

Debye Model For Specific Heat

The Debye model is a method developed by Peter Debye in 1912^[7] for estimating the phonon contribution to the specific heat (heat capacity) in a solid^[1]. This model correctly explains the low temperature dependence of the heat capacity, which is proportional to T^3 and also recovers the [Dulong-Petit law](#) at high temperatures. However, due to simplifying assumptions, its accuracy suffers at intermediate temperatures.

Introduction to Phonons

In 1912 Debye realized that, inconsistent with the Einstein model, low-energetic excitations of a solid material were not oscillations of a single atom^[2], but collective modes propagating through the material. Such vibrations can be considered to be sound waves, and their propagation speed is the speed of sound in the material^[3]. Moreover, these modes only accept energy in discreet amounts.

Quantum theory uses the concepts of phonons, which are “quasi-particles” with definite energies and directions of motion, to treat the vibrations. The concept of phonon is analogous with photons of the electromagnetic wave. The relations between the energy of a phonon ε , the angular frequency ω and the wave vector \vec{q} are:

$$\varepsilon = \hbar\omega \quad (1)$$

$$\omega = v_s |\vec{q}| \quad (2)$$

where v_s is the velocity of the sound wave.

As a kind of Bosons, phonons obey Bose–Einstein statistics. The expectation number of bosons in a state with energy E is^[6]:

$$n(E) = \frac{1}{e^{E/k_B T} - 1} = \frac{1}{e^{\hbar\omega/k_B T} - 1} \quad (3)$$

where $k_B = 1.380\,6504(24) \times 10^{-23} \text{J/K}$ is the Boltzmann constant.

Debye frequency and Debye Temperature

Unlike electromagnetic radiation in a box, a phonon cannot have infinite frequency. Its frequency is bound by the medium of its propagation — the atomic lattice of the solid. If there are N primitive cells in the specimen, the total number of phonon modes are N. A cut-off frequency ω_D , known as Debye frequency, is determined by the following manner^[4]:

In the 3 dimensional reciprocal space, the volume for each allowed wave vector \vec{q} is:

$$\left(\frac{2\pi}{L}\right)^3 = \frac{8\pi^3}{V} \quad (4)$$

Since there is a cut-off wave vector $q_D = \omega_D/v_s$, all the modes are confined within a sphere with radius q_D . Thus number of modes (not number of phonons) should be (5)

$$N = \left(\frac{4}{3}\pi q_D^3\right) / \left(\frac{8\pi^3}{V}\right) \quad (5)$$

or

$$q_D = \left(6\pi^2 \frac{N}{V}\right)^{\frac{1}{3}} \quad (6)$$

$$\omega_D = v_s \left(6\pi^2 \frac{N}{V}\right)^{\frac{1}{3}} \quad (7)$$

Debye temperature T_D is defined as

$$T_D = \frac{\hbar\omega_D}{k_B} = \frac{\hbar v_s}{k_B} \left(6\pi^2 \frac{N}{V}\right)^{\frac{1}{3}} \quad (8)$$

The significance of this physical term will be discussed below. For elements in the same group, heavier atoms have lower Debye temperatures, simply because the velocity of sound decreases as the density increases.^[4] The Debye temperatures of several substances are listed in Table 1.^[1]

Table 1: Debye Temperatures of several substances.

Aluminum	428K	Iron	470K	Silicon	645K	Tungsten	400K
Cadmium	209K	Lead	105K	Silver	225K	Zinc	327K
Chromium	630K	Manganese	410K	Tantalum	240K	Carbon	2230K
Copper	343.5K	Nickel	450K	Tin(white)	200K	Ice	192K
Gold	165K	Platinum	240K	Titanium	420K		

Note

Heavier atoms have **lower** Debye temperatures, because the velocity of sound **decreases** as the density increases.

Derivation for Specific Heat

In the Debye approximation, the velocity of sound v_s is taken as constant for each polarization type, as it would be for a classical elastic continuum. According to equation (7), the density of states is:

$$D(\omega) = \frac{dN}{d\omega} = \frac{V\omega^2}{2\pi^2 v_s^3} \quad (9)$$

Thus, thermal energy for each polarization type is given by^[4]:

$$U = \int d\omega D(\omega) n(\omega) \hbar\omega = \int_0^{\omega_D} d\omega \frac{V\omega^2}{2\pi^2 v_s^3} \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} \quad (10)$$

There are 3 polarization types, 1 longitude and 2 transverse. For brevity, we assume that phonon velocity is independent of polarization. Thus we multiply a factor 3 and use equation (7) to obtain the total energy of phonon:

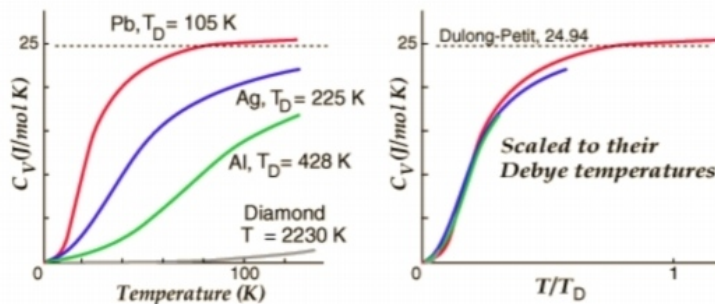
$$U = \frac{3V\hbar}{2\pi^2 v_s^3} \int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\hbar\omega/k_B T} - 1} = \frac{3Vk_B^4 T^4}{2\pi^2 v_s^3 \hbar^3} \int_0^{x_D} dx \frac{x^3}{e^x - 1} = 9Nk_B T \left(\frac{T}{T_D}\right)^3 \int_0^{x_D} dx \frac{x^3}{e^x - 1} \quad (11)$$

where $x = \hbar\omega/k_B T$ and $x_D \equiv T_D/T$.

The heat capacity is:

$$C_V = \frac{\partial U}{\partial T} = 9Nk_B \left(\frac{T}{T_D}\right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{(e^x - 1)^2} \quad (12)$$

At the left of Figure 1^[3] below, the experimental results of specific heats of four substances are plotted as a function of temperature and they look very different. But if they are scaled to T/T_D , they look very similar and are very close to the Debye theory.



High and Low Temperature Limits

The integral in Equation (12) cannot be evaluated in closed form. But the high and low temperature limits can be assessed.

High Temperature Limit

For the high temperature case where $T \gg T_D$, the value of x is very small throughout the range of the integral. This justifies using the approximation to the exponential $e^x \approx 1 + x$ and reduces equation (11) and (12) to

$$U = 9Nk_B T \left(\frac{T}{T_D} \right)^3 \int_0^{x_D} x^2 dx = 3Nk_B T \quad (13)$$

$$C_V = 3Nk_B \quad (14)$$

which is the classical *Dulong-Petit result*.

When the temperature is above the Debye temperature, the heat capacity is very close to the classical value $3Nk_B T$. For temperatures below the Debye temperature, quantum effects become important and C_v decreases to zero. Note that diamond, with a Debye temperature of 1860K, is a “quantum solid” at room temperature. [8]

Low Temperature Limit

At very low temperature where $T \ll T_D$, only long wavelength acoustic modes are thermally excited. These are just the modes that can be treated as elastic continuum with macroscopic elastic constants. The energy of those short wavelength modes are too high to be populated significantly at low temperatures. We may approximate $x_D \equiv T_D/T$ to infinity and make use of the standard integral

$$\int_0^{\infty} dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{15} \quad (15)$$

to obtain

$$U = \frac{3\pi^4 Nk_B T^4}{5T_D^3} \quad (16)$$

$$C_V = \frac{12\pi^4 Nk_B T^3}{5T_D^3} \cong 324Nk_B \frac{T^3}{T_D^3} \quad (17)$$

For actual crystals, the temperatures at which the T^3 approximation holds are quite low, even may be below $T_D/50$. It is easy to understand T/T_D^3 with a simple argument. Only the modes with $\hbar\omega < k_B T$ will be excited to any appreciable extent at a low temperature T . Define $\omega_T \equiv kT/\hbar$ as the largest frequency excited at this temperature. In the reciprocal space, the fraction occupied by the excited states is $(q_T/q_D)^3$ or $(w_T/w_D)^3 = (T/T_D)^3$.

Extension: Einstein-Debye Specific Heat

This T dependence of the specific heat at very low temperatures agrees with experiment for nonmetals. For metals the specific heat of highly mobile conduction electrons is approximated by Einstein Model, which is composed of single-frequency quantum harmonic oscillators. The temperature dependence of Einstein model is just T . It becomes significant at low temperatures and is combined with the above lattice specific heat in the Einstein-Debye specific heat [3].

$$C_{metal} = C_{electron} + C_{phonon} = \frac{\pi^2 Nk^2}{2E_f} T + \frac{12\pi^4 Nk_B}{5T_D^3} T^3 \quad (18)$$

Finally, experiments suggest that amorphous materials do not follow the Debye T^3 law even at temperatures below $0.01T_D$ [8]. There is more yet to be learned.