PHYS-F308 - Soft matter and solid state physics
Notes on soft matter

Moeil Juian

Université Libre de Bruxelles
Academic year 2022-2023
November 12, 2022

Contents

In this course, we are considering a large class of materials featuring certain properties. In particular, we are interested in materials that are "soft" such as simple liquids, polymers, gels, glasses, liquid crystals, ... or even biological materials!

Definition 0.1. *A particular object is defined to be soft matter when its interactions are of the order of $k_B T$.*

Being defined at such an order, *soft matter* presents a series of particularly interesting properties:

- Lack of long-range order.

- Relevance of the entropic contribution to the energy balance.

- Corrections from quantum mechanics not needed.

Part I
Intermolecular forces

Abstract

In the study of matter, one defines several different states. In this course, we will focus on the study of the properties of condensed matter. Crystals and liquids are examples of such condensed matter - the interaction between molecules of the latter is of the order of $E_{int} >> k_B T$ whereas the former preents an interaction energy $E_{int} \geq k_B T$ which can be put in contrast to a gas' $E_{int} << k_B T$. Let us note that thermal energy is much larger than the interactions between particules in the gaseous states.

1 Microscopic interaction potential

Let us consider the interaction between two different molecules. The total energy in the system can be written as

$$E_{tot}(r) = E_A + E_B + w(r) \tag{1.1}$$

where r is the distance between the molecules A and B and $w(r)$ is the *potential of interaction*, defined as

$$w(r) = E_{tot}(r) - E_{tot}(\infty) \tag{1.2}$$

$$w(r) = -\int_r^\infty F(r)dr \quad \Leftrightarrow \quad F(r) = -\frac{dw}{dr} \tag{1.3}$$

Beware to the minus sign between the two: the interaction is *attractive* when the potential is negative, and *repulsive* when the potential

2 L1 : Molecular interactions via electrostatic potentials

We will perform a review of the electrostatic potential interaction, with an increasing level of complexity. In particular, we will consider the interaction between...

- Two single point charges (approximation for two ions), dipole moments (approximation for two molecules)

- A single point charge and a non-rotating dipole moment

- Two non rotating dipole moments

- A single point charge and a rotating dipole moment

- Two rotating dipole moments

2.1 Electrostatic interaction between two point charges

Let us consider two single points charges Q_1 and Q_2 separated by a distance r. As a reminder, let us note that the electric field of a charge Q at a distance r is given by $E = \frac{Q}{4\pi\epsilon_r\epsilon_0 r^2}$. Therefore, the electric force of charge Q_1 on charge Q_2 is given by $F = E_1 Q_2 = \frac{Q_1 Q_2}{4\pi\epsilon_r\epsilon_0 r^2} = \frac{z_1 z_2 e^2}{4\pi\epsilon_r\epsilon_0 r^2}$ by introducing the valence numbers z_i. We deduce the macroscopic electrostatic potential

$$w(r) = -\frac{z_1 z_2 e^2}{4\pi\epsilon_r\epsilon_0 r} \tag{2.1}$$

Electrostatic interaction: application to $NaCl$

In a vaccum, one finds that $w_{NaCl} = -8.4 \times 10^{-19} J$. However, at room temperature one has that $U_T = k_B T \approx 1.38 \times 10^{-23} J/K \cdot 291 J = 4 \times 10^{-21} J$. Given that $w_{NaCl} > 200 k_B T$[1], NaCl is stable at room temperature in a vaccum. However, put it in a medium with high dielectric constant such as water and $w_{NaCl}^{H_2O}(r) \approx 2.5 k_B T$.

2.1.1 Dipole moments

Asymetric molecules bounded by covalent bounds often contains dipole moments. One defines the units of *Debye* for this purpose: take two charges e and $-e$ separated by a distance of one *Angstrum*:

$$\mu = 4.8D$$

Dipole moment of water

Example 2.1. *The molecule of water can be seen as two OH molecules separated by an angle of* 104.5ř. *Given that $\mu_{OH} = 1.51D$, we deduce that the dipole moment of water is given by*

$$\mu_{H_2O} = 2\cos\left(\frac{H\hat{O}H}{2}\right)\mu_{HO} = 1.85D \tag{2.2}$$

2.1.2 Ion-dipole interaction

Instead of looking a two single point charges and a dipole seperately, let us put them together and see what happens as shown in figure 1. The resulting macroscopic electrostatic potential is

$$w(r) = -\frac{qQ}{4\pi\epsilon_0 r_A} + \frac{qQ}{4\pi\epsilon_0 r_B} = \frac{qQ}{4\pi\epsilon_0}\left(\frac{1}{r_B} - \frac{1}{r_A}\right) \tag{2.3}$$

Let us note that $r_A \approx r - \frac{l}{2}\cos\theta$ whereas $r_B \approx r + \frac{l}{2}\cos\theta$. Applying the approximation $\frac{r_A - r_B}{r_A r_B} \approx -\frac{l\cos\theta}{r^2}$, one finds that (2.3) can be rewritten as

$$w(r) \approx -\frac{qQ}{4\pi\epsilon_0}\frac{l\cos\theta}{r^2} = -\mu\frac{Q\cos\theta}{4\pi\epsilon_0 r^2} \quad w(r) = -\mu E(r)\cos\theta \tag{2.4}$$

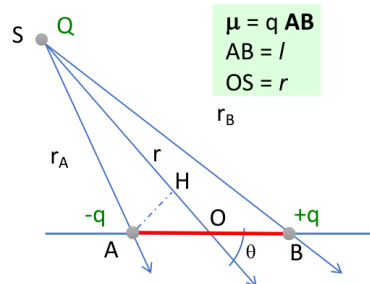The potential is either attractive or repulsive, depending on the orientation of the molecule.

Figure 1: Ion-dipole interaction

---

[1]Why do we ignore the negative sign?

2.1.3 Ion-ion interaction

Part II
Phase transitions I : Thermodynamics

Test