

Lattice dynamics in crystals (CLASSICAL THEORY)

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Let us consider a three-dimensional crystal with N unit cells. These unit cells correspond to vectors \vec{T}_n ($n=1, N$) and contain n_b atoms each (the basis) positioned at $\vec{T}_n + \vec{d}_\nu$ ($\nu=1, n_b$). Thus we can denote the atomic positions with two indices (n, ν) . If $\vec{u}_{n\nu} \equiv \{u_{n\nu\alpha} | \alpha=x, y, z\}$ are ^{the} displacements of the atoms from their equilibrium positions, then the expansion of the total lattice energy up to second order in these displacements (HARMONIC APPROXIMATION) reads

$$E_{\text{TOT}}^{(\text{harmonic})}(\{\vec{u}_{n\nu}\}) = E_{\text{TOT}}(0) + \frac{1}{2} \sum_{\substack{n\nu\alpha \\ n'\nu'\alpha'}} D_{n\nu\alpha, n'\nu'\alpha'} u_{n\nu\alpha} u_{n'\nu'\alpha'} + \dots$$

Here $D_{n\nu\alpha, n'\nu'\alpha'} \equiv \left(\frac{\partial^2 E_{\text{TOT}}}{\partial u_{n\nu\alpha} \partial u_{n'\nu'\alpha'}} \right) \Big|_0$ are the force constants.

(obviously $\frac{\partial E_{\text{TOT}}}{\partial u_{n\nu\alpha}} \Big|_0 = 0$, which is why the first order term in the above expansion vanishes!)

These force constants respect the following symmetries:

1. $D_{n\nu\alpha, n'\nu'\alpha'} = D_{n'\nu'\alpha', n\nu\alpha}$ (real symmetric matrix)
2. $D_{n\nu\alpha, n'\nu'\alpha'} = D_{m\nu\alpha, m'\nu'\alpha'}$ if $\vec{T}_n - \vec{T}_{n'} = \vec{T}_m - \vec{T}_{m'}$
(consequence of the translational symmetry of the crystal)
3. $\sum_{n'\nu'} D_{n\nu\alpha, n'\nu'\alpha'} = 0$ (sum rule)

Where does this sum rule come from?

The classical equations of motion for the atoms read $\left\{ \begin{array}{l} \text{the corresponding forces are given by } \vec{F}_{nv} = - \frac{\partial E_{TOT}}{\partial \vec{u}_{nv}} \end{array} \right\}$

$$(*) \quad M_v \ddot{u}_{nv\alpha} = - \sum_{n'\nu'\alpha'} D_{nv\alpha, n'\nu'\alpha'} u_{n'\nu'\alpha'}$$

These equations can be rewritten as

$$M_v \ddot{u}_{nv\alpha} = - \sum_{\alpha'} \underbrace{\sum_{n'\nu'} D_{nv\alpha, n'\nu'\alpha'}}_{\text{sum rule}} u_{n'\nu'\alpha'}$$

If $u_{n'\nu'\alpha'} = u_{\alpha'}$ (independent of n', ν') then the forces on all the atoms should be zero and the right hand side of the last equation implies that

$$u_{\alpha'} \sum_{n'\nu'} D_{nv\alpha, n'\nu'\alpha'} = 0,$$

which proves the above sum rule.

We now look for the solutions of the coupled equations (*) in the form

$$(\#) \quad \vec{u}_{nv}(t) = \vec{A}_v(\vec{r}, \omega) e^{i(\vec{r} \cdot \vec{T}_n - \omega t)},$$

where $\vec{A}_v(\vec{r}, \omega)$ are the polarization vectors.

Note that $\vec{A}_v(\vec{r}, \omega) = \{ A_{v\alpha}(\vec{r}, \omega) \mid \alpha = x, y, z \}$

By substituting (#) into (*) we get :

$$-M_\nu \omega^2 A_{\nu\alpha}(\vec{q}, \omega) = -\sum_{n'\nu'\alpha'} D_{\nu\alpha, n'\nu'\alpha'} e^{-i\vec{q}\cdot(\vec{r}_n - \vec{r}_{n'})} A_{\nu'\alpha'}(\vec{q}, \omega)$$

$$\Leftrightarrow -M_\nu \omega^2 A_{\nu\alpha}(\vec{q}, \omega) = -\sum_{\nu'\alpha'} \left(\sum_{n'} D_{\nu\alpha, n'\nu'\alpha'} e^{-i\vec{q}\cdot(\vec{r}_n - \vec{r}_{n'})} \right) A_{\nu'\alpha'}(\vec{q}, \omega)$$

$$\Leftrightarrow \boxed{-M_\nu \omega^2 A_{\nu\alpha}(\vec{q}, \omega) = -\sum_{\nu'\alpha'} D_{\nu\alpha, \nu'\alpha'}(\vec{q}) A_{\nu'\alpha'}(\vec{q}, \omega)}$$

(**)

where we introduced the dynamical matrix with elements

$$\boxed{D_{\nu\alpha, \nu'\alpha'}(\vec{q}) \equiv \sum_{n'} D_{\nu\alpha, n'\nu'\alpha'} e^{-i\vec{q}\cdot(\vec{r}_n - \vec{r}_{n'})}}$$

Then Eq. (**) represents a set of homogeneous linear equations for $A_{\nu\alpha}$, which has nontrivial solutions provided that the corresponding determinant is zero:

$$\| D_{\nu\alpha, \nu'\alpha'}(\vec{q}) - M_\nu \omega^2 \delta_{\alpha\alpha'} \delta_{\nu\nu'} \| = 0.$$

The solutions to the last equation (at each \vec{q} and ω) are the normal modes of the crystal.

How many normal modes are there?

At each \vec{q} there are $3N_b$ modes in a 3D crystal (or, more generally, dN_b modes in a d -dimensional crystal!)

To get the total number of modes one should

multiply this with the total number of permissible \vec{q} vectors; remember that with periodic boundary conditions the number of allowed \vec{q} vectors equals the total number of unit cells $\equiv N!$

Hence the total number of modes is $\boxed{3M_b N}$.

\Rightarrow we have $3M_b$ phonon branches as \vec{q} is varied in the Brillouin zone!

The modes whose polarization vectors are parallel to \vec{q} are called longitudinal (L) and those with polarization vectors perpendicular to \vec{q} are transverse (T).

The sum rule we discussed above can be rewritten in terms of the dynamical matrix as

$$\sum_{\nu'} D_{\nu\alpha, \nu'\alpha'}(\vec{q}=0) \equiv 0.$$

The implication of the last result is the following:

if all the atoms of the basis have the same amplitudes

$$A_{\nu\alpha'} \equiv A_{\alpha'} \quad (\text{independent of } \nu!)$$

then Eqs. (**) are satisfied with $\omega = 0!$
(for $\vec{q} = 0$)

Thus any 3D crystal has three acoustic branches with the property that $\boxed{\omega \rightarrow 0 \text{ as } \vec{q} \rightarrow 0}$.

The $\vec{q} = 0$ ACOUSTIC MODES (also known as the Goldstone modes of a crystal) correspond to all the atoms moving in phase and with the same amplitude!

So each 3D crystal has 3 acoustic branches
and $3N_b - 3 = 3(N_b - 1)$ optical branches!

{ more generally, a d -dimensional crystal has d
acoustic branches and $d(N_b - 1)$ OPTICAL branches }

⇒ MONOATOMIC CRYSTALS ONLY HAVE ACOUSTIC BRANCHES!

In crystals with short-range interatomic forces
{ e.g. homopolar elemental semiconductors such as }
{ silicon and germanium }

one has to take into account several shells of neighbors of a given atom (~ 10) to accurately calculate the normal modes of a crystal.

In crystals where interatomic forces also have a long-range component, the calculation is typically more involved and requires the so-called Ewald summation method for the long-range parts of forces.

It is important to remember the difference between the optical and acoustic modes:

the acoustic ones assume motion of all the atoms within the same unit cell as a whole (i.e., in phase), and in the special case $\vec{q} = 0$ the motion of all the atoms in the whole crystal with the same amplitude and phase!

The optical modes are "pulsations" of a unit cell.

The optical branches usually do not disperse much and are very often approximated as Einstein modes!
(COMPLETELY DISPERSIONLESS)

The ^{optical} modes at the Γ -point ($\vec{q} = 0$) are often called the ZONE-CENTER modes.

In the appended illustrations of typical phonon spectra, you can see that aluminum (Al) only has acoustic branches (since it is a monoatomic crystal!) while silicon (Si) and germanium (Ge) have both acoustic and optical branches (crystals with bases!).

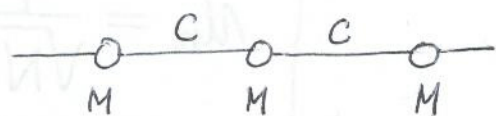
The typical optical phonon energies are of the same order of magnitude as the room-temperature $k_B T$ ($\approx 25.5 \text{ meV}$). Among the highest optical phonon energies are those found in carbon-based systems (such as graphene) -- they go up to almost 200 meV !

Quantum theory of the harmonic crystal

The previous discussion of the lattice dynamics was based on classical equations of motion. As it turns out, the classical and quantum treatments are completely equivalent as far as the mode dispersions (i.e., the dependence $\omega = \omega(\vec{q})$) are concerned!

The new aspect brought about by the quantum treatment is that ^{the} lattice displacements are quantized, the corresponding quanta being called PHONONS.

We will illustrate the quantum approach on the example of a linear monoatomic chain of atoms. Its Hamiltonian reads



$$H = \sum_n \frac{p_n^2}{2M} + \frac{C}{2} \sum_n (2u_n^2 - u_n u_{n+1} - u_n u_{n-1})$$

in the harmonic approximation (if only nearest neighbor interactions are taken into account).

Here $[u_n, p_{n'}] = i\hbar \delta_{nn'}$, $[u_n, u_{n'}] = [p_n, p_{n'}] = 0$ are the usual commutation relations.

We can perform a canonical transformation, i.e., introduce the following phonon creation and annihilation operators:

$$(*) \begin{cases} a_q = \frac{1}{\sqrt{N}} \sum_{t_n} e^{-iq t_n} \left[\sqrt{\frac{M\omega(q)}{2\hbar}} u_n + i \sqrt{\frac{1}{2M\hbar\omega(q)}} p_n \right], \\ a_q^\dagger = \frac{1}{\sqrt{N}} \sum_{t_n} e^{iq t_n} \left[\sqrt{\frac{M\omega(q)}{2\hbar}} u_n - i \sqrt{\frac{1}{2M\hbar\omega(q)}} p_n \right], \end{cases}$$

where $\omega(q)$ is the as yet unspecified frequency.

It is easy to check that the transformation from the set of operators $\{u_n, p_n\}$ to $\{a_q, a_q^\dagger\}$ is

indeed canonical, i.e., that $[a_q, a_{q'}^\dagger] = \delta_{q,q'}$ as well as $[a_q, a_{q'}] = [a_q^\dagger, a_{q'}^\dagger] = 0$

The transformations (*) are inverted as

$$U_n = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} \sqrt{\frac{\hbar}{2M\omega(\mathbf{q})}} e^{i\vec{q}\cdot\vec{r}_n} [a_{\mathbf{q}} + a_{-\mathbf{q}}^\dagger],$$

$$P_n = -\frac{i}{\sqrt{N}} \sum_{\mathbf{q}} \sqrt{\frac{\hbar M\omega(\mathbf{q})}{2}} e^{i\vec{q}\cdot\vec{r}_n} [a_{\mathbf{q}} - a_{-\mathbf{q}}^\dagger].$$

Using the last two expressions, the Hamiltonian H can be recast as

$$H = -\frac{1}{4} \sum_{\mathbf{q}} \hbar\omega(\mathbf{q}) [a_{\mathbf{q}} - a_{-\mathbf{q}}^\dagger][a_{-\mathbf{q}} - a_{\mathbf{q}}^\dagger] + \frac{1}{4} \sum_{\mathbf{q}} \frac{\hbar}{\omega(\mathbf{q})} \frac{C}{M} [a_{\mathbf{q}} + a_{-\mathbf{q}}^\dagger][a_{-\mathbf{q}} + a_{\mathbf{q}}^\dagger][2 - 2\cos(qa)]$$

On a closer look, the last Hamiltonian is diagonalized for

$$\omega(\mathbf{q}) = \frac{2C}{M\omega(\mathbf{q})} (1 - \cos(qa)) \iff$$

$$\omega(\mathbf{q}) = \sqrt{\frac{2C}{M} (1 - \cos(qa))} \iff \boxed{\omega(\mathbf{q}) = 2\sqrt{\frac{C}{M}} \sin\left(\frac{qa}{2}\right)},$$

and reads

$$H = \sum_{\mathbf{q}} \hbar\omega(\mathbf{q}) \left(a_{\mathbf{q}}^\dagger a_{\mathbf{q}} + \frac{1}{2} \right),$$

a sum of the Hamiltonians of N independent linear harmonic oscillators with frequencies $\omega(\mathbf{q})$.

A SIMILAR ANALYSIS, ONLY WITH A MORE COMPLICATED NOTATION, CARRIES OVER TO A 3D CRYSTAL.