Homework 9 – Solution

9.1. This problem on the cohesive energy of bcc and fcc neon compares the subtle difference between different types of crystal structures for Lennard-Jones solids and is based on Kittel Chapter 3, Problem #2. Using the Lennard-Jones potential, calculate the ratio of the cohesive energies of neon in the bcc and fcc structures. The lattice sums are

$$C_{12}(bcc) = \sum_j{}' p_j^{-12} = 9.11418 \; ; \; C_6(bcc) = \sum_j{}' p_j^{-6} = 12.2533$$

for the bcc lattice and

$$C_{12}(fcc) = \sum_j{}' p_j^{-12} = 12.13188 \; ; \; C_6(fcc) = \sum_j{}' p_j^{-6} = 14.45392$$

for the fcc lattice.

Solution:

At the equilibrium interatomic separation,

$$E_{coh} = \epsilon \left(\frac{C_6^2}{2C_{12}} \right) \; .$$

With the values for C_{12} and C_6 provided, we get $E_{coh}(fcc) = \epsilon \times 8.6100$ and $E_{coh}(bcc) = \epsilon \times 8.2368$. Thus,

$$\frac{E_{coh}(bcc)}{E_{coh}(fcc)} = \frac{8.2368}{8.6100} = 0.957 \; .$$

9.2. This problem on solid molecular hydrogen is based on Kittel Chapter 3, Problem #3. For H_2 one finds from measurements on the gas that the Lennard-Jones parameters are $\epsilon = 50 \times 10^{-16}$ erg and $\sigma = 2.96$ Å. Find the cohesive energy in kJ per mole of H_2; do the calculation for an fcc structure. Treat each H_2 molecule as a sphere. The observed value of the cohesive energy is 0.751 kJ/mol, much less than what you get, so that quantum corrections must be very important.

Solution:

$$\begin{aligned} \frac{E_{coh}}{mol} &= 4\epsilon \times 2.1525 \times N_A = 4 \times 50 \times 10^{-16} \text{ erg} \times \frac{10^{-7} \text{ J}}{\text{erg}} \times 6.022 \times 10^{23} \; , \\ E_{coh} &= 2.59 \text{ kJ/mol} \; . \end{aligned}$$

This value decreases significantly by quantum corrections, so it is reasonable to find the same melting point for H_2 and the much heavier rare gas Ne.

9.3. This problem involving the Madelung energy and repulsive energy for a linear ionic crystal is based on Kittel Chapter 3, Problem #5. Consider a line of $2N$ ions of alternating charge $\pm q$ with a repulsive potential energy A/R^n between nearest neighbors.

(a) Show that, in *cgs* units, at the equilibrium separation

$$U(R_0) = -\frac{2Nq^2 \ln 2}{R_0}\left(1 - \frac{1}{n}\right).$$

(b) Let the crystal be compressed so that $R_0 \rightarrow R_0(1+\delta)$. Show that the work done in compressing a unit length of the crystal has the leading term $\frac{1}{2}C\delta^2$, where, in *cgs* units,

$$C = \frac{(n-1)q^2 \ln 2}{R_0}.$$

To obtain the results in SI, replace q^2 by $q^2/4\pi\epsilon_0$. Note: Do not expect to obtain this result from the expression for $U(R_0)$; you must use the complete expression for $U(R)$.

Solution:

$$U = N\left[\frac{ZA}{R^n} - \frac{\alpha q^2}{R}\right] \quad \text{with } \alpha = 2\ln 2 \text{ and } Z = 2$$

$$\frac{dU}{dR} = 0$$

$$R_0^{n-1} = \frac{ZnA}{\alpha q^2}$$

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

$$U(R_0) = -\frac{2N\ln 2\, q^2}{R_0}\left[1 - \frac{1}{n}\right].$$

Now we can expand $U(R)$ near $R = R_0$. The linear terms vanish since the first derivative of $U(R)$ vanishes at R_0. The quadratic terms is the first correction.

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

$$U(R) = U(R_0(1+\delta)) = U(R_0) + \frac{1}{2}N\delta^2\frac{(n-1)q^2 2\ln 2}{R_0},$$

$$\frac{U(R)}{2N} = \frac{U(R_0)}{2N} + \frac{1}{2}C\delta^2 \quad \text{with } C = \frac{(n-1)q^2 \ln 2}{R_0}.$$

9.4. This problem about ionic crystals and their most stable ionic configuration is based on Kittel Chapter 3, Problem #7. Barium oxide has the NaCl structure. Estimate the cohesive energies per molecule of the hypothetical crystals Ba^+O^- and $Ba^{++}O^{--}$ with respect to separated neutral atoms. The observed nearest-neighbor internuclear distance is $R_0 = 2.76$ Å. The first and second ionization potentials of Ba are 5.19 eV and 9.96 eV, respectively. The electron affinities of the first and second electrons added to the neutral oxygen atom are 1.5 eV and -9.0 eV, respectively. The first electron affinity of the neutral oxygen atom is the energy released in the reaction $O + e \rightarrow O^-$. The second electron affinity is the energy released in the reaction $O^- + e \rightarrow O^{--}$. Which valence state do you predict will occur? Assume R_0 is the same for both forms, and neglect the repulsive energy.

Solution:

We have to first calculate the cohesive energy when the charges are $\pm 1\,e$ and $\pm 2\,e$. Here we will calculate the energy per dimer, U/N, because we will correct for the ionization energy and electron affinity for a dimer.

We may ignore the short-range repulsion, which gives about a 10% correction, and focus on the main Madelung energy. We will express the charge as $|q| = e\epsilon$, where $\epsilon = 1, 2$. Then, for an fcc lattice,
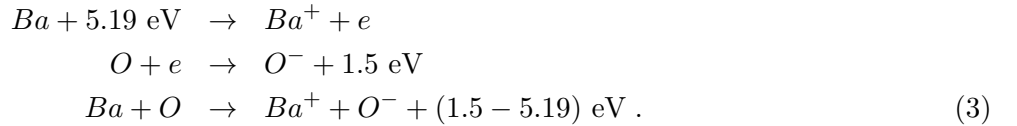
$$\frac{U}{N} = -\frac{\alpha q^2}{R_0} = -\frac{1.747565}{2.76}\left(\frac{e^2}{1\,\text{Å}}\right)\epsilon^2 \ \text{with} \ \epsilon = 1, 2 \ .$$

$$\frac{U}{N} = -9.11 \text{ eV} \ \text{for} \ \epsilon = 1 \ , \tag{1}$$

$$\frac{U}{N} = -36.44 \text{ eV} \ \text{for} \ \epsilon = 2 \ . \tag{2}$$

Clearly the $+2/-2$ charge state is more stable than the $+1/-1$ charge state due to the larger attraction of the larger charges. But we should not forget the energies to produce a particular ionization state from isolated neutral Ba and O atoms. Consequently, we need to combine the above results with the energy investments associated with ionizing the isolated atoms.
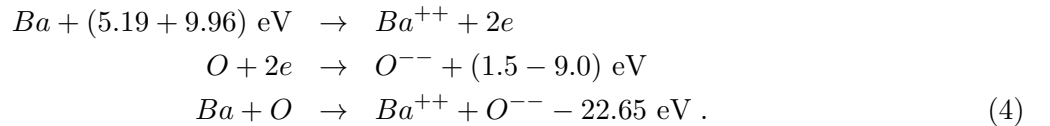
For the charge state $+1/-1$ we get

$$\begin{aligned} Ba + 5.19 \text{ eV} &\rightarrow Ba^+ + e \\ O + e &\rightarrow O^- + 1.5 \text{ eV} \\ Ba + O &\rightarrow Ba^+ + O^- + (1.5 - 5.19) \text{ eV} \ . \end{aligned} \tag{3}$$

Combining the results of Eq. (1) and Eq. (3) we get for the cohesive energy of a Ba^+O^- fcc lattice

$$E_{coh}(Ba^+O^-) = 9.11 \text{ eV} - 3.69 \text{ eV} = 5.42 \text{ eV} \ .$$

Now consider the charge state $+2/-2$. We get

$$\begin{aligned} Ba + (5.19 + 9.96) \text{ eV} &\rightarrow Ba^{++} + 2e \\ O + 2e &\rightarrow O^{--} + (1.5 - 9.0) \text{ eV} \\ Ba + O &\rightarrow Ba^{++} + O^{--} - 22.65 \text{ eV} \ . \end{aligned} \tag{4}$$

Combining the results of Eq. (2) and Eq. (4) we get for the cohesive energy of a $Ba^{++}O^{--}$ fcc lattice

$$E_{coh}(Ba^{++}O^{--}) = 36.44 \text{ eV} - 22.65 \text{ eV} = 13.79 \text{ eV} \ .$$

The cohesive energy of $Ba^{++}O^{--}$ is obviously larger than that of Ba^+O^-. So the more stable compound is $Ba^{++}O^{--}$.