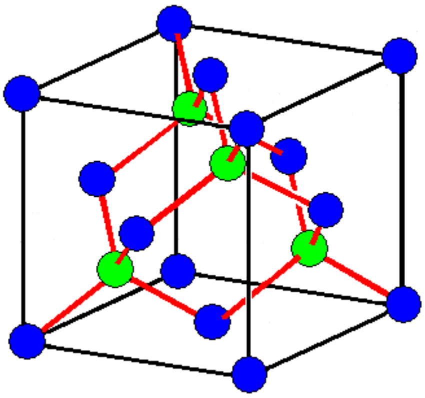

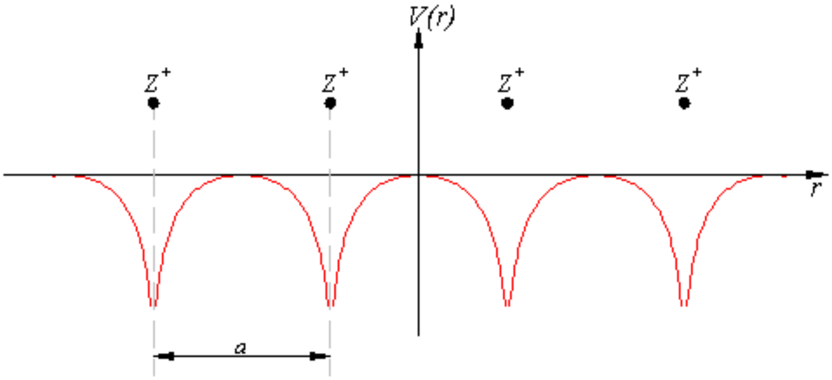

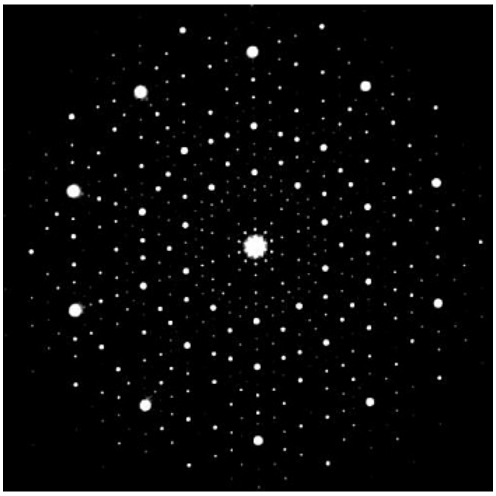

KYA322

Solid State Physics

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Phonons: Crystal Vibrations

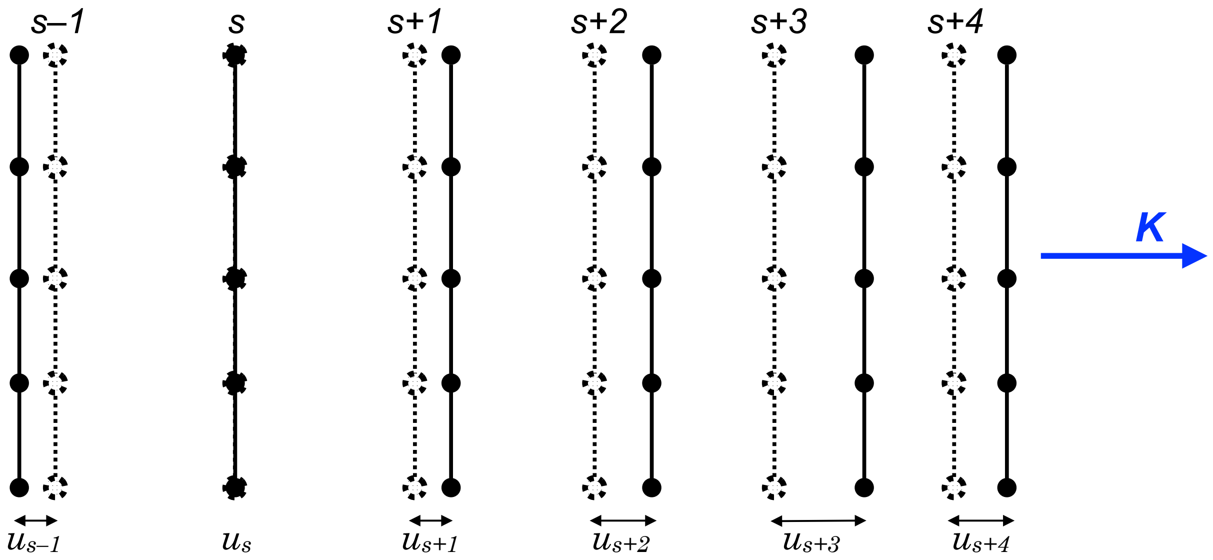
In the previous section we worked out the wave vectors of elastic waves in solids, by relating the stresses on displaced of atoms to the allowed wavevectors that described traveling waves in the solid.

However, the treatment so far has only been valid for the case that the lattice constants a are very small compared to the wavelength (the continuum approximation).

To do better, we need to deal with the fact that the vibrations are quantised. By analogy to the quantum of electromagnetic radiation, the quantum of elastic waves is known as a *phonon*.

In the case of waves in the [100] (edge), [110] (face diagonal), and [111] (body diagonal) directions, the solution of the wave equation is simple, because entire planes of atoms move together, and the wave can be described by a 1-dimensional displacement vector u_s.

Vibrations within crystal planes



A longitudinal displacement wave: planes of atoms are displaced by an amount u with respect to their equilibrium position (shown by the dotted lines). There are two other polarizations, the transverse waves, not shown.

Vibrations for Monatomic Basis

When the atomic basis on the lattice is monatomic, the problem is 1-dimensional.

Assume the potential energy of interaction between planes is quadratic in u (the *harmonic approximation*). For small displacements, cubic and higher terms will tend to be negligible; linear terms from opposite sides will cancel out.

Then the force between neighbouring planes is proportional to their separation. For plane s, we have $F_s = C(u_{s+1} - u_s) + C(u_{s-1} - u_s)$, under the conditions that

1) we only include nearest-neighbours to a first approximation, and
2) C is the force constant *per atom*. C differs for longitudinal and transverse waves.

The equation of motion is $M\dfrac{d^2u_s}{dt^2} = C(u_{s+1} + u_{s-1} - 2u_s)$, which has travelling wave solutions for frequency $\omega^2 = -\dfrac{C}{Mu_s}(u_{s+1} + u_{s-1} - 2u_s)$

Vibrations for Monatomic Basis

The solutions for the travelling wave are $u_{s\pm1} = u\exp(isKa)\exp(\pm iKa)$

Substitution of the expression for ω^2 and cancelling $u\exp(isKa)$ from both sides of the equation, we can get $\omega^2 = -\frac{C}{M}[\exp(iKa) + \exp(-iKa) - 2]$

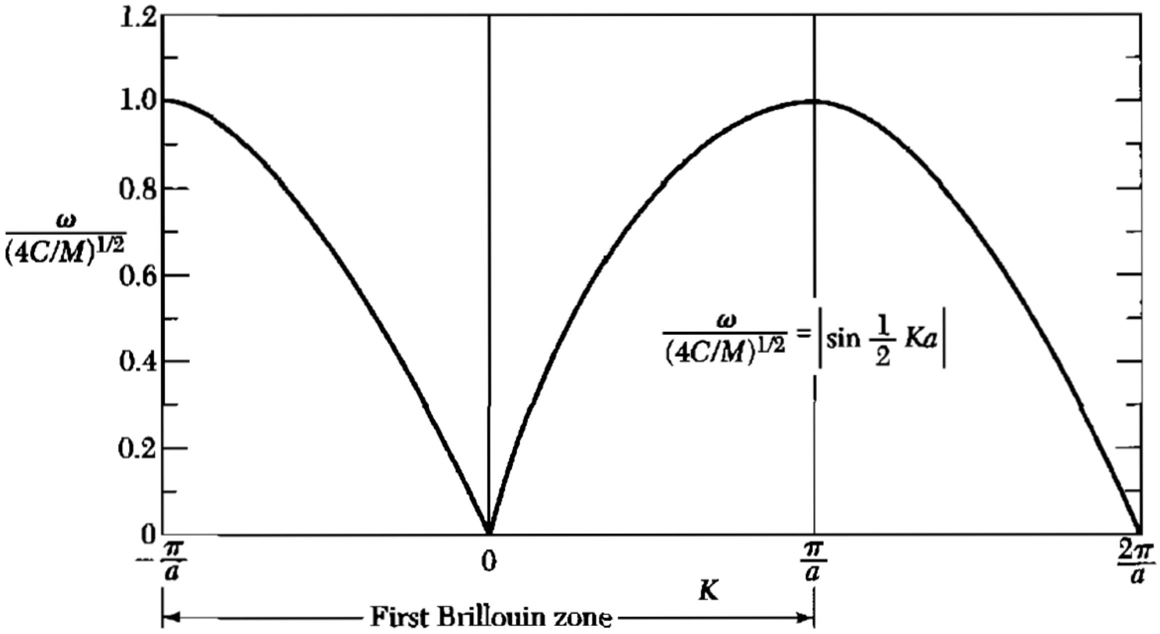
From the definition of $\cos(Ka)$, this is rewritten as the ***phonon dispersion relation:***

$$\omega^2 = \frac{2C}{M}(1 - \cos Ka)$$

This has a special relationship to the boundaries of the first Brillouin zone, which lie at $K = \pm\pi/a$. Consider the derivative $\frac{d\omega^2}{dK} = \frac{2Ca}{M}\sin Ka$. The derivative vanishes at the edge of the first Brillouin zone.

Dispersion Relation

Another trig identity allows us to write $\omega = (4C/M)^{1/2}|\sin\frac{1}{2}Ka|$



The area right around $K = 0$ ($K \ll 1/a$; $\lambda \gg a$) corresponds to the continuum approximation, where $\omega \propto K$.

The First Brillouin Zone

The range of independent wavenumbers K is given by $-\pi/a < K \leq \pi/a$.

This exactly corresponds to the range of the first Brillouin zone in the reciprocal lattice; any other values of K describe the same physical motions, shifted by an integer multiple of $2\pi/a$.

Some points to note:

- At $K = \pm\pi/a$, the group velocity goes to zero. Energy is not transmitted through the crystal by waves of that wavelength and direction.
- At the zone boundaries, the wave motion becomes a standing wave:

$$u_s = u\exp(isKa) = u\exp(\pm is\pi)$$

$$u_s = u(-1)^s$$

Alternate planes of atoms move in opposite phases.

- wavevectors along the Brillouin zone boundary are analogous to the Bragg condition (with $\theta = \pi/2$, $d = a$, n = 1).

The Long Wavelength Limit

For $\lambda >> a$, the prodcut $Ka << 1$. That means the cos(Ka) term can be expanded as $\cos(Ka) \approx 1 - \frac{1}{2}(Ka)^2$. The dispersion relation $\omega^2 = \frac{2C}{M}(1 - \cos Ka)$ simplifies to $\omega^2 = (C/M)K^2a^2$.

In the long wavelength limit the frequency is linearly proportional the wavevector, so that the sound speed v = ω/K is a constant in this limit.

In the continuum limit the classical result for elastic waves is recovered. **The complex spectrum of energy transmission in solids is only apparent when the wavelengths are small compared to the interatomic spacing.**

Long Range Forces

All of the preceding was derived by only considering the interaction between nearest neighbours. Sometimes this is a bad assumption (as in metals).

If an integer number of planes p contributes to the restoring force of the oscillation, then the dispersion relation can be generalised

$$\omega^2 = (2/M)\sum_{p>0} C_p(1-\cos pKa)$$

where the strength of each interaction between crystal planes separated by p units is given by the appropriate force constant Cp.

By experimental observation of the dispersion relation for waves in a solid, the force constants C_p can be determined.

For some metals, up to 20 terms may be needed to accurately describe the observed waves: that is, crystal planes separated by up to 20 lattice units are influencing the wave energy transmission.

Two or More Atoms per Basis

The phonon dispersion relation is relatively simple when there is only one atom per primitive cell, as in the previous discussion.

If there are p different atoms in the basis, where p is an integer, the dispersion relation splits into $3p$ independent branches. These are known as the *acoustic* (3) and the *optical* ($3p$–3) branches.

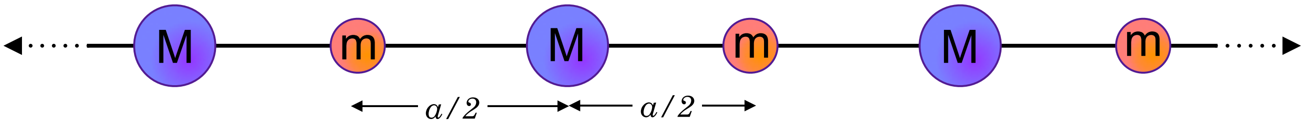
Consider a crystal with a two-atom basis, e.g., NaCl, or diamond. These would have six different possible waves represented in the dispersion relation: one longitudinal and two transverse acoustic waves (LA, TA), and one longitudinal and two transverse optical waves (LO, TO).

The optical modes get their name because they can be excited by absorption of electromagnetic radiation (if the atoms in the basis have opposite charge)

The acoustic modes correspond to classic sound waves (in the long wavelength limit). Note that sound waves in solids have both longitudinal AND transverse components.

Diatomic Linear Chain

Consider a linear chain with two atoms per primitive unit cell. A cell with length a contains two atoms/ions. One atom with mass M is located at sa, and one atom with mass m is located at $(s+1/2)a$, for any integer s.



In general a chain of N atoms will have N different normal modes of oscillation.

For a given value of s, making the harmonic approximation (Hooke's law), we can write the displacements as

$$M\frac{d^2u_{Ms}}{dt^2} = C_{Mm}\left[u_{ms} + u_{ms-1} - 2u_{Ms}\right]$$

$$m\frac{d^2u_{ms}}{dt^2} = C_{Mm}\left[u_{Ms} + u_{Ms+1} - 2u_{ms}\right]$$

Diatomic Linear Chain

The displacements of all atoms of mass M are equivalent to each other, as are those for atoms m, so we can write down the solutions for unit cell s as

$$u_{Ms}(t) = A_M\, e^{i(qsa-\omega t)}$$

$$u_{ms}(t) = A_m\, e^{i(qsa+qa/2-\omega t)}$$

We can start to solve for the frequencies, velocities, and phases by substitution back into the equations of motion, which give us two relations:

$$-M\omega^2 A_M = 2C_{Mm}\left[A_m\cos\left(qa/2\right) - A_M\right]$$

$$-m\omega^2 A_m = 2C_{Mm}\left[A_M\cos\left(qa/2\right) - A_m\right]$$

An important point for a linear diatomic chain is that there is only one frequency for the two resulting waves.

There is a trivial solution where the amplitudes equal zero, which corresponds to no wave energy, but to find non-trivial solutions we solve a quadratic using the determinant of a matrix.

Diatomic Linear Chain

There are two roots, $\omega^2 = C_{Mm}\left(\frac{1}{\mu}\right) \pm C_{Mm}\left[\left(\frac{1}{\mu}\right)^2 - \frac{4}{Mm}\sin^2(qa/2)\right]^{1/2}$ where μ is the reduced mass of M and m together.

As with any periodic lattice, waves with propagation constants q and $q + 2\pi h/a$ are identical, so we only discuss waves with $-\pi/a \le q \le \pi/a$.

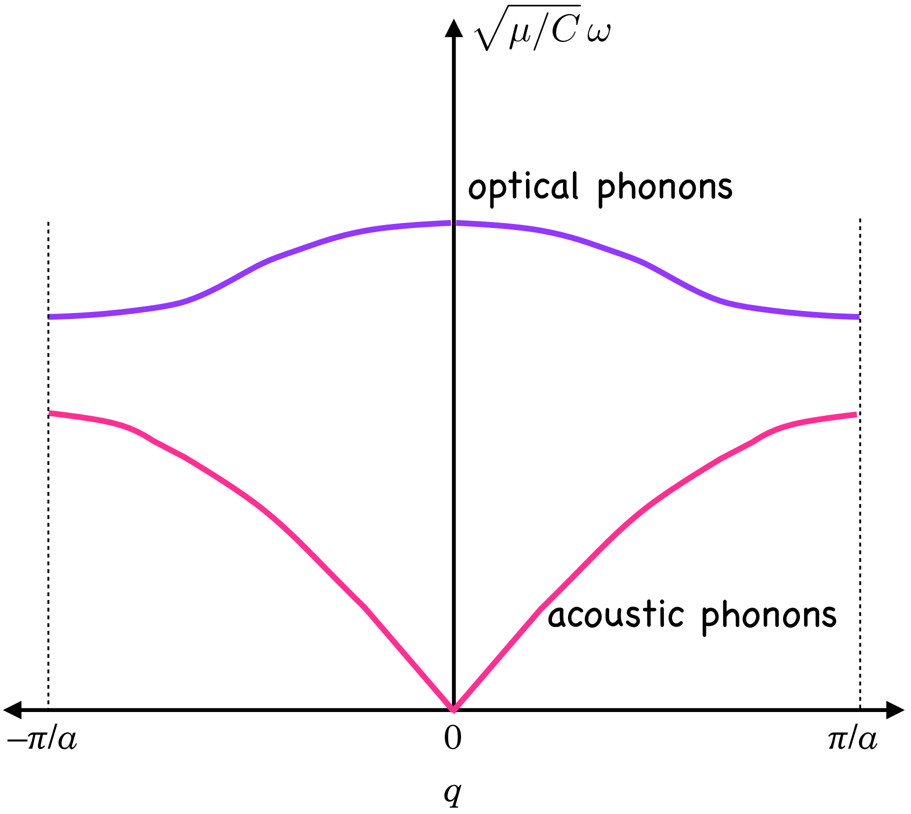
For N total atoms, there are 2N total modes of oscillation, and there is a significant difference with the monatomic case: There are two possible frequencies for each allowed value of q (the optical branch and the acoustic).

The upper branch of solutions and the lower branch merge for some values of q if the two masses are equal, but if they are not, then there will be a frequency gap. If a disturbance affects the diatomic chain with a frequency between the high and low branches, then it will rapidly be attenuated, and won't travel far within the chain.

In polyatomic lattices, there is a frequency gap where no waves can exist (unless $M_1 = M_2$).

Optical phonons have nonzero frequency at the centre of the Brillouin zone (long wavelength limit).

Acoustic phonons have a linear relationship between ω and K at long wavelength.



The optical and acoustic branches of the dispersion relation for an idealised diatomic lattice of atoms with mass M_1 and M_2.

The minimum and maximum frequencies of the branches can be found by setting $q = 0$ and $q = \pi/a$, respectively.

For optical phonons:

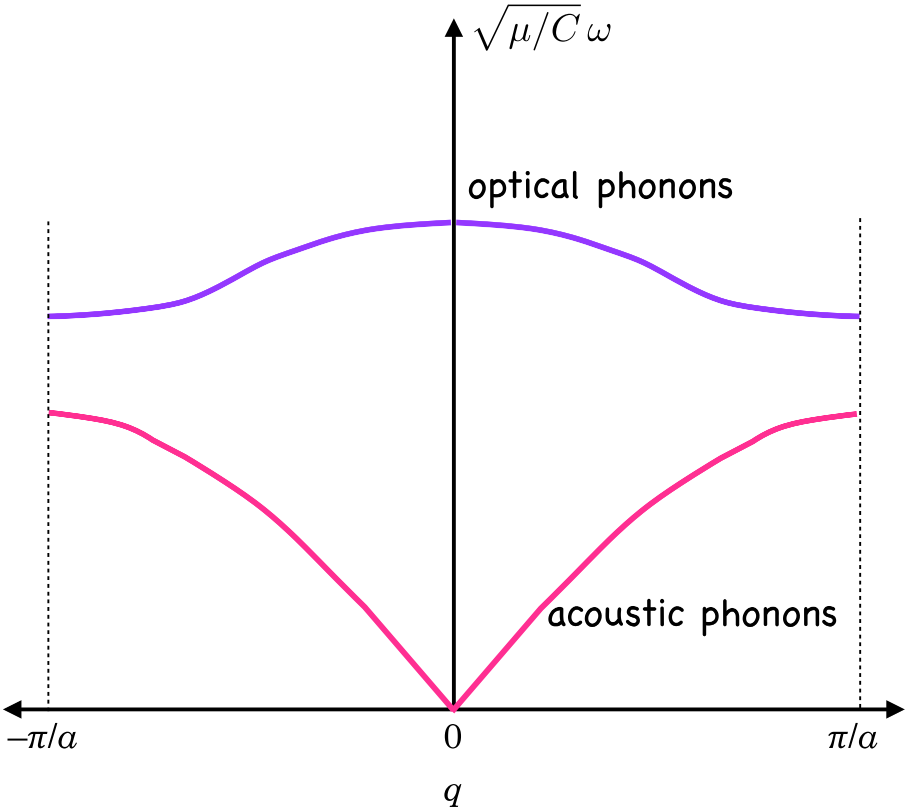
$$\omega_{op,max} = [2C/\mu]^{1/2}$$

$$\omega_{op,min} = [2C/m]^{1/2}$$

For acoustic phonons:

$$\omega_{op,max} = [2C/M]^{1/2}$$

The frequency gap vanishes when $m = M$.



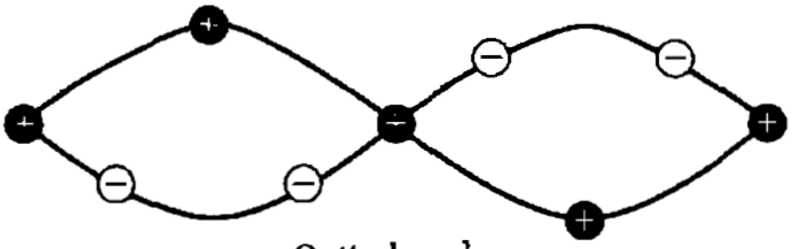
The optical and acoustic branches of the dispersion relation for an idealised diatomic lattice of atoms with mass M_1 and M_2.

Acoustic & Optical Modes

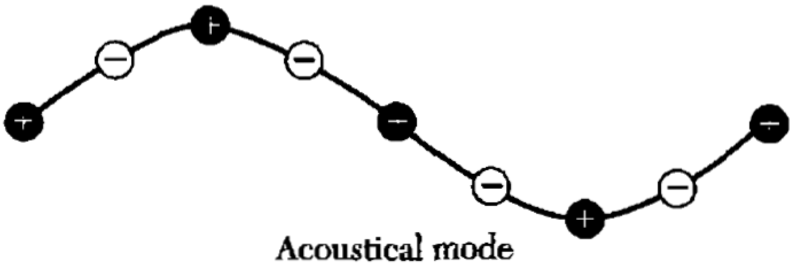
The two modes are shown here for a diatomic basis, with equal mass atoms.

The optical modes occur where atoms oscillate out of phase with each other. This resulting charge separation means that infrared light shining on a crystal can excite these vibrations.

In the acoustic mode the different atoms oscillate coherently.



Optical mode



Acoustical mode

If the masses differ, the atoms have different displacements. For the optical branch, the displacements are in the ratio $u_1/u_2 = -M_2/M_1$

Quantization

The name *phonon* was invented by Igor Tamm in the 1920s during his work on the quantum mechanics of solids.

Lattice vibrations must be quantized, like any other atomic scale oscillator.

If the angular frequency of a particular mode is ω, then the energy in the mode is $\epsilon = (n+½)\hbar\omega$.

Phonons have a zeropoint energy where n = 0, and the quantum number n describes the amplitude of that mode of oscillation.

We can go through the steps to quantization by considering the case of a standing wave, $u = u_0 \cos Kx \cos \omega t$.

Because this is a harmonic oscillator, expectation value of the potential energy is equal to the expectation value of the kinetic energy.

Quantization

For a unit volume of material with density ρ, the kinetic energy density is $½\rho(\partial u/\partial t)^2$. Substitution of the standing wave expression for u and integrating over the unit volume gives instantaneous total kinetic energy

$$KE(t) = \frac{1}{4}\rho V \omega^2 u_0^2 \sin^2(\omega t)$$

and integration over time gives $\langle KE \rangle = \frac{1}{8}\rho V \omega^2 u_0^2$.

This is half the total energy, so $\frac{1}{8}\rho V \omega^2 u_0^2 = \frac{1}{2}\left(n + \frac{1}{2}\right)\hbar\omega$

Algebra gives $u_0^2 = 4\left(n + \frac{1}{2}\right)\hbar/(M\omega)$ where M is the mass of the primitive cell.

Phonon Momentum

A phonon of wavenumber K interacts with photons, electrons, neutrons, ions, etc., just as if it had momentum given by p = $\hbar K$.

However, the phonon does not actually carry physical momentum. This is because the phonons only involve motion of the <u>relative</u> coordinates. Averaged over a full cycle, the net momentum transfer is zero.

Put another way: phonons do not correspond to centre of mass translation motion of the crystal.

Conservation of phonon momentum leads to certain *selection rules* that dictate which phonons can be emitted or absorbed under what circumstances.

An example of a selection rule for photons is the Laue condition for x-ray elastic scattering, $k' = k + G$, where G is a vector in the reciprocal lattice. Momentum is always conserved.

Phonon Momentum

Scattering can also be inelastic, resulting in the creation or destruction of a phonon, i.e.,

$$k' + K = k + G$$

or

$$k' = k + K + G$$

The first case shows the creation of a phonon (exciting a crystal vibration, increasing quantum number n), and the second case shows destruction of a phonon ("damping out" the vibration, decreasing quantum number n)

In neutron scattering experiments to determine the structure of materials, the incident and scattered neutrons and the crystal vibrations are measured; further constraints are applied from conservation of energy, knowing that 1 phonon of frequency ω has E = $\hbar\omega$.

Thermal Properties of Solids

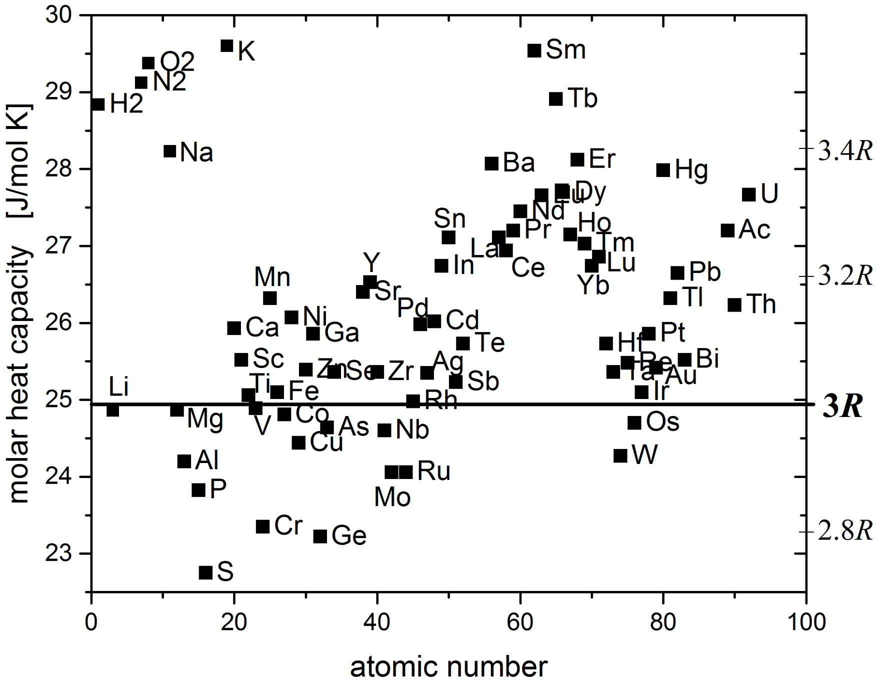
The conductivity, specific heat, and other thermal properties of solids depend critically on the spectrum of phonons that can be supported in the material.

Some properties, like heat capacity, can be derived from the statistics of phonon energy distribution; others depend on deviations from the harmonic oscillator potential, and interactions of the phonons with the lattice.

The contribution of phonons to the heat capacity is known as the "lattice heat capacity" and over a wide range of temperatures may be the dominant contribution.

The total energy of all the phonons in a solid in thermal equilibrium depends on the temperature. For total energy U, the specific heat is $C_V \equiv (\partial U/\partial T)_V$*.

*C_V and C_P are usually nearly the same for solids. As $T \to 0$, $C_V \to C_P$



In modern units, the law of Dulong & Petit says that solids have molar heat capacities of approximately 3R.

The horizontal line shows what is termed "the Law of Dulong & Petit", which says that all solids have the same molar specific heat.

This is not a great law, and is more famous for being first than for being useful (it was stated only 2 years after the idea of atomic masses was postulated).

Lattice Heat Capacity

Basic kinetic theory calculations can be used to show that the specific heat of three dimensional solids should be approximately constant, classically.

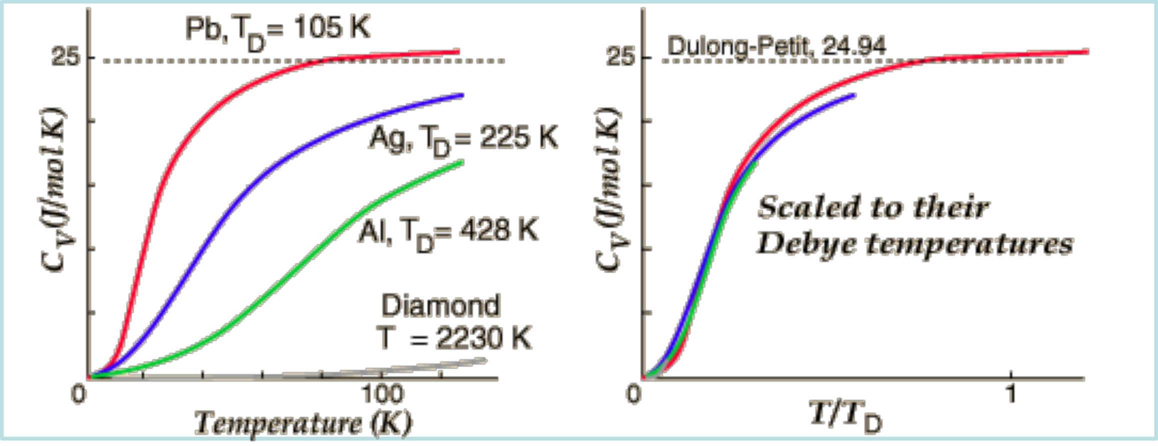
This applies if heat capacity is calculated per atom, or per mole of material. The heat capacity per unit mass is predicted to vary depending on the density of the material.

Later work showed this law to arise from the equipartition theorem: each atom contributes an equal amount $3k\mathrm{T}/2$ of translational kinetic energy to the total energy of a solid, plus lattice vibration energy also equal to $3k\mathrm{T}/2$. The heat capacity per atom is then just $c_v = 3k = 4.14\times10^{-23}$ J/K/atom, or 24.94 J/K/mol.

In reality, this law only applies at very high temperatures, because it is based on Maxwell-Boltzmann statistics. Phonons obey Bose-Einstein statistics, and at low temperatures they are a major contributor to the internal energy of a solid (below what is known as the Debye temperature).

Einstein model for D(ω)

The Law of Dulong and Petit (constant molar heat capacity for solids) was known to fail dramatically at low temperatures.



Einstein (1907) tried to explain this failure by applying the new idea of quantization to the vibrational energy levels in solids, for energies less than the thermal energy kT. N quantum oscillators with frequency ω have total vibrational energy $U = \dfrac{N\hbar\omega}{\exp(\hbar\omega/kT) - 1}$

Phonon Heat Capacity

At temperature T, we have to sum over all phonon modes, described by wavevector K and polarization p.

Each mode has energy $\hbar\omega$ per phonon, and in equilibrium there will be an average number of phonons per mode given by $\langle n \rangle$.

From the Planck distribution, $\langle n \rangle = \dfrac{1}{\exp(\hbar\omega/kT) - 1}$.

The total energy then $U_{\text{lat}} = \sum_K \sum_p \langle n_{Kp} \rangle \hbar\omega_{Kp}$

$$U_{\text{lat}} = \sum_K \sum_p \frac{\hbar\omega_{Kp}}{\exp\left(\hbar\omega_{Kp}/kT\right) - 1}$$

Normal Mode Enumeration

In many cases there are so many discrete states that we can replace the sums by an integral, if we define the density of states as a function of frequency, $D_p(\omega)d\omega$.

$$U_{\text{lat}} = \sum_p \int d\omega D_p(\omega) \frac{\hbar\omega_{Kp}}{\exp\left(\hbar\omega_{Kp}/kT\right) - 1}$$

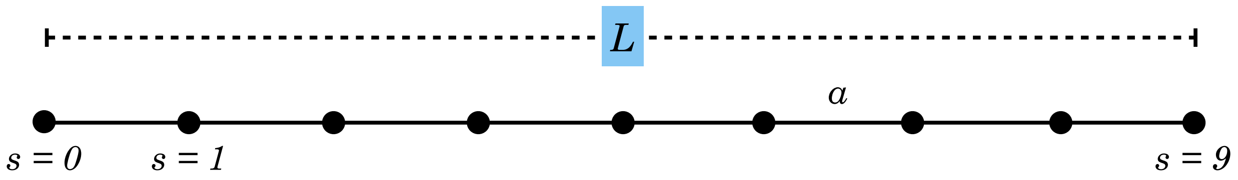
The lattice heat capacity is found by differentiating this with respect to temperature. For convenience, define $x \equiv \hbar\omega/kT$.

$$C_{\text{lat}} = k \sum_p \int d\omega D_p(\omega) \frac{x^2 \exp x}{(\exp x - 1)^2}$$

The integral is doable provided we can define the density of states $D(\omega)$ - the number of modes per unit frequency range, between ω and $\omega + d\omega$.

State Density - 1d

To illustrate the calculation of D(ω), we can look at a one-dimensional system: an elastic line of N+1 atoms, with the ends fixed. The atom positions are labelled like the crystal planes *s*, separated by *a*.



This is a system of N harmonic oscillators, with displacements given by $u_s \propto u_0 \exp(-i\omega t) \sin sKa$.

Of the N+1 atoms, only N–1 can move. Solving the problem of N–1 linked oscillators in classical mechanics shows there are N–1 allowed values of *K:*

$$K = \frac{\pi}{L}, \frac{2\pi}{L}, \ldots, \frac{(N-1)\pi}{L} \quad .$$

Allowed Phonon energies

There are N–1 allowed independent values of *K*, with each one associated with a standing wave. In one-dimension, the density of states per unit *K* is L/π for $K \leq \pi/a$, and 0 for $K > \pi/a$.

In addition there are 3 polarizations for each *K*, two transverse and one longitudinal.

For each polarization, the density of states is $D(\omega)d\omega = \frac{L}{\pi}\frac{dK}{d\omega}d\omega.$

This is more useful expressed in in terms of the dispersion relation,

$$D(\omega)d\omega = \frac{L}{\pi}\left(\frac{d\omega}{dK}\right)^{-1} d\omega$$

This way we can see that there's a singularity in D(ω) whenever the group velocity goes to zero.

The above analysis uses fixed boundary conditions, but the same result can be obtained by using periodic boundary conditions, which are more easily extended to 3-dimensions.

Density of states in 3-d

We can extend the analysis to three dimensions, but it will only remain this simple for waves along certain directions in the lattice, e.g., [100].

The periodic boundary condition means that the displacement of a crystal plane and its velocity must be continuous across the boundary between adjacent primitive cells, which means that:

$$\exp\left[i(K_x x + K_y y + K_z z)\right] = \exp\left[i(K_x(x+L) + K_y(y+L) + K_z(z+L)\right]$$

For N^3 primitive cells within a cube of length L, there will be 3 independent components of K, (e.g., x, y, z), each of which can be $\pm m\pi/L$, where m is an even integer between 0 and N.

There are $(L/2\pi)^3$ allowed values of K per unit volume for each polarization and each branch of the dispersion relation.

The number of modes with $K < K_{\max}$ is then $N = \frac{L^3}{8\pi^3}\left(\frac{4\pi K_{\max}^3}{3}\right)$

and $D(\omega) = dN/d\omega = \left(\frac{VK_{\max}^2}{2\pi^2}\right)\left(\frac{d\omega}{dK}\right)^{-1}$

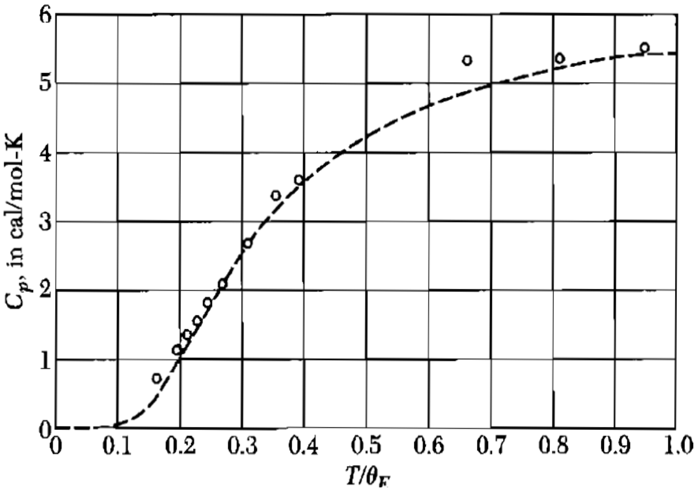
Einstein Model for Heat Capacity

The heat capacity of the quantum oscillators is found by differentiating with respect to temperature, and multiplying by 3 to account for the independent modes of a 3-d oscillator.

$$C_v = Nk\left(\frac{\hbar\omega}{kT}\right)^2 \frac{\exp \hbar\omega/kT}{\left[\exp(\hbar\omega/kT) - 1\right]^2}$$

This is Einstein's result for the heat capacity of N identical oscillators.

- In the high-T limit, this approaches the constant Dulong & Petit value.
- In the low-T limit, this decreases (in agreement with experiment), but decreases like $\exp(-\hbar\omega/kT)$, which is not observed.



molar heat capacity of diamond compared to the prediction of the Einstein model, for θ_E = 1320 K

- This is a useful first approximation and is historically important as one of the first (partially) successful applications of quantum mech. to solids.

Debye Model for Density of States

The density of states obtained by considering the volume of phonon modes in phase space, $D(\omega) = dN/d\omega = \left(\frac{VK_{\max}^2}{2\pi^2}\right)\left(\frac{d\omega}{dK}\right)^{-1}$, needs a dispersion relation to be useful in calculation.

In the Debye approximation, the velocity of sound is taken as a constant for each polarization type, which is only strictly true for a classical continuum solid. Under this approximation, $\omega = vK$.

The density of states simplifies to $D(\omega) = \frac{V\omega^2}{2\pi^2 v^3}$

A key aspect of the phonon mode distribution is that there is a maximum wavevector, dictated by the spacing between atoms. This is the fundamental difference between the Planck function for photon energies and the distribution of phonon energies.

We can work out the maximum wavevector and the corresponding frequency in terms of the number density of atoms by going back to the expression for the maximum number of modes, $N = \frac{L^3}{8\pi^3}\left(\frac{4\pi K_{\max}^3}{3}\right) = \frac{V}{6\pi^2}K_{\max}^3$.

Using the sound speed v, the frequency corresponding to $K_{\max}$ is $\omega_D = 6\pi^2 v^3 (N/V)$

Under this model we can calculate the total thermal energy in phonons of a given polarization:

$$U = \int d\omega D(\omega)\langle n\rangle\hbar\omega \qquad = \int_0^{\omega_D} d\omega \left(\frac{V\omega^2}{2\pi^2 v^3}\right)\left(\frac{\hbar\omega}{\exp(\hbar\omega/kT) - 1}\right)$$

We assume the sound speed v is constant for the three polarizations and do the integral

Debye Temperature

To express the results compactly, we define $x = \hbar\omega/kT$ and $x_D = \hbar\omega_D/kT = \theta/T$

$\hbar\omega/k$ defines the Debye Temperature θ in terms of the cutoff frequency for waves in the crystal. Using the definition of ω_D, $\theta = \frac{\hbar v}{k}\left(\frac{6\pi^2 N}{V}\right)^{1/3}$

θ can be thought of as a convenient collection of constants and factors, but there is a useful physical interpretation as well. The quantity $k\,\theta$ is approximately equal to the phonon energy of the minimum wavelength phonon.

For T > θ, all phonon modes are excited.

Debye temperatures for some common elements: Li: 344 K, Be: 1440 K, Si: 645 K
Na: 168 K; K 91 K; Ca: 230 K; Fe: 470 K; Ne 75 K.

Debye Specific Heat

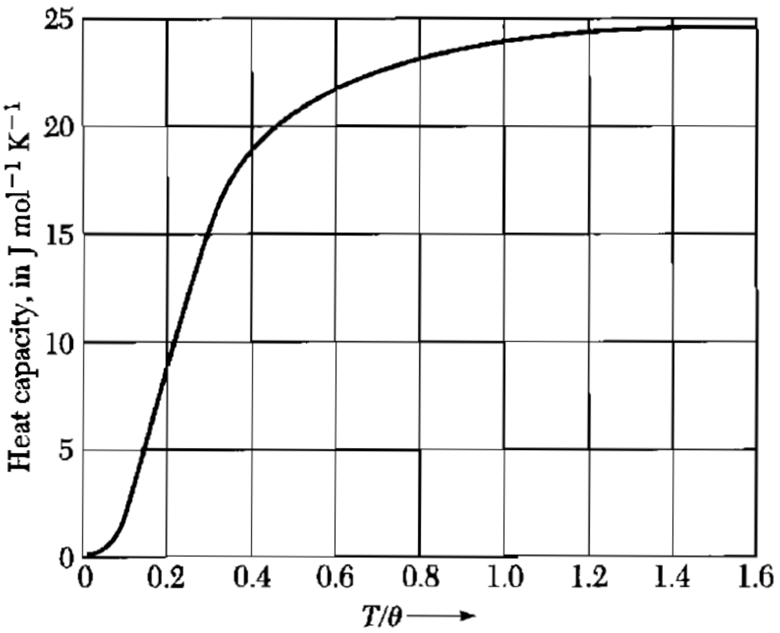
The total phonon energy in this model is $U = 9NkT\left(\frac{T}{\theta}\right)^3 \int_0^{x_D} dx \frac{x^3}{e^x - 1}.$

Differentiation gives

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

At T >> θ, the heat capacity asymptotically approaches the classical value of 3Nk.

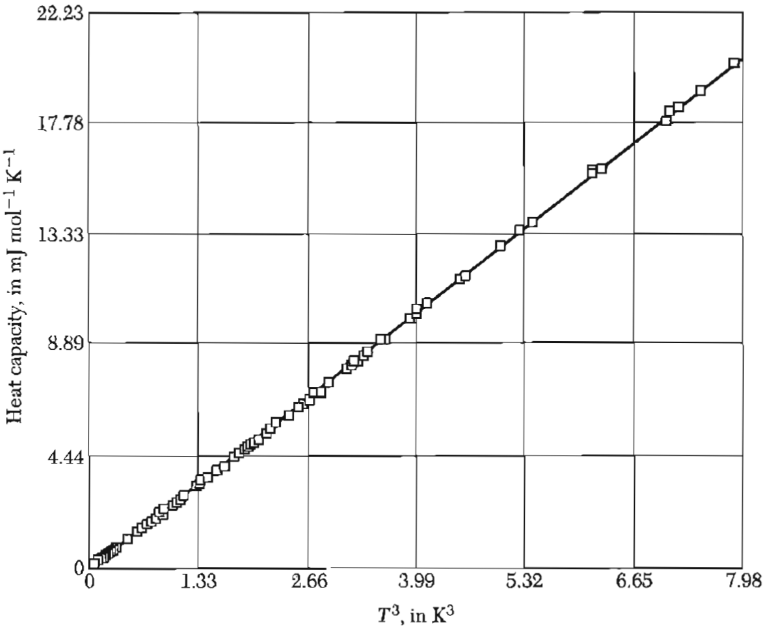
At low temperatures, the heat capacity varies like T^3, which reproduces the observed behaviour of a very wide range of materials.



Debye T^3 Law

At very low temperatures the integral takes on the approximate value $\pi^4/15$, independent of temperature. Therefore the heat capacity can be written as $C_V \approx 234Nk(T/\theta)^3$.

The T^3 approximation is quite good at sufficiently low temperatures, e.g., the figure shows the specific heat of argon (θ = 92 K) vs. the prediction of the T^3 law.

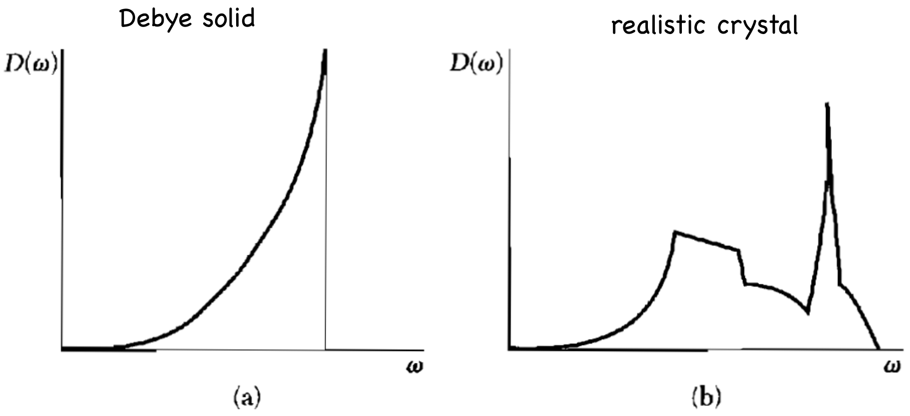


For $T \ll \theta$, only the very long wavelength phonon modes are excited. For these, the solid can be treated as an elastic continuum.

Good approx. for $T < \theta/50$.

D(ω), General Case

In the most general case, the challenge is to identify all possible wave modes within a given frequency range. Because many different waves exist with different dispersion relations, this can be a challenge and is better done experimentally as opposed to from basic theory.



(a) (b)

The points at which the group velocity goes to zero are interesting because the density of states changes quite abruptly at the corresponding frequencies. These are known as van Hove singularities.

Anharmonic Vibrations

Everything so far has concerned vibrations which the energies are quadratic in terms of the separation between atoms. This is a reasonable approximation, which has the following consequences:

- Two waves do not interact.
- Single waves are transmitted without decay.
- There is no thermal expansion.
- Elastic constants are independent of P and T.
- Adiabatic and isothermal elastic constants are equal.

In real solids none of these conditions are exactly true, because *anharmonic* terms in the potential energy (higher than quadratic) influence the motion.