

An introduction to lattice vibrations

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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 therefore is 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. These collective distortions can be classified by vibration modes $\propto e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$ where each \mathbf{k} only allows for a finite set of (angular) frequencies $\omega_n(\mathbf{k})$. Here this basic concept is motivated and a few results are presented. 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 a quantized excitation of a vibration mode is called a phonon. However, frequently the term phonon spectrum is used the spectrum $\omega_n(\mathbf{k})$ of vibration modes as well.

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 n^{th} atom has 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 at $V'(x) = 0$ 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 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 $f = V''(a) > 0$. (This actually a *parabolic approximation* for the potential $V(x) \approx V(a) + f(x - a)^2/2$.) Thus we obtain

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

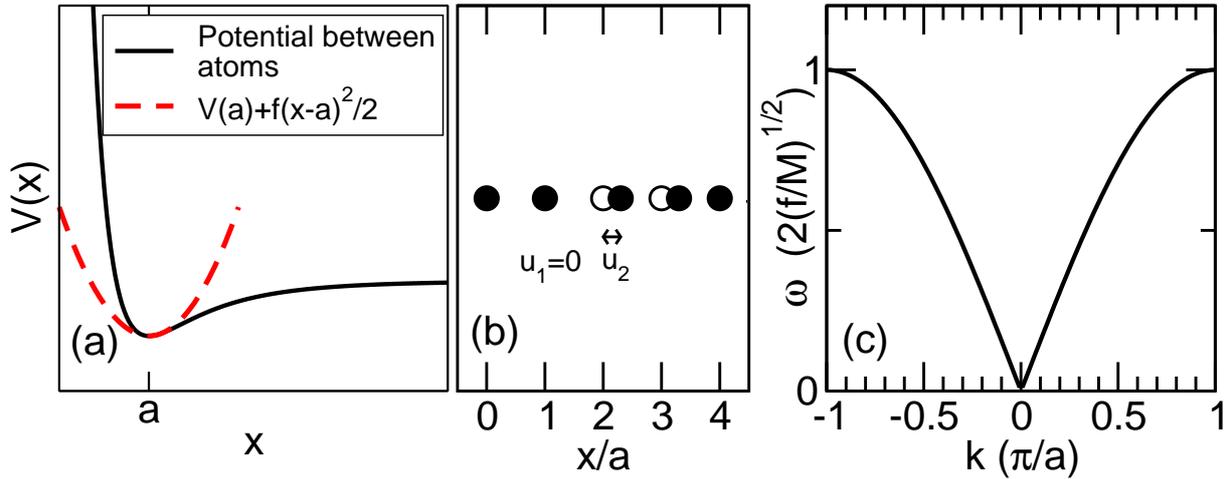


Figure 1: The one dimensional chain: (a) Characteristic potential for the interaction between atoms together with the parabolic approximation (dashed). (b) Atoms (full circles) in the chain, the open circles indicate the positions having the lowest energy. (c) vibrational spectrum from Eq. (3).

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

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

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

$$\omega = 2\sqrt{\frac{f}{M}} |\sin(ka/2)| = \omega(k) \quad (3)$$

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 $\omega(k)$.

Now we can limit k to the interval $-\pi/a < k \leq \pi/a$. Otherwise we can write $k = \tilde{n}2\pi/a + \tilde{k}$ with $\tilde{n} \in \mathbb{Z}$ and $-\pi/a < \tilde{k} \leq \pi/a$. Then we see $e^{ikna} = e^{i\tilde{k}na}$ for all lattice points and thus all elongations in Eq. (2) are identical.

Now we can estimate the average elongation by lattice oscillations in real crystals. If the oscillations are in thermal equilibrium the average potential energy is $\langle f(x-a)^2/2 \rangle = k_B T/2$. Thus $\langle (x-a)^2 \rangle = k_B T/f \approx k_B T/(2M\omega_{\text{typ}}^2)$. At room temperature we find for a typical frequency $\omega_{\text{typ}}/2\pi = 9$ THz and a mass of 27u (Al), the elongation 0.03 Å. Thus the amplitude of the lattice oscillations is of the order of 1% of the interatomic distance (2.86 Å for Al).

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

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

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

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

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

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

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 – more details can be found in the notes <http://www.matfys.lth.se/Andreas.Wacker/Scripts/wavepacket.pdf>.

For small $|k_0|$, Eq. (3) provides $v_g = \pm a \sqrt{\frac{f}{M}}$ 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 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

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 interatomic potential compensates the force, i.e. $-V'(x) + F_{\text{ext}} = 0$. In the quadratic approximation, this becomes $f(x - a) = F_{\text{ext}}$. Now $(x - a)/a = \varepsilon$ is the strain and $F/A = \sigma$ is the stress (if we assume an area A of the chain). From elasticity theory we know, that for small elongations $\sigma = (\lambda + 2\mu)\varepsilon$ [The Lamé coefficients λ , μ are related to the Young's modulus E and Poisson's ratio ν via $\lambda + 2\mu = \frac{(1-\nu)E}{(1-2\nu)(1+\nu)} \approx E(1 + \mathcal{O}(\nu^2))$]. Thus we can identify

$$\frac{f}{M} = \frac{F_{\text{ext}}}{M(x - a)} = \frac{A\sigma}{Ma\varepsilon} = \frac{\lambda + 2\mu}{\rho_m a^2}$$

where $\rho_m = M/(aA)$ is the mass density of the crystal. Thus the group velocity at $k \approx 0$ becomes $v_g = \pm \sqrt{\frac{\lambda + 2\mu}{\rho_m}}$, which is precisely the longitudinal sound velocity obtained by continuum mechanics. We further conclude that materials with a large elastic modulus and low mass densities have high phonon frequencies.

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 $n = 1, 2, \dots, N$? 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 be actually be realized by a ring of N atoms. Here this periodicity implies $e^{iNna} = 1$, 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.

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. Adding solutions of the form (2) with k and $-k$ (which have the same frequency) using $A_{\pm k} = e^{\mp ika/2}$, we obtain

$$u_n(t) = 2 \cos(k(n - 1/2)a) \cos(\omega t)$$

which matches the boundary condition $u_0 = u_1$. 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 is satisfied if $kNa = \pi * j$ with $j \in \mathbb{Z}$. Thus we have precisely N different values $j = 0, 1, 2, \dots, N - 1$ which match the interval $0 \leq k < \pi/a$.

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.

In all cases we find that the number of different vibration modes is equal to the number of atoms which are allowed to move. 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. For a D -dimensional system with N point-like particles this is just ND provided that there are no constraints. generally the 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

$$\begin{aligned} M_1 \ddot{u}_n &\approx f(v_n - 2u_n + v_{n-1}) \\ M_2 \ddot{v}_n &\approx f(u_{n+1} - 2v_n + u_n) \end{aligned}$$

The Ansatz

$$u_n(t) = A_1 e^{i(knd - \omega t)} \quad \text{and} \quad v_n(t) = A_2 e^{i(knd - \omega t)} \quad (7)$$

provides a matrix equation

$$-\omega^2 \begin{pmatrix} M_1 & 0 \\ 0 & M_2 \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \end{pmatrix} = f \begin{pmatrix} -2 & 1 + e^{-ikd} \\ 1 + e^{ikd} & -2 \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \end{pmatrix}$$

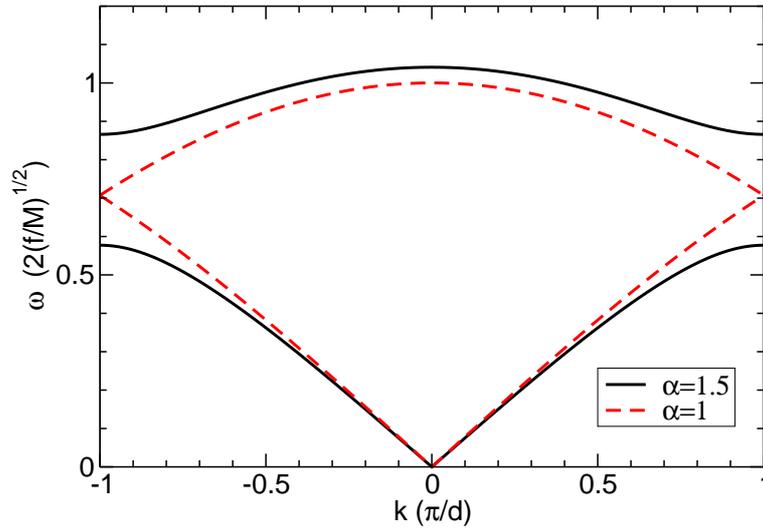


Figure 2: Vibrational spectrum for the diatomic chain with masses $M_1 = \alpha M$ and $M_2 = M/\alpha$ for different values of α . The result for $\alpha = 1$ is equal to the one plotted in Fig. 1(c), however now the range of k values is half as big as $d = 2a$ and correspondingly there are two branches.

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

$$0 = \begin{vmatrix} M_1\omega^2 - 2f & f(1 + e^{-ikd}) \\ f(1 + e^{ikd}) & M_2\omega^2 - 2f \end{vmatrix} = M_1M_2\omega^4 - 2f(M_1 + M_2)\omega^2 + \underbrace{[2 - 2\cos(kd)]}_{=4\sin^2(kd/2)} f^2$$

with the solutions

$$\omega^2 = f \frac{M_1 + M_2}{M_1M_2} \left(1 \pm \sqrt{1 - \frac{4M_1M_2}{(M_1 + M_2)^2} \sin^2(kd/2)} \right)$$

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

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 $\omega = \sqrt{2f \frac{M_1 + M_2}{M_1M_2}}$ and $M_1A_1 = -M_2A_2$. 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*.

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 there are two branches, the total number of vibration modes, $2N$ is again equal to the total number of atoms.

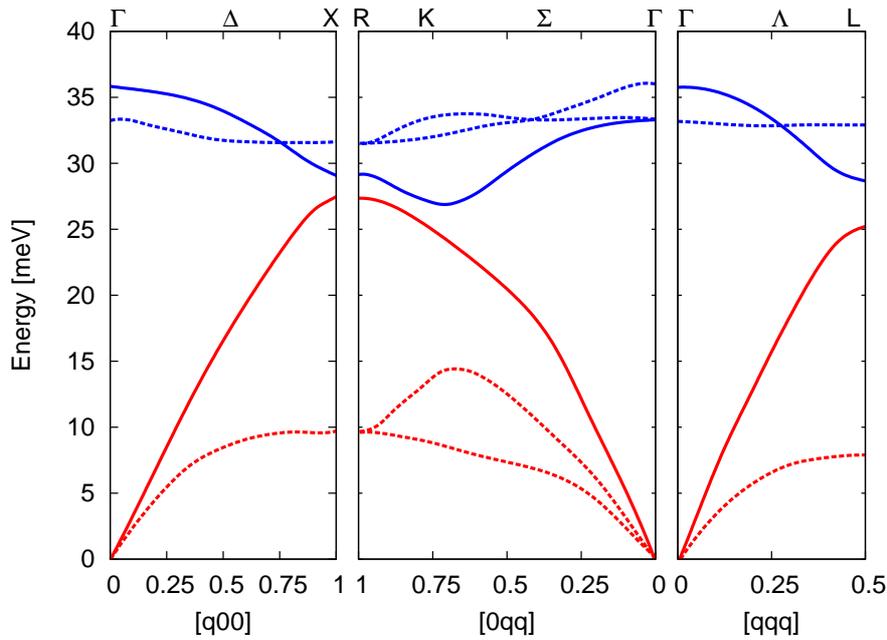


Figure 3: Phonon spectrum of GaAs with optical (blue) and acoustic (red) phonons. The full lines refer to longitudinal and the dashed lines to transverse phonons. The vector $\mathbf{q} = [q_x, q_y, q_z]$ displayed on the abscissa is in units $2\pi/a$, where $a = 5.653 \text{ \AA}$ is the cubic lattice constant of GaAs. [After J.S. Blakemore, J. Appl. Phys **53**, R123 (1982)]

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 \mathbf{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, of which D are of acoustic and $(N_\alpha - 1)D$ of optical character. For a finite crystal containing N primitive unit cells, the Brillouin zone contains precisely N different \mathbf{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 of freedom.

Figure 3 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 $35\mu\text{m}$. This is, like all(?) molecular and lattice vibrations in the infrared region, of the electromagnetic spectrum. Further note, that the thermal energy $k_B T = 25 \text{ meV}$ at room temperature is of comparable magnitude.

Question 3: Why are there six different branches in the vibration spectrum of GaAs?