# Lectures 13, 14: Phonons: thermal properties

Lattice vibrations in 3-D: the contribution to the thermal properties of solids

♦ **Aims:**

➤ Phonons in real, 3-D crystals:

- some examples: Rare gas solids, Alkali halides

➤ Lattice thermal properties:

➤ Heat capacity:

- Debye treatment

- T^3 law for low temperature heat capacity

➤ Thermal conductivity

- Phonon scattering

- Mean-free path

ω_D

Debye model

Measured

$g(\omega)$

ω

Debye, T^3 Law

$$c_V = \left.\frac{\partial U}{\partial T}\right|_V \propto T^3$$
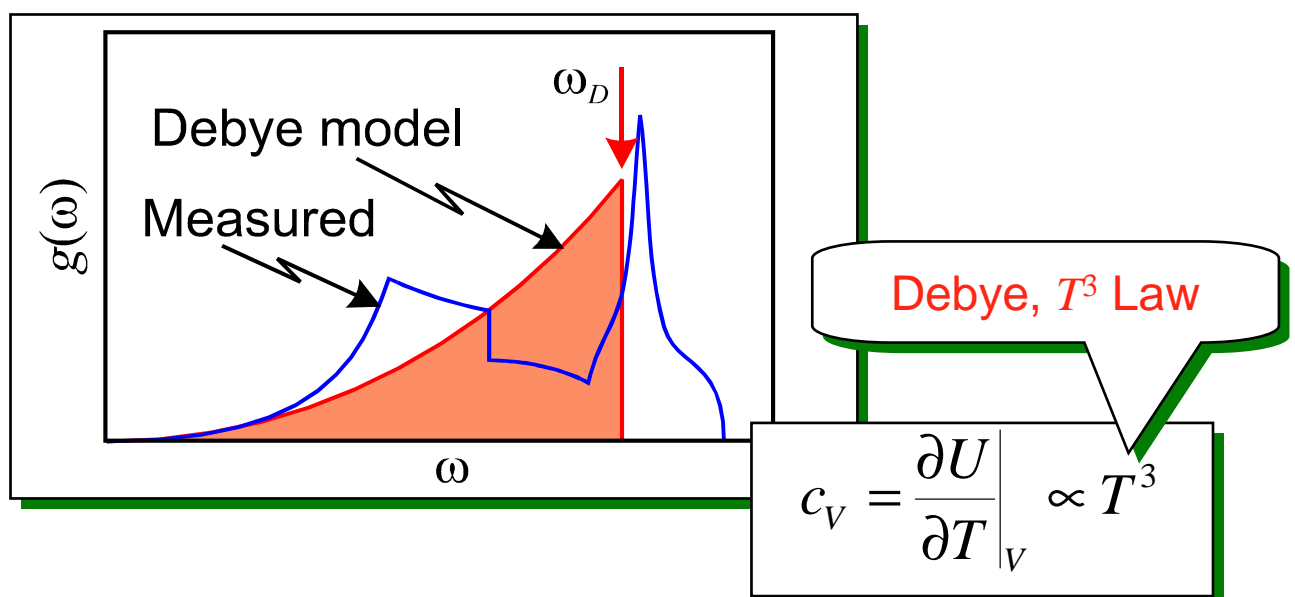
Phonons in 3-D crystals: Monatomic lattice

♦ **Example: Neon, an f.c.c. solid:**

➤ Inelastic neutron scattering results in different crystallographic directions
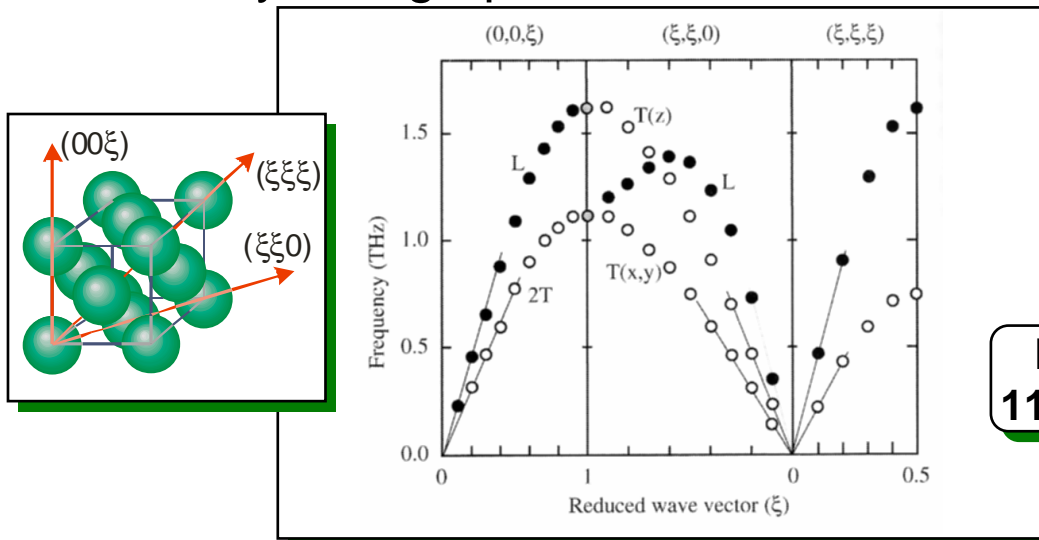
➤ Many features are explained by our 1-D model:

➤ Dispersion is sinusoidal (n.n. interactions)

➤ All modes are acoustic (monatomic system)

➤ Two types of mode:

◻ Longitudinal (L): generally have higher energy

◻ Transverse (T): generally have lower energy

◻ often degenerate in high symmetry directions (not along $(\xi\xi 0)$ above)

➤ Minor point: L mode along $(\xi\xi 0)$ has 2 Fourier components, suggesting next-n.n. interactions (see problem 10, sheet 2). (In Neon, the effect arises purely from 3-D nature of fcc structure.)

Phonons in 3-D crystals: Diatomic lattice

♦ **Example: NaCl,** has sodium chloride structure!

➤ Two interpenetrating f.c.c. lattices

Note energy scales: 8 THz ~ 30 meV (c.f. Neon)

Phys. Rev. **178** 1496, (1969)
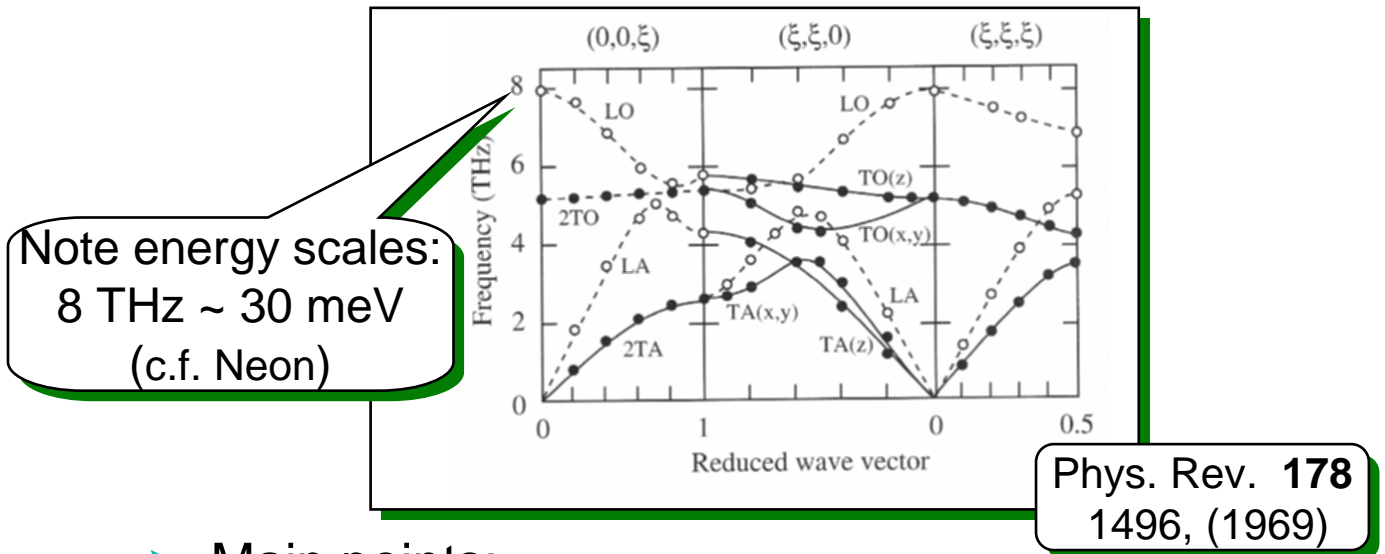
➤ Main points:

➤ Again, the 1-D model gives several insights:

➤ Optical and acoustic modes;

➤ Longitudinal and transverse modes;

➤ Dispersion along ($\xi\xi\xi$) is simplest and most like our 1-D model

   ◻ ($\xi\xi\xi$) planes contain, alternately, Na atoms and Cl atoms (other directions have Na and Cl mixed)

➤ Minor point:

   ◻ Modes with same symmetry cannot cross, hence the avoided crossing between acoustic and optical modes in (00ξ) and ($\xi\xi$0) directions.

   ◻ Ignore the detail for present purposes

Lattice heat-capacity

♦ **Heat capacity**

➤ Follows from differentiating the internal energy (as usual).

➤ Internal energy

$$U = \int_0^\infty \left[\frac{\hbar\omega}{\exp(\hbar\omega/kT) - 1} \right] g(\omega)d\omega$$

> No. of phonons in $d\omega$ at ω

> Energy per phonon (Planck formula, Lecture 6)

➤ Density of modes $g(\omega)$.

- Einstein Approximation: all modes have the same frequency, ω_E. (See lecture 6)
- Debye approximation: In the low temperature limit acoustic modes, with small q, dominate. So assume $\omega = v_s q$.
- Exact: calculate $g(\omega)$, numerically, from the phonon dispersion curves

➤ Einstein approximation gave the correct high-temperature behaviour ($C = 3NkT$) and gave $C \rightarrow 0$ as $T \rightarrow 0$ though the exact temperature dependence was inaccurate (the reason, we can now understand from the phonon dispersion curves)

Debye Model

♦ **Density of states**

➤ Assume $\omega = v_s q$. i.e. dispersionless waves

➤ Result is therefore similar to that for photons in a 3-D cavity (black body radiation), except for a numerical constant.

$$g(q)\,\mathrm{d}\,q = 3 \cdot \frac{a^3}{2\pi^2} q^2\,\mathrm{d}\,q$$

$g(q)\,\mathrm{d}\,q = g(\omega)\,\mathrm{d}\,\omega$

$$g(\omega)\,\mathrm{d}\,\omega = 3\frac{a^3}{\pi^2 v_s^3}\omega^2\,\mathrm{d}\,\omega$$

3 acoustic modes for each q

where $\omega = v_s q$ has been substituted in RHS.

➤ Energy becomes:

Upper limit on integral guarantees the correct, total number of modes ($3N$). It is known as the Debye frequency.

$$U = \int_0^{\omega_D} \frac{3V\omega^2}{2\pi^2 v_s^3}\hbar\omega\frac{1}{\exp(\hbar\omega/kT)-1}\,d\omega$$

Vol, $V = a^3$.

$$= \frac{3V\hbar}{2\pi^2 v_s^3}\int_0^{\omega_D}\omega^3\frac{1}{\exp(\hbar\omega/kT)-1}\,d\omega$$

➤ Formula gives the full T dependence. We are interested in the behaviour at low T.

heat capacity at low-temperture

♦ **Limiting behaviour as $T \to 0$.**

➤ At low temperature the higher frequency modes are not excited. Thus contributions to the integral for large $\omega\,(\sim\omega_D)$ can be ignored and ω_D replaced by ∞.

$$U = \frac{3V\hbar}{2\pi^2 v_s^3} \int_0^\infty \omega^3 \frac{1}{\exp(\hbar\omega/kT)-1}\, d\omega$$

$$= \frac{3V\hbar}{2\pi^2 v_s^3} \left(\frac{kT}{\hbar}\right)^4 \int_0^\infty x^3\left(\exp(x)-1\right)^{-1} d\omega$$

$$U = \frac{V\pi^2 k^4}{10(v_s\hbar)^3} T^4$$

Integral $= \pi^4/15$

➤ Differentiating gives the heat capacity as

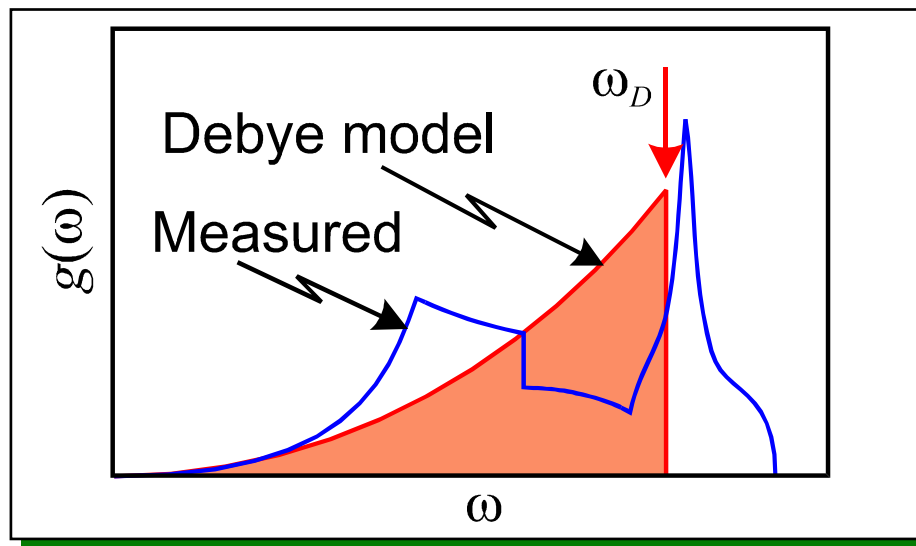$$c_V = \left.\frac{\partial U}{\partial T}\right|_V \propto T^3$$

Debye, T^3 Law

gives the correct, observed dependence at low temperatures. Recall the Einstein model gave an exponential dependence at low T.

Measured density of states

♦ **Example: Aluminium** (shows common features)

➤ Measured density of states compared with Debye approximation.

➤ Both measured and Debye density of states are similar at low ω, as expected ($\omega \propto q$).

➤ Debye frequency chosen to give same total number of modes (i.e. equal area under both curves)

➤ Largest deviations where phonon modes approach zone boundary.

➤ Measured curve is complex because the 3-D zone has a relatively complicated shape, and the transverse and longitudinal modes have different dispersions (as we have seen earlier)
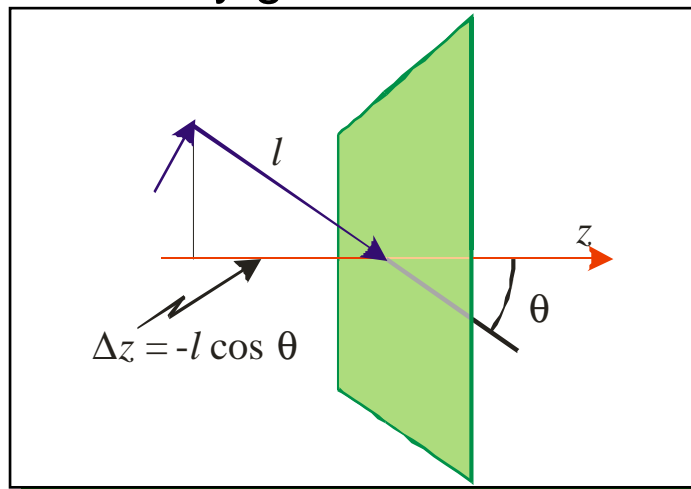
Thermal conductivity

♦ **Phonons and thermal conductivity**

  ➤ Phonons have energy and momentum and, therefore, can conduct heat.
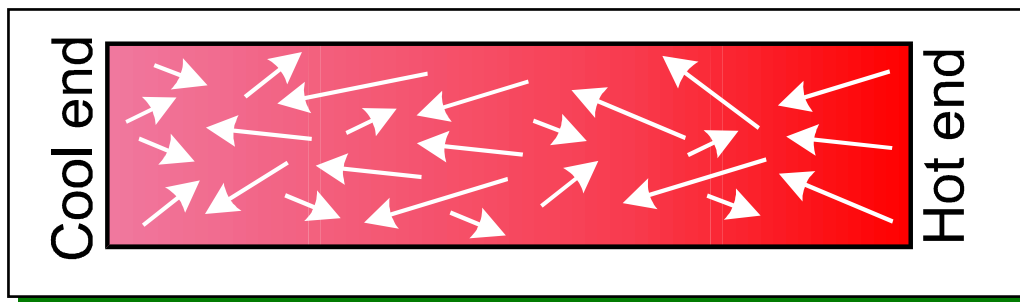
  ➤ Kinetic theory gives the thermal conductivity

  ◩ Excess temperature of phonons crossing plane

  $$\Delta T = \frac{dT}{dz} \Delta z = -\frac{dT}{dz} l \cos\theta$$

  ◩ Excess energy of each phonon
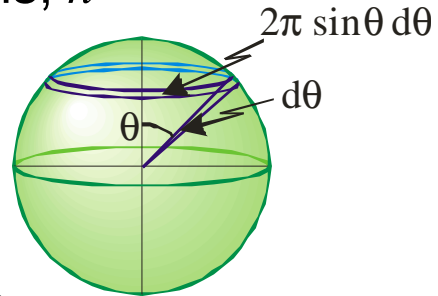
  $$c_{ph} \Delta T = -c_{ph} \frac{dT}{dz} l \cos\theta$$

  heat capacity of a phonon

conductivity..........

► Number density of phonons, n

2π sinθ dθ

dθ

θ

number with
speed c to $c+dc$

fraction with
angles θ to $\theta+d\theta$

$$n\,f(c)dc$$

$$2\pi \sin\theta\,d\theta/4\pi = \sin\theta\,d\theta/2$$

speed normal to plane

net heat per phonon

► Heat flux across plane

$$H = \int_0^\pi \int_0^\infty [nf(c)dc\,\sin\theta\,d\theta/2][c\cos\theta][-c_{ph}l\cos\theta\,dT/dz]$$

$$H = -\frac{1}{2}c_{ph}nl\frac{dT}{dz}\int_0^\pi \sin\theta\cos^2\theta\,d\theta \int_0^\infty c\,f(c)dc$$

$$H = +\frac{1}{2}c_{ph}nl\frac{dT}{dz}\langle c\rangle \int_0^\pi \cos^2\theta\,d(\cos\theta)$$

$\langle c\rangle$

$$H = +\frac{1}{3}c_{ph}nl\langle c\rangle\frac{dT}{dz} = \kappa\frac{dT}{dz}$$

$$\kappa = c_{ph}nl\langle c\rangle/3$$

Definition of thermal conductivity

► Thermal conductivity

$$\kappa = \frac{1}{3}C\langle c\rangle l$$

Mean free path

Average speed

Heat capacity per unit vol

Temperature dependence of thermal conductivity

♦ **Mean free path** – limited by scattering processes

➤ With many scattering processes:
$$1/l = 1/l_1 + 1/l_2 + \cdots$$
Thus, shortest mean free path dominates

➤ "Geometric" scattering:

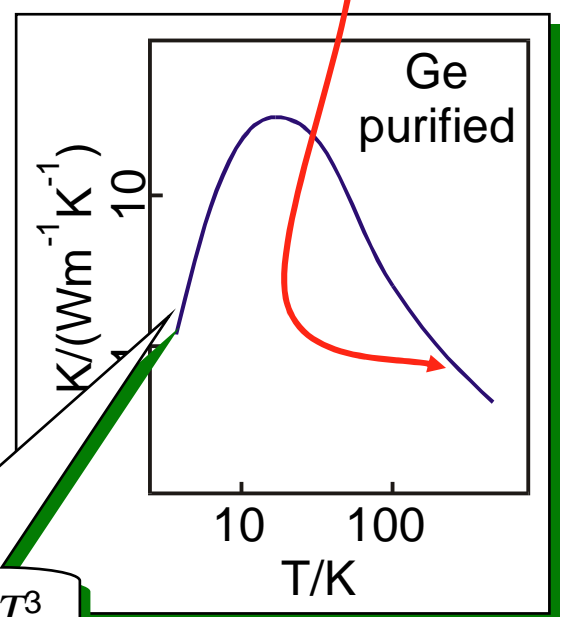🔹 Sample boundaries (only significant for purest samples at low temperatures).

🔹 Impurities: scattering rate ~ independent of T.

➤ Phonon-phonon scattering:

🔹 Phonons, being normal modes, should not affect each other. However, in an anharmonic lattice, they can scatter. Free path ~ $1/T$.

♦ **Insulators** (no contribution from electrons).

➤ In pure crystalline form the conductivity can be very high (larger than metals)

➤ N.B. Non-crystalline systems (eg glass) have much lower conductivity. l ~ local order

C, and hence $\kappa \sim T^3$

Ge purified

$K/(Wm^{-1}K^{-1})$ 10

10   100

T/K