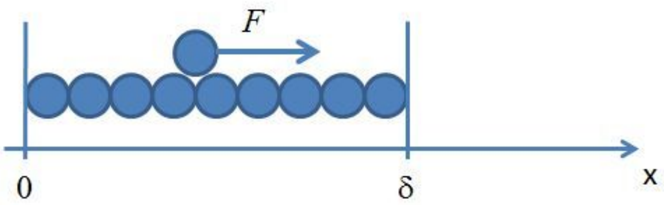
Example Sheet #1

**1.** *First passage time*
Calculate how long it takes a linear polymer to polymerize to a length $\delta$. Consider two separate cases, first without force ($F = 0$) acting on the diffusing monomer and then with a driving force ($F > 0$) acting on the monomer in steady state.




In order to approach this problem, first calculate the first passage time $\tau_1$ for a monomer to diffuse a distance $0 \to \delta$ for $F = 0$. You may assume that the particle reappears at the origin, when it reaches position $\delta$ and thus ensuring that probability $p$ of finding the particle in the interval $(0, \delta)$ is $p = 1$ . With this boundary condition you obtain the steady-state diffusion current $j = -D\partial p/\partial x$ with $D$ the diffusion constant.
Solve the steady-state diffusion equation $\partial^2 p/\partial x^2 = 0$ extracting $j$ and the first passage time $\tau_1 = \delta^2/2D$. Now add a driving force $F$ which acts on the monomer with friction coefficient $\gamma$ and solve the inhomogeneous equation

$$j = -D\frac{\partial c}{\partial x} - \frac{F}{\gamma}p$$

Discuss your result for $\tau_1$ in the case $F\delta \gg k_B T$.

**2.** *Sedimentation*
Consider identical small particles uniformly suspended in a vessel filled with solvent, where the average concentration of particles is $c_0$. Now let a gravitational force $F = mg$ act on these particles, where $m$ is the particle mass corrected for buoyancy. Write down the equation for the diffusion current for this situation and solve it to obtain the equilibrium distribution of particles $c(z)$. Explain this result heuristically.
Suppose that the suspended particles are in fact droplets of fat in water (e.g. milk) with diameters of around 1 $\mu$m. Assume a density for butterfat of 0.91 g/cm$^3$. Calculate the ratio $c(h)/c(0)$ for a container with height $h = 25$ cm . What do you conclude from this value?

**3.** *Protein Unfolding* [1]
In some naturally occurring membranes, bacteriorhodopsin proteins order in a near-perfect periodic lattice as shown in the paper by Oesterheldt *et al.*. Yet Fig. 1C from that paper shows a defect in this lattice. Explain why the defect is present and its significance.
By analyzing the data in Fig. 2, estimate the length per amino acid of an unfolded protein. Assume that the freely-jointed chain model provides a good description of this polymer.
The authors are using the lever arm of an atomic force microscope in their experiments. The lever arm extracting the protein can be seen as a harmonic spring with spring constant $k_c$. Estimate the spring constant from the data in Fig. 1B.

[1]This question is based on the paper *Unfolding pathways of individual bacteriorhodopsins* by Oesterhelt *et al.*, Science **288**, 143 (2000). You may download this paper from the course homepage or directly from the Science webpage through a library computer (or computer with Cambridge IP address).

**4.** *Electrophoresis in AC fields* [2]
Consider a spherical particle with radius $r$ in water held in an optical trap far from any surface. The particle has charge $q$ and is moving due to an homogeneous electric field alternating with angular frequency $\omega$ giving rise to an electrophoretic force $F_e$. Assume that the optical trap forms a harmonic potential with linear force distance relation $F = -\kappa \Delta x$ where $\kappa = \gamma \omega_c$. Estimate the maximum force on a particle with $q = 20,000e$ in an electric field of 50 V/m. Assuming that the trap has $\omega_c = 1000\ \mathrm{s}^{-1}$ and the particle $r = 1\ \mu$m compare the maximum $\Delta x$ with the thermal fluctuations of the particle in the trap. How is it still possible to measure the motion in the electric field? Now, write down the 1D-equation of motion for the particle in the field. In the overdamped regime, some terms can be safely neglected, which?
In case the colloid is held close to a charged surface and the AC-field is parallel to it, the equation of motion has to be adapted. How is the particle affected and which other forces become relevant?

**5.** *Polymer chains*
(a) Consider a freely jointed chain (FJC) polymer consisting of two different types of monomers with length $a$ and $b$ with $a \neq b$. The polymer has a sequence *babababa*... with $N/2$ monomers of each type. Calculate the room-mean-square end-to-end distance for the absence of any applied stretching force. For very low forces, this is a harmonic spring with $F = \kappa \langle z \rangle$. Calculate the value for the spring constant $\kappa$ of this chain.

(b) Now consider an almost ideal FJC with monomers $a$ only. In this chain of length $N$ the maximum bending angle of the bonds between adjacent monomers is unconstrained between 0 and $\pi/2$ and restricted from exceeding $pi/2$. Introduce $\vec{a_n}$ representing the unit vector indicating the direction of monomer $n$. Calculate $\langle \vec{a_n} \cdot \vec{a_{n+1}} \rangle$ where $\langle .. \rangle$ represents the average over all possible configurations.

**6.** *Stretching in electric fields*
Consider an ideal chain with $N = 1000$ segments of length $a = 0.5$ nm held at one end. Assume that in aqueous solution the chain carries $2e$ charges at the free end. What will be the average dnd-to-end distance $\langle z \rangle$ in a field $E = 30,000$ V/cm? At which field would $\langle z \rangle \approx 0.5(Na)$.

**7.** *Internal energy of a liquid.*
Suppose there is a pairwise interaction potential $u(r)$ acting between molecules in a liquid of uniform density $\rho$, 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

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

**8.** *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 $\delta_1$ and $\delta_2$, 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 $d \ll R$. You may wish to consult Hamaker's paper.

[2] The solution to this problem is e.g. discussed in Semenov, et al., "Single colloid electrophoresis" J. Coll. Interface Sci. (2009), can be downloaded from the course webpage.

**9.** *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 a fixed charge density $\sigma_0$. 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 $H = (1/R_1 + 1/R_2)/2$ 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 $\sigma_0$.

**10.** *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 $\sigma_0$, 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 energy to second order in $h$. Compare with the results in Problem 3.

**11.** *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 $c$,

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

away from a surface with fixed potential $\phi_0$.
(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.

**12.** *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

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

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 $\xi$, the length scale for decay of $C(y)$.

**13.** *Brownian motion with inertia.*
(a) Consider the Langevin equation for a single particle of mass $m$, drag coefficient $\gamma$ and random forcing $\mathbf{A}'(t)$,

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

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 $\tau$ 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.