$$\coth(x) = \frac{1}{x} + \frac{x}{3} - \frac{x^3}{45} + ---$$

Hence, $\coth(x) - \frac{1}{x} \to 0$ linearly as $x \to 0$.

We will now try to understand what happens when the rod has some bending rigidity. This time we will get an effective energy

$$\frac{E}{k_BT} = \int_0^L \frac{\xi_p}{2} \left(\frac{d\hat{t}}{ds}\right)^2 ds - \frac{f}{k_BT} \hat{e}_3 \cdot \left(\underline{r}(L) - \underline{r}(0)\right)$$

where the force 'f' is assumed to act along the z-direction. We will assume that 'f' is large enough so that $\hat{t}$ fluctuates around $\hat{e}_3$. The fluctuations are assumed to be small. Now let us write $\hat{t} = [t_x \ t_y \ t_z]$ then,

$$t_z = 1 - \frac{t_\perp^2}{2} + O(t_\perp^4) \quad \text{where} \quad t_\perp = [t_x \ t_y].$$

Similarly, $K^2 = \left(\frac{d\hat{t}}{ds}\right)^2 = \left(\frac{dt_\perp}{ds}\right)^2$ upto quadratic order.

$$\frac{E}{k_BT} = \frac{1}{2} \int_0^L \left(\xi_p \left(\frac{dt_\perp}{ds}\right)^2 + \frac{f}{k_BT} t_\perp^2\right) ds - \frac{fL}{k_BT}$$

where we have used $Z = (\underline{r}(L) - \underline{r}(0)) \cdot \hat{e}_3 = \int ds \ \hat{t}_z$

We have neglected terms higher than quadratic.
Now we will decouple the energy using normal modes and Fourier transforms.

$$\int_{-\infty}^{+\infty} ds \ e^{iqs} t_\perp(s) = \tilde{t}_\perp(q) \Rightarrow \hat{t}_\perp(s) = \int_{-\infty}^{\infty} \frac{dq}{2\pi} \tilde{t}_\perp(q) e^{-iqs}$$

$$\frac{E}{k_BT} = \frac{1}{2} \int \frac{dq}{2\pi} \left(\xi_p q^2 + \frac{f}{k_BT}\right) |\tilde{t}(q)|^2 - fL/k_BT$$

fL is just a constant term that has nothing to do with the modes. At equilibrium we expect equipartition, meaning each mode will have energy $\frac{k_BT}{2}$. Hence, ⌞I find this unsatisfying.

Invoke Parseval's thm here

$$\langle |t_\perp(s)|^2 \rangle = \int \frac{dq}{2\pi} \langle |\tilde{t}_\perp(q)|^2 \rangle = 2 \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{1}{\xi_p q^2 + \frac{f}{k_BT}}$$

The 2 appears because there are two independent components of $t_\perp$.

Parseval's theorem $\rightarrow$ $\int_{-\infty}^{+\infty} |f(x)|^2 dx = \int_{-\infty}^{+\infty} |\tilde{f}(q)|^2 dq$

We get $\left\langle |t_\perp(s)|^2 \right\rangle = \dfrac{1}{\sqrt{\dfrac{f\,\xi_p}{k_B T}}}$
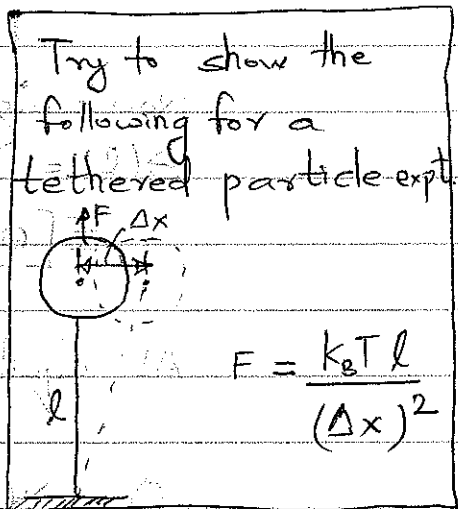
Now this is a constant. We already know that

$$Z = \int_0^L t_z\, ds = \int_0^L \left(1 - \frac{t_\perp^2}{2}\right) ds$$

Hence, $\langle Z \rangle = L - \int_0^L \left\langle \dfrac{t_\perp^2}{2} \right\rangle ds$

$$= L - \int_0^L \frac{1}{2} \frac{ds}{\sqrt{\dfrac{f\,\xi}{k_B T}}}$$

Or, $\dfrac{\langle Z \rangle}{L} = 1 - \dfrac{\sqrt{k_B T}}{\sqrt{4 f \xi_p}}$

Try to show the following for a tethered particle-expt

$$F = \frac{k_B T\, \ell}{(\Delta x)^2}$$

Note the distinct $\dfrac{1}{\sqrt{f}}$ dependence of this function. Unfortunately this does not reduce to the FJC in the limit as $\xi_p \to 0$ or $f \to 0$. We have relied on the quadratic approximation which fails to be valid in that limit. But starting at about $\dfrac{\langle Z \rangle}{L} = 0.3$ or so this formula works very well. The side-to-side excursions of the chain can also be computed exactly in the fluctuating rod model. We are interested in:

$$R_\perp^2(s) = \left\langle \left[r_\perp(s) - r_\perp(0) \right]^2 \right\rangle$$
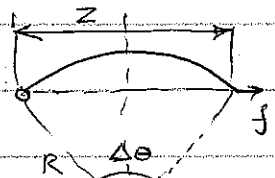
$$= \int_0^s \int_0^s du\, dv \, \left\langle t_\perp(u) \cdot t_\perp(v) \right\rangle$$

$$= \frac{2}{f} \left(s - \frac{1 - \exp\left[- s \sqrt{\dfrac{f}{\xi_p k_B T}} \right]}{\sqrt{\dfrac{f}{\xi_p k_B T}}} \right)$$

There is an unmistakable resemblance to the formula for the end-to-end distance for a chain with no force. The correlation length is $\sqrt{\dfrac{\xi_p k_B T}{f}}$ instead of ξ_p.

A sketch of why this should be the case is as follows. We do a 2D calculation.

$$E = \int_0^L \frac{A}{2}\left(\frac{d\hat{t}}{ds}\right)^2 ds - F\int(\hat{t}\cdot\hat{e}_3)\,ds$$

Now imagine a small circular arc with $\theta(0) = 0$ and $\theta(\ell) = \Delta\theta_\ell$. Then,

$$E[\theta] = \frac{A(\Delta\theta_\ell)^2}{2\ell} - f\ell + \frac{f\ell(\Delta\theta)^2}{24} \quad \left(\begin{array}{l}\text{we used } z = 2R\sin\frac{\Delta\theta}{2}\\ \text{and } R\Delta\theta = \ell\end{array}\right)$$

At equilibrium, we expect that (with $f=0$)

$$\frac{A\langle(\Delta\theta_\ell)^2\rangle}{2\ell} = \frac{k_BT}{2}$$

Or, $$\frac{\langle(\Delta\theta_\ell)^2\rangle}{2} = \ell\frac{k_BT}{2\left(A+\frac{f\ell^2}{12}\right)} + \frac{f\ell^2}{A}$$

If f is large then the first term is negligible in comparison to the second term and

$$\frac{\langle(\Delta\theta_\ell)^2\rangle}{2} = \frac{f\ell^2}{A}$$

Now, $$\langle \underline{t}(s)\underline{t}(s+\ell)\rangle = \langle\cos\Delta\theta_\ell\rangle \simeq 1 - \frac{1}{2}(\Delta\theta)^2 = 1 - \frac{\ell k_BT}{2A} - \frac{f\ell^2}{A}$$

$$\langle\underline{t}(s)\underline{t}(s+2\ell)\rangle = \langle\cos\Delta\theta_{\ell,1}\rangle\langle\cos\Delta\theta_{\ell,2}\rangle - \langle\sin\Delta\theta_{\ell,1}\rangle\langle\sin\Delta\theta_{\ell,2}\rangle^0$$

$$= \langle\underline{t}(s)\underline{t}(s+\ell)\rangle\langle\underline{t}(s+\ell)\underline{t}(s+2\ell)\rangle$$

$$= \left(1 - \frac{\ell k_BT}{2A} - \frac{f\ell^2}{A}\right)^2$$

We have used the fact that $\Delta\theta_{\ell,1}$ and $\Delta\theta_{\ell,2}$ are independent.

$$\langle\underline{t}(s)\underline{t}(s+n\ell)\rangle = \left(1 - \frac{\ell k_BT}{2A} - \frac{f\ell^2}{2A}\right)^n$$

Now if we assume f is very large then,

$$\langle\underline{t}(s)\underline{t}(s+L)\rangle = \left(1 - \ell\frac{k_BT}{2A} - \frac{fL^2}{An^2}\right)^n$$

Take $n\to\infty$ then we should get $e^{-\frac{L}{\ell_c}}$ where $\ell_c = \sqrt{\frac{A}{f}}$.

FORCE-EXTENSION MEASUREMENTS OF PROTEINS

We have talked about force-elongation of DNA and of freely-jointed chain polymers such as PEG. But when forces are exerted on proteins or on RNA they tend to unfold. The persistence length of the unfolded region is shorter than that of the folded region. They are much more floppy. (Can we account for this?
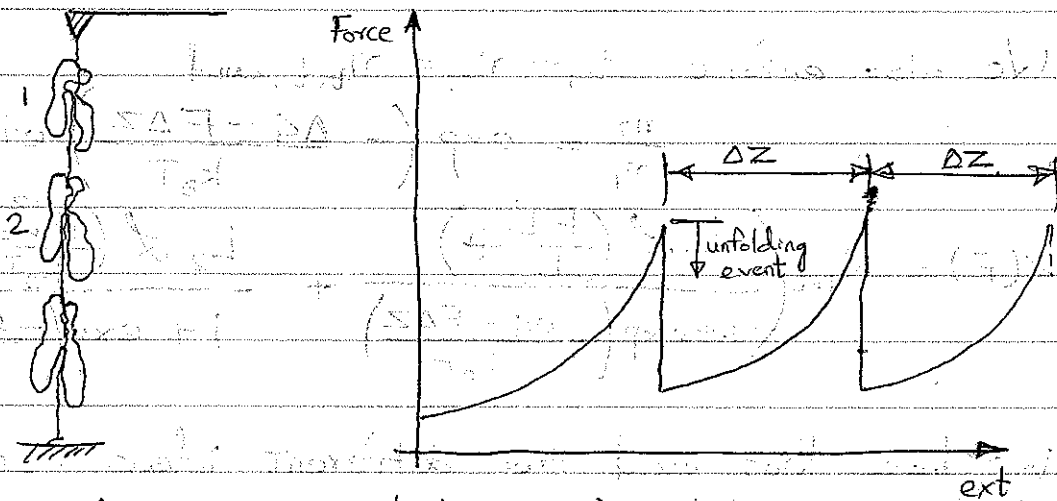
Consider a two state system where a population of molecules can be in one of two states. The two states differ in free-energy by ΔG. By applying a force the free-energy is titled. We know that the populations will be connected at equilibrium by the relation:

$$\frac{[S_1]}{[S_2]} = \exp\left(-\frac{\Delta G - F\Delta z}{k_B T}\right)$$

Hence, $p(S_2) = \dfrac{[S_2]}{[S_1]+[S_2]} = \dfrac{1}{1 + \exp\left(\dfrac{\Delta G - F\Delta x}{k_B T}\right)}$ etc.

In the unfolded (2) state the molecule has a different force-extension curve compared to that in the folded (1) state. The different force-extn relation is governed by a single constant which is the Kuhn-length, L_{seg}.

In fact we know that

$$\frac{z}{L} = \coth\left(\frac{F L_{seg}}{k_B T}\right) - \frac{k_B T}{F L_{seg}}$$

So if we have a molecule which consists of n_1 molecules in state 1 and n_2 molecules in state 2 then,

$$Z(F) = n_1 L_1 \mathcal{L}\left(\frac{F L'_{seg}}{k_B T}\right) + n_2 L_2 \mathcal{L}\left(\frac{F L^2_{seg}}{k_B T}\right)$$

We also enforce $n_1 + n_2 = n_{tot}$, and

$$\frac{n_2}{n_1} = \exp\left(-\frac{\Delta G - F \Delta z}{k_B T}\right) \text{etc.}$$

$$Z(F) = n_{tot}\left(\frac{L_1 \mathcal{L}\left(\frac{F L'_{seg}}{k_B T}\right)}{1 + \exp\left(-\frac{\Delta G - F \Delta z}{k_B T}\right)} + \frac{L_2 \mathcal{L}\left(\frac{F L^2_{seg}}{k_B T}\right)}{1 + \exp\left(-\frac{\Delta G - F \Delta z}{k_B T}\right)}\right)$$

We have thus used two different ideas : <u>entropic elasticity</u> and <u>two-state</u> equilibria in order to come out with force-extension relation for a complex macromolecule. The formula above works very well for dextran, PEG (in water) and for RNA. This works when the folded and unfolded states of the molecule are in equilibrium and not otherwise. For non-equilibrium calculations one has to resort to Kramer's rate theory or other non-eqbm theories.

This was the conclusion of our treatment of the mechanics of macromolecules where deterministic and stochastic forces were both responsible for determining the force-extension relation. Ideas of this type can also be extended to networks of these molecules and to membranes but we do not discuss them here.

POISSON-BOLTZMANN EQUATION.

Instead we will consider another situation which is important in biology where deterministic and stochastic physics collude with each other. This is the Poisson-Boltzmann equation for electrostatics in solution. The first thing to understand is when will stochastic effects become important in electrostatics. The electrostatic energy between two unit charges is $\frac{e^2}{4\pi\varepsilon r}$ where r is the separation between the charges. When this becomes comparable to $k_B T$ then we say that stochastic effects are important. We define the Bjerrum length as $l_B = \frac{e^2}{4\pi\varepsilon k_B T}$. For water at 300 K with a dielectric constant 80, we know that $l_B = 7 A° = 0.7$ nm. To get this substitute $e = 1.6021 \times 10^{-19}$ Coulombs, $\varepsilon = 80 \times \varepsilon_0$.
$= 80 \times 8.85 \times 10^{-12}$ C^2/Nm^2, $k_B T = 4.1$ pN nm.

Let us now write the theory of electrostatics for solutions. Gauss Law says that

$$\int \underline{E} \cdot \underline{dA} = \frac{1}{\varepsilon} \int \rho_{ch} dV$$

where ρ_{ch} is the charge density within a volume V and $\underline{E}$ is the electric field on the surface. ε is the permittivity of the medium. The divergence theorem allows us to write

$$\nabla \cdot \underline{E} = \frac{\rho_{ch}}{\varepsilon} \quad \text{or} \quad -\nabla^2 \psi = \frac{-\rho_{ch}}{\varepsilon}$$

where $\psi(\underline{x})$ is the potential such that $-\nabla\psi = \underline{E}$.
Now density of charges will be determined by the Maxwell-Boltzmann statistics. We assume for now that only one species of mobile ions is present, each ion with charge q experiencing a potential energy $q\psi(\underline{x})$. Defining ρ_0 as the

ion density at reference point $\psi = 0$, the density profile will be given by

$$\rho(\underline{x}) = \rho_o \exp\left(-q \frac{\psi(\underline{x})}{k_B T}\right)$$

Plugging this back into the Poisson equation we get

$$\nabla_{\underline{x}}^2 \psi = -\frac{q\rho_o}{\varepsilon} \exp\left(-\frac{q\psi(\underline{x})}{k_B T}\right)$$

Let us assume now that there are more than one type of ion. The charge density would be $\rho_+ + \rho_- = \rho$.
$\rho_{\pm} = e Z_{\pm} n_{\pm}(x)$ where Z_+ and Z_- are the valencies of the ions and n_+ and n_- are the number of ions. Clearly,

$$n_{\pm} = n_{\pm}^o \exp\left(-\frac{e Z_{\pm} \psi(\underline{x})}{k_B T}\right)$$

Plugging all this back into the Poisson-equation,

$$\nabla_{\underline{x}}^2 \psi = -\sum_{i=\pm} \frac{e n_i^o Z_i}{\varepsilon} \exp\left(-\frac{e z_i \psi(\underline{x})}{k_B T}\right)$$

This is the Poisson-Boltzmann equation. It is a non-linear partial differential equation for the potential $\psi(\underline{x})$. That is difficult to solve, so it is good to linearise this equation. As an example consider the equation with only ~~two~~ type of counter-ion species with $Z_+ = Z_- = 1$

$$\nabla_{\underline{x}}^2 \psi = + \frac{2 e n_o}{\varepsilon} \sinh\left(+ \frac{e \psi(\underline{x})}{k_B T}\right)$$

We have set $n^o_- = n_o^+$. If we linearise this we get,

$$\nabla_{\underline{x}}^2 \psi = \frac{2e^2 n_o}{\varepsilon k_B T} \psi(\underline{x}) = \lambda_D^{-2} \psi(\underline{x})$$

The new-parameter $\lambda_D = \sqrt{\dfrac{\varepsilon k_B T}{2e^2 n_0}} = (\ell_B n_0)^{-1/2}$ is called the screening length. The screening length varies with the conc^n of the medium. For 1M NaCl it is 0.3nm and it is 1μm for pure water (OH^- and H^+ ions). To a first approximation, one can say that for $r < \lambda_D$ the coulombic interaction $\sim r^{-1}$ is lightly screened but for $r \gg \lambda_D$ it is strongly screened. The linearised theory is also known as the Debye-Huckel theory.

With $-ve$ charge on plate and $+ve$ ions in solution the force on the $+ve$ ions is always directed downward or it is $-ve$. Hence, $-\nabla\psi$ is $-ve$. $\nabla\psi$ is positive and therefore ψ increases as Z increases.
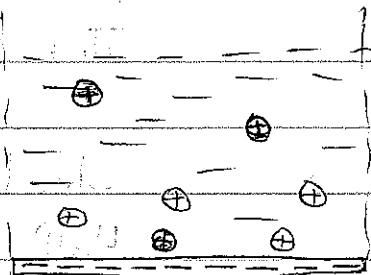
SOLUTIONS TO THE P-B EQN.

We will consider some analytical solutions to the P-B eqn. With only one type of ion next to a charged plate shown below we will get,

$$\frac{d^2\psi}{dz^2} = -\frac{e\rho_0}{\varepsilon}\exp\left(-\frac{e\psi}{k_BT}\right)$$

Let us define $\Psi = \frac{e\psi}{k_BT}$ then,

$$\frac{d^2\Psi}{dz^2} = -\rho_0\left(\frac{e^2}{\varepsilon k_BT}\right)\exp\left(-\Psi\right)$$

Remember $\ell_B = \frac{e^2}{4\pi\varepsilon k_BT}$ is the Bjerrum length. Let us define another length scale, K, by

$$K^2 = 2\pi \ell_B \rho_0$$

So that the P-B eqn now takes the form

$$\frac{d^2\Psi}{dz^2} = -2K^2 e^{-\Psi}$$

Or, $\frac{d}{dz}\left[\frac{d\Psi}{dz}\right]^2 = 4K^2 \frac{d}{dz}e^{-\Psi}$

Electric field should vanish for large distances z.

Or, $\frac{d\Psi}{dz} = 2K e^{-\Psi/2} \longrightarrow \textcircled{1}$

We have chosen the integration constant equal to zero to ensure that $\frac{d\Psi}{dz}$ vanishes for large values of Ψ expected as $z \to \infty$. Positive root is chosen because the potential increases with z when the plate is negatively charged. Integrating eqn $\textcircled{1}$ gives

$$\exp(\Psi/2) = K(z+c)$$

where 'c' is a constant. We have determined that

$$e^{-\Psi} = \frac{1}{(K(z+c))^2} \implies \Psi = 2\log(K(z+c)).$$

hence, $\rho(z) = \rho_0 e^{-\Psi} = \dfrac{\rho_0}{K^2(z+c)^2} = \dfrac{1}{2\pi \ell_B (z+c)^2}$

The integration constant is fixed by the known surface
charge density, which should be neutralised by solution charge

$$+ \sigma_s = \int e\rho \, dz = \frac{e}{2\pi \ell_B} \int_0^\infty \frac{dz}{(z+c)^2}$$

This gives $\quad c = \frac{\mp e}{\pm 2\pi \ell_B |\sigma_s|} = \frac{2\epsilon k_B T}{\pm e |\sigma_s|}$

Clearly the density of ions falls as the square of the distance
Half the counter-ions are within a distance 'c' from the
plate and the width of the distribution increases with
temperature linearly.
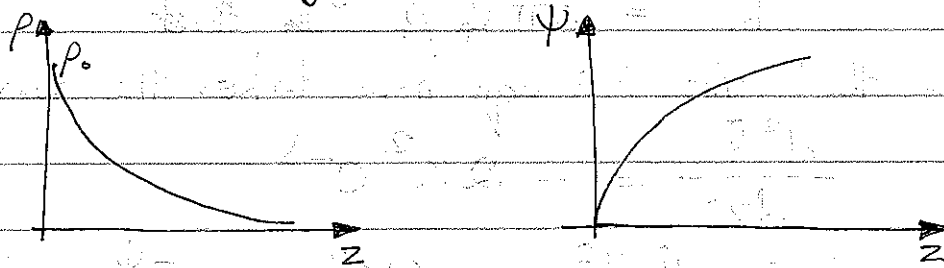
We will consider next a charged plate in a salt bath.
Both the interior and exterior of cells contain ions like
Na^+, K^+, Cl^-, PO_4^- etc, which we will refer to as
bulk ions. In this case, we intuitively expect the following
density distribution. Can we arrive at this using the
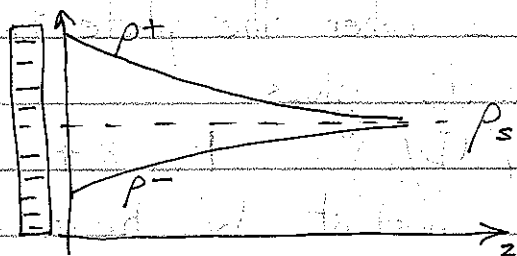
Poisson-Boltzmann equation? This time we have,

$$\rho_+(z) = \rho_s \exp\left(\frac{-e\,\psi(z)}{k_B T}\right) \quad \text{and}$$

$$\rho_-(z) = \rho_s \exp\left(\frac{+e\,\psi(z)}{k_B T}\right)$$

$$\nabla^2 \psi = -\frac{e\rho_s}{\varepsilon}\left[\exp\left(-\frac{e\psi(z)}{k_B T}\right) - \exp\left(\frac{e\psi(z)}{k_B T}\right)\right]$$

Once again define $\Psi(z) \equiv \dfrac{e\psi(z)}{k_B T}$ and $\lambda_D^{-2} = 8\pi \ell_B \rho_s$.
Then the equation can be recast as,

$$\frac{d^2\Psi}{dz^2} = -\frac{1}{2\lambda_D^2}\left(e^{-\Psi} - e^{+\Psi}\right) = \frac{1}{\lambda_D^2}\sinh(\Psi)$$

Integrating after multiplying with $\dfrac{d\Psi}{dz}$, we obtain,

$$\left(\frac{d\Psi}{dz}\right)^2 = \frac{1}{\lambda_D^2}\left(2\cosh(\Psi) - 2\right)$$

The last 2 comes from an integration constant since
we want $\dfrac{d\Psi}{dz} \to 0$ as $z \to \infty$. By taking a
square-root on both sides, we get

$$\frac{d\Psi}{dz} = \pm\frac{2}{\lambda_D}\sinh\left(\frac{\Psi}{2}\right) \qquad \left(\frac{d\Psi}{dz}\Big|_{z=0} = -\frac{\sigma}{\varepsilon}\right)$$

This equation can also be integrated to yield,

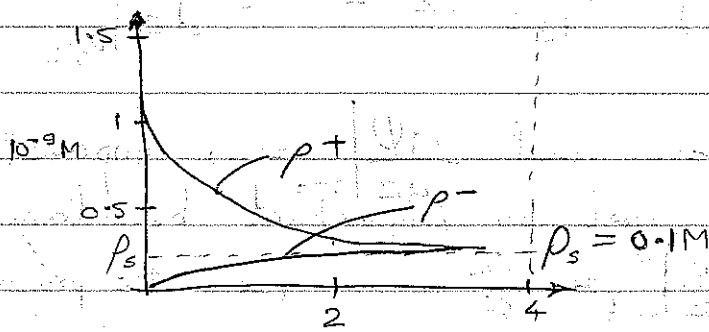$$\psi(z) = -\frac{2k_B T}{e}\log\frac{1 + \gamma e^{-z/\lambda_D}}{1 - \gamma e^{-z/\lambda_D}}$$

$$\rho_\pm(z) = \rho_s\left(\frac{1 \pm \gamma e^{-z/\lambda_D}}{1 \mp \gamma e^{-z/\lambda_D}}\right)^2$$
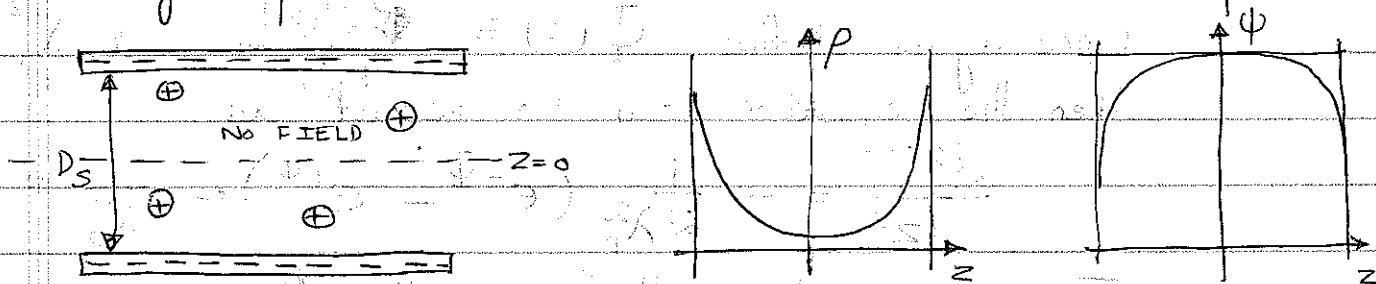
— Bjerrum length.

where the parameter γ is the positive root of the
equation $\gamma = -\dfrac{b}{\lambda_D} \pm \sqrt{\left(\dfrac{b}{\lambda_D}\right)^2 + 1}$ and the surface
potential $\psi(s) = \psi(0)$ is related to γ through

$$\psi_s = \psi(0) = -\frac{4k_B T}{e}\tanh^{-1}(\gamma)$$

Next we want to consider what happens between two charged plates. The electric field between the plates is

Zero since _one_ plate contributes a field $\frac{\sigma_s}{2\varepsilon}$ (Gauss Thm) and they are in opposite directions, so they cancel. The field outside is $\frac{\sigma_s}{\varepsilon}$ because the fields add there. If we now put a positive ion any-where between the plates it experiences no force. But if there is more than one positive ion then they will repel each other and pile up on the plates. Thermal fluctuations will try to have them uniformly distributed. By symmetry we expect $z=0$ to be the symmetry axis; we choose $\psi(z=0)=0$. Also, at the mid-plane $\frac{d\rho}{dz}=0$ and $\frac{d\psi}{dz}=0$. By overall charge neutrality, we expect

$$\sigma_s = -e\int_0^{D_s/2} \rho \, dz \qquad \begin{array}{l}\text{(plate and ions have opposite}\\ \text{sign)}\end{array}$$

From Poisson's equation we know $e\rho = -\varepsilon\nabla^2\psi$ which in this case is $-\varepsilon\frac{d^2\psi}{dz^2}$. Hence,

$$\sigma_s = \varepsilon\int_0^{D_s/2} \frac{d^2\psi}{dz^2} \, dz = \left.\varepsilon\frac{d\psi}{dz}\right|_{D_s/2}$$

where we have used $\left.\frac{d\psi}{dz}\right|_{z=0}=0$ imposed by symmetry. But now we get an important boundary condition,

$$\left.\frac{d\psi}{dz}\right|_{z=\frac{D_s}{2}} = \frac{\sigma_s}{\varepsilon} \qquad \text{(with the proper sign)}$$

We want to integrate the differential equation

$$\frac{d^2\psi}{dz^2} = -\frac{e\rho_0}{\varepsilon}\exp\left(-\frac{e\psi(z)}{k_BT}\right)$$

Use $\frac{e\psi(z)}{k_BT} = \Psi(z)$ and $K^2 = \frac{e^2\rho_0}{2\varepsilon k_BT} = 2\pi l_B\rho_0$

The solution to the equation above is simply,

$$\Psi(z) = -\log\left(\cos^2(Kz)\right)$$

$$\frac{d\Psi}{dz} = -2K\tan(Kz)$$

From the boundary condition we want,

$$-2K\tan\left(\frac{KD_s}{2}\right) = \frac{e\sigma_s}{\varepsilon k_BT} \longrightarrow \text{(1)}$$

This will fix K (remember we do not know what ρ_0 is).
We also have,

$$\rho(z) = \rho_0/\cos^2(Kz) = \rho_0 + \rho_0\tan^2(Kz)$$

We see that the density of ions at the plate is

$$\rho\left(\frac{D_s}{2}\right) = \rho_0 + \frac{\sigma_s^2}{2\varepsilon k_BT} \qquad (\text{using } \text{(1)})$$

Clearly, the counter-ion density at the plates declines with temperature as expected. It is known that the pressure P between charged plates is given by an appealing formula

$$P = \rho_0 k_BT \qquad (\text{Israelachvilli})$$

where ρ_0 is the density of ions at the center-line. But this looks like the ideal gas law. So we wonder under what conditions do the counter-ions fill the gap between the plates and behave like a gas.

This would happen if σ_s is small or T is large which implies a small value of K. In that case,

$$K^2 = \frac{-e\sigma_s}{\varepsilon k_B T D_s} \implies \rho_0 = \frac{-2\sigma_s}{e D_s}$$

which is obtained using $K^2 = \frac{e^2 \rho_0}{2\varepsilon k_B T} = 2\pi l_B \rho_0$,

which is just the density expected if the counter-ions are evenly spread across the gap. Hence for the pressure we get,

$$P = \frac{-2\sigma_s k_B T}{e D_s} \quad \text{(electrostatics, ideal gas limit)}$$

As usual σ_s and e have opposite signs making $P > 0$ and repulsive. If the charges are more concentrated at the plates then we want to solve for K in

$$\frac{K D_s}{2} \tan\left(\frac{K D_s}{2}\right) = -\underbrace{\frac{e D_s \sigma_s}{4\varepsilon k_B T}}_{\psi}$$

At large value of ψ the pressure is given by

$$P = \frac{\pi k_B T}{2 l_B D_s^2} \quad \text{(electrostatics, large } D_s, \text{ no screening)}$$

The reason lies in the fact that $K D_s \sim \pi$ and therefore $\rho_0 \sim K^2 \sim \frac{1}{D_s^2}$ etc. But note that the electrostatic pressure does not depend on the charge-density at all. The charges on the plates are being screened by the mobile ions available in large numbers.

At times the solution of the P-B eqn can give unrealistic values for the densities of ions right-next to the plates. In this case the P-B equation needs to be modified and the only other added ingredient is the entropy of the solvent in addition to those of the ions. In the case of 1:1 electrolyte, the PB equation with entropy modification looks like the following:

$$\rho_{\pm}(z) = \frac{\rho_0 \exp(\mp e\Psi/k_BT)}{1 - \phi_0 + \phi_0 \cosh(e\Psi/k_BT)}$$

$$\nabla^2 \Psi = -\frac{e}{\varepsilon}(\rho_+ - \rho_-) = \frac{2e\rho_0}{\varepsilon} \frac{\sinh(e\Psi/k_BT)}{1 - \phi_0 + \phi_0 \cosh(e\Psi/k_BT)}$$

where $\phi_0 = \frac{\pi a^3 \rho_0}{3}$ is the volume fraction of ions at bulk electrolyte conc^n and ρ_0 and 'a' is the molecular size of the solute and solvent. For small potentials

modified P-B
normal P-B

(Borukhov, 1997)

$Z(A°)$ 40$\mathring{A}$
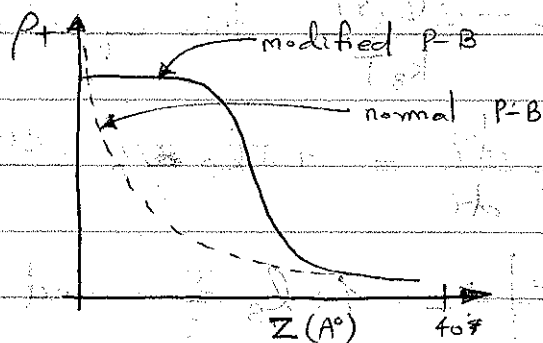
$\frac{e\Psi}{k_BT} \ll 1$, the distribution reduces to the usual Boltzmann one but for high potential the counterion density saturates at close packing densities of $1/a^3$.
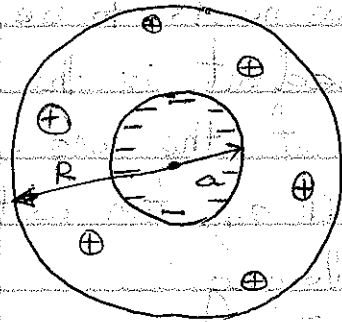
Next we want to consider the analytical solution of the P-B equation in cylindrical coordinates. This is especially useful for DNA, actin and other charged rod like polymers and colloidal particles. It is the cell model.

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2\psi}{\partial\theta^2} + \frac{\partial^2\psi}{\partial z^2} = -\frac{e\rho_0}{\varepsilon}\exp\left(-\frac{e\psi}{k_B T}\right)$$

THE CELL-MODEL

The model consists of two concentric cylinders with ionic solution in between. The inner cylinder of radius 'a' has a charge density $\sigma_s < 0$. The outer cylinder of radius R defines the total volume of the aqueous solution per cylinder.

By cylindrical symmetry and charge neutrality the electric field must vanish at R. Hence the boundary conditions are as follows:

$$\left.\frac{d\psi}{dr}\right|_{r=a} = -\frac{\sigma_s}{\varepsilon} \qquad \left.\frac{d\psi}{dr}\right|_{r=R} = 0$$

The P-B equation is

$$\nabla^2\psi = -\frac{e\rho_0}{\varepsilon}\exp\left(-\frac{e\psi}{k_B T}\right)$$

Defining $\eta(r) = -\frac{e\psi(r)}{k_B T}$ this equation reduces to,

$$\frac{d^2\eta}{dr^2} + \frac{1}{r}\frac{d\eta}{dr} = 4\pi l_B \rho_0 e^{\eta(r)}$$

with b.c $\left.\frac{d\eta}{dr}\right|_{r=a} = 4\pi l_B \frac{\sigma}{e}$ and $\left.\frac{d\eta}{dr}\right|_{r=R} = 0$

Substitutions

① $z = -\log r$

Eqn:

$e^{-2z}\frac{\partial^2\eta}{\partial z^2} = \kappa^2 e^{-2z}$

② $\eta = 2z - \log(f(z))$

We can recast this equation as,

$$\frac{d^2\eta}{dr^2} + \frac{1}{r}\frac{d\eta}{dr} = \kappa^2 e^{\eta(r)}$$

The solution is: $\eta(r) = -2\log r - \log\left(\frac{\kappa^2 \alpha^2}{2}\cos^2(\alpha\log r + \beta)\right)$ where α and β are two constants to be determined from boundary conditions. There are few other known analytical solutions to the P-B eqn.

$$\frac{d^2y}{dr^2} + \frac{1}{r}\frac{dy}{dr} = K^2 e^y$$

Here $y = y(r)$. If we take $y = y(z) = y(-\ln r)$ then

$$\frac{dy}{dz} = -r\frac{dy}{dr} \quad ; \quad -z = \ln r \Rightarrow e^{-z} = r$$

Let us now rewrite the equation above.

$$\frac{1}{r} r \frac{d}{dy}\left(\frac{1}{r} r \cdot \frac{dy}{dr}\right) = \frac{-1}{r^2} r \frac{dy}{dr} = K^2 e^y$$

Or, $e^{z}\frac{d}{dz}\left(e^{z}\frac{dy}{dz}\right) = -e^{2z}\frac{dy}{dz} = K^2 e^y$

Or, $+e^{+2z}\frac{dy}{dz} + e^{+2z}\frac{d^2y}{dz^2} - e^{2z}\frac{dy}{dz} = K^2 e^y$

Or, $e^{2z}\frac{d^2y}{dz^2} = K^2 e^y$

Or, $e^{-y}\frac{d^2y}{dz^2} = K^2 e^{-2z}$ variables separated,

Now suppose $y = 2z + \log(f(z))$

$$\frac{dy}{dz} = 2 - \frac{f'}{f}$$

$$\frac{d^2y}{dz^2} = \frac{-f''}{f} + \frac{f'^2}{f^2} \qquad\qquad \checkmark$$

This leads to

$$f\left(-\frac{f''}{f} + \frac{f'^2}{f^2}\right) = K^2$$

Or, $-f'' + \frac{f'^2}{f} - K^2 = 0$

This is a non-linear differential equation. Now suppose

$f = A\cos^2(\alpha z + B) = \frac{A}{2}(1 + \cos(2\alpha z + 2B))$

$f' = -\frac{A}{2}\times 2\alpha \sin(2\alpha z + 2B) = -A\alpha \sin(2\alpha z + 2B)$

$f'' = -2A\alpha^2 \cos(2\alpha z + 2B)$

$$-ff'' + f'^2 - k^2 f = 0$$

$$\Rightarrow A^2\alpha^2 \cos^2(2\alpha z + 2B) + A^2\alpha^2 \cos(2\alpha z + 2B)$$
$$+ A^2\alpha^2 \sin^2(2\alpha z + 2B) - \frac{k^2 A}{2}\left(\cos(2\alpha z + 2B) + 1\right) = 0$$

To satisfy this we need,

$$-\frac{k^2 A}{2} = -A^2\alpha^2$$

and

$$A^2\alpha^2 = \frac{k^2 A}{2}$$

Or,

$$A\alpha^2 = \frac{k^2}{2} \qquad \Rightarrow \qquad \sqrt{2A} = k\alpha$$

The solution to the equation is

$$f(z) = \frac{k^2\alpha^2}{2}\cos^2\left(\alpha z + B\right)$$

where α and B are arbitrary. Now, $-z = \ln r$ and

$$y(z) = 2z - \log\left(f(z)\right)$$

$$\Rightarrow y(r) = -2\log r - \log\left(\frac{k^2\alpha^2}{2}\cos^2\left(\alpha \lg r + B\right)\right)$$

So we have infact recovered the solution of the original equation. If we had $-ve$ ions istead of positive then

$$\frac{d^2 y}{dr^2} + \frac{1}{r}\frac{dy}{dr} = k^2 e^{-y}$$

Again use $z = -\ln r$ and that leads to

$$e^{2z}\frac{d^2 y}{dz^2} = k^2 e^{-y}$$

Now use $-y = 2z + \log\left(f(z)\right)$

$$\Rightarrow y = -2z + \log\left(f(z)\right)$$

$$\Rightarrow y' = -2 + \frac{f'}{f}$$

$$\Rightarrow y'' = + \frac{f'^2}{f^2} + \frac{f''}{f}$$

$$+ \frac{f'^2}{f^2} \ominus \frac{f''}{f} = \frac{K^2}{f}$$

Or, $-ff'' + f'^2 - K^2 f = 0$

The equation is the same and the solution is again,

$$f(z) = \frac{K^2 \alpha^2}{2} \cos^2(\alpha z + B)$$

$$y(z) = -2z - \log(f(z))$$

Or, $y(r) = 2\log r - \log\left(\frac{K^2 \alpha^2}{2} \cos^2(-\alpha \log r + B)\right)$

Of course α and B will be determined by the boundary conditions. And these will be different for the +ve charges and −ve charges.

It is possible to map exactly the two cylinder problem to the two-plate problem and this leads to an interesting idea. First we change the distance variable r into u.

$$u = \log \frac{r}{a} \qquad \text{(a is the radius of inner cylinder)}$$

The P-B equation then takes the form,

$$\frac{d^2 \eta}{du^2} = 4\pi \tilde{\rho}_0 \, e^{\eta + 2u}$$

where $\tilde{\rho}_0 = \ell_B a^2 \rho_0$. Make another change of variable $\psi = -\eta - 2u$ then,

$$\frac{d^2 \psi}{du^2} = -4\pi \tilde{\rho}_0 \, e^{-\psi} = -4\pi \tilde{p}(\psi)$$

with b.c $\left. \dfrac{d\psi}{du} \right|_{u=0} = 2(\ell_B c - 1)$ and $\left. \dfrac{d\psi}{du} \right|_{u=d=\log(\frac{R}{a})} = -2$.

If 'c' is the line charge density per unit length of the cylinder then $c = 2\pi a \sigma_s$, where σ_s is the surface charge density. The term $(\ell_B c - 1)$ can be positive or negative, but the b.c corresponding to outer cylinder is always negative. For $\ell_B c < 1$ the two b.c have same sign and when $\ell_B c > 1$ then the b.c have opposite sign. When $\ell_B c < 1$ then the charge density at $u = 0$ is positive and it repels the $\oplus$ counter-ions. When $\ell_B c > 1$ then the $u = 0$ surface attracts the counter-ions. This idea manifests itself in the fact that even when $R \to \infty$ some charge remains attracted towards the inner cylinder. This is called <u>Manning condensation</u>. This is a pretty non-trivial idea.

The cell-model can be used to determine the forces between macromolecules in equbm distribution of counter-ions and salt ions. We first obtain a stress-tensor on the outer surface of the cell:

$$\sigma_{ij} = \underbrace{\varepsilon \left(E_i E_j - \frac{1}{2} E^2 \delta_{ij} \right)}_{\text{Maxwell stress}} - k_B T \underbrace{\sum_p n_p \left(\phi(r) \right) \delta_{ij}}_{\text{vant-Hoff pressure}}$$

The last term is simply the van't Hoff ideal gas pressure. It has a $-ve$ sign since positive pressure is the smae as $-ve$ stress. On the outer-wall of a cell the Electric field is zero by symmetry.

$$\Pi(R) = -\sigma_{rr} = + k_B T \sum_i n_i (r = R)$$

We already know what $n_i (r=R)$ is in the case of charged rod with counter-ions only, we can substitute this above and get expression for $\Pi(R)$. This is the osmotic pressure difference between the bulk reservoir and the cell. The result is only approximate

ENTROPIC ELASTICITY OF MEMBRANES

We had considered the entropic elasticity of a one-dimensional fluctuating rod in our earlier analysis. We will now do the analysis for a lipid membrane. First some pre-liminaries. The type of membranes that we are considering consist of lipid bilayers as shown below.
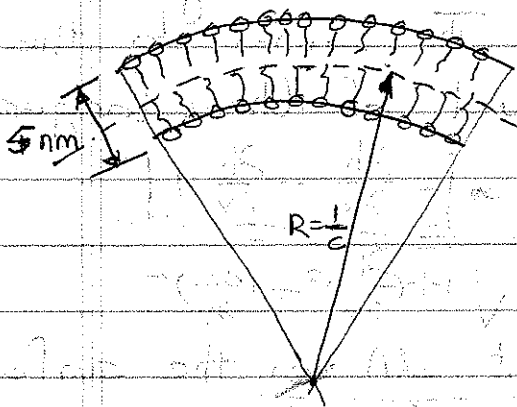

Typically, these bilayers are micrometers in spatial extent but only a few-nms thick. One therefore thinks of them as a 2D-surface embedded in 3D-space. The repulsion between the head-groups of the lipids together with the entropy of the hydrocarbon chains manifests itself as a bending rigidity of the membrane. In particular if c_1 and c_2 are the two principal curvatures at any point on the surface then the energy of the membrane is written as:

$$E = \tau \int dA + \frac{K_b}{2} \int (c_1 + c_2)^2 \, dA$$

where τ is a tension, K_b is a bending modulus and dA is an element of surface area. To integrate this expression in curvilinear co-ordinates on the surface of a membrane is an exercise in differential geometry and we do not want to do it. Instead, we will use the Monge representation in which we say that the co-ordinates of a point $\underline{r}$ on the surface are: $\underline{r} = [x \ y \ h(x,y)]$. We assume that $h(x,y)$ is single valued — a good
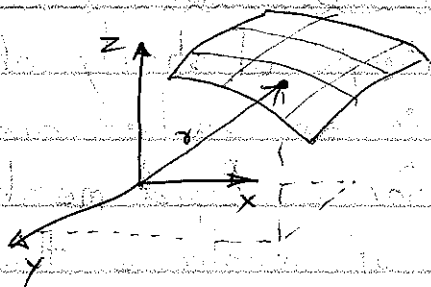
assumption if the sizes of the membrane we consider are not much larger than the bending persistence length. Clearly,

$$\frac{d\underline{r}}{dx} = \left[1, 0, \frac{\partial h}{\partial x} \right], \quad \frac{\partial \underline{r}}{\partial y} = \left[0, 1, \frac{\partial h}{\partial y} \right]. \quad \text{These are}$$

the tangents of the surface along the x and y directions respectively. The normal to the surface is the cross-product of these tangents.

$$\underline{n} = \frac{\frac{d\underline{r}}{dx} \times \frac{d\underline{r}}{dy}}{\left| \frac{d\underline{r}}{dx} \times \frac{d\underline{r}}{dy} \right|} = \frac{\left[-\frac{\partial h}{\partial x}, -\frac{\partial h}{\partial y}, 1 \right]}{\sqrt{1 + \left(\frac{\partial h}{\partial x}\right)^2 + \left(\frac{\partial h}{\partial y}\right)^2}}$$

Similarly the area element dA on the surface is

$$dA = dxdy \left| \frac{\partial \underline{r}}{\partial x} \times \frac{\partial \underline{r}}{\partial y} \right| = \sqrt{1 + h_x^2 + h_y^2} \, dx \, dy$$

where we have used short-hand $h_x = \frac{\partial h}{\partial x}$ etc. Note, here that $dxdy$ is the projected area on the xy-plane and dA is the area on the surface. They are related through the _metric_ $g = 1 + h_x^2 + h_y^2$ as $dA = \sqrt{g} \, dx \, dy$. We need to get the curvatures C_1 and C_2. These will be related to the 2nd derivative of $\underline{r}$. After going through a lengthy exercise in differential geometry one finds that,

$$C_1 + C_2 = \frac{\left[(1 + h_x^2) h_{yy} + (1 + h_y^2) h_{xx} - 2 h_x h_y h_{xy} \right]}{\left[1 + h_x^2 + h_y^2 \right]^{3/2}}$$

When the undulations are gentle $h(x,y)$ is a slowly varying function and we get,

$$C_1 + C_2 \approx h_{xx} + h_{yy}.$$

The energy in the Monge-representation then simplifies to

$$E = \int \left[\frac{\tau}{2} (h_x^2 + h_y^2) + \frac{K_b}{2} (h_{xx} + h_{yy})^2 \right] dx\, dy \longrightarrow Ⓐ$$

where we wrote $[1 + h_x^2 + h_y^2]^{1/2} = 1 + \frac{1}{2}(h_x^2 + h_y^2)$
and threw out an additive constant of the form $\int \tau\, dx\, dy$.
Just like the one-dimensional fluctuating rod we now take a fourier transform:

$$h(\underline{X}) = \frac{A}{4\pi^2} \int d\underline{q}\, \exp(i\, \underline{q} \cdot \underline{X}) h(\underline{q})$$

where $\underline{X} = \begin{bmatrix} x \\ y \end{bmatrix}$ and $\underline{q} = \begin{bmatrix} q_x \\ q_y \end{bmatrix}$ etc. We can immediately write,

$$h_x^2(\underline{X}) + h_y^2(\underline{X}) = \left[\frac{A}{4\pi^2} \right]^2 \int \left[q_x q_x' + q_y q_y' \right] h(\underline{q}) h^*(\underline{q}')$$
$$\exp(i[\underline{q} - \underline{q}'] \cdot \underline{x})\, dq_x\, dq_y\, dq_x'\, dq_y'$$

$h^*(\underline{q}')$ is the complex conjugate of $h(\underline{q}')$. Now we recall $\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(iyx)\, dy$ so that we can replace,
$\frac{1}{4\pi^2} \int \exp(i[\underline{q} - \underline{q}'] \cdot \underline{x})\, d\underline{x}$ in integral Ⓐ by $\delta(\underline{q} - \underline{q}')$.
Then integration over q_x' and q_y' results in,

$$\int dx\, dy \left[h_x^2(\underline{X}) + h_y^2(\underline{X}) \right] = \frac{A^2}{4\pi^2} \int (q_x^2 + q_y^2) h(\underline{q}) h^*(\underline{q})\, dq_x\, dq_y$$

By doing the same exercise for $(h_{xx} + h_{yy})^2$ one finds

$$\int dx\, dy \left[h_{xx}(\underline{X}) + h_{yy}(\underline{X}) \right]^2 = \frac{A^2}{4\pi^2} \int (q_x^2 + q_y^2)^2 h(\underline{q}) h^*(\underline{q})\, dq_x\, dq_y$$

Hence we are left with

$$E = \frac{1}{2} \frac{A^2}{4\pi^2} \int dq_x\, dq_y\, (\tau q^2 + K_b q^4)\, h(\underline{q}) h^*(\underline{q})$$

where $q^2 = q_x^2 + q_y^2$

Exactly in analogy to the fluctuating rod we will now compute an esemble average and get,

$$\langle h(\underline{q}) \, h^*(\underline{q}) \rangle = \frac{k_B T}{A(\tau q^2 + K_b q^4)}$$

since $\int dq_x \, dq_y$ is a sum over oscillator modes with one mode per $\frac{(2\pi)^2}{A}$ in q-space. (Recall how we define the Fourier transform of $h_x(\underline{x})$ etc.). We see clearly from above that as temperature increases the amplitude of oscillation increases as well.

But we want to determine how much area is eaten up by fluctuations at some tension. For doing this remember that

$$A = \int \sqrt{g} \, dx \, dy = \int (1 + h_x^2 + h_y^2)^{1/2} dx \, dy$$

When h_x and h_y are small then,

$$A \cong \underbrace{\int dx \, dy}_{\text{projected area}} + \underbrace{\frac{1}{2} \int (h_x^2 + h_y^2) \, dx \, dy}_{\text{area in thermal undulations}}$$

When we increase τ then we expect that the undulations will be ironed out and the projected area and true area will begin to get closer in value. We write

$$A_{red}(\tau) = \frac{1}{2} \left\langle \int (h_x^2 + h_y^2) \, dx \, dy \right\rangle$$

$$= \frac{A \, k_B T}{8 \pi^2} \int \frac{dq_x \, dq_y}{\tau + K_b q^2}$$

where we have used equipartition and the fact

$$\int (h_x^2 + h_y^2) \, dx \, dy = \frac{A^2}{4\pi^2} \int (q_x^2 + q_y^2) \, h(\underline{q}) \, h^*(\underline{q}) \, dq_x \, dq_y$$

$$\frac{\Delta A}{A} = \frac{A_{red}(0) - A_{red}(\tau)}{A}$$

We will now say $dq_x dq_y = \frac{1}{2} dq^2 d\theta$ and integrate over $d\theta$ from 0 to 2π to get

$$\frac{A_{red}(\tau)}{A} = \frac{k_B T}{8\pi} \int \frac{dq^2}{\tau + K_b q^2} \quad (q^2 = q_x^2 + q_y^2)$$

What are the limits of integration? The low value of q is $\sqrt{\frac{\pi}{Af}}$ and high value is $\frac{\pi}{b}$ where 'b' is the spacing of the molecules (lipids). We immediately get,

$$\frac{A_{red}(\tau)}{A} = \frac{k_B T}{8\pi K_b} \log \frac{\frac{\pi^2}{b^2} + \frac{\tau}{K_b}}{\frac{\pi^2}{A} + \frac{\tau}{K_b}}$$

This expression was obtained by Helfrich in 1975. The (fluctuating) component of the area vanishes when $\frac{k_B T}{K_b} \rightarrow 0$ or $\frac{\tau}{K_b} \rightarrow \infty$, both as expected. If we add the effect of how the lipid spacing changes with tension then,

$$\frac{\Delta A}{A} = \frac{k_B T}{8\pi K_b} \log \left(1 + \frac{\tau A}{\pi^2 K_b}\right) + \frac{\tau}{K_A}$$

where K_A is the area compression modulus. Using this expression one can determine both K_A and K_b in a single experiment. This was done by Evans & Rawicz in 1990 through micro-pipette aspiration experiments.

linear gives K_b

linear gives K_A
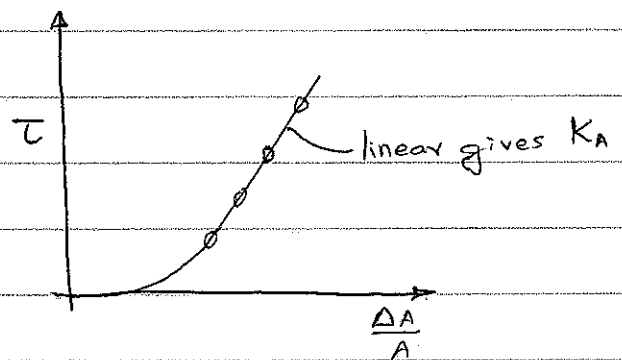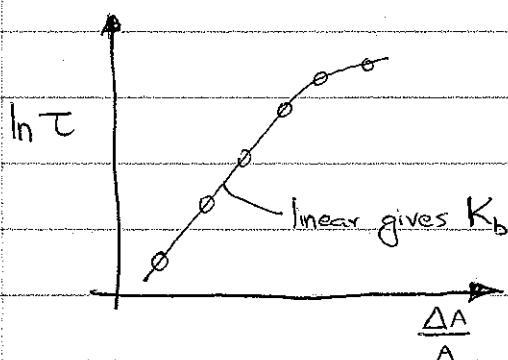
Within our theory we can also compute the amplitude of the thermal fluctuations.

$$[h(\underline{x})]^2 = \left(\frac{A}{4\pi^2}\right)^2 \int dq_x dq_y dq'_x dq'_y \, e^{i\underline{q}\cdot\underline{x}} e^{-i\underline{q}'\cdot\underline{x}} \, h(\underline{q}) h^*(\underline{q}')$$

Take an average over A by integrating over $dx\,dy$.

$$\langle h^2(\underline{x}) \rangle_{pos} = \left(\frac{A}{4\pi^2}\right)^2 \frac{1}{A} \int dx\,dy \int dq_x dq_y dq'_x dq'_y \, e^{i\underline{q}\cdot\underline{x}} e^{-i\underline{q}'\cdot\underline{x}} \, h(\underline{q}) h^*(\underline{q}')$$

The integral $\int dx\,dy \, \exp\left(i[\underline{q}-\underline{q}']\cdot\underline{x}\right) = 4\pi^2 \delta(\underline{q}-\underline{q}')$ can be removed from the above and we will be left with
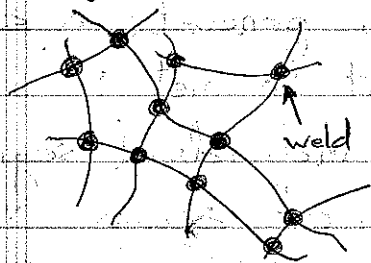
$$\langle h^2 \rangle = \frac{A}{4\pi^2} \int dq_x\,dq_y \, \langle h(\underline{q}) h^*(\underline{q}) \rangle$$

$$= \frac{A k_B T}{A \, 4\pi^2} \int \frac{dq_x \, dq_y}{\tau q^2 + K_b q^4}$$

Or, $\langle h^2 \rangle = \frac{k_B T}{4\pi\tau} \log\left(1 + \frac{\tau A}{\pi^2 K_b}\right)$

This shows how the membrane fluctuations depend on the area of the membrane. Clearly for larger tensions the amplitude of the fluctuations is smaller.

ENTROPIC ELASTICITY OF NETWORKS

Most cells consist of a lipid bilayer together with a cytoskeleton. The cytoskeleton is a two dimensional network of filaments cross-linked at various locations. For example, the RBC cytoskeleton has a spectrin network cross-linked by actin filaments. These networks endow the membrane with shear resistance. Can we write a mathematical model for ~~XXX~~ estimating the properties of this network of filaments. First let us see how networks are constructed. Throw a bunch of chains together such that they have a sufficient density to cross several ~~times~~ at locations. Then $\underline{weld}$ them together at the crossing points. After welding there are 'n' chain segments. Each of these is a FJC in its own right with the r_{ee} obeying a Gaussian probability distribution.

$$P(x) = (2\pi\sigma^2)^{-1/2} \exp\left(-\frac{r_{ee,x}^2}{2\sigma^2}\right)$$

The network nodes are not fixed. They fluctuate and the instantaneous end-to-end distance can change. Now suppose we deform the network so that the three stretches are $\Lambda_x, \Lambda_y, \Lambda_z$. The probability that a given chain 'i' has a displacement vector $\underline{r}_i = (x_i, y_i, z_i)$ $\underline{after}$ deformation can be determined from the probability that it had a displacement vector $\left(\frac{x_i}{\Lambda_x}, \frac{y_i}{\Lambda_y}, \frac{z_i}{\Lambda_z}\right)$ $\underline{before}$ deformation. Hence, the probability that the displacement of a chain lies in the range $\underline{r}_i$ and $\underline{r}_i + \Delta \underline{r}_i$ $\underline{after\ deformation}$ is

$$P\left(\frac{x_i}{\Lambda_x}, \frac{y_i}{\Lambda_y}, \frac{z_i}{\Lambda_z}\right)\left(\frac{\Delta x}{\Lambda_x}\right) \cdot \left(\frac{\Delta y}{\Lambda_y}\right) \cdot \left(\frac{\Delta z}{\Lambda_z}\right)$$

where $P(x,y,z) = \dfrac{1}{(2\pi\sigma^2)^{3/2}} \exp\left(-\dfrac{x^2+y^2+z^2}{2\sigma^2}\right)$

The actual number of chains with this value of $\underline{r}_i$ is

$$n_i = \frac{n}{(2\pi\sigma^2)^{3/2}} \frac{\Delta x \, \Delta y \, \Delta z}{\Lambda_x \Lambda_y \Lambda_z} \exp\left(\frac{-1}{2\sigma^2}\left[\left(\frac{x_i}{\Lambda_x}\right)^2 + \left(\frac{y_i}{\Lambda_y}\right)^2 + \left(\frac{z_i}{\Lambda_z}\right)^2\right]\right)$$

For instance, we can use $\sigma^2 = \dfrac{Nb^2}{3}$ for a 3D chain with N segments of equal length 'b'. We want to determine the change in free-energy during deformation. The free-energy is entirely <u>entropic</u>.

We need to evaluate the entropy, so we need to compute some probabilities. To generate a specific configuration two conditions must be met:

(a) The distribution of 'n' individual segments must have the correct number of chains n_i ~~in~~ in each range of r_i. Call it Probability P_a.

(b) each weld-site must be within the appropriate distance of a site from the neighbouring chain. Call this probability P_b.

For the weld to happen if one chain is at centre, other has to be within δv.

snap together

If n_i is the number of chains available in the original configuration to change to the new configuration and p_i is the probability that any one of these n_i chains has the correct $\underline{r}_i$ then the probability that all n_i chains have the correct $\underline{r}_i$ is $p_i^{n_i}$.

For all 'n' chains the total probability of being in the correct position is $\prod_i p_i^{n_i}$. The individual chains can be permuted in $\dfrac{\lfloor n}{\lfloor n_1 \lfloor n_2 ---\cancel{\lfloor}}$ different ways.
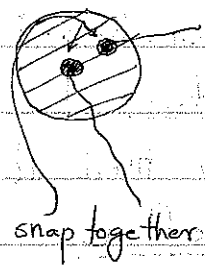
Hence, $\quad P_a = \lfloor n \prod_i \dfrac{P^{n_i}}{\lfloor n_i}$

Now, how about P_b? Remember that there are $\dfrac{n}{2}$ welds and there are 'n' weld-sites. Pick a site 1. The prob that 1 out of $n-1$ remaining sites is within a volume δV is $(n-1)\dfrac{\delta V}{V}$, where V is the volume of the network. After the first weld two welding sites are gone. For the second weld $(n-3)$ sites are available. The probability that it is within δV is $(n-3)\dfrac{\delta V}{V}$. We repeat this for $\dfrac{n}{2}$ welds.

$$P_b = (n-1)(n-3)(n-5)\cdots 1 \cdot \left(\dfrac{\delta V}{V}\right)^{n/2}$$
$$\simeq \lfloor \dfrac{n}{2} \left(2\dfrac{\delta V}{V}\right)^{n/2} \quad \left(\text{using } \left(\dfrac{n}{2}-\dfrac{1}{2}\right)\left(\dfrac{n}{2}-\dfrac{3}{2}\right)\cdots\left(\dfrac{1}{2}\right)=\lfloor\dfrac{n}{2}\right)$$

Probability for the network to have a particular shape is $P_a P_b$ and the entropy is $S = k_B \log P_a + k_B \log P_b$.

We are treating n_i as discrete here. Change to cont. and then the sum turns into an integral

$$\log P_a = n\log n + \sum_i n_i \log\left(\dfrac{P_i}{n_i}\right)$$
$$= \sum_i n_i \log\left(\dfrac{nP_i}{n_i}\right) \quad \text{since } \sum_i n_i = n.$$

This calculation is hard to do but the bottom-line is

$$\log P_a = -\dfrac{n}{2}\left[\Lambda_x^2 + \Lambda_y^2 + \Lambda_z^2 - 3 - 2\log\left(\Lambda_x \Lambda_y \Lambda_z\right)\right]$$

$$\log P_b = \log\lfloor\dfrac{n}{2} + \dfrac{n}{2}\log\left(\dfrac{2\delta v}{V_0}\right) - \dfrac{n}{2}\log\left(\Lambda_x \Lambda_y \Lambda_z\right)$$

where we wrote $V = \Lambda_x \Lambda_y \Lambda_z V_0$. So finally,

$$S = -\dfrac{k_B n}{2}\left[\Lambda_x^2 + \Lambda_y^2 + \Lambda_z^2 - 3 - \log\left(\Lambda_x \Lambda_y \Lambda_z\right) - \log\lfloor\dfrac{n}{2}\right.$$
$$\left. - \dfrac{n}{2}\log\left(\dfrac{2\delta v}{V_0}\right)\right]$$

The last two terms are independent of the deformation. So we are left with

$$\Delta F = -T\Delta S = \frac{k_B T n}{2}\left[\Lambda_x^2 + \Lambda_y^2 + \Lambda_z^2 - 3 - \log\left(\Lambda_x \Lambda_y \Lambda_z\right)\right]$$

If we require conservation of volume then $\Lambda_x \Lambda_y \Lambda_z = 1$ so that,

$$\Delta F = \frac{k_B T n}{2}\left[\Lambda_x^2 + \Lambda_y^2 + \Lambda_z^2 - 3\right]$$

Now for a pure shear $\Lambda_x = \Lambda = \frac{1}{\Lambda_y}$ and $\Lambda_z = 1$ so that

$$\Delta F = \frac{k_B T n}{2}\left(\Lambda^2 + \frac{1}{\Lambda^2} - 2\right)$$

$$= \frac{k_B T n}{2}\left(\Lambda - \frac{1}{\Lambda}\right)^2$$

Now letting $\Lambda = 1 + \delta$ where δ is small gives us

$$\Delta F = \frac{k_B T n}{2} 4\delta^2$$

and $\frac{\Delta F}{V_0} = 2\delta^2 \rho k_B T$ where ρ is the density of chains. Now let us map to macroscopic free energy density from continuum mechanics.

$$\frac{\Delta F}{V_0} = \mu \sum_{ij}\left(u_{ij} - \delta_{ij}\frac{tr\, u}{3}\right)^2 + \frac{1}{2}K_v\left(tr\, u\right)^2$$

For pure shear take $u_{xx} = \delta$, $u_{yy} = -\delta$ and $u_{zz} = 0$ then we get,

$$\frac{\Delta F}{V_0} = 2\delta^2 \mu$$

So, we finally obtain

$$\mu = \rho k_B T.$$

MEAM 663 Presentation

December 7, 2008

Contents

1 Continuous Markov processes and their Langevin equations

Central Question: What is the formula for a continuous Markov process?
   Key to the solution: Self-consistency of the formula

1.1 What is a Continuous Markov process

If X is a random variable, and its ditribution depends on time t. Then $X(t)$ is called a process.
   A continous Markov process is a process which:

1. $X(t + dt) - X(t) = \Delta(t, x, dt)$. The increasement does not depend on the history before t, or, the information before time t will not help to predict X after time t.

2. $\Delta(x, t, dt) \rightarrow 0$ as $dt \rightarrow 0$.

1.2 Central limit theorem

The sum of any K statistically independent random variables with finite means and variances will become a normal variable in the limit $K \rightarrow +\infty$.
   Mathematically, we can write:

$$\sum_{i=1}^{\infty} \xi_i = N(m, \sigma_2) \tag{1}$$

if ξ_i are independent random variables with finite means and variances. We use $N(m, \sigma_2)$ to represent a normal distribution with mean m and variance σ^2 here.

1.3 $N(m_1, \sigma_1^2) + N(m_2, \sigma_2^2) = N(m_1 + m_2, \sigma_1^2 + \sigma_2^2)$

Let x_1, x_2 be 2 normal distributions. The sum of these 2 random variables is a new random variable: $x = x_1 + x_2$, we ask the question: what is the distribution of x?

Denote

$$P(x_1) = N(m_1, \sigma_1^2) \tag{2}$$

$$P(x_2) = N(m_2, \sigma_2^2) \tag{3}$$

then we have:

$$
\begin{aligned}
P(x) &= \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \delta(x - x_1 - x_2) P(x_1) P(x_2) dx_1 \, dx_2 \tag{4} \\
&= \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \delta(x - x_1 - x_2) \frac{1}{\sqrt{2\pi}\sigma_1} e^{-\frac{(x_1 - m_1)^2}{2\sigma_1^2}} \cdot \frac{1}{\sqrt{2\pi}\sigma_2} e^{-\frac{(x_2 - m_2)^2}{2\sigma_2^2}} dx_1 \, dx_2 \tag{5} \\
&= \frac{1}{2\pi\sigma_1\sigma_2} \int_{-\infty}^{+\infty} e^{-\frac{(x_1 - m_1)^2}{2\sigma_1^2}} \cdot e^{-\frac{(x - x_1 - m_2)^2}{2\sigma_2^2}} dx_1 \tag{6} \\
&= \frac{1}{2\pi\sigma_1\sigma_2} e^{-\frac{m_1^2\sigma_2^2 + \sigma_1^2(m_2 - x)^2}{2\sigma_1^2\sigma_2^2}} \int_{-\infty}^{+\infty} e^{-ax_1^2 - 2bx_1} dx_1 \tag{7} \\
&= \frac{1}{2\pi\sigma_1\sigma_2} e^{-\frac{m_1^2\sigma_2^2 + \sigma_1^2(m_2 - x)^2}{2\sigma_1^2\sigma_2^2}} \sqrt{\frac{\pi}{a}} e^{\frac{b^2}{a}} \tag{8}
\end{aligned}
$$

where

$$a = \frac{\sigma_1^2 + \sigma_2^2}{2\sigma_1^2\sigma_2^2} \tag{9}$$

$$b = -\frac{\sigma_2^2(m_2 - x) - \sigma_2^2 m_1}{2\sigma_1^2\sigma_2^2} \tag{10}$$

Substitute a to b to Eq. 8, we finally obtain the result we want:

$$P = \frac{1}{\sqrt{2\pi(\sigma_1^2 + \sigma_2^2)}} e^{-\frac{(x - m_1 - m_2)^2}{2(\sigma_1^2 + \sigma_2^2)}} \tag{11}$$

Hence, we prove that:

$$N(m_1, \sigma_1^2) + N(m_2, \sigma_2^2) = N(m_1 + m_2, \sigma_1^2 + \sigma_2^2) \tag{12}$$

This means 2 normal random variables add up to be a new normal random variable. The mean and variance of the new variable are the sum of the means and variances of the original 2 variables.

1.4 Identifying a linear function

Show that if $h(z)$ is a smooth function, and $h(z) = nh(z/n)$ for any positive integer n, then $h(z)$ is a linear function $h = Cz$, in which C is independent of z.

Since

$$h(z) = nh\left(\frac{z}{n}\right), \quad \forall n \in \mathbf{Z}^+ \tag{13}$$

we take the derivative for both sides and get:

$$\left(\frac{dh}{dz}\right)_{z=z_0} = \left(\frac{dh}{dz}\right)_{z=z_0/n}, \quad \forall n \in \mathbf{Z}^+ \tag{14}$$

where z_0 is any real number.

Now pick any 2 real numbers z_1 and z_2

$$\left(\frac{dh}{dz}\right)_{z_1} = \lim_{n \to +\infty} \left(\frac{dh}{dz}\right)_{z_1/n} = \left(\frac{dh}{dz}\right)_{z=0} = \lim_{n \to +\infty} \left(\frac{dh}{dz}\right)_{z_2/n} = \left(\frac{dh}{dz}\right)_{z_2} \tag{15}$$

Since z_1 and z_2 are arbitrary, we conclude that:

$$\frac{dh}{dz} = C \tag{16}$$

where C is a constant, and thus:

$$h = Cz + D \tag{17}$$

where C and D are constant.

But plugging $z = 0$ into Eq. 13 gives us $h(0) = 0$, therefore $D = 0$ and we finally get:

$$h(z) = Cz \tag{18}$$

1.5 Update formula for a general continuous Markov process

Idea: for a memoryless continuous stochastic process, the increasement (if smooth) must be a normal distribution with its mean value and variace proportional to dt.

Mathematical Expression: The mathematical expression for the idea is: for a random process $x(t)$:

$$X(t + dt) = X(t) + \Delta \tag{19}$$

where Δ is random, if

1. $\Delta = \Delta(x, t, dt)$,   (memoryless condition)

2. $\Delta(x, t, dt) \to 0$ as $dt \to 0$,   (continuous condition)

3. $\Delta(x, t, dt)$ is smooth with respect to x, t and dt.

Then Δ must have the form:

$$\Delta(x, t, dt) = N\left(A(x, t)dt, D(x, t)dt\right) = A(x, t)dt + D^{1/2}(x, t) \cdot \sqrt{dt} \cdot N(0, 1) \tag{20}$$

Proof:
The formula must be self-consistent, i.e.,

$$\Delta(x, t, dt) = \sum_{i=1}^{N} \Delta(x_i, t_i, \frac{dt}{N}) \tag{21}$$

Since $\Delta \to 0$ as $dt \to 0$, the mean and variance of $\Delta(x_i, t_i, dt/N)$ must be finite. Moreover, $\Delta(x_i, t_i, dt/N)$ is independent because of the memoryless property. We take $N \to \infty$, then using the central limit theorem, we know Δ is a normal distribution.

Also, since dt is very small, we have:

$$\Delta(x, t, dt) = \sum_{i=1}^{M} \Delta(x_i, t_i, \frac{dt}{M}) \tag{22}$$

$$\approx \sum_{i=1}^{M} \Delta(x, t, \frac{dt}{M}) \tag{23}$$

$$= M\Delta(x, t, \frac{dt}{M}) \tag{24}$$

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Therefore,

$$\bar{\Delta}(x, t, dt) = M \cdot \bar{\Delta}(x, t, \frac{dt}{M}) \tag{25}$$

$$Var(\Delta)(x, t, dt) = M \cdot Var(\Delta)(x, t, \frac{dt}{M}) \tag{26}$$

Thus:

$$\begin{align} \Delta(x, t, dt) &= N\left(A(x,t)dt, D(x,t)dt\right) \tag{27} \\ &= A(x,t)dt + D^{1/2}\sqrt{dt} \cdot N(0,1) \tag{28} \end{align}$$

And the continuous Markov process has the general formula:

$$X(t + dt) = X(t) + A(x,t)dt + D(x,t)^{1/2}\sqrt{dt} \cdot N(0,1) \tag{29}$$

In general, the process is not differentiable unless $D(x,t) = 0$, but we still write:

$$\frac{dX}{dt} = A(x,t) + D(x,t)^{1/2}\Gamma \tag{30}$$

1.6 Comments

1. The update formula with $\sqrt{dt}$ and dt is non-trivial.

   Consider a ordinary deterministic function X(t), if you are told that $X(t)$ is smooth, then:

$$X(t + dt) = X(t) + A(X,t)dt \tag{31}$$

   can be derived from Taylor expansion or from

$$\frac{dX(t)}{dt} = A(x,t) \tag{32}$$

   but both these 2 methods depend on the fact the $X(t)$ is smooth.

   Here we only assume that the process is continous and get the results discussed above. In fact, the continous Markov process is not differentiable unless $D = 0$.

2. The $\sqrt{dt}$ term is larger than the dt term as $dt \to 0$. But the $\sqrt{(dt)}$ term is randomless with zero mean. So the dt term cannot be ignored. The $\sqrt{dt}$ term is strong but erratic whereas the dt term is weak and steady. They are comparable.

2 The Ornstein-Uhlenbeck process

The Ornstein-Uhlenbeck process is a continuous Markov process in which $A(x,t) = -x/\tau$ and $D(x,t) = c$.
   Central Question: What is the property of the O-U process?

2.1 General O-U process

2.1.1 Methods talked about in class

Since the general formula for the O-U process is:

$$X(t + dt) = X(t) - \frac{X}{\tau}dt + c^{1/2} \cdot (dt)^{1/2}N(0,1) \tag{33}$$

We first conclude that $X(t + dt)$ is a normal distribution because both $X(t)$ and $\Delta(x,t,dt)$ are normal distributions.
   Then we try to find its mean value and variace.
   We have from Eq. 33:

$$\frac{d<X>}{dt} = -\frac{1}{\tau}<X> \tag{34}$$

which gives us:

$$<X(t)> = x_0 \cdot e^{-\frac{t-t_0}{\tau}} \tag{35}$$

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Squaring Eq. 33 gives us:

$$X^2(t + dt) = X^2(t) - \frac{2}{\tau}X^2(t)dt + 2c^{1/2}X(t) \cdot N(t)(dt)^{1/2} + cN^2(t)dt \tag{36}$$

So:

$$\frac{d < X^2 >}{dt} = -\frac{2}{\tau} < X^2 > +c \tag{37}$$

the solution of which is:

$$< X^2 >= \frac{c\tau}{2}(1 - e^{-\frac{t-t_0}{\tau/2}}) + Ee^{\frac{t-t_0}{\tau/2}} \tag{38}$$

where E is a constant that is not determined yet.

Then:

$$Var(X) = \frac{c\tau}{2}(1 - e^{-\frac{t-t_0}{\tau/2}}) + Ee^{\frac{t-t_0}{\tau/2}} - x_0^2 e^{\frac{t-t_0}{\tau/2}} \tag{39}$$

using $Var(X)_{t=0} = 0$, we get:

$$Var(X) = \frac{c\tau}{2}(1 - e^{-\frac{t-t_0}{\tau/2}}) \tag{40}$$

Therefore,

$$X(t) = N\left(x_0 \exp(-\frac{t-t_0}{\tau}), \frac{c\tau}{2}\left(1 - \exp(-\frac{t-t0}{\tau/2})\right)\right) \tag{41}$$

To find the integral of $X(t)$: First, we have:

$$Y(t) = Y_0 + X(t_0)dt \tag{42}$$

So the fact that X(t) is normal distribution ensures Y(t) is also a normal distribution. Then we need to find the mean value and variance of $Y(t)$:

From

$$\frac{d < Y >}{dt} = < X(t) > \tag{43}$$

we get:

$$< Y(t) >= x_0\tau\left(1 - e^{-\frac{t-t_0}{\tau}}\right) \tag{44}$$

From

$$Y(t + dt) = Y(t) + X(t)dt \tag{45}$$

we get:

$$Y^2(t + dt) = Y^2(t) + 2Y(t)X(t)dt \tag{46}$$

that is:

$$< Y^2 >= 2\int_0^t < Y(t')X(t') > dt' \tag{47}$$

To get $< YX >$, we multiply the update formula for X and Y together:

$$X(t + dt)Y(t + dt) = X(t)Y(t) - \frac{X(t)Y(t)}{\tau}dt + c^{1/2}\sqrt{dt}N(0,1)Y(t) \tag{48}$$

Hence:

$$\frac{d < XY >}{dt} = -\frac{< XY >}{\tau} + < x^2 > \tag{49}$$

Now we get solve for $< XY >$ and use Eq. 47 to get Y^2 and covariance of Y:

$$Var\{Y(t)\} = c\tau^2\left[(t - t_0) - 2\tau\left(1 - e^{-\frac{t-t_0}{\tau}}\right) + \frac{\tau}{2}\left(1 - e^{-\frac{t-t_0}{\tau/2}}\right)\right] \tag{50}$$

To find the auto-covariance of $X(t)$, we first put $t = t2$ and $dt = dt_2$ in Eq. 33 and then multiply through by $X(t_1)$:

$$X(t_1)X(t_2 + dt_2) = X(t_1)X(t_2) - \frac{1}{\tau}X(t_1)X(t_2)dt_2 + c^{1/2}X(t_1)N(t_2)(dt_2)^{1/2} \tag{51}$$

Averaging this equation:

$$\frac{d}{dt_2} < X(t_1)X(t_2) >= -\frac{1}{\tau} < X(t_1) \cdot X(t_2) > \tag{52}$$

So
$$< X(t_1)X(t_2) >= E \exp(-\frac{t_2}{\tau}) \tag{53}$$

And
$$cov\{X(t_1)X(t_2)\} = E \exp(-\frac{t_2}{\tau}) - x_0^2 \exp(-\frac{t_1+t_2}{\tau}) \tag{54}$$

Using the variance at $t = t_1$, we get:

$$cov\{X(t_1)X(t_2)\} = \frac{c\tau}{2}\left(1 - e^{-\frac{t_1-t_0}{\tau/2}}\right)e^{-\frac{t_2-t_1}{\tau}} \tag{55}$$

2.1.2 Method used in Nelson's book

At $t = t_0$, we have

$$
\begin{aligned}
X(t_0 + dt) &= (1 - \frac{dt}{\tau})X(t_0) + c^{1/2}\sqrt(dt)N(0,1) && (56)\\
&= (1 - \frac{dt}{\tau})N(x_0,0) + c^{1/2}\sqrt(dt)N(0,1) && (57)\\
&= N\left((1 - \frac{dt}{\tau})x_0, cdt\right) && (58)
\end{aligned}
$$

$$
\begin{aligned}
x(t_0 + 2dt) &= (1 - \frac{dt}{\tau})X(t_0 + dt) + c^{1/2}\sqrt{dt}N(0,1) && (59)\\
&= N\left((1 - \frac{dt}{\tau})^2 x_0, \left(1 - \frac{dt}{\tau}\right)^2 \cdot (cdt) + (cdt)\right) && (60)
\end{aligned}
$$

Let $(1 - dt/\tau) = $p, we get:

$$X(t_0 + mdt) = N\left(p^m X_0, ct\left(1 + p^2 + p^3 + \cdots + p^{2(m-1)}\right)\right) \tag{61}$$

Take the limit $m \to +\infty$ (Note that p is itself a function of m), we can get the right result:

$$X(t) = N\left(x_0 e^{-\frac{t-t_0}{\tau}}, \frac{c\tau}{2}(1 - e^{-\frac{t-t_0}{\tau/2}})\right) \tag{62}$$

2.2 Special O-U process

2.2.1 Time limit process

The time limit process is ($t \to +\infty$ or $t_0 \to -\infty$):

$$X^* = N(0, \frac{c\tau}{2}) \tag{63}$$

$$Y^* = N(x_0\tau, c\tau^2(t - t_0)) \tag{64}$$

$$C_{X^*} = (\frac{c\tau}{2})e^{\frac{-t'}{\tau}} \tag{65}$$

$$S_{X^*} = \frac{2c\tau^2}{1 + (2\pi\tau\nu)^2} \tag{66}$$

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2.2.2 Zero-τ limit

In the limit $\tau \to 0$ with $\tau c^{1/2} = \epsilon$ fixed, the process become:

$$\tau \frac{dX(t)}{dt} + X(t) = \tau x^{1/2} \Gamma \tag{67}$$

Thus in the zero-τ limit, the process becomes a white noise process:

$$X(t) = \epsilon \Gamma \tag{68}$$

$$Y(t) = N(0, \epsilon^2 (t - t_0)) \tag{69}$$

$$C_{\epsilon\Gamma} = \epsilon^2 \delta(t') \tag{70}$$

$$S_{\epsilon\Gamma} = 2\epsilon^2 \tag{71}$$

2.2.3 Infinite-τ limit

When $\tau \to$, the formula is:

$$X(t + dt) = X(t) + c^{1/2} \sqrt{dt} \cdot N(0, 1) \tag{72}$$

The process is called the driftless Wiener process:

$$X(t) = N\left(x_0, \frac{c\tau}{2}\right) \tag{73}$$

$$Y(t) = N(x_0(t - t_0), \frac{C(t - t_0)^3}{3}) \tag{74}$$

3 Brownian motion

3.1 Problem description

We will begin with the equation:

$$m \frac{dv}{dt} = \gamma v + F(t) \tag{75}$$

and 3 assumptions:

1. The process is a continuous Markov process.

2. Equipartion holds: $\frac{1}{2} m < v_\infty^2 > = \frac{1}{2} k_B T$.

3. Experimental fact: $< x_\infty^2 > = D(t - t_0)$.

The following section try to give derivations of all the principal results of Bownian motion.

3.2 Solution of the Browin motion

Since the process is a continuous Markov process, from Section 1, we know that $F(t)$ must be a white noise term and thus we rewrite the Langevin's equation as:

$$\frac{dV}{dt} = -\frac{1}{\tau} + c^{1/2} \Gamma(t) \tag{76}$$

where

$$\tau = \frac{m}{\nu} \tag{77}$$

$$F(t) = m c^{1/2} \Gamma(t) \tag{78}$$

The solution of this O-U process is provided in section 2:

$$V(t) = N(V_0 e^{-\frac{t-t_0}{\tau}}, \frac{c\tau}{2}(1 - e^{-\frac{2(t-t_0)}{\tau}})) \tag{79}$$

$$x(t) = N(v_0 \tau (1 - e^{-\frac{t-t_0}{\tau}}), c\tau^2(t - t_0 - 2\tau(1 - e^{-\frac{t-t_0}{\tau}}) + \frac{\tau}{2}(1 - e^{-\frac{2(t-t_0)}{\tau}}))) \tag{80}$$

$$cov\{v(t) \cdot v(t + t')\} = \frac{c\tau}{2}(1 - e^{-\frac{2(t-t_0)}{\tau}}) e^{-\frac{t'}{t}} \tag{81}$$

3.3 Solution as $t \to +\infty$

The time infinity solution is also provided in section 2:

$$v_\infty = N(0, \frac{c\tau}{2})$$ (82)

$$x_\infty = N(v_0\tau, c\tau^2(t - t_0))$$ (83)

Using the equipartition theorem and also the experimental fact that $< x_\infty^2 >= 2D(t - t_0)$, we get:

$$\frac{c\tau}{2} = \frac{k_BT}{m}, c\tau^2 = 2D$$ (84)

which gives us:

$$\tau = \frac{Dm}{k_BT}, \quad c = \frac{2}{D}\left(\frac{k_BT}{m}\right)^2$$ (85)

Compared with Eq. 77 and Eq. 78, we get:

$$D = \frac{k_BT}{\nu}$$ (86)

$$F(t) = \sqrt{2k_BT\nu}\Gamma(t)$$ (87)

Further, the above equation gives:

$$\int_{-\infty}^{+\infty} < F(t) \cdot F(t + t') > dt' = \int_{-\infty}^{+\infty} 2k_BT\nu < \Gamma(t) \cdot \Gamma(t + t') > dt' = 2k_BT\nu$$ (88)

Finally, as $t \to \infty$, we have:

$$cov\{v(t) \cdot v(t + t')\} = \frac{c\tau}{2}e^{-\frac{t'}{\tau}}$$ (89)

Since at t infinity, the average of $v(t)$ is 0, so:

$$< v(t) \cdot v(t + t') >= cov\{v(t) \cdot v(t + t')\} = \frac{c\tau}{2}e^{-\frac{t'}{\tau}}$$ (90)

the integral of which gives:

$$\int_0^{+\infty} < v(t) \cdot v(t + t') > dt' = D$$ (91)

3.3.1 Connection with Eistein's analysis

Usually, $\tau = m/\nu$ is very small, so we can approximate the process by a zero-τ limit process (with $\tau c^{1/2} = (2D)^{1/2}$ fixed), the solution of which is given in section 2:

$$v(t) = (2D)^{1/2}\Gamma(t)$$ (92)

$$x(t) = N(0, 2D(t - t_0))$$ (93)

We recover the results:

$$< x(t) >= 0, \quad < x^2(t) >= 2D(t - t_0)$$ (94)