Announcement for Maths Students

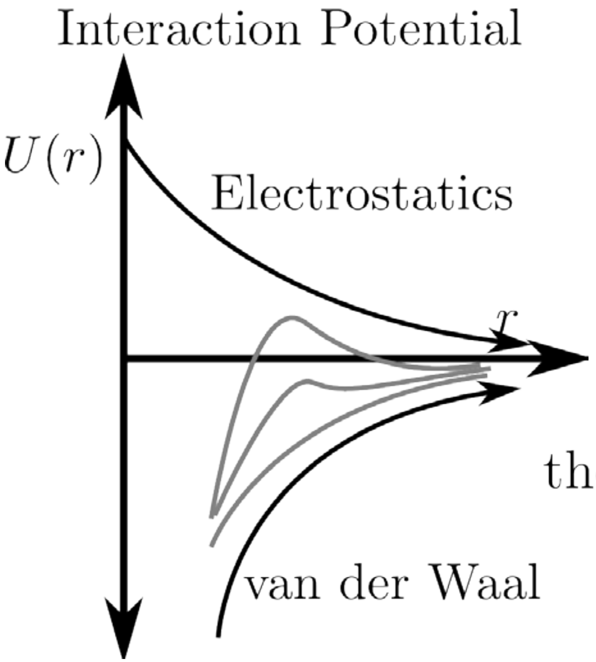
Could all Part III lecturers during their lecture, remind Part III students that if they have not registered on the computer they need to do so immediately in the Part III room (BL.16).
Go to the following web address:

http://www.maths.cam.ac.uk/postgrad/casm/registration/pt3.pl

username pt3reg
no password!

This includes all students who have been at Cambridge for the past 3 years but excludes Astrophysics students. Having their University card programmed at reception is not registering as a Part III student. Any Part III student not registered will not be on the Part III email distribution list or exam list.

DLVO Theory



Two charges in vacuum separated by a distance r have an electrostatic energy

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

If we measure r in the molecule scale of Å 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* λ_B as the point of balance:

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

Screened Interactions

There are two basic ingredients in the calculation of screened electrostatic interactions (in the so-called Poisson-Boltzmann theory).

1. The Poisson equation relating the electrostatic potential ϕ to the charge density ρ:

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

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

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

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

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

Screened Interactions - continued

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:

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

In the weak field limit, when $\beta e\phi \ll 1$, we can linearize the PB equation (using $\sinh(x) \simeq x + \cdots$):

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

This suggests a characteristic length scale, the Debye-Huckel length λ_{DH}:

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

This finally shows that the Debye-Huckel limit is governed by the modified Helmholtz equation

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

Screened Interactions - continued

The most elementary situation to consider is the one-dimensional problem of a surface held at fixed potential ϕ_0, bounded by a semi-infinite electrolyte. The relevant solution of

$$\left(\frac{\partial^2}{\partial x^2} - \lambda_{DH}^{-2}\right)\phi = 0 \qquad \text{is} \qquad \boxed{\phi = \phi_0 e^{-x/\lambda_{DH}}}$$

There is an induced charge density σ on the surface which can be computed in the usual way (Gaussian pillbox):

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

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:

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

Screened Interactions - continued

This was obtained with the general Euler-Lagrange formula

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

where $(\cdots)$ is the integrand of the functional.

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,

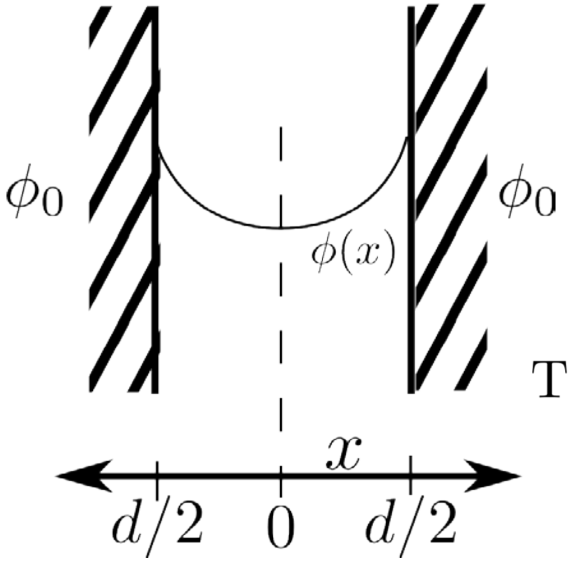
$$\tilde{\mathcal{F}} = \frac{\epsilon}{8\pi}\int_S dS\phi\hat{\mathbf{n}}\cdot\nabla\phi - \frac{\epsilon}{8\pi}\int d^3r\phi\left(\nabla^2\phi - \lambda_{DH}^{-2}\phi\right)\boxed{= \frac{1}{2}\int_S dS\sigma\phi,}$$

where σ is the surface charge. The bulk term vanishes by the DH equation (!).

For situations with fixed surface potential rather than fixed charge, the surface free energy must be Legendre transformed:

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

Interaction of Two Surfaces – Fixed Potentials



For fixed potential ϕ_0 on each surface, the solution of the DH equation is

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

The induced charge density is

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

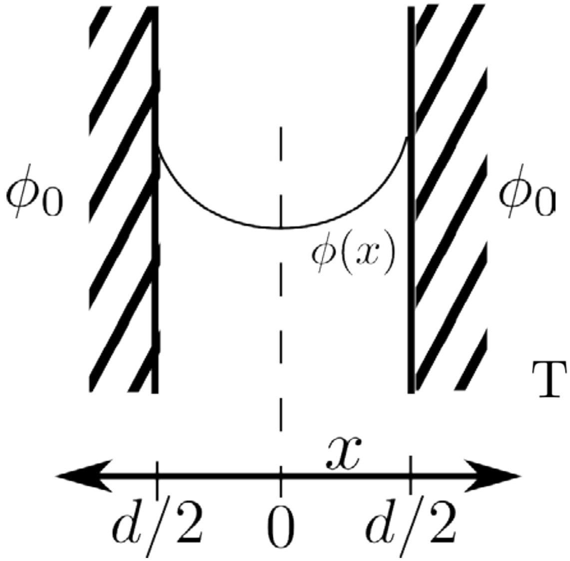
And finally the free energy per unit area is

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

And the interesting quantity is the difference between this and the energy at infinite separation:

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

Interaction of Two Surfaces – Fixed Charge



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

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

The potential at the surface is

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

And the interaction energy per unit area is

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

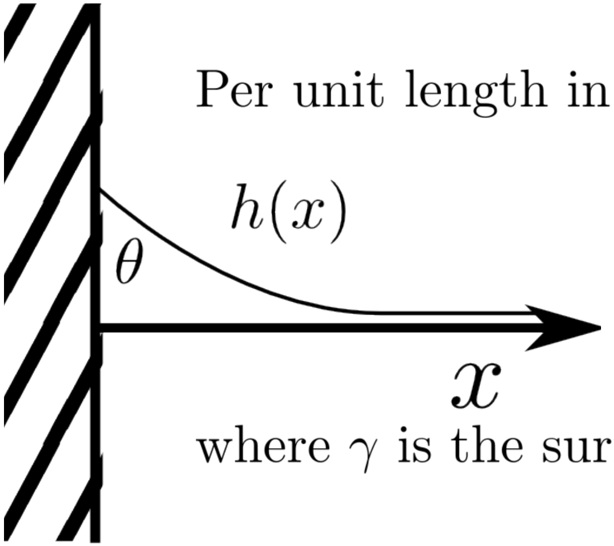
Screened Interactions - continued

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

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

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

An Aside on Quadratic Energy Functionals



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

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

where γ is the surface tension.

Screened Interactions - continued

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

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

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

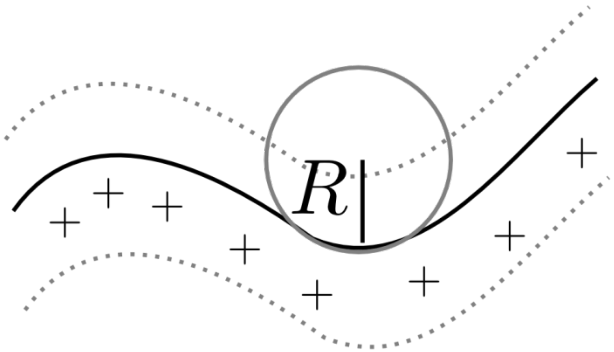
Note that we use the shorthand notation $h_x \equiv \partial h(x)/\partial x$.

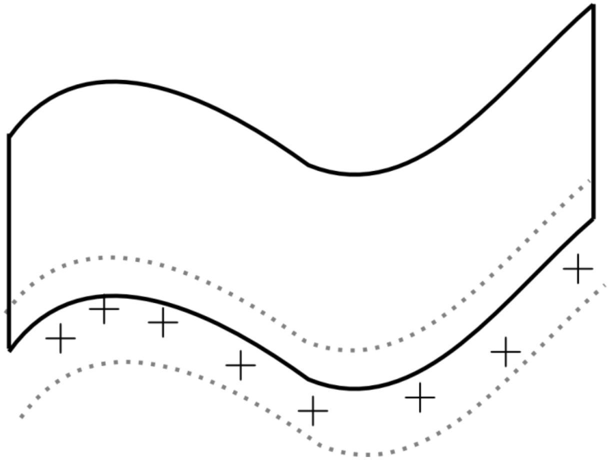
Again we will find a characteristic length scale by balancing the two terms. Here it is the *capillary length* l_c,

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

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

Geometrical Aspects





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

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

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

Geometrical Aspects

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

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

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

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

Various Approaches

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

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

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

Geometric Expansion

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

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

with

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

Rearranging, we obtain

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

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

Geometric Expansion - continued

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

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

and the free energy will involve a ratio of the form

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

Here, we use the asymptotic expansion of Bessel functions:

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

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

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