Heat capacity

Heat capacity of oscillator

$$\varepsilon_{\mathrm{n}} = \left(n + \frac{1}{2} \right) \hbar\omega$$

$$\bar{\varepsilon} = \sum_{n=0}^{\infty} p_n \varepsilon_n$$

$$p_n = A \exp[-\varepsilon_n / k_B T], \quad \sum_{n=0}^{\infty} p_n = 1$$

$$\bar{\varepsilon} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}$$

Planck distributions for phonons

$$\bar{\varepsilon} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} = \left(n(\omega) + \frac{1}{2} \right)\hbar\omega$$

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

High temperature limit

$$\bar{\varepsilon} = \left(n(\omega) + \frac{1}{2} \right) \hbar\omega, \qquad n(\omega) = \frac{1}{e^{\hbar\omega / k_B T} - 1}$$

$$\hbar\omega \ll k_B T$$

$$n(\omega) \simeq \frac{k_B T}{\hbar\omega} - \frac{1}{2}$$

$$\frac{1}{\exp(x) - 1} \simeq \frac{1}{x + x^2/2} \simeq \frac{1}{x} - \frac{1}{2}, \quad x \to 0$$

$$\bar{\varepsilon} \simeq \left(\frac{k_B T}{\hbar\omega} - \frac{1}{2} + \frac{1}{2} \right) \hbar\omega = k_B T$$

Low temperature limit

$$\bar{\varepsilon} = \left(n(\omega) + \frac{1}{2} \right) \hbar\omega$$

$$k_B T \ll \hbar\omega$$

$$n(\omega) = \frac{1}{e^{\hbar\omega/k_B T} - 1} \approx e^{-\hbar\omega/k_B T}$$ - exponentially small

$$\bar{\varepsilon} = \left(e^{-\hbar\omega/k_B T} + \frac{1}{2} \right) \hbar\omega$$

Heat capacity

$$C = \frac{d\overline{\varepsilon}}{dT} = k_B \left(\frac{\Theta}{T}\right)^2 \frac{e^{\Theta/T}}{\left(e^{\Theta/T} - 1\right)^2}, \quad \Theta = \hbar\omega / k_B$$

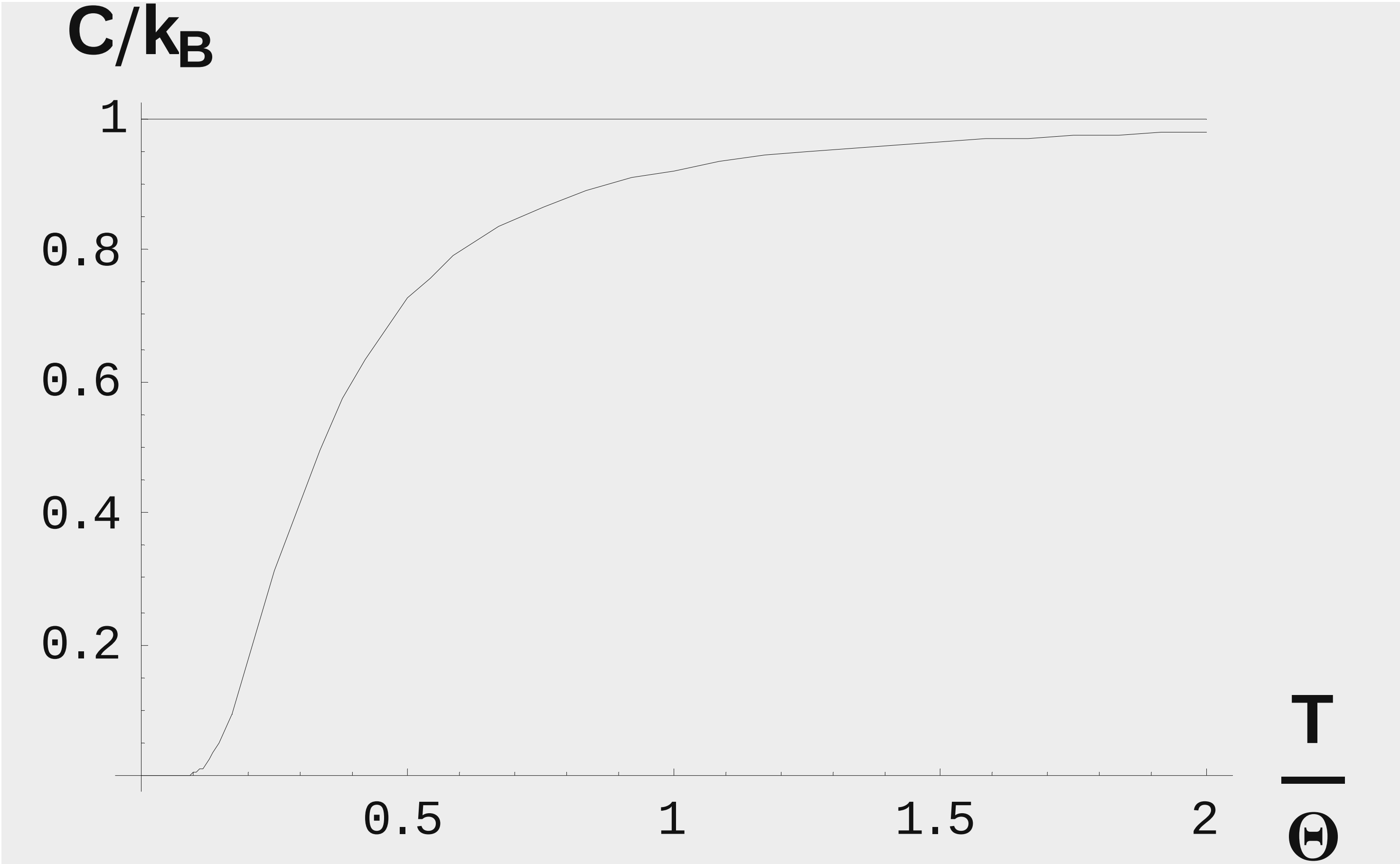
High temperature $\Theta \ll \mathrm{T}$

$$\mathrm{C} \simeq k_B \left(1 - \frac{1}{12}\left(\frac{\Theta}{T}\right)^2\right)$$

Low temperature $\mathrm{T} \ll \Theta$

$$C = k_B \left(\frac{\Theta}{T}\right)^2 \exp(-\Theta / T)$$

Heat capacity of the oscillator



Heat capacity of lattice

$$E = \sum_i \int \bar{\varepsilon}_i(\mathbf{k}) \frac{V d^3 k}{(2\pi)^3}, \quad \bar{\varepsilon}_i(\mathbf{k}) = \left(\frac{1}{2} + \frac{1}{e^{\hbar\omega_i(\mathbf{k})/k_B T} - 1} \right) \hbar\omega_i(\mathbf{k})$$

$$\sum_i \int k^2 \frac{dk}{d\omega} \frac{V d\Omega}{(2\pi)^3} = g(\omega)$$

$$E = \int_0^\infty \bar{\varepsilon}(\omega) g(\omega) d\omega$$

Density of states g

$$\sum_i \int k^2 \frac{dk}{d\omega} \frac{Vd\Omega}{(2\pi\hbar)^3} = g(\omega)$$

In the model in which there are only three identical sound waves $\omega = \mathrm{v}_S k$

$$3k^2 \frac{dk}{d\omega} \frac{V4\pi}{(2\pi)^3} = \frac{3}{2\pi^2} \frac{V\omega^2}{\mathrm{v}_S{}^3} = g(\omega)$$

If one distinguishes longitudinal $\omega = v_L k$, and two transverse $\omega = v_T k$ modes

$$\frac{1}{2\pi^2} V\omega^2 \left(\frac{1}{\mathrm{v}_L{}^3} + \frac{2}{\mathrm{v}_T{}^3} \right) = g(\omega)$$

Calculation of heat capacity

$$E = \int_0^\infty \bar{\varepsilon}(\omega) g(\omega) d\omega, \quad \bar{\varepsilon}(\omega) = \left(\frac{1}{2} + \frac{1}{e^{\hbar\omega/k_B T} - 1} \right) \hbar\omega$$

$$g(\omega) = \frac{1}{2\pi^2} V \omega^2 \left(\frac{1}{v_L{}^3} + \frac{2}{v_T{}^3} \right)$$

$$E = E_0 + \frac{1}{2\pi^2} V \left(\frac{1}{v_L{}^3} + \frac{2}{v_T{}^3} \right) \int_0^\infty \frac{\hbar\omega^3 d\omega}{e^{\hbar\omega/k_B T} - 1}$$

$$C = \frac{dE}{dT}$$

Energy

$$E = E_0 + \frac{1}{2\pi^2} V \left(\frac{1}{{v_L}^3} + \frac{2}{{v_T}^3} \right) \int_0^\infty \frac{\hbar\omega^3 d\omega}{e^{\hbar\omega/k_B T} - 1} =$$

$$E = E_0 + \frac{V}{2\pi^2} \left(\frac{1}{{v_L}^3} + \frac{2}{{v_T}^3} \right) \frac{(k_B T)^4}{\hbar^3} \int_0^\infty \frac{x^3 dx}{e^x - 1}$$

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

$$E = E_0 + \frac{\pi^2 V}{30} \left(\frac{1}{{v_L}^3} + \frac{2}{{v_T}^3} \right) \frac{(k_B T)^4}{\hbar^3}$$

Heat capacity

$$E = E_0 + \frac{\pi^2 V}{30}\left(\frac{1}{{v_L}^3} + \frac{2}{{v_T}^3}\right)\frac{(k_B T)^4}{\hbar^3}$$

$$C = \frac{dE}{dT} = \frac{2\pi^2 V}{15}\left(\frac{1}{{v_L}^3} + \frac{2}{{v_T}^3}\right)\left(\frac{k_B T}{\hbar}\right)^3$$

The Debye interpolation

Assume that the density of states satisfy

$$g(\omega) = \frac{1}{2\pi^2} V\omega^2 \left(\frac{1}{\mathrm{v}_L{}^3} + \frac{2}{\mathrm{v}_T{}^3} \right)$$

Introduce parameter ω_D

$$\int_0^{\omega_D} g(\omega) d\omega = 3N \ - \text{number of all possible oscillators}$$

$$\frac{1}{6\pi^2} V\omega_D^3 \left(\frac{1}{\mathrm{v}_L{}^3} + \frac{2}{\mathrm{v}_T{}^3} \right) = 3N,$$

Assume $\mathrm{v}_L = \mathrm{v}_T = \mathrm{v}, \quad \omega_D = \left(6\pi^2 \frac{N}{V} \right)^{1/3} \mathrm{v} \sim \left(6\pi^2 \right)^{1/3} \frac{\mathrm{v}}{a} \approx 4 \frac{\mathrm{v}}{a}$

Debye energy and temperature

ω_D Debye fequency

$\hbar\omega_{\mathrm{D}}$ Debye energy

$$\hbar\omega_{\mathrm{D}} = k_B T_D$$

$$\Theta_D = \frac{\hbar\omega_D}{k_B}$$ Debye temperature

Numericals

$$\mathrm{v} = 10^{3} 10^{2} = 10^{5}\ \mathrm{cm/c}$$

$$a = 310^{-8}\ \mathrm{cm}$$

$$\omega_{\mathrm{D}} = 4\frac{\mathrm{v}}{a} = 4\frac{10^{5}}{310^{-8}} = 10^{13}\ 1/\mathrm{c}$$

$$\Theta_{\mathrm{D}} = \frac{10^{-27}}{1.3810^{-16}} 10^{13} = 100^{0}\ \mathrm{K}$$

Energy in the Debye approx

$$g(\omega) = \frac{1}{2\pi^2} V\omega^2 \left(\frac{1}{\mathrm{v}_L^{\;3}} + \frac{2}{\mathrm{v}_T^{\;3}} \right)$$

$$\frac{1}{6\pi^2} V\omega_D^3 \left(\frac{1}{\mathrm{v}_L^{\;3}} + \frac{2}{\mathrm{v}_T^{\;3}} \right) = 3N$$

$$E = \int_0^\infty \left(\frac{1}{2} + \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} \right) g(\omega) d\omega =$$

$$N \left(\frac{9}{8} \hbar\omega_D + \frac{9}{\omega_D^3} \int_0^{\omega_D} \frac{\hbar\omega^3 d\omega}{e^{\hbar\omega/k_B T} - 1} \right)$$

Debye heat capacity

$$C = 9Nk_B\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x dx}{\left(e^x - 1\right)^2}, \qquad x = \frac{\hbar\omega}{k_B T}$$

$$T \to 0 \qquad C = \frac{12\pi^4}{5} Nk_B\left(\frac{T}{\Theta_D}\right)^3,$$

T^3 behaviour, not the exponent (!) as for an oscillator

$$T \to \infty \qquad C \to 3N\,k_B$$

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