Equation of Motion and Dynamical Matrix

Here, we recall the equations of motion (EoM) and the derivation of the dynamical matrix for the nuclear motion in a crystal. Let us assume a perfect crystal with periodic boundary conditions at 0 Kelvin. We define $\mathbf{R}_\alpha$ as the position vectors to the α-th atom within an arbitrarily chosen 'zero' unit cell, and the position vector to the n-th unit cell is denoted by $\mathbf{R}_n$. Hence the equilibrium position of atom α in unit cell n can be written as $\mathbf{R}_{n\alpha} = \mathbf{R}_n + \mathbf{R}_\alpha$. If we denote the Cartesian components of the displacement vector of atom α in unit cell n with $s_{n\alpha i}$, where i takes the three values x, y, z, we can write for the kinetic energy:

$$T = \sum_{n=1}^{N} \sum_{\alpha=1}^{r} \sum_{i=1}^{3} \frac{M_\alpha}{2} \left(\frac{ds_{n\alpha\, i}\,(t)}{dt} \right)^2 . \tag{1}$$

Here, M_α is the mass of atom α, and N is the number of unit cells, r the number of atoms per unit cell, and i stands for the three Cartesian coordinates x, y, z. Hence the total number of degrees of freedom is $3rN$. The potential energy W – as a function of the nuclei coordinates $\mathbf{x}$ – can be expanded into a Taylor series in the atomic coordinates.

$$\begin{aligned} W(s_{n\alpha i}) &= W(\mathbf{R}_{n\alpha}) + \sum_{n\alpha i} \left[\frac{\partial W(\mathbf{x}}{\partial s_{n\alpha i}} \right]_{\mathbf{x}=\mathbf{R}_{n\alpha}} s_{n\alpha i} \\ &+ \frac{1}{2} \sum_{n\alpha i} \sum_{n'\alpha' i'} \left[\frac{\partial^2 W(\mathbf{x}}{\partial s_{n\alpha i} \partial s_{n'\alpha' i'}} \right]_{\mathbf{x}=\mathbf{R}_{n\alpha}} s_{n\alpha i} s_{n'\alpha' i'} + O(s^3) \end{aligned} \tag{2}$$

The linear terms in s vanish, on account of our assumption that we expand around the equilibrium configuration (vanishing forces), and we can introduce the force constants

$$\Phi_{n\alpha i}^{n'\alpha' i'} = \left[\frac{\partial^2 W(\mathbf{x}}{\partial s_{n\alpha i} \partial s_{n'\alpha' i'}} \right]_{\mathbf{x}=\mathbf{R}_{n\alpha}} \tag{3}$$

Note that we neglect higher terms than the harmonic ones. In order to obtain the equations of motion we define the Lagrange function for our problem $\pounds = T - W$, and recall the Euler–Lagrange equations

$$\frac{d}{dt} \frac{\partial \pounds}{\partial\, \dot{s}_{n\alpha i}} - \frac{\partial \pounds}{\partial s_{n\alpha i}} = 0. \tag{4}$$

Inserting the expressions for the kinetic energy T and the potential expansion W into the Euler-Lagrange equation and taking account of the symmetry of the

force constants $\Phi_{n\alpha i}^{n'\alpha' i'} = \Phi_{n'\alpha' i'}^{n\alpha i}$ leads to:

$$M_\alpha \frac{d^2 s_{n\alpha i}}{dt^2} = -\sum_{n'\alpha' i'} \Phi_{n\alpha i}^{n'\alpha' i'} s_{n'\alpha' i'}. \tag{5}$$

With the ansatz

$$s_{n\alpha i}(t) = \frac{1}{\sqrt{M_\alpha}} u_{n\alpha i}\, e^{-i\omega t} \tag{6}$$

we obtain

$$\omega^2 u_{n\alpha i} = \sum_{n'\alpha' i'} \frac{\Phi_{n\alpha i}^{n'\alpha' i'}}{\sqrt{M_\alpha M_{\alpha'}}} u_{n'\alpha' i'} \tag{7}$$

which is an eigenvalue equation for the $3rN$ normal frequencies ω. On account of the translational symmetry, the force constants $\Phi_{n\alpha i}^{n'\alpha' i'}$– which can be identified as the i–th component of the force on atom α in unit cell n, when atom α' in unit cell n' is displaced a unit distance in i'–direction – only depend on the difference $n - n'$, i.e. $\Phi_{n\alpha i}^{n'\alpha' i'} = \Phi_{\alpha i}^{\alpha' i'}(n - n')$. In order to take account of the translational symmetry we make the ansatz:

$$u_{n\alpha i} = c_{\alpha i} e^{i\mathbf{q}\mathbf{R}_n} \tag{8}$$

and we find

$$\sum_{\alpha' i'} D_{\alpha i}^{\alpha' i'}(\mathbf{q}) c_{\alpha' i'} = \omega^2(\mathbf{q}) c_{\alpha i} \tag{9}$$

where we have introduced the dynamical matrix as

$$D_{\alpha i}^{\alpha' i'}(\mathbf{q}) = \left[\sum_n \frac{\Phi_{\alpha i}^{\alpha' i'}(n)}{\sqrt{M_\alpha M_{\alpha'}}} e^{i\mathbf{q}\mathbf{R}_n} \right] \tag{10}$$

Thus, we have arrived at an eigenvalue equation (9) which is only $3r$–dimensional, but now the eigenfrequencies ω are functions of $\mathbf{q}$ which is a wave vector inside the first Brillouin zone.