7. Lattice dynamics

7.1 Basic consideratons

In this section we'll follow a number of well-known textbooks, and only try to keep the notations consistent. Suppose we have a system of N atoms, m=1, . . . , N, with their positions defined by some (arbitrary chosen) set of coordinates q_i, i=1, . . . , $3N$. In classical treatment, one has to solve the system of Lagrangian equations of motion:

$$\frac{d}{dt}\frac{\partial T}{\partial \dot{q}_i} + \frac{\partial V}{\partial q_i} = 0, \qquad j = 1, \ldots, 3N \tag{7.1}$$

Let us first assume the coordinates q_j to be Cartesian,

$$X_{mi}, \quad \left\{ \begin{array}{c} i = 1, 3 \\ m = 1, N \end{array} \right. ,$$

and consider a more general case later on. Then

$$T = \frac{1}{2}\sum_{m=1}^{N} M_m \sum_{i=1}^{3} \dot{X}_{mi}^2 \, , \tag{7.2}$$

$$V = V_0 + \sum_{m=1}^{N}\sum_{i=1}^{3} \underbrace{\left(\frac{\partial V}{\partial X_{mi}}\right)}_{\substack{i\,=\,0 \\ \text{in the} \\ \text{equilibrium}}} X_{mi} + \frac{1}{2}\sum_{\substack{m=1 \\ n=1}}^{N}\sum_{\substack{i=1 \\ j=1}}^{3} \frac{\partial^2 V}{\partial X_{mi}\,\partial X_{nj}} X_{mi}\, X_{nj}\, r; \, . \tag{7.3}$$

the neglection of higher expansion terms for V corresponds to the harmonic approximation that we introduce here. With

$$\begin{aligned} \frac{\partial T}{\partial \dot{X}_{mi}} &= M_m \dot{X}_{mi} \, , \\ \frac{\partial V}{\partial X_{mi}} &= \sum_{n=1}^{N}\sum_{j=1}^{3} \left(\frac{\partial^2 V}{\partial X_{mi}\,\partial X_{nj}}\right) X_{nj} \, , \end{aligned}$$

the equation of motion

$$M_m \ddot{X}_{mi} + \sum_{n=1}^{N}\sum_{j=1}^{3} \left(\frac{\partial^2 V}{\partial X_{mi}\,\partial X_{nj}}\right) X_{nj} = 0 \tag{7.4}$$

is a system of $3N$ coupled equations, labeled by $\{m, i\}$. For a finite cluster or a molecule, one may try to simplify the problem by choosing appropriate symmetry coordinates, reduce the matrix of force constants to block-diagonal form making use of the point

group symmetry, and project out 3 global translation and 3 global rotation modes – see details below. For a perfect periodic crystal, a simplification is possible through applying periodic boundary conditions. The "individual" atom displacements are then labeled by the index of the unit cell in crystal, α, and the index of atom in each cell, l, e.g.:

$$X_{mi} \to X^{\alpha}_{l\,i}\,; \quad X_{nj} \to X^{\beta}_{k\,j}\,.$$

l and k run now from 1 to n, number of atoms per unit cell, and i, j remain the Cartesian indici. Similarly we emphasize the dependency on cell index and atomic position in the cell for the force constants:

$$\frac{\partial^2 V}{\partial X_{mi}\,\partial X_{nj}} \quad \to \quad \Phi^{\alpha\,\beta}_{li,\,kj}\,.$$

We search for solutions in lattice-periodic form,

$$X^{\alpha}_{li} = A_{li}(\mathbf{q})\exp[-i\omega t + i\mathbf{q}\mathbf{R}_{\alpha}]\,. \tag{7.5}$$

$\mathbf{R}_{\alpha}$ is the origin of the α'th unit cell, and the atomic displacements get the dependency on $\mathbf{q}$. There are exactly as many allowed $\mathbf{q}$ values as there are unit cells in crystal, with periodic boundary conditions imposed. So, Eq. (7.5) still defines $3N$ individual displacements. The trick is, due to imposing of periodic boundary conditions the equations of motion become decoupled in q. Substituting the second derivative of (7.5) into Eq. (7.4) yields

$$-M_l\,\omega^2 A_{li}(\mathbf{q})\exp[-i\omega t + i\mathbf{q}\mathbf{R}_{\alpha}] + \sum_{\beta}\sum_{k=1}^{n}\sum_{j=1}^{3}\Phi^{\alpha\,\beta}_{li,\,kj}\,A_{kj}(\mathbf{q})\exp[-i\omega t + i\mathbf{q}\mathbf{R}_{\beta}] = 0\,.$$

Multiplying by $\exp[i\omega t - i\mathbf{q}\mathbf{R}_{\alpha}]$ yields:

$$-M_l\,\omega^2 A_{li}(\mathbf{q}) + \sum_{k=1}^{n}\sum_{j=1}^{3}\underbrace{\left[\sum_{\beta}\Phi^{\alpha\,\beta}_{li,\,kj}\,A_{kj}(\mathbf{q})\exp[i\mathbf{q}(\mathbf{R}_{\beta}-\mathbf{R}_{\alpha})]\right]}_{\equiv D_{li,\,kj}(\mathbf{q})} A_{kj}(\mathbf{q}) = 0\,. \tag{7.6}$$

The summation in β must be done over all cells, and since real-space force constants depend only on relative distances between the atoms, the origin α does not play a role anymore (and could be set to 0). The system (7.6) becomes that of matrix equation, decoupled in q, of the size $3n$:

$$\sum_{k=1}^{n}\sum_{j=1}^{3}\Big[M_l\,\omega^2\delta_{lk}\delta_{ij} - D_{li,\,kj}(\mathbf{q})\Big]\,A_{kj}(\mathbf{q}) = 0\,. \tag{7.7}$$

The matrix to diagonalize is not symmetric, that may be unconvenient. One can redefine eigenvectors (incorporating there square root of mass), in order to restore the symmetry:

$$\sum_{k=1}^{n}\sum_{j=1}^{3}\left[\omega^2\delta_{lk}\,\delta_{ij} - \frac{D_{li,\,kj}(\mathbf{q})}{\sqrt{M_l\,M_k}}\right]\,\left[\sqrt{M_k}A_{kj}(\mathbf{q})\right] = 0\,. \tag{7.8}$$

More precisely, the matrix is now Hermitian. Indeed,

$$\begin{aligned} D^*_{li,\,kj}(\mathbf{q}) &= \sum_\beta \underbrace{\Phi^{\alpha\,\beta}_{li,\,kj}}_{\text{real}} e^{-i\mathbf{q}(\mathbf{R}_\beta-\mathbf{R}_\alpha)} = \sum_\beta \underbrace{\Phi^{\alpha\,\beta}_{li,\,kj}}_{\equiv \Phi^{\beta\,\alpha}_{kj,\,li}} e^{i\mathbf{q}(\mathbf{R}_\alpha-\mathbf{R}_\beta)} = \\ &= \sum_\alpha \Phi^{\beta\,\alpha}_{kj,\,li} e^{i\mathbf{q}(\mathbf{R}_\alpha-\mathbf{R}_\beta)} = D_{kj,\,li}(\mathbf{q})\,. \end{aligned}$$

It was used that since the lattice summation runs over relative vectors $(\mathbf{R}_\alpha - \mathbf{R}_\beta)$, instead of summing over β for $\alpha = 0$ we can as well fix β and run over α. The force constants matzrix is related to the forces as follows:

$$F^\alpha_{li} = -\frac{\partial V}{\partial X^\alpha_{li}} = -\sum_\beta \sum_{k=1}^{N} \sum_{j=1}^{3} \Phi^{\alpha\,\beta}_{li,\,kj}\, X^\beta_{kj}\,. \tag{7.9}$$

Inversely,

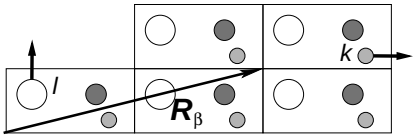
$$\Phi^{\alpha\,\beta}_{li,\,kj} = -\frac{\partial F^\alpha_{li}}{\partial X^\beta_{kj}} \left(= -\frac{\partial F^\beta_{kj}}{\partial X^\alpha_{li}} \right)\,. \tag{7.10}$$

This can be used for calculating force constants if forces due to displacements of all cartesian displacements of all atoms are available. If we make use of the electronic-structure code that makes use of periodic boundary conditions, we cannot displace just one atom in an infinite crystal. But we can choose different supercells and try different collective displacements. Once again,

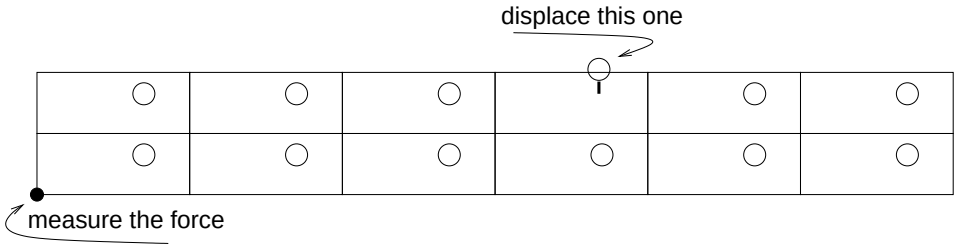
$$D_{li,\,kj}(\mathbf{q}) = -\sum_\beta \frac{\partial F^\beta_{kj}}{\partial X^\alpha_{li}} \exp[i\mathbf{q}(\mathbf{R}_\beta - \mathbf{R}_\alpha)]\,,$$

if we displace the atom at the origin only (in the cell α) and sum over forces induced all over the lattice. The relation between dynamical matrices in real and reciprocal spaces:

$$\begin{aligned} D_{li,\,kj}(\mathbf{q}) &= \sum_\beta \Phi^{0\,\beta}_{li,\,kj}\, e^{i\mathbf{q}\mathbf{R}_\beta}\,, \\ \Phi^{0\,\beta}_{li,\,kj}(\mathbf{R}_\beta) &= \sum_{\mathbf{q}} D_{li,\,kj}(\mathbf{q})\, e^{-\mathbf{q}\mathbf{R}_\beta}\,. \end{aligned}$$

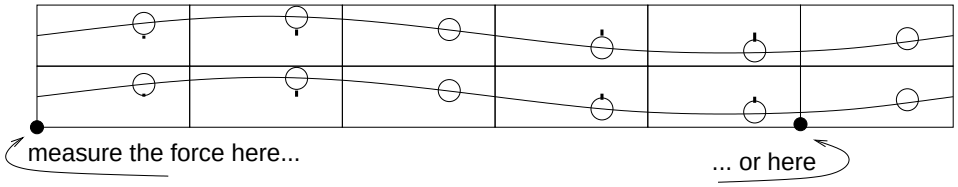


In principle it would be nice to displace atoms one by one (running through $\mathbf{R}_\beta$ and k) in all three cartesian directions and look at the force on the atom of our choise (say, l), and then make Fourier transformation to recover $\mathbf{q}$-dependent force constants:

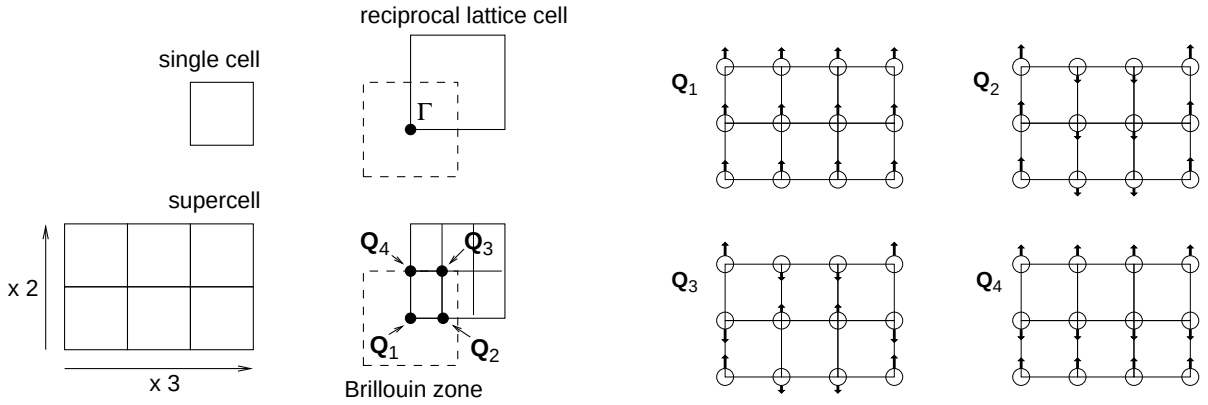


Unfortunately, this is not possible without breaking translation symmetry of the lattice. What is more feasible is either creation of a phonon with a given $\mathbf{q}$, or individual displacements of atoms in a supercell.

Let us first consider the first approach, that is the *frozen phonon* one. In this approach, the atoms of type k are displaced in *every* cell, proportionally to $\exp(i\mathbf{q}\mathbf{R}_\beta)$:

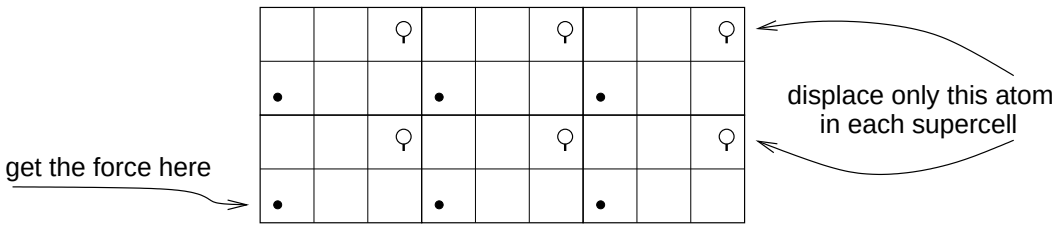


This becomes quite straightforward if the calculation of forces is done in a supercell, and the frozen phonon in question is commensurable with this supercell. Inversely, a choice of supercell defines several commensurable vectors $\mathbf{Q}$, for which the elements of dynamical matrix can be sampled exactly. Consider an example for 2-dim. lattice:



A reduced reciprocal cell maps onto four different vectors in the original Brillouin zone, which correspond to the following displacement patterns (according to the $e^{i\mathbf{Q}\mathbf{R}}$ wave).

Of course the displacement patterns need not be necessarily harmonic inside the supercell. Disregarding the symmetry, we can displace any atom individually and probe different force constants. Of course this "any" refers to atom in a supercell, and in the adjacent supercell we'll have an identically displaced atom:



In the lattice summation we'll now specify $\mathbf{R}_\beta = \mathbf{L} + \mathbf{\Delta}$, where $\mathbf{L}$ runs over supercells in crystal, and $\mathbf{\Delta}$ numbers single cells within a supercell. X^β_{kj} is then $X^{\mathbf{\Delta}}_{kj}$ for all $\mathbf{L}$.

$$F^{\alpha=0}_{li} = -\sum_\beta \sum_{k=1}^{n} \sum_{j=1}^{3} \Phi^{0\,\beta}_{li,\,kj} X^\beta_{kj} = -\sum_\beta \sum_{k=1}^{n} \sum_{j=1}^{3} \sum_{\mathbf{q}} D_{li,\,kj}(\mathbf{q}) e^{-i\mathbf{q}\mathbf{R}_\beta} X^\beta_{kj} =$$

$$= -\sum_{k=1}^{n}\sum_{j=1}^{3} X_{kj}^{\mathbf{\Delta}} \sum_{\mathbf{q}} D_{li,\,kj}(\mathbf{q})\, \exp[-i\mathbf{q}\mathbf{\Delta}] \underbrace{\sum_{\mathbf{L}} e^{-i\mathbf{q}\mathbf{L}}}_{=\delta_{\mathbf{q}\mathbf{Q}_L}} =$$

$$= -\sum_{k=1}^{n}\sum_{j=1}^{3} X_{kj}^{\mathbf{\Delta}} \sum_{\mathbf{Q}_L} D_{li,\,kj}(\mathbf{Q}_L) \exp[-i\mathbf{Q}_L\mathbf{\Delta}]\,. \tag{7.11}$$

$\mathbf{Q}_L$ have been introduced here as vectors in the reciprocal space, which are "conjugated" to the supercell vectors: $\mathbf{L}\cdot\mathbf{Q}_L = 2\pi\times$(integer). Note that $D_{li,\,kj}(\mathbf{Q}_L)$ from different $\mathbf{Q}_L$ are now mixed in the final force, but they can be recovered if we try all possible $\mathbf{\Delta}$, since there are so many different $\mathbf{Q}_L$ (in the first Brillouin zone) as there are $\mathbf{\Delta}$'s.

Let us skip for brevity the (li) and (kj) indices and concentrate on the dependencies on $\mathbf{\Delta}$ and $\mathbf{Q}_L$:

$$\begin{aligned} F(\mathbf{\Delta}) &= -\sum_{\mathbf{Q}_L} D(\mathbf{Q}_L) X(\mathbf{\Delta}) e^{-i\mathbf{Q}_L\mathbf{\Delta}}\,; \\ \left(\frac{F}{X}\right)_{\mathbf{\Delta}} &= -\sum_{\mathbf{Q}_L} \left[e^{-i\mathbf{Q}_L\mathbf{\Delta}}\right] D(\mathbf{Q}_L)\,; \\ D(\mathbf{Q}_L) &= -\sum_{\mathbf{\Delta}} \left[e^{-i\mathbf{Q}_L\mathbf{\Delta}}\right]^{-1} \left(\frac{F}{X}\right)_{\mathbf{\Delta}}\,. \end{aligned}$$

This is a matrix equation with the dimension equal to that of the supercell size (= number of different Δ), that will be, say S. Since on top of it we'll have mixing up of (kj) and (li) components everywhere, the full problem of finding all elements of D amounts to the matrix inversion of the size $3nS$. The use of point symmetry may help to reduce this number considerably.[46]

[46] Of course matrix inversion as such is not a problem; expensive are total energy/force calculations for large number of different displacements in the supercell. The symmetry analysis may hopefully help to reduce the number of trial displacements below $3n+1$ (three Cartesian displacements for each atom in the unit cell, plus equilibrium). For the forces, we assume that all $3nS$ components are available from each displacement pattern.