Chapter 2 Crystal Dynamics

2.1 Lattice Vibration

2.2 Phonon Heat Capacity

2.2.1 Dulong-Petit Law

2.2.2 Einstein Heat Capacity Model

2.2.3 Debye Heat Capacity Model

Heat capacity

$$C = \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T}$$

According to first law of thermodynamics

$$\Delta Q = \Delta U + p\Delta V$$

$$\Delta V = 0$$

$$C_V = \lim_{\Delta T \to 0} \frac{\Delta U_V}{\Delta T} = \left(\frac{\partial U}{\partial T}\right)_V$$

The energy in a solid includes:

- ✦ The energy given to lattice vibrations ---dominant contribution to the heat capacity in most solids.
- ✦ The energy given to electrons' movement.

◈ Calculation of the lattice energy and heat capacity of a solid falls into two steps:

- ✦ the evaluation of the contribution of lattice waves with the frequency of ω
- ✦ the summation over all frequency distribution of lattice waves.

$$C_V = \lim_{\Delta T \to 0} \frac{\Delta U_V}{\Delta T} = \left(\frac{\partial U}{\partial T}\right)_V$$

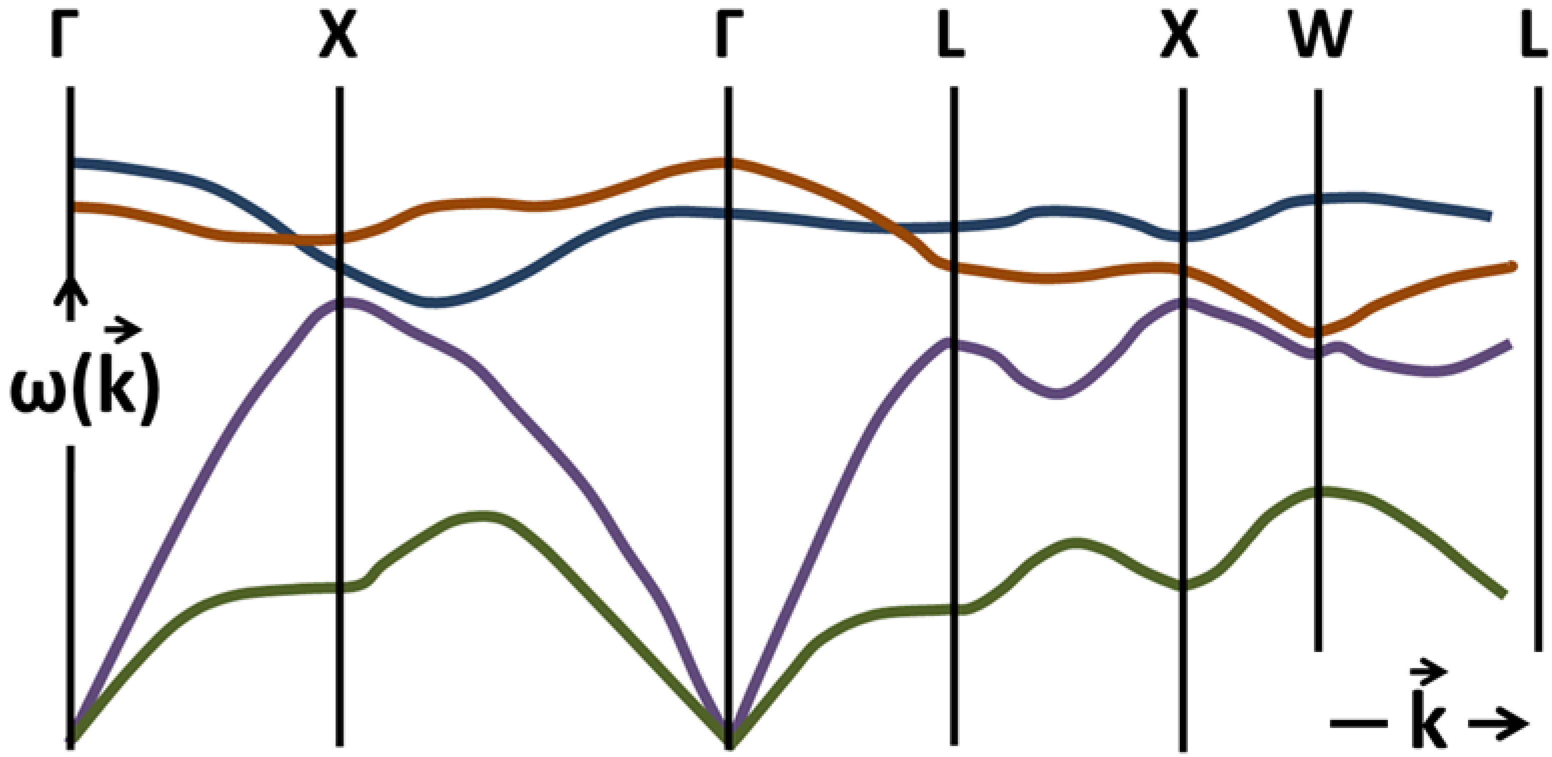
$$\overline{E} = E_0 + E(T) = \sum_{j=1}^{3P} \left(\int_0^{\omega_m} \frac{1}{2} \hbar \omega_j \mathbf{g_j}(\boldsymbol{\omega}) \mathrm{d}\omega_j + \int_0^{\omega_m} \frac{\hbar \omega_j}{e^{\hbar \omega_j / k_B T} - 1} \mathbf{g_j}(\boldsymbol{\omega}) \mathrm{d}\omega_j \right)$$

$$C_V = \left(\frac{\partial \overline{E}}{\partial T}\right)_V = \sum_{j=1}^{3P} \left(\int_0^{\omega_m} k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{\exp\left(\frac{\hbar\omega}{k_B T}\right)}{\left[\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right]^2} g(\omega) \mathrm{d}\omega \right)$$

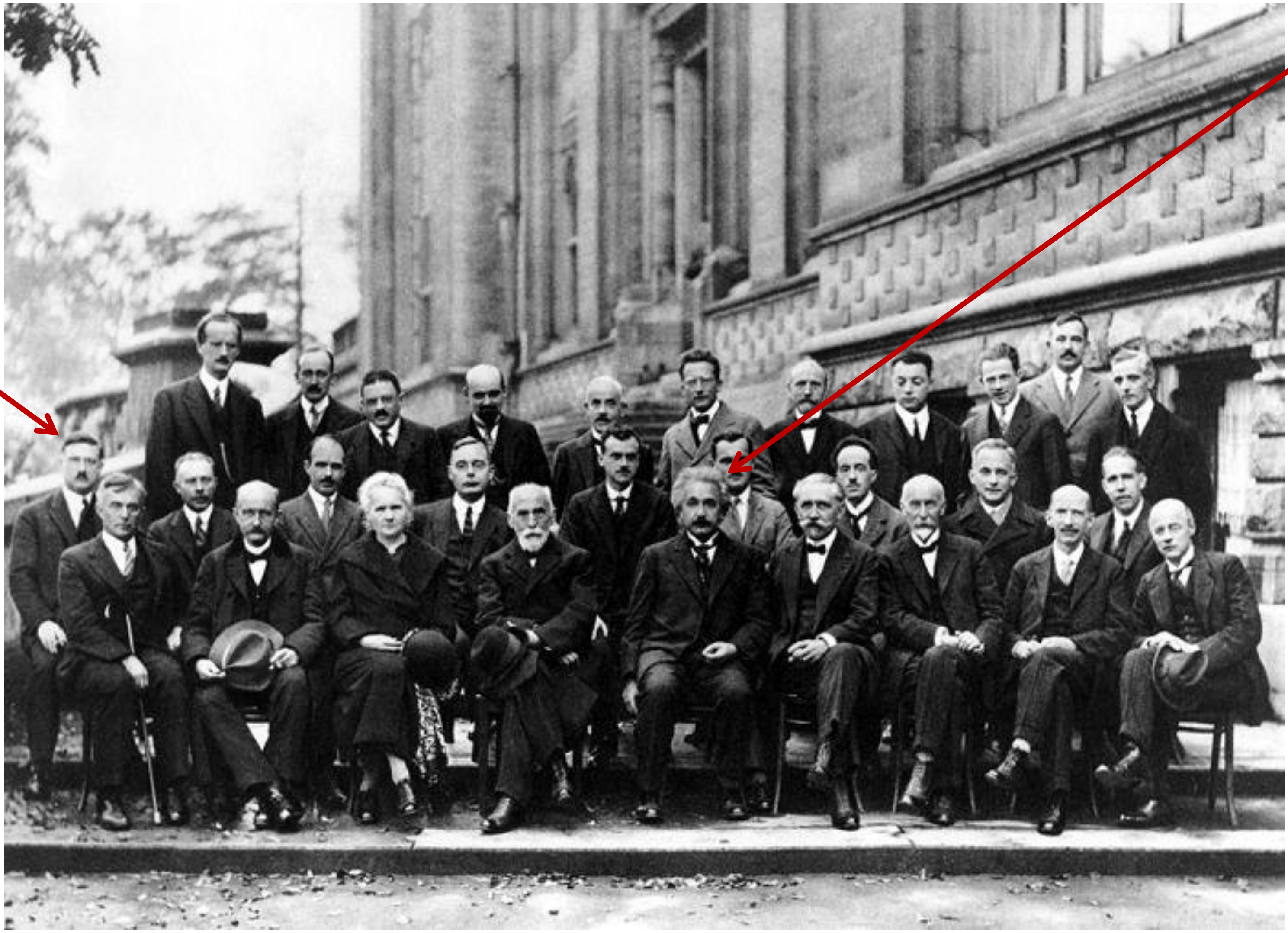
$$g_j(\omega) = \rho_j(k) \frac{\mathrm{d}k}{\mathrm{d}\omega_j}$$

y=1/(u-1), u=e^v, v=hw/kT $\quad \frac{\mathrm{d}y}{\mathrm{d}T} = \frac{\mathrm{d}y}{\mathrm{d}u} \frac{\mathrm{d}u}{\mathrm{d}v} \frac{\mathrm{d}v}{\mathrm{d}T}$

· Heat capacity · **Dispersion relation / Phonon spectrum**



·Heat capacity · Dispersion relation / Phonon spectrum



A. Piccard, E. Henriot, P. Ehrenfest, E. Herzen, Th. De Donder, E. Schrödinger, J.E. Verschaffelt, W. Pauli, W. Heisenberg, R.H. Fowler, L. Brillouin;
B. P. Debye, M. Knudsen, W.L. Bragg, H.A. Kramers, P.A.M. Dirac, A.H. Compton, L. de Broglie, M. Born, N. Bohr;
I. Langmuir, M. Planck, M. Skłodowska-Curie, H.A. Lorentz, A. Einstein, P. Langevin, Ch. E. Guye, C.T.R. Wilson, O.W. Richardson

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2.3 Anharmonic Effect

Translational motion

$$\bar{\varepsilon}_{k\text{-}Translation} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT \qquad \because \overline{v_x^{\,2}} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3}\overline{v^2}$$

$$\frac{1}{2}m\overline{v_x^{\,2}} = \frac{1}{2}m\overline{v_y^2} = \frac{1}{2}m\overline{v_z^2} = \frac{1}{3}\left(\frac{3}{2}kT\right) = \frac{1}{2}kT$$

Since the kinetic energy is quadratic in the components of the velocity, by equipartition these three components each contribute $1/2k_BT$ to the average kinetic energy in thermal equilibrium. Thus the average kinetic energy of the particle is $(3/2)k_BT$.

According to theorem of equipartition of energy

The original idea of equipartition was that, in thermal equilibrium, **energy is shared equally** among all of its various forms; for example, the average kinetic energy **per degree of freedom** in the translational motion of a molecule should equal that of its rotational motions.

Rotation and Vibration

Kinetic energy of a molecule with translation freedom degree t, rotation freedom degree r and vibration freedom degree s

$$\overline{\varepsilon_k} = \frac{1}{2}(t+r+s)kT$$

Total energy

$$\overline{\varepsilon_{\text{total}}} = \frac{1}{2}(t+r+s)kT + \frac{1}{2}skT$$

simple harmonic vibration

For monatomic molecule: t=3, r=s=0

$$\overline{\varepsilon_{\text{total}}} = \frac{3}{2}kT$$

For diatomic molecule: t=3, r=2, s=1

$$\overline{\varepsilon_{\text{total}}} = \frac{7}{2}kT$$

Ideal gas

$$E^{\mathrm{mol}} = \overline{\varepsilon_{\mathrm{total}}} N_A = \frac{1}{2}(t + r + 2s)N_A kT = \frac{1}{2}(t + r + 2s)RT$$

Molar heat capacity

$$C_V^{\mathrm{mol}} = \frac{\mathrm{d}E^{\mathrm{mol}}}{\mathrm{d}T} = \frac{1}{2}(t + r + 2s)R$$

For monatomic molecule: t=3, r=s=0

$$C_V^{\mathrm{mol}} = \frac{3}{2}R$$

For diatomic molecule: t=3, r=2, s=1

$$C_V^{\mathrm{mol}} = \frac{7}{2}R$$

For solid, t=0, r=0, s=3

$$\bar{\varepsilon}_i = \frac{3}{2} k_B T$$

For the simple harmonic vibration

$$\bar{\varepsilon}_{pi} = \bar{\varepsilon}_i = \frac{3}{2} k_B T$$

Total energy of 1mol solid state matter

$$E = N_A(\bar{\varepsilon}_{pi} + \bar{\varepsilon}_i) = 3N_A k_B T = 3RT$$

Molar heat capacity of solid state matter

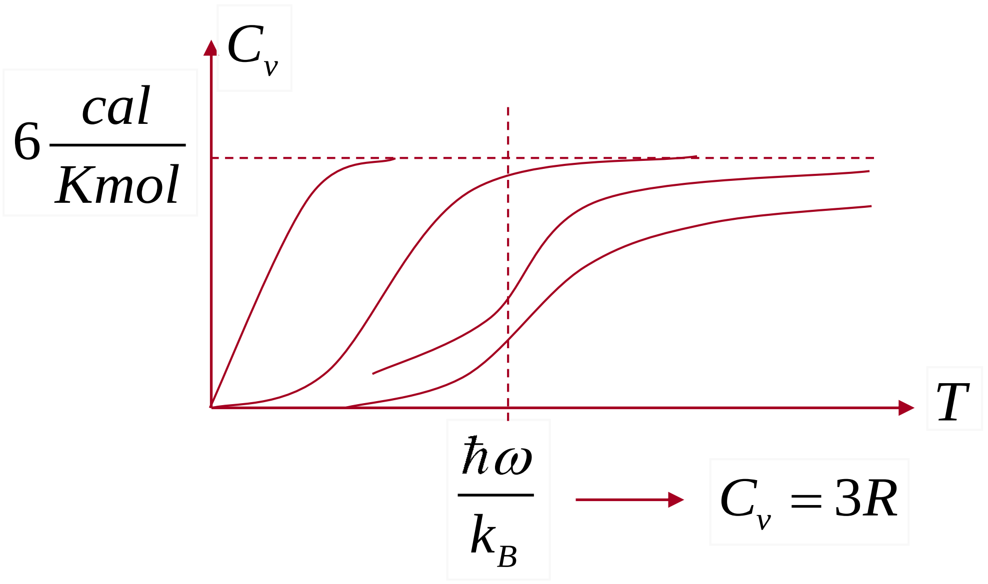
$$C_V^{\mathrm{mol}} = \frac{\partial E}{\partial T} = 3N_A k_B = 3R = 3\times 6.02\times 10^{23}\times 1.38\times 10^{-23}$$

$$= 24.6(\mathrm{J/mol\cdot K})$$

$$= 6(\mathrm{cal/mol\cdot K})$$

This law states that the mole specific heat of any solid is independent of temperature and is the same for all materials!

Matter	C^{mol}/R	Matter	C^{mol}/R
Al	3.09	Sn	3.34
Fe	3.18	Pt	3.16
Au	3.20	Ag	3.09
Cd	3.08	Diamond	0.68
Cu	2.97	Si	2.36
Zn	3.07	B	1.26



$\longrightarrow C_v = 3R$

At high temperatures, all crystalline solids have a specific heat of *25J/K* (or 6cal/K) per mole;

At room temperatures and below, the specific heat of solids is not a universal constant and decreases towards zero. PROBLEM!

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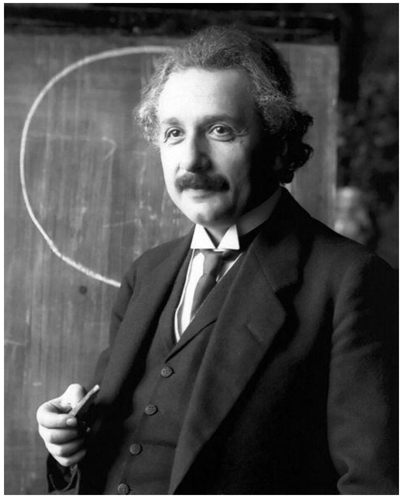
1905 – Annus Mirabilis papers

Title (translated)	Area of focus	Received	Published	Significance
On a Heuristic Viewpoint Concerning the Production and Transformation of Light	Photoelectric effect	18 March	9 June	Resolved an unsolved puzzle by suggesting that energy is exchanged only in discrete amounts (quanta).[133] This idea was pivotal to the early development of quantum theory.[134]
On the Motion of Small Particles Suspended in a Stationary Liquid, as Required by the Molecular Kinetic Theory of Heat	Brownian motion	11 May	18 July	Explained empirical evidence for the atomic theory, supporting the application of statistical physics.
On the Electrodynamics of Moving Bodies	Special relativity	30 June	26 September	Reconciled Maxwell's equations for electricity and magnetism with the laws of mechanics by introducing major changes to mechanics close to the speed of light, resulting from analysis based on empirical evidence that the speed of light is independent of the motion of the observer.[135] Discredited the concept of a "luminiferous ether."[136]
Does the Inertia of a Body Depend Upon Its Energy Content?	Matter–energy equivalence	27 September	21 November	Equivalence of matter and energy, $E = mc^2$ (and by implication, the ability of gravity to "bend" light), the existence of "rest energy", and the basis of nuclear energy.

Einstein Heat Capacity Model



In 1907, Einstein proposed a model of matter where each atom in a lattice structure is an independent harmonic oscillator. In the Einstein model, each atom oscillates independently—a series of equally spaced quantized states for each oscillator. Einstein was aware that getting the frequency of the actual oscillations would be different, but he nevertheless proposed this theory because it was a particularly clear demonstration that quantum mechanics could solve the specific heat problem in classical mechanics. Peter Debye refined this model.

Assumption: All lattice waves have the same frequency:

$$\bar{E} = \sum_i \bar{E}_i = \sum_i \left(\frac{1}{2} + \frac{1}{e^{\hbar\omega_i / k_B T} - 1} \right) \hbar\omega_i = \sum_i \frac{1}{2}\hbar\omega_i + \sum_i \frac{\hbar\omega_i}{e^{\hbar\omega_i / k_B T} - 1}$$

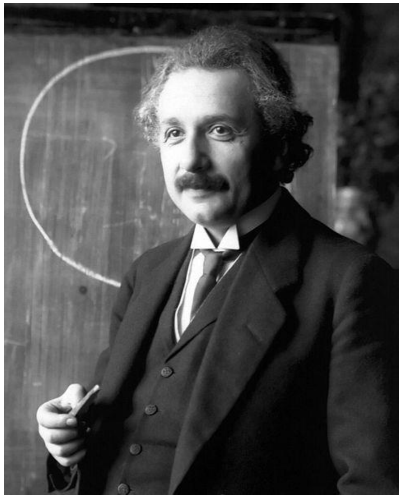
$$\omega = \omega_0 = const.$$

If a solid contains N atoms, the total lattice vibration energy can be written as:

$$\bar{E} = \frac{3N}{2}\hbar\omega_0 + \frac{3N\hbar\omega_0}{e^{\hbar\omega_0 / k_B T} - 1}$$

Then the heat capacity would be

$$\therefore C_V = \frac{\partial \bar{E}}{\partial T} = 3Nk_B \left(\frac{\hbar\omega_0}{k_B T} \right)^2 \cdot \frac{\exp\left(\frac{\hbar\omega_0}{k_B T} \right)}{\left[\exp\left(\frac{\hbar\omega_0}{k_B T} \right) - 1 \right]^2}$$



In this model, the atoms are treated as independent oscillators, but the energy of the oscillators are taken quantum mechanically as phonons.

Discussion: High and Low Temperature Limits for Einstein Model

Definition: $\boxed{\Theta_E = \frac{\hbar\omega_0}{k_B}}$ Einstein temperature.

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

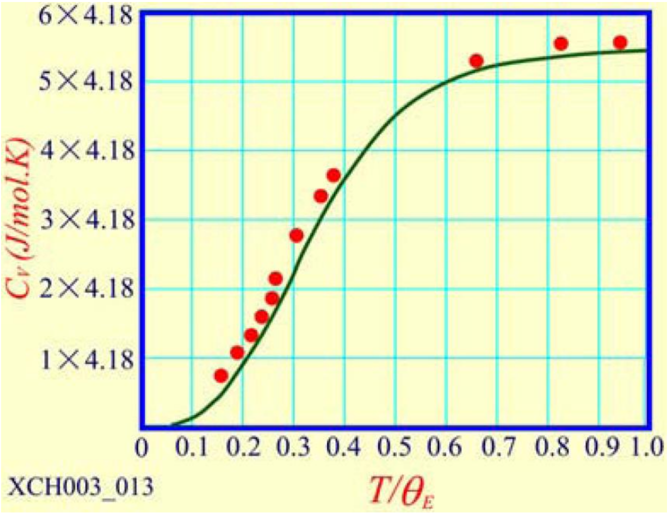
- At high temp.: $T >> \Theta_E$ that is $k_BT >> \hbar\omega_0$

$$C_v \approx 3Nk_B = 3R$$

Coincided with Dulong-Petit law !

- At low temp.: $T << \Theta_E$ that is $k_BT << \hbar\omega_0$

$$C_V \approx 3Nk_B\left(\frac{\hbar\omega_0}{k_BT}\right)^2 \cdot \exp\left(-\frac{\hbar\omega_0}{k_BT}\right) \xrightarrow{T\to 0} 0$$

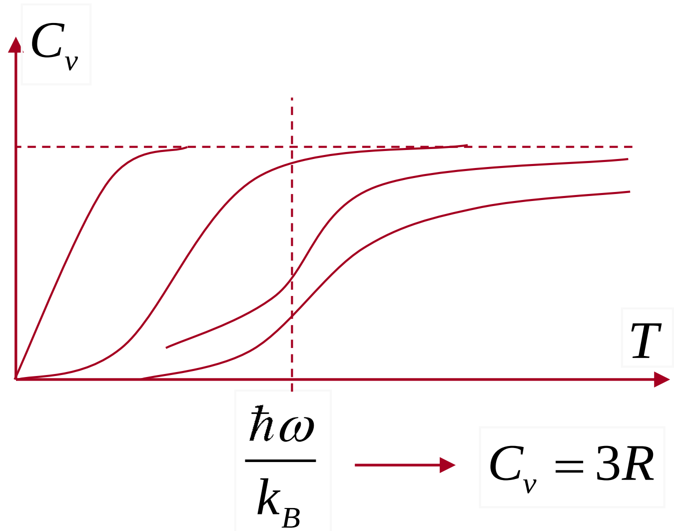


$$C_V = 3Nk_B\left(\frac{\theta_E}{T}\right)^2 \cdot \frac{e^{\theta_E/T}}{\left(e^{\theta_E/T}-1\right)^2} \qquad \Theta_E = \frac{\hbar\omega_0}{k_B}$$

$T >> \Theta_E$

$$C_V = 3Nk_B\left(\frac{\hbar\omega_0}{k_BT}\right)^2 \cdot \frac{\exp\left(\frac{\hbar\omega_0}{k_BT}\right)}{\left[\exp\left(\frac{\hbar\omega_0}{k_BT}\right)-1\right]^2} = 3Nk_B\left(\frac{\hbar\omega_0}{k_BT}\right)^2 \cdot \frac{1}{\left[\exp\left(\frac{\hbar\omega_0}{2k_BT}\right)-\exp\left(-\frac{\hbar\omega_0}{2k_BT}\right)\right]^2}$$

$$\approx 3Nk_B\left(\frac{\hbar\omega_0}{k_BT}\right)^2 \cdot \frac{1}{\left(1+\frac{\hbar\omega_0}{2k_BT}-1+\frac{\hbar\omega_0}{2k_BT}\right)^2} = 3Nk_B$$



$\longrightarrow C_v = 3R$

$x<<1$， $e^x \approx 1+x$

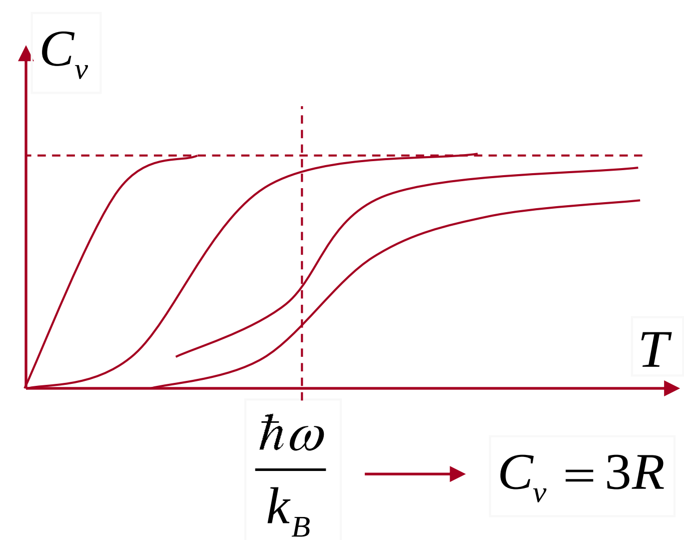
$$C_V = 3Nk_B\left(\frac{\theta_E}{T}\right)^2 \cdot \frac{e^{\theta_E/T}}{\left(e^{\theta_E/T}-1\right)^2} \qquad \Theta_E = \frac{\hbar\omega_0}{k_B}$$

$T << \Theta_E$

$$C_V = 3Nk_B\left(\frac{\hbar\omega_0}{k_B T}\right)^2 \cdot \frac{\exp\left(\frac{\hbar\omega_0}{k_B T}\right)}{\left[\exp\left(\frac{\hbar\omega_0}{k_B T}\right)-1\right]^2} \approx 3Nk_B\left(\frac{\hbar\omega_0}{k_B T}\right)^2 \cdot \exp\left(-\frac{\hbar\omega_0}{k_B T}\right)$$

$T \to 0$

$C_V \to 0$

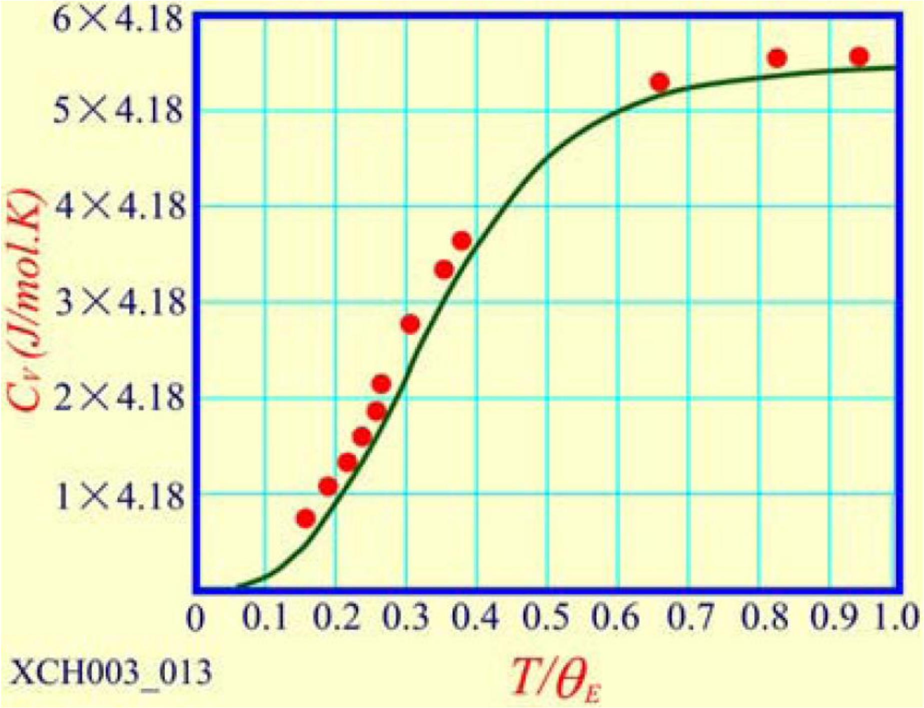


Dulong-Petit Law | Einstein Heat Capacity Model | Debye Heat Capacity Model

· Assumption · Results · Math Details · Problem

For most solids,

$$\Theta_E = 100K \sim 300K$$



Problem: A correct C_v tendence to zero at *0K*, but an incorrect temperature dependence near *0K* $(T \to 0,\ \ C_V \propto T^3)$.

Problem: the assumption of all lattice waves having the same frequency

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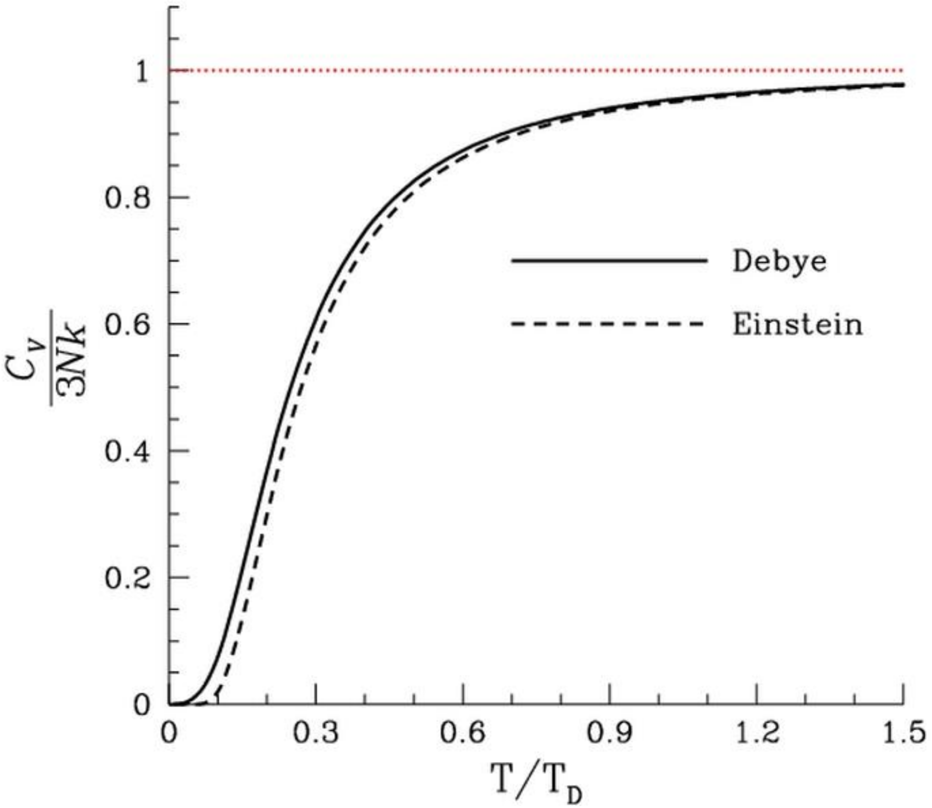
Peter Joseph William Debye, FRS, (March 24, 1884 – November 2, 1966) was a Dutch physicist and physical chemist, and Nobel laureate in Chemistry.



Debye vs. Einstein. Predicted heat capacity as a function of temperature.

$$C_\upsilon = \lim_{\Delta T \to 0}\left(\frac{\Delta E}{\Delta T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V$$

$$\overline{E} = \sum_i \overline{E}_i = \sum_i \frac{1}{2}\hbar\omega_i + \sum_i \frac{\hbar\omega_i}{\exp\left(\frac{\hbar\omega_i}{k_B T}\right)-1} = E_0 + E(T)$$

$$g(\omega) = \frac{\mathrm{d}n}{\mathrm{d}\omega}$$

Einstein — 1907

Einstein, Debye — 1911

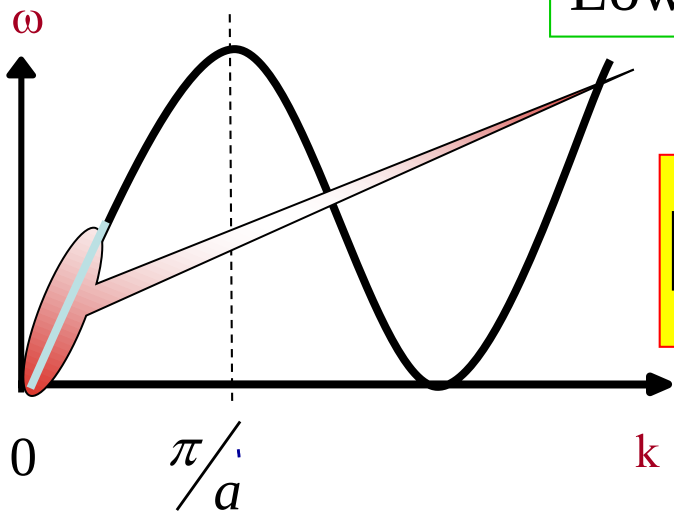
$\omega(k)$ — 1912

$$\overline{E} = E_0 + E(T) = \int_0^{\omega_m} \frac{1}{2}\hbar\omega \mathbf{g}(\boldsymbol{\omega}) d\omega + \int_0^{\omega_m} \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right)-1} \mathbf{g}(\boldsymbol{\omega}) d\omega$$

$$\mathrm{d}n = g_j(\omega)\mathrm{d}\omega = \rho_j(k)\mathrm{d}k \qquad g_j(\omega) = \rho_j(k)\frac{\mathrm{d}k}{\mathrm{d}\omega_j}$$

$$\rho_j(k) = \begin{cases} \dfrac{L}{2\pi} & \text{one dimensional} \\ \dfrac{S}{4\pi^2} & \text{two dimensional} \\ \dfrac{V}{8\pi^3} & \text{three dimensional} \end{cases}$$

At low *T*'s, only lattice waves with low frequencies can be excited from their ground states.



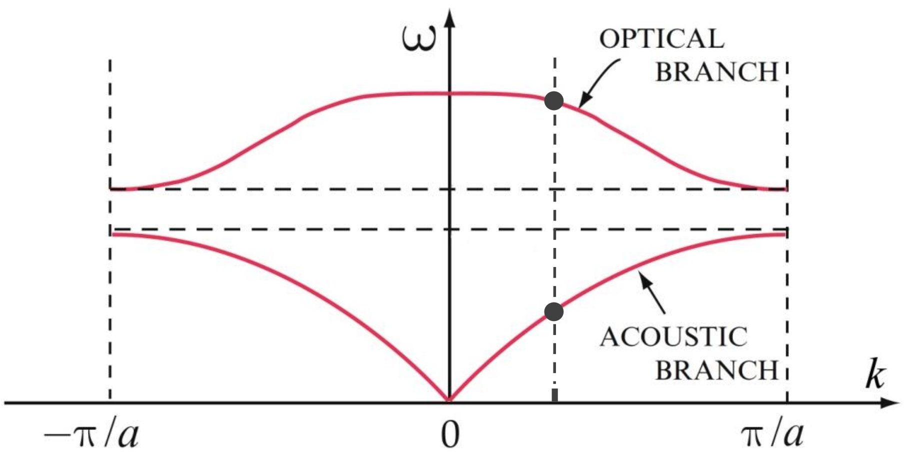
Low frequency → long λ → *sound waves* → $\omega = ck$

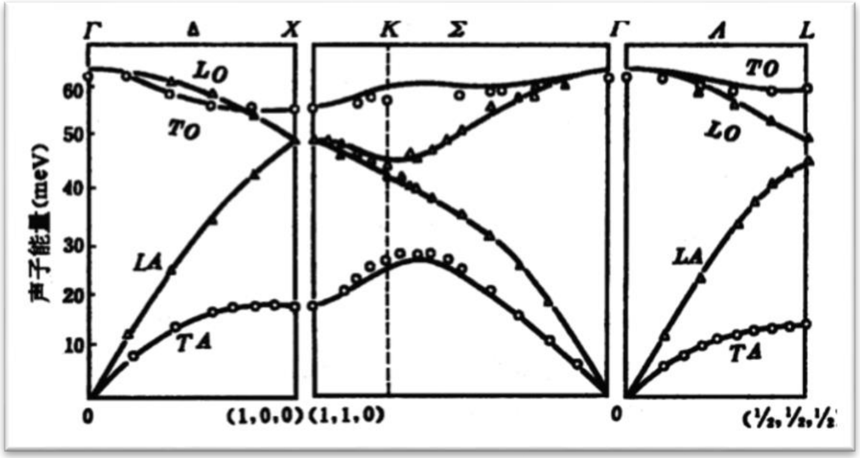
$$\left|\nabla_k \omega\right| = \left|\frac{\mathrm{d}\omega}{\mathrm{d}k}\right| = c = const$$

c: velocity of sound wave.

In the Debye approximation, the velocity of lattice wave is taken as a constant, as it would be for a classical elastic continuum.

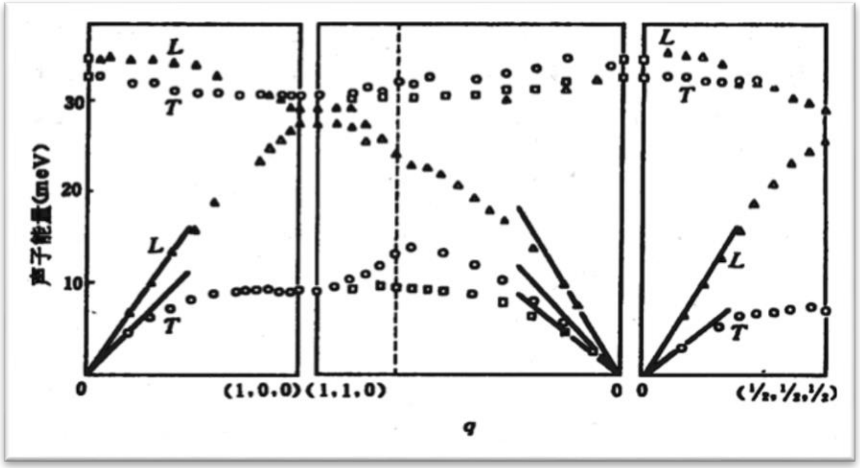
At low T's, only lattice waves with low frequencies can be excited from their ground states.





Si

$$\omega_{-}^{2}=\frac{\beta(M+m)}{Mm}\left\{1-\sqrt{1-\frac{4Mm}{(M+m)^{2}}\sin^{2}\left(\frac{1}{2}ak\right)}\right\}$$



GaAs

k→0

$$\omega_{-}\approx\frac{1}{2}a\sqrt{\frac{2\beta}{M+m}}\cdot k\propto k$$

$$g(\omega) = \sum_{j=1}^{3} g_j(\omega)$$

$$g_j(\omega) = \rho_j(k)\frac{\mathrm{d}k}{\mathrm{d}\omega_j} \overset{3D}{=} \rho(k)4\pi k^2 \frac{\mathrm{d}k}{\mathrm{d}\omega_j} = \frac{V}{8\pi^3}4\pi k^2 \frac{\mathrm{d}k}{\mathrm{d}\omega_j} = \frac{V}{2\pi^2}k^2\frac{\mathrm{d}k}{\mathrm{d}\omega_j} = \frac{V\omega_j^2}{2\pi^2 v_j^3}$$

For *ka*<<1, that is λ>>a, we have $\frac{\omega}{k} = v = \frac{\mathrm{d}\omega}{\mathrm{d}k}$

$$g_l(\omega) = \frac{V\omega_j^2}{2\pi^2 v_l^3} \qquad g_t(\omega) = \frac{V\omega_j^2}{2\pi^2 v_t^3} \qquad \Longrightarrow \qquad g(\omega) = g_l(\omega) + 2g_t(\omega)$$

Make $\frac{3}{v^3} = \left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right)$ Then $g(\omega) = \frac{3V\omega_j^2}{2\pi^2 v^3}$

For $$g(\omega)=\frac{3V\omega_j^2}{2\pi^2 v^3}$$

Define ω_D named Debye frequency or cutoff frequency, that is

$$\int_0^{\omega_D} g_j(\omega)\mathrm{d}\omega = N \qquad \int_0^{\omega_D} g(\omega)\mathrm{d}\omega = 3N$$

Then we get

$$\omega_D^3 = 3N\frac{2\pi^2 v^3}{V} \qquad \omega_D = \left(6\pi^2\frac{N}{V}\right)^{1/3} v$$

So

$$g(\omega)=\sum_{j=1}^{3} g_j(\omega) = 9N\frac{\omega^2}{\omega_D^3} \quad , \qquad \omega <= \omega_D$$

$$=0, \qquad \omega > \omega_D$$

With $g(\omega) = 9N\dfrac{\omega^2}{\omega_D^3}$ $\qquad \omega_D = \left(6\pi^2\dfrac{N}{V}\right)^{1/3} v$

and $$C_V = k_B \int_0^{\omega_m} \left(\frac{\hbar\omega}{k_B T}\right)^2 \cdot \frac{\exp\left(\frac{\hbar\omega}{k_B T}\right)}{\left[\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right]^2} g(\omega)\,\mathrm{d}\omega$$

Define $\Theta_D = \dfrac{\hbar\omega_D}{k_B}$ named Debye Temperature and $x_D = \dfrac{\hbar\omega_D}{k_B T} = \dfrac{\Theta_D}{T}$

The difference with Einstein temp.?

We'll obtain

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

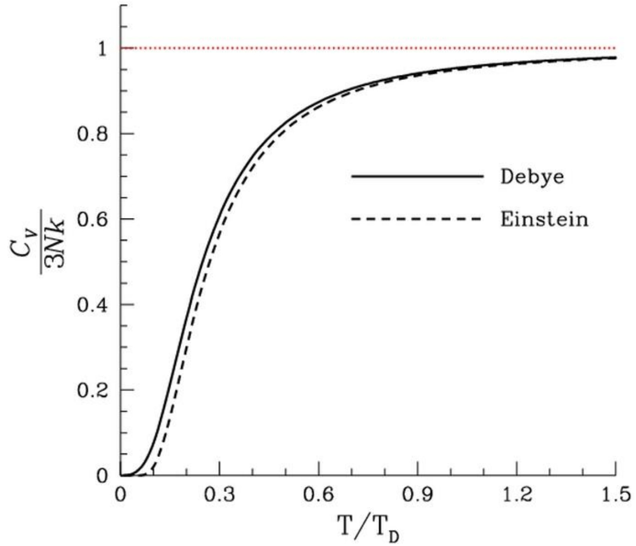
$$C_V = 9Nk_B\left(\frac{T}{\Theta_D}\right)^3 \int_0^{x_D} \frac{x^4 e^x dx}{\left(e^x - 1\right)^2}$$

High temp. limit : $T >> \Theta_D$

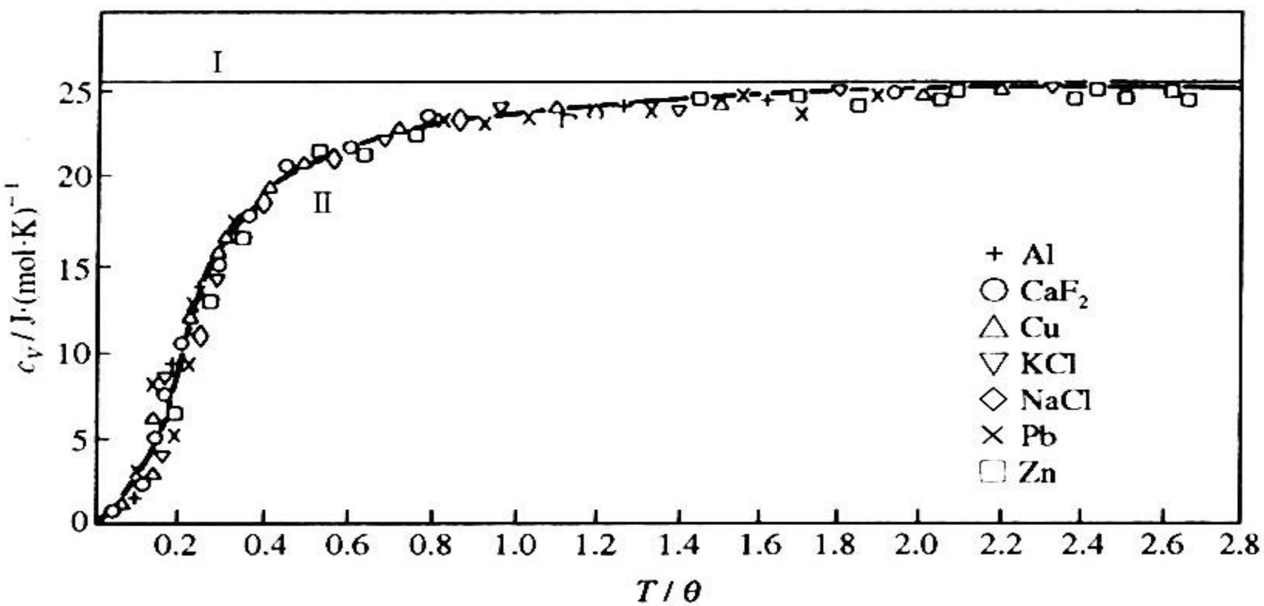
$$C_V \approx 9Nk_B\left(\frac{T}{\Theta_D}\right)^3 \int_0^{x_D} x^2 \mathrm{d}x = 3Nk_B$$

Low temp. limit: $T << \Theta_D$

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



In Debye model, the heat capacity of solids varies as T^3 at low temperature. This is referred to as Debye T^3 law.



Comparison Between Experiment and Theory

❖**The Debye model gives quite a good representation of the heat capacity of most solids.**

❖**For actual crystals, the temperatures at which the T^3 approximation holds are quite low (~ $T=\Theta_D/50$).**

$$\Theta_D = \frac{\hbar\omega_m}{k_B}$$

Debye Temperatures of Some Elements

element	Θ_D (K)	element	Θ_D (K)	element	Θ_D (K)
Ag	225	Cd	209	Ir	108
Al	428	Co	445	K	91
As	282	Cr	630	Li	344
Au	165	Cu	343	La	142
B	1250	Fe	470	Mg	400
Be	1440	Ga	320	Mn	410
Bi	119	Ge	374	Mo	450
diamond	2230	Gd	200	Na	158
Ca	230	Hg	71.9	Ni	450

Debye frequency and Debye temperature scale with the velocity of sound in the solid. So solids with low densities and large elastic moduli have high Θ_D.

Molar heat capacity of some matters

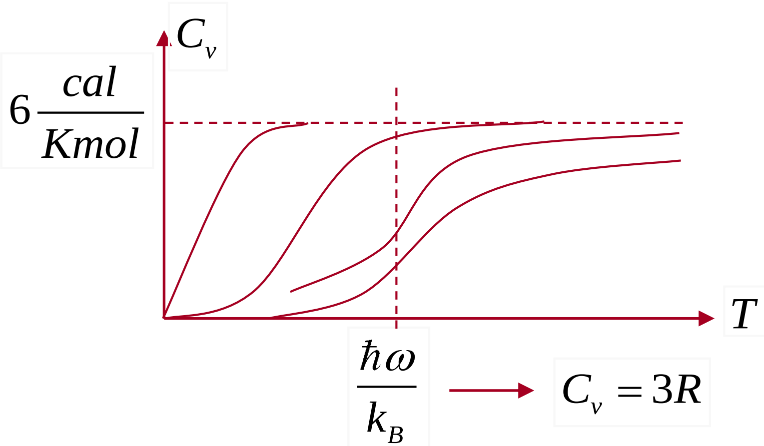
Matter	C^{mol}/R	Matter	C^{mol}/R
Al	3.09	Sn	3.34
Fe	3.18	Pt	3.16
Au	3.20	Ag	3.09
Cd	3.08	Diamond	0.68
Cu	2.97	Si	2.36
Zn	3.07	B	1.26

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

High Temp： T >> Θ_D， that is $x_D=\frac{\Theta_D}{T}\to 0$

$$C_V = 9Nk_B\left(\frac{T}{\Theta_D}\right)^3\int_0^{x_D}\frac{x^4e^x\mathrm{d}x}{\left(e^x-1\right)^2} = 9Nk_B\left(\frac{T}{\Theta_D}\right)^3\int_0^{x_D}\frac{x^4\mathrm{d}x}{\left(e^{\frac{1}{2}x}-e^{-\frac{1}{2}x}\right)^2}$$

$$C_V \approx 9Nk_B\left(\frac{T}{\Theta_D}\right)^3\int_0^{x_D}\frac{x^4\mathrm{d}x}{\left(1+\frac{1}{2}x-1+\frac{1}{2}x\right)^2} \approx 9Nk_B\left(\frac{T}{\Theta_D}\right)^3\int_0^{x_D}x^2\mathrm{d}x = 3Nk_B$$



x<<1， $e^x \approx 1+x$

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

Low Temp: T << Θ_D , that is $x_D = \frac{\Theta_D}{T} \to \infty$

$$C_V \approx 9Nk_B\left(\frac{\mathrm{T}}{\Theta_\mathrm{D}}\right)^3 \int_0^{\infty} \frac{x^4 e^x \mathrm{d}x}{\left(e^x - 1\right)^2} = 9Nk_B\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\infty} \frac{x^4 e^{-x} \mathrm{d}x}{\left(1 - e^{-x}\right)^2}$$

With Taylor's expansion

$$\left(1+\xi\right)^{-n} = 1 + (-n)\xi + \frac{(-n)(-n-1)}{2!}\xi^2 + \frac{(-n)(-n-1)(-n-2)}{3!}\xi^3 + \cdots$$

$$\therefore C_V = 9Nk_B\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\infty} x^4 e^{-x}\left(1 + 2e^{-x} + 3e^{-2x} + \cdots\right)\mathrm{d}x$$

$$= 9Nk_B\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\infty} x^4 \sum_{n=1}^{\infty} n e^{-nx}\mathrm{d}x = 9Nk_B\left(\frac{T}{\Theta_D}\right)^3 \sum_{n=1}^{\infty} n\int_0^{\infty} x^4 e^{-nx}\mathrm{d}x$$

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

Low Temp: T << Θ_D , that is $x_D = \frac{\Theta_D}{T} \to \infty$

$$C_V \approx 9Nk_B\left(\frac{\mathrm{T}}{\Theta_{\mathrm{D}}}\right)^3 \int_0^{\infty} \frac{x^4 e^x \mathrm{d}x}{\left(e^x - 1\right)^2} = \ldots = 9Nk_B\left(\frac{T}{\Theta_D}\right)^3 \sum_{n=1}^{\infty} n \int_0^{\infty} x^4 e^{-nx} \mathrm{d}x$$

With the integration formula:

$$\int_0^{\infty} \xi^m e^{-a\xi} d\xi = \frac{\Gamma(m+1)}{a^{m+1}} = \frac{m!}{a^{m+1}}$$

We'll get

$$C_V = 9Nk_B\left(\frac{T}{\Theta_D}\right)^3 \sum_{n=1}^{\infty} n \cdot \frac{4!}{n^5} \Longrightarrow C_V = \frac{12\pi^4 Nk_B}{5}\left(\frac{T}{\Theta_D}\right)^3 \propto T^3$$

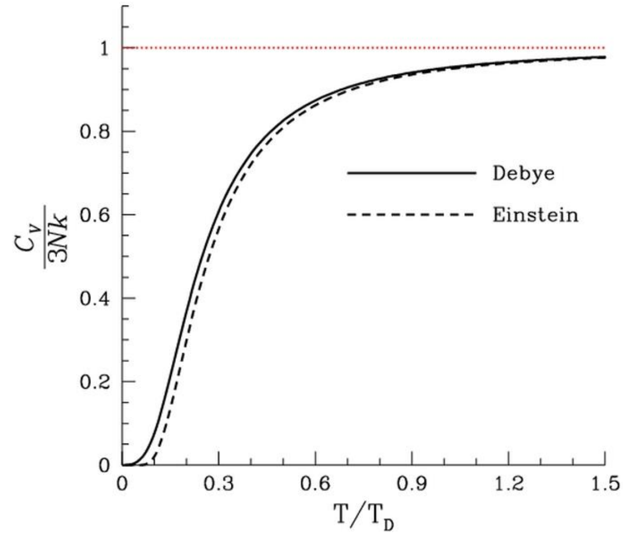
$$\sum_{n=1}^{\infty} \frac{1}{n^4} = \frac{\pi^4}{90}$$

Debye's Law

· Summary

Dulong-Petit Law

$$C_V^{\text{mol}} = \frac{\partial E}{\partial T} = 3N_A k_B = 3R = 24.6(\text{J/mol}\cdot\text{K})$$



Einstein Heat Capacity Model

At high temp.: $T >> \Theta_E$ $\quad C_V \approx 3Nk_B = 3R$

At low temp.: $T << \Theta_E$ $\quad C_V \approx 3Nk_B \left(\frac{\hbar\omega_0}{k_B T}\right)^2 \cdot \exp\left(-\frac{\hbar\omega_0}{k_B T}\right)$

Debye Heat Capacity Model

High temp. limit : $T >> \Theta_D$ $\quad C_V \approx 9Nk_B \left(\frac{T}{\Theta_D}\right)^3 \int_0^{x_D} x^2 dx = 3Nk_B$

Low temp. limit: $T << \Theta_D$ $\quad C_V = \frac{12\pi^4 Nk_B}{5}\left(\frac{T}{\Theta_D}\right)^3 \propto T^3$