Example Sheet #1

1. *Internal energy of a liquid.* (Rowlinson & Widom) Suppose there is a pairwise interaction potential $u(r)$ acting between molecules in a liquid of uniform density ρ, and that potential has a finite range d, so $u(r) = 0$ for $r > d$. Consider a particle P in the vicinity of the fluid-air interface, at some depth r below. Clearly, if $r > d$ there is no net force on the particle, due to its spherically-symmetric environment. Find the net force $F(r)$ on the particle for $r < d$, and thereby deduce the work needed to remove the particle from the fluid. Hence conclude that the internal energy per particle can be written as

$$\frac{1}{2}\rho \int_0^d d^3r u(r) \ .$$

2. *Van der Waals interactions between objects.* Assume that the fundamental pairwise interaction between individual atoms is $V(r) = -C/r^6$. Calculate the following:
(a) The interaction between two infinite slabs of thicknesses δ_1 and δ_2, a distance d apart.
(b) (Hamaker) The interaction between two spheres of radius R, whose distance of closest approach is d, and the limiting behaviour when $d \ll R$.

3. *Electrostatic contributions to elastic energy of surfaces.* Using Debye-Hückel theory, calculate the following:
(a) The electrostatic potential inside and outside of an infinite cylinder of radius R and thickness d and a sphere of radius R and thickness d when the surfaces have a fixed charge density σ_{in} inside and σ_{out} outside. Calculate the associated electrostatic energies.
(b) (Winterhalter & Helfrich) By comparing the energies from (a), along with that of a plane with charge densities σ_{in} on one side and σ_{out} on the other, in the regime such that the screening length $\lambda_{DH} \ll R$, deduce the electrostatic contribution to the elastic modulus k, Gaussian curvature modulus k_G, and spontaneous curvature H_0 in the Helfrich elastic energy

$$\mathcal{E} = \frac{1}{2}k \int dS \left(H - H_0\right)^2 + \frac{1}{2}k_G \int dSK \ ,$$

where $H = 1/R_1 + 1/R_2$ is the mean curvature (with R_1 and R_2 the principal radii of curvature), and $K = 1/R_1R_2$ is the Gaussian curvature.
(c) Estimate k, k_G, and the spontaneous radius $R_0 = 1/H_0$ for typical values of σ_0.

4. *Interaction of charged surfaces with nonuniform charge density.* Two parallel charged, planar, laterally-infinite membranes are located at $z = \pm d/2$. The upper one has charge density $\sigma_+ = \alpha\cos(kx)$, while the lower has $\sigma_- = \alpha\cos(kx+\theta)$, where θ is a constant phase shift. Within Debye-Hückel theory, find the electrostatic energy as a function of θ by computing the electrostatic potential ϕ in the region between the sheets. Find the value of θ that minimizes the energy, averaged over one wavelength of the charge modulation, and explain the physical content of this result.

5. *The Poisson-Boltzmann equation in one dimension and DLVO theory.* Here we explore the basic features of the nonlinear theory and the competition between electrostatics and van der Waals interactions.
(a) Find the electrostatic potential that satisfies the Poisson-Boltzmann equation for a $1:1$ electrolyte with mean concentration c,

$$\frac{d^2\phi}{dz^2} - \frac{8\pi ce}{\epsilon}\sinh\left(\beta e\phi\right) = 0 \ ,$$

away from a surface with charge density σ_0.
(b) Find the relationship between the surface charge density and the surface potential, and thus calculate the electrostatic free energy of that surface. Verify that the proper weak-field limit is recovered for small σ_0.
(c) Combine the weak-field results discussed in lecture for the interaction of two surfaces with charge density σ_0 with those of Problem 2 to obtain the complete energy per unit area of interaction of two membranes. Plot the potential for a range of relative strengths of the van der Waals and electrostatic energies and deduce the existence of a barrier to flocculation for a range of parameter values.

6. *Sedimentation.* Consider a uniform suspension of small particles of radius a, density ρ_p in a fluid of density ρ_f, at concentration c_0 in a chamber of height h. If gravity is now introduced the particles will settle, producing an equilibrium concentration profile $c(z)$ in which a gravitational flux balances that of diffusion. Find the normalized equilibrium concentration profile and explain why it is plausible. Suppose now that the suspended particles are in fact droplets of fat in water (e.g. milk) with $a = 0.5\ \mu$m. Assume a density for butterfat of 0.91 g/cm^3. Calculate the ratio $c(h)/c(0)$ for a container of height $h = 25$ cm. Rationalize your answer.