Interaction of Two Surfaces – Fixed Charge

For fixed charges \( \sigma_0 \) on each surface, the solution of the DH equation is

\[
\phi = \frac{4\pi \lambda_D H \sigma_0}{\varepsilon} \frac{\cosh(x/\lambda)}{\sinh(d/2\lambda)}
\]

The potential at the surface is

\[
\phi(d/2) = \frac{4\pi \lambda_D H \sigma_0}{\varepsilon} \coth(d/2\lambda_D H)
\]

And the interaction energy per unit area is

\[
\frac{\tilde{F}(d) - \tilde{F}(\infty)}{2A} = \frac{2\pi \sigma_0^2 \lambda_D H}{\varepsilon} \left[ \coth \left( \frac{d}{2\lambda_D H} \right) - 1 \right]
\]
Screened Interactions - continued

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

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

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

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An Aside on Quadratic Energy Functionals

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

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

where $\gamma$ 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:

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

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

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* $l_c$,

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

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

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

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

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

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 $\lambda_{DH}/R$ 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

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

The solutions to this are $K_0(\kappa r)$ (outer problem), and $I_0(\kappa r)$ inner problem, where these are modified Bessel functions.
Thus, the inner problem has a solution of the form (fixed charge)

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

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 \( \kappa R \).
Review of Classical Statistical Physics

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

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

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

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

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

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

where $q$ is some generalized coordinate.
Statistical Physics - continued

The partition function for a system of $N$ particles is simply

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

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 $\Lambda$ is

$$\Lambda = \frac{\hbar}{\sqrt{2\pi mk_B T}}$$

Note, that $\hbar$ 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

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

This means that we can view $\ln Z$ as a generating function. Now change variables in $Z$, pulling the constants out in front,

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

and so

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

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

$$z = \sum_{n=1}^{N} bs_n$$

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

$$Z = \sum_{s_1} ... \sum_{s_N} \exp \left( \beta mgb \sum_{n=1}^{N} s_n \right)$$

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

$$Z = \prod_{n=1}^{N} \sum_{s_n=\pm 1} e^{\beta mgb s_n} = \left[ 2 \cosh(\beta mgb) \right]^N$$
Polymers and Entropic Forces - continued

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

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

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

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

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:

$$x = \sum_{n=1}^{N} b \cos \theta_n$$

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

The partition function is then

$$Z = \prod_{n} 2\pi \int d\theta_n \sin \theta_n e^{f \cos \theta_n}$$

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

$$f = \frac{Fb}{k_BT}$$

The average extension follows by differentiation:

$$\langle x \rangle = b \frac{\partial (\ln Z)}{\partial f} = Nb \mathcal{L}(f)$$

$$\mathcal{L}(f) = \coth(f) - \frac{1}{f}$$

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

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

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

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

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:

\[
\langle A_n \rangle = 0
\]

\[
\langle E_n \rangle = \frac{k_B T}{2} = \frac{\gamma \pi^2 n^2}{4L} \langle A_n^2 \rangle \quad \rightarrow \quad \langle A_n^2 \rangle = \frac{2k_B T}{\gamma \pi^2 n^2} L
\]

The average variance of the string can then be calculated:

\[
\langle h^2(x) \rangle = \sum_{n} \sum_{m} \langle A_m A_n \rangle \sin \left( \frac{m \pi x}{L} \right) \sin \left( \frac{n \pi x}{L} \right) = \frac{2k_B T L}{\gamma \pi^2} \sum_{n=1}^{\infty} \frac{\sin^2 \left( \frac{n \pi x}{L} \right)}{n^2}
\]

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