Problem 8.1

Problem #2, Chapter 3
Compares the subtle difference between different types of crystal structures for Lennard Jones solids.

\[ E_{\text{coh}} = 4\varepsilon \left( \frac{C_2^3}{8C_1} \right) \]
\[ C_1 = \sum_{f} \frac{1}{p_{f}^{12}} = 12.13100 \text{ (FCC)}; \quad 9.11440 \text{ (BCC)} \]
\[ C_2 = \sum_{f} \frac{1}{p_{f}^{6}} = 14.45392 \text{ (FCC)}; \quad 12.2533 \text{ (BCC)} \]
\[ E_{\text{coh}} = 4\varepsilon (2.1525) \text{ (FCC)} \]
\[ E_{\text{coh}} = 4\varepsilon (2.0592) \text{ (BCC)} \]
\[ \frac{(E_{\text{coh}})_{\text{BCC}}}{(E_{\text{coh}})_{\text{FCC}}} = \frac{2.0592}{2.1525} = 0.957 \]

Problem 8.2
Problem #3, Chapter 3

\[ \frac{E_{\text{coh}}}{\text{mole}} = 4\varepsilon (2.1525) N_A = 4 \times 50 \times 10^{-16} \text{ erg} \times \frac{10^{-7} J}{\text{erg}} \times 6.022 \times 10^{23} \]
\[ \frac{E_{\text{coh}}}{\text{mole}} = 2.592 \text{ kJ} \]

Problem 8.3
Problem #5, Chapter 3
Nice problem involving Madelung energy and repulsive energy for a 1-dimensional ionic crystal

\[ U = N \left[ \frac{zA}{R^\alpha} - \frac{\alpha q^2}{R} \right] = 2 \ln 2 \Rightarrow z = 2 \]
\[ \frac{dU}{dR} = 0; \quad R_0^\alpha = \frac{2nA}{\alpha q^2} \]
Now we can expand $U(R)$ near $R=R_0$. The linear terms vanish because the first derivative of $U(R)$ vanishes at $R_0$. The quadratic term is the first correction.

$$U(R) = U(R_0(1+\delta)) = N \left[ \frac{2A}{R_0^n (1+\delta)^n} \right] - \frac{\alpha q^2}{R_0^2} \left[ 1 - \frac{1}{n} \right]$$

Problem 8.4
Problem #7, Chapter 3
Nice problem about ionic solids and the stable ionic configuration.

We have to first calculate the Madelung energy when the charges are $\pm 1$ (in units of electron charge) and when $\pm 2$. Here we will calculate energy/molecule, $U/N$, because we will correct for ionization energy and electron affinity for a molecule.

Madelung energy (ignore short range repulsion which is about 10% correction).
We will write the charge $q = e\varepsilon$; $\varepsilon=1,2$

FCC lattice

$$\frac{U}{N} = -\frac{\alpha q^2}{R_0} = -\frac{1.747565 \left( \frac{e^2}{143} \right) e^2}{2.76} ; \varepsilon = 1,2$$

$$\frac{U}{N} = -8.61 \text{ eV} ; \varepsilon = 1$$

$$\frac{U}{N} = -34.44 \text{ eV} ; \varepsilon = 2$$

(1)

(2)

Clearly the $+2$-$-2$ charge state has lower (more attractive and hence large cohesive energy) energy. But we have to compare this energy with that for isolated neutral Ba and O atoms.
Cohesive energy calculation

Charge states are +1,-1 (e=1)

\[
\begin{align*}
Ba + 5.19 \text{ eV} &= Ba^{1+} + e \\
O + e &= O^{1-} + 1.5 \text{ eV} \\
Ba + O &= Ba^{1+} + O^{1-} + (1.5 - 5.9) \text{ eV}
\end{align*}
\]

Using Eq.1 and Eq.3, the cohesive energy of Ba$^{1+}$O$^{1-}$ is given by

\[
E_{coh} = 6.61 - 4.1 = 4.51 \text{ eV}
\]

Now consider the charge +2,-2

\[
\begin{align*}
O + 2e &= O^{2-} + (1.5 - 9.0) \text{ eV} \\
Ba + (5.19 + 9.96) \text{ eV} &= Ba^{2+} + 2e
\end{align*}
\]

Putting these two equations together

\[
Ba + O = Ba^{2+} + O^{2-} - 22.65 \text{ eV}
\]

Using Eq.2 and Eq.4, the cohesive energy of Ba$^{2+}$O$^{2-}$ is given by

\[
E_{coh} = 34.44 - 22.65 = 11.79 \text{ eV}
\]

Cohesive energy of Ba$^{2+}$O$^{2-}$ is larger than that of Ba$^{1+}$O$^{1-}$. So the stable compound is indeed Ba$^{2+}$O$^{2-}$.