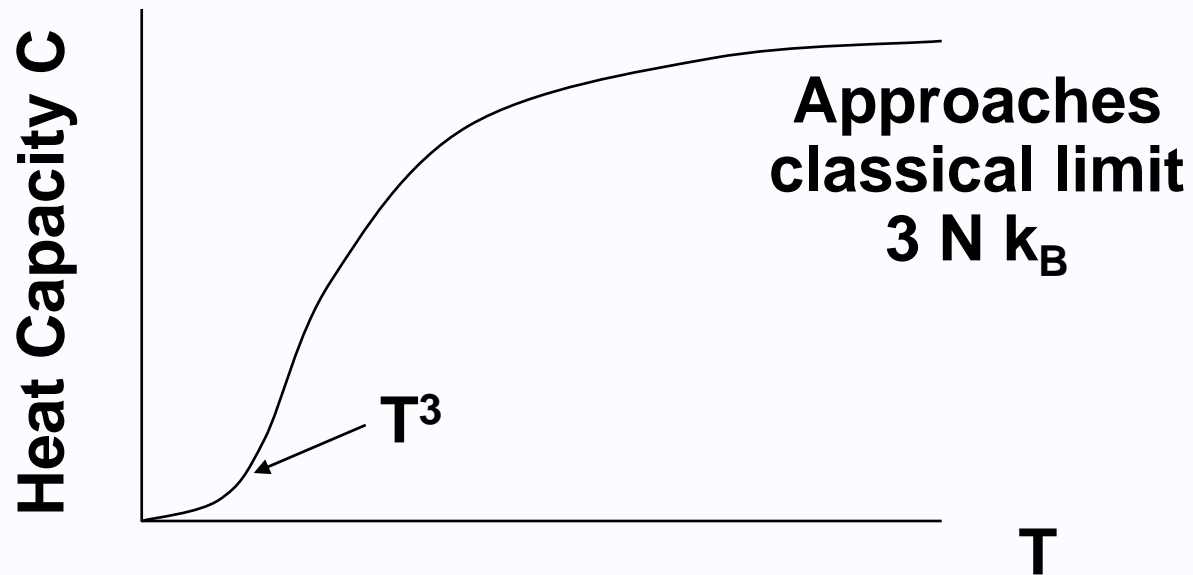# Phonons II - Thermal Properties
(Kittel Ch. 5)

Heat capacity

- Heat capacity is the measure of how much energy it takes to raise the temperature of a unit mass of an object a certain amount.

- Two heat capacities: constant volume, C_V, and constant pressure, C_P. For a gas $C_P > C_V$. For a solid $C_P \approx C_V$.

- The contribution of the phonons (lattice vibrations) to the heat capacity of a crystal is called the lattice heat capacity.

- Classical result: $C \approx 3NN_{cell}\,k_B$, where N is the number of atoms in a unit cell and N_{cell} is the number of cells in the crystal.

Lattice heat capacity

- The heat that goes into a solid to raise its temperature shows up as internal vibrational energy U (phonons).
- Determine U(T), then we can calculate $C_V = (\partial U/\partial T)_V$.

- In calculating U we need to consider the following:
  - (1) what is the average energy of each phonon;
  - (2) what is the average number of phonons existing at any T for each type (mode) of vibration;
  - (3) how many different types (modes) of vibration are there.

Quantization of vibration waves

- Vibrations in a crystal are independent waves, each labeled by <u>k.</u>
- There are 3N wave types in a 3D crystal with N atoms per cell

- Each independent harmonic oscillator has quantized energies:
$$E_n = (n + 1/2) h\nu = (n + 1/2) \hbar\omega$$
- Quanta are called phonons, each phonon carries energy $\hbar\omega$
- These can be viewed as particles
- For each independent oscillator (i.e., for each independent wave in a crystal), there can be any integer number of phonons
- Need to find out the average number of phonons and the average energy associated with each independent oscillator (mode).

Thermal Properties - Key Points

- Fundamental law of a system in thermal equilibrium:
  If two states of the system have total energies E_1 and E_2, then the ratio of probabilities for finding the system in states 1 and 2 is $P_1 / P_2 = \exp (- (E_1 - E_2) / k_B T)$ where k_B is the Boltzman constant
- Larger probability of smaller energy

- Applies to all systems - whether classical or quantum and whether the particles are bosons (like phonons) or fermions (like electrons)

Thermal Properties - Phonons

- Phonons are examples of bosons.

- There can be any number n phonons for each oscillator, i.e., the energy of each oscillator can be $E_n = (n + \frac{1}{2}) \hbar \omega$, $n = 0,1,2,...$

  The probability of finding an oscillator with n phonons (and not another value)

  $$P_n = \exp(-E_n / k_B T) \; / \; \sum_{n'=0}^{\infty} \exp(-E_{n'} / k_B T)$$

  and the average phonon occupation is

  $$\langle n \rangle = \sum_{n=0}^{\infty} P_n \, n$$
  $$= \sum_{n=0}^{\infty} n \exp(-E_n / k_B T) \; / \; \sum_{n'=0}^{\infty} \exp(-E_{n'} / k_B T)$$

Planck Distribution

- Using the formulas:

  $1/(1 - x) = \sum_{s=0}^{\infty} x^s$ and $x/(1 - x)^2 = \sum_{s=0}^{\infty} s\, x^s$

  $<n> = 1 / [\, \exp(\hbar\omega / k_B T) - 1\,]$ Planck Distribution

Average energy of an oscillator at temperature T:

  $U = <(n + \tfrac{1}{2})\,\hbar\omega> = \hbar\omega\,(<n> + \tfrac{1}{2})$

  $= \hbar\omega\,(1 / [\, \exp(\hbar\omega / k_B T) - 1\,] + \tfrac{1}{2})$

- At high T, $U \to \hbar\omega / [\,\hbar\omega / k_B T\,] \to k_B T$
  which is the classical result

Total thermal energy of a crystal

- The crystal is a sum of independent oscillators (in the harmonic approximation). The independent oscillators are waves labeled by $\underline{k}$ and an index m = 1, ..., 3N. Therefore, the total energy of the crystal is:

Fixed atoms

3 dimensions

N atoms per cell

$$U = U_0 +$$

$$\sum_{\underline{k},m} \hbar\, \omega_{\underline{k},m}\, (1 / [\, \exp(\hbar\, \omega_{\underline{k},m} / k_B\, T) - 1\,] + \tfrac{1}{2}\,)$$

Added thermal energy

Zero point energy

Question: How to do the sum over **$\underline{k}$** ??

Sum over vibration modes of a crystal

- The sum over $\underline{k}$ and the index m = 1, ..., 3N can be thought of as follows:
  One $\underline{k}$ point for each unit cell
  The index m counts the atoms per unit cell N multiplied by the number of independent ways each atoms can move (3 in 3D).

- The entire crystal has 3 N N_{cell} degrees of freedom(i.e. number of ways the atoms can move) . This must not change when we transform to the independent oscillators.

1D, two boundary conditions

- Demonstration that the sum over $\underline{k}$ is equivalent to one $\underline{k}$ point for each unit cell
- N atoms at separation a, $u_s = u \exp(ik (s\,a) - i\omega_{k,m} t)$
- Fixed boundary conditions: $u_0 = u_N = 0$
  - Standing waves only
  - Possible k values: $k = \pi/Na$, $2\pi/Na$, .. $n\pi/Na$, $(N-1)\pi/Na$
  - One k value per mobile atom, one k value per cell
- Periodic boundary conditions: $u_s = u_{N+s}$
  - traveling waves, need $kNa = +-2n\pi$
  - Possible k values: $k = 0$, $+-2\pi/Na$, $+-4\pi/Na$, .. $2n\pi/Na$
  - One k value per mobile atom, one k value per cell

Density of states

- All we need is the number of states per unit energy, and we can integrate over energy to find the thermal quantities

- Total energy
$$U = \sum_{k=1}^{N_{cell}} \sum_{m=1}^{3N} \frac{\hbar \omega_{k,m}}{exp(\hbar \omega_{k,m}/k_B T)-1}$$

- We know that there are N_{cell} possible k values

- In a large crystal one can replace the sum over k with an integral

- Since ω and k are related by the dispersion relation we can change variables
$$U = \sum_{m} \int d\omega \, D_m(\omega) \frac{\hbar \omega}{exp(\hbar \omega /k_B T)-1}$$

- $D_m(\omega)d\omega$ – number of modes (states) in frequency range ω to $\omega+d\omega$

Relation between k and ω

- Total energy $\quad U = \sum_m \int d\omega\, D_m(\omega) \dfrac{\hbar\omega}{exp(\hbar\omega / k_B T) - 1}$

- $D_m(\omega)d\omega$ – number of modes (states) in frequency range ω to $\omega + d\omega$ for branch m

  dispersion relation: $\omega_k = 2\,(\,C\,/\,M\,)^{1/2}\,|\sin(ka/2)|$

- Modes in interval (ω, k, E) to ($\omega + \Delta\omega$, k+ Δk, E+ ΔE)

  $\Delta N = D(\omega)\,\Delta\omega = N(k)\,\Delta k = N(E)\,\Delta E$

  $$D(\omega)d\omega = N(k)\dfrac{dk}{d\omega}d\omega = \dfrac{N(k)}{v_g}d\omega$$

  Group velocity

Density of states in 1D

- $D_m(\omega)d\omega$ – number of modes (states) in frequency range ω to $\omega+d\omega$

$$D(\omega)d\omega = \frac{N(k)}{v_g}d\omega$$

- N(k) - number of modes per unit range of k

- number of modes between $-\pi/a < k < \pi/a$ = N = L/a (the number of atoms)

- N(k)=N/(2π /a)

$$D(\omega)d\omega = \frac{Na}{2\pi}\frac{1}{v_g}d\omega = \frac{L}{2\pi}\frac{1}{v_g}d\omega$$

Possible wavevectors in 3D

- Assume $N_{cell} = n^3$ primitive cells, each a cube of side a
- volume of the crystal $V = (na)^3 = L^3$
- vibrations: $\vec{u}_s = \vec{u}\, exp(i\vec{k}\cdot\vec{r} - i\omega_{\vec{k},m}\, t)$

$$\vec{r} = x\vec{i} + y\vec{j} + z\vec{k} \qquad\qquad \vec{k} = k_x\vec{i} + k_y\vec{j} + k_z\vec{k}$$

- periodic boundary conditions:

$$exp[\,i(k_x x + k_y y + k_z z\,)] = exp\{\,i[\,k_x(x+L) + k_y(y+L) + k_z(z+L)]\}$$

$$k_x, k_y, k_z = 0, +\text{-}2\pi/L\,, +\text{-}4\pi/L, ..\ 2m\pi/L$$

na= L

- There is one allowed value of **k** in each volume $(2\pi/L)^3 = 8\pi^3/V$

  V - volume of the crystal

Density of states in 3D

- one allowed value of $\underline{\mathbf{k}}$ per volume $8\pi^3/V$
- $D(\omega)d\omega$ – number of modes (states) in frequency range ω to $\omega+d\omega$

$$\Delta N = D(\omega)\,\Delta\omega = N(\underline{\mathbf{k}})\,\Delta\underline{\mathbf{k}}$$

In a cubic lattice the 1D dispersion relation holds - ω only depends on k - spherical symmetry

$$D(\omega)d\omega = N(\vec{k})4\pi k^2 \frac{dk}{d\omega}d\omega$$

$$N(\underline{\mathbf{k}}) = V/8\pi^3$$

- $D(\omega)=k^2 V/2\pi^2\, dk/d\omega$

Heat Capacity

- The internal energy is found by summing over all modes

$$U = \sum_m \int d\omega\, D_m(\omega) \frac{\hbar\omega}{exp(\hbar\omega/k_B T) - 1}$$

- The heat capacity is found by differentiating U with respect to temperature, C = dU/dT

$$C = k_B \sum_m \int d\omega\, D_m(\omega) \frac{x^2\, exp(x)}{[exp(x) - 1]^2} \qquad x = \frac{\hbar\omega}{k_B T}$$

- Need to express D(ω) and dω as a function of x to do the integral

Debye Approximation

- Approximate crystal with an elastic continuum,
- $\omega = vk$ (v= sound velocity)
- In 3D cubic crystal $D(\omega) = k^2 V/2\pi^2 \, dk/d\omega$
- $D(\omega) = V\omega^2/2\pi^2 v^3$
- In this approximation the maximum ω is not known, we need to determine it from the fact that there are N_{cell} modes in each branch

$$\int_{\omega=0}^{\omega_D} d\omega \, D(\omega) = N_{cell}$$

- $\omega_D^3 = 6\pi^2 \, v^3 \, N_{cell} /V$ $N_{cell} /V = 1/V_{cell}$
- maximum wavevector $k_D = \omega_D/v = (6\pi^2 \, N_{cell} /V)^{1/3}$

Debye temperature

- Thermal energy (3 polarizations)

$$U = 3 \int_0^{\omega_D} d\omega \, D(\omega) \frac{\hbar\omega}{exp(\hbar\omega/k_B T)-1} = \frac{3Vk_B^4 T^4}{2\pi^2 v^3 \hbar^3} \int_0^{x_D} dx \frac{x^3}{exp(x)-1}$$

$$x_D = \frac{\hbar\omega_D}{k_B T} = \frac{\theta}{T}$$

- Characteristic Debye temperature $\theta = \hbar v/k_B (6\pi^2 N_{cell}/V)^{1/3}$

$$U = 9N_{cell}k_B T \left(\frac{T}{\theta}\right)^3 \int_0^{x_D} dx \frac{x^3}{exp(x)-1}$$

$$C_V = 9N_{cell}k_B \left(\frac{T}{\theta}\right)^3 \int_0^{x_D} dx \frac{x^4 exp(x)}{(exp(x)-1)^2}$$

Ex. Debye temperature $\theta = \hbar v / k_B (6\pi^2 N_{cell} / V)^{1/3}$

What material characteristics does the Debye temperature depend on?

Limits of heat capacity in the Debye appr.

$$C_V = 9 N_{cell} k_B \left(\frac{T}{\theta}\right)^3 \int_0^{x_D} dx \, \frac{x^4 \exp(x)}{(\exp(x)-1)^2}$$

- For T>>θ, $x_D \rightarrow 0$, exp(x)~1+x

  C_V~$3N_{cell} k_B$ - equal to classical limit
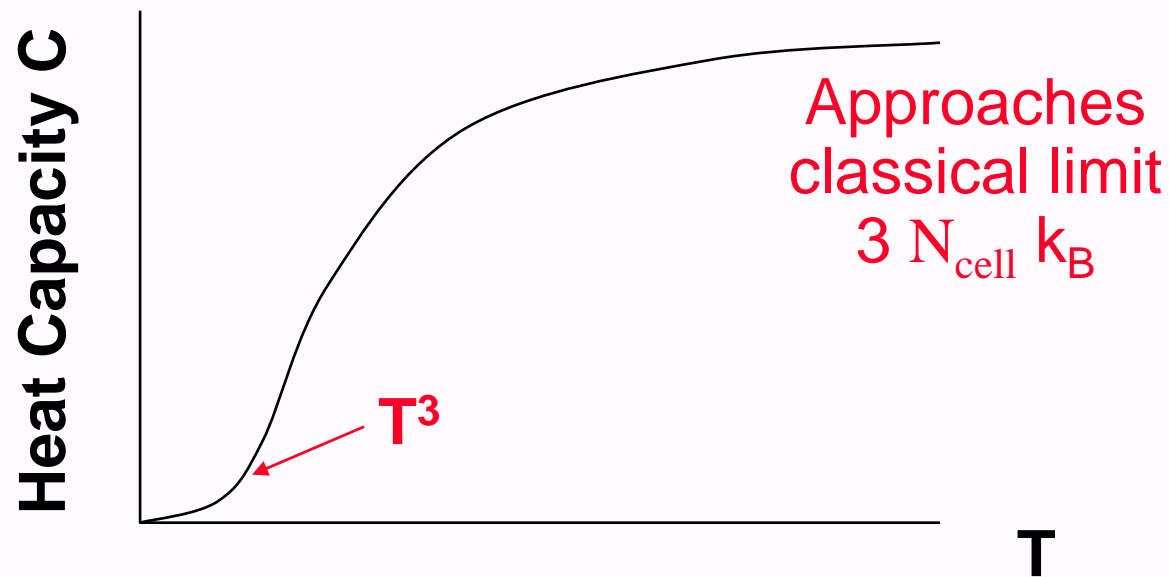
- For T<<θ, $x_D \rightarrow \infty$,

$$C_V = 9 N_{cell} k_B \left(\frac{T}{\theta}\right)^3 \int_0^{\infty} dx \, \frac{x^4 \exp(x)}{(\exp(x)-1)^2} = 9 N_{cell} k_B \left(\frac{T}{\theta}\right)^3 \frac{4\pi^4}{15}$$

  C_V~T^3

Debye Approximation
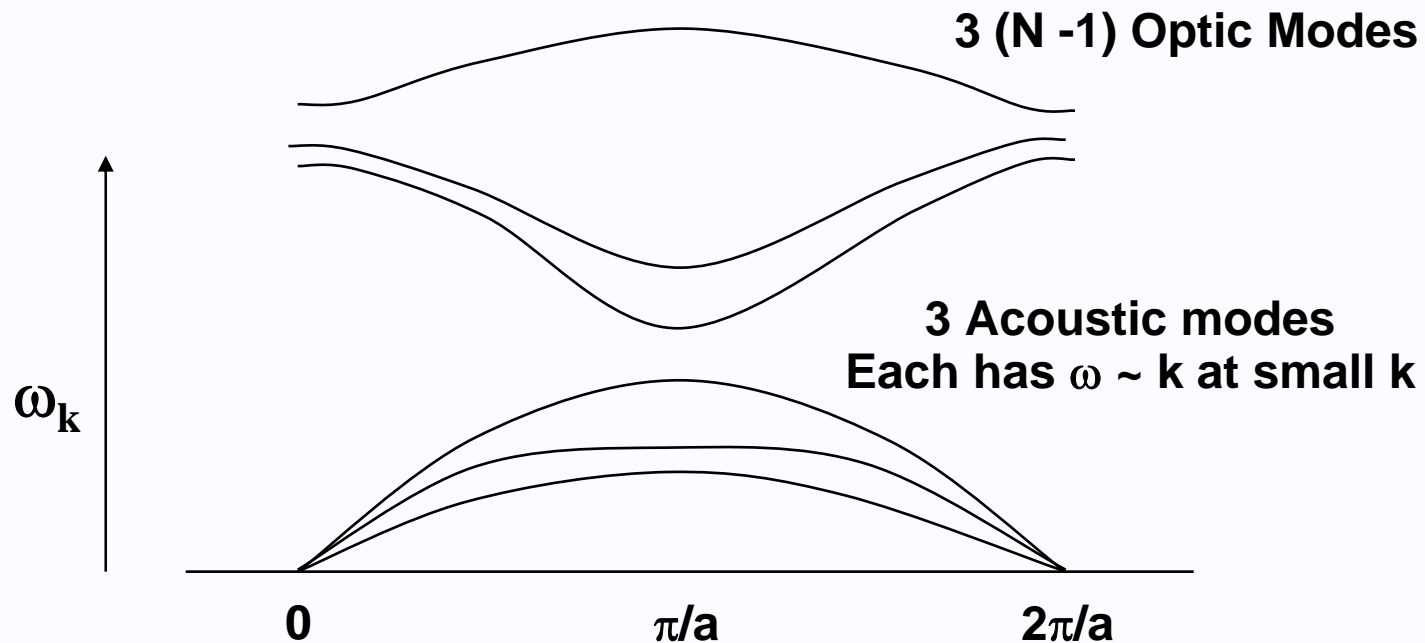
$$C_V = 9N_{cell}k_B\left(\frac{T}{\theta}\right)^3 \int_0^{x_D} dx \frac{x^4 \exp(x)}{(\exp(x)-1)^2}$$

C_v has correct general behavior that must be found in all crystals. For 3 dimensions

Einstein Approximation

- The Debye approximation is valid for acoustic modes
- For optic modes one can assume a constant frequency-
  Einstein approximation

3 (N -1) Optic Modes

3 Acoustic modes
Each has $\omega \sim k$ at small k

ω_k

0   π/a   2π/a

Einstein Approximation

- Assume each oscillator has $\omega=\omega_0$
- $D(\omega)=N_{cell}\delta(\omega-\omega_0)$

$$U = 3N_{cell}\frac{\hbar\omega_0}{exp(\hbar\omega_0/k_BT)-1}$$

$$C_V = 3N_{cell}k_B\left(\frac{\hbar\omega_0}{k_BT}\right)^2\frac{exp(\hbar\omega_0/k_BT)}{(exp(\hbar\omega_0/k_BT)-1)^2}$$

- For $T\rightarrow0$, $C_V\sim exp(-h\omega/k_BT)$
- For $T\gg0$, $C_V\sim3N_{cell}k_B$ - equal to classical limit

General expression for D(ω)

- In 1D $\quad D(\omega) = \dfrac{N(k)}{v_g}$, v_g=group velocity

- In 3D $\quad \Delta N = D(\omega)\, \Delta\omega = N(\underline{\mathbf{k}})\, \Delta\underline{\mathbf{k}}$

  $$D(\omega)d\omega = N(\vec{k}) \int_{shell} d^3k$$

- integral over the volume of the shell in $\underline{k}$ space bounded by the surfaces with ω and $\omega+d\omega$

$$\int_{shell} d^3k = \int dS_\omega dk_\perp = \int dS_\omega \frac{d\omega}{v_g} \qquad v_g = \left| \Delta_{\vec{k}}\omega \right|$$

$$D(\omega) = \frac{V}{(2\pi)^3} \int_{shell} \frac{dS_\omega}{v_g} \qquad \text{integral over } \omega = \text{const surface}$$

- v_g=0 - Van Hove singularities

$$D(\omega) = \frac{V}{(2\pi)^3} \int_{shell} \frac{dS_\omega}{v_g}$$

- Plot the density of states as a function of ω for a Debye solid, $D(\omega) = V\omega^2/2\pi^2 v^3$

- How does this plot change for an actual crystal structure?

Energy & Force due to Displacements

- The energy of the crystal changes if the atoms are displaced.
- The change in energy can be written as a function of the positions of all the atoms:

$$E(\underline{R}_1, \underline{R}_2, \underline{R}_3, \ldots) = E(\underline{R}_1^0 + \Delta\underline{R}_1, \underline{R}_2^0 + \Delta\underline{R}_2, ..)$$

- To lowest order in the displacements the energy is quadratic - Hooke's law - harmonic limit

$$E = E_0 + (1/2) \, \Sigma_{i\,j} \, \Delta\underline{R}_i \cdot D_{i\,j} \cdot \Delta\underline{R}_j + \ldots.$$

(There are no linear terms if we expand about the equilibrium positions)

Consequences of anharmonicity

- If we expand the energy beyond the harmonic order:

$$E = E_0 + (1/2) \Sigma_{ij} \ \Delta\underline{R}_i \cdot D_{ij} \cdot \Delta\underline{R}_j +$$
$$(1/6) \Sigma_{ijk} \ D_{ijk} \cdot \Delta\underline{R}_i \ \Delta\underline{R}_j \ \Delta\underline{R}_k + \ldots$$

$\longleftarrow$ **Difficult and Messy**

- The problem is fundamentally changed:

  No longer exactly solvable

- 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
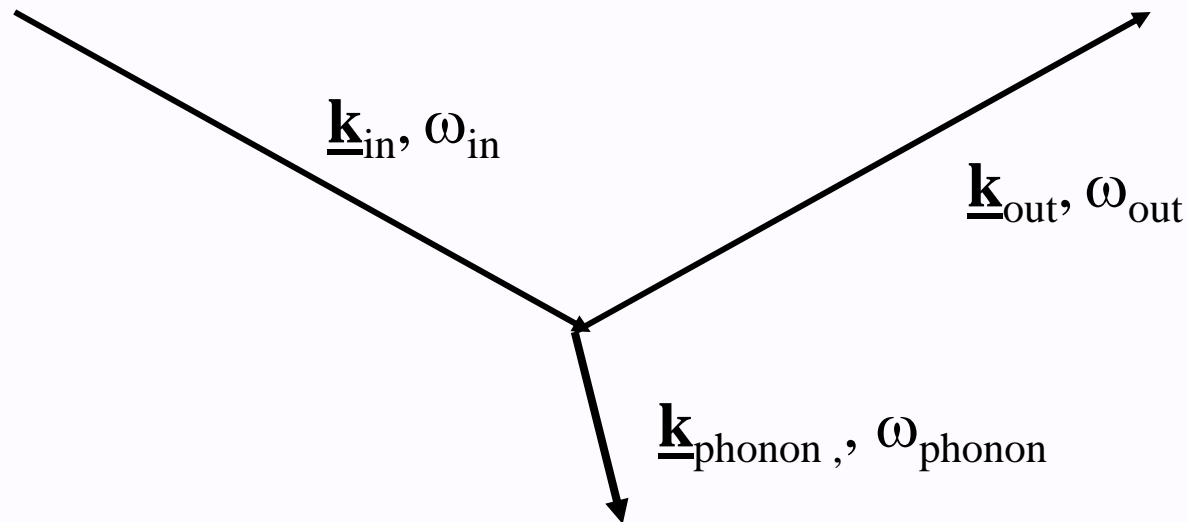
  Phonons can establish thermal equilibrium and

  conduct heat like a "gas" of particles

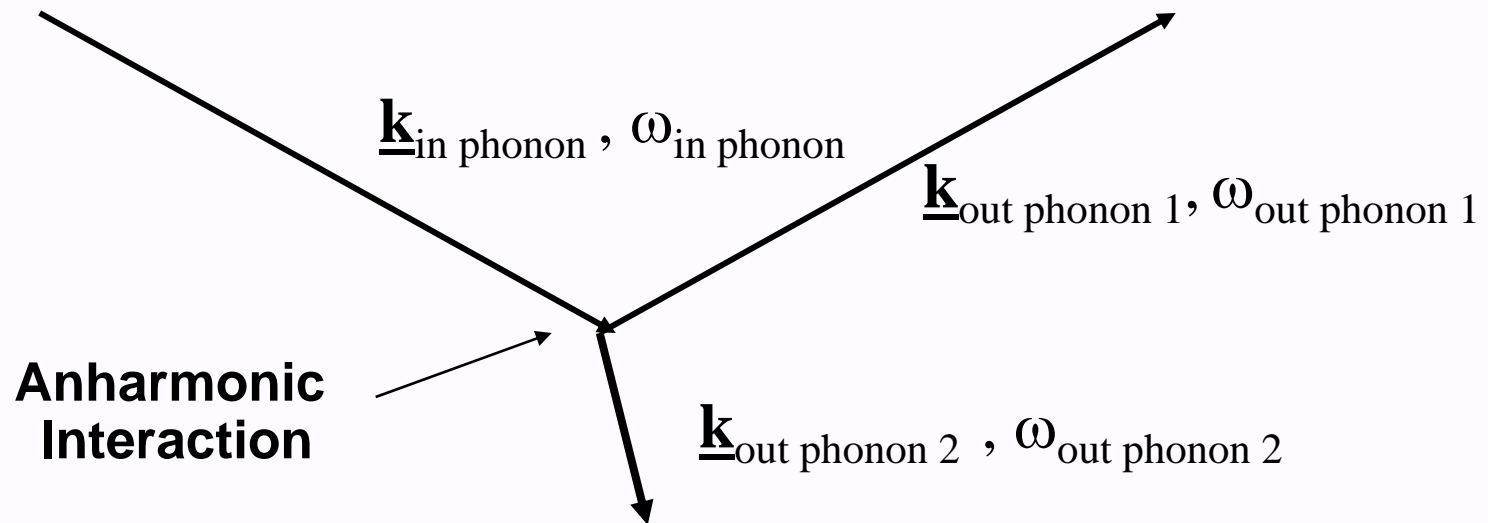# Inelastic Scattering and Fourier Analysis

Inelastic diffraction occurs for

$$\underline{k}_{in} - \underline{k}_{out} = \underline{G} \pm \underline{k}_{phonon}$$

$$\omega_{in} - \omega_{out} = \pm \, \omega_{phonon} \; \text{or} \; E_n - E_{out} = \pm \, \hbar\omega_{phonon}$$

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

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

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

Scattering of Phonons - I

- **The same idea applies to phonons**. One phonon can scatter to create two.
- Scattering can occur for

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

$$\omega_{in\ phonon} = \omega_{out\ phonon\ 1} + \omega_{out\ phonon\ 2}$$

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

$\underline{\mathbf{k}}_{out\ phonon\ 1}$, $\omega_{out\ phonon\ 1}$

Anharmonic Interaction

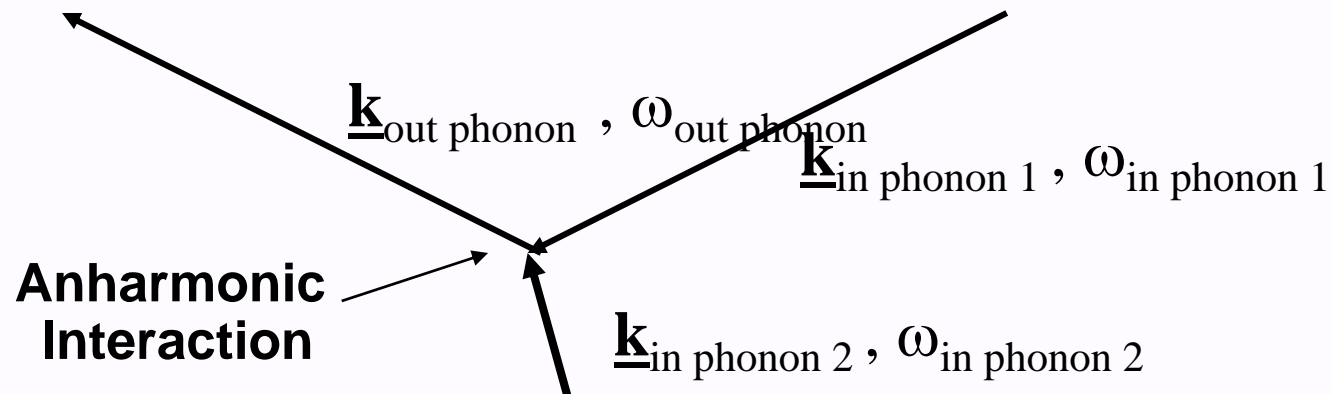$\underline{\mathbf{k}}_{out\ phonon\ 2}$, $\omega_{out\ phonon\ 2}$

Scattering of Phonons - II

- Two phonons can interact to create one.

- This is called "up conversion (umklapp)", which can be done with intense phonon beams and occurs for

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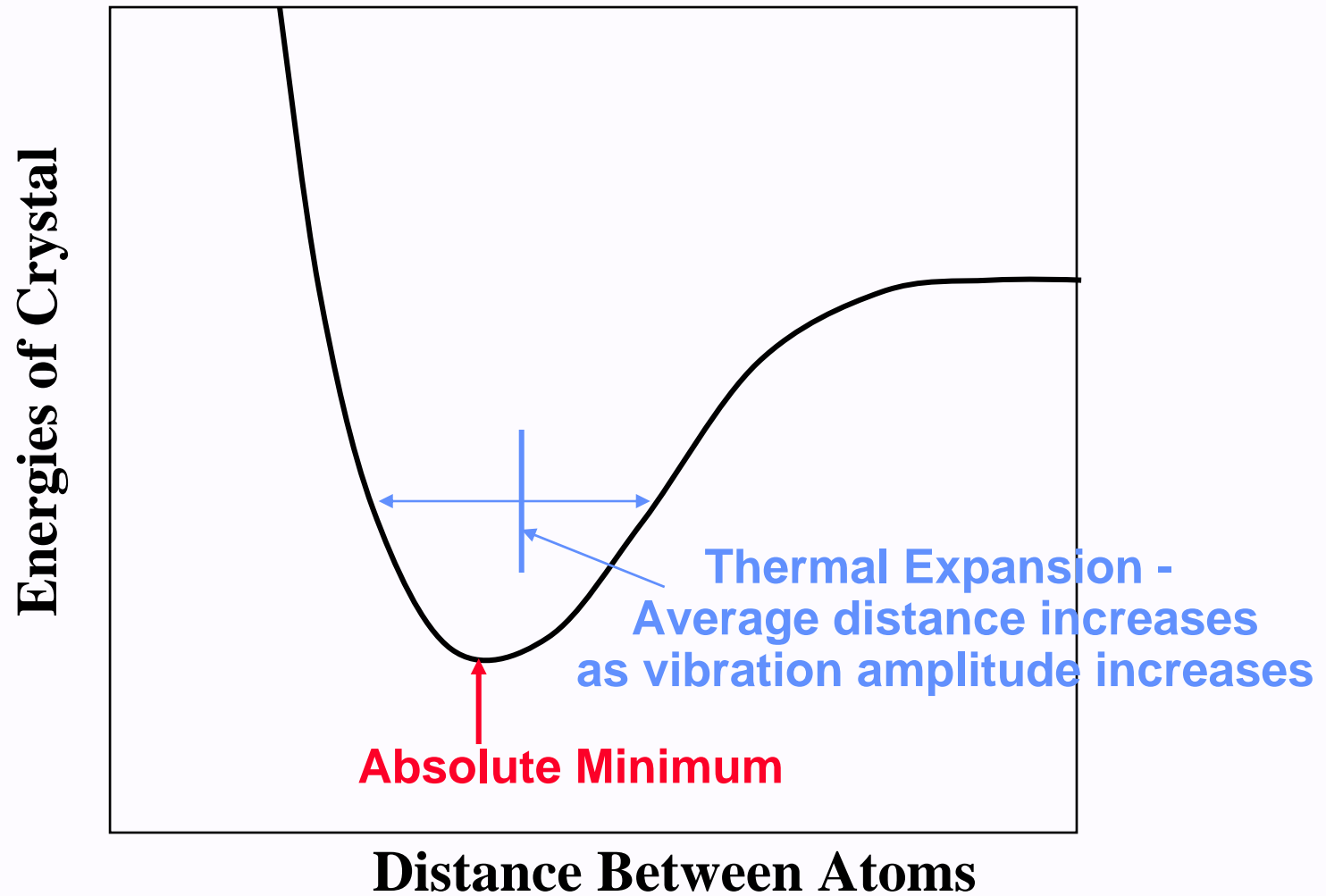
$$\omega_{\underline{\text{out}}\ \text{phonon}} = \omega_{\text{in phonon 1}} + \omega_{\text{in phonon 2}}$$

$\underline{\mathbf{k}}_{\text{out phonon}}$, $\omega_{\text{out phonon}}$

$\underline{\mathbf{k}}_{\text{in phonon 1}}$, $\omega_{\text{in phonon 1}}$

Anharmonic Interaction

$\underline{\mathbf{k}}_{\text{in phonon 2}}$, $\omega_{\text{in phonon 2}}$

Thermal expansion

- The energy of a pair of atoms depends on the displacement x from their equilibrium separations, $U(x) = cx^2 - gx^3 - fx^4$

- The average displacement $\langle x \rangle$ is determined by the condition that the average force vanishes.

- In the harmonic approximation $F = cx$. Therefore $\langle x \rangle = 0$, $\langle F \rangle = 0$, and there is no thermal expansion

- Anharmonicity adds additional terms:
  $F = cx - 1/2\, g\, x^2 - \ldots, \langle F \rangle = 0 \Rightarrow \langle x \rangle = 1/2\, (g/c)\, \langle x^2 \rangle$

- In general, this means thermal expansion.

Thermal expansion

Energies of Crystal

Distance Between Atoms

Thermal Expansion -
Average distance increases
as vibration amplitude increases

Absolute Minimum

Characterizing thermal dilation

- Average displacement of atoms, <x>

$$\langle x \rangle = \frac{\int\limits_{-\infty}^{\infty} dx\, x\, exp\left[-U(x)/k_BT\right]}{\int\limits_{-\infty}^{\infty} dx\, exp\left[-U(x)/k_BT\right]} \cong \frac{3g}{4c^2} k_BT$$

- U(x) – potential energy of a pair of atoms.
- Thermal expansion of a crystal or cell: $\delta = dV/V$
- For cubic crystals $dV/V = 3\, dx/x$

From the theory of elastic media:

- Potential energy of a unit cell due to dilation:
  $U_{cell}(T) = V_{cell}\, B\, \delta^2/2$, where B is the bulk modulus

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 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 one 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
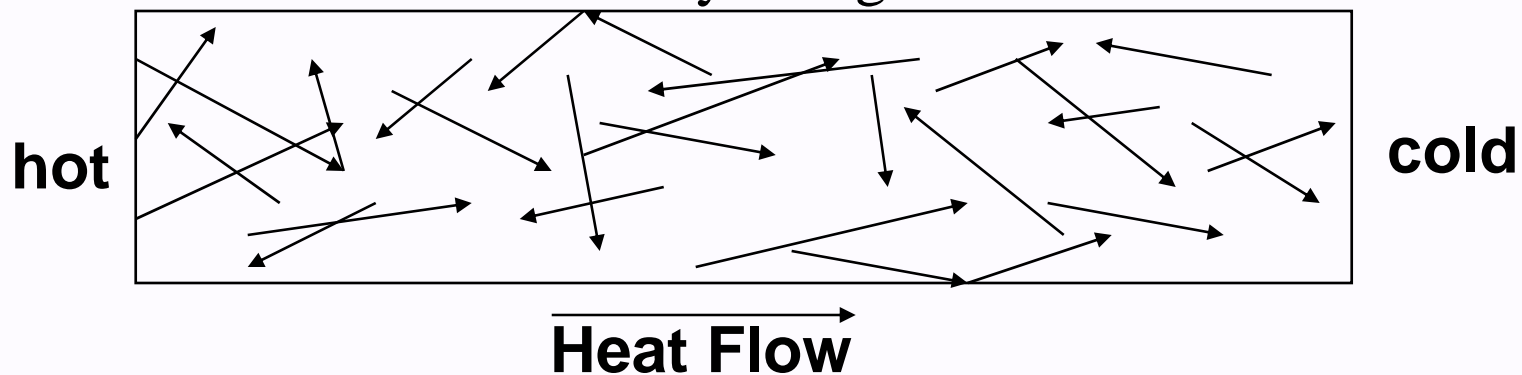
Heat Flow
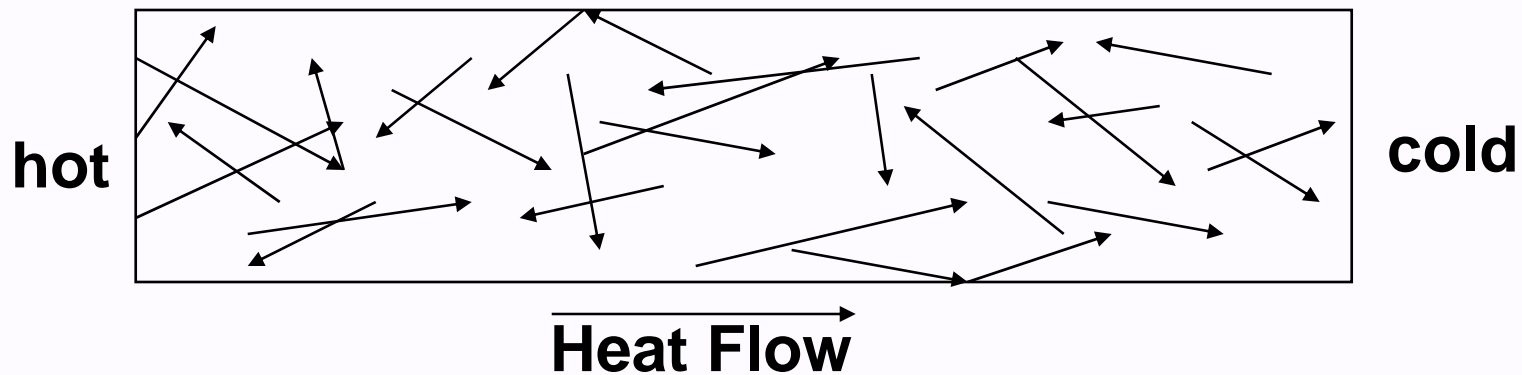
Phonons also act like a gas

- A phonon is a particle - a quantum of vibration

- It carries energy just like a molecule.

- Phonons can come to equilibrium by scattering just like molecules (phonon scattering is due to defects and to anharmonicity).

- What is different?
Phonons can be created and destroyed. But we will see that we can treat them exactly like gas.

Thermal conductivity of phonons

- Definition: j = heat flow (energy per unit area per unit time) = $- K \, dT/dx$; K – thermal conductivity

- If a phonon moves from a region with local temperature T to one with local temperature $T - \Delta T$, it supplies excess energy $c \, \Delta T$, where c = heat capacity per phonon.   (Note ΔT can be positive or negative).

- Temperature difference between the ends of a free path :
  $\Delta T = (dT/dx) \, v_x \, \tau$, 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

Phonon Heat Transport - continued

- This can be simplified in an isotropic case, since averaging over directions gives $(v_x^2)_{average} = (1/3) v^2$

- This leads to $j = - (1/3) n c v^2 \tau \, dT/dx$

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

- Then $j = - (1/3) C v L \, dT/dx$
  and
    $K = (1/3) C v L$ = thermal conductivity
  (just like an ordinary gas!)

Phonon Heat Transport - continued

- What determines mean free path $L = v \, \tau$?

- At low temperature, the thermal phonons are sound waves that have long mean free paths -
  $$L \sim \text{sample size}$$

- At high temperature, phonons scatter from other phonons.

- ONLY Umklapp scattering limits the energy flow.
  The density of other phonons is $\sim T$, so
  $$L \sim 1/T$$

- At intermediate temperature, phonon scatter from defects and other phonons.
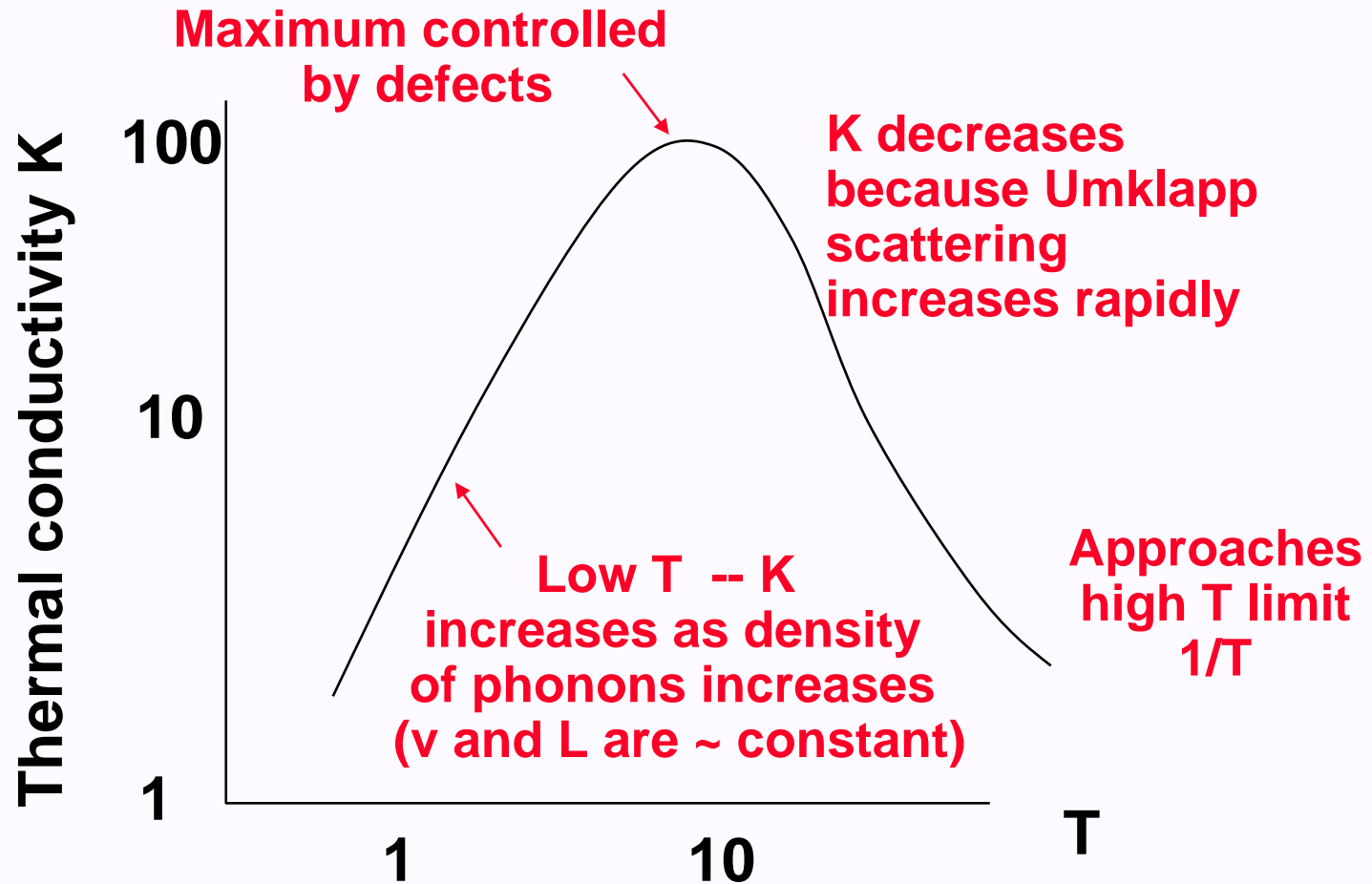
Phonon Heat Transport - continued

- Low T - K increases with T because density of phonons increases with roughly constant v and L
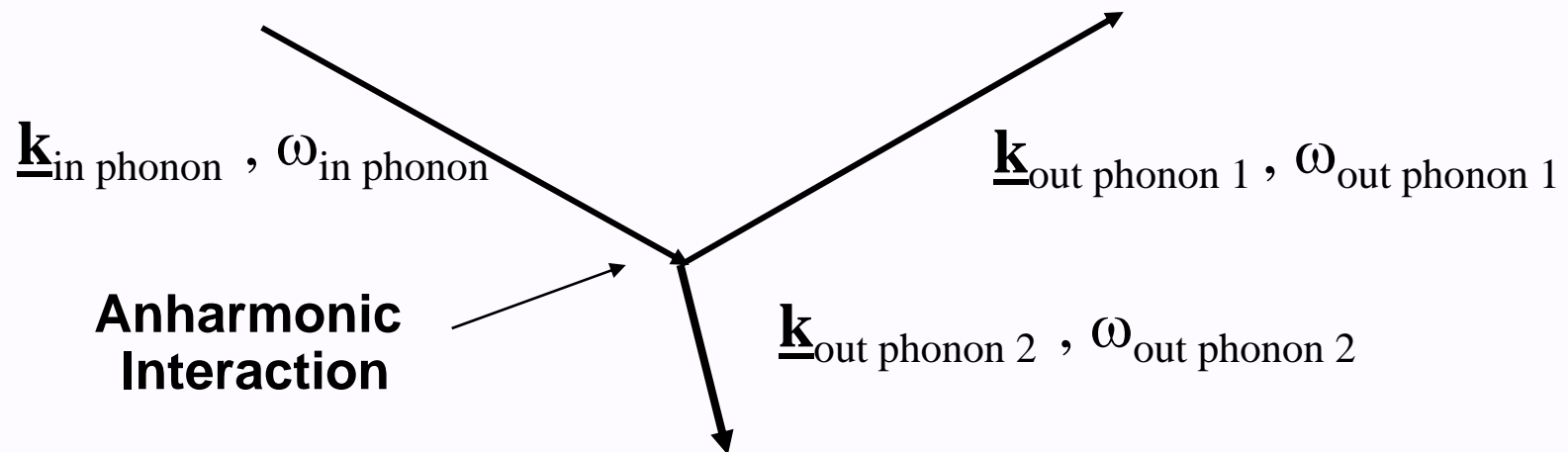
- High T - K decreases with T as Umklapp scattering

Low T

High T

hot

Heat Flow

cold
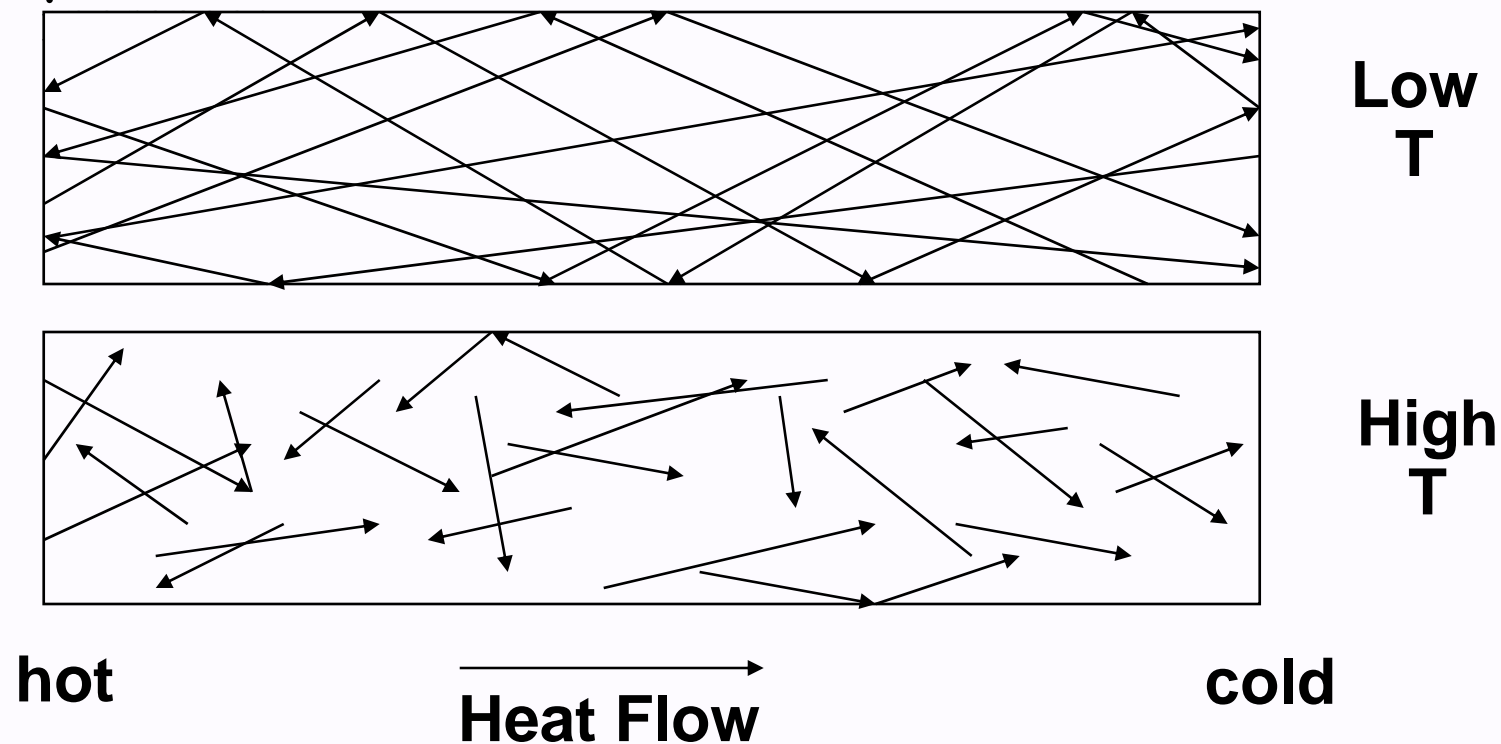
Phonon Heat Transport - continued

• Behavior in an excellent quality crystal:

Umklapp Scattering

- Scattering that changes total crystal momentum by a reciprocal lattice vector.

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

  $\omega_{\text{in phonon}} = \omega_{\text{out phonon 1}} + \omega_{\text{out phonon 2}}$

$\underline{\mathbf{k}}_{\text{in phonon}} , \omega_{\text{in phonon}}$

$\underline{\mathbf{k}}_{\text{out phonon 1}} , \omega_{\text{out phonon 1}}$

Anharmonic Interaction

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

Unless $G \neq 0$, the scattering does not change the total phonon momentum or energy. Therefore only Umklapp scattering limits the heat flow. It also leads to thermal equilibrium.

- **Vibrations of atoms**
  - **Harmonic approximation**
  - **Exact solution for waves in a crystal**
    - **Labeled by $\underline{k}$ and index m = 1, …, 3N**
- **Quantization of vibrations**
  - **Phonons act like particles**
  - **Can be created or destroyed by inelastic scattering experiments**
- **Thermal properties**
  - **Fundamental law of probabilities**
  - **Planck distribution for phonons**
  - **Heat Capacity C**
    - **Low T: C ~ T^3 -- High T: C ~ constant**
    - **Thermal conductivity K**
    - **Maximum as function of T**