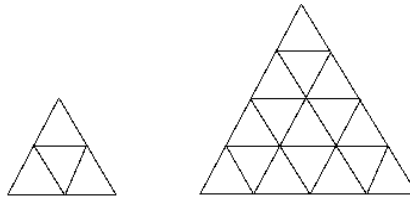


10.420 / 10.520
Problem Set #4/Solutions

1. Consider a molecule with a geometrical shape approximating a flat triangle.
- a) Determine the number of actual and potential favorable packing forces for the illustrated 4-mer and 16-mer. Assume that each edge-wise interaction with another molecule is worth $\alpha kT/3$ per molecule.



For the geometrical determination of packing forces, all interactions are double counted. For example, in a system A--B there are two interactions: one for A interacting with B, and one for B interacting with A.

Consider the 4--mer (a, b, c, d). Each molecule has 3 possible interactions, thus for the four molecules combined there are 12 possible interactions. From these possible interactions there are 6 actual interactions: a--b, b--a, b--c, c--b, b--d, d--b. The actual interactions can also be computed by subtracting the total number of exterior walls from the total potential interactions:

$$12 \text{ potential interactions} - 6 \text{ interacting walls} = 6 \text{ actual interactions}$$

On a per molecule basis, there are 6 interactions divided by 4 molecules or 1.5 interactions/ molecule.

Now, consider that each edgewise interaction is worth $-1/3 \alpha kT$ per molecule. Thus for a 4--mer

$$(1.5 \text{ Molecules})(-1/3 \alpha kT) = -0.5 \alpha kT/ \text{ molecule}$$

For a 16--mer, there are $(16 \times 3 =)$ 48 total potential interactions and a total of 12 exterior walls, thus there are $(48 - 12 =)$ 36 actual interactions. One a per molecule basis there are $(36/ 16 =)$ 2.25 interactions/ molecule. Thus the force per molecule is:

$$2.25 (-1/3 \alpha kT) = -0.75 \alpha kT/ \text{ molecule}$$

- b) Provide the equations that generalize these forces for an n-mer.

$$\frac{3N - 3N^{\frac{1}{2}}}{N} \left(-\frac{\alpha KT}{3} \right) = -\alpha KT \left(1 - N^{-\frac{1}{2}} \right) = \Delta\mu$$

- c) For the n-mer, derive an expression for μ_0^N that is a function of μ_0^∞ and N.

$$\Delta\mu = \mu_0^N - \mu_0^1 = \alpha KT (1/N^{1/2} - 1)$$

We can think of $\Delta\mu$ as the difference in standard state chemical potential between an n-mer and a monomer. Thus rewriting, we get

$$\mu_0^N = \mu_0^1 + \alpha KT (1/N^{1/2} - 1)$$

For $N = \infty$, we get

$$\mu_0^\infty = \mu_0^1 - \alpha KT$$

thus if we subtract the two equations we have

$$\mu_0^N = \mu_0^\infty + \alpha KT / N^{1/2}$$

2. Consider a molecule that "self-assembles" into a rod at 25 °C with an interaction energy between subunits of $\alpha kT = 24.75$ kJ/mol (10 kT).

- a) Produce plots of X_N vs. N for total concentrations, C, of 0.01 mM, 1 mM, and 10 mM for N = 1 to N = 25. (hint: you will need eqns 16.18 and 16.19 in your Israelachvili handout and/or lecture notes).

The equation from lecture ($\chi_N = N (1 - 1/(C e^\alpha))^N e^{-\alpha}$) is not applicable here since $C e^\alpha$ must be $\gg 1$ for it to give accurate results. Instead, we'll use

$$\chi_N = N (\chi_1 e^\alpha)^N e^{-\alpha}$$

In order to use this, we must first calculate χ_1 from $C = \chi_1 / (1 - \chi_1 e^\alpha)^2$. This can be rearranged to give

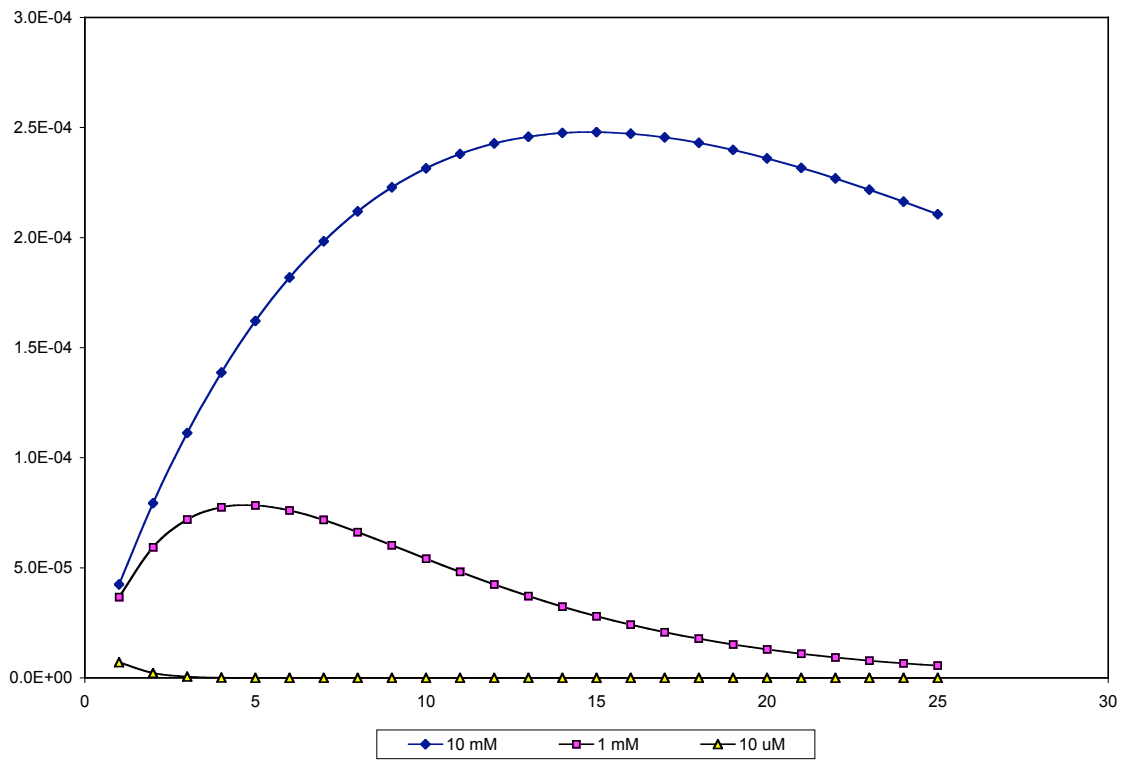
$$C e^{2\alpha} \chi_1^2 - (2C e^\alpha + 1) \chi_1 + C = 0$$

We can solve the quadratic above to get

$$\chi_1 = \frac{(1 + 2C e^\alpha) - \sqrt{1 + 4C e^\alpha}}{2C e^{2\alpha}}$$

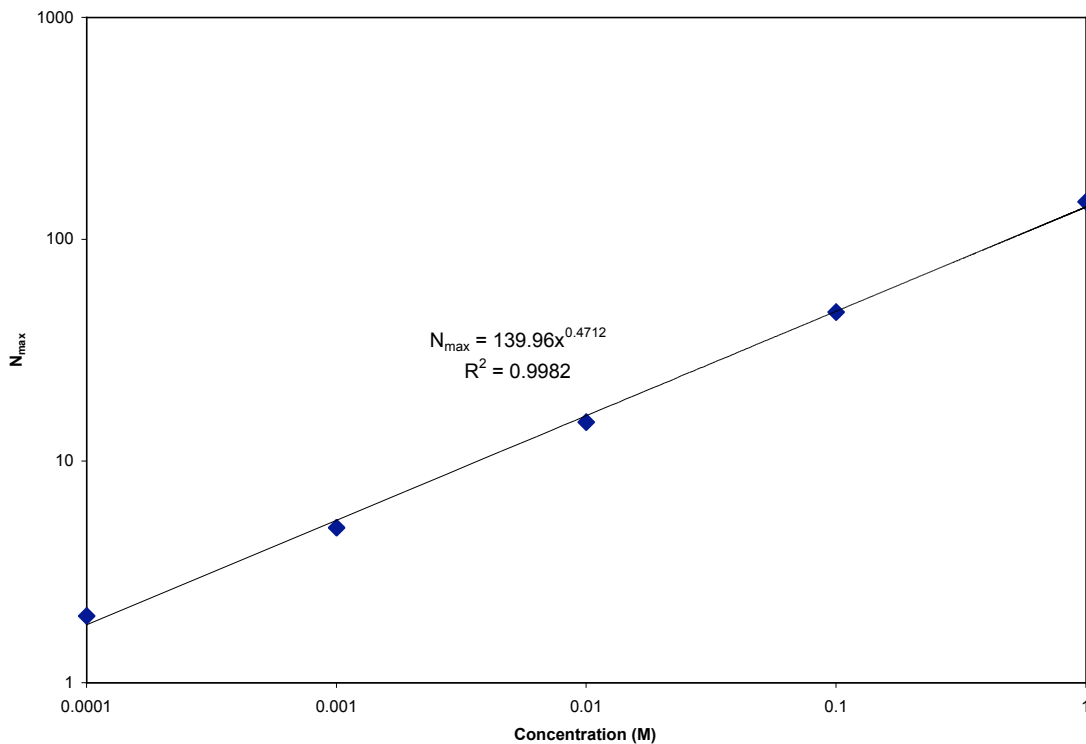
In this case we use the negative root as the positive root leads to unrealistic concentrations. Now that we have χ_1 we can compute χ_N from the previously given equation.

The plot shows the values of χ_N as a function of N for three different concentrations. From these plots, we see that the value where χ_N reaches a maximum, N_{max} , increases with the concentration, as we would anticipate. For example, one would form more 150-mers at greater concentrations than at lower concentrations.



- b) Determine the value of N where X_N reaches a maximum for total concentrations, C , of 0.1 mM, 1 mM, 10 mM, 100 mM, and 1 M.

The trend in N_{max} is additionally illustrated if we plot N_{max} as a function of concentration on a log-log graph. C [0.0001, 0.001, 0.01, 0.1, 1], N_{max} [2, 5, 15, 47, 148]



- c) N_{\max} , the value of N where X_N reaches a maximum, is a function of the concentration of C . Plot $\log(N_{\max})$ vs. $\log(C)$ and determine the relationship between these two parameters. In your analysis, plot all values, but only use values of $N_{\max} > 3$.

Solution given above.

3. Provide a physical (P) and/or molecular (M) reason for the following observations. Molecular (M) rationales should include a rough figure.

- a) Hexadecane wets glass (P).

Glass is a fairly high energy surface ($\gamma_{sv} = \text{high}$), while hexadecane is a low γ_{LV} liquid with dispersive interactions.

$$\cos \theta = (\gamma_{sv} - \gamma_{sL}) / \gamma_{LV}$$

thus as $\cos \theta$ increases, θ decreases.

- b) Hexadecane containing stearic acid, $\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$, does not wet glass (M).

γ_{sL} is increased due to polar functionalities migrating to the glass-liquid interface, which increases theta. Interface now looks more like water/glass than hexadecane/glass.

- c) Addition of small amounts of sodium dodecyl sulfate (SDS) increases the spreading of water on polyethylene (P/M).

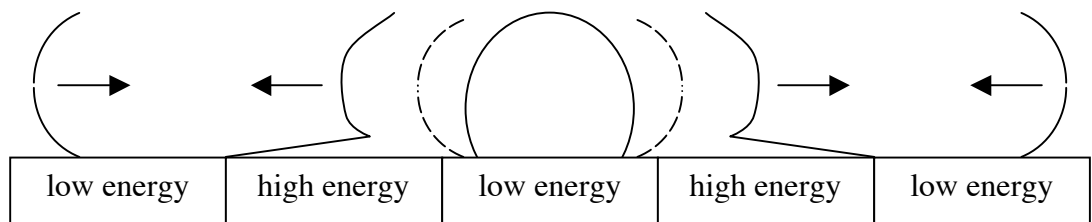
Addition of SDS reduced γ_{LV} and γ_{sL} by replacing water with lower energy hydrocarbons at the interface. Lower γ_{LV} and γ_{sL} decreases theta.

- d) Continued addition of SDS to water begins to have no effect on the spreading nature of water on polyethylene (M).

Further addition of SDS raises us over the CMC, so no further benefit is achieved.

- e) The contact angle for a drop of rainwater on the hood of a car is greater during a falling rain than afterwards (P).

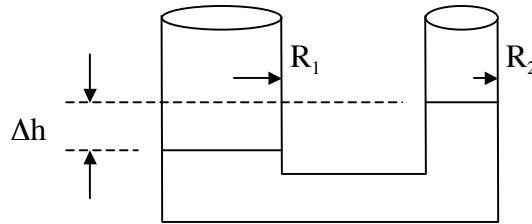
During rain, the drops are growing (i.e., advancing) due to additional water added to the drops. Following a rain, when the sun comes out, the drops begin to evaporate and recede on the car's surface. Advancing angles are greater than receding angles.



All real surfaces are heterogeneous. Liquid drops, upon advancing, move past the high energy patches and hold up on the low energy patches. Upon receding, liquid drops hold up on the high energy patches.

4. One method for measuring surface tension is to use a U-tube with a smaller radius on one side and a larger radius on the other. In such a system, a liquid that wets glass was determined to have a Δh of 19 mm between the levels of the two menisci in the U-tube.

- a) Draw the U-tube and liquid identifying Δh and the two radii.



- b) If the radii are 1 mm and 10 mm, and ρ is 950 kg/m^3 , determine the surface tension of the liquid.

$$P_{atm} - P_{surf} = 2\gamma / R_i$$

Applying the equation to each surface, and then subtracting them leads to

$$P_A - P_B = 2\gamma (1/R_1 - 1/R_2) = \rho g \Delta h$$

$$\gamma = \rho g \Delta h / [2(1/R_1 - 1/R_2)] = 0.0983 \text{ N/m}$$

5. a) Given the surface tensions of heptane (20.14 dyn/cm) and diethylene glycol (30.9 dyn/cm), calculate the works of cohesion for these solvents. The work of cohesion is the energy (erg/cm^2) required to separate one body of liquid/material into two. If two $1 \mu\text{L}$ drops of heptane that are suspended in air combine to form one $2 \mu\text{L}$ drop, estimate the energy gain (erg/cm^3) for this process and a temperature rise for the heptane..

$$W_H = 2 \gamma_H = 2 (20.14 \text{ dyn/cm}) = 40.28 \text{ dyn/cm}$$

$$W_{DG} = 2 \gamma_D = 2 (30.9 \text{ dyn/cm}) = 61.80 \text{ dyn/cm}$$

The energy change for two heptane drops coming together can be calculated as the difference between twice the energy change of a $1 \mu\text{L}$ drop and once the change in energy of a $2 \mu\text{L}$ drop. Once the work is found, the temperature change corresponding to the change in energy can be calculated.

$$\Delta E = 2(W_H SA_1) - W_H SA_2 = W_H (2SA_1 - SA_2) =$$

$$= 8 \pi (3/4\pi)^{2/3} (20.14 \text{ mJ/m}^2) [2(1 \times 10^{-9} \text{ m}^3)^{2/3} - (2 \times 10^{-9} \text{ m}^3)^{2/3}] = 8.04 \times 10^{-5} \text{ mJ}$$

or $4.02 \times 10^{-5} \text{ J/mL}$

$$\Delta T = \Delta E / (\rho V_2 C_p)$$

$$= (8.04 \times 10^{-8} \text{ J})(0.1 \text{ kg/mol}) / [(682 \text{ kg/m}^3)(2 \times 10^{-9} \text{ m}^3)(230 \text{ J/mol/L})] = 2.56 \times 10^{-5} \text{ K}$$

b) Given the interfacial tension of heptane-diethylene glycol (10.6 dyn/cm), calculate the work of adhesion for the heptane-diethylene glycol interface.

$$W_{HD} = \gamma_H + \gamma_D - \gamma_{HD} = (20.14 + 30.9 - 10.6) \text{ dyn/cm} = 40.44 \text{ dyn/cm}$$

6. a) A fabric is made of wool fibers of individual diameter 20 μm and density of 1.3 g/cm^3 . The contact angle for water on a single fiber is 120° . Calculate the contact angle of water on fabric woven so that its bulk density is 0.8 g/cm^3 .

Rearrange the Cassie Equation to get

$$\theta_{fab} = \arccos \left[\left(1 - \frac{\rho_{fab}}{\rho_{wool}} \right) \cos \theta_{air} - \frac{\rho_{fab}}{\rho_{wool}} \cos \theta_{wool} \right]$$

Substituting values and solving for theta gives $\theta_{fab} = 133.8^\circ$.

- b) If the fibers are chemically modified so that the contact angle of water on the individual fiber is 60° , what would be the contact angle on the above woven fabric?

Substituting values and solving for theta using 60° gives $\theta_{fab} = 94.4^\circ$