### Soft Matter and Biological Physics

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## Preface

How to use this handout:

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 examples sheets are also part of the course, and worked out solutions will be made available towards the end of the course.

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 determine if you are understanding the material.

Don'ts:

- Expect to study only from these notes. You will need the other main 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! 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 and primary literature.

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## Disclaimer

# 1

The topics of soft matter and biological are not like quantum mechanics or thermal and statistical physics. In most respects the latter are complete and done. In our opinion, it is unlikely that both will fundamentally change in the next decades, if ever. The situation is completely different for soft matter and biological physics, which are topics which only in the last two decades became a focus of physics departments around the world. This makes the field exciting to work in but also poses problems for students and for us; there is no single standard textbook that covers all of soft matter and biological physics. Thus we decided to provide some notes in the present form, not to replace a textbook but to help accessing the material of the course.

These are notes for the Part III 'soft and biological physics' course and they are and probably always will 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 fully understand the topics covered in the course. Notes like these can almost never replace a proper textbook (until they become one). This even more so in an advanced course covering 'hot' topics discussed at the moment in the scientific community. This makes it 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 - so this is another, perhaps more painful but also more useful, exercise than you realize during the course.

Please send corrections to Ulrich Keyser (ufk20 (at) cam.ac.uk) or Ray Goldstein (reg53 (at) damtp.cam.ac.uk).

## Introduction

# 2

#### 2.1 Recommended books

Books best suited for introductory reading for the course:

- (1) Biological Physics, P. Nelson, W. H. Freeman (2007)
- (2) Mathematical Biology I. and II., J. D. Murray, Springer (2007, 2008)
- (3) Molecular Driving Forces, K. Dill and S. Bromberg, Garland Science (2009)

And we recommend the following books for advanced and complementary reading

- (1) Soft Condensed Matter Physics in Molecular and Cell Biology, D. Andelman and W. Poon, Taylor and Francis (2006)
- (2) Van der Waals Forces, A. Parsegian, CUP (2005)
- (3) Intermolecular and Surface Force, J. N. Israelachvili, Academic Press (1992)
- (4) The Theory of Polymer Dynamics, M. Doi and S. Edwards, OUP (1986)
- (5) Theory of the Stability of Lyophobic Colloids, E. Verwey and J. Overbeek, Elsevier (1948)

Other interesting books are,

- (1) What is life? (Schrödinger)
- (2) Stochastic Processes
- (3) Mathematical Biology (Murray)
- (4) Molecular Biology of the Cell, Alberts, et al.
- (5) Lectures on the Physiology of Plants, J. Sachs
- (6) for diffusion, random walks, nice introduction: H. C. Berg "Random Walks in Biology"

#### 2.2 Overview of Course

#### 2.2.1 Microscopic Physics

- Inter-molecular attraction (Van der Waals, Lennard Jones potentials, fluctuating dipoles, etc.)
- Charged Particles in Solution (Debye-Huckel theory)

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- Membranes of a cell (deformed, charged sheets of positive ions)
- Bending energy of membranes

#### 2.2.2 Fluctuations and Fluctuation Induced Forces

- Dynamics of polymer chains and DNA (entropic springs)
- Brownian Motion (stochastic differential equations)

#### 2.2.3 Elasticity

• Curve dynamics, elasticity, bending energies, curve shortening, elasticity in higher dimensions (membranes, etc.)

#### 2.2.4 Chemical Kinetics and Pattern Formation

- Simple kinetic models (Michaelis Mentin, etc.)
- Reaction/diffusion equations, slaving, multiple time scales
- Interface dynamics
- Pattern formation in the Fitz-Hugh Nagumo model

#### 2.2.5 Bioconvection

- Gyrotaxis
- bio-convection/diffusion equations
- Instabilities

#### 2.2.6 Electrokinetic phenomena

- Electrophoresis
- Electroosmosis
- Single molecule sensing
- Coupled Poisson-Boltzmann Navier-Stokes equation

#### 2.2.7 Techniques

- Optical tweezers (calibration)
- Atomic force microscopy
- Single particle tracking
- Resistive-pulse sensing

### **Microscopic Physics**

## 3

#### 3.1 Review of Molecular Physics

The ideal gas law, as normally used, is

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

where p is the pressure, V is the volume, T is the (absolute) temperature,  $\rho$  is the density, R is the ideal gas constant, N is the number of molecules, n is the number of moles, and  $k_B$  is Boltzmann's constant. In real gases,  $\rho$  if often not linearly related to the pressure, and if the density is sufficiently low p can be expanded in a so-called 'virial expansion' as

$$\frac{p}{k_B T} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \dots$$

Intuitively, the quadratic term accounts for two-body effects, the third term to triplet effects etc. Measurements of the second virial coefficient  $B_2$  show the following qualitative curve (left):



As  $B_2$  changes sign with temperature it is clearly not simply related to the underlying intermolecular potential u(r) governing the pairwise interaction between particles. The point where  $B_2 = 0$  is known as the Boyle point, after the chemist Robert Boyle.

Initial attempts to understand molecular interactions resulted in a general understanding of the interaction potential (above, right). Van der Waals conceived of a mean field averaging argument in the derivation of his eponymous equation of state. He partitioned the interaction potential into an infinite contribution below a critical radius, responsible for the non-overlapping of the atoms or molecules, and an attractive interaction  $u_{\rm attr}$  beyond

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that. The strength of that attraction is given by the integral

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

Thus, a is a temperature-independent constant characteristic of a given species. In a mean-field calculation in which each of the N particles in a gas sees an average potential whose strength is a, the total attractive energy is

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

The pressure arising from this contribution is

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

Modifying the ideal gas pressure with this contribution leads to the next approximation,

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

Further, Van der Waals realized that the effective volume available to the particles in the gas is reduced from the container volume V by the "excluded volume" arising from the hard core interactions of the particles. If b is the excluded volume per particle (4 times the physical volume of each particle), then:

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

Rearranging, we obtain

$$\frac{Pp}{k_BT} \simeq \rho + (b - \frac{a}{k_BT})\rho^2 + \dots \; .$$

This is the start of a virial expansion and indicates that the second virial coefficient  $B_2(T)$  has the form shown in the figure. It is negative at low temperatures as the attractive interaction dominates, and positive at high temperatures due to volume exclusion.

Another way of viewing this is in terms of the radial distribution function g(r). The RDF is shown below for a semi-realistic (Lennard Jones) gas and for the assumed gas of Van der Waals, in which the RDF is constant beyond the hard-core radius.

**Radial Distribution Function** 



#### 3.2 Quantum-mechanical argument for attraction among neutral molecules

One way to obtain a semi-quantitative understanding of the origin of the attraction between two polarizable (but neutral) molecules is to model each as a pair of charges connected by a simple spring, with the positive charges fixed in place at a separation R (Holstein, 2001).



If we let  $x_1$  and  $x_2$  be the displacements of each of the electrons from its associated nucleus, then the Hamiltonian of the system is

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_0 + \mathcal{H}_1 = \text{Spring Energy} + \text{Coulombic Energy} \\ \mathcal{H}_0 &= \frac{p_1^2}{2m} + \frac{1}{2}m\omega_0^2 x_1^2 + \frac{p_2^2}{2m} + \frac{1}{2}m\omega_0^2 x_2^2 \\ \mathcal{H}_1 &= e^2 \left[ \frac{1}{R} + \frac{1}{R - x_1 + x_2} - \frac{1}{R - x_1} - \frac{1}{R + x_2} \right] \sim -\frac{2e^2 x_1 x_2}{R^3}, \end{aligned}$$

The final approximation, which holds in the interesting limit in which the internal charge separation of each "atom" is small compared to the interatomic spacing, has a bilinear dependence on  $x_1$  and  $x_2$  which is intuitive; if either one is zero the associated atom is neutral and has no Coulombic interaction with the other.

It seems intuitive that given the bilinear form of the perturbation  $\mathcal{H}_1$  some sort of completion-of-squares make sense to simplify the problem, so we consider the coordinate changes

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

Then, the total energy can be rewritten as a sum of two new independent oscillators,

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

The two parenthetical terms define two new frequencies,

$$\omega_{+}^{2} = \omega_{0}^{2} - \frac{2e^{2}}{mR^{3}} \qquad \qquad \omega_{-}^{2} = \omega_{0}^{2} + \frac{2e^{2}}{mR^{3}}$$

,

so we can finally write the energy as

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

Rather than resorting to some complicated second-order perturbation theory in quantum mechanics, we can simply read off the

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change in the ground state energy of the system due to the Coulombic interactions as the change in the zero-point energies of these oscillators. The interaction energy is thus

$$U(r) = \frac{1}{2}\hbar\omega_{+} + \frac{1}{2}\hbar\omega_{-} - 2 \cdot \frac{1}{2}\hbar\omega_{0}$$
$$\approx -\frac{\hbar e^{4}}{2m^{2}\omega_{0}^{2}R^{6}} = -\frac{1}{2}\hbar\omega_{0}\frac{(e^{2}/m\omega_{0}^{2})^{2}}{R^{6}}$$

where, in writing the final form, we have factored out the characteristic electronic energy  $\hbar\omega_0$ , leaving the remaining terms in a form that highlights the fact that the factor  $e^2/m\omega_0^2$  is a volume. We shall see that this volume is the polarizability of the model atom, indicating that the van der Waals energy arises from fluctuating dipoles in which a fluctuation within one atom sets up an electric field (falling off as  $R^{-3}$  which polarizes the second. To see this, we recall the relation between the dipole moment **d** induced by an electric field **E** acting on a polarizable atom,

#### $\mathbf{d} = \alpha \mathbf{E}$ .

Since the dimensions of a dipole moment **d** are  $Q \cdot L$ , and those of an electric field are  $Q/L^2$ , indeed the dimensions of  $\alpha$  are  $L^3$ (a volume). To confirm that the volume we obtained above is properly associated with the atomic polarizability, we generalize the Hamiltonian to include an electric field,

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_0 + eE_0 x_1 + eE_0 x_2 \\ &= \frac{1}{2} m \omega_0^2 \left( x_1^2 + \frac{2eE_0 x_1}{m \omega_0^2} \pm \left( \frac{eE_0}{m \omega_0^2} \right)^2 \right) + (1 \leftrightarrow 2) \\ &= \frac{1}{2} m \omega_0^2 z_1^2 + \cdots \\ z_{1,2} &= x_{1,2} + \frac{eE_0}{m \omega_0^2} \;, \end{aligned}$$

where in the second relationship the notation  $\pm$  indicates that one adds and subtracts the given quantity, allowing completion of the square. Ignoring the additive constant we see that the new Hamiltonian corresponds to oscillators with shifted coordinates  $z_{1,2}$ . At equilibrium we should have  $z_{1,2} = 0$ , allowing us to see from the induced dipole moment that the polarizability is indeed

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

The attractive (van der Waals) interaction energy can thus be expressed in the very simple form

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

## 3.2.1 Attractive interaction of extended neutral objects

The attraction between two neutral sheets of atoms can be inferred from the calculated scaling through a progression of geometries:

First, let us denote the attraction between two point molecules as

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

Then, the attraction between a neutral atom and a slab is

$$V_{1S}(h) = \int_{h}^{\infty} dz \int_{0}^{2\pi} d\phi \int_{0}^{\infty} r dr \rho V_{11}(\sqrt{z^{2} + r^{2}})$$
$$= -\int_{h}^{\infty} dz \int_{0}^{2\pi} d\phi \int_{0}^{\infty} r dr \rho \frac{C}{(z^{2} + r^{2})^{3}}$$
$$= -\frac{\pi C \rho}{6h^{3}}$$

Finally, extending to two neutral slabs  $(A\rho dz \text{ atoms each per thickness } dz)$ :

$$V_{ss} = A \int_{h}^{\infty} \rho V_{1s}(z) dz \Rightarrow \frac{V_{ss}}{A} = -\frac{A_H}{12\pi} \frac{1}{h^2} \, .$$

where  $A_H$  is the Hamaker constant. In a more general form, allowing for different densities of particles in the two slabs,

$$A_H = \pi^2 \rho_1 \rho_2 C_{12} \sim \pi^2 \hbar \omega (\alpha \rho)^2$$

 $A_H$  scales with  $\pi^2 \hbar \omega (\alpha \rho)^2$ , allowing an estimate of  $5 \times 10^{-20} J$ , 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, permitting relatively long-range forces. This work is related to DLVO theory (Derjagum, London, Verway, Overbeck) (Verwey, 1947), as will be discussed below.

#### 3.2.2 Attraction of Finite Slabs and Spheres

One interesting application of these calculations is to the interaction between two lipid membranes, modeled as polarizable slabs of finite thickness.



Integrating up the pairwise interactions as before one finds, for example, the interaction between two slabs of thickness  $\delta$  spaced a distance d apart

$$V(d) = -\frac{A_H}{48\pi} \left\{ \frac{1}{d^2} + \frac{1}{(d+\delta)^2} - \frac{2}{(d+\delta/2)^2} \right\}$$

At large distances this attraction decays as  $\sim -\delta^2/d^4$ , whereas at short distances it diverges as  $\sim -1/d^2$ . In the question sheet we will look at the sphere-sphere interactions which are extensively discussed in the book by Verwey and Overbeek.

#### 3.2.3 Competition between electrostatic attraction and van der Waals interactions

The total interaction between surfaces is a combination of screened electrostatics and van der Waals interactions. As the electrostatic interactions will be seen below to fall off exponentially, the van der Waals forces are more important at both very short and very long ranges. However, for intermediate r, the electrostatic contribution can be important.



We start with the electrostatic interaction between two point charges of magnitude e in vacuum,

$$\varepsilon = e\phi(r) = \frac{e^2}{r}$$

If we measure r in  $\mathring{A}$  the ratio of electrostatic to thermal energy is

$$\frac{\varepsilon}{k_B T} = \frac{(4.8 \times 10^{-10})^2}{4 \times 10^{-14} \cdot r \cdot 10^{-8} \text{cm}} = \frac{580}{r [\text{\AA}]}$$

This seems absurdly large, suggesting that Coulombic interactions are vastly more important than thermal effects. But of course water has a large dielectric constant (ca. 80), so even without accounting for screening effects the relevant ratio is more on the order of 7/r. This suggests a characteristic length, the "Bjerrum length", which represents the separation at which the electrostatic interaction between two elemental charges is comparable to the thermal energy scale  $k_B T$ ,

$$\ell_B = \frac{e^2}{\epsilon k_B T} \; .$$

At 300K,  $\ell_B$  is about  $7\mathring{A}$ .

#### 3.3 Screening Effect of Water (Debye-Huckel)

Even pure water has small amounts of ionic species  $(H^+/OH^-)$  at equilibrium. These ions will have a screening effect on any interactions, effectively forming a neutralizing layer around any charged species. This interaction can be modeled through the Poisson-Boltzmann equation, named after the two equations on which it is based. The Poisson equation,

$$\nabla^2 \phi = -\frac{4\pi\rho}{\epsilon}$$

relates the electrostatic potential  $\phi$  to the charge density  $\rho$ , where as usual the electric field is  $\mathbf{E} = -\nabla \phi$ . A second relation between  $\rho$  and  $\phi$  is needed to have a closed system, and this is the Boltzmann distribution for the concentration c of charges,

$$c_s = c_{s,0} e^{-z_s e\phi/k_B T} \, .$$

where  $c_{s,0}$  is the background concentration of charges of species s, with valence  $z_s$ . Combining these two equations into one self consistent equation (and defining  $\beta = 1/k_B T$ ) we obtain

$$abla^2 \phi = -\frac{4\pi}{\epsilon} \sum_s z_s e c_{s,0} e^{-\beta z_s e \phi} \, ,$$

the general form of the Poisson-Boltzmann (PB) equation.

If we consider the specific case of a z : z electrolyte (1:1, NaCl, 2:2, CuSO<sub>4</sub> etc.), we can write this in the compact form

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

In the weak field limit,  $\beta ze\phi \ll 1$ , we can linearize the PB equation (using  $\sinh(x) \simeq x + \cdots$ ) to obtain the Debye-Hückel (DH) equation,

$$\nabla^2 \phi \simeq \frac{8\pi z^2 e^2 c_0}{\epsilon k_B T} \phi \ .$$

From dimensional arguments it is thus clear that there is a characteristic length, the Debye-Huckel length  $\lambda_{DH}$ ,

$$\lambda_{DH}^2 = \frac{\epsilon k_B T}{8\pi z^2 e^2 C_0} \sim \frac{10nm}{z^2 c_0 [mM]} \; ,$$

where we have used typical material constants, and expressed  $c_0$  in mM. The DH equation then takes the form of a modified Helmholtz equation,

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

In one dimension this becomes

$$\left(\frac{d^2}{\partial x^2} - \frac{1}{\lambda_{DH}^2}\right)\phi = 0 ,$$

whose general solution is

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

This provides the basis for the linearized interaction between surfaces, provided we implement the proper boundary conditions to obtain the amplitudes A and B.

If we consider a single surface, away from which the field must decay to zero at infinity, we set A = 0 and  $B = \phi_0$ , the surface potential, so

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

We are now interested in finding the charge density on the surface if we fix the the potential at  $\phi_0$ . From electrostatics we know that the normal component of the electric field is related to the charge density and the dielectric constant via

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

It is important to note here that the charge density depends on the potential. Within DH theory the relationship between the  $\sigma_0$ and  $\phi_0$  is linear, which is a direct consequence of the linearization of the PB equation. In a more general case the relationship is of course non-linear, which leads to more interesting problems like Manning condensation (Manning, 1969). As a general statement we see that next to the surface there is an excess of counterions (oppositely charged from the surface) which accumulate within the screening layer. The charged surface and the charged layer of counter ions together are referred to as the double layer.

We now turn to a calculation of the free energy of this configuration. First observe that the DH equation  $\nabla^2 \phi - \lambda_{DH}^{-2} \phi = 0$  is the Euler-Lagrange equation for the functional

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

where we have used the general Euler-Lagrange formula

$$rac{\delta \mathcal{F}}{\delta \phi} = -rac{\partial}{\partial x} rac{\partial \mathcal{L}}{\partial \phi_x} + rac{\partial \mathcal{L}}{\partial \phi} \; ,$$

where  $\mathcal{L}$  is the integrand of  $\mathcal{F}$ . Thus, we see that the DH free energy is the sum of the contributions of the electrical energy (with energy density  $\epsilon \mathbf{E}^2/8\pi$ ) and an entropic contribution. If we integrate by parts the gradient-squared term above we obtain

$$\mathcal{F} = \frac{\epsilon}{8\pi} \int_{S} \phi \hat{\mathbf{n}} \cdot \boldsymbol{\nabla} \phi - \frac{\epsilon}{8\pi} \int \phi \left( \nabla^{2} \phi - \frac{1}{\lambda_{DH}^{2}} \phi \right) \;,$$

where S is the surface of the domain under consideration. The integral term above vanishes by the DH equation, leaving  $\mathcal{F}$  expressibly completely as an integral over the surfaces bounding the domain. Recognizing the expression for the surface charge above, we finally obtain

$$\mathcal{F} = -\frac{1}{2} \int_{S} \sigma \phi dS$$

. In the more general nonlinear case, this expression is replaced by a charging integral

$$\mathcal{F} = -\int_{S} dS \int_{0}^{\phi_{0}} \sigma(\phi') d\phi'$$

For situations with fixed charge rather than fixed potential, we Legendre transform the free energy to obtain

$$\tilde{\mathcal{F}} = \mathcal{F} + \int dS\sigma\phi = \frac{1}{2}\int dS\sigma\phi \text{ or } \int_{S} dS \int_{0}^{\sigma_{0}} \phi(\sigma')d\sigma' .$$

If we apply these ideas to a single surface at fixed surface charge we find the free energy per unit area of

$$\frac{\mathcal{F}}{A} = \frac{2\pi\lambda_{DH}\sigma_0^2}{\epsilon}$$

#### 3.3.1 Potential Between Two Surfaces

We now move on to study the interaction of two surfaces bounding a domain with screening charges. As we will see, there is an interesting distinction in this problem for surfaces with fixed charge or fixed potentials. Consider two surfaces located at  $\pm d/2$ , and solve the DH equation in between assuming fixed potentials.



By symmetry and inspection the (symmetric) potential distribution is

$$\phi = \phi_0 \frac{\cosh(x/\lambda_{DH})}{\cosh(d/2\lambda_{DH})}$$

The charge density at one surface follows as

$$\sigma(d/2) = \frac{\varepsilon}{4\pi} \frac{\phi_0}{\lambda_{DH}} \tanh(d/2\lambda_{DH}) ,$$

which properly tends to the previously-established value as  $d \rightarrow \infty$ . Finally we calculate the free energy,

$$\frac{F}{2A} = -\frac{1}{2} \int dS \sigma \phi = -\frac{\varepsilon \phi^2}{8\pi \lambda_{DH}} \tanh(d/2\lambda_{DH})$$

If we subtract from this energy the value as  $d \to \infty$  we obtain the interaction energy

$$\frac{\Delta calF}{2A} = \frac{\epsilon \phi^2}{8\pi \lambda_{DH}} \left[1 - \tanh(d/2\lambda_{DH})\right] \; .$$

This is a repulsive interaction energy tending to a constant at short distances (so the force vanishes in that limit) and, when  $d/\lambda_D H \gg 1$  following an exponential form (note  $\tanh(x) \simeq 1 - 2e^{-2x} + \cdots$ ),

$$\frac{\Delta F}{2A} \simeq \frac{\epsilon \phi^2}{4\pi \lambda_{DH}} e^{-d/\lambda_{DH}} \ .$$

#### 3.3.2 Fixed charge

As shown before, there will be an exponentially decaying potential

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

The charge at the surface can then be calculated

$$\frac{4\pi\sigma_0}{\varepsilon} = \frac{\phi_0}{\lambda_{DH}} \Rightarrow \phi_0 = \frac{4\pi\lambda_{DH}\sigma_0}{\varepsilon} \qquad \phi = \frac{4\pi\lambda_{DH}\sigma_0}{\varepsilon}e^{-x/\lambda}$$

The energy of interaction between two surfaces of fixed charge is then

$$\frac{\Delta F}{2A} = \frac{2\pi\sigma_0^2\lambda_{DH}}{\varepsilon} \left[\coth(d/2\lambda_{DH}) - 1\right]\sigma_0$$

In contrast to the fixed-potential case, this energy diverges at short distances, and this can be understood as a consequence of forcing those charges together. A typical charge density would be a single elementary charge per  $50\text{\AA}^2$ , which yields a surface energy per unit area of 50 erg/cm<sup>2</sup> (in cgs units). This is a very large energy, comparable to the surface tension of the air-water interface.

#### **3.4** Surface tension and wetting

To continue gaining familiarity with the kinds of quadratic energy functionals that show up frequently in soft matter and biological physics we turn to the problem of understanding the shape of a meniscus formed when a liquid is in contact with a wall. The equilibrium shape will be a compromise between the (usually favorable) interactions with the wall, which causes the fluid to rise to form a contact angle, and gravity, which acts to keep the surface flag.



Referencing the figure, in which the meniscus has height h(x), we assume that the three-dimensional is invariant along the direction perpendicular to the plane of the paper. The energy per unit length in that direction is

$$\frac{E}{L} = \int_0^L dx \left[ \gamma \sqrt{1 + h_x^2} + \frac{1}{2} \Delta \rho g h^2 \right]$$

where  $\gamma$  is the surface tension,  $\Delta \rho$  is the density difference between the fluid and the vapor above it, and g is the acceleration of gravity. We adopt the notation  $h_x \equiv \partial h/\partial x$ . The first term represents the extra arclength of the curve h(x) and we note that the second term has the quadratic form due to the fact that we are counting the energy in infinitesimal *columns* of fluid of height h(x).

Pedagogically we focus on the case of a gently tilted interface, with  $|h_x| \ll 1$  and expand the square root as  $\sqrt{1+h_x^2} = 1 + (1/2)h_x^2 + \ldots$  to obtain for the energy difference from the flat state

$$\frac{E[h]-E_0}{L}\approx \int_0^L dx \left[\frac{1}{2}\gamma h_x^2+\frac{1}{2}\Delta\rho g h^2\right] \ , \label{eq:E-E-field}$$

a form that is just like the Debye-Hückel energy in the electrostatic problem considered earlier. Again we will find that there is a characteristic length scale in the system, termed the capillary length  $l_c$ 

$$l_c = \sqrt{\frac{\gamma}{\Delta \rho g}}$$

which, for water/air, is about  $3\text{mm}(\sqrt{100/1/1000})$ . For a full analysis of the system we must account the interaction between the liquid and the surface and enforce the specific contact angle. A full description of wetting angles etc. can be found in the notes of the Part II Soft Matter Physics course (?).

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

Here we make some comments about the phenomenon of Manning condensation (Manning, 1969), an important feature of the energetics of long polyelectrolytes.

Charge Separation 
$$\hat{\underline{r}}$$
  
 $\underline{b}$   
 $\underline{\hat{z}}$   
Charge Density,  $\gamma = 3z_p e/b$ 

Consider a line of even charges separated by b as depicted in the figure, with a linear charge density

$$\lambda = \frac{z_p \epsilon}{b}$$

where  $z_p$  is the valence and e is the charge of an electron. In 2D 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 (concentration) based on this energy we obtain

$$e^{-\beta U_{ip}(r)} = r^{2z_i z_p l_B/b}$$

where  $l_B$  is the Bjerrum length. The integral of this probability density is then:

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

If the test charge is a counterion  $(z_i z_p < 0)$  and  $l_B/b \ge |z_i z_p|^{-1}$ the normalization will fail at the origin. This is accounted for with Manning condensation (counter-ion collapse or condensation) (Manning, 1969) which cancels the bare charges, reducing  $\gamma$  to the point of convergence.

## 3.6 Geometrical aspects of screened electrostatic interraction

We turn now to the quantification of the charges on an object such as a membrane to its stiffness or bending rigidity. Here, we will discuss two methods to find a solution to this problem. In each it is necessary to work in a regime in which there is a small parameter to organize the calculation. As we have already established the existence of the screning length  $\lambda$  we require a second length, and this is provided by the radius of curvature R of the surface, or more generally by  $R_1$  and  $R_2$  the two principal radii of a general surface at a given point. The regime of interest is then  $\lambda/R \ll 1$ , where the screening charges are confined to a region close to the surface on the scale of the local inscribed circle(s) that define the curvatures. Is this a realistic assumption for biological systems? Cells live on length scales of many microns, artificial vesicles as well, while the Debye-screening length is on the range of nm in realistic conditions, so indeed our assumption that  $\lambda/R \ll 1$  is valid. 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.

We will start by evaluating a situation where a charged membrane has a certain curvature. For a surface there are obviously two principle radii  $R_1$  and  $R_2$  associated with any point on the surface. Using  $R_1$  and  $R_2$  we can construct two second order quantities. One of which we call the mean curvature defined as  $H = (1/2)(1/R_1 + 1/R_2)$  and the Gaussian curvature  $K = 1/(R_1R_2)$ . With the help of these curvatures we can now write down the energy function of a membrane proposed and studied separately by Canham and Helfrich, the quadratic form

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

This energy is associated with non-stretching membranes subject only to a bending energy. The elastic constants  $k_c$  and  $\overline{k}_c$  each have units of energy, and are typically some multiple of  $k_BT$ . The "spontaneous curvature"  $H_0$  represents an equilibrium preferred curvature set by asymmetries between the two sides of the membrane.

We see the electrostatic contributions to  $k_c$ ,  $\overline{k}_c$  and  $H_0$ . There are three ways to solve this problem.

- 1. compare the energy of several different membrane geometries in which calculations are straightforward, i.e. where the curvatures are constant, and then deduce the unknown by comparison. For the planar calculation we did earlier we have  $R_1 = R_2 = \infty$ . If we extend this to a cylinder (with  $R_1 = R$  and  $R_2 = \infty$  and a sphere  $R_1 = R_2 = R$  we can complete the calculations.
- 2. construct a perturbation theory around a flat surface. For a slightly deformed flat plane which is bending according to h(x, y) one can calculate the electrostatic energy by an expansion of the solution of the Debye-Hückel problem. We will outline the essential features of this 'boundary perturbation' method.
- 3. a 'multiple scattering method'. This is much more difficult and not covered in the course, but is the most powerful and general. It relies on the use of an integral expression for the Green's function of th DH problem in an arbitrary domain.



#### 3.6.1 Geometric comparison method

We will now start with the geometric comparison method and consider the simple geometries given below



We now solve the modified Helmholtz equation in a cylindrical coordinate system, with only radial dependence to the potential. To simplify notation we use  $\kappa = 1/\lambda$ . The governing equation is

$$\phi'' + \frac{\phi'}{r} - \kappa^2 \phi = 0$$

Multiplying through by  $r^2$  we recognize this as the equation defining the modified Bessel functions  $I_0$  and  $K_0$  this equation is solved by Bessel functions. There are two solutions to this equation, one for field inside the cylinder and one for the outer problem. Demanding that the potential be finite at the origin yields

$$\phi = \phi_0 \frac{I_0(\kappa r)}{I_1(\kappa r)}$$

while the solution for the outer problem (with the potential vanishing at infinity) is given by the Bessel function  $K_0(\kappa r)$ . As before one calculates the energy per unit area of the system as  $(1/2)\sigma\phi$ .

Apart from the cylinder we can find the **Solution for a Plane**, which we already developed in class, and led to

$$\phi = \begin{cases} \phi_0 e^{-(x-a)/\lambda_{DH}} & x > a \\ \phi_0 e^{-(a-x)/\lambda_{DH}} & x < -a \end{cases}$$

For a surface of fixed charge, the potential at the surface will be

$$\phi_0 = \lambda_{DH} \frac{\sigma}{\epsilon}$$

The associated energy, as discussed in class, is determined through the energy necessary to build up the relevant charge

$$E = \int_0^\sigma \phi d\sigma = \int_0^\sigma \lambda_{DH} \frac{\sigma}{\epsilon} e^{-(x-a)/\lambda_{DH}} d\sigma = \frac{\sigma}{2} \phi = \frac{\sigma^2 \lambda_{DH}}{\epsilon}$$

The third simple geometry is the **Solution for a Sphere**. Expanding the Laplacian (for only the radial term, due to symmetry)

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

The general solution is

$$\phi = A \frac{e^{\pm r/\lambda_{DH}}}{r}$$

Since the solution that decays at infinity is desired (outside the sphere), one solution can be eliminated so that

$$\phi = A \frac{e^{-r/\lambda_{DH}}}{r}$$

For a sphere of radius b with fixed potential  $\phi_0$ , this becomes:

$$\phi = \phi_0 b \frac{e^{-(r-b)/\lambda_{DH}}}{r}$$

Inside of the sphere, the potential must be bounded at zero so that the two terms cancel.

$$\phi = \phi_0 \frac{a}{e^{a/\lambda_{DH}} - e^{-a/\lambda_{DH}}} \left( \frac{e^{r/\lambda_{DH}} + e^{-r/\lambda_{DH}}}{r} \right)$$

Simplifying to hyperbolic functions and incorporating solutions for both inside and outside the sphere

$$\phi = \begin{cases} \phi = \phi_0 a \frac{\sinh(r/\lambda_{DH})}{r\cosh(a/\lambda_{DH})} & r < a \\ \phi = \phi_0 b \frac{\exp[-(r-b)/\lambda_{DH}]}{r} & r > b \end{cases}$$

For fixed charge, the potential (taken from Hunter) will be

$$\phi_0 = \frac{\sigma \lambda_{DH}}{\epsilon (1 + \lambda_{DH}/a)}$$

#### 3.7 Solution with perturbation theory

Here we want to look at and understand how perturbation theory can be applied to solve a problem with a field equation of this kind. The surface or membrane of interest is not trivial. This non-trivial shape makes the solution complicated, however with the method discussed in the following we will be able to find a solution. It is interesting to note that this kind of problem is very common and physics and is found both in hard and soft matter physics.

We will now have to solve this respecting the surface boundary condition  $\phi_{surf}$ 

$$\phi_{surf} = \phi_0 = \phi(x, h(x))$$

which means essentially that this is a function of both x and y = h(x). In electrostatics we could use Green's function if the surface would have a simple geometry. However, this is not the case here so we have to find another way. We introduce a counting device  $\epsilon$ , which reflects the fact that h is small. Small in this context means that the curvature is in the range of the screening length i.e.  $\lambda_{DH}/R \approx 1$ . With  $\epsilon$  we can rewrite  $\phi$  as

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

We now use a Taylor expansion which yields

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

where the subscript denotes a partial derivative with respect to  $y \phi_y = \partial \phi / \partial y$ . This is an expansion for the boundary condition at y = 0.

However, We are interested in the two-dimensional case. Assuming that the two-dimensional problem  $\phi(x, y)$  can be written in a similar way, as expansion in  $\epsilon$ ,

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

and remembering that we have the governing equation is

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

The governing equation does not change due to boundary conditions and thus we solve on every order the same equation. This means that

$$\phi_0 = \phi^{(0)}(x,0) + \epsilon \phi^{(1)}(x,0) + \epsilon^2 \phi(2)(x,0) + \dots + \epsilon h(x)(\phi_y^{(0)}(x,0)) + \epsilon \phi_y^{(1)}(x,0) + \dots) + \frac{1}{2} \epsilon^2 h^2(x)(\phi_{yy}^{(0)}(x,0)) + \dots)$$

We can write down the terms now considering the boundary conditions given above and identify the terms with the boundary conditions and write down the solution for different orders of  $\epsilon$ . For the zero order  $\epsilon^0$  this is simple as this should be the same solution as for a flat surface:

$$O(\epsilon^0): \phi^{(0)}(x,0) = \phi_0 \Rightarrow \phi^{(0)}(x,y) = \phi_0 e^{-\kappa y}$$

For the first order  $\epsilon^1$  we get

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

which replaces the problem with a boundary condition on a curved surface with a problem involving a spatially varying potential on a 'flat' surface.

## Fluctuations and Fluctuation-Induced Forces

## 4

#### 4.1 Brownian Motion

The diffusion equation is (Brown, 1828; Einstein and F "urth, 1956):

$$\frac{\partial C}{\partial t} = -\boldsymbol{\nabla} \cdot \mathbf{J} = D\nabla^2 C$$

where  $J = -D\nabla C$  is the flux from Fick's law. To understand the typical values of diffusion coefficients (say, for small molecules in water:  $10^{-5}$  cm<sup>2</sup>/s) we consider a one-dimensional system in which particles diffuse and are acted on by a deterministic force, so

$$J = J_{\text{Diffusive}} + J_{\text{Force}} = -D\frac{dC}{dx} + cv$$

where v is the velocity that results from the balance of the force and viscous drag. Since at small length scales (and thus low Reynolds number), inertia is negligible and those forces balance, we can write

$$\zeta = F = -\frac{d\phi}{dx} \; ,$$

where  $\phi$  is the potential energy from which the force is derived. Thus,

$$J = -D\frac{dC}{dx} - \frac{C}{\zeta}\frac{d\phi}{dx} \; .$$

At equilibrium, where the principles of statistical mechanics hold, the total flux must vanish and we can integrate to obtain

$$C = C_0 e^{-\phi/D\zeta} \sim e^{-E/k_B T} ,$$

where the second relation is just the Boltzmann factor associated with an energy. Thus,

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

which is the celebrated Stokes-Einstein relation. Since the diffusion coefficient can be measured from the Brownian motion of microscopic particles, and the gas constant is known, Einstein showed that such measurements yield a determination of Avogadro's number. This decisive demonstration of the reality of atoms and molecules as discrete entities was one of the main results of Einstein's 1905 paper on Brownian motion (Einstein and F

"urth, 1956). Assuming a spherical particle, with  $\zeta = 6\pi\eta R$  in a fluid of viscosity  $\eta$ , and taking R = 2Å, we obtain  $D \sim 10^{-5} \text{cm}^2/\text{s}$ .

#### 4.2 **Review of Statistical Physics**

We will not give a whole review of classical statistical physics as this would require a full lecture course. However, it will be useful to briefly introduce the main concepts that are relevant for the material discussed in this course. The probability p(E) of finding a system in a state of energy E is given by

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

The factor Z that is needed to normalize this probability is called the partition function,

$$Z = \sum_{i} e^{-\beta E_i}$$

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

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

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

a sum of the values in each state  $A(E_i)$  weighted by the probability of the system being in that state.

Z, the partition function, can be interpreted in various ways. Here, we will often consider Z to be a generating function of averages. For most of the problems we will encounter in this course we will discuss continuous states of energy. One example is a microscopic particle in an optical trap, which can be found at any position in the parabolic potential. For example, in the case of a single particle, the energy is a sum of the kinetic and potential contributions,

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

For an N-particle system we use the notation  $\{p^N\}$  and  $\{q^N\}$  to denote the set of N momenta and positions. The partition function of such a system is then the multiple integral

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

read Einstein's paper

where the integrals run over all possible momenta and positions. The prefactor is a consequence of the assumption of indistinguishable particles and a proper normalization of phase space volumes (the factor involving Planck's constant h).

In this classical picture of course the momentum integral can be done directly, yielding

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

where we define the thermal de Broglie wavelength  $\Lambda$  as

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

Thus h appears only in the prefactor  $\Lambda$  in classical system. Unless we are interested in a few particular quantities like the absolute entry, h will not enter into any of the observables we compute.

The most important result we shall use is the equipartition theorem, which states that each degree of freedom that enters the energy quadratically will have on average the same energy. This is easily seen. Consider a potential energy of the form

$$E = \frac{1}{2}kx^2 \; .$$

The average energy is

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

where the last relationship highlights the use of Z as a generating function. The partition function Z can be simplified by changing variables so as to remove all constants from the exponential (the trick is simply multiplying by 1),

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

 $\ln Z$  then has a simple  $\beta$ -dependence and remaining terms (···) independent of  $\beta$ ,

$$\ln Z = -\frac{\ln \beta}{2} + \cdots \qquad -\frac{\partial \ln Z}{\partial \beta} = \frac{1}{2\beta} = \frac{1}{2}k_BT$$

Thus, the energy per mode or degree of freedom is

$$\left\langle \frac{1}{2}kx^2 \right\rangle = \frac{1}{2}k_BT \; ,$$

which is precisely the equipartition theorem.

#### 4.3 Review of Polymer Physics

In this section we develop the notion of an entropic force by examining the statistical properties of polymers, which act like entropic springs.. This is one of the most important concepts for polymers is directly related to the statistical nature of these objects. Before we start discussing the physics we will introduce a few - well-known - examples for polymers.

Polymers are defined as long chain molecules with repeating (identical) sub-units. A few examples are:

- (1) DNA: Covalently bonded polymer with nucleotide units
- (2) Microtubules: Aggregates of protein monomers, held together with electrostatics and van der Waal forces. Due to the weak bonding these polymers can 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.

An example of a polymer is styrene, with monomers of ethyl benzene. One important degree of freedom of this chain is the freedom of rotation around single bonds, such as C - C bonds in proteins. This introduced (potentially many) additional internal degrees of freedom to the chain. As discussed before, both short and long range interactions are possible. For example, one region might interact with a polymer segement far down the chain, both by electrostatics and by excluded-volume interactions. Local physical and chemical interactions are also very important and determine for example the chain stiffness.

## 4.3.1 Simplest model of polymers: A Chain Units with Discrete Conformations

The simplest model of a polymer is a chain of N links, each with length b, which can point up or down. Let us imagine the chain is stretched by a weight which pulls the chain with force mg, as in the figure.

7777. M mq

The change in energy of a configuration relative to the state with highest energy is directly related to the length z of the chain

$$\Delta E = mgz \qquad \qquad z = \sum_{n=1}^{N} bs_n$$

where  $s_n = \pm 1$ , denotes whether the element *n* is pointing up or down. The partition function is simply a sum over all possibilities of the spin variables  $s_n$ ,

$$Z = \sum_{s_1} \dots \sum_{s_2} \exp\left(\beta bmg \sum s_n\right) \;.$$

Since all the sums are independent of each other

$$Z = [2\cosh(\beta mgb)]^N .$$

Thus, the average extension z is

$$\langle z \rangle = b \langle \sum_{N} s_n \rangle = \frac{-\partial \ln Z}{\partial (\beta m g)} = Nb \tanh(\beta m g b) = L \tanh(\beta m g b) ,$$

where L is the total length of the chain. This defines a forceextension curve z/L vs.  $\beta mbg$  as in the figure.



For a weak gravitational force, the length z can be Taylor expanded to yield

$$z = \frac{Nb^2mg}{k_BT} + \dots \approx \left(\frac{Nb^2}{k_BT}\right)mg$$

This is analogous to a Hookean force F = -kx, with spring constant k. Here we have

$$k = \frac{k_B T}{N b^2}$$

This result is especially interesting because the restoring force stems entirely from entropic forces. 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.

#### 4.3.2 More realistic freely jointed chain

After discussing the easiest chain model we now consider a more realistic one in which every link is free to move in continuously in three dimensions (two angles). Applying a force F to the chain end we have a configuration as in the figure.

For this situation the projected length x and energy E are:

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

The partition function is then

$$Z_N = \prod_n \int d\theta_n \sin \theta_n 2\pi e^{f \cos \theta_n} \qquad f = \frac{Fb}{k_B T}$$
$$= \left[\frac{4\pi \sinh(f)}{f}\right]^N.$$

This can then be used to find the average extension

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

where  $\mathcal{L}$  is known as the Langevin function. The spring constant for this model is easily calculated,

$$k = \frac{3k_BT}{Nb^2}$$

This is intuitively sensible, since there are two more degrees of freedom than in the simple case above. This is exactly analogous to molecular velocity distributions, with each degree of freedom having an energy of  $k_B T/2$ .

These considerations are true as long as we leave the chain freely hinged, meaning that there is no energy associated with bending the chain by an angle. However, for most realistic scenarios, an energy is associated with this and then we will have to develop another description. This will lead to the worm-like chain model.

#### 4.3.3 Fluctuating continuous objects

Our model for the freely hinged chain can be generalized to continuous surfaces. This is relevant for the description of filaments like microtubules or a membrane. We start with a simple 1D string that is stretched by two masses and hence under tension.



The energy of this string, relative to the straight state, is simply the tension multiplied by the extra arclength,

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

Here,  $h_x \equiv \partial h/\partial x$  is the local slopen and  $\gamma$  is the tension. Adopting a 'long-wavelength' approximation we expand the square root and obtain

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

We cannot apply equipartition directly to this integral as the degrees of freedom are not isolated. Instead we decompose the displacement field h(x) into discrete modes. Considering the boundary conditionsh(0) = 0 and h(L) = 0 we use sin-waves for the modes, essentially taking the Fourier sine transform,

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

The energy of the surface is then just a sum over the energy of each constituent mode.

$$\Delta E = \frac{1}{2} \gamma \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} A_n A_m \left(\frac{n\pi}{L}\right) \left(\frac{m\pi}{L}\right) \int_0^L dx \cos\left(\frac{n\pi x}{L}\right) \cos\left(\frac{m\pi x}{L}\right)$$
$$= \frac{1}{2} \gamma \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} A_n A_m \left(\frac{n\pi}{L}\right) \left(\frac{m\pi}{L}\right) \left(\frac{\delta_{mn}L}{2}\right)$$
$$= \frac{\gamma L}{4} \sum_{n=1}^{\infty} \left(\frac{n\pi}{L}\right)^2 A_n^2$$

If the string is in thermal equilibrium (e.g. connected to a heat bath), so the probability distribution of the coefficients  $A_n$  is a Gaussian centered at zero, then we immediately deduce from equipartition that

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

and hence

$$\langle A_n \rangle = 0$$
  
 $\langle A_n^2 \rangle = \frac{2k_B T}{\gamma \pi^2 n^2} L .$ 

The average variance of the string position can then be calculated,

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

On dimensional grounds,  $\gamma$  has units of Energy/Length, so that the sum has units of Length<sup>2</sup>.

#### 4.3.4 Energy Calculations in Fourier Space

Rather than focusing explicitly on the boundary conditions and the modes they determine, we can adopt a more general Fourier space description, eventually passing to a continuous distribution of modes. Starting again from the initial string energy and introducing the Fourier representation of  $h_x$ , we write

$$h(x) = \sum_{q} e^{-iqx} \hat{h}(q)$$

where  $\hat{h}(q)$  is the discrete Fourier transform of h(x). We can then write down the energy as

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

This can be simplified with the help of

$$\int_{0}^{L} dx e^{-ipx} = L\delta_{p,0} \qquad \text{so } \hat{h}(q)\hat{h}(q') = \frac{\gamma L}{2} \sum_{q} q^{2}|\hat{h}(q)|^{2}$$

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 have been using the angular bracket notion  $\langle h^2 \rangle$  to denote as thermal average. It is useful to introduce the concept of a systemaverage, denoted by  $\overline{\cdots}$ , where

$$\overline{\cdots} = \frac{1}{L} \int_0^L dx \cdots$$

One finds easily that the thermal average of the system average is

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

In the continuum limit, we replace the sum by the rule

$$\frac{1}{L}\sum_{q} \to \int \frac{dq}{2\pi}$$

,

which leads to

$$\left<\overline{h^2}\right> = \frac{k_BT}{2\pi\gamma}\int \frac{dq}{q^2}$$

Now we must address the need for cutoffs on this integral. These usually occur in either of two forms:

- (1) Small scale: The continuum theory does not hold below some molecular length a which limit small scale behavior
- (2) Large scale: The system size L prevents fluctuations on arbitrarily large wavelengths

Introducing these cutoffs we have

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

Clearly, we can safely take  $a \to 0$ , but must keep L finite, to obtain a finite result. On the other hand, if we calculate the energy itself we find

$$\Delta E \propto \int h_x^2 \Rightarrow \left\langle \overline{h_x^2} \right\rangle \sim \frac{k_B T}{\gamma} \int \frac{dq}{q^2} q^2 \sim \frac{k_B T}{\gamma} (q_{max} - q_{min})$$

Now there is no problem setting  $L \to \infty$ ,  $q_{min} \to 0$ , but the energy is dominated by the small-scale cutoff a,

$$\Delta E \approx \frac{k_B T}{\gamma} \frac{\pi}{a}$$

#### 4.3.5 Check against physical systems

Since  $k_B T \sim 4 \times 10^{-14} erg$ ,  $\gamma \sim 1 - 100$  erg/cm,  $a \sim 10^{-8}$  cm, the average slope  $\langle \overline{h_x^2} \rangle^{1/2}$  is on the order of  $10^{-3} - 10^{-2}$ , which is quite small indeed.

## 4.3.6 Fluctuations of an interface in a gravitational field

Now we add a gravitational field to the problem and consider a two-dimensional surface.

$$\Delta p \left( \begin{array}{c} \text{Tension, } \sigma \\ \text{air } h(x, y) \\ \text{water} \end{array} \right)$$

The energy is

$$\Delta E = \int \int dx dy \left[ \frac{1}{2} \sigma (\boldsymbol{\nabla} h)^2 + \frac{1}{2} \Delta \rho g h^2 \right] \; .$$

Now we represent h in Fourier space,

$$h(\mathbf{r}) = \sum_{q} e^{-i\mathbf{q}\cdot\mathbf{r}} \hat{h}(\mathbf{q}) \;,$$

and use

$$\int d^2 r e^{i(\mathbf{q}+\mathbf{q}')\cdot\mathbf{r}} = A \delta_{\mathbf{q}+\mathbf{q}',\mathbf{0}} ,$$

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to obtain

$$\Delta E = \frac{\sigma A}{2} \sum_{\underline{q}} (q^2 + l_c^{-2}) |\hat{h}(q)|^2$$

where  $l_c$  is once again the capillary length. The average displacement is then

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

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

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

#### 4.4 Brownian Motion and Diffusion

As discussed earlier, the diffusion equation and Stokes-Einstein relation are

$$C_t = D\nabla^2 C \qquad \qquad D = \frac{k_B T}{\zeta}$$

where  $\zeta$  is the drag coefficient. The diffusion equations suggests the dimensional relationship between time and length  $l \sim \sqrt{Dt}$ . For example, with the diffusion of a small molecules in water  $(D = 10^{-5} cm^2/s, l = 30 \mu m \sqrt{t}$  we expect in one second for molecules to explore a region of size  $30 \mu m$ , which is very much larger than a bacterium and greater even then many eukarytoic cells. This suggests that the concentrations of free molecules inside such cells would rapidly homogenize without additional mechanisms at work (e.g. membrane localization, etc.). On the other hand, for the very largest eukaryotic cells found in aquatic plants, which can be up to 10 cm in length, the diffusive time scales reach to months, and cells require additional active transport mechanisms (e.g. cytoplasmic streaming) in order to survive. comparable to the length of a cell.

#### 4.4.1 Brownian particle in harmonic force field

Brownian motion is now studied routinely using the latest techniques of image acquisition and manipulation, particular that of optical trapping. This method was first invented in the 1970s at Bell Labs (Ashkin, 1970). A laser beam is shined through a high numerical aperture microscope objective to a diffraction-limited spot. For sufficiently tight focus the beam waist acts as a trap in the sense that the are inward forces drawing a dielectric particle to the center of the trap dominate over radiation pressure pushing the particle along the beam path.



The forces acting on a moving particle within the trap are Stokes drag, the restoring force of the trap, and random, fluctuating forces from collisions of water molecules with the particle. Near the trap centre the restoring force is harmonic, and a model equation of motion for the position x of the particle is

$$\zeta \dot{x} = -kx + \xi'(t) \; ,$$

which is known as a Langevin equation.



For  $\mu$ m size spheres and moderate laser power, the spring constant k is typically on the order of 10 fN/nm or 0.01 pN/nm.



Interestingly, the so-called 'stall force' for motor proteins is typically a few pN. This implies that a particle displaced a few hundred nm from the trap centre will experience forces comparable to those of motors. Note from the Langevin equation that there is a characteristic time  $\tau = \zeta/k \sim 4$ ms. This is the relaxation time of the particle moving back towards the trap centre. At the same time, recalling that thermal energy  $k_BT \sim 4pN \cdot nm$ , we see by equipartition that the typical excursion of a particle in a trap will be hundreds of nm.

Let us now try to solve the Langevin equation in the sense of deducing its statistical predictions about the motion of a particle and determining the strength of the noise needed for consistency with statistical mechanics. Dividing through by the drag coefficient  $\zeta$ and rescaling the noise as  $\xi = \xi'/\zeta$  we see observe a convenient

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integrating factor  $e^{t/\tau}$ , which allows a solution to be found,

$$\dot{x} + \frac{1}{\tau}x = \xi(t) \quad (\xi \text{ rescaled})$$
$$e^{t/\tau} \left( \dot{x} + \frac{1}{\tau}x \right) = e^{t/\tau}\xi(t)$$
$$x(t) - x_0 e^{-t/\tau} = \int_0^t dt' e^{-(t-t')/\tau}\xi(t') ,$$

where  $x_0$  is the initial position. Before deducing anything further, we observe from this formula that the relaxation time introduces a memory into the system.

If we denote averages over realizations of the noise by angular brackets, the average position of the particle obeys

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

and since the noise must have zero mean so as not to bias the particle we obtain

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

Next we examine the variance in the position,

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

Here we invoke the assumed separation of time scales between the random forcing and the deterministic motion of the particle. That is, we assume that the last term is a sharply peaked function of |t - t''|, say  $\phi(t' - t'')$ . With the change of variables

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

the r.h.s. of the previous equation becomes

$$\frac{1}{2}e^{-2t/\tau}\int_0^{2t}ds e^{s/\tau}\int_{-\infty}^{\infty}dq\phi(q)\;.$$

Note that we have extended the integration limits on the final equation to  $\pm \infty$  in recognition of the separation of time scales. The final integral is then just a constant we term  $\Gamma$ . The average deviation squared is then

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

To determine  $\Gamma$  we take the limit  $t/\tau \to \infty$  where we expect equilibrium statistical mechanics to hold, and obtain

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

But we know from equipartition that

$$\frac{1}{2}k\langle x^2\rangle = \frac{1}{2}k_BT$$
 so  $\Gamma = \frac{2k_BT}{\zeta}$ 

Returning to the original formulation, we clearly might just as well have assumed from the beginning that the noise is  $\delta$ -function correlated,

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

Let us consider the small-t behavior of the variance,

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

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.

As an aside, we can justify the assumption of no inertia for small particles. If a  $1\mu$ m bacterium moving under it's own power at  $10\mu$ m/sec stops propulsion, it will stop within a subatomic distance. Thus, there is negligible inertia and no drifting at these length scales.

#### 4.4.2 Brownian Diffusion

The diffusion coefficient is just the average of the movement rate per time at long times

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

where  $\mathbf{r}(t)$  is

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

The diffusion coefficient term above holds provided that the correlation of velocities  $(\langle \mathbf{u}(t') \cdot \mathbf{u}(t'') \rangle$  falls off fast enough. This yields

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

For *E. coli* the average velocity is about 20  $\mu$ m/s, and the bacterium executes 1s of movement before randomly changing direction. This yields a diffusion coefficient of  $4 \times 10^{-6}$  cm<sup>2</sup>/s, which is approximately the diffusion coefficient of a small molecule in water. Thus, *E. coli* use propulsion to achieve diffusion that their large size does not allow, allowing them to effectively explore space.

#### 4.4.3 Brownian Motion and Polymers

Consider a free polymer



with each segment labeled as  $\mathbf{r}_n$ . Each segment is followed by another random segment of equal length

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

The total and average length of the polymer is then

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

by symmetry. The average of the displacement squared is

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

Now, more generally we can say that the probability that a polymer will have segment positions at  $\{\mathbf{r}_k\}$  is

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

We will consider the case in which the energy U is a local function,

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

where W represents an external potential (electric, gravitational, etc.). 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. Following Doi & Edwards, we then define a term to represent the energy exponential between two elements

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

The function  $\tau_j$  is assumed to be normalized, and can also be used to calculate the end position, assuming the starting position is the origin **0**,

$$\int d\mathbf{R}_i \tau_i(\mathbf{R}_i) = 1 \qquad \mathbf{r}_N = \sum_{j=1}^N \mathbf{R}_j \ .$$

Thus, molecular level structures are effectively abstracted away and we can consider a whole class of models for the distribution of segments,

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For example, one could even imagine a spring connecting beads together, so

$$p(x) \sim \exp(-kx^2/2k_BT)$$

Eventually, we are interested in the probability distribution of the end-to-end vector of the polymer and the way it depends on properties of the function  $\tau$ . The quantity of interest is the fixed end-to-end vector partition function, the integral over all degrees of freedom for which the end position is **R**, is then

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

#### 4.4.4 Example of Nearest Neighbor Interaction

An example of  $\tau$  is that for a fixed-length distribution,

$$\tau(\mathbf{R}_j) = \frac{1}{4\pi l^2} \delta(|\mathbf{R}_j| - l) \; ,$$

which is the simplest model for a self-avoiding chain. The trick to performing the calculation is the use an integral representation of a delta function,

$$\delta\left(\sum_{j=1}^{N}\mathbf{R}_{j}-\mathbf{R}\right) = \int \frac{d^{3}k}{(2\pi)^{3}} \exp\left[i\mathbf{k}\cdot\left(\sum_{j=1}^{N}\mathbf{R}_{j}-\mathbf{R}\right)\right] .$$

The distribution function is then

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

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

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

.

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We are interested in the regime  $N \gg 1$  and thus need only focus on the small-k behavior of K,

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

Thus, we obtain

$$G(\underline{R}_j; N) = \int \frac{d^3k}{(2\pi)^3} \exp(-i\mathbf{k} \cdot \mathbf{R}) \exp(-Nl^2k^2/6)$$
$$= \left(\frac{3}{2\pi l^2 N}\right)^{3/2} \exp\left(\frac{-3R^2}{2Nl^2}\right) .$$

More generally we would recognize an effective bond length defined in terms of the second moment of the distribution function  $\tau$ . Provided there is nothing pathological about  $\tau$  the central limit theorem guarantees us a Gaussian distribution.

#### 4.4.5 Self-avoidance and Flory Theory

Real polymers have excluded-volume interactions that change the relationship between the end-to-end distance R and the number of segments N.

We saw previously that the probability distribution for the free chain takes the form

$$P(R) \sim e^{-3R^2/2Nl^2}$$

and this can be used to define an effective free energy via the relation

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

This looks like the energy of a spring (quadratic in the displacement R), with a spring constant of entropic origin.

In the simplest treatment of self-avoidance, we introduces an energetic cost of contact interactions between segments,

$$k_B T v \delta(\mathbf{R}_m - \mathbf{R}_n)$$

where we measure the interaction energy for convenience by  $k_B T$ . In the mean field argument pioneered by Flory, we estimate the contribution of this term to the free energy through the segment concentration  $N/R^3$  as

$$vk_BT\cdot N\cdot \frac{N}{R^3}$$

Adding this to the entropic contribution we arrive at the total free energy

$$F_{tot} = k_B T \left[ \frac{3R^2}{2Nl^2} + \frac{vN^2}{R^3} \right] \ . \label{eq:ftot}$$

Thus, there is a trade-off between the two competing effects, with entropic elasticity favoring a compact chain and self-avoidance swelling it.

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Minimizing  $F_{tot}$  with respect to R we find

$$fracRN \sim \frac{N^2}{R^4}$$

and hence

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

It is conventional to denote the exponent of the relation  $\nu$ . For the ideal random walk we have

$$\langle R \rangle \sim N^{\nu}, \nu = 1/2$$
,

and thus self-avoidance does indeed swell the chain. Note that the concentration of segments is

$$C_{seg} \sim \frac{N}{R^3} \sim N^{1-3\nu} \begin{cases} \sim N^{-1/2} & \text{ideal} \\ \sim N^{-4/5} & \text{self-avoidance} \end{cases}$$

so the concentration is reduced.

If we generalize this to d dimensions the only change is in the expression for the concentration of segments, so balancing the terms in the free energy yields

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

This relation is remarkably close to the available results for  $1 \le d \le 4$ :

d = 1	$R \sim N$	exact (trivial)
d = 2	$R \sim N^{3/4}$	exact (solved)
d = 3	$R \sim N^{3/5}$	Renormalization group and 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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