

§3. Vibration of lattice

3.1 Harmonic vibration of 1d one atomic lattice.

We supposed that the lattice is one dimensional. All atoms are chemically identical. The temperature of lattice is zero, it means that atoms are fixed in their own lattice nodes.



As we shall subsequently learn, all the regularities obtained for this artificial one-dimensional model prove to be true for three-dimensional lattices as well.

Our general aim is a calculation of thermal capacity of crystal and dependence of thermal capacity on temperature. The total number of atoms in lattice equal to N , and we presume that this number is sufficiently large (the order of Avogadro's number 10^{23}). For small deflections of atoms from their equilibrium positions the interaction forces may be considered quasi-elastic, i.e., proportional to the variation of the interionic distance. The force acting on each atom is proportional to deflection of atoms from equilibrium position or by the other words we can use the Hooke's law for calculation of this forces. If all atoms are numbered and u_n is a displacement of the atom with number n from equilibrium position. We presume that nearest atoms are connected by spring with elastic constant g : So the total potential energy of total crystal could be written in the next form:

$$V = \frac{1}{2} g \sum_n (u_n - u_{n-1})^2 \quad (1)$$

Here u_n is displacement of atom with number n from its equilibrium position. In this equation $(u_n - u_{n-1})$ is an extending or compression of linear spring connecting two atoms with numbers n and $n+1$. This is a quite classical equation. The equation of motion or second Newton's law or the equation describing the dependence of displacement u_n on time and is look like so:

$$m \cdot a_k = m \cdot \ddot{u}_k = F_k, \text{ here } m - \text{ is mass of atoms.} \quad (2)$$

F_k - force acting on atom with number k . This force can be calculated from (1) with general expression:

$$F_k = - \frac{dV}{du_k} \quad (3)$$

So for atom with number k the equation of motion is looks like so:

$$\ddot{u}_k = \frac{g}{m} [u_{k+1} - 2 \cdot u_k + u_{k-1}] \quad (4)$$

For calculation force action on this atom (number k) we taken into account only two members of this sum consisting the deflections of this atom. In our case the total number of equations is equal to number of atoms. All equations are depend on each other. So we have a very complicated system of the second order differential equations. How to solve this problem? But if the forces acting between the atoms are linear (as in the our case) so the solution of such problem is well known this is a harmonic function or harmonic traveling wave propagating along the chain in the both directions. I'll write the harmonic functions in exponential form. So we get:

$$u_k(t) = \frac{1}{\sqrt{mN}} \cdot A \cdot e^{i(\omega t + qak)} \quad (5)$$

Here A is a amplitude of given wave, ω is a cycle frequency, q-wave vector (it is well known that the length of this vector is equal to $\frac{2\pi}{\lambda}$, λ is a wave length) and a-distance between nearest atoms. Do not forget that the sum of the solutions is also a solution of the equation. Or by the other words if we wish describe the motion of atom with number k, we have to take into the account total set of all harmonic waves. The parameter q here is a numbering index for different harmonic waves. If we substitute the solution (5) into the equation (4) we will get :

$$-\omega^2 \cdot A \cdot e^{i(\omega t + qak)} = \frac{g}{m} (A \cdot e^{i(\omega t + qa(k+1))} - 2A \cdot e^{i(\omega t + qak)} + A \cdot e^{i(\omega t + qa(k-1))})$$

$$-\omega^2 \cdot e^{iqak} = \frac{g}{m} (e^{iqa(k+1)} - 2e^{iqa(k)} + e^{iqa(k-1)})$$

$$-\omega^2 = \frac{g}{m} (e^{iqa} - 2 + e^{-iqa})$$

$$\omega^2 = \frac{2g}{m} (1 - \cos(qa))$$

$$\omega^2 = \frac{4g}{m} \cdot \sin^2\left(\frac{qa}{2}\right)$$

after replacement $\omega_0 = \sqrt{\frac{4g}{m}}$ we have:

$$\omega(q) = \omega_0 \cdot \left| \sin\left(\frac{qa}{2}\right) \right| \quad (6)$$

So we got the dependence of cyclic frequency from the wave vector or dispersion relations (figure 1). Due to the periodicity of frequency(sin function), it is not sense to take into the account all values of wave vector but only nonequivalent vectors located in the interval from 0 to 2π (figure 2).

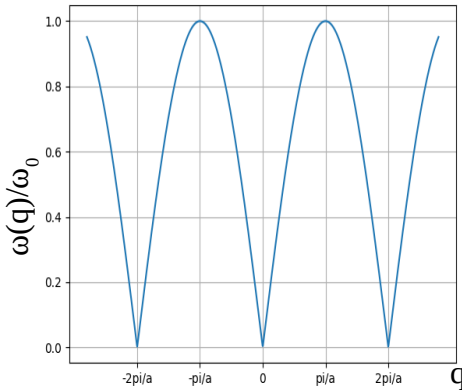


Figure 1

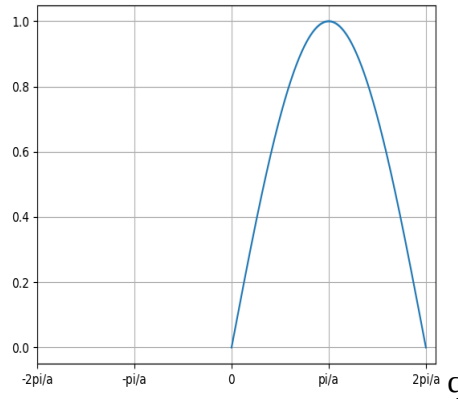


Figure 2

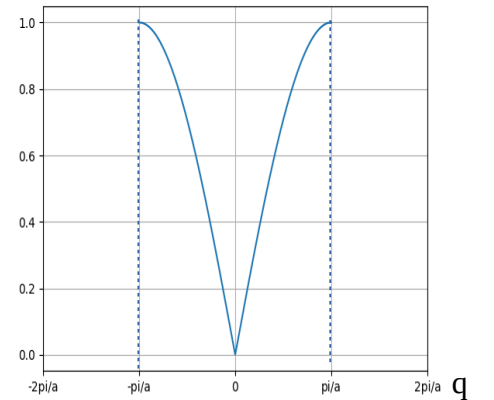


Figure 3

It is clear that $\omega(q) = \omega_0 \cdot \left| \sin\left(\frac{qa}{2}\right) \right| = \omega_0 \cdot \left| \sin\left(\frac{(q + \frac{2\pi n}{a})a}{2}\right) \right| = \omega(q + \frac{2\pi n}{a})$, here n is any integer number. .

For displacements (5) we have the same result:

$$u_k(t) = \frac{1}{\sqrt{mN}} \cdot A \cdot e^{i(\omega t + qak)} = \frac{1}{\sqrt{mN}} \cdot A \cdot e^{i(\omega t + (q + \frac{2\pi n}{a})ak)} = \frac{1}{\sqrt{mN}} \cdot A \cdot e^{i(\omega t + qak)} e^{i(2\pi n \cdot k)}, \text{ here } n \text{ and } k \in \mathbb{Z}$$

Make sense to use more symmetrical representation of this dependency, we will use the wavevector values from region from $-\pi/a$ to π/a (figure 3).

Now we can use equation (5) to describe the vibration of any atom in crystal, but before that it is necessary to determine the value of the wave vectors q . How to calculate it? We use for this aim the periodic boundary conditions, it means that the atoms with number k and $k+N$ this is the same atoms. Mathematically it's means that displacement of the atoms k and $k+N$ from the equilibrium position are equal:

$$u_k = u_{k+N} \quad (7)$$

After apply equation (5)

$$u_k(t) = \frac{1}{\sqrt{(mN)}} \cdot A \cdot e^{i(\omega t + qak)} = \frac{1}{\sqrt{(mN)}} \cdot \underbrace{A \cdot e^{i\omega t}}_{\text{replacement}} \cdot e^{iqak} = \frac{1}{\sqrt{(mN)}} \cdot A(t) \cdot e^{iqak} \quad (8)$$

After substitution into the equation (7) we get:

$$e^{iqka} = e^{iq(k+N)a}$$

After a little simplification:

$$e^{iqNa} = 1$$

This is possible if $q \cdot N \cdot a = 2 \cdot \pi \cdot n$, here $n \in \mathbb{N}$ and $q = \frac{2\pi n}{Na} = \frac{2\pi n}{L}$ here, L — total length of 1d crystall. If we take into account figure 3, The non equivalent values of wave vector located in the range $[-\frac{\pi}{a}, \frac{\pi}{a}]$ and could be calculated as follows:

$$q = \frac{2\pi n}{L}, \text{ and } n \in [-\frac{N}{2}, +\frac{N}{2}] \quad (9)$$

As you see the wave vector is discrete parameter which have N valid values in the range from $-\frac{\pi}{a}$ to $\frac{\pi}{a}$.

The wave vector can be interpreted as the number of a harmonic wave propagating in a 1d chain of atoms. The total number of distinct, nonequivalent harmonic waves is equal to N (a large but finite number). Once the wave vector is determined (take it from (9)), we can calculate the frequency of the corresponding wave using (6). And at the last stage, we can calculate the displacement of any atom in the chain that participated in the creation of this harmonic wave using (5).

An important note: if we want to calculate the real displacement of the k atom, we need to take into account the combination of all harmonic waves. Each atom participates in the creation of all harmonic waves at the same time:

$$u_k(t) = \sum_{q=-\frac{\pi}{a}}^{+\frac{\pi}{a}} \frac{1}{\sqrt{(mN)}} \cdot A_q \cdot e^{i(\omega(q)t + qak)}, \text{ here} \quad (10)$$

A_q — is an amplitude of harmonic wave for corresponding wave vector q . Total number of sum members is N .

Now I want to calculate the useful function, density of vibrations which definition is:

$$g(\omega) = \frac{dn}{d\omega} \quad (11)$$

The physical meanings is the number of harmonic waves with frequencies in the range from ω to $\omega+d\omega$. The integral

$\int_{\omega_1}^{\omega_2} g(\omega) d\omega = n_{12}$ is equal to number of harmonic waves in region of frequency from ω_1 to ω_2 .

We start from equation (9) $q = \frac{2\pi}{L} n$. The differentiation give :

$$dq = \frac{2\pi}{L} dn \quad (12)$$

Or for dn:

$$dn = \frac{L}{2\pi} dq \quad (13)$$

After replacement to (11):

$$g(\omega) = \frac{L}{2\pi} \frac{dq}{d\omega} = \frac{L}{2\pi} \frac{1}{\frac{d\omega}{dq}} \quad (14)$$

Derivative $\frac{d\omega}{dq}$ can be calculated from (6):

$$\frac{d\omega}{dq} = \frac{\omega_0 \cdot a}{2} \left| \cos\left(\frac{qa}{2}\right) \right| \quad (15)$$

Substitution to the (13) give:

$$g(\omega) = \frac{L}{2\pi} \frac{dq}{d\omega} = \frac{L}{2\pi} \frac{2}{\omega_0 \cdot a \left| \cos\left(\frac{qa}{2}\right) \right|} = \frac{L}{\pi a} \frac{1}{\omega_0 \left| \cos\left(\frac{qa}{2}\right) \right|} = \frac{L}{\pi a} \frac{1}{\omega_0 \sqrt{1 - \sin^2\left(\frac{qa}{2}\right)}} = \frac{N}{\pi} \frac{1}{\sqrt{\omega_0^2 - \omega^2}} \quad (16)$$

It is make sense to correctly normalize this function. We know that:

$$\int_0^{\omega_0} g(\omega) d\omega = N \neq \frac{N}{\pi} \int_0^{\omega_0} \frac{1}{\sqrt{\omega_0^2 - \omega^2}} d\omega = N/2.$$

It means that we need take into the account both branches (left and right on figure 3) and multiply (16) to 2.

The graphic of function $G(\omega) = \frac{g(\omega)}{\frac{N}{\pi}}$ you can see on

figure 4.

There is a useful formula which can be used to simplify the calculation of specific physical properties of crystals in further:

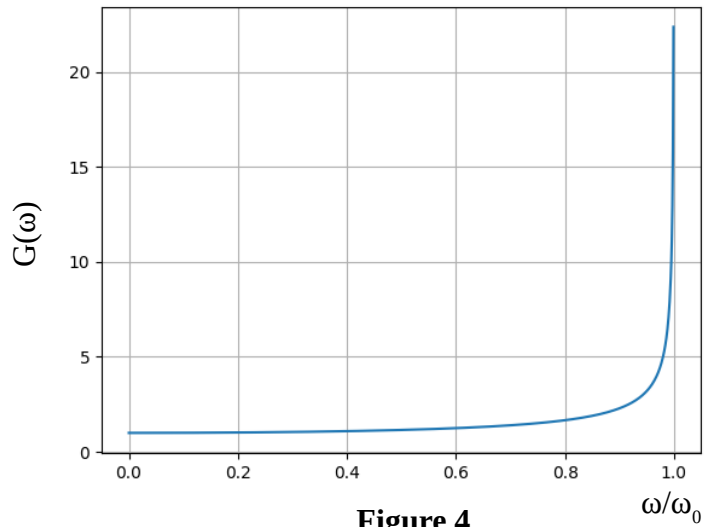


Figure 4

$$dq = \frac{L}{2\pi} g(\omega) d\omega \quad (17)$$

So, now we are ready to start the calculation of heat capacity of the one dimensional artificial crystal from the point of view of classical physics.

The first assessment for heat capacity can be done with a very simple classical approach. From the classical point of view if the total number of atoms is N and lattice is one dimensional, in this case the total number of the degrees of freedom is equal to N (1 for each atom, we assume that there is only longitudinal displacements of atoms along the chain of atoms). If the temperature of crystal is not zero, so the average thermal kinetic energy associated with one degree of freedom is equal $\frac{kT}{2}$ and the total thermal kinetic energy of whole crystal is equal to $\frac{kTN}{2}$. The average **kinetic** and **potential** energies associated with thermal motion are equal to the total internal energy of the crystal and equal to kTN . So as you see we can calculate the heat capacity of lattice (need to calculate the derivative with respect to T) and we get simple kN . The result do not depend on the temperature. This result is conflicting with the experimental data. Experiment show that for low temperature the heat capacity have a very strong dependence on temperature and proportional to T^n , here n is the dimension of crystal.

But what give us the quantum mechanical approach ? We start from the exact calculation of internal energy of the crystal. The classical formula for calculating the internal energy of crystal is look like so:

$$E = E_{kin} + E_{pot} = \frac{m}{2} \sum_k \dot{u}_k^2 + \frac{g}{2} \sum_k (u_k - u_{k+1})^2, \text{ summation over the all atoms.} \quad (18)$$

The calculation of kinetic energy give:

$$E_{kin} = \frac{m}{2} \sum_k \dot{u}_k^2 = \frac{m}{2} \sum_k \dot{u}_k \cdot \dot{u}_k^* \quad (19)$$

After using (8) we have:

$$E_{kin} = \frac{m}{2} \sum_k \dot{u}_k \cdot \dot{u}_k^* = \frac{1}{2N} \sum_k \sum_q \dot{A}_q e^{iqka} \sum_{q'} \dot{A}_{q'}^* e^{-iq'ka} \quad (20)$$

After reordering of summation:

$$E_{kin} = \frac{m}{2} \sum_k \dot{u}_k \cdot \dot{u}_k^* = \frac{1}{2N} \sum_{qq'} \dot{A}_q \dot{A}_{q'}^* \sum_k e^{-i(q-q')ka} \quad (21)$$

The last sum in (21) could be represented by delta function():

Figure 4

$$\sum_k e^{-i(q-q')ka} = \delta_{qq'} \cdot N \quad (22)$$

if $q \neq q'$ then $e^{-i(q-q')ka}$ is a fast oscillating function and corresponding sum is equal to zero.

After simplification we have:

$$E_{kin} = \frac{m}{2} \sum_k \dot{u}_k \cdot \dot{u}_k^* = \frac{1}{2} \sum_q \dot{A}_q^2 \quad (23)$$

As you see , in comparison with (19), the summation over the atoms is replaced by the summation over the wave vectors.

By the same way for potential energy:

$$E_{pot} = \frac{g}{2} \sum_k (u_k - u_{k+1})^2 = \frac{g}{2} \sum_k (u_k - u_{k+1}) \cdot (u_k - u_{k+1})^* = \frac{g}{2} \sum_k (u_k \cdot u_k^* + u_{k+1} \cdot u_{k+1}^* - u_{k+1} u_k^* - u_k u_{k+1}^*) \quad (24)$$

The corresponding amounts can be calculated separately (prove it!):

$$\frac{g}{2} \sum_k u_k \cdot u_k^* = \frac{g}{2m} \sum_q A_q^2 \quad \frac{g}{2} \sum_k u_{k+1} \cdot u_{k+1}^* = \frac{g}{2m} \sum_q A_q^2 \quad \frac{g}{2} \sum_k u_{k+1} u_k^* = \frac{g}{2m} \sum_q A_q^2 \cdot e^{iqa} \quad \frac{g}{2} \sum_k u_k u_{k+1}^* = \frac{g}{2m} \sum_q A_q^2 \cdot e^{-iqa}$$

After the substitution to (19) we will get:

$$E_{pot} = \frac{2g}{2m} \sum_q A_q^2 (1 + \cos(qa)) = \frac{1}{2} \sum_q \frac{4g}{m} A_q^2 \sin^2\left(\frac{qa}{2}\right) \quad \text{and after using (6)} = \frac{1}{2} \sum_q \omega^2(q) \cdot A_q^2$$

Finally for total energy of vibrating crystal:

$$E_{tot} = \sum_q \frac{1}{2} (\dot{A}_q^2 + \omega^2(q) \cdot A_q^2) \quad (25)$$

Does this equation remind you of something? This equation means that we can represent the lattice as a set of independent harmonic oscillators, and each oscillator is associated with one harmonic wave with specific wave vector q . The total number of such oscillators is N , and the wave vector is the number of the oscillator. But if so, we can use an exact quantum mechanical expression for the energy of harmonic oscillators. So:

$$E_{tot} = \sum_q (\hbar \cdot \omega(q) \cdot (n_q + \frac{1}{2})) \quad (26)$$

For a nonzero temperature value, it is necessary to take into account the filling of the upper energy levels for each harmonic oscillator. To do this, we must use the average for quantum numbers n_q described by the Bose-Einstein distribution.

$$\bar{n}_q = \frac{1}{e^{\frac{\hbar \omega(q)}{kT}} - 1} \quad (27)$$

After substitution to (26) and ignoring of zero point energy:

$$E_{tot}^- = \sum_q \frac{\hbar \omega(q)}{e^{\frac{\hbar \omega(q)}{kT}} - 1} \quad (28)$$

Summation over the q -vector can be replaced by integration using the following standard relations:

$$\sum_q \dots \rightarrow \frac{V}{(2\pi)^3} \int_q \dots dq^3 \quad \text{-for 3d space and}$$

$$\sum_q \dots \rightarrow \frac{L}{(2\pi)} \int_q \dots dq \quad \text{-for 1d space, here V and L are volume and length of crystal .}$$

Now for total energy we have:

$$E_{tot} = \frac{L}{2\pi} \int_{-\pi/2}^{\pi/2} \frac{\hbar \omega(q)}{e^{\frac{\hbar \omega(q)}{kT}} - 1} dq = \frac{L}{\pi} \int_0^{\pi/2} \frac{\hbar \omega(q)}{e^{\frac{\hbar \omega(q)}{kT}} - 1} dq \quad (29)$$

after using (17) and (16) :

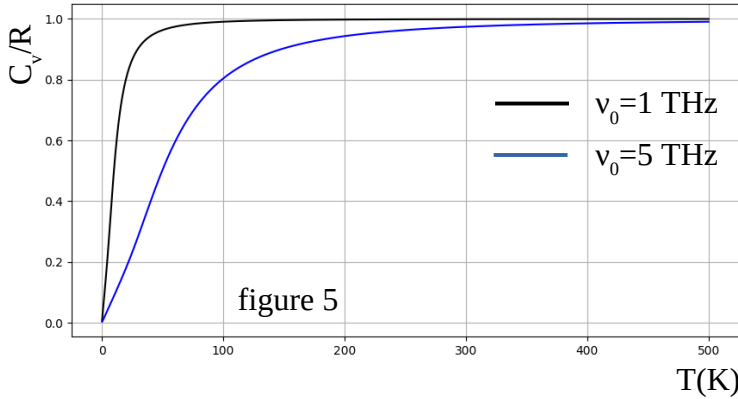
$$E_{tot} = \frac{2N}{\pi} \int_0^{\omega_0} \frac{\hbar \omega}{\sqrt{(\omega_0^2 - \omega^2)} \left(e^{\frac{\hbar \omega}{kT}} - 1 \right)} d\omega, \text{ here } \omega_0 = \sqrt{\frac{4g}{m}} \quad (30)$$

The heat capacity for a fixed volume can be calculated as a derivative of the total energy with respect to temperature.

$$C_v = \frac{dE_{tot}}{dT} = \frac{2N}{\pi} \int_0^{\omega_0} \frac{(\hbar \omega)^2 \cdot e^{\frac{\hbar \omega}{kT}}}{\sqrt{(\omega_0^2 - \omega^2)} \left(e^{\frac{\hbar \omega}{kT}} - 1 \right)^2 \cdot kT^2} d\omega \quad (31)$$

Using new variable $x = \frac{\hbar \omega}{kT}$:

$$C_v = kN \frac{2}{\pi} \int_0^{x_0} \frac{x^2 \cdot e^x}{\sqrt{(x_0^2 - x^2)} (e^x - 1)^2} dx, \text{ here } x_0 = \frac{\hbar \omega_0}{kT} = \frac{h \nu_0}{kT} \quad (32)$$



For one mole of atoms $N=N_A$ and $kN_A=R$. On figure 5 you can see the result of calculations of specific heat for two different values of ν_0 . For high temperatures, C_v tends to the classical limit R .

It is well known, from the theory of elasticity, that the speed of propagation of sound impulses in a solid rod $\nu_0 = \sqrt{E/\rho}$. For chain of atoms $\rho = \frac{m}{a}$ and Young modulus :

$$E = \frac{\text{tention force}}{\text{relative extension}} = \frac{g \cdot (u_k - u_{k-1})}{|u_k - u_{k-1}|/a} = g \cdot a$$

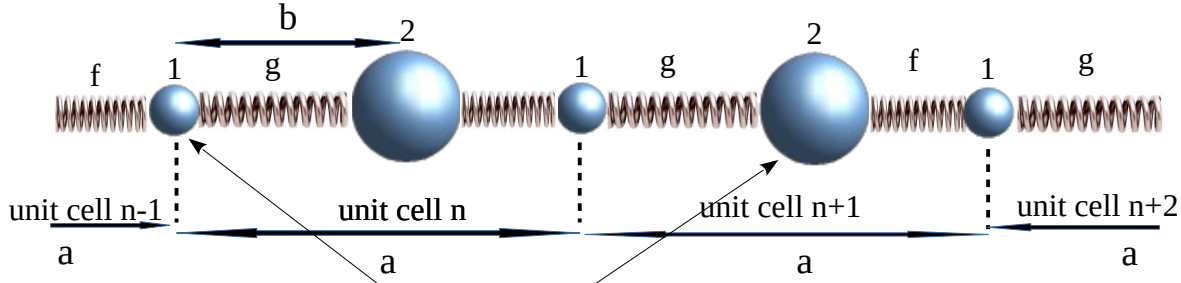
from where do we get $\nu_0 = a \cdot \sqrt{\frac{g}{m}}$.

There are two different types of speeds describing propagation of waves in matter, phase velocity (velocity of harmonic wave with fixed q) $\nu_p = \frac{\omega}{q}$ and group velocity (the rate of energy transfer in the crystal) $\nu_g = \left| \frac{d\omega}{dq} \right|$. For chain of

atoms: $\nu_p = \nu_0 \left| \frac{\sin \frac{aq}{2}}{\frac{aq}{2}} \right|$ and $\nu_g = \nu_0 \left| \cos \frac{aq}{2} \right|$. For small wave vectors (very long wave length) $\nu_p = \nu_g = \nu_0$.

3.2 Harmonic vibration of 1d two atomic lattice.

We supposed that the lattice is one dimensional but each elementary cell consist two different atoms per elementary cell. The masses of atoms are different and equal to m_1 and m_2 . The force constant of the spring connecting the atoms 1-2 is g and 2-1 is f . The length of basis vector is equal a .



Each unit cell contains two atoms of types 1 and 2. To denote the displacement of atoms from the equilibrium position, we need to use two indices. The first index must be used for numbering unit cells, and second for numbering the type of atom within a given unit cell. For example: u_n^1 - describes the displacement of an atom of type 1 in unit cell n , u_{n+1}^2 - describes the displacement of an atom of type 2 in unit cell $n+1$.

The temperature of lattice is zero, it means that atoms are fixed in their own lattice nodes. In this case we have two different springs connecting the atom. So the expression for potential energy is like so:

$$E_{pot} = \frac{g}{2} \sum_n (u_n^1 - u_n^2)^2 + \frac{f}{2} \sum_n (u_n^2 - u_{n+1}^1)^2 \quad \text{- summation over unit cells.} \quad (33)$$

Equation of motion for atoms in unit cell with number k can be obtained by the same way as in previous part. The general equations (2) and (3) give us the desired equations:

$$\begin{aligned} m_1 \ddot{u}_k^1 &= -\frac{dV}{du_k^1} = -g(u_k^1 - u_k^2) - f(u_k^1 - u_{k-1}^2) \\ m_2 \ddot{u}_k^2 &= -\frac{dV}{du_k^2} = -g(u_k^2 - u_k^1) - f(u_k^2 - u_{k+1}^1) \end{aligned} \quad (34)$$

In fact, the total number of differential equations to be solved is $2N$, where N is the order of Avogadro's number 10^{23} . But due to the linearity of the problem, the solution can be written directly:

$$\begin{aligned} u_k^1(t) &= \frac{1}{\sqrt{2Nm_1}} A^1 \cdot e^{i(\omega t + qak)} \\ u_k^2(t) &= \frac{1}{\sqrt{2Nm_2}} A^2 \cdot e^{i(\omega t + q(ak+b))} \end{aligned} \quad (35)$$

Substituting the solution into the equations of motion (34), we obtain :

$$\begin{aligned} \left(\omega^2 - \frac{(g+f)}{m_1} \right) A^1 + \left(\frac{g+f \cdot e^{-iaq}}{\sqrt{m_1 m_2}} \right) A^2 &= 0 \\ \left(\frac{g+f \cdot e^{iaq}}{\sqrt{m_1 m_2}} \right) A^1 + \left(\omega^2 - \frac{(g+f)}{m_2} \right) A^2 &= 0 \end{aligned} \quad \text{, or in matrix form } D_{ss'} \cdot A^{s'} = \omega^2 \cdot A^s \quad \text{, here} \quad (36)$$

$$D^{ss'} = \begin{pmatrix} \left(\frac{(g+f)}{m_1} \right) & -\left(\frac{g+f \cdot e^{-iaq}}{\sqrt{m_1 m_2}} \right) \\ -\left(\frac{g+f \cdot e^{iaq}}{\sqrt{m_1 m_2}} \right) & \left(\frac{(g+f)}{m_2} \right) \end{pmatrix} \text{--so called 'dynamical matrix,' and } A^s = \begin{pmatrix} A^1 \\ A^2 \end{pmatrix} \quad (37)$$

This is a system of linear equations to find the amplitude of vibrations of atoms 1 and 2 and have non trivial solution if determinant of system is equal to zero:

$$\begin{vmatrix} -\frac{g+f}{m_1} & \frac{g+f \cdot e^{-iaq}}{\sqrt{m_1 m_2}} \\ \frac{g+f \cdot e^{iaq}}{\sqrt{m_1 m_2}} & -\frac{g+f}{m_2} \end{vmatrix} = 0 \quad (38)$$

This is a 4th order equation with respect to frequency. The solutions are looks like so:

$$\omega_1^2(q) = \frac{1}{2} \omega_0^2 \left(1 - \sqrt{1 - \gamma^2 \sin^2 \left(\frac{qa}{2} \right)} \right) \quad (39.1)$$

$$\omega_2^2(q) = \frac{1}{2} \omega_0^2 \left(1 + \sqrt{1 - \gamma^2 \sin^2 \left(\frac{qa}{2} \right)} \right) \quad (39.2)$$

, here $\omega_0^2 = \frac{(g+f)(m_1+m_2)}{m_1 m_2}$, $\gamma^2 = 16 \frac{g \cdot f}{(g+f)^2} \cdot \frac{m_1 m_2}{(m_1+m_2)^2}$. (39)

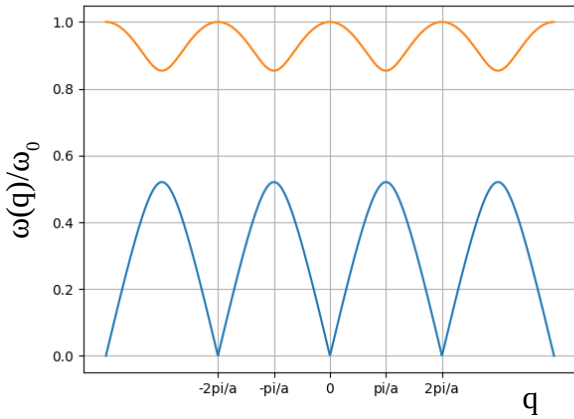


Figure 6

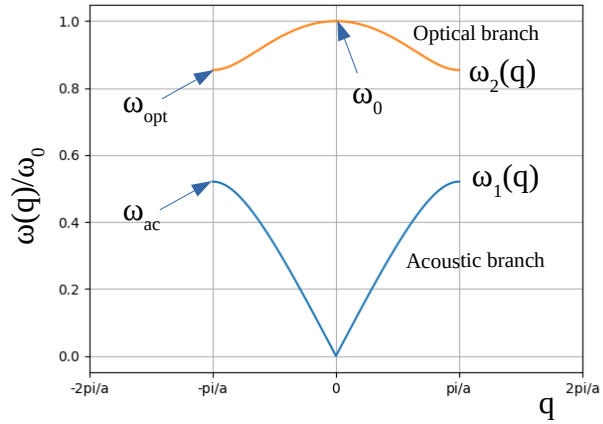


Figure 7

The expression (38) define two dispersion branches , one of which (39.1) shall be termed acoustic and the other (39.2) optical.

The first solution have the name “acoustic” because in low frequency region (near zero point) frequency of harmonic wave is proportional to wave vector $\omega = v \cdot q$, v -the speed of sound propagating along a chain of atoms.

Let consider the nature of atomic motion for optical and acoustic branches near zero value of q .

For $q=0$, $\omega_1=0$ and $\omega_2=\omega_0$. Here $\omega_0^2 = \frac{(g+f)(m_1+m_2)}{m_1 m_2}$.

For first solution, describing the vibrations of atoms for acoustic long wave harmonic wave we have from (36):

$$\frac{A_1}{A_2} = \sqrt{\frac{m_1}{m_2}} \text{ by using (5) for displacement of atoms } \frac{u_1}{u_2} = 1 \text{ or } u_1 = u_2 \quad (40)$$

This means that for long waves acoustic vibration all atoms move synchronously at the same distance. The crystal is displaced as a whole.

For second solution, describing the vibrations of atoms for optical long wave harmonic wave we have from (36):

$$\frac{A_1}{A_2} = -\sqrt{\frac{m_2}{m_1}} \text{ by using (5) for displacement of atoms } \frac{u_1}{u_2} = -\frac{m_2}{m_1} \text{ or } u_1 \cdot m_1 + u_2 \cdot m_2 = 0 \quad (41)$$

The last expression can be interpreted like this: there are two sublattices formed by type 1 and type 2 atoms. In the long-wavelength limit of optical vibrations, the two sublattices vibrate in opposite phases, so that the center of mass remains stationary. If these atoms have opposite charges, this type of vibration becomes active in the optical range and can emit and absorb electromagnetic energy. That why this type of vibration is called "optical vibration".

The density of vibrations can calculating by the same equation (14). But now we have two functions: $g(\omega)_1$ and $g(\omega)_2$ for the acoustic and optical branches, respectively:

$$E_{tot} = \frac{2N}{\pi} \int_0^{\omega_{ac}} \frac{g_1(\omega) \hbar \omega}{\left(e^{\frac{\hbar \omega}{kT}} - 1 \right)} d\omega + \frac{2N}{\pi} \int_{\omega_{opt}}^{\omega_0} \frac{g_2(\omega) \hbar \omega}{\left(e^{\frac{\hbar \omega}{kT}} - 1 \right)} d\omega \quad (42)$$

3.3 Harmonic vibration of 3d lattice.

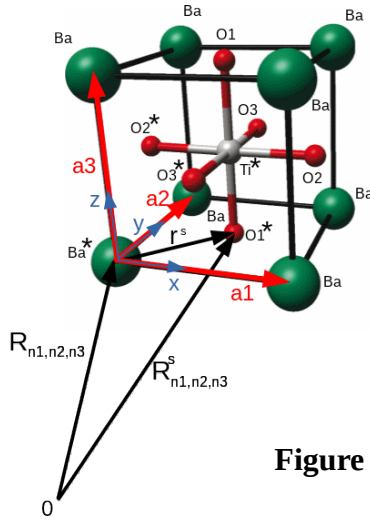


Figure 8

We assume that we have a complex 3d crystal containing a set of different atoms in a unit cell. As always all unit cells are equivalent. The crystal temperature is zero and the lattice is stable.

We will start by describing the arrangement of atoms in the lattice and we do this for a BaTiO3 crystal (figure 8). The unit cell is cubic (O_h -symmetry) and each unit cell contains 5 atoms: one titanium Ti, one barium Ba, and three oxygen atoms O1, O2, O3. All these atoms are marked with an asterisk in Figure 8 (all other atoms are located in the next unit cells.). Note that the oxygen atoms are chemically identical, but from a crystallographic point of view (in terms of symmetry) they are different, so they are marked with different symbols. The position of unit cell defines the vector:

$$R_{n_1, n_2, n_3} = a_1 \cdot n_1 + a_2 \cdot n_2 + a_3 \cdot n_3, \text{ here, } a_1, a_2, a_3 - \text{basis vectors}$$

and n_1, n_2, n_3 – integer numbers. The position of atom with type s (for example in our case $s=1$ for Ti, 2 for Ba, 3 for O1, 4 for O2 and 5 for O3) can be calculated as follows:

$$R_{n_1, n_2, n_3}^s = R_{n_1, n_2, n_3} + r^s \quad (43)$$

r^s - gives the position of s -atom inside of the given unit cell (we assume that zero point inside of unit cell coincide with position of Ba* atom). The lengths of basis vectors are the same and equal to a (for barium titanate it equal $4A$).

The positions of the atoms (the coordinate of the vector r) can be determined from the table 1. Denote the displacement of atom type s in unit cell $n=\{n_1, n_2, n_3\}$ in direction α as:

$$u_{\alpha,n}^s, \text{ here } n \text{ is a combination of three indices } \{ n_1, n_2, n_3 \} \quad (44)$$

If the number of unit cells in x direction is equal N_1 in y direction N_2 and in z direction N_3 , so the total number of unit cell in whole crystal $N = N_1 \cdot N_2 \cdot N_3$ and total number of atoms can be calculated as follows:

	Cartesian coordinates (in Å)			Fractional coordinates		
	r_x	r_y	r_z	$q1=r_x/a_1$	$q2=r_y/a_2$	$q3=r_z/a_3$
Ti	2.	2.	2.	0.5	0.5	0.5
Ba	0.	0.	0.	0.0	0.0	0.0
O1	2.	2.	0.	0.5	0.5	0.0
O2	0.	2.	2.	0.0	0.5	0.5
O3	2.	0.	2.	0.5	0.0	0.5

Table 1

$$N_{atoms} = N \cdot N_{atoms \text{ in unit cell}} \quad (45)$$

The total potential energy of crystal can be expanded into a power series with respect to displacement of atoms:

$$V = V(0) + \sum_{\alpha,n,s} \frac{dV}{du_{\alpha,n}^s} \Big|_{u=0} \cdot u_{\alpha,n}^s + \frac{1}{2} \cdot \sum_{\substack{\alpha,n,s \\ \beta,n',s'}} \frac{d^2V}{du_{\alpha,n}^s du_{\beta,n'}^{s'}} \Big|_{u=0} \cdot u_{\alpha,n}^s \cdot u_{\beta,n'}^{s'} + \dots \quad (46)$$

In (46) $V(0)$ – total potential energy of the crystal in the ground state (all atoms are in their equilibrium positions).

The second term is zero due to the stability of the crystal (all derivatives $\frac{dV}{du_{\alpha,n}^s} = 0$ for $u_{\alpha,n}^s = 0$).

We investigate the vibrations of atoms in a harmonic approximation, which means that all terms in (46) with an order higher than the second must be neglected (linear approximation). Finally for harmonic crystal total energy is looks like so:

$$V = V(0) + \frac{1}{2} \cdot \sum_{\substack{\alpha,n,s \\ \beta,n',s'}} \frac{d^2V}{du_{\alpha,n}^s du_{\beta,n'}^{s'}} \Big|_{u=0} \cdot u_{\alpha,n}^s \cdot u_{\beta,n'}^{s'} \quad (47)$$

Instead of the second order derivative, you can use the corresponding 6th order matrix:

$$\Phi_{\alpha\beta} \begin{pmatrix} ss' \\ nn' \end{pmatrix} = \frac{d^2V}{du_{\alpha,n}^s du_{\beta,n'}^{s'}} \Big|_{u=0} \quad (48)$$

Matrix (48) can be interpreted as a force constant for a spring connecting atoms (s,n) and (s',n'), displaced in directions α and β , respectively (see (47)). After the replacement (48) to (47):

$$V = V(0) + \frac{1}{2} \cdot \sum_{\substack{\alpha,n,s \\ \beta,n',s'}} \Phi_{\alpha\beta} \begin{pmatrix} ss' \\ nn' \end{pmatrix} \cdot u_{\alpha,n}^s \cdot u_{\beta,n'}^{s'} \quad (49)$$

Force acting on atom $\{s,n\}$ in α -direction could be calculated as follows:

$$F_{\alpha,n}^s = -\frac{dV}{du_{\alpha,n}^s} = -\sum_{\beta,n',s'} \Phi_{\alpha\beta} \left(\begin{smallmatrix} ss' \\ nn' \end{smallmatrix} \right) \cdot u_{\beta,n'}^{s'} \quad (50)$$

The equation (50) gives us another important relationship for the elements of the force matrix. For atoms in equilibrium positions (all displacements are zero), the force 50 should also be zero. If we move all the atoms the same distance and in the same direction, the situation will not change. it means that:

$$0 = \sum_{\beta} u_0 \sum_{n',s'} \Phi_{\alpha\beta} \left(\begin{smallmatrix} ss' \\ nn' \end{smallmatrix} \right) = \sum_{n',s'} \Phi_{\alpha\beta} \left(\begin{smallmatrix} ss' \\ nn' \end{smallmatrix} \right) = 0 \quad (51)$$

The classical equation of motion is:

$$m_s \cdot \ddot{u}_{\alpha,n}^s = -\frac{dV}{du_{\alpha,n}^s} \quad (52)$$

By using (48):

$$m_s \cdot \ddot{u}_{\alpha,n}^s = -\sum_{\beta,n',s'} \Phi_{\alpha\beta} \left(\begin{smallmatrix} ss' \\ nn' \end{smallmatrix} \right) u_{\beta,n'}^{s'} \quad (53)$$

Total number of the second order differential equations is $3sN$ and at the same time this is a dimension of matrix (48). Do not forget that n is complex index $\{n_1, n_2, n_3\}$.

Due to the linearity of the equation of motion (forces acting on an atom have a linear dependence on displacement) solution of (53) is harmonic function :

$$u_{\alpha,n}^s = \frac{1}{\sqrt{2m_s N}} A_q e_{\alpha}^s(q) e^{i(\omega(q)t + q R_n^s)} \quad (54)$$

here A_q – amplitude of harmonic wave with fixed value of wave vector $\mathbf{q} = \{q_1, q_2, q_3\}$, $\mathbf{e}_{\alpha}^s(q)$ – polarization vector (basis vector) describing the direction of atoms displacement.

After the substitution to (53):

$$\omega^2 \cdot \sqrt{m_s} \cdot A_q \cdot e_{\alpha}^s(q) \cdot e^{iqR_n^s} = \sum_{\beta,s',n'} \Phi_{\alpha\beta} \left(\begin{smallmatrix} ss' \\ nn' \end{smallmatrix} \right) \cdot e^{iqR_{n'}^{s'}} \cdot \frac{A_q}{\sqrt{m_{s'}}} \cdot e_{\beta}^{s'}(q) \quad (55)$$

or after a little simplification:

$$\omega^2(q) e_{\alpha}^s(q) = D_{\alpha\beta}^{ss'}(q) e_{\beta}^{s'}(q) \quad (56)$$

here

$$D_{\alpha\beta}^{ss'}(q) = -\frac{1}{\sqrt{m_s m_{s'}}} \sum_{n'} \Phi_{\alpha\beta} \left(\begin{smallmatrix} ss' \\ 0n' \end{smallmatrix} \right) \cdot e^{iq(R_{n'}^{s'} - R_0^s)} \text{ is the dynamical matrix of crystal, here } n=0 \quad (57)$$

(56) is a system of $3s$ linear equations for $3s$ variables $e_{\alpha}^s(q)$. The nontrivial solution exist if determinant of this system of equations is equal to 0.

$$|D_{\alpha\beta}^{ss'}(q) - \omega^2(q) \delta_{\alpha\beta} \delta_{ss'}| = 0 \quad (58)$$

If we assume that the elements of the dynamic matrix $D_{\alpha\beta}^{ss'}(q)$ are predefined (This can be done by fitting to experimental data or from direct calculations by solving the Schrödinger equation and using the Hellman-Feynman theorem (we will talk about this a little later)) the (58) give us the equation order $3s$ with respect to ω^2 . Clear that total number of different functions $\omega^2(q)$ in this case is equal to $3s$ of which 3 are acoustic and $3s-3$ optical branches (or the different harmonic waves). For example for BaTiO₃ we have 15 (3 acoustic, 12 optical) specific harmonic waves. Substitution calculated functions $\omega_j^2(q), j=1\dots 3s$ to (56) we will get the polarization vectors $e_\alpha^s(q)$.

Mathematically, this problem can be solved as the problem of diagonalizing a dynamic matrix $D_{\alpha\beta}^{ss'}(q)$. There is a large set of programs in Fortran, Matlab, Python for that. After diagonalization, everything the required frequencies and polarization vectors will be found automatically. Do not forget to repeat this procedure for different values of the wave vector \mathbf{q} (independent parameter). **But where can we get the values of the projections of the wave vector $\mathbf{q}=\{q_1, q_2, q_3\}$?** We can use for that the periodical boundary conditions (see (7)).

NB! To be more specific, we will carry out further calculations for the CsCl crystal.

The simple cubic unit cell (Γ^c lattice, space group symmetry is Pm-3m (221); <https://www.cryst.ehu.es/>) of CsCl contain two atoms marked by asterisk on figure 9. The length of basis vector (Cs-Cs or Cl-Cl minimal distance) equal to 4.1 Å. Fractional (Direct) coordinate of atoms inside of unit cell are looks like so: Cs (0.5,0.5,0.5); Cl (0.,0.,0.). Clear that $\mathbf{a}_1=\mathbf{a}_2=\mathbf{a}_3=\mathbf{a}$.

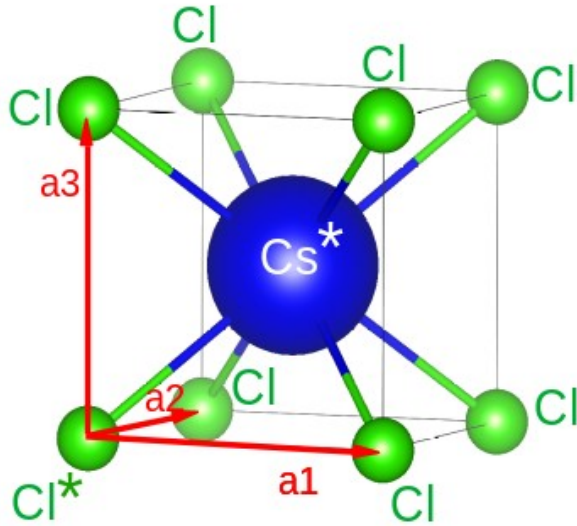


figure 9

We assume that the crystal is sufficiently large and have N_1 unit cells in a_1 direction, N_2 in a_2 direction and N_3 in a_3 direction. The lengths of lattice in every direction is equal $L_1=N_1 a$, $L_2=N_2 a$ and $L_3=N_3 a$ respectively. Due to periodical boundary condition and using (7) we can write:

$$\begin{aligned} \mathbf{u}_{x,n_1,n_2,n_3}^s &= \mathbf{u}_{x,n_1+N_1,n_2,n_3}^s \\ \mathbf{u}_{y,n_1,n_2,n_3}^s &= \mathbf{u}_{y,n_1,n_2+N_2,n_3}^s \\ \mathbf{u}_{z,n_1,n_2,n_3}^s &= \mathbf{u}_{z,n_1,n_2,n_3+N_3}^s \end{aligned} \quad (59)$$

Using $R_{n_1,n_2,n_3} = \mathbf{a}_1 \cdot n_1 + \mathbf{a}_2 \cdot n_2 + \mathbf{a}_3 \cdot n_3$, and (54,59):

$$e^{iqaN_1q_1} = 1 \quad e^{iqaN_2q_2} = 1 \quad e^{iqaN_3q_3} = 1, \quad (60)$$

do non forget that in case of CsCl $q_1=q_x$, $q_2=q_y$, $q_3=q_z$.

$\mathbf{e}_\alpha^s(\mathbf{q})$

Analogically (9) we will get equation for calculating the values for wave vectors:

$$\begin{aligned} q_x &= q_1 = \frac{2\pi}{L_1} n_1, \text{ and } n_1 \in \left[-\frac{N_1}{2}, +\frac{N_1}{2}\right] \\ q_y &= q_2 = \frac{2\pi}{L_2} n_2, \text{ and } n_2 \in \left[-\frac{N_2}{2}, +\frac{N_2}{2}\right] \quad \text{or in general } q_\alpha = \frac{2\pi}{a_\alpha} k_\alpha, \text{ and } k_\alpha \in \left[-\frac{1}{2}, +\frac{1}{2}\right], \text{ here} \\ q_z &= q_3 = \frac{2\pi}{L_3} n_3, \text{ and } n_3 \in \left[-\frac{N_3}{2}, +\frac{N_3}{2}\right] \quad k_\alpha \text{ is dimensionless wave vectors.} \end{aligned} \quad (61)$$

$\mathbf{e}_\alpha^s(\mathbf{q})$ Similarly to (9), nonequivalent values of wave vectors fill a cube with the side length equal to $\frac{2\pi}{a_\alpha}$. The corresponding cube (have the name **Brillouin zone**) with some standard symmetrical directions (but only for Γ_c lattice) is shown in figure 10 and table 2. The **Brillouin zone** (https://en.wikipedia.org/wiki/Brillouin_zone) is a Wigner-Seits primitive unit cell for reciprocal lattice. The description of **Brillouin zones** for different crystals (space groups) you can find here https://www.cryst.ehu.es/cryst/get_kvec.html.

figure 10

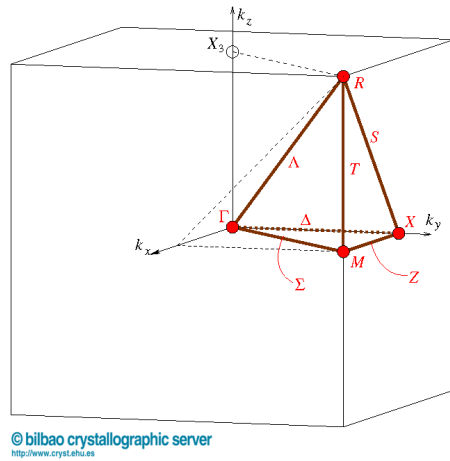


table 2

Symmetrical Points	k_x	k_y	k_z
Γ	0	0	0
X	0	0	0.5
M	0.5	0.5	0
R	0.5	0.5	0.5

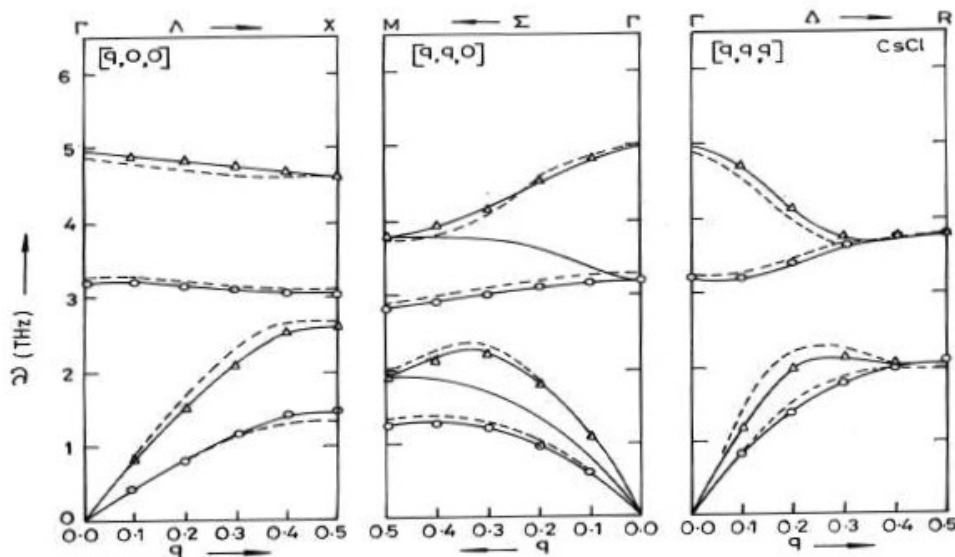


Figure 11.
Phonon Dispersion Curve for CsCl at 78 K.
 Δ -longitudinal (L-vibration), o-transverse waves(T-vibration).

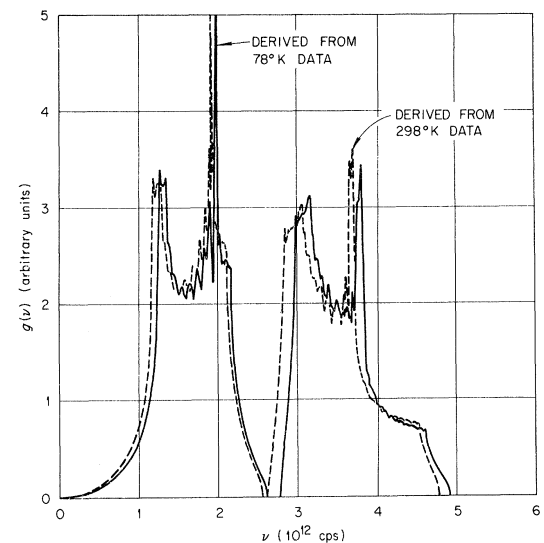


Figure 12.
Density of state (DOS function)

The analytical calculation of phonons (harmonic vibration) for CsCl you can find in article:
S.K.Shukla, K.K.Mishra , A.N. Pandey , G.K.Upadhyay and K.S.Upadhyaya “Theoretical analysis of phonon dynamical behaviour of Cesium Chloride at various temperatures”, *Journal of Applied Physics (IOSR-JAP) Volume 2, Issue 4 (Nov. - Dec. 2012), PP 26-34*

Step by step calculation process is looks like this:

1. Potential energy is separated into two parts LR (long range interactions) or Coulomb and SR (short range interactions).
2. At the next step, the element of the matrix of force constants is calculating using (48).

There are other methods for calculating the members of the force constant matrices (48):

2.1 The **analytical method**. This approach is acceptable if we know the form of potential energy (analytical expression or as a set of numerical data). Only in this case the derivatives (48) can be calculated directly.

2.2 The **semi-empirical method** is based on fitting the elements of matrix (48) to experimental data such as: infrared absorption, Raman (photons scattering) spectra, neutron scattering, elastic constants C_{ij} , bulk modulus and shear modulus, heat capacity, etc. Now this method is not used, since it does not allow understanding the physics of processes. This is just a description without understanding why this is so.

2.3 **Ab-initio (modern method)** approach is implemented in the VASP and PHONOPY software packages. If we move atoms from equilibrium positions to the vector $u_{\alpha,n}^s$, knowledge of this displacement allow to calculate the elements of elastic matrix (48) by using equation (50). The equation (50) is a system of linear equations with respect to elements of matrix (48). What about the forces acting on atoms $F_{\alpha,n}^s$? Answer is: They can be calculated by using of quantum mechanics. The use of crystal symmetry properties makes it possible to sufficiently reduce the number of different bias combinations. Currently, this method is the most used because one have a clear quantum mechanical, physical basis.

3. Substitution (48) to (57) give the elements of dynamical matrix.

4. Diagonalization of dynamical matrix for different values of wave vectors q (result of diagonalization presented on figure 11) give the frequency of vibrations, functions $\omega_j(q)$ and polarization vectors $e_{\alpha}(q)$. These parameters can be further used to calculate physical quantities and optical spectra related to vibrational properties of crystals (Infrared and Raman spectra, elastic properties, heat capacity and so on). For high symmetry directions ($\Gamma \rightarrow X$ or $\Gamma \rightarrow R$) transverse vibrations are twofold degenerate, so the total number of branches is 6 (for CsCl lattice), as it should be.

5. The density of vibrations (DOS function) $g(\omega)$ -function can be calculated as follows:

$$g_j(\omega) = \sum_q \delta(\omega - \omega_j(q)) \quad (62)$$

The equation (62) is easy to implement in program code and result of this calculations you can see on figure 12.

3.4 LT-splitting in ionic crystals.

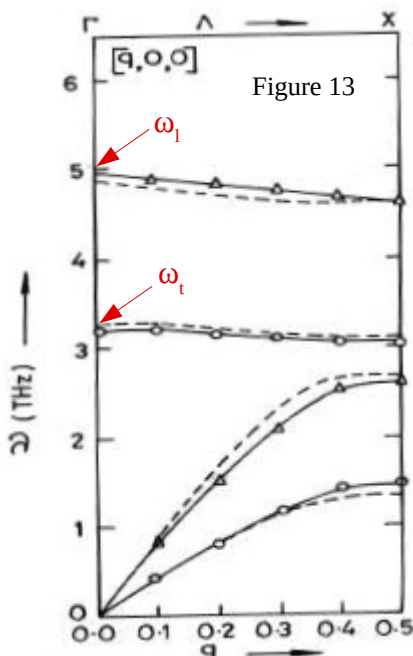


Figure 13

As you can see, longitudinal vibrations have a higher frequency than transverse vibrations. For optical vibration at the Γ -point, this effect is related to so called LT-splitting of vibrations for ionic crystals (figure 13).

It should be emphasized that this effect takes place only for crystals with charged atoms. For pure covalent crystals such as Ge or Si, no splitting is observed. Why the charge of atoms is so important?

Detailed theory of this effect you can find in [1](see first lecture). Here we will consider only qualitative description.

Suppose we have two sublattices formed by atoms with opposite charges. Lattice like NaCl. For long wave limit ($q=0$ and wavelength of harmonic wave $\lambda \rightarrow \infty$) this two sublattices are vibrating in opposite phase (we need to distinguish between longitudinal fig. 14a and transversal vibrations fig. 14b).

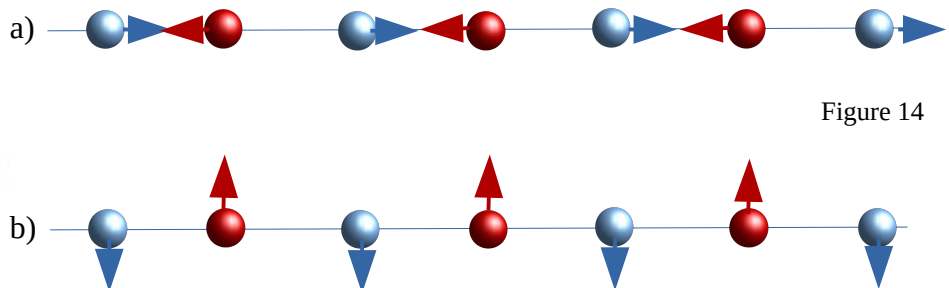


Figure 14

If the charge of atoms is equal to Q , masses of positive and negative atoms are m_+ and m_- respectively. and u_+ and u_- are the displacement of positive and negative ions from their equilibrium positions. Then the equations of motion for ions are looks like so (at $q = 0$, atoms in one sublattice vibrate synchronously, which means that now it is quite sufficient to describe the motion of only one atom of a given type):

$$m_+ \frac{d^2 u_+}{dt^2} = -k \cdot (u_+ - u_-) + Q \cdot E \quad m_- \frac{d^2 u_-}{dt^2} = k \cdot (u_+ - u_-) - Q \cdot E \quad (63)$$

In (63) E -electric field strength vector generated by relative displacement of sublattices. By using of reduced mass $\frac{1}{m_r} = \frac{1}{m_+} + \frac{1}{m_-}$ of ions and normalized relative displacement of sublattices $w = \sqrt{N_e m_r} (u_+ - u_-)$ (see [1]) we will get two separate equations of motion for longitudinal and transversal longwave waves:

$$\begin{aligned} \frac{d^2 w_t}{dt^2} &= -\omega_t^2 \cdot w_t \\ \frac{d^2 w_l}{dt^2} &= -\omega_t^2 \frac{\epsilon_0}{\epsilon_\infty} \cdot w_l \end{aligned} \quad (64)$$

Comparison of this equations we obtain Lyddane–Sachs–Teller relation [https://en.wikipedia.org/wiki/Lyddane%E2%80%93Sachs%E2%80%93Teller_relation]:

$$\frac{\omega_l}{\omega_t} = \sqrt{\frac{\epsilon_0}{\epsilon_\infty}} \quad (65)$$

The polarization vector is related to electrical strength vector as follows:

$$\vec{P} = \frac{\epsilon - 1}{4\pi} \vec{E} \quad (66)$$

ϵ - dielectric constant describing the response of crystal on external electric field. This response is related to the deformation of electron shells of ions (electron part of dielectric constant) and to the displacement of ions (ionic part of dielectric constant). In practice, a static dielectric constant ϵ_0 describes the reaction of a crystal to a constant external electric field (includes the ionic and electronic parts) and high-frequency dielectric constant ϵ_∞ (includes only the electronic part, since the massive ions do not just have time to shift in a high-frequency electric field).

It is clear that if the frequency of external electric field is sufficiently large (practically $=\infty$) in this case always for any crystal $\epsilon_\infty = 1$ and $\vec{P} = \frac{\epsilon - 1}{4\pi} \vec{E} = 0$ - the crystal is not polarizable.

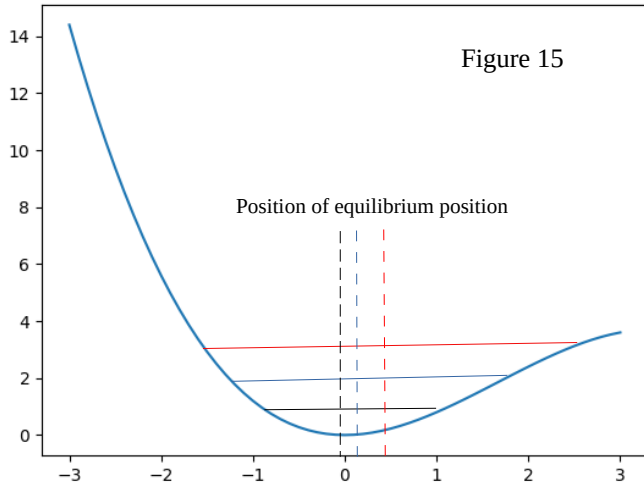
According to [65], long-wave longitudinal vibrations in ionic crystals have a higher frequency than transverse waves. This effect is associated with the generation of an additional electric field in the direction of longitudinal vibrations, which effectively strengthens the lattice. This effect decays quickly with distance from the $q=0$ point.

3.5 Effects related to anharmonicity

The effects of anharmonicity appear if we take into account a terms of order greater than two (third order, fourth order, etc.) in expansion (46). The anharmonicity is leads to such very important effects as thermal expansion of solids, thermal resistance, etc. Let's start from thermal expansion.

Consider a very simple model containing two atoms at a distance R_0 at $T = 0$. For small deflection from equilibrium position the corresponding potential energy of interaction is(see Figure 15):

$$U = \frac{\beta x^2}{2} - \frac{\gamma x^3}{3} \quad (67)$$



As seen this curve a little unsymmetrical due to anharmonic cubic term. The corresponding force can be calculated directly :

$$F = -\frac{dU}{dx} \Big|_{x=0} = -\beta x + \gamma x^2 \quad (68)$$

The probability of an atom deviating from the equilibrium position is by Boltzmann :

$$f(x) = A e^{-\frac{U}{kT}} \approx A e^{-\frac{\beta x^2}{2kT}} \left(1 + \frac{\gamma x^3}{3kT}\right) \quad (69)$$

The unknown parameter **A** can be determined from the normalization condition:

$$\int_{-\infty}^{+\infty} f(x) dx = 1 \text{ the calculations gives } A = \left(\frac{\beta}{2\pi kT}\right)^{1/2} \quad (70)$$

Now let's calculate the average deviation of the atom from the equilibrium position:

$$\bar{x} = \int_{-\infty}^{+\infty} x f(x) dx = \left(\frac{\beta}{2\pi kT}\right)^{1/2} \int_{-\infty}^{+\infty} e^{-\frac{\beta x^2}{2kT}} \left(x + \frac{\gamma x^4}{3kT}\right) dx = \frac{\gamma kT}{\beta^2} \quad (71)$$

The definition for coefficient of linear thermal expansion is:

$$\frac{dl}{l_0} = \alpha dT \text{ or } \alpha = \frac{d\bar{x}}{dT} \frac{1}{R_0} = \frac{\gamma k}{R_0 \beta^2} \quad (72)$$

As you see the coefficient of linear thermal expansion depend on parameter of anharmonicity γ . A harmonic (linear) crystal does not exhibit thermal expansion.

The physical explanation for this effect is simple and is associated with the asymmetry of the potential energy due to the anharmonic term. This leads to a dynamic displacement of the equilibrium position of the atom and thermal expansion of the lattice.

The physical phenomenon of thermal conductivity in crystals is associated with the transfer of thermal energy (thermal vibrations of atoms) from one point of the lattice to another. For a harmonic crystal, the crystal contains a set of independent and non-interacting harmonic waves, which can be represented as a set of quasiparticle -phonons. Each phonon have quasimomentum $\vec{p} = \hbar \vec{k}$, here \vec{k} – wave vector of phonon. In harmonic crystals, phonons do not interact and can transfer thermal energy at the speed of sound to any point in the lattice. This means that in this case the thermal conductivity is infinitely large. But experiment shows that this is not the case.

But in an anharmonic crystal (cubic term in (67)), phonons begin to interact. In this case, it is necessary to take into account the so-called three-phonon processes. In this case, a phonon can decay into two phonons, or two phonons for collision can create a new phonon. This three-phonon process leads to the appearance of resistance to the movement of phonons. The calculation gives the following expression for the thermal conductivity coefficient:

$$\chi \propto \frac{1}{\gamma^2 T} \quad (73)$$

The coefficient decreases with temperature, because the number of three-photon processes increases with growing temperature.