Chem. Engr. 06-607 Physical Chemistry of Colloids and Surfaces

Homework #6 **3-26-02**

Due: 4-9-02, beginning of class.

1. Starting from the expression for the van der Waals energy of interaction between flat plates, and using the Derjaguin approximation, derive expressions for the van der Waals (VDW) energy of interaction between:

a) sphere and wall
b) sphere and sphere
c) crossed cylinders

2. a) Plot the interaction energy (U_{ss}, in mJ) vs. separation distance (h, from 1 nm to 100 nm) for two similar charged spheres of radius 10^{-7} m and a surface potential of –50 mV. The NaCl concentration of the aqueous medium is 10 mM and the Hamaker constant is (H_{121} = 5 x 10^{-20} J). You may use the weak overlap approximation and assume that EDL and VDW are additive.

b) Determine the separation *(h_o)* for which the interactions energy goes through zero between the barrier and the primary minimum.

3. Because of its exceedingly low polarizability, the condensed material with the lowest Hamaker constant is liquid helium. As such, Hamaker constants for the van der Waals interaction of various substrates and air through thin films of liquid helium will always be negative, so that the substrate and air repel each other. Films of liquid helium will climb up the walls of containers, thickening the film of liquid helium on the sides to relieve the repulsion between substrate and air as shown below. A competing force is gravity, acting to pull the liquid back into its reservoir at the bottom. Measuring changes in film thickness with height is a useful measure of the Hamaker constant in these systems (see *Phys. Rev. A.* 7:790 (1973)).

a) Approximate the Hamaker constant (H_{132}) for the interaction of calcium fluoride and vapor through a thin film of liquid helium. Use the attached table of Hamaker constants and describe any approximations you make.

b) Derive a simple expression for the free energy (G) of a slice of liquid helium of thickness h and length dl at height l above the surface of the liquid helium reservoir. Be sure to account for differences in van der Waals interaction energy and gravitational potential energy.

c) Find the equilibrium thickness (h) at l by setting dG/dh to zero and solving for h. Calculate the thickness (h) at $l = 1$ cm and $l = 1000$ cm (the density of liquid helium is 140 kg/m^3, and the acceleration due to gravity (g) is 9.8 m/s^2).

d) The experimentally obtained values are $h = 21.5$ nm at $l = 1$ cm and $h = 2.8$ nm at $l = 1000$ cm. Explain any discrepancies between your theoretical values and the real ones.