Heat capacity

Harmonic oscillator

$$\varepsilon_n = \left(n + \tfrac{1}{2}\right)\hbar\omega \qquad (1)$$

$$\overline{\varepsilon} = \sum W_n \varepsilon_n \qquad (2)$$

$$\begin{cases} W_n = A\, e^{-\varepsilon_n / kT} & (3) \\ \sum\limits_n W_n = 1 & (4) \end{cases}$$

$$\overline{\varepsilon} \underset{(1-4)}{=} \left(\overline{n} + \tfrac{1}{2}\right)\hbar\omega \qquad (5)$$

$$\overline{n} = \frac{1}{e^{\frac{\hbar\omega}{kT}} - 1} = \frac{1}{e^{x} - 1} \qquad (6)$$

$$x = \frac{\hbar\omega}{kT} \qquad (7)$$

$$C = \frac{d\bar{\varepsilon}}{dT} \underset{(5,6)}{=} k \frac{x^2 e^x}{(e^x - 1)^2} \qquad (8)$$

High-temperature (classical) limit

$$kT \gg \hbar\omega \underset{(7)}{\Longrightarrow} x \ll 1 \qquad (9)$$

$$\bar{n} \underset{(6,9)}{\cong} \frac{1}{x + \frac{x^2}{2}} \cong \frac{1}{x} - \frac{1}{2} \qquad (10)$$

$$\bar{\varepsilon} \underset{(5,10)}{=} \frac{1}{x}\hbar\omega \underset{(7)}{=} kT \qquad (11)$$

$$C = k \qquad (12)$$

Low-temperature limit (quantum)

$$kT \ll \hbar\omega \qquad x \gg 1 \tag{13}$$

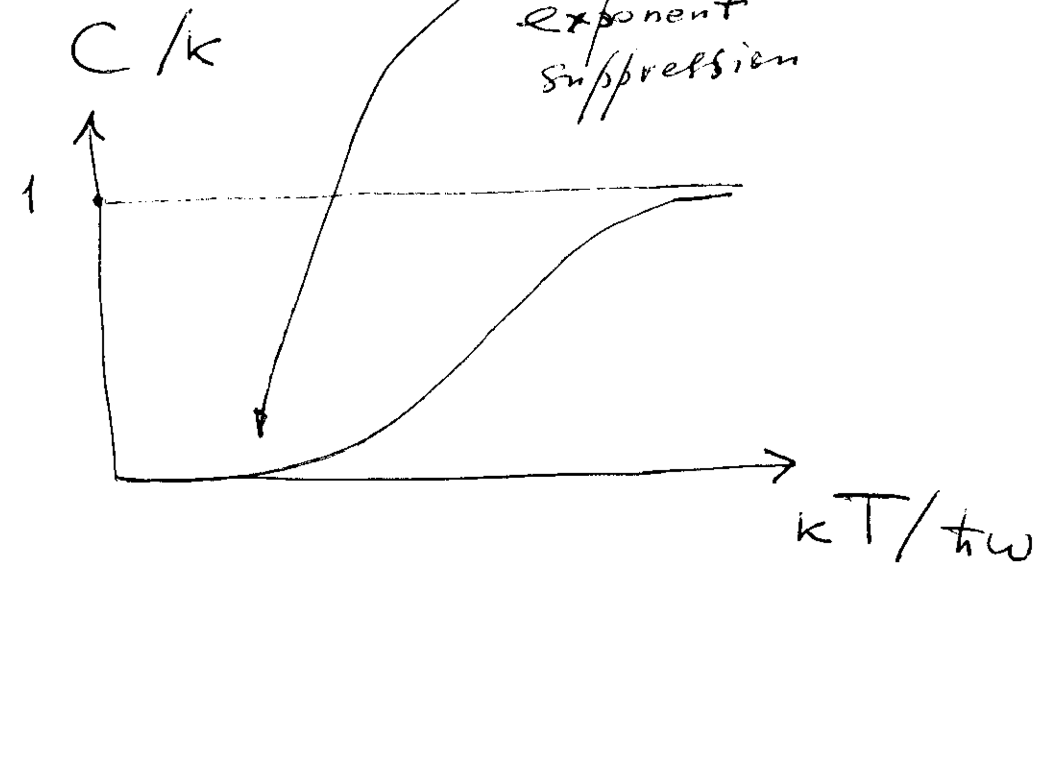
$$\bar{n} \underset{(6,13)}{\cong} e^{-x}$$

$$\bar{\varepsilon} = \left(e^{-\frac{\hbar\omega}{kT}} + \frac{1}{2} \right) \hbar\omega \tag{14}$$

$$C \underset{(8)}{=} k\, x^2 e^{-x} =$$

$$= k \left(\frac{\hbar\omega}{kT} \right)^2 e^{-\frac{\hbar\omega}{kT}} \tag{15}$$

exponent suppression



Phonon contribution to heat capacity

$$E = \sum_{\vec{k},i}{}' \left(n(\omega_{\vec{k},i}) + \frac{1}{2} \right) \hbar \omega_{\vec{k},i} \qquad (1)$$

$$\sum_i{}' \Rightarrow \sum_{\substack{\text{sound} \\ \text{waves}}}{}' = \sum_{i = L, T} \qquad (2)$$

for simplicity (see below)

doubly degenerate

$$\sum_{\vec{k}}{}' \Rightarrow \int \frac{V\, d^3k}{(2\pi)^3} =$$

$$= \frac{V}{2\pi^2} \int k^2 dk = \frac{V}{2\pi^2} \int k^2 \frac{dk}{d\omega}\, d\omega \qquad (3)$$

If sound waves dominate then (4)

$$k = \frac{\omega}{v} \quad \leftarrow \text{sound wave} \qquad (5)$$

$$\sum_{\vec{k}} \underset{(4,5,6)}{=} \frac{V}{2\pi^2} \frac{1}{v^3} \omega^2 d\omega \qquad (6)$$

$$\sum_{\vec{k},i}' \underset{(2,6)}{=} \underbrace{\frac{V}{2\pi^2} \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \omega^2 d\omega}_{g(\omega)\, d\omega} \qquad (7)$$

$$E = \int \left(\bar{n}(\omega) + \frac{1}{2} \right) \hbar\omega \, g(\omega) \, d\omega \qquad (8)$$

$$g(\omega) d\omega = \frac{V}{2\pi^2} \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \omega^2 d\omega \qquad (9)$$

$$E = \underset{\frac{1}{2}\hbar\omega}{E_0} + E_1(T)$$

$$E_1(T) \underset{(8,9)}{=} \frac{V}{2\pi^2}\left(\frac{1}{v_L^3}+\frac{2}{v_T^3}\right)\hbar \cdot \qquad (10)$$

$$\cdot \underbrace{\int \bar{n}(\omega)\,\omega^3 d\omega}_{\displaystyle\int_0^\infty \frac{\omega^3 d\omega}{e^{\frac{\hbar\omega}{kT}}-1}}$$

$$\frac{\hbar\omega}{kT} = x \qquad \omega = \frac{kT}{\hbar}x \qquad (11)$$

$$E_1(T) = \frac{V}{2\pi^2}\left(\frac{1}{v_L^3}+\frac{2}{v_T^3}\right)\frac{(kT)^4}{\hbar^3}\underbrace{\int_0^\infty \frac{x^3 dx}{e^x-1}}_{\frac{\pi^4}{15}} \qquad (11)\ (12)$$

$$E_1 = \frac{\pi^2 V}{30} \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \frac{(kT)^4}{\hbar^3} \qquad (13)$$

$$C = \frac{dE}{dT} = \frac{dE_1}{dT} =$$

$$= k \left(\frac{2\pi^2}{15} \right) V \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \left(\frac{kT}{\hbar} \right)^3 \qquad (14)$$

Debye temperature

Model — keep only the sound waves, but cut the integration at high ω by ω_D in such a way that the number of states is $3N$ (15)

$$\left(\frac{1}{v_L^3}+\frac{2}{v_T^3}\right)\frac{V}{2\pi^2}\int_0^{\omega_D}\omega^2 d\omega = 3N \qquad (16)$$

$$\frac{V}{\underbrace{3\cdot 2\pi^2}_{6}}\left(\frac{1}{v_L^3}+\frac{2}{v_T^3}\right)\omega_D^3 = 3N \qquad (17)$$

$$\omega_D = \left(6\pi^2\frac{N}{V}\right)^{1/3} v \underset{v_L = v_T}{=} \left[\frac{1}{2\pi}\left(6\pi^2\right)^{1/3}\right]\frac{2\pi v}{a} \qquad (18)$$

$$\omega_D \sim \frac{2\pi v}{a}$$

$$E = N\left(\frac{9}{8}\hbar\omega_D + \frac{9}{\omega_D^3}\int_0^{\omega_D}\frac{\hbar\omega^3 d\omega}{e^{\frac{\hbar\omega}{kT}}-1}\right) \quad (19)$$

$$C = 9Nk_B\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_T/T}\frac{x^4e^x dx}{(e^x-1)^2} \quad (20)$$

$$\begin{cases} T\to 0 & C = \dfrac{12\pi^4}{5}Nk_B\left(\dfrac{T}{\theta_D}\right)^3 \\ T\to\infty & C = 3Nk_B \end{cases} \quad (21)$$