Lecture 11 - Phonons II - Thermal Prop. Continued

Phonons II - Thermal Properties - Continued (Kittel Ch. 5)

Low T

High T

hot

Heat Flow

cold

Outline

- **Anharmonicity**
  - **Crucial for Thermal expansion and other changes with pressure and temperature**
  - **Gruneisen Constant**

- **Thermal Heat Transport Phonon Heat Conductivity**

  Low T and High T behaviors

- **(Read Kittel Ch 5)**

Consequences of Anharmonicity

- If we expand the energy beyond the harmonic order:
  $E = E_0 + (1/2) \Sigma_{ij} \Delta \underline{R}_i \cdot \underline{D}_{ij} \cdot \Delta \underline{R}_j +$
  $(1/6) \Sigma_{ijk} \underline{D}_{ijk} \cdot \Delta \underline{R}_i \ \Delta \underline{R}_j \ \Delta \underline{R}_k + \ldots$ ⟵ **Difficult and Messy**

- The problem is fundamentally changed:
  No longer exactly soluble

- Consequences:
  There is thermal expansion and other changes with temperature
  The heat capacity is not constant at high T
  Phonons decay in time
  Two phonons can interact to create a third
  Phonons can establish thermal equilibrium and conduct heat like a "gas" of particles

Thermal expansion - I

Energies of Crystal

The general shape applies for any type of binding

Increases more rapidly at short distances

Thermal Expansion - Average distance increases as vibration amplitude increases

Absolute Minimum

Distance Between Atoms

Thermal expansion - II

- There is no thermal expansion In the harmonic approximation!

Why?
In the harmonic approximation the magnitude of the force is symmetric around the minimum (F = -Cx). Therefore, the vibrations are symmetric $\Rightarrow$ the average position <x> is always the center, i.e.,
<x> = 0
and
there is no thermal expansion

Harmonic Approximation
$E = \frac{1}{2} C x^2$

Energies of Crystal

Minimum

Distance Between Atoms

Thermal expansion - III

- Anharmonicity causes thermal expansion.

Why?
If the potential energy curve is not symmetric, the vibrations are not symmetric $\Rightarrow$ the average position <x> changes as the magnitude of the vibration increases, i.e.,
<x> increases
and
there is thermal expansion

Anharmonic potential energy
$E = \frac{1}{2} C x^2 + (1/6) A x^3$

Energies of Crystal

Minimum

Distance Between Atoms

1

Lecture 11 - Phonons II - Thermal Prop. Continued

Gruneisen Constant γ

- Anharmonicity is very complicated because there are all the possible terms involving 3 atoms!
- A simple characterization requires finding a typical measurable quantity.
- This is given by the dimensionless Gruneisen constant γ defined as an average value of the change of vibration frequency per unit dilation:
  $$\Delta\omega/\omega = \gamma\,(\Delta V/V) = 3\gamma\,(\Delta R/R)$$
  where L is a characteristic near-neighbor distance .
- Thus $\gamma = (1/3)(\Delta\omega/\omega)/(\Delta R/R)$
- On the next slide we consider a simple case that shows the relation to anharmonicity

Physics 460 F 2006 Lect 11   7

Gruneisen Constant γ

- From previous slide: The Gruneisen constant γ defined as an average value of the change of vibration frequency per unit dilation:
  $$\Delta\omega/\omega = \gamma\,(\Delta V/V) = 3\gamma\,(\Delta R/R)$$
  where L is a characteristic near-neighbor distance .
- An example is a nearest neighbor interaction with
  $$E = \tfrac{1}{2} C\,\Delta R^2 + (1/6)\,A\,\Delta R^3$$
- Then the force is given by
  $$F = -dE/dR = -C(\Delta R) - \tfrac{1}{2} A\,(\Delta R)^2 + \ldots$$
  $$= -C\,[1 + \tfrac{1}{2} A\Delta R/C]\,\Delta R$$
  Since $\omega^2 \sim C/M \Rightarrow \Delta\omega/\omega = \tfrac{1}{2}\Delta C/C = \tfrac{1}{2} A\,\Delta R / C$
- Thus $\gamma = (1/3)(\Delta\omega/\omega)/(\Delta R/R) = (1/6)\,(A/C)\,\Delta R$
  is a measure of anharmonicity

Physics 460 F 2006 Lect 11   8

Other effects of Anharmonicity

- Anharmonicity
  - Crucial for Thermal expansion and other changes with pressure and temperature
  - Gruneisen Constant

- **Thermal Heat Transport**
  Phonon Heat Conductivity

  Low T and High T behaviors

- **(Read Kittel Ch 5)**

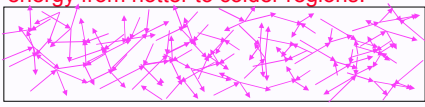Physics 460 F 2006 Lect 11   9

Thermal Energy (Heat) Transport

- **First consider heat transport in an ordinary gas**
- **Molecules in the gas have average energy**

  $$\tfrac{1}{2} m\,v^2 = 3[\tfrac{1}{2} k_B T]$$

  and move with average speed v   ← **Factor of 3 in 3 dimensions**

- **Two limiting cases**
  - Ordinary case where molecules scatter from one another very often as they move
    The molecules diffuse and thermalize with one another
    This is the usual case for gases like the air in this room
  - Cases where the molecules hit the walls of the container without hitting one another – the molecules transport energy directly from one wall to another

Physics 460 F 2006 Lect 11   10

Transport of heat in an ordinary gas

- Molecules move in all directions and scatter so that they come to local thermal equilibrium in each region.
- How can random motion of molecules cause heat flow in one direction?
- On average, in hotter regions molecules have more kinetic energy. A molecule that moves from a hotter region to a colder region brings energy above the local average. The opposite for a molecule moving from a colder to a hotter region. Either way, there is transport of energy from hotter to colder regions.

hot   **cold**

Heat Flow   Physics 460 F 2006 Lect 11   11

Heat Transport due Molecular Motion

- Definition:
  j = heat flow (energy per unit area per unit time)
    = $- K\,dT/dx$
- If a particle moves from a region with local temperature T to one with local temperature T - ΔT, it supplies excess energy c ΔT, where c = heat capacity per particle.   (Note ΔT can be positive or negative).
- On the average for a particle with average thermal speed v in the x direction:
  $\Delta T = (dT/dx)\,v_x\,\tau$, where τ = mean time between collisions
- Then $j = - n\,v_x\,c\,v_x\,\tau\,dT/dx = - n\,c\,v_x^2\,\tau\,dT/dx$

Density   **Flux**

Physics 460 F 2006 Lect 11   12

Lecture 11 - Phonons II - Thermal Prop. Continued

Heat Transport due Molecules - II

- This can be simplified in an isotropic case, since averaging over directions gives $(v_x^2)_{average} = (1/3) v^2$
- This leads to $j = -(1/3) n c v_x^2 \tau \, dT/dx$

- Finally we can define the mean free path:
    $L = v \tau$
    and
    $C = nc =$ total heat capacity per unit volume

- Then $j = -K \, dT/dx = -(1/3) C v L \, dT/dx$
    and
    $K = (1/3) C v L =$ thermal conductivity

    This is a general result for thermal conductivity due to thermal motion of particles - Eq. 42 in Kittel

Heat Transport due Molecules - III

- For molecules in a gas we can use classical expressions for C and v, and we can understand some facts about L
- Heat capacity: $C = 3Nk_B$
- Average speed: v determined by $\frac{1}{2} Mv^2 = (3/2) k_B T$
- Mean free path L is distance between collisions – increases with density – temperature independent
- Then
    $K = (1/3) C v L = Nk_B (3k_B T/M)^{1/2} L$
- Increases with T for fixed density because v increases

Heat Transport due Molecules - IV

- What happens if the mean free path is long compared to the size of the container
    $L \sim$ dimension of container

    and the thermal conductivity is given by
    $K = (1/3) C v L$
- And the basic idea are still the same

What causes heat transport in a solid?

- **Motion of the atoms is thermal energy**
- **But the atoms vibrate around their sites and do not move through the solid**

- **How does energy moves from hot to cold?**

- **The amplitude of the vibrational motion is transferred through the solid – hotter atoms transfer energy to colder atoms**
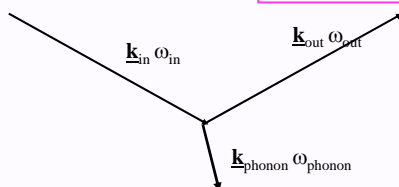
- **How do we describe this?**

From Before
Inelastic Scattering and Fourier Analysis

- Scattering of neutrons, x-rays, ….
- Inelastic diffraction occurs for
    $\underline{k}_{in} - \underline{k}_{out} = \underline{G} \pm \underline{k}_{phonon}$
    $\omega_{in} - \omega_{out} = \pm \omega_{phonon}$ or $E_n - E_{out} = \pm \hbar\omega_{phonon}$
    Quantum Mechanics

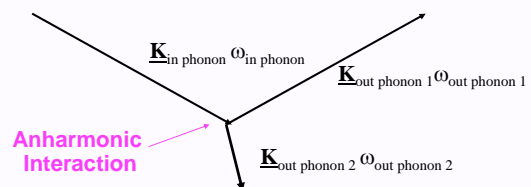$\underline{k}_{in} \, \omega_{in}$ $\underline{k}_{out} \, \omega_{out}$

$\underline{k}_{phonon} \, \omega_{phonon}$

Scattering of Phonons - I

- The same idea applies to phonons. One phonon can scatter to create two.
- We can say one phonon is destroyed and two are created. This can occur if
    $\underline{k}_{in \, phonon} = \underline{k}_{out \, phonon \, 1} + \underline{k}_{out \, phonon \, 2} \pm \underline{G}$
    $\omega_{in \, phonon} = \omega_{out \, phonon \, 1} + \omega_{out \, phonon \, 2}$

$\underline{K}_{in \, phonon} \, \omega_{in \, phonon}$

$\underline{K}_{out \, phonon \, 1} \omega_{out \, phonon \, 1}$

Anharmonic Interaction

$\underline{K}_{out \, phonon \, 2} \, \omega_{out \, phonon \, 2}$

3

Lecture 11 - Phonons II - Thermal Prop. Continued

Scattering of Phonons - II

- Also a phonon can absorb (destroy) another phonon and create a different phonon.
- Thus two phonons are destroyed and one is created which can occur if

$$\underline{k}_{out\ phonon} = \underline{k}_{in\ phonon\ 1} + \underline{k}_{in\ phonon\ 2} \pm \underline{G}$$
$$\omega_{out\ phonon} = \omega_{in\ phonon\ 1} + \omega_{in\ phonon\ 2}$$

$\underline{K}_{in\ phonon\ 1}\ \omega_{in\ phonon\ 2}$

$\underline{K}_{out\ phonon}\ \omega_{out\ phonon}$

Anharmonic Interaction

This is proportional to the average occupation of phonons in state 2 – the probability vanishes if there are no phonons to destroy!

$\underline{K}_{in\ phonon\ 2}\ \omega_{in\ phonon\ 2}$

Physics 460 F 2006 Lect 11   19

Phonons also act like a gas

- A phonon is a particle - a quantum of vibration
- It carries energy just like a molecule.
- Phonon can come to equilibrium by scattering just like molecules
- Scattering is due to defects and anharmonicity.
- Leads to heat transport just as for molecules

$$K = (1/3)\ C\ v\ L = \text{thermal conductivity}$$

hot   cold

Heat Flow   Physics 460 F 2006 Lect 11   20

Phonons also act like a gas

- What is different about phonons and gas molecules?
- Speed = v_{group} is largest for low energy (v_{sound}) and smaller for high energy
- The heat capacity ~ T^3 at low T, ~ $3Nk_B$ at high T
- The density of phonons <n> increases with T. Scattering increases ~ <n> since each phonon has scatters from other phonons. Therefore we expect the mean free path to decrease with T

hot   cold

Heat Flow   Physics 460 F 2006 Lect 11   21

Phonon Heat Transport

- The same logic applies for phonons as for molecules
  j = heat flow (energy per unit area per unit time)
  = - K dT/dx
- If a phonon moves from a region with local temperature T to one with local temperature T - ΔT, it supplies excess energy c ΔT, where c = heat capacity per phonon.
- Then j = - (1/3) C v L dT/dx
  and
  $$K = (1/3)\ C\ v\ L\ = \text{thermal conductivity}$$

  where L = mean free path,
  C = nc = total heat capacity (a function of temperature)

Physics 460 F 2006 Lect 11   22

Phonon Heat Transport - continued

- What determines mean free path L = v τ ?
- At low temperature, the thermal phonons are sound waves that have long mean free paths -
  L ~ sample size
- At high temperature, phonons scatter from other phonons. The density of other phonons is ~ T, so
  L ~ 1/T
- At intermediate temperature, phonon scatter from defects and other phonons. The latter decreases very rapidly as T decreases because ONLY Umklapp scattering limits the energy flow.

Physics 460 F 2006 Lect 11   23

Phonon Heat Transport - continued

- Behavior in an excellent quality crystal:

Maximum controlled by defects

K decreases as Umklapp scattering increases rapidly

Thermal conductivity K 100

High T
$K = CvL/3 \sim 1/T$
since L~1/T
(C and v are ~ constant)

10

Low T
$K = CvL/3 \sim T^3$
since C ~ T^3
(v and L are ~ constant)

1

1   10   T

Physics 460 F 2006 Lect 11   24

4

Lecture 11 - Phonons II - Thermal Prop. Continued

Phonon Heat Transport - continued

- Low T – K ~ T^3 - increases because density of phonons increases with roughly constant v and L
- High T – K ~ 1/T - decreases as scattering increases

Low T

High T

hot ←— **Heat Flow** —→ **cold**

Umklapp Scattering

- What is Umklapp scattering? Scattering that changes total crystal momentum by a reciprocal lattice vector.
- Recall: scattering can occur for

$$\underline{k}_{\text{in phonon}} = \underline{k}_{\text{out phonon 1}} + \underline{k}_{\text{out phonon 2}} \pm \underline{G}$$
$$\omega_{\text{in phonon}} = \omega_{\text{out phonon 1}} + \omega_{\text{out phonon 2}}$$

$\underline{K}_{\text{in phonon}} \, \omega_{\text{in phonon}}$

$\underline{K}_{\text{out phonon 1}} \omega_{\text{out phonon 1}}$

Anharmonic Interaction

$\underline{K}_{\text{out phonon 2}} \, \omega_{\text{out phonon 2}}$

Unless G ≠ 0, the scattering does not change the total phonon momentum or energy. Therefore only Umklapp scattering limits the heat flow.

Other effects

- Maximum value of K affected by all scattering mechanisms

- Impurities scatter phonons

- Isotope effects
    Isotopes do not affect chemical properties, but they do change phonon frequencies and cause scattering of phonons - limits the maximum value of K in high quality crystals

Recent developments

- How did the collapse of the Soviet Union affect thermal conductivity?

Recent developments

- Availability of pure isotopes from Soviet nuclear program has made possible growth of large crystals of pure isotope materials
- New record for heat conductivity for all crystals - isotopically pure diamond - better than any metal at room temperature

- Stimulated new research to create better diamond heat sinks for lasers, etc.

Thermal conductivity K

Record Value

T

Recent developments

- Are there special aspects of thermal conductivity in nanosystems?

An electron can "fall" into the well only if it can give up energy to phonons – the rate is reduced because the phonons have only quantized energies
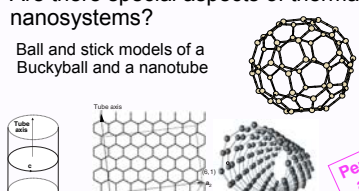
e⁻

More later

Ball and stick model of a 1-atom wide gold "wire" actually made and seen in an electron microscope

An electrical current leads to very high current densities, heating, …

"Quantum well" for electrons in a semiconductor – used to contain electrons for lasers, electronic devices, ….

Lecture 11 - Phonons II - Thermal Prop. Continued

Recent developments

- Are there special aspects of thermal conductivity in nanosystems?

Ball and stick models of a Buckyball and a nanotube

Buckyball with 60 carbon atoms now made in quantity

Perhaps later we can say a little about electrons in nanotubes

A nanotube is a sheet of graphite rolled up into a long thin tube

Work now to use nanotubes as wires in semiconductor circuits

An electrical current in the nanotube leads to very high current densities, heating, … phonons scatter very little in the tube – good for removing heat --- but the mismatch with other materials makes it hard for the heat to excape – "burn" in the middle

Summary

- Anharmonicty crucial for certain effects
  Thermal expansion, ….
  Phonon scattering
- Gruneisen Constant γ
- Heat transport due to thermal motion of particles
  $j = - K\, dT/dx$, $K = (1/3)\, C\, v\, L$
  K = thermal conductivity
  C = heat capacity
  v = mean velocity
  L = mean free path

  The same ideas are used later for both thermal and electrical conductivity of electrons!

- Gas of molecules – $K \sim = Nk_B\,(3k_BT/M)^{1/2}\,L$
- Phonons act like particles in a gas
  (We treat heat transport due to electrons later)
- Low T $K \sim T^3$ ($C \sim T^3$ and v, L ~ constant)
- $K \sim 1/T$ ($C \sim 3Nk_B$, v ~ constant and L ~ 1/T)

Next time

- **Start next Part of Course:**
  Electronic Properties of Solids

- **Free electron Fermi Gas**

- **Energy levels in one dimension and three dimensions**

- **Heat Capacity**

- **(Read Kittel Ch 6)**

- **Remember: EXAM MONDAY, OCTOBER 9**

Summary of Part I

- This is an incomplete list of concepts, topics, equations, examples!

Summary of Part I --- 1

- Solids are defined by their "solidity" - i.e., to ability to resist shear stress and keep a shape
- A crystal is truly solid (as opposed to a glass which is like a "slow"liquid")
  A crystal has a true long range crystalline order
- Crystalline order is defined by the regular positions of the nuclei
  Crystal Structure = Lattice + Basis
- Bravais lattice of points in real space
  Examples:
  line, square, simple cubic, hexagonal, fcc, hcp, bcc
- Primitive Cell
  Parallelpiped in 3d
  Wigner-Seitz cell
- Examples of crystals:
  line, square, simple cubic
  fcc, hcp, bcc, NaCl, ZnS, diamond, graphene

Summary of Part I --- 2

- Diffraction and experimental studies of crystal structures
  Examples: X-ray, neutron diffraction
  Appropriate wavelength ($k = 2\pi/\lambda$)

- Bravais lattice on points in real space and Reciprocal Lattice
  Reciprocal lattice
  Brillouin Zone – diffraction occurs only on boundary of BZ

- Diffraction and experimental studies of crystals
  Bragg Law - easier to describe in terms of reciprocal lattice
  Elastic scattering : $k_{in} = k_{out} + G$
  Examples:
  line, square, simple cubic, hexagonal, fcc, hcp, bcc

- Structure factor – example of diamond
  Here it is the idea that is important not the details

Lecture 11 - Phonons II - Thermal Prop. Continued

Summary of Part I --- 3

- Binding of Crystals
  - 5 basic types
- Simplest examples: pair potentials $\phi(r)$
  - Van der Waals. Attractive and Repulsive terms
  - Coulomb interactions in ionic crystals
- For pair potentials, binding is sum of over pairs
  - Count each interaction as ½ for each atom in the pair
- Binding curve
  - Minimum energy – equilibrium structure
- Bulk modulus
  - Curvature – $B = Vd^2E/dV^2$
- Elastic properties
  - Stress – strain relations - elastic constants C_{ij}
  - (The ideas that are most important – not the details)
  - Example: cubic crystals – C_{11}, C_{12}, C_{44} $B = (C_{11} + 2C_{12})/3$
  - Sound waves - $v_s = (C_{ij}/\rho)^{1/2}$,
  - C_{ij} = appropriate elastic constant, ρ = mass density

Summary of Part I --- 4

- Vibrations of atoms
  - Harmonic approximation
  - Exact solution for waves in a crystal
  - Dispersion curves $\omega_{k,m}$ where $\underline{k}$ is the wavevector
    in Brillouin Zone and $m = 1, \ldots, 3N$
- Counting k states
  - The number of k states = number of cells in crystal N
  - Example in 1 dimension
    - Same ideas in 2 and 3 dimensions
  - Result
    - Each k state corresponds to a volume of reciprocal
      space $= (2\pi)^3/V = V_{BZ}/N$ ($2\pi/L$ in 1 dimension)
    - $(1/N) \Sigma k$ inside BZ $\Rightarrow (1/V_{BZ}) \int_{BZ} dk$
- Quantization of vibrations
  - For each vibration with frequency ω, the quantum is $\hbar\omega$
  - Phonons act like particles
  - Observed in inelastic scattering experiments (neutrons, …)
- Inelastic scattering is a central idea that is used again in transport

Summary of Part I --- 5

- Thermal properties
  - Fundamental law of probabilities – $\exp(-E/k_BT)$
  - Planck distribution for phonons

  $$<n> = \frac{1}{\exp(\hbar\omega/k_BT) - 1}$$

- Debye and Einstein models
  - Debye captures critical features of acoustic modes

- Heat Capacity C
  - Low T: $C \sim T^3$ High T: $C \sim$ constant

- Thermal conductivity K
  - Low T: $K \sim T^3$ High T: $K \sim 1/T$
  - Maximum as function of T

Summary of Part I
Looking Forward

- What will be important in describing electrons?
- In order to understand:
  - Metals, insulators, semiconductors, ….
  - We need:
    - The structure of the crystal – Lattice, basis, Recip. Lattice
    - Electronic states in periodic crystal
    - Electrons act like waves/particles
      - The same Brillouin zone as for phonons
      - The same counting of states in the BZ
      - Density of states D(E)
- Conductivity – transport of charge
  - The same ideas as for thermal energy
    - $j = \sigma E = \sigma dV/dx$, $\sigma = (1/3) e^2 v L$
    - (Ohm's law!)
    - Scattering - essential for resistance (and for Ohm's law) –
      is due to phonons, impurities, …
- And we need to understand the crucial differences between electrons
  and phonons!
  - Specific heat – ideas the same but very different result
  - Conductivity – ….

7