1. We know that in 2D, Xe atoms want to form a triangular lattice (or hexagonal lattice). But there may be a possibility that Xe atoms can also form a locally stable square lattice. (Although the square lattice has a higher energy than the triangular lattice, any small deformations of the square lattice may always increase its energy. If this happens, the square lattice is said to be locally stable.) In this problem, we will investigate if the square lattice of Xe is really locally stable or not.

The interaction potential \( V(r) \) between two Xe atoms is given by eq. (10) on page 58 of Kittle. The parameters can be found in the table on page 53.

(a) Assume that the Xe atoms form a square lattice, find that lattice constant \( a \) that minimizes the total potential energy. (Hint: for square lattice \( \gamma_6 = \sum'_j 1/p^6_{ij} = 4.66 \) and \( \gamma_{12} = \sum'_j 1/p^2_{ij} = 4.06. \))

(b) If we use the spring-bead model to describe the above Xe lattice with springs connecting the nearest-neighbor and the next-nearest-neighbor Xe atoms, what should be the spring constant \( K_1 \) for the springs connecting the nearest neighbors and what should be the spring constant \( K_2 \) for the springs connecting the next nearest neighbors? (Hint: For the spring that connects the \( i^{th} \) and the \( j^{th} \) atoms, its spring constant is \( K_{ij} = \partial^2 V(r_{ij})/\partial r^2_{ij} \) where \( r_{ij} \) is the distance between the two atoms.)

(c) Using the result from the lecture note, determine if the square lattice of Xe is locally stable or not.

Solution:
Interaction potential between Xe atoms in lattice (Kittel, p. 58, eq. 10)

\[ U_{\text{int}} = 2NE \left[ \frac{\sigma_j (\sigma_j \cdot \mathbf{r}_{ij})}{\sigma_j} \right]^{12} - \frac{1}{r_{ij}} \]  
\[ U_{\text{ext}} = 2NE \left[ \gamma_{12} \left( \frac{\sigma_j}{\mathbf{r}_{ij}} \right)^{12} - \gamma_6 \left( \frac{\sigma_j}{\mathbf{r}_{ij}} \right)^6 \right] \]

Note: \( \sigma_{\text{lat}} \) = lattice constant (notational differences)

\( \sigma_6 = 4.66 \)
\( \sigma_12 = 4.06 \)

a. To minimize \( U_{\text{int}} / N \):

\[ \frac{\sigma}{a} = \left( \frac{\sigma_6}{2\gamma_{12}} \right)^{1/6} \quad \text{(result from lecture)} \]

\[ \text{Using the value } \sigma = 3.97 \text{ Å (from Kittel p. 53)} \]

\[ a = \left( \frac{4.66}{2 \times 4.06} \right)^{1/6} (3.97 \text{ Å}) = 4.35 \text{ Å} = a \]

b. The interaction potential between 2 atoms is:

\[ V_{ij} = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right] \]

The force constant is:

\[ K_{ij} = \frac{\partial^2 V_{ij}}{\partial (\sigma_{ij})^2} \]

\[ K_{ij} = 4\epsilon \left[ 15 \frac{\sigma^2}{r_{ij}^6} - 42 \frac{\sigma^2}{r_{ij}^8} \right] \]

\( \sigma = 3.97 \text{ Å} \)

For nearest neighbors: \( r_1 = 4.35 \text{ Å} \) (Kittel p. 53)
For 2nd nearest neighbors:

\[ r_2 = \frac{r_1}{\sqrt{2}} \]

\( \epsilon = 320 \text{ eV} \) (Kittel p. 53)
\( K_1 = 4\epsilon \left[ 15 \frac{\sigma_{12}^2}{r_{12}^6} - 42 \frac{\sigma_{12}^2}{r_{12}^8} \right] \approx 1.88 \text{ eV/Å}^2 \)
\( K_2 = 4\epsilon \left[ 15 \frac{\sigma_{12}^2}{r_{12}^6} - 42 \frac{\epsilon}{r_{12}^8} \right] \approx -7.59 \text{ eV/Å}^2 \)

C. The lattice is locally stable if all \( \omega \) (frequencies of modes) are real (e.g., any deformation causes destabilization of the lattice).
For a square 2D lattice:

\[ \omega = \frac{1}{\sqrt{m}} \left[ \frac{a+b}{2} + \sqrt{\left(\frac{a-b}{2}\right)^2 + c^2} \right]^{1/2} \]

where

- \( a = 2k_1(1 - \cos k_x) + k_2 [2 - \cos (k_x k_y) - \cos (k_x - k_y)] \)
- \( b = 2k_1(1 - \cos k_y) + k_2 [2 - \cos (k_x + k_y) - \cos (k_x - k_y)] \)
- \( c = k_2 [\cos (k_x + k_y) - \cos (k_x - k_y)] \)
- \( \vec{k} = \left( \frac{k_x}{a}, \frac{k_y}{b} \right) \) (direction of mode)

1. \( |k_1| > |k_2| \)
2. \( k_1 > 0, \ k_2 < 0 \)

Define

\[ \omega_1 = \frac{1}{\sqrt{m}} \left[ \frac{a+b}{2} + \sqrt{\left(\frac{a-b}{2}\right)^2 + c^2} \right]^{1/2} \]

\[ \omega_2 = \frac{1}{\sqrt{m}} \left[ \frac{a+b}{2} - \sqrt{\left(\frac{a-b}{2}\right)^2 + c^2} \right]^{1/2} \]

\( \omega_1 \) is always real.
However, \( \omega_2 \) becomes imaginary: \( \left( \frac{a+b}{a} \right) \) is not always greater than \( \left[ \left( \frac{a-b}{a} \right)^2 + c^2 \right]^{1/2} \).

See attached plots.

So the Xe square lattice is not locally stable.
\[ f[x_] = (a \div x)^{12} - (a \div x)^{6} \quad (A = 0) \text{ sorry bad notation} \]

\[ g[x_] = D_t[f[x], \{x, 2\}, \text{Constants} \to \{a\}] \]

Solving for \(K_{ij}\) gives the following function (epsilon -> e, Rij->x):

\[
h[x_, e_, a_] = 4 \times e \times g[x]
\]

\[
4 e \left( \frac{156 a^{12}}{x^{14}} - \frac{42 a^{6}}{x^{8}} \right)
\]

The spring constant for the spring connecting nearest neighbors \((\text{erg/(Angstrom)}^2)\):

\[
K_1 = h[4.35, 320 \times 10^{-16}, 3.97]
\]

\[
1.80179 \times 10^{-13}
\]

The spring constant for the spring connecting next nearest neighbors \((\text{erg/(Angstrom)}^2)\):

\[
K_2 = h[6.14, 320 \times 10^{-16}, 3.97]
\]

\[
-7.59181 \times 10^{-15}
\]

\[
a[kx_, ky_] = 2 \times K_1 \times (1 - \cos[kx]) \times K_2 \times (2 - \cos[kx + ky] - \cos[kx - ky])
\]

\[
b[kx_, ky_] = 2 \times K_1 \times (1 - \cos[ky]) \times K_2 \times (2 - \cos[kx + ky] - \cos[kx - ky])
\]

\[
c[kx_, ky_] = K_2 \times (-\cos[kx + ky] - \cos[kx - ky])
\]

The two possible solutions for the frequencies of the two modes are:

\[
w_1[kx_, ky_] = (1 / \sqrt{m}) \times \sqrt{\left( \frac{1}{4} \left( 3.76359 \times 10^{-13} (1 - \cos[kx]) - 3.76359 \times 10^{-13} (1 - \cos[ky]) + 0.2 \times \cos[kx - ky] + \cos[kx + ky] \right)^{2} + 5.76355 \times 10^{-29} \times (-\cos[kx - ky] - \cos[kx + ky])^{3} \right) + \frac{1}{2} \left( 3.76359 \times 10^{-13} (1 - \cos[kx]) + 3.76359 \times 10^{-13} (1 - \cos[ky]) - 1.51836 \times 10^{-14} \times (2 - \cos[kx - ky] - \cos[kx + ky]) \right)}
\]
\[
\begin{align*}
\text{w2[\text{kx, ky}]} &= \left(1 / \text{Sqrt[m]}\right) * \\
&\quad \text{Sqrt}[(\text{a[kx, ky]} + \text{b[kx, ky]}) / 2] - \text{Sqrt}[((\text{a[kx, ky]} - \text{b[kx, ky]}) / 2) ^ 2 + \text{c[kx, ky]} ^ 2] \\
&\quad \frac{1}{\sqrt{m}} \\
&\quad \left(\sqrt{\frac{1}{4} \left(3.76359 \times 10^{-13} \left(1 - \text{Cos[kx]}\right) - 3.76359 \times 10^{-13} \left(1 - \text{Cos[ky]}\right) + 0. \left(2 - \text{Cos[kx - ky]} - \text{Cos[kx + ky]}\right)\right)^2 + 5.76355 \times 10^{-29} \left(-\text{Cos[kx - ky]} - \text{Cos[kx + ky]}\right)^2} + \\
&\quad \frac{1}{2} \left(3.76359 \times 10^{-13} \left(1 - \text{Cos[kx]}\right) + 3.76359 \times 10^{-13} \left(1 - \text{Cos[ky]}\right) - 1.51836 \times 10^{-14} \left(2 - \text{Cos[kx - ky]} - \text{Cos[kx + ky]}\right)\right)\right)
\end{align*}
\]

Set \(m = 1\) since it does not affect whether the frequency is real or imaginary.

\[
\begin{align*}
\text{m} &= 1 \\
1
\end{align*}
\]

A plot of the first root: it is positive and real.

\[
\text{Plot3D[w1[kx, ky], \{kx, 0, 1\}, \{ky, 0, 1\}]}
\]

A plot of the second root: it becomes imaginary (parts of the plot that are missing).
Plot3D[w2[kx, ky], {kx, 0, 1}, {ky, 0, 1}]

For instance, it is imaginary at \((kx, ky) = (0, 0)\):

\[
w2[0, 0] = 0. + 1.23222 \times 10^{-7} i
\]

A plot of the imaginary sections of the solution:

Plot3D[I*w2[kx, ky], {kx, 0, 1}, {ky, 0, 1}]
2. (20 pts) Beads of mass $m$ are connected by springs of length $a = 1$ and form a triangular lattice (see the figure below).

![Triangular Lattice Diagram]

The spring constants of the springs are all given by $C$.

(a) Find the fundamental translation vectors $(a_1, a_2)$ of the triangular lattice. Find the fundamental translation vectors $(b_1, b_2)$ of the reciprocal lattice. We choose the Wigner-Seitz unit cell of the reciprocal lattice as the Brillouin zone. Draw such a Brillouin zone.

(b) An lattice vibration mode (a sound wave mode) is described by

$$u_i = \tilde{u}_k e^{i\mathbf{k} \cdot \mathbf{i}}$$

where $i = \text{int.} \times a_1 + \text{int.} \times a_2$ labels the lattice point and the wave vector $\mathbf{k}$ labels different vibration modes. Show that two wave vectors $\mathbf{k}$ and $\mathbf{k}'$ differ by a vector in reciprocal lattice

$$\mathbf{k} - \mathbf{k}' = \mathbf{G}, \quad \mathbf{G} = \text{int.} \times \mathbf{b}_1 + \text{int.} \times \mathbf{b}_2$$

actually describe the same vibration mode. So only the wave vectors in the Brillouin zone (the cell of the reciprocal lattice) label distinct modes of vibration.

(c) Find an expression of the total potential energy $U_{\text{tot}}$ of the deformed lattice in terms of the displacements $u_i$. The total potential energy $U_{\text{tot}}$ has a form

$$U_{\text{tot}} = \frac{1}{2} \sum_{ij} u_i C_{ij} u_j$$

where $i$ is the location of a point in the triangular lattice and $u_i$ is the displacement of the bead at the location $i$. You need to calculate the two by two matrices $C_{ij}$.

(d) Calculate the dispersion relation $\omega_k$ of the two branches of sound waves. (Hint: you may want to introduce $(k_1, k_2)$ through $k = k_1 \frac{b_1}{2\pi} + k_2 \frac{b_2}{2\pi}$ and express $\omega_k$ as a function of $k_1$ and $k_2$.)

(e) (optional, no points) Plot the dispersion relations along the following lines $k = 0 \rightarrow k_c \rightarrow k_e \rightarrow 0$, where $k_c$ is a corner of the Brillouin zone (here chosen as the Wigner-Seitz unit cell of the reciprocal lattice), and $k_e$ is the center of the Brillouin-zone edge that connects to $k_c$. Mark those lines in your Brillouin zone. (This is also the good time to plot the dispersion relation along several directions that are related by symmetry to check your result.)

Solution:
a) \[ \hat{a}_1 = \hat{e}_1, \quad \hat{a}_2 = \frac{1}{2} \hat{e}_1 + \frac{\sqrt{3}}{2} \hat{e}_2 \]
\[ \hat{a}_1 \wedge \hat{a}_2 = \frac{\sqrt{3}}{2} \hat{e}_{12} = \mathbf{v} \]
\[ \hat{b}_1 = 2 \pi \hat{a}_1 \mathbf{v}^{-1} = -2 \pi \left( \frac{1}{2} \hat{e}_1 + \frac{\sqrt{3}}{2} \hat{e}_2 \right) \frac{2}{\sqrt{3}} \hat{e}_{12} \]
\[ = -2 \pi \left( \frac{1}{\sqrt{3}} \hat{e}_2 - \hat{e}_1 \right) \]
\[ \hat{b}_2 = -2 \pi \hat{a}_2 \mathbf{v}^{-1} = 2 \pi \hat{e}_1 \frac{2}{\sqrt{3}} \hat{e}_{12} \]
\[ = 4 \pi \frac{1}{\sqrt{3}} \hat{e}_2 \leftarrow \text{Triangular Lattice.} \]
\[ \hat{b}_4 = 4 \pi \frac{1}{\sqrt{3}} \left( \frac{1}{2} \hat{e}_2 - \frac{\sqrt{3}}{2} \hat{e}_1 \right) \]

Lattice:

Reciprocal Lattice:

Wigner-Seitz Unit Cell
b) \[ u_i = u_k e^{i k \cdot i}, \quad k' = k + G \]

\[ i = i_1 a_1 + i_2 a_2 \]

\[ G = G_1 b_1 + G_2 b_2 \]

where, \( i_1, i_2, G_1, \) and \( G_2 \) are all integers.

\[ u(i_1, i_2) = u_k e^{i(k \cdot i + G \cdot i)} \]

\[ G \cdot i = i_1 G_1 + i_2 G_2 = 2\pi n, \quad n \in \mathbb{Z} \]

\[ u(i_1, i_2) = u_k e^{i k \cdot i} e^{i 2\pi n} \]

\[ e^{i 2\pi n} = 1 \]

\[ u(i_1, i_2) = u_k e^{i k \cdot i} \]

Therefore, \( k \) and \( k' \) describe the same vibrational mode.
\( K_{12} = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} 1 & 0 \end{bmatrix} K = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} K \)

\( K_{13} = \begin{bmatrix} 1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{bmatrix} \begin{bmatrix} 1/4 & \sqrt{3}/4 \\ \sqrt{3}/4 & 3/4 \end{bmatrix} K \)

\( K_{23} = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix} \begin{bmatrix} 1/4 & -\sqrt{3}/4 \\ -\sqrt{3}/4 & 3/4 \end{bmatrix} K \)

\[
\mathcal{U}_\text{TOT} = \frac{\hbar}{2} \sum_{m,n} (U_{m+n} - U_{mn}) K_{12} (U_{m+n} - U_{mn}) + (U_{m+1} - U_{mn}) K_{13} (U_{m+1} - U_{mn}) + (U_{m-1} - U_{mn}) K_{23} (U_{m-1} - U_{mn})
\]
\[ u_{\text{tor}} = \frac{1}{2} \sum_k \hat{u}_k \hat{C}_k \hat{u}_k \]

\[
\hat{C}_k = \sum_\mu 2(1 - \cos(k \cdot \mu)) K_{\mu}
\]

\[
= 2(1 - \cos(k_1)) \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} K
\]

\[
+ 2(1 - \cos(k_2)) \begin{bmatrix} 2/4 & \sqrt{3}/4 \\ \sqrt{3}/4 & 3/4 \end{bmatrix} K
\]

\[
+ 2(1 - \cos(k_2 - k_1)) \begin{bmatrix} 2/4 & -\sqrt{3}/4 \\ \sqrt{3}/4 & 3/4 \end{bmatrix} K
\]
The two frequencies are given by:

\[ \omega_1 = \sqrt{3 - \cos[k_1] - \cos[k_1 - k_2] - \cos[k_2]} \]
\[ \omega_2 = \sqrt{3 - \cos[k_1] - \cos[k_1 - k_2] + \cos[k_2]} \]
\[ \sqrt{\cos[k_1]^2 - \cos[k_1] \cos[k_1 - k_2] + \cos[k_1 - k_2]^2} - (\cos[k_1] + \cos[k_1 - k_2]) \cos[k_2] + \cos[k_2]^2 \]

Plot of the two frequencies:

Plot of Omega for \((k_1, k_2) = (\pi, 0)k\)

\[ \vec{b}_c = \left( \frac{1}{2}, \frac{1}{2}, 0 \right) \]
\[ (k_1, k_2)_c = (\pi, 0) \]

Plot of Omega for \((k_1, k_2) = (4\pi/3, 2\pi/3)k\)

\[ \vec{k}_c = \left( \frac{1}{2}, \frac{1}{2}, 0 \right) \]
\[ (k_1, k_2)_c = \left( \frac{4\pi}{3}, \frac{2\pi}{3} \right) \]
$0 \rightarrow k_c$

Plot of Omega for $(k_1,k_2) = (\pi,0) + (\pi/3,2\pi/3)*k$

$k_e \rightarrow k_c$

Plot of Omega for $(k_1,k_2) = (\pi,\pi)*k$

Plot of Omega for $(k_1,k_2) = (\pi,0)*k$