Solid State Physics Homework 3

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Problem 1 Consider the ionic crystal NaCl. Model the total energy of the system in the standard way as a sum of an attractive electrostatic term (Madelung part) and a repulsive part with the usual $1/r^{12}$ dependence between atom pairs. Show that at the equilibrium conventional lattice parameter a (or equivalently at the equilibrium nearest neighbor distance R), the total energy is dominated to high precision by the electrostatic part and that the repulsive contribution is small. [Note: this happens because the electrostatic part is gentle and changing like $1/r$ while the repulsive one is very steep.]

Solution The total energy is

$$E = \sum_{i \neq j} E_{ij} = \frac{N}{2} \sum_{i \neq 0} E_{0i}. \tag{1}$$

We can replace the integer index i by $\boldsymbol{i}$, where $a/2 \cdot (i_x, i_y, i_z)$ are the coordinates of each atom in the crystal. (That is, $\boldsymbol{i}$ is *not* the index of unit cells.) Without the loss of generality, we assume at $\boldsymbol{i} = 0$ lies a Na atom. Then, if $i_x + i_y + i_z$ is an odd number, then the atom at $\boldsymbol{i}$ is a Cl atom; otherwise it's a Na atom. So we have

$$E_{0i} = \frac{e^2}{4\pi\epsilon_0} \frac{(-1)^{i_x+i_y+i_z}}{\frac{a}{2}\sqrt{i_x^2 + i_y^2 + i_z^2}} + \frac{C}{\left(\frac{a}{2}\right)^{12} \left(i_x^2 + i_y^2 + i_z^2\right)^6}. \tag{2}$$

The values of

$$\sum_{\boldsymbol{i} \neq 0} \frac{(-1)^{i_x+i_y+i_z}}{\sqrt{i_x^2 + i_y^2 + i_z^2}} \tag{3}$$

and

$$\sum_{\boldsymbol{i} \neq 0} \frac{1}{\left(i_x^2 + i_y^2 + i_z^2\right)^6}. \tag{4}$$

have already been calculated in the literature, but they actually don't matter here: from (1) and (2) we know

$$E = \frac{C_1}{a} - \frac{C_2}{a^{12}}, \quad C_1, C_2 > 0. \tag{5}$$

The first term is the electrostatic term, and the second term is the Lennard-Jones term. Now by taking the derivative we can find the minimum point:

$$\frac{\mathrm{d}E}{\mathrm{d}a} = -\frac{C_1}{a^2} + \frac{12C_2}{a^{13}} = 0 \Rightarrow a^{11} = \frac{12C_2}{C_1}.$$

Putting this back to (5), we get

$$E = -\frac{C_1}{a_{\min}} \left(1 - \frac{C_2}{C_1} \frac{1}{a_{\min}^{11}}\right) = -\frac{11}{12} \frac{C_1}{a} = 0.92 E_{\text{electrostatic}}. \tag{6}$$

Note that this result doesn't depend on the exact value of C_1 and C_2: as long as the repulsive part is $\sim a^{-12}$, the total energy is 0.92 times of the electrostatic energy. When the repulsive potential goes steeper, the total energy and the electrostatic energy get closer (12/13, 13/14, and so on).

Problem 2 Consider the compound La_2O_3 in its lowest energy crystal structure. What do you believe is the dominant type of bonding in this material? Look up the ionization energies of Y and La and thereby decide which of La_2O_3 and Y_2O_3 has more covalent character (assume for this problem that they have same crystal structure).

Solution lists the ionization energies together with the periodic table. The ionization energy of Y is $616\,\text{kJ/mol}$. The ionization energy of La is $538\,\text{kJ/mol}$. The electron affinity of O is $141\,\text{kJ/mol}$, so O atoms easily get electrons and La atoms easily lose electrons and thus the dominant type of bonding in La_2O_3 is likely to be ionic bond. The ionization energy of Y is higher, so Y is harder to ionize, so Y_2O_3 has more covalent character.

Note that it's not sufficient to just look at the ionization of O and conclude that O atoms easily get electrons, because it's of course possible for an atom to reject both ionization and electron injection.

Problem 3 Consider a one-dimensional monoatomic chain of atoms as discussed in Kittel or A&M: e.g., the situation described by equation (2) of Chapter 4 of Kittel: $M\ddot{u}_s = C\left(u_{s+1} + u_{s-1} - 2u_s\right)$. Following Kittel's notations, C is the spring constant between neighbors and M is the mass of each atom. Show that for long wavelength vibrational modes, the displacements u obey the continuum wave equation

$$\frac{\partial^2 u}{\partial t^2} = v^2 \frac{\partial^2 u}{\partial x^2}$$

Where u is now a function of continuous x and v is the velocity of sound. Hint: the main issue to convert from discrete positions (integer s in Kittel labelling the atoms that spaced by a) to continuous ones and figure out how to convert the derivative. The simplest approach is to use $x = a$ and then assume that changing by one lattice unit $\pm a$ is a small displacement so you can Taylor expand in powers of the shift a. Long wavelength means u varies gently in space.

Solution In the long wavelength limit, the lattice is almost continuous, and the distance between neighbor atoms is small enough. Thus

$$\frac{\partial u}{\partial x} \approx \frac{u(x) - u(x-a)}{a} = \frac{u_i - u_{i-1}}{a}, \tag{7}$$

and

$$\begin{aligned}
\frac{\partial^2 u}{\partial x^2} &= \frac{1}{a}\left(\left.\frac{\partial u}{\partial x}\right|_{x+a} - \left.\frac{\partial u}{\partial x}\right|_x \right) \\
&= \frac{1}{a}\left(\frac{u_{i+1} - u_i}{a} - \frac{u_i - u_{i-1}}{a} \right) \\
&= \frac{u_{i+1} - 2u_i + u_{i-1}}{a^2}.
\end{aligned} \tag{8}$$

So the EOM of atoms

$$M\ddot{u}_i = C(u_{i+1} + u_{i-1} - 2u_i) \tag{9}$$

now reads

$$M\frac{\partial^2 u}{\partial t^2} = Ca^2 \frac{\partial^2 u}{\partial x^2},$$

and we get

$$\frac{\partial^2 u}{\partial t^2} = v^2 \frac{\partial^2 u}{\partial x^2}, \quad v^2 = \frac{Ca^2}{M}. \tag{10}$$