

Physics 170:
Statistical Mechanics and Thermodynamics
Lecture 7A

Heat Capacity of Solids

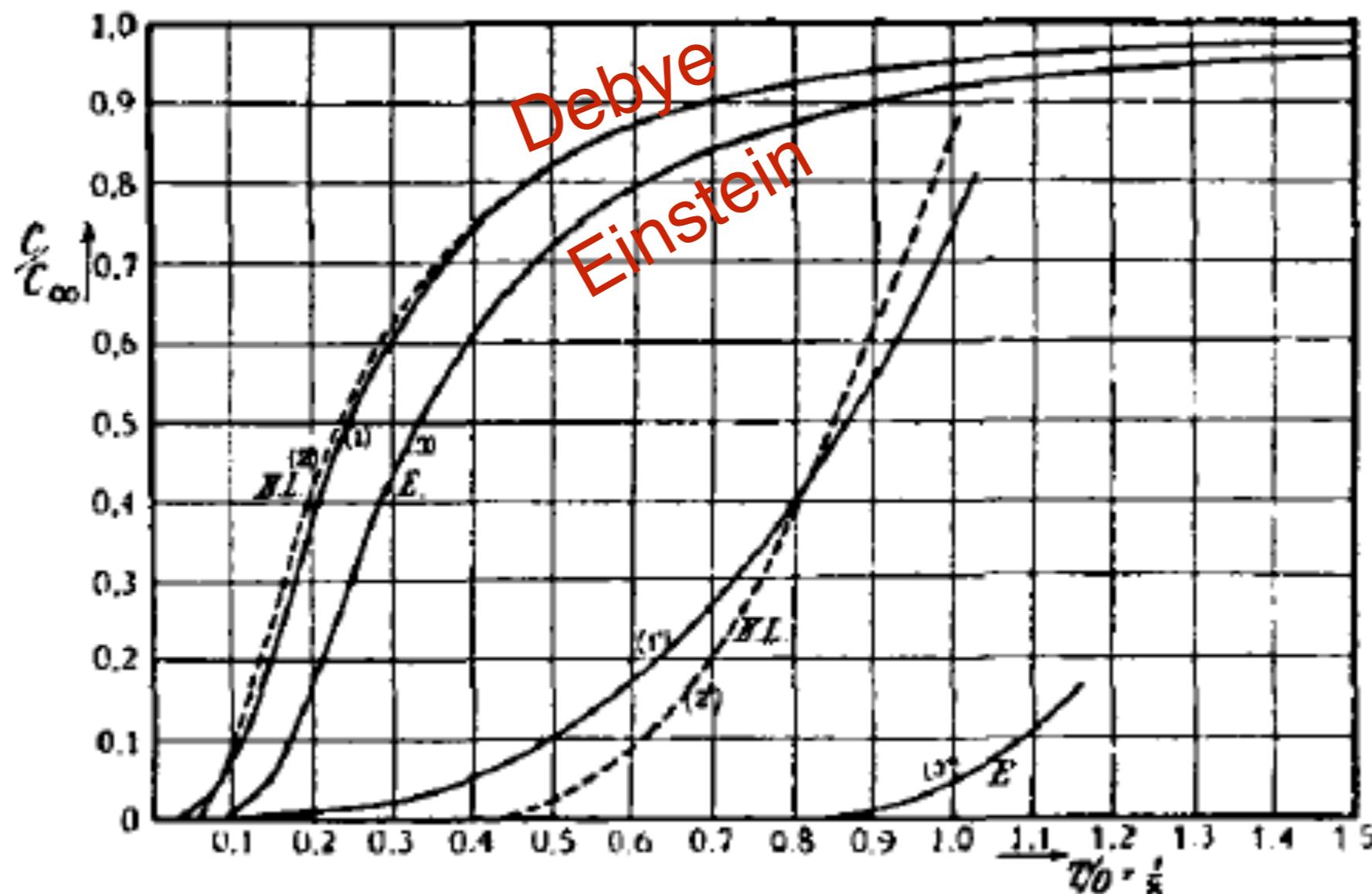


Fig. 1.

Debye Model

Aluminum

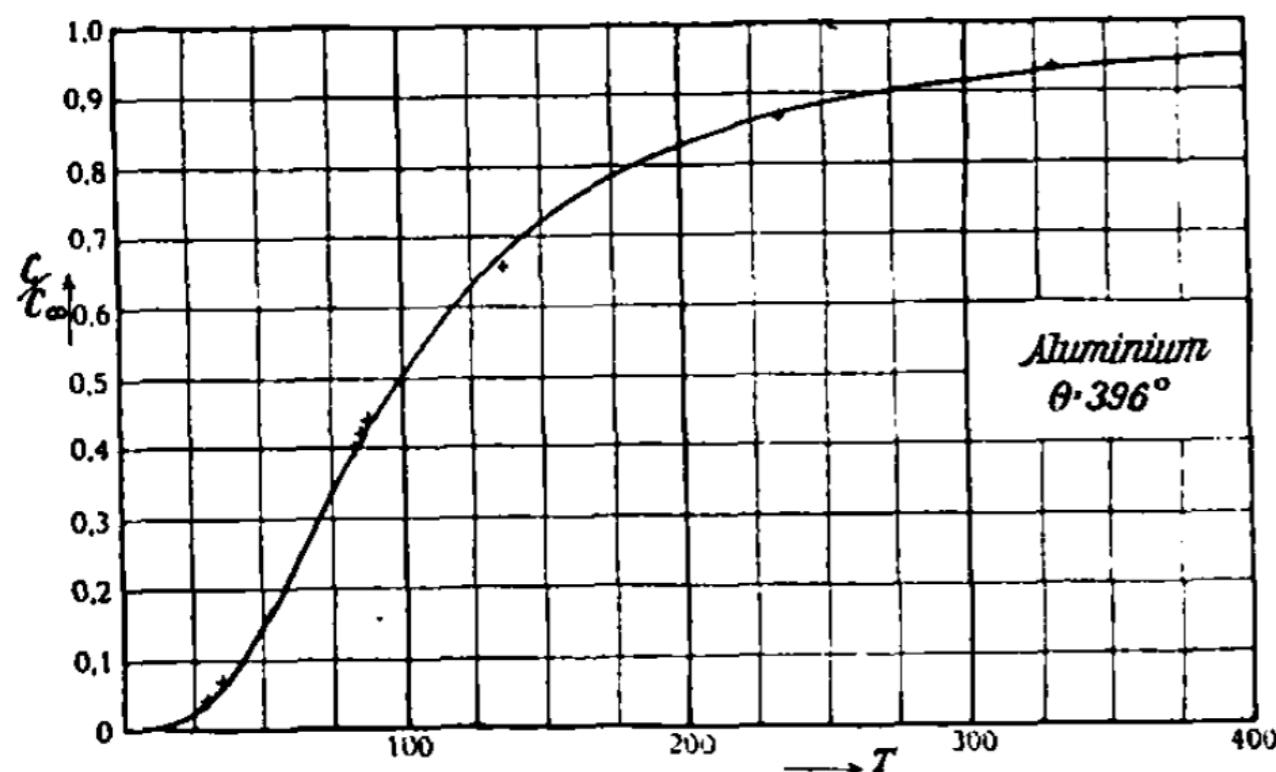


Fig. 3.

Silver

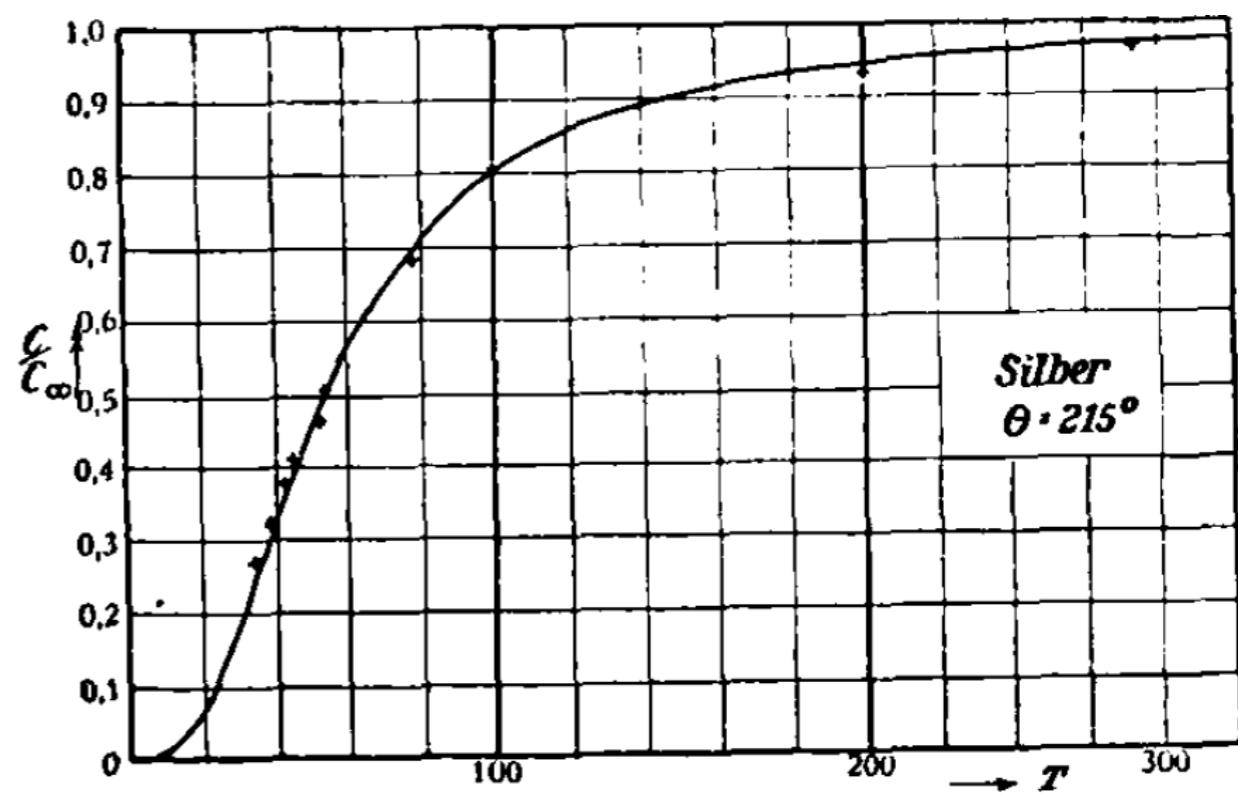


Fig. 5.

EXERCISE 7A: DEBYE THEORY OF PHONONS*Objectives:*

- Understand the limitations of the Einstein model of the solid (1907)
- Calculate the heat capacity of phonons in a solid (Debye theory) - 1912

Useful past results:

- Planck distribution: $\langle s \rangle_\omega = \frac{1}{e^{\hbar\omega/kT} - 1}$
- Wave equation: $\nabla^2 u = \frac{1}{v^2} \frac{\partial^2 u}{\partial t^2}$
- A definite integral: $\int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{15}$

1. *Law of Dulong and Petit.* Early in the term, we encountered the **Einstein's model of the solid**, which treated each atom as an independent 3D harmonic oscillator of frequency ω .

- a. In the Einstein model, you showed that high-temperature limit of the heat capacity of a solid consisting of N atoms is $C_V \rightarrow 3Nk_B$. Give a simple argument for this limit, specifying what constitutes "high temperature."

$$\text{Equipartition : } H = \sum_{i=1}^N \sum_{\alpha=x,y,z} \left(\frac{1}{2} k \alpha_i^2 + \frac{1}{2} m \dot{\alpha}_i^2 \right)$$

$$2 \times 3N \text{ quadratic terms} \Rightarrow E = 6N \left(\frac{1}{2} k_B T \right) = 3Nk_B T$$

$$\Rightarrow C_V = \left(\frac{\partial E}{\partial T} \right)_V = 3Nk_B$$

- b. In reality, atoms that are near each other interact, so that their motion is coupled (Fig. 1a). Remind yourself of the physics of coupled harmonic oscillators by considering just $N = 2$ such oscillators confined to move in the xz -plane (Fig. 1b).

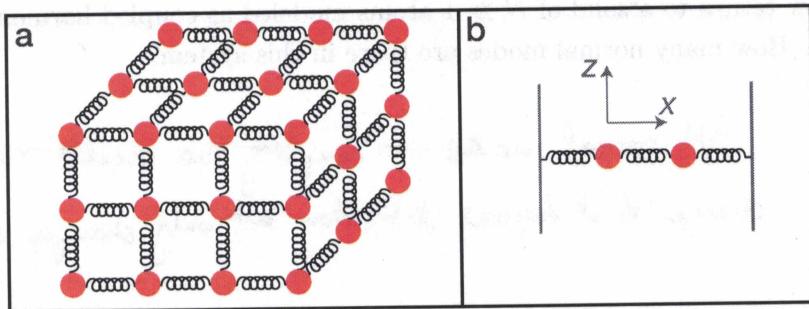
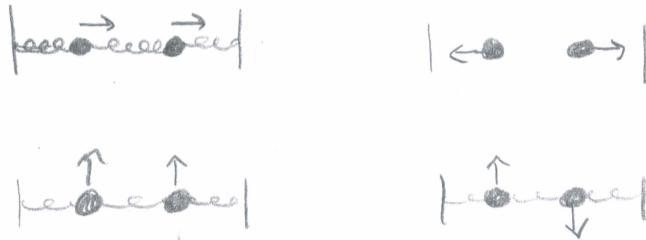


FIG. 1. (a) Debye model of a solid as a set of N coupled harmonic oscillators. (b) Minimal instance, consisting of just $N = 2$ two coupled harmonic oscillators.

- i. How many normal modes are there for the system of $N = 2$ coupled oscillators? Illustrate them in a set of sketches with arrows indicating directions of motion.



Four normal modes — same as # of modes for $N=2$
independent oscillators in 2D, but different linear combinations

- ii. Consider the normal modes involving motion along \hat{x} . Are their frequencies the same or different?

Different — lower frequency for moving together $\rightarrow \rightarrow$,
higher frequency for moving apart b/c opposed by the
central spring

See PhET simulations of normal modes:

<https://phet.colorado.edu/en/simulation/normal-modes>

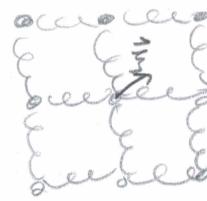
- c. Now return to a solid of $N \gg 1$ atoms modeled as coupled harmonic oscillators.
- i. How many normal modes are there in this system?

$3N$ normal modes — coupling the oscillators doesn't
change # of degrees of freedom but only changes eigenstates.

Comment: Generate system of N coupled oscillators in 1D

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i,j} \underbrace{k_{ij}}_{\substack{\text{coupling} \\ \text{displacement}}} (\xi_i - \xi_j)^2$$

$$= \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i,j} K_{ij} \xi_i \xi_j$$



Can diagonalize to $H = \sum_i \left(\frac{1}{2} k_i \xi_i^2 + \frac{1}{2} \mu_i \dot{\xi}_i^2 \right)$

↑ Normal modes $\xi_i = \sum_j c_{ij} \xi_j$

- $\cdots \cdots - k_B T$
- $\vdots \vdots$
- $\omega_1 \quad \omega_2 \quad \omega_{\max}$
- ii. How should we define the high-temperature limit for the system of N coupled oscillators? Does the result $C_V \rightarrow 3Nk_B$ still hold in the high-temperature limit? Why or why not?

Consider the maximum normal mode frequency ω_{\max} ... the high-T limit is given by $T \gg \hbar \omega_{\max}$. Here, we should still be able to treat the motion classically, so the result from equipartition still holds.

$$\therefore \text{still } C_V = 3Nk_B \text{ @ high T} \\ \text{"Law of Dulong and Petit"}$$

2. *Acoustic waves.* In the thermodynamic limit, the normal modes of the solid are acoustic waves. The quantized excitations of these normal modes are called *phonons* (by analogy with the photons constituting electromagnetic waves). The acoustic waves in a solid of dimensions $L \times L \times L$ take the form

$$\xi(x, y, z, t) = \xi_0 \sin(\omega t + \phi) \sin(n_x \pi x/L) \sin(n_y \pi y/L) \sin(n_z \pi z/L), \quad (1)$$

where ξ denotes the displacement of an atom from its equilibrium position (x, y, z) .

- a. Find a relationship between the frequency ω , the indices (n_x, n_y, n_z) , and the speed of sound v_s .

$$\text{Wave equation: } \nabla^2 \vec{\xi} = \frac{1}{v_s^2} \frac{\partial^2 \vec{\xi}}{\partial t^2} \Rightarrow \left(\frac{n_x \pi}{L}\right)^2 + \left(\frac{n_y \pi}{L}\right)^2 + \left(\frac{n_z \pi}{L}\right)^2 = \frac{\omega^2}{v_s^2}$$

$$\Rightarrow \omega = v_s \cdot \frac{\pi}{L} \sqrt{n_x^2 + n_y^2 + n_z^2}$$

(c.f. what we just did for photons, but $c \rightarrow v_s$).

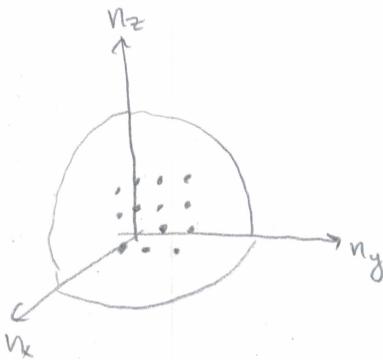
- b. How many basis vectors are required to describe the polarization of the acoustic wave (i.e., the direction of oscillation ξ) for a fixed direction of propagation? How does your answer compare with the case of an electromagnetic wave?

Three basis vectors: 2 transverse + 1 longitudinal polarization,

3. *Debye Model.* In a solid composed of a discrete lattice of N atoms, the discretization places an upper bound on the frequency of the acoustic modes, $\omega \leq \omega_D$. The maximum frequency ω_D is called the **Debye frequency**.

- a. Calculate the Debye frequency:

- i. First find a general expression for the total number of modes $N(\omega)$ with frequency $\leq \omega$.



$$\omega = v_s \frac{\pi}{L} |n| \iff |n| = \frac{\omega L}{v_s \pi}$$

$$\begin{aligned} N(\omega) &= \frac{1}{8} \times 3 \times \frac{4}{3} \pi |n_\omega|^3 \\ &= \frac{1}{2} \pi \left(\frac{\omega L}{v_s \pi} \right)^3 = \frac{\omega^3 V}{2\pi^2 v_s^3} \end{aligned}$$

- ii. The Debye frequency is given by $N(\omega_D) = 3N$. Why?

There are $3N$ normal modes in total, as we argued previously. So we can determine the frequency of the highest one by equating $N(\omega_D) = 3N$.

- iii. Find ω_D in terms of N , the volume $V = L^3$, and the speed of sound v .

$$3N = \frac{\omega_D^3 V}{2\pi^2 v_s^3} \Rightarrow \omega_D^3 = \frac{6\pi^2 v_s^3 N}{V}$$

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

- iv. The Debye frequency is associated with a minimum possible wavelength $\lambda_D = 2\pi v_s/\omega_D$. Find λ_D in terms of N and V .

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

- v. Give a physical interpretation for the lower bound λ_D . (Don't worry about details of the numerical pre-factor.)

$$\lambda_D \propto \left(\frac{V}{N}\right)^{1/3} \sim \text{interatomic spacing}$$

Makes sense — cannot define a shorter wavelength on a discrete lattice (c.f. Nyquist frequency).



- b. Determine the density of phonon modes $D(\omega) = dN/d\omega$ for frequencies $\omega < \omega_D$.

$$D(\omega) = \frac{dN}{d\omega} = \frac{3\omega^2 V}{2\pi^2 v_s^3}$$

per unit volume

- c. Determine the energy spectral density u_ω of phonons at frequency $\omega < \omega_D$ in a solid at temperature τ , using the Planck distribution for the average occupation of each phonon mode.

$$u_\omega = \frac{D(\omega)}{V} \langle s \rangle_\omega \hbar \omega = \frac{3\omega^2 V}{2\pi^2 v_s^3} \frac{\hbar \omega}{e^{\hbar \omega / kT} - 1}$$

Names:

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- d. Write down an integral representing the vibrational energy density U/V of the solid at temperature τ . Express the definite integral \mathcal{I} in terms of a dimensionless parameter $x = \hbar\omega/\tau$ and a cutoff $x_D = \tau_D/\tau$.

$$\begin{aligned} U/V &= \int_0^{\infty} d\omega \cdot u_{\omega} = \frac{3\hbar}{2\pi^2 V_s^3} \int_0^{\omega_D} d\omega \cdot \frac{\omega^3}{e^{\hbar\omega/\tau} - 1} & x = \hbar\omega/\tau \\ &= \frac{3\hbar}{2\pi^2 V_s^3} \left(\frac{\tau}{\hbar}\right)^4 \int_0^{x_D} dx \cdot \frac{x^3}{e^x - 1} & x_D = \frac{\hbar\omega_D}{\tau} \equiv \frac{\tau_D}{\tau} \\ &= \frac{3\tau^4}{2\pi^2 V_s^3 \hbar^3} \underbrace{\int_0^{x_D} dx \cdot \frac{x^3}{e^x - 1}}_{\mathcal{I}} \end{aligned}$$

- e. Give the value of the **Debye temperature** $\theta_D \equiv \tau_D/k_B$ and explain its physical significance.

$$\tau_D = \hbar\omega_D \quad \text{or} \quad \theta_D = \frac{\hbar\omega_D}{k_B} = \frac{\hbar}{k_B} V_s \left(\frac{6\pi^2 N}{V}\right)^{1/3}$$

The Debye temperature is equivalent to the energy of the highest phonon mode (up to a factor k_B). For $T \gg \theta_D$, all modes can be occupied.

For $T \ll \theta_D$, some modes are too high in energy to be occupied appreciably.

- f. Give the total vibrational energy U in terms of N , τ , τ_D , and \mathcal{I} . Your answer should include no other dimensionful quantities.

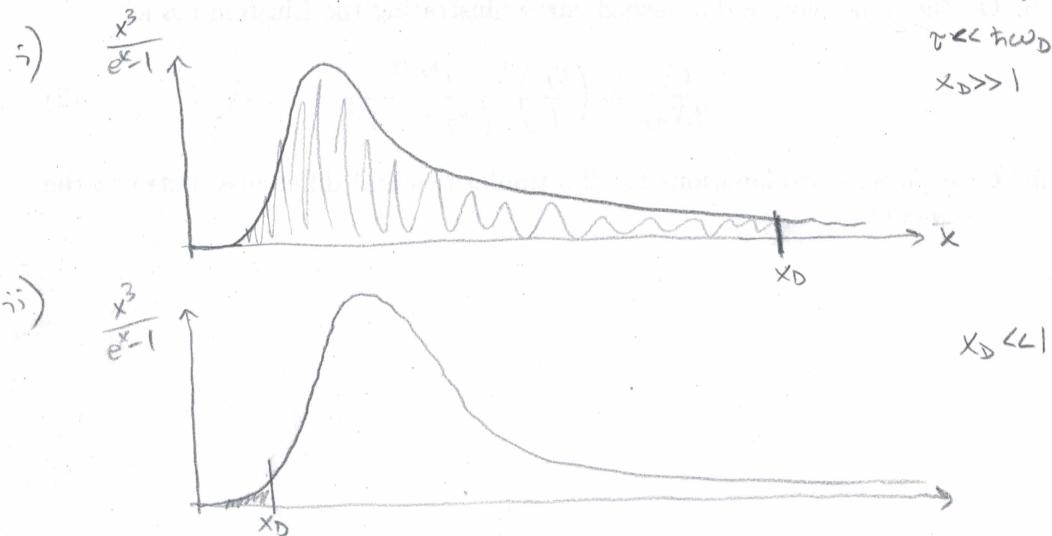
$$\text{We have } \tau_D = \hbar V_s (6\pi^2 N/V)^{1/3}, \text{ so } (\hbar V_s)^3 = \tau_D^3 \cdot \left(\frac{V}{6\pi^2 N}\right)$$

$$\text{Thus, } U = V \cdot \frac{3\tau^4}{2\pi^2 \tau_D^3} \left(\frac{6\pi^2 N}{V}\right) \mathcal{I}$$

$$\therefore U = \frac{9N\tau^4}{\tau_D^3} \cdot \mathcal{I}$$

g. Sketch the integrand from d., shading in the region of integration, for two cases:

- i. Low temperature: $T \ll \theta_D$
- ii. High temperature: $T \gg \theta_D$



h. Evaluate the integral \mathcal{I} and determine the heat capacity:

- i. ... in the low-temperature limit $T \ll \theta_D$
- ii. ... in the high-temperature limit $T \gg \theta_D$

i) In low-T limits can approximate as

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

$$\rightarrow U = \frac{9N\tau^4}{\tau_D^3} \cdot \frac{\pi^4}{15} = \frac{3N\tau^4 \pi^4}{5\tau_D^3} \Rightarrow C_V = \left(\frac{dU}{d\tau}\right)_V = \frac{12\pi^4 N}{5} \left(\frac{\tau}{\tau_D}\right)^3$$

We stopped here.

ii) High-T: $\mathcal{I} \approx \int_0^{x_D} \frac{x^3 dx}{x} \approx \int_0^{x_D} x^2 dx \approx \frac{1}{3} x_D^3$

$$\Rightarrow U = \frac{9N\tau^4}{\tau_D^3} \cdot \frac{1}{3} \left(\frac{\tau_D}{\tau}\right)^3 = 3N\tau \Rightarrow C_V = 3N$$

consistent w/
classical limit.