

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 α of its displacement. For an N atom cluster in 3D, τ varies from 1 to $3N$, and Φ 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: $E(\mathbf{u} + c) = E(\mathbf{u})$; $\mathbf{F}(\mathbf{u} + c) = \mathbf{F}(\mathbf{u})$. Substituting for the forces its harmonic expression, we find:

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

implying, since the displacements are arbitrary:

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

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

Other relations come from symmetry operations, such a rotations or mirror symmetries, elements of its point group, 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 Φ 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 \mathcal{S} .

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}_τ and frequencies ω 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{e}_τ become:

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

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, Φ is positive definite). For each eigenvalue ω_λ , there is an eigenvector of $3N$ components, defined by \mathbf{e}_τ^λ , which is also called the **normal mode**. For this mode λ , the polarization vector \mathbf{e}_τ^λ 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 τ oscillates in that mode λ .

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

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 $m\omega^2 e^2/2$), 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 phonon¹ 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 τ , 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:

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

¹The 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_λ 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_λ, π_λ) . To write \mathbf{Q}_τ in terms of π_λ one needs to invert \mathbf{e}_τ^λ which can be thought of as a matrix of row index τ and column index λ . It is the matrix of the eigenvectors which is also the orthogonal matrix that takes one from the “ τ ” basis to the “ λ ” basis. Its inverse is its transpose as one can also see from the completeness relation^{1,7} 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 ω_λ . The eigenvalues of \mathcal{H} are well-known²:

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

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

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

1.2 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

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

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.

1.2.1 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 Φ 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 $\Phi_{\mathbf{R}\tau,\mathbf{R}'\tau'} = \Phi_{0\tau,\mathbf{R}'-\mathbf{R}\tau'}$, 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 τ , including, as in the case of clusters, the cartesian component of the displacement, so that τ 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 τ in the cell defined by the translation vector \mathbf{R} can be written as

$$\mathbf{u}_{\tau\mathbf{R}}(t) = \sum_{\mathbf{k}} \frac{1}{\sqrt{Nm_\tau}} \mathbf{u}_{\tau\mathbf{k}}(t) e^{i\mathbf{k}\cdot\mathbf{R}}. \quad (1.12)$$

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

$$E - E_0 = \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}',\tau\tau'} \mathbf{u}_{\tau\mathbf{R}} \mathbf{u}_{\tau'\mathbf{R}'} \Phi_{\mathbf{R}\tau,\mathbf{R}'\tau'} \quad (1.13)$$

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

The second line was obtained using the translational invariance of the force-constants matrix Φ , 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 Γ 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:

$$\sum_{\tau'} D_{\tau\tau'}(\mathbf{k}) \mathbf{e}_{\tau'}^\lambda(\mathbf{k}) = \omega_{\lambda\mathbf{k}}^2 \mathbf{e}_\tau^\lambda(\mathbf{k}) \Rightarrow D_{\tau\tau'}(\mathbf{k}) = \sum_{\lambda} \omega_{\lambda\mathbf{k}}^2 \mathbf{e}_\tau^\lambda(\mathbf{k}) \mathbf{e}_{\tau'}^\lambda(\mathbf{k})^\dagger \quad (1.14)$$

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:

$$\begin{aligned} \sum_{\tau} \mathbf{e}_{\tau}^{\lambda}(\mathbf{k})^{\dagger} \mathbf{e}_{\tau}^{\lambda'}(\mathbf{k}) &= \delta_{\lambda, \lambda'} \text{ orthonormality} \\ \sum_{\lambda} \mathbf{e}_{\tau}^{\lambda}(\mathbf{k}) \mathbf{e}_{\tau'}^{\lambda}(\mathbf{k})^{\dagger} &= \delta_{\tau, \tau'} \text{ completeness} \end{aligned} \quad (1.15)$$

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:

$$E - E_0 = \frac{1}{2} \sum_{\mathbf{k}\lambda} \mathbf{u}_{\lambda\mathbf{k}} \mathbf{u}_{\lambda-\mathbf{k}} \omega_{\lambda\mathbf{k}}^2, \quad (1.16)$$

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 a system of $3N$ uncoupled 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:

$$\frac{d^2 \mathbf{u}_{\tau\mathbf{k}}(\mathbf{t})}{dt^2} = - \sum_{\tau'} D_{\tau\tau'}(\mathbf{k}) \mathbf{u}_{\tau'\mathbf{k}}(\mathbf{t}) \quad (\forall \tau \in \{\mathbf{1}, \dots, \mathbf{3p}\}). \quad (1.17)$$

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

The dynamical matrix D for a crystal is the analog of the force-constants matrix Φ for a cluster (within a mass factor in the denominator). Their eigenvalues are the squares of the vibrational frequencies of the system. As we mentioned this whole treatment is, very analogous to the tight-binding formalism. The hopping matrix is replaced by the force constants matrix and the electronic energy levels by the square of the phonon frequencies. They would follow the same symmetry rules if the orbitals are of p ($L=1$) symmetry, otherwise the TB Hamiltonian can have different symmetry transformation properties if ($L \neq 1$).

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

$$\mathbf{u}_{\tau\mathbf{R}}(t) = \frac{1}{\sqrt{Nm_{\tau}}} \sum_{\mathbf{k}\lambda} \mathbf{e}_{\tau}^{\lambda}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{R}} A_{\lambda}(\mathbf{k}) \cos(\omega_{\lambda\mathbf{k}}t + \phi_{\lambda\mathbf{k}}). \quad (1.18)$$

where the $6N$ integration constants (A, ϕ) can be found from the initial conditions.

1.2.2 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 :

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

leading to

$$\mathbf{u}_{\tau\mathbf{R}}(t) = \sum_{\lambda\mathbf{k}} \sqrt{\frac{\hbar}{2N m_\tau \omega_{\lambda\mathbf{k}}}} \mathbf{e}_\tau^\lambda(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{R}} (a_{\lambda\mathbf{k}} e^{-i\omega_{\lambda\mathbf{k}}t} + a_{\lambda-\mathbf{k}}^\dagger e^{i\omega_{\lambda\mathbf{k}}t}) \quad (1.19)$$

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...

1.3 Phonon density of states in the harmonic approximation

DEFINE DOS AND THE VELOCITY AUTOCORRELATION FUNCTION. SHOW THAT THE LATTER GOES TO THE LOCAL DOS IN HARMONIC CRYSTALS AND TO THE VISCOSITY IN THE CASE OF LIQUIDS.

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 χ and ξ 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 2×2 , 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 (see eq. 1.17), 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.1.14. Since atom A is second neighbor to itself, there is only FCs of the type AB (let us use χ for the hard spring or short AB bond, and ξ for the soft spring or the long AB bond).

Due to the translational invariance constraint on Φ , 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 form the dynamical matrix. For the diagonal terms, since only the $R = 0$ term contributes to the sum, we have:

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

In the off-diagonal terms, there are the contributions of $R = 0$ and $R = \pm 2a$ depending on which off-diagonal term we are considering:

$$D_{AB}(k) = -\frac{1}{\sqrt{m_A m_B}}(\Phi_{AB} + \Phi_{A+R,B}e^{2ika}) = -\frac{\chi + \xi e^{2ika}}{\sqrt{m_A m_B}}$$

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

$$D(k) = \begin{bmatrix} \frac{\chi + \xi}{m_A} & -\frac{\chi + \xi e^{2ika}}{\sqrt{m_A m_B}} \\ -\frac{\chi + \xi e^{-2ika}}{\sqrt{m_A m_B}} & \frac{\chi + \xi}{m_B} \end{bmatrix}$$

Note that the lattice constant is $2a$, and a is the interatomic distance. The eigenvalues can in principle be calculated analytically from $\det(D(k) - \omega^2) = 0$.

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

$$\omega^2 = \frac{\chi + \xi}{m} \pm \frac{1}{m} \sqrt{\chi^2 + \xi^2 + 2\chi\xi \cos 2ka} \quad (1.20)$$

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:

$$\omega^2 \rightarrow \frac{\chi + \xi}{m} \pm \frac{\chi + \xi}{m} \left(1 - \frac{\chi\xi 4k^2 a^2}{2(\chi + \xi)^2}\right)$$

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

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

The fact that this mode is linear in k near $k = 0$ is not always 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) waves. The latter can be obtained from the “wave equation” derived within elasticity theory, which is the long wavelength limit of the phonon theory.

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 π . 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 .

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

Note that in the case where both masses and spring constants are equal ($m_A = m_B$; $\chi = \xi$), then we have a simple linear chain with one atom per unit cell. The representation that we have just used has a twice larger unit cell and hence a twice smaller first Brillouin zone. The eigenvalues in both representations should however be the same. What we have found (eq. 1.20) becomes in this limit:

$$\omega^2 = \frac{2\chi}{m} \pm \frac{2\chi \cos ka}{m} = \frac{2\chi}{m} (1 \pm \cos ka) \quad (1.21)$$

with a being the distance between two nearest neighbor atoms, also the lattice constant of the uniform chain for which it is straightforward to derive

that the dispersion relation is $\omega = 2\sqrt{\chi/m} \sin ka/2$. From fig.1.1, one can see that this is the unfolded representation of the previous dispersion with two branches.

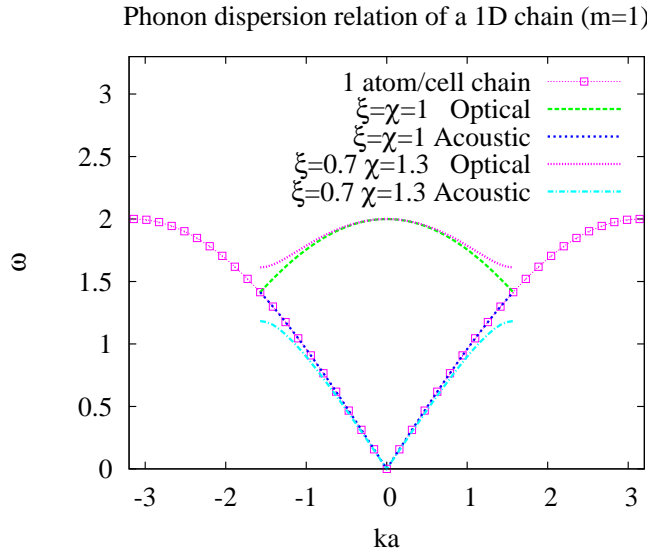


Figure 1.1: Dispersion relations of the 1D chain with two atoms per unit cell for two different couplings, compared to the uniform chain (unfolded dispersion)

1.5 Thermodynamic properties

In general, it is difficult to calculate thermodynamic properties such as entropy or free energy of a cluster or a solid. 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 $3N - 6$ uncoupled ones, the partition function of the system is therefore the product of the partition functions for each normal mode, and the free energy 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 ω . The free energy is $F = -k_B T \ln Z = \hbar\omega/2 + k_B T \ln(1 - e^{-\beta\hbar\omega}) = k_B T \ln 2 \sinh(\beta\hbar\omega/2)$ so that for a general molecule with many degrees of freedom, we can write

$$Z_{vib} = \prod_{\lambda}^{vib} \frac{1}{2 \sinh(\beta\hbar\omega_{\lambda}/2)} \quad (1.22)$$

$$F = k_B T \sum_{\lambda} \ln 2 \sinh(\beta\hbar\omega_{\lambda}/2) \quad (1.23)$$

$$E = \sum_{\lambda} \frac{1}{2} \coth(\beta\hbar\omega_{\lambda}/2) \hbar\omega_{\lambda} = \sum_{\lambda} (n_{\lambda} + \frac{1}{2}) \hbar\omega_{\lambda} \quad (1.24)$$

$$\frac{S}{k_B} = \frac{E - F}{k_B T} = \sum_{\lambda} \beta\hbar\omega_{\lambda}/2 \coth(\beta\hbar\omega_{\lambda}/2) - \ln 2 \sinh(\beta\hbar\omega_{\lambda}/2) \quad (1.25)$$

Note that the above formulas are only the contributions of the vibrational degrees of freedom, and one must also add to them the contributions of rotational and translational degrees of freedom in order to obtain the total free/total energy.

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

The heat capacity is defined as $C_v = (\partial E / \partial T)_V = k_B \sum_{\lambda} (x_{\lambda} / \sinh x_{\lambda})^2$ where $x_{\lambda} = \beta\hbar\omega_{\lambda}/2$. We can clearly see that at high temperatures $x_{\lambda} \rightarrow 0$, and therefore $C_v = k_B \sum_{\lambda} 1 = N_{\lambda} k_B$ with $N_{\lambda} = 3N - 6$ being the number of vibrational modes in a N atom cluster in 3 dimensions. The total energy also has a simple expression and goes to $E = k_B T(3N - 6)$.

The equation of state relating the pressure P , volume Ω and temperature T can be obtained from the definition of $P = -(\partial F / \partial \Omega)_T$. We find

$$P = -\frac{dE_0}{d\Omega} - \sum_{\lambda} \left(\frac{1}{2} + n_{BE}(\beta\omega_{\lambda}) \right) \frac{d\hbar\omega_{\lambda}}{d\Omega} \quad (1.26)$$

If we introduce the **Gruneisen parameters**³, $\gamma_{\lambda} = d \ln \omega_{\lambda} / d \ln \Omega$ we can write the equation of state in terms of these parameters (supposed to be

³Gruneisen parameters for each mode show by how many percents its frequency changes if there is a one percent change in the volume.

known) as follows:

$$P = -\frac{dE_0}{d\Omega} - \sum_{\lambda} \left(\frac{1}{2} + n_{\text{BE}}(\beta\omega_{\lambda}) \right) \frac{\hbar\omega_{\lambda}\gamma_{\lambda}}{\Omega} \quad (1.27)$$

which looks like a γ times the total energy divided by the volume, if γ_{λ} were constant.

In all above formulas the sum over modes can be replaced by a frequency integral of the frequency distribution function (or $g(\omega)$ =DOS). For instance

$$\begin{aligned} E &= E_0 + \int d\omega g(\omega) \left(n_{\text{BE}}\beta\omega + \frac{1}{2} \right) \hbar\omega \\ C_v &= k_B \int d\omega g(\omega) \left(\frac{\beta\hbar\omega/2}{\sinh \beta\hbar\omega/2} \right)^2 \end{aligned} \quad (1.28)$$

1.5.1 Einstein model

The simplest possible model for atoms vibrating about their equilibrium position in a cluster or solid is to assume that each atom is oscillating independent of all the other ones with a characteristic (constant) frequency ω_o . This approximation is Einstein's model, and assumes that while the atom is oscillating, all others are effectively fixed. It ignores correlations between motion of neighboring atoms, and is a reasonably good model for optical phonons. In this case, the sums are reduced to a multiplicative factor, which is the number of vibrational degrees of freedom⁴ ($3(N - N_0)$ in three dimensions, where N_0 is the number of unit cells in the crystal, and therefore $3N_0$ is the number of acoustic branches for which the Debye model could be used):

$$\begin{aligned} E &= E_0 + 3(N - N_0) \left(\frac{1}{2} + n_{\text{BE}}(\beta\omega_o) \right) \hbar\omega_o \\ F &= E_0 + 3(N - N_0) k_B T \left[\frac{1}{2} \frac{\hbar\omega_o}{k_B T} + \ln(1 - e^{-\beta\hbar\omega_o}) \right] \\ C_v &= 3(N - N_0) k_B \left(\frac{x_o}{\sinh x_o} \right)^2 \end{aligned} \quad (1.29)$$

where $x_o = \beta\hbar\omega_o/2$.

⁴for a crystal, the number of translational and rotational degrees of freedom, 6, is negligible compared to N , which is of the order of 10^{23} .

1.5.2 Debye model

This is a model to describe the low-temperature thermodynamic properties of the acoustic dispersion branches in the long wavelength limit. A priori, in 3 dimensions there are 3 acoustic branches, one longitudinal and two transverse. A **longitudinal mode** is a mode where the polarization vector is parallel to the wavevector $\mathbf{e}(\mathbf{k}) \parallel \mathbf{k}$, and in a **transverse mode**, the polarization vector is perpendicular to the wavevector $\mathbf{e}(\mathbf{k}) \cdot \mathbf{k} = 0$. This is not always true: in anisotropic crystals, the polarization vectors may be neither parallel nor perpendicular to their wavevector. In the longwavelength limit, however, if the crystal can be seen as isotropic, the above relations hold, and the two transverse-acoustic branches will be degenerate. In the Debye model, the dispersion is approximated by a linear one: $\omega_{l,t}(\mathbf{k}) = c_{l,t}k$. The Brillouin zone is replaced by a sphere of radius k_D which is determined so that the total number of acoustic modes per unit cell in d -dimensions is d . If the phonon DOS per unit volume is represented by $g(\omega)$, then the relation defining the Debye frequency ω_D is:

$$\int_0^{\omega_D} g(\omega) d\omega = d \frac{N}{\Omega} = dn \quad (1.30)$$

where N is the number of unit cells, and n would be the inverse of the volume of the unit cell. The phonon DOS can be easily calculated knowing the linear dispersion.

$$g_{l,t}(\omega)d\omega = \frac{1}{(2\pi)^d} s_d k^{d-1} dk = \frac{1}{(2\pi)^d} s_d \frac{\omega^{d-1}}{c_{l,t}^d} d\omega$$

with s_d being the surface of a sphere of radius 1 in d dimensions: $s_d = 2, 2\pi, 4\pi$ for $d = 1, 2, 3$ respectively. Since there are d acoustic branches, their contributions add in the formula for the total DOS. For convenience, we also define the ‘‘average’’ speed of sound \bar{c} as:

$$\frac{d}{\bar{c}^d} = \frac{1}{c_l^d} + \frac{d-1}{c_t^d}$$

so that the total DOS is:

$$g(\omega) = g_l(\omega) + (d-1)g_t(\omega) = \frac{d}{(2\pi)^d} s_d \frac{\omega^{d-1}}{\bar{c}^d} \quad (1.31)$$

Finally, we obtain for the Debye frequency in d dimensions:

$$\omega_D = 2\pi\bar{c}\left(\frac{nd}{s_d}\right)^{1/d} \quad (1.32)$$

This allows one to write the vibrational DOS per unit volume as:

$$g(\omega) = n d^2 \omega^{d-1} / \omega_D^d \quad (1.33)$$

The total energy per unit volume of the acoustic modes is given by:

$$\begin{aligned} E_{ac} &= \frac{1}{\Omega} \sum_{\mathbf{k}, \lambda=ac} (n_{\mathbf{k}\lambda} + \frac{1}{2}) \hbar \omega_{\mathbf{k}\lambda} = \frac{1}{\Omega} \sum_{\mathbf{k}, \lambda=ac} \frac{\hbar \omega_{\mathbf{k}\lambda}}{2} + \frac{1}{\Omega} \sum_{\mathbf{k}, \lambda=ac} \langle n_{\mathbf{k}\lambda} \rangle \hbar \omega_{\mathbf{k}\lambda} \\ &= ZPE + \int_0^{\omega_D} d\omega g(\omega) n_{\text{BE}}(\beta\omega) \hbar \omega \\ &= ZPE + \int_0^{\omega_D} d\omega \frac{n d^2}{\omega_D^d} \omega^{d-1} n_{\text{BE}}(\beta\omega) \hbar \omega \\ &= ZPE + n d^2 \frac{(k_B T)^{d+1}}{(\hbar \omega_D)^d} \int_0^{\beta \hbar \omega_D} n_{\text{BE}}(x) x^d dx \end{aligned} \quad (1.34)$$

The first term, $ZPE = \sum_{\mathbf{k}, \lambda=ac} \hbar \omega_{\mathbf{k}\lambda} / 2\Omega$, is the zero point energy per unit volume, which is the value of the total energy at $T = 0$. It is coming from Heisenberg uncertainty principle which implies that even at $T = 0$ in the ground state, atoms can not be confined to a point, and must have a zero point motion. Clearly, this term does not depend on temperature. There are two energy scales in this problem, the Debye energy $\hbar \omega_D = k_B \theta_D$, defining also a Debye temperature θ_D , and the actual thermal energy $k_B T$. All thermodynamic properties depend therefore on the ratio of these two terms. We define a low temperature regime characterized by $k_B T \ll \hbar \omega_D = k_B \theta_D$. In this case, the upper limit of the integral can be taken to infinity, and the result of the integral is $\Gamma(d+1)\zeta(d+1)$, with $\Gamma(d+1) = \int_0^\infty x^d e^{-x} dx$, and $\zeta(d) = \sum_{n=1}^\infty 1/n^d$. The latter function appears after writing the Bose-einstein distribution function in the integral as:

$$n_{\text{BE}}(x) = \frac{1}{e^x - 1} = \frac{e^{-x}}{1 - e^{-x}} = e^{-x} + e^{-2x} + \dots = e^{-x} \sum_{n=0}^\infty e^{-nx}$$

Finally the temperature-dependent part of the total energy per unit volume can be written in the $T \ll \theta_D$ limit as:

$$E_{ac} - ZPE \rightarrow n d^2 \frac{T^{d+1}}{\theta_D^d} \Gamma(d+1) \zeta(d+1) \quad (1.35)$$

and therefore the heat capacity per unit volume at low temperatures is given by:

$$\frac{C_v}{k_B} = \frac{\partial E_{ac}}{\partial T} \rightarrow n(d+1)d^2 \Gamma(d+1) \zeta(d+1) \left(\frac{T}{\theta_D}\right)^d \quad (1.36)$$

It is thus proportional to T^d at low temperatures.

So we see that according to the Debye model, the heat capacity of any material follows the same temperature dependence which only depends on its Debye frequency. In other words, at equal T/θ_D , all materials have the same temperature-dependence of their heat capacity. This fact has been experimentally verified with a good accuracy. Even Einstein model has very good predictions for the heat capacity, except of course at low temperatures where the distribution of the frequencies becomes important. The agreement between these simple models and experimental results shows that the thermal properties are not very sensitive to the details of the DOS except at temperatures much smaller than the Debye or Einstein temperatures.

The free energy, according to eq. 1.25 is $F = k_B T \sum_{\lambda} \ln 2 \sinh(\beta \hbar \omega_{\lambda}/2)$. Similar to the total energy, the contribution of acoustic modes in the free energy per unit volume can be written as the integral:

$$\begin{aligned} F_{ac} &= \int_0^{\omega_D} d\omega g(\omega) \ln 2 \sinh(\beta \hbar \omega/2) \\ &= \frac{n d^2}{(\hbar \omega_D)^d} (k_B T)^{d+1} \int_0^{\beta \hbar \omega_D} x^{d-1} \ln 2 \sinh x/2 dx \end{aligned} \quad (1.37)$$

If we use $\ln 2 \sinh x/2 = \ln(e^{x/2} - e^{-x/2}) = x/2 + \ln(1 - e^{-x}) \approx x/2 - e^{-x}$ for large x , then it is possible to subtract the contribution of the ZPE, and write the remaining term as $\ln(1 - e^{-x}) = -\sum_{m=1}^{\infty} e^{-mx}/m$. One can find the temperature dependence of the free energy at low T to be:

$$\begin{aligned} F_{ac} - ZPE &\rightarrow -n d^2 \frac{(k_B T)^{d+1}}{(\hbar \omega_D)^d} \sum_{m=1}^{\infty} \frac{1}{m} \int_0^{\beta \hbar \omega_D} x^{d-1} e^{-mx} dx \\ &= -n d^2 \frac{k_B T^{d+1}}{\theta_D^d} \Gamma(d) \zeta(d+1) \end{aligned} \quad (1.38)$$

Leading to a low-temperature entropy per unit volume of:

$$\frac{S}{k_B} = -\frac{\partial F_{ac}}{\partial k_B T} \rightarrow n(d+1) d^2 \Gamma(d) \zeta(d+1) \left(\frac{T}{\theta_D}\right)^d = n d \Gamma(d+2) \zeta(d+1) \left(\frac{T}{\theta_D}\right)^d \quad (1.39)$$

This can also be obtained from the thermodynamic relation relating C_v to the entropy. $C_v = T\partial S/\partial T$, which implies that at low temperatures $C_v = dS$.

It can be shown that a quite general equation of state due to Mie and Gruneisen holds for crystals: $P + dE_0/d\Omega = \gamma(E - E_0)/\Omega$. This can be obtained from the general definition of the pressure in eq. 1.27 if we assume all γ_λ are equal.

For a general yet simple discussion of thermal properties, it is possible to fit the exact formula for the heat capacity versus temperature, to that obtained from the Debye approximation. Thus at each temperature, we can find a best Debye frequency which fits the exact result, leading to temperature-dependent Debye frequency! If this is done, we find that the obtained Debye frequency becomes nearly constant at high temperatures, implying that viewing the real crystal as an elastic medium is fine at high T ⁵. However this breaks down at low T , implying the importance of the optical modes in describing thermal properties at low temperatures.

1.5.3 High-temperature limit

The high temperature limit is defined by $T \gg \theta_D$. Since $n_{\text{BE}}(\beta\omega) \rightarrow k_B T/\hbar\omega$, according to the third line in eq.1.34, the total energy becomes $n d k_B T$ and thus C_v goes to a constant which is equal to $n d k_B$ due to equipartition theorem which says that the total energy per degree of freedom must be $k_B T$, which in d dimensions leads to $C_v/\text{atom} = d k_B$.

The expression for the free energy can be simplified in this limit: We need to replace $\ln(1 - e^{-x})$ by $\ln x$ for small x ; then the integral to compute is

$$\int_0^{\theta_D/T} x^{d-1} \ln x dx = \frac{(\theta_D/T)^d}{d^2} (d \ln \frac{\theta_D}{T} - 1) \rightarrow \frac{(\theta_D/T)^d}{d} \ln \frac{\theta_D}{T}$$

So that the free energy per unit volume becomes:

$$F_{ac} - ZPE \rightarrow n d k_B T \ln \frac{\theta_D}{T} \quad (1.40)$$

⁵The temperature must still be low enough so that the crystal remains harmonic and the effect of higher derivatives of the potential can be neglected.