

7.1 Harmonic vibration of 1d one atomic lattice (application of a quantum harmonic oscillator).

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. **Very important to emphasize that atoms in this model can be displaced only along (not perpendicularly) the chain of atoms, we have longitudinal type of atomic vibrations.**

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 arising interaction forces may be considered quasielastic, i.e., proportional to the variation of the interatomic 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. 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 the whole crystal could be written as follows:

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

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 of n -th atom from equilibrium position u_n on time is looks 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 the force action on the atom with number k we need to taken into the account only two members of this sum included the deflections of this atom from equilibrium position $(u_{k+1} - u_k)^2$ and $(u_k - u_{k-1})^2$ (we assume that in our model only the nearest atoms interact). 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 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:

$$u_k(t) = \frac{1}{\sqrt{2mN}} \cdot A \cdot e^{i(\omega t + qak)}, \text{ m-mass of atom and N-total number of atoms.} \quad (5)$$

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 is a distance between nearest atoms. Do not forget that the linear combination of the harmonic solutions is also a solution of the equation (4). Or by the other words if we need to describe the motion of atom with number k , we have to take into the account total set of all possible harmonic waves.

$$u_k(t) = \frac{1}{\sqrt{N}} \cdot \sum_q A_q \cdot e^{i(\omega t + qak)}.$$

The q parameter can be used as an index for numbering 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 the cyclic frequency on the wave vector or so called **dispersion relation** (Figure 1). Due to the periodicity of frequency (**sine** function), it is not sense to take into the account all possible values of wave vector but only nonequivalent values of wave vectors located in the interval from 0 to 2π (figure 2) or more symmetrical option (figure 3).

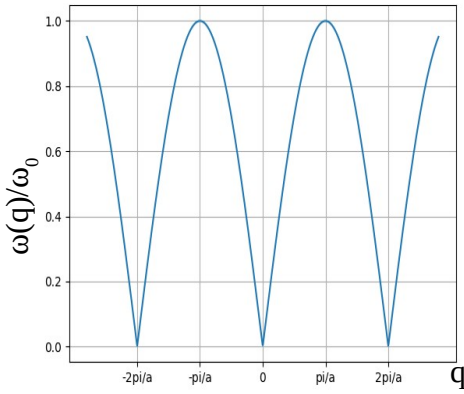


figure 1

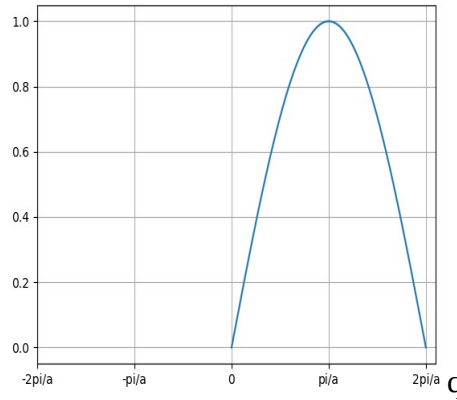


figure 2

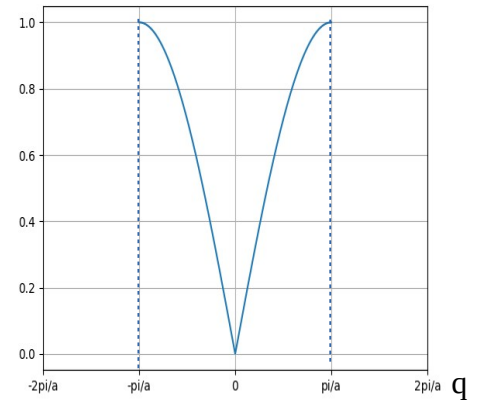


figure 3

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

For displacements (5) we have the same result:

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

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 \mathbf{q} . How to calculate it? We use for this aim the **periodic boundary conditions**, it means that the atoms with number \mathbf{k} and $\mathbf{k} + \mathbf{N}$ are the same atoms. Mathematically it's means that displacement of the atoms \mathbf{k} and $\mathbf{k} + \mathbf{N}$ from the equilibrium position are equal:

$$u_k = u_{k+N} \quad \text{This replacement is needed to eliminate an explicit time dependency.} \quad (7)$$

After applying the equation (5):

$$u_k(t) = \frac{1}{\sqrt{N}} \cdot A \cdot e^{i(\omega t + qak)} = \frac{1}{\sqrt{N}} \cdot A \cdot e^{i\omega t} \cdot e^{iqak} = \frac{1}{\sqrt{N}} \cdot A(t) \cdot e^{iqak} \quad (8)$$

After substitution one into the equation (7) we get:

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

A little simplification give:

$$e^{iqNa} = 1$$

This is possible if $q \cdot N \cdot a = 2 \cdot \pi \cdot n$, here $n \in Z$ and $q = \frac{2\pi n}{Na} = \frac{2\pi n}{L}$ here, L — total length of 1d crystal. 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:

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

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

with step $\Delta q = \frac{2\pi}{L}$.

The wave vector can be interpreted as the order 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:

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

A_q- is an amplitude of harmonic wave for coresponding wave vector **q**. Total number of terms of this sum 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 **ω+dω**. The integral

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

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):

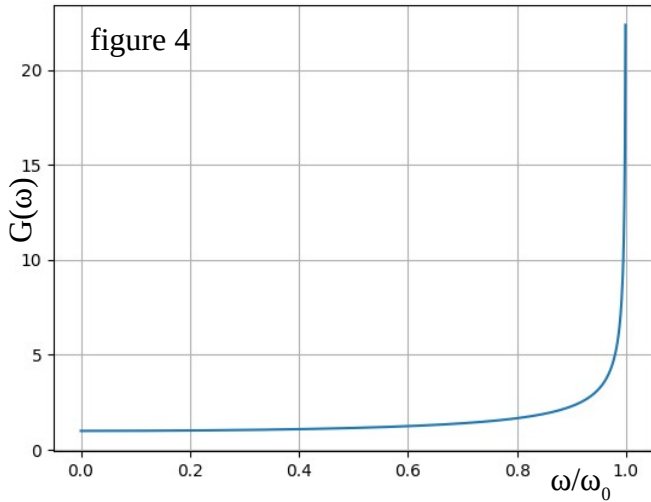
$$\frac{d\omega}{dq} = \frac{\omega_0 \cdot a}{2} \left| \cos\left(\frac{qa}{2}\right) \right| \quad (15)$$

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:

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



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

$$G(\omega) = \frac{g(\omega)}{\frac{N\pi}{\omega_0}}$$

The graphic of function you can see on figure 4.

There is a useful formula that can be used to further simplify the calculation of specific physical properties of crystals.

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

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. It means that the total internal energy of the crystal is equal to **kTN**. So as you see we can calculate the heat capacity of lattice (need to calculate the derivative with respect to temperature **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 **Tⁿ**, 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:

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

The calculation of kinetic energy give:

$$E_{kin} = \frac{1}{2} m \sum_k \dot{u}_k^2 = \frac{1}{2} m \sum_k \dot{u}_k \cdot \dot{u}_k^* \quad (19)$$

After using (8) we have:

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

After reordering of summation:

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

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

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

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:

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

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:

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

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

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

After the substitution to (19) we will get:

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

Finally for total energy of vibrating crystal:

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

Does this equation remind you of something? This equation means that we can represent the lattice vibration as a vibration of the set of independent harmonic oscillators, and each oscillator is associated with one harmonic wave with specific wave vector \mathbf{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 value for quantum numbers \mathbf{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 \mathbf{q} -vector can be replaced by integration using the following standard relations:

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

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

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 $x = \frac{\hbar \omega}{kT}$ give :

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

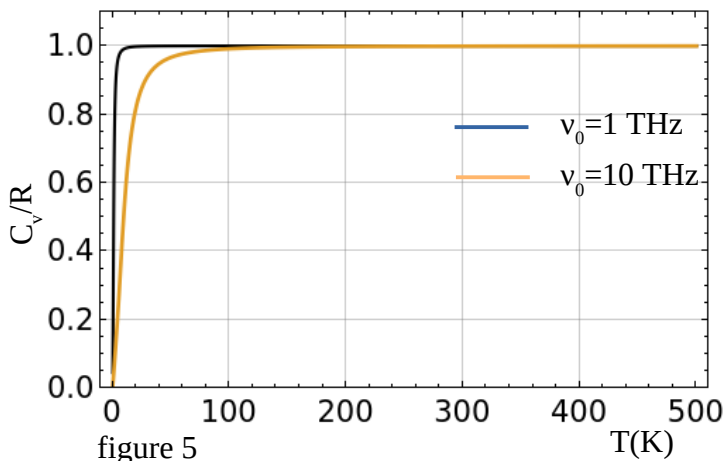


figure 5

For one mole of atoms $N=N_A$ we have $kN_A=R$. 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 $\nu_0 = \sqrt{E/\rho}$.

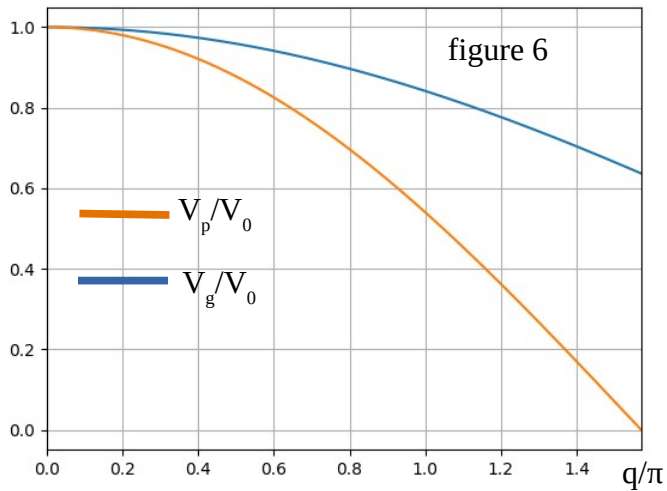
For chain of atoms $\rho = \frac{m}{a}$ and Young modulus :

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

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) $v_p = \frac{\omega}{q}$ and **group velocity** (the rate of energy transfer in the crystal) $v_g = \left| \frac{d\omega}{dq} \right|$. For

chain of atoms: $v_p = v_0 \left| \frac{\sin \frac{aq}{2}}{\frac{aq}{2}} \right|$ and $v_g = v_0 \left| \cos \frac{aq}{2} \right|$. For small wave vectors (very long wave limit) $v_p = v_g = v_0$.



On figure 6 presented the the dependence of group and phase velocities on wavevector.