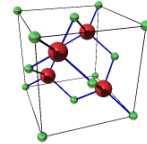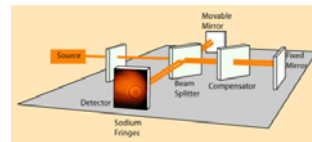# Phys 446:

Solid State Physics / Optical Properties

Lattice vibrations:
Thermal, acoustic, and optical properties

Fall 2007

Solid State Physics

Lecture 5

Last week: (Ch. 3)

• Phonons

• Today:

  Einstein and Debye models for thermal capacity

  Thermal conductivity

  HW2 discussion

Material to be included in the test
Oct. 12th 2007

• Crystalline structures.
  7 crystal systems and 14 Bravais lattices

• Crystallographic directions
  and Miller indices
  $$d_{hkl} = \frac{n}{\left(\dfrac{h^2}{a^2} + \dfrac{k^2}{b^2} + \dfrac{l^2}{c^2} \right)^{1/2}}$$

• Definition of reciprocal lattice vectors:

$$\mathbf{b}_1 = \frac{2\pi}{V}\mathbf{a}_2 \times \mathbf{a}_3, \quad \mathbf{b}_2 = \frac{2\pi}{V}\mathbf{a}_3 \times \mathbf{a}_1, \quad \mathbf{b}_3 = \frac{2\pi}{V}\mathbf{a}_1 \times \mathbf{a}_2$$

• What is Brillouin zone

• Bragg formula: $2d \cdot \sin\theta = m\lambda$; $\Delta\mathbf{k} = \mathbf{G}$

• Factors affecting the diffraction amplitude:

  Atomic scattering factor (form factor): reflects distribution of electronic cloud. $f_a = \int n(\mathbf{r})e^{i\Delta\mathbf{k}\cdot\mathbf{r}_l}d^3r$

  In case of spherical distribution $f_a = \int_0^{r_0} 4\pi r^2 n(r)\frac{\sin(\Delta k \cdot r)}{\Delta k \cdot r}dr$

• Structure factor $F = \sum_j f_{aj} e^{2\pi i(hu_j + kv_j + lw_j)}$

• Elastic stiffness and compliance. Strain and stress: definitions and relation between them in a linear regime (Hooke's law):

$$\sigma_{ij} = \sum_{kl} C_{ijkl}\varepsilon_{kl} \qquad \varepsilon_{ij} = \sum_{kl} S_{ijkl}\sigma_{kl}$$

• Elastic wave equation: $\dfrac{\partial^2 u}{\partial t^2} = \dfrac{C_{eff}}{\rho}\dfrac{\partial^2 u_x}{\partial x^2}$ sound velocity $v = \sqrt{\dfrac{C_{eff}}{\rho}}$

- Lattice vibrations: acoustic and optical branches
  In three-dimensional lattice with s atoms per unit cell there are
  $3s$ phonon branches: 3 acoustic, $3s - 3$ optical

- Phonon - the quantum of lattice vibration.
  Energy $\hbar\omega$; momentum $\hbar\mathbf{q}$

- Concept of the phonon density of states

- Einstein and Debye models for lattice heat capacity.

  Debye temperature $\quad \theta_D = \dfrac{\hbar v}{k_B}\left(\dfrac{6\pi^2 N}{V}\right)^{1/3}$

  Low and high temperatures limits of Debye and Einstein models

- Formula for thermal conductivity $\quad K = \dfrac{1}{3}Cvl$

- Be able to obtain scattering wave vector or frequency from
  geometry and data for incident beam (x-rays, neutrons or light)

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Summary of the Last Lecture

❖ Elastic properties – crystal is considered as continuous anisotropic medium

❖ Elastic stiffness and compliance tensors relate the strain and the stress in a linear region (small displacements, harmonic potential)

Hooke's law: $\quad \sigma_{ij} = \sum_{kl} C_{ijkl}\varepsilon_{kl} \qquad \varepsilon_{ij} = \sum_{kl} S_{ijkl}\sigma_{kl}$

❖ Elastic waves $\quad \dfrac{\partial^2 u}{\partial t^2} = \dfrac{C_{eff}}{\rho}\dfrac{\partial^2 u_x}{\partial x^2}\quad$ sound velocity $\quad v = \sqrt{\dfrac{C_{eff}}{\rho}}$

❖ Model of one-dimensional lattice: linear chain of atoms

❖ More than one atom in a unit cell – acoustic and optical branches

❖ All crystal vibrational waves can be described by wave vectors within the first Brillouin zone in reciprocal space

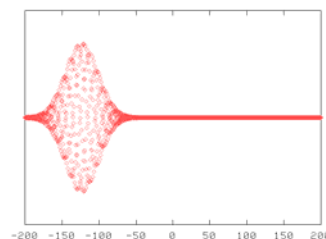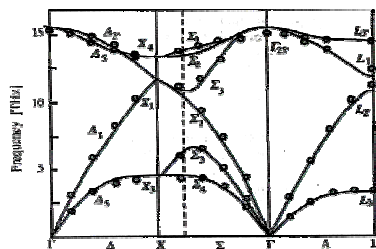What do we need?   3D case consideration
Phonons. Density of states

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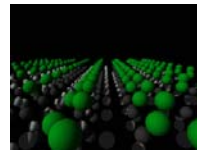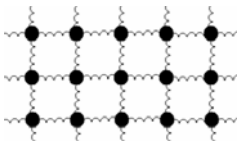
Vibrations in three-dimensional lattice.

Phonons

Phonon Density of states

Specific heat

(Ch. 3.3-3.9)

Three-dimensional lattice

In simplest 1D case with only nearest-neighbor interactions we had

equation of motion

$$M\frac{\partial^2 u}{\partial t^2} = F_n = C(u_{n+1} - u_n) + C(u_{n-1} - u_n)$$

solution

$$u(x,t) = Ae^{i(qx_n - \omega t)}$$

In general 3D case the equations of motion are:

$$M_\alpha \frac{\partial^2 \mathbf{u}_{\mathbf{n}\alpha}}{\partial t^2} = \sum_{\mathbf{m},\beta} F_{\mathbf{n}\alpha}^{\mathbf{m}\beta}$$
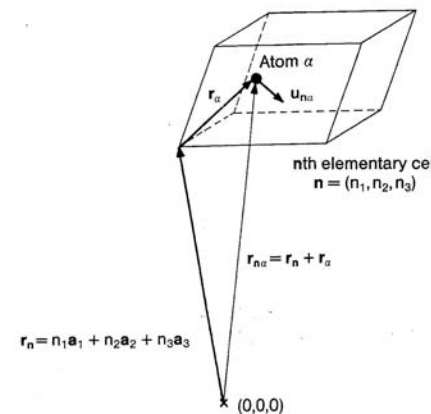
N unit cells, s atoms in each $\rightarrow$ $3N's$ equations

Fortunately, have 3D periodicity $\Rightarrow$
Forces depend only on difference $\mathbf{m-n}$

Write displacements as

$$u_{n\alpha i}(x,t) = \frac{1}{\sqrt{M_\alpha}} u_{\alpha i}(\mathbf{q})e^{i(\mathbf{q}\cdot\mathbf{r}_n - \omega t)}$$

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substitute into equation of motion, get

$$-\omega^2 u_{\alpha i}(\mathbf{q}) - \sum_{\beta,j}\underbrace{\sum_{\mathbf{m}}\frac{1}{\sqrt{M_\alpha M_\beta}}F_{\mathbf{n}\alpha i}^{\mathbf{m}\beta j}e^{i\mathbf{q}\cdot(\mathbf{r_m}-\mathbf{r_n})}}_{D_{\alpha i}^{\beta j}(\mathbf{q})\text{ - dynamical matrix}}u_{\beta j}(\mathbf{q}) = 0$$

$$-\omega^2 u_{\alpha i}(\mathbf{q}) + \sum_{\beta,j}D_{\alpha i}^{\beta j}(\mathbf{q})u_{\beta j}(\mathbf{q}) = 0$$

$$\Rightarrow \ \mathbf{Det}\left\{D_{\alpha i}^{\beta j}(\mathbf{q}) - \omega^2\mathbf{1}\right\} = 0$$
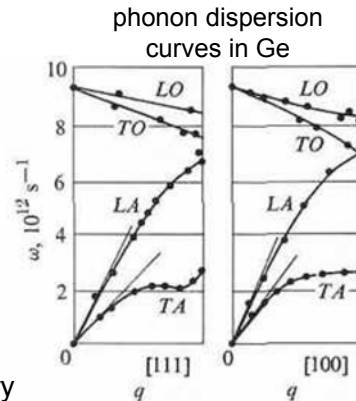
- dispersion relation

3s solutions – dispersion branches

3 acoustic, 3*s* - 3 optical

direction of *u* determines *polarization*
(longitudinal, transverse or mixed)

Can be degenerate because of symmetry

phonon dispersion curves in Ge

- Quantum mechanics: energy levels of the harmonic oscillator are quantized
- Similarly the energy levels of lattice vibrations are quantized.
- The quantum of vibration is called a *phonon*
  (in analogy with the photon - the quantum of the electromagnetic wave)

Allowed energy levels of the harmonic oscillator: $E = (n + \tfrac{1}{2})\hbar\omega$

  where *n* is the quantum number

A normal vibration mode of frequency ω is given by $\mathbf{u} = \mathbf{A}e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)}$

mode is occupied by *n phonons* of energy $\hbar\omega$; momentum $\mathbf{p} = \hbar\mathbf{q}$

Number of phonons is given by :
      (*T* – temperature) $n(\omega, T) = \dfrac{1}{e^{\hbar\omega/kT} - 1}$

The total vibrational energy of the crystal is the sum of the energies of the individual phonons:
  (*p* denotes particular phonon branch)

$$E = \sum_{\mathbf{q}p}E_{\mathbf{q}p} = \sum_{\mathbf{q}p}(n_{\mathbf{q}p} + \tfrac{1}{2})\hbar\omega_p(\mathbf{q})$$

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Phonon Momentum

- You might think that these phonons have momentum which is p = ħK, just like photons have momentum p = E/c.
- Be careful! Phonons don't carry momentum like photons due. They can interact with particles like they have a momentum (for example, a neutron can hit a crystal, and start a wave by transferring momentum to the lattice).
- However, you have to think of this momentum as being transferred to the <u>whole lattice</u>. The atoms themselves are not being translated permanently from their equilibrium positions.
- The only exception to this rule is the K = 0 mode, where the whole lattice translates. This, of course, carries momentum.

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Phonon Momentum

- For all practical purposes, a phonon acts as if it carries a momentum p = ħK, which is sometimes called the crystal momentum.
- We have already seen examples of where this is used. For example, if an x-ray interacts with a lattice, then we know that the scattered ray($\vec{k'}$) and incident ray ($\vec{k}$) have to be related by:

$$\vec{k'} = \vec{k} + \vec{G}$$

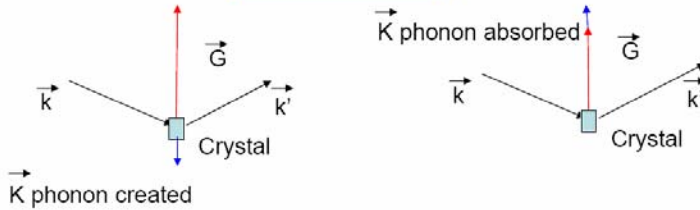- Where $\vec{G}$ is a reciprocal lattice vector. In this process, the whole crystal recoils with momentum -ħG

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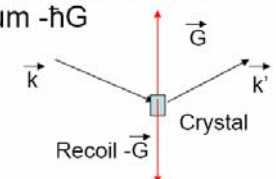
Phonon Momentum

- If this photon interacts inelastically with the lattice, then we have:

$$\vec{k'} + \vec{K} = \vec{k} + \vec{G}$$ (phonon is created)

- Or:

$$\vec{k'} = \vec{k} + \vec{K} + \vec{G}$$ (phonon is absorbed)

Density of states

Consider 1D longitudinal waves. Atomic displacements are given by:

$$u = Ae^{iqx}$$

Boundary conditions: external constraints applied to the ends

Periodic boundary condition: $u(x = 0) = u(x = L)$

Then $e^{iqL} = 1$ $\Rightarrow$ condition on the admissible values of q:

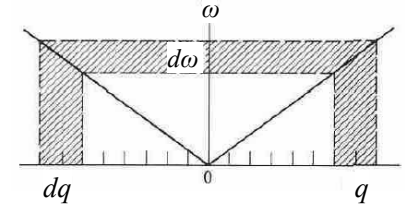$$q = \frac{2\pi}{L}n \quad \text{where} \quad n = 0, \pm 1, \pm 2, ...$$

regularly spaced points, spacing $2\pi/L$

Number of modes in the interval dq in q-space : $\dfrac{L}{2\pi}dq$

Number of modes in the frequency range $(\omega, \omega + d\omega)$: $D(\omega)d\omega = \dfrac{L}{2\pi}dq$

$D(\omega)$ - *density of states* determined by dispersion $\omega = \omega(q)$

$$D(\omega) = \frac{L}{\pi}\frac{1}{d\omega/dq}$$

Density of states in 3D case

Now have $\mathbf{u} = \mathbf{A}e^{i(q_x x + q_y y + q_z z)}$

Periodic boundary condition: $e^{iq_x L} = e^{iq_y L} = e^{iq_z L} = 1$

$\Rightarrow$ $(q_x, q_y, q_z) = \left(l\dfrac{2\pi}{L}, m\dfrac{2\pi}{L}, n\dfrac{2\pi}{L}\right)$ l, m, n - integers
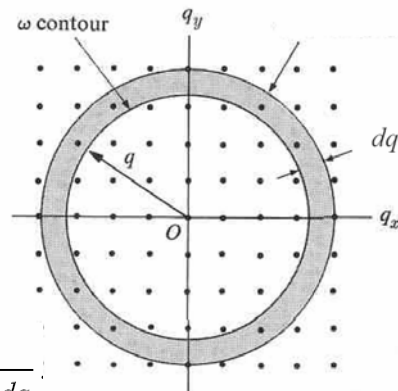
Plot these values in a q-space, obtain a 3D cubic mesh

number of modes in the spherical shell between the radii q and $q + dq$:

$$\left(\frac{L}{2\pi}\right)^3 4\pi q^2 dq = \frac{V}{(2\pi)^3} 4\pi q^2 dq$$

$V = L^3$ – volume of the sample

$\Rightarrow$ *Density of states* $D(\omega) = \dfrac{Vq^2}{2\pi^2}\dfrac{1}{d\omega/dq}$

Few notes:

- Equation we obtained is valid only for an *isotropic solid*, (vibrational frequency does not depend on the direction of **q**)

- We have associated a single mode with each value of **q**. This is not quite true for the 3D case: for each **q** there are 3 different modes, one longitudinal and two transverse.

- In the case of lattice with basis the number of modes is 3*s*, where *s* is the number of non-equivalent atoms. They have different dispersion relations. This should be taken into account by index *p* =1…3*s* in the density of states.

Lattice specific heat (heat capacity)

Defined as (per mole) $C = \dfrac{dQ}{dT}$ If constant volume V $C_V = \left(\dfrac{\partial E}{\partial T}\right)_V$

The total energy of the phonons at temperature T in a crystal:

$$E = \sum_{\mathbf{q},p} \left\langle n_{\mathbf{q}p}\right\rangle \hbar\omega_p(\mathbf{q}) = 0$$ (the zero-point energy is chosen as the origin of the energy).

$$\langle n \rangle = \frac{1}{e^{\hbar\omega/kT} - 1}$$ - Planck distribution   Then $E = \sum_{\mathbf{q}p} \dfrac{\hbar\omega_p(\mathbf{q})}{e^{\hbar\omega_p(\mathbf{q})/k_BT} - 1}$

replace the summation over q by an integral over frequency:

$$E = \sum_p \int d\omega\, D_p(\omega) \frac{\hbar\omega}{e^{\hbar\omega/k_BT} - 1}$$

Then the lattice heat capacity is:

$$C_V = \frac{\partial E}{\partial T} = k_B \sum_p \int d\omega\, D_p(\omega) \frac{\left(\dfrac{\hbar\omega}{k_BT}\right)^2 e^{\hbar\omega/k_BT}}{(e^{\hbar\omega/k_BT} - 1)^2}$$

Central problem is to find the density of states

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Debye model

• assumes that the acoustic modes give the dominant contribution to the heat capacity

• Within the Debye approximation the velocity of sound is taken a constant independent of polarization (as in a classical elastic continuum)

The dispersion relation: $\omega = vq,$ v is the velocity of sound.

In this approximation the density of states is given by:

$$D(\omega) = \frac{Vq^2}{2\pi^2} \frac{1}{d\omega/dq} = \frac{Vq^2}{2\pi^2} \frac{1}{v} = \frac{V\omega^2}{2\pi^2 v^3}$$

Need to know the limits of integration over ω. The lower limit is 0.

How about the upper limit ? Assume N unit cells is the crystal, only one atom in per cell $\Rightarrow$ the total number of phonon modes is $3N \Rightarrow$

$$\sum_p \int_0^{\omega_D} D(\omega)d\omega = 3N \Rightarrow \omega_D = \left(\frac{6\pi^2 v^3 N}{V}\right)^{1/3} = v\left(6\pi^2 n\right)^{1/3}$$ *Debye frequency*

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The cutoff wave vector which corresponds to this frequency is

$$q_D = \frac{\omega_D}{v} = \left(\frac{6\pi^2 N}{V}\right)^{1/3}$$ modes of wave vector larger than q_D are not allowed - number of modes with $q \le q_D$ exhausts the number of degrees of freedom

Then the thermal energy is $E = 3\int_0^{\omega_D} d\omega \dfrac{V\omega^2}{2\pi^2 v^3} \dfrac{\hbar\omega}{e^{\hbar\omega/k_BT} - 1}$

where is "3" from ?

$$\rightarrow \quad E = \frac{3V\hbar}{2\pi^2 v^3} \int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\hbar\omega/k_BT} - 1} = \frac{3Vk_B^4 T^4}{2\pi^2 v^3 \hbar^3} \int_0^{x_D} dx \frac{x^3}{e^x - 1}$$

where $x \equiv \hbar\omega/k_BT$ and $x_D \equiv \hbar\omega_D/k_BT \equiv \theta_D/T$

Debye temperature:

$$\theta_D = \frac{\hbar v}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{1/3}$$

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The total phonon energy is then $E = 9Nk_BT\left(\dfrac{T}{\theta_D}\right)^3 \int_0^{x_D} dx \dfrac{x^3}{e^x - 1}$

where N is the number of atoms in the crystal and $x_D \equiv \theta_D/T$

To find heat capacity, differentiate

$$E = \frac{3V\hbar}{2\pi^2 v^3} \int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\hbar\omega/k_BT} - 1}$$

So,

$$C_V = \frac{3V\hbar^2}{2\pi^2 v^3 k_B T^2} \int_0^{\omega_D} d\omega \frac{\omega^4 e^{\hbar\omega/k_BT}}{\left(e^{\hbar\omega/k_BT} - 1\right)^2} = 9Nk_B\left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{\left(e^x - 1\right)^2}$$

In the limit $T \gg \theta_D$, $x \ll 1$, $\Rightarrow$ $C_v = 3Nk_B$ - *Dulong-Petit law*

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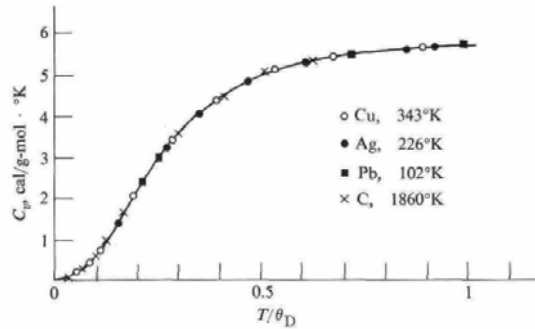Opposite limit, $T << \theta_D$: let the upper limit in the integral $x_D \to \infty$

Get

$$E = 9Nk_B T \left(\frac{T}{\theta_D}\right)^3 \int_0^\infty dx \frac{x^3}{e^x - 1} = 9Nk_B T \left(\frac{T}{\theta_D}\right)^3 \frac{\pi^4}{15} = \frac{3\pi^4}{5} Nk_B T \left(\frac{T}{\theta_D}\right)^3$$

$$\Rightarrow \quad C_V = \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\theta_D}\right)^3$$

within the Debye model at low temperatures $C_v \propto T^3$

The Debye temperature is normally determined by fitting experimental data.

Curve $C_v(T/\theta)$ is *universal* – it is the same for different substances

o Cu, 343°K
● Ag, 226°K
■ Pb, 102°K
× C, 1860°K

Einstein model

The density of states is approximated by a δ-function at some ω_E :

$D(E) = N\delta(\omega - \omega_E)$ where N is the total number of atoms – simple model for optical phonons

Then the thermal energy is $E = \dfrac{3N\hbar\omega_E}{e^{\hbar\omega_E / k_B T} - 1}$

The heat capacity is then

$$C_V = \frac{\partial E}{\partial T} = 3Nk_B \left(\frac{\hbar\omega_E}{k_B T}\right)^2 \frac{e^{\hbar\omega_E / k_B T}}{\left(e^{\hbar\omega_E / k_B T} - 1\right)^2}$$

The high temperature limit is the same as that for the Debye model:

$C_v = 3Nk_B$ - the Dulong-Petit law

At low temperatures $C_v \sim e^{-\hbar\omega/k_B T}$ - different from Debye T^3 law

Reason: at low T acoustic phonons are much more populated $\Rightarrow$ the Debye model is much better approximation that the Einstein model


Real density of vibrational states is much more complicated than those described by the Debye and Einstein models.

This density of states must be taken into account in order to obtain quantitative description of experimental data.

The density of states for Cu.

The dashed line is the Debye approximation.

The Einstein approximation would give a delta peak at some frequency.
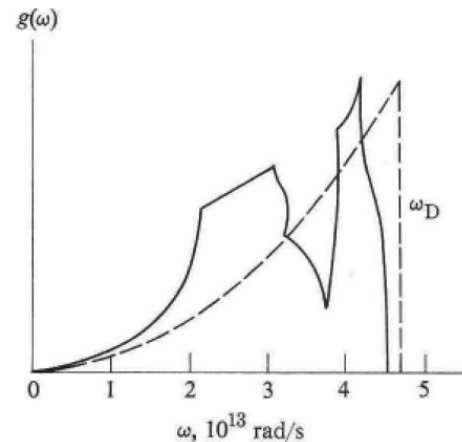
Summary

❖ In three-dimensional lattice with s atoms per unit cell there are 3s phonon branches: 3 acoustic, 3s - 3 optical

❖ **Phonon** - the quantum of lattice vibration. Energy $\hbar\omega$; momentum $\hbar\mathbf{q}$

❖ *Density of states* is important characteristic of lattice vibrations; It is related to the dispersion $\omega = \omega(q)$. Simplest case of isotropic solid, for one branch: $D(\omega) = \dfrac{Vq^2}{2\pi^2}\dfrac{1}{d\omega/dq}$

❖ Heat capacity is related to the density of states.

❖ Debye model – good when acoustic phonon contribution dominates. At low temperatures gives $C_v \propto T^3$

❖ Einstein model - simple model for optical phonons ($\omega(q)$ is constant)

❖ At high T both models lead to the Dulong-Petit law: $C_v = 3Nk_B$

❖ Real density of vibrational states is more complicated

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Thermal Conductivity

Temperature gradient in a material → heat flow from the hotter to the cooler end.
Heat current density j (amount of heat flowing across unit area per unit time) is proportional to the temperature gradient (dT/dx):

$$j_u = -K \frac{dT}{dx} \qquad K \text{ - thermal conductivity}$$

- In metals the heat is carried both by electrons and phonons; electron contribution is much larger

- In insulators, there are no mobile electrons ⇒ heat is transmitted entirely by phonons

Heat transfer by phonons

- *phonon gas*: in every region of space there are phonons traveling randomly in all directions, much like the molecules in an ordinary gas

- phonon concentration is larger at the hotter end →they move to the cooler end

- the advantage of using this gas model: can apply familiar concepts of the kinetic theory of gases

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Elementary kinetic considerations:

if c is the heat capacity of the single particle, then moving from region with $T+\Delta T$ to a T,   particle will give up energy $c\Delta T$

ΔT between the ends of the free path length l_x : $\quad \Delta T = \frac{dT}{dx} l_x = \frac{dT}{dx} v_x \tau$

where τ is the average time between collisions

The net energy flux (n – concentration) :

$$j_u = -n \langle v_x^2 \rangle \frac{dT}{dx} c\tau = -\frac{1}{3} n \langle v^2 \rangle c\tau \frac{dT}{dx}$$

for phonons, v is constant. $nc = C$; $l = v\tau$

$$\Rightarrow \quad j_u = -\frac{1}{3} Cvl \frac{dT}{dx} \quad \Rightarrow \quad K = \frac{1}{3} Cvl \qquad \begin{array}{l} \text{- phonon thermal} \\ \text{conductivity} \end{array}$$

Dependence of the thermal conductivity on temperature

– C_v dependence on temperature has already been discussed

– Sound velocity v essentially insensitive to temperature

– The mean free path l depends strongly on temperature

Three important mechanisms are to be considered:

(a) collision of a phonon with other phonons

(b) collision of a phonon with imperfections in the crystal

(c) collision of a phonon with the external boundaries of the crystal

The phonon-phonon scattering is due to the *anharmonic interaction.*
If interatomic forces are purely harmonic – no phonon-phonon interaction.

At high temperature atomic displacements are large ⇒ stronger anharmonism ⇒ phonon-phonon collisions become more important

At high T the mean free path $l \propto 1/T$: number of phonons $n \propto T$ at high T

collision frequency $\propto n \Rightarrow l \propto 1/n$

Suppose that two phonons of vectors $\mathbf{q}_1$ and $\mathbf{q}_2$ collide, and produce a third phonon of vector $\mathbf{q}_3$.

Momentum conservation: $\mathbf{q}_3 = \mathbf{q}_1 + \mathbf{q}_2$

$\mathbf{q}_3$ may lie inside the Brillouin zone, or not. If it's inside → momentum of the system before and after collision is the same.

This is a *normal process*. It has no effect at all on thermal resistivity, since it has no effect on the flow of the phonon system as a whole.
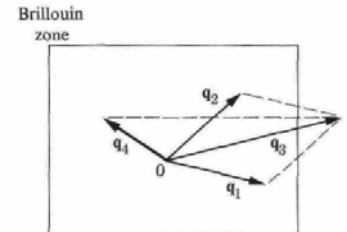
If $\mathbf{q}_3$ lies outside the BZ, we reduce it to equivalent $\mathbf{q}_4$ inside the first BZ: $\mathbf{q}_3 = \mathbf{q}_4 + \mathbf{G}$

Momentum conservation: $\mathbf{q}_1 + \mathbf{q}_2 = \mathbf{q}_4 + \mathbf{G}$

The difference in momentum is transferred to the center of mass of the lattice.

This type of process is is known as the *umklapp process*

- highly efficient in changing the momentum of the phonon

- responsible for phonon scattering at high temperatures

The second mechanism - phonon scattering results from defects. Impurities and defects scatter phonons because they partially destroy the periodicity of the crystal.

At very low T, both phonon-phonon and phonon-defect collisions become ineffective:

– there are only a few phonons present,

– the phonons are long-wavelength ones = not effectively scattered by defects, which are much smaller in size

In the low-temperature region, the primary scattering mechanism is the external boundary of the specimen - so-called *size* or *geometrical effects.*

Becomes effective because the phonon wavelengths are very long - comparable to the size of the sample L.

The mean free path here is $l \sim L$
$\Rightarrow$ independent of temperature.

low T:
$K \sim T^3$
due to C_v

high T:
$K \sim 1/T$
due to l
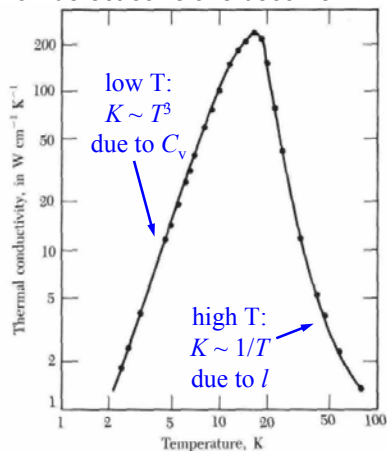
Thermal conductivity of NaF
(highly purified) [29]

Anharmonism

So far, lattice vibrations were considered in harmonic approximation. Some consequences:

– Phonons do not interact; no decay

– No thermal expansion

– Elastic constants are independent of pressure and temperature

– Heat capacity is constant at high T ($T >> \theta_D$).

Anharmonic terms in potential energy:

$$U(x) = cx^2 - gx^3 - fx^4 \qquad x \text{ - displacement from equilibrium separation at T = 0}$$

Thermal expansion

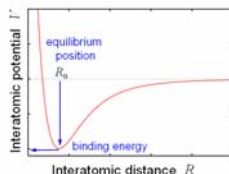Calculate average displacement using Boltzmann distribution function:

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x e^{-U(x)/k_B T} dx}{\int_{-\infty}^{\infty} e^{-U(x)/k_B T} dx}$$

If anharmonic terms are small, can use Taylor expansion for exponent

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} dx e^{-cx^2/k_B T} \left(x + \frac{gx^4}{k_B T} + \frac{fx^5}{k_B T} \right)}{\int_{-\infty}^{\infty} dx e^{-cx_2/k_B T}} = \frac{\frac{3\pi^{1/2}}{4} \frac{g}{c^{5/2}} (k_B T)^{3/2}}{\left(\frac{\pi}{c} \right)^{1/2} (k_B T)^{1/2}} = \boxed{\frac{3g}{4c^2} k_B T}$$
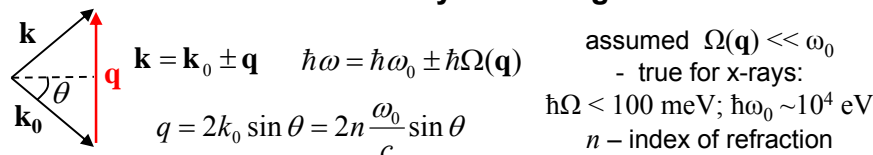
thermal expansion

Origin of thermal expansion – asymmetric potential

Techniques for probing lattice vibrations

• Inelastic X-ray scattering
• Neutron scattering
• Infrared spectroscopy
• Brillouin and Raman scattering

Inelastic X-ray scattering

$\mathbf{k} = \mathbf{k}_0 \pm \mathbf{q}$

$\hbar\omega = \hbar\omega_0 \pm \hbar\Omega(\mathbf{q})$

$q = 2k_0 \sin\theta = 2n\frac{\omega_0}{c}\sin\theta$

assumed $\Omega(\mathbf{q}) << \omega_0$
- true for x-rays:
$\hbar\Omega < 100$ meV; $\hbar\omega_0 \sim 10^4$ eV
n – index of refraction

measuring $\omega - \omega_0$ and θ sin one can determine dispersion $\Omega(\mathbf{q})$

main disadvantage – difficult to measure $\omega - \omega_0$ accurately

This difficulty can be overcome by use of ***neutron scattering***

Energy of "thermal" neutrons is comparable with $\hbar\Omega$ (80 meV for $\lambda \approx 1$Å)

Brillouin and Raman spectroscopy

Inelastic light scattering mediated by the *electronic polarizability* of the medium

- a material or a molecule scatters irradiant light from a source
- Most of the scattered light is at the same wavelength as the laser source (elastic, or *Raileigh scattering*)
- but a small amount of light is scattered at different wavelengths (inelastic, or *Raman scattering*)
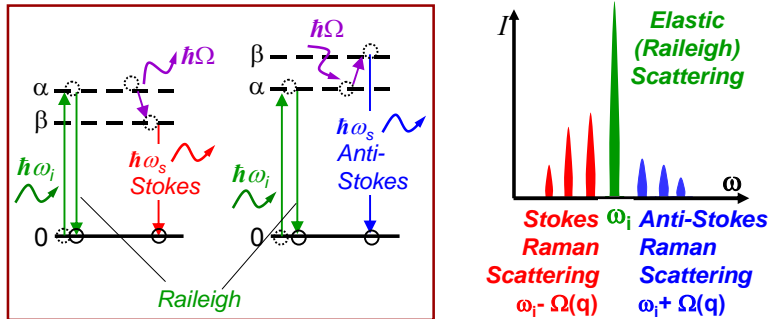
Analysis of scattered light energy, polarization, relative intensity provides information on lattice vibrations or other excitations
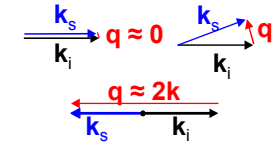
Raman scattering in crystalline solids

Not every crystal lattice vibration can be probed by Raman scattering. There are certain *Selection rules*:

1. Energy conservation:
$$\hbar\omega_i = \hbar\omega_s \pm \hbar\Omega;$$

2. Momentum conservation:
$$\mathbf{k}_i = \mathbf{k}_s \pm \mathbf{q} \implies 0 \le |\mathbf{q}| \le 2|\mathbf{k}| \implies 0 \le |q| \le \frac{4\pi n}{\lambda_i}$$

$$\lambda_i \sim 5000 \text{ Å}, \ a_0 \sim 4\text{-}5 \text{ Å} \implies \lambda_{phonon} \gg a_0$$

$\implies$ *only small wavevector (cloze to BZ center) phonons are seen in the 1st order (single phonon) Raman spectra of bulk crystals*

3. Selection rules determined by crystal symmetry

Summary

❖ Phonon thermal conductivity $\qquad K = \frac{1}{3}Cvl$

❖ Mechanisms of phonon scattering affecting thermal resistivity:
- umklapp processes of phonon-phonons collision – important at high T
- collision of a phonon with defects and impurities in the crystal
- collision of a phonon with the external boundaries of the crystal – important at low T

❖ Anharmonism of potential energy is responsible for such effects as:
- phonon-phonon interaction
- thermal expansion

❖ Techniques for probing lattice vibrations:

Inelastic X-ray scattering, Neutron scattering, Infrared spectroscopy, Brillouin and Raman scattering Electron energy loss spectroscopy

SOME USEFUL SLIDES
FROM Physics-I

Avogadro's number and Ideal Gases

Tactic 1: *Avogadro's Number of What?*

In Eq. 20-1 , Avogadro's number is expressed in terms of mol^{-1}, which is the inverse mole, or 1/mol. We could instead explicitly state the elementary unit involved in a given situation. For example, we might write $N_A = 6.02 \times 10^{23}$ atoms/mole if the elementary unit is an atom. If, instead, the elementary unit is a molecule, then we might write $N_A = 6.02 \times 10^{23}$ molecules/mole.
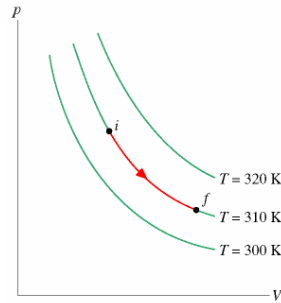
Ideal Gases $\quad pV = nRT \quad$ (ideal gas law) $\quad R = 8.31$ J/mol·K.

$$k = \frac{R}{N_A} = \frac{8.31 \text{ J/mol·K}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 1.38 \times 10^{-23} \text{ J/K}.$$

Ideal Gas at Constant Temperature

$$p = nRT\frac{1}{V} = (\text{a constant})\frac{1}{V}.$$

R is a gas constant"

(graph: p vs V with curves $T = 320$ K, $T = 310$ K, $T = 300$ K)

The Kinetic Theory of Gases; Mole

➤One mole is the number of atoms in a 12 g sample of carbon-12.

Avogadro's Number

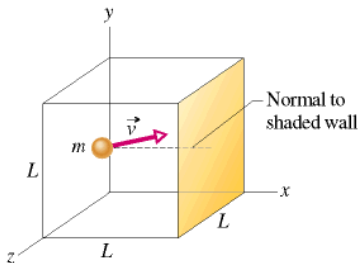$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1} \quad \text{(Avogadro's number)},$$

$$n = \frac{N}{N_A}. \qquad\qquad n = \frac{M_{sam}}{M} = \frac{M_{sam}}{mN_A}.$$

M is molar mass;   m is molecular mass

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Pressure, Temperature, and Speed of molecules

$$v_{rms} = \sqrt{\frac{3RT}{M}}.$$

mN_A is the molar mass *M*
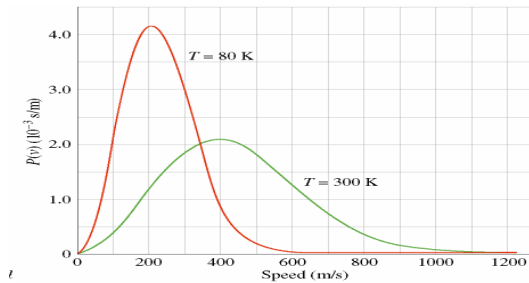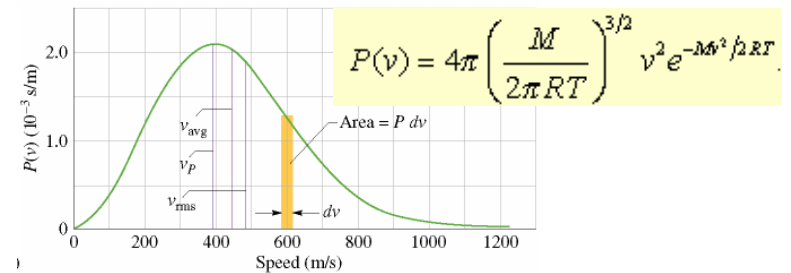
Root-mean-square speed

$$K_{avg} = \frac{3}{2}kT.$$

Some Molecular Speeds at Room Temperature ($T = 300$ K)

Gas	Molar Mass (10^{-3} kg/mol)	v_{rms} (m/s)
Hydrogen (H_2)	2.02	1920
Helium (He)	4.0	1370
Water vapor (H_2O)	18.0	645
Nitrogen (N_2)	28.0	517
Oxygen (O_2)	32.0	483
Carbon dioxide (CO_2)	44.0	412
Sulfur dioxide (SO_2)	64.1	342

For convenience, we often set room temperature = 300 K even though (at 27°C or 81°F) that represents a fairly warm room.

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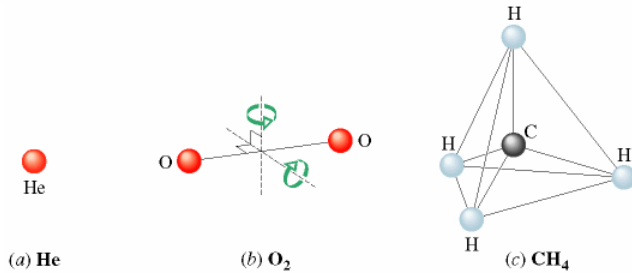---

The Distribution of Molecular Speeds

$$P(v) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

(graphs: $P(v)$ vs Speed (m/s); with v_{avg}, v_P, v_{rms}, Area = $P\,dv$; and curves for $T = 80$ K and $T = 300$ K)

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View at the molecular theory of an ideal Gas

$$C_V = \tfrac{3}{2} R$$

$$C_p = C_V + R.$$

(a) He (b) O_2 (c) CH_4

Degrees of Freedom for Various Molecules

| Molecule | Example | Degrees of Freedom | | | Predicted Molar Specific Heats | |
		Translational	Rotational	Total (f)	C_V (Eq. 20-51)	$C_p = C_V + R$
Monatomic	He	3	0	3	$\tfrac{3}{2}R$	$\tfrac{5}{2}R$
Diatomic	O_2	3	2	5	$\tfrac{5}{2}R$	$\tfrac{7}{2}R$
Polyatomic	CH_4	3	3	6	$3R$	$4R$

Heat Capacity

$$Q = C\,\Delta T = C(T_f - T_i)$$

Specific Heat

$$Q = cm\,\Delta T = cm(T_f - T_i)$$

Specific Heats of Some Substances at Room Temperature

Substance	Specific Heat cal/g·K	Specific Heat J/kg·K	Molar Specific Heat J/mol·K
Elemental Solids			
Lead	0.0305	128	26.5
Tungsten	0.0321	134	24.8
Silver	0.0564	236	25.5
Copper	0.0923	386	24.5
Aluminum	0.215	900	24.4
Other Solids			
Brass	0.092	380	
Granite	0.19	790	
Glass	0.20	840	
Ice (-10°C)	0.530	2220	
Liquids			
Mercury	0.033	140	
Ethyl alcohol	0.58	2430	
Seawater	0.93	3900	
Water	1.00	4190	

Heat Transfer Mechanisms

- **Convection**
- **Radiation**
- **Conduction**

Some Thermal Conductivities [a]

Substance	k (W/m·K)
Metals	
Stainless steel	14
Lead	35
Aluminum	235
Copper	401
Silver	428
Gases	
Air (dry)	0.026
Helium	0.15
Hydrogen	0.18
Building Materials	
Polyurethane form	0.024
Rock wool	0.043
Fiberglass	0.048
White pine	0.11
Window glass	1.0

[a]Conductivities change somewhat with temperature. The given values are at room temperature.
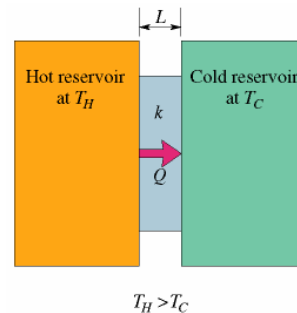
Q=kA(ΔT/L)t,
Where k is
the thermal conductivity