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1 Problem 1

Find the first four terms of the Madelung constant for the cubic lattice in which the unit cell has one kind of ion at the corners of the cube and the other oppositely charged ion at the center of the cube. Is the series quickly converging?

1.1 Solution

Medelung's constant is given by (Week 1 Slide - 20):

$$\alpha = \sum_{j \neq i} \frac{\pm 1}{p_{ij}}$$

Where p_{ij} is given by (Week 1 Slide - 18):

$$p_{ij} = \frac{r_{ij}}{R}$$

Where R is the nearest neighbor distance, and r_{ij} is the distance of the from the *i*th element of the crystal to the *j*th element. If we pick the reference ion *i* to be in the center of cubic lattice with charge $-q$, then we can rewrite Madelung's constant as follows (Kittel, EQ 25):

$$\frac{\alpha}{R} = \sum_{j} \frac{\pm}{r_j}$$

As such, we can determine the first four terms of the constant as follows: The first outwards step is to the 8 oppositely charged ions at the corners of the cube; the second outwards step is to the 6 identically charged ions at the center of the face-adjacent cubes; the thirds outwards step is to the 12 identically charged centers of the edge-adjacent cubes; the fourth outwards step is to the 24 oppositely charged ions at the outside corners of the face adjacent cubes. Therefore we can construct the following expansion of the Madelung's constant infinite series:

$$\frac{\alpha}{R} = \left[\frac{1}{8R} - \frac{1}{6\sqrt{2}R} - \frac{1}{12(2)R} + \frac{2}{24\sqrt{11}R} \cdots \right]$$

The series is obviously converging, but not at a particularly quick rate.

2   Problem 2 - Kittel 3.2

Cohesive energy of bcc and fcc neon.

Using the Lennard-Jones potential, calculate the ratio of cohesive energies of neon in the bcc and fcc structures (Ans. 0.958). The lattice sums for the bcc structures are:

$$\sum_j p_{ij}^{-12} = 9.11418$$

$$\sum_j p_{ij}^{-6} = 12.2533$$

2.1   Solution

The Lennard-Jones potential is given by (Week 1 Slide - 28):

$$U(R) = 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^{6} \right]$$

And the total energy of the crystal is determined by the following summation of the Lennard-Jones potential (Week 1 Slide - 29):

$$U_{tot} = \frac{1}{2} N(4\epsilon) \left[\sum_{j \neq i} \left(\frac{\sigma}{p_{ij} R} \right)^{12} - \sum_{j \neq i} \left(\frac{\sigma}{p_{ij} R} \right)^{6} \right]$$

Given the following lattice sums for an fcc crystal (Week 1 Slide - 29):

$$\sum_j p_{ij}^{-12} = 12.13188$$

$$\sum_j p_{ij}^{-6} = 14.45392$$

We can find the equilibrium value R_0 using the following derivation of U_{tot}:

$$\frac{dU_{tot}}{dR} = 0 = -2N\epsilon \left[-12 \sum_{j \neq i} \left(\frac{1}{p_{ij}} \right)^{12} \frac{\sigma^{12}}{R^{13}} + \sum_{j \neq i} \left(\frac{1}{p_{ij}} \right)^{6} \frac{\sigma^{12}}{R^{13}} \right]$$

From which we can calculate:

$$R_0 = \sigma \left(\sum_{j \neq i} \frac{p_{ij}^{-12}}{p_{ij}^{-6}} \right)$$

From Table 4 in Kittel, we can pull the following information: fcc: $R_0 = 1.0902$; bcc: $R_0 = 1.0684$, $\epsilon = 50$; $\sigma = 2.74$, and use it to calculate the following:

$$U_{tot-bcc} = -4.1181(2N\epsilon)$$

$$U_{tot-fcc} = -4.30341(2N\epsilon)$$

From which we can show that:

$$\frac{U_{tot-bcc}}{U_{tot-fcc}} = \frac{-4.1181}{-4.30341} = 0.9569$$

3 Problem 3 - Kittel 3.5

Linear ionic crystal.

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 at the equilibrium separation:

CGS:

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

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

CGS:

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

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

3.1 Solution

Part A) To begin, we utilize the following equation (Week 1 Slide - 20) for the total energy of the system, given the repulsive potential A/R^n:

$$U_{tot} = \left(\frac{NA}{R^n} - \alpha\frac{Nq^2}{R}\right)$$

Where α is the Madelung constant of an infinite chain of oppositely charged particles and equal $2\ln 2$ (Week 1 Slide - 21). In order to compute the equilibrium separation, we must take the first derivative of the total energy in terms of R, and set it equal to zero:

$$\frac{dU}{dR} = \left(\frac{-nNA}{R^{n+1}} + \alpha \frac{Nq^2}{R^2} \right) = 0$$

$$\frac{nA}{R_0^{n+1}} = \frac{\alpha q^2}{R_0^2}$$

$$\frac{nA}{R_0^n} = \frac{\alpha q^2}{R_0}$$

From which we see that:

$$\frac{A}{R_0^n} = \frac{\alpha q^2}{nR_0}$$

Which we can return to our original equation as such:

$$U_{tot}(R_0) = \left(\frac{\alpha q^2}{nR_0} - \alpha \frac{q^2}{R_0} \right)$$

Which we can simplify to:

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

Part B)

First, we can see that the work done to compress the crystal is simply the difference between the potential energy of the uncompressed crystal and the compressed crystal:

$$\Delta U = U_{tot}(R_0) - U_{tot}(R(1 - \delta)) = U_{tot}(R_0 - R_0\delta)$$

In order to find the work needed to compress a unit length of the crystal, we can calculate the following:

$$W = \frac{\Delta U}{2N}$$

Now, in order to examine what happens as $R_0 \to R_0(1 - \delta)$, we must expand ΔU into its Taylor series approximation:

$$\Delta U = U(R_0 - R_0\delta) + U'(R_0 - R_0\delta)R_0\delta + \frac{1}{2}U''(R_0 - R_0\delta)R_0^2\delta^2 + \dots$$

At equilibrium, the first derivative is zero, and therefore the leading term is:

$$\Delta U \approx \frac{1}{2}\frac{\delta^2 U}{\delta R^2}R_0^2\delta^2 = N \left(\frac{-n(n+1)A}{R_0^{n+2}} - \frac{2\alpha q^2}{R_0^3} \right) R_0^2\delta^2$$

Using the definition from part A:

$$\frac{A}{R_0^n} = \frac{\alpha q^2}{nR_0}$$

We can simplify to the following:

$$\Delta U \approx \frac{1}{2}\frac{\delta^2 U}{\delta R^2}R_0^2\delta^2 = N\left(\frac{(n+1)\alpha q^2}{R_0^3} - \frac{2\alpha q^2}{R_0^3}\right)R_0^2\delta^2$$

$$\Delta U \approx \frac{1}{2}\frac{\delta^2 U}{\delta R^2}R_0^2\delta^2 = \frac{N\alpha q^2}{2R_0}(n-1)\delta^2$$

Which we can insert into our equation for work and show that:

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

Or, in the terms specified by the problem:

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

And therefore the leading term of the work required to compress a unit length of the crystal is:

$$W = \frac{C\delta^2}{2}$$

4   Problem 4 - Kittel 3.7

Divalent ionic crystals.

Barium oxide has the NaCl structure. Estimate the cohesive energies per molecule of the hypothetical crystals Ba^+O^- and $Ba^{++}O^{--}$ referred to to separated neutral atoms. The observed nearest-neighbor internuclear distance is $R_0 = 2.67$ Å; the first and second ionization potentials of BA are 5.19 and 9.96 eV; and the electron affinities of the first and second electrons added to the neutral oxygen atom are 1.5 and -9.0 eV. 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.

4.1   Solution