Exercise 3.1

Lennard-Jones potential. The Lennard-Jones potential is widely used to describe the interactions between similar atoms or molecules in liquidus or gaseous phases. It has the simple analytical form

$$U(r) = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}],$$

where ϵ is the depth of the potential well, σ is the distance at which the potential between the two atoms is zero, and r is the distance between the two atoms. For argon crystal ($\epsilon = 0.0104\,\text{eV}$ and $\sigma = 3.40\,\text{Å}$),

a) Calculate the equilibrium interatomic distance.

b) Calculate the energy at the minimum (called cohesive energy).

c) Calculate the effective spring constant between two argon atoms.

Solution

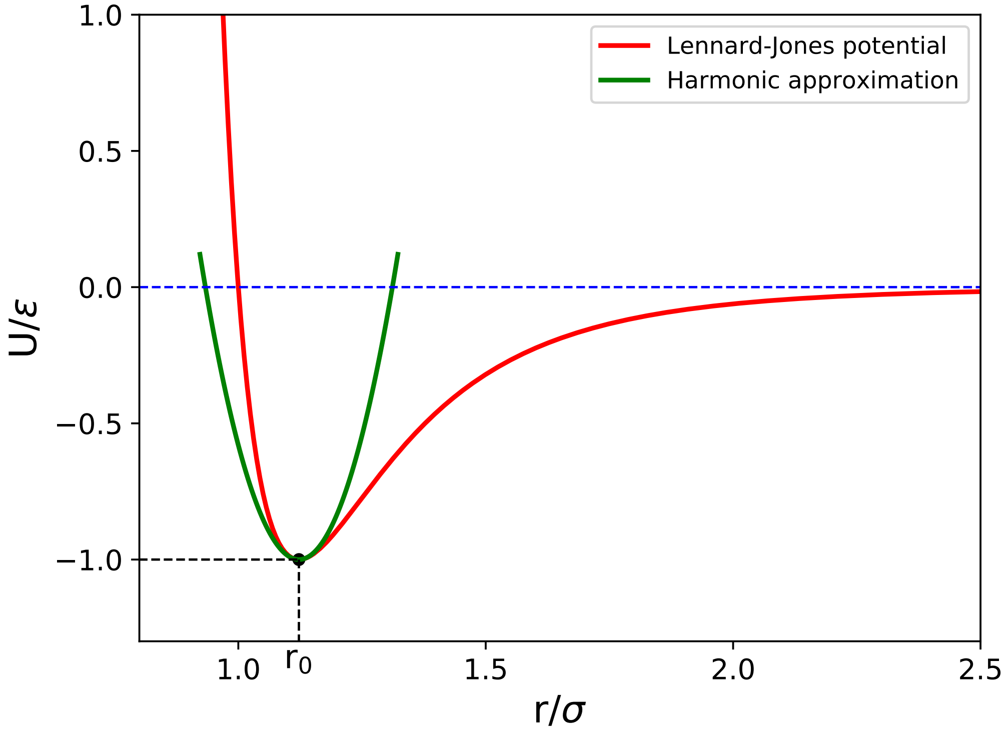

Figure 1: Graph of the Lennard-Jones potential

(a) At the equilibrium, the potential has its lowest energy. To obtain the interatomic distance, we take the derivative of the potential U with respect to the interatomic distance r and get its zero,

$$\frac{dU}{dr} = -4\epsilon[12(\frac{\sigma}{r})^{12}\frac{1}{r} - 6(\frac{\sigma}{r})^{6}\frac{1}{r}] = 0.$$

The physically meaningful solution is $r = 2^{1/6}\sigma$. So the equilibrium interatomic distance is

$$r_0 = 2^{1/6} \times 3.40 \approx 3.82\,\text{Å}.$$

(b) Substituting $r_0 = 3.82\,\text{Å}$ obtained in (a) into the Lennard-Jones potential, we have the energy at the minimum as

$$U_{min} = 4 \times 0.0104 \times [(\frac{3.40}{3.82})^{12} - (\frac{3.40}{3.82})^{6}] \approx -0.0104\,\text{eV}.$$

You can see that this energy is just the depth of the potential well ϵ (also called cohesive energy). By absorbing this amount of energy, the interatomic bonding is broken and atoms in the crystal would be free. In other words, atoms arranged periodically in certain order form the crystal, releasing the amount of energy σ, and that is where the name cohesive energy comes from.

(c) The effective spring constant is the second-order derivative of the potential U with respect to interatomic distance r, we can do it in the Taylor expansion around the equilibrium interatomic distance r_0,

$$U(r) = U(r_0) + \frac{1}{2}\frac{d^2U}{dr^2}\bigg|_{r=r_0}(r-r_0)^2 + O[(r-r_0)^3].$$

The first-order derivative does not appear in the above equation because it vanishes at the equilibrium interatomic distance (you can understand this through the fact that the forces exerted on atoms at the equilibrium are zero). Hence, the effective spring constant for the Lennard-Jones potential is

$$K_{eff} = \frac{d^2U}{dr^2}\bigg|_{r=r_0} = [4\epsilon(\frac{156\sigma^{12}}{r^{14}} - \frac{42\sigma^6}{r^8})]\bigg|_{r=r_0} = 4\times0.0104\times(\frac{156\times3.40^{12}}{3.82^{14}} - \frac{42\times3.40^6}{3.82^8}) \approx 0.0504\,\mathrm{eV}/\text{Å}^2.$$

From the plot, it can also be concluded that harmonic approximation (the Taylor expansion of the potential up to the second order) is only valid close to the equilibrium.

Exercise 3.2

Phonon spectra of a diatomic lattice chain. Consider a diatomic chain of atoms as shown in figure 2. The masses of the two atoms are different but the spacing and the spring constant between them are the same. Derive the following given expression for the phonon dispersion in this diatomic lattice chain and schematically draw it:

$$\omega^2 = K(\frac{M_1 + M_2}{M_1 M_2}) \pm K\sqrt{(\frac{M_1 + M_2}{M_1 M_2})^2 - \frac{4\sin^2{(ka/2)}}{M_1 M_2}},$$

where K is the spring constant and k the wavevector with the following values

$$k = 0, \pm\frac{2\pi}{Na}, \pm\frac{4\pi}{Na}, ..., \frac{\pi}{a},$$

and N is the total number of lattice points in the chain.

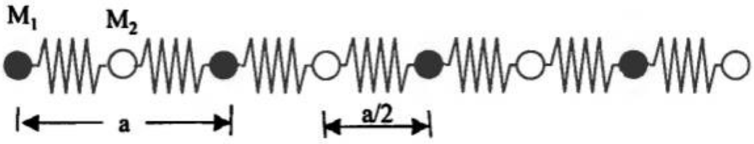

Figure 2: A diatomic lattice chain

Solution

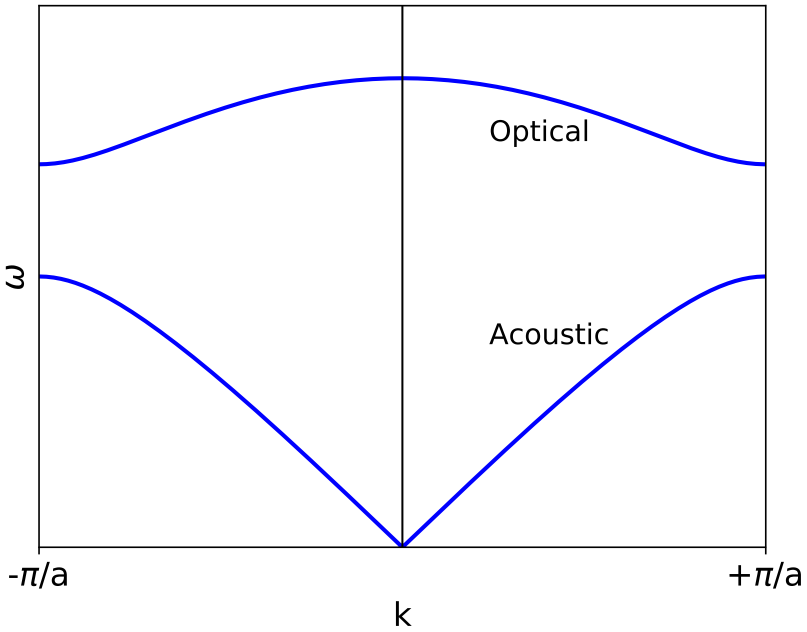

Figure 3: Phonon spectra of a 1D diatomic lattice chain

There are N lattice sites (labelled as 0, 1, ..., $N-1$) in the chain with two different atoms at each site. For an arbitrary lattice site n, the atom of mass M_1 occupies the sublattice position $R_n^1 = na$ and the one of mass M_2 occupies the position $R_n^2 = (n + \frac{1}{2})a$, as shown in the figure. We further denote their displacements by u_n and v_n, respectively. If we only consider the nearest-neighbor interactions by spring constant K and apply the Hooke's law, the classical equations of motion for the two types of atoms from Newton's Second Law read:

$$M_1 \frac{d^2 u_n}{dt^2} = -K(u_n - v_{n-1}) - K(u_n - v_n), \tag{1}$$

$$M_2 \frac{d^2 v_n}{dt^2} = -K(v_n - u_n) - K(v_n - u_{n+1}). \tag{2}$$

These two differential equations are coupled and can be readily solved by the traveling waves ansatzs,

$$u_n(t) = A_1 e^{i(kna-\omega t)}, \tag{3}$$

$$v_n(t) = A_2 e^{i[k(n+1/2)a-\omega t]}. \tag{4}$$

By substituting Eq. (3)-(4) into Eq. (1)-(2), we obtain

$$(M_1\omega^2 - 2K)A_1 + 2K\cos(ka/2)A_2 = 0, \tag{5}$$

$$2K\cos(ka/2)A_1 + (M_2\omega^2 - 2K)A_2 = 0. \tag{6}$$

In order to have a non-trivial solution, i.e. $A_1 \neq 0$ and $A_2 \neq 0$, the determinant of the coefficient matrix of the equation set (5)-(6) must be zero,

$$\begin{vmatrix} M_1\omega^2 - 2K & 2K\cos(ka/2) \\ 2K\cos(ka/2) & M_2\omega^2 - 2K \end{vmatrix} = 0. \tag{7}$$

The solutions thus are

$$\omega^2 = K(\frac{M_1 + M_2}{M_1 M_2}) \pm K\sqrt{(\frac{M_1 + M_2}{M_1 M_2})^2 - \frac{4\sin^2{(ka/2)}}{M_1 M_2}}.$$

For this 1D diatomic lattice chain, the phonon spectra is shown in the above figure. There is one acoustic branch and one optical branch. In general, a d-dimensional system with m atoms in the primitive cell, having d acoustic branches and $d(m-1)$ optical branches.

Additional questions (if you are interested): How does the phonon spectrum change qualitatively if $M_1 = M_2$? At the Brillouin zone border, is there still an energy gap between acoustic and optical phonons?