

Phonons and Thermal Properties of Solids

Phonons and Thermal Properties of Solids: Reading

C. Kittel “Introduction to Solid State Physics”

J. R. Hook and H. E. Hall “Solid State Physics”

N. W. Ashcroft and N. D. Mermin “Solid State Physics”

Phonons and Thermal Properties of Solids: The Plan

Lecture 1 Vibrations in Crystals – the 1D **monatomic** chain

Lectures 2-3 Vibrations in Crystals – the 1D **diatomic** chain

Lectures 4-5 Quantum Approaches for Understanding Heat Capacity

Lectures 6-7 Anharmonic Effects on Thermal Properties

Lectures 8 Feedback on Assignment 1 ?

Please Fill-in the 2nd Year Experience Survey

The FYE and SYE surveys can be completed via any electronic device by accessing the following

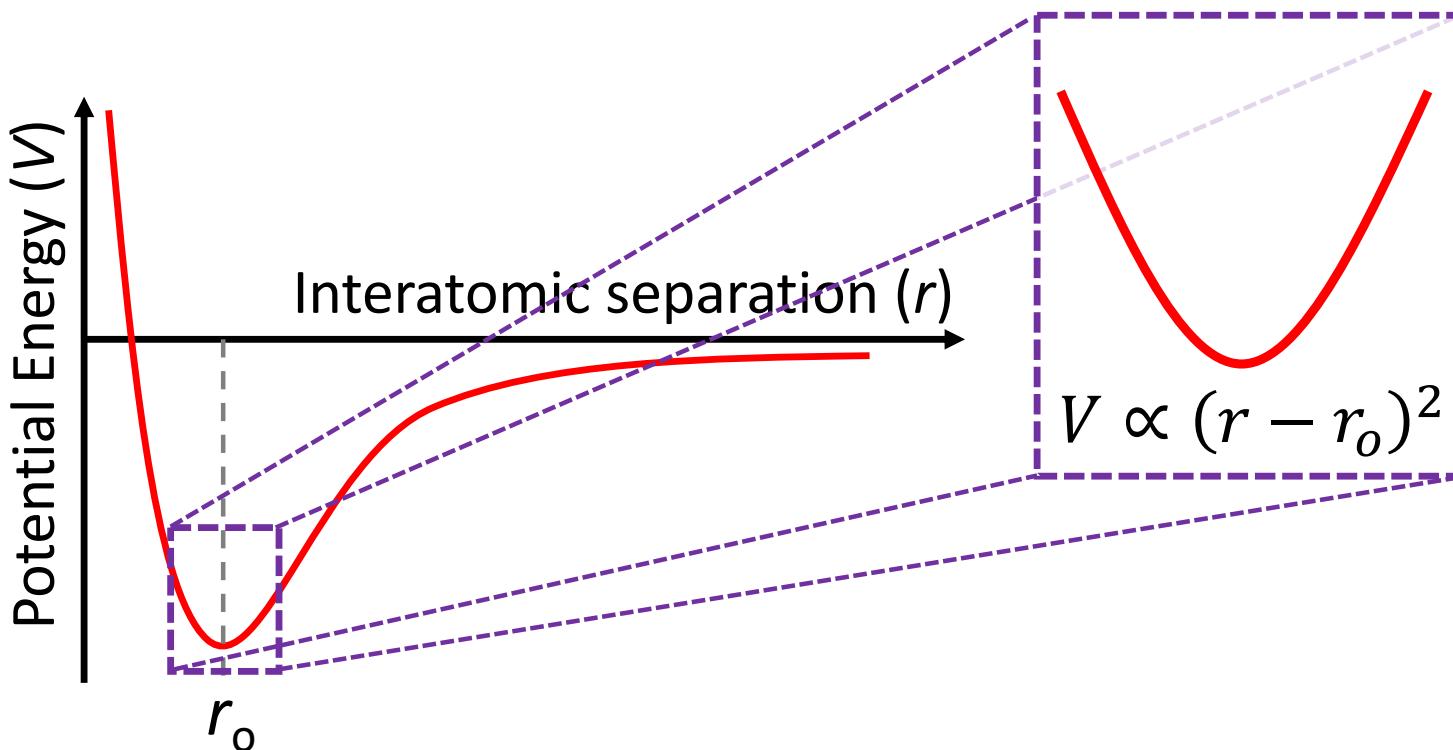
link: <https://eur02.safelinks.protection.outlook.com/?url=http%3A%2F%2Fgo.qub.ac.uk%2FSES2021&data=04%7C01%7Csim%40qub.ac.uk%7Cbdfe5143aecd4a7c2ee208d8d983f6af%7Ceaab77eab4a549e3a1e8d6dd23a1f286%7C0%7C0%7C637498508082170585%7CUnknown%7CTWFpbGZsb3d8eyJWljojMC4wLjAwMDAiLCJQIjoiV2luMzliLCJBtil6Ik1haWwiLCJXVCI6Mn0%3D%7C1000&sdata=kgYYMw7uWls0MbGmcBk8u5FMMIStRUm3Z2uCsvz0oo0%3D&reserved=0>

The survey will take students approximately 6-7 minutes and they need to complete the whole survey in one visit.

The survey will remain open until 30 April 2021.

We would really appreciate any efforts to promote the surveys to all student cohorts below the 50% response rate target.

Interatomic Potential and the Harmonic Approximation

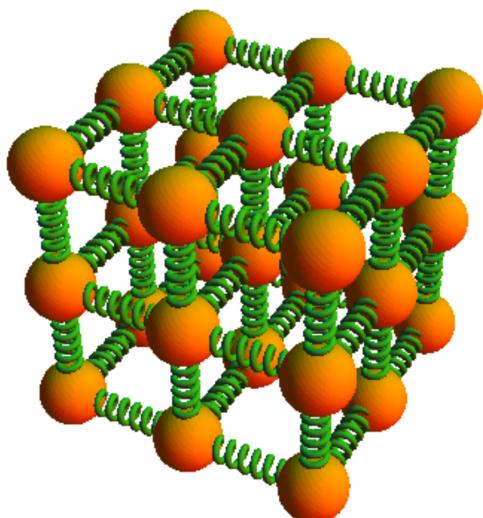


Potential (and hence potential energy) varies approximately as the square of a change in position from that at equilibrium. This function (parabola) has exactly the same form as that associated with a spring:

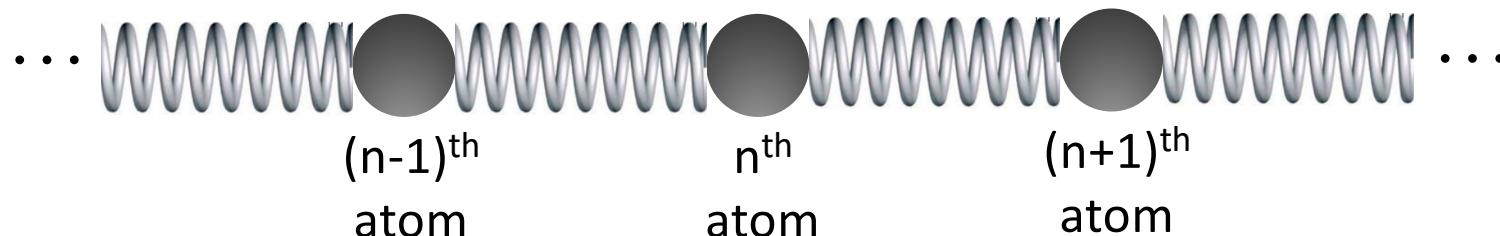
$$E = \frac{1}{2} kx^2$$

Suggests any force that acts to restore the equilibrium position of the atom will obey Hooke's Law: $F = -kx$
Motion under these conditions will be simple harmonic – hence **Harmonic Approximation**

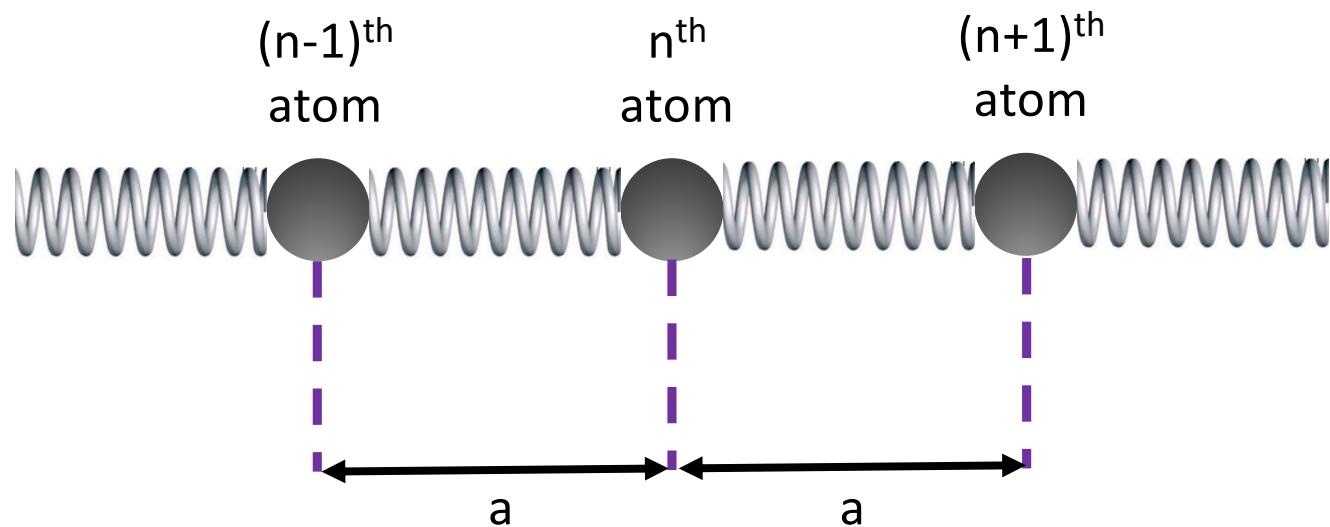
Ball and Spring Models for Crystalline Solids



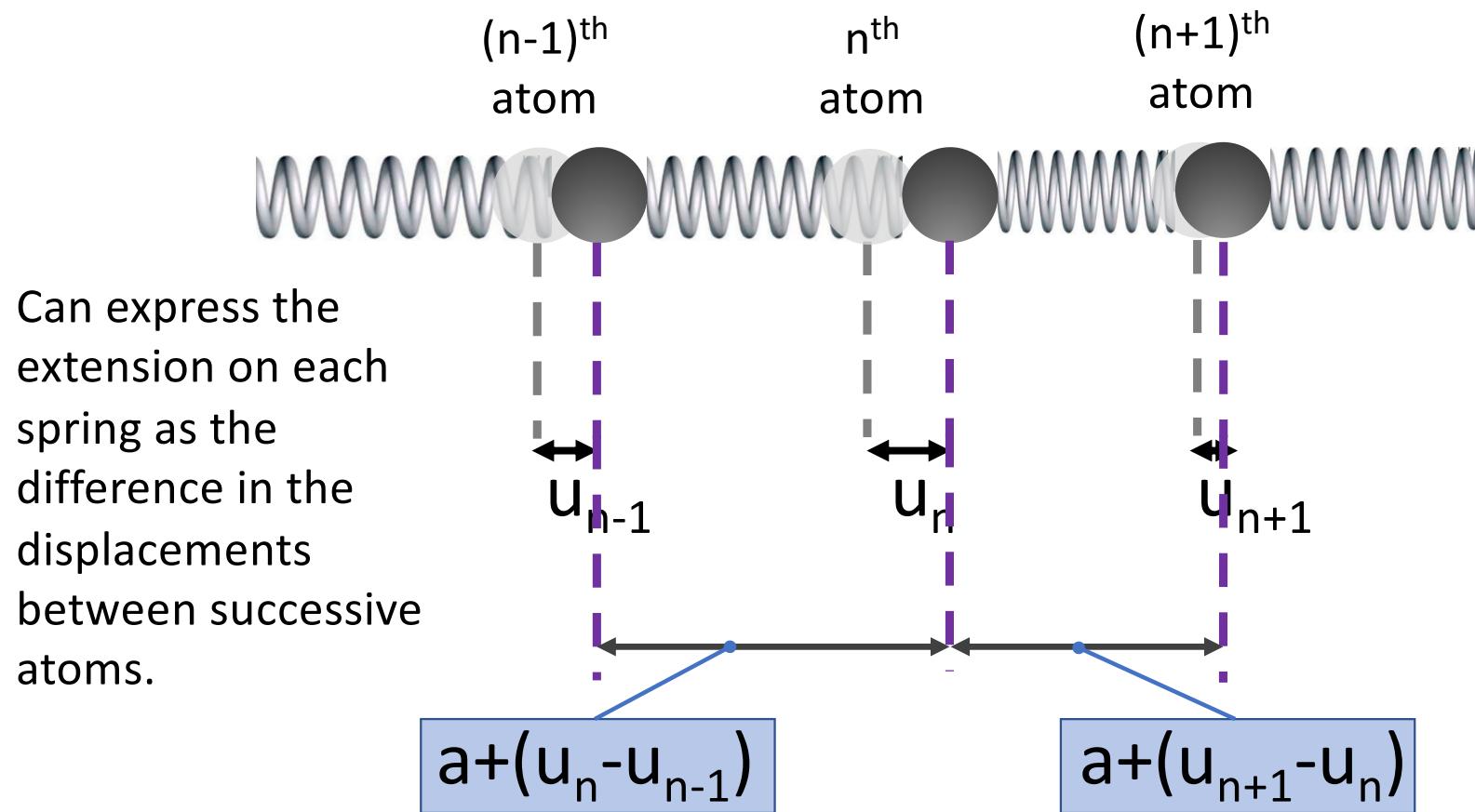
For developing simple model of vibrations in crystals, initially consider a single atomic type and a 1D chain of atoms (the **monatomic chain**):



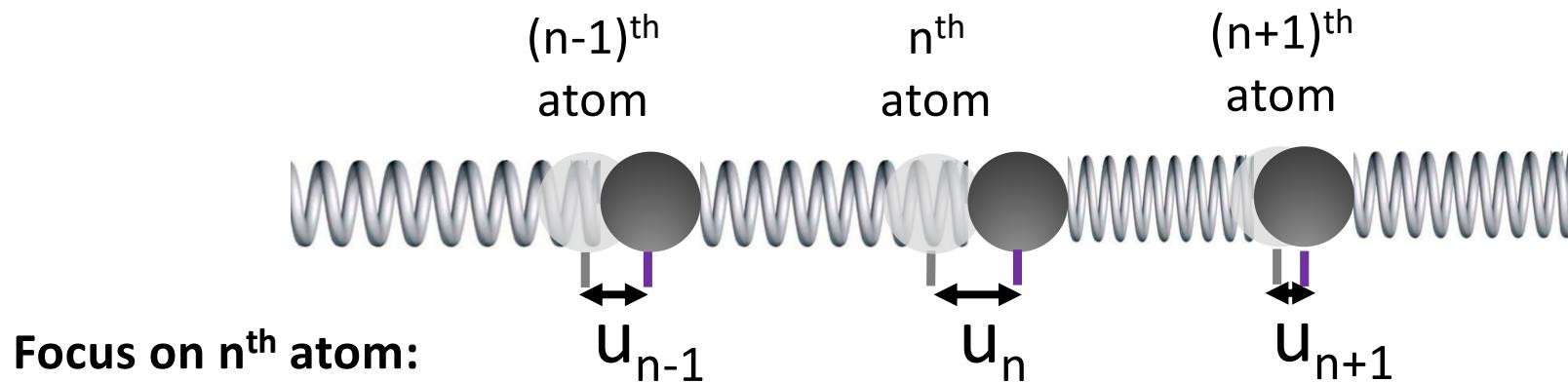
Vibrations along the Monatomic Chain



Vibrations along the Monatomic Chain



Vibrations along the Monatomic Chain



Focus on n^{th} atom:

Left-hand-side bond extension: $u_n - u_{n-1}$

Right-hand-side bond 'extension': $u_{n+1} - u_n$

Resultant force on the n^{th} atom (Hooke's Law): $F = \mu(u_{n+1} - u_n) - \mu(u_n - u_{n-1})$

Spring constant is μ NOT k – use k for wavevector later

Newton's 2nd law of motion: $m \frac{d^2 u_n}{dt^2} = \mu(u_{n+1} - u_n) - \mu(u_n - u_{n-1})$

Vibrations along the Monatomic Chain

$$m \frac{d^2 u_n}{dt^2} = \mu(u_{n+1} - u_n) - \mu(u_n - u_{n-1}) = \mu(u_{n+1} + u_{n-1}) - \mu(2u_n)$$

Waveform Trial Solution: $u_m = u_0 e^{i(kma - \omega t)}$

$$\frac{du_m}{dt} = -i\omega u_0 e^{i(kma - \omega t)}$$

$$\frac{d^2 u_m}{dt^2} = -\omega^2 u_0 e^{i(kma - \omega t)}$$

Where k is wavevector; ω is angular frequency; a the lattice repeat, m is a number for the m^{th} atom, a is lattice repeat and t is time.

$$-m\omega^2 u_0 e^{i(kna - \omega t)} = \mu(u_0 e^{i(k[n+1]a - \omega t)} + u_0 e^{i(k[n-1]a - \omega t)}) - \mu(2u_0 e^{i(kna - \omega t)})$$

$$-m\omega^2 u_0 e^{i(kna - \omega t)} = \mu(u_0 e^{i(kna - \omega t)} e^{ika} + u_0 e^{i(kna - \omega t)} e^{-ika}) - \mu(2u_0 e^{i(kna - \omega t)})$$

Vibrations along the Monatomic Chain

Divide both sides of equation by: $u_n = u_0 e^{i(kna - \omega t)}$

$$-m\omega^2 = \mu(e^{ika} + e^{-ika} - 2)$$

Given that: $e^{ika} = \cos ka + i \sin ka$ (Euler's formula)

$$e^{-ika} = \cos(-ka) + i \sin(-ka) = \cos ka - i \sin ka$$

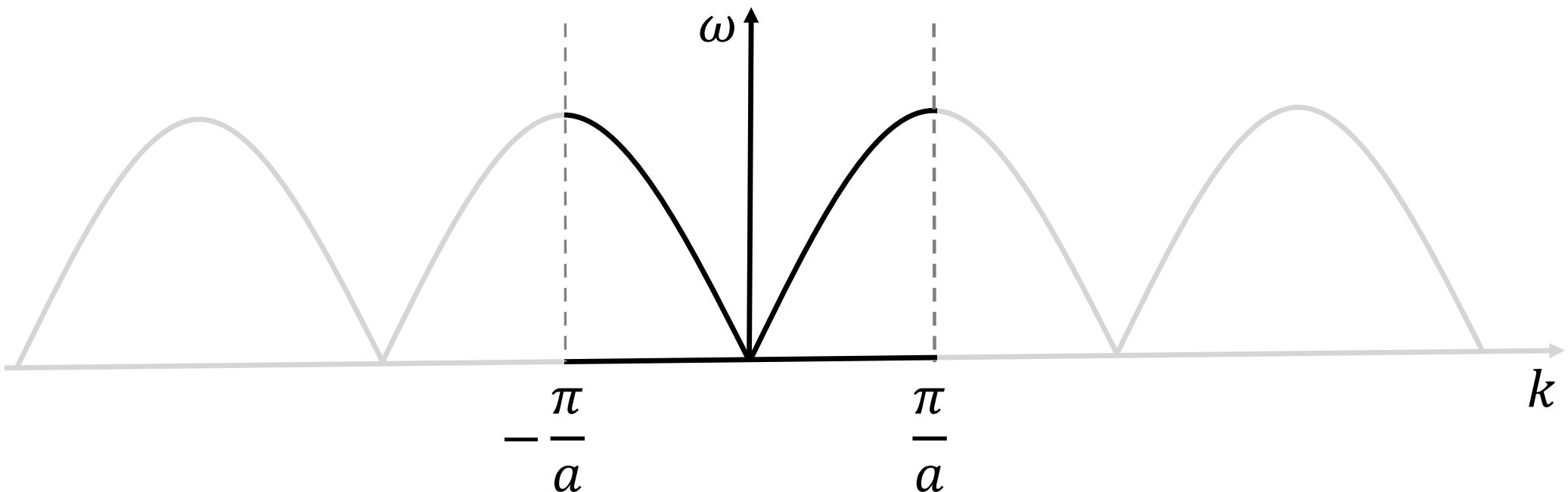
$$-m\omega^2 = 2\mu(\cos ka - 1) \quad \text{Double angle formula: } \cos ka = 1 - 2 \left(\sin \frac{ka}{2} \right)^2$$

$$\omega^2 = \frac{4\mu}{m} \left(\sin \frac{ka}{2} \right)^2$$

OR

$$\omega = 2 \sqrt{\frac{\mu}{m}} \left| \sin \left(\frac{ka}{2} \right) \right|$$

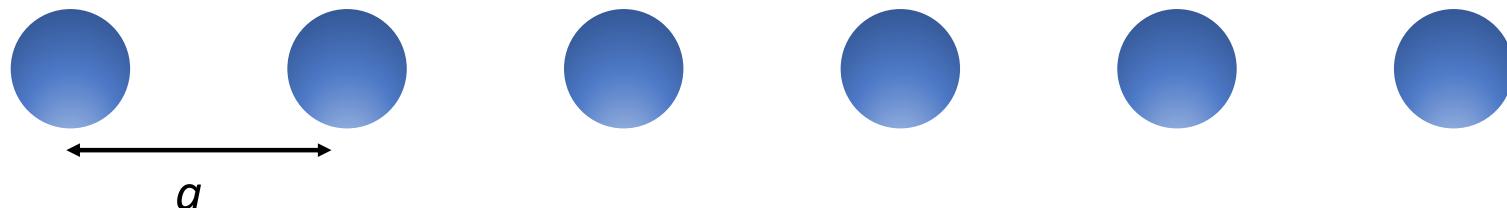
Vibrations along the Monatomic Chain



Periodic function. All vibration frequencies contained within a “unit cell” which extends from $-\pi/a$ to π/a – known as the Brillouin Zone.

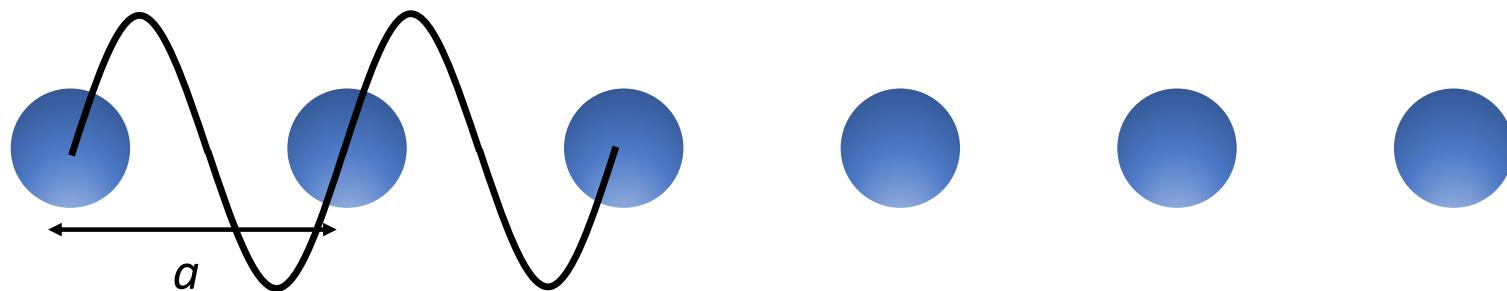
Note that the periodic “lattice” exists in reciprocal space !! – here sometimes refer to it as k-space.

Vibrations in each unit cell of k-space



Infinite wavelength – all atomic motion in phase: $k=0$

What if $k=2\pi/a$?in other words $\lambda=a$



The vibration state at $k+2\pi/a$ in “2nd” Brillouin Zone (or indeed $k+n2\pi/a$) reflects exactly the same atomic motion as k – hence redundant.

Longitudinal and Transverse Modes



Longitudinal: atomic displacements parallel to the wavevector (k)



Transverse: atomic displacements perpendicular to the wavevector (k)

Two transverse modes (in plane perpendicular and out-of-plane perpendicular).

Vibrations along the Monatomic Chain

Velocity of sound in a crystal:

Group velocity (velocity of wavepackets): $\frac{d\omega}{dk}$

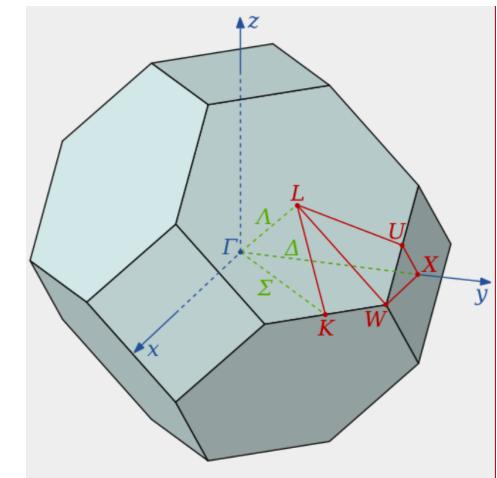
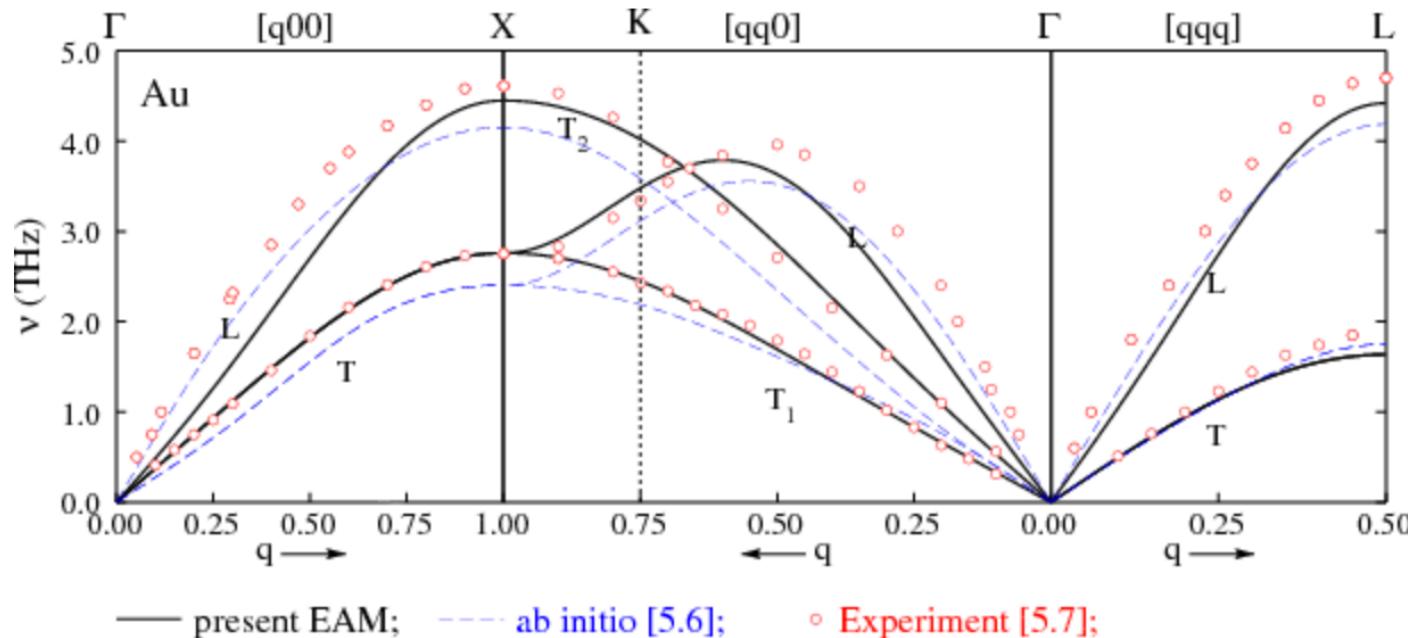
Phase velocity (velocity of individual maxima and minima): $\frac{\omega}{k}$

For the vibrations in the monatomic chain, the group and phase velocity are equal as $k \rightarrow 0$.

This “conventional” behavior of sound results in these vibrations being called “acoustic phonons”

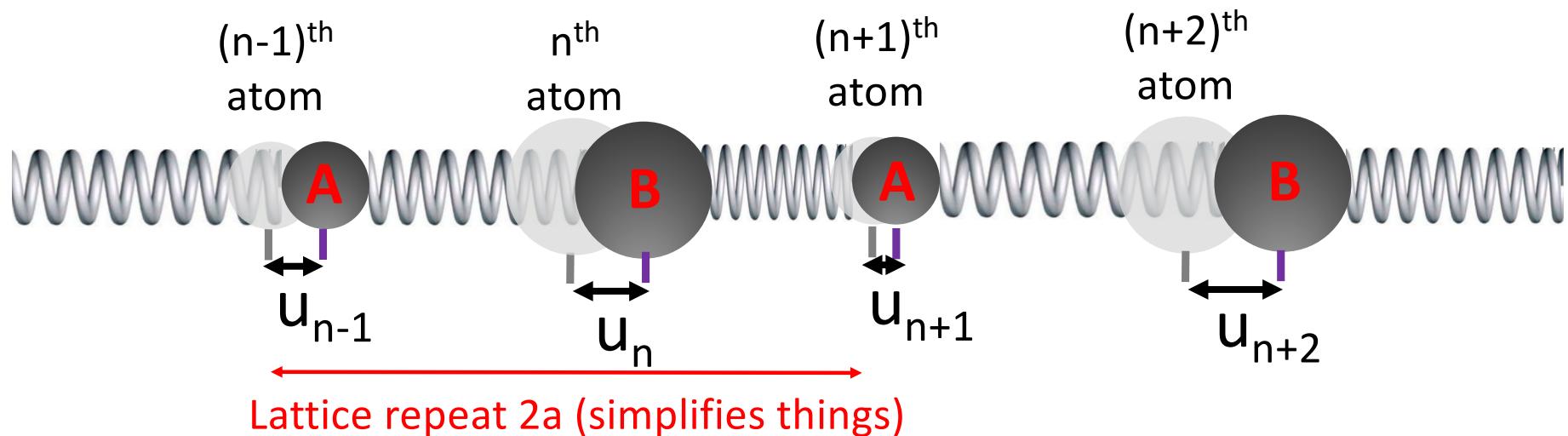
Monatomic Chain: Does it Work?

<https://sites.google.com/site/eampotentials/Au>



Capital (sometimes Greek) Letters indicate “high symmetry points” in the Brillouin Zone: Γ is the Zone Centre; X the Zone Boundary (ZB) along 010; L the ZB along 111; K the ZB along 110. Often “Reduced Wavevector” notation used.

Vibrations along the Diatomic Chain



Two different atomic types (A and B) with different masses (M_A and M_B).

Consider net forces on the n^{th} and $(n+1)^{\text{th}}$ atoms in similar manner as before:

$$n^{\text{th}} \text{ atom: } (1) \quad M_B \frac{d^2 u_n}{dt^2} = \mu(u_{n+1} + u_{n-1} - 2u_n)$$

$$(n+1)^{\text{th}} \text{ atom: } (2) \quad M_A \frac{d^2 u_{n+1}}{dt^2} = \mu(u_{n+2} + u_n - 2u_{n+1})$$

Vibrations along the Diatomic Chain

$$(1) \ M_B \frac{d^2 u_n}{dt^2} = \mu(u_{n+1} + u_{n-1} - 2u_n)$$

$$(2) \ M_A \frac{d^2 u_{n+1}}{dt^2} = \mu(u_{n+2} + u_n - 2u_{n+1})$$

Trial Solutions for u_n and u_{n+1}

$$u_n = u_B e^{i(kna - \omega t)}$$

$$\frac{du_n}{dt} = -i\omega u_B e^{i(kna - \omega t)}$$

$$\frac{d^2 u_n}{dt^2} = -\omega^2 u_B e^{i(kna - \omega t)}$$

$$u_{n+1} = u_A e^{i(k(n+1)a - \omega t)}$$

$$\frac{du_{n+1}}{dt} = -i\omega u_A e^{i(k(n+1)a - \omega t)}$$

$$\frac{d^2 u_{n+1}}{dt^2} = -\omega^2 u_A e^{i(k(n+1)a - \omega t)}$$

Vibrations along the Diatomic Chain

$$(1) \ M_B \frac{d^2 u_n}{dt^2} = \mu(u_{n+1} + u_{n-1} - 2u_n) \quad \text{Using terms from trial solution:}$$

$$-M_B \omega^2 u_B e^{i(kna - \omega t)} = \mu(u_A e^{i(k(n+1)a - \omega t)} + u_A e^{i(k(n-1)a - \omega t)} - 2u_B e^{i(kna - \omega t)})$$

$$-M_B \omega^2 u_B e^{i(kna - \omega t)} = \mu(u_A e^{i(kna - \omega t)} e^{ika} + u_A e^{i(kna - \omega t)} e^{-ika} - 2u_B e^{i(kna - \omega t)})$$

Cancelling terms in $e^{i(kna - \omega t)}$

$$-M_B \omega^2 u_B = \mu(u_A e^{ika} + u_A e^{-ika} - 2u_B)$$

Hence:

$$(2\mu - M_B \omega^2)u_B = \mu u_A (e^{ika} + e^{-ika}) = (2\mu \cos ka)u_A$$

$$\text{Or: } (M_B \omega^2 - 2\mu)u_B + (2\mu \cos ka)u_A = 0$$

Vibrations along the Diatomic Chain

(2) $M_A \frac{d^2 u_{n+1}}{dt^2} = \mu(u_{n+2} + u_n - 2u_{n+1})$ Using terms from trial solution:

$$-M_A \omega^2 u_A e^{i(k(n+1)a - \omega t)} = \mu(u_B e^{i(k(n+2)a - \omega t)} + u_B e^{i(kna - \omega t)} - 2u_A e^{i(k(n+1)a - \omega t)})$$

$$-M_A \omega^2 u_A e^{i(k(n+1)a - \omega t)} = \mu \begin{pmatrix} u_B e^{i(k(n+1)a - \omega t)} e^{ika} + u_B e^{i(k(n+1)a - \omega t)} e^{-ika} \\ -2u_A e^{i(k(n+1)a - \omega t)} \end{pmatrix}$$

Cancelling terms in $e^{i(k(n+1)a - \omega t)}$

$$-M_A \omega^2 u_A = \mu \begin{pmatrix} u_B e^{ika} + u_B e^{-ika} \\ -2u_A \end{pmatrix}$$

$$(M_A \omega^2 - 2\mu)u_A + (2\mu \cos ka)u_B = 0$$

Vibrations along the Diatomic Chain

Now simultaneous equations have the form:

$$(1) \quad (2\mu \cos ka)u_A + (M_B \omega^2 - 2\mu)u_B = 0$$

$$(2) \quad (M_A \omega^2 - 2\mu)u_A + (2\mu \cos ka)u_B = 0$$

So following matrix statement is true:

$$\begin{pmatrix} (2\mu \cos ka) & (M_B \omega^2 - 2\mu) \\ (M_A \omega^2 - 2\mu) & (2\mu \cos ka) \end{pmatrix} \cdot \begin{pmatrix} u_A \\ u_B \end{pmatrix} = 0$$


 M

True if determinant of M is zero: i.e. $(2\mu \cos ka)^2 - [(M_B \omega^2 - 2\mu)(M_A \omega^2 - 2\mu)] = 0$

Vibrations along the Diatomic Chain

$$(2\mu \cos ka)^2 - [(M_B \omega^2 - 2\mu)(M_A \omega^2 - 2\mu)] = 0$$

Expanding gives quartic function in ω , or quadratic in ω^2

$$M_A M_B \omega^4 - 2\mu(M_A + M_B)\omega^2 + 4\mu^2[1 - (\cos ka)^2] = 0$$

$$\omega^2 = \frac{\mu(M_A + M_B)}{M_A M_B} \pm \frac{\sqrt{4\mu^2(M_A + M_B)^2 - 16\mu^2 M_A M_B (\sin ka)^2}}{2M_A M_B}$$

$$\omega^2 = \frac{\mu(M_A + M_B)}{M_A M_B} \pm \frac{\mu\sqrt{(M_A + M_B)^2 - 4M_A M_B (\sin ka)^2}}{M_A M_B}$$

Vibrations along the Diatomic Chain

Several points:

Since it is a quadratic, there are two distinct solutions in the relationship between ω and k

When considering the solution where the two terms are subtracted:

As $k \rightarrow 0, \sin ka \rightarrow 0$

$$\omega^2 \rightarrow \frac{\mu(M_A + M_B)}{M_A M_B} - \frac{\mu(M_A + M_B)}{M_A M_B} = 0$$

and when $k = \frac{\pi}{2a}, \omega^2$ is at a maximum; conversely, when $k = \frac{\pi}{a}, \omega^2$ is zero once more.

Hence it is a periodic function similar to the acoustic phonon mode in the monatomic chain.

Vibrations along the Diatomic Chain

Considering the solution where the two terms are added:

As $k \rightarrow 0, \sin ka \rightarrow 0$

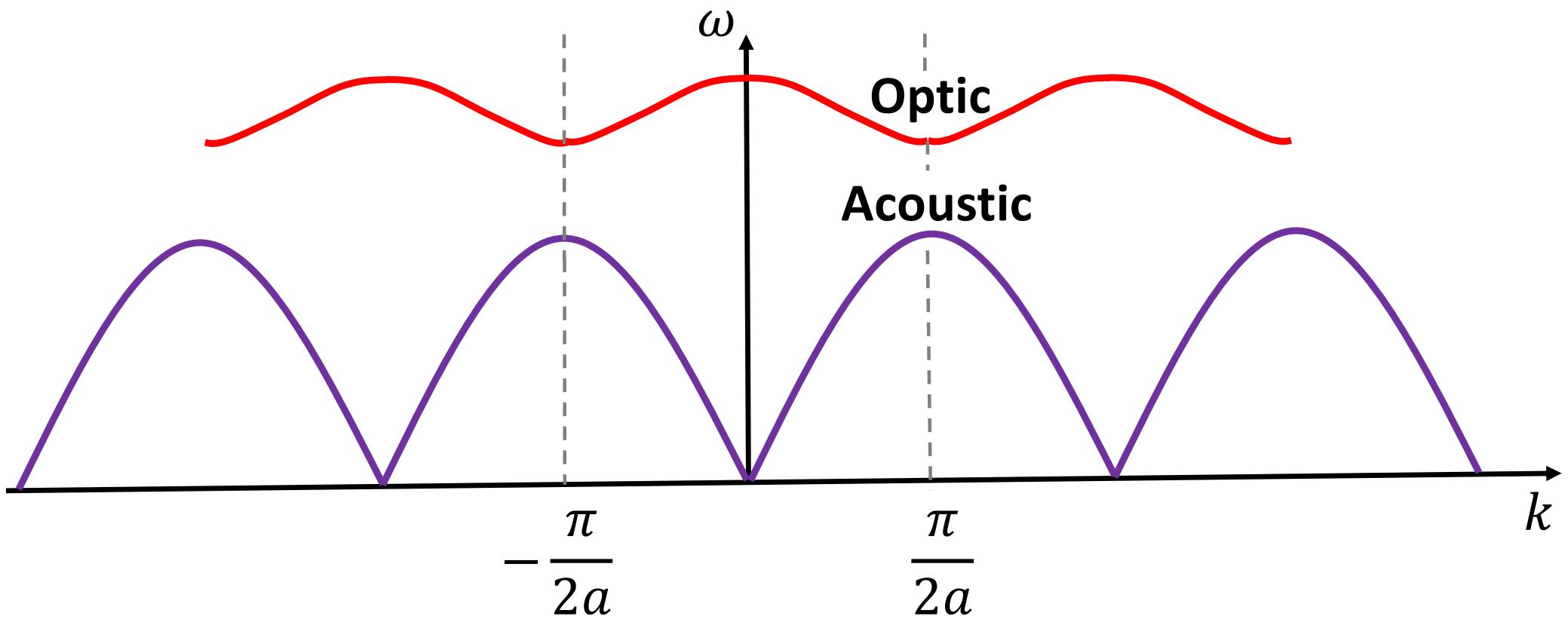
$$\omega^2 = \frac{\mu(M_A + M_B)}{M_A M_B} + \frac{\mu(M_A + M_B)}{M_A M_B} = \frac{2\mu(M_A + M_B)}{M_A M_B}$$

when $k = \frac{\pi}{2a}, \sin ka = 1$

ω^2 decreases by relatively small amount of $\frac{2\mu\sqrt{M_A M_B}}{M_A M_B}$

Hence it is a different periodic function NOT found in the monatomic chain.

Vibrations along the Diatomic Chain



Diatomeric Chain: at Zone Boundary

At boundary of Brillouin Zone: $k = \frac{\pi}{2a}$, $\sin ka = 1$

$$\omega^2 = \frac{\mu(M_A + M_B)}{M_A M_B} \pm \frac{\mu\sqrt{(M_A + M_B)^2 - 4M_A M_B}}{M_A M_B}$$

$$\omega^2 = \frac{\mu(M_A + M_B)}{M_A M_B} \pm \frac{\mu\sqrt{M_A^2 + M_B^2 - 2M_A M_B}}{M_A M_B} = \frac{\mu(M_A + M_B)}{M_A M_B} \pm \frac{\mu(M_A - M_B)}{M_A M_B}$$

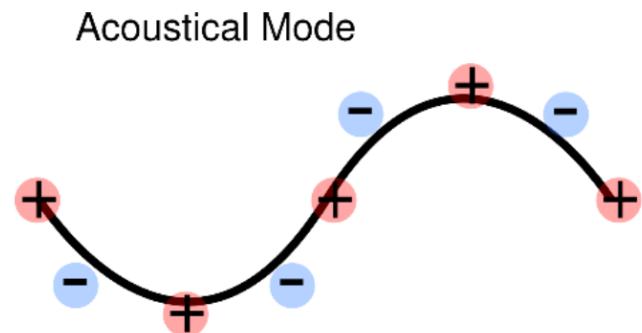
Optic Mode:

$$\omega^2 = \frac{\mu(M_A + M_B)}{M_A M_B} + \frac{\mu(M_A - M_B)}{M_A M_B} = \frac{2\mu}{M_B}$$

Acoustic Mode:

$$\omega^2 = \frac{\mu(M_A + M_B)}{M_A M_B} - \frac{\mu(M_A - M_B)}{M_A M_B} = \frac{2\mu}{M_A}$$

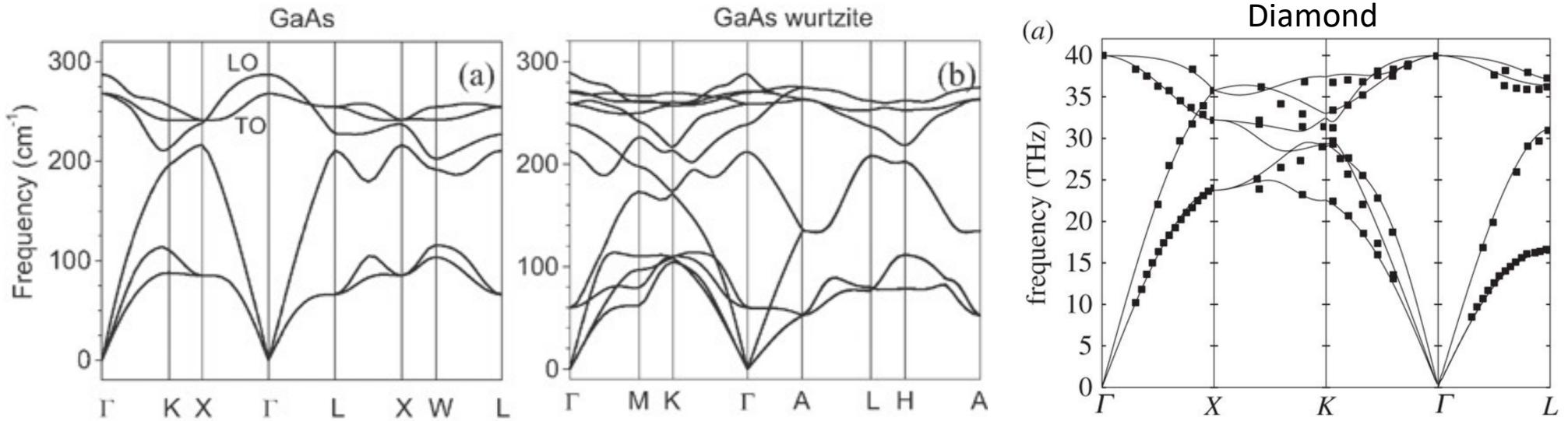
Significant Real Space Difference between Optic and Acoustic Vibrations



In acoustic modes in the diatomic chain, the phase of the motion of individual atoms is independent of the atomic type.

In optic modes in the diatomic chain, the phases of the motions of individual atoms is opposite for the two different atomic types. If the two atoms are cations and anions, then the vibration would be that associated with a propagating ac electric field – like light ! Hence these are called “optic” modes.

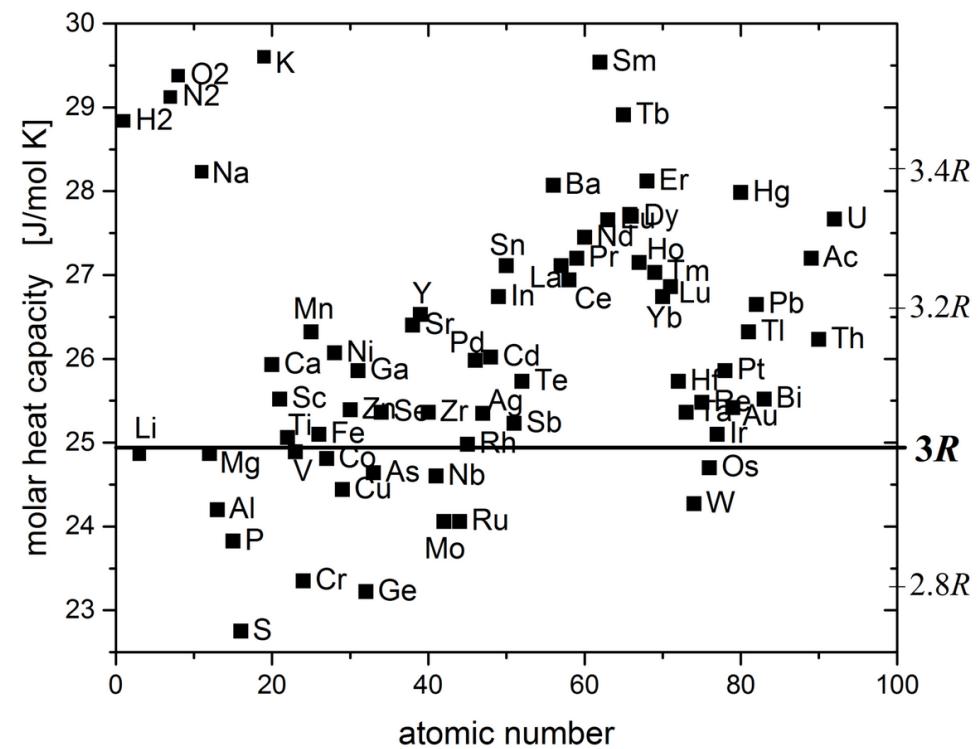
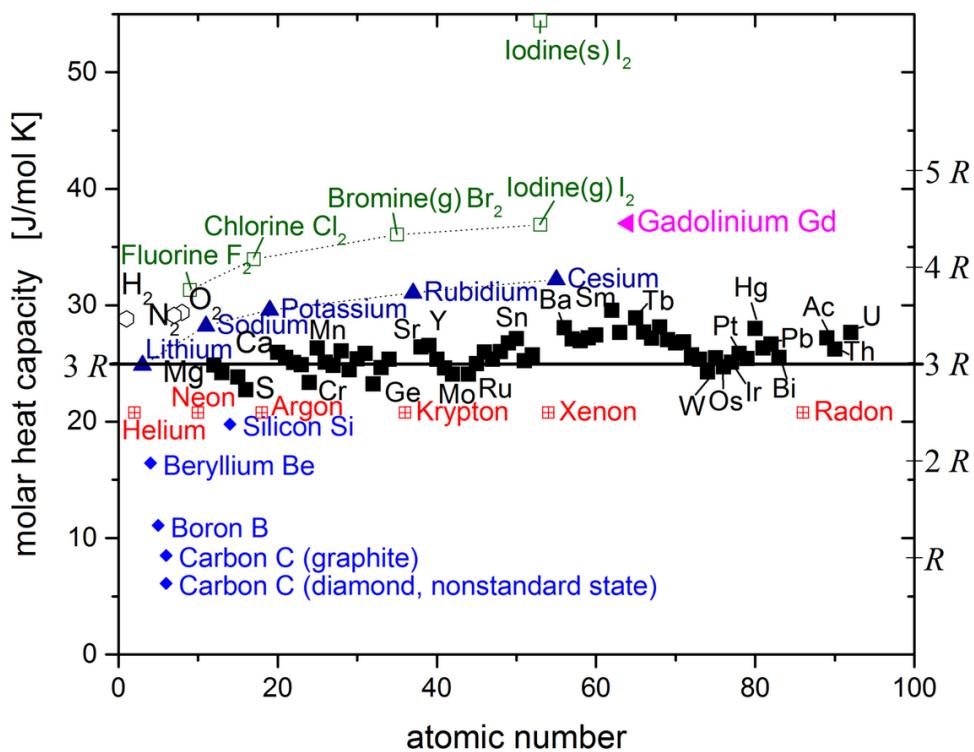
Experimental Diatomic Vibration Dispersion Curves



Diatom systems give optic as well as acoustic modes. Worryingly diamond (above right) also shows optic modes, despite being monatomic (carbon atoms only). In this case though, the lattice is primitive and still has two atoms in the motif (two atoms are in non-identical crystallographic positions).

Phonons and the Heat Capacity: Dulong and Petit (1819)

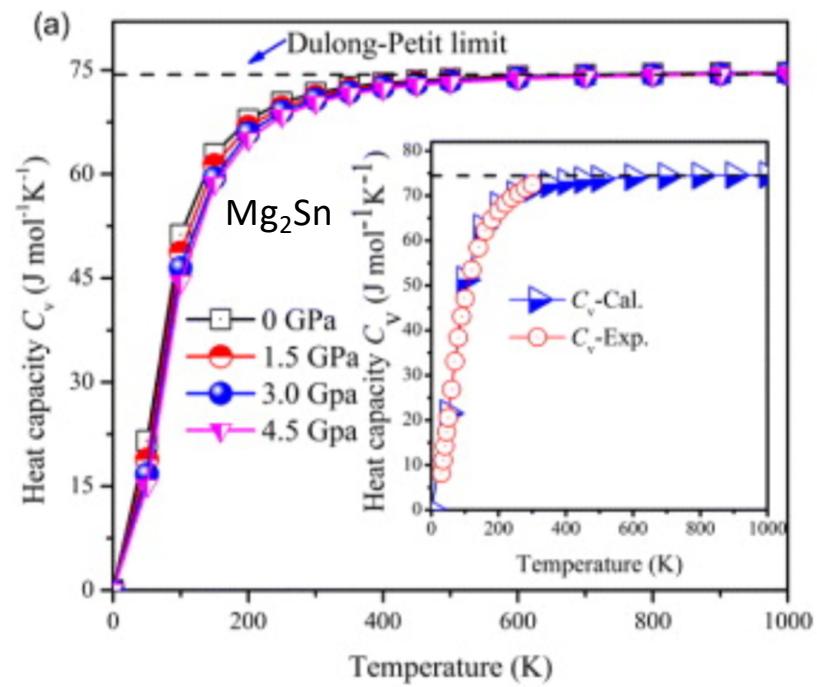
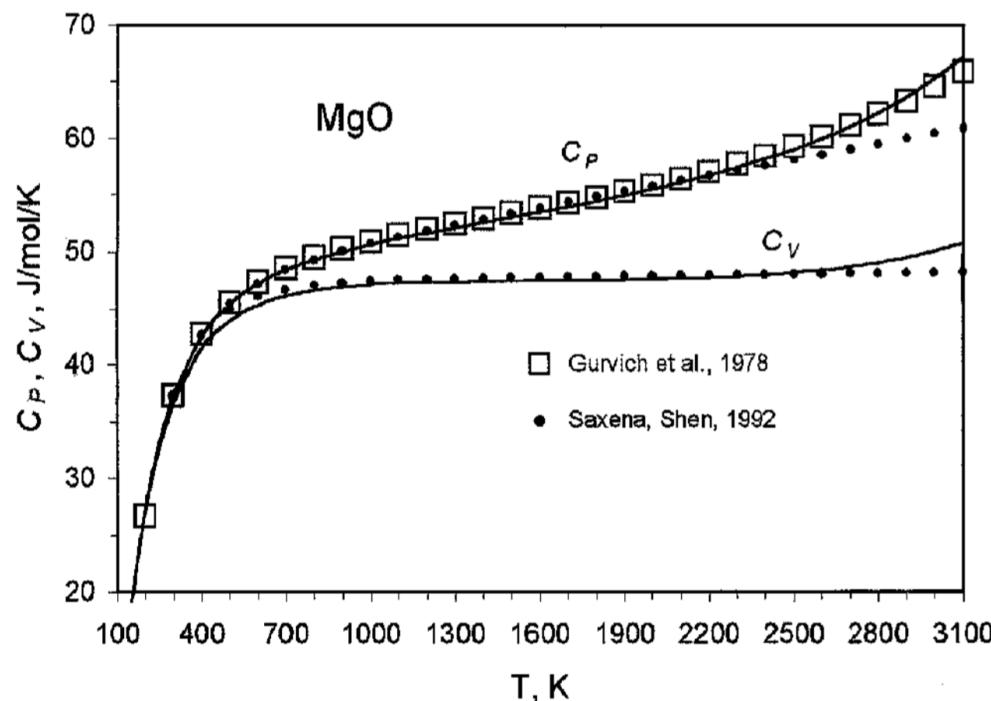
Heat capacity per mole at room temperature seems to have a value of about three times the gas constant for all elements. Experimental report made by Dulong and Petit.



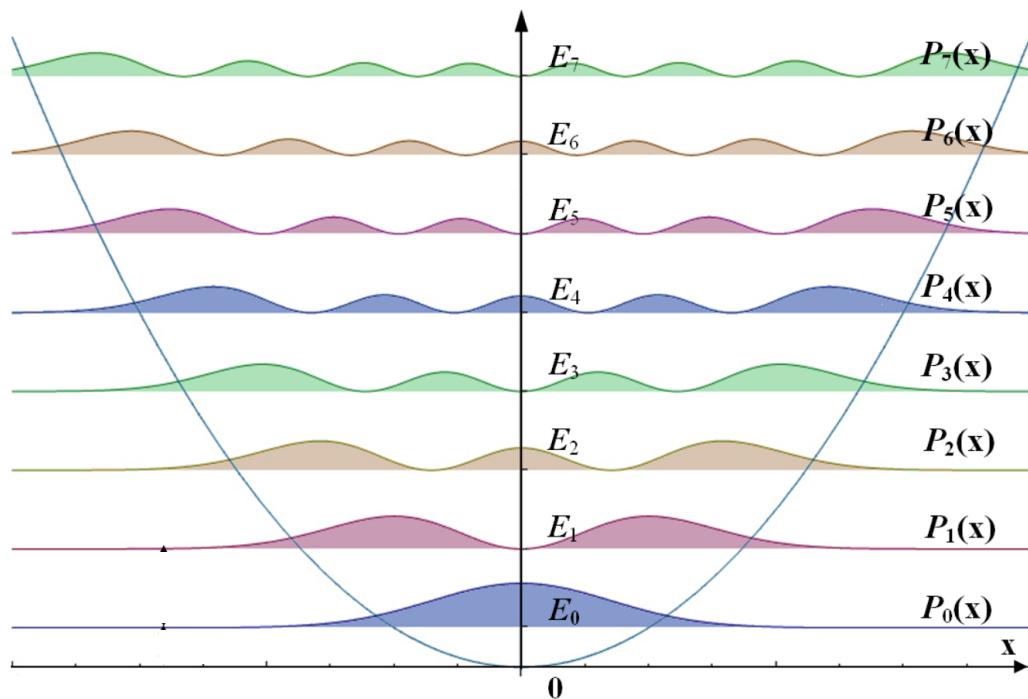
Phonons and the Heat Capacity: Dulong and Petit (1819)

While true for most elements at high temperatures, the Dulong-Petit observation fails as temperatures are reduced.

Given the importance of heat capacity as a window into internal energy, entropy and free energy (and hence phase transitions), need more physical insight than offered by Dulong-Petit.



Quantum Approach to Phonons



So far used classical “ball and spring” model for behaviour in the interatomic potential well (assumed to be parabolic).

Now develop quantum solutions to associated energy states (assume atoms possess wavefunctions which require a quantum, rather than classical treatment).

Revision of Schrodinger (for electrons in this case)

An obvious statement is that the total energy of an atom (E) can be represented as the sum of its kinetic (KE) and potential (PE) energies:

$$E = KE + PE = \frac{p^2}{2m} + U \quad (13)$$

where the atom momentum is p and its mass is m .

Revision of Schrodinger

Since, for a wave, $p = \frac{h}{\lambda} = \hbar k$ and hence $k = \frac{p}{\hbar}$ (where \hbar is Planck's constant, λ is the wavelength, \hbar Planck's constant divided by 2π and k is the wave-vector) equation (16) can be expressed as:

$$\frac{d^2\psi}{dx^2} = -\frac{p^2}{\hbar^2}\psi \text{ or}$$
$$-\hbar^2 \frac{d^2\psi}{dx^2} = p^2\psi \quad (17)$$

Quantum Approach to Phonons

1D Time-independent Schrodinger Equation: $(U - E)\psi = \frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2}$

Use harmonic potential well for U and spring constant μ : $\left(\frac{1}{2}\mu x^2 - E\right)\psi = \frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2}$

Trial Solution: $\psi = Ae^{-\frac{\alpha x^2}{2}}$

$$\frac{d\psi}{dx} = -\alpha x A e^{-\frac{\alpha x^2}{2}}$$
$$\frac{d^2\psi}{dx^2} = (\alpha^2 x^2 - \alpha) A e^{-\frac{\alpha x^2}{2}} = (\alpha^2 x^2 - \alpha)\psi$$

Quantum Approach to Phonons

Substitution of trial solution: $\left(\frac{1}{2}\mu x^2 - E\right)\psi = \frac{\hbar^2}{2m}(\alpha^2 x^2 - \alpha)\psi$

Rearranging and gathering terms in x^2 :

$$x^2 \left(\underbrace{\frac{\hbar^2 \alpha^2}{2m} - \frac{1}{2} \mu}_{0} \right) \psi + \left(E - \underbrace{\frac{\alpha \hbar^2}{2m}}_{0} \right) \psi = 0$$

Generally true only if both terms in brackets are zero:

$$\frac{\hbar^2 \alpha^2}{2m} - \frac{1}{2} \mu = 0 \text{ hence } \alpha^2 = \frac{\mu m}{\hbar^2} = \frac{\omega^2 m^2}{\hbar^2}$$

Using harmonic oscillation relation: $\omega^2 = \frac{\mu}{m}$ $\alpha = \frac{\omega m}{\hbar}$

$$E = \frac{\omega m \hbar^2}{2m \hbar} = \frac{\hbar \omega}{2}$$

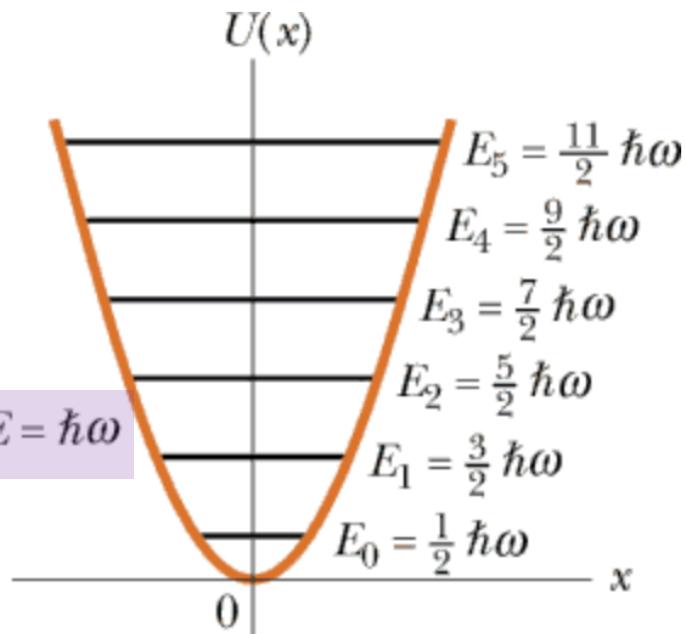
This is the **GROUND STATE** solution

Quantum Approach to Phonons

General Solution, including excited states is: $E_n = \left(n + \frac{1}{2}\right) \hbar\omega$

Important statement

$$\Delta E = \hbar\omega$$



Quantum Approach to Phonons: Mean Quantum No.

Given Boltzmann probability behaviour, the ratio of the number of quantum oscillators (N) at state ($n+1$) to that at n can be given as follows:

$$\frac{N_{n+1}}{N_n} = \frac{e^{-\frac{(n+1)\hbar\omega}{kT}}}{e^{-\frac{n\hbar\omega}{kT}}} = \frac{e^{-\frac{n\hbar\omega}{kT}} \cdot e^{\frac{\hbar\omega}{kT}}}{e^{-\frac{n\hbar\omega}{kT}}} = e^{\frac{\hbar\omega}{kT}}$$

The fraction of all of the quantum oscillators in the n^{th} state is:

$$\frac{N_n}{\sum_{s=0}^{\infty} N_s} = \frac{e^{-\frac{n\hbar\omega}{kT}}}{\sum_{s=0}^{\infty} e^{-\frac{s\hbar\omega}{kT}}}$$

Quantum Approach to Phonons: Mean Quantum No.

Average “quantum number” (n where energy state is E_n): $\langle n \rangle = \frac{\sum_s s e^{-\frac{s\hbar\omega}{kT}}}{\sum_s e^{-\frac{s\hbar\omega}{kT}}}$

Let $x = e^{-\frac{\hbar\omega}{kT}}$, then $e^{-\frac{s\hbar\omega}{kT}} = x^s$

Since $x < 1$ $\sum_s [x]^s = \frac{1}{1-x}$ (sum to infinity of a geometric series)

Rather neatly: $\sum_s s[x]^s = x \frac{d}{dx} \left(\sum_s [x]^s \right) = \frac{x}{(1-x)^2}$

Multiply through by: $\frac{e^{\frac{\hbar\omega}{kT}}}{e^{\frac{\hbar\omega}{kT}}}$

$$\langle n \rangle = \frac{\sum_s s[x]^s}{\sum_s [x]^s} = \frac{x}{(1-x)^2} \cdot (1-x) = \frac{x}{(1-x)} = \frac{e^{\frac{\hbar\omega}{kT}}}{1 - e^{\frac{\hbar\omega}{kT}}}$$

$$\langle n \rangle = \frac{1}{e^{\frac{\hbar\omega}{kT}} - 1}$$

Quantum Approach to Phonons: Mean Quantum No.

$$\sum_s [x]^s = 1 + x + x^2 + x^3 + \dots = \frac{1}{1-x} \quad (\text{sum to infinity of a geometric series})$$

$$\frac{d}{dx} \left(\sum_s [x]^s \right) = \sum_s \frac{d}{dx} [x]^s = \underbrace{0 + 1 + 2x + 3x^2 + 4x^3 + \dots}_{\text{Multiplied by "x" from above}} = \frac{d}{dx} \frac{1}{(1-x)} = \frac{1}{(1-x)^2}$$

$$x \frac{d}{dx} \left(\sum_s [x]^s \right) = 0 + x + 2x^2 + 3x^3 + 4x^4 + \dots = \frac{x}{(1-x)^2} = \sum_s s[x]^s$$

$$\langle n \rangle = \frac{\sum_s s[x]^s}{\sum_s [x]^s} = \frac{x}{(1-x)^2} \cdot (1-x) = \frac{x}{(1-x)} = \frac{e^{\frac{\hbar\omega}{kT}}}{1 - e^{\frac{\hbar\omega}{kT}}}$$

Einstein's Approach to Heat Capacity

- N harmonic oscillators (quantum behaviour);
- Each oscillator supports 3 modes (two transverse and one longitudinal in 1D chain);
- Entire system behaves as if all vibration modes had the mean quantum number.

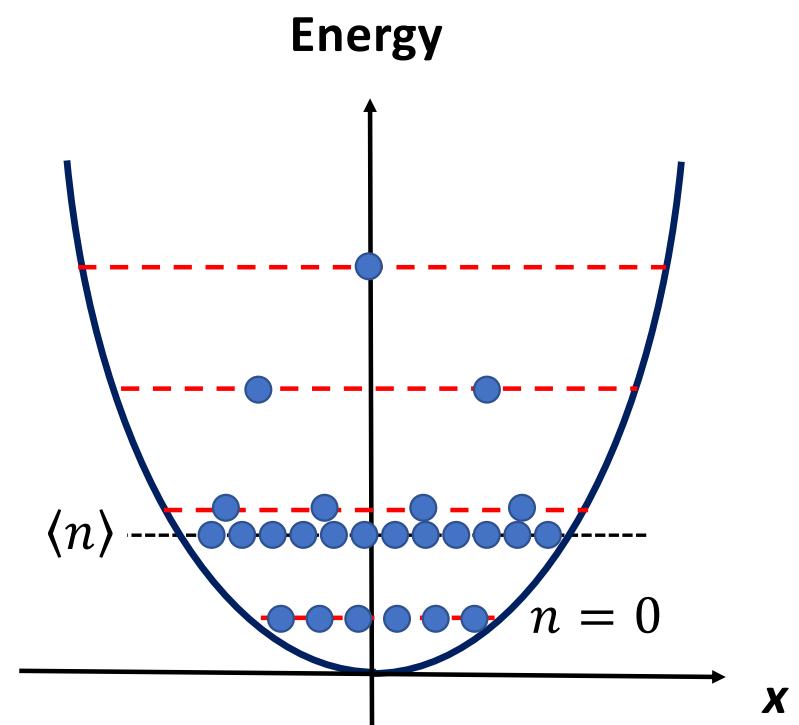
Internal Energy developed during heating

$$U = 3N\langle n \rangle \hbar\omega$$

Number of oscillator modes

Mean quantum number above ground state.

Additional energy above ground state per quantum number



Einstein's Approach to Heat Capacity

$$U = 3N\langle n \rangle \hbar\omega$$

Substituting for $\langle n \rangle$:
$$U = \frac{3N\hbar\omega}{e^{\frac{\hbar\omega}{kT}} - 1}$$

Remembering: $C_v = \frac{dU}{dT}$

and that: $\frac{d}{dx} e^{f(x)} = e^{f(x)} f'(x)$ then:
$$\frac{dU}{dT} = -3N\hbar\omega \left(e^{\frac{\hbar\omega}{kT}} - 1 \right)^{-2} \cdot \frac{d}{dT} e^{\frac{\hbar\omega}{kT}}$$

$$= -3N\hbar\omega \left(e^{\frac{\hbar\omega}{kT}} - 1 \right)^{-2} \cdot \left(-\frac{\hbar\omega}{k} \right) T^{-2} e^{\frac{\hbar\omega}{kT}} = 3Nk \left(\frac{\hbar\omega}{kT} \right)^2 \frac{e^{\frac{\hbar\omega}{kT}}}{\left(e^{\frac{\hbar\omega}{kT}} - 1 \right)^2}$$

Let Einstein Temperature
(Θ_E) be:

$$\Theta_E = \frac{\hbar\omega}{k}$$

$$C_v = 3Nk \left(\frac{\Theta_E}{T} \right)^2 \frac{e^{\frac{\Theta_E}{T}}}{\left(e^{\frac{\Theta_E}{T}} - 1 \right)^2}$$

Einstein's Approach to Heat Capacity

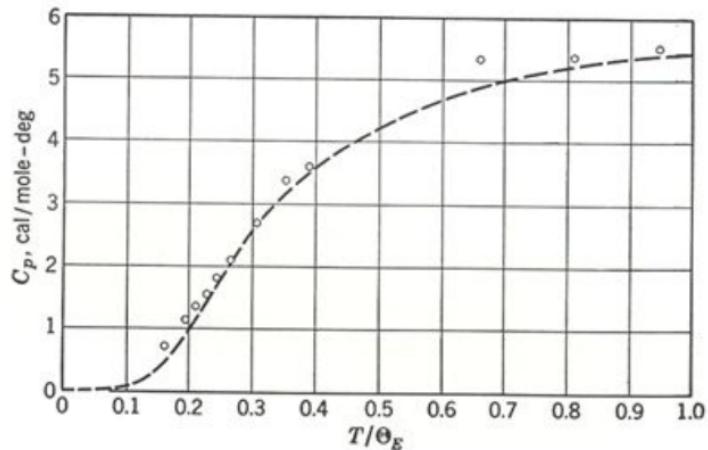


Fig. 6.2. Comparison of experimental values of the heat capacity of diamond and values calculated on the Einstein model, using $\Theta_E = 1320^\circ\text{K}$. [After A. Einstein, Ann. Physik **22**, 180 (1907).]

Temperature
Heat Capacity
Einstein Model
Comparison
Experimental Data
Calculated Curve

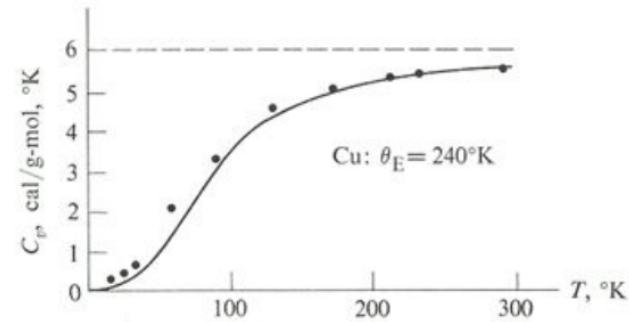


Fig. 3.10 Specific heat of copper versus temperature. The dots represent experimental values, and the curve is given by the Einstein expression.

Einstein Model works very well: $T \rightarrow 0; C_v \rightarrow 0$

$T \rightarrow \infty; C_v \rightarrow 3Nk = 3R$ if $N = N_A$

(compare with Dulong-Petit measurements)

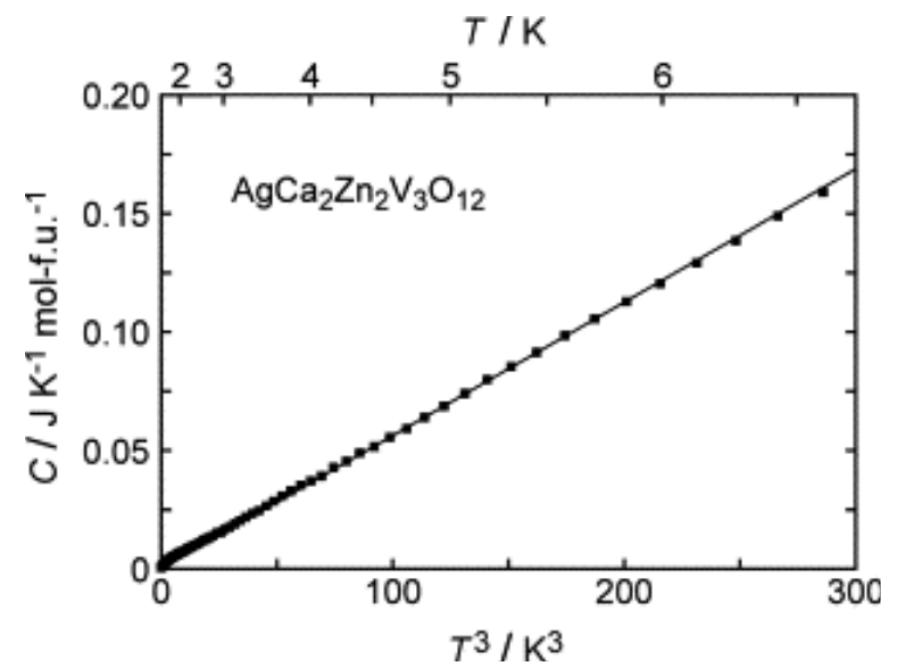
Einstein's Approach to Heat Capacity

Einstein Model: slight disagreement with experimental data at low temperatures, where C_v known to vary with T^3 , but predicted by Einstein to vary as $e^{-\frac{\hbar\omega}{kT}}$.

Einstein missed a key conceptual element in modelling of heat capacity.....

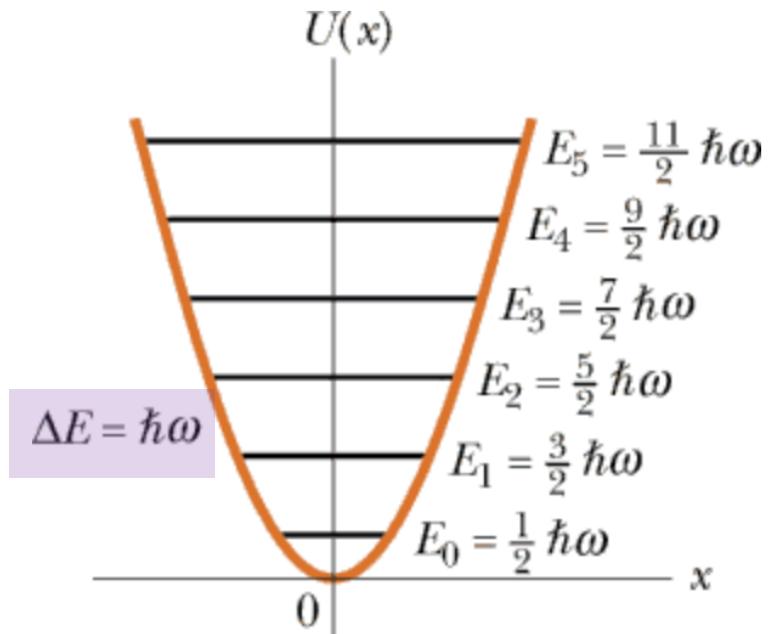
The DENSITY of STATES

Probability of each quantum oscillator state (of energy above ground state of $n\hbar\omega$) is given by Boltzmann statistics weighted by the number density of that state compared to other states.

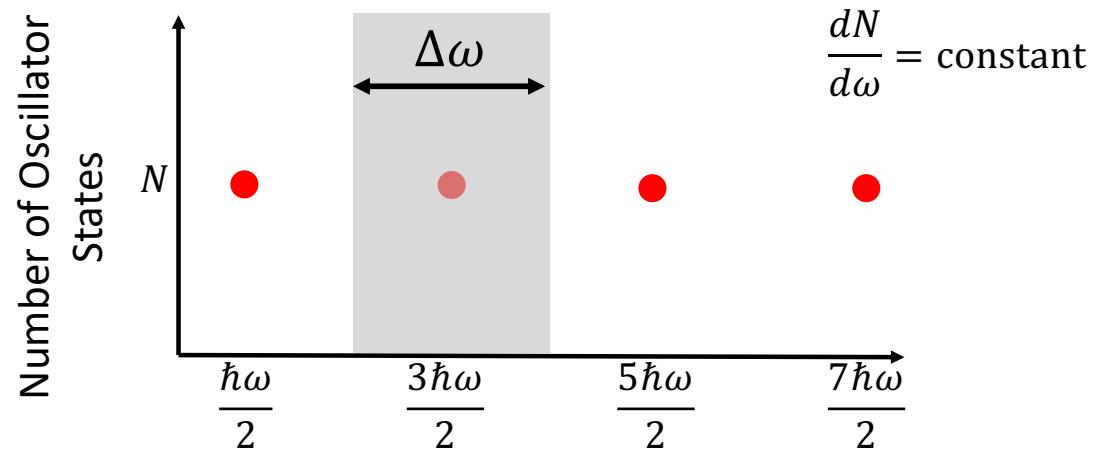


Density of States in 1D

General Solution, including excited states is: $E_n = \left(n + \frac{1}{2}\right) \hbar\omega$

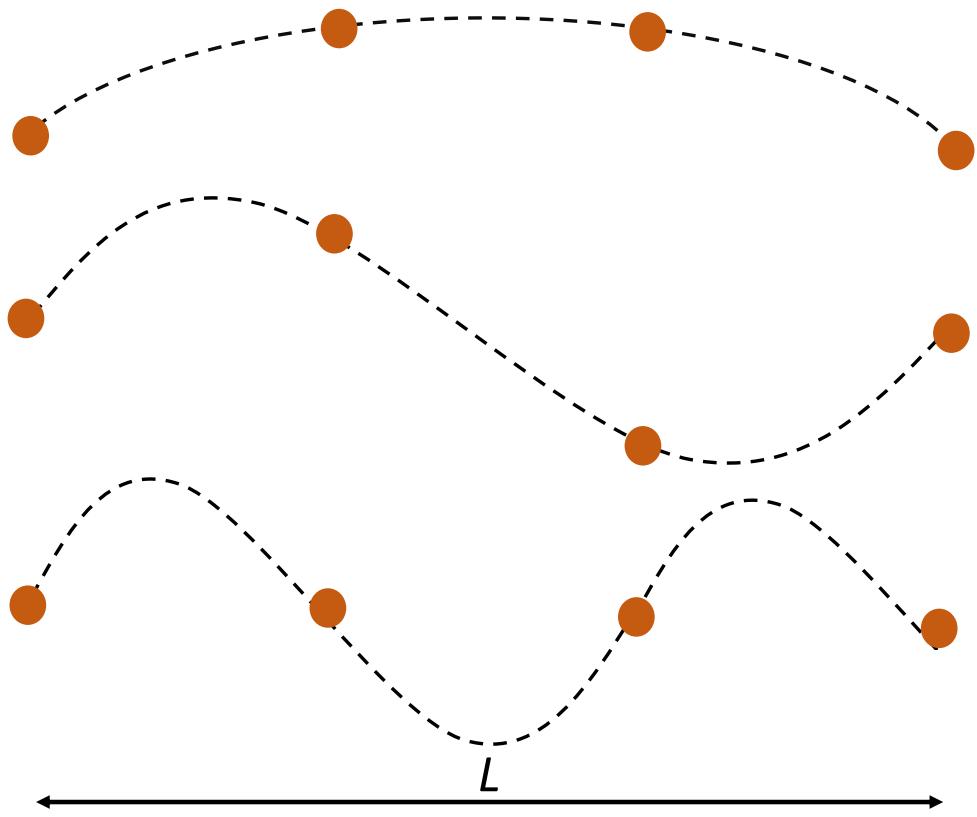


This set of wavefunction solutions (for the parabolic approximation to the interatomic potential well – The Harmonic Approximation) in 1D gives states that are evenly distributed in energy.



Density of States: uniform density of wavevectors

Allowed wavevectors have uniform distribution in k-space: consider balls and springs again and the standing modes that can exist:

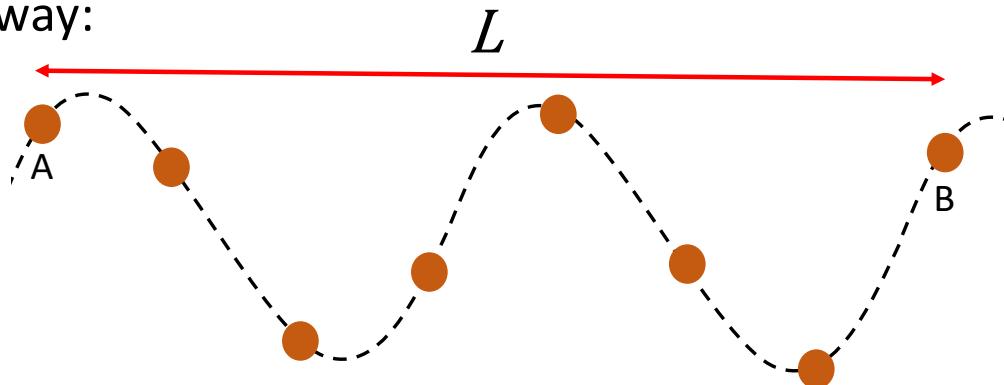


$$\begin{aligned}\lambda &= 2L & k &= \frac{2\pi}{2L} = \frac{\pi}{L} \\ \lambda &= L & k &= \frac{2\pi}{L} = 2\frac{\pi}{L} \\ \lambda &= \frac{2L}{3} & k &= \frac{6\pi}{2L} = 3\frac{\pi}{L}\end{aligned}$$

One mode every
 $\Delta k = \frac{\pi}{L}$.
Uniform
wavevector
density = $\frac{L}{\pi}$

Density of States: periodic boundary conditions

More realistic approach than standing waves: use “periodic boundary conditions” where the displacement of the first atom in the chain must be the same as another one a number of lattice vectors away:



At atom “A” (the n^{th} atom) wave displacement: $= A_0 e^{i(kna - wt)}$

At atom “B” (the $(n+7)^{\text{th}}$ atom in this case) wave displacement: $= A_0 e^{i(k[na+L] - wt)}$

Under periodic boundary condition, these displacement functions are the same:

$$A_0 e^{i(k[na+L] - wt)} - A_0 e^{i(kna - wt)} = 0$$

$$\text{Divide through by } A_0 e^{i(kna - wt)}: \quad e^{ikL} = 1 \quad \text{Solutions: } k = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \pm \frac{6\pi}{L}, \dots$$

Density of States in 1D: influence of the dispersion curves

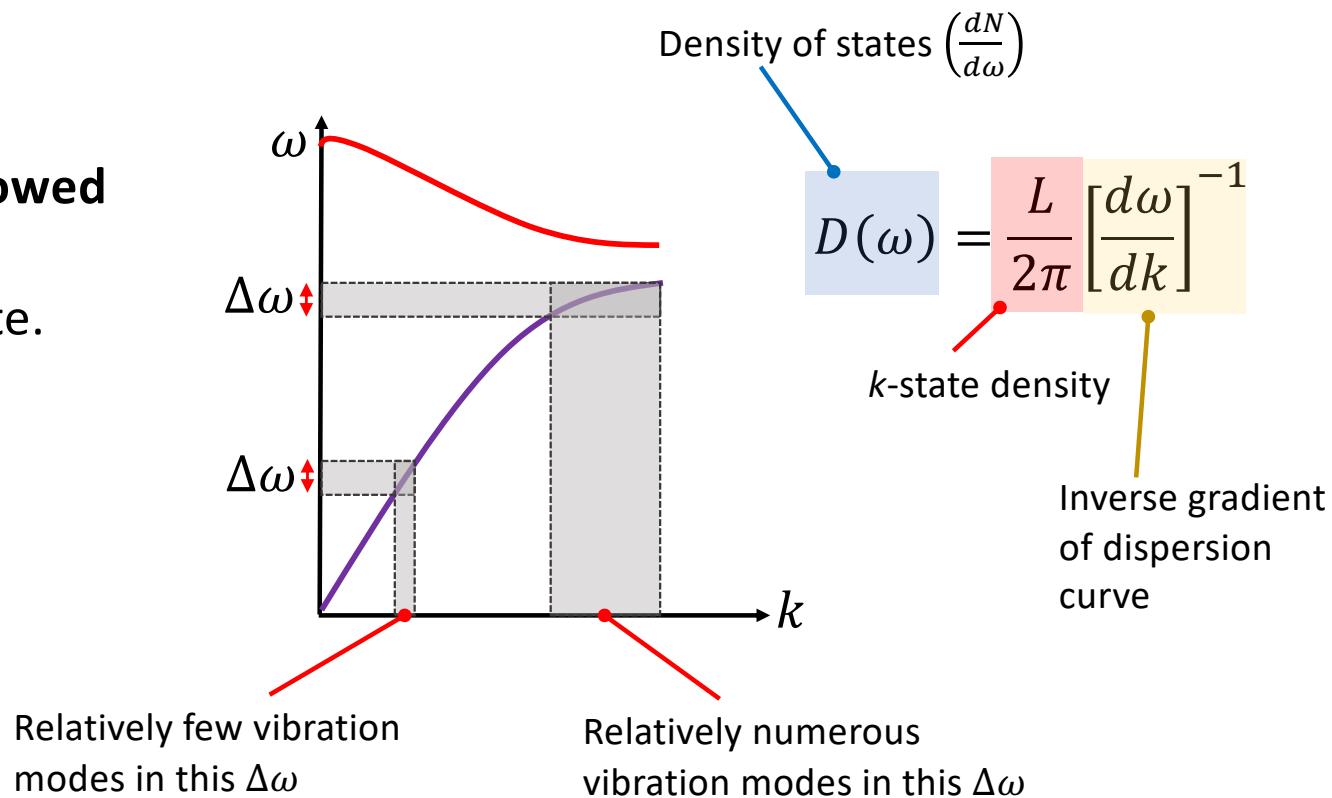
$$k = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \pm \frac{6\pi}{L} \dots \dots$$

Still means evenly distributed allowed wavevectors.

Each wavevector is a vibration state.

In other words $dN \propto dk$

BUT is $dk \propto d\omega$ and hence $\frac{dN}{d\omega}$ a constant? NO – remember 1D atomic chain dispersion relations:



Density of States from Experimental Dispersion Curves

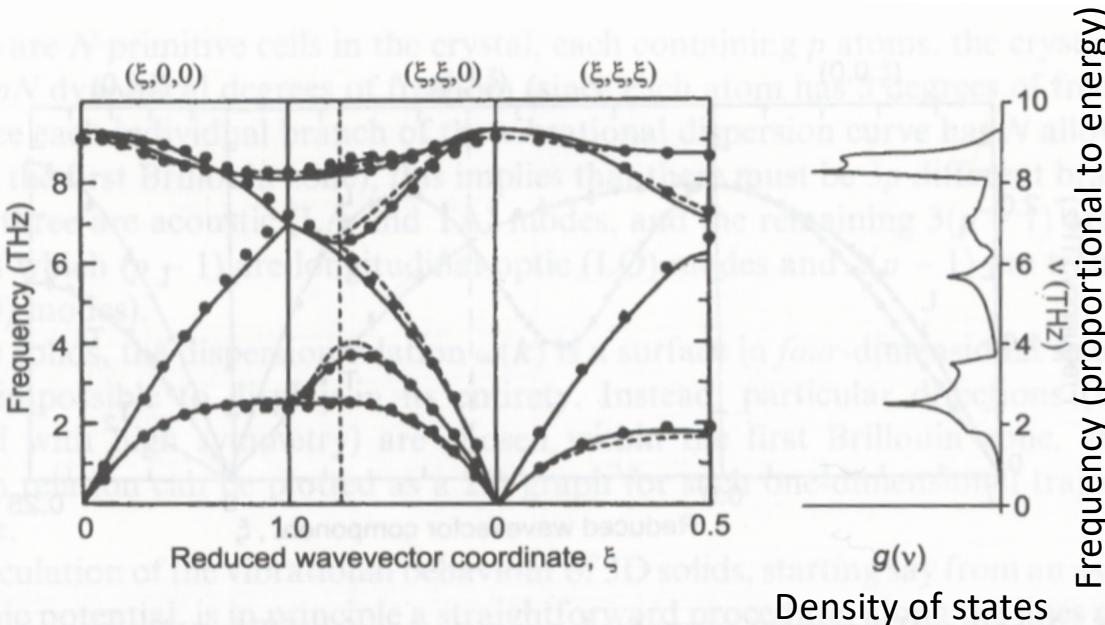
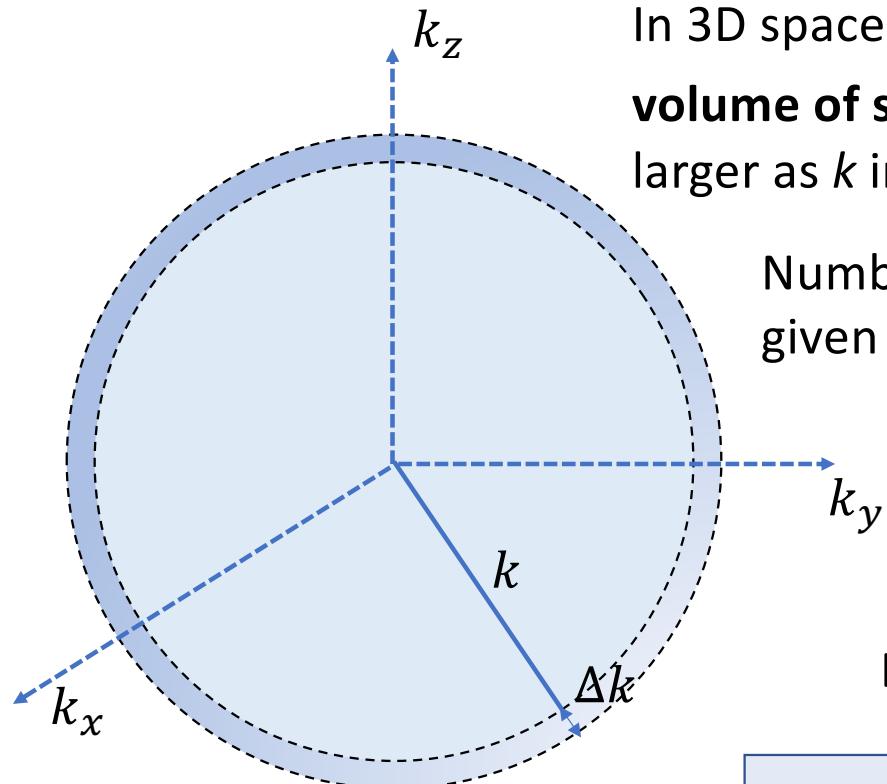


Fig. 4.17 Vibrational dispersion curves for Ge: the points are experimental data and the lines are calculated curves for the bond-charge model, where a covalent bond is modelled by positioning charges at the mid-bond sites. Note the degeneracy of the transverse modes in high-symmetry directions ($(\xi, 0, 0)$ and (ξ, ξ, ξ)) and the absence of an LO–TO splitting at $k = 0$ (Reprinted with permission from Weber (1977), *Phys. Rev. B* **15**, 4789. © 1977. The American Physical Society). Also shown is the corresponding density of states.

Density of States in 3D (rather than 1D)



In 3D space, number of k -states per unit volume is $\left(\frac{L}{2\pi}\right)^3$, BUT the **volume of space**, associated with progressive increases in k , gets larger as k increases:

Number of vibration modes (ΔN) in a given Δk range:

$$\Delta N = \text{Volume of shell element} \cdot \text{No. of } k\text{-states per unit volume}$$

$$\Delta N = 4\pi k^2 \Delta k \cdot \left(\frac{L}{2\pi}\right)^3 = \left(\frac{L^3}{2\pi^2}\right) k^2 \Delta k$$

Dividing both sides by $\Delta\omega$:

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

Hence density of states:

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

Debye Model for Heat Capacity

Einstein's 3D number of oscillator states

Einstein's approach ignoring influence of density of states: $U = 3N\langle n \rangle \hbar\omega$

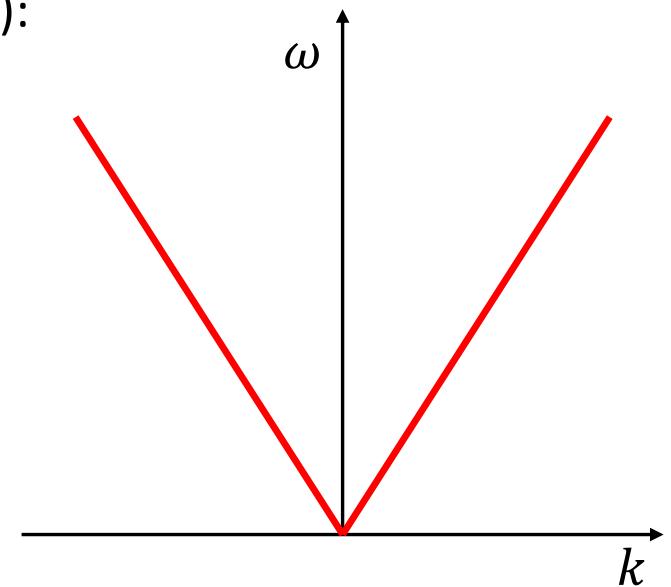
Including influence of density of states: $U = \int_0^{\omega_D} D(\omega) d\omega [\langle n \rangle \hbar\omega]$
More realistic number of oscillator states in 3D

Debye assumes $\omega - k$ dispersion relation to be linear (sigh):

$$\omega = \nu k \quad \therefore k = \frac{\omega}{\nu} \text{ and } \frac{dk}{d\omega} = \frac{1}{\nu}$$

$$\text{Hence: } D(\omega) = \left(\frac{L^3}{2\pi^2} \right) k^2 \frac{dk}{d\omega} = \left(\frac{L^3}{2\pi^2} \right) \frac{\omega^2}{\nu^2} \frac{1}{\nu}$$

$$\text{and: } U = \frac{3L^3\hbar}{2\pi^2\nu^3} \int_0^{\omega_D} \frac{\omega^3}{e^{\frac{\hbar\omega}{kT}} - 1} d\omega$$



Debye Model for Heat Capacity

$$U = \frac{3L^3\hbar}{2\pi^2\nu^3} \int_0^{\omega_D} \frac{\omega^3}{e^{\frac{\hbar\omega}{kT}} - 1} d\omega$$

Substituting $x \equiv \hbar\omega/kT$: $U = \frac{3L^3k^4T^4}{2\pi^2\nu^3\hbar^3} \int_0^{x_D} \frac{x^3}{e^x - 1} dx$

Letting the Debye Temperature (θ_D)

$$\theta_D = \frac{\hbar\nu}{k} \left(\frac{6\pi^2 N}{L^3} \right)^{1/3}$$

$$U = 9NkT \left(\frac{T}{\theta_D} \right)^3 \int_0^{x_D} \frac{x^3}{e^x - 1} dx \sim \frac{\pi^4}{15}$$

$$C_v = \frac{dU}{dT} = 9Nk \left(\frac{T}{\theta_D} \right)^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

$$C_v \propto T^3$$

Brilliant at low temperatures where linear dispersion relation is relevant – otherwise.... needs more accurate assumptions about dispersion relations

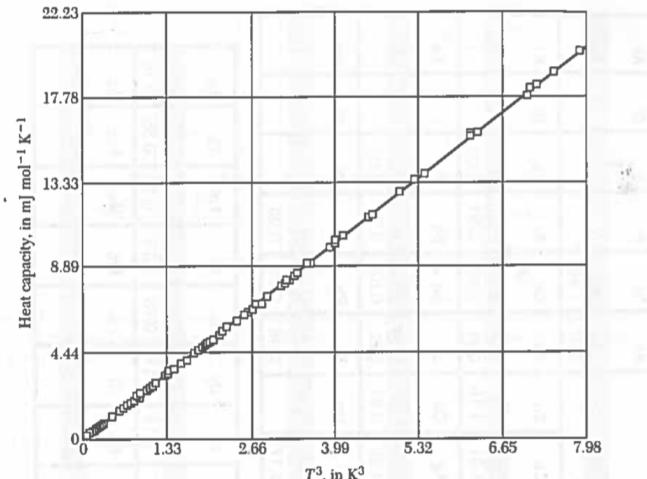
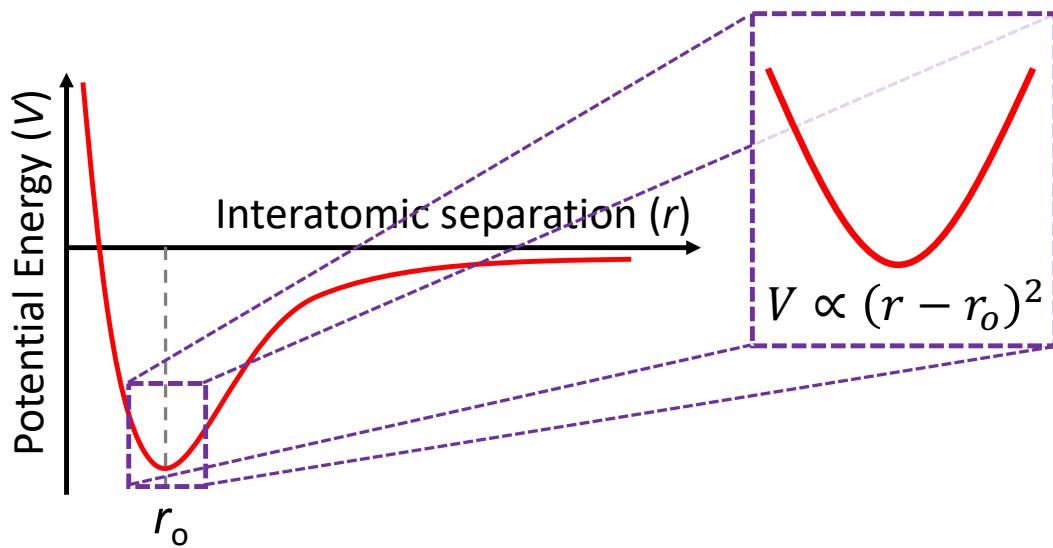


Figure 9 Low temperature heat capacity of solid argon, plotted against T^3 . In this temperature region the experimental results are in excellent agreement with the Debye T^3 law with $\theta = 92.0$ K. (Courtesy of L. Finegold and N. E. Phillips.)

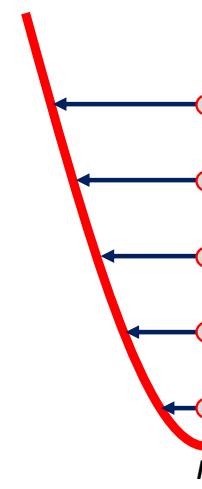
Anharmonic Effects: Thermal Expansion



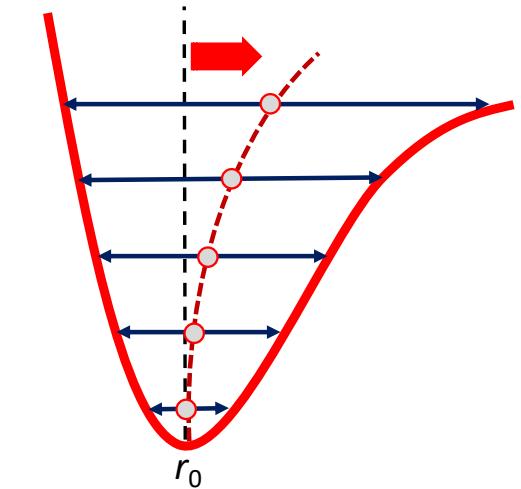
Thermal expansion – harmonic potential would see the mean atomic position being independent of vibrational energy. Need to consider influence anharmonic aspect of potential well.

Harmonic approximation is incapable of describing all of the physics associated with atomic disturbance around r_0 , because the potential well is NOT symmetric.

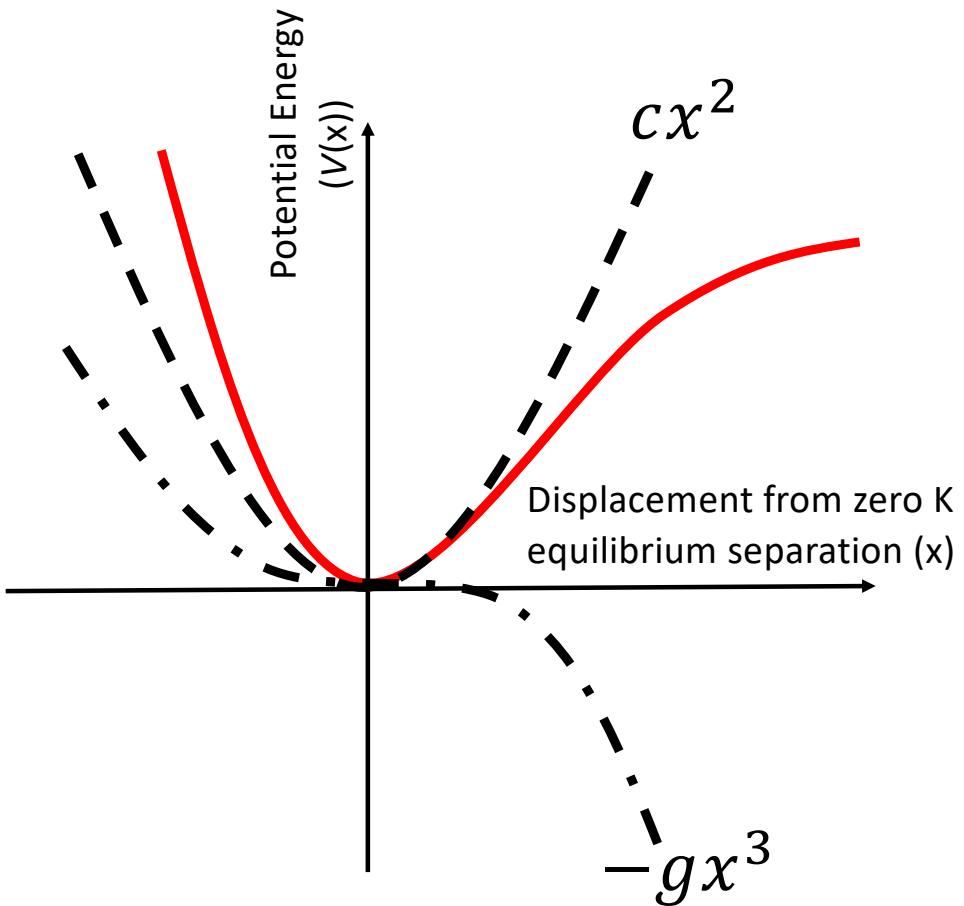
Mean atomic position across all excited states remains at r_0



Mean atomic separation increases as thermal energy is supplied



Anharmonic Effects: Thermal Expansion



Simplest anharmonic approximation for interatomic potential energy:

$$V(x) = cx^2 - gx^3$$

Average displacement from equilibrium atomic separation at zero K:

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} xe^{-\beta V(x)} dx}{\int_{-\infty}^{\infty} e^{-\beta V(x)} dx}$$

$$\text{where: } \beta \equiv \frac{1}{kT}$$

Anharmonic Effects: Thermal Expansion

Incorporating anharmonic form for $V(x)$:

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} xe^{-\beta V(x)} dx}{\int_{-\infty}^{\infty} e^{-\beta V(x)} dx} = \frac{\int_{-\infty}^{\infty} xe^{-\beta(cx^2 - gx^3)} dx}{\int_{-\infty}^{\infty} e^{-\beta(cx^2 - gx^3)} dx}$$

Solving these integrals is a painful experience, but can be done with a few tricks.

Trick one – use the series expansion of $e^x = 1 + x + \dots$ on the $e^{\beta gx^3}$ term

Focusing on the numerator: $\int_{-\infty}^{\infty} xe^{-\beta cx^2} e^{\beta gx^3} dx = \int_{-\infty}^{\infty} xe^{-\beta(cx^2)}(1 + \beta gx^3) dx$

$$= \int_{-\infty}^{\infty} xe^{-\beta(cx^2)} + \beta gx^4 e^{-\beta(cx^2)} dx$$

A

B

Anharmonic Effects: Thermal Expansion

$$A = \int_{-\infty}^{\infty} xe^{-\beta(cx^2)} dx = \left[-\frac{1}{2\beta c} e^{-\beta cx^2} \right]_{-\infty}^{\infty}$$

$$B = \int_{-\infty}^{\infty} \beta g x^3 x e^{-\beta(cx^2)} dx$$

B by parts (trick 2):

$$u = \beta g x^3 \quad v = -\frac{1}{2\beta c} e^{-\beta cx^2}$$

$$\frac{du}{dx} = 3\beta g x^2 \quad \frac{dv}{dx} = x e^{-\beta cx^2}$$

$$B = \left[-\frac{gx^3}{2c} e^{-\beta cx^2} \right]_{-\infty}^{\infty} - \underbrace{\int_{-\infty}^{\infty} -\frac{3gx^2}{2c} e^{-\beta(cx^2)} dx}_{C} \\ = 0$$

C by parts (trick 2 repeated):

$$u = \frac{3g}{2c} x \quad v = -\frac{1}{2\beta c} e^{-\beta cx^2}$$

$$\frac{du}{dx} = \frac{3g}{2c} \quad \frac{dv}{dx} = x e^{-\beta cx^2}$$

Anharmonic Effects: Thermal Expansion

$$C = \left[-\frac{3gx}{4\beta c^2} e^{-\beta cx^2} \right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} -\frac{3g}{4\beta c^2} e^{-\beta(cx^2)} dx$$

$= 0$ D

$$D: \frac{3g}{4\beta c^2} \int_{-\infty}^{\infty} e^{-\beta(cx^2)} dx$$

Using standard Gaussian integral solution (trick 3): $\int_{-\infty}^{\infty} e^{-Ax^2} dx = \sqrt{\frac{\pi}{A}}$

$$D: \frac{3g}{4\beta c^2} \sqrt{\frac{\pi}{\beta c}} = \frac{3\sqrt{\pi}}{4} \frac{g}{c^{\frac{5}{2}} \beta^{\frac{3}{2}}}$$

Anharmonic Effects: Thermal Expansion

Remember why we're doing this: to find average temperature-induced displacement from ground state equilibrium interatomic separation. So far only worked on numerator:

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} xe^{-\beta V(x)} dx}{\int_{-\infty}^{\infty} e^{-\beta V(x)} dx} = \frac{\int_{-\infty}^{\infty} xe^{-\beta(cx^2 - gx^3)} dx}{\int_{-\infty}^{\infty} e^{-\beta(cx^2 - gx^3)} dx} :$$

Similar pain allows the denominator to be approximated as $\left(\frac{\pi}{\beta c}\right)^{\frac{1}{2}}$ giving:

$$\langle x \rangle = \frac{\frac{3\sqrt{\pi}}{4} \frac{g}{c^{\frac{5}{2}} \beta^{\frac{3}{2}}}}{\frac{\frac{1}{\pi^{\frac{1}{2}}}}{c^{\frac{1}{2}} \beta^{\frac{1}{2}}}} = \frac{3g}{4\beta c^2} \text{ or remembering } \beta = \frac{1}{kT} : \langle x \rangle = \frac{3g}{4c^2} kT$$

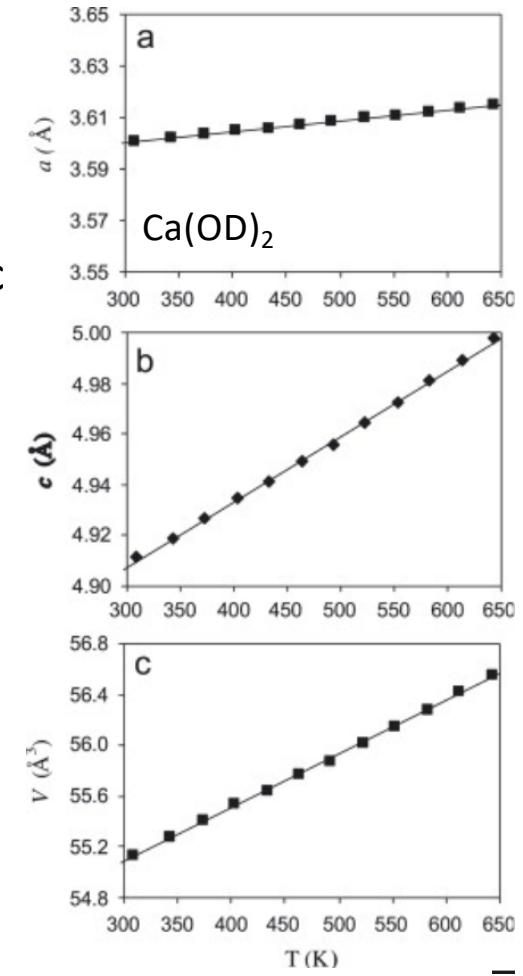
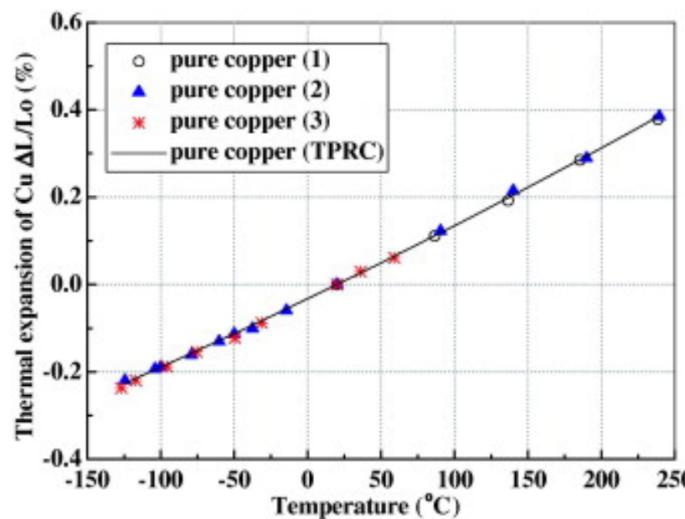
Anharmonic Effects: Thermal Expansion

$$\langle x \rangle = \frac{3g}{4c^2} kT$$

Anharmonic approximation, in which negative cubic term is included, predicts that the average change in the interatomic separation varies linearly with temperature and on the detailed shape of the interatomic potential energy: the ratio of anharmonic prefactor to square of harmonic prefactor. *Could use thermal expansion to map form of interatomic potential energy.*

Thermal expansion coefficient expected to be a constant:

$$\frac{d\langle x \rangle}{dT} = \frac{3kg}{4c^2}$$



Anharmonic Effects: Thermal Expansion

As $T \rightarrow 0$ lattice expansion / contraction is not linear with temperature. In fact, in the example given in Kittel (right) and those below from literature, the lattice does not expand as temperature is raised close to zero Kelvin: suggests that Harmonic approximation is better at lower temperatures: gradient in thermal expansion $\propto \frac{g}{c^2}$, so when gradient tends to zero, $g \rightarrow 0$ i.e. the anharmonic term becomes irrelevant.

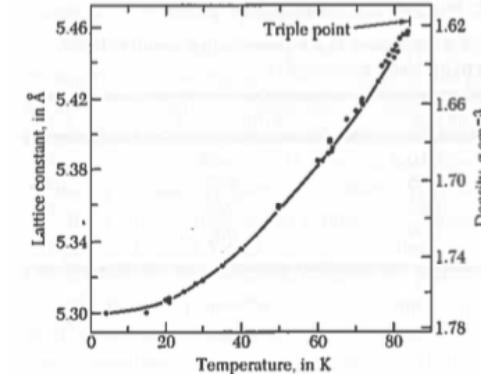
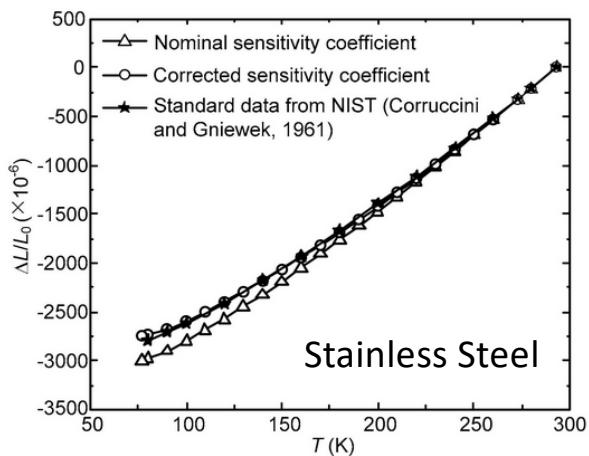
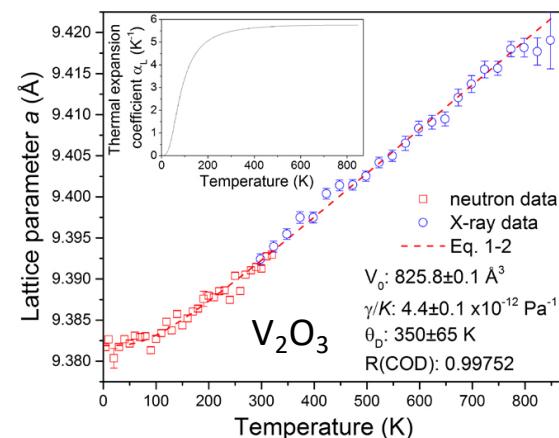


Figure 15 Lattice constant of solid argon as a function of temperature.



Anharmonic Effects: Phonon Scattering

Harmonic approximation leads to non-interacting atomic oscillators (treatments of heat capacity assumed independent oscillators). Need anharmonic terms to generate phonon-phonon collisions, which are important – particularly in thermal transport.

Normal (N) phonon-phonon scattering:
two phonons meet and coalesce to form a third, or a single phonon splits to form two others. Process must conserve energy and momentum.

Also need all phonons involved to exist in the dispersion relations ($\omega - k$ plots).

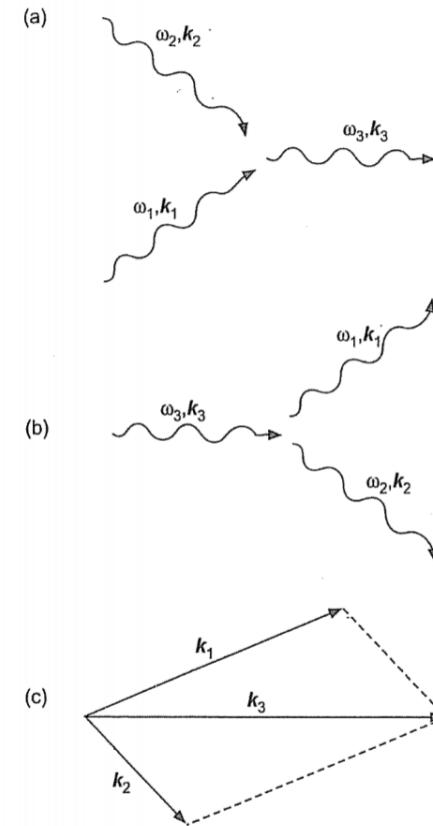
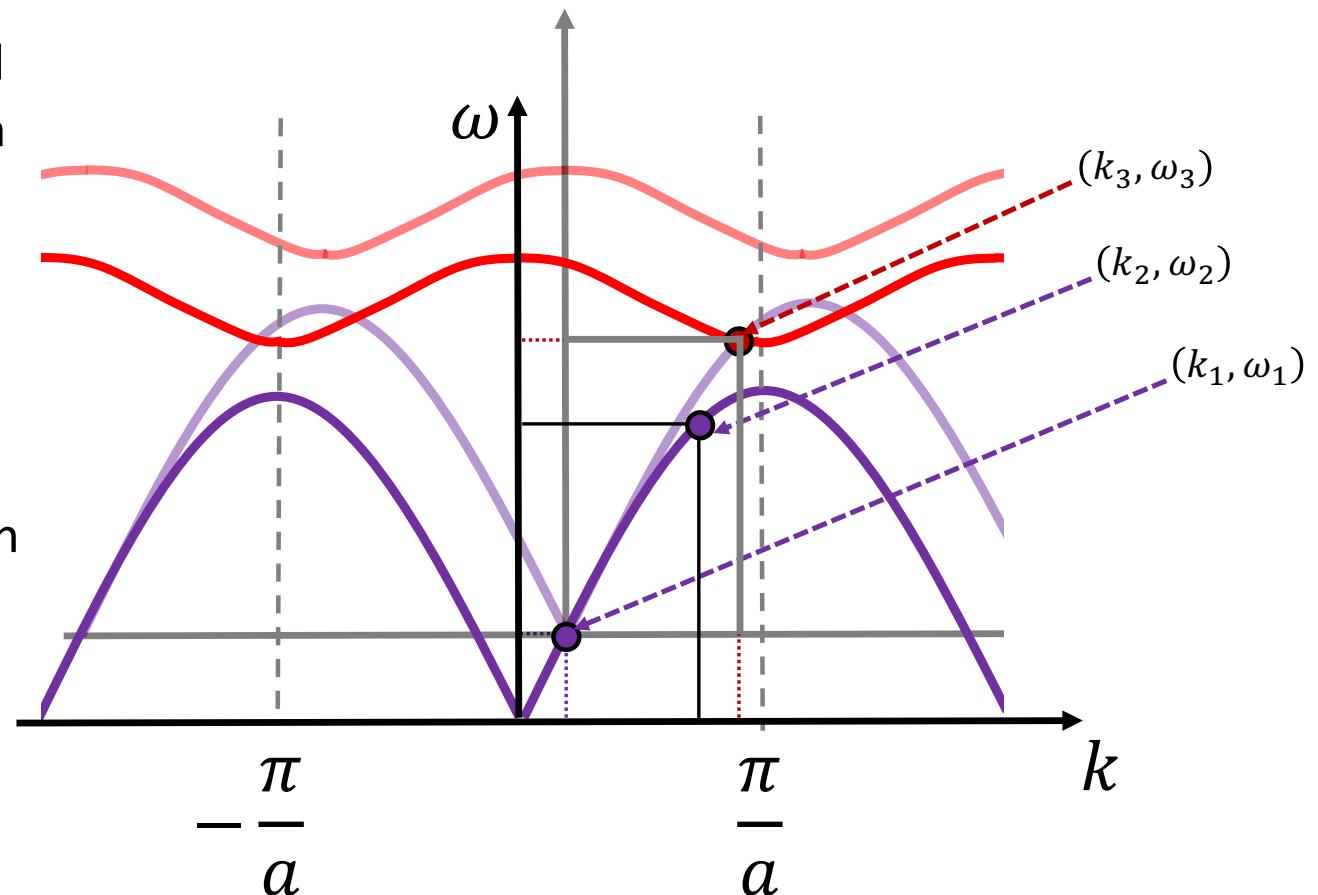


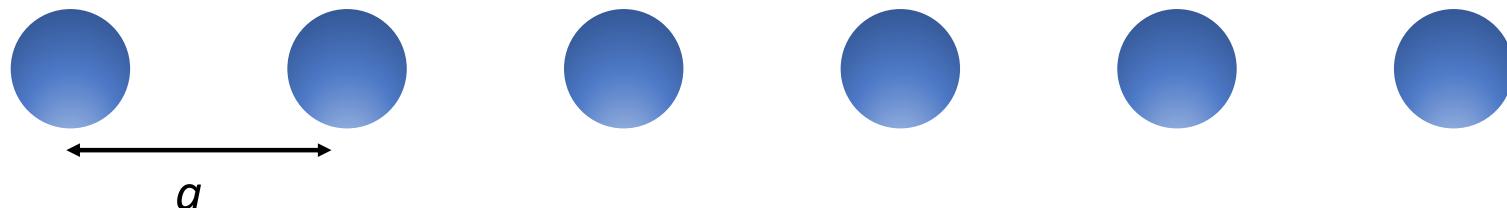
Fig. 4.41 Representation of the interactions between three phonons as a result of the cubic anharmonic term in the vibrational potential energy: (a) coalescence of two phonons to give a third; (b) decay of a phonon into two others; (c) 2D illustration of the conservation of crystal momentum in the first zone ($G = 0$) (normal, 'N', process).

Anharmonic Effects: Phonon Scattering

- Consider a phonon with wavevector k_1 and frequency ω_1
- To find a phonon in dispersion curve which might be produced from a collision, shift dispersion curve by (k_1, ω_1) and observe intersections between original and shifted functions
- Intersections on **unshifted** dispersion curve give possible resultant phonons after collision (k_3, ω_3)
- Intersections on **shifted** dispersion curve give phonon (k_2, ω_2) needed to produce resultant post-collision phonon

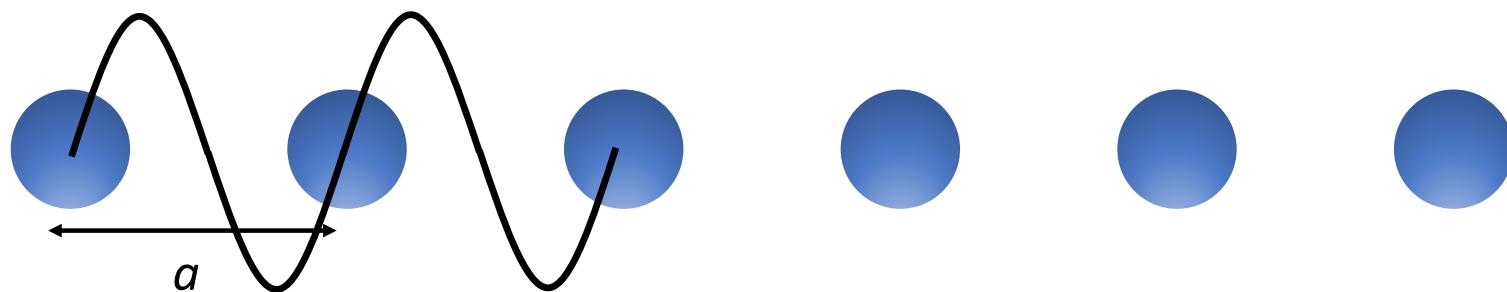


Vibrations in each unit cell of k-space



Infinite wavelength – all atomic motion in phase: $k=0$

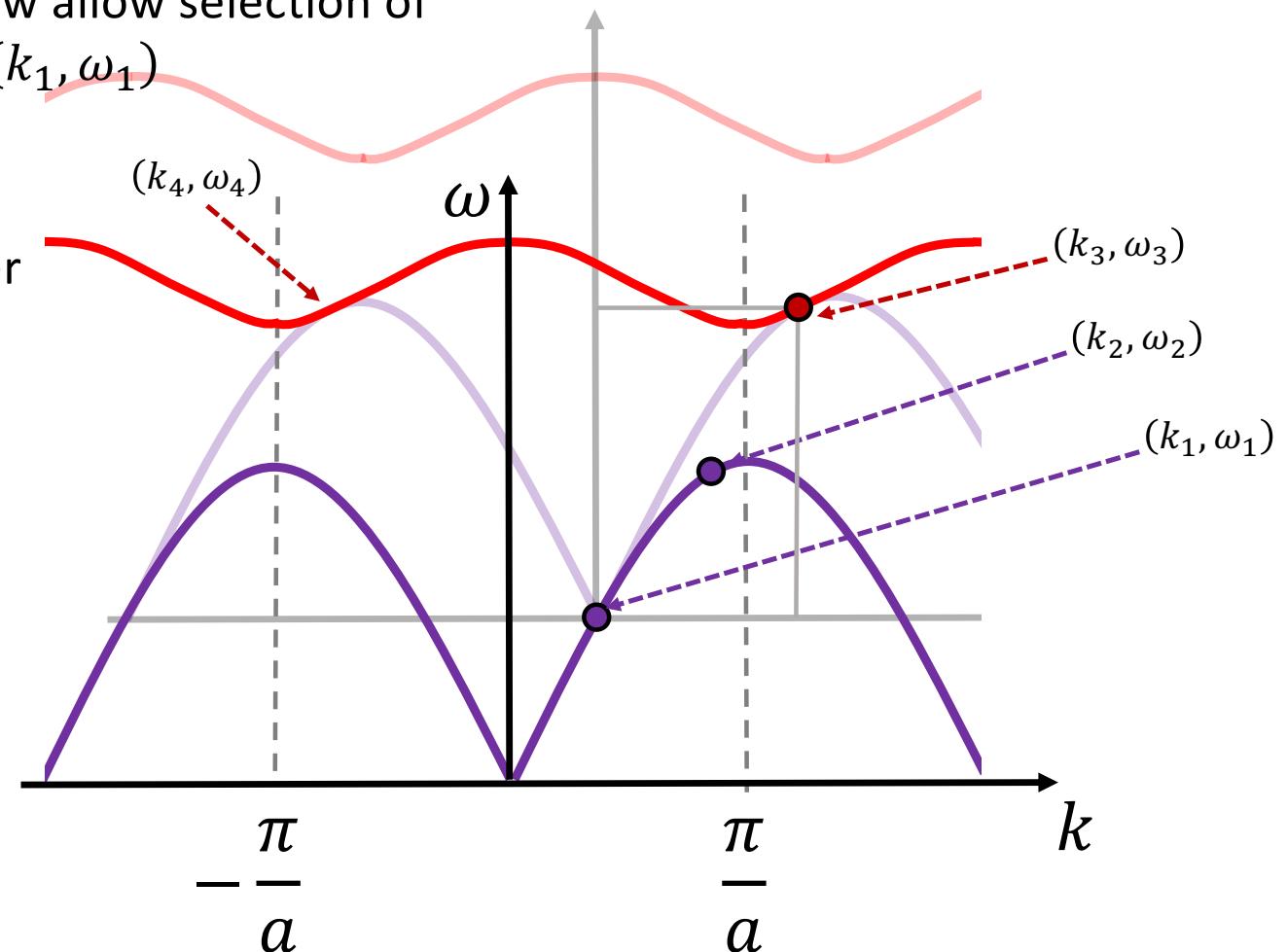
What if $k=2\pi/a$?in other words $\lambda=a$



The vibration state at $k+2\pi/a$ in “2nd” Brillouin Zone (or indeed $k+n2\pi/a$) reflects exactly the same atomic motion as k – hence redundant.

Anharmonic Effects: Umklapp (U) Phonon Scattering

- Same process as before, but now allow selection of relatively high energy phonon (k_1, ω_1)
- Intersections on **unshifted** dispersion curve which give possible resultant phonons after collision might generate (k_3, ω_3) outside of Brillouin Zone
- Periodic nature of dispersion curve means that resultant (k_3, ω_3) represented by alternative (k_4, ω_4) inside the Brillouin Zone shifted by $2\pi/a$
- Resultant wavevector after collision is hence **negative**



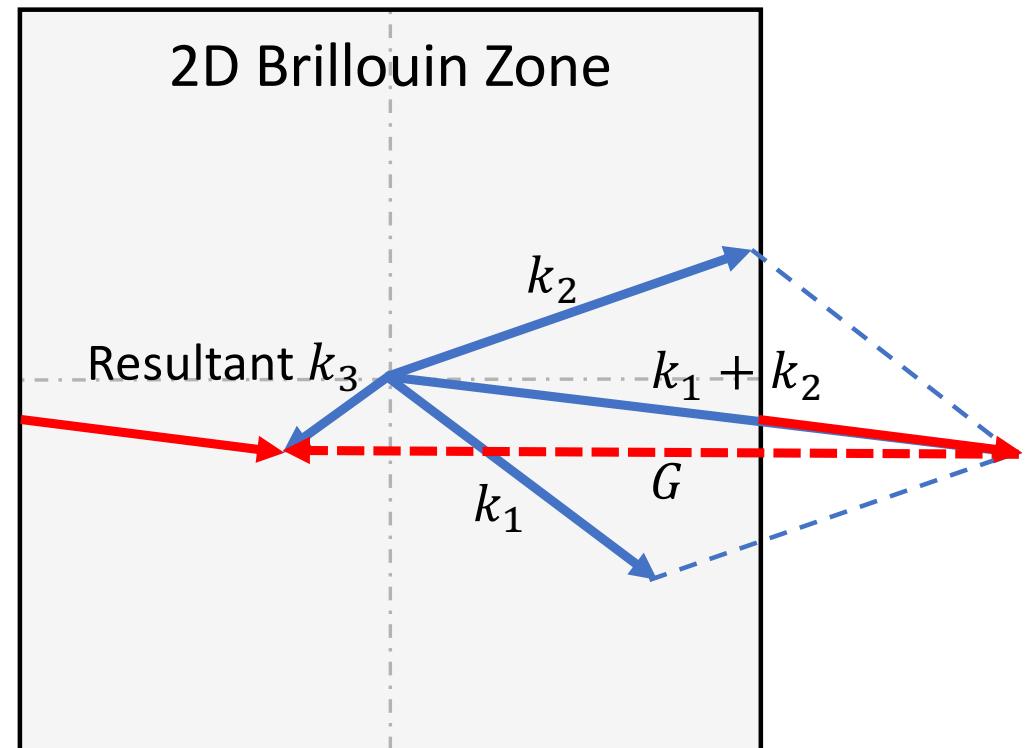
Anharmonic Effects: Umklapp (U) Phonon Scattering

This leads to an uncomfortable vector diagram for resultant phonon wavevector after Umklapp phonon-phonon collision:

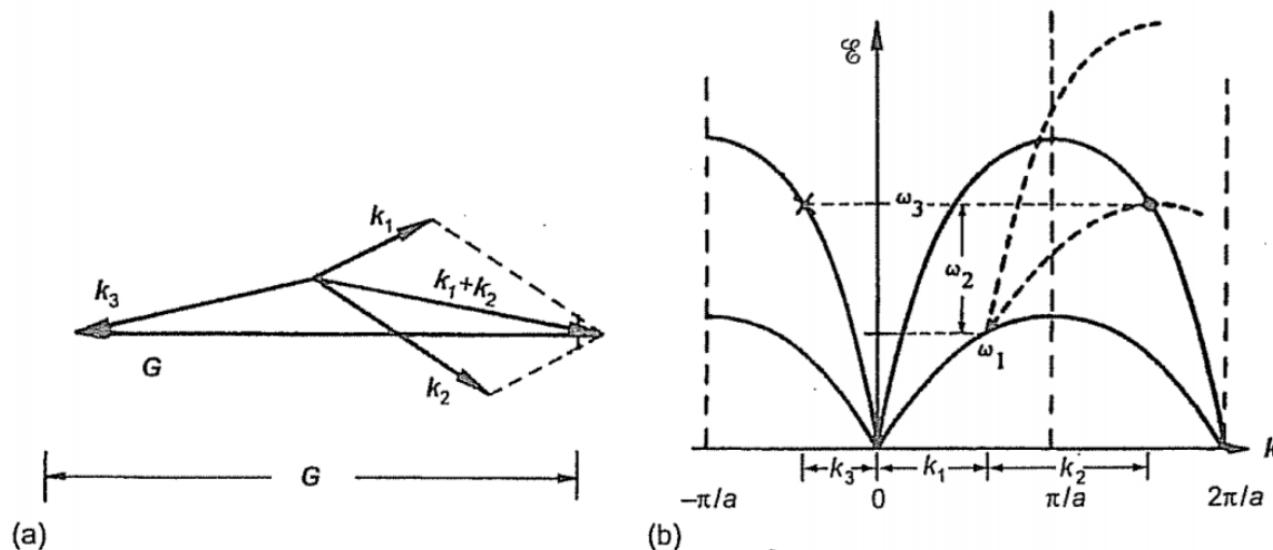
$$k_3 = k_1 + k_2 + G$$

Where G is a reciprocal lattice vector (such as $2\pi/a$).

Umklapp scattering requires coalescence of relatively long wavevector (high energy) phonons; such phonon states are not filled at low temperatures and so Umklapp processes absent at strongly cryogenic temperatures and develop progressively on heating.



Anharmonic Effects: Umklapp (U) Phonon Scattering



Taken from Elliott:
The Physics and
Chemistry of Solids

Fig. 4.45 Umklapp (U) phonon-phonon scattering process: (a) The wavevector k_3 of the phonon resulting from the combination of two others (k_1, k_2) lies outside the first Brillouin zone, and is brought back into it by the addition of a suitable reciprocal-lattice vector, \mathbf{G} (b) Geometric construction to find the allowed values of frequency (ω_3) and wavevector (k_3) of a phonon created in a U-process from the coalescence of two other phonons ($\omega_1 k_1, \omega_2 k_2$). It is assumed for simplicity that all three wavevectors are collinear. See Fig. 4.42 for an explanation of the construction.

Thermal Conduction: Kinetic Theory

In electrical insulators, heat energy is carried along thermal gradient by phonon quasiparticles, each with heat capacity c

Hot phonon moving from region of $T + \Delta T$ to region of T and then undergoing collision will give up energy of $c\Delta T$

ΔT can be given in terms of the thermal gradient and the length moved by the phonon (l_x):

$$\Delta T = \frac{dT}{dx} l_x = \frac{dT}{dx} v_x \tau$$

Where v_x is the phonon group velocity and τ the time taken prior to collision.

For a population density of n phonons, net energy flux (j_U) is heat energy per phonon multiplied by the phonon flux ($n\langle v_x \rangle$):

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

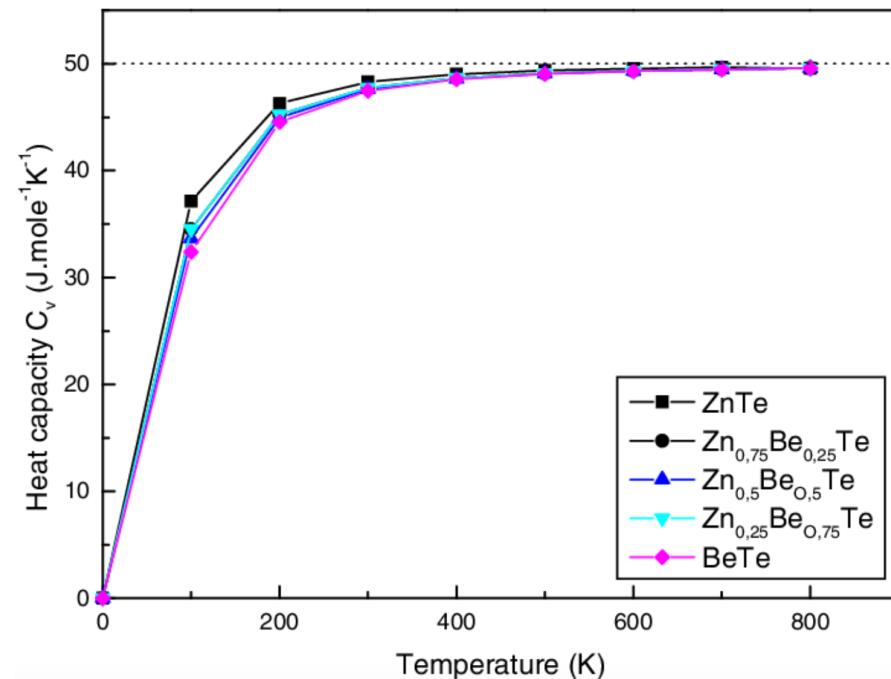
Where $C = nc$ and $l = v\tau$. The thermal conductivity is then $K = \frac{1}{3} C v l$

Thermal Conduction: Kinetic Theory

The thermal conductivity is $K = \frac{1}{3} C v l$

C is the heat capacity (behaviour as function of temperature known).

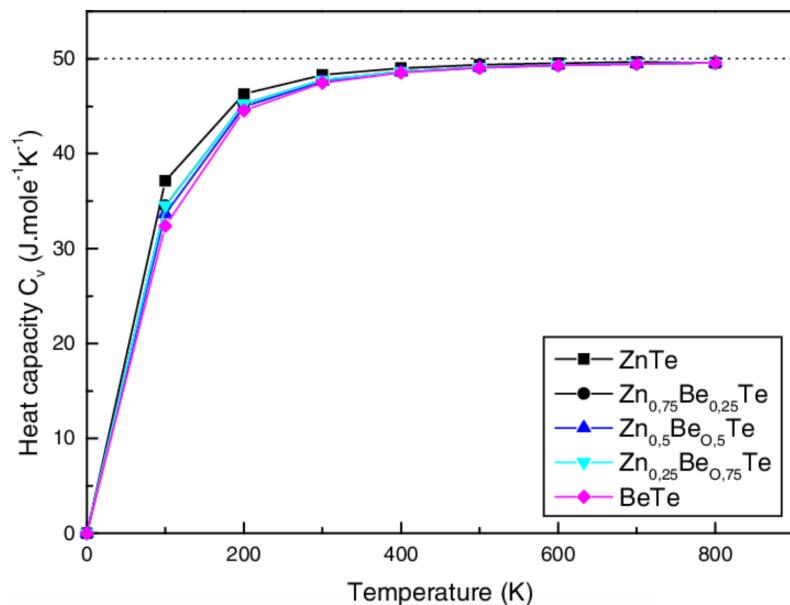
v is the phonon group velocity (assumed to be constant by Debye, but otherwise complex temperature dependence since $d\omega/dk$ is complex).



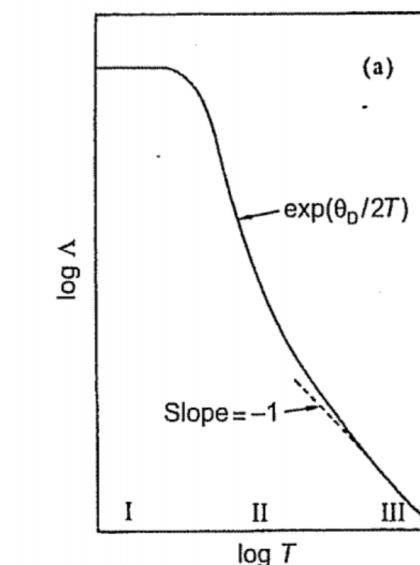
l is the mean free path, which is only limited by impurity scattering and sample surface scattering at low temperature (largely temperature independent); at higher temperatures, Umklapp phonon-phonon scattering progressively develops and number of phonons responsible increases.

Temperature Dependence of Thermal Conduction

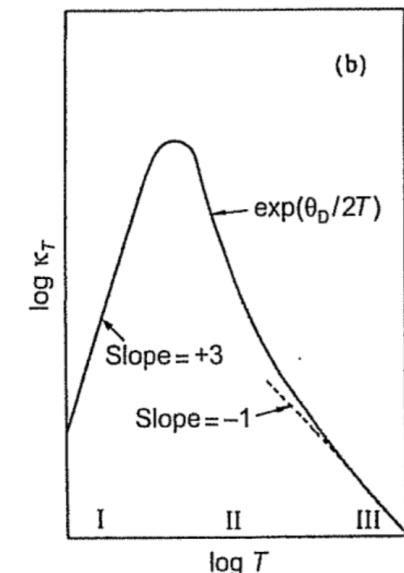
Heat Capacity



Mean Free Path



Thermal Conductivity



Taken from Elliott: The Physics
and Chemistry of Solids

Temperature Dependence of Thermal Conduction

