Introduction to lattice vibrations

Andreas Wacker[1]
Mathematical Physics, Lund University
November 11, 2019

1   Introduction

Ideally, the atoms in a crystal are positioned in a regular manner following the Bravais lattice. This configuration has the minimal total energy and is therefore taken at zero temperature. However, for finite temperature, there is a certain probability for the atoms to be elongated from these rest positions, which costs some energy. Now the elongation of a single atom affects all others via their mutual interaction, which leads to a dynamical distortion of the entire crystal. Due to the translational symmetry of the crystal, these collective distortions can be classified by vibration modes $\propto \mathrm{e}^{\mathrm{i}(\mathbf{k}\cdot\mathbf{r}-\omega t)}$ where each $\mathbf{k}$ only allows for a finite set of (angular) frequencies $\omega_n(\mathbf{k})$. The aim of this text is to motivate this basic concept and to present a few central results. While the problem is treated entirely classical here, one has to bear in mind that quantum physics tells us that any oscillator can take energy only in portions $\hbar\omega$. Such an quantized excitation of a vibration mode is called a *phonon*. However, frequently the term phonon spectrum is used for the spectrum $\omega_n(\mathbf{k})$ of vibration modes as well. Knowledge about lattice vibrations in crystals is central to understand the thermal properties, to quantify phonon scattering, limiting the electron conductivity, and to explain the absorption of far-infrared light.

2   The one-dimensional chain

Let us consider a chain of atoms, which are interacting with their nearest neighbors via a potential $V(x)$, which has a minimum at $x = a$, as sketched in Fig. 1(a). Then the lowest energy is obtained, if all atoms have the distance a of each other, i.e., they form a regular chain described by the Bravais lattice $\mathbf{R}_n = na\mathbf{e}_x$, see open circles in Fig. 1(b). Here we consider the dynamical behavior for small displacements $x_n = na + u_n$ of the individual atoms, where $u_n \ll a$.

2.1   Obtaining the dispersion relation

The nth atom is subjected to the potential $V(x_{n+1} - x_n) + V(x_n - x_{n-1})$ due to its interaction with the neighbors and thus it is subjected to the force $V'(x_{i+1} - x_i) - V'(x_i - x_{i-1})$. ($f'(x)$ denotes the derivative of the function f with respect to its argument. Derivatives with respect to time are denoted by $\dot{f}$ in the following.) If all atoms are at the regular positions, this force is zero as $V'(x) = 0$ at the minimum $x = a$. Things change if we consider small displacements $x_n = na + u_n$ of the individual atoms, where $u_n \ll a$, see Fig. 1(b). In this case, Newton's
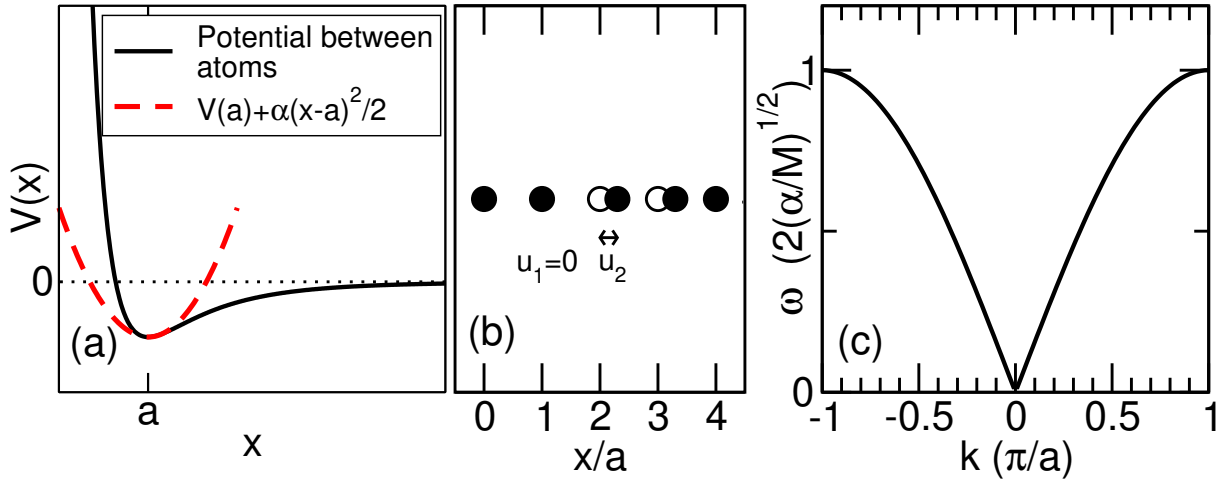
Figure 1: The one dimensional chain: (a) Characteristic potential for the interaction between atoms together with the parabolic approximation (dashed). (b) Atoms (full circles) in the chain, the open circles indicate the positions having the lowest energy. (c) vibrational spectrum from Eq. (3).

equation of motion for atoms with a mass M reads

$$M\ddot{u}_n = M\ddot{x}_n = V'(x_{n+1} - x_n) - V'(x_n - x_{n-1}) = V'(a + u_{n+1} - u_n) - V'(a + u_n - u_{n-1})$$

For small displacements we may write $V'(a + \delta x) \approx V'(a) + V''(a)\delta x$. As $V(x)$ has a minimum at $x = a$ we have $V'(a) = 0$ and $\alpha = V''(a) > 0$. (This is the *parabolic approximation* for the potential $V(x) \approx V(a) + \alpha(x - a)^2/2$, which we justify in Sec. 2.3) Thus we obtain

$$M\ddot{u}_n \approx \alpha(u_{n+1} - 2u_n + u_{n-1}) \tag{1}$$

Question 1: Can you motivate this equation for a chain of balls with a spring between neighbors?

This linear differential equation has solutions of the form

$$u_{kn}(t) = \text{Re}\left\{A_k e^{i(kna - \omega t)}\right\} \tag{2}$$

with a complex amplitude A_k. Inserting into Eq. (1) provides $-M\omega^2 = \alpha(e^{ika} - 2 + e^{-ika}) = -4\alpha \sin^2(ka/2)$ or

$$\omega = 2\sqrt{\frac{\alpha}{M}}\left|\sin\left(\frac{ka}{2}\right)\right| \equiv \omega(k) \tag{3}$$

which is called *dispersion relation*. This result is displayed in Fig. 1(c). Thus, for each k there is one *vibration mode* of the form (2) with a distinct frequency $\omega(k)$.

The possible values of k can be limited to the interval $-\pi/a < k \leq \pi/a$ (which is the first Brillouin zone of the one-dimensional lattice). This can be understood by the following argument: If k is not in this interval, we can write $k = 2\pi l/a + \tilde{k}$ with $l \in \mathbb{Z}$ and $-\pi/a < \tilde{k} \leq \pi/a$. Then the elongations in Eq. (2) satisfy $u_{nk}(t) = \text{Re}\{A_k e^{ikna}\} = \text{Re}\{A_k e^{i\tilde{k}na}\}$ for all lattice points n as $e^{i2\pi ln} \equiv 1$. Thus the vibration mode with k is identical to a vibration mode with $\tilde{k}$ satisfying $-\pi/a < \tilde{k} \leq \pi/a$, which can be chosen to represent the vibration considered.

2.2 Traveling localized distortions

We now consider a localized distortion at $t = 0$ of the form

$$u_n(0) = A e^{-(na/w)^2} e^{ik_0 na}$$

where $w \gg a$ is the effective width of the distortion and A is its maximal amplitude. The time dependence can be easily obtained by using the modes (2) evaluated above, which constitute a complete set of functions for the system. We set

$$u_n(t) = \frac{1}{2\pi} \int_{-\pi/a}^{\pi/a} dk\, A_k e^{i(kna - \omega(k)t)} \tag{4}$$

This holds in particular for $t = 0$, where we find

$$\frac{1}{2\pi} \int_{-\pi/a}^{\pi/a} dk\, A_k e^{ikna} = A e^{-(na/w)^2} e^{ik_0 na} \tag{5}$$

One can show that for $w \gg a$

$$A_k \approx \sqrt{\pi} w A e^{-(k-k_0)^2 w^2/4}$$

Thus for $w \gg a$, A_k is essentially restricted to a small range of k values around k_0.

For $k \approx k_0$, we can expand $\omega(k) \approx \omega(k_0) + \omega'(k_0)(k - k_0)$ and Eq. (4) becomes

$$u_n(t) \approx \frac{1}{2\pi} e^{i(k_0 na - \omega(k_0)t)} \int_{-\pi/a}^{\pi/a} dk\, A_k e^{i(k-k_0)(na - \omega'(k_0)t)} \tag{6}$$

Comparing with Eq. (5) this provides

$$u_n(t) \approx A e^{-(na - \omega'(k_0)t)^2/w^2} e^{i(k_0 na - \omega(k_0)t)}$$

Thus the elongation travels with the *group velocity* $v_g = \omega'(k_0) \equiv d\omega(k_0)/dk$. This is a rather general concept of localized wave-packets[2]. For small $|k_0|$, Eq. (3) provides

$$v_g = \pm v_{\text{sound}} \quad \text{with the sound velocity } v_{\text{sound}} = a\sqrt{\frac{\alpha}{M}} \tag{7}$$

if k_0 is positive/negative, respectively. Thus elongations can travel in both directions with constant velocities, if their wavelength $2\pi/k_0$ is large compared to the lattice. This is actually the common behavior of (here longitudinal) sound waves. If the wavelength becomes shorter, the velocity decreases and becomes zero at the boundaries $k_0 = \pm \pi/a$.

2.3 Relation to elasticity theory and orders of magnitudes

Consider two atoms with the potential $V(x)$ as shown in Fig. 1(a). The lowest energy is obtained for a distance a. If an external force F_{ext} is applied to the right atom, while the left is fixed, it will be elongated until the inter-atomic potential compensates the force, i.e. $-V'(x) + F_{\text{ext}} = 0$. In the quadratic approximation, this becomes $\alpha(x - a) = F_{\text{ext}}$. Now $(x - a)/a = \varepsilon$ is the strain and $F/A = \sigma$ is the stress (if we assume an area $A \sim a^2$ of the chain). From elasticity theory we know, that for small elongations $\sigma = Y\varepsilon$ with Young modulus Y. Thus we have

$$\alpha = \frac{F_{\text{ext}}}{(x - a)} \approx \frac{\sigma a^2}{\varepsilon a} = Ya \tag{8}$$

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[2]Details can be found in `http://www.matfys.lth.se/Andreas.Wacker/Scripts/wavepacket.pdf`.

Typical values for the Young modulus of crystals are of the order of 100 GPa. For $a \sim 3\text{Å}$, this provides $\alpha \sim 30$ N/m ~ 2 eV/Å^2, which appears very plausible as the binding energy between atoms is of the order eV, which relates to $-V(a)$ in Fig. 1(a). The sound velocity (7) is then of the order 6000 m/s (here for a mass of $M = 40u$), which is a typical (longitudinal) sound velocity in crystals.[3] Finally, the maximum frequencies of the dispersion relation are typically $\omega/2\pi = \sqrt{\alpha/M}/\pi \sim 7$ THz (for a mass of $M = 40u$). This corresponds to a wavelength of 40 μm or a photon energy of 30 meV, which is in the far-infrared region of the electromagnetic spectrum. All these values given here are characteristic orders of magnitude for common crystals. Extreme cases are diamond and lead with maximum frequencies around 40 THz and 2 THz, respectively. These crystals consist of particularly light/heavy atoms and also have a large/low Young modulus.

Using these typical values, we can also estimate the average elongation by lattice oscillations in real crystals. If the oscillations are in thermal equilibrium, the average potential energy is $\langle \alpha(x-a)^2/2 \rangle = k_B T/2$. Thus, we have an average elongation of $\sqrt{k_B T/\alpha} \sim 0.1$ Å at room temperature, which is more than an order of magnitude less than the atomic distance, so that the quadratic approximation of $V(x)$ used in Eq. (1) is essentially valid.

2.4 Counting the number of modes for finite length

For an infinite chain, there is a continuum of k values possible and thus there are infinitely many vibration modes. What happens for a finite chain of N atoms at $n = 1, 2, \ldots N$? In this case we have to specify boundary conditions.

The most simple choice are periodic boundary conditions, where $u_0 = u_N$ and $u_{N+1} = u_1$, which can actually be realized by a ring of N atoms. For the waves from Eq. (2) this periodicity implies $e^{iNka} = 1$, i.e., $Nka = 2\pi j$ with $j \in \mathbb{Z}$. Within the interval $-\pi/a < k \leq \pi/a$ this allows for N different k values $k_j = 2\pi j/Na$ [where $j = -N/2 + 1, = -N/2 + 2, \ldots, N/2$ for even N and $j = (1-N)/2, (3-N)/2, \ldots, (N-1)/2$ for odd N]. The corresponding frequencies, provided by Eq. (3), are $\omega_j = 2\sqrt{\alpha/M} \sin|j\pi/N|$.

A more realistic boundary condition is a vanishing force at the end of the chain. This is equivalent to $u_0 = u_1$ and $u_{N+1} = u_N$, as the force vanishes if the distance between the atoms is a and thus the elongations are equal. The modes can be written as linear combinations of the general solutions (2). As the frequency of all parts must be identical we can only combine solutions with a given k and $-k$ where we may choose arbitrary coefficients. The boundary condition $u_0 = u_1$ implies $A_{\pm k} = Ce^{\mp ika/2}$. Here we set $C = 1$ (more general complex numbers provide a different amplitude and a phase shift in time) and obtain

$$u_n^{\text{open}}(t) = \text{Re}\left\{e^{-ika/2}e^{i(kan-\omega(k)t)} + e^{ika/2}e^{i(-kan-\omega(k)t)}\right\} = 2\cos(k(n-1/2)a)\cos(\omega(k)t)$$

These solutions are different provided $0 \leq k < \pi/a$. (The value $k = \pi/a$ is excluded here as this provides $u_n(t) \equiv 0$.) The other boundary condition $u_{N+1} = u_N$ is satisfied if $kNa = j\pi$ with $j \in \mathbb{Z}$. Within the interval $0 \leq k_j < \pi/a$, we have N different values $k_j = j\pi/Na$ where the dispersion relation (3) provides the angular frequencies $\omega_j = 2\sqrt{\alpha/M} \sin|j\pi/2N|$. [4]

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[3]Elasticity theory provides for isotropic materials the longitudinal sound velocity $c_L = \sqrt{\frac{(1-\nu)Y}{(1-2\nu)(1+\nu)\rho}}$, where ρ is the mass density and ν is the Poisson ratio. Assuming $\rho \sim M/a^3$, $\nu \sim 0$, and $Y \sim f/a$ we obtain the sound velocity of our chain from Eq. (7).

[4]The modes $u_n^{open}(t)$ have actually the periodicity $2N$, where the elongations for $n = N+1, \ldots 2N$ satisfy $u_n = u_{2N+1-n}$ for $n = N+1, \ldots 2N$. Thus the mode-frequencies correspond to a periodic chain with length $2N$, except that the maximum frequency is missing and no degeneracy occurs.

Exercise 1: Determine the modes for a finite chain with the boundary conditions $u_0 = 0$ and $u_{N+1} = 0$, i.e., a chain of $N + 2$ atoms, where the outer ones are fixed.

Answer: The boundary condition $u_0 = 0$ is satisfied by choosing $A_k = -\mathrm{i}$ and $A_{-k} = \mathrm{i}$ providing

$$u_n^{fixed}(t) = \mathrm{Re}\left\{ \mathrm{i}e^{\mathrm{i}(-kan-\omega(k)t)} - \mathrm{i}e^{\mathrm{i}(kan-\omega(k)t)} \right\} = 2\sin(kan)\cos(\omega(k)t)$$

The boundary condition $u_{N+1} = 0$ requires $ka(N + 1) = j\pi$ with $\in \mathbb{Z}$. Restricting to non-negative k in the first Brillouin zone, we obtain N values $j = 1, \ldots N$. (For $j = 0$ and $j = N + 1$, all elongations are zero). Thus we have N different modes with frequencies $\omega_j = 2\sqrt{\alpha/M}\sin|j\pi/(2N+2)|$, which are standing waves. [Remark: The modes $u_n^{fixed}(t)$ have the periodicity $2(N+1)$, where the elongations for $n = N+2, \ldots 2N+2$ satisfy $u_n = -u_{2N+2-n}$ for $n = N+2, \ldots 2N+2$. Thus, the mode-frequencies correspond to a periodic chain with length $2N + 2$, except that the maximum and minimum frequency are missing and no degeneracy occurs.]

In all cases we find that *the number of different vibration modes is equal to the number of atoms which are allowed to move* (for one-dimensional systems considered here). This can be understood by the number of degrees of freedom from classical mechanics, which count the directions in which the particles are allowed to move. Generally, the number of collective modes of motion for the entire system is equal to this number of degrees of freedom.

3   The diatomic chain

Now we consider a chain where two different atoms with masses M_1 and M_2 alternate. The neighboring atoms 1 and 2 interact with each other via the potential $V(x)$, see Fig. 1(a). Now the period of the system is $d = 2a$ and there are two atoms in each unit cell which is labeled by the index n. Their positions are given by $x_n^{(1)} = 2na + u_n$ for atom 1 and $x_n^{(2)} = 2na + a + v_n$ for atom 2. In analogy to Eq. (1) the equation of motion for small elongations read

$$M_1\ddot{u}_n \approx \alpha(v_n - 2u_n + v_{n-1})$$
$$M_2\ddot{v}_n \approx \alpha(u_{n+1} - 2v_n + u_n)$$

The ansatz

$$u_n(t) = A_1 e^{\mathrm{i}(knd-\omega t)} \quad \text{and} \quad v_n(t) = A_2 e^{\mathrm{i}(knd-\omega t)} \tag{9}$$

provides a matrix equation

$$-\omega^2 \begin{pmatrix} M_1 & 0 \\ 0 & M_2 \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \end{pmatrix} = \alpha \begin{pmatrix} -2 & 1 + e^{-\mathrm{i}kd} \\ 1 + e^{\mathrm{i}kd} & -2 \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \end{pmatrix}$$

The existence of nontrivial solutions (i.e. solutions, where not both A_1 and A_2 are zero) provides the condition

$$0 = \begin{vmatrix} M_1\omega^2 - 2\alpha & \alpha(1 + e^{-\mathrm{i}kd}) \\ \alpha(1 + e^{\mathrm{i}kd}) & M_2\omega^2 - 2\alpha \end{vmatrix} = M_1 M_2\omega^4 - 2\alpha(M_1 + M_2)\omega^2 + \underbrace{[2 - 2\cos(kd)]}_{=4\sin^2(kd/2)}\alpha^2$$

with the solutions

$$\omega^2 = -\alpha\frac{M_1 + M_2}{M_1 M_2}\left(1 \pm \sqrt{1 - \frac{4M_1 M_2}{(M_1 + M_2)^2}\sin^2(kd/2)} \right)$$

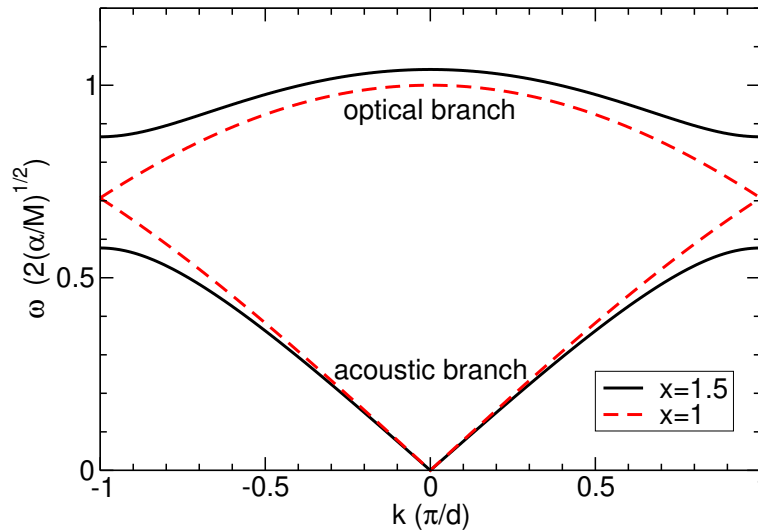These are plotted in Fig. 2, which displays two branches with solutions $\omega_j(k)$, with $j = 1, 2$.

Figure 2: Vibrational spectrum for the diatomic chain with masses $M_1 = xM$ and $M_2 = M/x$ for different values of x. The result for $x = 1$ is equal to the one plotted in Fig. 1(c), however now the range of k values is half as big as $d = 2a$ and correspondingly there are two branches.

Question 2: In which branch are localized distortions traveling faster?

Now we take a look at the spatial structure of the vibration modes for the two branches. This becomes most clear at $k = 0$: For the lower branch we have $\omega = 0$ and $A_1 = A_2$. Thus both atoms within a unit cell move in the same direction. This is the case for sound waves, and thus this branch is called *acoustic branch*. For the upper branch, we find $\omega = \sqrt{2\alpha \frac{M_1+M_2}{M_1 M_2}}$ and $M_1 A_1 = -M_2 A_2$. Thus, the two atoms in each period move against each other, while the center of mass is fixed. Typically the atoms have opposite electrical charge due to some charge transfer in the bonding process and thus this vibration is associated with an oscillating electric dipole moment strongly coupling to electromagnetic fields (i.e. light!). Therefore this branch is called the *optical branch*. This is further illustrated in Figs. 3,4.

Finally we count the number of vibration modes. By similar arguments as given above we find, that the number of k points in each branch is equal to the number N of unit cells (each with two atoms!) in the crystal. As their are two branches, the total number of vibration modes, $2N$ is again equal to the total number of atoms.

4   Generalization to three dimensions and summary

These results can be directly generalized to two- or three-dimensional systems which also summarizes the findings above. In higher dimensions the one-dimensional range $\pi/d < k \leq \pi/d$ becomes the first Brillouin zone, which is a set of **k**-vectors in reciprocal space (unit 1/length). Solving the mechanical equations for a lattice with N_α atoms per unit cell in D dimensions provides $N_\alpha D$ branches. D of these branches are acoustic and the frequency drops linearly to zero for $\mathbf{k} \to 0$ (they correspond to longitudinal Lund transverse sound waves). The other $(N_\alpha - 1)D$ branches are of optical character and have a finite frequency at $\mathbf{k} = 0$. For a finite crystal containing N primitive unit cells, the Brillouin zone contains precisely N different **k**-values matching the boundary condition. Thus the total number of vibration modes is given by $DN_\alpha N$, matching the fact that each atom has D degrees or freedom.
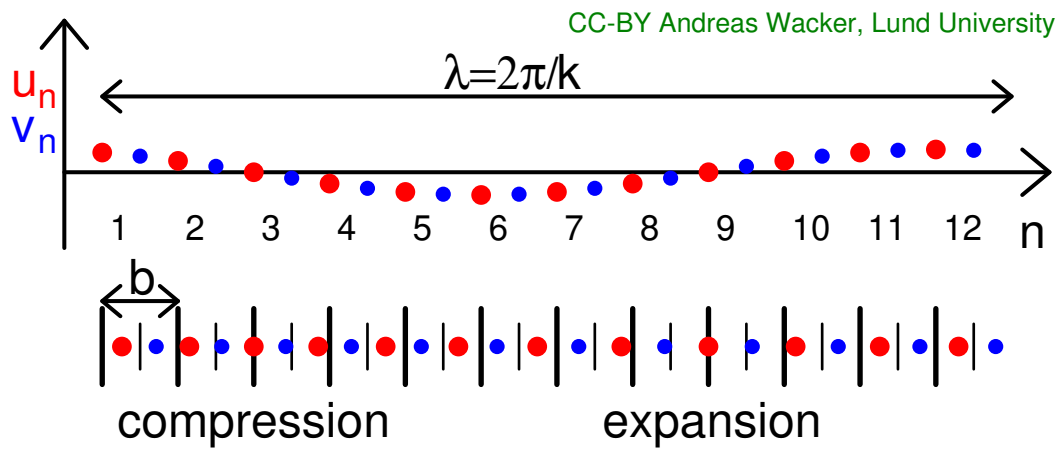
Figure 3: Vibration mode of the *acoustic* branch in a diatomic lattice for small k. The red and blue atoms follow the *same elongations* as can be seen in the upper diagram. Drawing the actual positions of the atoms in the lattice (lower diagram) together with their equilibrium positions (Long/short vertical lines for red/blue atoms) exhibits compressed and expanded regions for the lattice structure, which corresponds to a sound wave.
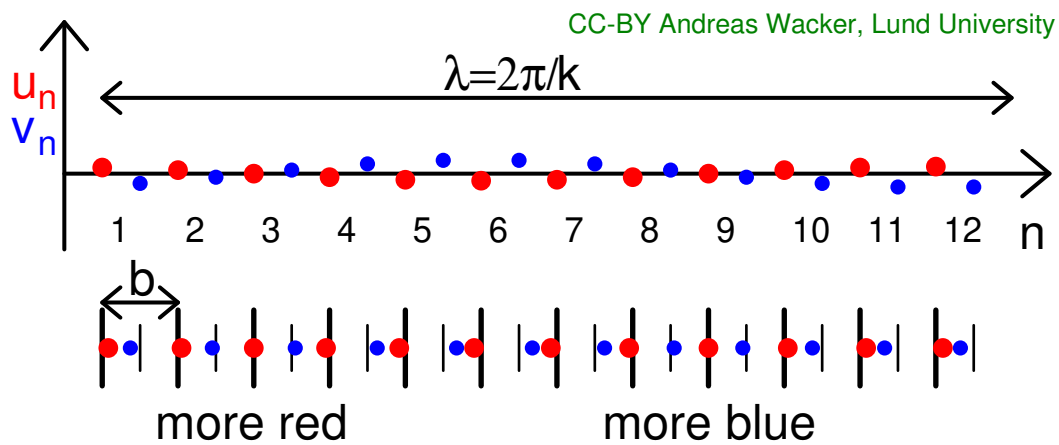

Figure 4: Vibration mode of the *optical branch* in a diatomic lattice for small k. The red and blue atoms follow *opposite elongations* as can be seen in the upper diagram. Drawing the actual positions of the atoms in the lattice (lower diagram) together with their equilibrium positions (Long/short vertical lines for red/blue atoms) exhibits dominance of blue or red atoms in different spatial regions. For different charges of the ionic atoms, this provides oscillating charges, which couple strongly to electromagnetic fields.

Figure 5 shows the vibration spectrum of GaAs where the frequencies are given as energies $\hbar\omega$. The maximal energy 36 meV corresponds to a frequency $\omega/2\pi$ of 8.7 THz and a vacuum wavelength of 35μm. This is, like almost all molecular and lattice vibrations[5] in the infrared region of the electromagnetic spectrum. Further note, that the thermal energy $k_B T = 25$ meV at room temperature is of comparable magnitude.

Question 3: Explain the number of branches in the vibration spectrum of GaAs!
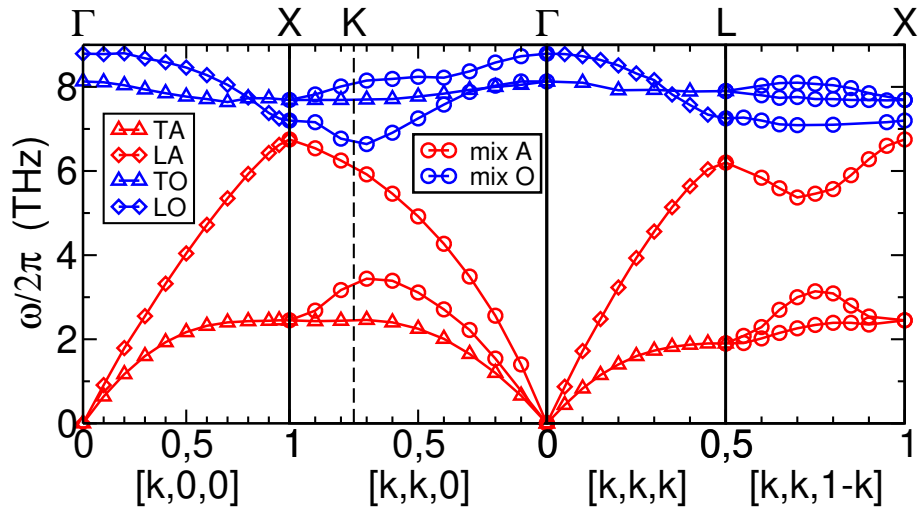
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[5]except for acoustic modes for small k

Figure 5: Neutron scattering data [Strauch and Dorner, J. Phys. C **2**, 1457 (1990)] for the vibration spectrum of GaAs exhibiting optical (blue, O) and acoustic (red, A) branches. The vector $\mathbf{k} = [k_x, k_y, k_z]$ displayed on the abscissa is in units $2\pi/a_0$, where $a_0 = 5.653$ Å is the cubic lattice constant of GaAs. On the top, the center of the Brillouin zone (Γ) and points on its boundary (X,K,L) are marked. The lines in $[k, k, 0]$ and $[k, k, 1 - k]$ direction have reduced symmetry, so mixtures between longitudinal (L) and transversal (T) oscillations occur.