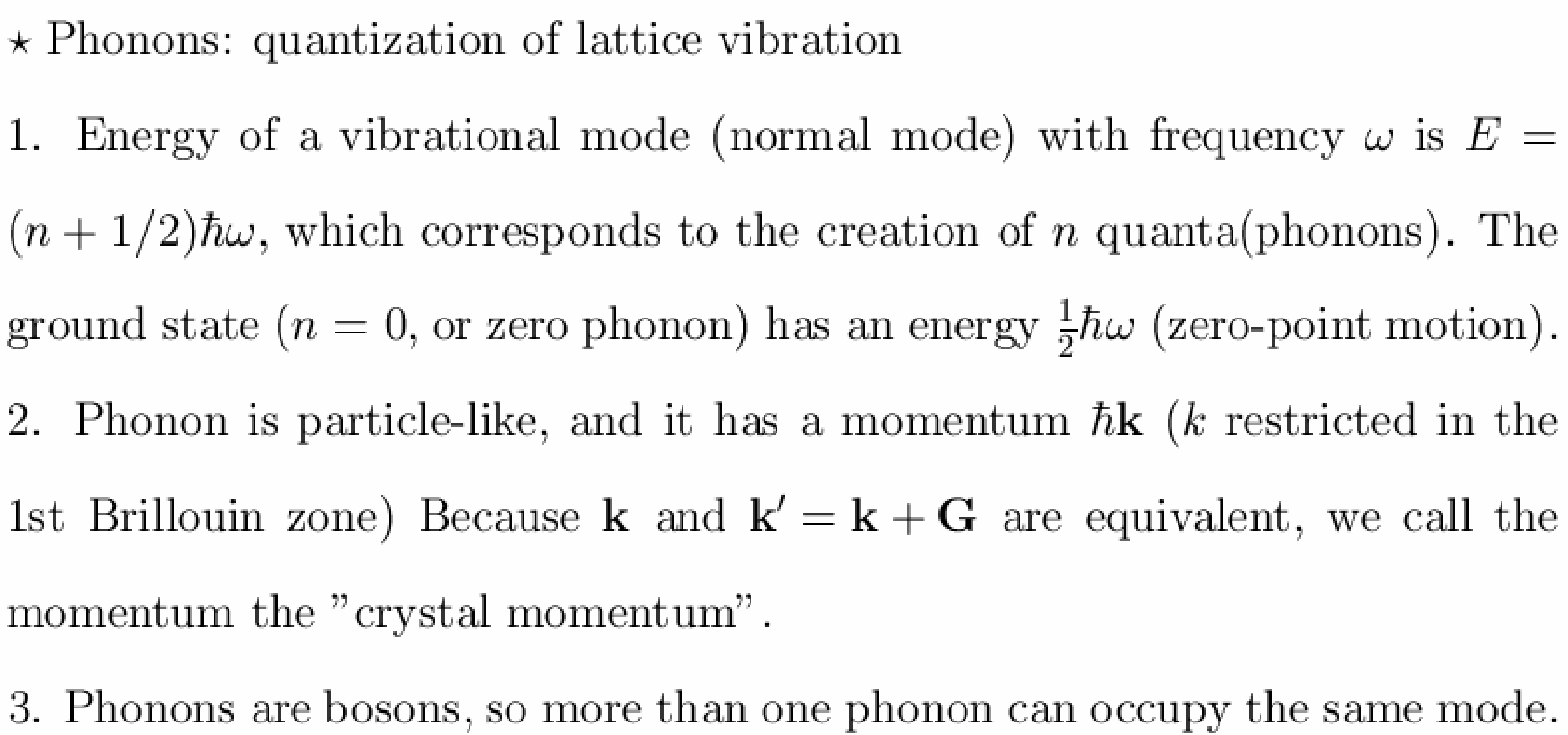
Lattice Thermal Properties

- Planck distribution
- Average thermal energy
- Density of states (DOS)
- Phase-space summation
- Debye model
- Anharmonicity
- Thermal conductivity

HW assignment: Ch. 8, p.5

Concept of Phonons



⋆ Phonons: quantization of lattice vibration

1. Energy of a vibrational mode (normal mode) with frequency ω is $E = (n + 1/2)\hbar\omega$, which corresponds to the creation of n quanta(phonons). The ground state ($n = 0$, or zero phonon) has an energy $\frac{1}{2}\hbar\omega$ (zero-point motion).

2. Phonon is particle-like, and it has a momentum $\hbar\mathbf{k}$ (k restricted in the 1st Brillouin zone) Because $\mathbf{k}$ and $\mathbf{k}' = \mathbf{k} + \mathbf{G}$ are equivalent, we call the momentum the "crystal momentum".

3. Phonons are bosons, so more than one phonon can occupy the same mode.

Average occupancy:

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

Planck distribution

Average occupancy of a state for bosons (phonons or photons) which behave like harmonic oscillators: In a given normal mode, the frequency is w and the energy of an n-particle state is $(n+1/2)\hbar\omega$. If the system is in thermal contact with a reservoir with temperature T, then the relative probability of finding the system in a given state $[E_n = (n+1/2)\hbar\omega]$ is proportional to the Boltzmann factor

$$p_n \sim e^{-E_n/k_BT} = e^{-E_n/\tau};\ \tau \equiv k_BT.$$

The thermal average of any physical quantity that depends on En is given by

$$< A > = \sum_n p_n A(E_n)/\sum_n P_n = \sum_n e^{-E_n/\tau} A(E_n)/\sum_n e^{-E_n/\tau}.$$

Let $A = n \Rightarrow$ Average occupancy $< n > = \sum_{n=0}^{\infty} e^{-\hbar\omega(n+1/2)/\tau} n / \sum_n e^{-\hbar\omega(n+1/2)/\tau}$

$$= \sum_{n=0}^{\infty} x^n n / \sum_n x^n;\ (x = e - \hbar\omega/\tau < 1)$$

Let $f(x) = \sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \Rightarrow \frac{\partial f(x)}{\partial x} = \sum_{n=0}^{\infty} n x^{n-1} = \frac{1}{(1-x)^2}$

$$\Rightarrow \sum_{n=0}^{\infty} n x^n = x\frac{\partial f}{\partial x} = \frac{2}{(1-x)^2}$$

or $< n > = \frac{x}{(1-x)^2}/(1-x)^{-1} = \frac{x}{1-x} = \frac{1}{x^{-1}-1} = \frac{1}{e^{\hbar\omega/\tau}-1}$

Average thermal energy in a given mode

$$U_\lambda =< E_\lambda >= \sum_n e^{-E_n/\tau}(n\hbar\omega_\lambda)/\sum_n e^{-E_n/\tau} = \hbar\omega_\lambda < n >_\lambda = \frac{\hbar\omega_\lambda}{e^{\hbar\omega\lambda/\tau}-1}.$$

$\Rightarrow$ Total thermal energy of the lattice is

$$U = \sum_\lambda U_\lambda = \sum_\lambda \frac{\hbar\omega_\lambda}{e^{\hbar\omega_\lambda/\tau}-1} = \int D(\omega)\frac{\hbar\omega}{e^{\hbar\omega/\tau}-1}d\omega,$$

where

$$D(\omega) = \sum_\lambda \delta(\omega-\omega_\lambda) = \sum_{\mathbf{k},p}\delta(\omega-\omega_p(\mathbf{k})) = \sum_p D_p(\omega)$$

is called the density of states (DOS)and

$$D_p(\omega) = \sum_{\mathbf{k}}\delta(\omega-\omega_p(\mathbf{k}))$$

is the DOS of branch p.

$$\text{Note:}\quad \int D(\omega)d\omega = \sum_\lambda \int \delta(\omega-\omega_\lambda)d\omega = \sum_\lambda = N_m$$

$=$ total number of phonon modes in the crystal

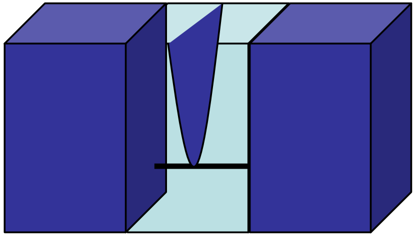
$=$ (dimensionality).(number of atoms in crystal) $=$ total number of degrees of freedom.

Density of states for various dimensions

$$N_d(E) \rightarrow \quad N_3(E) \propto \sqrt{E}, \quad N_2(E) \propto \theta(E), \quad N_1(E) = 1/\sqrt{E}$$

- Density of states (DOS) = #states per unit energy

$$\sum_{\vec{k}} = (\frac{L}{2\pi})^d \int dk^d$$



In 2D:

$$(\frac{L}{2\pi})^2 \int dk^2 = \int dE \qquad N(E)$$

DOS

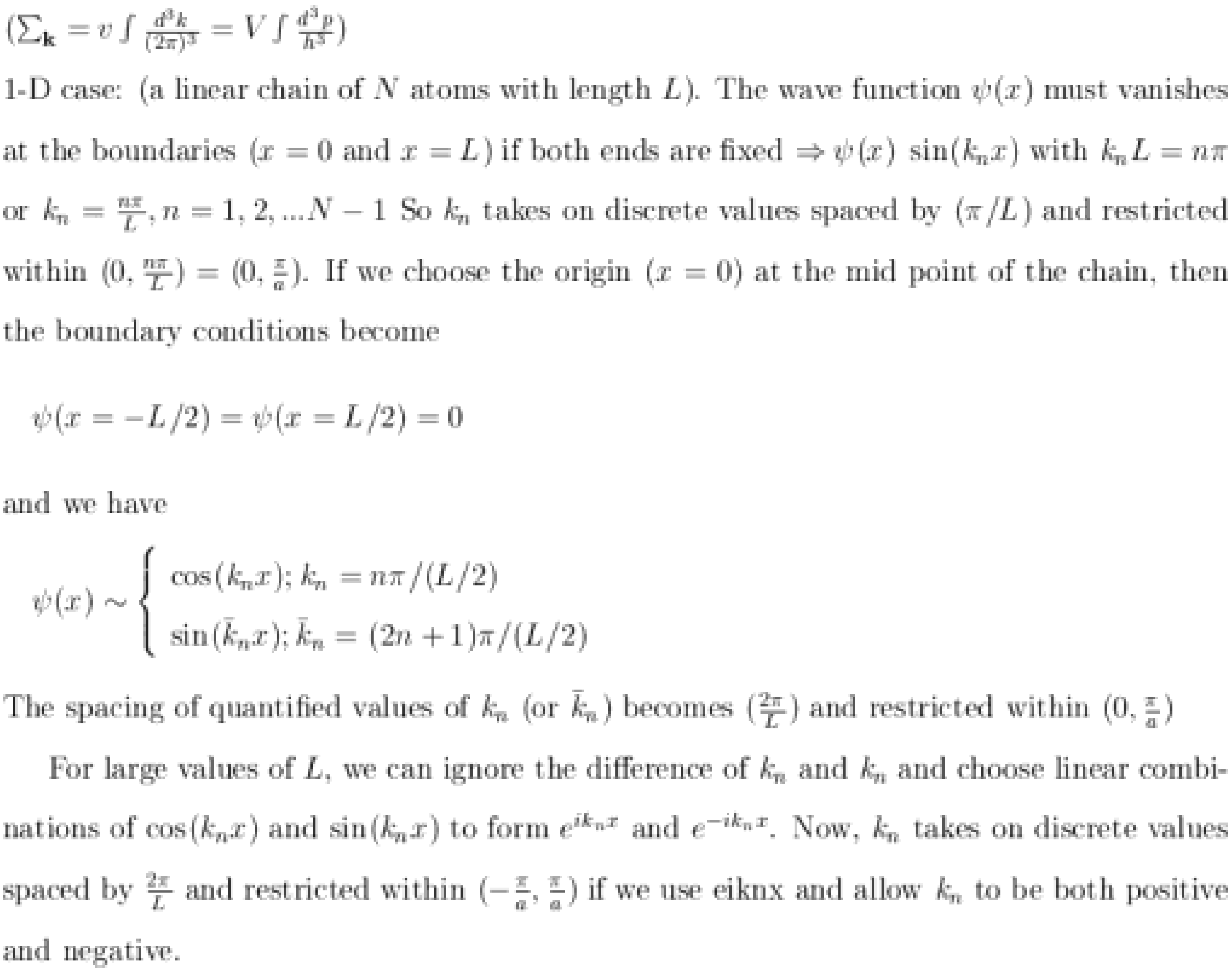
$$E = \frac{\hbar^2 k^2}{2m^*} \longrightarrow dE = \frac{\hbar^2\, 2\,kdk}{2\,m^*} \longrightarrow (\frac{L}{2\pi})^2 \int dk^2 = \int dE \qquad (\frac{L}{2\pi})^2 \frac{2m^*}{\hbar^2}$$

DOS, N(E)=constant

Phonon bottleneck in QD

- In polar semiconductor
- Quantum dots with discrete states

Meaning of the phase-space summation



($\sum_{\mathbf{k}} = v \int \frac{d^3k}{(2\pi)^3} = V \int \frac{d^3p}{h^3}$)

1-D case: (a linear chain of N atoms with length L). The wave function $\psi(x)$ must vanishes at the boundaries ($x = 0$ and $x = L$) if both ends are fixed $\Rightarrow \psi(x)$ $\sin(k_n x)$ with $k_n L = n\pi$ or $k_n = \frac{n\pi}{L}, n = 1, 2, ...N - 1$ So k_n takes on discrete values spaced by (π/L) and restricted within $(0, \frac{n\pi}{L}) = (0, \frac{\pi}{a})$. If we choose the origin ($x = 0$) at the mid point of the chain, then the boundary conditions become

$$\psi(x = -L/2) = \psi(x = L/2) = 0$$

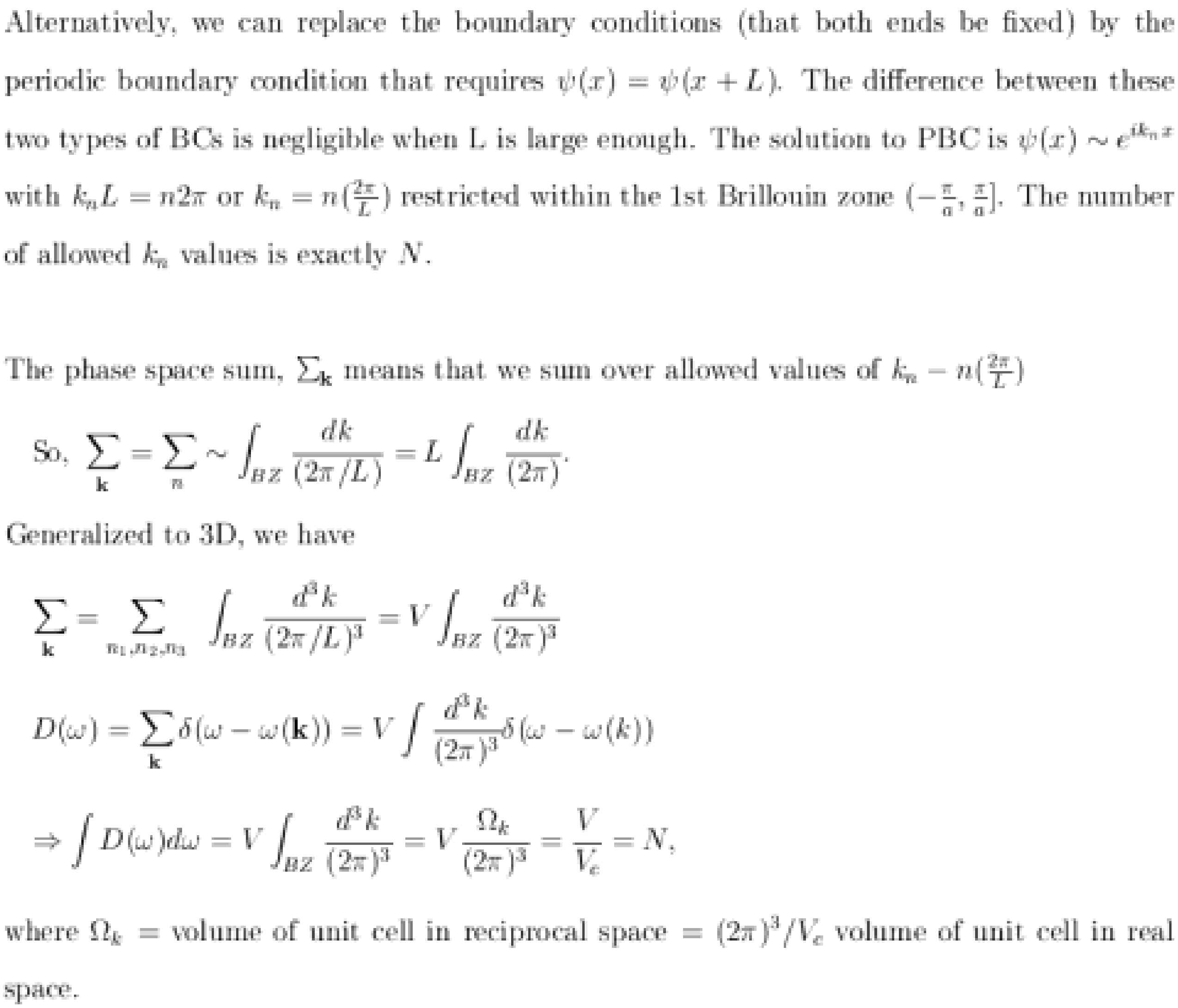
and we have

$$\psi(x) \sim \begin{cases} \cos(k_n x); k_n = n\pi/(L/2) \\ \sin(\bar{k}_n x); \bar{k}_n = (2n+1)\pi/(L/2) \end{cases}$$

The spacing of quantified values of k_n (or $\bar{k}_n$) becomes $(\frac{2\pi}{L})$ and restricted within $(0, \frac{\pi}{a})$

For large values of L, we can ignore the difference of k_n and k_n and choose linear combinations of $\cos(k_n x)$ and $\sin(k_n x)$ to form $e^{ik_n x}$ and $e^{-ik_n x}$. Now, k_n takes on discrete values spaced by $\frac{2\pi}{L}$ and restricted within $(-\frac{\pi}{a}, \frac{\pi}{a})$ if we use eiknx and allow k_n to be both positive and negative.

Periodic boundary condition (PBC)



Alternatively, we can replace the boundary conditions (that both ends be fixed) by the periodic boundary condition that requires $\psi(x) = \psi(x+L)$. The difference between these two types of BCs is negligible when L is large enough. The solution to PBC is $\psi(x) \sim e^{ik_n x}$ with $k_n L = n2\pi$ or $k_n = n(\frac{2\pi}{L})$ restricted within the 1st Brillouin zone $(-\frac{\pi}{a}, \frac{\pi}{a}]$. The number of allowed k_n values is exactly N.

The phase space sum, $\sum_{\mathbf{k}}$ means that we sum over allowed values of $k_n = n(\frac{2\pi}{L})$

$$\text{So, } \sum_{\mathbf{k}} = \sum_{n} \sim \int_{BZ} \frac{dk}{(2\pi/L)} = L \int_{BZ} \frac{dk}{(2\pi)}.$$

Generalized to 3D, we have

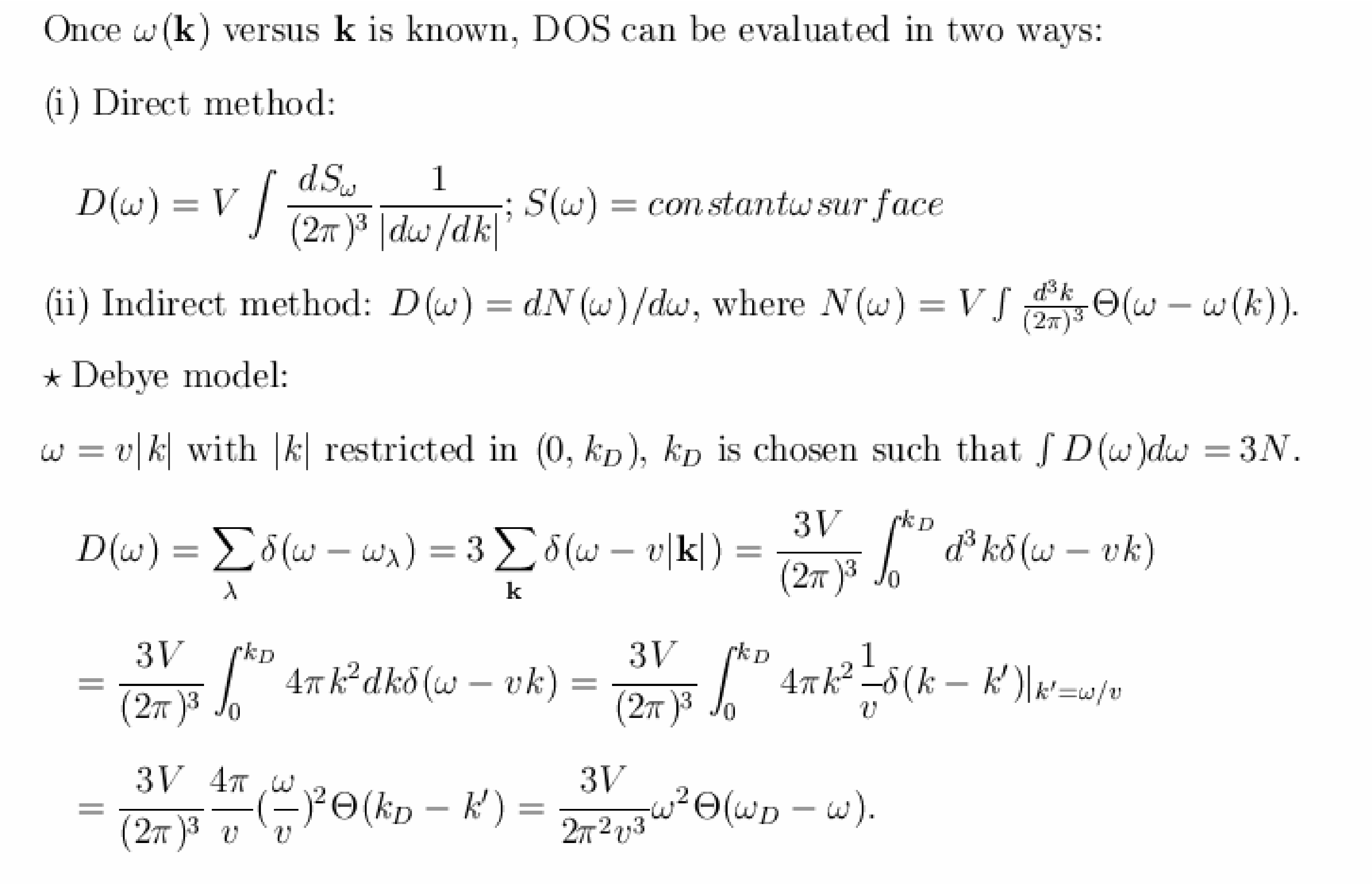
$$\sum_{\mathbf{k}} = \sum_{n_1,n_2,n_3} \int_{BZ} \frac{d^3k}{(2\pi/L)^3} = V \int_{BZ} \frac{d^3k}{(2\pi)^3}$$

$$D(\omega) = \sum_{\mathbf{k}} \delta(\omega - \omega(\mathbf{k})) = V \int \frac{d^3k}{(2\pi)^3} \delta(\omega - \omega(k))$$

$$\Rightarrow \int D(\omega) d\omega = V \int_{BZ} \frac{d^3k}{(2\pi)^3} = V \frac{\Omega_k}{(2\pi)^3} = \frac{V}{V_c} = N,$$

where Ω_k = volume of unit cell in reciprocal space = $(2\pi)^3/V_c$ volume of unit cell in real space.

Evaluation of DOS



Once $\omega(\mathbf{k})$ versus $\mathbf{k}$ is known, DOS can be evaluated in two ways:

(i) Direct method:

$$D(\omega) = V \int \frac{dS_\omega}{(2\pi)^3} \frac{1}{|d\omega/dk|}; \; S(\omega) = constant \omega surface$$

(ii) Indirect method: $D(\omega) = dN(\omega)/d\omega$, where $N(\omega) = V \int \frac{d^3k}{(2\pi)^3} \Theta(\omega - \omega(k))$.

$\star$ Debye model:

$\omega = v|k|$ with $|k|$ restricted in $(0, k_D)$, k_D is chosen such that $\int D(\omega) d\omega = 3N$.

$$D(\omega) = \sum_\lambda \delta(\omega - \omega_\lambda) = 3 \sum_{\mathbf{k}} \delta(\omega - v|\mathbf{k}|) = \frac{3V}{(2\pi)^3} \int_0^{k_D} d^3k \delta(\omega - vk)$$

$$= \frac{3V}{(2\pi)^3} \int_0^{k_D} 4\pi k^2 dk \delta(\omega - vk) = \frac{3V}{(2\pi)^3} \int_0^{k_D} 4\pi k^2 \frac{1}{v} \delta(k - k')|_{k' = \omega/v}$$

$$= \frac{3V}{(2\pi)^3} \frac{4\pi}{v} (\frac{\omega}{v})^2 \Theta(k_D - k') = \frac{3V}{2\pi^2 v^3} \omega^2 \Theta(\omega_D - \omega).$$

Alternatively, use

$$N(\omega) = \sum_{\lambda} \Theta(\omega - \omega_\lambda) = 3 \sum_{\mathbf{k}} \Theta(\omega - vk) = \frac{3V}{(2\pi)^3} \int_0^{k_D} d^3k \Theta(\omega - vk)$$

$$= \frac{3V}{(2\pi)^3} \int_0^{k_D} 4\pi k^2 dk \Theta(\omega/v - k) = \frac{3V}{(2\pi)^3} \int_0^{\omega/v} 4\pi k^2 dk (\text{if } \omega/v < k_D) = \frac{3V}{(2\pi)^3} \frac{4\pi}{3} (\omega/v)^3.$$

$$D(\omega) = \frac{dN(\omega)}{d\omega} = \frac{3V}{2\pi^2 v^3} \omega^2, \quad \text{if } \omega/v < k_D \equiv \omega_D/v.$$

To determine ω_D, we use

$$\int_0^{\omega_D} D(\omega) d\omega = 3N = \frac{3V}{2\pi^2 v^3} \int_0^{\omega_D} \omega^2 d\omega = \frac{V}{2\pi^2 v^3} \omega_D^3 = \frac{V}{2\pi^2} k_D^3$$

$$\Rightarrow k_D = (\omega_D/v) = (6\pi^2 N/V)^{1/3} \Rightarrow D(\omega) = \frac{9N}{\omega_D^3} \omega^2.$$

Lattice thermal energy in Debye model

$$U \int D(\omega)\frac{\hbar\omega}{e^{\hbar\omega/\tau}-1}d\omega = \frac{9N\hbar}{\omega_D^3}\int_0^{\omega_D}\frac{\omega^3}{e^{\hbar\omega/\tau}-1}d\omega$$

$$= \frac{9N\tau^4}{\omega_D^3\hbar^3}\int_0^{x_D}\frac{x^3}{e^x-1}dx = \frac{9Nk_BT^4}{\Theta^3}\int_0^{x_D}\frac{x^3}{e^x-1}dx,$$

$\Theta = \hbar\omega_D/k_B = \frac{\hbar v}{k}{}_B(6\pi 2N/V)^{1/3}$ is called "Debye temperature".

$$\int_0^{x_D}\frac{x^3}{e^x-1}dx \approx \begin{cases} \int_0^{\infty}\frac{x^3}{e^x-1}dx = \frac{\pi^4}{15} \text{ as } T \to 0 \\ \int_0^{x_D} x^2dx = \frac{1}{3}x_D^3 \quad \text{as } x = \hbar\omega/T \to 0 \text{ (high T limit)} \end{cases}$$

$$\Rightarrow U(T) = \begin{cases} \frac{3}{5}\pi^4 Nk_BT^4/\Theta^3 \text{ as } T \to 0 \\ 3Nk_BT \text{ as } T \to \infty \end{cases}$$

⋆ Heat capacity

$$C_V = \frac{\partial U}{\partial T} = \begin{cases} \frac{12\pi^4}{5}Nk_BT^3/\Theta^3 \text{ as } T \to 0 \\ 3NkB \text{ as } T \to \infty \end{cases}$$

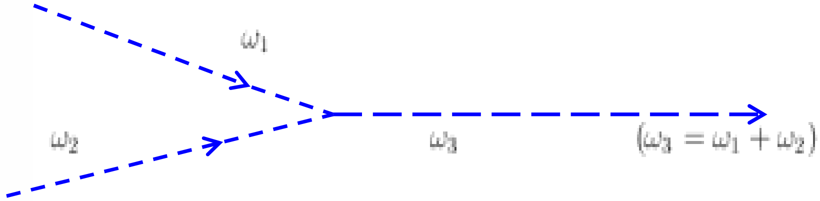
⋆ Einstein model:

$D(\omega) = 3N\delta(\omega - \omega_0)$ (appropriate for optical phonons)

$U = 3N\hbar\omega_0/(e^{\hbar\omega_0/\tau} - 1)$

$$C_V = \frac{\partial U}{\partial T} = 3Nk_B(\frac{\hbar\omega_0}{\tau})^2 \frac{e^{\hbar\omega_0/\tau}}{(e^{\hbar\omega_0/\tau} - 1)^2} \rightarrow \begin{cases} 3Nk_B(\hbar\omega_0/\tau)^2 e^{-\hbar\omega_0/\tau} \text{ as } T \rightarrow 0 \\ 3Nk_B \text{ as } T \rightarrow \infty \end{cases}$$

⋆ Anharmonicity:



Consequence of harmonic theory:

1. No phonon-phonon interaction
2. No thermal expansion
3. No pressure/temperature dependence in elastic constants
4. $C_v \rightarrow 3Nk_B$ as $T >> \Theta$.

Evidence of anharmonicity: sum frequency generation

Thermal Expansion (1D model)

$$U(x) = cx2 - gx3 + O(x^4)$$

$$<x>= \int dxe^{-\beta U(x)x} / \int dxe^{-\beta U(x)}; \beta = 1/\tau$$

$$= \int dxe^{-\beta cx^2} x(e^{\beta gx^3}) / \int dxe^{-(\beta cx^2 - \beta gx^3)}$$

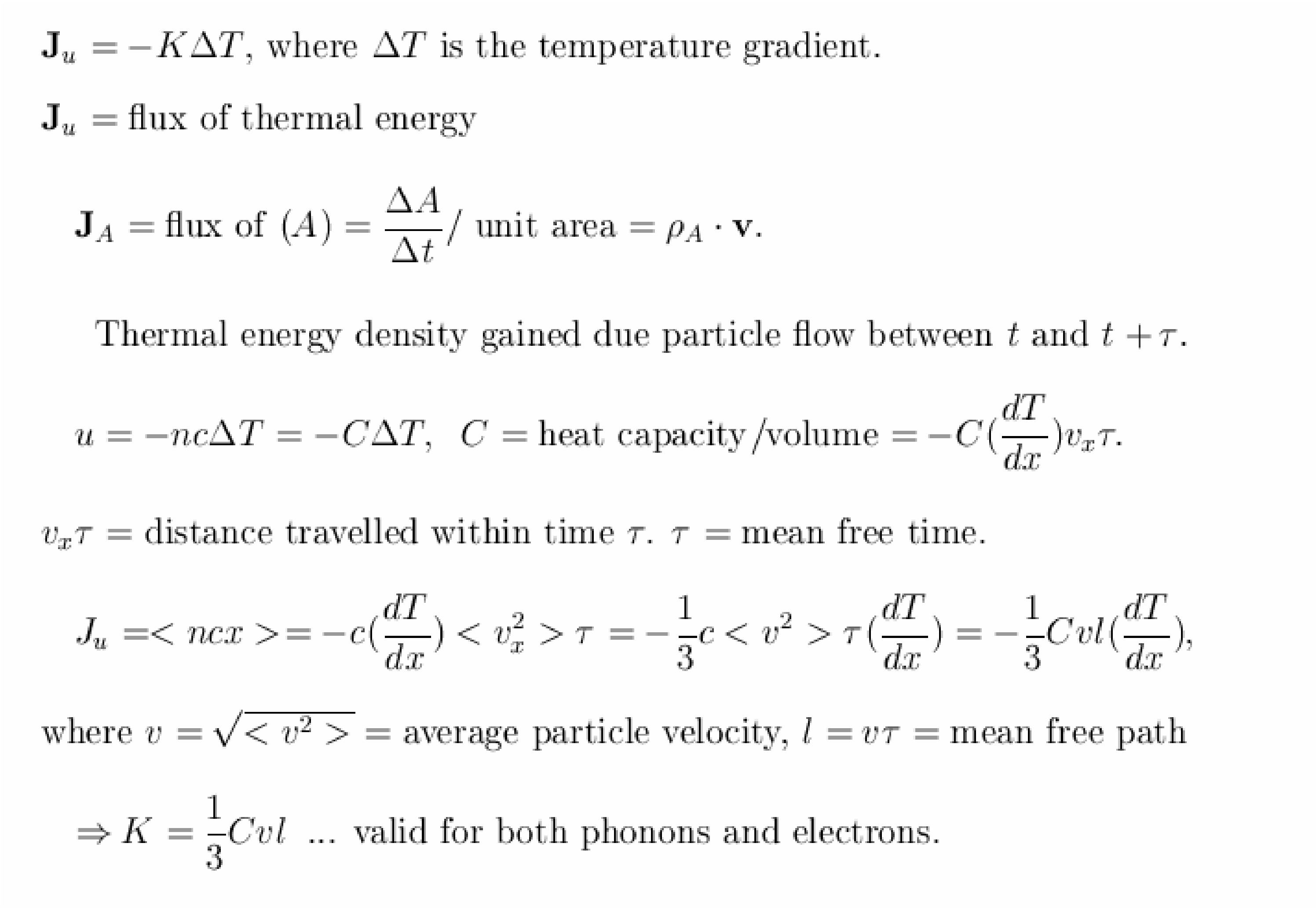
$$\sim \int dxe^{-\beta cx^2} x(1 + \beta gx^3) / \int dxe{-}\alpha x^2 I(\alpha) = \int dxe^{-\alpha x^2} = (\frac{\pi}{\alpha})^{1/2}; \ \alpha = \beta c$$

$$(\frac{\partial}{\partial\alpha})^2 I(\alpha) = \int x^4 e^{-\alpha x^2} dx = \frac{1}{2}\frac{3}{2}(\frac{\pi}{\alpha})^{1/2}\alpha^{-2}$$

$$\Rightarrow <x>= (\alpha g/c).\frac{3}{4}\alpha^{-2} = \frac{3}{4}\frac{g}{c\alpha} = \frac{3g}{4c^2}k_B T$$

$$\Rightarrow \text{Thermal expansion coef.} \ = (\frac{3g}{4c^2})k_B.$$

Thermal conductivity



$\mathbf{J}_u = -K\Delta T$, where ΔT is the temperature gradient.

$\mathbf{J}_u$ = flux of thermal energy

$$\mathbf{J}_A = \text{flux of } (A) = \frac{\Delta A}{\Delta t} / \text{ unit area} = \rho_A \cdot \mathbf{v}.$$

Thermal energy density gained due particle flow between t and $t+\tau$.

$$u = -nc\Delta T = -C\Delta T, \quad C = \text{heat capacity /volume} = -C(\frac{dT}{dx})v_x\tau.$$

$v_x\tau$ = distance travelled within time τ. τ = mean free time.

$$J_u =< ncx >= -c(\frac{dT}{dx}) < v_x^2 > \tau = -\frac{1}{3}c < v^2 > \tau(\frac{dT}{dx}) = -\frac{1}{3}Cvl(\frac{dT}{dx}),$$

where $v = \sqrt{< v^2 >}$ = average particle velocity, $l = v\tau$ = mean free path

$\Rightarrow K = \frac{1}{3}Cvl$ ... valid for both phonons and electrons.

Phonon mean free path is determined by phonon-defect scattering or phonon-phonon scattering.

$$l^{-1} \propto \text{ scattering rate } \propto \text{ number of phonons available}$$

$$< n >= (e^{\hbar\omega/k_BT} - 1)^{-1} = k_BT/\hbar\omega \;\text{ for } k_BT \ll \hbar\omega.$$

So, at high tempereature ($k_BT \ll \hbar\omega$) number of phonons $\propto T$ and $l \propto 1/T$ due to phonon-phonon scattering.

Note: Any momentum-conserving scattering ($\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_3$) (N-process) will lead to no change in thermal current. Only the Umbklapp process (U-rocess), in which $\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_3 + \mathbf{G}, \mathbf{G} =$ a nonzero reciprocal lattice vector, can change the thermal current and establish thermal equilibrium.

⋆ Geometric effect (phonon-scattering due to boundaries)

l is limited by the width of the sample (D). When phonon-phonon scattering becomes negligible at the low temperatures, the geometric effect prevails, and we have $K \sim CvD$. Thus,

$$K \sim \begin{cases} T^3 \text{ as } T \to 0 \\ T^{-1} \text{ as } T \ll \Theta \end{cases}$$