Homework Week 6:
Exercises 16, 17, 18, 19

Material to study for this weeks' material:
JN Israelachvilli: Intermolecular and surface forces:
Chapter 7: 7.1-7.3
Chapter 8: 8.1; 8.2; 8.5-8.7

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}
The gas constant: $R_g = kN_A$
Radius of Na^+ ion: 0.095 nm
Radius of Fe^{3+} ion: 0.064 nm
Radius of Cl^- ion: 0.181 nm
Radius of water molecule: 0.14 nm
Radius of CCl_4 molecule: 0.275 nm
Radius of a CH_4 molecule/CH_3 group: 0.275 nm
Effective radius of a benzene molecule: 0.265 nm
Effective radius of a cyclohexane molecule: 0.285 nm
The dielectric permittivity of free space: $\varepsilon_0 = 8.85 \times 10^{-12}$ C^2 J^{-1} m^{-1}
Dielectric constant of vacuum: $\varepsilon = 1$
Dielectric constant of water: $\varepsilon = 80$ (298 K)
Elementary charge: $e = 1.6 \times 10^{-19}$ C
Dipole moment of water: 1.85 D
1 D = 3.336 10^{-30} Cm
Interfacial tension air/water: 72 mJ/m^2
Interfacial tension benzene/water: 35 mJ/m^2
Interfacial tension cyclohexane/water 51 mJ/m^2

Useful Equations and entities (in SI units)

Boltzmann equation	$\frac{P(B)}{P(A)} = e^{\frac{-(\mu_b-\mu_a)}{kT}}$
Debye screening parameter	$\kappa = \left(\sum_i \frac{n_{0i}e^2z_i^2}{\varepsilon_0\varepsilon kT}\right)^{1/2}$
Coulomb Force	$F = \frac{q_1q_2}{4\pi\varepsilon\varepsilon_0 r^2}$
Force / E-field	$F=qE$
Energy vs force	$F = -\frac{dw}{dr}$
Field vs potential	$E = -\nabla\psi$
Energy of a permanent dipole u in a field E	$\omega(r,\theta) = -uE(r)cos\theta$
angle averages and integrals	$\langle\sin\theta\rangle = \langle\cos\theta\rangle = \langle\sin\theta\cos\theta\rangle=0$ $\langle\sin\phi\rangle = \langle\cos\phi\rangle = \langle\sin\phi\cos\phi\rangle=0$ $\langle\sin^2\phi\rangle = \langle\cos^2\phi\rangle = 1/2$ $\langle\sin^2\theta\rangle = 2/3$; $\langle\cos^2\theta\rangle = 1/3$ $\int_0^\infty e^{-ax^2}dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}$
Taylor series around x=0	$f(x) = \sum_{n=0}^{\infty} \frac{f(0)^{n'}}{n!}x^n$
Thermodynamic parameters and relations	U H = U + PV A = U - TS G = H - TS

Question about polarizability

Before considering questions about water we will first review some aspects of lecture 5 relating to the electronic and dipolar polarizability of molecules. We will use the Tables 1 and 2 as input (see the next page).

16.

a. Calculate the polarizability of diethyl ether, acetone and acetonitrile at T=298 K in SI units. Assume that for unsaturated bonds the bond angle is 109°.

Fig. 1 displays the dielectric constant for several liquids as a function of temperature.

b. Describe in words what is the relation between the dielectric constant and the polarizability?

c. Explain why the offsets and the slopes of the curves of diethyl ether, acetone and acetonitrile are different.

d. The graph only plots values above the melting point. What happens below the melting point? Give estimated values for the polarizability of the three solids of diethyl ether, acetone and acetonitrile.

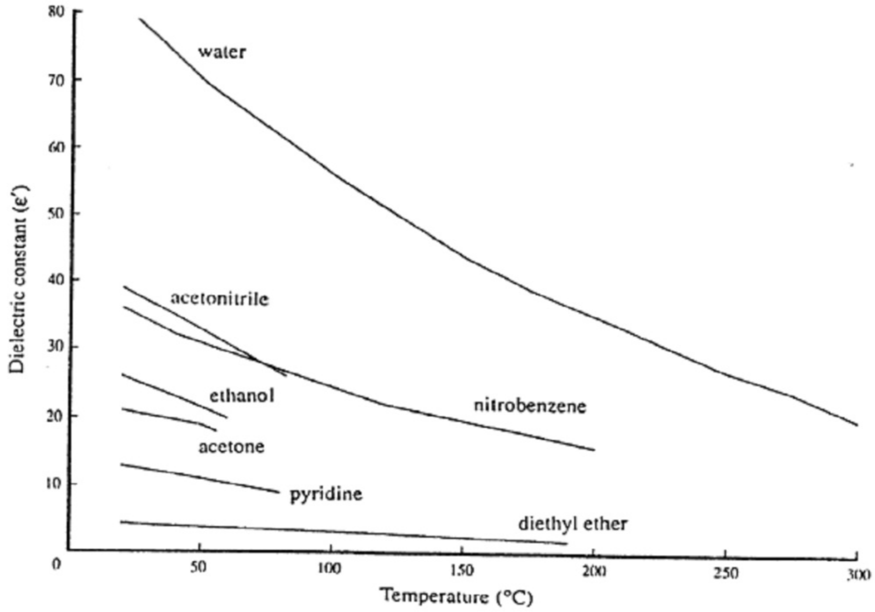

Figure 1: Dielectric constant of various liquids.

Polarizability and dielectric constant

The following table lists the dipole moments of a variety of molecules and molecular groups.

Table 1: Dipole moments of a variety of molecules and molecular groups (in Debye units)

Molecules			
Alkanes	0[b]	H_2O	1.85[c]
C_6H_6 (benzene)	0[d]	$C_nH_{2n+1}OH$ (alcohols)	1.7
CCl_4	0	$C_6H_{11}OH$ (cyclohexanol)	1.7
CO_2	0[e]	OMCTS[f]	0.42
CO	0.11	CH_3COOH (acetic acid)	1.7
$CHCl_3$ (chloroform)	1.06	C_2H_4O (ethylene oxide)	1.9
HCl	1.08	CH_3COCH_3 (acetone)	2.9
HF	1.91[c]	$HCONH_2$ (formamide)	3.7[c]
NH_3	1.47	C_6H_5OH (phenol)	1.5
CH_3Cl	1.87	$C_6H_5NH_2$ (aniline)	1.5
NaCl	8.5	C_6H_5Cl (chlorobenzene)	1.8
CsCl	10.4	$C_6H_5NO_2$ (nitrobenzene)	4.2

Bond Moments					
$C{-}H^+$	0.4	$C{-}C$	0	$C^+{-}Cl$	1.5–1.7
$N{-}H^+$	1.31	$C{=}C$	0	$N^+{-}O$	0.3
$O{-}H^+$	1.51	$C^+{-}N$	0.22	$C^+{=}O$	2.3–2.7
$F{-}H^+$	1.94	$C^+{-}O$	0.74	$N^+{=}O$	2.0

Group Moments					
$C{-}^+CH_3$	0.4	$C{-}^+COOH$	1.7	Adenine	~3
$C{-}^+OH$	1.65	$C{-}^+OCH_3$	1.3	Thymine	~4
$C{-}^+NH_2$	1.2–1.5	$C^+{-}NO_2$	3.1–3.8	Guanine	~7
				Cytosine	~8

Note the dipole moment of the -C≡N group is 3.52 D

The polarizabilities of several atoms, molecules and groups are given below in Table 2.

Table 2: Polarizabilities of several atoms, molecules and groups (in volume units, i.e. $4\pi\varepsilon_0 Å^3$):

Atoms and Molecules					
He	0.20	NH_3	2.3	$CH_2{=}CH_2$	4.3
H_2	0.81	CH_4	2.6	C_2H_6	4.5
H_2O	1.45–1.48	HCl	2.6	Cl_2	4.6
O_2	1.60	CO_2	2.9	$CHCl_3$	8.2
Ar	1.63	CH_3OH	3.2	C_6H_6	10.3
CO	1.95	Xe	4.0	CCl_4	10.5
Bond Polarizabilities					
C—C aliphatic	0.48	C—H	0.65	C—Cl	2.60
C⎓C aromatic	1.07	O—H	0.73	C—F	0.73
C═C	1.65	C—O	0.60	Si—Si	2.24
C≡C	2.39	C═O	1.36	Si—H	1.27
Molecular Groups					
C—O–H	1.3	—CH_2—	1.84	CF_3	2.4
C—O—C	1.1	CH_3	2.0	Si—O—Si	1.4
C—NH_2	2.0	—CF_2—	2.0	Si—OH	1.6

The electronic polarizability of the -C≡N group is 3.

Questions about Water and Hydrophobicity

17.

a. What is a hydrophobic molecule?
b. Which type of substances are more likely to be hydrophobic: ions, dipolar liquids, non-polar molecules, in their gas or liquid state.
c. What is solubility?
d. What is the difference between solubility and partitioning?
e. The solubility of N_2 in water is 0.018 g/kg. The solubility of CO_2 is 1.5 g/kg (20 °C). Both molecules are non-polar gasses at room temperature. Explain why CO_2 has such a high solubility compared to N_2.
HINT: CO_2 undergoes a chemical reaction when it is in contact with water.

Having defined hydrophobicity and solubility, two related terms we ask ourselves, what is the molecular reason behind hydrophobicity (and why oil and water don't mix).

18.
Thanks to the ability of water to form H bonds in three dimensions, liquid water will rearrange its H-bond network as soon as a non-polar molecule is put into water.

First we want to understand how this leads to an entropy penalty. The entropy of a system is given by:

$$S = k\ ln(W)$$

with *W* the number of configurations. Let us examine the number of configurations for two cases: (1) a water molecule in a tetrahedral environment, and (2) a water molecule at an non-polar or vacuum interface.

a. Sketch both situations
b, How many H bonds can 1 water molecule participate in if it sits in a 3 dimensional environment?
c. For case (1) how many possible configurations are there for a single water molecule?
d. For case (2) how many possible configurations are there for a single water molecule?
e. Show that at room temperature (298 K) the entropy cost for going from (1) to (2) is 1.7 kJ/mol H-bonds.

From a thermodynamic stand point we can also derive an expression for the free energy of solubility using the picture that we need to form a cavity if we are to dissolve a nonpolar molecule in water (see Figure 2).

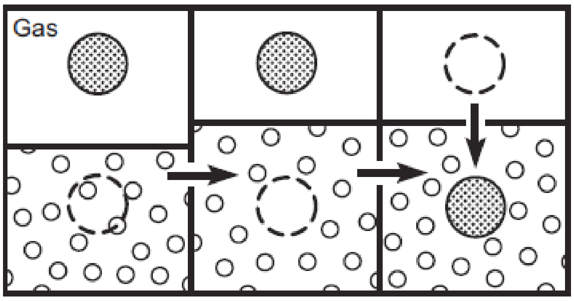

Figure 2: Cavity formation

The probability of finding a cavity in a state with energy μ_i (and radius r) is:

$$P(\mu_i(r)) = \frac{e^{-\mu_i(r)/kT)}}{\sum_i e^{-\mu_i(r)/kT}} \qquad (1)$$

f. Develop expression (1) so that it becomes a continuous expression that can be integrated. Show that the result is: $P(r) = 4\sqrt{\frac{\gamma}{kT}}e^{-\frac{4\pi\gamma r^2}{kT}}$

g. Show that for the solvation free energy, ΔG_s, we get:

$$\Delta G_s = 4\pi N_{av}\gamma r^2 - R_g T ln(4\sqrt{\frac{\gamma}{kT}})$$

h. For cyclohexane calculate the solvation free energy.
i. Assuming that $\Delta H_s = 0$ (for the enthalpy of solvation) and T=298 K, estimate how many H-bonds are restructured (assuming they each lose half of the available configurations).
j. How many water molecules are involved knowing that on average there are 3.6 H-bonds per water molecule? Does that make sense in terms of the range of the interactions that we have considered?

19.

The solubility of cyclohexane (C_6H_{12}) and benzene (C_6H_6) in water is, respectively, 55 and 1800 parts per million by weight at 20 ^oC.

a. Calculate the solubility for both compounds in mole fraction units.

b. Assuming that these organic molecules can be considered as macroscopic spheres with, calculate their interfacial energies per unit surface area exposed to water and compare your results with the known printed in the list of constants.

c. The measured solubility of water in cyclohexane and benzene is, respectively, 59 and 620 parts per million by weight at 20 ^oC. Assuming that water is a spherical molecule, calculate the values for the interfacial tension obtained from this reciprocal set of solubility data. Comment on possible reasons for the total lack of agreement in this case.

NOTE: consider what you have done in exercise 7 (Lecture 2).