

# LLI (Micro-390) Homework and Problems

## Homework

Exercises 12-15

Material to study for next week:

JN Israelachvili: Intermolecular and surface forces:

Chapter 4: paragraphs: 4.7; 4.10.

Chapter 5: paragraphs: 5.1-5.2; 5.3, 5.6; 6.1

### List of constants:

Boltzmann constant:  $k = 1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$

Avogadro number:  $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

Radius of water molecule: 0.14 nm

The dielectric permittivity of free space:  $\epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$

Dielectric constant of vacuum:  $\epsilon = 1$

Dielectric constant of water:  $\epsilon = 80$  (298 K)

Elementary charge:  $e = 1.6 \times 10^{-19} \text{ C}$

Dipole moment of water: 1.85 D

1 D =  $3.336 \times 10^{-30} \text{ Cm}$

**Table 4.2** Hydrated radii and Hydration Numbers of Ions in Water (Approximate)

Ion	Bare ion radius (nm)	Hydrated radius (nm)	Hydration number ( $\pm 1$ )	Lifetime/exchange rate (s)
$\text{H}_3\text{O}^+$	—	0.28	3	—
$\text{Li}^+$	0.068	0.38	5	$5 \times 10^{-9}$
$\text{Na}^+$	0.095	0.36	4	$10^{-9}$
$\text{K}^+$	0.133	0.33	3	$10^{-9}$
$\text{Cs}^+$	0.169	0.33	1	$5 \times 10^{-10}$
$\text{Be}^{2+}$	0.031	0.46	$4^a$	$10^{-3}$
$\text{Mg}^{2+}$	0.065	0.43	$6^a$	$10^{-6}$
$\text{Ca}^{2+}$	0.099	0.41	6	$10^{-8}$
$\text{Al}^{3+}$	0.050	0.48	$6^a$	0.1–1
$\text{Cr}^{3+}$	0.052	—	$6^a$	>3 hrs
$\text{OH}^-$	0.176	0.30	3	
$\text{F}^-$	0.136	0.35	2	
$\text{Cl}^-$	0.181	0.33	1	$\sim 10^{-11}$
$\text{Br}^-$	0.195	0.33	1	$\sim 10^{-11}$
$\text{I}^-$	0.216	0.33	0	$\sim 10^{-11}$
$\text{NO}_3^-$	0.264	0.34	0	
$\text{N}(\text{CH}_3)_4^+$	0.347	0.37	0	

## Hydration shells

Based on ion-dipole interactions we can explain the hydration of ions in water. When ions are solvated they carry a shell of water molecules that feel the influence of the ion. This is called the hydration or solvation shell. The hydrated radius is generally bigger than the bare ionic radius. The following table lists the hydration radii and numbers of several ions:

12.

- What is the trend for the increase from bare ion radius to solvated radius or hydration number in going from  $F^-$  to  $NO_3^-$ ? Explain the trend based on ion-dipole interactions.
- What is the trend for the increase from bare ion radius to solvated radius in going from  $Li^+$  to  $Cs^+$ ? What is the relative increase expressed in percentage? Explain the trend based on ion-dipole interactions.
- $Be^{2+}$  has a smaller hydration shell than  $Mg^{2+}$ . This seems to be at odds with the above explanations. What is going on here?

## Consequences of temperature dependent angle averaging

The interaction between a charge and a dipole can be represented by the graph in Figure 1.

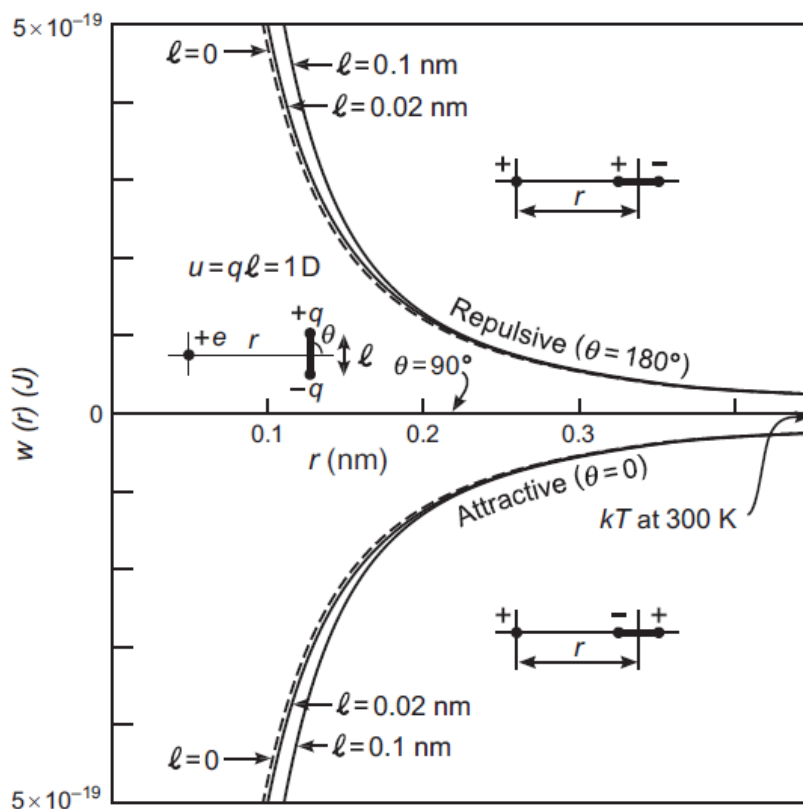


Figure 1: The interaction potential between a charge and a dipole

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13.

a. Using Fig. 1, suppose that at a spacing of 0.2 nm the dipole reverts its orientation from 180 to 0 degrees. Is energy freed or gained from the system? Can this energy be used to do work or has work been done on the system? How much energy is being gained or lost? Is this free energy?

b. Using Fig. 1, suppose that the dipole has a fixed angle of 0 degrees and is moved closer to the charge. Is energy freed or gained from the system? Can this energy be used to do work or has work been done on the system? How much energy is being gained or lost? Is this free energy?

From averaging over all possible dipole orientations using the Boltzmann factor as a weighing term we have obtained the following proportionality for the distance dependent interaction between a charge and a dipole:

$$w(r) \cong -\frac{Const}{\epsilon T r^4}$$

Unlike the interaction potential for a fixed dipole and a charge (which has  $w(r, \theta) \cong -\frac{Const}{\epsilon r^2}$ ), this interaction potential has a temperature dependence.

c. What is the origin of the temperature dependence?

If the number of molecules of the system is fixed and the volume is not changing, we may use the following expression for the molar free energy involved in the angle averaged interaction of dipoles and charges:

$$A = U - TS$$

with S the entropy and U the internal energy. We are now going to determine the free energy and the total internal energy of the two situations. For the entropy we can write:

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,N}$$

d. Show that for the case of the angle averaged interaction we have  $U=2A$ , while for the fixed dipole charge interaction we have  $U=A$ .

e. Why is the free energy only half the total internal energy for the case of angle averaged dipole charge interaction?

f. Do you expect the same to happen for dipole-dipole interactions?

## Magnitude and range of dipole-charge and dipole-dipole interactions

Just as with the charge-charge interaction we would like to determine what is the approximate strength and reach of the charge-dipole and dipole-dipole interaction.

14.

- Assuming that our charge is a  $\text{Fe}^{3+}$  ion and the dipole is a water molecule, determine the value of the maximum attractive energy in vacuum and in water and calculate for both systems at which separation distance the interaction energy falls below  $kT$ .
- How do those numbers change if we take angle averaging into account?
- Assuming that we have two dipoles in the form of two water molecules, determine the value of the maximum attractive energy in vacuum and in water and calculate for both systems at which separation distance the interaction energy falls below  $kT$ .
- How do those numbers change if we take angle averaging into account?

## Non-polar molecules: electronic polarizability.

In order to estimate the electronic polarizability of an atom, we consider the simplest model of an atom, namely the Bohr hydrogen atom. In this model the H atom is represented by a charged nucleus with mass  $M$  and charge  $+e$ . The electron orbits the nucleus in a spherical shell. The situation is depicted in Fig 2a.

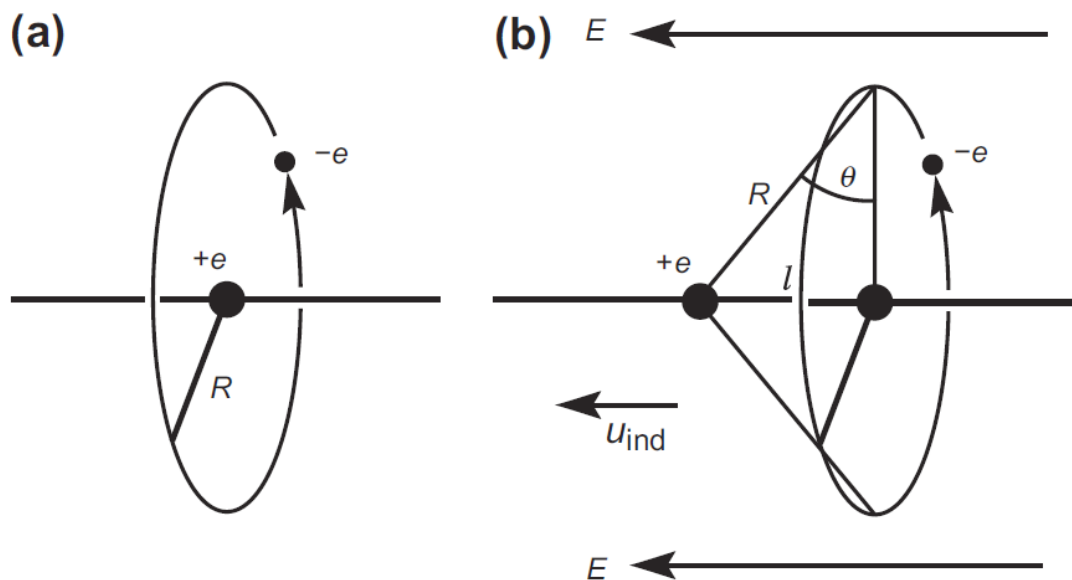


Figure 2: Sketch of a Bohr atom, without (a) and with (b) an external electrostatic field.

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15.

a. Which forces make sure that the electron keeps its steady orbit?

When an external electric field is present (from a neighboring charge for example) the atom will be distorted in shape until the forces are again in balance (Fig 2b).

b. Which part of the atom is actually distorted?

In the thus distorted atom a dipole moment is induced that can be written as:  $u_{ind} = \alpha_0 E$  with  $\alpha_0$  the electronic polarizability of the atom.

c. Starting from the expression for the force balance, show that  $\alpha_0 = 4\pi\epsilon_0 R^3$

d. Suppose that we have a positively charged ion with a charge  $+e$ ,  $+2e$  or  $+3e$  that is placed close to a  $\text{CCl}_4$  molecule in air. What distance should they be separated in order to induce a dipole moment equal to that of water?

e. If the same process occurs in octanol ( $\epsilon=10$ ), which ions can still induce the same dipole moment of water in  $\text{CCl}_4$ ?

f. What is the unit charge ( $e$ ) separation in  $\text{CCl}_4$  if we induce a dipole moment with  $u=1.85$  D?