Phonons II: Thermal properties

- **Heat capacity of a crystal**

    - Density of state

    - Einstein mode

    - Debye model

- **Anharmonic effect**

    - Thermal conduction

A technician holding a silica fiber thermal insulation tile at 1300 Celsius

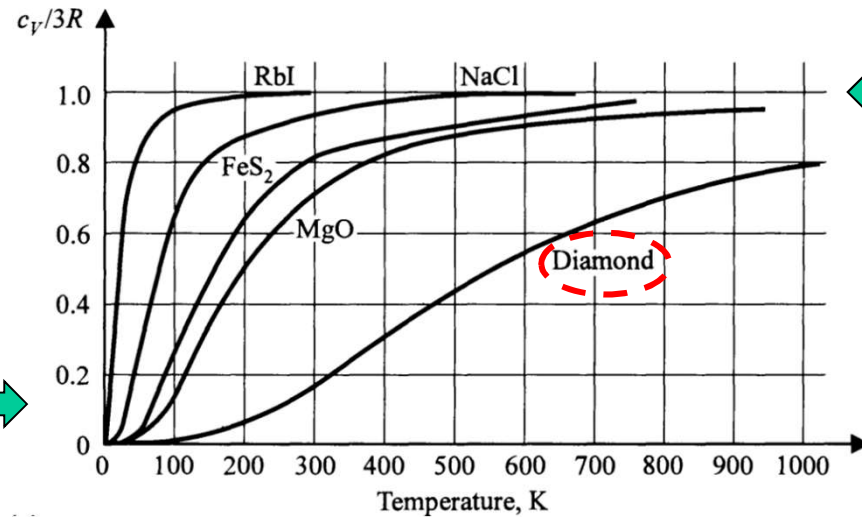See www.youtube.com/watch?time_continue=3&v=Pp9Yax8UNoM

Dept of Phys

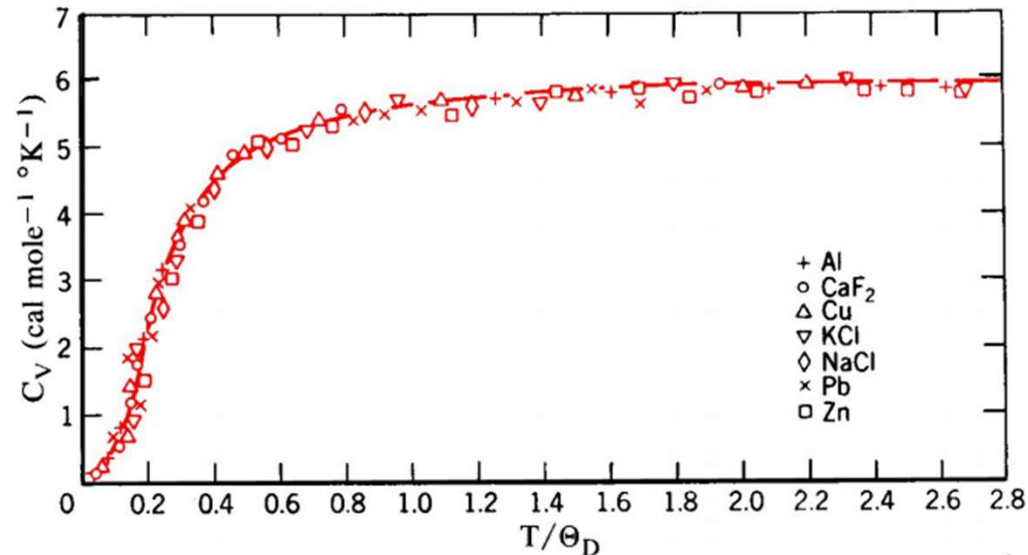M.C. Chang

Heat capacity: experiment

Heat capacity approaches 3R (~ 25 J/K) at high temperature

(Dulong-Petit law, 1819)

Heat capacity drops to zero at low temperature

1 mol of diamond, $\frac{1}{2}$ mol of RbI, NaCl, and MgO; and $\frac{1}{3}$ mol of FeS_2.

After rescaling the temperature by θ (Debye temperature), which differs from material to material, a universal behavior emerges:

Debye temperature

Table 1   Debye temperature and thermal conductivity[a]

In general, a harder material has a higher Debye temperature

important

Heat capacity: Quantum theory

- Internal energy U of a crystal is the summation of vibrational energies

(consider an insulator so there's no electronic energies)

$$U(T) = \sum_{k,s} (n_{k,s} + 1/2)\hbar\omega_{k,s}$$

where s sums over different phonon branches (L/T, A/O).

- Heat capacity C is nothing but the change of U(T) w.r.t. to T:

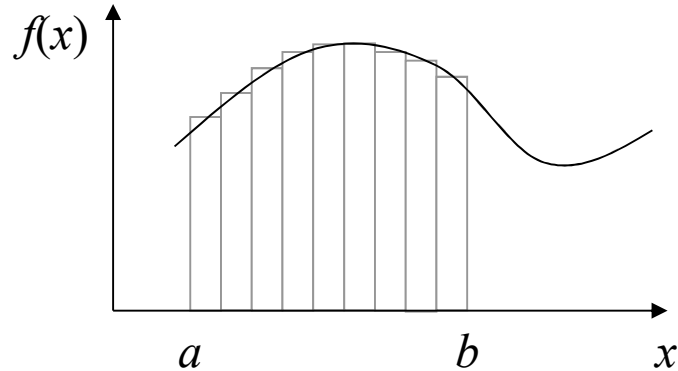$$C_V = \left(\partial U / \partial T\right)_V$$

- For a crystal in thermal equilibrium, the average phonon number
for k-mode is (see Kittel, p.107)

$$\langle n_{k,s} \rangle = \frac{1}{e^{\hbar\omega_{k,s}/kT} - 1}, \quad \text{Bose-Einstein distribution}$$

- Therefore, we have

$$U(T) = \sum_{k,s} \left(\frac{\hbar\omega_{k,s}}{e^{\hbar\omega_{k,s}/kT} - 1} + \frac{\hbar\omega_{k,s}}{2} \right)$$

Connection between *summation* and *integral*

$$\int_a^b dx f(x) = \lim_{\Delta x \to 0} \sum_i \Delta x \cdot f(x_i), \text{ or}$$

$$\sum_i f(x_i) \cong \int_a^b \frac{dx}{\Delta x} f(x).$$

Generalization to 3-dim:

$$\sum_{\vec{x}} f(\vec{x}) \cong \int \frac{d^3 x}{\Delta^3 x} f(\vec{x})$$

or $\quad \sum_{\vec{k}} f(\vec{k}) \cong \int \frac{d^3 k}{\Delta^3 k} f(\vec{k}) \quad$ in solid state

$$\Delta^3 k = \left(\frac{2\pi}{L} \right)^3$$

important

Density of states $D(\omega)$ (DOS, 態密度)

• $D(\omega)d\omega$ is the number of states within the surfaces of constant ω and $\omega + d\omega$

$$D(\omega)d\omega = \frac{\int_{shell} d^3k}{\Delta^3 k}, \quad \Delta^3 k = \left(\frac{2\pi}{L}\right)^3$$

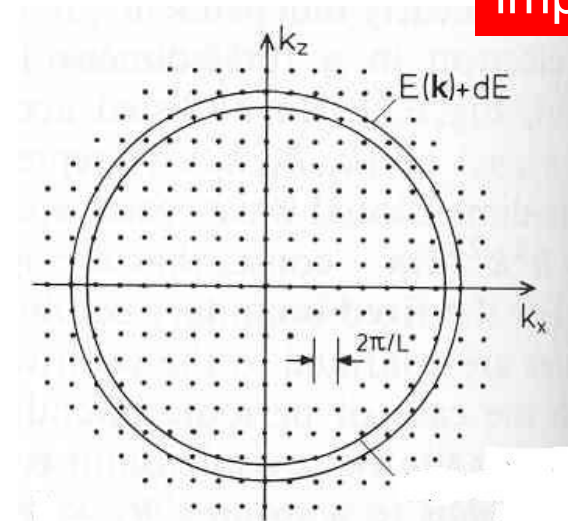$$\sum_{\vec{k}} f(\omega_{\vec{k}}) \cong \int \frac{d^3k}{\Delta^3 k} f(\omega_{\vec{k}})$$

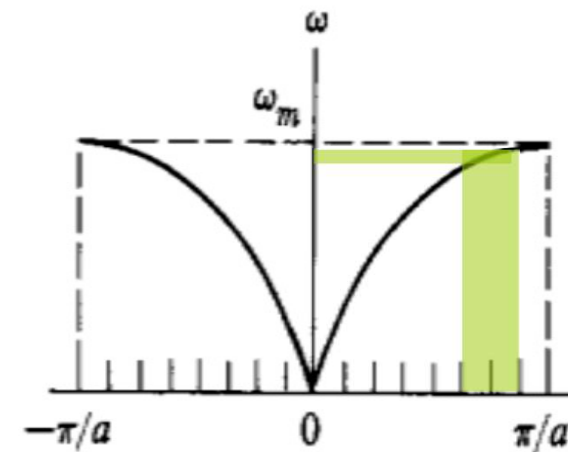not for $f(\boldsymbol{k})$

$$= \int d\omega D(\omega) f(\omega)$$

• Once we know the DOS, we can reduce the 3-dim $\boldsymbol{k}$-integral to a 1-dim ω integral.

Alternative definition:

$$D(\omega) = \int \frac{d^3k}{\Delta^3 k} \delta(\omega_{\vec{k}} - \omega)$$

• For example, assume N=16, then there are 2×2=4 states within the interval $d\omega$

• Flatter $\omega(k)$ curve, higher DOS.

DOS: 1-dim

$$D(\omega)d\omega = 2\frac{dk}{\Delta k} = 2\frac{dk/d\omega}{\Delta k}d\omega$$

$$\therefore D(\omega) = \begin{cases} \dfrac{L}{\pi}\dfrac{1}{d\omega/dk} & \text{for } \omega \le \omega_M \\ 0 & \text{otherwise} \end{cases}$$
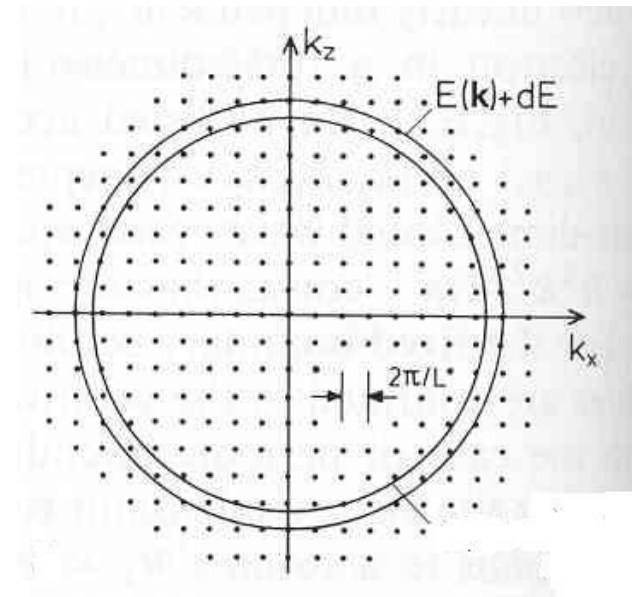
Ex: If $\omega(k) = vk$, then $D(\omega) = L/\pi v$.

Q: Calculate $D(\omega)$ for the 1-dim string with $\omega(k) = \omega_M|\sin(ka/2)|$
Prob.1(a)

DOS: 3-dim (assume $\omega(\boldsymbol{k}) = \omega(k)$ is isotropic)

$$D(\omega)d\omega = \int_{Shell}\frac{d^3k}{\Delta^3 k} = \frac{4\pi}{\Delta^3 k}k^2 dk = \frac{L^3}{2\pi^2}\frac{k^2}{d\omega/dk}d\omega$$

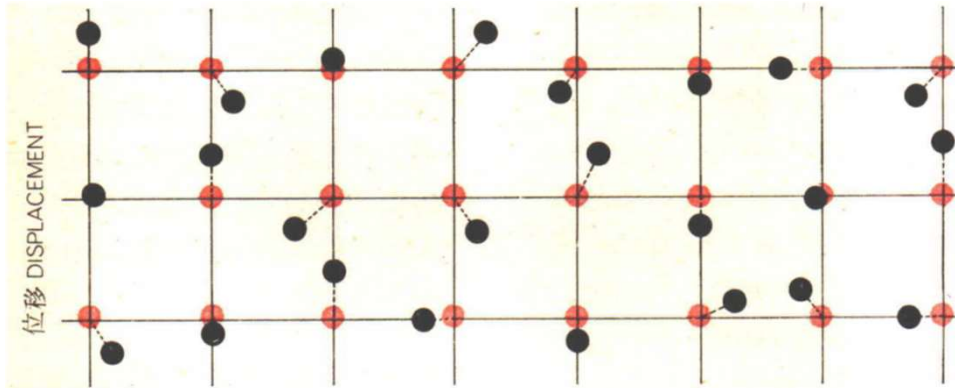for example, if $\omega = vk$, then $D(\omega) = V\omega^2/2\pi^2 v^3$

It's not necessary to memorize the result,
just remember the way of deriving it.

Einstein model (1907)

Assume that

1. each atom vibrates independently of each other, and

2. every atom has the same vibration frequency ω_0

- The DOS can be written as

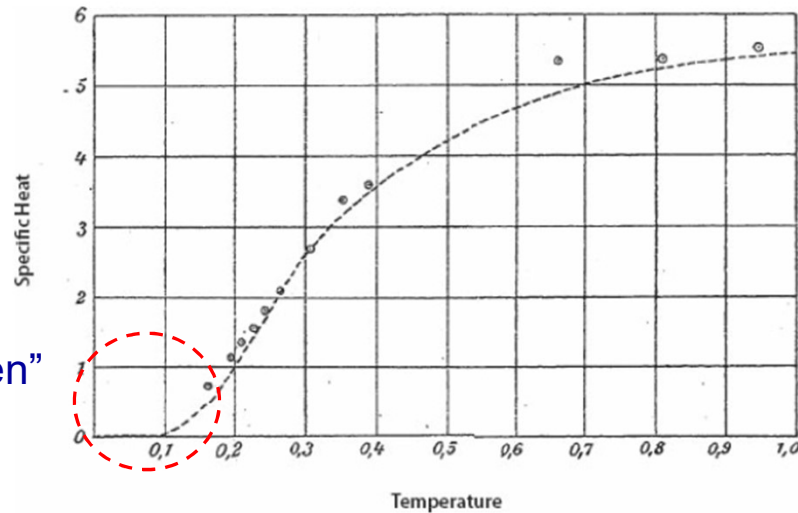$$D(\omega) = 3N\delta(\omega - \omega_0)$$

3 dim $\times$
number of atoms

Einstein model

$$U = 3N\left(\langle n \rangle + \frac{1}{2}\right)\hbar\omega_0 = 3N\frac{\hbar\omega_0}{\exp(\hbar\omega_0 / kT) - 1} + 3N\frac{\hbar\omega_0}{2}$$

$$C_V = (\partial U / \partial T)_V = 3Nk\left(\frac{\hbar\omega_0}{kT}\right)^2 \frac{e^{\hbar\omega_0/kT}}{\left(e^{\hbar\omega_0/kT} - 1\right)^2}$$

$$\approx e^{-\hbar\omega_0/kT} \text{ as } T \to 0\,K$$
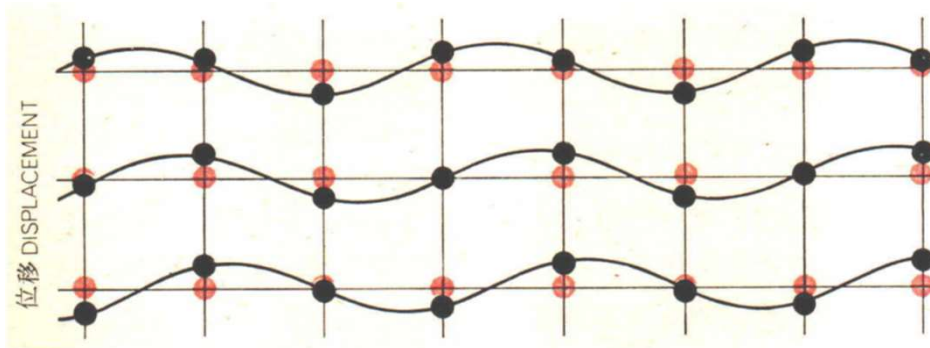
vibration is "frozen"
at low T

Data of diamond from Einstein's 1907 paper.

Debye model (1912)

Based on classical elasticity theory (continuous, before the classical theory of lattice dynamics).

Vibration produces waves

$$U(T) = \sum_{k,s} \langle n_{k,s} \rangle \hbar\omega_{k,s} \quad (\hbar\omega_{k,s}/2 \text{ neglected})$$

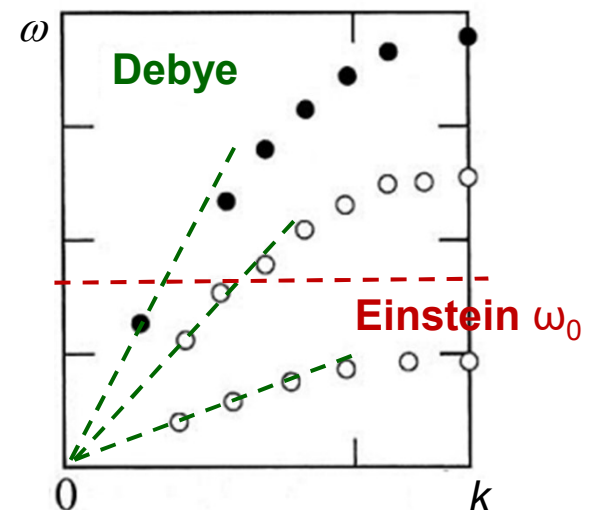$$= \sum_{s=1}^{3} \int d\omega D_s(\omega) \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1}$$

Debye assumed that

1. the wave is non-dispersive: $\omega = v_s k$ (s=L,T_1,T_2).

Therefore, $D_s(\omega) = V\omega^2 / 2\pi^2 v_s^3$ (quadratic)

(Iso-frequency surface is a sphere)

Frequency dispersion

Debye

Einstein ω_0

2. The 1st BZ is approximated by a sphere with the same volumne (# of states).

High-frequency cut-off ω_D (Debye frequency)

- A simple estimate

$$\frac{\frac{4}{3}\pi k_D^3}{\Delta^3 k} = N$$
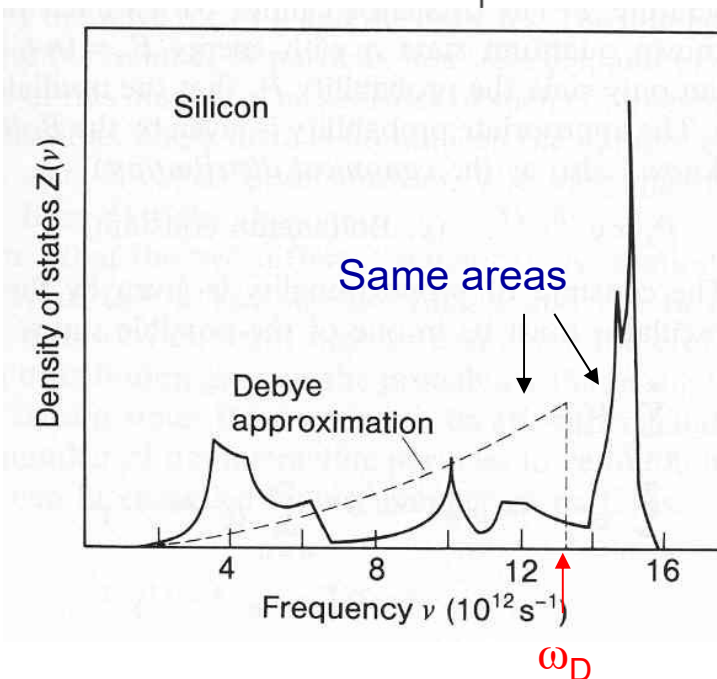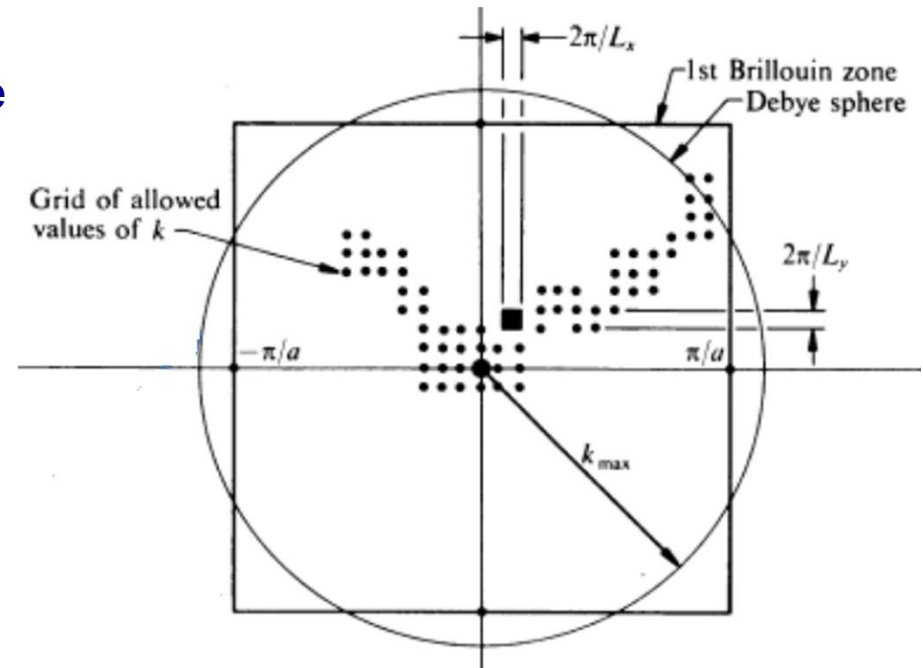
For every branch

$$\rightarrow \quad \omega_D = v k_D = v\left(6\pi^2 n\right)^{1/3}$$

- or $\quad \sum_{s=1}^{3}\int_0^{\omega_D} d\omega D_s(\omega) = 3N$

$$\rightarrow \sum_{s=1}^{3}\frac{V\omega_D^3}{6\pi^2 v_s^3} = 3N$$

$$\frac{3}{v^3} \equiv \sum_{s=1}^{3}\frac{1}{v_s^3}$$

$$\rightarrow \omega_D = v(6\pi^2 n)^{1/3}, \ n = N/V$$

Silicon

Density of states $Z(\nu)$

Same areas

Debye approximation

Frequency ν (10^{12} s^{-1})

ω_D

$2\pi/L_x$

1st Brillouin zone
Debye sphere

Grid of allowed values of k

$2\pi/L_y$

$-\pi/a$ π/a

k_{max}

Internal energy and heat capacity

$$U(T) = \sum_{s=1}^{3} \frac{V}{2\pi^2 v_s^3} \int_0^{\omega_D} d\omega\, \omega^2 \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}$$
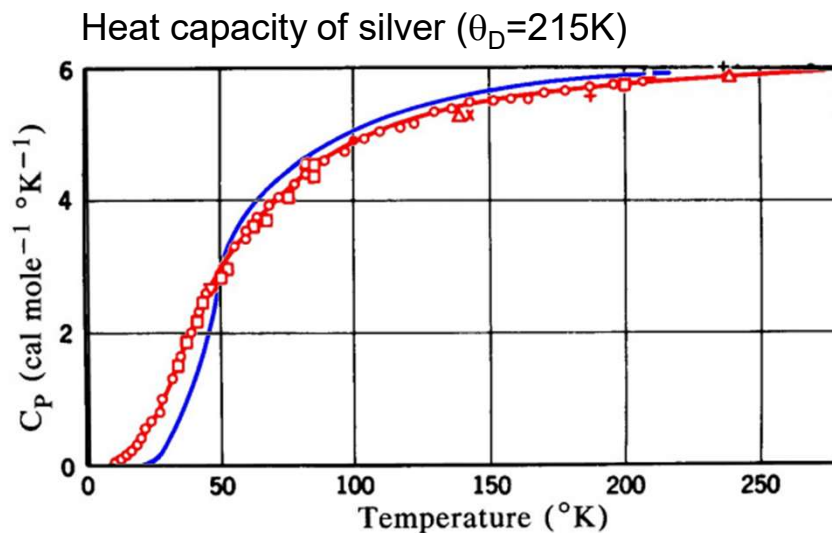
$$= \frac{3V}{2\pi^2 v^3} \hbar \left(\frac{k_B T}{\hbar}\right)^4 \int_0^{x_D} dx \frac{x^3}{e^x - 1}, \quad x_D = \frac{\hbar\omega_D}{k_B T} = \frac{\theta}{T}$$
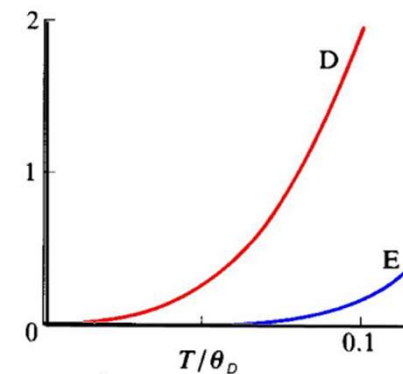
Debye temperature

$$k_B \theta \equiv \hbar\omega_D$$

$$= 9Nk_B T \left(\frac{T}{\theta}\right)^3 \boxed{\int_0^{x_D} dx \frac{x^3}{e^x - 1}} = \pi^4/15 \text{ as } T \to 0\ (x_D \to \infty)$$

$$\therefore C_V = \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\theta}\right)^3 \propto T^3 \text{ as } T \to 0 \qquad \text{(Debye } T^3 \text{ law)}$$

Heat capacity of silver (θ_D=215K)

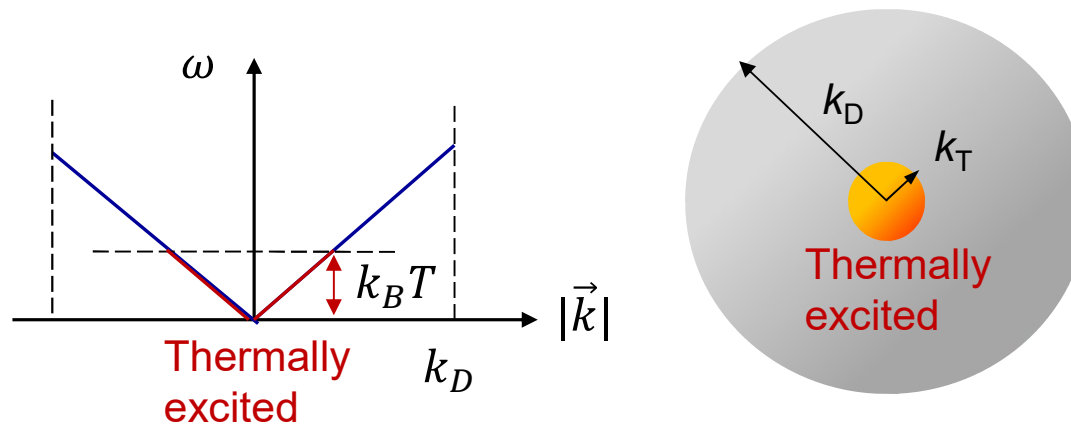**At low T, Debye's curve drops slowly because long wavelength vibration can still be excited.**

A simple explanation of the T^3-dependence (at low T):

First, define $\quad \hbar\omega_T = k_B T, \qquad \omega_T = v k_T$

$$\hbar\omega_D = k_B \theta, \qquad \omega_D = v k_D$$

Suppose that

1. All the phonons with wave vector $k < k_T$ are excited, while the modes between k_T and k_D are not excited.

2. Each excited mode roughly has thermal energy $k_B T$

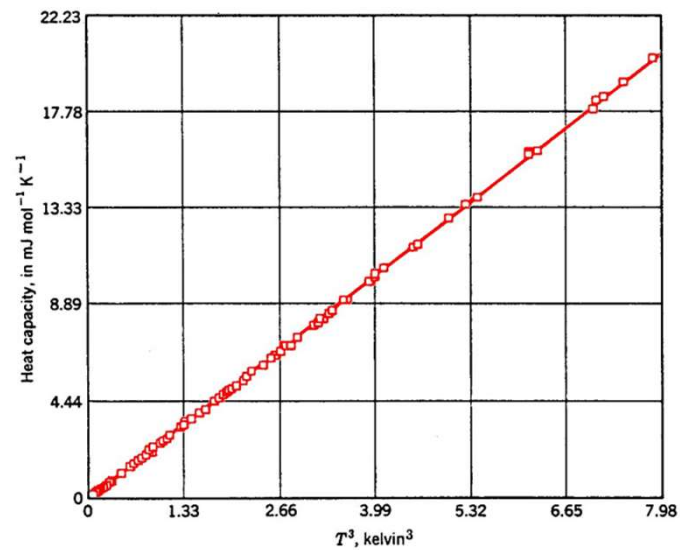$$\hbar\omega_D = \hbar v k_D = k_B \theta$$

- Then the fraction of excited modes

$= (k_T/k_D)^3 = (T/\theta)^3$.

# of normal modes

- Thermal energy $U \sim k_B T \cdot 3N(T/\theta)^3$

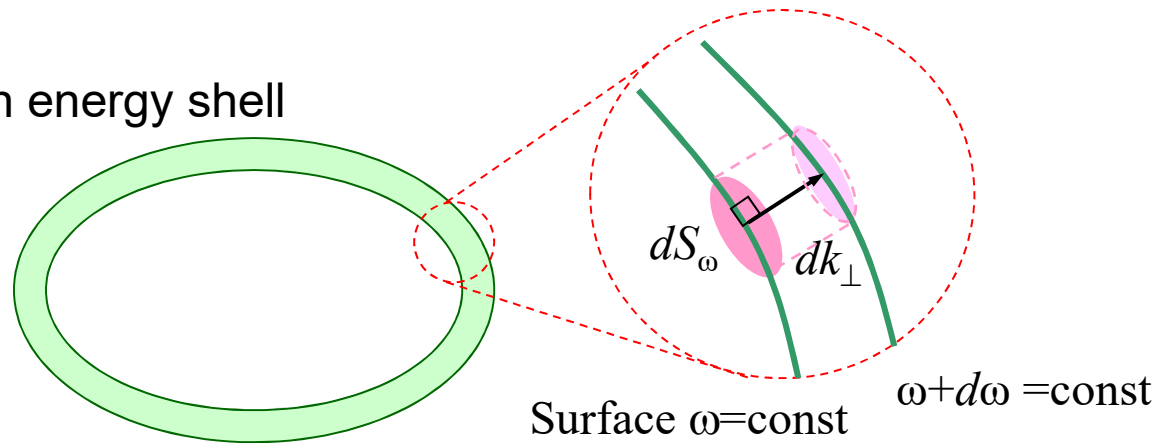- $\therefore$ Heat capacity $C \sim 12Nk_B(T/\theta)^3$

solid Argon (θ=92 K)

DOS for *general dispersion relation*

important

An energy shell

dS_ω $dk_\perp$

Surface ω=const   ω+$d\omega$ =const

$$D(\omega)d\omega = \left(\frac{L}{2\pi}\right)^3 \int_{Shell} d^3k$$

$\nabla_{\vec{k}}\omega \perp$ **Iso-frequency surface**

$$d^3k = dS_\omega dk_\perp$$

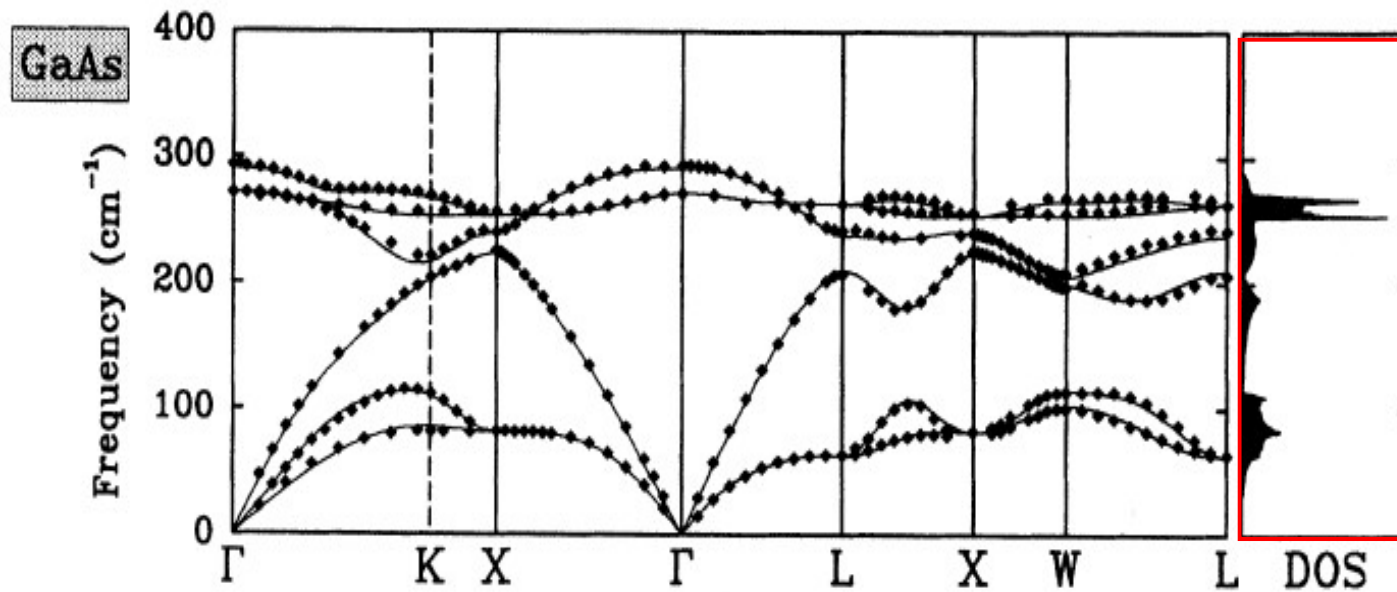$$d\omega = \nabla_{\vec{k}}\omega \cdot d\vec{k} = \left|\nabla_{\vec{k}}\omega\right| dk_\perp$$

$$\therefore d^3k = dS_\omega \frac{d\omega}{\left|\nabla_{\vec{k}}\omega\right|}$$

$$\Rightarrow D(\omega) = \left(\frac{L}{2\pi}\right)^3 \int \frac{dS_\omega}{\left|\nabla_{\vec{k}}\omega\right|}$$ ← **Group velocity**
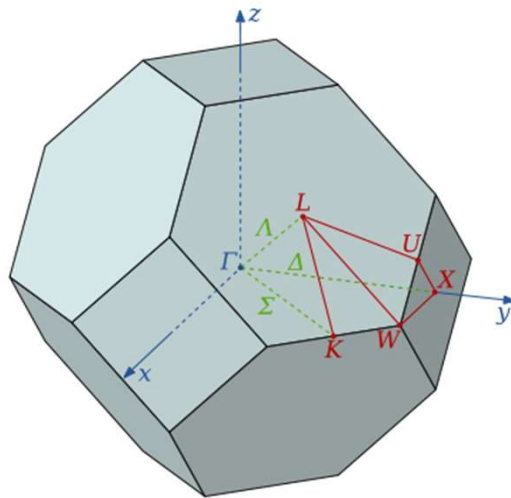
If $v_g = \left|\nabla_{\vec{k}}\omega\right| = 0$, then there is

"van Hove singularity" (1953)

Silicon

Density of states $Z(\nu)$

Debye approximation

Frequency ν (10^{12} s^{-1})

Dispersion relation and DOS

Giannozzi et al, PRB 43, 7231 (1991)

• Heat capacity of a crystal

    • density of states

    • Einstein model

    • Debye model

• anharmonic effect

    • thermal conduction

Aharmonic effect in crystals

If there is no aharmonic effect, then there is

• No thermal expansion

• Heat capacity becomes constant at high T

• No phonon-phonon interaction

• Thermal conductivity would be infinite (for a pure crystal)

•…

No thermal expansion   Thermal expansion

physics.stackexchange.com/questions/332524/what-is-thermal-expansion

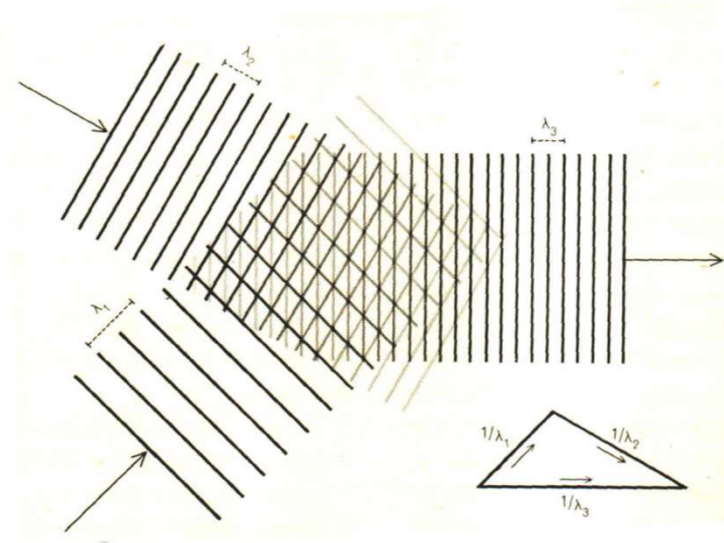## Phonon-phonon scattering

A result of the anharmonic vibration

Modulation of elastic const.
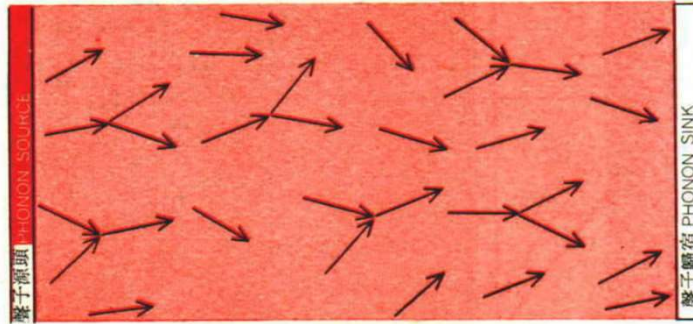(~ acoustic grating)

$$F = -kx + k'x^2$$
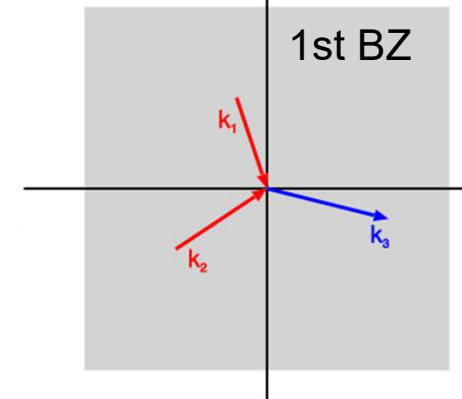$$= -(k - k'x)x$$
$$\therefore \quad k_{eff}(x) = k - k'x$$

• Total momentum of the 2 phonons remains the same

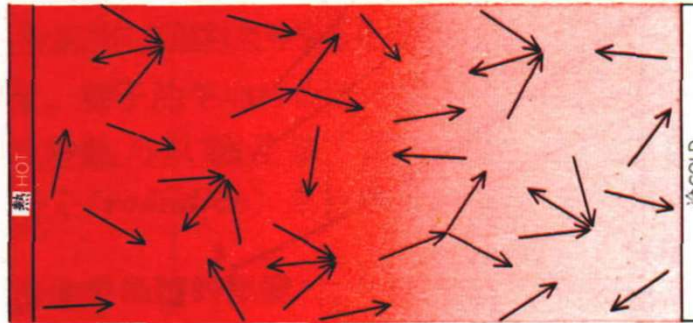during the scattering. No resistance to thermal current?
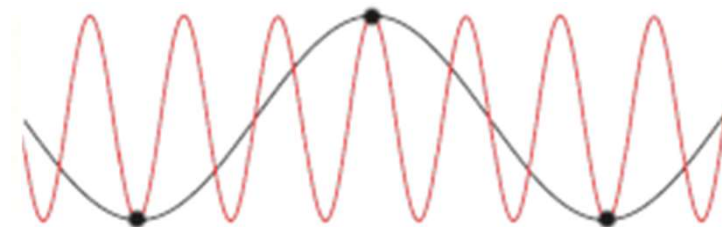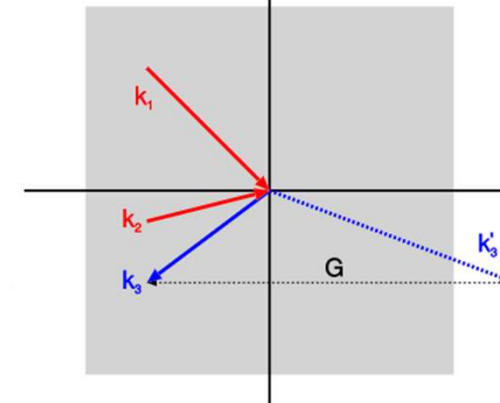
Phonon-phonon scattering

- Normal process:

N-Process

1st BZ

- Umklapp process (轉向過程, Peierls 1929):

U-Process

Figs from wiki

Thermal conductivity

- Thermal current density (Fourier's law, 1807)

$$\vec{J}_U = -K\nabla T \qquad \sim \qquad \vec{J} = -\sigma\nabla\phi$$

- In metals, thermal current is carried by both electrons and phonons. In insulators, only phonons can be carriers.

- The collection of phonons is similar to an ideal gas

THE CLASSICAL GAS vs. THE PHONON GAS

	CLASSICAL GAS OF MOLECULES	PHONON GAS
Container	A vessel with impenetrable walls	A crystal, which is the medium that sustains the phonons
Collisions	Molecules collide with each other and with walls of vessel	Phonons collide with each other, with surface of crystal, and with impurities
Energy conserved in collisions	Yes	Yes
(Crystal) momentum conserved in collisions	Yes (except at walls)	Yes (except at surfaces and in collisions with impurities), provided that $T \ll \Theta_D$, so that umklapp processes are frozen out
Number conserved in collisions	Yes	No

Ashcroft and Mermin, Chaps 23, 24

- **Thermal conductivity**

  K=1/3 *c v* ℓ

  c: C/volume

  v: phonon velocity

  ℓ: mean free path

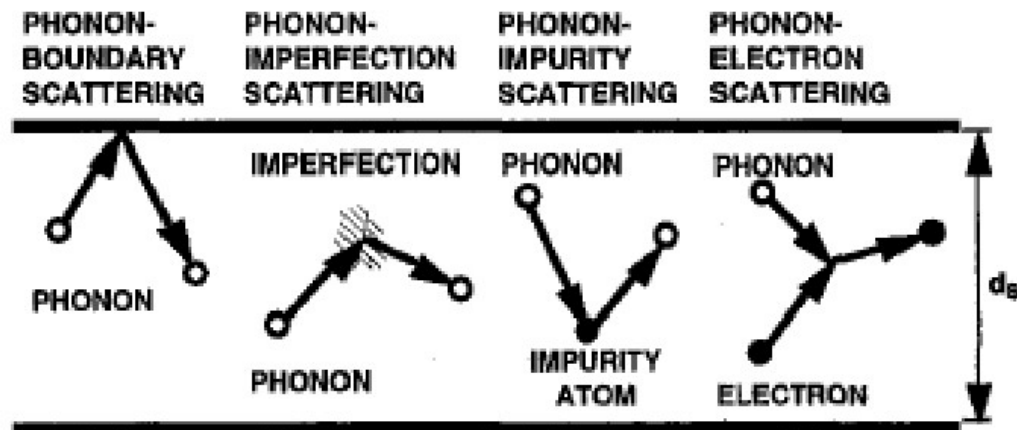 (Kittel p.122)

  Dimensional analysis:

  Assume $[K] = [c]^\alpha [v]^\beta [\ell]^\gamma$

  → $\alpha=\beta=\gamma=1$

- **The mean free path of a phonon can be affected by boundary, defects, electrons, and other phonons.**

◆ *T*-dependence of the phonon mean free path ℓ

• Low *T*: For a crystal with few defects, the mean free path is limited mainly by the boundary of the sample.

• High *T*: The number of phonons are proportional to *T*. The mean free path $\sim 1/T^x$ (x=1~2).

◆ *T*-dependence of the lattice thermal conductivity $K(T) \sim c(T)\, v\, \ell(T)$

• Low *T*: $K(T) \sim c(T) \sim T^3$

• High *T*: $K(T) \sim \ell(T) \sim 1/T$

Boer and Pohl, Semiconductor Physics 2018