1. Show that for the total energy in the jellium model

\[ U_{\text{total}}(r_s) = N \left( \frac{3}{5} \frac{\hbar^2}{2m} \left( \frac{9\pi}{4} \right)^{2/3} \frac{1}{r_s^2} - \frac{3e^2}{16\pi^2\epsilon_0} \left( \frac{9\pi}{4} \right)^{1/3} \frac{1}{r_s} \right) \]

the equilibrium radius \( r_s^0 = 2.5 \, \text{Å} \) and the binding energy \( U_{\text{total}}(r_s^0)/N = -1.3 \, \text{eV/atom} \).

**Solution**

The total energy can be defined as

\[ U_{\text{total}}(r_s) = N \left[ \frac{A}{r_s^2} - \frac{B}{r_s} \right], \]

with the constants are

\[ A = \frac{3}{5} \frac{\hbar^2}{2m} \left( \frac{9\pi}{4} \right)^{2/3} = 8.45 \, \text{eVÅ}^2 , B = \frac{3e^2}{16\pi^2\epsilon_0} \left( \frac{9\pi}{4} \right)^{1/3} = 6.63 \, \text{eVÅ}. \]

The equilibrium distance \( r_s^0 \) can be found again by searching for the minimum:

\[ \frac{dU_{\text{total}}(r_s)}{dr_s} = N \left[ -\frac{2A}{r_s^3} + \frac{B}{r_s^2} \right] = 0, \]

giving

\[ r_s^0 = \frac{2A}{B} \approx 2.55 \, \text{Å} \]

So the binding energy is

\[ U_{\text{total}}(r_s^0)/N = \left[ \frac{AB^2}{4A^2} - \frac{B^2}{2A} \right] = -\frac{B^2}{4A} \approx -1.3\,\text{eV/atom}. \]
2. Calculate the ratio of the binding energies of neon with fcc (face-centered cubic) and bcc (body-centered cubic) lattice structures. Use the Lennard-Jones potential \((\sigma = 2.74 \text{ Å}, \varepsilon = 3.1 \text{ meV})\) and the bcc lattice sums
\[
\sum_j p_{ij}^{-12} = 9.11418 \quad \text{ and } \quad \sum_j p_{ij}^{-6} = 12.2533.
\]
(The lattice fcc sums were mentioned in the lecture.) Also compare the bulk modulus. *Hint:* You need first the volume as a function of the distance to the next neighbors. You can also determine the solution graphically.

**Solution**

The total energy for the bcc lattice is:
\[
U_{bcc}(R) = 2N\varepsilon \left[ 9.11418 \left( \frac{\sigma}{R} \right)^{12} - 12.2533 \left( \frac{\sigma}{R} \right)^{6} \right].
\]

The equilibrium lattice constant or the nearest neighbor distance \(R_0\) can be found by minimizing the above energy (first derivative equal to zero)
\[
\frac{dU_{bcc}}{dR} = 2N\varepsilon \left[ 9.11418 \left( \frac{-12}{R} \right) \left( \frac{\sigma}{R_0} \right)^{12} - 12.2533 \left( \frac{-6}{R} \right) \left( \frac{\sigma}{R_0} \right)^{6} \right] = 0.
\]

Results in
\[
9.11418 \left( \frac{-12}{R_0} \right) \left( \frac{\sigma}{R_0} \right)^{12} = 12.2533 \left( \frac{-6}{R_0} \right) \left( \frac{\sigma}{R_0} \right)^{6}\]
\[
9.11418(-12)(\sigma)^{12} = 12.2533(-6)R_0^6(\sigma)^{6}
\]
\[
2\times 9.11418 \times 12.2533 \times R_0^6 = \sigma^6
\]
\[
R_0 = 1.068\sigma = 2.93\text{ Å}
\]

The binding energy is simply the total energy at minimum per atom:
\[
U_{bcc}(R_0)/N = -8.23\varepsilon = -25.5 \text{ meV}.
\]

These results can be compared with the results from the lecture for the fcc lattice:
\[
R_0 = 1.09\sigma = 2.99\text{ Å}, \quad U_{fcc}(R_0)/N = -8.61\varepsilon = -26.7 \text{ meV}.
\]

The arrangement of the atoms in the fcc lattice is therefore energetically more favorable.
In order to be able to calculate the bulk modulus, the volume of the crystal is required as a function of the nearest neighbor distance, for bcc lattice one atom sits at each corner of a cube (=unit cell) of side length $a$ (= lattice constant) and one atom in the middle of the cube (i.e. at position $(a/2, a/2, a/2)$). The atoms at the corners are part of 8 adjacent unit cells, i.e. each unit cell has $8 \times 1/8 + 1 = 2$ atoms and volume $a^3$. The nearest neighbor distance is $R = \sqrt{3}(a/2)^2 = \sqrt{3}(a/2)$. The volume of the crystal with $N$ atoms is accordingly

$$V = N \frac{a^3}{2} = \frac{N}{2 \left(\frac{2R}{\sqrt{3}}\right)^3} = \frac{4N}{3\sqrt{3}}R^3.$$

The bulk modulus can now be calculated using the equation from the lecture:

$$K = V \left(\frac{dV}{dR}\right)^{-2} \frac{\partial^2 U}{\partial R^2} \bigg|_{R=R_0}.$$

The derivatives are

$$\frac{dV}{dR} = \frac{4N}{\sqrt{3}}R^2$$

$$\frac{\partial^2 U}{\partial R^2} = 2N \varepsilon \left[ 9.11418 \frac{(-12)(-13)}{R^2} \left(\frac{\sigma}{R}\right)^{12} - 12.2533 \frac{(-6)(-7)}{R^2} \left(\frac{\sigma}{R}\right)^6 \right]$$

giving the result

$$K = \frac{4N}{3\sqrt{3}}R_0^3 \left(\frac{4N}{\sqrt{3}}R_0^2\right)^{-2} 2N \varepsilon \left[ 9.11418 \frac{(-12)(-13)}{R_0^2} \left(\frac{\sigma}{R_0}\right)^{12} - 12.2533 \frac{(-6)(-7)}{R_0^2} \left(\frac{\sigma}{R_0}\right)^6 \right]$$

$$= \frac{2N \varepsilon}{4N R_0 \sqrt{3}} \left[ 9.11418 \frac{156 \varepsilon R_0^{0.672^2 - 12.2533 \frac{42 R_0^{0.672}}{R_0^2} \left(\frac{\sigma}{R_0}\right)^6} \right]$$

$$= \frac{85.51 \varepsilon}{R_0^3} = \frac{85.51 \varepsilon}{R_0^3} \frac{70.1 \varepsilon}{\sigma^3} = 10.56 \text{ meVÅ}^{-3}.$$
3. For the description of colloids (nanoparticles distributed in a medium) the DLVO theory (according to Derjaguin, Landau, Verwey and Overbeek) is used. It is assumed that the interaction between the (spherical) particles by the attractive van der Waals energy $U_{vdW}$ (Hamaker theory) and an electrostatic repulsion $U_{el}(D)$ is given:

$$
U_{tot}(D) = U_{vdW}(D) + U_{el}(D),
$$

$$
U_{vdW}(D) = - \frac{16AHR^6}{9D^6} \quad (D \gg R),
$$

$$
U_{el}(D) = Be^{-\kappa D}.
$$

What are the differences to the Lennard-Jones model with regard to the binding energy, the equilibrium distance and the bulk modulus? (Assume that only neighbors are involved in the interaction).

**Solution**

The total energy of the “colloidal crystal” results from the summation of the pair interaction $U_{tot}(D)$ for all nearest neighbors. Assuming there are $Z$ nearest neighbors, the energy is

$$
U = \frac{1}{2}NZ \left( Be^{-\kappa D} - \frac{C}{D^6} \right) \quad \text{with} \quad C \equiv \frac{16AHR^6}{9}.
$$

The calculation of the binding energy, the equilibrium distance and the bulk modulus follows the previous scheme. Only the main results are given below; a similar calculation is carried out in more detail in connection with the ionic crystals.

- **Equilibrium distance**: Minimization of energy

  $$
  \frac{dU}{dD} = 0 = 6NZCZ^{-\kappa D} - BZ\kappa e^{-\kappa D} \quad \Rightarrow \quad \frac{e^{-\kappa D}}{C} = \frac{6C}{B}D^2
  $$

  This equation should be solved numerically or graphically for $D_0$.

- **Binding Energy**: Energy at minimum per atom

  $$
  U(D_0)/N = -\frac{1}{2} \left( \frac{ZC}{D_0^6} \left( 1 - \frac{6}{\kappa D_0} \right) \right) = U_B
  $$

- **Bulk modulus**: second derivative of the potential and volume as a function of distance (only the second derivative should be considered here)

  $K \propto \frac{d^2U}{dD^2} = \frac{3NZC\kappa}{D_0^5} \left( 1 - \frac{7}{D_0\kappa} \right) \approx 6|U_B|\frac{\kappa}{D_0}$