# Soft Matter and Biological Physics

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# Preface

How to use these lecture notes:

Where derivations are written out extensively here, they will probably not be reproduced in class, and vice versa. You will be expected to have understood all of these, and to be able to reproduce these results and variations that use the same methods. Derivations obtained in the exercises on the examples sheets are also part of the course, and worked-out solutions will be made available towards the end of the term.

Dos:

- Use the handout to follow progress through the course material. The structure of the handout is almost the same as the lectures.
- Integrate the lecture overheads and the handout material yourself. There is examinable material that only appears in one place.
- Follow suggestions and think about the questions in the notes. These are distributed through the text to help you spot if you are understanding the material.

Don'ts:

- Expect to study only from these notes. You will need the other primary references. Most of all you will need to understand how to use the material and methods presented, rather than memorising information.
- Expect these notes to be error free. They will contain a higher density of errors than a typical book! (They derive originally from one student's very generous but incomplete work). e-mail us if you think something is wrong or unclear, and the notes will improve.
- Expect these notes to be even in the level of presentation. Some paragraphs are minimal, and some section labels are only place holders for material that will be covered in class. Instead, use these notes to guide you through the books, articles, etc.

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# Introduction

# 1

Soft matter and biological physics are topics very much unlike the more standard subjects such as quantum mechanics or thermal and statistical physics. The latter are in many respects complete, certainly at the level of interest to advanced undergraduate or beginning graduate students. It is safe to say that the core material in these subjects will not change fundamentally in the next decades, if ever. In contrast, soft matter and biological physics are topics which only in the last two decades have become a strong focus in physics departments around the globe. This makes them exciting fields in which to work, but also poses the problem for students and professors in that there is no single standard textbook that covers the field. Thus we have decided to provide some notes in this form, not to replace a textbook, but to help in accessing the material of the course.

These are notes for the Part III 'soft and biological physics' course jointly convened between the Cavendish Laboratory and the Department of Applied Mathematics and Theoretical Physics. They are and will likely remain 'preliminary'. They are neither fully complete, nor fully correct and will be constantly updated. It is very important that you look at other material as well to understand fully the topics covered in the course. It is also important to realize that notes like these can almost never replace a proper textbook. Even more so in an advanced courses replace covering 'hot' topics discussed at the moment in the scientific community it is often necessary to read (very often recent) journal articles. We know that this can be a challenge but you are expected to be able to do this when you start to work on your Part III projects and essays.

# Microscopic Physics

# 2

## 2.1 Review of molecular physics

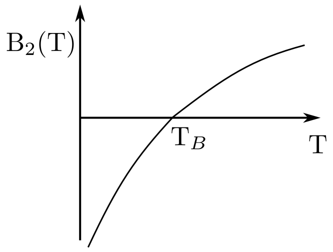
The ideal gas law,

$$pV = Nk_BT = nRT \qquad \text{or} \qquad \frac{p}{k_BT} = \rho \ ,$$

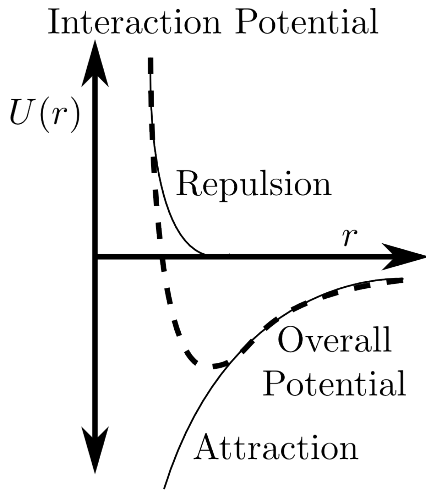
where $p$ is the pressure, $V$ is the volume, $N$ is the number of molecules, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $n$ is the number of moles, $R = N_Ak_B$ is the ideal gas constant (where $N_A$ is Avogadro's number), and $\rho = N/V$ is the density, is only an approximation. At low densities real gases are described by a "virial expansion", a power series in $\rho$,

$$\frac{p}{k_BT} \simeq \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \cdots \ .$$

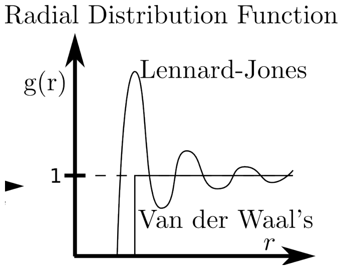
Intuitively, the quadratic term involves 2-body interactions, the cubic term captures 3-body effects, and so on. Experimental measurements (see figure below) of the second virial coefficient $B_2$ show that it is negative at low temperatures (indicating attraction between pairs) and becomes positive (repulsive) at high temperatures. The temperature $T_B$ at which $B_2 = 0$ is known as the Boyle point.



One of the great early triumphs of statistical physics was to show how $B_2(T)$ arises from the underlying intermolecular potential, which typically has a repulsive hard core and an attractive tail due to van der Waals interactions (figure).


Interaction Potential
$U(r)$
Repulsion
$r$
Overall Potential
Attraction

It was van der Waals who had the crucial idea that the potential could be thought of as the sum of a purely repulsive part, which led to excluded volume around each molecule, and a purely attractive part whose effects on the thermodynamics could be estimated by a kind of perturbation theory. In this "mean field" calculation of the latter, we imagine that the density of the gas is uniform throughout space, rather than trying to address the complex form of the radial distribution function (RDF) seen in the figure:


Radial Distribution Function
g(r)
Lennard-Jones
1
Van der Waal's
r

Under this assumption the energy $U_{\rm attr}$ associated with the attractive part of the potential $u_{\rm attr}$ is

$$U_{\rm attr} = \frac{1}{2} N\rho \int d^3r u_{\rm attr}(r) \ ,$$

where the factor of 1/2 avoids double-counting. It is convenient to define the quantity $a$,

$$a = -\frac{1}{2} \int d^3r u_{\rm attr}(\mathrm{r}) \ ,$$

which is a characteristic constant for a given species. The energy is then $U_{\rm attr} = -aN\rho = -aN^2/V$ and the contribution to the pressure is

$$p_{\rm attr} = -\frac{\partial U_{\rm attr}}{\partial V} = -a\rho^2 \ .$$

Thus, our first guess at a corrected equation of state is

$$p \simeq \rho k_B T - a\rho^2 \ .$$

Further, van der Waals realized that effect of the hard-core interactions could be accounted for by subtracting from the total volume $V$ an amount proportional to the number of particles $N$, with an effective excluded volume per particle $b$. Putting these two effects together one has the revised equation of state

$$(p + a\rho^2)(V - Nb) = Nk_BT$$

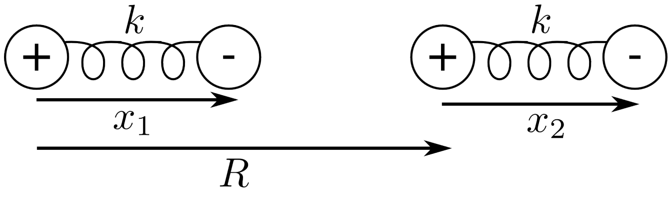
Expanding for small $\rho$ we find

$$\frac{p}{k_BT} \sim \rho + \left(b - \frac{a}{k_BT}\right)\rho^2 + \dots\ .$$

This shows that $B_2(T) = b - a/k_BT$, a form that is qualitatively like that seen in experiment. At high temperatures it saturates to a positive constant, reflecting entropic effects, whereas at low temperatures it is dominated by the attractive part of the potential. This shows the important point seen in many other contexts (such as polymer physics), that interaction terms quadratic in a density often must be interpreted as free energies (involving energy and entropy) rather than purely energetic.

## 2.2 Van der Waals interactions

Van der Waals' name is of course also associated with the long-range *fluctuating-dipole* interactions between neutral objects. Let us first get some insight into the physics responsible for the long-range attraction between neutral atoms or molecules. We reproduce essentially verbatim the very nice derivation in the literature (Holstein, 2001) which is based on the picture of two charged harmonic oscillators whose positive charges are fixed in place and whose negative charges can oscillate back and forth under the action of a spring of constant $k$:



With $\omega_0^2 = k/m$, where $m$ is the electron mass, the Hamiltonian is a sum of the electron kinetic energy, spring energy, and electrostatic interactions,

$$\begin{aligned}
\mathcal{H} &= \mathcal{H}_0 + \mathcal{H}_1 \\
\mathcal{H}_0 &= \frac{p_1^2}{2m} + \frac{1}{2}m\omega_0^2 x_1^2 + \frac{p_2^2}{2m} + \frac{1}{2}m\omega_0^2 x_2^2 \\
\mathcal{H}_1 &= e^2\left[\frac{1}{R} + \frac{1}{R - x_1 + x_2} - \frac{1}{R - x_1} - \frac{1}{R + x_2}\right]
\end{aligned}$$

This is exact but rather cumbersome. If we consider the physically-interesting limit in which the atoms are separated a distance large compared to their size, $|x_1|, |x_2| \ll R$, then

$$\mathcal{H}_1 \sim -\frac{2e^2 x_1 x_2}{R^3},$$

which we recognize as a dipole term from the $R^{-3}$ fall-off with distance. To simplify the situation, a coordinate change is made:

$$x_\pm = \frac{x_1 \pm x_2}{\sqrt{2}} \qquad x_1 = \frac{x_+ + x_-}{\sqrt{2}} \qquad x_2 = \frac{x_+ - x_-}{\sqrt{2}} \ ,$$

and the Hamiltonian becomes

$$\mathcal{H} = \frac{p_1^2}{2m} + \frac{1}{2}\left(m\omega_0^2 - \frac{2e^2}{R^3}\right)x_+^2 + \frac{p_2^2}{2m} + \frac{1}{2}\left(m\omega_0^2 + \frac{2e^2}{R^3}\right)x_-^2 \ .$$

The two terms in parenthesis are modified frequencies,

$$\omega_+^2 = \omega_0^2 - \frac{2e^2}{mR^3} \qquad \omega_-^2 = \omega_0^2 + \frac{2e^2}{mR^3} \ ,$$

and so

$$\mathcal{H} = \frac{p_1^2}{2m} + \frac{1}{2}m\omega_+^2 x_+^2 + \frac{p_2^2}{2m} + \frac{1}{2}m\omega_-^2 x_-^2 \ .$$

Having diagonalized the Hamiltonian, we can easily calculate the change to the ground state energy of the system due to the Coulomb interactions. This interaction potential $u(r)$ is just the shift in zero-point energies,

$$u(r) = \frac{1}{2}\hbar\omega_+ + \frac{1}{2}\hbar\omega_- - 2\cdot\frac{1}{2}\hbar\omega_0 \simeq -\frac{1}{2}\hbar\omega_0\frac{(e^2/m\omega_0^2)^2}{R^6} + \cdots \ ,$$

where we have expanded the frequencies $\omega_\pm$ to the lowest non-vanishing order. In grouping the terms as shown in the final form above we have isolated a characteristic energy ($\hbar\omega_0$) that sets the overall scale for the interaction (it would be typical of an internal excitation energy from an $s$ state to a $p$ state, since fundamentally the interaction is due to virtual transitions to states with dipole moments). Recognizing the $R^{-6}$ dependence, we observe that $e^2/m\omega_0^2$ must be a characteristic volume (remember we are working in cgs units!). To check this we note that the simplest relationship between an induced electric dipole moment $\mathbf{d}$ and an applied electric field $\mathbf{E}$ is

$$\mathbf{d} = \alpha\mathbf{E} \ ,$$

where $\alpha$ is known as the polarizability. As the dimensions of $\mathbf{d}$ are charge×length ($Q \cdot L$), and the units of $\mathbf{E}$ are $Q/L^2$ (cgs), the dimensions of $\alpha$ are $L^3$, that is a *volume.* That it is proper to interpret $e^2/m\omega_0^2$ as the polarizability can be seen by generalizing the original Hamiltonian to include an applied electric field of magnitude $E_0$ in the $x$-direction, acting to displace the electrons only (recall that the positive charges are fixed in place),

$$\begin{aligned}\mathcal{H} &= \mathcal{H}_0 + eE_0x_1 + eE_0x_2 \\ &= \frac{1}{2}m\omega_0^2\left(x_1^2 + \frac{2eE_0x_1}{m\omega_0^2} \pm \left(\frac{eE_0}{m\omega_0^2}\right)^2\right) + (1 \leftrightarrow 2) \\ &= \frac{1}{2}m\omega_0^2 z_1^2 + \cdots \\ z_{1,2} &= x_{1,2} + \frac{eE_0}{m\omega_0^2} \ ,\end{aligned}$$

where the ± term in the second line indicates that we can add the indicated term to complete a square and then subtract it off separately. We thus see that we have a new pair of oscillators whose equilibrium positions are linearly shifted by the field. The induced dipole moment is thus the electron charge times that shift, $e^2E_0/m\omega_0^2$, so the polarizability is indeed

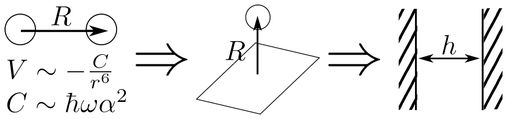
$$\alpha = \frac{e^2}{m\omega_0^2} \ .$$

Finally, in this model the interaction between the two fluctuating dipoles can be written in the simple form

$$u(r) = -\frac{1}{2}\frac{\hbar\omega_0\alpha^2}{r^6} \ .$$

### 2.2.1 Interaction of extended objects

Now can can use the basic result of the previous section to calculate the interaction energy between atoms and extended objects through a progression of geometries:



Let us denote the interaction between two point molecules as

$$V_{11}(r) = -\frac{C}{r^6} \ .$$

To calculate the attraction $V_{1\mathrm{S}}$ between one such neutral particle (at the origin) and a semi-infinite medium (a "slab") lateral in the $x-y$ plane, and filling the region $z > h$), we use cylindrical coordinates to obtain

$$\begin{aligned}V_{1\mathrm{S}}(h) &= \int_h^\infty dz \int_0^{2\pi} d\phi \int_0^\infty rdr\rho V_{11}(\sqrt{z^2+r^2}) \\ &= -2\pi C\rho \int_h^\infty dz \int_0^\infty rdr\frac{1}{(z^2+r^2)^3} \\ &= -\frac{\pi C\rho}{6h^3} \ ,\end{aligned}$$

where $\rho$ is the number density of particles in the slab. Note that the power law $r^{-6}$ of the particle-particle potential has become $r^{-3}$ by three spatial integrals $(x, y, z)$.

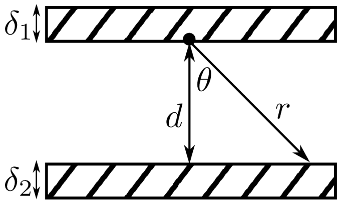
With this we can calculate the interaction between two semi-infinite slabs by adding up all the contributions of the particles at varying distances from one slab within the other. Since there are $A\rho dz$ atoms each per thickness $dz$, the interaction energy is

$$V_{\rm SS}(h) = A\int_h^\infty \rho V_{\rm 1S}(z)dz \Rightarrow \frac{V_{\rm SS}}{A} = -\frac{A_H}{12\pi}\frac{1}{h^2} \ ,$$

where $A_H$ is known as the Hameker constant. In the more general case of atoms of type 1 and 2 in the two slabs, with densities $\rho_{1,2}$ and a cross-interaction constant $C_{12}$ we have

$$A_H = \pi^2\rho_1\rho_2 C_{12} \ .$$

From a scaling point of view, $A_H \sim \pi^2\hbar\omega(\alpha\rho)^2$, so with $\pi^2 \sim 10$, $\hbar\omega_0 \sim 3$eV and $\alpha\rho \sim 0.1$ (typical of dense liquids), we estimate $A_h \sim 0.3$ eV $\sim 5\times 10^{-20}$ J $\sim 5 \times 10^{-13}$ erg, which is an order of magnitude larger than thermal energy at 300K. Just as importantly, this interaction scales with the inverse square of the distance, which produces a very long-range force.



A simple generalization of the previous calculation yields the interaction between two laterally-infinite slabs of *finite* thickness $\delta_1$ and $\delta_2$, relevant to the interaction of pairs of nearby lipid membranes. The interaction of a single atom a distance $d$ from the slab of thickness $\delta_1$ is

$$V_{\rm 1S}(d) = -\frac{\pi C\rho}{6}\left\{\frac{1}{d^3} - \frac{1}{(d+\delta_1)^3}\right\} \ ,$$

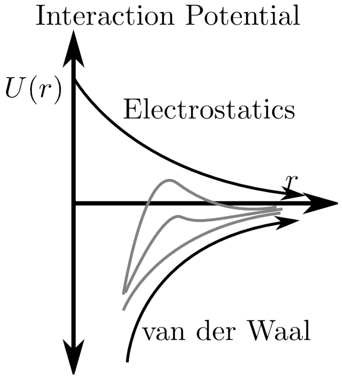
which, by integration over slab 2 yields the energy per unit area

$$\frac{V_{\rm SS}(d)}{A} = -\frac{\pi C\rho^2}{12}\left\{\frac{1}{d^2} - \frac{1}{(d+\delta_1)^2} - \frac{1}{(d+\delta_2)^2} + \frac{1}{(d+\delta_1+\delta_2)^2}\right\}$$

At long distances this interaction scales as $d^{-4}$. On the examples sheet we will examine the sphere-sphere interaction, which is discussed extensively in the book by Verwey and Overbeek.

## 2.3 Screened electrostatic interactions

Many of the interesting objects in biology interact both through van der Waals forces and (screened) electrostatic interactions. As the former typically decay as an inverse power of distance, and the latter (as we shall see) decays exponentially, the combined potential is attractive at long distances. Depending on the length scales and amplitudes in a given system, at shorter distances there can be a secondary minimum separated by a potential barrier from the minimum at the very close separations (see figure). This complex interplay between the two contributions can give rise to many interesting phenomena. Our first goal is to understand the electrostatic contribution.



Two charges in vacuum separated by a distance $r$ have an electrostatic energy (in cgs units) of

$$\mathcal{E} = e\phi(r) = \frac{e^2}{r} \ ,$$

where $\phi$ is the electrostatic potential. If we measure $r$ in the molecule scale of $\mathring{A}$ the ratio of electrostatic to thermal energy is

$$\frac{\mathcal{E}}{k_B T} = \frac{(4.8 \times 10^{-10})^2}{4 \times 10^{-14} \cdot 10^{-8}} = \frac{580}{r[\mathring{A}]}$$

However, the dielectric constant $\epsilon \sim 80$, so even apart from screening the energy is reduced to $e^2/\epsilon r$. Turning this around, we define the *Bjerrum length* $\lambda_B$ as the point of balance:

$$\lambda_B = \frac{e^2}{\epsilon k_B T} \sim 7\mathring{A}$$

Even pure water has small amounts of ionic species ($H^+/OH^-$) at equilibrium. These and other ions present will tend to screen the bare electrostatic interactions considered above. Effectively, mobile charges opposite in sign to a given charge will cluster around it in a diffuse cloud, screening it from other distant charges. The standard formalism to compute the ionic distribution and resulting interactions is known as Poisson-Boltzmann theory, or, in its linearized form, as Debye-Hückel theory. PB theory is based on two assumptions.

1. The Poisson equation relating the electrostatic potential $\phi$ to the charge density $\rho$:

$$\nabla^2\phi = -\frac{4\pi\rho}{\epsilon} \qquad \mathbf{E} = -\boldsymbol{\nabla}\phi$$

2. The Boltzmann distribution, relating the ionic concentrations $c_s$ of the species $s$ of valence $z_s$ to the electrostatic potential

$$c_s = c_0 e^{-z_s e\phi/k_B T} ,$$

where $c_0$ is a background concentration.

Combining these into a single self-consistent equation (with $\beta = 1/k_B T$), we obtain the *Poisson-Boltzmann equation*

$$\nabla^2 \phi = -\frac{4\pi}{\epsilon} \sum_{species\ s} z_s e c_0 e^{-\beta z_s e \phi} .$$

If we consider the specific case of a $z : z$ electrolyte (1:1, NaCl, 2:2, $CuSO_4$ etc.), we can write this in a more compact form

$$\nabla^2 \phi = \frac{8\pi z e c_0}{\epsilon} \sinh(\beta z e \phi) .$$

This is a very nonlinear equation for which analytical solutions can be found only in very simplified geometries. Much of the important physics of screened electrostatics can be seen in the *weak field* limit, when $\beta e \phi \ll 1$. We then linearize the PB equation (using $\sinh(x) \simeq x + \cdots$) to obtain

$$\nabla^2 \phi = \frac{8\pi z^2 e^2 c_0}{\epsilon k_B T} \phi + \ldots$$

Comparing the two sides of this equation we infer on dimensional grounds that there is a characteristic length scale, the Debye-Huckel length $\lambda_{DH}$:

$$\lambda_{DH} = \left[ \frac{\epsilon k_B T}{8\pi z^2 e^2 c_0} \right]^{1/2} \sim \frac{10 \text{ nm}}{\sqrt{c_0[\text{mM}]}} ,$$

where in the final expression we have expressed the concentration in the biologically relevant units of millimolar (mM). Our first important conclusion is that this length scale is nanometric for typical biophysical contexts.

In this Debye-Hückel limit the electostatics is governed by the *modified Helmholtz equation*,

$$\left( \nabla^2 - \lambda_{DH}^{-2} \right) \phi = 0 .$$

Solving this problem first for a surface occupying the $y - z$ plane ($x = 0$), we observe that the general solution of

$$\left( \frac{\partial^2}{\partial x^2} - \lambda_{DH}^{-2} \right) \phi = 0$$

is

$$\phi = A e^{x/\lambda_{DH}} + B e^{-x/\lambda_{DH}} .$$

In this case, $A = 0$ by the requirement of a bounded solution as $x \to \infty$, and if the surface potential is held at $\phi_0$, then

$$\phi = \phi_0 e^{-x/\lambda_{DH}}$$

There is an induced charge density $\sigma$ on the surface which can be computed in the usual way (Gaussian pillbox),

$$-\hat{\mathbf{n}} \cdot \boldsymbol{\nabla}\phi|_{\text{surf}} = \frac{4\pi\sigma}{\epsilon} \Rightarrow \sigma_0 = \frac{\epsilon}{4\pi\lambda_{DH}}\phi_0 \ ,$$

where $\hat{\mathbf{n}}$ is the *outward* normal to the surface.

It is important to note here that the charge density depends on the screening length in solution. This is a characteristic feature of this problem. In Debye-Hückel theory there is a linear relationship between the induced charge and $\phi_0$, while in the more general case the relationship is non-linear, which leads to more interesting problems like Manning condensation (Manning, 1969).

Once we have the potential everywhere and the charge on the surface we should be able to find the (free) energy of the system. Observe that $\nabla^2\phi - \lambda_{DH}^{-2}\phi = 0$ is the Euler-Lagrange equation for the functional

$$\tilde{\mathcal{F}} = \frac{\epsilon}{4\pi}\int d^3r \left[\frac{1}{2}(\boldsymbol{\nabla}\phi)^2 + \frac{1}{2}\lambda_{DH}^{-2}\phi^2\right]$$

where we employ the general Euler-Lagrange formula

$$\frac{\delta\tilde{\mathcal{F}}}{\delta\phi} = -\frac{\partial}{\partial x}\frac{\partial(\cdots)}{\partial\phi_x} + \frac{\partial(\cdots)}{\partial\phi} \ ,$$

where $(\cdots)$ is the integrand of the functional. We recognize the first term as the electrostatic energy density $\epsilon\mathbf{E}^2/8\pi$. The second is the weak-field approximation of an entropic contribution.

Now, here's the crucial point. If we take the original free energy and integrate by parts the term involving $(\nabla\phi)^2$, we obtain a surface term and a new bulk contributiion (that is, using Green's first identity),

$$\tilde{\mathcal{F}} = \frac{\epsilon}{8\pi}\int_S dS\phi\hat{\mathbf{n}}' \cdot \boldsymbol{\nabla}\phi - \frac{\epsilon}{8\pi}\int d^3r\phi\left(\nabla^2\phi - \lambda_{DH}^{-2}\phi\right) ,$$

where $\sigma$ is the surface charge and here $\hat{\mathbf{n}}'$ is the surface normal pointing *out* of the volume containing the ionic medium, and hence *into* the surface. Noting that the the bulk term vanishes by the DH equation, we are left only with the surface term. Re-expressed in terms of the outward normal of the surface we can rewrite the energy in terms of the surface charge density $\sigma$ as

$$\tilde{\mathcal{F}} = \frac{1}{2}\int_S dS\sigma\phi \ .$$

This is the appropriate energy for a system in which the surface charge is specified.

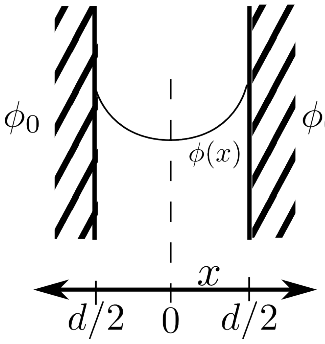
For situations with fixed surface potential rather than fixed charge, the surface free energy must be Legendre transformed, which is equivalent to accounting for the work done against the battery that held the potential fixed. This new free energy F is

$$\mathcal{F} = \tilde{\mathcal{F}} - \int_S dS\sigma\phi = -\frac{1}{2}\int_S dS\sigma\phi \quad \text{or} \quad -\int_S dS \int^{\phi_0} \sigma(\phi')d\phi' \ ,$$

the latter relation holding in the more general case of a nonlinear relationship between charge and potential.

### 2.3.1 Interaction between surfaces

Now we move on to calculate the interaction of two surfaces, noting some distinctions between the cases of fixed potential and fixed charge. For two surfaces held at the same potential $\phi_0$, located at $x = \pm d/2$ (see figure),



the potential is the symmetric combination of the fundamental exponential solutions found previously,

$$\phi = \phi_0 \frac{\cosh(x/\lambda)}{\cosh(d/2\lambda)} \ ,$$

where the denominator is chosen to enforce the boundary conditions, and we write $\lambda$ for the DH screening length. Using this we find the charge density at the plate at $z = d/2$. Here, $-\hat{\mathbf{n}} \cdot \boldsymbol{\nabla} = d/dz$, so

$$\sigma(d/2) = \frac{\epsilon\phi_0}{4\pi\lambda} \tanh(d/2\lambda) \ .$$

At the left-hand surface we have $-\hat{\mathbf{n}} \cdot \boldsymbol{\nabla} = -d/dz$, but with $\sinh(-d/2\lambda) = -\sinh(d/2\lambda)$ the charge density is the same. As the charge and potential do not vary with position over these flat surfaces the surface integration will just give a factor of the surface area $A$. Normalizing by the area of the *two* surfaces the free energy is

$$\frac{\mathcal{F}(d)}{2A} = -\frac{1}{4}\sigma\phi_0 = -\frac{\epsilon\phi_0^2}{8\pi\lambda} \tanh(d/2\lambda)$$

The interesting quantity is the difference between this and the energy at infinite separation,

$$\frac{\mathcal{F}(d)-\mathcal{F}(\infty)}{2A}=\frac{\epsilon\phi_0^2}{8\pi\lambda}\left[1-\tanh\left(\frac{d}{2\lambda}\right)\right]$$

At large arguments tanh approaches unity from below, so this is clearly a repulsion, as expected. In detail, if $d/\lambda \gg 1$ we note that $\tanh(z)\simeq 1-2\mathrm{e}^{-2z}+\cdots$, so

$$\frac{\Delta\mathcal{F}(d)}{2A}\simeq\frac{\epsilon\phi_0^2}{4\pi\lambda}\mathrm{e}^{-d/\lambda}\ ,$$

so the repulsive free energy has the same exponential decay as the electrostatic potential. The second point of interest is that the potential is bounded as $d\to 0$, as the induced charge density decreases monotonically.

Now we consider the case of two surfaces with fixed charge density $\sigma_0$. Since we require that the derivative of the potential be a given value on the surface it is easy to see that the required potential has a normalizing denominator that is the derivative of the numerator,

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

The potential at the surface is

$$\phi(d/2)=\frac{4\pi\lambda\sigma_0}{\epsilon}\coth(d/2\lambda)\ ,$$

and finally the interaction energy per unit area is

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

The function coth approaches its asymptote from above, so we again have a repulsive interaction, but this time there is a divergence at short distances due to the condition that the charge density is fixed.

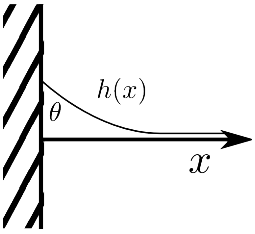
To put the scale of energies involved in perspective, we examine typical values of the charge density. A typical lipid has a cross sectional area of about $50-100\ \mathring{A}^2$. If each head group holds a single charge, and the Debye-Hückel length $\lambda_{DH}$ is about 1 nm, then the typical energy is:

$$\frac{\tilde{\mathcal{F}}}{A}\sim 50\frac{\mathrm{erg}}{\mathrm{cm}^2}$$

Remembering that the surface tension of water is about 80 $\mathrm{erg/cm}^2$ we see that these electrostatic effects can be large.

### 2.3.2 An aside on quadratic energy functionals

We will see a number of situations in which quadratic energy functionals show up in soft and biological systems, so it is worthwhile to remind ourselves of other places they occur. A good example is found in the computation of the shape of a liquid meniscus that meets a solid wall at some contact angle $\theta$ (figure below). The shape of the meniscus is a compromise between the effects of surface tension and gravity.



We assume that this three-dimensional system has translational invariance in the direction normal to the page, and formulate the energy per unit length in that orthogonal direction,

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

where $\sigma$ is the surface tension and $\delta\rho$ is the density difference between the fluid below the meniscus and above. The first term represents the arclength of the curve $h(x)$, while the second is the gravitational potential energy of the meniscus relative to $h = 0$. It is quadratic because it accounts for the potential energy in the infinitesimal *columns* of fluid of height $h$, rather than the linear-in-$h$ form for a point mass in a gravitational field.

As usual, the pedagogically interesting limiting case is the one in which the local slope of the interface is small, so we expand the square root assuming $|h_x(x)| \ll 1$, with $\sqrt{1 + h_x^2} \simeq 1 + (1/2)h_x^2 + \ldots$ and consider the difference in energy $\Delta E = E(h) - E(0)$ between that for a given function $h(x)$ and the flat state,

$$\frac{\Delta E}{L} \approx \frac{1}{2} \int_0^\infty dx \left[ \frac{1}{2} \sigma h_x^2 + \Delta\rho g h^2 \right] .$$

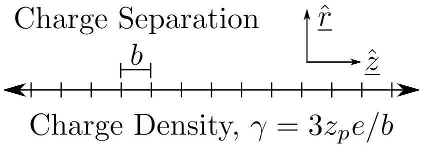
Again we will find that there is a characteristic length scale in the system, which is the capillary length $l_c$,

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

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

### 2.3.3 Long, linear, charged objects (e.g. DNA)

We will present a very brief discussion of the unusual statistical physics associated with charged linear objects, such as DNA. now try to merge the two concepts, surface tension and wetting on the one hand, and electrostatics on the other. We will investigate this by considering a flexible, charged object like DNA or a biological membrane. In equilibrium this object is flat, however, here we will try to see what happens when we are bending it.



Let us imagine there is a linear object of uniform charge density $\gamma$ (Manning, 1969):

$$\gamma = \frac{z_p e}{b}$$

where $z_p$ is the valence, $e$ is the charge of an electron, and $b$ the typical charge spacing. In cylindrical coordinates, the energy of a test charge of valence $z_i$ is

$$U_{ip} = -z_i e \frac{2\gamma}{\epsilon} \ln(r) \ .$$

If we assume a probability density that is based on this electrostatic energy we find the power-law form

$$e^{-\beta U_{ip}(r)} = \exp(2z_i z_p e^2/\epsilon b k_B T) = r^{2z_i z_p \lambda_B/b}$$

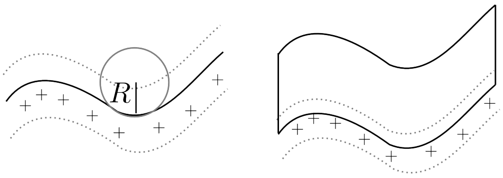
where $\lambda_B$ is the Bjerrum length we previously introduced. If we try to normalize this charge density we are confronted with an integral of the form

$$\int 2\pi dr e^{-\beta U_{ip}(r)} \sim \int dr r^{1+2z_i z_p \lambda_B/b}$$

If the test charge is a counterion ($z_i z_p < 0$) and $\lambda_B/b \geq |z_i z_p|^{-1}$ then the normalization will fail at the origin. This is the origin of what is known as *Manning condensation*, where counter-ions collapse to the linear polymer (Manning, 1969), canceling the bare charge and reducing $\gamma$ to the point of convergence.

## 2.4 Geometrical aspects of screened electrostatics

The problem now is to quantify the contribution of charges to the stiffness of an object. Here, we will use various methods to solve this problem within an approximation that takes advantage of a small parameter. We have already identified the screening length $\lambda$ which characterizes the width of the electric double layer. This can be compared to the radius of curvature $R$ of a bent object, whether a filament or a membrane. In most situations the bending radius is much larger than $\lambda$, so that $\lambda/R \ll 1$ serves as a dimensionless small parameter.



Our calculations will be based on the membrane problem, and we recall that at every point of a surface there are two principal radii $R_1$ and $R_2$ and from these we can construct two geometric quantities. One is the *mean curvature* $H = (1/2)(1/R_1 + 1/R_2)$ and the second is the *Gaussian curvature* $K = 1/(R_1 R_2)$. With the help of these curvatures we can now write down the energy function of a membrane, which is a quadratic form

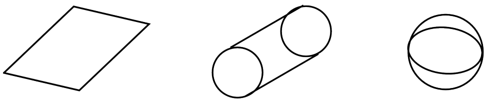
$$\varepsilon = \int dS \left[ \frac{1}{2} k_c (H - H_0)^2 + \frac{1}{2} \bar{k}_c K \right] .$$

This was introduced by Helfrich and others for a non-stretching, bending membrane. There are two elastic constants that describe the energy cost to produce bends. The quantity $H_0$ is known as the *spontaneous curvature* and represents the possibility of a preferred curvature in the ground state. It is often a constant, but can vary from place to place if the membrane composition is spatially variable, for instance.

Our goal is to find the electrostatic contributions to the elastic constants and the spontaneous curvature. This can be done three ways.

1. Dating back to work by Winterhalter and Helfrich (Winterhalter and Helfrich, 1988) and others, we can compare the energy of different simple geometries where the various curvatures are constant. For the 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. Use a variant of *multiple scattering theory.* This is very complicated and not covered in this course, but it is described in the references.

We will now start with the geometric comparison method and consider the geometries described above.



$R_1 = R_2 = \infty$ $\quad$ $R_1 = R, R_2 = \infty$ $\quad$ $R_1 = R_2 = R$

To simplify notation we use $\kappa = 1/\lambda_{DH}$. Since we already solved the electrostatic problem for a plane, we next consider the cylinder. We wish to solve the modified Helmholtz equation,

$$(\nabla^2 - \lambda_{DH}^{-2})\phi = 0 \ ,$$

with the radial part of the Laplacian

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

Rearranging, we obtain

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

As this is homogeneous in powers of $r$ the solution is only a function of $\kappa r$. The two solutions to this are $K_0(\kappa r)$ for the outer problem (decaying at infinity) and $I_0(\kappa r)$ for the inner problem (well-behaved at the origin). These are *modified Bessel functions*

In the case of a fixed charge, the inner problem has a solution of the form

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

and the free energy will involve a ratio of the form

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

This is very naturally set up for an expansion in inverse powers of $\kappa R$, using the asymptotic results

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

where $\mu = 4\nu^2$. We see that the prefactors in front of the large brackets cancel in the ratio $I_0/I_1$, leaving the desired expansion.

We leave it to the student to complete the calculation given in the examples sheet.

Next, we sketch the basic features of a perturbative approach to finding the energetics of electric double layers near a non-flat boundary. In the simplest case we imagine a surface that has some non-trivial height function $h(x)$ in one direction only, and the surface is held at a fixed potential $\phi_0$. That is

$$\phi(x, h(x)) = \phi_0.$$

The mathematical problem is centered around the fact that in general we do not know the Green's function of the modified Helmholtz operator for the domain bounded by some arbitrary height function $h(x)$. But, we can perturbatively connect the solutions at finite $h(x)$ to those at $h = 0$, where we know the solution.

Hence, we introduce a dimensionless small parameter $\epsilon$ as a counting device. The boundary condition can then be expanded as

$$\phi(x, \epsilon h(x)) \simeq \phi(x, 0) + \epsilon\phi_y(x, 0) + \frac{1}{2}\epsilon^2\phi_{yy}(x, 0) + ...$$

where the subscript denotes a partial derivative with respect to $y$, $\phi_y = \partial\phi/\partial y$.

Now, we expect that the solution itself (in the bulk) also has an expansion in powers of $\epsilon$,

$$\phi(x, y)) \simeq \phi^{(0)}(x, y) + \epsilon\phi^{(1)}(x, y) + \epsilon^2\phi(2)(x, y) + \cdots \ .$$

The governing equation does not depend on $\epsilon$, so at every order we will have

$$(\partial_{xx} + \partial_{yy} - \kappa^2)\phi^{(n)}(x, y) = 0 \ .$$

Merging the expansion of the boundary condition with the expansion of the solution we arrive at a sequence of boundary conditions for each order of solution. Up to second order in $\epsilon$ we have

$$\begin{aligned}\phi_0 = \phi^{(0)}(x, 0)) + \epsilon\phi^{(1)}(x, 0) + \epsilon^2\phi(2)(x, 0) + \cdots \\ +\epsilon h(x)\left[\phi_y^{(0)}(x, 0)) + \epsilon\phi_y^{(1)}(x, 0) + \cdots\right] \\ +\frac{1}{2}\epsilon^2 h^2(x)\left[\phi_{yy}^{(0)}(x, 0)) + \cdots\right] + \cdots\end{aligned}$$

At order $\epsilon^0$ we simply recover the boundary condition at a flat surface:

$$\mathcal{O}(\epsilon^0): \qquad \phi^{(0)}(x, 0) = \phi_0 \ ,$$

and we can immediately write down the solution for all $(x, y)$ as

$$\phi^{(0)}(x, y) = \phi_0 \mathrm{e}^{-\kappa y} \ .$$

At the next order we find the boundary condition

$$O(\epsilon^1): \qquad \phi^{(1)}(x, 0) = -h(x)\phi_y^{(0)}(x, 0) = \kappa h(x)\phi_0 \ .$$

Thus, the problem with a boundary condition on a curved surface has become one with a flat boundary but an inhomogeneous potential. At quadratic order we have a similar kind of result,

$$O(\epsilon^2): \qquad \phi^{(2)}(x, 0) = -\frac{1}{2}h^2(x)\phi_{yy}^{(0)}(x, 0) - h(x)\phi_y^{(1)}(x, 0) \ .$$

A convenient way to solve these boundary-value problems is to work in Fourier space. Let us define

$$\hat{\phi}^{(m)}(k, y) = \int dx \mathrm{e}^{ikx}\phi^{(m)}(x, y) \qquad \text{and} \qquad \hat{h}(q) = \int dx \mathrm{e}^{iqx}h(x) \ .$$

The modified Helmholtz equation $(\partial_{xx} + \partial_{yy} - \kappa^2)\phi = 0$ then becomes

$$\left(\partial_{yy} - \kappa_q^2\right) \hat{\phi}^{(n)}(q,y) = 0 \ , \qquad \text{where} \qquad \kappa_q^2 = \kappa^2 + q^2 \ .$$

This is easily solved, as

$$\hat{\phi}^{(n)}(q,y) = \hat{\phi}^{(n)}(q,0)\mathrm{e}^{-\kappa_q y} \ .$$

Thus, we need to know the Fourier transform of the functions at $y = 0$, but this can be determined directly from the order-by-order boundary conditions. For example, at order $\epsilon^1$ we have

$$\phi^{(1)}(x,0) = \kappa\phi_0 h(x) \ ,$$

so

$$\hat{\phi}^{(1)}(q,0) = \kappa\phi_0\hat{h}(q)$$

This we must do order by order. In addition, depending on the boundary conditions, we may need to expand the surface normal vector,

$$\hat{\mathbf{n}} = -\frac{-h_x\hat{\mathbf{e}}_x + \hat{\mathbf{e}}_y}{\sqrt{1+h_x^2}} \ ,$$

in order to compute the surface charge as

$$\sigma(x) = -\frac{\epsilon}{4\pi}\hat{\mathbf{n}} \cdot \boldsymbol{\nabla}\phi(x, \epsilon h(x)) \ .$$

We leave the details for the problem in the example sheet.

# Fluctuations and Fluctuation-Induced Forces

# 3

## 3.1 Review of Statistical Physics

We will not present a complete review of classical statistical physics, but instead will simply highlight a few key points relevant to the applications in this course. The fundamental relation is that 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

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

where the index $i$ runs over all possible states of the system. 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 system 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.

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

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

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

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

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

When the configurational energy is qudratic in the generalized coordinate,

$$E = \frac{1}{2} k x^2 \ ,$$

then the theorem of equipartition holds. Observe that

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

. 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

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

Thus, the energy per mode or degree of freedom is

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

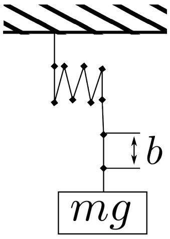
## 3.2 Polymers and Entropic Forces

In this section we will develop basic concepts of polymer physics, with emphasis on the concept of an *entropic spring.* Polymers are defined as long chain molecules with repeating sub-units. Examples include

(1) DNA: A covalently bonded polymer with nucleotide units
(2) Microtubules: Aggregates of protein monomers, held together with electrostatics and van der Waals forces. Due to the weak bonding these polymers fluctuate in length.
(3) Linear/branched: Most proteins are single chains, but molecules with multiple attachments are possible.
(4) Cross-linked networks: interlocked chains of polymers are necessary for many cellular functions.

### 3.2.1 Simplest model of polymers

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 pulled down by gravity.



With a reference point at zero extension, the energy is $E = -mgz$, where the extension $z$ is

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

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

$$Z = \sum_{s_1} ... \sum_{s_2} \exp\left(\beta mgb \sum s_n\right) \ ,$$

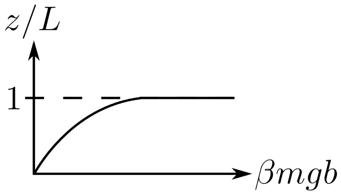
which, by the independence of the $s_n$, can be simplified to

$$Z = \prod_{n=1}^{N} \sum_{s_n=\pm 1} \mathrm{e}^{\beta mgbs_n} = [2\cosh(\beta mgb)]^N \ .$$

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

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

where $L$ is the fully-extended polymer length.



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

$$\langle z \rangle = \frac{Nb^2}{k_B T} F + \dots \ .$$

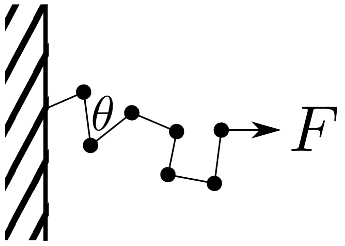
This is nothing but a Hookean spring relationship (force proportional to extnesion), with a spring constant.

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

This result is especially interesting because the restoring force stems entirely from entropy. Work is done to reduce the entropy when the chain is extended. For example, at full extension there is only one configuration, so a minimum in entropy.

### 3.2.2 The freely-jointed chain

Now we examine a more realistic model in which every link is freely-jointed. Applying a force F to this look 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

$$\begin{aligned} Z &= \prod_{n=1}^{N} 2\pi \int d\theta_n \sin\theta_n \mathrm{e}^{f\cos\theta_n} \qquad f = \frac{Fb}{k_B T} \\ &= \left[\frac{4\pi\sinh(f)}{f}\right]^N \ . \end{aligned}$$

The average extension follows by differentiation,

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

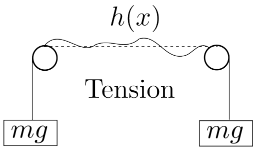
where $\mathcal{L}$ is the Langevin function. The spring constant for this new chain is

$$k = \frac{3k_B T}{Nb^2}$$

which reflects the three degrees of freedom per link.

## 3.3 Fluctuating continuous objects

No we consider how to generalize these kinds of analyses to fluctuating continuous objects such as membranes and biofilaments. of filaments like microtubules or a membrane. A simple place to being is with a 1D string stretched by two hanging masses, and thereby under tension:



The energy of this object, relative to that of a straight string, is the product of the line tension $\gamma$ and the excess arclength,

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

Where $h_x = \partial h / \partial x$. Expanding the squre root under the assumption of a weakly-sloping curve we have

$$\Delta E \sim \frac{\gamma}{2} \int_0^L dx h_x^2 + \dots$$

In this form we can not apply equipartition directly as there are no identifiable independent modes. But, if we note the pinned boundary conditions at $x = 0$ and $x = L$ we can use a Fourier series,

$$h(x) = \sum_{n=1}^{\infty} A_n \sin\left(\frac{n\pi x}{L}\right) .$$

By the orthogonality of the modes, a little algrebra show 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 $A_n$. Note the explicit appearance of the system size $L$. If the string is in thermal equilibrium (e.g. connected to a heat bath), then the probability distribution of the $A_n$ is just a Gaussian, with a mean of

$$\langle A_n \rangle = 0$$

and an energy per mode of

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

The average variance of the string can then be calculated:

$$\begin{aligned} \langle h^2(x) \rangle &= \sum_m^{\infty} \sum_n^{\infty} \langle A_m A_n \rangle \sin\left(\frac{m\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) \\ &= \frac{2 k_B T L}{\gamma \pi^2} \sum_{n=1}^{\infty} \frac{\sin^2 (N\pi x/L)}{n^2} . \end{aligned}$$

As a check, $\gamma$ has units of Energy/Length, so that the sum has units of Length$^2$. Note again the interesting dependence on the system size. The variance is linear in $L$, which should remind you of a random walk.

### 3.3.1 Energy Calculations in Fourier Space

Rather than doing summations over discrete modes, in many cases we would like to consider a system large enough that a continuum of modes is reasonable. To that end, we return to the string energy and write

$$E = \frac{\gamma}{2}\int dx h_x^2 \qquad\qquad h_x = \sum_q e^{-iqx}\hat{h}(q)$$

where $\hat{h}(q)$ is the discrete Fourier transform of $h(x)$. Substituting, we have

$$E = \frac{\gamma}{2}\int dx \sum_q \sum_{q'} (-iq)(-iq')e^{-i(q+q')x}\hat{h}(q)\hat{h}(q') \ .$$

This can be simplified with

$$\int_0^L dx e^{-ipx} = L\delta_{p,0} \rightarrow E = \frac{\gamma L}{2}\sum_q q^2|\hat{h}(q)|^2$$

where $\delta_{p,0}$ s the Kronecker $\delta$.

We are now able to use the equipartition theorem:

$$\left\langle |\hat{h}(q)|^2 \right\rangle = \frac{k_B T}{\gamma L}\frac{1}{q^2}$$

We denote the thermal average by $\langle h^2\rangle$. A second average of interest is the *system average*, denoted by $\overline{\langle h^2\rangle}$,

$$\overline{h^2} = \frac{1}{L}\int_0^L dx h^2 \ .$$

The thermal average fo the system average has a very compact form,

$$\overline{\langle h^2\rangle} = \sum_q \langle |\hat{h}(q)|^2\rangle \ .$$

This is still a discrete sum. In the continuum limit, we use the fundamental relation

$$\frac{1}{L}\sum_q \rightarrow \int dq/2\pi \ ,$$

so

$$\overline{\langle h^2\rangle} = \frac{k_B T}{2\pi\gamma}\int \frac{dq}{q^2} \ .$$

For this and other integrals of this type we may need to introduce integration cutoffs. These usually occur in either of two forms:

(1) Small scale: Molecular lengths $a$ limit small scale fluctuations.

(2) Large scale: Limited system size $L$ prevents long wavelength fluctuations.

Accounting for such cutoffs:

$$\overline{\langle h^2 \rangle} = \frac{k_B T}{2\pi\gamma}\left(\frac{1}{q_{\min}} - \frac{1}{q_{\max}}\right) \qquad q_{\min} = \frac{\pi}{L} \qquad q_{\max} = \frac{\pi}{a} \ .$$

Considering the basic object in the energy, we have

$$\overline{\langle h_x^2 \rangle} \sim \frac{k_B T}{\gamma} \int \frac{dq}{q^2} q^2 \sim \frac{k_B T}{\gamma}(q_{\max} - q_{\min}) \ .$$

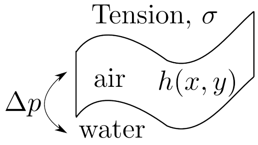
As we let $L \to \infty, q_{min} \to 0$, and $a \to 0, q_{max} \to \infty$, so that

$$\overline{\langle h_x^2 \rangle} \approx \frac{k_B T}{\gamma}\frac{\pi}{a}$$

If we generalize this calculation to $d$ dimensions of space and hence $d-1$ dimensions of the surface we find

$$\begin{aligned}
\langle \overline{h^2} \rangle &\sim \int \frac{d^{d-1}q}{(2\pi)^{d-1}} \frac{k_B T}{\gamma q^2} \sim \frac{k_B T}{\gamma} \int dq \frac{q^{d-2}}{q^2} \\
&\sim \frac{k_B T}{\gamma} \frac{q^{d-3}}{d-3}\bigg|_{\mathrm{q_{min}}}^{\mathrm{q_{max}}} \qquad (d > 3) \\
&\sim \frac{k_B T}{\gamma} \ln\left(\frac{\mathrm{q_{max}}}{\mathrm{q_{min}}}\right) \sim \frac{k_B T}{\gamma} \ln\left(\frac{L}{a}\right) \qquad (d = 3)
\end{aligned}$$

### 3.3.2 Fluctuations of an interface in a gravitational field



Now we consider a two-dimensional interface endowed with surface tension and in a gravitational field, with a density difference $\Delta\rho$ between the fluids on either side. Once again we expand the surface deformation

$$h(\mathbf{r}) = \sum_q \mathrm{e}^{-i\mathbf{q}\cdot\mathbf{r}} \hat{h}(\mathbf{q})$$

The quadratic energy functional is

$$\begin{aligned}
E &= \frac{1}{2}\int\int dxdy \left[\sigma(\nabla h)^2 + \Delta\rho g h^2\right] \\
&= \frac{\sigma A}{2} \sum_{\mathbf{q}} (q^2 + l_c^{-2}) |\hat{h}(\mathbf{q})|^2
\end{aligned}$$

where $l_c$ is once again the capillary length. Again by equipartition we find

$$\langle |\hat{h}(\mathbf{q})|^2 \rangle = \frac{k_B T}{\sigma A} \frac{1}{l_c^{-2} + q^2} \ .$$

This shows that the capillary length provides a cutoff on what would otherwise be divergent fluctuation amplitudes as $q \to 0$.

Introducing both large-scale and small-scale cutoffs, the average variance of the displacement field is

$$\begin{aligned}\overline{\langle h^2 \rangle} =& \frac{k_B T}{2\pi\sigma} \int \frac{q dq}{l_c^{-2} + q^2} \\ & \frac{k_B T}{4\pi\sigma} \ln \left[ \frac{1 + 2\left(\pi l_c / l\right)^2}{1 + 2\left(\pi l_c / L\right)^2} \right]\end{aligned}$$

In the thermodynamic limit ($L \to \infty$), which is now possible at finite $g$,

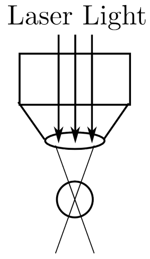
$$\langle \overline{h^2} \rangle \sim \frac{k_B T}{4\pi\sigma} \ln \left[ 1 + 2\left( \frac{\pi l_c}{l} \right)^2 \right]$$

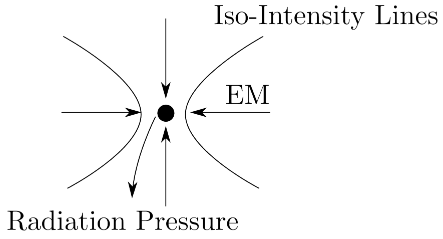
It is clear, with $k_B T \sim 10^{-14}$ erg and $\sigma \sim 50$ erg/cm$^2$ that even if $l_c / l \sim 10^7$ the fluctuations are still on the molecular scale.

## 3.4 Brownian Motion and Diffusion

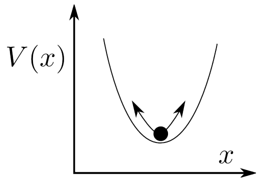
### 3.4.1 Brownian particle in harmonic force field

Brownian motion can be investigated in modern laser trapping systems, first invented in the 1970's at Bell Labs (Ashkin, 1970) The focus beam naturally converges on a small diffraction limited region:





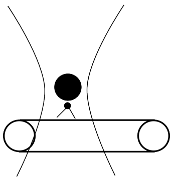
Radiation pressure acts to push the dielectric particle along the optical path, while gradients in the electric field magnitude all point toward the beam waist. If those gradients are sufficiently large there will be a stable trapping potential, which will be harmonic for small displacements. Note that the general result that a dielectric object moves to regions of higher electric field is applicable here as long as one recognizes that the typical microspheres have higher dielectric constants than water *at optical frequencies*, while their DC values are smaller than that of water.



Assuming that the trapping potential is quadratic in lateral displacements $x$, the overdamped equation of motion of a microsphere in the trap is

$$\zeta \dot{x} = -kx + \eta(t) \ ,$$

where $\eta(t)$ is a random force. For $\mu$m sized spheres and moderate lasers, $k \sim 10$ fN/nm, and the relaxation time scale $\tau$ in the well comes from the spring constant and drag coefficient:$\tau = \zeta/k \sim 4$ ms (see below). The scale of the trap stiffness implies that submicron displacements correspond to pN forces. Thus, attaching spheres onto motor proteins allows the stall force (typically several pN) of the motor to be determined from a *force clamp.*



There are two levels at which we can "solve" the Langevin equation. For any particular realization of the random noise $\xi(t)$ we can write down $x(t)$ directly. But we are also interested in *averages over realizations* of the noise, suitable to compare with experimental observations. In the first case, if we rescale the noise term the equation is

$$\dot{x} + \frac{1}{\tau}x = \xi(t)$$

We recognize an integrating factor:

$$e^{t/\tau}\left(\dot{x} + \frac{1}{\tau}x\right) = e^{t/\tau}\xi(t)$$

This allows a direct solution for any particular noise

$$x(t) - x_0 e^{-t/\tau} = \int_0^t dt' e^{-(t-t')/\tau}\xi(t')$$

Now we find averages over realizations of the noise.

$$\langle x(t) - x_0 e^{-t/\tau}\rangle = \int_0^t dt' e^{-(t-t')/\tau}\langle\xi(t')\rangle = 0 \ .$$

Clearly, the average of the noise must vanish for an unbiased system, so we conclude

$$\langle x(t)\rangle = x_0 e^{-t/\tau} \ .$$

Now we consider the square of the deviation from simple relaxation:

$$\langle (x(t) - x_0 e^{-t/\tau})^2\rangle = \int_0^t dt' \int_0^t dt'' e^{-(t-t'')/\tau} e^{-(t-t')/\tau}\langle\xi(t')\xi(t'')\rangle$$

The crucial assumption of the Langevin approach is that the correlation inside the integral is a sharply-peaked function of $|t'-t''|$, decaying much faster than any relevant timescale of the particle. Calling this function $\phi(t'-t'')$, we make the change of variables $(J = 1/2)$

$$s = t' + t'' \qquad\qquad q = t' - t''$$

The right hand side of the previous equation will then be (extending limits to $\pm\infty$)

$$\begin{aligned}&\int_0^t dt' \int_0^t dt'' e^{-(t-t'')/\tau} e^{-(t-t')/\tau} \langle \xi(t')\xi(t'')\rangle \\ &= \frac{1}{2} e^{-2t/\tau} \int_0^{2t} ds e^{s/\tau} \int_{-\infty}^{\infty} dq \phi(q) \ ,\end{aligned}$$

where the final integral is just a number $(\Gamma)$. The average deviation squared is then

$$\langle (x(t) - x_0 e^{-t/\tau})^2 \rangle = \frac{\Gamma\tau}{2}(1 - e^{-2t/\tau})$$

In the long time limit $(t/\tau \to \infty)$

$$\langle (x(t) - x_0 e^{-t/\tau})^2 \rangle = \langle x(t)^2 \rangle = \frac{\Gamma\tau}{2}$$

However, using the equipartition argument

$$\frac{1}{2}k\langle x^2\rangle = \frac{1}{2}k_B T \qquad \Rightarrow \qquad \Gamma = \frac{2k_B T}{\zeta}$$

Logically, we assume that there is a $\delta$ correlation for the noise:

$$\langle \xi(t)\xi(t')\rangle = \frac{2k_B T}{\zeta}\delta(t-t')$$

A further test of the result is to examine the short-time behaviour of the variance in the displacement. If we assume $x_0 = 0$ and $t/\tau \ll 1$, then

$$\langle x^2(t)\rangle \sim \frac{\Gamma\tau}{2}\left(\frac{2t}{\tau} + \ldots\right) \sim \frac{2k_B T}{\zeta} t + \cdots$$

which is just a random walk in 1D ($\langle x^2\rangle = 2Dt$). Thus

$$D = \frac{k_B T}{\zeta}$$

and the Stokes-Einstein relation is recovered. The fun calculation is to do this in the presence of inertia (see examples sheet).

The diffusion coefficient is just the average

$$D = \lim_{t\to\infty} \frac{1}{6t}\langle (\mathbf{r}(t) - \mathbf{r}(0))^2\rangle$$

$$\text{where} \quad \mathbf{r}(t) = \mathbf{r}(0) + \int \mathbf{u}(t')dt'$$

This holds provided that the correlation of velocities ($\langle \mathbf{u}(t') \cdot \mathbf{u}(t'') \rangle$) falls off fast enough. If $\tau$ is the time scale for that decay and $u$ is a typical velocity, then

$$D = \frac{1}{3} \int_0^\infty dt \langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle \sim u^2 \tau$$

We can apply this to the run-and-tumble locomotion of bacteria. For *E. coli* the average velocity is about 20 $\mu$m/s, and the bacteria executes 1s of movement before randomly changing direction. This yields a diffusion coefficient of $4 \times 10^{-6}$cm$^2$/s, which is approximately the diffusion coefficient of a small molecule in water.

## 3.5 Brownian Motion and Polymer Statistics

Consider an arbitrary free polymer with each segment labeled as $\mathbf{r}_n$. Each segment is followed by another random segment of equal length ($|\boldsymbol{\zeta}_n| = b$)

$$\mathbf{r}_{n+1} = \mathbf{r}_n + \boldsymbol{\zeta}_n$$

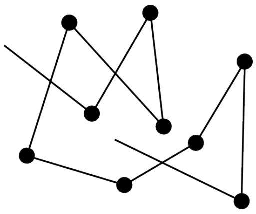
The end-to-end displacement of the polymer is

$$\mathbf{r}_N - \mathbf{r}_0 = \sum_{n=1}^{N} \boldsymbol{\zeta}_n \qquad \langle \mathbf{r}_N - \mathbf{r}_0 \rangle = \sum_{n=1}^{N} \langle \boldsymbol{\zeta}_n \rangle = 0$$

by symmetry. The average of the displacement squared is

$$\langle \mathbf{r}_N - \mathbf{r}_0)^2 \rangle = \sum_{m=1}^{N} \sum_{n=1}^{N} \langle \boldsymbol{\zeta}_m \cdot \boldsymbol{\zeta}_n \rangle = \sum_{m=1}^{N} \sum_{n=1}^{N} \delta_{mn} b^2 = Nb^2$$

The similarity with the Langevin formalism is apparent.



Let us try to formulate the problem more generally. defining the probability that a polymer will have segment positions at $\{\mathbf{r}_k\}$ as

$$p = \frac{1}{Z} G(\{\mathbf{r}_k\}) \qquad G = \mathrm{e}^{-\beta U(\{\mathbf{r}_k\})}$$

Let us suppose that the energy is a sum of near-neighbor interactions plus a contribution from some external potential,

$$U(\{\mathbf{r}_k\}) = \sum_{j=1}^{N} U_j(\mathbf{r}_{j-1}, \mathbf{r}_j) + W(\{\mathbf{r}_k\})$$

When $W = 0$, this is just a random flight model. Either way, this is a local model for the total energy, as it only relies on nearest neighbor interactions. We then introduce

$$\tau_j(\mathbf{R}_j) = \exp[-\beta U_j(\mathbf{R}_j)] \quad \text{where} \quad \mathbf{R}_j = \mathbf{r}_j - \mathbf{r}_{j-1}$$

and we can take it to be normalized ($\int d\mathbf{R}_j \tau(\mathbf{R}_j) = 1$).

We now define the fixed end-to-end-vector partition function as an integral over all degrees of freedom for which the end position is $\mathbf{R}$ (start at origin):

$$G(\mathbf{R}; N) = \int d\{\mathbf{R}_k\} G(\{\mathbf{R}_k\}) \delta(\mathbf{r}_N - \mathbf{R}) = \int d\{\mathbf{R}_k\} \prod_{j=1}^{N} \tau(\mathbf{R}_j) \delta\left(\sum_{j=1}^{N} \mathbf{R}_j - \mathbf{R}\right)$$

We shall see that molecular-level details will be coarse-grained away...

As an example, consider $\tau$ for a fixed-length segment:

$$\tau(\mathbf{R}_j) = \frac{1}{4\pi\ell^2} \delta\left(|\mathbf{R}_j| - \ell\right)$$

Now we use an integral representation of a delta function,

$$\delta\left(\sum_{j=1}^{N} \mathbf{R}_j - \mathbf{R}\right) = \int \frac{d^3k}{(2\pi)^3} \mathrm{e}^{i\mathbf{k}\cdot(\sum \mathbf{R}_j - \mathbf{R})}$$

The distribution function is then

$$G = \int \frac{d^3k}{(2\pi)^3} e^{-i\mathbf{k}\cdot\mathbf{R}} \left[\int d\mathbf{R}_j \tau(\mathbf{R}_j) \exp(i\mathbf{k} \cdot \mathbf{R}_j)\right]^N$$

The bracketed term is a characteristic function $K(\mathbf{k}; N)$, and in this particular case is

$$K(\mathbf{k}; N) = \left(\frac{\sin(k\ell)}{k\ell}\right)^N$$

We expect $N$ to be on the order of $R^2$ if dominated by diffusive behavior, and thus quite large. In the limit of large $N$ (small $k$)

$$K(\mathbf{k}; N) \approx \left(1 - \frac{k^2\ell^2}{6} + \dots\right)^N \sim \exp(-Nk^2\ell^2/6)$$

Inverse Fourier transforming,

$$\begin{aligned} G(\mathbf{R}; N) &= \int \frac{d^3k}{(2\pi)^3} \exp(-i\mathbf{k} \cdot \mathbf{R}) \exp(-N\ell^2k^2/6) \\ &= \left(\frac{3}{2\pi\ell^2 N}\right)^{3/2} \exp\left(\frac{-3R^2}{2N\ell^2}\right) \end{aligned}$$

This Gaussian distributiion is nearly universal - its existence depends primarily on the underlying bond length distribution having a finite second moment, so the central limit theorem holds. In the more general case, the characteristic length $\ell$ derives from the second moment of that distribution.

### 3.5.1 Self-avoidance

We saw previously that the probability distribution of the end-to-end vector $\mathbf{R}$ has the Gaussian form

$$P(R) \sim \mathrm{e}^{-3R^2/2N\ell^2} \ .$$

We are free to interpret the argument of the exponential as the Boltzmann factor of an effective free energy $F(R)$,

$$F(R) = -k_B T \ln P(R) = k_B T \frac{3R^2}{2N\ell^2}$$

which has the form of a (Hookean) entropic spring, with a minimum at $R = 0$. It costs entropy to extend the chain.

Let us now consider how excluded-volume interactions change this free energy. We imagine that there is a pairwise interaction of the form

$$\frac{1}{2} v k_B T \int_0^N dn \int_0^N dm \ \delta(\mathbf{R}_n - \mathbf{R}_m)$$

where we have called the amplitude of the interaction $v k_B T$ for convenience, and abstracted it into a delta function potential.

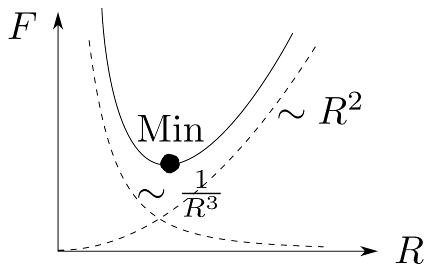
### 3.5.2 Flory Theory

Using the mean-field arguments of van der Waals, we estimate the contribution of these interactions to the free energy as

$$v k_B T \cdot N \cdot \frac{N}{R^3} \sim k_B T \frac{vN^2}{R^3}$$

where the local segment concentration is $N/R^3$ (in three dimensions). The total free energy in this *Flory theory* is thus

$$F_{\text{tot}} = k_B T \left[ \frac{3R^2}{2N\ell^2} + \frac{vN^2}{R^3} \right]$$



We see a competition between entropy, which favours the smallest $R$, and excluded-volume effects that tend to swell the chain. Differentiating to find the optimum, $R^*$, we obtain

$$R^* \sim N^{3/5}$$

Note: $3/5 > 1/2$, so excluded-volume interactions have swollen the chain from its ideal random-walk size.

Generalizing this to $d$-dimensions, the only change is that the local concentration is $N/R^d$, so the balance of terms is

$$\frac{R^2}{N} \sim \frac{N^2}{R^d} \Rightarrow R^{d+2} \sim N^3 \Rightarrow R \sim N^{3/(d+2)}$$

Thus, Flory theory predicts the exponent values

$$R \sim N^{\nu} \qquad \nu = \frac{3}{d+2}$$

This relation is remarkably accurate:

| | | |
|---|---|---|
| $d = 1$ | $R \sim N$ | correct |
| $d = 2$ | $R \sim N^{3/4}$ | exact (solved) |
| $d = 3$ | $R \sim N^{3/5}$ | numerical solution (0.589) |
| $d = 4$ | $R \sim N^{1/2}$ | correct |
| $d > 4$ | $R \sim N^{3/(d+2)}$ | wrong (should be $N^{1/2}$) |

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