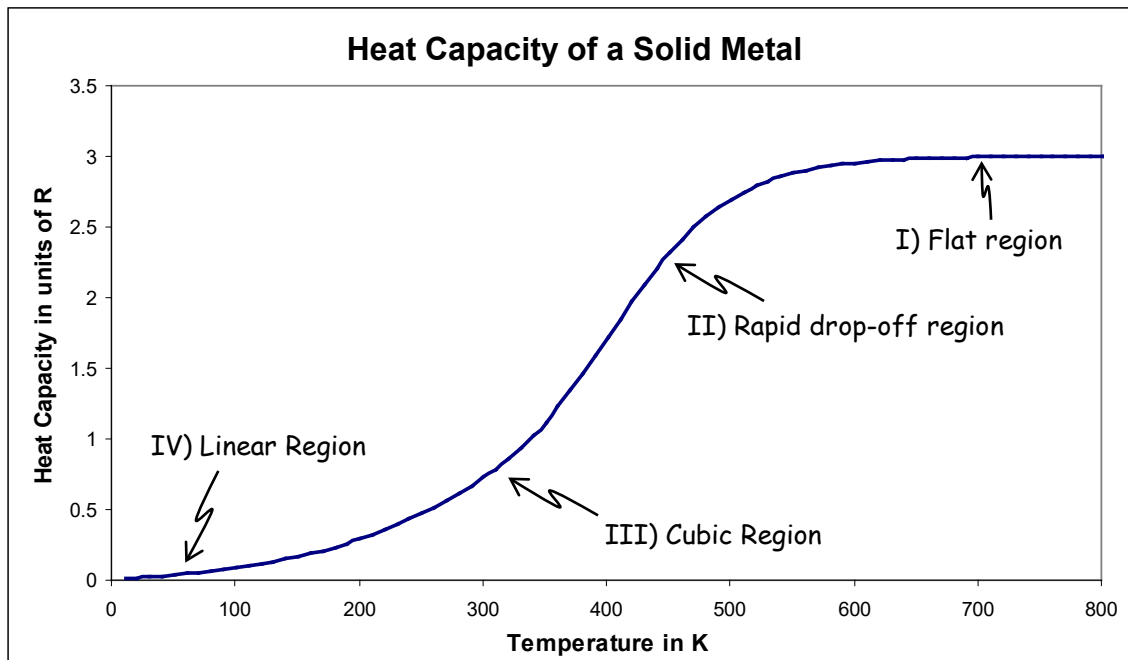


Heat Capacity: Classical and Quantum

The development of statistical mechanics was, in part, driven by the physics community striving to understand the dependence of heat capacity (at constant volume) on temperature as shown below.



I. Classical: The Dulong-Petit Law: Ion vibrations

Equipartition of energy according to Maxwell-Boltzmann statistics claims that each quadratic term in (mechanical) energy contributes $\frac{1}{2}kT$ in thermal energy. Each ion thus has mechanical and thermal energies of

$$E_{MB,ion} = \frac{1}{2}mv_x^2 + \frac{1}{2}mk_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mk_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}mk_z^2, \quad \text{and} \quad U_{MB,ion} = 6\left(\frac{1}{2}kT\right) = 3kT$$

A lattice of N atoms will have N times these energies. If there is a mole of ions, $N = N_A$ and since $kN_A = R$ (the gas constant), the thermal energy of the lattice is

$$U_{MB,lattice} = 3kN_A T = 3RT$$

The heat capacity at constant volume (C_V) is then

$$C_{V,MB} = \frac{dU_{MB,lattice}}{dT} = 3kN_A = 3R$$

Which is true at high temperatures as shown by the flat region on the plot.

II) Quantum Phonons: Einstein: Phonons: vibrations in lattice

Einstein postulated that vibrations in the lattice of ions behave as phonons of (a single) energy, $E_{ph} = \hbar\omega$ that is characterized by an Einstein Temperature

$$kT_E = \hbar\omega \quad \Rightarrow \quad T_E = \frac{\hbar\omega}{k}$$

Since phonons are bosons and any number can occupy the same energy state, he derived the heat capacity using Bose-Einstein statistics, finding

$$C_{V,E} = 3R \left(\frac{T_E}{T} \right)^2 \frac{e^{T_E/T}}{(e^{T_E/T} - 1)^2}$$

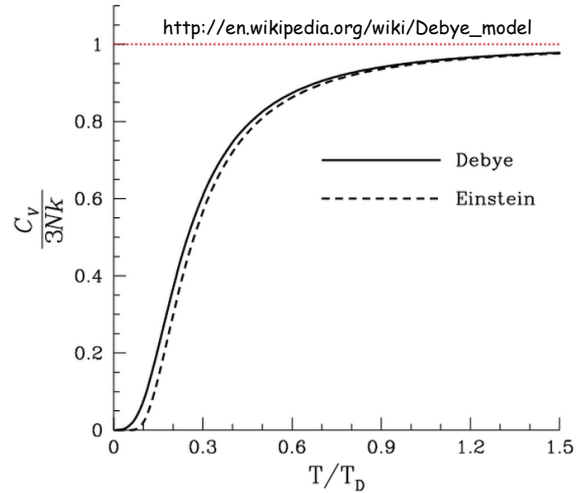
III) Quantum Phonons: Debye: Phonons

Debye refined Einstein's model by including phonons of frequencies ranging from zero to a maximum, Debye frequency, based on the density and sound speed that gives a Debye Temperature.

$$f_D = \left(\frac{3N}{4\pi V} \right)^{1/3} v_{\text{sound}} \Rightarrow T_D = \frac{hf_D}{k}$$

This allowed him to derive a slightly different heat capacity than Einstein:

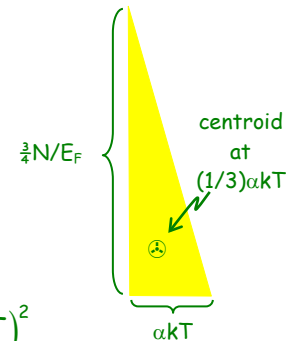
$$C_{V,D} = \frac{12\pi^4}{5} R \left(\frac{T}{T_D} \right)^3$$



The difference between the Einstein and Debye heat capacities are shown in the figure from the Wikipedia page. It is very small, but is important in accurately characterizing heat capacities at very low temperatures.

IV) Quantum Electrons: Fermi-Dirac: Energy into conduction e⁻'s

Only electrons close to the Fermi Energy can be excited to higher states. The thermal energy absorbed is the number of electrons excited times their average increase in energy. From area analysis of the Fermi-Dirac curve, we get



$$U_{EX} = n_{\text{excited}} \Delta E = \left[\left(\frac{1}{2} \right) \left(\frac{3N}{4E_F} \right) (\alpha kT) \right] \left[\left(E_F + \frac{1}{3} \alpha kT \right) - \left(E_F - \frac{1}{3} \alpha kT \right) \right] = \frac{1}{4} \frac{N(\alpha kT)^2}{E_F}$$

For a mole, so that $N_A k = R$, including Sommerfeld's finding that $\alpha = \pi$ and taking $E_F = kT_F$, the heat capacity of the electrons is

$$C_{V,e^-} = \frac{\pi^2}{2} R \frac{T}{T_F}$$

In general, $T_F \gg T$ rendering this a very small effect that is only consequential at very low temperatures.

Total Heat Capacity

The total heat capacity is the sum of these, though a choice needs to be made between the Einstein and Debye models. The Debye is the more accurate, but the Einstein model is very close. Thus,

$$C_V = C_{V,MB} + C_{V,D} + C_{V,e^-} \quad \text{or} \quad C_V = C_{V,MB} + C_{V,E} + C_{V,e^-}$$