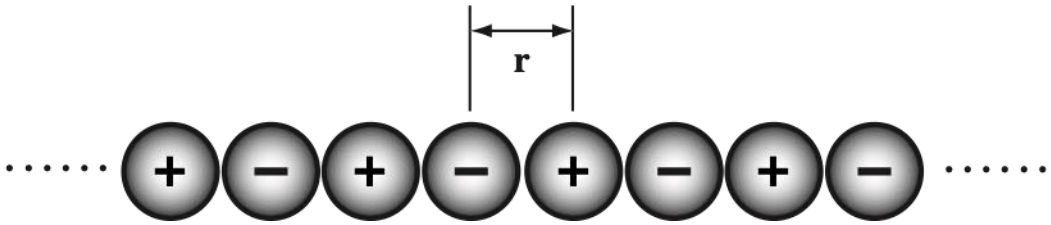
PHYSICS OF MATERIALS

Physics School Autumn 2024

Solution sets: Series 1 **20 September 2024**

Exercise #1

In an ionic chain such as the one in the following figure:



The Coulomb attraction-repulsion for the ion *i* is expressed by:

$$U_i = \sum_{i \neq j} \frac{\pm q^2}{4\pi\varepsilon_0 r_{ij}} = \frac{-2q^2}{4\pi\varepsilon_0}\left(\frac{1}{r} - \frac{1}{2r} + \frac{1}{3r} - \frac{1}{4r} + \cdots\right) = \frac{-2q^2}{4\pi\varepsilon_0 r}\left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots\right)$$

where *q* is the electric charge. The factor of 2 comes from the fact that we sum at the right and the left.

Thus, the Madelung constant is:

$$\alpha = 2\left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots\right)$$

Using the series development: $\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \cdots$

with $x=1$, we get:

$$\alpha = 2\ln(2) = 1.38629$$

The Coulomb potential decreases at long distances. Other potentials, such as those describing Van der Waals forces, decrease significantly at short distances. In these cases, we can give a good approximation of the Madelung constant with only a few terms of the series that can be calculated by hand as the series converges quickly.

Exercise #2

Let's consider the Lennard-Jones potential in the form of

$$U = 4\varepsilon\left(\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right).$$

The minimum of the energy potential gives the equilibrium distance between atoms:

$$\frac{dU}{dR} = 0 \Rightarrow \frac{-12\sigma^{12}}{R^{13}} + \frac{6\sigma^{6}}{R^{7}} = 0 \Rightarrow \frac{R}{\sigma} = \sqrt[6]{2} \simeq 1.12$$

Notice that the energy of free atoms (argon gas) to which we compare the energy of bound atoms is zero since their distance is always much larger than that of atoms in the solid. Indeed, the interaction potential of Lennart-Jones becomes negligible at large distances. On the other hand, there is no change (like in ionic crystals) in the configuration of valence electrons. Therefore, if we take the energy of N atoms in an FCC network

$$U_{tot} = \frac{1}{2}N4\varepsilon\left[\sum_{i,j}\left(\frac{\sigma}{p_{ij}R}\right)^{12} - \left(\frac{\sigma}{p_{ij}R}\right)^{6}\right] = \frac{1}{2}N4\varepsilon\left[\left(\frac{\sigma}{R}\right)^{12}\sum_{i,j}\left(\frac{1}{p_{ij}}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\sum_{i,j}\left(\frac{1}{p_{ij}}\right)^{6}\right]$$

We have seen (formula 1.12) that for an FCC structure

$$\sum_{i,j}\left(\frac{1}{p_{ij}}\right)^{12} = 12.13188 \text{ and } \sum_{i,j}\left(\frac{1}{p_{ij}}\right)^{6} = 14.45392$$

Notice that if we take just the nearest neighbors in the FCC structure, we should get 12. So, the variations for the factor with exponent 12 are minimal events taking the second and other nearest neighbors. Instead, the variations for the factor with exponent 6 are a little more important.

Therefore, we get a slightly modified formula:

$$\frac{dU}{dR} = 0 \Rightarrow \frac{-12\cdot 12.13\cdot\sigma^{12}}{R^{13}} + \frac{6\cdot 14.45\cdot\sigma^{6}}{R^{7}} = 0 \Rightarrow \frac{R}{\sigma} = \sqrt[6]{2\frac{12.13}{14.45}} \simeq 1.09$$

Thus, calculated R/σ values provide the following interatomic distances and cohesion energies table.

	Neon	Argon	Krypton	Xenon
R [Å]	3.05	3.8	3.9	4.4
r [Å]	1.58	1.88	2.00	2.17
U_{tot} [eV/atom]	-0.025	-0.086	-0.120	-0.164

The table of elements gives cohesion energies close to our calculations. It is the same for the interatomic distances (twice the atomic radius). We notice that the Van der Waals bonds (typical of the solid rare gases) are one or two orders of magnitude weaker than metallic, covalent, or ionic bonds. For instance, look at the example of NaCl in the course text (page 9). It thus readily dissociates solid argon into neutral atoms.

Exercise #3

a)

Ionic: There is an electrostatic attraction between oppositely charged ions. occurs between atoms with a large difference in electronegativity, where one atom donates an electron to another, resulting in positively and negatively charged ions that are held together by electrostatic forces.

Covalent: There is electron sharing between two adjacent atoms, typically between nonmetals, where each atom contributes one or more electrons to form a stable electron pair.

Metallic: bonding a lattice of positively charged ions immersed in a sea of delocalized electrons, allowing electrons to move freely and contribute to properties like conductivity and malleability.

b) The Pauli exclusion principle states that no two electrons can simultaneously occupy the same quantum state within an atom, i.e., they must have opposite spins. This principle leads to the filling of distinct energy levels by electrons, influencing the structure and stability of atoms in atomic bonding. Bonding theory ensures that electrons occupy different orbitals and contribute to bond formation by avoiding identical quantum states.

c) Covalently bonded materials are generally less dense than ionically or metallically bonded materials because covalent bonds involve the directional sharing of electrons, leading to more open and less compact structures. In contrast, ionic and metallic bonds allow for more efficient packing of atoms or ions in a lattice, resulting in denser and more closely packed structures.