Homework Week 3: Exercises 5, 6, 7

Material to study for next week:
JN Israelachvilli: Intermolecular and surface forces:
Chapter 3: paragraphs: 3.1 – 3.8

Exercises to aid with the lecture material: 5, 6,
Exercises as exam practice: 7

List of constants:

Boltzmann constant: $k = 1.38 \times 10^{-23}$ m^2 kg s^{-2} K^{-1}
Avogadro number: $N_A = 6.022 \times 10^{23}$ mol^{-1}

kT as a criterion of energy

We have seen that the translational energy of a molecule in a gas is between $^3/_2\,kT$ or $^7/_2\,kT$, depending on the structure of the molecule. The energy increases depending on the degrees of vibrational and rotational energy that are available. We proceed by examining the molecular energy available in the liquid phase. We therefore switch our attention to the interaction energy μ_{I}, which also takes into account the interactions that a molecule has with other molecules, which is virtually absent in the gas phase.
We seek to determine the total average interaction free energy per molecule (μ_i) in a liquid. This can be done by considering a chemical equilibrium between a liquid and a vapor of the same chemical. This procedure will be very useful, because, without knowing yet the exact types of interactions, it is still possible to predict an approximate value for the average magnitude of μ_I and thus get some insight in the magnitude of the relevant interactions without knowing them in detail. We thus use the macroscopic energy together with the *assumption* that this will reflect on the average molecular energy.

The following exercise is meant as an aid for the material of chapter 2.6.

5.
One can measure the heat released by vaporizing a liquid into a gas. We assume that the gas is ideal. The released heat is given by the enthalpy of vaporization ($H_{vap}=U_{vap}+PV$). An experiment is typically performed as illustrated in Figure 1:

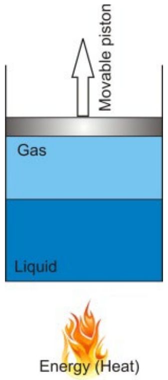

***Fig. 1**: Vaporizing a liquid.*

Taking water as an example, we have for the molar volume of water vapor, V_g = 22400 mL/mol, and P = 1 atm, and T = 273 K. The molar volume of liquid water V_l is 18 mL/mol.

a. What is the thermodynamic condition for chemical equilibrium between a liquid and its vapor?

$\mu_{i,g}$ and $\mu_{i,l}$ represent the standard chemical potential of water in its gas or liquid state (at the same temperature since the system is in equilibrium). Another way to describe the chemical potential is to say that $\mu_{i,g}$ or $\mu_{i,l}$ represent the average total free energy, or the total interaction energy of a molecule with its surroundings plus the thermal energy that it possesses.

b. Can we expect that the total interaction energy depends on the density of each phase? Depending on your answer, which of the following approximations do you expect is most true:
1. $\mu_{i,g} = \mu_{i,l}$
2. $\mu_{i,g} >> \mu_{i,l} \rightarrow \mu_{i,l} \approx 0$
3. $\mu_{i,g} << \mu_{i,l} \rightarrow \mu_{i,g} \approx 0$

c. Using 5a. and 5b., show that: $\mu_{i,l} \approx - 7\ kT$

Now, we want to know if this approximation is generally applicable. If this expression is generally applicable, we need to show two things:
(1) The expression in 5c is insensitive to temperature, so that it can also be applied up to the boiling point (T_b), and
(2) The expression in 5c is generally applicable for all liquids.

d. Assuming that we can use the ideal gas law and that any liquid is always approximately three orders of magnitude more dense than its gas phase (verify this for yourself by randomly picking three of your favorite liquids – e.g. beer, benzene and alcohol), show that the result of 5c will not vary more than ~ 15 % if we raise the temperature up to the boiling point (T_b), so that we can write: $\mu_{i,l} \approx - 7\ kT_b$

e. Now that we have an expression for the average interaction energy per molecule in the liquid, what can we say about the molar energy of vaporization (U_{vap})?

f. What is the expression for the molar enthalpy of vaporization?

Thus, to take a molecule out of its liquid at constant temperature, we need to break bonds. Bonds correspond to an attractive and thus negative pair potential $w(r)$. Breaking bonds requires energy and thus means that a positive amount of energy is supplied to the system. The created extra gas phase molecule will need to occupy a volume that needs to be created. This pressure-volume work needs to be done in addition to breaking bonds. The piston in Fig. 1 will go up, by an amount PdV.

The experimental value of the molar enthalpy of vaporization also known as the molar cohesive energy is 9RT, which is quite close to our crude approximation. Thus, to obtain an estimate of the interaction energy that a molecule has in its liquid phase, the energy value kT can be used as a good reference point.

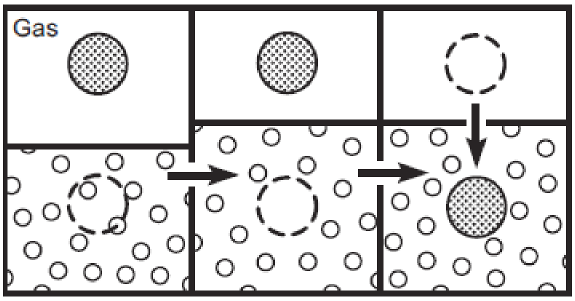

***Fig. 2:** Illustration of the process of cavity formation*

The cohesive energy

6.

We have found that μ_i = - 9kT. For a molecule in its own liquid $\mu_{i,l}$ represents the cohesive energy. The **cohesive energy** as we have seen in exercise 5 is defined as:
<u>The sum of interactions with all surrounding molecules. It is the energy needed to break up a substance in its individual compounds.</u>

We have also seen in the lecture that the relationship between the cohesive energy, that is, the average interaction energy μ_i per medium (m) molecule and the pair potential w_{mm} (the interaction energy between two m molecules) is:

$$\mu_i \approx 6w_{mm}$$

a. What magnitude should the pair potential w_{mm} minimally have, for a molecule to be released from or inserted into its own liquid? Compute the value for T = 298 K.

The thermal energy is therefore an important parameter. It provides us with an estimate of the energy needed to remove a molecule from its surroundings. Another approach to obtain a crude estimate of what the value of the pair potential is from experimental observables is to use the picture in Figure 2. In this approximation we create a cavity in the liquid with a size equal to the size of the molecule that is inserted. To create a cavity, we need to create an interface. The energy thus required can be estimated by measuring the interfacial tension or energy (γ, in mJ/m^2). Taking water at 298 K as an example, the interfacial energy of the air/water interface is 72 mJ/m^2.

b. First we need to estimate the size of a water molecule. At 298 K the density of water is 999.8 g/L and the molar mass is 18.02 g/mol. Calculate: (1) the density of water in terms of molecules / nm^3, and (2) show that the radius (σ) of a water molecule will be 0.19 nm, if we approximate the shape of a water molecule as a sphere.

c. Now, using the spherical approximation show that $w_{mm} \approx \frac{2}{3}\pi\sigma^2\gamma$.

d. Calculate the value for w_{mm} and show that the difference between both methods (in 6a and 6d) is ~ 12 % which is not bad at all for such a crude approximation of a molecular property.

Boltzmann Distribution and solubility

7.

The following exercise is meant to test your understanding of the concepts of Boltzmann distribution and chemical equilibrium. This time we seek to use it to try and find molecular properties of water and oil by mixing them. The solubility (S) is defined as the maximum concentration of a molecule that can be inserted in another medium. We can expect that it will depend on the molecular structure, the temperature and the pressure. The solubility of cyclohexane (C_6H_{12}, m_c = 84.16 g/mol) in water (m_w=18.02 g/mol) is only 55 parts per million by weight at 293 K. As we have seen, the interfacial energy γ is a macroscopic measurement that is given by the amount of energy that is needed to create an interface. The interfacial energy of the cyclohexane / water interface is found to be γ = 50 mJ/m^2. We can use this value to determine a rough estimate of the cohesive energy (as we have seen), but also of the solvation energy, which is the topic of the below exercise. The energy of solvation is the amount of energy associated with dissolving a solute in a solvent. The difference between cohesive and solvation energy is that solute and solvent molecules are not the same. The cohesive energy can be viewed as a special form of the solvation energy where solvent = solute.

a. Show that the radius of the cyclohexane molecule (σ, assuming a spherical shape for the molecule) is given by the following expression:

$$\sigma = \sqrt{-\frac{kT}{4\pi\gamma}\ln(S\frac{m_w}{m_c})}$$

Start with the condition for chemical equilibrium and define clearly the two reference states that are being compared.

b. Calculate the radius of the cyclohexane molecule.

c. For the opposite case, the solubility of water in cyclohexane, we have the value S = 100 ppm. Calculate the radius of a water molecule.

d. Every model depends on measured data. Small deviation in the measured values can alter the final result tremendously. Which parameter has the biggest influence in the determination of the molecular radius? (Hint: inspect the equation and consider the functional form of each measurable parameter).

e. According to literature values the radii of the molecules are σ (C_6H_{12}) = 0.26 nm and σ (H_2O) = 0.14 nm. Why are the calculated values deviating from the literature value?