Lecture notes: Phonons III

Phonon heat capacity

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1 Lattice heat capacity

The heat capacity at constant volume is defined as:

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V \tag{1}$$

where U is the internal thermal energy and T is the absolute temperature. Although experiments typically measure the heat capacity at constant pressure C_p, the two quantities are related thermodynamically by $C_p - C_V = 9\alpha^2 BVT$ (where α is the linear thermal expansion coefficient, B is the bulk modulus, and V is the volume). In solids, the fractional difference between C_p and C_V is small and vanishes as $T \to 0$.

The contribution of lattice vibrations (phonons) to the heat capacity of a crystal is called the **lattice heat capacity**, denoted C_{lat}. At temperature $\tau \equiv k_B T$, the total thermal energy of the phonons is the sum over all wavevectors $\mathbf{K}$ and polarization branches p:

$$U_{\text{lat}} = \sum_{\mathbf{K}} \sum_{p} U_{\mathbf{K},p} = \sum_{\mathbf{K}} \sum_{p} \langle n_{\mathbf{K},p} \rangle \hbar\omega_{\mathbf{K},p} \tag{2}$$

where $\langle n_{\mathbf{K},p} \rangle$ is the thermal equilibrium occupancy of phonons in mode $(\mathbf{K}, p)$, given by the **Planck distribution function**:

$$\langle n \rangle = \frac{1}{\exp(\hbar\omega/\tau) - 1} \tag{3}$$

To obtain (3) from first principles, consider a large ensemble of identical, independent quantum harmonic oscillators of angular frequency ω in thermal equilibrium with a heat reservoir at temperature T, characterized by the thermal energy scale $\tau \equiv k_B T$. From quantum mechanics, the allowed energy eigenvalues of a one-dimensional harmonic oscillator of angular frequency ω are discrete and equally spaced:

$$\epsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega, \qquad n = 0, 1, 2, \ldots \tag{4}$$

where n is the excitation quantum number and $\frac{1}{2}\hbar\omega$ is the ground-state zero-point energy. According to the canonical Boltzmann distribution of statistical mechanics, the number of oscillators N_n occupying the n-th quantum state in thermal equilibrium is proportional to the Boltzmann factor $\exp(-\epsilon_n/\tau)$:

$$N_n = A \exp\left(-\frac{(n + \frac{1}{2})\hbar\omega}{\tau}\right) = A \exp\left(-\frac{\hbar\omega}{2\tau}\right) \exp\left(-\frac{n\hbar\omega}{\tau}\right) \tag{5}$$

where A is a state-independent normalization constant. Similarly, the number of oscillators in the adjacent $(n+1)$-th state (with energy $\epsilon_{n+1} = \epsilon_n + \hbar\omega$) is:

$$N_{n+1} = A \exp\left(-\frac{(n + 1 + \frac{1}{2})\hbar\omega}{\tau}\right) = A \exp\left(-\frac{\hbar\omega}{2\tau}\right) \exp\left(-\frac{(n+1)\hbar\omega}{\tau}\right) \tag{6}$$

Taking the ratio of N_{n+1} to N_n cancels both the normalization constant A and the common zero-point factor $\exp(-\hbar\omega/2\tau)$, leaving only the exponential of the energy spacing $\epsilon_{n+1} - \epsilon_n = \hbar\omega$:

$$\frac{N_{n+1}}{N_n} = \frac{A\exp(-\hbar\omega/2\tau)\exp\left[-(n+1)\hbar\omega/\tau\right]}{A\exp(-\hbar\omega/2\tau)\exp(-n\hbar\omega/\tau)} = \exp\left(-\frac{\hbar\omega}{\tau}\right), \qquad \tau \equiv k_B T. \tag{7}$$

Applying (7) repeatedly starting from the ground-state population N_0 expresses the population of any n-th excited state as:

$$N_1 = N_0 e^{-\hbar\omega/\tau}, \quad N_2 = N_1 e^{-\hbar\omega/\tau} = N_0 e^{-2\hbar\omega/\tau}, \quad \cdots \implies N_n = N_0 \exp\left(-\frac{n\hbar\omega}{\tau}\right) \tag{8}$$

The total number of oscillators across all quantum states in the ensemble is obtained by summing N_s over every non-negative integer $s = 0, 1, 2, \ldots$:

$$N_{\text{tot}} = \sum_{s=0}^{\infty} N_s \tag{9}$$

The fraction of oscillators residing in the n-th quantum state—that is, the normalized probability P_n of observing an oscillator with excitation quantum number n—is the ratio N_n/N_{tot}. Substituting (8) into both the numerator and every term of the denominator, and factoring the s-independent constant N_0 out of the sum so that it cancels cleanly, yields:

$$P_n = \frac{N_n}{\sum_{s=0}^{\infty} N_s} = \frac{N_0 \exp(-n\hbar\omega/\tau)}{N_0 \sum_{s=0}^{\infty} \exp(-s\hbar\omega/\tau)} = \frac{\exp(-n\hbar\omega/\tau)}{\sum_{s=0}^{\infty} \exp(-s\hbar\omega/\tau)} \tag{10}$$

In thermal equilibrium, individual oscillators fluctuate among different quantum levels, so we compute the ensemble-average excitation quantum number $\langle n \rangle$ (which represents the mean number of phonons occupying the mode). By definition of a statistical expectation value, $\langle n \rangle$ is the weighted average of the quantum number s over all states $s = 0, 1, 2, \ldots$, where each state is weighted by its occupation probability P_s from (10):

$$\langle n \rangle = \sum_{s=0}^{\infty} s\, P_s = \sum_{s=0}^{\infty} s \left[\frac{\exp(-s\hbar\omega/\tau)}{\sum_{s'=0}^{\infty} \exp(-s'\hbar\omega/\tau)}\right] \tag{11}$$

Because the partition sum $\sum_{s'=0}^{\infty} \exp(-s'\hbar\omega/\tau)$ in the denominator does not depend on the outer summation index s, it can be pulled outside the numerator sum (and its dummy index relabeled $s' \to s$), giving:

$$\langle n \rangle = \frac{\sum_{s=0}^{\infty} s\, \exp(-s\hbar\omega/\tau)}{\sum_{s=0}^{\infty} \exp(-s\hbar\omega/\tau)} \tag{12}$$

To evaluate the two infinite series in (12), introduce the dimensionless Boltzmann factor:

$$x \equiv \exp\left(-\frac{\hbar\omega}{\tau}\right) \tag{13}$$

For any positive frequency $\omega > 0$ and finite positive temperature $\tau = k_B T > 0$, the exponent $-\hbar\omega/\tau$ is strictly negative, which guarantees $0 < x < 1$. In terms of x, the denominator of (12) is a standard infinite geometric series. Its M-th partial sum $S_M = 1 + x + x^2 + \cdots + x^M$ satisfies $S_M - xS_M = 1 - x^{M+1}$, so $S_M = \frac{1-x^{M+1}}{1-x}$. Since $|x| < 1$, $x^{M+1} \to 0$ as $M \to \infty$, giving:

$$\sum_{s=0}^{\infty} x^s = 1 + x + x^2 + x^3 + \cdots = \frac{1}{1-x} \tag{14}$$

Differentiating (14) with respect to x and multiplying by x evaluates the numerator:

$$\sum_{s=0}^{\infty} s\, x^s = x \frac{d}{dx} \left(\sum_{s=0}^{\infty} x^s \right) = x \frac{d}{dx} \left(\frac{1}{1-x} \right) = \frac{x}{(1-x)^2} \tag{15}$$

Now substitute (14) and (15) into the numerator and denominator of (12) and cancel one common factor of $(1-x)$:

$$\langle n \rangle = \frac{x/(1-x)^2}{1/(1-x)} = \frac{x}{(1-x)^2} \cdot \frac{1-x}{1} = \frac{x}{1-x} = \frac{\exp(-\hbar\omega/\tau)}{1 - \exp(-\hbar\omega/\tau)} \tag{16}$$

Finally, multiplying both the numerator and the denominator by $\exp(\hbar\omega/\tau)$ eliminates the negative exponents and yields the **Planck distribution function**:

$$\langle n \rangle = \frac{\exp(-\hbar\omega/\tau) \cdot \exp(\hbar\omega/\tau)}{[1 - \exp(-\hbar\omega/\tau)] \exp(\hbar\omega/\tau)} = \frac{1}{\exp(\hbar\omega/\tau) - 1} = \frac{1}{\exp(\hbar\omega/k_B T) - 1} \tag{17}$$

- **Low-temperature quantum limit ($k_B T \ll \hbar\omega$):** $\exp(\hbar\omega/k_B T) \gg 1$, so $\langle n \rangle \approx \exp(-\hbar\omega/k_B T) \to 0$. High-frequency modes are thermally frozen out.
- **High-temperature classical limit ($k_B T \gg \hbar\omega$):** Expanding $\exp(\hbar\omega/k_B T) \approx 1 + \frac{\hbar\omega}{k_B T}$ gives $\langle n \rangle \approx \frac{k_B T}{\hbar\omega}$, so each mode carries average thermal energy $\langle n \rangle \hbar\omega \approx k_B T$ in agreement with classical equipartition.

Substituting the Planck distribution (17) into the lattice thermal energy (2) gives:

$$U = \sum_{\mathbf{K}} \sum_{p} \frac{\hbar\omega_{\mathbf{K},p}}{\exp(\hbar\omega_{\mathbf{K},p}/\tau) - 1} \tag{18}$$

For a macroscopic crystal, allowed wavevectors $\mathbf{K}$ are closely spaced, so we replace the summation over $\mathbf{K}$ by an integral over angular frequency ω. Let $D_p(\omega)\, d\omega$ be the number of normal modes of polarization p in the frequency interval $[\omega, \omega + d\omega]$. The function $D_p(\omega)$ is called the **density of states** (or density of modes). The total thermal energy becomes:

$$U = \sum_{p} \int d\omega\, D_p(\omega) \frac{\hbar\omega}{\exp(\hbar\omega/\tau) - 1} \tag{19}$$

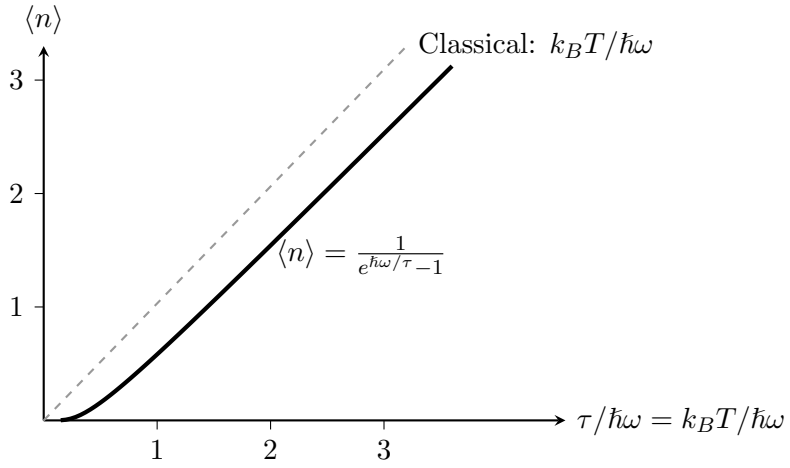


Figure 1: Thermal equilibrium phonon occupancy $\langle n\rangle$ as a function of dimensionless temperature $\tau/\hbar\omega = k_BT/\hbar\omega$.

To find the lattice heat capacity $C_{\text{lat}} = (\partial U/\partial T)_V$, let $x = \frac{\hbar\omega}{\tau} = \frac{\hbar\omega}{k_BT}$. Differentiating x with respect to T at fixed ω gives:

$$\frac{\partial x}{\partial T} = -\frac{\hbar\omega}{k_BT^2} = -\frac{x}{T} \tag{20}$$

Applying the chain rule to the temperature-dependent factor inside (19):

$$\begin{aligned}\frac{\partial}{\partial T}\left(\frac{\hbar\omega}{e^x-1}\right) &= \hbar\omega\cdot\frac{-e^x}{(e^x-1)^2}\cdot\frac{\partial x}{\partial T}\\ &= \hbar\omega\cdot\frac{-e^x}{(e^x-1)^2}\left(-\frac{\hbar\omega}{k_BT^2}\right)\\ &= k_B\left(\frac{\hbar\omega}{k_BT}\right)^2\frac{e^x}{(e^x-1)^2} = k_B\frac{x^2e^x}{(e^x-1)^2}\end{aligned} \tag{21}$$

Thus, the general expression for the lattice heat capacity is:

$$C_{\text{lat}} = k_B\sum_p\int d\omega\, D_p(\omega)\frac{x^2e^x}{(e^x-1)^2}, \qquad x = \frac{\hbar\omega}{k_BT} \tag{22}$$

2 Density of states

Apply periodic boundary conditions over a cubic crystal of side L and volume $V = L^3$ containing N primitive cells:

$$\exp\left[i(K_xx + K_yy + K_zz)\right] = \exp\left\{i\left[K_x(x+L) + K_y(y+L) + K_z(z+L)\right]\right\} \tag{23}$$

This restricts each Cartesian component of $\mathbf{K}$ to:

$$K_x,\, K_y,\, K_z = 0,\, \pm\frac{2\pi}{L},\, \pm\frac{4\pi}{L},\, \ldots,\, \frac{N^{1/3}\pi}{L} \tag{24}$$

Consequently, there is one allowed wavevector $\mathbf{K}$ per volume $(2\pi/L)^3 = 8\pi^3/V$ in $\mathbf{K}$-space. The density of allowed $\mathbf{K}$-points per unit volume of $\mathbf{K}$-space (for each polarization and branch) is:

$$\rho_{\mathbf{K}} = \left(\frac{L}{2\pi}\right)^3 = \frac{V}{8\pi^3} \tag{25}$$

To visualize this mode-counting procedure in Fourier space, consider first the two-dimensional analog shown in Fig. 2 for a square lattice of lattice constant a with periodic boundary conditions applied over a square of side $L = 10a$. Each allowed wavevector occupies an area $(2\pi/L)^2$ in $\mathbf{K}$-space, so the smoothed number of allowed states within a circle of radius K is $\pi K^2 (L/2\pi)^2$.

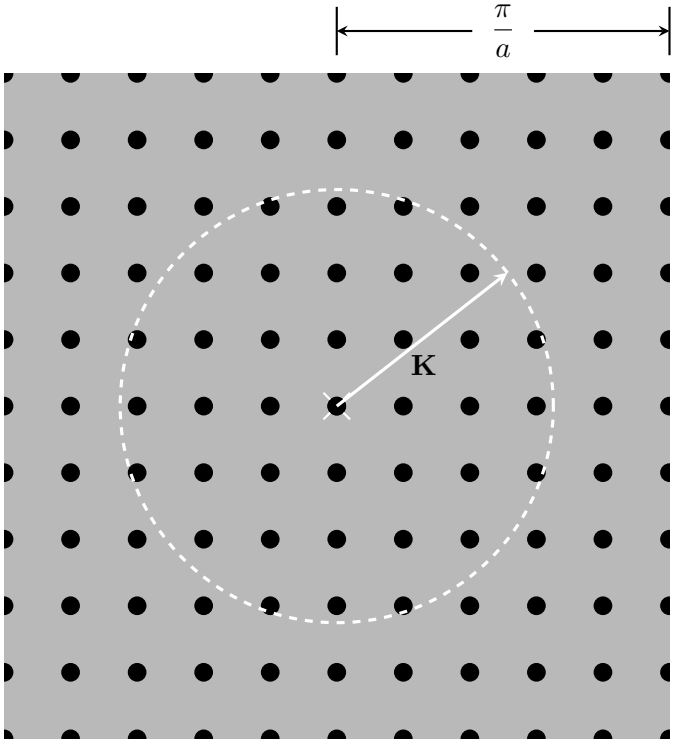


Figure 2: Allowed values in Fourier space of the phonon wavevector $\mathbf{K}$ for a square lattice of lattice constant a with periodic boundary conditions over a square of side $L = 10a$. The uniform mode ($\mathbf{K} = 0$) is marked with a cross. There is one allowed value of $\mathbf{K}$ per area $(2\pi/10a)^2 = (2\pi/L)^2$, so within a circle of area πK^2 the smoothed number of allowed points is $\pi K^2 (L/2\pi)^2$.

Extending this geometric counting from two dimensions to three dimensions, for an isotropic dispersion relation $\omega(K)$ the total number of modes $\mathcal{N}(K)$ with wavevector magnitude less than K equals $\rho_{\mathbf{K}}$ multiplied by the volume of a sphere of radius K:

$$\mathcal{N}(K) = \left(\frac{V}{8\pi^3}\right)\left(\frac{4}{3}\pi K^3\right) = \frac{VK^3}{6\pi^2} \tag{26}$$

By definition, $D(\omega)\, d\omega$ is the number of allowed states with frequencies between ω and $\omega + d\omega$, which equals the differential increment $d\mathcal{N}$ of the mode count. Differentiating

$\mathcal{N}(K)$ with respect to ω and applying the chain rule to express $D(\omega) = d\mathcal{N}/d\omega$ via K yields the 3D density of states per polarization branch:

$$D(\omega) = \frac{d\mathcal{N}}{d\omega} = \frac{d\mathcal{N}}{dK}\frac{dK}{d\omega} = \frac{d}{dK}\left(\frac{VK^3}{6\pi^2}\right)\frac{dK}{d\omega} = \left(\frac{VK^2}{2\pi^2}\right)\frac{dK}{d\omega} \tag{27}$$

3 The Debye model and the T^3 law

In the **Debye approximation**, the discrete crystal lattice is replaced by a continuous, isotropic elastic medium in which the speed of sound v is constant and independent of wavevector direction or magnitude for each acoustic polarization. Under this continuum assumption, the angular frequency is strictly proportional to the wavevector magnitude:

$$\omega = vK \tag{28}$$

This is a linear equation and may be called linear Debye dispersion relation. Inverting $\omega = vK$ from (28) gives $K = \omega/v$, and differentiating with respect to ω at constant sound speed v gives the inverse group velocity:

$$\frac{dK}{d\omega} = \frac{d}{d\omega}\left(\frac{\omega}{v}\right) = \frac{1}{v} \tag{29}$$

Substituting both $K = \omega/v$ and $dK/d\omega = 1/v$ into (27) yields the **Debye density of states** for each individual polarization type:

$$D(\omega) = \frac{V}{2\pi^2}\left(\frac{\omega}{v}\right)^2\left(\frac{1}{v}\right) = \frac{V\omega^2}{2\pi^2 v^3} \tag{30}$$

Notice that in three dimensions $D(\omega)$ grows quadratically with frequency ($D(\omega) \propto \omega^2$) because the surface area $4\pi K^2$ of a constant-frequency sphere in $\mathbf{K}$-space expands as $K^2 = (\omega/v)^2$ while the radial shell thickness $dK = d\omega/v$ remains constant. If the crystal contains N primitive cells, there are exactly N independent modes per acoustic polarization. Setting $\mathcal{N}(K_D) = N$ in (26) defines the **Debye cutoff wavevector** K_D and the **Debye cutoff frequency** ω_D:

$$N = \frac{VK_D^3}{6\pi^2} \implies K_D = \left(\frac{6\pi^2 N}{V}\right)^{1/3}, \qquad \omega_D = vK_D = v\left(\frac{6\pi^2 N}{V}\right)^{1/3} \tag{31}$$

For $\omega > \omega_D$, $D(\omega) = 0$ so that the total number of modes across all 3 acoustic polarizations equals $\int_0^{\omega_D} 3D(\omega)\,d\omega = 3N$, exhausting the vibrational degrees of freedom of a monatomic lattice.

Assuming identical sound speed v for all three acoustic polarizations (1 LA + 2 TA), we multiply (30) by 3 and substitute into the thermal energy integral (19):

$$U = 3\int_0^{\omega_D} d\omega \left(\frac{V\omega^2}{2\pi^2 v^3}\right)\frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1} = \frac{3V\hbar}{2\pi^2 v^3}\int_0^{\omega_D}\frac{\omega^3\,d\omega}{e^{\hbar\omega/\tau} - 1} \tag{32}$$

Introduce the dimensionless variable $x \equiv \frac{\hbar\omega}{\tau} = \frac{\hbar\omega}{k_B T}$ (so $\omega = \frac{k_B T}{\hbar} x$ and $d\omega = \frac{k_B T}{\hbar} dx$), and define the **Debye temperature** θ:

$$\theta \equiv \frac{\hbar\omega_D}{k_B} = \frac{\hbar v}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{1/3}, \qquad x_D \equiv \frac{\hbar\omega_D}{k_B T} = \frac{\theta}{T} \tag{33}$$

Changing the integration variable in (32) from ω to x:

$$U = \frac{3V\hbar}{2\pi^2 v^3}\left(\frac{k_B T}{\hbar}\right)^4 \int_0^{x_D} \frac{x^3\, dx}{e^x - 1} = \frac{3V k_B^4 T^4}{2\pi^2 v^3 \hbar^3} \int_0^{x_D} \frac{x^3\, dx}{e^x - 1} \tag{34}$$

From (31) and (33), note that $\omega_D^3 = \frac{6\pi^2 v^3 N}{V} \implies \frac{V}{2\pi^2 v^3} = \frac{3N}{\omega_D^3} = \frac{3N\hbar^3}{k_B^3 \theta^3}$. Substituting this gives Debye thermal energy as:

$$U = 9N k_B T \left(\frac{T}{\theta}\right)^3 \int_0^{x_D} \frac{x^3\, dx}{e^x - 1} \tag{35}$$

Differentiating (32) with respect to T (using (22)) gives the **Debye heat capacity**:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3V\hbar^2}{2\pi^2 v^3 k_B T^2} \int_0^{\omega_D} \frac{\omega^4 e^{\hbar\omega/\tau}}{(e^{\hbar\omega/\tau} - 1)^2}\, d\omega = 9N k_B \left(\frac{T}{\theta}\right)^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2}\, dx \tag{36}$$

3.1 Step-by-step derivation of the Debye heat capacity

To obtain the Debye heat capacity at constant volume $C_V = (\partial U/\partial T)_V$, we differentiate the frequency-integral expression for the total phonon thermal energy (32) directly with respect to temperature:

a. Passing the temperature derivative inside the integral: Writing $\tau = k_B T$ explicitly in (32), notice that the prefactor $\frac{3V\hbar}{2\pi^2 v^3}$ and the cutoff frequency $\omega_D = v(6\pi^2 N/V)^{1/3}$ depend only on the crystal volume V and material constants, so they remain constant during partial differentiation at fixed V. Applying the Leibniz rule to pass $\frac{\partial}{\partial T}$ inside the integral gives:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3V\hbar}{2\pi^2 v^3} \int_0^{\omega_D} \omega^3 \frac{\partial}{\partial T}\left[\left(e^{\hbar\omega/k_B T} - 1\right)^{-1}\right] d\omega \tag{37}$$

b. Differentiating the Planck occupancy factor via the power and chain rules: First apply the power rule $\frac{\partial}{\partial T}[f(T)]^{-1} = -[f(T)]^{-2}\frac{\partial f}{\partial T}$ with $f(T) = e^{\hbar\omega/k_B T} - 1$:

$$\frac{\partial}{\partial T}\left[\left(e^{\hbar\omega/k_B T} - 1\right)^{-1}\right] = -\left(e^{\hbar\omega/k_B T} - 1\right)^{-2} \frac{\partial}{\partial T}\left(e^{\hbar\omega/k_B T} - 1\right) \tag{38}$$

Next, differentiate the exponential term using the chain rule with exponent $\frac{\hbar\omega}{k_B}T^{-1}$ (using $\frac{d}{dT}(T^{-1}) = -T^{-2}$):

$$\frac{\partial}{\partial T}\left(e^{\hbar\omega/k_BT} - 1\right) = e^{\hbar\omega/k_BT}\left(-\frac{\hbar\omega}{k_BT^2}\right) \tag{39}$$

Combining these results, the two minus signs cancel to yield:

$$\frac{\partial}{\partial T}\left[\left(e^{\hbar\omega/k_BT} - 1\right)^{-1}\right] = \frac{\hbar\omega}{k_BT^2}\frac{e^{\hbar\omega/k_BT}}{\left(e^{\hbar\omega/k_BT} - 1\right)^2} \tag{40}$$

c. Evaluating the frequency-integral form of C_V: Substitute (40) back into (37), pull the ω-independent factor $\frac{\hbar}{k_BT^2}$ outside the integral, combine $\hbar \cdot \hbar = \hbar^2$ and $\omega^3 \cdot \omega = \omega^4$, and restore $\tau \equiv k_BT$:

$$\begin{aligned} C_V &= \frac{3V\hbar}{2\pi^2v^3}\int_0^{\omega_D}\omega^3\left[\frac{\hbar\omega}{k_BT^2}\frac{e^{\hbar\omega/k_BT}}{\left(e^{\hbar\omega/k_BT} - 1\right)^2}\right]d\omega \\ &= \frac{3V\hbar^2}{2\pi^2v^3k_BT^2}\int_0^{\omega_D}\frac{\omega^4e^{\hbar\omega/\tau}}{\left(e^{\hbar\omega/\tau} - 1\right)^2}\,d\omega \end{aligned} \tag{41}$$

d. Transforming to the dimensionless variable $x = \hbar\omega/k_BT$: Change the integration variable from ω to $x = \frac{\hbar\omega}{k_BT}$ using $\omega = \frac{k_BT}{\hbar}x$ and $d\omega = \frac{k_BT}{\hbar}dx$. The integration limits $\omega \in [0, \omega_D]$ transform to $x \in [0, x_D]$, where $x_D = \frac{\hbar\omega_D}{k_BT} = \frac{\theta}{T}$:

$$\begin{aligned} C_V &= \frac{3V\hbar^2}{2\pi^2v^3k_BT^2}\int_0^{x_D}\left(\frac{k_BT}{\hbar}x\right)^4\frac{e^x}{(e^x-1)^2}\left(\frac{k_BT}{\hbar}\,dx\right) \\ &= \frac{3V\hbar^2}{2\pi^2v^3k_BT^2}\left(\frac{k_BT}{\hbar}\right)^5\int_0^{x_D}\frac{x^4e^x}{(e^x-1)^2}\,dx \\ &= \frac{3Vk_B^4T^3}{2\pi^2v^3\hbar^3}\int_0^{x_D}\frac{x^4e^x}{(e^x-1)^2}\,dx \end{aligned} \tag{42}$$

e. Expressing the prefactor in terms of N and θ: From (31) and (33), recall that $\omega_D^3 = \frac{6\pi^2v^3N}{V}$ and $\omega_D = \frac{k_B\theta}{\hbar}$, which gives the identity:

$$\frac{V}{2\pi^2v^3} = \frac{3N}{\omega_D^3} = \frac{3N\hbar^3}{k_B^3\theta^3} \tag{43}$$

Substituting this into the prefactor of (42) cancels $\hbar^3$ and k_B^3:

$$\frac{3Vk_B^4T^3}{2\pi^2v^3\hbar^3} = 3\left(\frac{3N\hbar^3}{k_B^3\theta^3}\right)\frac{k_B^4T^3}{\hbar^3} = 9Nk_B\left(\frac{T}{\theta}\right)^3 \tag{44}$$

Combining (41) with this dimensionless integral form yields the **Debye heat capacity**:

$$C_V = \frac{3V\hbar^2}{2\pi^2v^3k_BT^2}\int_0^{\omega_D}\frac{\omega^4e^{\hbar\omega/\tau}}{(e^{\hbar\omega/\tau}-1)^2}\,d\omega = 9Nk_B\left(\frac{T}{\theta}\right)^3\int_0^{x_D}\frac{x^4e^x}{(e^x-1)^2}\,dx \tag{45}$$

3.2 High-temperature limit ($T \gg \theta$): Dulong–Petit law

When $T \gg \theta$, the upper limit $x_D = \theta/T \ll 1$, so $x \ll 1$ across the entire integration range. Expanding the exponential $e^x \approx 1 + x$ gives:

$$\frac{x^4 e^x}{(e^x - 1)^2} \approx \frac{x^4(1)}{x^2} = x^2 \tag{46}$$

Substituting into (36) and integrating:

$$C_V \approx 9Nk_B \left(\frac{T}{\theta}\right)^3 \int_0^{x_D} x^2\, dx = 9Nk_B \left(\frac{T}{\theta}\right)^3 \left(\frac{x_D^3}{3}\right) = 9Nk_B \left(\frac{T}{\theta}\right)^3 \frac{1}{3} \left(\frac{\theta}{T}\right)^3 = 3Nk_B \tag{47}$$

For one mole of atoms ($N = N_A$), $C_V = 3N_A k_B = 3R \approx 24.94$ J mol^{-1} K^{-1}, recovering the classical **Dulong–Petit limit**.

3.3 Low-temperature limit ($T \ll \theta$): Debye T^3 law

At very low temperatures ($T \ll \theta$), $x_D = \theta/T \to \infty$, so we replace the upper integration limit in (35) by ∞. Expanding $\frac{1}{e^x - 1} = \frac{e^{-x}}{1 - e^{-x}} = \sum_{s=1}^{\infty} e^{-sx}$:

$$\int_0^\infty \frac{x^3\, dx}{e^x - 1} = \sum_{s=1}^{\infty} \int_0^\infty x^3 e^{-sx}\, dx = \sum_{s=1}^{\infty} \frac{3!}{s^4} = 6 \sum_{s=1}^{\infty} \frac{1}{s^4} = 6 \left(\frac{\pi^4}{90}\right) = \frac{\pi^4}{15} \tag{48}$$

Substituting $\pi^4/15$ into (35) yields the low-temperature thermal energy:

$$U \cong 9Nk_B T \left(\frac{T}{\theta}\right)^3 \left(\frac{\pi^4}{15}\right) = \frac{3\pi^4}{5} Nk_B \frac{T^4}{\theta^3} \tag{49}$$

Differentiating with respect to T gives the **Debye T^3 law**:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \cong \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\theta}\right)^3 \approx 233.8\, Nk_B \left(\frac{T}{\theta}\right)^3 \qquad (T \ll \theta) \tag{50}$$

Physical K-space picture of the T^3 law: Define a thermal wavevector K_T by $\hbar v K_T = k_B T$. At low temperature $T \ll \theta$, only long-wavelength acoustic modes inside the sphere of radius K_T have $\hbar\omega < k_B T$ and are thermally excited (carrying $\sim k_B T$ each), whereas modes between K_T and K_D remain unexcited. The fraction of occupied **K**-space volume is:

$$\frac{\text{Volume of thermal sphere}}{\text{Volume of Debye sphere}} = \left(\frac{K_T}{K_D}\right)^3 = \left(\frac{T}{\theta}\right)^3 \tag{51}$$

Hence, roughly $3N(T/\theta)^3$ modes are excited, giving $U \sim 3Nk_B T(T/\theta)^3$ and $C_V = \partial U/\partial T \sim 12Nk_B(T/\theta)^3$.

(a) Debye heat capacity curve **(b) Excited modes in K-space ($T \ll \theta$)**

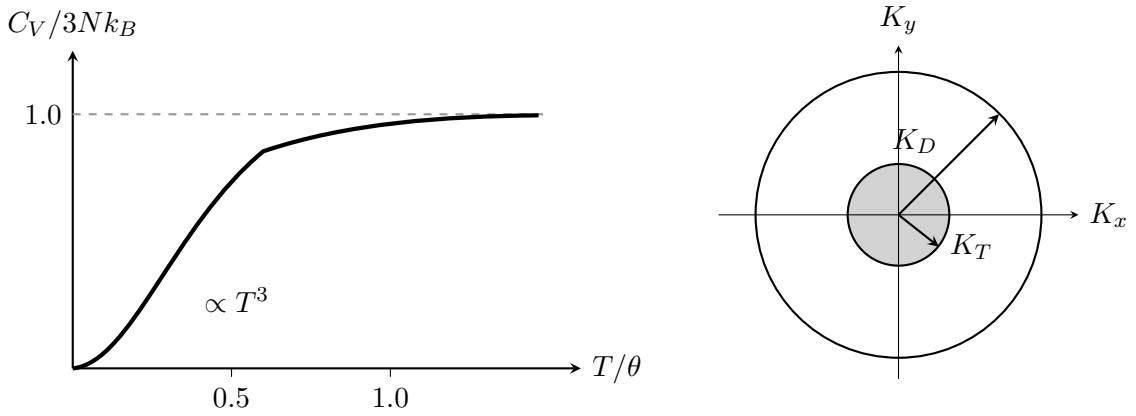


Figure 3: The Debye model: (a) normalized heat capacity $C_V/3Nk_B$ versus T/θ showing the low-temperature T^3 regime and high-temperature Dulong–Petit plateau, and (b) thermal sphere of excited modes ($K \leq K_T$) inside the Debye cutoff sphere ($K \leq K_D$).

3.4 Advantages and limitations of the Debye model

While the Debye continuum approximation provides the foundational framework for lattice specific heat, its physical assumptions introduce both notable strengths and well-defined boundaries of validity.

Advantages

- **Accurate low-temperature T^3 law:** At cryogenic temperatures ($T \ll \theta$), the Debye model reproduces the experimentally observed $C_V \propto T^3$ scaling, predicting $C_V \cong \frac{12\pi^4}{5} N k_B (T/\theta)^3$. This holds because only long-wavelength acoustic modes ($\hbar\omega < k_B T$) are thermally populated, and these modes propagate accurately as continuum elastic waves.

- **Correct high-temperature classical limit:** For $T \gg \theta$, all $3N$ vibrational degrees of freedom are fully excited and the model smoothly recovers the classical Dulong–Petit value, $C_V \to 3Nk_B$.

- **Single-parameter universality:** The entire lattice heat capacity curve of a monatomic solid is governed by a single material-dependent parameter, the Debye temperature $\theta = \frac{\hbar v}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{1/3}$. Plotting C_V against the scaled temperature T/θ collapses experimental heat capacity data for different crystals onto a universal curve.

- **Captures collective acoustic vibrations:** Unlike the Einstein model—which treats atoms as uncoupled oscillators at a single frequency and decays exponentially as $\exp(-\hbar\omega/k_B T)$ at low temperatures—the Debye model incorporates coupled, collective lattice waves spanning a continuous frequency spectrum down to $\omega \to 0$.

Limitations

- **Linear dispersion (elastic continuum) approximation:** Assuming a constant speed of sound ($\omega = vK$) neglects the downward bending of real dispersion curves near the Brillouin zone boundary, where the group velocity $v_g = d\omega/dK \to 0$. Consequently, strictly pure T^3 behavior is confined to very low temperatures (often requiring $T < \theta/50$ in real crystals), and θ treated as an empirical fitting parameter varies slightly with temperature.
- **Spherical cutoff versus true Brillouin zone geometry:** The true polyhedral First Brillouin Zone of a discrete crystal lattice is replaced by an isotropic sphere of radius $K_D = (6\pi^2 N/V)^{1/3}$ containing the same total number of states, ignoring directional variations of the zone boundary along different crystallographic axes.
- **Neglect of polarization and elastic anisotropy:** The standard formulation uses a single average sound velocity v for all three acoustic branches. In actual crystals, longitudinal acoustic (LA) waves travel faster than transverse acoustic (TA) waves ($v_L > v_T$), and sound velocities depend on propagation direction in anisotropic crystals.
- **Omission of optical branches and Van Hove singularities:** Because the Debye density of states is a smooth parabola $D(\omega) \propto \omega^2$ terminating abruptly at ω_D, it omits **Van Hove singularities** (sharp kinks and peaks where $|\nabla_{\mathbf{K}}\omega| = 0$) and does not account for the $3p - 3$ **optical phonon branches** in polyatomic solids ($p \geq 2$ atoms per primitive basis), which are typically modeled by adding Einstein terms to the Debye acoustic contribution.
- **Harmonic assumption and non-lattice contributions:** Built within the harmonic approximation, the model ignores anharmonic interactions and thus cannot describe thermal expansion or the high-temperature difference $C_p - C_V = 9\alpha^2 BVT$. Moreover, it describes only the lattice heat capacity C_{lat}, omitting electronic ($C_{\text{el}} \propto T$) and magnetic contributions in metals and magnetic solids.

4 The Einstein model of heat capacity

In the **Einstein model** (1907), every atom in a crystal is modeled as an independent quantum harmonic oscillator vibrating at a single identical angular frequency ω_0 (written simply as ω for convenience), neglecting interatomic coupling and wavevector dispersion across **K**-space.

4.1 Thermal energy in the Einstein model

To obtain the thermal energy of the Einstein solid, we first construct its density of states $D(\omega')$ and integrate over all frequencies:

1. **One-dimensional ensemble (N oscillators):** Because all N oscillators vibrate at the exact same angular frequency ω_0, every vibrational mode is concentrated at $\omega' = \omega_0$. Mathematically, this sharp spectral line is represented by a Dirac delta function normalized to the total number of oscillators N:

$$D(\omega') = N\,\delta(\omega' - \omega_0) \tag{52}$$

which satisfies $\int_0^\infty D(\omega')\,d\omega' = N$. Substituting (52) into the general thermal energy integral (19) gives:

$$U = \int_0^\infty D(\omega')\langle n(\omega')\rangle\hbar\omega'\,d\omega' = \int_0^\infty N\,\delta(\omega' - \omega_0)\frac{\hbar\omega'}{e^{\hbar\omega'/\tau} - 1}\,d\omega' \tag{53}$$

Applying the sifting property of the Dirac delta function, $\int_0^\infty f(\omega')\delta(\omega' - \omega_0)\,d\omega' = f(\omega_0)$ for $\omega_0 > 0$, collapses the integral to a single term evaluated at ω_0. Writing ω in place of ω_0 for convenience yields the 1D Einstein thermal energy:

$$U = N\langle n\rangle\hbar\omega = \frac{N\hbar\omega}{e^{\hbar\omega/\tau} - 1} \qquad \text{(1D)} \tag{54}$$

2. **Three-dimensional crystal ($3N$ oscillators):** In a three-dimensional crystal of N atoms, each atom has three independent orthogonal vibrational degrees of freedom (along the x, y, and z axes), giving $3N$ identical oscillators of frequency ω ($D(\omega') = 3N\,\delta(\omega' - \omega)$). Multiplying (54) by 3 gives the 3D Einstein thermal energy:

$$U = \frac{3N\hbar\omega}{e^{\hbar\omega/\tau} - 1} \qquad \text{(3D)} \tag{55}$$

4.2 Derivation of the Einstein heat capacity

To obtain the heat capacity at constant volume $C_V = (\partial U/\partial T)_V$ from Equation (33), we first substitute $\tau = k_B T$ into (54) so that the explicit temperature dependence is visible:

$$U(T) = \frac{N\hbar\omega}{e^{\hbar\omega/k_B T} - 1} = N\hbar\omega\left(e^{\hbar\omega/k_B T} - 1\right)^{-1} \tag{56}$$

Holding the number of oscillators N, the frequency ω, and the crystal volume V fixed, we differentiate $U(T)$ with respect to T using the power rule $\frac{d}{dT}[f(T)]^{-1} = -[f(T)]^{-2}\frac{df}{dT}$:

$$\begin{aligned} C_V = \left(\frac{\partial U}{\partial T}\right)_V &= N\hbar\omega\cdot\frac{\partial}{\partial T}\left[\left(e^{\hbar\omega/k_B T} - 1\right)^{-1}\right] \\ &= N\hbar\omega\cdot(-1)\left(e^{\hbar\omega/k_B T} - 1\right)^{-2}\cdot\frac{\partial}{\partial T}\left(e^{\hbar\omega/k_B T} - 1\right) \end{aligned} \tag{57}$$

Next, we evaluate the inner derivative of the exponential term by applying the chain rule to the exponent $u(T) = \frac{\hbar\omega}{k_B}T^{-1}$. Since $\frac{d}{dT}(T^{-1}) = -T^{-2}$, we obtain:

$$\frac{\partial}{\partial T}\left(e^{\hbar\omega/k_B T} - 1\right) = e^{\hbar\omega/k_B T}\cdot\frac{\partial}{\partial T}\left(\frac{\hbar\omega}{k_B}T^{-1}\right) = e^{\hbar\omega/k_B T}\left(-\frac{\hbar\omega}{k_B T^2}\right) \tag{58}$$

Substituting (58) back into (57), the two minus signs cancel, and the factors of $\hbar\omega$ combine into $(\hbar\omega)^2$:

$$C_V = -N\hbar\omega \frac{1}{\left(e^{\hbar\omega/k_BT}-1\right)^2}\left(-\frac{\hbar\omega}{k_BT^2}e^{\hbar\omega/k_BT}\right)$$
$$= N\frac{(\hbar\omega)^2}{k_BT^2}\frac{e^{\hbar\omega/k_BT}}{\left(e^{\hbar\omega/k_BT}-1\right)^2} \tag{59}$$

Finally, multiplying numerator and denominator by k_B groups the prefactor into Nk_B multiplied by the square of the dimensionless ratio $\frac{\hbar\omega}{k_BT} = \frac{\hbar\omega}{\tau}$. Restoring $\tau \equiv k_BT$ yields the 1D Einstein heat capacity:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = Nk_B\left(\frac{\hbar\omega}{k_BT}\right)^2\frac{e^{\hbar\omega/k_BT}}{\left(e^{\hbar\omega/k_BT}-1\right)^2} = Nk_B\left(\frac{\hbar\omega}{\tau}\right)^2\frac{e^{\hbar\omega/\tau}}{\left(e^{\hbar\omega/\tau}-1\right)^2} \qquad \text{(1D)} \tag{60}$$

For a three-dimensional solid with $3N$ vibrational modes, replacing N by $3N$ gives:

$$C_V = 3Nk_B\left(\frac{\hbar\omega}{k_BT}\right)^2\frac{e^{\hbar\omega/k_BT}}{\left(e^{\hbar\omega/k_BT}-1\right)^2} \qquad \text{(3D)} \tag{61}$$

Defining the **Einstein temperature** $\theta_E \equiv \hbar\omega/k_B$, equation (61) takes the compact form:

$$C_V = 3Nk_B\left(\frac{\theta_E}{T}\right)^2\frac{e^{\theta_E/T}}{(e^{\theta_E/T}-1)^2} \tag{62}$$

4.3 Limiting behavior and comparison with the Debye model

- **High temperatures ($T \gg \theta_E$):** Expanding $e^{\theta_E/T} \approx 1 + \frac{\theta_E}{T}$ gives $C_V \approx 3Nk_B(\theta_E/T)^2\frac{1}{(\theta_E/T)^2} = 3Nk_B$, reproducing the Dulong–Petit law.
- **Low temperatures ($T \ll \theta_E$):** Since $e^{\theta_E/T} \gg 1$, we have $(e^{\theta_E/T}-1)^2 \approx e^{2\theta_E/T}$, so:

$$C_V \approx 3Nk_B\left(\frac{\theta_E}{T}\right)^2 e^{-\theta_E/T} \qquad (T \ll \theta_E) \tag{63}$$

  At very low temperatures, the Einstein heat capacity drops **exponentially** rather than following the experimental T^3 law, because a single-frequency model neglects long-wavelength, low-frequency acoustic phonons. Nevertheless, the Einstein model provides an accurate description of the heat capacity contribution from **optical phonon branches**, whose frequencies vary only weakly across the Brillouin zone.

4.4 Advantages and limitations of the Einstein model

Although the Einstein model relies on a highly simplified picture of atomic vibrations, it marked a crucial conceptual breakthrough in quantum solid-state physics and remains valuable for describing specific vibrational modes.

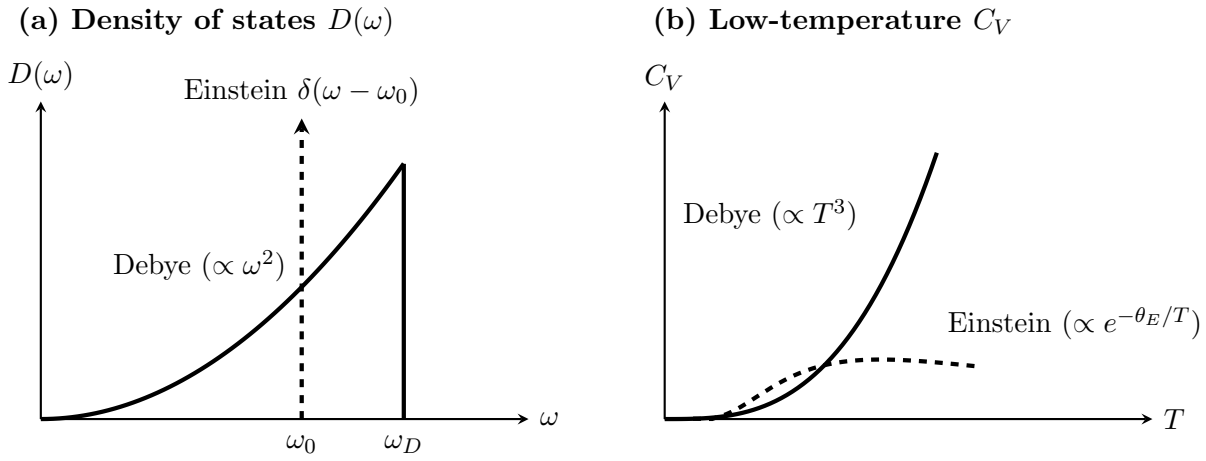


Figure 4: Comparison between the Debye and Einstein models: (a) assumed phonon density of states $D(\omega)$, and (b) resulting low-temperature heat capacity $C_V(T)$.

Table 1: Summary of the Debye and Einstein Models of Lattice Heat Capacity

Property	**Debye Model**	**Einstein Model**
Dispersion assumption	Linear acoustic ($\omega = vK$)	Single frequency ($\omega = \omega_0$)
Density of states $D(\omega)$	$\frac{3V\omega^2}{2\pi^2 v^3}$ for $\omega \leq \omega_D$	$3N\,\delta(\omega - \omega_0)$
Characteristic temperature	$\theta = \hbar\omega_D/k_B$	$\theta_E = \hbar\omega_0/k_B$
High-T limit ($T \gg \theta, \theta_E$)	$3Nk_B$ (Dulong–Petit)	$3Nk_B$ (Dulong–Petit)
Low-T limit ($T \ll \theta, \theta_E$)	$\frac{12\pi^4}{5} Nk_B(T/\theta)^3$	$3Nk_B(\theta_E/T)^2 e^{-\theta_E/T}$
Primary physical role	Acoustic phonon spectrum	Optical phonon branches

Advantages

- **First quantum explanation of the low-temperature drop in C_V:** Proposed in 1907, the Einstein model was the first theory to apply Planck's energy quantization ($\hbar\omega$) to lattice vibrations, successfully explaining why the heat capacity of solids falls well below the classical Dulong–Petit value at low temperatures (such as in hard crystals like diamond, where $\theta_E = \hbar\omega/k_B \approx 1320$ K).

- **Correct high-temperature classical limit:** At high temperatures ($T \gg \theta_E$, or $k_B T \gg \hbar\omega$), all $3N$ vibrational degrees of freedom are fully excited and the model smoothly recovers the classical Dulong–Petit result, $C_V \to 3Nk_B$.

- **Mathematical simplicity and analytical tractability:** Treating all $3N$ modes as oscillating at a single characteristic frequency ω_0 with $D(\omega) = 3N\,\delta(\omega - \omega_0)$ avoids wavevector integration over the Brillouin zone and yields a compact, closed-form analytical expression for $C_V(T)$.

- **Accurate representation of optical phonon branches:** In polyatomic crystals with $p \geq 2$ atoms per primitive basis, optical branches have nearly flat dispersion relations ($\omega(\mathbf{K}) \approx$ constant) at high frequencies. Because a nearly dispersionless branch corresponds to a sharp peak in $D(\omega)$, the Einstein model provides a natural and accurate approximation for optical-phonon contributions to C_V.

Limitations

- **Incorrect exponential decay at very low temperatures:** As $T \to 0$ ($T \ll \theta_E$), the Einstein heat capacity vanishes exponentially as $C_V \propto (\theta_E/T)^2 e^{-\theta_E/T}$, falling off far more rapidly than the experimentally observed T^3 power law.
- **Independent oscillator assumption:** Modeling atoms as uncoupled oscillators vibrating at a single fixed frequency ω_0 ignores interatomic coupling. In real crystals, coupled atomic motions generate collective acoustic waves whose frequencies extend continuously down to $\omega \to 0$; omitting these low-frequency modes creates an artificial energy gap $\hbar\omega_0$ that freezes out thermal excitations prematurely at cryogenic temperatures.
- **Omission of phonon dispersion and Van Hove singularities:** Replacing the full vibrational spectrum by a single spike $D(\omega) \propto \delta(\omega - \omega_0)$ neglects wavevector dispersion $\omega(\mathbf{K})$, distinctions between longitudinal and transverse acoustic velocities, and Van Hove singularities.
- **Harmonic approximation constraints:** Like the Debye model, the Einstein model assumes purely harmonic restoring forces and therefore cannot account for thermal expansion, phonon–phonon scattering, or the high-temperature difference $C_p - C_V = 9\alpha^2 BVT$.

5 Model comparison: Which one is better, and why?

Overall, **the Debye model is better for describing the total lattice heat capacity of a crystal across the full temperature range**, especially for monatomic solids and in the low-temperature regime:

- **Superior accuracy at low temperatures:** At $T \ll \theta$, thermal energy $k_B T$ can excite only long-wavelength, low-frequency acoustic phonons ($\hbar\omega < k_B T$). By modeling the solid as an elastic continuum with a continuous density of states $D(\omega) \propto \omega^2$ extending down to $\omega = 0$, the Debye model naturally reproduces the experimental $C_V \propto T^3$ law. In contrast, the Einstein model assigns every mode the same finite quantum $\hbar\omega_0$, causing an unphysical exponential freeze-out $e^{-\theta_E/T}$. At high temperatures ($T \gg \theta, \theta_E$), both models perform equally well and converge to the classical Dulong–Petit limit $3Nk_B$.
- **Complementary role of the Einstein model (hybrid Debye–Einstein approach):** The Einstein model is **better suited for optical phonon branches** and localized vibrational modes (such as guest atoms in cage-like crystals or internal molecular vibrations), because optical branches are nearly flat ($\omega \approx \omega_0$) rather than linearly dispersive ($\omega = vK$). Consequently, for a polyatomic crystal with p atoms per primitive cell ($3p$ total branches), standard practice combines both models: a **Debye term** is used for the 3 acoustic branches, while $3p - 3$ **Einstein terms** are added to represent the optical branches.

6 Historical timeline: What Debye corrected in the Einstein model

Historically, Albert Einstein formulated the first quantum theory of solid-state specific heat in **1907**, and Peter Debye resolved its low-temperature discrepancy five years later in **1912**. Understanding this chronological progression clarifies why each approximation behaves as it does:

1. **1819 — Classical Dulong–Petit Law:** Pierre Louis Dulong and Alexis Thérèse Petit empirically established that the molar heat capacity of many solid elements near room temperature is approximately constant ($C_V \approx 3R \approx 24.94$ J mol^{-1} K^{-1}), later explained by classical statistical equipartition ($\frac{1}{2}k_BT$ per kinetic and potential degree of freedom). However, classical theory failed completely to explain why C_V drops precipitously toward zero as temperature decreases (notably in light, stiff crystals such as diamond, boron, and silicon).

2. **1907 — Einstein's Quantum Model (Independent Oscillators):** Applying Max Planck's energy quantization ($\epsilon_n = (n + \frac{1}{2})\hbar\omega$) to atomic vibrations, Einstein modeled a crystal of N atoms as $3N$ *independent* quantum harmonic oscillators all vibrating at a single identical angular frequency ω_0, corresponding to a sharp delta-function density of states $D(\omega) = 3N\,\delta(\omega - \omega_0)$ [1]. This landmark paper successfully explained both the high-temperature $3Nk_B$ classical limit and the dramatic drop in C_V upon cooling. However, because every vibrational mode was assigned the same minimum excitation energy $\hbar\omega_0$, thermal energy could not excite any vibrations once $k_BT \ll \hbar\omega_0$. As a result, Einstein's formula predicted an exponential freeze-out, $C_V \propto (\theta_E/T)^2 e^{-\theta_E/T}$, falling significantly faster than experimental measurements at cryogenic temperatures.

3. **1912 — Debye's Continuum Correction (Coupled Collective Modes):** Debye recognized that Einstein's low-temperature error stemmed from treating atoms as isolated, uncoupled oscillators rather than a mechanically coupled crystal lattice [2]. In a real solid, interatomic restoring forces couple atomic displacements into collective elastic waves (acoustic phonons) whose frequencies extend continuously all the way down to $\omega \to 0$. By replacing Einstein's single spectral line $D(\omega) = 3N\,\delta(\omega - \omega_0)$ with a continuous quadratic density of states $D(\omega) = \frac{3V\omega^2}{2\pi^2 v^3}$ up to a cutoff frequency ω_D, Debye accounted for the long-wavelength, low-frequency acoustic modes ($\hbar\omega < k_BT$) that remain thermally excited even near absolute zero. Including these low-frequency collective modes eliminated the artificial energy gap and reproduced the experimental $C_V \propto T^3$ power law.

4. **Modern Synthesis — Hybrid Debye–Einstein Treatment:** Although Debye corrected Einstein's model for acoustic vibrations, Einstein's single-frequency approximation later found an important complementary role in polyatomic crystals ($p \geq 2$ atoms per primitive basis). Because Debye's linear dispersion ($\omega = vK$) captures only the 3 acoustic branches and omits the $3p - 3$ nearly dispersionless optical branches ($\omega(\mathbf{K}) \approx$ constant), modern solid-state analyses combine both frameworks by adding $3p - 3$ Einstein terms to the Debye acoustic contribution.

Table 2: Summary of Key Physical Corrections Made by Debye (1912) to Einstein's Model (1907)

Feature	**Einstein Model (1907)**	**Debye Correction (1912)**
Atomic motion	Independent, uncoupled oscillators	Coupled, collective elastic waves
Frequency spectrum	Single discrete frequency ω_0	Continuous spectrum $0 \leq \omega \leq \omega_D$
Density of states $D(\omega)$	$3N\,\delta(\omega - \omega_0)$	$\frac{3V\omega^2}{2\pi^2 v^3}$ $(\omega \leq \omega_D)$
Low-frequency modes ($\omega \to 0$)	Absent (artificial energy gap $\hbar\omega_0$)	Present (long-wavelength acoustic waves)
Low-T heat capacity ($T \to 0$)	Exponential decay: $\propto (\theta_E/T)^2 e^{-\theta_E/T}$	Power law: $\propto (T/\theta)^3$ (matches experiment)

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