Examples Sheet #1

1. *Internal energy of a liquid.*
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

$$-\rho \int_0^d d^3r u(r) \ .$$

2. *van der Waals interactions between objects.*
(a) In terms of the fundamental interaction between individual atoms, $V(r) = -C/r^6$, calculate the interaction between two infinite slabs of thicknesses δ_1 and δ_2, separated by a distance d.
(b) Calculate the limiting behaviour of the interaction between two spheres of radius R, whose distance d of closest approach satisfies $d \ll R$.

3. *Electrostatic contributions to elastic energy of surfaces.*
(a) Using Debye-Hückel theory, calculate the electrostatic potential inside and outside of flat, cylindrical, and spherical surfaces with either fixed charge density σ_0 or fixed potential ϕ_0. Calculate the associated electrostatic energies.
(b) By comparing these energies from (a) in the regime that the screening length $\lambda_{DH} \ll R$, where R is the cylinder or sphere radius, deduce the electrostatic contribution to the elastic modulus k, Gaussian curvature modulus k_G, and spontaneous curvature H_0 in the elastic energy

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

where $H = 1/R_1 + 1/R_2$ is the mean curvature (with R_1 and R_2 the principal radii of curvature), and $K = 1/R_1 R_2$ is the Gaussian curvature.
(c) Estimate k, k_G, and the spontaneous radius $R_0 = 1/H_0$ for typical values of σ_0 and ϕ_0.

4. *Debye-Hückel theory near a rippled surface.* Membranes and surfaces in physical and biological systems are often not flat and smooth, but may exhibit undulations of various periodicities. Suppose a two-dimensional surface deviates from flatness by a one-dimensional modulation $h(x)$.
(a) If the surface has a constant surface charge density σ_0, find within Debye-Hückel theory the electrostatic potential away from the surface to second order in the displacement h and its derivatives.
(b) Using the results in (a), find the electrostatic potential to second order in h. Compare with the results in Problem 3.

5. *The Poisson-Boltzmann equation in one dimension.*
(a) Find the electrostatic potential that satisfies the Poisson-Boltzmann equation for a $1:1$ electrolyte with mean concentration c,

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

away from a surface with fixed potential ϕ_0.
(b) Find the relationship between the surface charge density and the surface potential, and thus calculate the electrostatic free energy of that surface.
(c) Generalize (a) and (b) to the case of two parallel surfaces, and thus find the energy of interaction as a function of separation. Compare with the weak-field limit.
(d) Combine these results with those of Problem 2 to obtain the complete DLVO potential 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. *The wormlike chain.*
(a) A wormlike polymer of contour length L is subject to an external force f acting at its two ends, directed along the z axis. The effective energy is

$$\mathcal{E} = \frac{1}{2}A\int_0^L ds\kappa^2 - fz \ ,$$

where A is the bending modulus and z is the end-to-end extension. Consider the high-force limit, where the chain's configuration deviates only slightly from a straight line. Then the tangent vector $\hat{\mathbf{t}}$ fluctuates only slightly around $\hat{\mathbf{z}}$, the unit vector in the z direction. If we take t_x and t_y as independent fluctuating components, the constraint $|\hat{\mathbf{t}}| = 1$ shows that t_z deviates from unity quadratically in the vector $\mathbf{t}_\perp \equiv (t_x, t_y)$. Show that to quadratic order the energy is

$$\mathcal{E} = \frac{1}{2}\int ds \left[A(\partial_s \mathbf{t}_\perp)^2 + f\mathbf{t}_\perp^2\right] - fL \ .$$

Use equipartition to find the thermal average $\langle \mathbf{t}_\perp^2 \rangle$, being careful to account for the two independent components of $\mathbf{t}_\perp$. From this, show that in this high-force limit the force-extension relation takes the form

$$\frac{z}{L} = 1 - \frac{1}{\sqrt{4fA}} \ . \qquad (1)$$

Compare this asymptotic result with that for the freely-jointed chain composed of N links, each of length b.

Calculate the correlation function $C(y) = \langle (1/L)\int_0^L ds\mathbf{t}_\perp(s)\cdot\mathbf{t}_\perp(s+r)\rangle$ of the tangent vector and thereby find the correlation length ξ, the length scale for decay of $C(y)$.

7. *Brownian motion with inertia.*

(a) Consider the Langevin equation for a single particle of mass m, drag coefficient γ and random forcing $\mathbf{A}'(t)$,

$$m\frac{d\mathbf{u}}{dt} = -\gamma\mathbf{u} + \mathbf{A}'(t)\ . \tag{1}$$

Assume the random force has zero mean and a variance $< \mathbf{A}'(t) \cdot \mathbf{A}'(t') >$ that is a function $\phi(|t-t'|)$ decaying very rapidly with $t-t'$, satisfying $\int_{-\infty}^{\infty} dy\phi(y) = m^2\tau$. If $\mathbf{u}(0) = \mathbf{u}_0$ and $\mathbf{r}(0) = \mathbf{r}_0$ are the initial velocity and position, solve (1) to obtain $\mathbf{U} \equiv \mathbf{u}(t) - \mathbf{u}_0 \mathrm{e}^{-\zeta t}$ formally in terms of $\mathbf{A}$, where $\zeta = \gamma/m$ and $\mathbf{A} = \mathbf{A}'/m$. From this deduce the variance $\langle U^2 \rangle$ and thereby determine τ from equipartition.

In order to evaluate higher moments of $\mathbf{U}$, assume that the random process $A(t)$ is Gaussian, so

$$\langle A(t_1)A(t_2)\cdots A(t_{2n+1})\rangle = 0\ ,$$

and

$$\langle A(t_1)A(t_2)\cdots A(t_{2n})\rangle = \sum_{\text{all pairs}} \langle A(t_i)A(t_j)\rangle\langle A(t_k)A(t_l)\rangle\cdots$$

Considering carefully the number of pairs in the above sum, show that the moments satisfy

$$\langle U^{2n+1}\rangle = 0 \qquad \langle U^{2n}\rangle = (2n-1)!!\langle U^2\rangle^n$$

and hence that the probability distribution of $\mathbf{U}$ is Gaussian,

$$W(\mathbf{u}, t; \mathbf{u}_0) = \left[\frac{m}{2\pi k_B T(1-\mathrm{e}^{-2\zeta t})}\right]^{3/2} \exp\left[-\frac{m|\mathbf{u} - \mathbf{u}_0\mathrm{e}^{-\zeta t}|^2}{2k_B T(1-\mathrm{e}^{-2\zeta t})}\right]\ .$$

Integrate the equation for $\mathbf{u}$ to obtain the position vector $\mathbf{r}$. Find the mean and variance of $\mathbf{r}$. Examine the short and long-time behaviour and explain the distinction between the two.