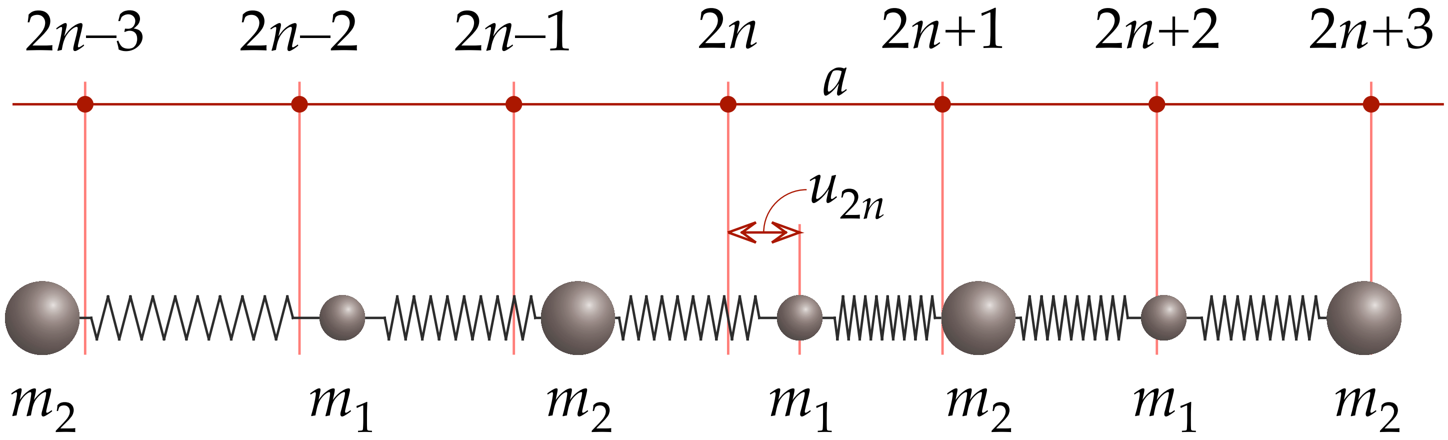
Normal modes of a one-dimensional lattice with a basis

Consider a linear chain in which the spacing of atoms is a, and alternate atoms have mass m_1 and m_2.

Assume again that only nearest neighbors interact and that this interaction is equivalent to a connection by a spring with spring constant K.



The equations of motion are

$$\begin{aligned} m_1\, \ddot{u}_{2n} &= -K\left(u_{2n} - u_{2n-1}\right) + K\left(u_{2n+1} - u_{2n}\right) \\ &= K\left(u_{2n-1} + u_{2n+1} - 2u_{2n}\right), \\ m_2\, \ddot{u}_{2n+1} &= -K\left(u_{2n+1} - u_{2n-2}\right) + K\left(u_{2n} - u_{2n+1}\right) \\ &= K\left(u_{2n-2} + u_{2n} - 2u_{2n+1}\right). \end{aligned} \tag{4.44}$$

We seek solutions to (4.44) representing plane waves with angular frequency ω and wave vector k:

$$\begin{aligned} u_{2n} &= Ae^{i(2kna-\omega t)}, \\ u_{2n+1} &= Be^{i[k(2n+1)a-\omega t]}. \end{aligned} \tag{4.45}$$

We substitute (4.45) into the equations of motion (4.44) and find that

$$\left(\omega^2-\omega_1^2\right)A+\omega_1^2\left(e^{ika}+e^{-ika}\right)B=0\ , \tag{4.46}$$

$$\omega_2^2\left(e^{ika}+e^{-ika}\right)A+\left(\omega^2-2\omega_2^2\right)B=0\ , \tag{4.47}$$

where $\omega_1=\sqrt{K/m_1}$ and $\omega_2=\sqrt{K/m_2}$.

This system of two homogenous equations in the two variables A and B has a nontrivial solution when

$$\left(\omega^2-2\omega_1^2\right)\left(\omega^2-2\omega_2^2\right)-4\omega_2^2\omega_1^2\cos^2 ka=0\ , \tag{4.48}$$

or

$$\omega^4-2\omega^2\left(\omega_1^2+\omega_2^2\right)-4\omega_1^2\omega_2^2\sin^2 ka=0\ . \tag{4.49}$$

The solution of equation 4.49 is

$$\omega^2 = \omega_1^2 + \omega_2^2 \pm \sqrt{\left(\omega_1^2 + \omega_2^2\right)^2 - 4\omega_1^2\omega_2^2 \sin^2 ka}$$

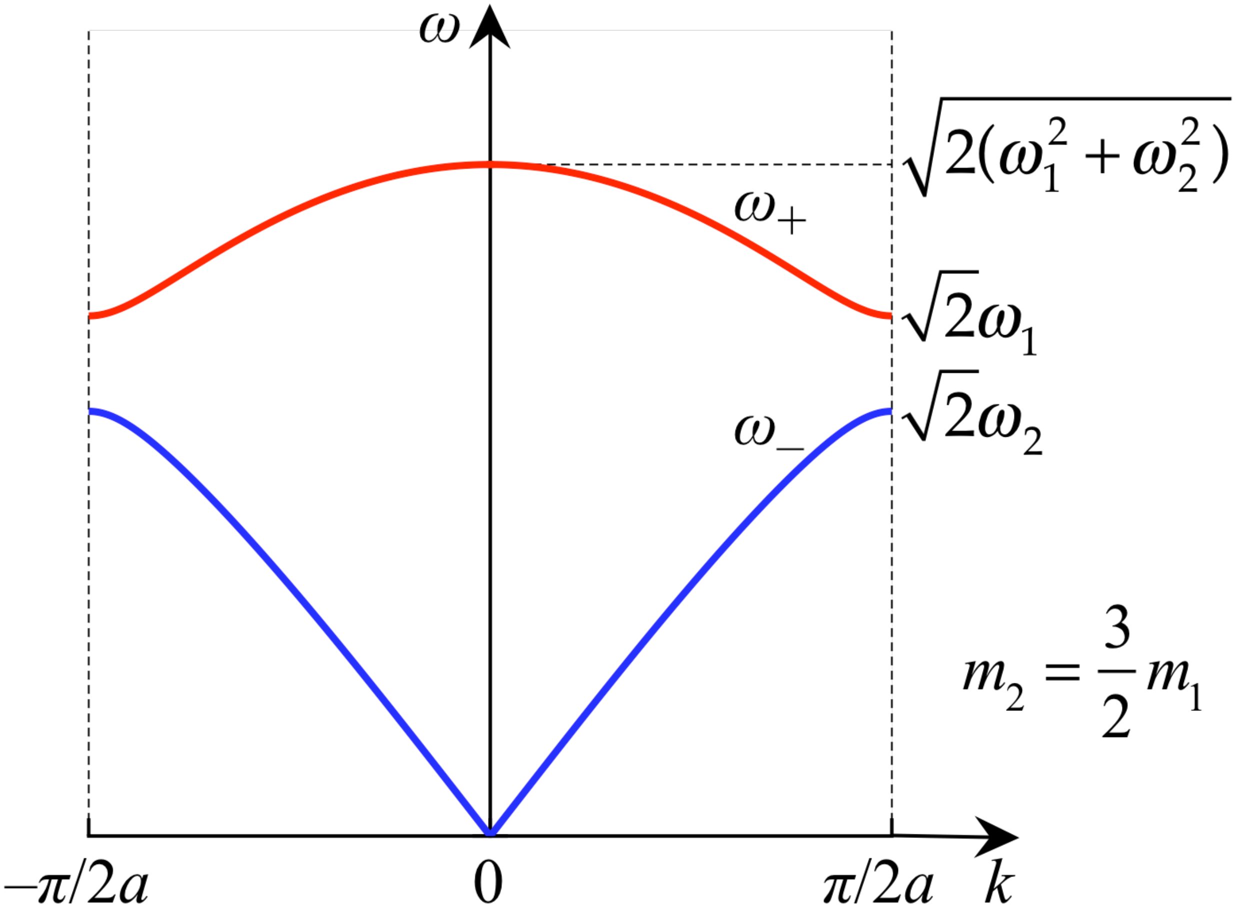
or

$$\omega^2 = \omega_1^2 + \omega_2^2 \pm \sqrt{\omega_1^4 + \omega_2^4 + 2\omega_1^2\omega_2^2 \cos 2ka} \quad . \qquad (4.50)$$

The wave vectors k take the values only between $-\pi/2a$ and $\pi/2a$.

This is because the lattice parameter of a diatomic chain is $2a$, i.e., twice the lattice parameter of the monatomic chain.

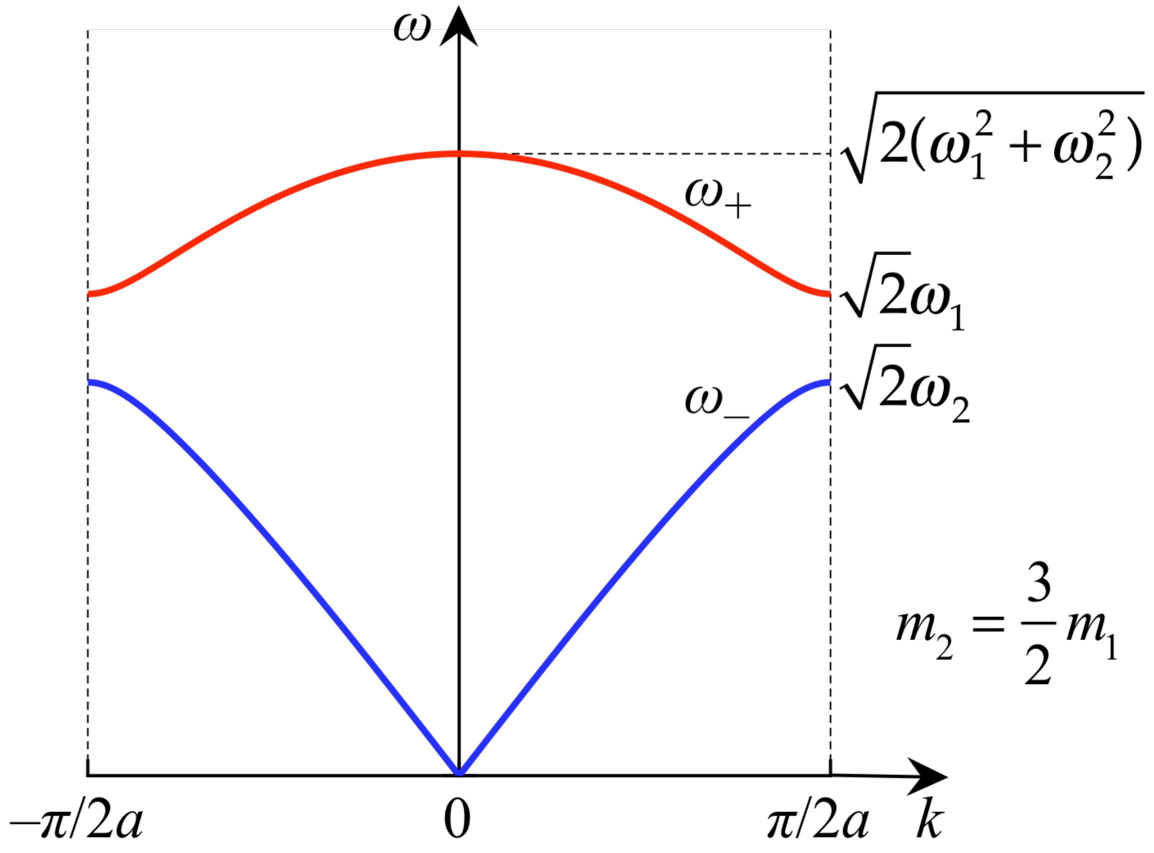
Here the dispersion curve $\omega(k)$ is plotted for $m_2/m_1 = 3/2$, and the branches ω_+ и ω_- correspond to the signs in (4.50).



The ranges of allowed frequencies ω:

ω_-: ω varies between zero and $\omega_2\sqrt{2}$,

ω_+: ω varies between $\omega_1\sqrt{2}$ and $\sqrt{2(\omega_1^2+\omega_2^2)}$.



The width of a gap formed at $k=\pi/2a$ is $\Delta\omega=\sqrt{2}(\omega_1-\omega_2)$.

We first discuss the branch ω_- because it looks similar to the dispersion curve of the monatomic chain.

Surprisingly, the maximum frequency $\sqrt{2}\omega_2=\sqrt{2K/m_2}$ of the ω_- branch is independent of m_1, the mass of light atoms.

The origin of this phenomenon becomes lies in the actual motions of the light and heavy atoms.

Because $\omega_1>\omega_2$, A and B are the amplitude of oscillations of light and heavy atoms, respectively.

From (4.46) we find

$$\frac{B}{A} = \frac{2\omega_1^2 - \omega^2}{2\omega_1^2 \cos ka} \,, \tag{4.51}$$

and from (4.47) we find

$$\frac{B}{A} = \frac{2\omega_2^2 \cos ka}{2\omega_2^2 - \omega^2} \,. \tag{4.52}$$

For $\omega = 0$ and $k = 0$ the both conditions (4.51) and (4.52) lead to $B/A = 1$.

The neighboring atoms move in phase and with the same amplitude, as in a common sound wave in the limit $\lambda \gg a$.

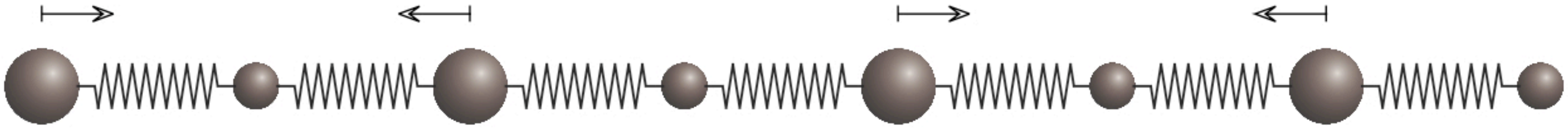
Therefore, $\omega_{-}(k)$ is known as the acoustic branch.

At $k = \pm\pi/2a$, i.e., the boundaries of the Brillouin zone, the frequency ω reaches $\sqrt{2}\,\omega_2$. According to (4.51) this leads to

$$\frac{B}{A} = \infty \quad .$$

The light atoms do not move at all, and therefore the maximum frequency is independent of their mass m_1.

The corresponding mode of oscillations is shown here.



We now discuss the branch ω_+.

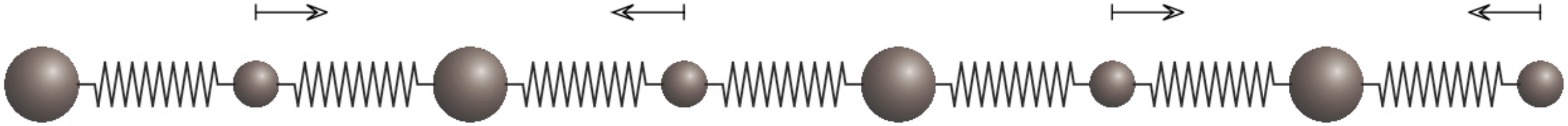
At $k=0$ the frequency is $\omega=\sqrt{2\left(\omega_1^2+\omega_2^2\right)}$, and according to (4.51) or (4.52)

$$\frac{B}{A}=-\frac{\omega_2^2}{\omega_1^2}=-\frac{m_1}{m_2} \quad . \tag{4.53}$$

The light and heavy atoms move out of phase.

If the light and heavy atoms also bear different charges, such motion can lead to an oscillating dipole moment, which can interact with electromagnetic waves. Therefore, $\omega_+(k)$ is known as the optical branch; the name remain also when the atoms do not bear different charges.

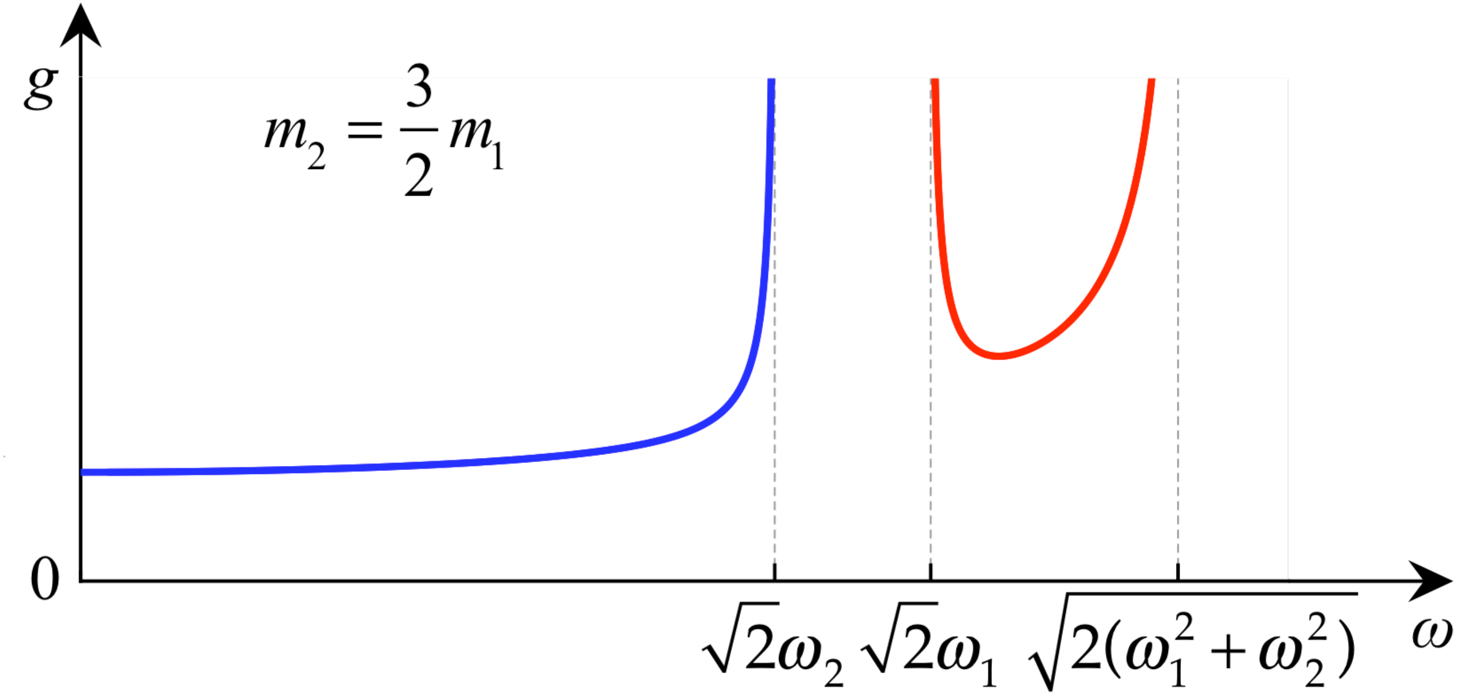
At the edges of the Brillouin zone $k = \pm\pi/2a$ we find from (4.52) that $B/A = 0$, i.e., the heavy atoms do not move.



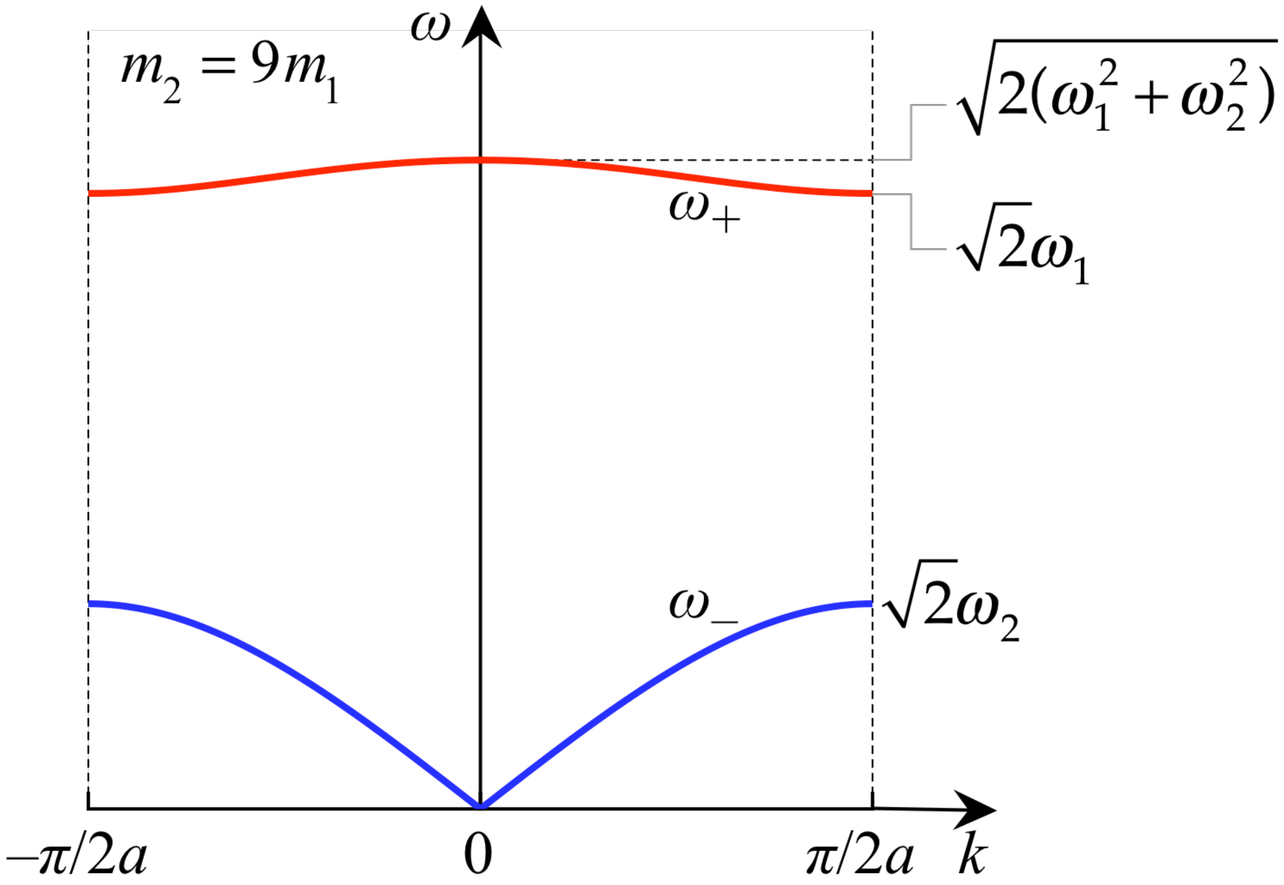
For this mode, the dipole moment does not oscillate.

Therefore, electromagnetic waves cannot exite lattice vibrations of the optical branch at the the edges of the Brillouin zone.

The density of normal modes of the acoustic branch $\omega_-(k)$ is similar to $g(\omega)$ of the monatomic chain. The density of normal modes of the optical branch diverges as the frequency ω approaches the minimum $\sqrt{2}\,\omega_2$ and maximum $\omega = \sqrt{2\left(\omega_1^2 + \omega_2^2\right)}$ frequencies.



If the limit $m_1 \ll m_2$, the frequency of the optical branch ω_+ weakly depends on k, the group velocity $\partial\omega/\partial k$ is small, and the width of the optical branch is $\Delta\omega_+ \approx \omega_+(0)m_1/2m_2$.



If the limit $m_1 \ll m_2$ the density of normal modes $g(\omega)$ of the optical branch can be approximated by a δ-function.

In this case the Einstein model can describe the specific heat due to excitations of the optical modes.

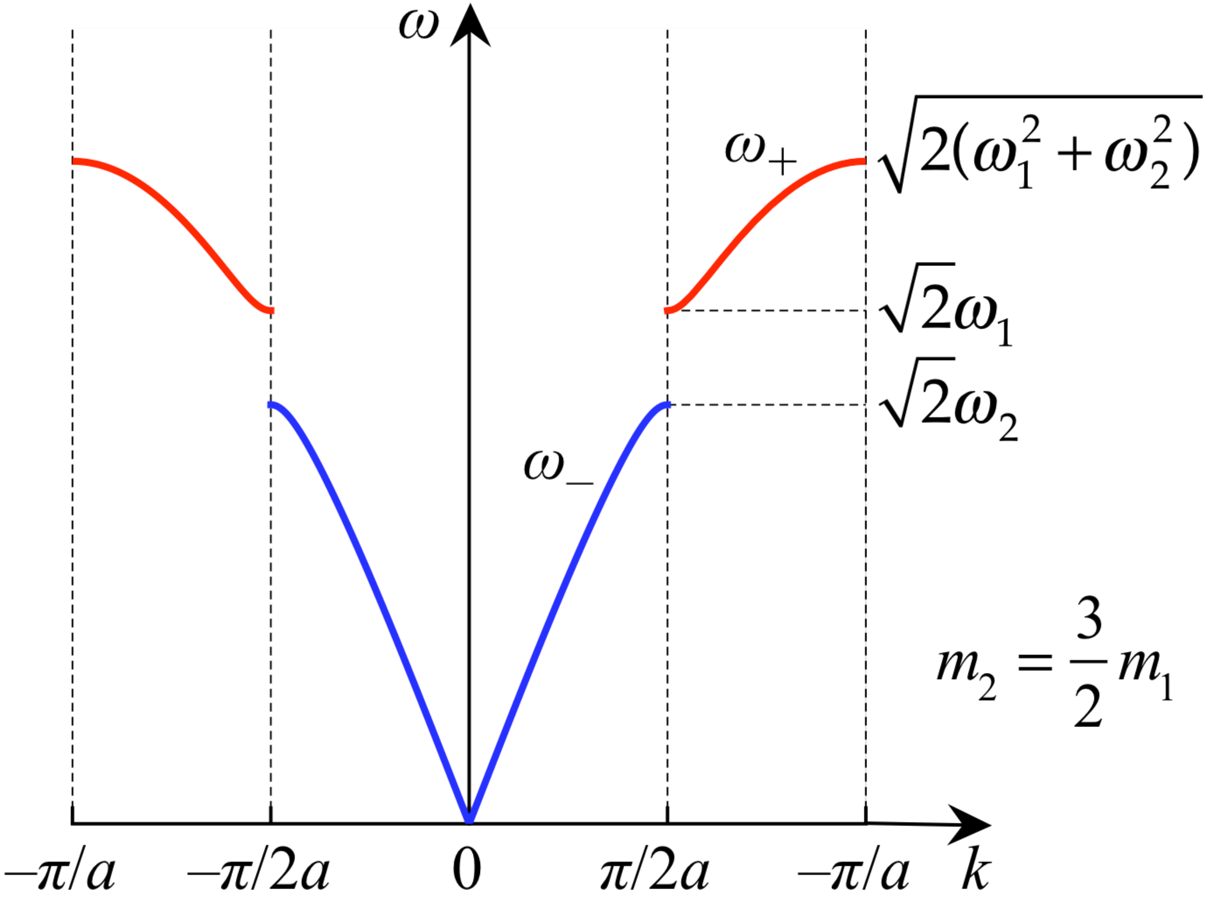
The acoustic contribution to the specific heat can be described by the Debye model.

The both contributions are additive.

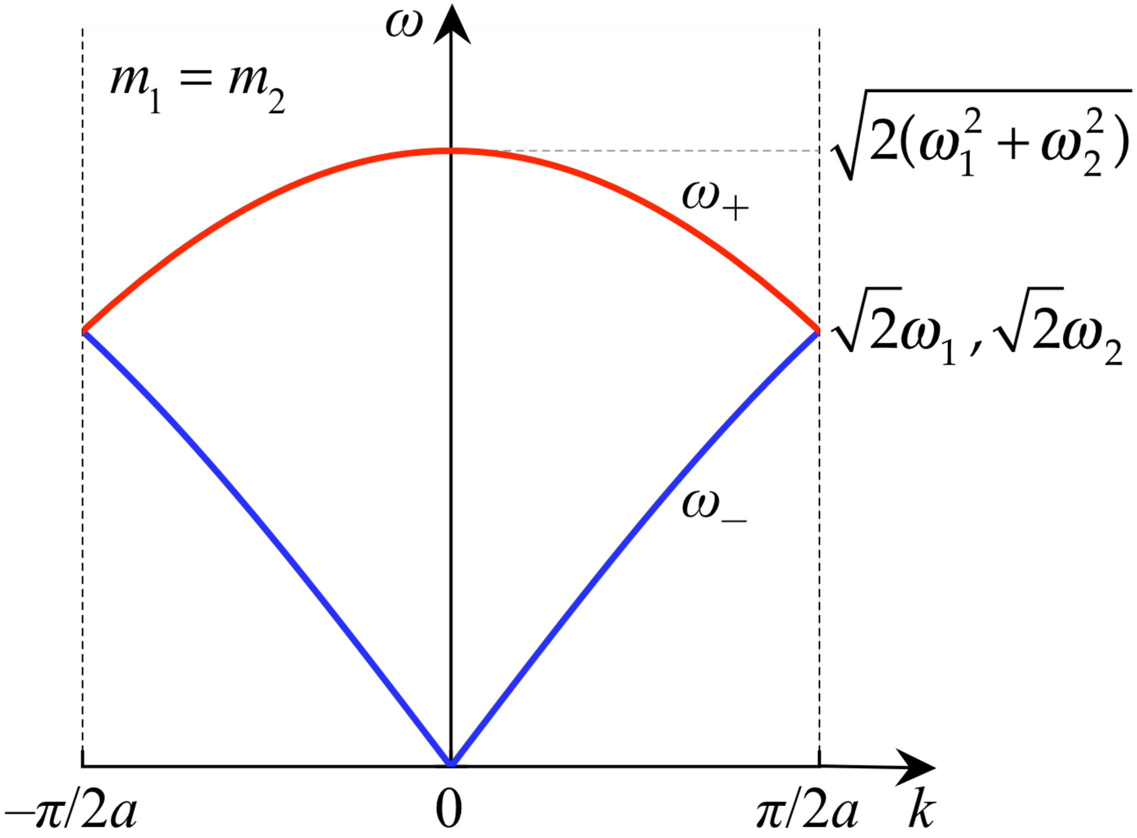
The lattice specific heat of several solids is in fact best described by the sum of the Einstein and Debye terms.

Example is the filled antimony scutterudite $Tl_{0.8}Co_4Sb_{11}Sn$ [R. P. Hermann *et al.*, 2003].

Considering the lattice excitation spectrum of the diatomic chain, we could arrive at the same solution, at least in the wave vector range between $-\pi/a$ and π/a, if we would regard our chain as a one-dimensional lattice with the constant a and two atoms in the basis.

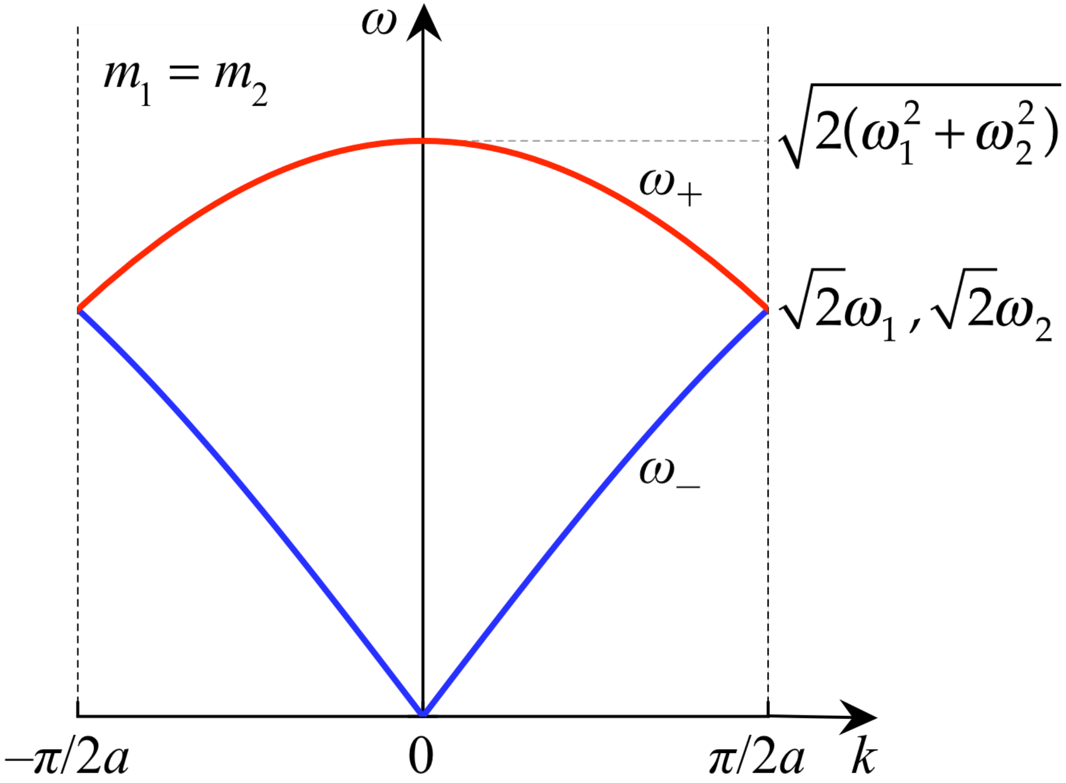


Optical branches appear in the excitation spectrum of the Bravais lattice with the basis that contain two or more atoms. An optical branch appears even when a diatomic basis contains two identical atoms.



At the edges of the Brillouin zone the highest frequency $\omega_-(\pi/2a)$ of the acoustic branch, however, coincides with the lowest frequency $\omega_+(\pi/2a)$ of the optical branch.

The lattice excitation spectrum therefore remains gapless, and the mode with the wave vector $k=\pi/2a$ becomes doubly degenerated.



Lattice excitations in three-dimensional crystals

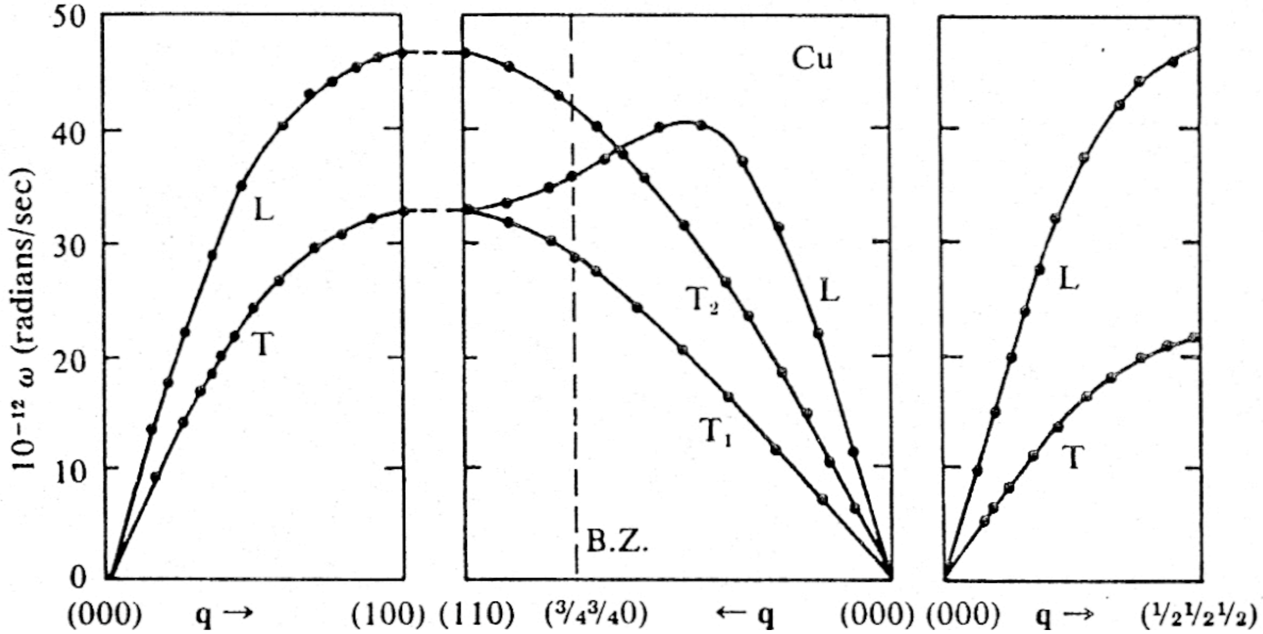
In general, our arguments for one-dimensional lattices remain valid also in three dimensions. In our discussion of the lattice excitations in 1D chains we considered only longitudinal modes. There are two additional transverse modes in three-dimensional crystals.

The density of normal modes can be obtained from the same relation $g(\omega) = g(k)\,\partial k/\partial\omega$, as in one-dimensional case.

We now discuss the dispersion relations $\omega(k)$ for copper and diamond, measured using inelastic neutron scattering, to illustrate typical features of $\omega(k)$ in three dimensions.

Copper (Cu) — fcc lattice with a monatomic basis

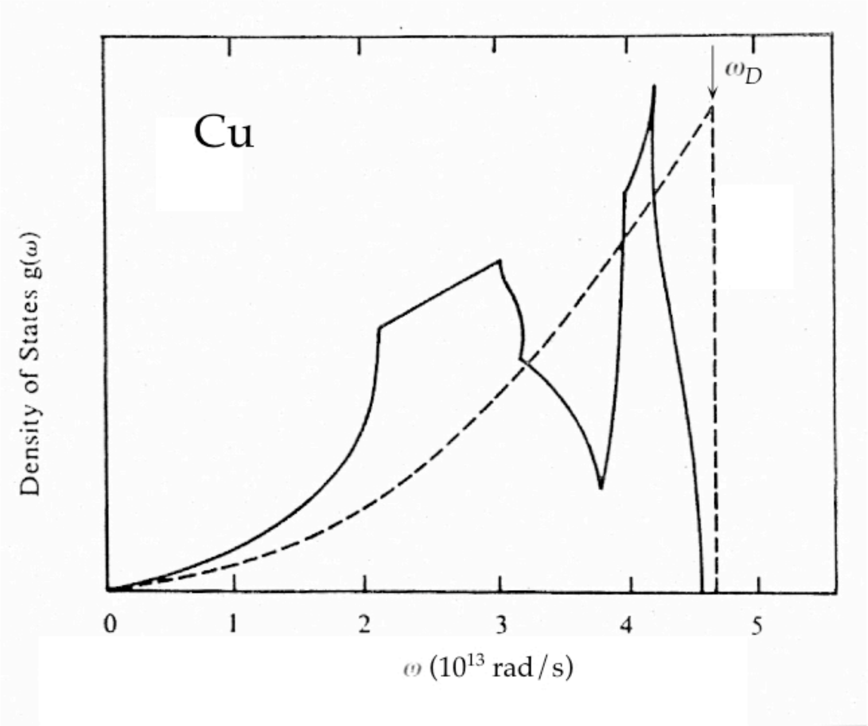
Only acoustic modes are expected.



[from E. C. Swensson *et al.*, Phys. Rev. **155**, 619 (1967)]

The wave vector is plotted in units $ka/2\pi$. Data points correspond to excitations with certain frequency ω and wave vector k, i.e., to phonons. For some high-symmetry directions the transverse modes are degenerate.

In three dimensions the density of normal modes $g(\omega)$ becomes quite complex because ω now depends both on the absolute value and on the direction of the wave vector $\mathbf{k}$.



The density of normal modes in copper [from E. C. Swensson, B. N. Brockhouse, and J. M. Rowe, Phys. Rev. **155**, 619 (1967)]

Contrary to the 1D case, the critical points of $g(\omega)$, or van Hove singularities, are now infinities only in the $g(\omega)$ derivatives, but not in $g(\omega)$ itself.

The density of normal modes in copper is a superposition of separate densities for one longitudinal and two transverse branches.

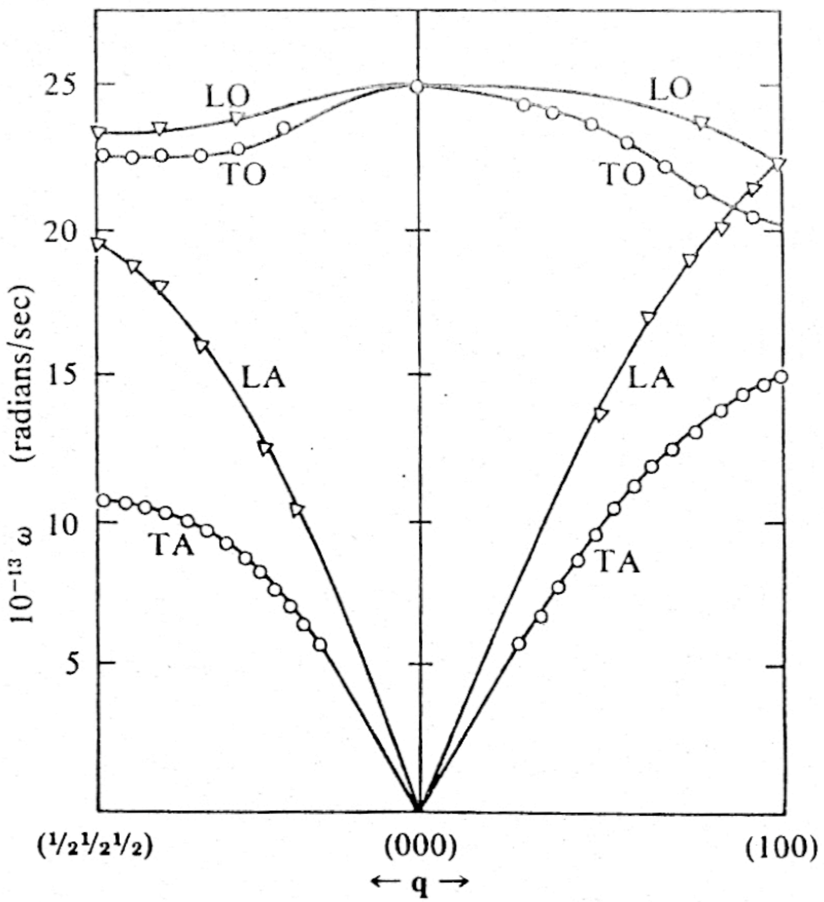
Diamond (C) — fcc lattice with a diatomic basis

One acoustic and two optical branches are expected.

The branches LO и LA at the edge of the Brillouin zone along the [100] direction are degenerate.

The branches LO и TO at the Brillouin zone center are also degenerate.

This degeneracy is lifted for ionic crystals, e.g., for NaCl.



[From J. L. Warren *et al.*, Inelastic Scattering of Neutrons (IAEA, Vienna, 1965) Vol. I, p. 361]

Connection with the Theory of Elasticity

The theory of elasticity treats a solid as a continuum, ignoring its microscopic atomic structure.

The theory of elasticity can be derived from the theory of lattice vibrations by considering lattice deformations that vary gradually on a scale determined by the range of the interatomic forces.

Assumption: one can specify the deformation of the basis atoms within each primitive cell entirely in terms of the vector field $\mathbf{u}(\mathbf{r})$, specifying the displacement of the whole primitive cell.

The number of independent elastic constants

Crystal System	Point Groups	Elastic Constants
Triclinic	all	21
Monoclinic	all	13
Orthorhombic	all	9
Tetragonal	C_4, C_{4h}, S_4	7
	$C_{4v}, D_4, D_{4h}, D_{2d}$	6
Rhombohedral	C_3, S_6	7
	C_{3v}, D_3, D_{3d}	6
Hexagonal	all	5
Cubic	all	3
Decagonal	all	5
Icosahedral	all	2
Isotropic Media		2

Elastic isotropy and transverse elastic isotropy

The elastic modulus matrix c_{ij} of an isotropic solid has only two independent components:

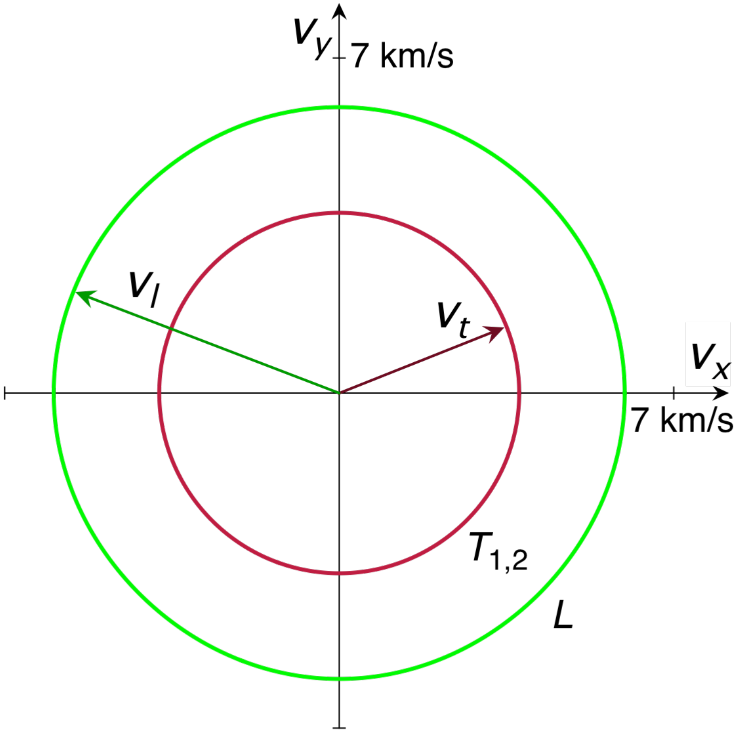
$$\begin{pmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c' & 0 & 0 \\ 0 & 0 & 0 & 0 & c' & 0 \\ 0 & 0 & 0 & 0 & 0 & c' \end{pmatrix},$$

where $c' = \frac{1}{2}(c_{11} - c_{12})$.

By contrast, the simplest elastic modulus matrix for a periodically ordered crystal (cubic) has three independent components c_{11}, c_{12} and c_{44}:

$$\begin{pmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{44} \end{pmatrix}.$$

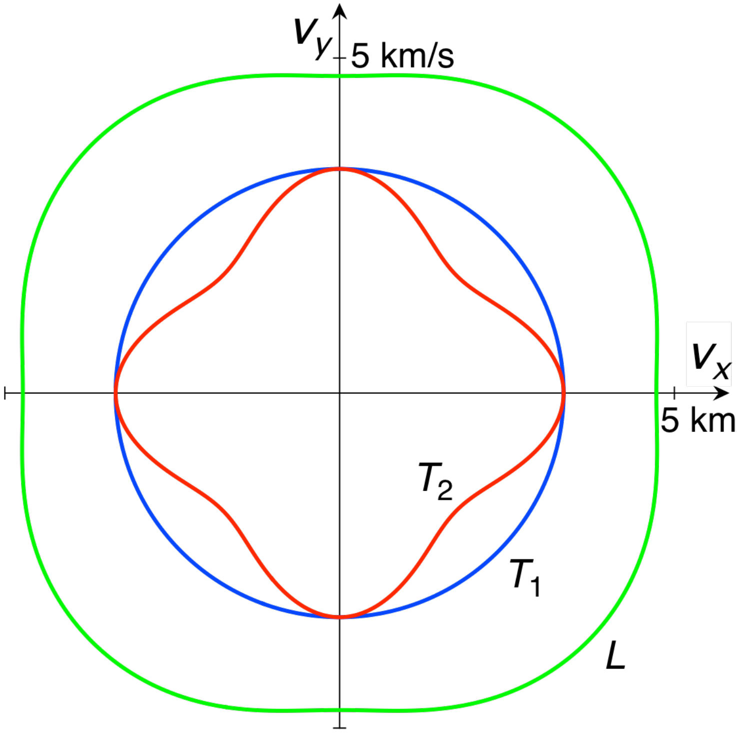
Vitreous silica – arbitary plane



$v_l = (c_{11}/\rho)^{\frac{1}{2}}$

$v_t = (c_{44}/\rho)^{\frac{1}{2}}$

Cubic GaAs – (001) plane



The isotropic and cubic elastic tensors are identical, except that for an isotropic solid $c_{44} = \frac{1}{2}(c_{11} - c_{12})$. An anisotropy parameter A is defined as

$$A = \frac{c_{11} - c_{12}}{2c_{44}} \quad ,$$

so that for an isotropic solid $A = 1$.

With $A = 1.007 \pm 0.002$ tungsten has the smallest elaslic anisotropy among all periodic crystals. The sound velocity in tungsten varies with direction by less than 0.5%.

Icosahedral quasicrystals possess elastic isotropy, and for icosahedral Al-Cu-Li, elastic isotropy was verified to within 0.07% (Spoor *et al.*, 1995).

The elastic modulus matrix of a transversely elastically isotropic solid

$$\begin{pmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c' \end{pmatrix}$$

The number of independent elastic moduli c_{ij} is five

The elastic modulus matrix of a tetragonal crystal (Laue class $4/mmm$)

$$\begin{pmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66} \end{pmatrix}$$

The number of independent elastic moduli c_{ij} is six

The elastic modulus matrix of the tetragonal Laue class $4/mmm$ differs from that of a transversely isotropic solid only in that the elastic modulus combination $c_{66} = \frac{1}{2}(c_{11} - c_{12})$ is nonzero. A measure of the deviation from transverse isotropy is the ratio

$$A_\mathrm{s} = \frac{c_{11} - c_{12}}{2c_{66}}$$

of the squares of the velocities of the pure shear waves polarized in the (001) plane and propagating along the [110] and [100] directions, respectively. For transversely isotropic solids $A_\mathrm{s} = 1$.

For transversely elastically isotropic solids, the equality $c_{66} = \frac{1}{2}(c_{11} - c_{12})$ reduces the number of independent elastic moduli c_{ij} that determine a deformation in the quasiperiodic plane to two, as for an isotropic medium.

Among ordered solids only hexagonal and decagonal phases are transversely elastically isotropic.

For example, for the decagonal Al-Ni-Co phase (five-dimensional space group $P10_5/mmc$) $A_{\mathrm{s}} = 1.0002 \pm 0.0004$ (Chernikov *et al.*, 1997).

We now determine the degree of polar elastic anisotropy, i.e., the deviation from complete elastic isotropy.

For transversely isotropic solids, two parameters may be used to quantify polar anisotropy, i.e., the anisotropy of shear $P_{\mathrm{s}} = c_{44} / c_{66}$ and the compressional anisotropy $P_{\mathrm{c}} = c_{33} / c_{11}$.

For decagonal Al-Ni-Co $P_{\mathrm{s}} = 0.794$ and $P_{\mathrm{c}} = 0.991$, revealing a very weak polar elastic anisotropy.

For comparison, for hexagonal Zn $P_{\mathrm{s}} = 0.65$ and $P_{\mathrm{c}} = 0.38$.

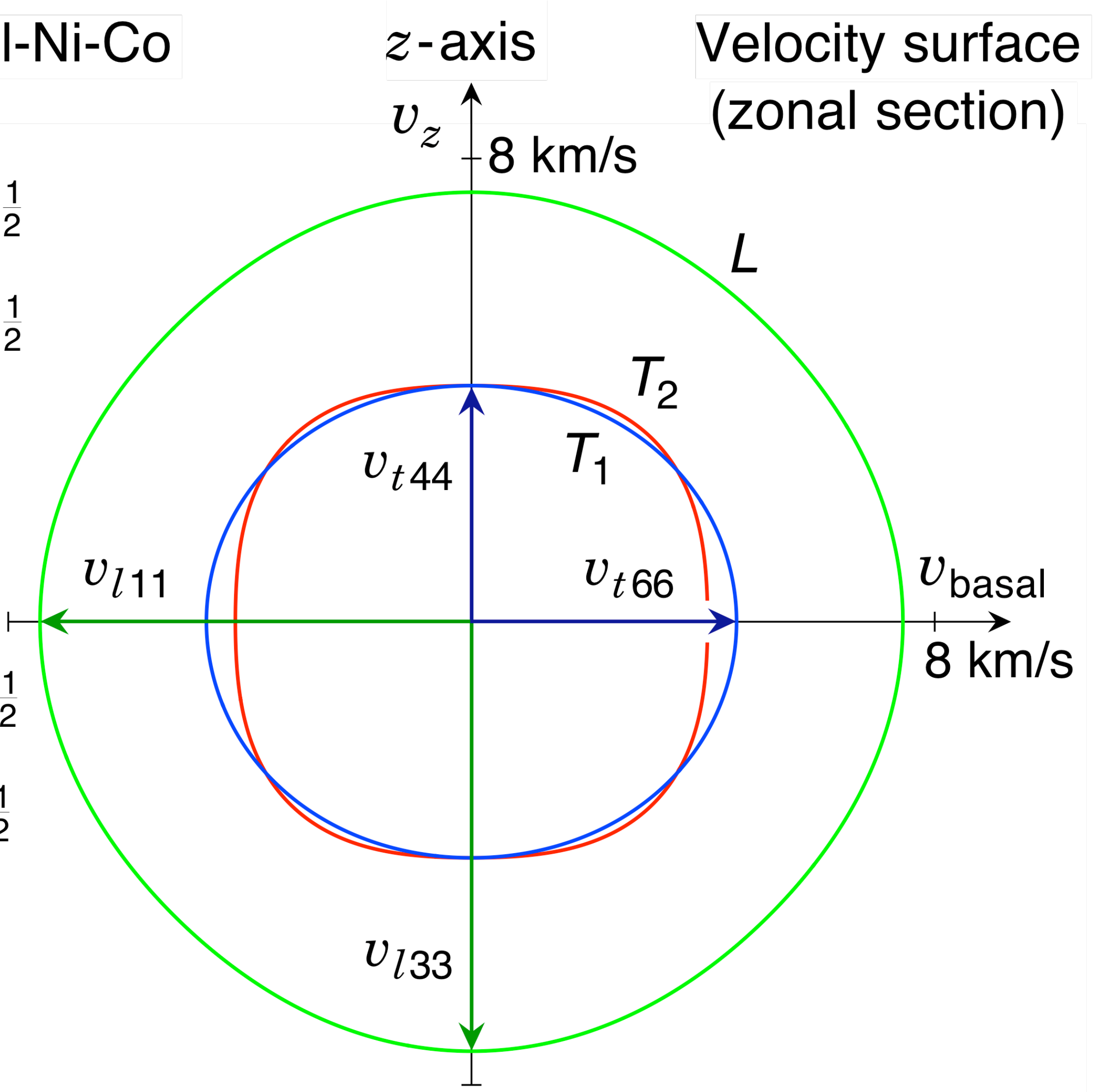
Decagonal Al-Ni-Co

Velocity surface (zonal section)

$$v_{t44} = (c_{44}/\rho)^{\frac{1}{2}}$$

$$v_{t66} = (c_{66}/\rho)^{\frac{1}{2}}$$

$$\frac{c_{44}}{c_{66}} = 0.79$$



$$v_{l33} = (c_{33}/\rho)^{\frac{1}{2}}$$

$$v_{l11} = (c_{11}/\rho)^{\frac{1}{2}}$$

$$\frac{c_{33}}{c_{11}} = 0.99$$

Hexagonal Zinc

Velocity surface (zonal section)

$$\frac{c_{44}}{c_{66}} = 0.65$$

$$\frac{c_{33}}{c_{11}} = 0.38$$