

Phonon theory by the Born-von Karman method

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This is the first part of the Phonon chapter for the Neutron Scattering Notes, turning into a textbook. The part is separated because I need to develop the description of the Born-von Karman method - and the full note text takes forever to compile...

1 Lattice vibrations

In chapter ??, we investigated diffraction from the lattice planes of crystals. Here, we worked under the assumption that the nuclei of the crystalline material were fixed in position. This is, of course, not a completely accurate description. In this chapter, we will investigate how the nuclei in the crystal may move coherently - and how this motion will scatter neutrons inelastically. However, as we shall see, the major part of the scattering from a crystal will still take place as the diffraction described in chapter ??.

First, we will treat the physics of lattice vibrations in crystalline materials purely classically, later the result from a quantum mechanical treatment is given, leading to quantized vibrations, or *phonons*. The latter is necessary for the detailed understanding of the inelastic neutron scattering cross section from crystals.

Along with the description of phonons, we will discover how lattice vibrations affect the intensity of the diffraction signals, leading to the Debye-Waller factor, already loosely described in chapter ??.

The quantum mechanical derivation of some of the results in this chapter are presented in chapter ??.

1.1 Lattice vibrations, classical treatment

We will here describe lattice vibrations in general. This section deals with the purely classical description, while section ?? introduces the quantum mechanical treatment that lead to the description of phonons.

Dynamical description of nuclei in crystals

Let us follow the nomenclature from section ?? and denote the equilibrium position of the nuclei with \mathbf{r}_j - or for a non-Bravais lattice $\mathbf{r}_j + \Delta_i$ - with j being the index for the unit cell and i labeling the atom within

the unit cell. These lattice positions are constant in time (assuming that the crystal center-of-mass is at rest). We describe the motion of the nuclei with the (small) displacement vector $\mathbf{u}_{ij}(t)$. The time-dependent nuclear position now reads

$$\mathbf{R}_{ij}(t) = \mathbf{r}_j + \mathbf{\Delta}_i + \mathbf{u}_{ij}(t). \quad (1.1)$$

We approximate the potential energy between two neighbour atoms by a quadratic form in the difference between their displacements:

$$V_{jj'} = \frac{1}{2} K_{jj'} (\mathbf{u}_j(t) - \mathbf{u}_{j'}(t))^2 + V_{0,jj'}, \quad (1.2)$$

where $K_{jj'}$ is the spring constant for the (in this case isotropic) atom-atom interaction. The constant $V_{0,jj'}$ is an unimportant zero point of the energy, which we omit in the following.

This model for describing lattice vibrations was introduced more than a century ago and is known as the Born-von Karman model after its inventors[Born1912].

The one-dimensional nearest neighbour model

We will now start with a few one-dimensional examples, which will give much insight into the physics of lattice vibrations. We first consider a model of N identical particles (atoms) of mass M , with equilibrium spacing a , and identical nearest neighbour spring constants K . This system is illustrated in figure 1.1. The equilibrium distance between atoms is a , so we can write $r_j = ja$.

The net spring force between two particles is zero in equilibrium (where all $u_j = 0$). In the general case, the force on particle j from particle $j + 1$ reads:

$$F_{j,j+1}(t) = K(-u_j(t) + u_{j+1}(t)). \quad (1.3)$$

Including also the similar coupling $F_{j-1,j}(t)$, the equation of motion

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Figure 1.1: A classical illustration of a system showing lattice vibrations in one dimension. A series of equal masses (atoms) are connected by identical harmonic forces and can vibrate around their equilibrium positions.

for u_j can be written using Newton's second law:

$$\begin{aligned} M \frac{d^2}{dt^2} u_j(t) &= -F_{j-1,j}(t) + F_{j,j+1}(t) \\ &= K(u_{j-1}(t) + u_{j+1}(t) - 2u_j(t)). \end{aligned} \quad (1.4)$$

To simplify the calculations, Born and von Karman assumed periodic boundary conditions, *i.e.* we assume that atom 1 is connected with atom N with a force term equivalent to $F_{j,j+1}$. This is equivalent to defining $u_{N+1} \equiv u_1$. The error introduced by this boundary condition will vanish in the thermodynamic limit ($N \rightarrow \infty$) and hence it is safe for us to make this choice that makes the problem mathematically simpler.

We search for solutions to equation (1.4) of the plane wave form

$$u_j(t) = A \exp(iqja - i\omega_q t), \quad (1.5)$$

where the real value of $u_j(t)$ represent the physical displacement, while the imaginary part contains information on the phase of the vibrations. The amplitude for the vibrations, A , can be any complex number. The modulus of A describes the physical amplitude of the vibration and the complex phase represents an overall phase shift of the vibration.

The Born-von Karman periodic boundary condition implies that the phase is invariant under a translation of a distance Na (equal N atom sites). This gives a choice of possible values of the wave vector:

$$q = \frac{l}{N} a^*, \quad (1.6)$$

where l is any integer and the reciprocal lattice constant is $a^* = 2\pi/a$.

Inserting equation (1.5) into (1.4), we reach

$$-\omega_q^2 M u_j(t) = K u_j(t) (\exp(iqa) + \exp(-iqa) - 2). \quad (1.7)$$

This simplifies directly into the dispersion relation we are looking for
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phonon dispersion relation for the one-atom chain]

$$\omega_q^2 = 2\omega_0^2 (1 - \cos(qa)) = 4\omega_0^2 \sin^2(qa/2). \quad (1.8)$$

We have here defined the characteristic frequency, ω_0 , as the resonance frequency of the related single-particle harmonic oscillator, [colback=mintlight!80!,colframe=mint!80!,colbacktitle=mint!80!,coltitle=mintddark!80!,title=mintddark!80!]
particle resonance frequency]

$$\omega_0 = \sqrt{K/M}. \quad (1.9)$$

The dispersion relation for one Brillouin zone, $|\mathbf{q}| \leq \pi/a = |\mathbf{a}^*|/2$, is shown in figure 1.2.

In general, the speed of a wave signal is given as the *group velocity*,

which is in turn given as

$$c(\omega) = \left. \frac{\partial \omega_q}{\partial q} \right|_{\omega}. \quad (1.10)$$

At small q , the dispersion (1.8) is approximately linear, so it is meaningful to define the speed of (low-energy) sound of the lattice vibrations by using equation (1.10) in the limit $\omega \rightarrow 0$:

$$c = \left. \frac{\partial \omega_q}{\partial q} \right|_0 \approx \omega_0 a. \quad (1.11)$$

These long-wavelength lattice vibrations are, in fact, the same as sound waves in materials. Therefore, these types of vibrations are known as *acoustic*. The related low-energy phonons are in analogy with the discussion above denoted *acoustic phonons*.

Optical lattice vibrations

When considering a crystal with more than one atom in the unit cell acoustic vibrations are no longer the only type of solution to the equations of motion. We will illustrate this with a simple example.

A symmetry breaking in the Bravais crystal can cause a doubling of the unit cell, $a_2 = 2a$, even if it may have little effect on the vibration physics. This leads to reduction of the Brillouin zone by a factor 2, $a_2^* = a^*/2$. The vibration modes are now denoted differently. The part of the dispersion relation that has the highest values of $|q|$ is “folded back” by a reciprocal lattice vector, $q_2 = q - a_2^*$, in effect creating a second branch of the dispersion relation. This new branch is now denoted the *optical branch*. The optical and acoustic branches of the simple one-dimensional example are shown in figure 1.2.

The optical mode for $q = 0$ is particularly easy to interpret: In the system with a one-atom unit cell, this would correspond to a vibration with a wave vector at the zone boundary: $q = \pi/a$. However, with a two-atom unit cell, all unit cells behave identically, while the two atoms in the unit cell vibrate in counter phase. The frequency at this position is $\omega_{\pi/a} = 2\omega_0$.

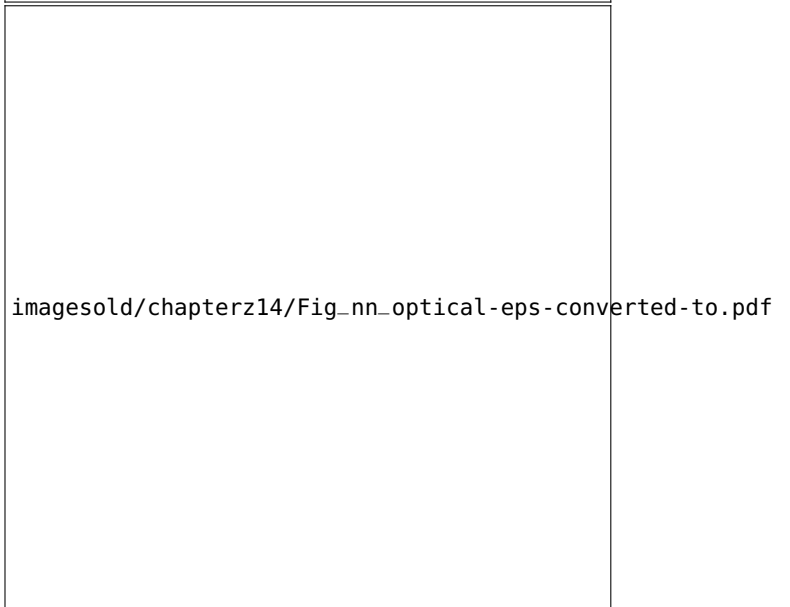


Figure 1.2: (top) dispersion relation for the nearest neighbour one-dimensional lattice model within one Brillouin zone. (bottom) dispersion relation for the nearest neighbour one-dimensional phonon model when the unit cell is doubled without change in the vibration physics. This means that the reciprocal lattice vector is halved with respect to the top panel, $a_2^* = a^*/2$. Note the occurrence of a low (acoustic) and a high (optical) branch.

For the sake of consistency, let us calculate the above result explicitly. To describe this motion quantitatively, we denote the displacement of the first atom in the j 'th unit cell $u_j(t)$, while the second atom is denoted $v_j(t)$. The equations of motion now read

$$\begin{aligned} M \frac{d^2}{dt^2} u_j(t) &= K(v_{j-1}(t) + v_j(t) - 2u_j(t)), \\ M \frac{d^2}{dt^2} v_j(t) &= K(u_{j+1}(t) + u_j(t) - 2v_j(t)). \end{aligned} \quad (1.12)$$

Since $q = 0$, the motion is independent of j . Hence, we can reduce the expression to:

$$\begin{aligned} \omega^2 u(t) &= 2\omega_0^2 (u(t) - v(t)), \\ \omega^2 v(t) &= 2\omega_0^2 (v(t) - u(t)). \end{aligned} \quad (1.13)$$

This is the same equation of motion as for two identical particles connected by one spring with strength $2K$. When we take into account that the two atoms in the unit cell move in counter phase, we have $u(t) = -v(t)$, leading to $\omega = 2\omega_0$, as we aimed to show.

In general, for a crystal with n atoms in the unit cell, there will be 1 acoustic and $n - 1$ optical vibration modes, which will in general all vary with the wave vector, \mathbf{q} .

One-dimensional models with two different atoms


Let us now treat the one-dimensional system with identical springs of constant K , but two different atoms per unit cell. This is illustrated in figure 1.3.

The masses of the two atoms are denoted m and M , respectively, with M being the largest of the two. We define

$$\beta = \frac{m}{M} < 1, \quad (1.14)$$

and ω_0 is defined as in equation (1.9).

Solving the equations of motion for the two atoms (see problem ??), we reach the dispersion relation [colback=mintlight!80!,colframe=mint!80!,



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Figure 1.3: The two-atom phonon problem in one dimension. Two different masses (atoms) are connected by identical harmonic forces (springs).

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$$\omega_q^2 = 2\omega_0^2(1 - \cos(qa/2)\alpha^{-1}), \quad (1.15)$$

where α is the ratio of vibration amplitudes for the two types of atoms:

$$\alpha = \frac{1 - \beta \pm \sqrt{(1 - \beta)^2 + 4\beta \cos^2(qa/2)}}{2 \cos(qa/2)}. \quad (1.16)$$

For $q \rightarrow 0$, we have the two solutions $\alpha_1 = 1$, long-wave acoustic phonons; and $\alpha_2 = -\beta$, the $q = 0$ optical phonons, where the atoms move in counter phase and the light atoms vibrate with a larger amplitude. The resulting dispersion relation for $\beta = 1/3$ is shown in figure 1.4. We notice that a gap has now opened at the zone boundary between the two modes. This is a typical feature for (the vast majority of) crystals that contain different atomic species

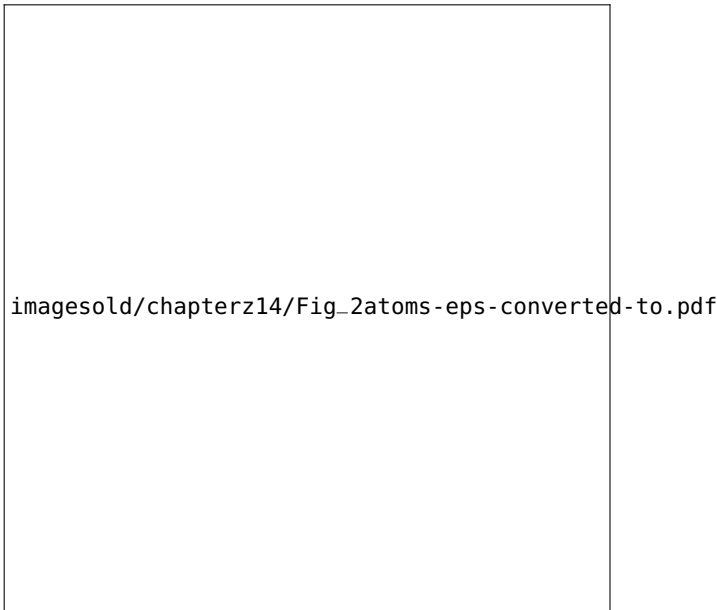


Figure 1.4: Dispersion relation for the simple two-atom one-dimensional phonon model with $\beta = 1/3$.

Lattice vibrations in three dimensions, overview

We here describe the main characteristics of three-dimensional lattice vibrations. For a description of the model and calculations behind the results, we refer to subsection 1.1. The solution is very similar to the one-dimensional case, except that the phonons now have both a (three-dimensional) \mathbf{q} and a polarization vector, $\mathbf{e}_{\mathbf{q},p}$, which represents the direction of the vibration that depend on both the wave vector, \mathbf{q} , and the mode index p .

In general, there are two types of polarization:

- **Longitudinal.** The polarization vector $\mathbf{e}_{\mathbf{q},p}$ is parallel to \mathbf{q} .
- **Transverse.** The two polarization vectors $\mathbf{e}_{\mathbf{q},p}$ are perpendicular to \mathbf{q} . Usually, these modes have lower energies than the longitudinal ones.

For a non-Bravais lattice with n atoms per unit cell, there are only 3 acoustic modes: 1 longitudinal and 2 transverse. The remaining $3(n - 1)$ are optical modes with a non-zero frequency (often a local

maximum) at $q = 0$. Typical sets of phonon dispersion curves for a two-atom unit cell (Si) and a four-atom unit cell (graphite) are presented in the example section.

Lattice vibrations in three dimensions, Born-von Karman treatment

The problems of three-dimensional phonons was first tackled by Born and von Karman [Born1912] and is also treated in a number of textbooks, *e.g.* in Squires, Appendix G [squires] (CHECK). We here present a simplified version of the calculations. This section may, however, be skipped by students less interested in the mathematical details, since the main points were already mentioned in the previous section.

Within the Born-von Karman model, we assume that forces in all three dimensions depend linearly on the displacement of atoms from the equilibrium positions, *i.e.* relative to the positions of their neighbouring atoms. However, in general we must expect cross terms, *e.g.* that a displacement along the x -direction could give a force component also in the y -direction. We thus write the force equation analogous to (1.3) as

$$F_{ij}^\alpha(t) = \Phi_{ij}^{\alpha\beta} \times (-u_i^\beta(t) + u_j^\beta(t)), \quad (1.17)$$

where α and β are cartesian coordinates and Φ_{ij} represent the three dimensional force constant matrix between atoms i and j . As before, we set up Newtons second law for each atom:

$$M_i \frac{d^2 \mathbf{u}_i(t)}{dt^2} = \sum_j F_{ij}^\alpha(t). \quad (1.18)$$

We now assume that the motion of the atoms consists of harmonic plane waves with propagation vector \mathbf{q} and frequency $\omega_{q,p}$. We also assume that the lattice is a Bravais lattice, *i.e.* one atom per unit cell. With these assumptions, one can reach an equation of motion, analogous with (1.7) of the one-dimensional system: (MAKE A PROBLEM OUT OF THIS)

$$M\omega_{q,p}^2 u_j^\alpha(t) = \sum_\beta D^{\alpha\beta}(\mathbf{q}) u_j^\beta(t), \quad (1.19)$$

where the Fourier transformed force constants are given by [svensson67]

$$D^{\alpha\beta}(\mathbf{q}) = \sum_j \Phi_{0,j}^{\alpha\beta} \times (1 - \cos(\mathbf{q} \cdot \mathbf{r}_j)), \quad (1.20)$$

(CHECK THE SIGN - IT IS OPPOSITE FROM THE REFERENCE). The solution to the equation-of-motion (1.19) is found for each value of \mathbf{q} by finding the three directions $\mathbf{e}_{q,p}$ that are eigenvectors to the matrix equation (1.19), as well as the corresponding eigenfrequencies, $\omega_{q,p}$. This is equivalent to solving the determinant equation

$$0 = \left| D^{\alpha\beta}(\mathbf{q}) - M\omega_{q,p}\delta_{\alpha\beta} \right|, \quad (1.21)$$

where $\delta_{\alpha\beta}$ is the Kronecker delta function that assumes a value of unity if α and β are equal, zero otherwise.

? AND THEN WHAT TO DO IF THIS IS NOT A BRAVAIS LATTICE ? YOU ARE JUGGLING BOTH CARTESIAN COORDINATES AND UNIT CELL COORDINATES - DOES THIS BECOME 4D TENSORS ???

The role of lattice vibrations in materials

The lattice vibrations determine a number of properties of materials. A straightforward example is the acoustic properties, where the long-wavelength acoustic lattice vibrations are equal to sound waves.

An important consequence of the lattice vibrations is the thermodynamic properties of materials. In fact the heat capacity and thermal conductivity in insulating materials stem from the lattice vibrations. As we will show in detail in the optional section ??, the lattice vibrations quantize in energy units of $\hbar\omega_q$. These *quasiparticles* are denoted *phonons* and are approximately Bosons, *i.e.* there can be several phonons with the same \mathbf{q} and p ; a larger number of phonons corresponds to larger classical vibration amplitudes. The occupation numbers of phonons are thus given by Bose-Einstein statistics,

$$n_{q,p} = n_B(\hbar\omega_{q,p}/k_B T). \quad (1.22)$$

where n_B is the Bose occupation number

$$n_B \left(\frac{\hbar\omega}{k_B T} \right) = \frac{1}{\exp \left(\frac{\hbar\omega}{k_B T} \right) - 1}. \quad (1.23)$$

These equations form, together with knowledge of the dispersion relation, $\omega_{q,p}$, the basis for the description of the thermal properties of phonons, which is elaborated on in many textbooks of condensed matter physics, *e.g.* the one by Kittel [Kittel]. For the thermal conductivity, also the phonon life time is important. This can be found by measuring the phonon spectra, since a finite life time will result in an energy broadening, from the Heisenberg uncertainty relations, $\delta E \delta t \leq \hbar/2$.

Another aspect phonon science is the study of crystal anharmonicities, caused by higher order terms in the atomic potentials. Anharmonicities give rise to *e.g.* thermal expansion, and can be inferred from studies of phonon lifetimes. This is, however, beyond the scope of these notes.

Phonons also contribute strongly to electrical conductivity, since collision between conduction electrons and phonons will give a contribution to the material resistivity. This is the reason why resistivity in metals in general decrease upon cooling. On the other hand, phonons can serve as a "glue" that at very low temperature in some metals will serve to form "Cooper pairs" of electrons that will in turn lead to superconductivity.

Is it therefore in general of large importance to know details of the phonon dispersion relations in order to understand physical properties of materials and their temperature dependence.

1.2 Examples

TO BE MERGED WITH THE EXISTING EXAMPLES SECTION.

In 1967, Svensson, Brockhouse, and Rowe published a study of the phonon spectrum in Cu metal [svensson67]. The study was performed at a thermal-neutron triple-axis spectrometer at Chalk River (CAN) and showed very clearly the dispersion relations of the two transverse

n	\mathbf{r}_n/a	$K_{n,l}$ [N/m]	$K_{n,t}$ [N/m]
1	(1/2 1/2 0)	28.02	-1.07
2	(1 0 0)	0.20	-0.19
3	(1 1/2 1/2)	0.0	0.0
4	(1 1 0)	0.53	-0.30

Table 1.1: Born-von Karman force constants for metallic copper, listed as transverse and longitudinal force constants, K_t and K_l , respectively. Adapted from Ref. [svensson67].

and one longitudinal phonon branches in the fcc Bravais lattice of copper. In the study, the authors convert their measured dispersion relations into Born-von Karman force constants for up to 8th nearest neighbours. We here deal with the 1st and 2nd neighbours only and present the force constants in table 1.1. We see that the dominating force is, as expected, the 1st neighbour longitudinal force.

Figure 1.5 compares the measured phonon dispersion along the [1 1 0] direction with the results of the Born-von Karman model (1.19) using only the two nearest neighbour interactions. The figure also shows the direction cosines of the three branches, separating the longitudinal branch from the transverse ones. We see that the model corresponds to the measurements, although the match is not perfect, with deviations of the 3% level. For a more precise modeling, see the full 8th neighbour treatment in the original publication [svensson67].

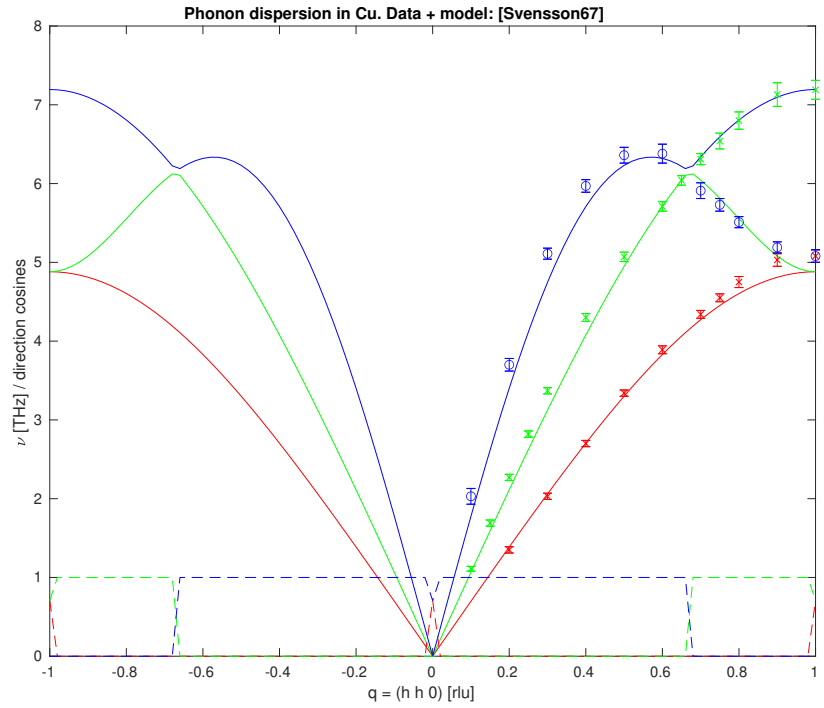


Figure 1.5: Measured phonon dispersion in Cu (points) along the $[1\ 1\ 0]$ direction. The full lines show a model of the dispersion calculated from the 1st and 2nd neighbour Born-von Karman force constants, listed in Table 1.1. The dashed lines show the direction cosines of the three eigenmodes; a value of unity reveals the longitudinal mode.