Solid State Physics Homework 3

Jinyuan Wu

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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 oxygen is $1314 \, \text{kJ/mol}$. The ionization energy of Y is $616 \, \text{kJ/mol}$. The ionization energy of La is $538 \, \text{kJ/mol}$. The difference between the ionization energies of La and O is $776 \, \text{kJ/mol}$, much greater than $600 \, \text{kJ/mol}$, 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 difference between the ionization energies of Y and O is smaller, so Y_2O_3 has more covalent character.

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

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