We compute the heat capacity of solids in the Debye model.

First, we construct the partition function.

The energy of a phonon is given by $E = \hbar \omega$. Since phonon number is not conserved, the partition function for phonons at a given frequency ω is given by

$$Z_\omega = \sum_{n=0}^{\infty} e^{-\beta \hbar \omega n} = \frac{1}{1 - e^{-\beta \hbar \omega}}$$

To compute the total partition function, we take the product $Z = \prod_\omega Z_\omega \Rightarrow$

$$\log Z = \sum_\omega \log Z_\omega \approx -\int_0^{\omega_0} d\omega \, g(\omega) \log\left(1 - e^{-\beta \hbar \omega}\right),$$

Where we are treating the density of states $g(\omega) d\omega$ as our integration measure, and we integrate to some maximum frequency ω_0 because the crystal structure limits the minimum wavelength (and hence the maximum frequency).

Debye's hypothesis equates the number of degrees of freedom in the solid with the number of phonon states:

$$3N = \int_0^{\omega_0} g(\omega) d\omega = \frac{3V}{2\pi^2 c_s^3} \frac{\omega_0^3}{3}.$$

(The density of states is the massless, relativistic density of states with 3 polarization states and $c \mapsto c_s$.)

Also, we will use $T_D = \hbar \omega_D / k_B \implies$

$$3N = \frac{V k_B^3}{2\pi^2 \hbar^3 c_s^3} T_D^3$$

The average energy can now be computed

$$\langle E \rangle = \frac{-\partial}{\partial \beta} \log Z = \frac{3V}{2\pi^2 c_s^3} \int_0^{\omega_D} \omega^2 \frac{\hbar \omega \, e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \, d\omega =$$

$$\frac{3V\hbar}{2\pi^2 c_s^3} \int_0^{\omega_D} \frac{\omega^3}{e^{\beta \hbar \omega} - 1} \, d\omega = \frac{3V\hbar}{2\pi^2 c_s^3} \int_0^{\beta \hbar \omega_D} \frac{(\beta \hbar \omega)^3 \cdot \frac{1}{(\beta \hbar)^3}}{e^{\beta \hbar \omega} - 1} \, d(\beta \hbar \omega) \cdot \frac{1}{\beta \hbar}$$

$$= \frac{3V (k_B T)^4}{2\pi^2 \hbar^3 c_s^3} \int_0^{T_D / T} \frac{x^3}{e^x - 1} \, dx \quad .$$

This integral has no analytic form. We consider two limits.

High temperature limit: $T_D / T \ll 1$.

In this limit, $x \ll 1 \implies x^3 / (e^x - 1) \approx x^2 \implies$

$$\langle E \rangle \approx \frac{3V (k_B T)^4}{2\pi^2 \hbar^3 c_s^3} \left(\frac{T_D}{T} \right)^3 \cdot \frac{1}{3} = \frac{k_B^4 V T_D^3 T}{2\pi^2 \hbar^3 c_s^3}$$

The heat capacity in the high temperature limit is thus given by

$$C_v = \frac{\partial \langle E \rangle}{\partial T} = \frac{K_B^4 V T_D^3}{2\pi^2 \hbar^3 C_s^3} = \boxed{3 N K_B}$$

This is the Dulong-Petit law, which can also be computed using the Einstein solid Hamiltonian,

$$H = \sum_{i=1}^{N} \vec{P}_i^2/2m + \frac{1}{2} K \vec{x}_i^2.$$

Low Temperature Limit: $T_D/T \gg 1$

In this case, $\langle E \rangle \approx \frac{3V(K_B T)^4}{2\pi^2 \hbar^3 C_s^3} \int_0^{\infty} \frac{x^3}{e^x - 1} dx$

$$\frac{3V(K_B T)^4}{2\pi^2 \hbar^3 C_s^3} \cdot \frac{\pi^4}{15} \implies C_v = \frac{12 V K_B^4 T^3 \pi^4}{2\pi^2 \hbar^3 C_s^3} \cdot \frac{1}{15}$$

$$3N K_B \pi^4 \cdot \frac{12}{15} \left(\frac{T}{T_D}\right)^3 = \boxed{\frac{12}{5} N K_B \pi^4 \left(\frac{T}{T_D}\right)^3}$$

Thus, we expect cubic temperature dependence of the heat capacity for small temperatures, and constant dependence at large temperatures.