

PHYS-F308 - Soft matter and solid state physics

Notes on soft matter

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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

L1 : 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 $E_{int} \gg k_B T$ whereas the former presents an interaction energy $E_{int} \geq k_B T$ which can be put in contrast to a gas' $E_{int} \ll k_B T$. Let us note that thermal energy is much larger than the interactions between particles 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

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

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

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

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

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

2 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

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

2.1.1 Electrostatic interaction: application to NaCl

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

2.2 Dipole moments

Asymmetric molecules bounded by covalent bonds 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 *Angstrom*:

$$\mu = 4.8D$$

2.2.1 Dipole moment of water

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

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

2.3 Ion-dipole interaction

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

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

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

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

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

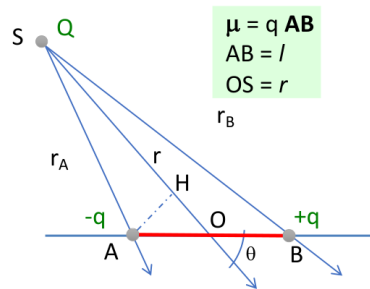


Figure 1: Ion-dipole interaction

¹Why do we ignore the negative sign?

2.4 Dipole-dipole interaction

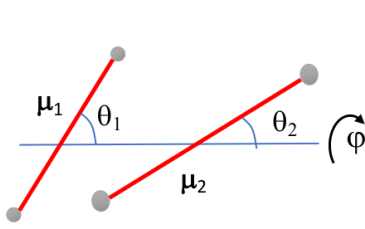
Assuming the two dipoles can freely move in the xyz space, one would need to replace the angle θ used previously by three different angles - θ_1, θ_2 and φ as shown in figure 2a. The interaction potential can then be written as

$$w(r, \theta_1, \theta_2, \varphi) = -\frac{\mu_1 \mu_2}{4\pi\epsilon_0\epsilon_r r^3} (2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \varphi) \quad (2.5)$$

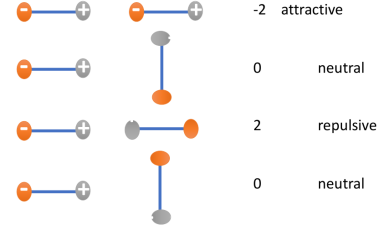
To simplify the problem, let us assume the angles θ_1 is equal to 0, meaning that the only allowed variation is in θ_2 and in the rotation angle φ . Then,

- $\theta_2 = 0 \Leftrightarrow w(r, 0, 0, \varphi) = -\frac{2\mu_1\mu_2}{4\pi\epsilon_r\epsilon_0 r^3}$. The two dipoles are attracted to each other.
- $\theta_2 = 90$. The dipoles are neither attracted nor repulsed by each other - they are said to be neutral.
- $\theta_2 = 180$. The dipoles are repelled by each other.
- $\theta_2 = 270$. The dipoles are neither attracted nor repulsed by each other - they are said to be neutral.

Let us note that in all situations, if the dipoles are free to rotate, then they tend to align themselves (situation with the lowest potential). This is shown in figure 2b.



(a) Dipole-Dipole interaction



(b) Summary of the different possible states with $\theta_1 = 0$.

2.5 Interactions involving freely rotating molecules

To take into account all different orientations, one would need to average the potential over the solid angle. Unfortunately, that is difficult to obtain analytically. How can we appropriately approximate the consequences of all the angles? Let us average all the possible orientations over the solid angle Ω .

$$e^{-\frac{w(r)}{kT}} = \frac{\int e^{-\frac{w(r, \Omega)}{kT}} d\Omega}{\int d\Omega} = \left\langle e^{-\frac{w(r, \Omega)}{kT}} \right\rangle \quad (2.6)$$

When $kT \gg w(r, \Omega)$, one finds

$$\left\langle \exp \left[-\frac{w(r, \Omega)}{kT} \right] \right\rangle = \left\langle 1 - \frac{w(r, \Omega)}{kT} + \frac{1}{2} \left[\frac{w(r, \Omega)}{kT} \right]^2 + (\dots) \right\rangle \quad (2.7)$$

As the potential is expanded over a Taylor series, it loses its angular contribution and acquires a temperature dependence which leads to

$$\bar{w}(r, T) \approx \left\langle w(r, \Omega) - \frac{w(r, \Omega)^2}{2kT} + (\dots) \right\rangle \quad (2.8)$$

2.5.1 Interaction between a charge and a flexible dipole

Reminding ourselves that $\langle \sin \theta \rangle = 0 = \langle \cos \theta \rangle$, and noting that

$$\int d\Omega = \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta = 4\pi, \quad (2.9)$$

$$\langle \cos^2 \theta \rangle = \frac{1}{4\pi} \int_0^\pi \cos^2 \theta \sin \theta d\theta \int_0^{2\pi} d\phi = \frac{1}{3}, \quad (2.10)$$

one shows that

$$\bar{w}(r, T) \approx \left\langle -\frac{Q\mu}{4\pi\epsilon_0\epsilon_r r^2} \cos\theta - \left(\frac{Q\mu}{4\pi\epsilon_0\epsilon_r r^2}\right)^2 \frac{\cos^2\theta}{2kT} + (\dots) \right\rangle = -\frac{Q\mu}{4\pi\epsilon_0\epsilon_r r^2} \langle \cos\theta \rangle - \frac{1}{2kT} \left(\frac{Q\mu}{4\pi\epsilon_0\epsilon_r r^2}\right)^2 \langle \cos^2\theta \rangle + (\dots) \quad (2.11)$$

meaning that in the limit $kT \gg w(r, \Omega)$,

$$\bar{w}(r, T) \approx -\frac{1}{6kT} \frac{(Q\mu)^2}{(4\pi\epsilon_0\epsilon_r)^2 r^4}. \quad (2.12)$$

2.5.2 Interaction between two freely rotating molecules

Using the results of 2.4, one finds at the high temperature limit $kT > \frac{\mu_1\mu_2}{4\pi\epsilon_0\epsilon_r r^3}$ the expression of the *Keesom forces* (1921)

$$\bar{w}(r, T) \approx -\frac{1}{3kT} \frac{\mu_1^2 \mu_2^2}{(4\pi\epsilon_r \epsilon_0)^2} \frac{1}{r^6} \quad (2.13)$$

2.5.3 Interactions between a charge and a nonpolar molecule

The proximity of an ion induces a dipole moment in the nonpolar molecule to appear. If ΔE is the difference in the electric field induced within the molecule, the magnitude of the dipole acting on the nonpolar molecule is

$$E = \mu \frac{\sqrt{1 + 3 \cos^2 \theta}}{4\pi\epsilon_0\epsilon_r r^3} \quad (2.14)$$

The interaction potential can then be written as

$$w(r, \theta) = -\int f dr = -\int \alpha_0 E dE = -\frac{1}{2} \alpha_0 E^2 \quad (2.15)$$

where we introduced the polarizability constant $\alpha_0 = \frac{\mu}{E}$. Merging (2.14) and (2.15), one finds

$$w(r, \theta) = -\frac{\alpha_0 \mu^2}{2} \frac{1 + 3 \cos^2 \theta}{(4\pi\epsilon_0\epsilon_r)^2 r^6} \quad (2.16)$$

which can be averaged over θ . The interaction between the different molecules is then given by

$$w(r) = -\frac{\alpha_{01}\mu_1^2 + \alpha_{02}\mu_2^2}{(4\pi\epsilon_0\epsilon_r)^2 r^6} \quad (2.17)$$

This is the expression of the *Debye forces* (1920's).

2.5.4 Interactions between neutral particles

Quantum fluctuations of the charge density inside a nonpolar molecule can induce the formation of an instantaneous dipole moment. This permits interactions with other nonpolar molecules - it is an induced dipole moment. London derived the interaction between *s-electrons* of two neighboring atoms and solved the problem considering quantum oscillator of frequency ν and thus of ionization potential $I = h\nu$. The *London (dissipative) forces* (1937) can be written as

$$w(r) \approx -\frac{1}{2(4\pi\epsilon_0\epsilon_r)^2} \frac{\alpha_1 \alpha_2}{r^6} \frac{I_1 I_2}{I_1 + I_2} \quad (2.18)$$

2.5.5 Van der Waals interactions

The Van der Waals forces are comprised of three terms, corresponding to (2.13) (dipole-dipole), (2.17) (dipole-induced dipole) and (2.18) (induced dipole-induced dipole). The largest contribution is given by London (20-99%) and Keesom forces.

Part II

L2: Phase transitions I : Thermodynamics