Part III: Biological Physics and Complex Fluids (Michaelmas, 2016)
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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

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

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) The limiting behaviour of the interaction between two spheres of radius R, whose distance d of closest approach satisfies $d \ll R$. You may wish to consult Hamaker's paper.

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 a sphere of radius R when the surfaces have a fixed charge density σ_0. Calculate the associated electrostatic energies.
(b) By comparing the energies from (a), along with that of a plane with charge density σ_0, in the regime such 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 Helfrich elastic energy

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

where $H = (1/R_1 + 1/R_2)/2$ 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.

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.* Here we explore the basic features of the nonlinear theory.
(a) Find the electrostatic potential that satisfies the Poisson-Boltzmann equation for a $1:1$ electrolyte with mean concentration c,

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

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.
(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. *Brownian motion with inertia.* Here we generalize the Langevin equation discussed in lecture to a particle 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,

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

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.

7. *The wormlike chain.* As we saw in lecture, the wormlike chain is perhaps the simplest model of a polymer that accounts for its bending elasticity.
(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

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

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

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

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 $C(y)$.

8. *A paper from the literature.* Read the paper: D.K. Fygenson, J.F. Marko, and A. Libchaber, "Mechanics of Microtubule-Based Membrane Extension," *Phys. Rev. Lett.* **79**, 4497-4500 (1997), available on the course website. Explain the origin of the free energy quoted in Eq. 1, the calculation of the buckling force in Eq. 2, the proposed ratcheting mechanism for microtubule growth, and the essential features of the calculation of the vesicle shapes.