Ab initio methods in solid state physics

IX. Lattice dynamics - harmonic approximation

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Lattice dynamics

- Atoms vibrate → lattice vibrations → thermodynamics
- Lattice dynamics:[1][2]
  - heat conductance
  - heat capacity
  - thermodynamic stability
  - mechanical stability
  - phase transitions
  - thermoelectricity

[1] A. A. Maradudin, *Theory of Lattice Dynamics in the Harmonic Approximation* / (New York :, 1963.).
[2] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, 1988).

Energy of the crystal

Atomic positions in crystal lattice are described by the position vector $\mathbf{R}(\mathbf{n}, i)$:

$$\mathbf{R}(\mathbf{n}, i) = n_a \mathbf{a} + n_b \mathbf{b} + n_c \mathbf{c} + \mathbf{r}_i$$

where i numbers atoms in the primitive unit cell and vector of integers $\mathbf{n} = [n_a, n_b, n_c]$ numbers unit cells in the lattice while $\mathbf{r}_i$ is a position of the i-th atom relative to the origin of the unit cell with cell vectors $\mathbf{a}, \mathbf{b}, \mathbf{c}$. Symmetry operations of the lattice act only on indexes $i, j, k, ...$, while the periodicity is encapsulated in the integer vector $\mathbf{n}$ and lattice vectors $\mathbf{a}, \mathbf{b}, \mathbf{c}$.

Potential energy of the lattice can be expanded as a function of the atomic displacements $s_{ni\alpha}$, where $\alpha = x, y, z$, (assuming small vibrations and negligible in quantum effects):

$$V(s) = V_0 + \sum_{ni\alpha} \left.\frac{\partial V}{\partial s_{ni\alpha}}\right|_{s=0} s_{ni\alpha} + \frac{1}{2} \sum_{ni\alpha} \sum_{n'i'\alpha'} \left.\frac{\partial^2 V}{\partial s_{ni\alpha} \partial s_{n'i'\alpha'}}\right|_{s=0} s_{ni\alpha} s_{n'i'\alpha'} + O(s^3)$$

The linear term vanishes due to the equilibrium point assumption and we neglect higher order terms assuming they are small.

Equation of motion

We can now write the Lagrangean $L = T - V$ and the Euler-Lagrange equation:

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{s}_{ni\alpha}} = \frac{\partial L}{\partial s_{ni\alpha}}$$

resulting in the equation of motion:

$$m_i \ddot{s}_{ni\alpha} = -\sum_{n'i'\alpha'} \Phi_{ni\alpha}^{n'i'\alpha'} s_{n'i'\alpha'}$$

where we have introduced force constants matrix Φ denoting the second derivative term:

$$\Phi_{ni\alpha}^{n'i'\alpha'} = \left.\frac{\partial^2 V(s)}{\partial s_{ni\alpha}\partial s_{n'i'\alpha'}}\right|_{s_{ni\alpha}=0}$$

Obviously, $\Phi_{ni\alpha}^{n'i'\alpha'} = \Phi_{n'i'\alpha'}^{ni\alpha}$ is symmetric.

Solution of EOM

We can search for the solution of EOM with the standard oscillating ansatz:

$$s_{ni\alpha}(t) = \frac{1}{\sqrt{m_i}} u_{ni\alpha} e^{-i\omega t}$$

The equation of motion now takes form of eigen-equation:

$$\omega^2 u_{ni\alpha} = \sum_{n'i'\alpha'} \Phi_{ni\alpha}^{n'i'\alpha'} u_{n'i'\alpha'}$$

Note that the interaction between atoms $ni\alpha$ and $n'i'\alpha'$ depend only on relative positions of unit cells n and n'. Thus, we can select arbitrary unit cell for the origin and consider one of the indexes constant $n' = 0$ and replace $\Phi_{ni\alpha}^{n'i'\alpha'}$ with $\Phi_{i\alpha}^{i'\alpha'}(n)$ taking care of the translational symmetry of the crystal.

Dynamical matrix

We can further simplify the solution by taking into account the periodicity of the crystal lattice and taking another ansatz for a solution – this time oscillating in spatial coordinates with wave vector $\mathbf{q}$:

$$u_{ni\alpha} = \varepsilon_{i\alpha} e^{i\mathbf{q}\cdot\mathbf{R}_n}$$

where $\mathbf{R}_n$ denotes relative positional vector of the n^{th} unit cell and $\mathbf{q}$ is the point in the first Brillouin zone.

Finally, the equation of motion takes form of eigenequation:

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

where dynamical matrix D is defined by the equation:

$$D_{i\alpha}^{i'\alpha'}(\mathbf{q}) = \sum_n \frac{\Phi_{i\alpha}^{i'\alpha'}(n)}{\sqrt{m_i m_{i'}}} e^{i\mathbf{q}\cdot\mathbf{R}_n}$$

above and $\varepsilon_{i\alpha}$ present themselves as eigenvectors of the dynamical matrix – i.e. polarisation vectors or normal base vectors.

Force constants

Atomic displacements $s_{ni\alpha}$ are connected with forces acting on atoms $F_{ni\alpha}$ with linear relation:

$$F_{ni\alpha} = -\frac{\partial V}{\partial s_{ni\alpha}} = -\sum_{mj\beta} \Phi_{ni\alpha}^{mj\beta} s_{mj\beta}$$

This is again a linear force-displacement relation similar to the one we encountered while calculating elastic tensor in Lecture 8. And we can use similar trick to derive matrix Φ from sets of forces and displacements

Similar to the elastic tensor case the Φ matrix is subject to symmetries of a particular crystal. Unfortunately, here it is much more complicated. But still we can symbolically rewrite above relation as following large set N of linear equations ($a = 1 \dots N$):

$$F^a = S(s^a) I_\Phi$$

Where a numbers set of displacements, $S(s^a)$ is a symmetry-encoding matrix which is a function of displacements and I_Φ is a set of independent parameters of Φ.

Direct (Finite Displacements) method

The force-displacement relation can be approximately solved by fitting the I_Φ parameters to make the sides of the equation as close as possible in the least-squares sense.[3] Again, we often use SVD for this, but this is by far not the only method of solving this problem (e.g. Elastic-net regression, Adaptive LASSO).[4] [5]

The remaining problems are: * Construction of the matrix $S(s^a)$ and vector I_Φ * Selection of displacement sets s^a * Multiple subtle issues (supercell selection, exact points, etc.)

[3] K. Parlinski, Z. Q. Li, and Y. Kawazoe, Phys. Rev. Lett. 78, 4063 (1997)
[4] T. Tadano, Y. Gohda, and S. Tsuneyuki, J. Phys.: Condens. Matter 26, 225402 (2014)
[5] ALAMODE manual

Direct method in practice

- Construction of $S(s)$ is coded in multiple phonon-calculation programs (ALAMODE, PhonoPy, Phonon, Phon, GULP, ...)
- Selection of I_Φ follows directly from the S matrix
- The same goes for the rest of computational details
- Selection of displacements:
  - Elementary displacements (minimal set: PhonoPy, Phonon, ...)
  - Random or thermodynamic displacements (ALAMODE, HECSS)
- Selection of the supercell:
  - Smallest cell containing interaction range
  - Preferably commensurate with important points in reciprocal space
  - Preferably not braking symmetry of the crystal

Goals

- Frequencies $\omega(\mathbf{q})$
- Polarization vectors ε
- Density of states $p(\omega)$
- Structure stability
- Phase transitions
- Phonon heat capacity