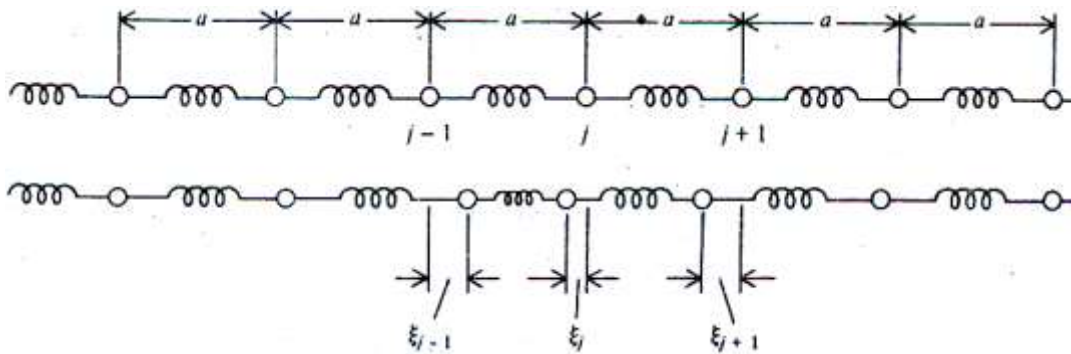


experimental temperature dependence of C_V for solids

We will now discuss about two successful theories which have resolved the issue.

Monatomic Crystals

Let us consider a one dimensional crystal where atoms are connected by spring. This description works for crystals because each atom/molecule at corresponding lattice site is confined by a step potential.



Schematic representation of one dimensional crystal system of masses and springs.

In the course of vibration, atoms can displace by small amount, ξ_j . We can write the energy U of such a crystal of N atoms as a Taylor series expansion in ξ_j

$$U(\xi_1, \xi_2, \dots, \xi_n) = U(0, 0, \dots, 0) + \sum_{j=1}^N \left(\frac{\partial U}{\partial \xi_j} \right)_0 \xi_j + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \left(\frac{\partial^2 U}{\partial \xi_i \partial \xi_j} \right)_0 \xi_i \xi_j + \dots$$

The 2nd term on the RHS is zero because U is minimum at zero displacement (equilibrium state). We can write the expansion as

$$U(\xi_1, \xi_2, \dots, \xi_n) = U(0, 0, \dots, 0) + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N K_{ij} \xi_i \xi_j$$

where we have truncated the series after the quadratic term. Here K_{ij} is the force constant of the bond between the bond involving atom i and j . Also the all the $K_{ij} = K$, as the crystal is monatomic. Now, this quadratic function can be diagonalized by introducing **normal coordinate**, just as we do in vibrational spectroscopy of polyatomic molecules.

If we have N atoms in the crystals, then 3N-6 vibrational modes will be there. Since here N is of O(10²³), then 3N-6 ≈ 3N. So, we will have 3N normal modes of frequency of the jth mode be

$$\nu_j = \frac{1}{2\pi} \sqrt{\frac{k_j}{\mu_j}}$$

We do not really need the precise form of k_j, μ_j, and ν_j in this treatment (we can get them from considering lattice dynamics). We shall replace ν_j by a distribution which is called phonon density of state (the normal modes are called phonons).

Now the crystal does not translate and rotate, so the partition function of the crystals is

$$Z_N(V, T) = e^{-\beta U_0} \prod_{j=1}^{3N} z_{vib,j}$$

Here z_{vib,j} is the vibrational partition function (PF) of the jth normal mode. Let us now evaluate the vibrational PF. Consider a harmonic oscillator of frequency ν. Energy levels are

$$E_j = \left(j + \frac{1}{2}\right) h\nu, \quad j = 0, 1, 2, 3, \dots$$

Partition function is

$$z_{vib} = \sum_{j=0}^{\infty} e^{-\beta E_j} = e^{-\frac{1}{2}\beta h\nu} \sum_{j=0}^{\infty} e^{-j\beta h\nu} = \frac{e^{-\frac{1}{2}\beta h\nu}}{1 - e^{-\beta h\nu}}$$

So, the total canonical PF is

$$Z_N(V, T) = e^{-\beta U_0} \prod_{j=1}^{3N} \left(\frac{e^{-\frac{1}{2}\beta h\nu_j}}{1 - e^{-\beta h\nu_j}} \right)$$

Also we can write the logarithm of the PF as

$$\ln Z_N(V, T) = -\frac{U_0}{k_B T} - \sum_{j=1}^{3N} \left[\ln(1 - e^{-h\nu_j/k_B T}) + \frac{h\nu_j}{k_B T} \right]$$

Now, we introduce a phonon density of states g(ν) which should follow the following equation

$$\int_0^{\infty} d\nu g(\nu) = 3N$$

So the logarithm of the PF can be written as the following integral equation

$$-\ln Z_N(V, T) = \frac{U_0}{k_B T} + \int_0^{\infty} \left[\ln(1 - e^{-h\nu/k_B T}) + \frac{h\nu}{2k_B T} \right] g(\nu) d\nu$$

Now we will try to get integral equation of different thermodynamics properties of the crystal using this PF. Let us get the integral equation for energy of the system E. Using the relation of canonical

ensemble $E = k_B T^2 \left(\frac{\partial \ln Z_N(V, T)}{\partial T} \right)_V$, we get

$$E = U_0 + \int_0^{\infty} \left[\frac{h\nu e^{-h\nu/k_B T}}{(1 - e^{-h\nu/k_B T})} + \frac{h\nu}{2} \right] g(\nu) d\nu$$

We can also get an expression for heat capacity C_V using the thermodynamics relation ($C_V = \left(\frac{\partial E}{\partial T}\right)_V$) as

$$C_V = k_B \int_0^{\infty} \frac{(h\nu / k_B T)^2 e^{-h\nu/k_B T} g(\nu) d\nu}{(1 - e^{-h\nu/k_B T})^2}$$

At this point given a suitable expression for phonon density of states $g(\nu)$, one can get the thermodynamics properties and their temperature dependence.

A. Einstein Theory: In order to explain non-classical, low temperature behavior of specific of solids, Einstein proposed a simple quantum model and assumes the following:

- 1- The crystal consists of atoms which may be regarded as identical and fixed at the lattice points.
- 2- The atoms in a crystal vibrate independently of each other about fixed lattice points.
- 3- These vibrations are all assumed to be simple harmonic, all with the same frequency.
- 4- The vibrations of any one atom can be split into three independent vibrations one along each coordinate axis.

Hence a solid containing N atoms is equivalent to $3N$ harmonic oscillators vibrating independently of each other all with the same frequency, say ν . The value of this frequency depends on the strength of the restoring force. Consider any simple solid with N atoms. These atoms are free to vibrate about their equilibrium positions. (Such vibrations are called "lattice vibrations"). The total energy of the system is written as

$$E = \sum_{i=1}^{3N} E_i, \quad E_i = \frac{p_i^2}{2m} + \frac{1}{2} k_i q_i^2 \quad (1)$$

Thus the total energy is considered as that of $3N$ independent one dimensional harmonic oscillator. If the temperature T is high enough so that classical description is applicable, then the application of the equipartition theorem allows one to conclude that the total mean energy (internal energy of the crystal) is

$$U = 6N \left(\frac{1}{2} k_B T \right) = 3N k_B T = 3RT \quad (\text{if } N = N_a)$$

Thus the specific heat at constant volume becomes

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 3R = 25 \text{ J mole}^{-1} \text{K}^{-1} \quad (\text{Douling-Petit})$$

Of course, the preceding arguments are not valid for solids at appreciably lower temperatures, which required that $\lim_{T \rightarrow 0} C_V \approx 0$. To do so, Einstein introduced the following assumptions:

- a- All atoms in the solid vibrate with the same angular frequency ω_E , which implies $k_i = m\omega_E^2$ for all terms i in equation (1).
- b- The mole of solid is equivalent to an assembly of $3N_a$ independent one dimensional harmonic oscillators, which could be easily treated by quantum mechanics with the following results:

Using the quantum energy levels in the form $\epsilon_n = (n + \frac{1}{2})h\nu_E = (n + \frac{1}{2})\hbar\omega_E$, the single particle partition function will be:

$$Z_{\text{sp}} = \sum_n e^{-\beta \epsilon_n} = \frac{e^{-a}}{1 - e^{-2a}} = \frac{1}{e^a - e^{-a}} = (2 \sinh a)^{-1}, \quad a = \frac{\beta \hbar \omega_E}{2},$$

$$Z = Z_{\text{sp}}^{3N} = (2 \sinh a)^{-3N}$$

Internal energy and heat capacity of the Einstein solid

- Now that we have the partition function, it is straightforward to determine thermodynamic quantities for the Einstein solid. First, let's derive the internal energy:

$$\text{(Eqn 1)} \quad U = \langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$$

$$\text{(Eqn 2)} \quad \ln Z = \frac{3N\beta h\nu}{2} - 3N \ln(e^{\beta h\nu} - 1)$$

$$\text{(Eqn 3)} \quad \therefore U = -\left[\frac{3Nh\nu}{2} - \frac{3Nh\nu e^{\beta h\nu}}{(e^{\beta h\nu} - 1)} \right] = \frac{3}{2}Nh\nu \frac{(e^{\beta h\nu} + 1)}{(e^{\beta h\nu} - 1)} = \frac{3}{2}Nh\nu + \frac{3Nh\nu}{(e^{\beta h\nu} - 1)}$$

- INTERPRET THE BEHAVIOR**

- Using the internal energy, we can calculate the heat capacity of the Einstein solid:

$$\text{(Eqn 4)} \quad C_V = \left(\frac{dq}{dT} \right)_V = \left(\frac{dU}{dT} \right)_V$$

- Since $\beta = 1/kT$:

$$\text{(Eqn 5)} \quad \frac{d\beta}{dT} = -\frac{1}{kT^2}$$

- Thus we can write the derivative dU/dT in the more convenient form:

$$\text{(Eqn 6)} \quad C_V = \left(\frac{dU}{dT} \right)_V = \left(\frac{dU}{d\beta} \right)_V \left(\frac{d\beta}{dT} \right) = -\frac{1}{kT^2} \left(\frac{dU}{d\beta} \right)_V$$

$$\text{(Eqn 7)} \quad C_V = 3Nk\beta^2 (h\nu)^2 \frac{e^{\beta h\nu}}{(e^{\beta h\nu} - 1)^2} = 3Nk \left(\frac{1}{kT} \right)^2 (h\nu)^2 \frac{e^{\frac{h\nu}{kT}}}{\left(e^{\frac{h\nu}{kT}} - 1 \right)^2}$$

- The Einstein solid heat capacity is plotted below as calculated for Diamond, compared to the experimentally measured heat capacity- and we see quite good agreement over a broad range of temperatures. In particular, at high temperatures, we see the limiting behavior of the heat capacity is:

$$\text{(Eqn 8)} \quad C_V(T \rightarrow \infty) \approx 3Nk\beta^2 (h\nu)^2 \frac{(1 + \beta h\nu + \dots)}{(1 + \beta h\nu + \dots - 1)^2} = 3Nk\beta^2 (h\nu)^2 \frac{1}{(\beta h\nu)^2} = 3Nk = 3R$$

- o ...correctly predicting the limiting value of C_V observed experimentally for many solids.

$$U = 3N_a \hbar \omega_E \left(\frac{1}{2} + \frac{1}{e^{2a} - 1} \right),$$

$$C_V = 3R \left(\frac{\Theta_E}{T} \right)^2 \frac{e^{2a}}{(e^{2a} - 1)^2}$$

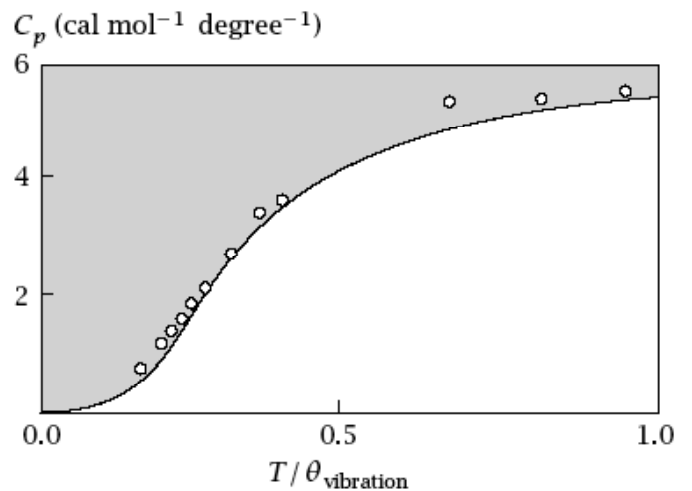
by introducing the characteristic "Einstein temperature" $\Theta_E = \frac{\hbar \omega_E}{k_B}$, then

$$C_V = \begin{cases} 3R & T \gg \Theta_E \\ 3R \left(\frac{\Theta_E}{T} \right)^2 e^{-\Theta_E/T} & T \ll \Theta_E \end{cases}$$

Thus the specific heat should approach zero exponentially as $T \rightarrow 0$.

○

Figure 11.14 Experimental values of the heat capacity of diamond (○) compared with values calculated by the Einstein model (—), using the characteristic temperature $\theta_{\text{vibration}} = h\nu/k = 1320$ K. Vibrations are frozen out at low temperatures. Source: RJ Borg and GJ Dienes, *The Physical Chemistry of Solids*, Academic Press Inc, San Diego, 1992. The data are from A Einstein, *Ann Phys* 22, 180 (1907).



▪ **PHYSICAL INTERPRETATION**

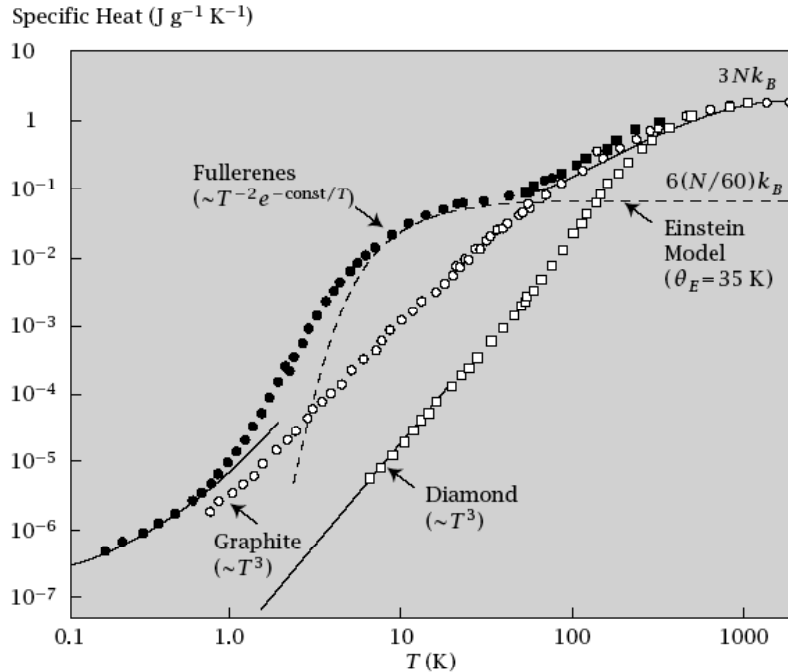


Figure 11.15 Specific heat (heat capacity per gram) versus temperature T for solids: diamond (\square), graphite (\circ), and fullerenes (\bullet). This log-log plot emphasizes the behavior at low temperatures. The Einstein model of independent oscillators ($\sim T^{-2}e^{-a/T}$) characterizes fullerenes from about $T = 5\text{ K} - 100\text{ K}$, but the more sophisticated Debye model of coupled oscillators $\sim T^3$ is a better model for diamond and graphite at low temperatures. Source: JR Olson, KA Topp and RO Pohl, *Science* 259, 1145-1148 (1993).

Experimentally the specific heat approaches zero more slowly than this, indeed $C_v \propto T^3$ as $T \rightarrow 0$. The reason for this discrepancy is the crude assumption that all atoms vibrate with the same characteristic frequency. In reality this is not the case (even if all the atoms are identical). Nevertheless, the crude assumptions of Einstein approximation give a reasonably good description of the specific heats of solids. It also makes clear the existence of the a characteristic parameter Θ_E which depends on the properties of the solid under consideration.

The normal modes of the crystal are its various standing waves of free vibration whose lowest frequencies are in the sonic range (wavelength = half or a third or a tenth of crystal size) and highest frequencies are in the infrared (wavelength = size of interatomic distance). Sometimes the quantized standing waves are called **phonons**. Then n_i is the number of phonons in the i^{th} wave. The phonons are related to the vibrations of the lattice in a crystal in the same fashion as photons are related to the vibrations of the electromagnetic field.

B Debye theory:

The disagreement between Einstein's result and the experimental data is due to the fact that Einstein's assumptions about the atoms in a crystal do not strictly apply to real crystals. The main problem lies in the assumption that a single frequency of vibration characterizes all $3N$ oscillators. Debye improved on Einstein's theory by considering the vibrations of a body as a whole, regarding it as a **continuous elastic solid**. He associated the internal energy of the solid with stationary elastic sound waves. Each independent mode of vibration (or normal mode) is treated as a degree of freedom.

In Debye's theory a solid is viewed as a **phonon gas**. Vibrational waves are matter waves, each with its own de Broglie wavelength and associated particle. The particle is called a phonon, with characteristics similar to those of a photon. If the interatomic distance is small as compared to the wavelength of elastic waves, the crystal can be regarded as a continuum from the point of view of the wave. Based on this idea, Debye based his theory on the following assumptions:

- a- The motion of each atom in a solid is not independent of the motions of its neighbors, as assumed by Einstein.
- b- The single frequency of Einstein should be replaced by a spectrum of vibrational frequency, with an upper frequency limit ν_m (or ω_m), for the solid. ν_m is called Debye (or cut-off) frequency.
- c- Solids regard as a gas of non-interacting particles (phonons), enclosed in a volume V .

The density of states for photons in the frequency range ω to $\omega+d\omega$ is:

$$g(\omega)d\omega = \frac{V}{2\pi^2} \left(\frac{2}{c_T^3} + \frac{1}{c_L^3} \right) \omega^2 d\omega.$$

Where the factor of 3 takes into account that there are 3 polarizations (2 transverse with speed c_T and 1 longitudinal with speed c_L). Note that **in the Debye theory we assumed that the speed of sound is constant for all phonon frequencies**. In practice this is not the case, but the Debye theory is generally used at low temperatures, where only low frequency phonons are excited, and where the approximation that they all travel at the same speed is a good one.

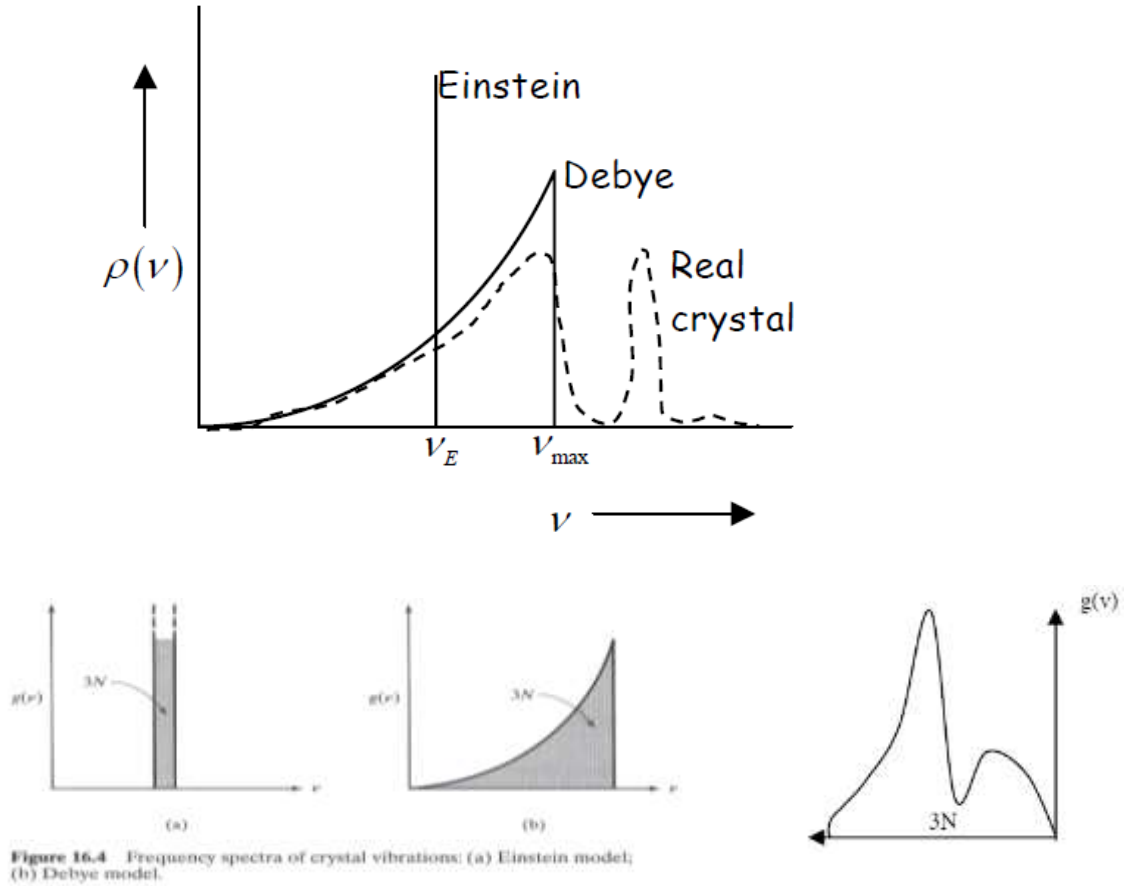
Since each oscillator of the assembly vibrates with its own frequency, and we are considering an assembly of $3N$ linear oscillator, there must be an upper limit to the frequency spectrum. The maximum frequency ω_m is determined from the fact that there are only $3N$ phonons:

$$\int_0^{\omega_m} g(\omega)d\omega = 3N,$$

$$\frac{V}{2\pi^2} \left(\frac{2}{c_T^3} + \frac{1}{c_L^3} \right) \int_0^{\omega_m} \omega^2 d\omega = 3N$$

where we obtain for the cut-off frequency

$$\omega_m^3 = 18\pi^2 \frac{N}{V} \left(\frac{2}{c_T^3} + \frac{1}{c_L^3} \right)^{-1}$$



i.e. the maximum frequency $\omega_m \propto \left(\frac{N}{V}\right)^{1/3}$ is determined by the average interatomic spacing. Thus the structure of the crystal sets a lower limit to the wavelength $\lambda_{\min} \propto \left(\frac{V}{N}\right)^{1/3}$; higher frequencies (shorter wavelength) do not lead to new modes of atomic vibration. Consequently,

$$g(\omega) = \begin{cases} 9N \frac{\omega^2}{\omega_m^3} & \text{for } \omega \leq \omega_m \\ 0 & \text{for } \omega \geq \omega_m \end{cases}$$

From Bose-Einstein distribution law

$$dn = \frac{g(\omega_m)d\omega_m}{e^{\beta\hbar\omega_m} - 1}$$

then the total number of phonons per unit volume is

$$\frac{dn}{V} = \frac{3\pi}{2\pi^2c^3} \frac{\omega_m^2}{e^{\beta\hbar\omega_m} - 1} d\omega_m$$

If the above equation multiplied by the energy of photon $E = \hbar\omega_m$ the result is the energy per unit volume, i.e. the energy density

$$\frac{dU}{V} = \frac{3\pi}{2\pi^2c^3} \frac{\hbar\omega_m^3}{e^{\beta\hbar\omega_m} - 1} d\omega_m$$

By using the dimensionless parameter

$$\eta = \frac{\hbar\omega_m}{k_B T} = \frac{\Theta_D}{T},$$

where $\Theta_D = \frac{\hbar\omega_m}{k_B}$ is the "Debye's temperature", one can have

$$\frac{dU}{V} = \frac{3\hbar}{2\pi^2 c^3} \left(\frac{k_B T}{\hbar} \right)^4 \frac{\eta^3}{e^\eta - 1} d\eta$$

Hence the internal energy per unit volume is

$$\begin{aligned} \frac{U}{V} &= \int_0^{\omega_m} U(\omega, T) d\omega = \frac{3\hbar}{\pi^2 c^3} \left(\frac{k_B T}{\hbar} \right)^4 \int_0^{\beta\hbar\omega_m} \frac{\eta^3}{e^\eta - 1} d\eta \\ &= \frac{9N}{\pi^2} \left(\frac{k_B T}{\hbar\omega_m} \right)^4 \int_0^{\beta\hbar\omega_m} \frac{\eta^3}{e^\eta - 1} d\eta \\ &= 3Nk_B T \frac{3}{x^3} \int_0^x \frac{\eta^3}{e^\eta - 1} d\eta, \quad x = \beta\hbar\omega_m \end{aligned}$$

Define Debye's function $D(x)$ by:

$$D(x) = \frac{3}{x^3} \int_0^x \frac{\eta^3}{e^\eta - 1} d\eta = \begin{cases} 1 - \frac{3}{8}x + \frac{1}{20}x^2 + \dots & x \ll 1 \Rightarrow T \rightarrow \infty \\ \frac{\pi^4}{5x^3} + O(e^{-x}) & x \gg 1 \Rightarrow T \rightarrow 0 \end{cases}$$

At high temperatures, $x \ll 1$

$$\frac{U}{V} = 3Nk_B T,$$

$$C_V = 3k_B, \quad (\text{Douling-Petit})$$

At very low temperatures, $x \gg 1$

$$\frac{U}{V} = \frac{3\pi^4 (k_B T)^4}{5\Theta_D^3},$$

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

Consequently,

This is Debye's famous " T^3 -law", which is valid at low temperatures.

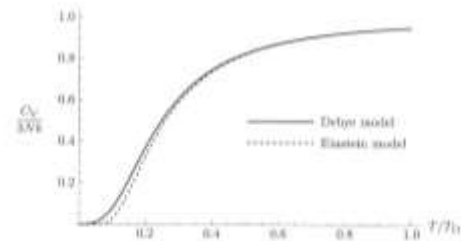


Figure 7.20: The Debye prediction for the heat capacity of a solid, with the prediction of the Einstein model plotted for comparison. The constant ϵ in the Einstein model has been chosen to obtain the best agreement with the Debye model at high temperatures. Note that the Einstein curve is much flatter than the Debye curve at low temperatures.

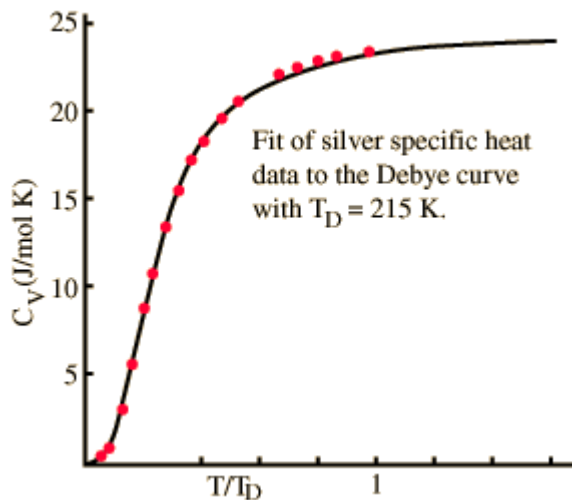
Substance	Θ_D (K)
Lead	88
Mercury	97
Silver	215
Copper	315
Iron	453

Diamond	1860
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Table Debye temperatures of some material

Limitations of the Debye Model

- i. The Debye's continuum model is valid for long wavelengths only, i.e., only low frequencies are active in the solid.
- ii. The total numbers of vibrational modes are assumed to be $3N$. This is difficult to justify as the solid is considered to be an elastic continuum which should possess infinite frequencies.
- iii. The cut off frequency is assumed to be the same for both longitudinal and transverse waves. This is again difficult to justify because different velocities of transverse and longitudinal waves should imply different values of cut off frequency for these waves.
- iv. According to the Debye's theory, Θ_D is independent of temperature, whereas actually it is found to vary up to an extent of 10% or even more.
- v. The theory does not take into account the actual crystalline nature of the solid. The theory cannot be applied to crystals comprising more than one type of atoms.
- vi. The theory completely ignores the interaction among th atoms and the contribution of electrons to the specific heat.



The data for silver shown at left is from Meyers. It shows that the specific heat fits the Debye model at both low and high temperatures.