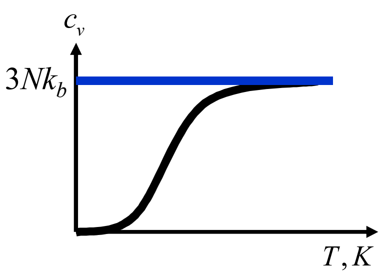
THERMAL PROPERTIES

Einstein's Theory: Discrepancies

- Einstein's theory: exponential temperature dependence
- Experiment: T^3 temperature dependence.
- **Limitations:** Independent oscillators and single frequency.
- **MUST** include vibrational frequency spectrum with dispersion relation and the quantization of the oscillator energies.

→ **Debye Theory**



Debye Theory

- Harmonic oscillators are coupled together by interatomic forces.
- Considers allowed normal modes of oscillations rather than the individual oscillators.
- We have seen that a 1-D linear crystal has N independent vibrational modes, provided that the number of atoms N is large.
- The energies of the modes are given by:

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

$$n = 0, 1, 2, 3, \ldots$$

Internal Energy

- Total vibrational energy can be found by finding the internal energy associated with the normal modes having frequencies in a range $d\omega$ about any given frequency ω, and integrating over frequency.
- The differential energy:

$$dU = \langle \varepsilon(\omega) \rangle g(\omega) d\omega$$

$\langle \varepsilon(\omega) \rangle$: Mean energy

$g(\omega)d\omega$: Number of modes in $d\omega$ about ω

Mean Energy

- We derived the mean energy while discussing Einstein Theory of specific heat:

$$\langle \varepsilon(\omega) \rangle = \hbar\omega \left[\frac{1}{2} + \frac{1}{e^{\hbar\omega/k_b T} - 1} \right]$$

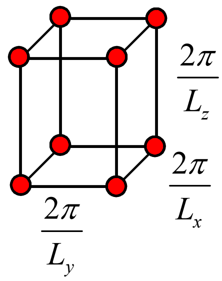
Density of States

- In practice, it is easier to calculate $g(k)dk$ instead of $g(\omega)d\omega$.

$$dU = \langle \varepsilon(\omega) \rangle g(\omega) d\omega$$
$$= \langle \varepsilon(\omega) \rangle g(k) \frac{dk}{d\omega} d\omega$$

Density of States

- Assume a rectangular crystal of dimensions L_x, L_y, L_z, with volume V in periodic boundary conditions.
- Allowed propagation vectors: $k_x = \frac{2\pi n_x}{L_x}, k_y = \frac{2\pi n_y}{L_y}, k_z = \frac{2\pi n_z}{L_z}$
- Unit cell corresponding to a single normal mode

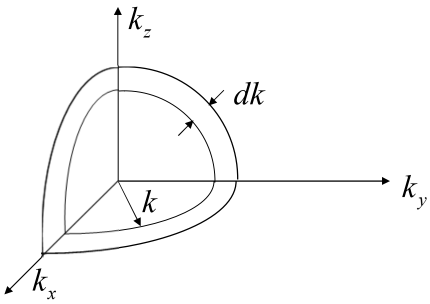


- Volume of k-space occupied by a single mode: $\frac{8\pi^3}{L_x L_y L_z} = \frac{8\pi^3}{V}$

Density of States

- Spherical surfaces corresponding to constant values k and $k + dk$
- Volume in dk: $4\pi k^2 dk$

$$g(k)dk = \frac{4\pi k^2 dk}{8\pi^3 / V} = \frac{k^2 V dk}{2\pi^2}$$



- Considering one longitudinal and two transverse modes:

$$g(k)dk = \frac{3k^2 V dk}{2\pi^2}$$

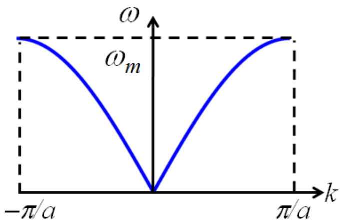
dk/dω

$$dU = \langle \varepsilon(\omega) \rangle g(k) \frac{dk}{d\omega} d\omega$$

- Debye assumptions:
  - Linear dispersion relation

$$\omega = v_0 k, \quad (k < k_m)$$

v_0 : Constant velocity



  - Cutoff frequency

$$\frac{4}{3}\pi k_m^3 = N\frac{8\pi^3}{V}, \quad \text{or} \qquad k_m = \left(6\pi^2 \frac{N}{V}\right)^{1/3}$$

9

Internal Energy

$$U = \int_0^{\omega_m} dU = \int_0^{\omega_m} \langle \varepsilon(\omega) \rangle g(k) \frac{dk}{d\omega} d\omega$$

$$U = \int_0^{\omega_m} \left(\frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/k_bT} - 1} \right) \frac{3k^2V}{2\pi^2} \frac{1}{v_0} d\omega$$

$$= \frac{3V}{2\pi^2} \frac{1}{v_0} \int_0^{\omega_m} \left(\frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/k_bT} - 1} \right) \frac{\omega^2}{v_0^2} d\omega$$

$$= \frac{3\hbar V}{2\pi^2 v_0^3} \int_0^{\omega_m} \left(\frac{\omega^3}{2} + \frac{\omega^3}{e^{\hbar\omega/k_bT} - 1} \right) d\omega$$

$$= \frac{3\hbar V}{2\pi^2 v_0^3} \frac{\omega_m^4}{8} + \frac{3\hbar V}{2\pi^2 v_0^3} \int_0^{\omega_m} \frac{\omega^3}{e^{\hbar\omega/k_bT} - 1} d\omega$$

10

Internal Energy

$$U = \frac{3\hbar V}{2\pi^2 v_0^3}\frac{\omega_m^4}{8} + \frac{3\hbar V}{2\pi^2 v_0^3}\int_0^{\omega_m}\frac{\omega^3}{e^{\hbar\omega/k_bT}-1}d\omega$$

$$\frac{4}{3}\pi k_m^3 = N\frac{8\pi^3}{V} \Rightarrow V = \frac{6\pi^2 N}{k_m^3} = \frac{6\pi^2 N v_0^3}{\omega_m^3}$$

- Replacing V

$$U = \frac{9}{8}N\hbar\omega_m + \frac{9N\hbar}{\omega_m^3}\int_0^{\omega_m}\frac{\omega^3 d\omega}{e^{\hbar\omega/k_bT}-1}$$

11

Specific Heat

$$U = \frac{9}{8}N\hbar\omega_m + \frac{9N\hbar}{\omega_m^3}\int_0^{\omega_m}\frac{\omega^3 d\omega}{e^{\hbar\omega/k_bT}-1}$$

$$c_v = \frac{\partial U}{\partial T}$$

$$= \frac{9N\hbar}{\omega_m^3}\int_0^{\omega_m}\omega^3\frac{-1}{\left(e^{\hbar\omega/k_bT}-1\right)^2}e^{\hbar\omega/k_bT}\frac{-\hbar\omega}{k_bT^2}d\omega$$

$$= \frac{9N\hbar^2}{\omega_m^3 k_b T^2}\int_0^{\omega_m}\frac{\omega^4 e^{\hbar\omega/k_bT}}{\left(e^{\hbar\omega/k_bT}-1\right)^2}d\omega$$

12

Specific Heat

$$c_v = \frac{9N\hbar^2}{\omega_m^3 k_b T^2}\int_0^{\omega_m}\frac{\omega^4 e^{\hbar\omega/k_bT}}{\left(e^{\hbar\omega/k_bT}-1\right)^2}d\omega$$

Let $\frac{\hbar\omega}{k_bT} = x \Rightarrow d\omega = \frac{k_bT}{\hbar}dx$

Boundary values:

$$\omega \to 0 \Rightarrow x \to 0$$

$$\omega \to \omega_m \Rightarrow x \to \frac{\hbar\omega_m}{k_bT} = \frac{\Theta}{T},\ \Theta: \text{Debye Temperature}$$

$$c_v = 9Nk_b\left(\frac{T}{\Theta}\right)^3\int_0^{\Theta/T}\frac{x^4 e^x}{\left(e^x-1\right)^2}dx$$

13

$T \to \infty$

$$U = \frac{9}{8}N\hbar\omega_m + \frac{9N\hbar}{\omega_m^3}\int_0^{\omega_m}\frac{\omega^3}{e^{\hbar\omega/k_bT}-1} = \frac{9}{8}N\hbar\omega_m + 9Nk_bT\left(\frac{T}{\Theta}\right)^3\int_0^{\Theta/T}\frac{x^3}{e^x-1}dx$$

- Simplification:

$$\frac{x^3}{e^x-1} \approx \frac{x^3}{1+x-1} = x^2$$

$$U \approx \frac{9}{8}N\hbar\omega_m + 9Nk_bT\left(\frac{T}{\Theta}\right)^3\int_0^{\Theta/T}x^2\,dx = \frac{9}{8}N\hbar\omega_m + 9Nk_bT\left(\frac{T}{\Theta}\right)^3\left[\frac{x^3}{3}\right]_0^{\Theta/T}$$

$$= \frac{9}{8}N\hbar\omega_m + 3Nk_bT\left(\frac{T}{\Theta}\right)^3\left(\frac{\Theta}{T}\right)^3 = \frac{9}{8}N\hbar\omega_m + 3Nk_bT$$

$c_v = 3Nk_b \rightarrow$ Independent of temperature

14

$T \to 0$

$$U = \frac{9}{8} N\hbar\omega_m + \frac{9N\hbar}{\omega_m^3}\int_0^{\omega_m} \frac{\omega^3}{e^{\hbar\omega/k_bT}-1} = \frac{9}{8} N\hbar\omega_m + 9Nk_bT\left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \frac{x^3}{e^x-1}dx$$

- Simplification:

$$\frac{1}{e^x-1} = \left(\frac{1}{e^x}\right)\left(\frac{1}{1-e^{-x}}\right) = \frac{1}{e^x}\sum_{n=0}^{\infty}\left(e^{-x}\right)^n = \sum_{n=1}^{\infty}\left(e^{-x}\right)^n = \sum_{n=1}^{\infty} e^{-nx}$$

$$\int_0^{\Theta/T} \frac{x^3}{e^x-1}dx = \int_0^{\infty} \frac{x^3}{e^x-1}dx = \int_0^{\infty}\left(\sum_{n=1}^{\infty} x^3 e^{-nx}\right)dx$$

$$= \sum_{n=1}^{\infty}\left(\int_0^{\infty} x^3 e^{-nx} dx\right) = \sum_{n=1}^{\infty} I_n$$

15

Integration

$$I_n = \int_0^{\infty} x^3 e^{-nx} dx = \left[-x^3\frac{e^{-nx}}{n}\right]_0^{\infty} + \int_0^{\infty} 3x^2 \frac{e^{-nx}}{n} dx = 0 + \frac{3}{n}\int_0^{\infty} x^2 e^{-nx} dx$$

$$= \frac{3}{n}\left[-x^2\frac{e^{-nx}}{n}\right]_0^{\infty} + \frac{3}{n}\int_0^{\infty} 2x\frac{e^{-nx}}{n}dx = 0 + \frac{6}{n^2}\int_0^{\infty} xe^{-nx}dx$$

$$= \frac{6}{n^2}\left[-x\frac{e^{-nx}}{n}\right]_0^{\infty} + \frac{6}{n^2}\int_0^{\infty} \frac{e^{-nx}}{n}dx = 0 + \frac{6}{n^3}\int_0^{\infty} xe^{-nx}dx$$

$$= \frac{6}{n^3}\left[-\frac{e^{-nx}}{n}\right]_0^{\infty} = \frac{6}{n^4}$$

16

$T \rightarrow 0$

$$\int_0^{\Theta/T} \frac{x^3}{e^x - 1} dx = 6\sum_{n=1}^{\infty} \frac{1}{n^4}$$

- Riemann zeta function:

$$\zeta(4) = \sum_{n=1}^{\infty} \frac{1}{n^4} = 1 + \frac{1}{2^4} + \frac{1}{3^4} + \frac{1}{4^4} + \cdots = \frac{\pi^4}{90}$$

$$U = \frac{9}{8} N\hbar\omega_m + 9Nk_b T\left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \frac{x^3}{e^x - 1} dx = \frac{9}{8} N\hbar\omega_m + 9Nk_b T\left(\frac{T}{\Theta}\right)^3 \frac{6\pi^4}{90}$$

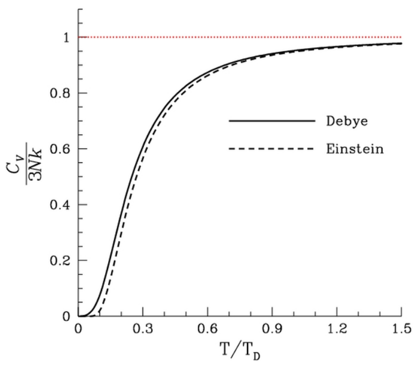
$$= \frac{9}{8} N\hbar\omega_m + \frac{3\pi^4}{5} Nk_b T\left(\frac{T}{\Theta}\right)^3$$

$$c_v = \frac{12\pi^4}{5} Nk_b \left(\frac{T}{\Theta}\right)^3$$

17

Specific Heat

- $T \rightarrow \infty$: $c_v = 3Nk_b$
- $T \rightarrow 0$: $c_v = \frac{12\pi^4}{5} Nk_b \left(\frac{T}{\Theta}\right)^3$



18