Major Project: Phonon spectra of an fcc crystalline lattice

PHZ 5156

1. The atoms in a crystalline lattice at low enough temperatures can be described as a collection of independent simple-harmonic oscillators. The starting point is to expand the potential energy $U$ of the crystal in terms of small atomic displacements from the ground state as,

$$U = U_0 + \frac{1}{2} \sum_{i\mu,j\nu} \frac{\partial^2 U}{\partial r_{i\mu} \partial r_{j\nu}} |_{0} u_{i\mu} u_{j\nu}$$

Here $i,j$ label the atoms, and $\mu,\nu$ label the Cartesian components, $r_{i\mu}$ are the atomic coordinates in equilibrium, and $u_{i\mu}$ represents a small displacement from equilibrium. From this expansion, we define the force constant matrix,

$$\Phi_{i\mu,j\nu} = \frac{\partial^2 U}{\partial r_{i\mu} \partial r_{j\nu}}$$

where the derivatives of the potential energy $U$ are performed at the equilibrium coordinates. In the harmonic approximation, it is easy to show that the time-dependent displacements are given by

$$u_{i,\mu}(t) = \frac{1}{m_i^{1/2}} \sum_{\lambda} a_{\lambda} \epsilon_{\lambda\mu} \exp \left(-i\omega_{\lambda} t\right)$$

Since the lattice is periodic, we could also write for the $\mu$‘th Cartesian component of the time-dependent displacement of atom $i$ in unit cell $l$,

$$u_{il,\mu}(t) = \frac{1}{m_i^{1/2}} \sum_{\lambda,\vec{k}} a_{\lambda\vec{k}} \epsilon_{\lambda\mu}(\vec{k}) \exp \left[i\vec{k} \cdot \vec{R}_l - i\omega_{\lambda}(\vec{k}) t\right]$$

1. In this project, we will directly compute the phonon frequencies of a collection of atoms. Using your MD code from project 4, you can create a $8 \times 8 \times 8$ fcc argon lattice. How big should the force-constant matrix be? Analytically determine the needed expressions for the force-constant matrix using the Lennard Jones potential, and write a code to populate the matrix. Use periodic boundary conditions. The normal modes frequencies and eigenvectors are obtained by diagonalization of the force-constant matrix. Plot the number of states in found as a function of frequency. This is the density-of-states (DOS). It is important to understand that this is the
DOS for a finite system, and so it looks rather discrete. It is actually easy to do this for an infinite system, and actually requires diagonalization of a smaller matrix, although repeated many times.

2. Show analytically that the DOS can be found from the Fourier transform of the velocity-velocity autocorrelation function. The velocity-velocity correlation is defined as

\[ \langle \vec{v}(\tau) \cdot \vec{v}(0) \rangle = \frac{1}{NT} \sum_{i=1}^{N} \int_{0}^{T} \vec{v}_i(t + \tau) \cdot \vec{v}_i(t) dt \]

where \( N \) is the total number of atoms and \( T \) is the total simulation time for the averaging. Show that the Fourier transform gives

\[ D(\omega) = \sum_{\lambda} \delta(\omega - \omega_{\lambda}) = \int_{0}^{\infty} \langle \vec{v}(\tau) \cdot \vec{v}(0) \rangle \exp(-i\omega\tau) d\tau \]

This can be done in a computer code, although obviously we don’t have the possibility of \( \tau \to \infty \), but the Fourier transform can be done for large enough times and using some tricks to get good results.

Of course, in reality the harmonic assumption is only an approximation, and anharmonic coupling between the modes exists to redistribute energy between the modes. For a classical system, or at fairly high temperature, this leads to \( k_B T \) of energy per mode. In a quantum system, which is relevant at lower temperatures, the energy in each mode is quantized. The quanta are called phonons, and the average number of phonons per mode is given by a Bose-Einstein distribution.