

# Chapter 1

## Phonons and lattice dynamics

### 1.1 Vibration modes of a cluster

Consider a cluster or a molecule formed of an assembly of atoms bound due to a specific potential. First, the structure must be relaxed to its ground state, or at least a local minimum. This can be done numerically by several local optimization methods. The most widely used methods are steepest descent (SD), conjugate gradients (CG) and quasi-Newton (QN). Once the local minimum is reached, one can expand the potential energy about this minimum in terms of the powers of atomic displacements. Since all forces on all atoms are zero, the Taylor expansion does not have linear terms. The Harmonic approximation (HA) consists in neglecting all the powers of displacements larger or equal to 3. Being at a local minimum, the matrix of second derivatives must be positive definite, and thus will have only positive eigenvalues. The potential energy thus becomes:

$$E(r_1, \dots, r_N) = E_0 + \frac{1}{2} \sum_{\tau, \tau'} \Phi_{\tau, \tau'} \mathbf{u}_\tau \mathbf{u}_{\tau'} \quad (1.1)$$

where  $\mathbf{u}$  is the “small” displacement vector from the equilibrium position:  $\mathbf{r}_i(t) = \mathbf{R}_i^0 + \mathbf{u}_\tau(\mathbf{t})$ , and the label  $\tau = (i, \alpha)$  refers to an atom  $i$  and the cartesian component  $\alpha$  of its displacement. For an  $N$  atom cluster in 3D,  $\tau$  varies from 1 to  $3N$ , and  $\Phi$  is a  $3N \times 3N$  matrix. The latter is the second derivative of the potential energy evaluated at the equilibrium position and is called the **force constants matrix**.

$$\Phi_{\tau, \tau'} = \frac{\partial^2 E}{\partial \mathbf{u}_\tau \partial \mathbf{u}_{\tau'}} = -\frac{\partial \mathbf{F}_\tau}{\partial \mathbf{u}_{\tau'}} = -\frac{\partial \mathbf{F}_{\tau'}}{\partial \mathbf{u}_\tau} = \Phi_{\tau', \tau}$$

### 1.1.1 Symmetries of the force constants

Apart from the invariance under permutation of atoms expressed above, which comes from the fact that the total energy is an analytic function of the atomic coordinates, there are other relations between different elements of this tensor due to symmetries of the system. An important relation satisfied by the force constants comes from the translational invariance of the potential energy: under any arbitrary translation, the potential energy and the forces should remain the same:  $E(\mathbf{u} + \mathbf{c}) = E(\mathbf{u})$ ;  $\mathbf{F}(\mathbf{u} + \mathbf{c}) = \mathbf{F}(\mathbf{u})$ . Substituting for the forces its harmonic expression, we find:

$$\sum_{\tau'} \Phi_{\tau, \tau'} \mathbf{u}_{\tau'} = \sum_{\tau'} \Phi_{\tau, \tau'} (\mathbf{u}_{\tau'} + \mathbf{c})$$

implying, since the displacements are arbitrary:

$$\sum_{\tau'} \Phi_{\tau, \tau'} = 0 \quad (1.2)$$

This relation defines the diagonal element of the force constant matrix as a function of its non-diagonal elements:  $\Phi_{\tau, \tau} = -\sum_{\tau' \neq \tau} \Phi_{\tau, \tau'}$  meaning that, effectively, the atom  $\tau$  is bound by a spring to its equilibrium position.

Other relations come from symmetry operations, such as rotations or mirror symmetries, which leave the molecule invariant. If such a symmetry operation is denoted by  $\mathcal{S}$ , we must have

$$\Phi_{\mathcal{S}\tau, \mathcal{S}\tau'} = \Phi_{\tau, \tau'}$$

As  $\Phi$  is a second rank tensor, we have by definition:

$$\Phi_{\mathcal{S}\tau, \mathcal{S}\tau'}^{\alpha, \beta} = \sum_{\alpha', \beta'} \Phi_{\tau, \tau'}^{\alpha', \beta'} \mathcal{S}_{\alpha, \alpha'} \mathcal{S}_{\beta, \beta'} = \Phi_{\tau, \tau'}^{\alpha, \beta}$$

where  $\mathcal{S}_{\alpha, \alpha'}$  are the 3x3 matrix elements of the operation  $\mathcal{S}$ . The above relation implies that for any symmetry operation, the matrix of the force constants must commute with that of  $\Phi$ .

### 1.1.2 Classical theory of vibrations

Given the expression for the potential energy as a function of displacements, it is an easy task to derive the Newtonian equations of motion:

$$m_{\tau} \frac{d^2 \mathbf{r}_{\tau}(t)}{dt^2} = \mathbf{F}_{\tau} \simeq - \sum_{\tau'} \Phi_{\tau \tau'} [\mathbf{r}_{\tau'}(t) - \mathbf{R}_{\tau'}^0] = - \sum_{\tau'} \Phi_{\tau \tau'} \mathbf{u}_{\tau'}(t) \quad (\forall \tau \in \{1, \dots, 3N\}), \quad (1.3)$$

This formula is linear in the atomic coordinates, and can be interpreted, within the harmonic approximation, as the particles being connected by “springs”. A (harmonic) solution of the form  $\mathbf{u}_\tau(t) = \mathbf{e}_\tau \cos(\omega t + \phi)$  can be substituted in (1.3). The resulting set of linear equations in the amplitudes  $\mathbf{e}_\tau$  and frequencies  $\omega$  define the vibrational modes of the system. First to make the system of equations symmetric, one needs to make a change of variable by setting  $\sqrt{m_\tau} \mathbf{u}_\tau = \mathbf{v}_\tau$ . The resulting equations on  $\mathbf{v}_\tau$  become:

$$\sum_{\tau'} \left( \frac{\Phi_{\tau\tau'}}{\sqrt{m_\tau m_{\tau'}}} - \omega^2 \delta_{\tau\tau'} \right) \mathbf{v}_{\tau'} = 0 \quad (\forall \tau \in \{1, \dots, 3N\}). \quad (1.4)$$

This linear system has a nonzero solution for  $\mathbf{e}$  if the determinant of the matrix  $\Phi_{\tau\tau'}/\sqrt{m_\tau m_{\tau'}} - \omega^2$  is equal to zero. Consequently, the square of the vibrational frequencies of the cluster are the eigenvalues of the matrix  $\Phi_{\tau\tau'}/\sqrt{m_\tau m_{\tau'}}$ . The system is  $3N \times 3N$ , in three dimensions, and has  $3N$  eigenvalues, six of which will be due to pure translations (3) and rotations (3), and therefore equal to zero. All the rest are positive, reflecting the fact that the total energy was a minimum and any deviation of the atoms from their equilibrium position results in an increase in  $E$  (in other words,  $\Phi$  is positive definite). For each eigenvalue  $\omega_\lambda$ , there is an eigenvector of  $3N$  components, defined by  $\mathbf{e}_\tau^\lambda$ , which is also called the **normal mode**. For this mode  $\lambda$ , the polarization vector  $\mathbf{e}_\tau^\lambda$  can be represented by  $N$  three-dimensional vectors associated with the  $N$  atoms in the cluster, and showing the amplitude and the direction along which the atom  $\tau$  oscillates in that mode  $\lambda$ .

$$\sum_{\tau'} \frac{\Phi_{\tau\tau'}}{\sqrt{m_\tau m_{\tau'}}} \mathbf{e}_{\tau'}^\lambda = \omega_\lambda^2 \mathbf{e}_\tau^\lambda \quad (1.5)$$

Furthermore the eigenvectors  $\mathbf{e}$  being a complete orthonormal set satisfy two relations of orthonormality and completeness:

$$\sum_{\tau} \mathbf{e}_\tau^\lambda \mathbf{e}_\tau^{\lambda'} = \delta_{\lambda,\lambda'} \quad \text{orthonormality} \quad (1.6)$$

$$\sum_{\lambda} \mathbf{e}_\tau^\lambda \mathbf{e}_{\tau'}^\lambda = \delta_{\tau,\tau'} \quad \text{completeness} \quad (1.7)$$

A general displacement of the atoms defined by the two initial conditions on positions and velocities and the equations of motion, can be expanded on the set of eigenvectors which form a complete orthonormal basis of the

3N-dimensional space:

$$\mathbf{u}_\tau(t) = \frac{1}{\sqrt{m_\tau}} \sum_{\lambda=1}^{3N} A_\lambda \mathbf{e}_\tau^\lambda \cos(\omega_\lambda t + \phi_\lambda)$$

where the 6N coefficients  $(A_\lambda, \phi_\lambda)$  must be determined from the 6N initial conditions on positions and velocities of the particles. The eigenvectors not only give information about the polarization of the mode, but also allow one to calculate mechanical properties of the system under study. They can also be used to calculate infrared (IR) or Raman active spectra of molecules if information on the induced charge distribution (dipole moment in the case of IR, and polarizability in case of Raman) under that mode are available. From the frequencies, one can deduce a criterion for mechanical stability: if the lowest eigenvalue is small, this means the period of the oscillations for that mode is large, and the corresponding increase of the energy is small (since it depends on  $m\omega^2\mathbf{e}^2/2$ ), or, in other words, the mode is *soft*. The softening of a mode ( $\omega \rightarrow 0$ ) is a signature of its becoming mechanically unstable, and thus leading to a phase transition.

### 1.1.3 Quantum theory of vibrations of a cluster

It is also possible to obtain the vibrational frequencies of a cluster by using the quantum formalism and start from the Hamiltonian of the system. For the sake of completeness, we will derive phonon<sup>1</sup> frequencies from both methods. Again, using the Harmonic approximation, we keep up to second order terms in the potential energy of the particles, and write the Hamiltonian as follows:

$$\mathcal{H} = \sum_{\tau} \frac{\mathbf{P}_\tau^2}{2m_\tau} + \frac{1}{2} \sum_{\tau\tau'} \Phi_{\tau\tau'} \mathbf{u}_\tau \mathbf{u}_{\tau'} \quad (1.8)$$

The index  $\tau$ , as before, labels the atom and its cartesian component and goes from 1 to 3N. This is a system of 3N coupled harmonic oscillators. To solve it, we can first make the change of variable  $\sqrt{m_\tau} \mathbf{u}_\tau = \mathbf{v}_\tau$ . The corresponding conjugate momenta become  $\mathbf{Q}_\tau = -i\partial/\partial\mathbf{v}_\tau = \mathbf{P}_\tau/\sqrt{m_\tau}$ , and the Hamiltonian, in terms of  $\mathbf{v}_\tau, \mathbf{Q}_\tau$  becomes:

$$\mathcal{H} = \frac{1}{2} \sum_{\tau} \mathbf{Q}_\tau^2 + \frac{1}{2} \sum_{\tau\tau'} \frac{\Phi_{\tau\tau'}}{\sqrt{m_\tau m_{\tau'}}} \mathbf{v}_\tau \mathbf{v}_{\tau'} \quad (1.9)$$

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<sup>1</sup>The word phonon is actually mostly used for quanta of vibrations in crystals.

As before, one can diagonalize the matrix  $D_{\tau\tau'} = \Phi_{\tau\tau'}/\sqrt{m_\tau m_{\tau'}}$  and write the Hamiltonian in the basis of its eigenvectors, which are real since  $D$  is symmetric:

$$\sum_{\tau'} D_{\tau\tau'} \mathbf{e}_{\tau'}^\lambda = \omega_\lambda^2 \mathbf{e}_\tau^\lambda$$

Using  $\mathbf{v}_\tau = \sum_{\lambda=1}^{3N} v_\lambda \mathbf{e}_\tau^\lambda$ , with  $v_\lambda = \sum_\tau \mathbf{v}_\tau \cdot \mathbf{e}_\tau^\lambda$ , and taking  $v_\lambda$  as the new dynamical variables having as conjugate momenta  $\pi_\lambda = -i\partial/\partial v_\lambda = \sum_\tau \mathbf{Q}_\tau \cdot \mathbf{e}_\tau^\lambda$ , then the Hamiltonian can be rewritten in terms of  $(v_\lambda, \pi_\lambda)$ . To write  $\mathbf{Q}_\tau$  in terms of  $\pi_\lambda$  one needs to invert  $\mathbf{e}_\tau^\lambda$  which can be thought of as a matrix of row index  $\tau$  and column index  $\lambda$ . It is the matrix of the eigenvectors which is also the orthogonal matrix that takes one from the “ $\tau$ ” basis to the “ $\lambda$ ” basis. Its inverse is its transpose as one can also see from the completeness relation<sup>1,7</sup> We have therefore  $\mathbf{Q}_\tau = \sum_\lambda \mathbf{e}_\tau^\lambda \pi_\lambda$ , and using the orthogonality of the eigenvectors  $\sum_\tau \mathbf{e}_\tau^\lambda \mathbf{e}_\tau^{\lambda'} = \delta_{\lambda\lambda'}$ , the Hamiltonian becomes:

$$\mathcal{H} = \sum_\lambda \frac{\pi_\lambda^2}{2} + \frac{1}{2} \sum_\lambda \omega_\lambda^2 v_\lambda^2 \quad (1.10)$$

which is now a set of  $3N$  **decoupled** oscillators each oscillating independently with the frequency  $\omega_\lambda$ . The eigenvalues of  $\mathcal{H}$  are well-known<sup>2</sup>:

$$\sum_{\lambda=7}^{3N} \hbar \omega_\lambda \left( n_\lambda + \frac{1}{2} \right)$$

and from it, one can easily extract thermodynamic properties within the harmonic approximation. The expression for the displacement operator becomes now:

$$\mathbf{u}_\tau(t) = \sum_{\lambda=7}^{3N} \sqrt{\frac{2}{m_\tau \omega_\lambda}} \mathbf{e}_\tau^\lambda (a_\lambda e^{-i\omega_\lambda t} + a_\lambda^\dagger e^{i\omega_\lambda t}) \quad (1.11)$$

## 1.2 Thermodynamic properties of a cluster

In general, it is difficult to calculate thermodynamic properties such as entropy or free energy of a cluster or a molecule. At very low temperatures, however, it is possible to use the harmonic approximation, and calculate exactly these properties. As the system of coupled oscillators was reduced to

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<sup>2</sup>To consider purely vibrational states for a cluster, we need to exclude the 6 rotational and translational modes with frequency zero, and strictly sum  $\lambda$  from 7 to  $3N$

$3N - 6$  uncoupled ones, the partition function of the system is therefore the product of the partition functions for each normal mode, and the free energy is the sum of the free energies. For a single harmonic oscillator, we have:

$$Z = \sum_{n=0}^{\infty} e^{-\beta \hbar \omega (n+1/2)} = e^{-\beta \hbar \omega / 2} \frac{1}{1 - e^{-\beta \hbar \omega}} = \frac{1}{2 \sinh(\beta \hbar \omega / 2)}$$

where the geometric series converged due to positivity of the frequency  $\omega$ . The free energy is  $F = -k_B T \ln Z = k_B T \ln 2 \sinh(\beta \hbar \omega / 2)$  so that for a general molecule with many degrees of freedom, we can write

$$Z_{vib} = \prod_{\lambda}^{vib} \frac{1}{2 \sinh(\beta \hbar \omega_{\lambda} / 2)} \quad (1.12)$$

$$F = k_B T \sum_{\lambda} \ln 2 \sinh(\beta \hbar \omega_{\lambda} / 2) \quad (1.13)$$

$$E = \sum_{\lambda} \frac{1}{2} \coth(\beta \hbar \omega_{\lambda} / 2) \hbar \omega_{\lambda} = \sum_{\lambda} (n_{\lambda} + \frac{1}{2}) \hbar \omega_{\lambda} \quad (1.14)$$

$$\frac{S}{k_B} = \frac{E - F}{k_B T} = \sum_{\lambda} \beta \hbar \omega_{\lambda} / 2 \coth(\beta \hbar \omega_{\lambda} / 2) - \ln 2 \sinh(\beta \hbar \omega_{\lambda} / 2) \quad (1.15)$$

Note that the above formulas are only the contributions of the vibrational degrees of freedom, and must also add to them the rotational and translational free/total energies:

$$Z = Z_{vib} Z_{rot} Z_{trans}; \quad F = F_{vib} + F_{rot} + F_{trans} \dots$$

### 1.3 Vibration modes of a crystal

The treatment of a crystal is very similar to that of a cluster except that the number of atoms, or degrees of freedom becomes infinite. In this case, use has to be made of symmetry properties of the crystal, namely translational invariance, to simplify the decoupling problem. As mentioned in the case of a cluster, in the harmonic approximation, the Hamiltonian is quadratic, and therefore exactly solvable. This is called the **non-interacting** problem, because in principle, one can reduce it to a set of uncoupled harmonic oscillators. The interacting problem of lattice dynamics will consist in including higher anharmonic terms in the potential energy of the lattice. Perturbation theory is the most widely used method to treat this problem, but we will not discuss these methods here.

### 1.3.1 Classical theory of lattice vibrations

As in the case of a cluster, one can get rid of unequal masses by making a first change of variables from the displacements  $\mathbf{u}$  to  $v = \mathbf{u}\sqrt{m}$ , at the cost of modifying the force constant matrix from  $\Phi$  to  $\Phi_{\tau,\tau'}/\sqrt{m_\tau m_{\tau'}}$ . Formally one can write this change of variable as:

$$M \frac{d^2 \mathbf{u}}{dt^2} = -\Phi \mathbf{u} \iff \frac{d^2(\sqrt{M} \mathbf{u})}{dt^2} = -\sqrt{M^{-1}} \Phi \sqrt{M^{-1}} (\sqrt{M} \mathbf{u})$$

where  $\sqrt{M}$  is the matrix with atomic masses on its diagonal. Next, using invariance of the crystal under discrete translation by vectors  $\mathbf{R}$ , we have  $\Phi_{\mathbf{R}\tau,\mathbf{R}'\tau'} = \Phi_{\mathbf{R}-\mathbf{R}',0\tau\tau'}$ , where each atom is identified by the unit cell it is in (denoted by the translation vector  $\mathbf{R}$ ), and its label within the unit cell (denoted by  $\tau$ , including, as in the case of clusters, the cartesian component of the displacement, so that  $\tau$  runs from 1 to  $3p$ ,  $p$  being the number of atoms per unit cell).

Now we can use Bloch's theorem and go to new variables. The displacements  $\mathbf{u}$  about the equilibrium position for an atom  $\tau$  in the cell defined by the translation vector  $\mathbf{R}$  can be written as

$$\mathbf{u}_{\tau\mathbf{R}}(t) = \sum_{\mathbf{k}} \frac{1}{\sqrt{Nm_\tau}} \mathbf{u}_{\tau\mathbf{k}}(t) e^{i\mathbf{k}\cdot\mathbf{R}}. \quad (1.16)$$

the sum over  $\mathbf{k}$  being restricted to the first Brillouin zone (FBZ). Note that the above definition of  $\mathbf{u}_{\tau\mathbf{k}}$  has the periodicity of the reciprocal space:  $\mathbf{u}_{\tau\mathbf{k}} = \mathbf{u}_{\tau\mathbf{k}+\mathbf{G}}$ . Substituting this into the expansion of the potential energy in powers of the displacements about the equilibrium positions, and truncating the sum at the second powers of  $\mathbf{u}$  (harmonic approximation), we find

$$\begin{aligned} E - E_0 &= \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}',\tau\tau'} \mathbf{u}_{\tau\mathbf{R}} \mathbf{u}_{\tau'\mathbf{R}'} \Phi_{\mathbf{R}\tau,\mathbf{R}'\tau'} \quad (1.17) \\ &= \frac{1}{2N} \sum_{\mathbf{R}\mathbf{R}'\mathbf{k}\mathbf{k}'\tau\tau'} \mathbf{u}_{\tau\mathbf{k}} \mathbf{u}_{\tau'\mathbf{k}'} \frac{\Phi_{\mathbf{R}-\mathbf{R}',0\tau\tau'}}{\sqrt{m_\tau m_{\tau'}}} e^{i\mathbf{k}\cdot\mathbf{R}} e^{i\mathbf{k}'\cdot\mathbf{R}'} \\ &= \frac{1}{2N} \sum_{\mathbf{k}\mathbf{k}'\tau\tau'} \mathbf{u}_{\tau\mathbf{k}} \mathbf{u}_{\tau'\mathbf{k}'} \left( \sum_{\mathbf{R}} \frac{\Phi_{\mathbf{R},0\tau\tau'}}{\sqrt{m_\tau m_{\tau'}}} e^{i\mathbf{k}\cdot\mathbf{R}} \right) \left( \sum_{\mathbf{R}'} e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{R}'} \right) \\ &= \frac{1}{2} \sum_{\mathbf{k}\tau\tau'} \mathbf{u}_{\tau\mathbf{k}} \mathbf{u}_{\tau'-\mathbf{k}} \left( \sum_{\mathbf{R}} \frac{\Phi_{\mathbf{R},0\tau\tau'}}{\sqrt{m_\tau m_{\tau'}}} e^{i\mathbf{k}\cdot\mathbf{R}} \right) \\ &= \frac{1}{2} \sum_{\mathbf{k}} \left[ \sum_{\tau\tau'} \mathbf{u}_{\tau\mathbf{k}} \mathbf{u}_{\tau'-\mathbf{k}} D_{\tau\tau'}(\mathbf{k}) \right]. \end{aligned}$$

The second line was obtained using the translational invariance of the force-constants matrix  $\Phi$ , implying that it depends only on the distance between the two cells, and the last line maybe taken as the definition of the dynamical matrix  $D$ . Note that this definition of  $D$  is very similar to the definition of the Hamiltonian matrix in the tight-binding formalism??, which contained a sum of the neighboring cells of a short-ranged matrix. In the case of TB, the short-ranged matrix was that of the Hamiltonian, and in the case of lattice dynamics, it is that of the force constants which also extends to the neighboring atoms only. Note that similar to the TB case,  $D(-\mathbf{k}) = D(\mathbf{k})^*$  implying, since both have the same set of eigenvalues, that the eigenvalues  $\omega_{\lambda\mathbf{k}}$  are even functions of  $\mathbf{k}$ . Note that here again, using the “Bloch” transformation, one was able to do the uncoupling in the  $\mathbf{k}$  space and change the force constants matrix to the dynamical matrix which is block-diagonal in the  $\mathbf{k}$  space, meaning that it does not couple  $\mathbf{k}$  to any other vector  $\mathbf{k}'$  within the first Brillouin zone. A last remark concerns the correspondance between the eigenvalues:  $\epsilon_\lambda \Leftrightarrow \omega_\lambda^2$  where both have a quadratic dispersion near  $\mathbf{k} = 0$ , implying that the phonon dispersion at the  $\Gamma$  point is linear in  $\mathbf{k}$  for acoustic modes. This will be discussed in more detail in the next section where an example will illustrate better this theory.

Now that modes of different  $\mathbf{k}$  are separated, and one can diagonalize the hermitian matrix  $D_{\tau\tau'}(\mathbf{k})$  for each  $\mathbf{k}$  in the FBZ:

$$\sum_{\tau'} D_{\tau\tau'}(\mathbf{k}) \mathbf{e}_{\tau'}^\lambda(\mathbf{k}) = \omega_{\lambda\mathbf{k}}^2 \mathbf{e}_\tau^\lambda(\mathbf{k}) \Rightarrow D_{\tau\tau'}(\mathbf{k}) = \sum_\lambda \omega_{\lambda\mathbf{k}}^2 \mathbf{e}_\tau^\lambda(\mathbf{k}) \mathbf{e}_{\tau'}^\lambda(\mathbf{k})^\dagger \quad (1.18)$$

where, similar to the case of a crystal, we have a completeness and orthonormality constraint on the eigenvectors of  $D$ , which are now complex. They form therefore a unitary matrix, as opposed to a orthogonal one in the case of a cluster. The two constraints can be written as:

$$\begin{aligned} \sum_\tau \mathbf{e}_\tau^\lambda(\mathbf{k})^\dagger \mathbf{e}_\tau^{\lambda'}(\mathbf{k}) &= \delta_{\lambda,\lambda'} \text{ orthonormality} \\ \sum_\lambda \mathbf{e}_\tau^\lambda(\mathbf{k}) \mathbf{e}_{\tau'}^\lambda(\mathbf{k})^\dagger &= \delta_{\tau,\tau'} \text{ completeness} \end{aligned} \quad (1.19)$$

Recall that the vector  $\mathbf{e}^\lambda(\mathbf{k})^\dagger$  is the transpose and conjugate of  $\mathbf{e}^\lambda(\mathbf{k})$ , and that changing  $\mathbf{k}$  to  $-\mathbf{k}$  transforms  $\mathbf{e}$  to  $\mathbf{e}^*$ . One can finally write the potential energy in the new basis as:

$$E - E_0 = \frac{1}{2} \sum_{\mathbf{k}\lambda} \mathbf{u}_{\lambda\mathbf{k}} \mathbf{u}_{\lambda-\mathbf{k}} \omega_{\lambda\mathbf{k}}^2, \quad (1.20)$$



where  $\mathbf{u}_{\lambda\mathbf{k}} = \sum_{\tau} \mathbf{e}_{\tau}^{\lambda}(\mathbf{k})^{\dagger} \cdot \mathbf{u}_{\tau\mathbf{k}}$ . The potential energy is now diagonal in  $\mathbf{u}_{\lambda\mathbf{k}}$  and can be combined with the transformed kinetic energy to yield an uncoupled  $3N$  system of one-dimensional harmonic oscillators. Alternatively, one may write down the equation of motion for  $\mathbf{u}_{\tau\mathbf{k}}(\mathbf{t})$  from the Newtonian equations for  $\mathbf{u}_{\tau\mathbf{R}}(\mathbf{t})$ . It is easy to verify that this equation is:

$$\frac{d^2 \mathbf{u}_{\tau\mathbf{k}}(\mathbf{t})}{dt^2} = - \sum_{\tau'} D_{\tau\tau'}(\mathbf{k}) \mathbf{u}_{\tau'\mathbf{k}}(\mathbf{t}) \quad (\forall \tau \in \{\mathbf{1}, \dots, \mathbf{3p}\}). \quad (1.21)$$

After multiplying both sides by  $\mathbf{e}_{\tau}^{\lambda}(\mathbf{k})$  and summing over  $\tau$ , we recover the uncoupled set of 1D harmonic oscillator equations for each  $u_{\lambda\mathbf{k}}$  with frequency  $\omega_{\lambda\mathbf{k}}$ :  $-\omega_{\lambda\mathbf{k}}^2 u_{\lambda\mathbf{k}} = -\omega_{\lambda\mathbf{k}}^2 u_{\lambda\mathbf{k}}$ .

The dynamical matrix  $D$  for a crystal is the analog of the force-constants matrix  $\Phi$  for a cluster (within a mass factor). The eigenvalues of both of them are the squares of the vibrational frequencies of the system.

The general displacement of an atom can now be written in terms of the normal modes:

$$\mathbf{u}_{\tau\mathbf{R}}(t) = \frac{1}{\sqrt{Nm_{\tau}}} \sum_{\mathbf{k}\lambda} \mathbf{e}_{\tau}^{\lambda}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{R}} A_{\lambda}(\mathbf{k}) \cos(\omega_{\lambda\mathbf{k}}t + \phi_{\lambda\mathbf{k}}). \quad (1.22)$$

where the integration constants  $(A, \phi)$  can be found from the initial conditions.

### 1.3.2 Quantum theory of phonons in a crystal

Now we can also quantize the theory, and consider the displacement  $\mathbf{u}$  as an operator. In the uncoupled case, we have :

$$u_{\lambda\mathbf{k}}(t) = \sqrt{\frac{1}{2\omega_{\lambda\mathbf{k}}}} (a_{\lambda\mathbf{k}} e^{-i\omega_{\lambda\mathbf{k}}t} + a_{\lambda-\mathbf{k}}^{\dagger} e^{i\omega_{\lambda-\mathbf{k}}t})$$

leading to

$$\mathbf{u}_{\tau\mathbf{R}}(t) = \sum_{\lambda\mathbf{k}} \sqrt{\frac{1}{2N m_{\tau} \omega_{\lambda\mathbf{k}}}} \mathbf{e}_{\tau}^{\lambda}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{R}} (a_{\lambda\mathbf{k}} e^{-i\omega_{\lambda\mathbf{k}}t} + a_{\lambda-\mathbf{k}} e^{i\omega_{\lambda-\mathbf{k}}t}) \quad (1.23)$$

This expression can be used when computing thermal or ground state averages of quantities such as  $\langle \mathbf{u}_{\tau\mathbf{R}}(t) \mathbf{u}_{\tau'\mathbf{R}'}(t') \rangle$  which appear in the calculation of structure factors etc...

## 1.4 An example

To illustrate the theory previously outlined, let us consider a linear chain with two atoms A and B per unit cell and two different spring constants  $\chi$  and  $\xi$  between nearest neighbors only. The hard part in the lattice dynamics calculations is the correct set up of the force constants and then the dynamical matrix. The rest is a matter of a matrix diagonalization. There are two degrees of freedom in this problem, and the dynamical matrix is therefore  $2 \times 2$ , and can therefore be analytically diagonalized, and modes can easily be characterized. We can start by writing down the equations of motion for the two atoms. But this has been done before, and we know that we first need to form the force constant matrix, renormalized by the mass factors, and Fourier transform it to get the dynamical matrix as in eq.1.18. Since atom A is second neighbor to itself, there is only FCs of the type AB (let us use  $\chi$  for the hard spring or short AB bond, and  $\xi$  for the soft spring or the long AB bond).

Due to the translational invariance constraint on  $\Phi$ , we have  $\Phi_{AA} = -\chi - \xi = \Phi_{BB}$ , whereas  $\Phi_{AB} = \chi$  or  $\Phi_{AB} = \xi$  depending on our choice for the unit cell. Let us choose the unit cell as the one containing the strong bond. In this case  $\Phi_{AB} = \chi$ .

Now, we can go to form the dynamical matrix:

$$D_{AA}(k) = -\Phi_{AA}/m_A = (\chi + \xi)/m_A$$

because only the  $R = 0$  term contributes to the sum.

$$D_{AB}(k) = -\frac{1}{\sqrt{m_A m_B}}(\Phi_{AB} + \Phi_{A+R,B}e^{ika}) = -\frac{\chi + \xi e^{ika}}{\sqrt{m_A m_B}}$$

Likewise, we can calculate  $D_{BA}$  but we know that  $D$  is hermitian. Finally  $D_{BB}(k) = (\chi + \xi)/m_B$ .

$$D(k) = \begin{bmatrix} \frac{\chi + \xi}{m_A} & -\frac{\chi + \xi e^{ika}}{\sqrt{m_A m_B}} \\ -\frac{\chi + \xi e^{-ika}}{\sqrt{m_A m_B}} & \frac{\chi + \xi}{m_B} \end{bmatrix}$$

The eigenvalues can in principle be calculated analytically from  $\det(D(k) - \omega^2) = 0$ .

Solving this equation for  $\omega^2$  assuming for simplicity that the masses are equal, we obtain:

$$\omega^2 = \frac{\chi + \xi}{m} \pm \frac{1}{m} \sqrt{\chi^2 + \xi^2 + 2\chi\xi \cos ka} \quad (1.24)$$

Here we are mostly interested in their behavior near the zone center at  $k = 0$ . In this case, we can see that the determinant is zero implying, as expected, that one of the eigenvalues is zero. This corresponds to the translation of the whole lattice which does not cost any energy, and all crystals have such modes in  $d$  dimensions. These are called the **acoustic modes** since the motion of the atoms within the unit cell are in phase. For small  $k$  one can simplify the dispersion relation:

$$\omega^2 \rightarrow \frac{\chi + \xi}{m} \pm \frac{\chi + \xi}{m} \left(1 - \frac{\chi \xi k^2 a^2}{2(\chi + \xi)^2}\right)$$

The acoustic brach, obtained with the  $(-)$  sign has therefore a linear dispersion:

$$\omega_-(k) = ka \sqrt{\frac{\chi \xi}{2m(\chi + \xi)}}$$

The fact the this mode is linear in  $k$  near  $k = 0$  is not generally true, but it occurs in most cases where there are no long-range forces present in the system, and no peculiar interactions among the particles.

The slope at the origin is the group velocity of that mode and is called the **speed of sound**, as it is also the speed of propagation of elastic (long wavelength limit) vibrations.

The other mode is called the **optical mode**, and as can be deduced from the analysis of the eigenvectors of  $D$ , the two atoms in the unit cell are vibrating with a phase difference of  $\pi$ . This usually creates a dipole moment, and therefore couples to electromagnetic waves, hence the name of optical for these modes. The frequency of optical modes at the zone center are particle like i.e. quadratic in  $k$ .

$$\omega_+(k) = \sqrt{\frac{\chi + \xi}{m}} \left(1 - \frac{\chi \xi k^2 a^2}{4(\chi + \xi)^2}\right)$$