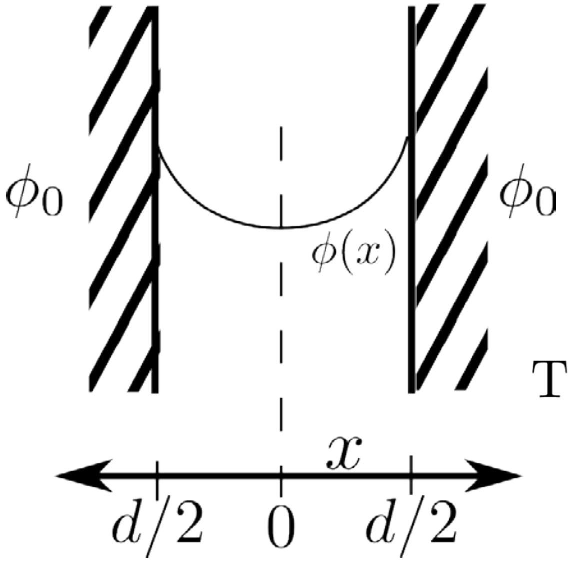
Interaction of Two Surfaces – Fixed Charge



For fixed charges σ_0 on each surface, the solution of the DH equation is

$$\boxed{\phi = \frac{4\pi\lambda_{DH}\sigma_0}{\epsilon}\frac{\cosh(x/\lambda)}{\sinh(d/2\lambda)}}$$

The potential at the surface is

$$\boxed{\phi(d/2) = \frac{4\pi\lambda_{DH}\sigma_0}{\epsilon}\coth(d/2\lambda_{DH})}$$

And the interaction energy per unit area is

$$\boxed{\frac{\tilde{\mathcal{F}}(d) - \tilde{\mathcal{F}}(\infty)}{2A} = \frac{2\pi\sigma_0^2\lambda_{DH}}{\epsilon}\left[\coth\left(\frac{d}{2\lambda_{DH}}\right) - 1\right]}$$

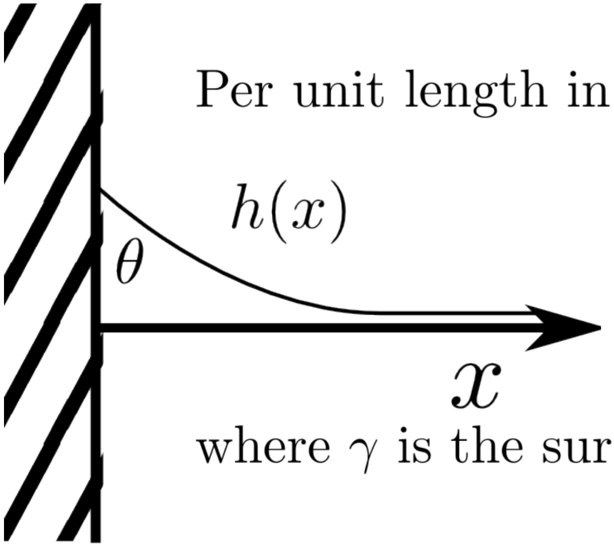
Screened Interactions - continued

A typical lipid has a cross sectional area of about $50 - 100\ \mathring{A}^2$. If each head group holds a single charge, and the Debye-Hückel length λ_{DH} is about 1 nm, then the typical energy is:

$$\frac{\tilde{\mathcal{F}}}{A} \sim 50 \frac{\text{erg}}{\text{cm}^2} \sim \text{Surface Tension of Water } (80[\text{erg/cm}^2])$$

So, these effects are comparable surface tension etc., and thus quite relevant.

An Aside on Quadratic Energy Functionals



Per unit length in the direction perpendicular to the plane the energy is

$$\frac{E}{L} = \int dx \left[\gamma \sqrt{1 + \left(\frac{\partial h}{\partial x}\right)^2} + \frac{1}{2} \Delta \rho g h^2 \right]$$

where γ is the surface tension.

Screened Interactions - continued

We are interested in the limiting case of small slopes to the surface, so we expand the square root for $|h(x)| \ll 1$, and obtain the energy difference from the flat state:

$$\sqrt{1+h_x^2} = 1 + \frac{1}{2}h_x^2 + \dots$$

$$\frac{E[h]-E_0}{L} \approx \boxed{\int dx \left[\frac{1}{2}\gamma h_x^2 + \frac{1}{2}\Delta\rho g h^2\right]}$$

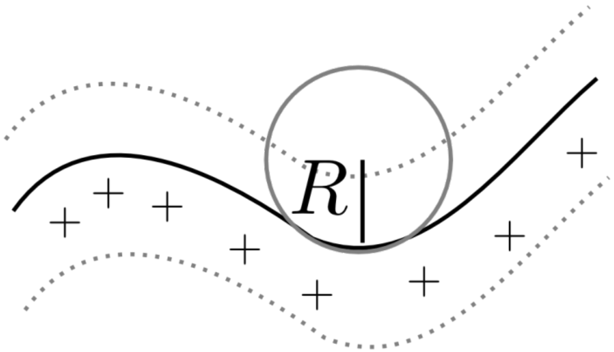
Note that we use the shorthand notation $h_x \equiv \partial h(x)/\partial x$.

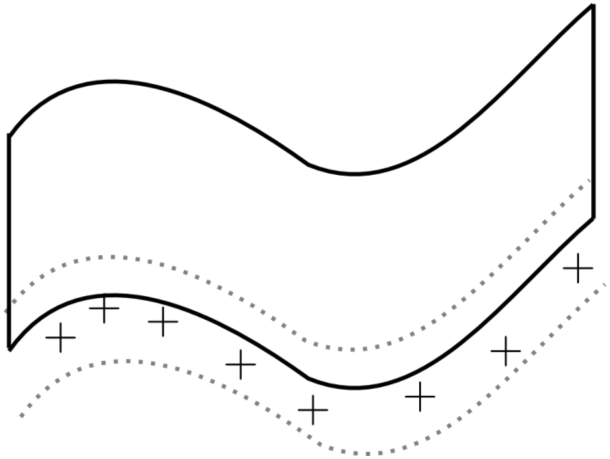
Again we will find a characteristic length scale by balancing the two terms. Here it is the *capillary length* l_c,

$$\frac{1}{l_c^2} \sim \frac{\Delta\rho g}{\gamma} \qquad \Rightarrow \qquad \boxed{l_c \sim \sqrt{\frac{\gamma}{\Delta\rho g}}}$$

which, for water/air, is about 3 mm ($\sqrt{100/1/1000}$).

Geometrical Aspects





Cells have length scales of many microns, artificial vesicles as well, while the Debye-screening length is in the range of nm, which means that we can exploit the separation of length scales

$$\boxed{\frac{\lambda_{DH}}{R} \ll 1}$$

For highly charged molecules like DNA this is not the case as there bends can happen on the scale of a few nm, which sets a limit to this analysis.

Geometrical Aspects

We will start by considering a curved, charged membrane. At each point on the surface there are two principal radii of curvature, R_1 and R_2. Using these we construct two quadratic quantities, the *mean curvature*, defined as $H = (1/2)(1/R_1 + 1/R_2)$ and the *Gaussian curvature* $K = 1/(R_1 R_2)$. The general energy functional for a membrane takes the form

$$\boxed{\mathcal{E} = \int dS \left[\frac{1}{2}k_c(H - H_0)^2 + \frac{1}{2}\bar{k}_c K\right]}$$

which was introduced by Helfrich and others for a non-stretching but bending membrane. There are two elastic constants that describe the stiffness of the membrane, and H_0 is known as the *spontaneous curvature*.

Each of these elastic constants has units of energy, and are typically some multiple of $k_B T$. H_0 arises from asymmetries between the two sides of the membrane.

Various Approaches

1. Compare the energy of different simple geometries where the various curvatures are constant. For a plane we have $R_1 = R_2 = \infty$. For a cylinder we have one vanishing curvature, and for the sphere $R_1 = R_2$. Comparing the results with the terms in the Helfrich energy in an expansion in powers of λ_{DH}/R we can find the elastic constants and the spontaneous curvature.

2. Construct a perturbation theory around a flat surface. This provides a good context to understand "boundary perturbation theory".

3. Multiple scattering method (very hard, not covered in this course)

Geometric Expansion

To simplify notation we use $\kappa = 1/\lambda$. Consider cylindrical geometry. We wish to solve the modified Helmholtz equation

$$(\nabla^2 - \kappa^2)\phi = 0$$

with

$$\nabla^2\phi = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial\phi}{\partial r}\right) = \phi'' + \frac{1}{r}\phi'$$

Rearranging, we obtain

$$\left(r^2\partial_{rr} + r\partial_r - (\kappa r)^2\right)\phi = 0$$

The solutions to this are $K_0(\kappa r)$ (outer problem), and $I_0(\kappa r)$ inner problem, where these are *modified Bessel functions*.

Geometric Expansion - continued

Thus, the inner problem has a solution of the form (fixed charge)

$$\boxed{\phi(r) = \frac{4\pi\sigma}{\epsilon\kappa}\frac{I_0(\kappa r)}{I_1(\kappa R)}}$$

and the free energy will involve a ratio of the form

$$\tilde{\mathcal{F}} \sim \frac{I_0(\kappa R)}{I_1(\kappa R)}$$

Here, we use the asymptotic expansion of Bessel functions:

$$I_\nu(z) = \frac{e^z}{\sqrt{2\pi z}}\left\{1 - \frac{\mu - 1}{8z} + \frac{(\mu - 1)(\mu - 9)}{2!(8z)^2} + \cdots\right\}$$

where $\mu = 4\nu^2$.

Thus, $I_0(\kappa R)/I_1(\kappa R)$ has an expansion in inverse powers of κR.

Review of Classical Statistical Physics

The probability $p(E)$ of finding a system in a state of energy E is

$$p(E) = \frac{\mathrm{e}^{-\beta E}}{Z}$$

where $\beta = 1/k_B T$, and the partition function Z is

$$Z = \sum_i \mathrm{e}^{-\beta E_i} .$$

The expectation value of a physical quantity A of the system is

$$\langle A \rangle = \sum_i A(E_i) \frac{e^{-\beta E_i}}{Z}$$

We will typically deal with systems for which the energy is simply the sum of kinetic and potential contributions. For a single particle this might look like

$$\boxed{E = \frac{p^2}{2m} + U(q) \ ,}$$

where q is some generalized coordinate.

Statistical Physics - continued

The partition function for a sytem of N particles is simply

$$\boxed{Z = \frac{1}{N!h^{3N}} \int d^3p^N \int d^3q^N \exp\left(-\beta\left[\sum_i \frac{p_i^2}{2m} + U(q^N)\right]\right)}$$

where we use the notation p^N and q^N to stand for the whole set of variables. The prefactor is appropriate for indistinguishable particles, and there is a phase space normalization factor of h (Planck's constant) for every pair of p and q.

Since there is no issue of the non-commutation of positions and momenta we can perform the momentum integrals exactly, yielding

$$Z = \frac{1}{N!}\frac{1}{\Lambda^{3N}} \int d^3q^N \exp\left(-\beta U(q^N)\right)$$

where the thermal de Broglie wavelength Λ is

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

Note, that h appears only as a prefactor, and thus will play no role in almost all observables.

Equipartition Theorem

When the configurational energy is quadratic in the generalized coordinate $E = (1/2)kq^2$, then the theorem of equipartition holds. Observe that

$$\left\langle \frac{1}{2}kx^2 \right\rangle = \frac{\int dx \frac{1}{2}kx^2 e^{-\beta k x^2/2}}{\int dx e^{-\beta k x^2/2}} = -\frac{\partial \ln Z}{\partial \beta}$$

This means that we can view $\ln Z$ as a *generating function.*

Now change variables in Z, pulling the constants out in front,

$$Z = \int dx e^{-\beta k x^2/2} \sqrt{\frac{\beta k}{2}} \sqrt{\frac{2}{\beta k}} = \sqrt{\frac{2}{\beta k}} \int dq e^{-q^2}$$

and so

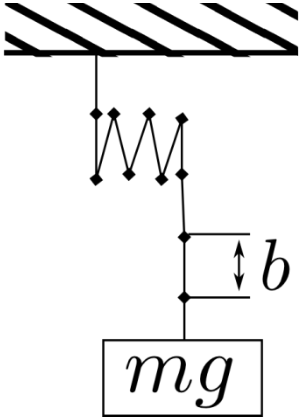
$$\ln Z = -\frac{\ln \beta}{2} + \text{terms independent of } \beta \qquad -\frac{\partial \ln Z}{\partial \beta} = \frac{1}{2\beta} = \frac{1}{2}k_B T$$

Thus, the energy per mode or degree of freedom is

$$\left\langle \frac{1}{2}kx^2 \right\rangle = \frac{1}{2}k_B T \ .$$

Polymers and Entropic Forces

The simplest model of a polymer is one in which there are N identical links of length b, each of which can be oriented up or down. Consider the case in which it is stretched by a mass m pulled down by gravity: The energy is then $E = -mgz$, where the extension z is



$$z = \sum_{n=1}^{N} b s_n$$

where $s_n = \pm 1$ denotes the orientation of the nth link.
The partition function is thus

$$Z = \sum_{s_1} \dots \sum_{s_N} \exp\left(\beta m g b \sum s_n\right)$$

which, by the independence of the s_n, can be simplified to

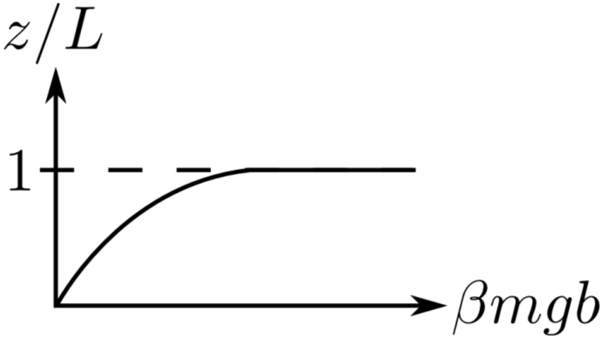
$$Z = \prod_{n=1}^{N} \sum_{s_n = \pm 1} \mathrm{e}^{\beta m g b s_n} = \boxed{[2 \cosh(\beta m g b)]^N}$$

Polymers and Entropic Forces - continued

From this we can calculate the mean extension as a function of the force $F = mg$,

$$\langle z \rangle = \langle b \sum_N s_n \rangle = -\frac{\partial \ln Z}{\partial \beta F} = Nb \tanh(\beta F b) = \boxed{L \tanh(\beta F b)},$$

where L is the fully-extended polymer length.



For a weak force, the average length $\langle z \rangle$ can be Taylor expanded

$$\langle z \rangle \simeq \frac{Nb^2}{k_B T} F + \cdots$$

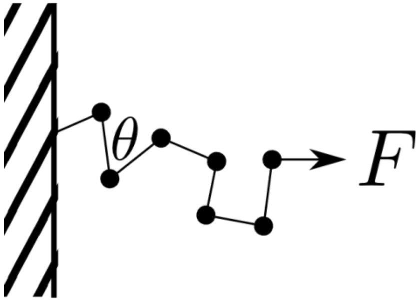
This is nothing but a Hookean spring relationship (force proportional to extension), with a spring constant

$$\boxed{k = \frac{k_B T}{Nb^2}}$$

An “entropic spring”

More Realistic Freely-Jointed Chain

Now we examine a more realistic model in which every link is freely jointed. Applying a force F to looks like this: The extension x and energy E are:



$$x = \sum_{n=1}^{N} b\cos\theta_n \qquad E[\{\theta_n\}] = -Fb\sum_{n=1}^{N}\cos\theta_n$$

The partition function is then

$$Z = \prod_N 2\pi \int d\theta_n \sin\theta_n \mathrm{e}^{f\cos\theta_n} \qquad f = \frac{Fb}{k_B T}$$

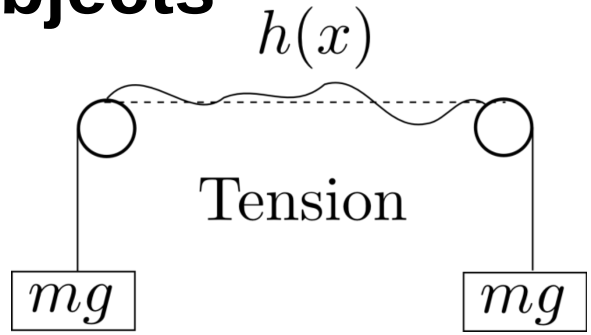
$$\boxed{Z = \left[\frac{4\pi\sinh(f)}{f}\right]^N}$$

The average extension follows by differentiation:

$$\langle x\rangle = b\frac{\partial(\ln Z)}{\partial f} = Nb\mathcal{L}(f) \qquad \boxed{\mathcal{L}(f) = \coth(f) - \frac{1}{f}}$$

The spring constant for this new chain is then $k = 3k_BT/Nb^2$ reflecting 3 degrees of freedom per link.

Fluctuating Continuum Objects



Now we generalize the model to a continuous object, using a simple 1D string that is under tension from e.g. two hanging masses. Relative to the flat state $h = 0$, the energy is

$$\Delta E = \gamma \left[\int_0^L dx \sqrt{1 + h_x^2} - L \right] \simeq \boxed{\frac{\gamma}{2} \int_0^L dx h_x^2 + \dots}$$

We can not directly apply equipartition since there are no identifiable independent degrees of freedom. But, if we note the boundary conditions at $x = 0$ and L we can use a Fourier series,

$$h(x) = \sum_n A_n \sin\left(\frac{n\pi x}{L}\right)$$

By the orthogonality of the modes, a little algebra shows that

$$\boxed{\Delta E = \frac{\gamma L}{4} \sum_{n=1}^{\infty} \left(\frac{n\pi}{L}\right)^2 A_n^2}$$

This decomposition holds for any particular realization of the Fourier coefficients. Next we turn to the thermal averages...

Fluctuating Continuum Objects - continued

If the string is in thermal equilibrium (e.g. connected to a heat bath), then the average of each coefficient will be:

$$\langle A_n \rangle = 0$$

$$\langle E_n \rangle = \frac{k_B T}{2} = \frac{\gamma \pi^2 n^2}{4L} \langle A_n^2 \rangle \rightarrow \boxed{\langle A_n^2 \rangle = \frac{2k_B T}{\gamma \pi^2 n^2} L}$$

The average variance of the string can then be calculated:

$$\langle h^2(x) \rangle = \sum_n^\infty \sum_m^\infty \langle A_m A_n \rangle \sin\left(\frac{m\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right)$$

$$= \boxed{\frac{2k_B T L}{\gamma \pi^2} \sum_{n=1}^\infty \frac{\sin^2\left(\frac{n\pi x}{L}\right)}{n^2}}$$

Note the interesting dependence on the system size. The variance is linear in L. This should remind you of a random walk...