

Crystal vibrations and the classical theory:

The assumption will be made to consider that the mean equilibrium position \vec{R} of each ion is at a Bravais lattice site. The ions oscillate about this mean position. Thus the instantaneous position of the ion $\vec{r}(\vec{R})$ will deviate from its mean position by the displacement $\vec{u}(\vec{R})$, as shown in figure 59. This means that

$$\vec{r}(\vec{R}) = \vec{R} + \vec{u}(\vec{R}).$$

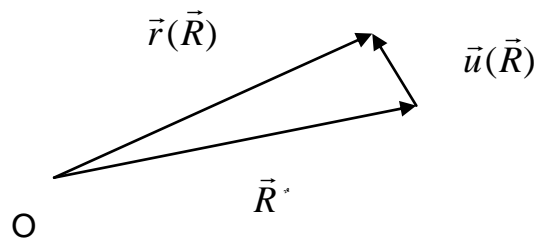


Figure 59: The instantaneous position of an ion is defined in terms of its mean position (the Bravais lattice vector) \vec{R} and the ionic displacement $\vec{u}(\vec{R})$.

The static lattice model as compared to the dynamic model:

As mentioned before that the pair of atoms in noble gases, for example, separated by \vec{r} contributes a potential energy $U(\vec{r})$ to the total potential energy of the whole crystal where the assumption is made that these atoms are fixed at their Bravais lattice sites (with zero kinetic energies). The total potential energy is the sum of all potential energies of the pairs of atoms and has the expression:

$$U = \frac{1}{2} \sum_{\vec{R}\vec{R}'} U(\vec{R} - \vec{R}') = \frac{N}{2} \sum_{\vec{R} \neq 0} U(\vec{R}).$$

Now if our assumption is changed such that allowing the atoms to oscillate about their mean positions, the above relation must be modified and written as:

$$U = \frac{1}{2} \sum_{\vec{R}\vec{R}'} U(\vec{r}(\vec{R}) - \vec{r}(\vec{R}')) = \frac{1}{2} \sum_{\vec{R}\vec{R}'} U(\vec{R} - \vec{R}' + \vec{u}(\vec{R}) - \vec{u}(\vec{R}'))$$

However, the new expression of the total potential energy depends on the dynamical variables $\vec{u}(\vec{R})$. Therefore the Hamiltonian of the system is expressed as:

$$H = \sum_{\vec{R}} \frac{\vec{P}(\vec{R})^2}{2M} + U,$$

where $\vec{P}(\vec{R})$ is the momentum of the atom whose equilibrium position is \vec{R} and its atomic mass is M .

The harmonic Approximation:

This approximation is based on the concept that the atoms will have very small deviations $\vec{u}(\vec{R})$ from their mean positions \vec{R} . In such circumstances the total potential energy may be expanded using the Taylor's theorem, that is,

$$U(\vec{r} + \vec{a}) = U(\vec{r}) + \vec{a} \cdot \vec{\nabla} U(\vec{r}) + \frac{1}{2} (\vec{a} \cdot \vec{\nabla})^2 U(\vec{r}) + \frac{1}{3!} (\vec{a} \cdot \vec{\nabla})^3 U(\vec{r}) + \dots O(r^3)$$

Put $\vec{r} = \vec{R} - \vec{R}'$, $\vec{a} = \vec{u}(\vec{R}) - \vec{u}(\vec{R}')$ and insert the above-mentioned dynamical definition of the total potential energy we may get:

$$U = \frac{N}{2} \sum U(\vec{R}) + \frac{1}{2} \sum_{\vec{R}\vec{R}'} (\vec{u}(\vec{R}) - \vec{u}(\vec{R}')) \cdot \nabla U(\vec{R} - \vec{R}') \\ + \frac{1}{4} \sum_{\vec{R}\vec{R}'} [(\vec{u}(\vec{R}) - \vec{u}(\vec{R}')) \cdot \nabla]^2 U(\vec{R} - \vec{R}') + O(u^3)$$

The first term is the potential energy at equilibrium and can be given the expression:

$$U^{eq} = \frac{1}{2} \sum_{\vec{R}\vec{R}'} U(\vec{R} - \vec{R}') = \frac{N}{2} \sum_{R \neq 0} U(\vec{R}).$$

The second term represents the linear term which has the coefficient $\sum_{\vec{R}} \nabla U(\vec{R} - \vec{R}')$. This coefficient gives us the net

force on any atom in equilibrium. Thus this term must vanish because the net force on any atom in such conditions is zero.

All higher order terms can be taken as corrections to U^{eq} . The most important term among such high order terms is the quadratic term U^{quad} (or called U^{harm}), namely,

$$U^{quad} = \frac{1}{4} \sum_{\vec{R}\vec{R}'} [(\vec{u}(\vec{R}) - \vec{u}(\vec{R}')) \cdot \nabla]^2 U(\vec{R} - \vec{R}')$$

or

$$U^{quad} = \frac{1}{4} \sum_{\substack{\vec{R}\vec{R}' \\ \mu, \nu = x, y, z}} [\vec{u}_{\mu}(\vec{R}) - \vec{u}_{\mu}(\vec{R}')] U_{\mu\nu}(\vec{R} - \vec{R}') [\vec{u}_{\nu}(\vec{R}) - \vec{u}_{\nu}(\vec{R}')],$$

$$\text{where } U_{\mu\nu}(\vec{r}) = \frac{\partial^2 U(\vec{r})}{\partial r_{\mu} \partial r_{\nu}}.$$

Note:

- In several dynamical applications the constant term U^{eq} can be neglected because it is independent of the \vec{u} 's and \vec{P} 's and the total potential energy turns out to be the quadratic term only.
- Further corrections to the total potential energy may be considered. Such corrections are like the third and fourth order terms and they are called the anharmonic terms. Those are treated as small perturbations on the dominant harmonic term.

Vibrations of crystals with monatomic basis in one-dimension:

In order to study the elastic vibrations of a crystal when one atom in the primitive cell is considered, we need to know the direction by which the elastic wave may propagate along. The propagation of such wave causes the entire planes of atoms to move in phase with two displacements:

- a. Either one is parallel to the direction of wave vector \vec{k} (called longitudinal vector).
- b. Or the other is perpendicular to the direction of wave vector \vec{k} (called transverse vector)

However each wave vector may have three modes, one in longitudinal polarization and two transverse polarizations.

Let us take a linear array of atoms along the x -axis as an example. Each atom with mass M and separated by a distance $x = na$, where n is an integer. The displacement of the n^{th} ion along the x -axis from its equilibrium position is defined by $u(na)$, as shown in figure 60. If the assumption is made that only neighboring ions will interact, then harmonic approximation will be adopted where the quadratic term in the expanded elastic potential energy may be considered, namely:

$$U^{quad} = \frac{1}{2} C \sum_n [u(na) - u((n+1)a)]^2 .$$

Here it is assumed that the force on an atom in the plane of atoms n caused by the displacement of the plane of atoms $n+1$ is proportional to the change in displacements $[u(n+1) - u(n)]$. The elastic constant $C = \frac{\partial^2 U}{\partial x^2}$, where U is the elastic potential energy of the two interacting ions separated by a distance x .

Note: It must be emphasized that if only nearest-neighbor forces are kept, the harmonic approximation for the 1-D Bravais lattice describes a model in which each ion is tied to its neighbor by perfect springs of spring constant C .

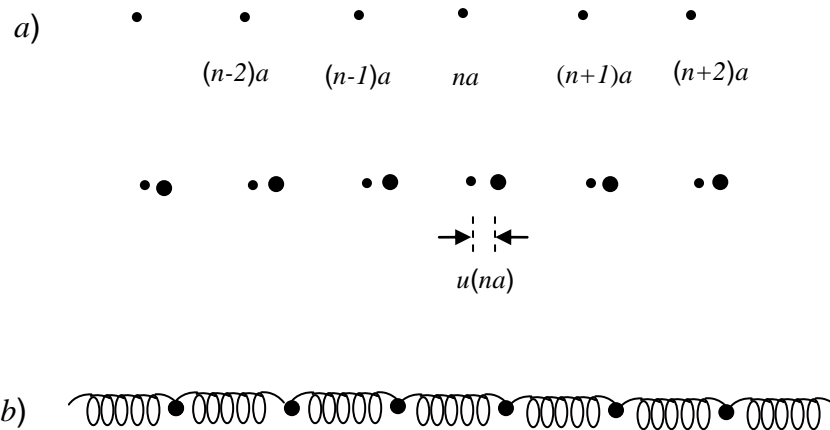


Figure 60: a) The displacement $u(na)$ of an ion from its equilibrium position at na , at any instant.

b) The harmonic approximation for 1-D Bravais lattice describes a model in which each ion is tied to its nearest-neighbor by perfect springs with spring constant C .

The equations of motion can be simply obtained from the above form of elastic potential energy as:

$$M\ddot{u}(na) = -\frac{\partial U^{quad}}{\partial u(na)} = -C[2u(na) - u(\{n+1\}a) - u(\{n-1\}a)]$$

Considering the normal mode of oscillations the same as a wave traveling on a continuous string, the displacement of the n^{th} atom may be represented by:

$$u(na, t) = ue^{i(kna - \omega t)}$$

If we are seeking solutions of such form to the above equations of motion, then these solutions must satisfy the equations of motion, i.e.:

$$-M\omega^2 ue^{i(kna - \omega t)} = -C[2ue^{i(kna - \omega t)} - ue^{i(k\{n+1\}a - \omega t)} - ue^{i(k\{n-1\}a - \omega t)}],$$

$$M\omega^2 = C[2 - e^{ika} - e^{-ika}] = 2C(1 - \cos ka),$$

$$\therefore \omega^2(k) = \frac{2C(1 - \cos ka)}{M},$$

$$\Rightarrow \omega(k) = \sqrt{\frac{2C(1 - \cos ka)}{M}} = 2\sqrt{\frac{C}{M}} \left| \sin \frac{ka}{2} \right|,$$

(where $\cos ka = 1 - 2\sin^2 \frac{ka}{2}$).

Or
$$\omega^2(k) = \frac{4C}{M} \sin^2 \frac{ka}{2}.$$

This is the dispersion relation for normal modes of a linear chain of atoms and it is depicted in figure 61.

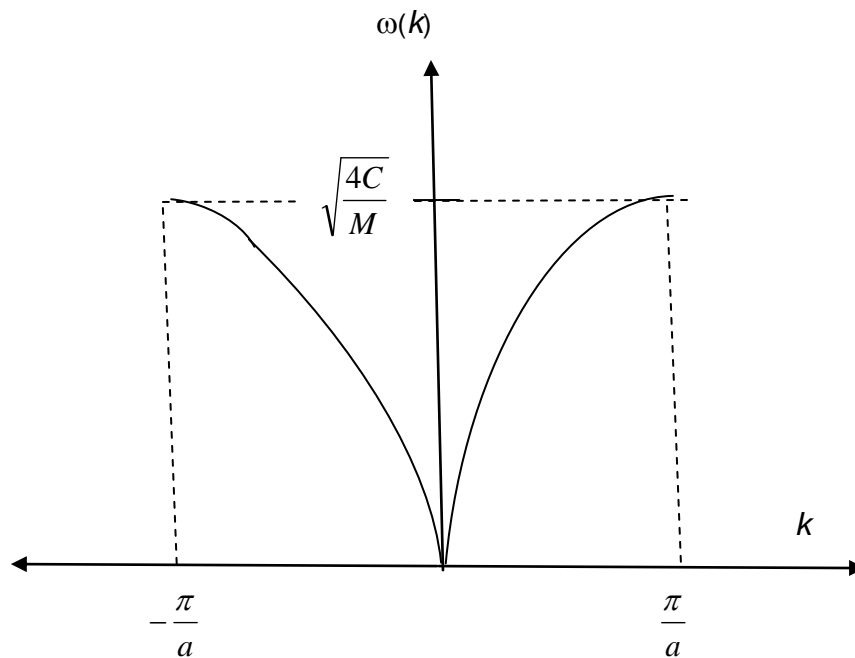


Figure 61: The dispersion plot for a monatomic linear chain with only nearest-neighbor interactions.

The boundary of the first Brillouin Zone:

The boundary of the first Brillouin zone can be checked out as follows: The first derivative with respect to k of the last relation is

zero, i.e. $\frac{d\omega^2}{dk} = 0$. Since $\frac{d\omega^2}{dk} = \frac{2Ca}{M} \sin ka \Rightarrow \sin ka = 0$ at $k = \pm \frac{\pi}{a}$.

Two extreme limits of ω or wavelength λ :

- i) For very small values of k (or very long wavelengths), i.e. $ka \ll 1$, $\cos ka$ can be expanded such that $\cos ka \approx 1 - \frac{1}{2}(ka)^2$. Thus $\omega(k) \rightarrow \omega_{min}$ and the dispersion relation give $\omega_{min} = \left(\frac{C}{M}\right)^{1/2} ka$.

Conclusion:

The elastic (or sound) waves have frequencies that are directly proportional to k in this region of the dispersion curve. The slope of this linear relation gives us the velocity of sound, namely: $v_{sound} = \left(\frac{C}{M}\right)^{1/2} a$. Some physics might be extracted from this, if we define the linear mass density (or mass per unit length) of the chain of atoms as $\eta = \frac{M}{a}$, then Ca may represent the tension of the chain T . This will obviously give us a physical picture similar to the problem of a wave traveling in a string where the velocity of wave is written as $v = \left(\frac{T}{\eta}\right)^{1/2}$. Thus the frequency ω in our real problem can be expressed as $\omega = v_{sound} k$, as shown in figure 62.

- ii) When large values of k are considered $\omega(k) \rightarrow$

$$\omega_{max} \text{ at } k = \pm \frac{\pi}{a}, \text{ and } \omega_{max} = \left(\frac{4C}{M}\right)^{1/2}.$$

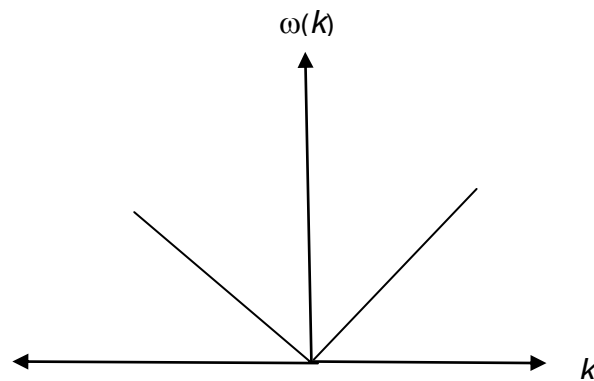


Figure 62: The linear part of the dispersion plot at very small values of k for a monatomic linear chain with only nearest-neighbor interactions.

Remark: There are no normal modes that can have angular frequency greater than ω_{max} .

Limitations on the wave vector k within the first Brillouin zone):

Since the dispersion curve is periodic in k in intervals of $2\pi/a$, atomic displacements are the same for normal modes. This means that the most convenient way to specify the boundary conditions is to join the two remote ends of the chain back together by one more of the same springs that connect internal atoms as shown in figure 63. If we take the atoms to occupy sites $a, 2a, Na$, where N represents the total number of atoms, then we can solve the equation of motion N times (where $n = 1, 2, N$) provided that the boundary conditions are:

$$u(a) = u([N+1]),$$

$$\text{and } u(Na) = u(0).$$

This requires that $e^{ikNa} = 1$ which may also require that $k = \frac{2\pi n}{aN}$. This is the well-known Born-von Karman periodic boundary condition.

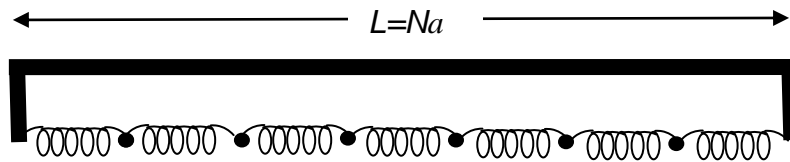


Figure 63: The Born-von boundary condition. A massless rigid rod of length $L=Na$ connects the ion on the extreme right with the spring on the extreme left.

Notes:

- Any two modes with a wave vector that differ by $2\pi/a$ are the same and the smallest wave vector for any given mode is restricted to the range $-\frac{\pi}{a} \leq k \leq +\frac{\pi}{a}$. The maximum wave vector $k_{\max} = \pm \frac{\pi}{a}$.
- At the boundaries $k_{\max} = \pm \frac{\pi}{a}$ of the first Brillouin zone, the solution $u e^{i(kna - \omega t)}$ does not represent a traveling wave, but a standing wave. This means that in such a standing wave, alternate atoms oscillate in opposite phases, because $u_n = e^{\pm in\pi} = (-1)^n$, where the phase factor $e^{-i\omega t}$ is ignored here. Thus u_n is either equal +1 or -1 which depends on whether n is an even integer (where the wave moves to the right) or odd integer (where the wave moves to the left).

Standing wave and Bragg reflection of x-rays:

When the Bragg condition is satisfied a standing wave is set up and no more traveling wave propagation does exist in a lattice. Substituting the values $k_{\max} = \pm \frac{\pi}{a}$ into the Bragg law ($2d \sin \theta = m\lambda$) will give $2d \sin \theta = m(2a)$, where $\lambda = 2a$. Here the above condition may be satisfied when $d = a$, $\theta = \pi/2$ and $m = 1$.

Conclusion:

Only wave lengths longer than $2a$ are required to represent the lattice motion. This occurs by having values of k within the first Brillouin zone (*i.e.* within limits $k_{\max} = \pm \frac{\pi}{a}$).