

Crystal Vibrations and Elasticity

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Born-Oppenheimer Approximation

The many-particle Schrödinger wave equation is $\mathcal{H}_c \psi = i\hbar \frac{\partial \psi}{\partial t}$,

the wave function ψ , in general, is a function of all electronic and nuclear coordinates and of the time t . That is,

$$\psi = \psi(\mathbf{r}_i, \mathbf{R}_l, t),$$

where the \mathbf{r}_i are the electronic coordinates and the \mathbf{R}_l are the nuclear coordinates. The Hamiltonian \mathcal{H}_c of the crystal is

$$\begin{aligned} \mathcal{H}_c = & -\sum_i \frac{\hbar^2}{2m} \nabla_i^2 - \sum_l \frac{\hbar^2}{2M_l} \nabla_l^2 + \frac{1}{2} \sum_{i,j}' \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \\ & - \sum_{i,l} \frac{e^2 Z_l}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_l|} + \frac{1}{2} \sum_{l,l'}' \frac{e^2 Z_l Z_{l'}}{4\pi\epsilon_0 |\mathbf{R}_l - \mathbf{R}_{l'}|}. \end{aligned}$$

m is the electronic mass, M_l is the mass of the nucleus located at \mathbf{R}_l , Z_l is the atomic number of the nucleus at \mathbf{R}_l , and e has the magnitude of the electronic charge.

By simplification, we can also write

$$\mathcal{H}_c = T_E + U + T_N = \mathcal{H}_0 + T_N, \quad \mathcal{H}_0 = T_E + U.$$

Here, T_E be the kinetic energy of the electrons, T_N be the kinetic energy of the nuclei, and U be the total Coulomb energy of interaction of the nuclei and the electrons.

Nuclei have large masses and hence in general they have small kinetic energies. Thus in the above expression, it makes some sense to regard T_N as a perturbation on \mathcal{H}_0 . Under the adiabatic approximation, the total wave function $\psi_n(\mathbf{r}_i, \mathbf{R}_l)$ can be written as a product of the electronic wave function $\varphi_n(\mathbf{r}_i)$ (with the nuclei fixed) times the nuclear wave function $X(\mathbf{R}_l)$ (with the electrons in some fixed state). In this approximation the electrons provide a potential energy for the motion of the nuclei while the moving nuclei continuously deform the wave function of the electrons.

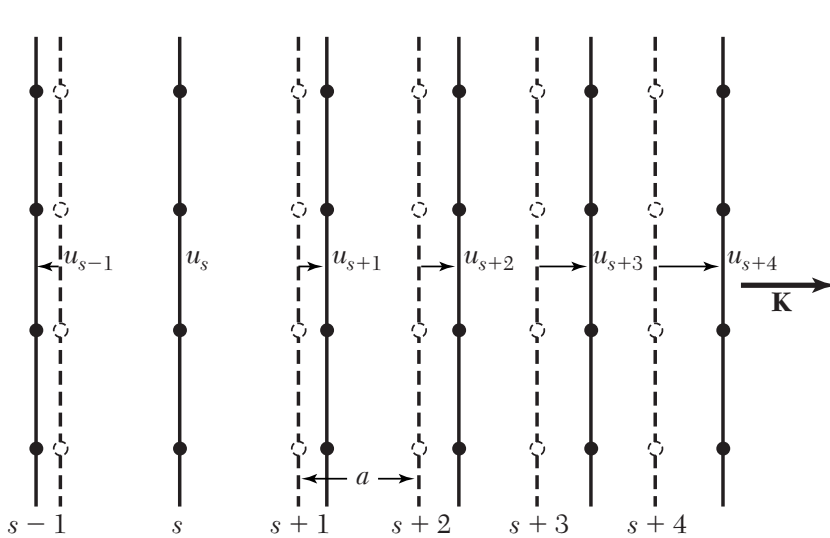
$$\psi_n(\mathbf{r}_i, \mathbf{R}_l) = \varphi_n(\mathbf{r}_i)X(\mathbf{R}_l), \quad \text{where } n \text{ labels an electronic state.}$$

Crystal Dynamics

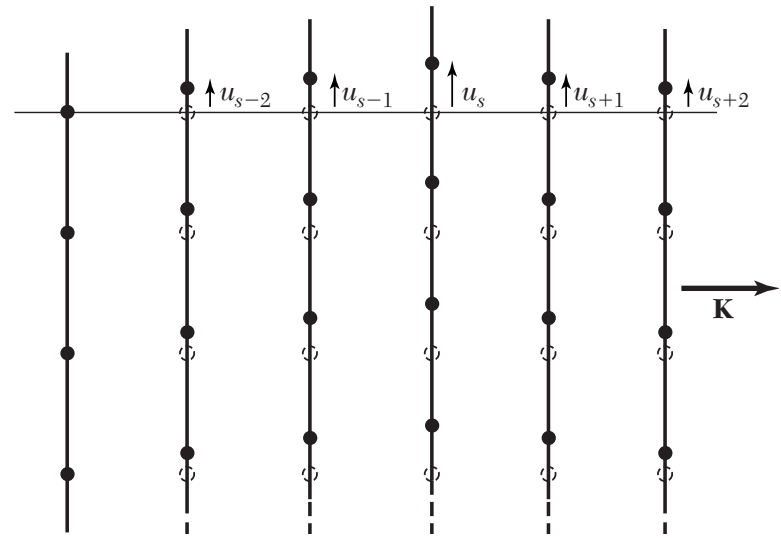
- Atomic motions are governed by the forces exerted on atoms when they are displaced from their equilibrium positions.
- At any finite temperature, the lattice structure is not static and there will be thermal vibrations.
- These lattice vibrations can be described in terms of normal modes describing the collective vibration of atoms. The quanta of these normal modes are called phonons.
- To calculate the forces it is necessary to determine the wavefunctions and energies of the electrons within the crystal. Fortunately many important properties of the atomic motions can be deduced without doing these calculations.
- The phonons mainly contribute both to the specific heat and the thermal conduction of the crystal, and they are also important because of their interaction with other energy excitations, causing electrical resistivity and thermal expansion.

Three Modes of Plane Waves

When a wave propagates along one of symmetric directions in cubic crystals, entire planes of atoms move in phase with displacements u either parallel or perpendicular to the direction of the wavevector. We can simplify the problem to one dimension. For each wavevector there are three modes as solutions for u , one of longitudinal polarization and two of transverse polarization.



Longitudinal Plane Waves



Transverse Plane Waves

Longitudinal Plane Waves

For brevity we consider only nearest-neighbor interactions, with $p = \pm 1$.

The total force on plane s is

$$F_s = C(u_{s+1} - u_s) + C(u_{s-1} - u_s), \quad u \ll a$$

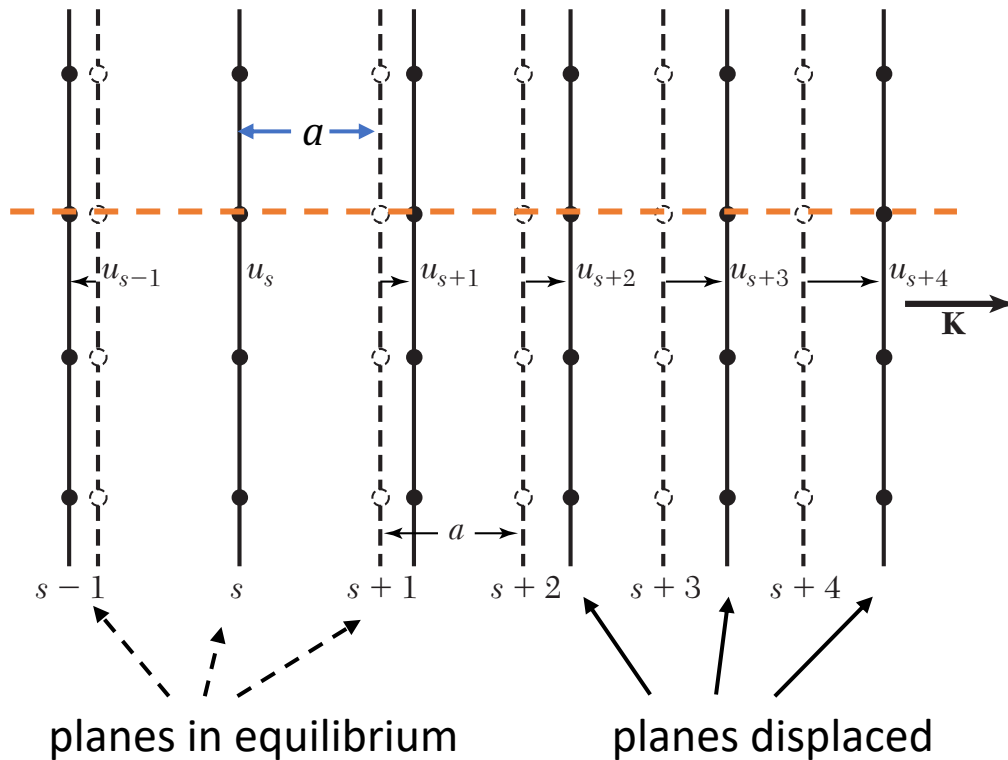
The equation of motion of an atom in plane s is

$$M \frac{d^2 u_s}{dt^2} = C(u_{s+1} + u_{s-1} - 2u_s)$$

where M is the mass of an atom.

Assume the solution contains time dependent term $e^{-i\omega t}$, then

$$-M\omega^2 u_s = C(u_{s+1} + u_{s-1} - 2u_s)$$



$-M\omega^2 u_s = C(u_{s+1} + u_{s-1} - 2u_s)$ is a difference equation and has traveling wave solution of the form: $u_s = u \exp(isKa) \exp(-i\omega t)$

where a is the spacing between planes and K is the wavevector and $a \parallel K$.

We then have

$$-\omega^2 M u \exp(isKa) = C u \{ \exp[i(s+1)Ka] + \exp[i(s-1)Ka] - 2 \exp(isKa) \}$$

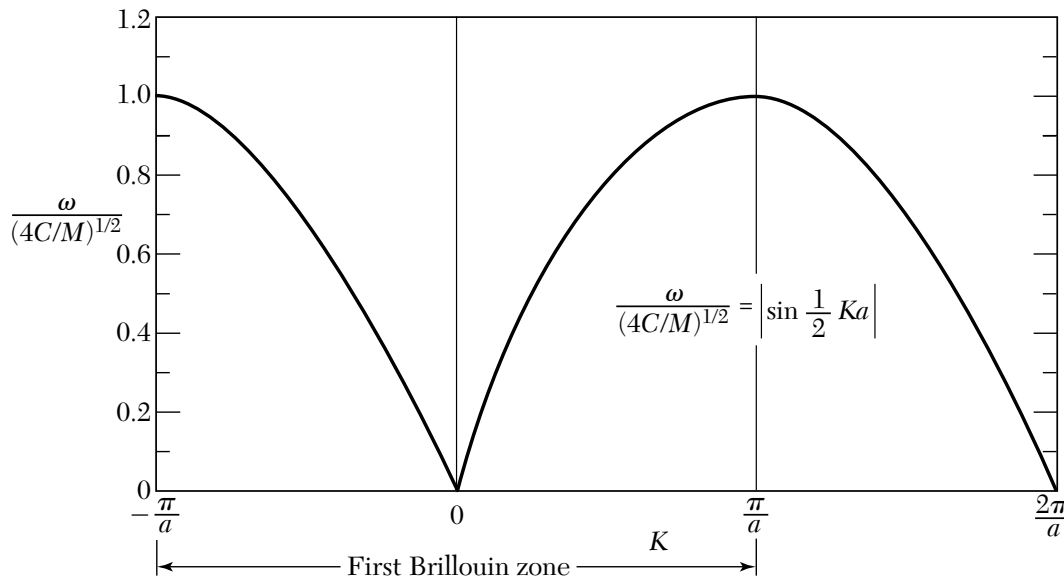


$$\omega^2 M = -C [\exp(iKa) + \exp(-iKa) - 2] \rightarrow$$

$$\omega^2 = (2C/M)(1 - \cos Ka)$$

or

$$\omega = (4C/M)^{1/2} \left| \sin \frac{1}{2} Ka \right|$$



First Brillouin Zone

The ratio of the displacements of two successive planes is given by

$$\frac{u_{s+1}}{u_s} = \frac{u \exp[i(s+1)Ka]}{u \exp(isKa)} = \exp(iKa)$$

The range $-\pi$ to $+\pi$ for the phase Ka covers all independent values of the exponential.

The first Brillouin zone of a linear lattice is defined by $-\frac{\pi}{a} < K \leq \frac{\pi}{a}$, and all the displacement can be described by a wavevector within the first zone.

At the zone boundaries, $K = \pm \pi/a$, whence

$$u_s = u \exp(\pm is\pi) = u (-1)^s$$

This is a standing wave: alternate atoms oscillate in opposite phases, because $u_s = \pm 1$ according to whether s is an even or an odd integer. The wave moves neither to the right nor to the left.

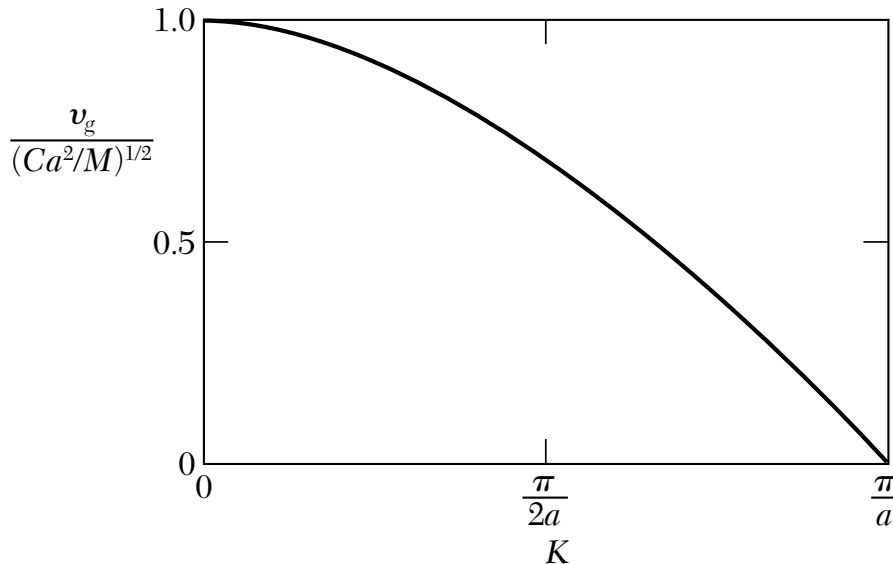
Group Velocity

The transmission velocity of a wave packet is the **group velocity**, given as

$$v_g = d\omega/dK ,$$

the gradient of the frequency with respect to **K**.

For the linear lattice, we thus have $v_g = (Ca^2/M)^{1/2} \cos \frac{1}{2} Ka$



Near zone center where $Ka \ll 1$,

$$\omega^2 = (C/M)K^2a^2$$

$$v_g = \text{const.}$$

At zone boundaries where $Ka = \pm\pi$,

$$v_g = 0$$

Force Beyond Nearest Neighbors

The dispersion relation generalized to include p nearest planes is

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

To obtain C_p , multiplying both sides by $\cos(rKa)$ and integrating over K

$$\begin{aligned} M \int_{-\pi/a}^{\pi/a} dK \omega_K^2 \cos rKa &= 2 \sum_{p>0} C_p \int_{-\pi/a}^{\pi/a} dK (1 - \cos pKa) \cos rKa \\ &= -2\pi C_r / a . \end{aligned}$$

The integral vanishes except for $p = r$. Thus

$$C_p = -\frac{Ma}{2\pi} \int_{-\pi/a}^{\pi/a} dK \omega_K^2 \cos pKa$$

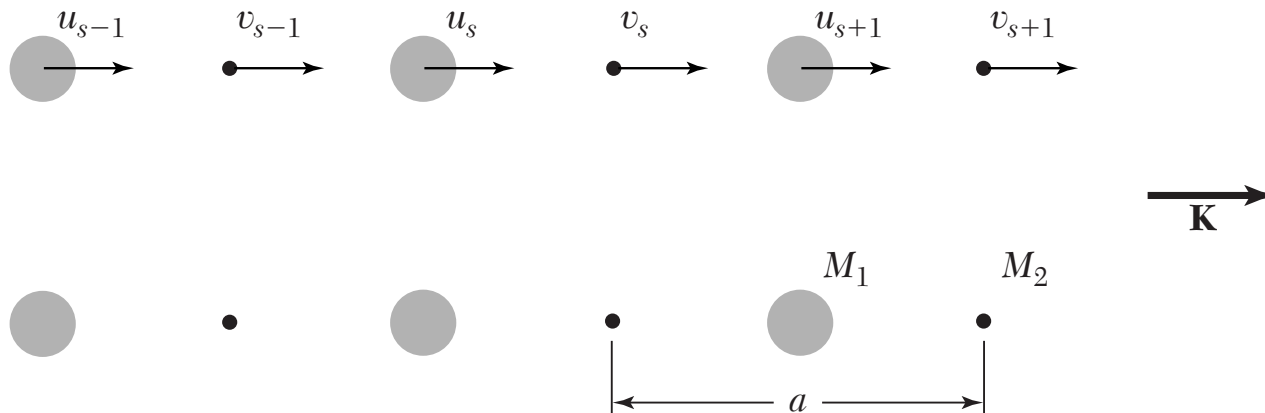
gives the force constant at range pa , for a structure with a monatomic basis.

Vibrations of Diatomic Crystal

Considering forces from the nearest planes only, the equations of motion are

$$M_1 \frac{d^2 u_s}{dt^2} = C(v_s + v_{s-1} - 2u_s) ;$$

$$M_2 \frac{d^2 v_s}{dt^2} = C(u_{s+1} + u_s - 2v_s) .$$



We look for a solution in the form of a traveling wave such as

$$u_s = u \exp(isKa) \exp(-i\omega t) ; \quad v_s = v \exp(isKa) \exp(-i\omega t) .$$

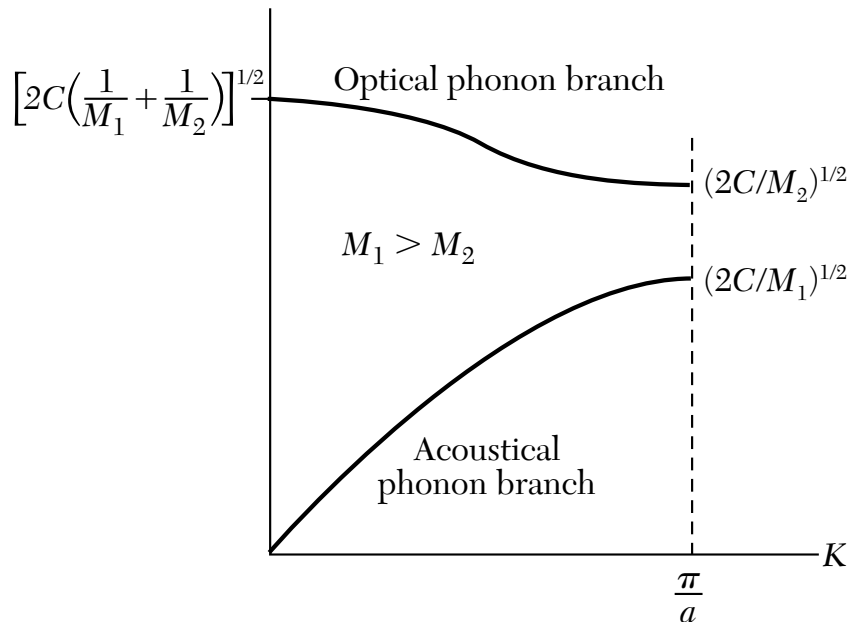
Here a is the distance between nearest identical planes, not nearest neighbor planes. We then have

$$-\omega^2 M_1 u = Cv[1 + \exp(-iKa)] - 2Cu ;$$

$$-\omega^2 M_2 v = Cu[\exp(iKa) + 1] - 2Cv .$$

or

$$M_1 M_2 \omega^4 - 2C(M_1 + M_2)\omega^2 + 2C^2(1 - \cos Ka) = 0 .$$



Near zone center where $Ka \ll 1$,

$$\omega^2 \cong 2C \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \quad (\text{optical branch})$$

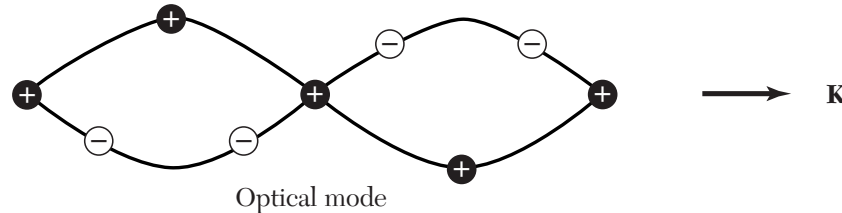
$$\omega^2 \cong \frac{\frac{1}{2}C}{M_1 + M_2} K^2 a^2 \quad (\text{acoustical branch})$$

At zone boundaries where $Ka = \pm\pi$,

$$\omega^2 = 2C/M_1 ; \quad \omega^2 = 2C/M_2 .$$

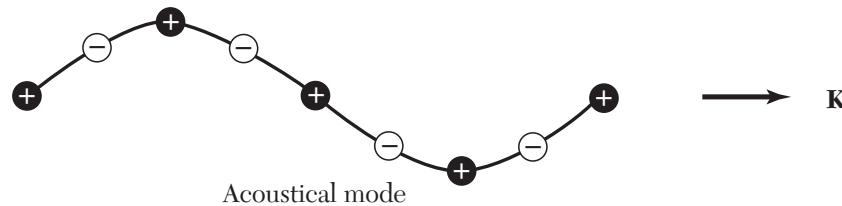
Illustration of Optical and Acoustic Modes

The atoms vibrate against each other, but their center of mass is fixed.



$$\frac{u}{v} = -\frac{M_2}{M_1}$$

M_1 and M_2 vibrate out of phase which can be excited by the electromagnetic waves.



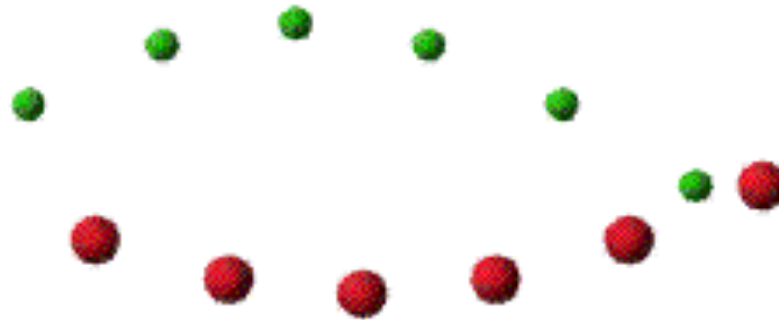
$$u \simeq v \text{ at } K \sim 0,$$

whence the term acoustic branch.

- With p atoms in the primitive cell and N primitive cells, there are a total of $3pN$ degrees of freedom for the crystal. Acoustical modes (TA and LA) will contribute $3N$ of the total degrees of freedom. The remaining $(3p - 3)N$ are accommodated by the optical branches.
- Wavelike solutions do not exist for certain frequencies, which is characteristic of elastic waves in polyatomic lattices.

Transverse optical mode for diatomic chain

The optical branch is a higher energy vibration. The term “optical” comes from how these were discovered - notice that if atom 1 is positively charged and atom 2 is negative, that the charges are moving in opposite directions. You can excite these modes with the oscillating electric fields of EM radiations.



Amplitude of vibration is strongly exaggerated!

Transverse acoustical mode for diatomic chain

The acoustic branch has this name because it gives rise to long wavelength vibrations - speed of sound.



Phonons

- The regular lattice of atoms are tied together with bonds, so they can't vibrate independently. The vibrations take the form of collective modes which propagate through the material.
- There should be energy associated with the vibrations of these atoms, which is quantized, the quantum of the vibration energy is a “phonon”. A phonon is an excited state in the quantum mechanical quantization of the modes of vibrations for elastic structures of interacting particles.
- The vibrational energies of molecules are quantized and treated as quantum harmonic oscillators with

$$\epsilon = (n + \frac{1}{2})\hbar\omega$$

when the mode is excited to quantum number n .

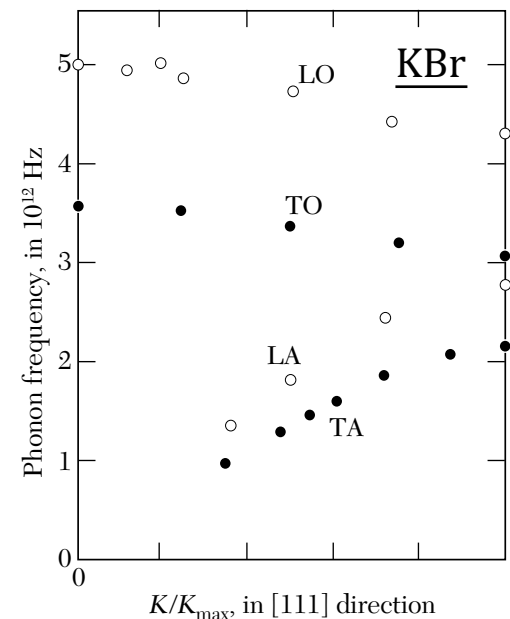
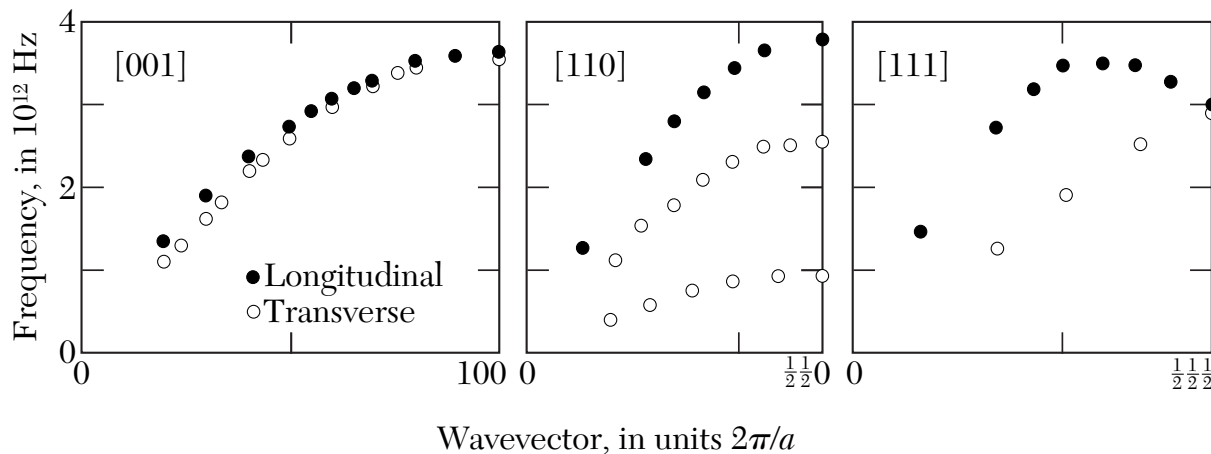
- Such propagating lattice vibrations can be considered to be sound waves, and their propagation speed is the speed of sound in the material.

Measurement of Phonon Dispersion

A phonon of wavevector K will interact with particles such as photons, neutrons, and electrons as if it had a momentum $\hbar K$. However, a phonon does not carry physical momentum.

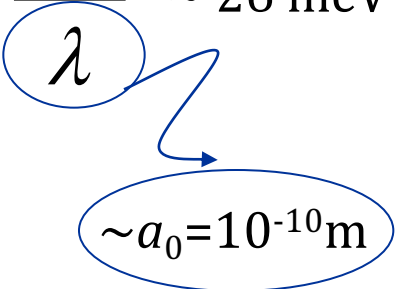
Phonon dispersion relations $\omega(\mathbf{K})$ are most often determined experimentally by the inelastic scattering of neutrons with the emission or absorption of a phonon. If a phonon of \mathbf{K} is emitted (+) or absorbed (-) in the scattering of a neutron \mathbf{k} by the crystal, then

$$\mathbf{k} + \mathbf{G} = \mathbf{k}' \pm \mathbf{K} \quad \text{and} \quad \frac{\hbar^2 k^2}{2M_n} = \frac{\hbar^2 k'^2}{2M_n} \pm \hbar\omega$$



PHONONS

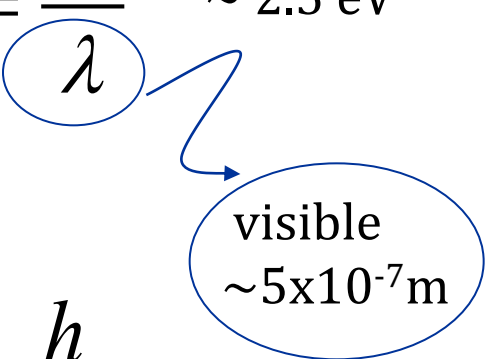
- Quanta of lattice vibrations
- Energies of phonons are quantized

$$E_{\text{phonon}} = \frac{h\nu_s}{\lambda} \sim 26 \text{ meV}$$


$$p_{\text{phonon}} = \frac{h}{\lambda}$$

PHOTONS

- Quanta of electromagnetic radiation
- Energies of photons are quantized as well

$$E_{\text{photon}} = \frac{hc}{\lambda} \sim 2.5 \text{ eV}$$


$$p_{\text{photon}} = \frac{h}{\lambda}$$

Phonon Heat Capacity

Energy given to lattice vibrations (or phonons) is the dominant contribution to the heat capacity in most solids. In non-magnetic insulators, it is the only contribution. Calculation of the lattice energy and heat capacity of a solid therefore falls into two parts: i) the evaluation of the contribution of a single mode, and ii) the summation over the frequency distribution of the modes. The heat capacity at constant volume is defined as

$$C_V = (\partial U / \partial T)_V, \text{ where } U \text{ is the energy and } T \text{ the temperature.}$$

The total energy of the phonons at temperature T in a crystal can be written as the sum of the energies over all phonon modes, here indexed by the wavevector K and polarization index p .

$$U_{\text{lat}} = \sum_K \sum_p U_{K,p} = \sum_K \sum_p \langle n_{K,p} \rangle \hbar \omega_{K,p}$$

where $\langle n_{K,p} \rangle$ is the thermal equilibrium occupancy of phonons of wavevector K and polarization p .

Planck Distribution

Boltzmann distribution (also called Gibbs distribution) is a probability measure P_i that gives the probability that a system will be in a certain state as a function of that state's energy ϵ_i and the temperature T of the system.

$$p_i \propto e^{-\epsilon_i/kT}$$

The ratio of probabilities of two states is known as the Boltzmann factor and characteristically only depends on the states' energy difference:

$$\frac{p_i}{p_j} = e^{(\epsilon_j - \epsilon_i)/kT}$$

Consider a set of identical harmonic oscillators in thermal equilibrium. The ratio of the number of oscillators in their $(n + 1)$ th quantum state of excitation to the number in the n th quantum state is

$$N_{n+1}/N_n = \exp(-\hbar\omega/\tau) , \quad \tau \equiv k_B T ,$$

The fraction of the total number of oscillators in the n th quantum state is

$$P_n = \frac{N_n}{\sum_{s=0}^{\infty} N_s} = \frac{\exp(-n\hbar\omega/\tau)}{\sum_{s=0}^{\infty} \exp(-s\hbar\omega/\tau)} .$$

We see that the average excitation quantum number of an oscillator is

$$\langle n \rangle = \sum_n n P_n = \frac{\sum_s s \exp(-s\hbar\omega/\tau)}{\sum_s \exp(-s\hbar\omega/\tau)} .$$

Since

$$\sum_s x^s = \frac{1}{1-x} ; \quad \sum_s s x^s = x \frac{d}{dx} \sum_s x^s = \frac{x}{(1-x)^2} , \quad \text{if } x \ll 1.$$

With $x = \exp(-\hbar\omega/\tau)$, we have the Planck distribution function:

$$\langle n \rangle = \frac{x}{1-x} = \frac{1}{\exp(\hbar\omega/\tau) - 1} , \quad \tau = k_B T$$

Thermal Energy of Oscillators

An oscillator in thermal equilibrium at temperature T , we can prove, using the similar procedure before, the average energy of an oscillator is

$\langle \epsilon \rangle = (\langle n \rangle + \frac{1}{2}) \hbar \omega$, and $\langle n \rangle$ is the expected value of the quantum number n of an oscillator in thermal equilibrium at temperature T .

The energy of a collection of oscillators of frequencies $\omega_{K,p}$ in thermal equilibrium at temperature T is found,

$$U_{\text{lat}} = \sum_K \sum_p U_{K,p} = \sum_K \sum_p \langle n_{K,p} \rangle \hbar \omega_{K,p} = \sum_K \sum_p \frac{\hbar \omega_{K,p}}{\exp(\hbar \omega_{K,p} / \tau) - 1}, \quad \tau = k_B T$$

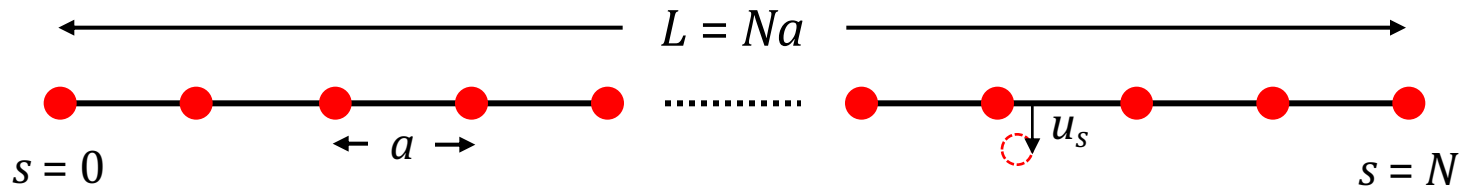
It is usually convenient to replace the summation over K by an integral. Suppose that the crystal has $D_p(\omega) d\omega$ modes of a given polarization p in the frequency range ω to $\omega + d\omega$. Then the energy is

$$U = \sum_p \int d\omega D_p(\omega) \frac{\hbar \omega}{\exp(\hbar \omega / \tau) - 1}.$$

The lattice heat capacity is found by differentiation with respect to temperature. Let $x = \hbar \omega / \tau = \hbar \omega / k_B T$: then $\partial U / \partial T$ gives

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

Density of Modes of a Linear Chain



We assume that the particles $s = 0$ and $s = N$ at the ends of the line with length L are held fixed. Each normal vibration mode of polarization p has the form of a standing wave, where u_s is the displacement of particle s :

$$u_s = u(0) \exp(-i\omega_{K,p}t) \sin sKa ,$$

where $\omega_{K,p}$ is related to K by the appropriate dispersion relation.

The wavevector K is restricted by the fixed-end boundary conditions to the values:

$$K = \frac{\pi}{L} , \quad \frac{2\pi}{L} , \quad \frac{3\pi}{L} , \dots , \quad \frac{(N-1)\pi}{L} .$$

The solution for $K = N\pi/L = \pi/a = K_{\max}$ has $u_s \propto \sin s\pi$; this permits no motion of any atom, because $\sin s\pi$ vanishes at each atom.

The number of modes per unit range of K is L/π for $K \leq \pi/a$, and 0 for $K > \pi/a$.

We need to know $D(\omega)$, the number of modes per unit frequency range for a given polarization. The number of modes $D(\omega) d\omega$ in $d\omega$ at ω is given in one dimension by

$$D_1(\omega) d\omega = \frac{L}{\pi} \frac{dK}{d\omega} d\omega = \frac{L}{\pi} \cdot \frac{d\omega}{d\omega/dK}$$

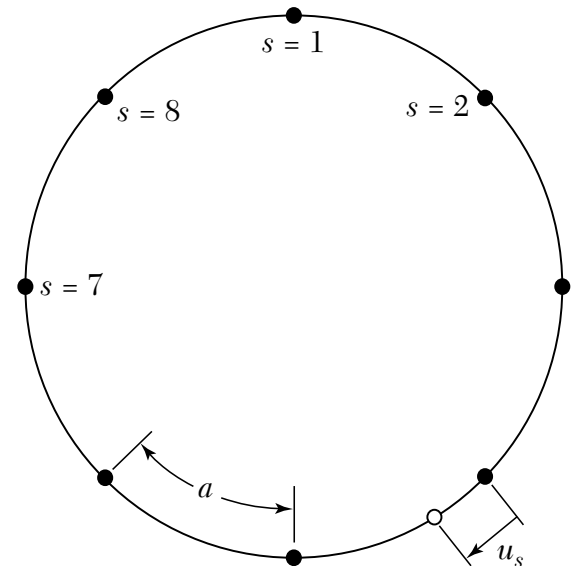
We can obtain the group velocity $d\omega/dK$ from the dispersion relation ω versus K .

With the periodic boundary conditions, $u(sa) = u(sa + L)$ and $u_s = u(0) \exp[i(sKa - \omega_K t)]$, the allowed values of K are

$$K = 0, \quad \pm \frac{2\pi}{L}, \quad \pm \frac{4\pi}{L}, \quad \pm \frac{6\pi}{L}, \quad \dots, \quad \frac{N\pi}{L}$$

We have now both plus and minus values of K , with the interval $\Delta K = 2\pi/L$.

The number of modes per unit range of K is $L/2\pi$ for $-\pi/a \leq K \leq \pi/a$, and 0 otherwise.



Density of Modes in 3D

We apply periodic boundary conditions over N^3 primitive cells within a cube of side L , so that \mathbf{K} is determined by the condition

$$\exp[i(K_x x + K_y y + K_z z)] \equiv \exp\{i[K_x(x + L) + K_y(y + L) + K_z(z + L)]\} ,$$

whence

$$K_x, K_y, K_z = 0 ; \quad \pm \frac{2\pi}{L} ; \quad \pm \frac{4\pi}{L} ; \quad \dots ; \quad \frac{N\pi}{L} .$$

Therefore, there is one allowed value of \mathbf{K} per volume $(2\pi/L)^3$ in \mathbf{K} space, or

$$\left(\frac{L}{2\pi}\right)^3 = \frac{V}{8\pi^3} \quad \text{allowed values of } \mathbf{K} \text{ per unit volume of } \mathbf{K} \text{ space, for}$$

each polarization and for each branch.

The total number of modes with wavevector less than K is

$$N = (L/2\pi)^3 (4\pi K^3/3)$$

The density of states for each polarization is

$$D(\omega) = dN/d\omega = (VK^2/2\pi^2)(dK/d\omega) .$$

Debye Model of Density of Modes

In the Debye approximation the velocity of sound is taken as constant for each polarization type, as it would be for a classical elastic continuum. The dispersion relation is written as

$$\omega = vK \quad , \quad \text{with } v \text{ the constant velocity of sound.}$$

The density of modes becomes $D(\omega) = V\omega^2/2\pi^2v^3$.

If there are N primitive cells in the specimen, the total number of acoustic phonon modes is N . A cutoff frequency ω_D is determined as

$$\omega_D^3 = 6\pi^2v^3N/V \quad .$$

To this frequency there corresponds a cutoff wavevector in \mathbf{K} space:

$$K_D = \omega_D/v = (6\pi^2N/V)^{1/3} \quad .$$

On the Debye model we do not allow modes of wavevector larger than K_D . The number of modes with $K \leq K_D$ exhausts the number of degrees of freedom of a monatomic lattice.

The thermal energy U for each polarization type is then

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

Assume the phonon velocity is independent of the polarization, we simply multiply the above U by 3, then

$$U = \frac{3V\hbar}{2\pi^2v^3} \int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\hbar\omega/\tau} - 1} = \frac{3Vk_B^4T^4}{2\pi^2v^3\hbar^3} \int_0^{x_D} dx \frac{x^3}{e^x - 1},$$

where $x \equiv \hbar\omega/\tau \equiv \hbar\omega/k_B T$ and $x_D \equiv \hbar\omega_D/k_B T \equiv \theta/T$.

Here we define Debye temperature θ as: $\theta = \frac{\hbar v}{k_B} \cdot \left(\frac{6\pi^2 N}{V} \right)^{1/3}$

The total thermal energy U is

$$U = 9Nk_B T \left(\frac{T}{\theta} \right)^3 \int_0^{x_D} dx \frac{x^3}{e^x - 1},$$

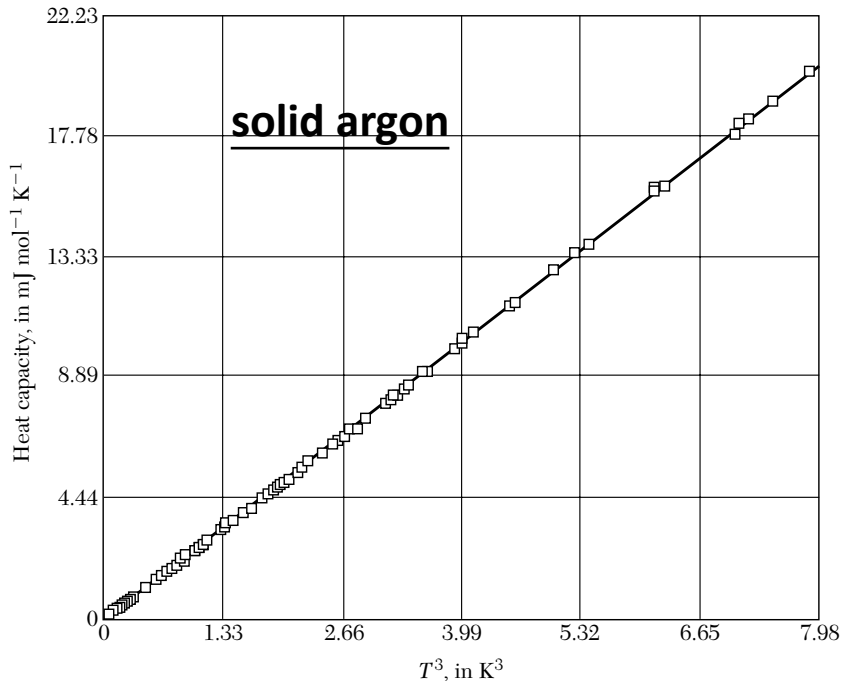
where N is the number of atoms in the specimen and $x_D = \theta/T$.

Heat Capacity with Debye Model

At very low temperature, i.e. $T \ll \theta$, we can replace the upper limit of the integral for the total thermal energy U to infinity. Since

$$\int_0^{\infty} dx \frac{x^3}{e^x - 1} = \int_0^{\infty} dx x^3 \sum_{s=1}^{\infty} \exp(-sx) = 6 \sum_{s=1}^{\infty} \frac{1}{s^4} = \frac{\pi^4}{15},$$

we have then $U \cong 3\pi^4 Nk_B T^4 / 5\theta^3$



The heat capacity C_V

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \cong \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\theta} \right)^3 \cong 234 Nk_B \left(\frac{T}{\theta} \right)^3,$$

which is the Debye T^3 approximation.

At very high temperature, i.e. $T \gg \theta$,

$$C_V \sim 3Nk_B, \text{ this is the classical limit.}$$

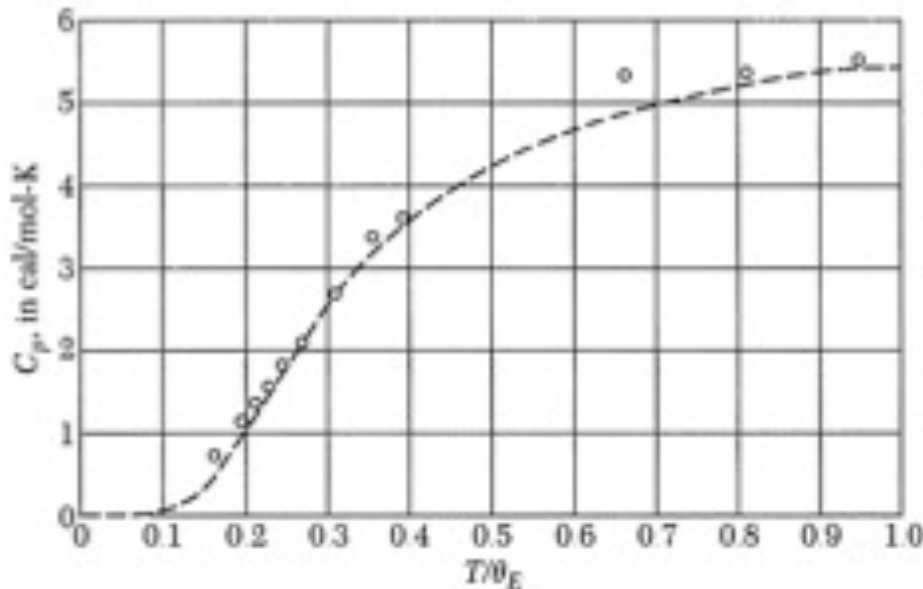
Einstein Model of Density of Modes

The Einstein density of states is $D(\omega') = N\delta(\omega' - \omega)$, where the delta function is centered at ω , considering N oscillators of the same frequency ω in one dimension. The thermal energy of the system is

$$U = N\langle n \rangle \hbar\omega = \frac{N\hbar\omega}{e^{\hbar\omega/\tau} - 1}$$

The heat capacity of the oscillators is

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = Nk_B \left(\frac{\hbar\omega}{\tau} \right)^2 \frac{e^{\hbar\omega/\tau}}{(e^{\hbar\omega/\tau} - 1)^2}$$



Experimental data of the heat capacity of Diamond compared with the values derived from the Einstein model

General Form of Density of Modes

$$D(\omega) d\omega = \left(\frac{L}{2\pi}\right)^3 \int_{\text{shell}} d^3K, \quad \text{and} \quad \int_{\text{shell}} d^3K = \int dS_\omega dK_\perp,$$

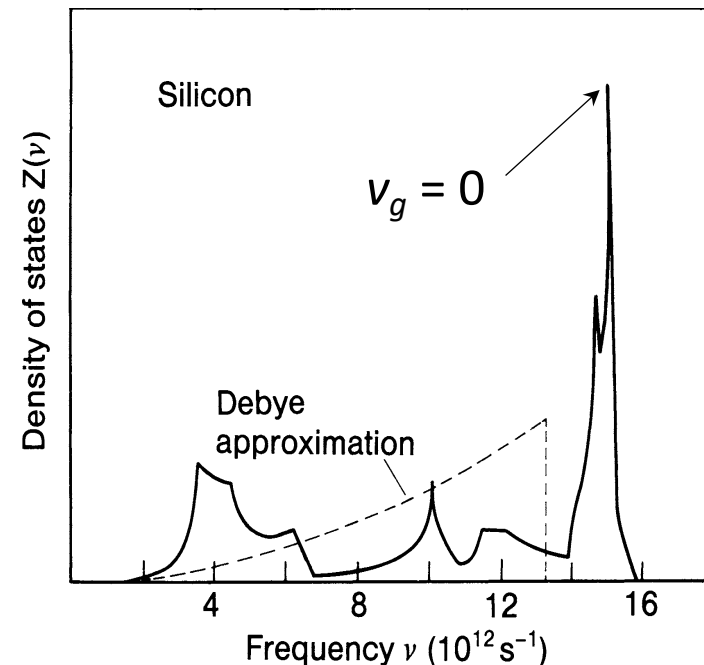
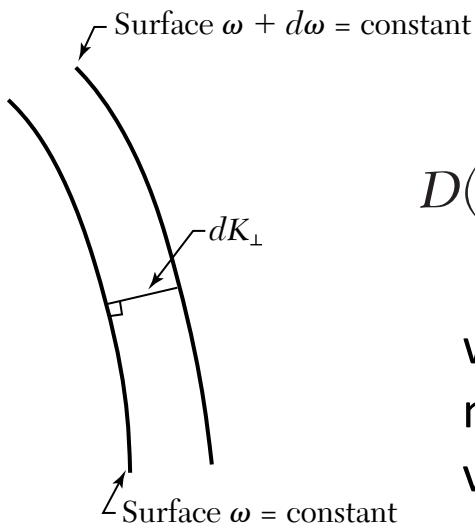
where the integral is extended over the volume of the shell in \mathbf{K} space bounded by the two surfaces on which the phonon frequency is constant, one surface on which the frequency is ω and the other on which the frequency is $\omega + d\omega$.

The gradient of ω , which is $\nabla_{\mathbf{K}}\omega$, is also normal to the surface ω constant, and the quantity

$$|\nabla_{\mathbf{K}}\omega| dK_\perp = d\omega$$

$$D(\omega) d\omega = \left(\frac{L}{2\pi}\right)^3 \int \frac{dS_\omega}{v_g} d\omega$$

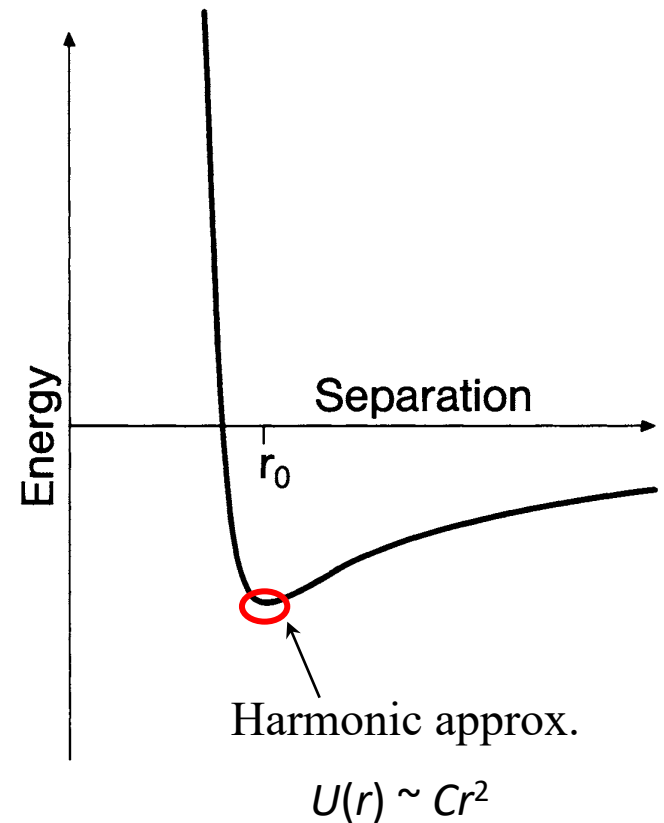
where $v_g = |\nabla_{\mathbf{K}}\omega|$ is the magnitude of the group velocity of a phonon.



Anharmonic Effects

Any real crystal resists compression to a smaller volume than its equilibrium value more strongly than expansion to a larger volume. This is due to the asymmetric shape of the interatomic potential curve. This is an anharmonic effect due to the higher order terms in potential which are ignored in harmonic approximation of $U(r) \sim Cr^2$.

Thermal expansion is an example to the anharmonic effect. In anharmonic effect phonons collide with each other and these collisions limit thermal conductivity which is due to the flow of phonons.



Thermal Expansion

We choose a representation of interatomic potential beyond the simple harmonic approximation for a two-atom system separated by x as

$$U(x) = cx^2 - gx^3 - fx^4, \text{ where } c, g, f \text{ all positive}$$

We calculate the average displacement by using the Boltzmann distribution function with $\beta \equiv 1/k_B T$.

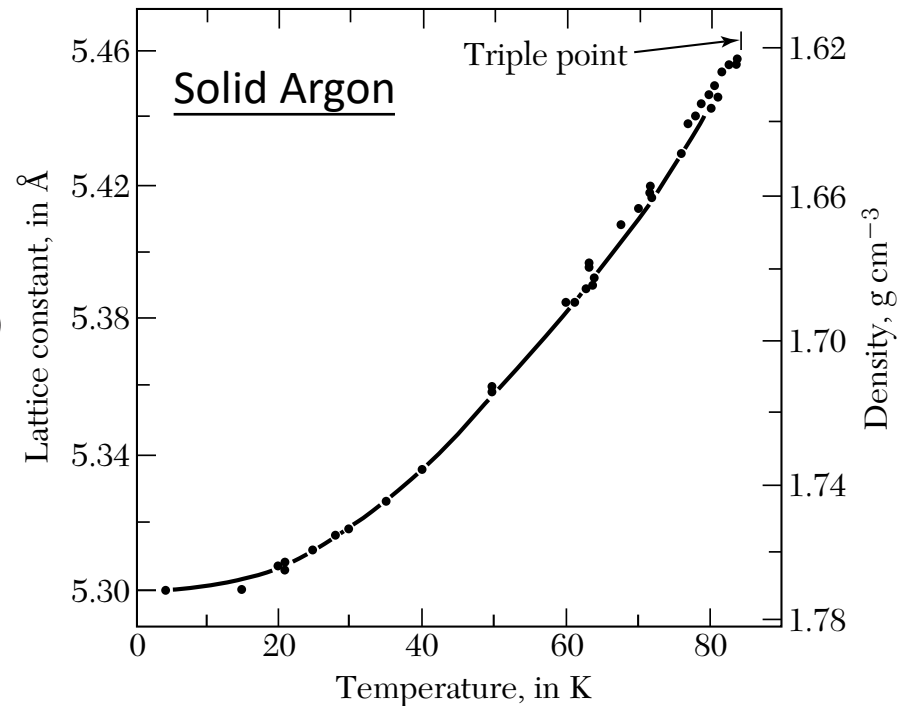
$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} dx x \exp[-\beta U(x)]}{\int_{-\infty}^{\infty} dx \exp[-\beta U(x)]},$$

$$\int dx x \exp(-\beta U) \cong \int dx [\exp(-\beta cx^2)](x + \beta gx^4 + \beta fx^5)$$

$$= (3\pi^{1/2}/4)(g/c^{5/2})\beta^{-3/2};$$

$$\int dx \exp(-\beta U) \cong \int dx \exp(-\beta cx^2) = (\pi/\beta c)^{1/2}$$

Thermal expansion is $\langle x \rangle = \frac{3g}{4c^2} k_B T$



Thermal Conductivity

The thermal conductivity coefficient K of a solid with the temperature gradient along x is defined as

$$j_U = -K \frac{dT}{dx} ,$$

where j_U is the flux of thermal energy, or the energy transmitted across unit area per unit time.

This process is a random process, which means the thermal energy was transferred through frequent collisions in the specimen. The random nature of the conductivity process brings the temperature gradient and a mean free path into the above expression.

The thermal conductivity coefficient for gases is

$$K = \frac{1}{3} C v \ell$$

Debye was first applying it to describe the thermal conductivity in solids, with C as the heat capacity of the phonons, v the phonon velocity, and ℓ the phonon mean free path.

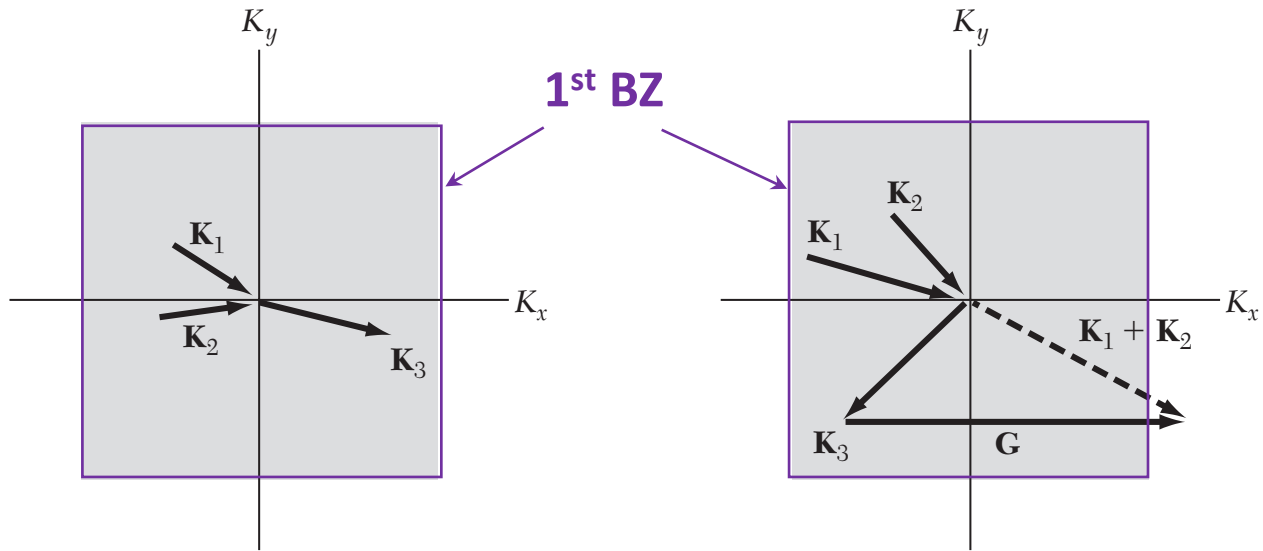
Phonon-Phonon Collisions

If the forces between atoms were purely harmonic, there would be no mechanism for collisions between different phonons. Then, the phonon mean free path ℓ is determined principally by collision with the lattice imperfections and boundaries. However, such collisions do not change the energy of individual phonons.

With anharmonic lattice interactions, there is a coupling between different phonons, which limits the value of the mean free path, and $\ell \propto 1/T$. In addition, we also need to establish a local thermal equilibrium distribution of phonons.

For a three-phonon collision process, it is remarkable that under normal scattering condition, $\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3$, the total momentum of the phonon gas is not changed by such a collision. So the process will not establish the thermal equilibrium.

Umklapp Processes

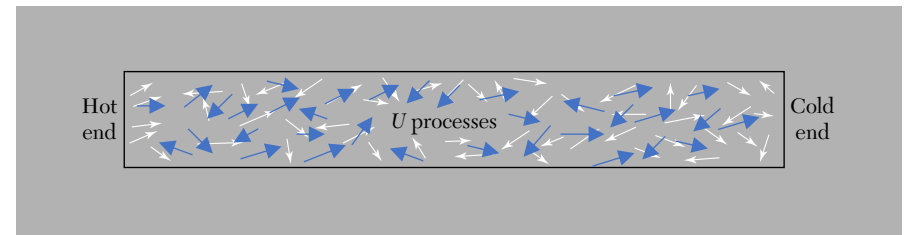
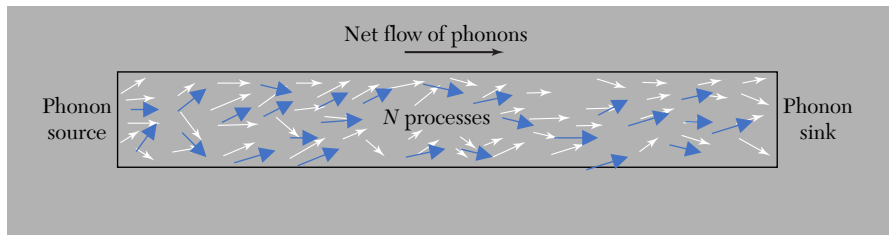


$$\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3$$

Normal Process or N process

$$\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3 + \mathbf{G}$$

Umklapp Process or U process



Raman Spectroscopy

Raman Spectroscopy is an important method using laser for investigating elementary excitations in solids, for example, phonons and plasmons. As for all scattering from time-varying structures, energy must be conserved and, to within a reciprocal lattice vector \mathbf{G} , wave vector too, i.e. we have

$$\hbar\omega_0 - \hbar\omega \pm \hbar\omega(\mathbf{K}) = 0 \quad \text{and} \quad \hbar\mathbf{k}_0 - \hbar\mathbf{k} \pm \hbar\mathbf{K} + \hbar\mathbf{G} = 0$$

where ω_0 , \mathbf{k}_0 and ω , \mathbf{k} characterize the incident and scattered light waves, respectively.

For light in the visible region of the spectrum, $|\mathbf{k}_0|$ and $|\mathbf{k}|$ are of the order of 1/1000 of a reciprocal lattice vector, which means that only excitations in the center of the Brillouin zone ($|\mathbf{K}| \sim 0$) can take part in Raman scattering.

The interaction of visible light with the solid occurs via the polarizability of the valence electrons. The electric field \mathcal{E}_0 of the incident light wave induces, via the susceptibility tensor χ a polarization \mathbf{P} , i.e.

$$\mathbf{P} = \varepsilon_0 \underline{\chi} \mathcal{E}_0 \quad \text{and} \quad \underline{\chi} = \underline{\chi}^0 + (\partial \underline{\chi} / \partial X) X$$

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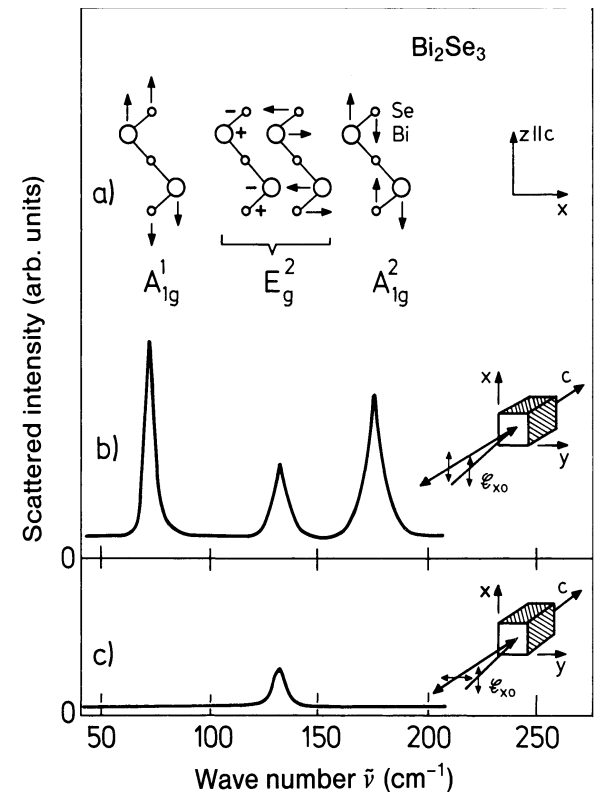
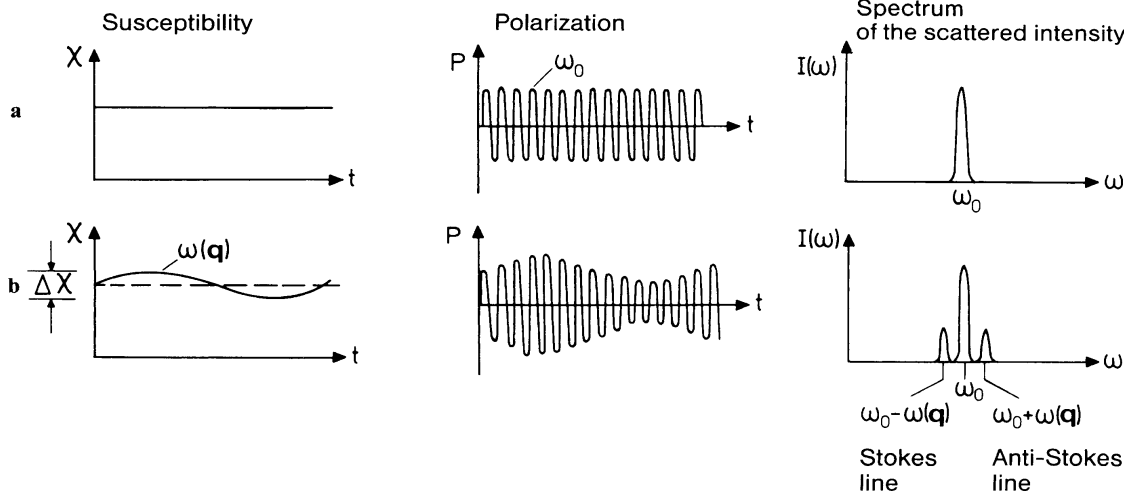
The energy flux density in direction \mathbf{s} , i.e. the Poynting vector \mathbf{S} , at distance r from the dipole as

$$\mathbf{S}(t) = \frac{\omega^4 P^2 \sin^2 \vartheta}{16\pi^2 \epsilon_0 r^2 c^3} \hat{\mathbf{s}}$$

If

$$X = X_0 \cos [\omega(\mathbf{q}) t] \quad \text{and} \quad \mathcal{E}_0 = \hat{\mathcal{E}}_0 \cos \omega_0 t,$$

$$\mathbf{P} = \epsilon_0 \underline{\chi}^0 \hat{\mathcal{E}}_0 \cos \omega_0 t + \frac{1}{2} \epsilon_0 \frac{\partial \underline{\chi}^0}{\partial X} X_0 \hat{\mathcal{E}}_0 \{ \cos[\omega_0 + \omega(\mathbf{q})] t + \cos[\omega_0 - \omega(\mathbf{q})] t \}$$



Problems

1. Monatomic linear lattice. Consider a longitudinal wave

$$u_s = u \cos(\omega t - sKa)$$

which propagates in a monatomic linear lattice of atoms of mass M , spacing a , and nearest-neighbor interaction C .

(a) Show that the total energy of the wave is

$$E = \frac{1}{2} M \sum_s (du_s/dt)^2 + \frac{1}{2} C \sum_s (u_s - u_{s+1})^2 .$$

where s runs over all atoms.

(b) By substitution of u_s in this expression, show that the time-average total energy per atom is

$$\frac{1}{4} M\omega^2 u^2 + \frac{1}{2} C(1 - \cos Ka)u^2 = \frac{1}{2} M\omega^2 u^2 ,$$

where in the last step we have used the dispersion relation (9) for this problem.

2. Singularity in density of states. (a) From the dispersion relation derived in Chapter 4 for a monatomic linear lattice of N atoms with nearest-neighbor interactions, show that the density of modes is

$$D(\omega) = \frac{2N}{\pi} \cdot \frac{1}{(\omega_m^2 - \omega^2)^{1/2}} .$$

where ω_m is the maximum frequency. (b) Suppose that an optical phonon branch has the form $\omega(K) = \omega_0 - AK^2$, near $K = 0$ in three dimensions. Show that $D(\omega) = (L/2\pi)^3 (2\pi/A)^{3/2} (\omega_0 - \omega)^{1/2}$ for $\omega < \omega_0$ and $D(\omega) = 0$ for $\omega > \omega_0$. Here the density of modes is discontinuous.

3. Heat capacity of layer lattice. (a) Consider a dielectric crystal made up of layers of atoms, with rigid coupling between layers so that the motion of the atoms is restricted to the plane of the layer. Show that the phonon heat capacity in the Debye approximation in the low temperature limit is proportional to T^2 . (b) Suppose instead, as in many layer structures, that adjacent layers are very weakly bound to each other. What form would you expect the phonon heat capacity to approach at extremely low temperatures?