

Phonons

Notes for Lecture 3 and Lecture 4

Vibrations of 1D monoatomic and diatomic Chains.

3. MOVEMENT OF IONS. PHONONS

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3.0. INTRODUCTION

At any temperature, even at absolute zero, the atoms that form a real solid are NOT static in their equilibrium positions, corresponding to the crystalline structure that we have seen so far, but constantly oscillate around them.

These atomic movements give rise to **collective oscillations of the lattice**, the study of which constitutes the objective of this topic.

The model that we will consider to study the vibrations of the lattice is based on **two hypotheses of a general nature**:

i) The equilibrium position of an atom corresponds to the position it would occupy in the ideal crystallographic structure (minimum potential energy).

For this reason, the atomic positions deduced from the crystallographic structure are actually average positions and NOT instantaneous fixed positions.

ii) The oscillation amplitudes of atoms around these equilibrium positions are much smaller than the interatomic distances.

The first hypothesis justifies the **existence of a crystalline structure in solids**, associated with the average positions of atoms, although, in reality, atoms oscillate continuously.

The second hypothesis is reasonable in most cases and ensures that only **small deformations** occur in the crystal, as a result of lattice vibrations.

All this makes it acceptable to consider the so-called **harmonic approximation**, which is based on the following hypotheses:

- i) The elastic energy of the crystal is only a quadratic function of the relative displacement of any two atoms of the solid.
- ii) All terms of order higher than quadratic are despised, although at sufficiently high temperatures they can have quite an influence and give rise to effects known as anharmonic effects.

In fact, there are many thermal properties of the solid that can only be explained within the framework of an anharmonic theory:

-Thermal expansion

-Existence of thermal resistance

-Dependence on specific heat temperature at constant volume, at high temperatures, ...

- iii) The solid behaves as if the atoms are bound together by harmonic forces.

Within the framework of the harmonic approximation, the movement of atoms can be reduced to a **classic problem of normal modes of oscillation**:

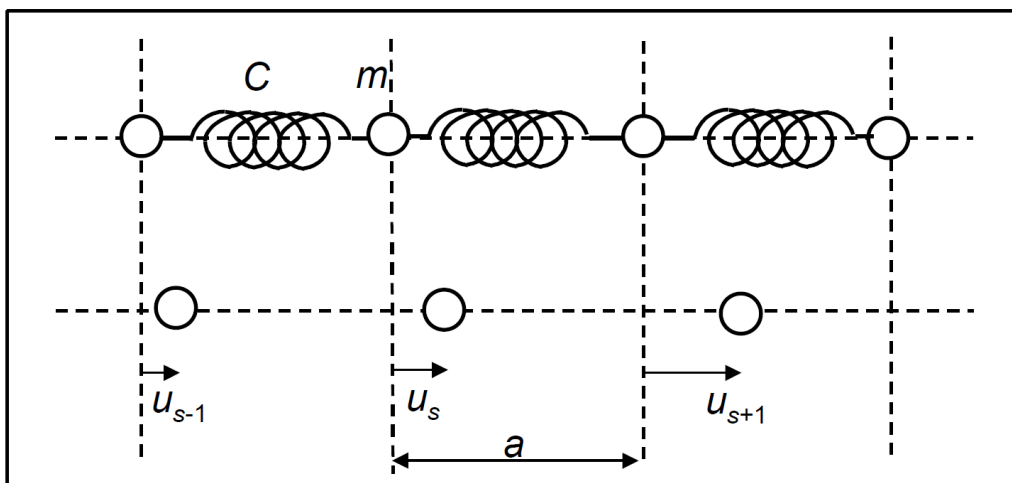
- These are collective modes of oscillation of atoms with \mathbf{k} and ω defined, similar to the case of a sound wave propagating through a solid.
- If frictions or anharmonic interactions are ignored, if a normal mode is excited in the solid, it is maintained over time.

[In a real solid, this happens with a more or less good degree of approximation, depending on the applicability of harmonic theory.]

3.1. 1D ACOUSTIC VIBRATION MODES

A. NORMAL VIBRATION MODES IN A 1D CRYSTAL WITH A MONOATOMIC BASIS

Consider a one-dimensional lattice, of lattice parameter a , and total length L , formed by N equal atoms ($L = Na$), of mass m , which are joined together by springs of recovery constant C , as indicated in the attached scheme.



We will solve this model considering two hypotheses:

- i) The recovering forces, which return atoms to their positions of balance, they act only between first neighbours.
- ii) Displacements occur only in the direction of the chain; i.e **longitudinal waves**.

If the first hypothesis is generalized to more distant interactions, they are obtained very similar results, but more mathematically complex.

If displacements are considered in the direction perpendicular to the chain, **transverse waves** with other force constants appear.

EQUATION OF MOTION OF THE ATOM S

We call u_s the displacement of the atom located in the cell S with respect to its equilibrium position, in the direction of the chain (see diagram on the previous page).

In the framework of the harmonic approximation to first neighbours, the elastic potential energy of the one-dimensional solid will be given by the summation

$$V = \sum_s \frac{C}{2} (u_{s+1} - u_s)^2,$$

and, therefore, the force acting on the atom will have the expression

$$F_s = -\frac{\partial V}{\partial u_s} = C[(u_{s+1} - u_s) + (u_{s-1} - u_s)]$$

In this classical approximation, the equation of motion of the atom located in the cells will be given by Newton's second law for this atom:

$$m \frac{d^2 u_s}{dt^2} = C[u_{s+1} + u_{s-1} - 2u_s]$$

If we look for solutions that correspond to collective modes of oscillation, all the atoms must oscillate with the same temporal dependence, that is, with the same frequency, ω :

$$u_s(x, t) = u_s(x) e^{-i\omega t}$$

If we replace this temporal dependence in Newton's second law, we calculate the second derivative and simplify terms, we get

$$-m\omega^2 u_s = C[u_{s+1} + u_{s-1} - 2u_s]$$

We propose a solution of the type (wave propagating through the solid):

$$u_s(x, t) = u e^{i(ksa - \omega t)}$$

where a is the lattice parameter, and it has been taken into account that the position, x , cannot take any value, but is fixed where there are atoms, that is, by the node of the lattice: $x = sa$.

This allows reducing the problem of solving N equations, one for each atom, to solve a single one, for any s .

Replacing this type of solution in the last equation of motion, we get:

$$-m\omega^2 u e^{iska} = Cu [e^{i(s+1)ka} + e^{i(s-1)ka} - 2 e^{iska}].$$

Simplifying the factor ue^{iska} , the equation remains as follows:

$$\omega^2 m = -C [e^{ika} + e^{-ika} - 2]$$

Isolating ω and using the relationship between cosine and imaginary exponentials, we achieve

$$\omega^2 = (2C/m) (1 - \cos ka)$$

If relation we consider that $\sin^2(ka/2) = (1 - \cos ka)/2$, we finally get the **dispersion relation** of elastic waves, $u_s(x, t) = u e^{i(sak - \omega t)}$, describing normal modes (collective modes) of oscillation of the atoms that make up the one-dimensional solid:

$$\omega = \sqrt{\frac{4C}{m}} \left| \sin\left(\frac{ka}{2}\right) \right|$$

PERIODIC CONTOUR CONDITIONS

Although we initially said that we had a length L of the chain, in the resolution of the equation of motion we considered a chain of infinite atoms, that is, we have NOT considered **any specific contour** condition.

As in the case of the study of electronic states (on the next unit), we will adopt periodic contour conditions (periodic Born-von Karman boundary conditions):

For a solid formed by a finite chain of N atoms, of length $L = Na$, this type of condition implies that atomic displacements verify the relationship

$$u(sa) = u(sa + L)$$

As we have seen, the solution for the atomic displacement corresponding to a mode oscillation normal can be represented by a plane wave with a defined wave vector, $u_s = u \exp(iksa)$.

The above relationship will simply limit the allowed values of the wave vector:

$$e^{iksa} = e^{ik(sa + L)} \Rightarrow e^{ikL} = 1 \Rightarrow kL = 2\pi n$$

That is, the wave vectors corresponding to waves, compatible with conditions contour periodic, are of the form

$$k_n = n \frac{2\pi}{L} = n \frac{2\pi}{Na} \quad (n \in Z)$$

where N is the number of primitive cells in the crystal.

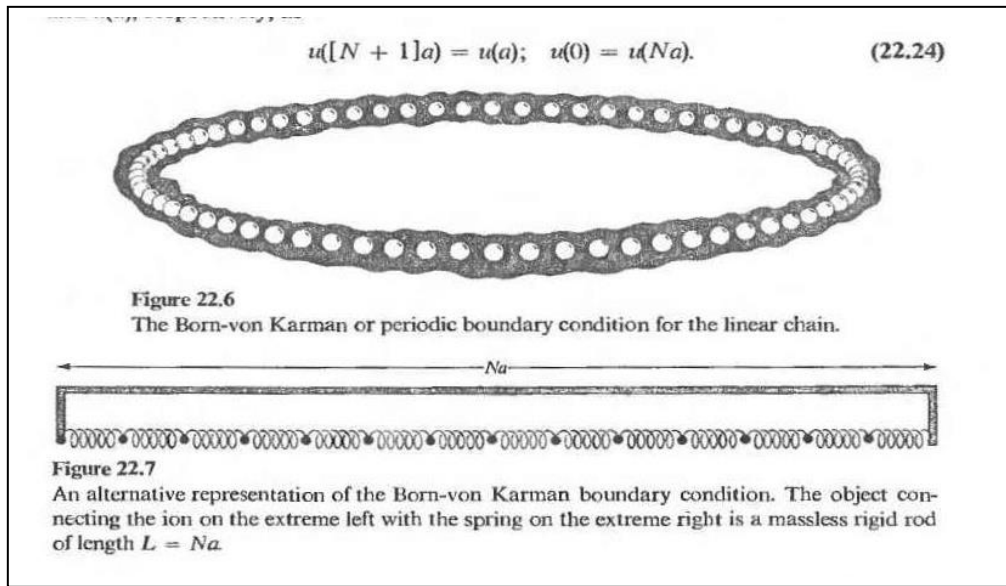


Figure: periodic Born-von Karman boundary conditions.

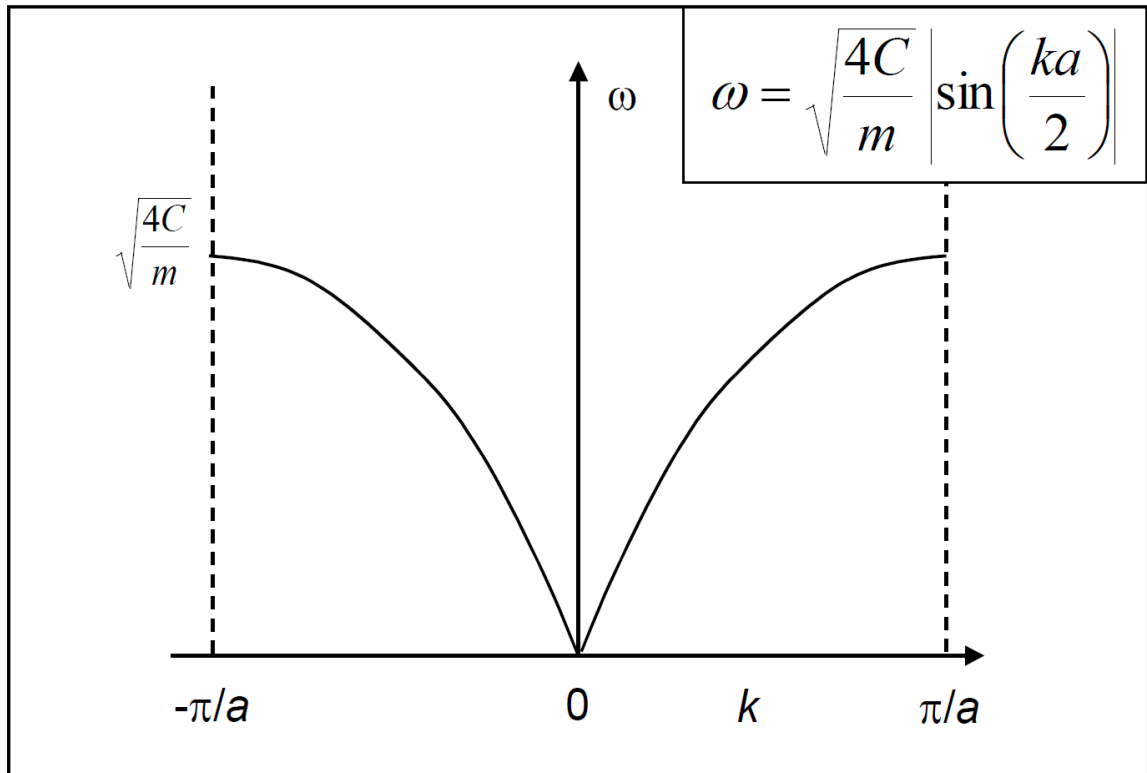
As we have seen, the function that provides the temporary dependence on displacement of the atom s is simply a plane wave, of the form

$$u_s = u e^{i(ksa - \omega t)},$$

if we assume that the system oscillates following a normal mode of oscillation.

Consequently, all atoms with a fixed value of k oscillate following a harmonic motion of the same frequency, ω , with a gap that depends on the position of each atom in the chain (ksa).

The dispersion relation of normal oscillation modes (which we have reached at the end of page 7) is a periodic function of the wave vector k , with the periodicity of the reciprocal lattice ($2\pi/a$).

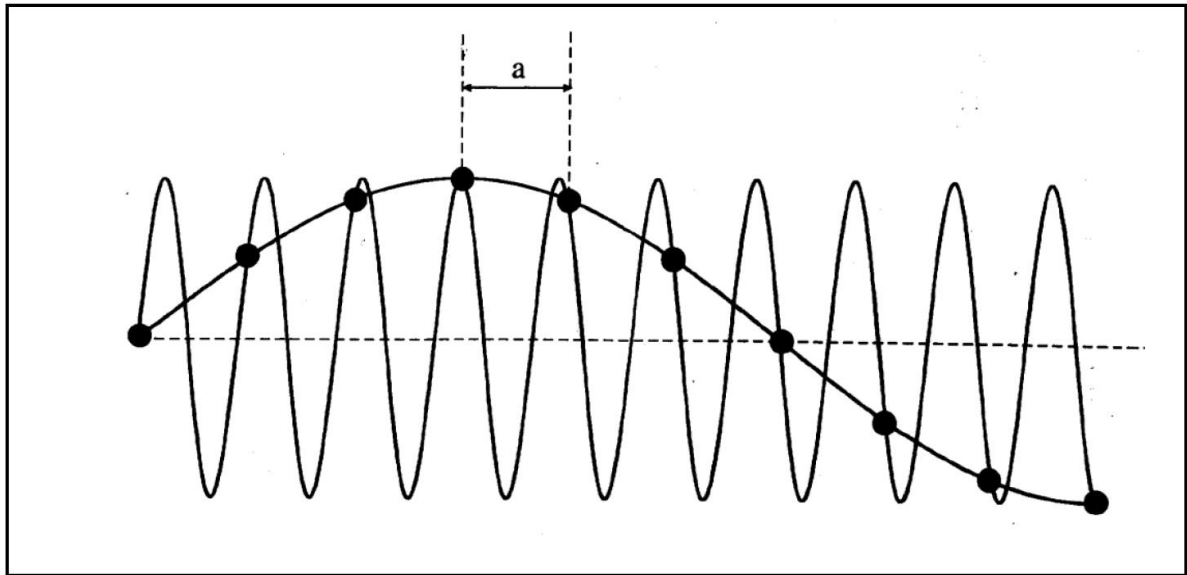


Therefore, any interval of the wave vector space, of width $2\pi/a$ (which is the size of a primitive cell), provides all possible frequencies corresponding to normal system oscillation modes.

In addition, the motion of elastic waves (normal modes) is defined only about atomic positions, u_s , since the chain we are dealing with is NOT a continuous medium.

For this reason, it is sufficient to use wave vectors corresponding to wave lengths greater than $2a$ to take into account all possible relative gaps between neighbouring atoms.

We can see this with an example in which, for clarity, they have been represented transverse displacements:



At a certain point in time, the oscillation amplitudes of atoms are equal for the wavelength $\lambda_1 > 2a$ and for the wavelength $\lambda_2 < 2a$.

That is, there are many possible representations of the same atomic displacement, with the same frequency, but each is associated with a different period of the graph $\omega(k)$.

Each of the possible representations must have the same value as ω .

Since waves can propagate to the right or left of the chain, we must use positive and negative values of the wave vector k , so it is more convenient to use the interval $-\pi/a < k \leq \pi/a$, instead of the interval $0 < k \leq 2\pi/a$, to define the possible values of the wave vector k , corresponding to normal oscillation modes.

FIRST BRILLOUIN AREA

The interval $-\pi/a < k \leq \pi/a$ it covers all independent values of the relative phase between two neighbouring atoms.

Demonstration:

Suppose k is a wave vector outside the first Brillouin zone ($|k| > \pi/a$).

We can always find an integer m that makes the vector k' defined as

$$k' = k - m(2\pi/a)$$

belongs to the first area of Brillouin ($|k'| < \pi/a$).

An elastic wave propagated by the one-dimensional solid, with wave vector k , produces a relative lag in the displacements of two neighbouring atoms equal to

$$u_{s+1}/u_s = e^{ika} = e^{i2\pi m} e^{i(ka - 2\pi m)} = e^{ik'a}$$

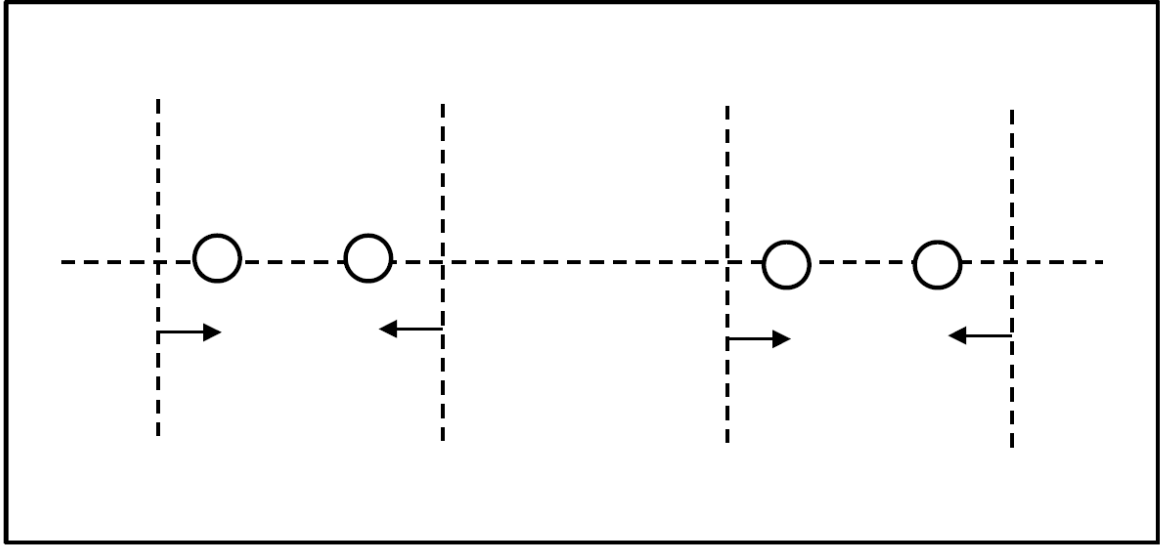
Therefore, you can always find a wave vector, k' , contained in the first Brillouin zone, the corresponding elastic wave that produces the same relative displacements of atoms as the elastic wave corresponding to another wave vector, k , outside the first Brillouin zone.

For $k=\pm\pi/a$ (i.e. at ends of the first Brillouin zone), the solution $u_s = u e^{iks a}$ does not represent a moving wave, but corresponds to a stationary wave. This is because, in the area limits, it is verified

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

and, consequently, two consecutive atoms oscillate with opposite phases, which depend on the fact that s is an even or odd number.

That is, if an atom moves in one direction and the adjacent atom moves in the opposite direction, with the same amplitude, there is NO net movement, so **the wave does not propagate**.



ENUMERATION OF NORMAL OSCILLATION MODES CANCELLATION

Each normal mode of oscillation is described by the elastic wave

$$u_s = u e^{i(ksa - \omega t)},$$

where the allowed values of k are only those that are compatible with the periodic contour conditions:

$$k_n = n \frac{2\pi}{L} = n \frac{2\pi}{Na} \quad (n \in \mathbb{Z})$$

This assumes that, if we consider a primitive cell between 0 and $2\pi/a$, the minimum value that k can take is $2\pi/Na$ and the maximum value that k can take is $2\pi/a$:

$$k = \frac{2\pi}{Na}, \frac{4\pi}{Na}, \frac{6\pi}{Na}, \dots, (N-1) \frac{2\pi}{Na}, \frac{2\pi}{a},$$

Or,

$$k = \frac{2\pi}{L}, \frac{4\pi}{L}, \frac{6\pi}{L}, \dots, (N-1) \frac{2\pi}{L}, N \frac{2\pi}{L}$$

[We don't count $k = 0$ because it represents the same state as $k = 2\pi/a$.]

If we limit ourselves, however, to the first Brillouin zone, that is, to the interval $-\pi/a < k \leq \pi/a$, the possible values of the wave vector k are

$$k = -\left(1 - \frac{2}{N}\right)\frac{\pi}{a}, \dots, -\frac{2\pi}{Na}, 0, \frac{2\pi}{Na}, \dots, \left(1 - \frac{2}{N}\right)\frac{\pi}{a}, \frac{\pi}{a},$$

which can be written compactly as

$$k = 0, \pm \frac{2\pi}{Na}, \pm \frac{4\pi}{Na}, \dots, \pm \left(1 - \frac{2}{N}\right)\frac{\pi}{a}, \frac{\pi}{a},$$

Or like

$$k = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \dots, \pm (N-2)\frac{\pi}{L}, N\frac{\pi}{L}$$

There are, therefore, **N values other than the wave vector within the first zone of Brillouin**, where N is the number of primitive cells in the crystal.

[We don't count the state $k = -N\pi/L$ because it represents the same state as $k = N\pi/L$.] $k = 0$ corresponds to the **uniform mode**, for which all atoms oscillate in phase:

$$u_s(k=0) = u e^{-i\omega t}, \forall s$$

C. SUPERPOSITION OF VIBRATION MODES AND GROUP SPEED

The general solution for the displacement of any atom is a superposition of normal modes of oscillation, of the form

$$u_s = \sum_k A_k \exp[i(ksa - \omega_k t)],$$

which is known as the **multiperiodic movement**.

The transmission speed of one of these wave packets is the **group velocity**, which is defined as

$$v_g = \left. \frac{d\omega}{dk} \right|_{k=k_0},$$

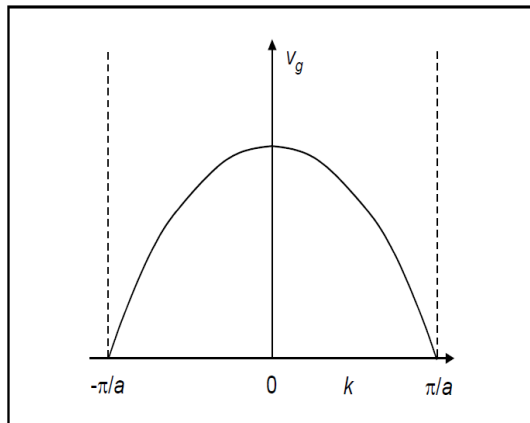
where k_0 is the value corresponding to the center of the package.

[The generalization in the 3D case of the group velocity gives the expression

$$v_g = \nabla_{\mathbf{k}} \omega(\mathbf{k}).]$$

Applying this definition to the dispersion relation, the following expression is obtained:

$$v_g = a \sqrt{\frac{C}{m}} \cos\left(\frac{ka}{2}\right)$$



For $k = \pm\pi/a$, we have already said that the elastic wave is stationary, and the propagation speed of the wave packet is zero:

$$v_g = 0$$

In this case, there is NO net transmission of elastic energy.

LIMIT OF LONG WAVE LENGTHS. SOUND SPEED

The scatter ratio is not a simple linear relationship between the angular frequency ω and the wave vector k ; therefore, it is as if the elastic waves in the solid propagate in a dispersive medium.

However, for $|k|$ small (long wavelengths), the ratio $\omega(k)$ is practically linear (there is no dispersion), since

$$\sin\left(\frac{ka}{2}\right) \approx \frac{ka}{2} \Rightarrow \omega \approx 2\sqrt{\frac{C}{m}} \frac{ka}{2} = \sqrt{\frac{C}{m}} ka \quad \left(|k| \ll \frac{\pi}{a} \right)$$

In this limit, the phase velocity, which is the speed of each wave in the packet and is, defines as $v_f = \omega/k$, becomes independent of the wave vector, k :

$$v_f = \frac{\omega}{k} \approx a \sqrt{\frac{C}{m}}$$

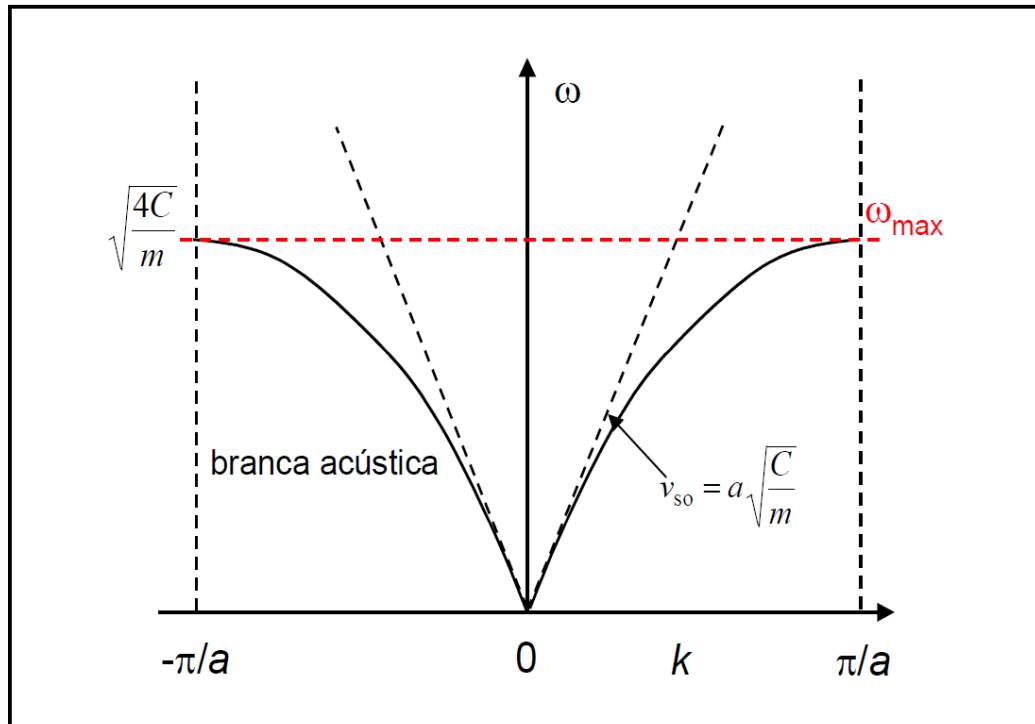
This speed, in addition, matches the group speed, v_g (which is the speed of the whole package), since for small values of k ,

$$\cos\left(\frac{ka}{2}\right) \approx 1 - \frac{1}{2}\left(\frac{ka}{2}\right)^2 \Rightarrow v_g \approx a \sqrt{\frac{C}{m}} \left[1 - \frac{1}{2}\left(\frac{ka}{2}\right)^2 \right] \approx a \sqrt{\frac{C}{m}}$$

This means that, at the limit of long wavelengths (much larger than twice the interatomic distance), the medium behaves as if it were an elastic and homogeneous continuum (interatomic spacing is negligible compared to wavelength), and v_g is then the speed of propagation of sound in the medium:

$$v_{so} = a \sqrt{\frac{C}{m}}$$

If we look at the representation of the dispersion relationship in the attached figure, we can see that this speed corresponds, in addition, to the maximum speed of propagation of elastic waves in the medium.



The approximation of low frequencies (long wavelengths) is applicable up to frequencies of the order of 10^{12} Hz (THz, terahertz).

On the other hand, in the same figure we see that there is a limit value for the frequency of propagation of the wave, a **cut-off frequency of the lattice**, which is determined by the spacing of the lattice, and that it is worth

$$\omega_{\text{max}} = \sqrt{\frac{4C}{m}} = \frac{2v_{\text{so}}}{a}$$

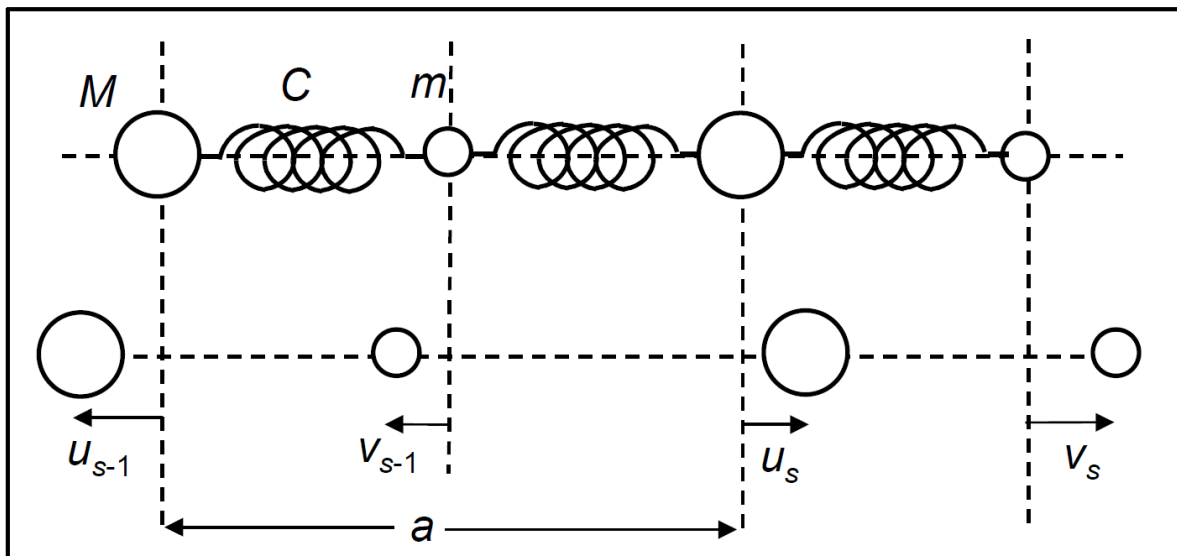
Elastic waves of frequency greater than ω_{max} cannot be transmitted by crystal.

The vibration modes studied in this section give rise to the so-called **acoustic branches** of the spectrum of collective oscillations of the solid.

3.2. OPTICAL 1D VIBRATION MODES

A. NORMAL MODES OF VIBRATION IN A 1D CRYSTAL WITH TWO ATOMS WITH DIFFERENT DISPLACEMENTS

Consider a one-dimensional lattice of lattice parameter a , with a atomic basis formed by two different atoms, of masses m and M ($m < M$), which are joined together by springs of recovery constant C , as indicated in the attached scheme.



We will solve this model considering two hypotheses:

- i) The recovery forces, which return atoms to their equilibrium positions, act only between first neighbours.
- ii) Displacements occur only in the direction of the chain (**longitudinal waves**).

We respectively call u_s and v_s the displacements of the mass atoms M and m belonging to the primitive cell s , with respect to their respective positions of equilibrium, in the direction of the chain (see diagram above).

EQUATIONS OF MOTION OF ATOMS IN THE PRIMITIVE CELL S

In the framework of the harmonic approximation to first neighbours, the force acting on each atom located in the primitive cell will have the expression

$$\begin{cases} F_{u_s} = -\frac{\partial V}{\partial u_s} = C[(v_s - u_s) + (v_{s-1} - u_s)] = C[v_s + v_{s-1} - 2u_s] \\ F_{v_s} = -\frac{\partial V}{\partial v_s} = C[(u_s - v_s) + (u_{s+1} - v_s)] = C[u_{s+1} + u_s - 2v_s] \end{cases}$$

In this classical approximation, the equation of motion corresponding to each atom according to Newton's second law will be as follows:

$$\begin{cases} M \frac{d^2 u_s}{dt^2} = C[v_s + v_{s-1} - 2u_s] \\ m \frac{d^2 v_s}{dt^2} = C[u_{s+1} + u_s - 2v_s] \end{cases}$$

We look for solutions that correspond to collective modes of oscillation, with the shape of an elastic wave with \mathbf{k} and ω defined, adopting an oscillation amplitude different on each type of atom of the atomic basis:

$$u_s = u e^{i(ksa - \omega t)} \quad v_s = v e^{i(ksa - \omega t)}$$

If we replace these expressions in Newton's second law, we calculate the derivative second and simplify terms, we obtain a homogeneous system of two equations, where the variables are u and v :

$$\begin{cases} -\omega^2 M u = C v [1 + e^{-ika}] - 2C u \\ -\omega^2 m v = C u [1 + e^{ika}] - 2C v \end{cases}$$

By fixing the system, we get

$$\begin{cases} (M\omega^2 - 2C) u + C[1 + e^{-ika}] v = 0 \\ C[1 + e^{ika}] u + (m\omega^2 - 2C) v = 0 \end{cases}$$

For this system to have a solution other than the trivial one ($u = v = 0$) the determinant of the coefficients must be nullified:

$$\begin{vmatrix} M\omega^2 - 2C & C(1 + e^{-ika}) \\ C(1 + e^{ika}) & m\omega^2 - 2C \end{vmatrix} = 0$$

By developing the determinant and grouping terms, the following equation is obtained:

$$Mm\omega^4 - 2C(m + M)\omega^2 + 2C^2(1 - \cos ka) = 0$$

Solving this equation of second degree in ω^2 , we obtain the **dispersion relation**:

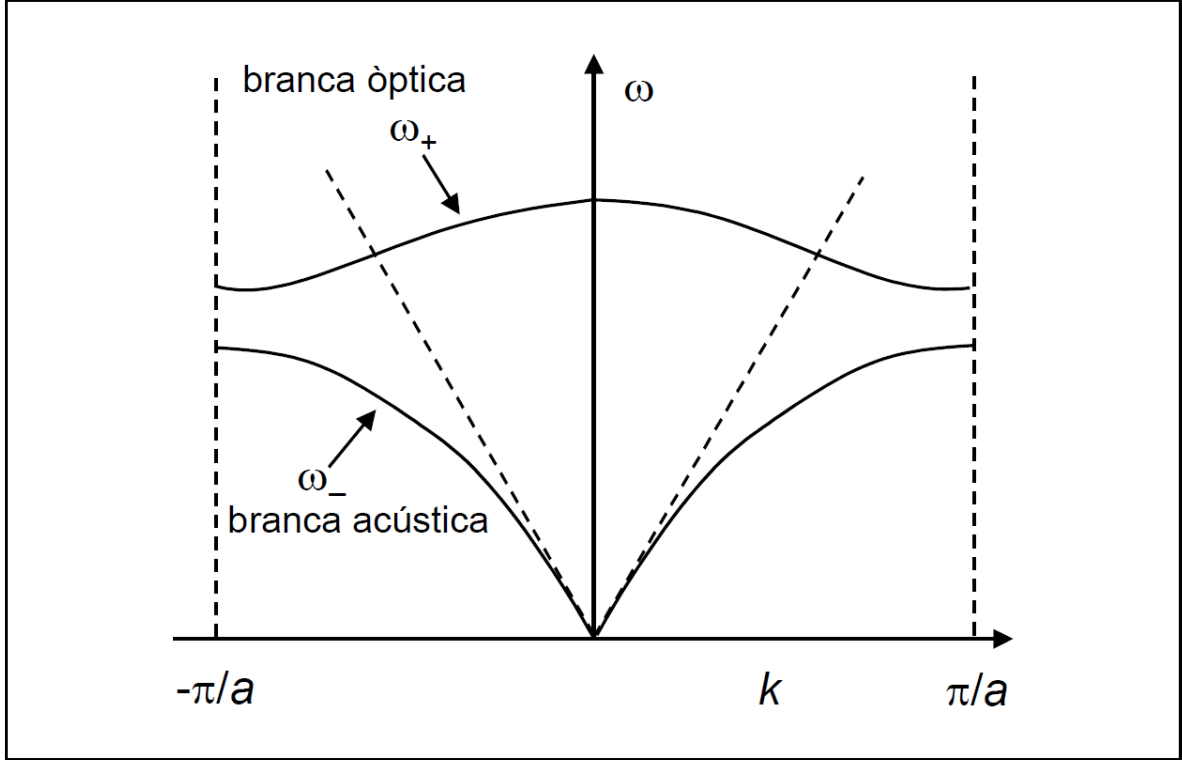
$$\omega^2 = C \left(\frac{m + M}{mM} \right) \pm C \left[\left(\frac{m + M}{mM} \right)^2 - \frac{2(1 - \cos ka)}{mM} \right]^{1/2}$$

In contrast to the monoatomic lattice, the dispersion relation of a lattice diatomic provides two possible values of ω (only positive values of ω they make physical sense) corresponding to a certain value of the wave vector k .

The representation of these two possible values as a function of k determines two branches, $\omega_+(k)$ and $\omega_-(k)$, for the dispersal relation, which are given the historical names of **optical branch** and **acoustic branch**, respectively.

As in the case of the monoatomic chain, $\omega(k)$ is a periodic function with the periodicity of the reciprocal lattice, $2\pi/a$.

B. DISPERSION RELATION



EXTREME VALUES OF THE ACOUSTIC AND OPTICAL BRANCHES

(i) Límit $k \rightarrow 0$ ($|k| \ll \pi/a$)

At this limit we can approximate $\cos ka$ by his Taylor development to around the origin, $\cos ka \approx 1 - (ka)^2/2$, and replace it with the dispersion relation:

$$\begin{aligned} \omega_{\pm}^2(k) &\approx C\left(\frac{m+M}{mM}\right) \pm C\left(\frac{m+M}{mM}\right) \left[1 - \frac{mM}{(m+M)^2} (ka)^2\right]^{1/2} \approx \\ &\approx C\left(\frac{m+M}{mM}\right) \pm C\left(\frac{m+M}{mM}\right) \left[1 - \frac{1}{2} \frac{mM}{(m+M)^2} (ka)^2\right] \end{aligned}$$

Optical branch:

$$\omega_+^2(k) \approx C \left(\frac{m+M}{mM} \right) + C \left[\left(\frac{m+M}{mM} \right)^2 - \frac{(ka)^2}{mM} \right]^{1/2} \approx 2C \left(\frac{m+M}{mM} \right);$$

$$\boxed{\omega_+(k) \approx \sqrt{2C} \left(\frac{m+M}{mM} \right)^{1/2}}$$

At this limit ($k \rightarrow 0$), $\omega_+(k)$ does not depend on k and therefore the group velocity it cancels and the phase speed becomes infinite:

$$v_f = \frac{\omega}{k} \rightarrow \infty \quad ; \quad v_g = \frac{d\omega}{dk} = 0$$

Acoustic branch:

$$\omega_-^2(k) \approx C \left(\frac{m+M}{mM} \right) - C \left(\frac{m+M}{mM} \right) \left[1 - \frac{1}{2} \frac{mM}{(m+M)^2} (ka)^2 \right] \approx \frac{C/2}{m+M} (ka)^2;$$

$$\boxed{\omega_-(k) \approx \left(\frac{C/2}{m+M} \right)^{1/2} ka}$$

At this limit, the acoustic branch has a linear relationship, indicating that the medium is very non-dispersive.

On the other hand, the expression is very similar to the one we already obtained for a monoatomic string [$\omega_{\text{mono}}(k) = (C/m)^{1/2} ka_{\text{mono}}$]. In fact, if the two masses are equal ($m = M$), considering that $a_{\text{dia}} = 2a_{\text{mono}}$, the two expressions exactly coincide.

Therefore, as in the case of the monoatomic lattice, the group velocity ($v_g = d\omega/dk$) and the phase velocity ($v_f = \omega/k$) match this limit:

$$v_f = v_g = a \left(\frac{C/2}{m+M} \right)^{1/2}$$

(ii) Limit $k = \pm \pi/a$ (ends of the first Brillouin zone)

At this limit, $\cos ka = -1$ and the scattering relation is simply reduced to

$$\omega_{\pm}^2 \left(\pm \frac{\pi}{a} \right) = C \left(\frac{m+M}{mM} \right) \pm C \left[\left(\frac{m+M}{mM} \right)^2 - \frac{4}{mM} \right]^{1/2} = C \left(\frac{m+M}{mM} \right) \pm C \left(\frac{M-m}{mM} \right),$$

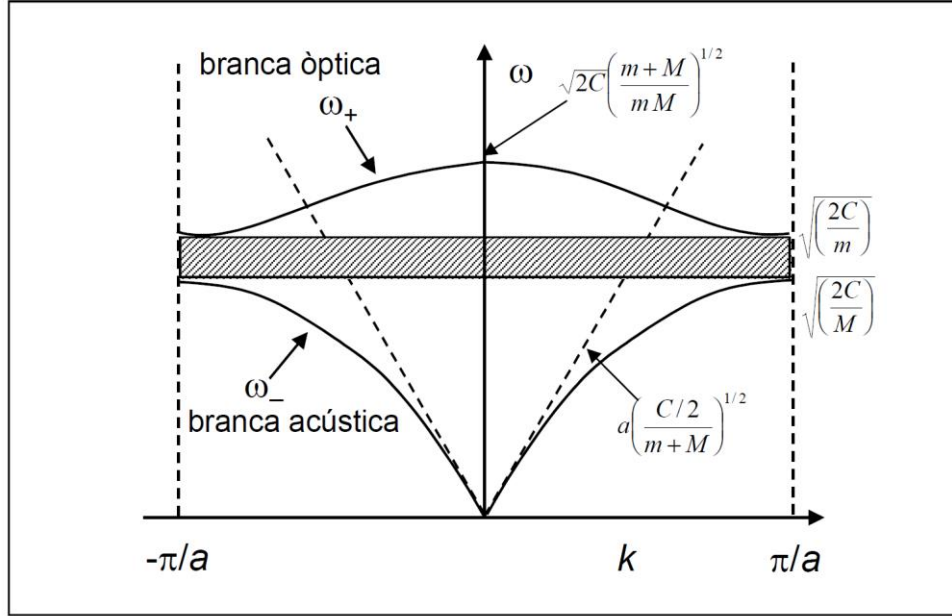
that has as solutions

$$\boxed{\omega_+ \left(\pm \frac{\pi}{a} \right) = \sqrt{\frac{2C}{m}} \quad ; \quad \omega_- \left(\pm \frac{\pi}{a} \right) = \sqrt{\frac{2C}{M}} \quad (m < M)}$$

Thus, a **region of forbidden frequencies** appears that separates the two branches, in which there are no solutions allowed:

$$(2C/M)^{1/2} < \omega < (2C/m)^{1/2}$$

In this region, the solutions for real ω correspond to complex k values, which give rise to elastic waves that quickly dampen when propagated.



C. ACOUSTIC MODES AND OPTICAL MODES

The difference in physical meaning between the two branches that have appeared in the dispersal relationship, and the origin of the historical names given to them, is best understood by analyzing the relationship between the oscillation amplitudes of the two atoms contained in the primitive cell s , in the center of each branch ($k \rightarrow 0$).

From the 1st equation of motion the following relationship is obtained:

$$\frac{u}{v} = C \frac{1 + e^{-ika}}{2C - M\omega^2} \xrightarrow{k \rightarrow 0} \frac{u}{v} \approx \frac{2C}{2C - M\omega^2}$$

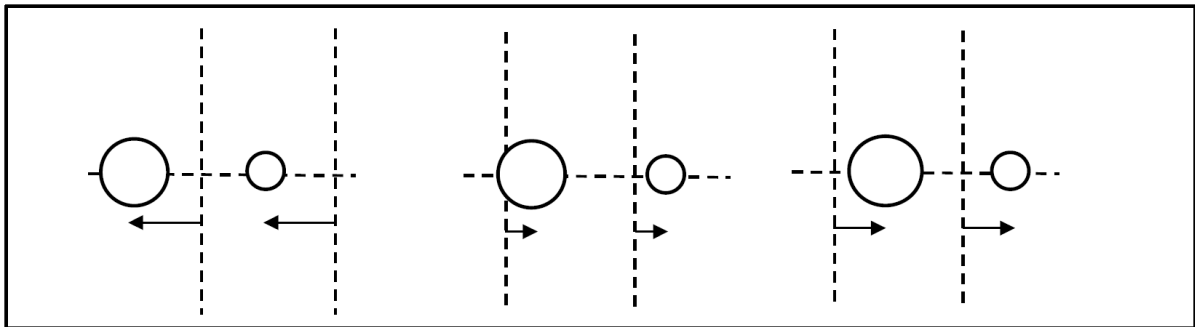
(i) Acoustic branch

In the center of the branch, that is, for $k \rightarrow 0$ and $\omega \rightarrow 0$, the above amplitude relation is simply

$$\frac{u}{v} \approx 1$$

This means that the atoms of the atomic basis move in phase and the primitive cell moves as a whole, similar to how an acoustic wave does in a continuous and elastic medium.

For this reason, this branch is historically called the **acoustic branch**.



[N.B. They are not consecutive cells.]

(ii) **Optical branch**

In the center of the branch, that is, for $k \rightarrow 0$, we have already seen before the expression of the dispersion relationship,

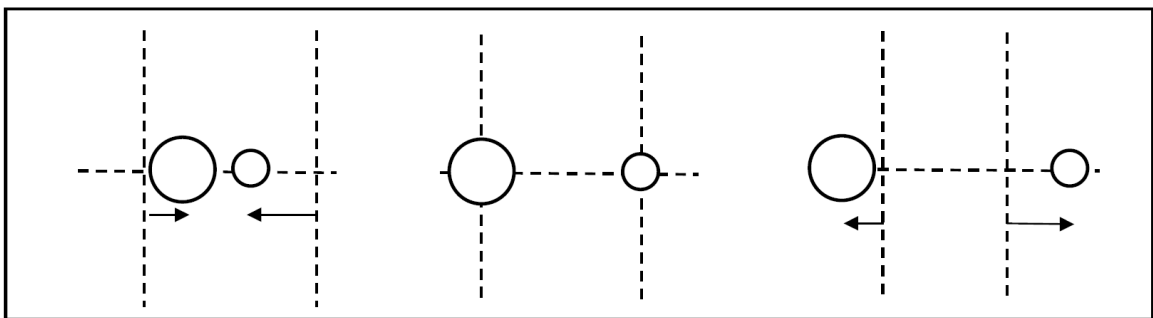
$$\omega_+(k) \approx \sqrt{2C} \left(\frac{m+M}{mM} \right)^{1/2},$$

so the amplitude ratio is

$$\frac{u}{v} \approx \frac{2C}{2C - M(2C) \frac{m+M}{mM}} = -\frac{m}{M} \longrightarrow Mu \approx -mv$$

This means that the two atoms of the atomic basis, contained in each primitive cell, oscillate in phase opposition (in opposite directions), with amplitudes inversely proportional to their masses. Accordingly, the center of mass of each cell does not move:

$$u_{\text{CM}} = \frac{Mu + mv}{m + M} \approx 0$$



[N.B. They are not consecutive cells.]

To understand the origin of the name of this branch, consider an ionic crystal, in which the two atoms at the basis have opposite charges.

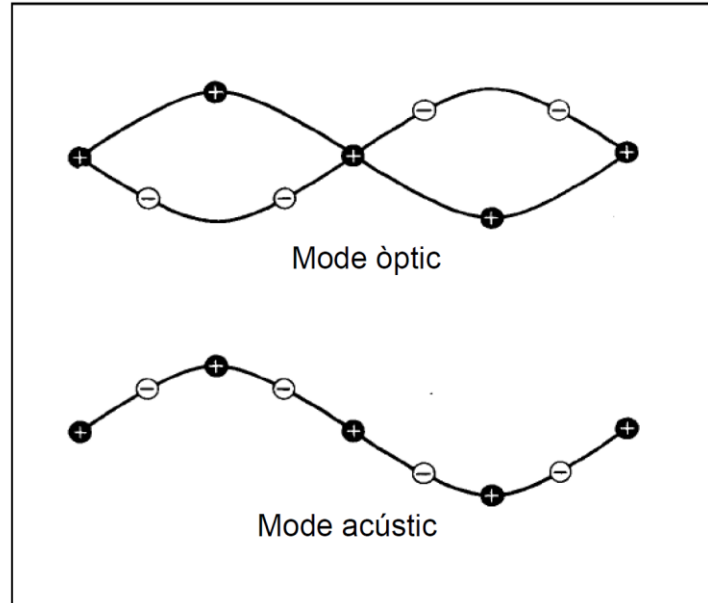
In these crystals, the movement of atoms when they follow an optical mode of k small creates an electric dipole moment

- which varies along the crystal with a long wavelength, and
- that strongly interacts with electromagnetic waves of the same frequency.

Because these waves fall into the infrared part of the spectrum (the frequency at $k \rightarrow 0$ is about THz), this branch is historically called the optical branch.

(iii) $k \neq 0$.

For any value of k , there is NO simple distinction between the oscillation modes in each of the two branches, although the designation of acoustic and optical modes is preserved throughout the range of values of k .



Example: Optical and acoustic modes for a transverse elastic wave.

D. ENUMERATION OF NORMAL OSCILLATION MODES
CANCELLATION

When it is imposed that elastic waves verify periodic contour conditions,

$$u(sa) = u(sa + L) \quad v(sa) = v(sa + L),$$

we already saw in the case of the monoatomic lattice that the permitted k -wave vectors are of the form

$$k_n = n \frac{2\pi}{L} = n \frac{2\pi}{Na} \quad (n \in Z)$$

Therefore, in the first Brillouin zone ($-\pi/a < k \leq \pi/a$, where we do not include the value $k = -\pi/a$, because it represents the same state as the value $k = \pi/a$), there are N values allowed of wave vector k , where N is the total number of primitive cells of the crystal:

$$k = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \dots, \pm (N-2)\frac{\pi}{L}, N\frac{\pi}{L}$$

Since for each value of k , there are two vibration modes (one acoustic and one optical), the **total number of normal oscillation modes is $2N$** .

That is, the number of normal modes of oscillation is equal to the total number of atoms.

[In fact, there are also so many equations of motion with atoms in the crystal, $2N$.]

3.3. 3D VIBRATION MODES

A. MONOATOMIC BASIS

In this section, we will extend the formulation prior to the case of three-dimensional solids.

In addition, we will consider interactions between all atoms, not just first neighbours.

The α component of the force, F_s , exerted on the atom located in the primitive cell s by the rest of the crystal, in the harmonic approximation, can be written as

$$F_{s,\alpha} = -\sum_r \sum_{\beta} \phi_{\alpha\beta}(s,r) u_{r,\beta} \quad ; \quad \alpha, \beta \in \{x, y, z\}$$

In this expression:

- The summation over the index r extends over the N primitive cells of the solid, including cell s .
- The summation on β sums over the three Cartesian coordinates, $\{x, y, z\}$.
- $\Phi_{\alpha\beta}(s, r)$ is the force constant for the interaction between atoms located in primitive cells s and r , when the displacements of these atoms occur in the Cartesian directions α and β , respectively

Force constants depend on the nature of atomic interactions (type of bond), and some are negative, as we saw in previous 1D cases.

These constants can be calculated from the interaction potential energy of the solid, V , for small displacements of atoms from their equilibrium positions (harmonic approximation), as follows:

$$\phi_{\alpha\beta}(s, r) = \frac{\partial^2 V}{\partial u_{s,\alpha} \partial u_{r,\beta}}$$

Newton's second law for an atom in the primitive cell is written as

$$m_s \frac{d^2 u_{s,\alpha}}{dt^2} = - \sum_r \sum_{\beta} \phi_{\alpha\beta}(s, r) u_{r,\beta} \quad ; \quad \alpha \in \{x, y, z\}$$

Therefore, we have three differential equations to describe the movement of each atom.

The component α of the displacement of the atom s , $u_{s,\alpha}$, when it oscillates following a normal oscillation mode, can be written as

$$u_{s,\alpha} = u_{s,\alpha}(\mathbf{k}) e^{-i\omega t}$$

By substituting this in Newton's 2nd law, of which it must be a solution, you get

$$m_s \omega^2 u_{s,\alpha}(\mathbf{k}) = \sum_r \sum_\beta \phi_{\alpha\beta}(s,r) u_{r,\beta}(\mathbf{k}),$$

which can be rewritten as

$$\sum_r \sum_\beta [\phi_{\alpha\beta}(s,r) - m_r \omega^2 \delta_{sr} \delta_{\alpha\beta}] u_{r,\beta}(\mathbf{k}) = 0$$

When considering the above equations for the N atoms of the solid, taking in note that the index s runs through the primitive N cells and, therefore, all atoms, a homogeneous system of $3N$ equations is obtained in the components of the atomic displacements, your, $u_{r,\beta}(\mathbf{k})$.

For this system to have a non-trivial solution, the determinant of the coefficients has been to cancel:

$$\text{Det}[\phi_{\alpha\beta}(s,r) - m_r \omega^2 \delta_{sr} \delta_{\alpha\beta}] = 0$$

Solving this determinant, a polynomial of degree $3N$ is obtained in ω^2 (3 equations x N cells), which has $3N$ solutions for ω with physical sense, as they are only allowed positive values of ω . The system therefore has **$3N$ normal oscillation modes**.

We consider that each atom in the crystal has mass m .

If we explain the displacement of the atom s , a normal mode of oscillation of this system has the form

$$\mathbf{u}_s(t) = \mathbf{A} e^{i(\mathbf{k} \cdot \mathbf{R}_s - \omega t)}$$

where \mathbf{A} is the vector that defines the amplitude of motion according to the three crystalline axes and \mathbf{R}_s is the equilibrium position of the atom s (it is a vector of the lattice of Bravais regarding a certain origin taken on a node in the net).

By substituting this expression in Newton's second law, one obtains

$$\sum_r \sum_\beta \left[\phi_{\alpha\beta}(s, r) - m\omega^2 \delta_{sr} \delta_{\alpha\beta} \right] A_\beta e^{i\mathbf{k} \cdot \mathbf{R}_r} = 0$$

However, two atoms with equilibrium positions \mathbf{R}_1 and $\mathbf{R}_1 + \mathbf{R}_d$ interact with the same force constant as two other atoms located at positions \mathbf{R}_2 and $\mathbf{R}_2 + \mathbf{R}_d$, since in both cases, the two atoms considered are displaced by one with respect to the other according to the translation vector \mathbf{R}_d .

If we define, in general, the \mathbf{R}_d vector as

$$\mathbf{R}_d = \mathbf{R}_r - \mathbf{R}_s,$$

and multiply the two members of the above equation by $e^{-i\mathbf{k} \cdot \mathbf{R}_s}$, we obtain

$$\sum_d \sum_\beta \left[\phi_{\alpha\beta}(d) - m\omega^2 \delta_{0d} \delta_{\alpha\beta} \right] A_\beta e^{i\mathbf{k} \cdot \mathbf{R}_d} = 0,$$

where the summation on the index r , which runs through all the atoms of the solid, has been replaced by a summation on all translation vectors, \mathbf{R}_d , which connect the atom s with all other atoms in the crystal, and it is considered that if $r = s$, then $\mathbf{R}_d \equiv \mathbf{R}_0 = 0$.

We define the dynamic matrix of the system as a 3X3 matrix of the form

$$D_{\alpha\beta}(\mathbf{k}) \equiv \frac{1}{m} \sum_d \phi_{\alpha\beta}(d) e^{i\mathbf{k} \cdot \mathbf{R}_d}$$

In this way, the last equation on the previous page becomes

$$\sum_{\beta} [D_{\alpha\beta}(\mathbf{k}) - \omega^2 \delta_{\alpha\beta}] A_{\beta} = 0$$

Considering the three possible values of α , this equation is actually a homogeneous system of three equations, where the unknowns are the components of the vector amplitude, \mathbf{A} .

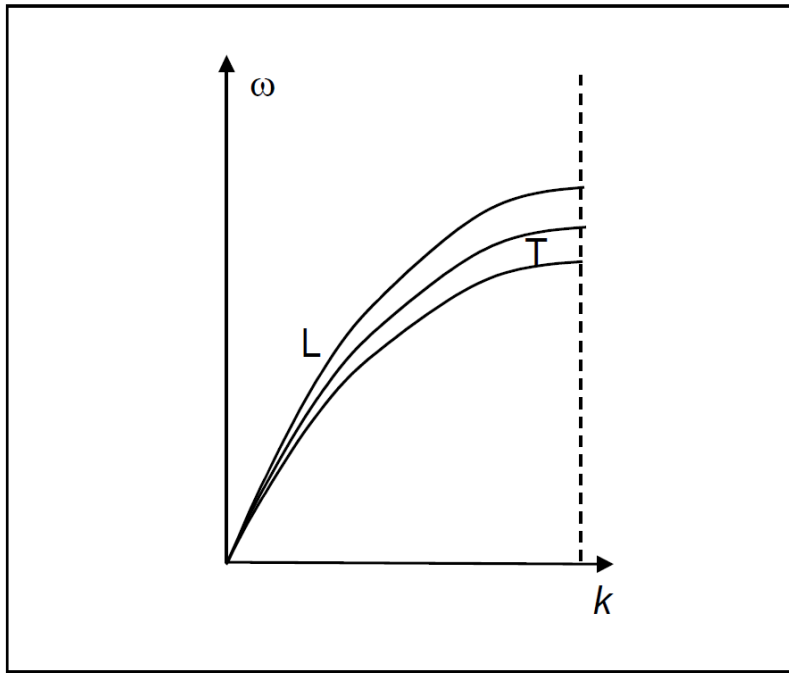
In order for this system to have a solution other than the trivial one, the determinant must be of the coefficients is annulled:

$$\begin{vmatrix} D_{xx} - \omega^2 & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} - \omega^2 & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} - \omega^2 \end{vmatrix} = 0$$

The characteristic polynomial, of degree 3 in ω^2 , provides 3 solutions physically acceptable of positive values for ω .

Therefore, for each allowed wave vector \mathbf{k} , there will be a dynamic matrix of the system that will give rise to a characteristic polynomial, from which three different normal modes of oscillation will be obtained as a solution, one for each value of the frequency ω .

The qualitative appearance of the three branches obtained in this general 3D case is very similar to that of the acoustic branch of one-dimensional examples, as you can check in the scheme on the next page.



Remarks:

- i) If \mathbf{k} is directed along an axis of symmetry of the crystal, two modes are obtained transverse (T), the amplitude vector, \mathbf{A} , of which is perpendicular to the direction of propagation of the wave associated with \mathbf{k} , and a **longitudinal mode (L)**, the vector amplitude of which is parallel to the direction of the wave vector.
- ii) For arbitrary directions of \mathbf{k} , the oscillation modes are neither pure transverse nor pure longitudinal (\mathbf{A} is neither parallel nor perpendicular to \mathbf{k}).
- iii) When $\mathbf{k} \rightarrow 0$ (long wavelength modes), ω depends linearly on \mathbf{k} (non-dispersive medium) for each branch, as in the one-dimensional case.
- iv) The speed of sound can then be defined from these linear regions, understood as the maximum speed at which an elastic wave can propagate through the solid, for a particular branch.
- v) For $\mathbf{k} \rightarrow 0$, an oscillation mode is always longitudinal or pure transverse, regardless of the direction of propagation of the wave (\mathbf{k}).
- vi) In a crystal the shear force constants (between crystalline planes) tend to be smaller than the compression force constants (within the same plane), so the transverse modes are slower than the Longitudinal modes.

B. PERIODIC CONTOUR CONDITIONS

Periodic contour conditions for atomic displacements according to crystallographic axes ($\alpha = 1, 2, 3$) are written in the form

$$u_{s,\beta}(\mathbf{R}_s + N_\alpha \mathbf{a}_\alpha, t) = u_{s,\beta}(\mathbf{R}_s, t),$$

where N_α is the number of primitive crystal cells in the direction of the axis α .

Considering that the component β of the displacement of the atom s is given by the expression $u_{s,\beta}(\mathbf{R}_s, t) = A_\beta e^{i(\mathbf{k} \cdot \mathbf{R}_s - \omega t)}$ the wave vectors \mathbf{k} compatible with the periodic contour conditions have the shape

$$\mathbf{k} = \sum_{\alpha=1}^3 \frac{m_\alpha}{N_\alpha} \mathbf{b}_\alpha \quad ; \quad m_\alpha \in Z$$

where $\mathbf{b}_1, \mathbf{b}_2$ and \mathbf{b}_3 are the primitive vectors of the reciprocal lattice.

Therefore, in the first area of Brillouin there are $N_1 N_2 N_3 = N$ allowed values of wave vectors \mathbf{k} , where N is the total number of primitive cells in the crystal.

As in the 1D case, these N wave vectors contained in the first Brillouin zone are enough to represent all the elastic waves that correspond to different oscillation modes.

Demonstration:

If \mathbf{k} is a vector outside the first Brillouin zone, it is always possible to find a vector of the reciprocal lattice, \mathbf{G} , so that $\mathbf{k}' = \mathbf{k} + \mathbf{G}$ is a contained vector in the first Brillouin zone, whose oscillation mode is the same as the mode corresponding to \mathbf{k} :

$$\mathbf{u}_s(t) = \mathbf{A} e^{i(\mathbf{k} \cdot \mathbf{R}_s - \omega t)} = \mathbf{A} e^{-i\mathbf{G} \cdot \mathbf{R}_s} e^{i(\mathbf{k} \cdot \mathbf{R}_s + \mathbf{G} \cdot \mathbf{R}_s - \omega t)} = \mathbf{A} e^{i(\mathbf{k}' \cdot \mathbf{R}_s - \omega t)}$$

C. POLYATOMIC BASIS

Let be a crystal with an atomic basis containing p atoms per primitive cell.

A normal mode of oscillation of this crystal will be written as

$$\mathbf{u}_{si}(t) = \mathbf{A}_i e^{i[\mathbf{k} \cdot (\mathbf{R}_s + \mathbf{\rho}_i) - \omega t]},$$

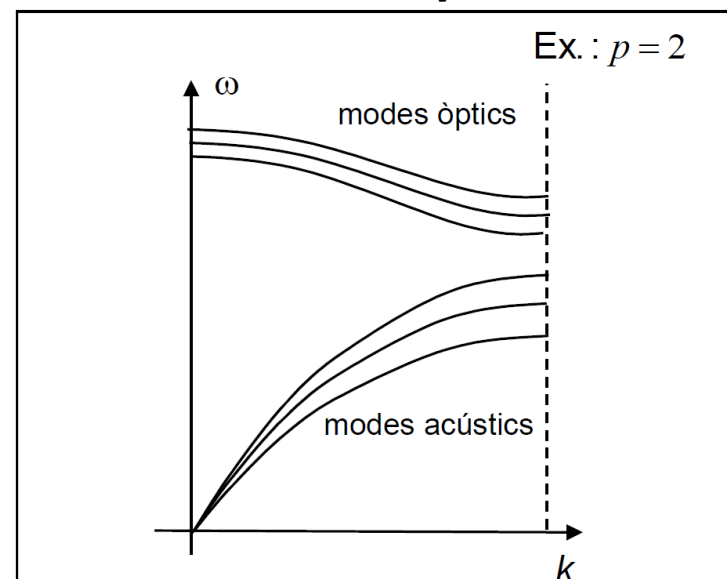
where s is the index of the primitive cell, and i is the index of the atom within the primitive cell s , \mathbf{R}_s is the vector of the Bravais lattice that indicates the origin of the primitive cell s , and $\mathbf{\rho}_i$ is the position vector of the atom i and within the primitive cell s .

The secular determinant obtained when replacing the previous oscillation mode in Newton's second law is a polynomial in ω^2 , of degree $3p$ (since there are p atoms to the atomic basis), which has $3p$ positive solutions for ω .

That is, for each value of the wave vector \mathbf{k} , there are $3p$ oscillation modes.

Of these $3p$ oscillation modes, there are 3 that give rise to acoustic branches and $3p - 3$ which give rise to optical branches.

[Simple reason: there are only 3 different ways to oscillate in phase, one second each crystallographic direction, and these correspond to the acoustic branches.]



3.4. PHONONS

A. OSCILLATE ONE-DIMENSIONAL HARMONIC INSTALLER. QUANTUM TREATMENT

The Hamiltonian of a one-dimensional harmonic oscillator of mass m is given by expression

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2,$$

where p is the quantity operator of motion and k is the force constant of the oscillator, which is related to the oscillation frequency ω as $k = m\omega^2$.

From the annihilation operators, a , and creation a^+ , defined as

$$a \equiv \sqrt{\frac{m\omega}{2\hbar}}x + i\sqrt{\frac{1}{2\hbar m\omega}}p,$$

$$a^+ \equiv \sqrt{\frac{m\omega}{2\hbar}}x - i\sqrt{\frac{1}{2\hbar m\omega}}p,$$

the Hamiltonian can be rewritten as

$$H = \hbar\omega\left(a^+a + \frac{1}{2}\right)$$

The own values of the Hamiltonian are:

$$E = \left(n + \frac{1}{2} \right) \hbar \omega \quad (n \in N),$$

and the own functions, $|n\rangle$, are characterized by the value of the main quantum number, n .

The energies and corresponding own states that we have obtained can be interpreted in terms of a simple model:

- The proper state $|n\rangle$ of the oscillator is equivalent to the state of a system with a only energy level $\hbar \omega$ in which n independent particles are placed.
- To the total energy of this level must be added the energy of the zero point, $(1/2) \hbar \omega$, so that the two models are equivalent.

In this interpretation, annihilation and creation operators simply **destroy** and **create**, respectively, a particle at the energy level $\hbar \omega$.

B. OSCILLATIONS IN A CRYSTAL. **QUANTUM TREATMENT. PHONONS**

The Hamiltonian of a **one-dimensional crystal**, of lattice parameter a , with N cells primitives and length L ($L = Na$), **with monoatomic basis** (see scheme in the page 5), can be written in the form

$$H = \sum_s \left[\frac{p_s^2}{2m} + \frac{1}{2} C (u_{s+1} - u_s)^2 \right],$$

where m is the mass of the atom at the basis, C is the spring force constant that joins two atoms located in adjacent cells, p_s is the amount of motion operator acting on the atom located in the primitive cell s , u_s is the displacement of this atom with respect to its equilibrium position, and the summation extends over all atoms of the crystal.

It can be shown that this Hamiltonian is separable in N Hamiltonians independent, one for each of the N classical oscillation modes (N values allowed of the wave vector k) that we have studied in section 3.1, and has the form of the hamiltonian of the simple harmonic oscillator

$$H = \sum_{i=1}^N \hbar \omega(k_i) \left[a_{k_i}^+ a_{k_i} + \frac{1}{2} \right]$$

In this scheme operators $a_{k_i}^+$ i a_{k_i} are respectively the operators of creation and annihilation of a quasiparticle called a **phonon** in the mode of oscillation k_i corresponding to the frequency $\omega(k_i)$, which is given by the classical scattering ratio.

The states of this Hamiltonian are of the form

$$\left| n_{k_1}, \dots, n_{k_N} \right\rangle,$$

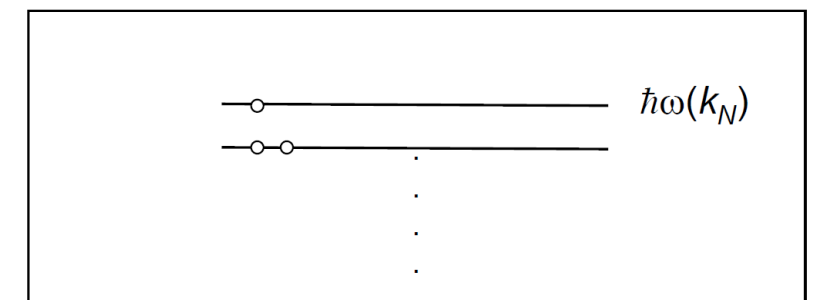
where $n_{k_1}, \dots, n_{k_N} \in \mathbb{N}$ and are the main quantum numbers associated with modes oscillation characterized by wave vectors k_1, \dots, k_N .

The energy of these states is simply the sum of their own energies of the Hamiltonian N equivalent to those of harmonic oscillators of frequencies $\omega(k_i)$

$$E = \sum_{i=1}^N \left(n_{k_i} + \frac{1}{2} \right) \hbar \omega(k_i)$$

Generalizing the model of a single energy level $\hbar\omega$, occupied by n independent particles, which we have used to interpret the results obtained for a harmonic oscillator in the previous subsection,

- we can introduce energy-independent quasiparticles $\hbar\omega(k_i)$, which we will call **phonons**,
- that will occupy the N levels corresponding to the N oscillation modes of the solid, in a larger or smaller number, depending on the degree of excitation energy of these modes.



phonon	Quantum excitation of an normal mode of oscillation of an solid
--------	---

The **phonons** of a solid are quasiparticles, since they can be assigned an energy $\hbar \omega(k_i)$ and a quasimomentum $\hbar k_i$.

For a real **three-dimensional crystal**, with N primitive cells and p atoms per cell

Primitive, there are **$3pN$ oscillation modes**, distributed in $3p$ branches (3 of acoustics and $3(p-1)$ of optics).

The energy of the i -th mode will be

$$E_i = \left(n_i + \frac{1}{2} \right) \hbar \omega_i$$

and the total energy of the crystal in the state $|n_1 \dots n_{3pN}\rangle$ will be

$$E = \sum_{i=1}^{3pN} \left(n_i + \frac{1}{2} \right) \hbar \omega_i ,$$

where n_i is the number of phonons with energy $\hbar \omega_i$ and in the i -th mode, and the summation it extends over the $3pN$ crystal oscillation modes.

When a crystal in the quantum state either creates or annihilates (emits or absorbs) a phonon, it passes into the quantum state $n_i + 1$ or $n_i - 1$, respectively.

C. QUANTITAT DE MOVIMENT DELS FONONS

[From there, we will use \mathbf{q} to present the wave vector of a phonon.]

A wave vector phonon \mathbf{q} interacts with other particles and quasiparticles (photons, neutrons, electrons, etc.) as if it had a moment $\hbar \mathbf{q}$.

However, a phonon does NOT carry any amount of physical motion, since its origin is the relative movement between atoms (except for $\mathbf{q} = 0$).

This is why $\hbar \mathbf{q}$ is a **quasi-moment**, and in reality, the phonon is a **quasiparticle**.

Normal modes of oscillation of a crystal DO NOT imply variation of the center of mass of the entire crystal.

For this reason, $\hbar \mathbf{q}$ is NOT a real moment.

For $\mathbf{q} = 0$, YES there is movement of the center of mass of the crystal, since it moves as a whole.

In this case, however, $\hbar \mathbf{q} = 0$.

D. INTERACTION OF PHONONS WITH OTHER PARTICLES AND QUASIPARTICLES

In crystals there are **selection rules** for wave vectors allowed for transitions between quantum states.

We already saw that the elastic dispersion of an X-ray photon by a crystal is governed by the following selection rule (Bragg condition):

$$\mathbf{k}' = \mathbf{k} + \mathbf{G},$$

where \mathbf{G} is a vector of the reciprocal lattice and \mathbf{k}' and \mathbf{k} are the wave vectors of the scattered and incident photons, respectively.

As a result of this reflection process, the crystal as a whole recedes with an amount of movement $-\hbar \mathbf{G}$.

If the dispersion of the photon is **inelastic** and in the process is created (emitted, sign +) or annihilated (absorbed, sign -) a wave vector phonon \mathbf{q} , the relationship is fulfilled

$$\mathbf{k}' \pm \mathbf{q} = \mathbf{k} + \mathbf{G}$$

Actually, the above equation is the **general rule of selection of wave vectors**, valid also for the interaction between crystal phonons and other particles (electrons, neutrons, etc.).

E. EXPERIMENTAL OBSERVATION OF INELASTIC DISPERSION

NEUTRONS FOR PHONONS

The scattering relationships of the phonons of a crystal, $\omega(q)$, are often determined through inelastic neutron scattering experiments with emission (creation) or absorption (annihilation) of phonons.

Neutrons interact mainly with atom nuclei and kinematics of dispersion is governed by a selection rule like the one we have seen in the previous page.

In this case, \mathbf{k} and \mathbf{k}' are respectively the wave vectors of the incident neutrons and dispersed, \mathbf{q} is the wave vector of the emitted and absorbed phonon, and \mathbf{G} is any vector of the reciprocal lattice.

In addition, in this dispersal process, the conservation **equation of total energy**,

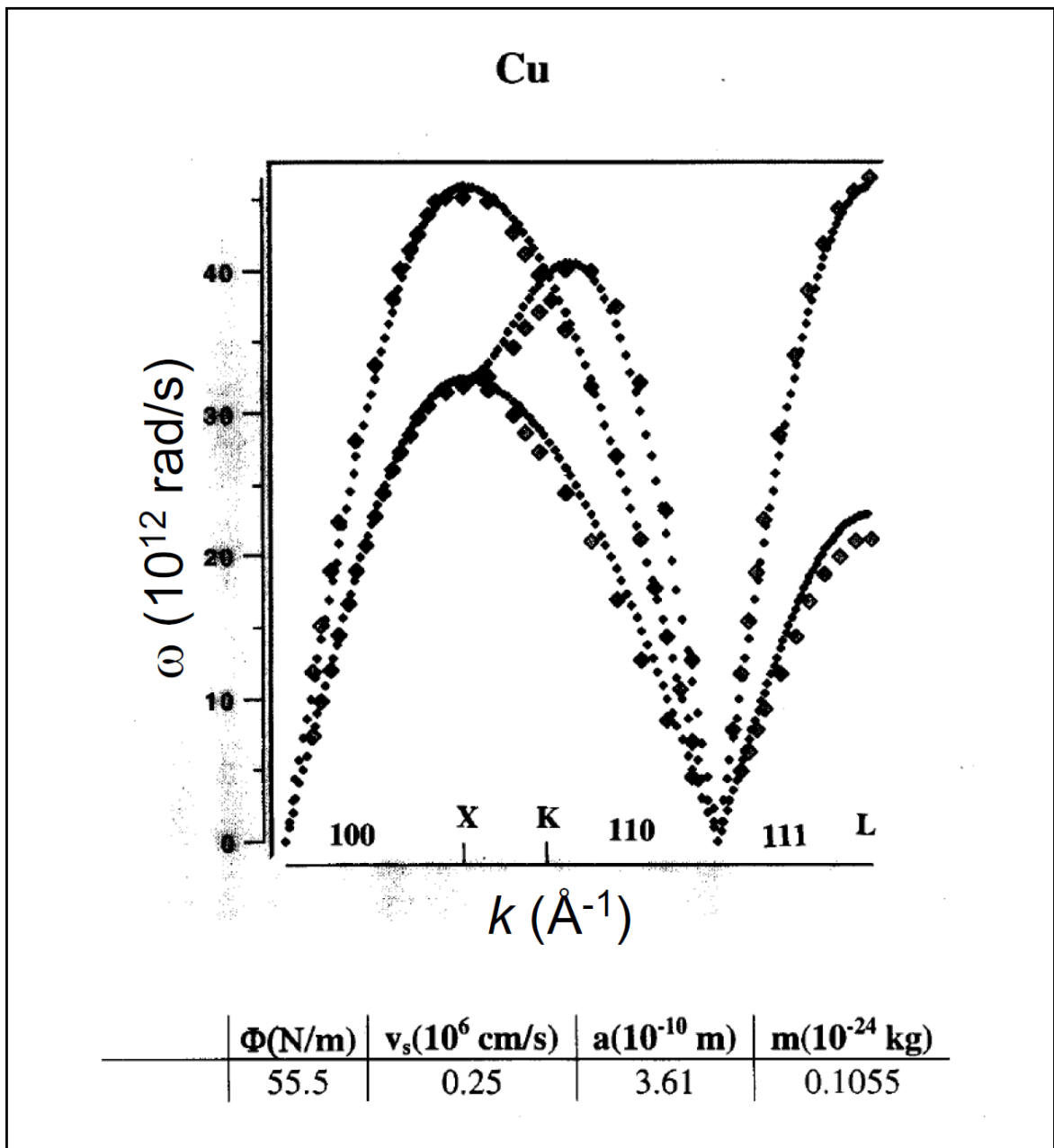
$$\frac{\hbar^2 k^2}{2M_n} = \frac{\hbar^2 k'^2}{2M_n} \pm \hbar\omega,$$

where $\hbar \omega$ is the energy of the phonon created (emitted, sign +) or annihilated (absorbed, sign -).

Studying the energy of scattered neutrons as a function of the scatter vector, $\mathbf{k} - \mathbf{k}'$, and using the conservation equations of momentum and energy, one can experimentally determine the phononic dispersion relation of a solid, $\omega(q)$.

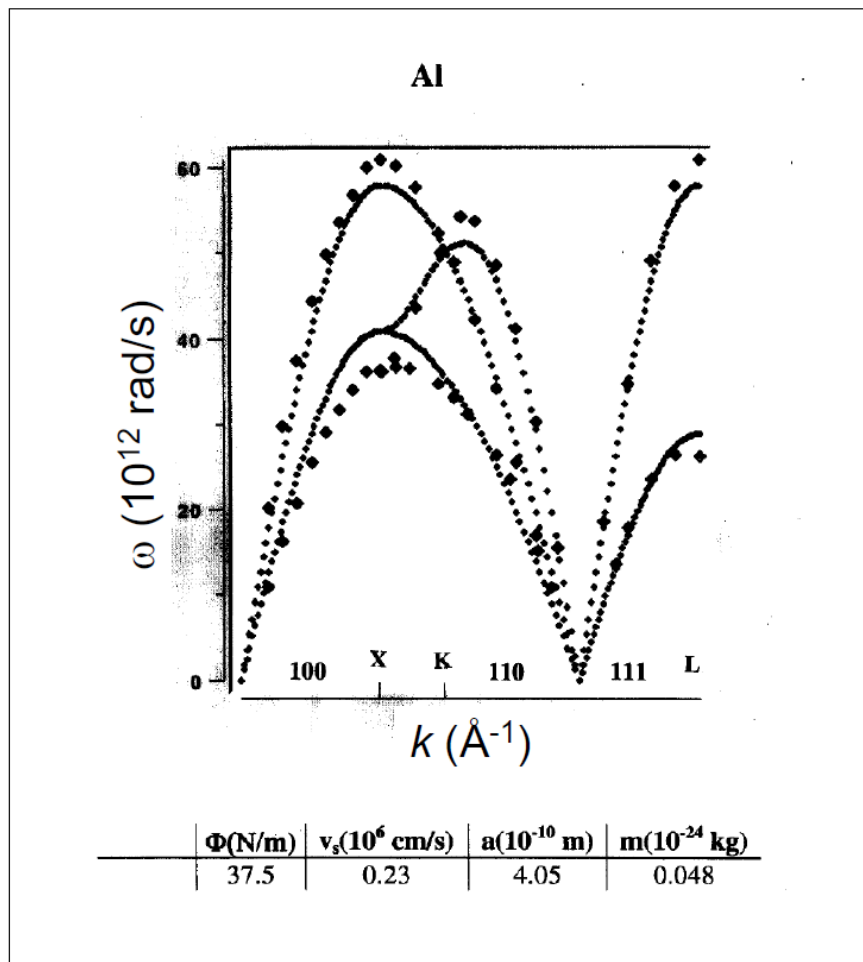
On the following pages you can see examples of dispersion relationships phononics obtained in this way for different metals (Pb, Al, Cu).

[In these experiments, **thermal neutrons** are used, with energies of the order of meV, because its wavelengths are similar to the spacing of the lattice, and so the neutron moment difference is adapted to the time of phonons.]



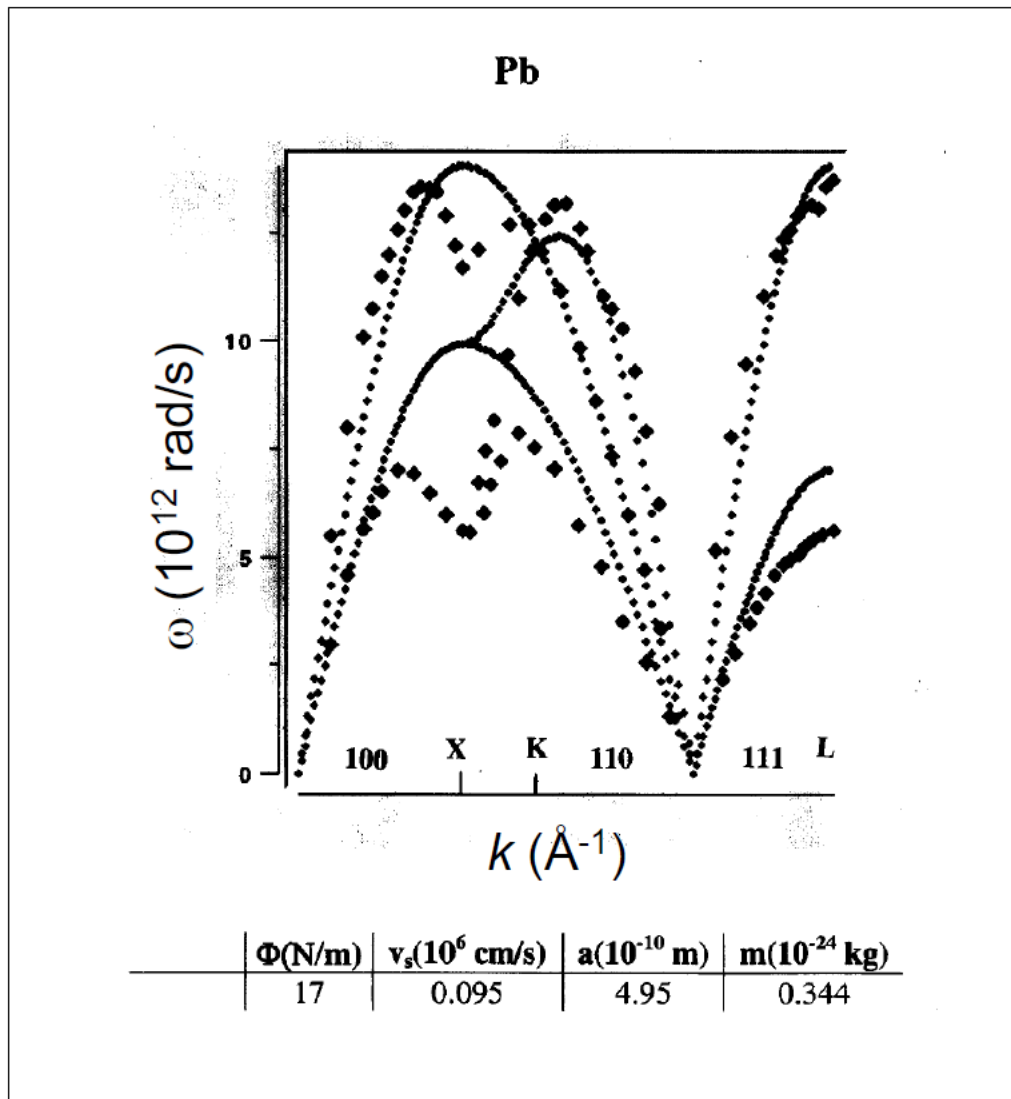
Remarks:

- i) The values of a (lattice parameter) and m (electron mass) are found in tables.
- ii) The value of the force constant in first neighbouring, Φ , is obtained from the highest maximum of $\omega(q)$, using $\omega_{\max} = 2(\Phi/m)^{1/2}$ as a one-dimensional approximation of a particular direction. The fact that it is a very large value means that the harmonic approximation (dotted curves) is good enough to adjust the data.



The force constant in close neighbours is not as large as in the case of copper, and this is reflected in the fact that experimental data

deviate from theoretical curves corresponding to the harmonic approximation.



The force constant in close neighbours in this case is relatively small, which is reflected in the fact that experimental data deviates greatly from the theoretical curves corresponding to the harmonic approximation.

This means that interactions with atoms that go beyond the first neighbours, because only these are not enough to describe the data experimental correctly.

F. ESTADÍSTICA DE BOSE-EINSTEIN

Phonons behave as if they were **bosons**, since there is no limitation on the maximum number of phonons that can exist in the same oscillation mode, that is, with the same quantum numbers.

In fact, creation and annihilation operators, a^+ and a , comply with the same switching rules for photons and for phonons.

For this reason, the average occupancy of the frequency oscillation mode ω_s and vector of wave \mathbf{k} in the branch s , $\langle n_{\mathbf{k}s} \rangle$, at a certain temperature T , is calculated by **the Bose-Einstein statistic**:

$$\langle n_{\mathbf{k}s} \rangle = \frac{\sum_{n=0}^{\infty} n \exp[-n\hbar\omega_s(\mathbf{k})/k_B T]}{\sum_{n=0}^{\infty} \exp[-n\hbar\omega_s(\mathbf{k})/k_B T]},$$

where $\omega_s(\mathbf{k})$ is the phononic scattering relationship.

If we introduce $z \equiv \exp[-\hbar\omega_s(\mathbf{k})/k_B T]$ and take into account

$$\left. \begin{aligned} \sum_{n=0}^{\infty} z^n &= \frac{1}{1-z}, \\ \sum_{n=0}^{\infty} n z^n &= z \frac{d}{dz} \left(\sum_{n=0}^{\infty} z^n \right) = z \frac{d}{dz} \left(\frac{1}{1-z} \right) = \frac{z}{(1-z)^2}, \end{aligned} \right\} \quad \langle n_{\mathbf{k}s} \rangle = \frac{\frac{z}{(1-z)^2}}{\frac{1}{1-z}} = \frac{1}{\frac{1}{z} - 1}$$

the average occupation adopts the following expression:

$$\langle n_{\mathbf{k}s} \rangle = \frac{1}{\exp[\hbar\omega_s(\mathbf{k})/k_B T] - 1}$$

G. AVERAGE ENERGY OF A NORMAL OSCILLATION MODE

CANCELLATION

The average energy of an oscillation mode is calculated as follows:

$$\langle E_{\mathbf{k}s} \rangle = \langle n_{\mathbf{k}s} \rangle \hbar\omega_s(\mathbf{k}) = \frac{\hbar\omega_s(\mathbf{k})}{\exp[\hbar\omega_s(\mathbf{k})/k_B T] - 1}$$

(i) Low temperature limit

In this case $\hbar\omega_s(\mathbf{k}) \gg k_B T$, so that

$$\langle n_{\mathbf{k}s} \rangle \cong \exp[-\hbar\omega_s(\mathbf{k})/k_B T]$$

The probability of phonons being excited is small and the average energy in one mode oscillation is

$$\langle E_{\mathbf{k}s} \rangle \cong \hbar\omega_s(\mathbf{k}) \exp[-\hbar\omega_s(\mathbf{k})/k_B T]$$

(ii) High temperature limit

In this case $\hbar\omega_s(\mathbf{k}) \ll k_B T$, so we can develop $\exp[\hbar\omega_s(\mathbf{k})/k_B T]$ in Taylor series to second order and replace it with the expression of $\langle n_{\mathbf{k}s} \rangle$:

$$\langle n_{\mathbf{k}s} \rangle = \frac{1}{e^{\hbar\omega_s/k_B T} - 1} \cong \frac{1}{\frac{\hbar\omega_s}{k_B T} + \frac{1}{2} \left(\frac{\hbar\omega_s}{k_B T} \right)^2} = \frac{k_B T}{\hbar\omega_s} \frac{1}{1 + \frac{1}{2} \frac{\hbar\omega_s}{k_B T}} \cong \frac{k_B T}{\hbar\omega_s} \left(1 - \frac{1}{2} \frac{\hbar\omega_s}{k_B T} \right)$$

In this way, the expressions for $\langle n_{\mathbf{k}s} \rangle$ and $\langle E_{\mathbf{k}s} \rangle$ they remain as follows:

$$\begin{cases} \langle n_{\mathbf{k}s} \rangle \cong \frac{k_B T}{\hbar \omega_s(\mathbf{k})} - \frac{1}{2} \\ \langle E_{\mathbf{k}s} \rangle \cong k_B T - \frac{1}{2} \hbar \omega_s(\mathbf{k}) \end{cases}$$

H. DENSITY OF MODES

Let's introduce the mode density function per unit frequency into the branch s , $Ds(\omega)$, so that $Ds(\omega)d\omega$ is the number of modes in branch s with frequencies between ω and $\omega + d\omega$.

We will do the deductution for a cubic crystal (3D) of edge L , with simple cubic lattice.

In this case, the values of \mathbf{k} compatible with the periodic conditions of outline are of the shape

$$k_i = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \dots, N \frac{\pi}{L} \quad (i = x, y, z)$$

Therefore, in the volume $(2\pi/L)^3$ of the wave vector space there is a single permissible value of \mathbf{k} and the density of states in that space is

$$\left(\frac{L}{2\pi} \right)^3 = \frac{V}{8\pi^3}$$

The number of modes corresponding to wave vectors \mathbf{k} with module smaller than one certain value k (i.e. the modes contained within a sphere of radius k) is

$$N = \left(\frac{V}{8\pi^3} \right) \left(\frac{4}{3} \pi k^3 \right) = \frac{V}{6\pi^2} k^3$$

Accordingly, the **density of modes per unit frequency in the branch \underline{s}** , $D_s(\omega)$, is given by the following expression:

$$D_s(\omega) = \frac{dN}{d\omega} = \frac{dN}{dk} \frac{dk}{d\omega} = \left(\frac{Vk^2}{2\pi^2} \right) \frac{dk}{d\omega}$$