Notes on Polymers

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Chapter 1

Notation

The position of the monomers is represented by $\boldsymbol{R}_i$, while the relative distance or the bond vector joining two consecutive monomers is $\boldsymbol{r}_i = \boldsymbol{R}_{i+1} - \boldsymbol{R}_i$.

Chapter 2

The size of a Polymer Coil

2.1 The ideal chain

The distribution of bond vectors for a random coil is

$$p(\boldsymbol{r}) = \frac{\delta(|\boldsymbol{r}| - b)}{4\pi b^2} \tag{2.1}$$

so that it is normalised to 1. Clearly, the average of the bond vector:

$$\langle \boldsymbol{r} \rangle = \int d\boldsymbol{r} p(\boldsymbol{r})\boldsymbol{r} = 0 \tag{2.2}$$

begin the integrand odd and integrated over a symmetric $\mathbb{R}^3$ domain. Also, one should notice that the end-to-end vector in this case is:

$$\boldsymbol{R}_{ee} = \sum_i \boldsymbol{r}_i = 0 \tag{2.3}$$

but its squared vaue is of course non zero

$$\boldsymbol{R}_{ee} = \sum_{nm} \boldsymbol{r}_n \boldsymbol{r}_m = \sum_n \boldsymbol{r}_n^2 + \sum_{n \neq m} \boldsymbol{r}_n \boldsymbol{r}_m = \sum_n \boldsymbol{r}_n^2 \overset{\delta(|\boldsymbol{r}|-b)}{=} Nb^2 \tag{2.4}$$

since for any $n \neq m$ the product of two bond vectors has zero mean being independent. Now, let us compute the probability $\Phi(\boldsymbol{R}, N)$ that a random coil made of N links has an end-to-end vector $\boldsymbol{R}$.

$$\Phi(\boldsymbol{R}, N) = \int d\boldsymbol{r}_1 \dots \int d\boldsymbol{r}_N \delta \boldsymbol{R} - \sum_i \boldsymbol{r}_i \frac{\delta(|\boldsymbol{r}_i| - b)}{4\pi b^2} \tag{2.5}$$

this can be rewritten using $(2\pi)^3\delta(\boldsymbol{r}) = \int d\boldsymbol{k}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$ therefore:

$$
\begin{aligned}
\Phi(\boldsymbol{R}, N) &= \frac{1}{(2\pi)^3}\int d\boldsymbol{k}e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\left(\int d\boldsymbol{r}\frac{\delta(|\boldsymbol{r}|-b)}{4\pi b^2}e^{-i\boldsymbol{r}\cdot\boldsymbol{k}}\right)^N = \\
&= \frac{1}{(2\pi)^3}\int d\boldsymbol{k}e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\left(\int_0^\pi d\theta\sin\theta\int_0^{2\pi} d\phi\int drr^2\frac{\delta(|\boldsymbol{r}|-b)}{4\pi b^2}e^{-i\boldsymbol{r}\cdot\boldsymbol{k}}\right)^N = \\
&= \frac{1}{(2\pi)^3}\int d\boldsymbol{k}e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\left(\int_{-1}^1 d\cos\theta\frac{1}{2}e^{-irk\cos\theta}\right)^N = \\
&= \frac{1}{(2\pi)^3}\int d\boldsymbol{k}e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\left(\frac{e^{ikb}-e^{-ikb}}{2kb}\right)^N = \frac{1}{(2\pi)^3}\int d\boldsymbol{k}e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\left(\frac{\sin kb}{kb}\right)^N = \\
&\overset{N\gg1\&kb\ll1}{\simeq} \frac{1}{(2\pi)^3}\int d\boldsymbol{k}e^{i\boldsymbol{k}\cdot\boldsymbol{R}}e^{\frac{-N\boldsymbol{k}^2b^2}{6}} = \frac{1}{(2\pi)^3}\prod_{\alpha=x,y,z}\int dk_\alpha e^{ik\alpha R_\alpha-\frac{Nk_\alpha^2b^2}{6}} = \\
&= \frac{1}{(2\pi)^3}\prod_{\alpha=x,y,z}\int dk_\alpha e^{-\frac{1}{2}\left(-\frac{3R_\alpha^2}{Nb^2}-2ik\alpha R_\alpha+\frac{Nk_\alpha^2b^2}{3}\right)}e^{-\frac{3R_\alpha^2}{2Nb^2}} = \\
&= \frac{1}{(2\pi)^3}\prod_{\alpha=x,y,z}\int dk_\alpha e^{-\frac{1}{2}\left(-i\frac{\sqrt{3}R_\alpha}{\sqrt{N}b}+\frac{\sqrt{N}k_\alpha b}{\sqrt{3}}\right)^2}e^{-\frac{3R_\alpha^2}{2Nb^2}} = \frac{1}{(2\pi)^3}\prod_{\alpha=x,y,z}\int dk_\alpha e^{-\frac{k_\alpha^2}{2}\frac{Nb^2}{3}}e^{-\frac{3R_\alpha^2}{2Nb^2}} = \\
&= \left(\frac{3}{2\pi Nb^2}\right)^{3/2}e^{-\frac{3(R_x^2+R_y^2+R_z^2)}{2Nb^2}} = \left(\frac{3}{2\pi Nb^2}\right)^{3/2}e^{-\frac{3\boldsymbol{R}^2}{2Nb^2}}
\end{aligned}
$$

using $\sin x/x \simeq 1 - x^2/6 \simeq e^{x^2/6}$.

2.2 Gaussian Chain

In practice the Gaussian chain approximation is much more used also because physically closer to the concept of Hamiltonian. For instance, for a chain whose bonds can be described by a distribution

$$\psi(\boldsymbol{r}) = \left(\frac{3}{2\pi b^2}\right)^{3/2}e^{-3\boldsymbol{r}^2/2b^2} = \left(\frac{3}{2\pi b^2}\right)^{3/2}e^{-3(\boldsymbol{R}_{i+1}-\boldsymbol{R}_i)^2/2b^2} \tag{2.6}$$

one can think the bonds as springs of energy

$$H = k_bT\frac{3}{2b^2}(\boldsymbol{R}_{i+1}-\boldsymbol{R}_i)^2 \tag{2.7}$$

which at equilibrium are distributed as (2.6). One of the most important properties of a Gaussian chain is that it is self=similar, meaning that any segment of a Gaussian chain is Gaussian:

$$\Phi(\boldsymbol{R}_m-\boldsymbol{R}_n, |m-n|) = \left(\frac{3}{2\pi|m-n|b^2}\right)^{3/2}e^{-3(\boldsymbol{R}_m-\boldsymbol{R}_n)^2/2b^2|m-n|} \tag{2.8}$$

which gives that the end-to-end distance of a Gaussian chain of $|n-m|$ links is

$$\langle(\boldsymbol{R}_n-\boldsymbol{R}_m)^2\rangle = |n-m|b^2. \tag{2.9}$$

Now, actually there is a better measure for a polymer, the radius of gyration, which is basically the second moment of its mass distribution, the mean being the centre of mass $\boldsymbol{R}_G = \sum_n \boldsymbol{R}_n/N$. The radius of gyration is defined as

$$R_g^2 = \frac{1}{N}\sum_n\langle(\boldsymbol{R}_n-\boldsymbol{R}_g)^2\rangle \tag{2.10}$$

another form of (2.10) can be found easily by noting:

$$R_g^2 = \frac{1}{N}\left\langle \sum_n \boldsymbol{R}_n^2 - 2\sum_n \boldsymbol{R}_n\boldsymbol{R}_G + \boldsymbol{R}_G^2 \right\rangle = \left\langle \frac{1}{N}\sum_n \boldsymbol{R}_n^2 - 2\frac{1}{N^2}\sum_n \boldsymbol{R}_n \cdot \sum_m \boldsymbol{R}_m + \frac{1}{N^3}\sum_m\sum_i \boldsymbol{R}_m \cdot \boldsymbol{R}_i \right\rangle =$$
$$= \left\langle \frac{1}{N}\sum_n \boldsymbol{R}_n^2 - 2\frac{1}{N^2}\sum_n \boldsymbol{R}_n \cdot \sum_m \boldsymbol{R}_m + \frac{1}{N^2}\sum_m \boldsymbol{R}_m^2 + \frac{1}{N^3}\sum_{m\neq i} \boldsymbol{R}_m \cdot \boldsymbol{R}_i \right\rangle =$$
$$= \left\langle \frac{1}{N}\sum_n \boldsymbol{R}_n^2 - \frac{1}{N^2}\sum_n\sum_m \boldsymbol{R}_n \cdot \boldsymbol{R}_m \right\rangle = \frac{1}{2N^2}\sum_{n,m}\langle(\boldsymbol{R}_n - \boldsymbol{R}_m)^2\rangle$$

By using this form for the gyration radius and eq.(2.9) it is easy to compute the radius of gyration of a Gaussian linear chain:

$$R_g^2 = \frac{1}{2N^2}\sum_{n=1}^{N}\sum_{m=1}^{N}\langle(\boldsymbol{R}_n - \boldsymbol{R}_m)^2\rangle = \frac{1}{2N^2}\sum_{n=1}^{N}\sum_{m=1}^{N}|n-m|b^2 =$$
$$= \frac{1}{2N^2}\int_0^N\int_0^N dndm|n-m|b^2 = \frac{1}{N^2}\int_0^N\int_0^n dndm(n-m)b^2 =$$
$$= \frac{1}{N^2}\left(\int_0^N n^2b^2dn - \int_0^N \frac{n^2}{2}b^2\right) = \frac{b^2}{N^2}\left(\frac{N^3}{3} - \frac{N^3}{6}\right) = \frac{Nb^2}{6}$$

2.3 Flexible Chains

2.3.1 Discrete Picture

In the case we are considering a semiflexible polymer with Kuhn length $l_K = Pb$ and contour length $L_c = Nb$ the formula for the radius of gyration becomes:

$$R_g^2 = 2l_K L_c\left[\frac{1}{6} - \frac{l_K}{2L_c} + \frac{l_K^2}{L_c^2} - \frac{l_K^3}{L_c^3}\left(1 - e^{-}L_c/l_k\right)\right] \tag{2.11}$$

also called Benoit-Doty equation (I can't find any derivation though). The other formula often used and derived in Doi-Edwards, is the formula for a Kratky-Porod chain with persistence length l_p. In this case the bending penalty is function of the type: $E_b = \cos\theta^{|s-t|}$, where $|s-t|$ is the contour distance of two segments which have are rotated by an angle θ w.r.t. each other, *i.e.*

$$\langle \boldsymbol{r}_i \cdot \boldsymbol{r}_j\rangle = b^2\langle\cos\theta_{ij}\rangle = b^2\prod_{k=i}^{j-1}\cos\theta_{k,k+1} = b^2\langle\cos\theta\rangle^{|i-j|} \tag{2.12}$$

In other words, any vector is rotate w.r.t. the previous by an amount $\cos\theta$, while the product of a vector with itself is the length b^2. Formally $\boldsymbol{r}_n = \cos\theta\boldsymbol{r}_{n-1}$ and

$$\langle \boldsymbol{r}_n \cdot \boldsymbol{r}_m\rangle = \langle \boldsymbol{r}_{n-1} \cdot \boldsymbol{r}_m\rangle\cos\theta \text{ with } \langle \boldsymbol{r}_n^2\rangle = b^2 \tag{2.13}$$

As usual, the end to end distance is the sum of all the vectors $\boldsymbol{r}$ as:

$$\langle \boldsymbol{R}_{ee}^2\rangle = \langle\sum_i \boldsymbol{r}_i \cdot \sum_j \boldsymbol{r}_j\rangle = \sum_{i,j=1}^{N}\langle \boldsymbol{r}_i \cdot \boldsymbol{r}_j\rangle \overset{\substack{i\to(i+j)/2=n\\ j\to i-n=k}}{=} \sum_{n=1}^{N}\sum_{k=-n+1}^{N-n}\langle \boldsymbol{r}_n \cdot \boldsymbol{r}_{n+k}\rangle \overset{(2.12)}{=}$$
$$\simeq \sum_{n=1}^{N}\sum_{k=-\infty}^{\infty}\langle \boldsymbol{r}_n \cdot \boldsymbol{r}_{n+k}\rangle = N\left(\langle \boldsymbol{r}_n^2\rangle + 2\sum_{k=1}^{\infty} b^2\cos\theta^k\right) = Nb^2\frac{1+\cos\theta}{1-\cos\theta}$$

Clearly here, one can call a new bead length $\bar{b}$ to be the rescaled version of b depending on the average value of $\underline{\cos\theta \text{ (and not! } \theta \text{ which would give } \langle\cos\theta\rangle = 1)}$. If this is zero, than one retrieves the random flight model, instead if $\theta = 0$ and $\langle\cos\theta\rangle = 1$ one gets a infinitely persistent walk!

2.3.2 Continuous Picture

The continuous version of the model described above is the Kratky-Porod model for worm like chains. The bending potential one usually uses to model this is the following:

$$U_{bend}(\boldsymbol{r}_i, \boldsymbol{r}_j) = \frac{\epsilon l_p}{\sigma} \left(1 + \frac{\boldsymbol{r}_i \cdot \boldsymbol{r}_j}{r_{ij}}\right) \tag{2.14}$$

where this is a function of the (complementary) angle between adjacent vectors, regulated by a spring of stiffness proportional to the persistence length l_p.

Another way of modelling this is the following; If we have a chain long L, and $\boldsymbol{u}(x) = \partial\boldsymbol{R}/\partial s(x)$ is the tangent along the contour at point x, one has a potential :

$$U_{bend} = \frac{E}{2} \int_0^L ds \left(\frac{\partial \boldsymbol{u}}{\partial s}\right)^2 \tag{2.15}$$

thus the conformation distribution of a polymer with this feature is described by a Boltzmann distribution for this energy, which is:

$$\Psi[\boldsymbol{u}] \propto \exp\left(\frac{-U_{bend}}{k_B T}\right) = \exp\left[-\frac{E}{2k_B T} \int_0^L ds \left(\frac{\partial \boldsymbol{u}}{\partial s}\right)^2\right] \tag{2.16}$$

$E/k_B T$ has measure of length, begin the argument of the exponential adimensional and the integral having dimensions of inverse length (curvature). This is why we an write E as in the model above, *i.e.* $l_p\epsilon$, visualising the stiffness of the spring as an energy ϵ typically equal to $k_B T$ times l_p.

Correlation $\langle \boldsymbol{u}(t) \cdot \boldsymbol{u}(0) \rangle$

At this point one has to compute the correlation between tangent vectors! This is written as:

$$\langle \boldsymbol{u}(t) \cdot \boldsymbol{u}(0) \rangle = \int d\boldsymbol{u} \int d\boldsymbol{u}' \boldsymbol{u} \cdot \boldsymbol{u}' G(\boldsymbol{u}, \boldsymbol{u}'; t) \Psi_{eq}(\boldsymbol{u}') \tag{2.17}$$

this equation simply says to compute the dot product between tangent vectors and give a weight $G(\dots)$ to a particular product. This is the conditional probability that a polymer takes direction $\boldsymbol{u}$ at time (or contour step) t, given that it start (at $t = 0$) in direction $\boldsymbol{u}'$. The last factor, Ψ is the equilibrium distribution of the vectors $\boldsymbol{u}'$ and gives a weight to the integral based on the particular starting direction (which actually is uniform in this case, as there s no preferred starting direction). Now, the conditional probability is nothing else than the Green function $G(\boldsymbol{u}, \boldsymbol{u}'; t)$ that describes the rotational Brownian motion with diffusion coefficient D_r, and that satisfies:

$$\frac{\partial G(\boldsymbol{u}, \boldsymbol{u}'; t)}{\partial t} = D_r \mathcal{R}^2 G(\boldsymbol{u}, \boldsymbol{u}'; t) \tag{2.18}$$

where $\mathcal{R}$ is the rotational operator, and it can be expressed as:

$$\mathcal{R} = \boldsymbol{u} \times \frac{\partial}{\partial u} \tag{2.19}$$

or in index notation $\mathcal{R}_\alpha = \epsilon_{\alpha\beta\gamma} u_\beta \partial_\gamma$, where $\partial_\gamma = \partial/\partial u_\gamma$. Also notice that the rotational operator is also used in Quantum mechanics and is Hermitian, *i.e.* $\int ds \mathcal{R}[AB] = 0 \leftrightarrow -\int ds[\mathcal{R}A]B = \int ds A[\mathcal{R}B]$. OK.

Let's go back to the computation of the correlation function. Let's take its time derivative:

$$\begin{aligned}\frac{\partial\langle \boldsymbol{u}(t)\cdot\boldsymbol{u}(0)\rangle}{\partial t} &= \int d\boldsymbol{u}\int d\boldsymbol{u}'\boldsymbol{u}\cdot\boldsymbol{u}'\frac{\partial}{\partial t}G(\boldsymbol{u},\boldsymbol{u}';t)\Psi_{eq}(\boldsymbol{u}') = \\ &= D_r\int d\boldsymbol{u}\int d\boldsymbol{u}'\boldsymbol{u}\cdot\boldsymbol{u}'\mathcal{R}^2 G(\boldsymbol{u},\boldsymbol{u}';t)\Psi_{eq}(\boldsymbol{u}') = \\ &= D_r\int d\boldsymbol{u}\int d\boldsymbol{u}'\left[\mathcal{R}^2\boldsymbol{u}\cdot\boldsymbol{u}'\right]G(\boldsymbol{u},\boldsymbol{u}';t)\Psi_{eq}(\boldsymbol{u}') \end{aligned} \tag{2.20}$$

at this point one uses this:

$$\mathcal{R}_\alpha u_k = \epsilon_{\alpha\beta\gamma}u_\beta\partial_\gamma u_k = \epsilon_{\alpha\beta\gamma}u_\beta\delta_{\gamma k} = \epsilon_{\alpha\beta\gamma}u_\beta = -\epsilon_{\alpha\gamma\beta}u_\beta = -\epsilon_{\alpha\beta\gamma}u_\gamma \tag{2.21}$$

and by applying this twice:

$$\mathcal{R}_\alpha^2 u_k = -\epsilon_{\alpha\beta\gamma}\mathcal{R}_\alpha u_\gamma = -\epsilon_{\alpha\beta\gamma}\epsilon_{\alpha\mu\nu}u_\mu\partial_\nu u_\gamma = -\left(\delta_{\beta\mu}\delta_{\gamma\nu} - \delta_{\beta\nu}\delta_{\gamma\mu}\right)u_\mu\delta_{\nu\gamma} = -3u_\beta + u_\beta = -2u_\beta \tag{2.22}$$

Perfect! And then by using this into eq. (2.20), one gets:

$$\frac{\partial\langle \boldsymbol{u}(t)\cdot\boldsymbol{u}(0)\rangle}{\partial t} = -2D_r\int d\boldsymbol{u}\int d\boldsymbol{u}'\boldsymbol{u}\cdot\boldsymbol{u}'G(\boldsymbol{u},\boldsymbol{u}';t)\Psi_{eq}(\boldsymbol{u}') = -2D_r\langle\boldsymbol{u}(t)\cdot\boldsymbol{u}(0)\rangle \tag{2.23}$$

which simply gives:

$$\langle\boldsymbol{u}(t)\cdot\boldsymbol{u}(0)\rangle = \exp\left(-2D_r t\right) \tag{2.24}$$

being the rotational correlation time (or the rotational correlation length) equal to $\tau_r = 1/2D_r$. Aslo it follows easily that the mean squared displacement is:

$$\langle(\boldsymbol{u}(t) - \boldsymbol{u}(0))^2\rangle = 2\langle\boldsymbol{u}\rangle^2 - 2\langle\boldsymbol{u}(t)\cdot\boldsymbol{u}(0)\rangle = 2\left(1 - e^{-2D_r t}\right) \tag{2.25}$$

in the limit $t \gg 1/2D_r$ than one can approximate this to the usual MSD:

$$\langle(\boldsymbol{u}(t) - \boldsymbol{u}(0))^2\rangle = 4D_r t. \tag{2.26}$$

Very well now, let's go back to the calculation of the end to end size for a flexible polymer. This can be computed as (here I'm using the continuous version of $\boldsymbol{r}$ *id est* $\boldsymbol{u}$):

$$\begin{aligned}\boldsymbol{R}_{ee}^2 &= \int dt\int ds\langle\boldsymbol{u}(t)\cdot\boldsymbol{u}(s)\rangle = \int_0^L ds\int_0^L dte^{-2D_r|t-s|} = \\ &= 2\int_0^L dt\int_0^t dse^{-2D_r(t-s)} = \frac{1}{D_r}\int_0^L dte^{-2D_r t}\left(e^{2D_r t} - 1\right) = \\ &= \frac{L}{D_r} - \frac{1}{2D_r^2}\left(1 - e^{-2D_r L}\right) = 2l_k L - 2l_k^2\left(1 - e^{-L/l_k}\right)\end{aligned}$$

where $l_k = 1/2D_r$ is the Kuhn length and is twice the persistence length l_p. *i.e.* . The radius of gyration R_g is related to this as $R_g^2 = R_{ee}^2/12$ and therefore one finally gets the Kratky-Porod form of the radius of gyration:

$$R_g^2 = \frac{l_k L}{6} - \frac{l_k^2}{6}\left(1 - e^{-L/l_k}\right) \tag{2.27}$$

where one gets the ideal random walk behaviour in the limit $L \gg l_k$ as $R_g^2 \sim l_k L = constNb^2$ (*i.e.* $\exp() \sim 1$), and in the other limit, $L \ll l_k$ one can expand the exp and gets $R_g^2 \sim L^2$, *i.e.* a rod-like behaviour.

2.4 Coil-to-Globule transition

TODO

Chapter 3

Excluded Volume Models

From Doi-Edwards: "In real polymers, the nature of the long range interaction is quite complicated: the interaction will include steric effects, van der Waals attraction, and also may involve other specific interactions mediated by solvent molecules. However, as far as the property of large length scale is concerned, the detail of the interaction will not matter because the excluded volume effect is controlled by the interaction between distant parts of the chain."

The exclude volume function is then some function of the distance $\boldsymbol{r}$, $v(\boldsymbol{r})$ which gives a total steric energy

$$U_{excl} = \int dn \int dm k_B T v(\boldsymbol{R}_n - \boldsymbol{R}_m) \simeq \frac{1}{2} k_B T v \int dn \int dm \delta(\boldsymbol{R}_n - \boldsymbol{R}_m) \tag{3.1}$$

where we approximated this un-known function with a delta function. We can go further, and consider the concentration of segments at $\boldsymbol{r}$,

$$c(\boldsymbol{r}) = \sum_n \delta(\boldsymbol{r} - \boldsymbol{R}_n) = \int_0^N dn \delta(\boldsymbol{r} - \boldsymbol{R}_n) \tag{3.2}$$

and use this as repulsive term for the steric energy:

$$U_{excl} = \frac{1}{2} k_B T v \int dn \int dm \delta(\boldsymbol{r} - \boldsymbol{R}_n) \delta(\boldsymbol{r} - \boldsymbol{R}_m) = \frac{1}{2} k_B T v c(\boldsymbol{r})^2 \tag{3.3}$$

This expression is the *first* virial term in the **virial expansion** which can, in principle, contain any term in power of the concentration c. Clearly, the higher the power of c, the smaller the term if c is small. Also, the concentration can be evaluated as the mass over the d-dimensional volume occupied:

$$c = \frac{N}{R_g^d} = N^{1-3\nu}, \text{where } \nu \text{ is the entropic exponent.} \tag{3.4}$$

3.1 The entropic exponent ν

The original idea of Flory for calculating the size of a polymer is to consider the balance of two effects: a repulsive excluded volume interaction which tends to swell the polymer, and the elastic energy arising from the chain connectivity which tends to shrink the polymer. This idea can be put into a particularly simple form of theory.

First: Recall that for a Gaussian chain the free energy can be found as the logarithm of its distribution. Hence the following is the free energy of a chain of N links with end-to-end vector $\boldsymbol{R}$:

$$A(\boldsymbol{R}) = -k_B T \log \Phi(\boldsymbol{R}, N) = \frac{3 k_B T \boldsymbol{R}^2}{2Nb^2} \tag{3.5}$$

This is forcing the chain to shrink due to its connectivity, if we were to try to pull such polymer we would feel a restoring force, as an entropic spring with energy (3.5).

Second: We also need to take into account the excluded volume interactions; these are described by an unknown exponent ν. Imagine to confine a gas in a volume $|\boldsymbol{R}|^3$ with a concentration $c = N/R^3$, the energy of the steric interaction would be

$$E = \frac{1}{2} v k_B T c^2 R^3 \simeq k_B T v \frac{N^2}{R^3} \tag{3.6}$$

Because of these two effects, we get a corrected free energy

$$A_{eff}(\boldsymbol{R}) \simeq k_B T \left(\frac{3R^2}{2Nb^2} + v \frac{N^2}{R^3} \right) \tag{3.7}$$

from which we can obtain the most likely value of the size R by minimising this w.r.t R:

$$\frac{\partial A_{eff}}{\partial R} \simeq k_B T \left(\frac{6R}{2Nb^2} - 3v \frac{N^2}{R^4} \right) \overset{!}{=} 0 \tag{3.8}$$

which gives:

$$\bar{R} = \left(v N^3 b^2 \right)^{1/5} \sim N^{3/5} \text{ as wanted/expected} \tag{3.9}$$

The Flory argument is actually wrong, and by luck mistakes cancel each others in this case producing a result close to experiments. It is wrong because the corrected free energy does not describe the free energy observed for polymers in solution in simulations. There must be something else going on (find out).

3.1.1 Are Polymer Coils Impenetrable?

Here I will talk about a very important point, which I believe it is at the very heart of my PhD. It all starts with Grosberg's paper [4] and then very interestingly pointed out more recently to compute the repulsion of knotted and circular polymer coils [5].

The question is: what is the energy penalty of two overlapping polymer coils? If this is increasing with the length of the polymers then in the limit of large coils, this divereges and coils are actually impenetrable. On the other hand, if this was a finite energy penalty for any value of M it would not represent a major obstacle to coils interpenetration.

Let M be the length of the coils and a the size of a monomer. Then following older works [**?**], the mean radius of gyration of the coil is $R \sim aN^{\nu}$ with $\nu = 0.588$ in 3D. The volume occupied is therefore $V \sim R^3 \sim a^3 M^{3\nu}$. Let's consider strongly overlapping coils, *i.e.* two coils share exactly the same volume V. It is clear that the energy penalty grows proportionally with the number of contacts between monomers. In particular, $F_{int} \sim k_B T S$, where S is the average number of contacts between polymers.

S can be estimated by the self-consistent mean field approximation where one visualises a coil as a cloud of monomers distributed independently in a volume R^3. In this case the number of contacts is equal to the product of the number of monomers of one of the coils in the overlap region ($\sim nV$) and of the contact probability for each of these monomers ($\sim na^3$), or $F_{int} \sim k_B T nV na^3$. The number of monomers in the overlapping region nV is given by the self density: $\rho_{self} = n = MR^{-3} = a^{-3}M^{1-3\nu}$. From which one finds $F_{int} \sim k_B T M^{2-3\nu}$. By plugging $\nu = 3/5$ for linear SAWs one gets $F_{int} \sim k_B T M^{1/5}$ which diverges with the length of the coil. This means that in the limit of large coils, they repel one another and tend to segregate.

Equivalently one can compute this as $S = \rho_{self}^2 R^3 \sim M^{2-3\nu}$.

The above calculation treats the coils and clouds of monomers whose interaction is independent of the neighbours. In reality, monomers are placed along the coil in "sub-clouds" and the interaction of these sub-clouds leads to an enhanced repulsion and a decreases in the contact probability. This changes the picture dramatically.

The contact probability of two monomers of different chains is of the order $(na^3)^{1/(3\nu-1)}$ [1] (instead of na^3 of the self-consistent field approximation). Therefore by using this one gets the estimate for the free energy:

$$F_{int} \sim k_B T nV (na^3)^{1/(3\nu-1)} \sim k_B T M \left(M^{1-3\nu}\right)^{1/(3\nu-1)} \sim k_B T \tag{3.10}$$

which is independent of the coil length and means that interpenetrations only cost few $k_B T$s and are therefore abundant!!

Following Marenduzzo [5] (using Duplantier's work [2]) one can find that two loops which are brought in contact can be described by a free energy difference which is given in terms of a change in one of the notes of a network of polymers. In fact two 2-legs vertices become one 4-legged one as two loops touch one another. Following Duplantier, this is captured by a new partition function $\mathcal{Z}' \simeq S^{\gamma_4 - 1}$ from $\mathcal{Z} \simeq S^{2\gamma_2 - 2}$ the difference in free energy is the log of their ratio:

$$\Delta F = -k_B T \frac{2\gamma_2 - \gamma_4 - 1}{\nu} \log(x) \tag{3.11}$$

where $S = N^\nu$ is the Hausdorff space covered by the polymer, *i.e.* $1/\nu = d_f$ is the Hausdorff dimension and $x = r/N^\nu$ is the ratio of distance of the two roots of the loops over the size of the loops.

I don't really get 100% of this.

3.1.2 Real Mean Field

A real mean field argument should be formulated as follows: take the average concentration $c(\boldsymbol{r}) = \int dn \delta(\boldsymbol{r} - \boldsymbol{R}_n)$, every segment would feel the same average potential $c(\boldsymbol{r})$, therefore we can describe the the statistical distribution as shifted by a virial term:

$$\Psi[\{\boldsymbol{r}_n\}] \sim \exp\left\{-\frac{3}{2Nb^2}\int dn \left(\frac{d\boldsymbol{R}_n}{dn}\right)^2 - \frac{v}{2}\int dr c(\boldsymbol{R}_n)\right\} \tag{3.12}$$

and its Green function can then be computed as a solution of the Schroedinger-like equation

$$\left[\frac{\partial}{\partial n} - \frac{b^2}{6}\frac{\partial^2}{\partial \boldsymbol{R}^2} + \frac{v}{2}c(\boldsymbol{R})\right] G(\boldsymbol{R}, 0, N) = \delta(\boldsymbol{R})\delta(N) \tag{3.13}$$

and with the Green function one can calculate self-consistently the concentration as

$$c(\boldsymbol{R}_n) = \frac{1}{G(\boldsymbol{R}, 0, N)} \int_0^N G(\boldsymbol{R}, \boldsymbol{r}, N-n) G(\boldsymbol{r}, 0, n) \tag{3.14}$$

which clearly is the integral over all the possible mid-points, of two paths covering the polymer. The integral over this, normalised, will give the concentration of the polymer segments in a volume.

3.2 Scaling Arguments for Predicting the Size

By only making some sound scaling arguments, one can get so much insight into the physics of the system. For instance, we want to express the size of the polymer; We can do that in many ways, R_g, $R_e e$ or other measures, but all of them must be related somehow. Clearly, they have to be a function of the only length-scale of the system, b. Also, given the Gaussian nature of the chain, we expect that by halving the number of links but multiplying the monomer size by $\sqrt{2}$, nothing should change, as $R = \sqrt{N}b = \sqrt{N/2}\sqrt{2}b$. Therefore we expect:

$$R = F(N)b \tag{3.15}$$

where $F(N)$ is a dimensionless function of the number of monomers N. Now, we know that this has to be invariant under re-scaling, i.e.

$$F(N/\lambda)\sqrt{\lambda}b = R = F(N)b \tag{3.16}$$

which is satisfied only when $F(N) = number \times \sqrt{N}$, and this is why any measure of the size of the polymers is related to each other by only numerical factors. For the excluded volume case, the transformation which leaves the system invariant is $N \to N/\lambda$ and $b \to b\lambda^{\nu}$

Chapter 4

Hydrodynamics

We want to capture how to describe the motion of particles in a viscoelastic medium. At first, one has to realise that the velocity field is caused by forces acting on the particles. This is given by:

$$V_n = H_{nm} F_m \tag{4.1}$$

where H_{nm} is the mobility tensor that describes the response of the medium to a force F_m. In the dilute limit, it is clear that the response of a particle is **only** due to the force applied on it, for this reason the mobility tensor is the more familiar

$$H_{nm} = \frac{\boldsymbol{I}\delta_{mn}}{\zeta} \tag{4.2}$$

where $\zeta = 6\pi\eta r$ is the friction on a particle of radius r in a medium with viscosity η. On the other hand, in general, the response of a particle to an external force is due to its interaction with the environment. For instance, in the case of hydrodynamic interaction, the motion of nearby particles create a flow which affects other particles. This is why H_{nm} takes in general more complicated forms. Let's see what are they.

4.1 Assumptions

First: Fluid is incompressible means that is divergence free in the velocity. There is no sink or source of velocity, *i.e.*

$$\frac{\partial v_\alpha}{\partial r_\alpha} = 0 \tag{4.3}$$

Second: The particles are moving in a system with low Reynolds number, which means that the inertia is negligible compared to the viscosity, *i.e.* $Re = \rho v L/\eta \ll 1$. For this reason one can write that the gradient of the stress on the system is equal to the external force $\boldsymbol{f}$ applied:

$$\frac{\partial \sigma_{\alpha\beta}}{\partial r_\beta} = -f_\alpha(\boldsymbol{r}) \tag{4.4}$$

4.2 The Equations

We first define the stress tensor as one diagonal part, and an off-diagonal part. The former is related to pressure, the other to shear, *i.e.*

$$\sigma_{\alpha\beta} = \eta\left(\frac{\partial v_\alpha}{\partial r_\beta} + \frac{\partial v_\beta}{\partial r_\alpha}\right) + P\delta_{\alpha\beta} \tag{4.5}$$

By using eq. (4.4) **and** eq. (4.3) one can write:

$$\frac{\partial \sigma_{\alpha\beta}}{\partial r_\beta} = \eta\left(\frac{\partial^2 v_\alpha}{\partial r_\beta^2} + \frac{\partial}{\partial r_\alpha}\frac{\partial v_\beta}{\partial r_\beta}\right) + \frac{\partial P}{\partial r_\alpha} \overset{(4.3)}{=} \eta\frac{\partial^2 v_\alpha}{\partial r_\beta^2} + \frac{\partial P}{\partial r_\alpha} = -f_\alpha \tag{4.6}$$

This, and the incompressibility equation are called the Stokes approximation.

Now, let's consider forces $\boldsymbol{F}$ applied on point-like particles at positions $\boldsymbol{R}_n$. Such that

$$f_\alpha(\boldsymbol{r}) = \sum_n F_\alpha \delta(\boldsymbol{r} - \boldsymbol{R}_n) \tag{4.7}$$

In this case eq. (4.6) becomes:

$$\eta\frac{\partial^2 v_\alpha}{\partial r_\beta^2} + \frac{\partial P}{\partial r_\alpha} = -\sum_n F_\alpha \delta(\boldsymbol{r} - \boldsymbol{R}_n) \tag{4.8}$$

or in vectorial notation

$$\eta\nabla^2 \boldsymbol{v} + \boldsymbol{\nabla} P = -\sum_n \boldsymbol{F}\delta(\boldsymbol{r} - \boldsymbol{R}_n) \tag{4.9}$$

Equations eq. (4.3) and eq. (4.9) are "easily" solved (see next section) and the result is that the velocity field can be written as

$$\boldsymbol{v}(\boldsymbol{r}) = \sum_n \boldsymbol{H}(\boldsymbol{r} - \boldsymbol{R}_n) \cdot \boldsymbol{F}_n \tag{4.10}$$

clearly, it has to be that the velocity field at $\boldsymbol{r}$ is the resultant of the forces applied to the point particles mediate by the **Oseen tensor**:

$$\boldsymbol{H}(\boldsymbol{r}) = \frac{1}{8\pi\eta r}\left(\boldsymbol{I} + \frac{\boldsymbol{rr}}{r^2}\right) \tag{4.11}$$

where $\boldsymbol{rr}/r^2$ is a tensor, *i.e.* $r_\alpha r_\beta$ divided by the squared length of $\boldsymbol{r}$.

4.3 Calculation of the Oseen tensor

A la Doi and Edwards:
Let's tart by Fourier transforming

$$\mathcal{F}(f_{\boldsymbol{r}}) = f_{\boldsymbol{k}} = \int \frac{d\boldsymbol{k}}{(2\pi)^d} f_{\boldsymbol{r}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \tag{4.12}$$

eqs. (4.3) and (4.9), this gives

$$\int \frac{d\boldsymbol{k}}{(2\pi)^d}\left(\eta\nabla^2 v_{\boldsymbol{r}} + \boldsymbol{\nabla} P\right) e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = -\int \frac{d\boldsymbol{k}}{(2\pi)^d} f_{\boldsymbol{r}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \qquad \int \frac{d\boldsymbol{k}}{(2\pi)^d} \boldsymbol{\nabla} v_{\boldsymbol{r}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = 0$$

which leads to

$$-\eta k^2 v_{\boldsymbol{k}} + i\boldsymbol{k}P_{\boldsymbol{k}} = -f_{\boldsymbol{k}} \qquad \boldsymbol{k}\cdot\boldsymbol{v}_{\boldsymbol{k}} = 0$$

Now, **first of all** obtain the expression for the pressure by using the incompressibility condition on the Stokes equation:

$$\boldsymbol{k}\cdot\left(-\eta k^2 v_{\boldsymbol{k}} + i\boldsymbol{k}P_{\boldsymbol{k}} = -f_{\boldsymbol{k}}\right) \tag{4.13}$$

which gives:

$$i\boldsymbol{k}\cdot\boldsymbol{k}P_{\boldsymbol{k}} = -\boldsymbol{k}\cdot f_{\boldsymbol{k}} \rightarrow \boxed{P_{\boldsymbol{k}} = -\frac{\boldsymbol{k}\cdot f_{\boldsymbol{k}}}{ik^2}} \tag{4.14}$$

Once one has this expression he can calculate back (now is better to use index notation):

$$-\eta k_\gamma k_\gamma v_{k,\alpha} - k_\alpha\left(\frac{k_\beta f_{k,\beta}}{k_\gamma k_\gamma}\right) = -f_{k,\alpha} \tag{4.15}$$

which gives the Fourier transformed flow:

$$v_{k,\alpha} = \frac{1}{\eta k_\gamma k_\gamma}\left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k_\gamma k_\gamma}\right) f_\beta \tag{4.16}$$

which in vectorial notation:

$$\boldsymbol{v_k} = \frac{1}{\eta k^2}\left(\boldsymbol{I} - \frac{\boldsymbol{k}\otimes\boldsymbol{k}}{k^2}\right)\boldsymbol{f_k} \tag{4.17}$$

Now we need to Fourier transform back to the real space. Reminding that the inverse fourier transform of the product of Fourier transformed function is their convolution in real space (*i.e.* $\mathcal{F}^{-1}\left[\mathcal{F}(f)\mathcal{F}(g)\right] = f\star g$) one has

$$\boldsymbol{v}(\boldsymbol{r}) = \int d\boldsymbol{r'}\boldsymbol{H}(\boldsymbol{r}-\boldsymbol{r'})\cdot\boldsymbol{f}(\boldsymbol{r'}) \tag{4.18}$$

where the tensor is the Oseen tensor

$$H(\boldsymbol{r}) = \int\frac{d\boldsymbol{k}}{(2\pi)^3}\frac{1}{\eta k^2}\left(\boldsymbol{I} - \frac{\boldsymbol{k}\otimes\boldsymbol{k}}{k^2}\right)e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \tag{4.19}$$

Now, the procedure to find this a la Doi and Edwards make use of the fact that the tensor $\boldsymbol{H}(\boldsymbol{r})$ depends only on the vector $\boldsymbol{r}$, therefore they infer that the functional form of the tensor can be in general

$$H_{\alpha\beta} = A\delta_{\alpha\beta} + B\hat{r}_\alpha\hat{r}_\beta \tag{4.20}$$

Now by taking the trace $H_{\alpha\alpha}$ and the product $H_{\alpha\beta}\hat{r}_\alpha\hat{r}_\beta$ one gets

$$\begin{aligned} H_{\alpha\alpha} &= 3A + B \\ H_{\alpha\beta}\hat{r}_\alpha\hat{r}_\beta &= A + B \end{aligned}$$

Fourier transformed these equations correspond to

$$3A + B = Tr\left[\int\frac{d\boldsymbol{k}}{(2\pi)^3}\frac{1}{\eta k^2}\left(\boldsymbol{I} - \frac{\boldsymbol{k}\otimes\boldsymbol{k}}{k^2}\right)e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\right] = \int\frac{d\boldsymbol{k}}{(2\pi)^3}\frac{1}{\eta k^2}\left(3-1\right)e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}$$

$$A + B = \int\frac{d\boldsymbol{k}}{(2\pi)^3}\frac{1}{\eta k^2}\left(\boldsymbol{I} - \frac{\boldsymbol{k}\otimes\boldsymbol{k}}{k^2}\right)\left(\frac{\boldsymbol{r}\otimes\boldsymbol{r}}{r^2}\right)e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} = \int\frac{d\boldsymbol{k}}{(2\pi)^3}\frac{1}{\eta k^2}\left(\frac{r^2}{r^2} - \frac{(\boldsymbol{k}\cdot\boldsymbol{r})^2}{r^2k^2}\right)e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}$$

The former reduces to a standard complex integral, as the imaginary part of $e^{ix} = \sin x$:

$$\begin{aligned} 3A + B &= \frac{2}{(2\pi)^3}\int_0^{2\pi}d\phi\int_0^\infty dkk^2\frac{1}{\eta k^2}\int_{-1}^1 d\cos\theta e^{-ikr\cos\theta} = \frac{2}{(2\pi)^2}\int_0^\infty dk\frac{1}{\eta}\frac{e^{ikr}-e^{-ikr}}{ikr} = \\ &\overset{\xi=kr}{=} \frac{4}{(2\pi)^2}\int_0^\infty\frac{d\xi}{\eta r}\frac{\sin\xi}{\xi} \overset{\star}{=} \frac{1}{\eta\pi^2 r}\Im\left[\int_0^\infty d\xi\frac{e^{i\xi}}{\xi}\right] = \frac{1}{2\eta\pi^2 r}\Im\left[\int_{-\infty}^\infty d\xi\frac{e^{i\xi}}{\xi}\right] = \\ &= \frac{1}{2\eta\pi^2 r}\Im\left[\int_{-\infty}^{-\varepsilon\to 0}d\xi\frac{e^{i\xi}}{\xi} + \int_{\varepsilon\to 0}^\infty d\xi\frac{e^{i\xi}}{\xi}\right] = \\ &\overset{\sum_{Res}=0}{=} \frac{1}{2\eta\pi^2 r}\Im\left[-\int_{\gamma_\varepsilon}d\xi\frac{e^{i\xi}}{\xi} - \int_{\gamma_R}d\xi\frac{e^{i\xi}}{\xi}\right] \overset{e^{i\xi}\overset{\gamma_R}{\to}0}{=} \frac{1}{2\eta\pi^2 r}\Im\left[-\int_{\gamma_\varepsilon}d\xi\frac{e^{i\xi}}{\xi}\right] = \\ &\overset{\gamma_\varepsilon\text{half clock-wise}}{=} \frac{1}{2\eta\pi^2 r}\Im\left[\pi i\lim_{\varepsilon\to 0}e^{i\epsilon}\right] = \frac{\pi}{2\eta\pi^2 r} \end{aligned}$$

The latter is reduced to a similar form, via the following trick (again using $t = \cos\theta = \hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{r}}$ and $\xi = |\boldsymbol{k}||\boldsymbol{r}|$):

$$A + B = \int \frac{d\boldsymbol{k}}{(2\pi)^3}\frac{1}{\eta k^2}\left(\frac{r^2}{r^2} - \frac{(\boldsymbol{k}\cdot\boldsymbol{r})^2}{r^2k^2}\right)e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} = \frac{1}{\eta(2\pi)^2 r}\int_0^\infty d\xi \int_{-1}^1 dt\left(1 - t^2\right)e^{-i\xi t} =$$
$$= \frac{1}{\eta(2\pi)^2 r}\int_0^\infty d\xi(1 + \frac{\partial^2}{\partial\xi^2})\int_{-1}^1 dte^{-i\xi t} \overset{\text{factor } 1/2 \text{ wrt}\star}{=} \frac{1}{\eta 2\pi^2 r}\int_0^\infty d\xi(1 + \frac{\partial^2}{\partial\xi^2})\frac{\sin\xi}{\xi} \overset{\partial^2\leftrightarrow\int d\xi}{=} \frac{\pi}{4\eta\pi^2 r} + 0$$

In light of these two equations one gets:

$$3A + B = \frac{1}{2\eta\pi r}$$
$$A + B = \frac{1}{4\eta\pi r}$$

which is satisfied only by

$$A = B = \frac{1}{8\eta\pi r} \tag{4.21}$$

and therefore the Oseen tensor is obtained:

$$H_{\alpha\beta} = \frac{1}{8\eta\pi r}\left(\delta_{\alpha\beta} + \frac{r_\alpha r_\beta}{r^2}\right) \tag{4.22}$$

which shows that while the diagonal part decreases as r^{-1}, the off-diagonal interactions go down as r^{-3}.

4.4 Hydrodynamic Screening in Systems of Polymers

Doi and Edwards (page 180) say that at high concentrations the presence of polymers affect the decay of the Oseen tensor, which is in free solution would be

$$H(r) \simeq \frac{1}{\eta_s r} \tag{4.23}$$

gains a further decay due to the increased viscosity of the medium due to the presence of polymers. When $\eta \gg \eta_s$ appears a hydrodynamic screening for which at any distance greater than ξ_H the polymers do not feel the velocity field induced at zero. This can written in the Fourier space as:

$$H(k) \simeq \frac{\mathbb{I} - \hat{k}\hat{k}}{\eta_s(k^2 + \xi_H^{-2})} \tag{4.24}$$

which in real space reads:

$$H(r) \simeq \frac{e^{-r/\xi_H}}{\eta_s r} \tag{4.25}$$

from which it is clear that exist a length ξ_H which kills the hydrodynamic interaction. This length can be written as [3]

$$\xi_H = \frac{2}{\pi c b^2} \tag{4.26}$$

In our systems of melts where the segment density $c \simeq 0.1\sigma^{-3}$, one gets that $\xi_H \simeq 5\sigma$ ($\sigma = b$) which is ten times shorter than our smallest system size. OK

Chapter 5

Brownian Motion

5.1 The Diffusion Eq.

Let's start by considering a concentration c of solute in a solvent. Clearly, this solute undergoes diffusion, and any unbalance in the distribution of concentration will create a flux, in response to the concentration gradient, so to level out the disparity. The flux is:

$$j = -D\frac{\partial c}{\partial x} \tag{5.1}$$

where D describes the rapidity of the response, *i.e.* the diffusion coefficient; together with the required continuity equation which states that any change in the concentration has to caused by a source or a sink of flux:

$$\frac{\partial c}{\partial t} = -\frac{\partial j}{\partial x} \tag{5.2}$$

one gets the famous diffusion equation:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}. \tag{5.3}$$

5.1.1 Adding a Potential

In the case an external potential $U(x)$ is applied to the system, a velocity will be produced, in which the solute is moving in response to the force $F = -dU/dx$. The velocity v will be proportional to the solute mobility $\mu = 1/\zeta$:

$$v = -\frac{1}{\zeta}\frac{dU}{dx} \tag{5.4}$$

This needs to be added to the flux equation, which will now read:

$$j = -D\frac{\partial c}{\partial x} + cv = -D\frac{\partial c}{\partial x} - \frac{c}{\zeta}\frac{dU}{dx} \tag{5.5}$$

clearly, at equilibrium, the concentration is **given** by the Boltzmann distribution, independently to what we see until now:

$$c_{eq}(x) \propto e^{U(x)/k_BT} \tag{5.6}$$

and we expect the flux to be null in this case:

$$0 \overset{!}{=} j = -D\frac{\partial c_{eq}}{\partial x} - -\frac{c_{eq}}{\zeta}\frac{dU}{dx} \tag{5.7}$$

which is satisfied only if:

$$D = \frac{k_B T}{\zeta} \tag{5.8}$$

which is the Einstein equation. This is a particular form of a more general law: the fluctuation-dissipation theorem.

The Smoluchowski equation can then be found by re-utilising the continuity equation onto this new flux and eq. (5.8):

$$-\frac{\partial j}{\partial x} = \frac{\partial c}{\partial t} = -D\frac{\partial^2 c}{\partial x^2} - \frac{\partial c}{\zeta \partial x}\frac{dU}{dx} = -\frac{1}{\zeta}\frac{\partial}{\partial x}\left(k_B T\frac{\partial c}{\partial x} + c\frac{dU}{dx}\right) \tag{5.9}$$

The same equation can be found in a more formal, and physically motivated way; let's consider the flux:

$$j(x) = -\frac{1}{\zeta}c\frac{\partial}{\partial x}\left(k_B T \log c(x) + U(x)\right) \tag{5.10}$$

this is the flux produced by non-interaction particles, whose concentration c induces an effective chemical potential $U + k_B T \log c$!!**In particular, this is more correct that before! In fact, what has to be constant at equilibrium is not the concentration, but the chemical potential!!!** If we now define the flux velocity as $v_f = j/c$ then the Smoluchowski equation can be derived by only the continuity equation where the chemical potential $U + k_B T \log c$ is considered, as:

$$\frac{\partial c}{\partial t} = -\frac{\partial (c v_f)}{\partial x}. \tag{5.11}$$

5.1.2 The Langevin Equation

In the case the diffusion coefficient does not depend on the position x, then the Sm. eq. is equivalent to the Langevin eq.

$$\zeta\frac{\partial x}{\partial t} = \frac{dU}{dx} + f(t) \tag{5.12}$$

where $f(t)$ is a random force such that

$$\langle f(t)\rangle = 0 \qquad \langle f(t_1)f(t_2)\rangle = 2\zeta k_B T\delta(t_1 - t_2) \tag{5.13}$$

Clearly eq. (5.12) can be easily integrated in the case $U = 0$ or a constant:

$$x(t) = x_0 + \frac{1}{\zeta}\int_0^t dt' f(t') \tag{5.14}$$

being a superposition of uncorrelated stochastic noise over time t, the position $x(t)$ needs to obey the central limit theorem, and needs to be Gaussian. Hence the probability distribution is:

$$\Psi(x,t) = (2\pi B)^{-1/2}\exp\frac{(x-A)^2}{2B} \tag{5.15}$$

with

$$A = \langle x\rangle \qquad B = \langle (x - \langle x\rangle)^2\rangle \tag{5.16}$$

Clearly, the average $\langle x\rangle = x_0$ being

$$A = x_0 + \langle\int_0^t dt' f(t')\rangle = x_0 \tag{5.17}$$

and

$$B = \frac{1}{\zeta^2}\langle\int_0^t dt' \int_0^t dt'' f(t')f(t''))\rangle = 2\frac{k_BT}{\zeta}\int_0^t\int_0^t dt'dt''\delta(t'-t'') = \frac{2k_BT}{\zeta}t \tag{5.18}$$

and by the Einstein realtion eq.(5.8):

$$B = \langle(x-\langle x\rangle)^2\rangle = 2Dt \tag{5.19}$$

which generalises to $2dDt$, where d is the number of dimensions.

5.2 Time Correlation and Response Functions

In this section we will see how to deal, in a general way, with correlation functions and response functions. The Smoluch. eq. 5.9 can be written:

$$\frac{\partial\Psi}{\partial t} = \frac{1}{\zeta}\frac{\partial}{\partial x}\left(k_BT\frac{\partial\Psi}{\partial x} + \frac{\partial U}{\partial x}\Psi\right) \tag{5.20}$$

and in the multidimensional case, where the mobility is, in general, different along different directions (see Oseen tensor and hydrodyn section), it can be written:

$$\frac{\partial\Psi}{\partial t} = \sum_{m,n}\frac{\partial}{\partial x_n}L_{nm}\left(k_BT\frac{\partial\Psi}{\partial x_m} + \frac{\partial U}{\partial x_m}\Psi\right) \tag{5.21}$$

and Ψ is the usual probability function at position $\boldsymbol{x}$ at time t. Very well. Now, in general, the correlation of a quantity with itself is a decaying function of time which can be defined as

$$C_{AA}(t) = \langle A(t)A(0)\rangle \tag{5.22}$$

which starts at $\langle A^2(0)\rangle$ at $t=0$ and decays to $\langle A\rangle^2$ at large t. Let's see how to compute these correlation functions. First, consider the conditional probability that a particle is found at position x at time time t having started at x' at time 0. This is given by the Green's function, $G(x,x';t)$ and <u>has to</u> satisfy the Smol. Eq.

$$\frac{\partial\Psi}{\partial G} = \sum_{m,n}\frac{\partial}{\partial x_n}L_{nm}\left(k_BT\frac{\partial G}{\partial x_m} + \frac{\partial U}{\partial x_m}G\right) \tag{5.23}$$

with B.C. $G(x,x'=0) = \delta(x-x')$ therefore, one can in general weight the (cross) correlation function of quantities A and B with the probability of having, first a particle at x' and then to have it at x at time t. This is clearly given by the expression:

$$\langle A(t)B(0)\rangle = \int\int dxdx'A(t)B(0)G(x,x';t)\Psi_{eq}(x') \tag{5.24}$$

very well. How do we now compute this? Actually, one uses a little trick. Consider its time derivative:

$$\frac{\partial}{\partial t}\langle A(x)B(x')\rangle = \int\int dxdx'A(t)B(0)\frac{\partial}{\partial t}G(x,x';t)\Psi_{eq}(x') = \tag{5.25}$$

$$= \int\int dxdx'A(x)\sum_{m,n}\frac{\partial}{\partial x_n}L_{nm}\left(k_BT\frac{\partial G}{\partial x_m} + \frac{\partial U}{\partial x_m}G\right)B(x')\Psi_{eq}(x') \tag{5.26}$$

at $t = 0$, *i.e.* for small t's, one can approximate the Green's function $G(x, x'; t)$ with its value at t=0, *i.e.* $\delta(x - x')$, this is handy! In fact,

$$\frac{\partial}{\partial t}\langle A(x)B(x')\rangle\bigg|_{t=0} = \int dx A(x)\sum_{m,n}\frac{\partial}{\partial x_n}L_{nm}\left(k_BT\frac{\partial(B(x)\Psi_{eq}(x))}{\partial x_m} + \frac{\partial U}{\partial x_m}B(x)\Psi_{eq}(x)\right) \tag{5.27}$$

Now, consider two things : (i) $\Psi_{eq}(x) = \exp\left(-U(x)/k_BT\right)/\int dx \exp\left(-U(x)/k_BT\right)$ which therefore leads to

$$B(x)\frac{\partial U}{\partial x}\Psi_{eq} = -k_BTB(x)\frac{\partial \Psi_{eq}}{\partial x} \tag{5.28}$$

and (ii)integration by parts....leading to:

$$\frac{\partial}{\partial t}\langle A(x)B(x')\rangle\bigg|_{t=0} = k_BT\int dx A(x)\sum_{m,n}\frac{\partial}{\partial x_n}L_{nm}\left(\frac{\partial B(x)}{\partial x_m}\Psi_{eq}(x) + \frac{\partial \Psi_{eq}(x)}{\partial x_m}B(x) - \frac{\partial \Psi_{eq}(x)}{\partial x_m}B(x)\right. \tag{5.29}$$

simplifies to

$$\frac{\partial}{\partial t}\langle A(x)B(x')\rangle\bigg|_{t=0} = k_BT\int dx A(x)\sum_{m,n}\frac{\partial}{\partial x_n}L_{nm}\left(\frac{\partial B(x)}{\partial x_m}\Psi_{eq}(x)\right) \tag{5.30}$$

and integrating again by parts (remember - sign)one finally gets:

$$\frac{\partial}{\partial t}\langle A(x)B(x')\rangle\bigg|_{t=0} = -k_BT\int dx \sum_{m,n}\frac{\partial A(x)}{\partial x_n}L_{nm}\left(\frac{\partial B(x)}{\partial x_m}\Psi_{eq}(x)\right) \tag{5.31}$$

or in concise form:

$$\frac{\partial}{\partial t}\langle A(x)B(x')\rangle\bigg|_{t=0} = -k_BT\sum_{m,n}\left\langle\frac{\partial A(x)}{\partial x_n}L_{nm}\frac{\partial B(x)}{\partial x_m}\right\rangle_{\Psi_{eq}} \tag{5.32}$$

which says that the initial slope of the decay of the correlation function of A and B is given by the correlation of the product of the derivatives mediated by the mobility matrix and averaged w.r.t. the equilibrium distribution. The initial decay rate defined as $\Gamma_0 = -\left.\partial\langle A(x)B(x')\rangle/\partial t\right|_{t=0}/(\langle AB\rangle - \langle A\rangle\langle B\rangle)$ is therefore given by eq. (5.32) opportunely normalised.

5.2.1 The Fluctuation-Dissipation Theorem

Let's say that I want to compute the response of an observable A as a function of time in response to a small perturbation, which takes the form of a potential

$$U(x, t) = h(t)B(x). \tag{5.33}$$

One can obtain the response by computing the expected value

$$\langle A(t)\rangle_h = \langle A\rangle_0 + \int_{-\infty}^{t} dt'\mu(t - t')h(t') \tag{5.34}$$

i.e. the deviation from the value at equilibrium $\langle A\rangle_0$ is a linear functional of the applied field and the response function $\mu(t)$. Now, it can be shown, (see below), that in the case the perturbation is expressed as eq. (5.33), one can write:

$$\mu(t) = -k_BT\frac{d}{dt}C_{AB}(t), \tag{5.35}$$

and it is the general formulation of the fluctuation-dissipation eq. Now, let us prove this equation!

Proof:

Let's consider a constant perturbation from $-\infty$ to 0, at which time is turned off (step-function). Clearly, the observable A changes, from the value $\langle A\rangle_h$ when the field was on, to $\langle A\rangle_0$ when the field is off. Now, this change is driven by the response function as follows

$$\langle A\rangle_h = \langle A\rangle_0 + \alpha(t)h(t) \tag{5.36}$$

where they are decoupled because of the form of the perturbation! and

$$\alpha(t) = \int_{-\infty}^{t} dt'\mu(t-t') = \int_{s}^{\infty} ds\mu(s). \tag{5.37}$$

Now, if the distribution function was known, the steady state of the observable A could be computed as

$$\langle A\rangle_h = \int dx A(x)\Psi(x,t) \tag{5.38}$$

but!! At $t=0$ there is no field on end therefore the distribution at larger times $t>0$ is given by

$$\Psi(x,t) = \int dx' G(x,x';t)\Psi(x,0) \tag{5.39}$$

where $G(x,x';t)$ is once again the probability of ending up at x at time t being at x' at time 0 and the distribution at time $t=0$ is clearly

$$\Psi(x,0) = \frac{\exp\left(-U(x)/k_BT + h(0)B(x)/k_BT\right)}{\int dx \exp\left(-U(x)/k_BT + h(0)B(x)/k_BT\right)} \tag{5.40}$$

which for small h can be expanded:

$$\Psi(x,0) = \frac{\exp\left(-U(x)/k_BT\right)\left[1+\dfrac{h(0)B(x)}{k_BT}\right]}{\int dx \exp\left(-U(x)/k_BT + h(0)B(x)\right)} \tag{5.41}$$

at the <u>denominator</u>, one can write

$$\int dx \exp\left(-U(x)/k_BT - h(0)B(x)\right) = \int dx \left[1+\frac{h(0)B(x)}{k_BT}\right]\exp\left(-U(x)/k_BT\right) \tag{5.42}$$

or simply

$$\int dx \exp\left(-U(x)/k_BT\right)\left[1+\frac{h(0)\langle B\rangle_0}{k_BT}\right] \tag{5.43}$$

which in the expression for the distribution function becomes:

$$\Psi(x,0) = \frac{\exp\left(-U(x)/k_BT\right)\left[1+\dfrac{h(0)B(x)}{k_BT}\right]}{\int dx \exp\left(-U(x)/k_BT\right)\left[1+\dfrac{h(0)\langle B\rangle_0}{k_BT}\right]} = \Psi_{eq}(x)\left[1+\frac{h(0)B(x)}{k_BT}\right]\left[1-\frac{h(0)\langle B\rangle_0}{k_BT}\right] =$$

$$\simeq \Psi_{eq}(x)\left[1+h(0)\frac{B(x)-\langle B\rangle_0}{k_BT}\right] + \mathcal{O}(h^2)$$

Ok, now that we have an expression for the distribution at non-zero field $\Psi(x,t)$ which gives!

$$\langle A(t)\rangle_h = \int dx A(x)\int dx' G(x,x';t)\Psi_{eq}(x')\left[1+h(0)\frac{B(x')-\langle B\rangle_0}{k_BT}\right] \tag{5.44}$$

now it is easy to compute:

$$\begin{aligned}\langle A(t)\rangle_h &= \int dxA(x)\int dx'G(x,x';t)\Psi_{eq}(x') + \int dxA(x)\int dx'G(x,x';t)\Psi_{eq}(x')h(0)\frac{B(x')-\langle B\rangle_0}{k_BT}\\ &= \langle A\rangle_0 + h(0)\frac{\langle A(t)B(0)\rangle - \langle A\rangle_0\langle B\rangle_0}{k_BT}\end{aligned}$$

by using the definitions of average and the property of equilibrium distribution $\Psi_{eq}(x) = \int dyG(x,y;t)\Psi_{eq}(y)$. Now it is clear that

$$\alpha(t) = \frac{1}{h(t)}(\langle A(t)\rangle_h - \langle A\rangle_0) = \frac{\langle A(t)B(0)\rangle - \langle A\rangle_0\langle B\rangle_0}{k_BT} = \int_t^\infty dt'\mu(t') \tag{5.45}$$

and its time derivative:

$$\mu(t) = -\frac{1}{k_BT}\frac{d}{dt}\langle A(t)B(0)\rangle = -\frac{1}{k_BT}\frac{d}{dt}C_{AB}(t) \tag{5.46}$$

□

The case in which A and B are the same quantity, is a special case. In this scenario, let's consider the case in which at time $t = 0$ a perturbation is turned on as a step function so that:

$$\langle A(t)\rangle_h - \langle A\rangle_0 = \beta(t)h \tag{5.47}$$

where once again the growth is described by the function

$$\beta(t) = \int_0^t ds\mu(s) \tag{5.48}$$

now using what we discovered with eq. (5.46) one gets:

$$\beta(t) = \int_0^t ds\mu(s) = -\frac{1}{k_BT}\int_0^t ds\frac{d}{ds}C_{AA}(s) = \frac{-C_{AA}(t)+C_{AA}(0)}{k_BT} \tag{5.49}$$

and now (not clear) using $\langle A(0)^2\rangle = \langle A(t)^2\rangle$

$$\beta(t) = \frac{-2\langle A(t)A(0)\rangle + \langle A(0)^2\rangle + \langle A(t)^2\rangle}{2k_BT} = \frac{\langle [A(t)-A(0)]^2\rangle}{2k_BT} \tag{5.50}$$

The Einstein relation is retrieved when A is position and the external field is a position dependent potential expressing a constant force so that B is linear in x. In this case, the field conjugate to $B(x) = x$ is simply the force $\partial U/\partial x = h = const$. Hence when the force is turned on, the particle starts to move in the direction of the field with speed given by $v = h/\zeta$. Therefore

$$\beta(t) = \int_0^t ds\mu(s)h = \int_0^t ds\frac{h}{\zeta} = \frac{t}{\zeta} \tag{5.51}$$

since the mobility $\mu = 1/\zeta = const$. Therefore the FDT eq. becomes:

$$\mu(t) = \frac{1}{\zeta} = -\frac{1}{k_BT}\frac{d}{dt}C_{xx}(t) = \frac{1}{2k_BT}\frac{d}{dt}\langle [x(t)-x(0)]^2\rangle = \frac{1}{k_BT}\frac{dDt}{dt} = \frac{D}{k_BT} \tag{5.52}$$

where we used the well-known fact: $\langle [x(t)-x(0)]^2\rangle = 2Dt$.

□

5.3 Practical Example pg. 62: Harmonic Potential

5.3.1 Smol. Eq.

Let's take an Harmonic potential centred in zero: $U(x) = \frac{k}{2}x^2$. This has equilibrium distribution:

$$\frac{\Psi(x)}{dt} = \frac{1}{\zeta}\frac{d}{dx}\left(k_BT\frac{d\Psi(x)}{dx} + \frac{dU}{dx}\Psi(x)\right) \tag{5.53}$$

at equilibrium this gives:

$$\frac{1}{\Psi_{eq}(x)}\frac{\Psi_{eq}(x)}{dt} = -\frac{k}{2k_BT}x^2 \tag{5.54}$$

and therefore

$$\Psi_{eq}(x) = \Psi_0 \exp\left[-\frac{k}{2k_BT}x^2\right] \text{ and } \int \Psi_{eq}(x)dx = 1 \tag{5.55}$$

therefore $\Psi_0 = \left(\frac{2\pi k_BT}{k}\right)^{-1/2}$.

Ok, now we want to comoute the correlation function of the position, using the standard trick:

$$\begin{aligned}\frac{d}{dt}\langle x(t)x(0)\rangle &= \int dx \int dx' xx' \frac{d}{dt}G(x,x';t)\Psi_{eq}(x') = \int dx \int dx' xx' \frac{1}{\zeta}\frac{d}{dx}\left(k_BT\frac{dG}{dx} + \frac{dU}{dx}G\right)\Psi_{eq}(x') = \\ &\overset{\text{by parts}}{=} \int dx \int dx' \frac{1}{\zeta}\left[k_BTG\frac{d}{dx}\frac{d(xx')}{dx} - kx\frac{d(xx')}{dx}\right]\Psi_{eq}(x') = \\ &= -\frac{k}{\zeta}\int dx \int dx' xx' G(x,x';t)\Psi_{eq}(x') = -\frac{k}{\zeta}\langle x(t)x(0)\rangle = -\frac{1}{\tau}\langle x(t)x(0)\rangle\end{aligned}$$

where τ is the decay time of the exponential function $\langle x(t)x(0)\rangle$. In fact:

$$\langle x(t)x(0)\rangle = \langle x(0)^2\rangle e^{-t/\tau} \tag{5.56}$$

where

$$\langle x(0)^2\rangle = \int_0^\infty dx x^2 \left(\frac{2\pi k_BT}{k}\right)^{-1/2} e^{-kx^2/2k_BT} = \frac{k_BT}{k} = \sigma^2$$

is the second moment of the equilbirum distribution.

5.3.2 Langevin Eq.

The same picture can be described by the (overdamped) Langevin eq.

$$\zeta\frac{dx}{dt} = -kx + f(t) \tag{5.57}$$

where the Harmonc potential is expressed as a constant force pointing toward $x = 0$. The random force $f(t)$ satisfies the usual constraints, where its mean $\langle f\rangle = 0$ and variance $\langle f(t)f(t')\rangle = 2\zeta k_BT\delta(t-t')$. Let's comoute the same correlation function, but first one can express the posiiton $x(t) = \int_{-\infty}^t dt' \exp\left(-(t-t')/\tau\right)f(t')/\zeta$ since the position $x(t)$ will respond to the potential as a decay function, like there was no external radnom force, but this has to be weighted by the effect of random collisions, therefore:

$$\begin{aligned}\langle x(t)x(0)\rangle &= \frac{1}{\zeta^2}\int_{-\infty}^{t} dt_1 \int_{-\infty}^{0} dt_2 e^{(t-t_1-t_2)/\tau}\langle f(t_1)f(t_2)\rangle = \\ &= \frac{1}{\zeta^2}\int_{-\infty}^{t} dt_1 \int_{-\infty}^{0} dt_2 e^{(t-t_1-t_2)/\tau} 2\zeta k_B T\delta(t_1-t_2) = \frac{2k_BT\tau}{2\zeta}e^{-t/\tau} \overset{\tau=\zeta/k}{=} \frac{k_BT}{k}e^{-t/\tau}\end{aligned}$$

which agrees with the one comouted with the Smol. Eq..

5.3.3 Green's Function

Now we want to compute the Green's function for this system explicitly. Again, since the result will be a linear combination of $f(t)$, the distribution of x will be a Gaussian only this time not centred in $\langle f(t)\rangle$ but it will have a shift induced by the harmonic potential. Therefore:

$$G(x,x';t) = (2\pi B)^{-1/2}\, e^{-\dfrac{(x-A)^2}{2B}} \tag{5.58}$$

where

$$A(t) = \langle x(t)\rangle \text{ and } B(t) = \langle [x(t)-A(t)]^2\rangle \tag{5.59}$$

To compute these quantities one should solve the Langevin equation under the condition that at time $t = 0$ the position is the generci x_0. So:

$$x(t) = x_0 e^{-t/\tau} + \frac{1}{\zeta}\int dt' e^{-(t-t')/\tau} f(t') \tag{5.60}$$

and therefore

$$A = \langle x(t)\rangle = x_0 e^{-t/\tau} + \frac{1}{\zeta}\int dt' e^{-(t-t')/\tau}\langle f(t')\rangle = x_0 e^{-t/\tau} \tag{5.61}$$

and

$$\begin{aligned}B = \langle [x(t)-A(t)]^2\rangle &= \frac{1}{\zeta^2}\int dt' \int dt'' e^{-[(t-t')+(t-t'')]/\tau}\langle f(t')f(t'')\rangle = \\ &= \frac{2k_BT}{\zeta}\int_0^t dt' e^{-2(t-t')/\tau} = \frac{k_BT}{k}\left[1-e^{-2t/\tau}\right]\end{aligned}$$

Therefore the Green's function is given by:

$$G(x,x_0;t) = \left[\frac{2\pi k_BT}{k}\left(1-e^{-2t/\tau}\right)\right]^{-1/2} \exp\left[-\frac{k(x-x_0\exp(-2t/\tau))^2}{2k_BT[1-\exp(-2t/\tau)]}\right] \tag{5.62}$$

One can consider the two limiting cases:

- $t \ll \tau$: In this case the time is much smaller than the relaxation time $\tau = \zeta/k$, i.e. either the fricition is very high or the spring k very small, in this case the distribution will be a Gaussian centred in x_0 and no force will be felt by the particle:

  $$G(x,x_0;t) = \left[\frac{2\pi k_BT}{\zeta}\right]^{-1/2} \exp\left[-\frac{\zeta(x-x_0)^2}{2k_BT}\right] \tag{5.63}$$

  which is the same as free diffusion.

- $t \gg \tau$: In this case the exponentials have relaxed and therefore the only effect left will be the one from the spring

  $$G(x,x_0;t) = \left[\frac{2\pi k_BT}{k}\right]^{-1/2} \exp\left[-\frac{kx^2}{2k_BT}\right] \tag{5.64}$$

  This is the equilbrium ditribution for a particle in a potential well.

Hermite Polynomials

A very interesting way of writing this result is via the Hermite polynomials. The Mehler's formula reads:

$$\sum_{p=1}^{\infty} \frac{H_p(\xi)H_p(\eta)}{2^p p!} s^p = (1-s^2)\exp\left[\xi^2 - \frac{(\xi-\eta s)^2}{1-s^2}\right] \tag{5.65}$$

where

$$H_p(\xi) = (-1)^p \exp\xi^2 \frac{d^p}{d\xi^p} \exp\xi^2 \tag{5.66}$$

and using this one can re-write eq. (5.62) in a eigen-values form:

$$G(x,x';t) = \sum_{p=0}^{\infty} \exp\left(-\lambda_p t\right)\psi_p(x)\psi_p(x_0)\Psi_{eq}(x) \tag{5.67}$$

with $\lambda_p = p/\tau$, $\psi_p(x) = (2^p p!)^{-1/2} H_p(x/\gamma)$ and $\gamma = (2k_B T/k)^{1/2}$.

Chapter 6

The Rouse Model

The Rouse model starts from the general description of a polymer made of beads of size b connected via harmonic springs. The general Smol eq. is:

$$\frac{d\Psi}{dt} = \sum_{nm} \frac{\partial}{\partial \boldsymbol{R}_n} L_{nm} \left(k_B T \frac{\partial \Psi}{\partial \boldsymbol{R}_m} + \frac{\partial U}{\partial \boldsymbol{R}_n} \Psi \right) \tag{6.1}$$

or, equivalently, the Langevin description:

$$\frac{d\boldsymbol{R}_n}{dt} = -\sum_m L_{nm} \left(\frac{dU}{d\boldsymbol{R}_m} + \boldsymbol{f}_m \right) + \frac{k_B T}{2} \sum_m \frac{dL_{nm}}{d\boldsymbol{R}_m} \tag{6.2}$$

where the last term is the equivalent of the derivative of the diffusion coefficient, or the mobility (using Einstein relation).
In this model the hydrodynamic interactions are neglected and therefore we can take the mobility tensor to be only a constant matrix of mobilities, rather than the Oseen tensor.

$$L_{nm} = \frac{\boldsymbol{I}}{\zeta} \delta_{nm} \tag{6.3}$$

This makes eq. (6.2) much easier, in fact:

$$\zeta \frac{d\boldsymbol{R}_n}{dt} = -\frac{dU}{d\boldsymbol{R}_n} + \boldsymbol{f}_n \tag{6.4}$$

By taking the potential describing the *local* interaction as:

$$U = \frac{k}{2} \sum_{n=1}^{\infty} (\boldsymbol{R}_n - \boldsymbol{R}_{n-1})^2 \tag{6.5}$$

one gets (for the bulk):

$$\zeta \frac{d\boldsymbol{R}_n}{dt} = -k \left(-\boldsymbol{R}_{n+1} + 2\boldsymbol{R}_n - \boldsymbol{R}_{n-1} \right) + \boldsymbol{f}_n \tag{6.6}$$

This can be written in “continuous mode” by taking $N \to \infty$ as

$$\zeta \frac{d\boldsymbol{R}_n}{dt} = k \frac{d^2 \boldsymbol{R}_n}{dn^2} + \boldsymbol{f}_n \tag{6.7}$$

where

$$\langle \boldsymbol{f}_n(t) \rangle = 0$$
$$\langle f_{n\alpha}(t) f_{m\beta}(s) \rangle = 2 k_B T \zeta \delta_{nm} \delta_{\alpha\beta} \delta(t-s)$$

For the two ends of the chain instead:

$$\zeta \frac{d\boldsymbol{R}_1}{dt} = -k\left(-\boldsymbol{R}_2 + 2\boldsymbol{R}_1 - \boldsymbol{R}_0\right) + \boldsymbol{f}_1$$
$$\zeta \frac{d\boldsymbol{R}_N}{dt} = -k\left(-\boldsymbol{R}_{N+1} + 2\boldsymbol{R}_N - \boldsymbol{R}_{N-1}\right) + \boldsymbol{f}_N$$

and by setting $\boldsymbol{R}_0 = \boldsymbol{R}_1$ and $\boldsymbol{R}_{N+1} = \boldsymbol{R}_N$ one gets that the two ends need to satisfy:

$$\left.\frac{d\boldsymbol{R}_n}{dn}\right|_{n=1} = 0 = \left.\frac{d\boldsymbol{R}_n}{dn}\right|_{n=N}. \tag{6.8}$$

It is to be noted that eq. (6.7) is the easiest equation describing local interactions, in fact one can start from somewhere else and end up with the same equation. Let's consider, for example, the most general Langevin eq. describing local interactions:

$$\frac{d\boldsymbol{R}_n}{dt} = \sum_m A_{nm}\boldsymbol{R}_m + \boldsymbol{g}_n \tag{6.9}$$

where A_{nm} is a matrix of constants which weight the interaction between beads forming the chain, which is a function only of their position. Because it is natural to describe the interaction along the chain in terms of a fixed point (n) and the relative distance from it (m) one can write:

$$\frac{d\boldsymbol{R}_n}{dt} = \sum_m A_{n,n+m}\boldsymbol{R}_{n+m} + \boldsymbol{g}_n \tag{6.10}$$

Assuming that the interaction is slowly varying with the relative distance m one can expand:

$$\sum_m A_{n,n+m}\boldsymbol{R}_{n+m} \equiv \sum_m A_m\left(\boldsymbol{R}_n + m\frac{d\boldsymbol{R}_n}{dn} + \frac{m^2}{2}\frac{d^2\boldsymbol{R}_n}{dn^2} + \ldots\right) = a_0\boldsymbol{R}_n + a_1\frac{d\boldsymbol{R}_n}{dn} + a_2\frac{d^2\boldsymbol{R}_n}{dn^2} + \ldots \tag{6.11}$$

Now, it is clear that a_0 needs to be zero since the interaction is invariant for translations, *i.e.* it cannot tell where it is along the chain, also the polymer cannot distinguish head-to-tail and therefore also a_1 needs to be zero. We are left only with

$$\frac{d\boldsymbol{R}_n}{dt} = a_2\frac{d^2\boldsymbol{R}_n}{dn^2} + \boldsymbol{g}_n \tag{6.12}$$

which agrees with eq. (6.7).

Also, it is worth noting that for **rings** this is not completely true. In fact, there are no ends!

In this case eq. (6.7) is valid for all the beads along the chain, not only in the bulk, and in particular, for the two beads which are at the end of the indexing one gets:

$$\zeta \frac{d\boldsymbol{R}_1}{dt} = -k\left(-\boldsymbol{R}_2 + 2\boldsymbol{R}_1 - \boldsymbol{R}_N\right) + \boldsymbol{f}_1$$
$$\zeta \frac{d\boldsymbol{R}_N}{dt} = -k\left(-\boldsymbol{R}_1 + 2\boldsymbol{R}_N - \boldsymbol{R}_{N-1}\right) + \boldsymbol{f}_N$$

by setting $\boldsymbol{R}_0 = \boldsymbol{R}_N$ and $\boldsymbol{R}_{N+1} = \boldsymbol{R}_1$.

6.1 Solving the Rouse Model with Modes

The best way to solve this model is by decomposing the eq. in modes, so that each mode is independent. This is done by introducing normal coordinates, as one would do in the case of a chain of oscillators.

6.1.1 Normal Coordinates

Let's introduce the normal coordinates in which the modes of the polymer should be non-interacting. We describe the modes as a linear super-position of the positions:

$$\boldsymbol{X}_p = \int_0^N dn \phi_{np} \boldsymbol{R}_n \tag{6.13}$$

in these coordinates we want the equation eq. (6.7) to become a standard Langevin-like as the following:

$$\zeta_p \frac{d\boldsymbol{X}_p}{dt} = -k_p \boldsymbol{X}_p + \boldsymbol{f}_p \tag{6.14}$$

in order to do so we first apply the latter equation to the normal coordinates eq. (6.13) which give:

$$\zeta_p \frac{d\boldsymbol{X}_p}{dt} = \frac{\zeta_p}{\zeta} \int_0^N dn \phi_{np} \overset{= d\boldsymbol{R}_n/dt \text{ eq. (6.7)}}{\left(k \frac{d^2 \boldsymbol{R}_n}{dn^2} + \boldsymbol{f}_p \right)} \overset{\text{by parts}}{=} \frac{\zeta_p}{\zeta} \left[\Big(k \phi_{np} \frac{d\boldsymbol{R}_n}{dn} \Big|_0^N - k \int_0^N dn \frac{d\phi_{np}}{dn} \frac{d\boldsymbol{R}_n}{dn} + \int_0^N dn \phi_{np} \boldsymbol{f}_n \right] =$$

$$\overset{B.C.+parts}{=} \frac{\zeta_p}{\zeta} \left[- k \frac{d\phi_{np}}{dn} \boldsymbol{R}_n \Big|_0^N + k \int_0^N dn \frac{d^2 \phi_{np}}{dn^2} \boldsymbol{R}_n + \int_0^N dn \phi_{np} \boldsymbol{f}_n \right] =$$

$$= \int_0^N dn (-k_p \phi_{np} \boldsymbol{R}_n) + \boldsymbol{f}_p = -k_p \boldsymbol{X}_p + \boldsymbol{f}_p$$

but the last line holds only if ϕ_{np} satisfies:

$$\frac{\zeta_p}{\zeta} k \frac{d^2 \phi_{np}}{dn^2} = -k_p \phi_{np} \tag{6.15}$$

with Von Neumann boundary conditions, *i.e.* $d\phi_{np}/dn|_{n=0,n=N} = 0$. Eq. (6.15) is the standard eq. for oscillators, and its solution is a linear combination of harmonic functions:

$$\phi_{np} = A \cos\left(\sqrt{\lambda} n\right) + BA \sin\left(\sqrt{\lambda} n\right) \tag{6.16}$$

by applying the two boundary conditions at $n = 0$ and $n = N$ on its first derivative one gets:

$$\phi_{np} = A \cos\left(\frac{p\pi n}{N}\right) \tag{6.17}$$

and

$$k_p = \frac{k\zeta_p}{\zeta} \left(\frac{p\pi}{N}\right)^2 \tag{6.18}$$

with $p = 0, 1, 2, \ldots$. Furthermore, the factor A should match the normalisation condition at $p = 0$, *i.e.* $\int_0^N dnA \cos(p\pi n/N)|_{p=0} = AN \overset{!}{=} 1$ which gives $A = 1/N$.
Clearly the random force $\boldsymbol{f}_p$ is a linear super-position of random forces $\boldsymbol{f}_n$ weighted with the functions ϕ_{np}, *i.e.*

$$\boldsymbol{f}_p = \frac{\zeta_p}{\zeta} \int_0^N dn \phi_{np} \boldsymbol{f}_n \tag{6.19}$$

which leads to

$$\begin{aligned}
&\langle \boldsymbol{f}_p(t)\rangle = 0 \\
&\langle f_{px}(t) f_{px}(0)\rangle = 2k_BT\zeta_p\delta(t)
\end{aligned}$$

so we can choose ζ_p in order to satisfy the fluctuation dissipation theorem. The left hand side can be computed in terms of the old $\boldsymbol{f}_n$ via the eigen-functions ϕ_{np}

$$\begin{aligned}
\langle f_{p\alpha}(t) f_{q\beta}(0)\rangle &= \frac{\zeta_p\zeta_q}{\zeta^2}\int dn \int dm \phi_{np}\phi_{mq}\langle f_{n\alpha}(t) f_{m\beta}(0)\rangle = \frac{\zeta_p\zeta_q}{\zeta^2}2\zeta k_BT\int dn\int dm \phi_{np}\phi_{mq}\delta_{mn}\delta_{\alpha\beta}\delta(t \\
&= \frac{\zeta_p\zeta_q}{N^2\zeta^2}2\zeta k_BT\int dn\int dm \cos{(p\pi n/N)}\cos{(q\pi m/N)}\delta_{mn}\delta_{\alpha\beta}\delta(t) = \\
&= \frac{\zeta_p\zeta_q}{N^2\zeta^2}2\zeta k_BT\int dn \cos{(p\pi n/N)}\cos{(q\pi n/N)}\delta_{\alpha\beta}\delta(t) = \\
&= \frac{\zeta_p\zeta_q}{N^2\zeta^2}2\zeta k_BT\int dn \frac{1}{2}\left(\cos{[(p+q)\pi n/N]} + \cos{[(p-q)\pi n/N]}\right)\delta_{\alpha\beta}\delta(t) = \\
&= \frac{\zeta_p^2}{N^2\zeta^2}2\zeta k_BT\frac{1+\overset{\text{maybe}}{(2)}\ \delta_{p0}}{2}N\delta_{pq}\delta_{\alpha\beta}\delta(t)
\end{aligned}$$

Now we are going to use this to solve eq. (6.7), as follows. We know that we need to solve an equation as

$$\zeta\frac{d\boldsymbol{R}_n}{dt} = k\frac{d^2\boldsymbol{R}_n}{dn^2} + \boldsymbol{f}_n \tag{6.20}$$

but this has (in the r.h.s.) a dependence on the neighbouring beads. Using the normal coordinates, one can reduce this equation to:

$$\zeta_p\frac{d\boldsymbol{X}_p}{dt} = -k_p\boldsymbol{X}_p + \boldsymbol{f}_p \tag{6.21}$$

given that

$$\begin{aligned}
\boldsymbol{X}_p &= \int_0^N dn\frac{1}{N}\cos{(p\pi n/N)}\boldsymbol{R}_n \\
k_p &= \frac{\zeta_p}{\zeta}k = \frac{\zeta_p}{\zeta}\frac{3k_BT}{b^2} \\
\boldsymbol{f}_p &= \int_0^N dn\frac{1}{N}\cos{(p\pi n/N)}\boldsymbol{f}_n
\end{aligned}$$

OK, now, first of all one want to compute the average of the p-mode, like:

$$\langle X_{p\alpha}(t)\rangle = \int_{-\infty}^t dt' e^{-(t-t')/\tau}\frac{\langle f_p(t')\rangle}{\zeta_p} = 0 \tag{6.22}$$

this can be seen in two ways. (1) Either you integrate the homogeneous eq. without $f(t)$ and use the result to integrate $f(t)$. (2) Or, equivalently one can see this by using the integrating factor $\exp{(-(t-t')/\tau)}$. For instance by taking the derivative w.r.t time in both sides of eq. (6.22) one gets:

$$\begin{aligned}
\frac{d}{dt}X_{p\alpha}(t) &= \frac{d}{dt}\int_{-\infty}^t dt' e^{-(t-t')/\tau}\frac{f_p(t')}{\zeta_p} = -\frac{\tau}{\zeta_p}\int_{-\infty}^t dt' e^{-(t-t')/\tau}\frac{f_p(t')}{\zeta_p} + \left(e^{-(t-t')/\tau}\frac{f_p(t')}{\zeta_p}\right|_{t'=t} \\
&= -\frac{k_p}{\zeta_p}X_{p\alpha}(t) + \frac{f_{p\alpha}(t)}{\zeta_p}
\end{aligned}$$

exactly as the eq. (6.21). Ok, now let's compute the correlation function between modes. As already computed this gives:

$$\langle X_{p\alpha}(t)X_{q\beta}(0)\rangle = \frac{1}{\zeta_p^2}\int_{-\infty}^{t}\int_{-\infty}^{0} dt_1 dt_2 \exp\left[-(t-t_1-t_2)/\tau\right]\langle f_{p\alpha}(t_1)f_{q\beta}(t_2)\rangle = \frac{2k_BT\zeta_p\tau}{2\zeta_p^2}\delta_{pq}\delta_{\alpha\beta}e^{-t/\tau} =$$
$$\overset{\tau=\zeta_p/k_p}{=} \frac{k_BT}{k_b}\delta_{pq}\delta_{\alpha\beta}e^{-t/\tau} \text{ for } p>0$$

and just to be clear,

$$\tau = \tau_p = \frac{\zeta_p}{k_b} \overset{k_b=\zeta_p p^2\pi^2 k/N^2\zeta}{=} \frac{N^2b^2\zeta}{3\pi^2 k_BT}\frac{1}{p^2} = \frac{\tau_1}{p^2} \tag{6.23}$$

But for $p=0$ the equation for the mode X_0 is rather different, as $k_0=0$ one gets:

$$\langle (X_{0\alpha}(t)-X_{0\alpha}(0))(X_{0\beta}(t)-X_{0\beta}(0))\rangle = \frac{1}{\zeta_p^2}\int_0^t dt_1\int_0^t dt_2\langle f_{0\alpha}(t_1)f_{0\beta}(t_2)\rangle =$$
$$\frac{2k_BT\zeta_p\delta_{\alpha\beta}}{\zeta_p^2}\int_0^t dt_1 \overset{p=0}{=} \frac{2k_BT\delta_{\alpha\beta}t}{N\zeta}$$

So! For any mode which is **not** the zeroth mode, the correlation function decays as an exponential, where the characteristic time decreases as p^2. The zeroth mode actually grows with t linearly! Let's look at the inverse of the modes, these are:

$$\boldsymbol{R}_n = \boldsymbol{X}_0 + 2\sum_{p=1}^{\infty}\cos\left(\frac{p\pi n}{N}\right)\boldsymbol{X}_p \tag{6.24}$$

Therefore one can express, for instance, the centre of mass as the zeroth mode *i.e.*

$$\boldsymbol{R}_{com} = \boldsymbol{X}_{p=0} = \frac{1}{N}\int_0^N dn\cos\left(0\pi n/N\right)\boldsymbol{R}_n$$

and its mean square displacement (or correlation between the difference in starting point):

$$\langle(\boldsymbol{R}_{com}(t)-\boldsymbol{R}_{com}(0))^2\rangle = \langle(\boldsymbol{X}_0(t)-\boldsymbol{X}_0(0))^2\rangle = \sum_{\alpha=x,y,z}\frac{2k_BT\delta_{\alpha\alpha}t}{N\zeta} = \frac{6k_BT}{N\zeta}t \tag{6.25}$$

From which the diffusion coefficient of the centre of mass can be calculated via the Einstein relation:

$$D_{com} = \lim_{t\to\infty}\frac{\langle(\boldsymbol{R}_{com}(t)-\boldsymbol{R}_{com}(0))^2\rangle}{6t} = \frac{k_BT}{N\zeta} \tag{6.26}$$

This is the main result of the Rouse model. And it works in regimes in which hydrodynamics is not too important. For instance when the fluid is very viscous, or there is no fluid, like in the melt..in this case short enough chains do not reptate but follow the Rouse model (picked up later in this notes). The other modes can be interpreted, for instance, as the distance between points along the chain. The end-to-end vector:

$$\boldsymbol{P}(t) = \boldsymbol{R}_N - \boldsymbol{R}_0 \tag{6.27}$$

can be interpreted as the difference:

$$\boldsymbol{P}(t) = \boldsymbol{X}_0(t) + 2\sum_{p=1}^{\infty}\cos\left(\frac{p\pi N}{N}\right)\boldsymbol{R}_N(t) - \boldsymbol{X}_p(t) - 2\sum_{p=1}^{\infty}\cos\left(\frac{p\pi 0}{N}\right)\boldsymbol{X}_p(t) = 2\sum_{p=1}^{\infty}\left(\cos\left(p\pi\right)-1\right)\boldsymbol{X}_p =$$
$$= -4\sum_{p:odd}\boldsymbol{X}_p$$

and its correlation function:

$$\langle \boldsymbol{P}(t)\cdot\boldsymbol{P}(0)\rangle = 16\sum_{p:odd}\langle \boldsymbol{X}_p(t)\cdot\boldsymbol{X}_p(0)\rangle \overset{p\geq 0}{=} \sum_{p=1,3,5,\ldots} 16\frac{3k_BT\zeta}{k_p}e^{-t/\tau_p} = N^2b^2\sum_{p=1,3,5,\ldots}\frac{8}{p^2\pi^2}e^{-tp^2/\tau_1} \tag{6.28}$$

In general $\boldsymbol{X}_p$ represents the local motion of a segment that contains N/p monomers and corresponds to the motion with the length-scale of the order of $(N/p)^{1/2}b$. Since N/p is the number of segments of size b and the size of that coiled segment is the number of segments to the $1/2$ = entropic exponent for a phantom chain. Finally, the longest relaxation time is given by the relaxation time of the first moment, *i.e.* τ_1

$$\tau_r = \frac{N^2b^2\zeta}{3\pi^2k_BT} \qquad \text{and} \qquad D_{com} = \frac{k_BT}{N\zeta} \tag{6.29}$$

Chapter 7

Reptation

7.1 The Tube Model

The rigorous account for topological interactions is extremely difficult and it has been shown that an entangled state can be described by an effective "tube model", where a single chain is surrounded by other polymers.

The tube models describes the motion of a probe chain in a midst of other chains, but it can't take into account the collective motion of chains. This is the main reason for which it fails to describe a system of rings.

Let's say that there is a chain in a network of fixed obstacles such that its primitive contour length is

$$L = \frac{Nb^2}{a} \tag{7.1}$$

which means that L times the number of entanglement lengths a equals the length of the Rouse chain Nb^2. Consider the end-to-end vector $\boldsymbol{P}(t) = \boldsymbol{R}(L,t) - \boldsymbol{R}(0,t)$. Its correlation function $\langle \boldsymbol{P}(t)\boldsymbol{P}(0)\rangle$ gives the quantity of length that is still inside the same tube after time t. This can be expressed as $a\langle\sigma(t)\rangle$ where $\sigma(t)$ is the number of entanglement lengths still in the tube. Define a function $\psi(s,t)$ which gives the probability that segment s is still in the tube at time t, then clearly

$$\sigma(t) = \int_0^L ds\psi(s,t) \tag{7.2}$$

Now, define a more complicated probability. Which is the probability that a chain moves a length ζ without hitting s with neither ends and time t: $\Psi(\zeta, t; s)$. This quantity undergoes 1D diffusion along the polymer contour:

$$\frac{\partial \Psi(\zeta,t;s)}{\partial t} = D_c \frac{\partial^2 \Psi(\zeta,t;s)}{\partial \zeta^2} \tag{7.3}$$

This equation is actually fairly similar to the Rouse equation. The boundary conditions are somewhat different. Here, in fact,

$$\Psi(\zeta,0;s) = \delta(\zeta) \tag{7.4}$$

which means that at time zero the chain has not moved yet and that the boundary conditions are:

$$\Psi(\zeta,t;s) = 0 \text{ if } \zeta = s \text{ or } \zeta = s - L \tag{7.5}$$

which means that the function vanishes if one of the two ends hits the segment s.

This expression could be identical for a branch of branched polymer, with the caveat that only one end can move and vanishes when hits the other end. Plus, add some delay for threadings.

The solution can be found in a similar way we found the solution for the Rouse chain (see Section on Rouse) and gives

$$\Psi(\zeta, t; s) = \sum_{p=1}^{\infty} \frac{2}{L} \sin\left(\frac{p\pi s}{L}\right) \sin\left(\frac{p\pi(s-L)}{L}\right) e^{-p^2 t/\tau_d} \tag{7.6}$$

where $\tau_d = L^2/D_c\pi^2$. After this, the function $\psi(s,t)$ is easily found as

$$\psi(s,t) = \int_{s-L}^{s} d\zeta \Psi(\zeta, t; s) = \sum_{p:odd} \frac{4}{p\pi} \sin\left(\frac{p\pi s}{L}\right) e^{-p^2 t/\tau_d} \tag{7.7}$$

and finally

$$\langle \boldsymbol{P}(t)\boldsymbol{P}(0) \rangle = La\psi(t) = La\frac{1}{L}\int_0^L ds\psi(s,t) = \sum_{p:odd} \frac{8}{p^2\pi} e^{-p^2 t/\tau_d} \tag{7.8}$$

which is exactly the same as for the Rouse chain, a part from the characteristic time

$$\tau_d = \frac{1}{\pi^2}\frac{\xi M^3 b^4}{k_B T a^2} \text{ while } \tau_R = \frac{M^2 b^2 \xi}{k_B T 3\pi^2}. \tag{7.9}$$

Chapter 8

Brownian Ratchet

One concept that might be interesting to keep in mind is that of "Brownian Ratchet". This had been advanced in the '90s to explain how cells move on a substrate (Peskin Odell Oster Biophys J. 1993). The network of actin tubules polymerise along the "+" end, therefore creating a flux of material in one direction. If one imagines a fluctuating membrane which is diffusing in front of a single microtubule then the competition between polymerisation timescale and diffusion timescale might be able to "rectify" the motion of the membrane and create directed motion.

The basic model is that of a fibre which is growing and in front of it there is a diffusing flat membrane. The fibre grows by adding monomers of size δ at rate k_{on} and removed with rate k_{off}. The diffusion is regulated by D and there might be a force f applied onto the membrane from the "outside".

The max speed of the ratchet is achieved when one monomer is added every time the membrane diffuses a space large enough that a new monomer can be inserted. This means $t_\delta = \delta^2/2D$. The speed is therefore $v_{ideal} = \delta/t_\delta = 2D/\delta$.

In the "real" case one can describe the situation in a more general terms. One in general has a distance x of the tip of the fibre from the surface of the membrane. The probability of being at distance x at time t can be written as a diffusion-advection equation

$$\begin{aligned}\frac{\partial p(x,t)}{\partial t} &= D\frac{\partial^2 p}{\partial x^2} + \frac{f}{\gamma}\frac{\partial p}{\partial x} + \\ &+ k_{on}\left[p(x+\delta,t) - p(x,t)\Theta(x-\delta)\right] + \\ &- k_{off}\left[p(x-\delta,t)\Theta(x) - p(x,t)\right]\end{aligned} \tag{8.1}$$

The last two term can be understood as a sort of Master equation-like terms that balance the mass lost and gained at a given timestep. The heaviside functions act to make sure that the move can be done (i.e. the membrane is or was, far enough to allow the move).

In this more complicated case one can then argue that the speed is given by

$$\begin{aligned}v_{ratchet} &= \delta k_{on} p(gap \geq \delta) - k_{off}\delta = \\ &= \delta k_{on}\frac{\int_\delta^\infty p_{ss}(x)}{\int_0^\infty p_{ss}(x)} - k_{off}\delta\end{aligned} \tag{8.2}$$

this is because each time the gap is greater than δ I can put a monomer. And this happen at rate k_{on}. The speed being $\sim \delta k_{on} - \delta k_{off}$. The steady state probability $p_{ss}(x)$ has therefore to be computed.

The important dimensionless parameters are $k_{on}\delta^2/D$ and $k_{off}\delta^2/D$. These reflect how many monomers are added or lost during one diffusion time $\sim \delta^2/D$. Now assuming

$k_{on}\delta^2/D \ll 1$ one can write the steady state solution as

$$\begin{aligned} 0 &= D\frac{\partial^2 p_{ss}}{\partial x^2} + \frac{Df}{k_BT}\frac{\partial p_{ss}}{\partial x} = \\ &= \frac{d}{dx}\left[D\frac{dp_{ss}}{dx} + \frac{Dfp_{ss}}{k_BT}\right] = \frac{dJ}{dx} \end{aligned} \tag{8.3}$$

with J being a "current". To satisfy this equation the current needs to be constant, and using the no-flux boundary condition (at the membrane there is no escape of probability) one can therefore set $J = 0$. The equation thus reduces to

$$J = 0 = \frac{dp_{ss}}{dx} + \frac{fp_{ss}}{k_BT} \tag{8.4}$$

which simply gives $p \propto e^{-fx/k_BT}$. Plugging this solution back to the equation for the velocity one obtains:

$$\begin{aligned} v_{ratchet} &= \delta k_{on}\frac{\int_\delta^\infty e^{-fx/k_BT}dx}{\int_0^\infty e^{-fx/k_{B_T}}dx} - k_{off}\delta = \\ &= \delta\left[k_{on}e^{-f\delta/k_BT} - k_{off}\right] \end{aligned} \tag{8.5}$$

Plugging in some realistic numbers (for instance $k_{on} \simeq 100s^{-1} \gg k_{off} \simeq s^{-1}$) one gets (for $f = 0$) $v_{ratchet} \simeq k_{on}\delta \simeq 300nms^{-1}$ not too far from the real case which is of order $100 - 200nms^{-1}$. From the same equation one can find the stalling force f so that easy exercise to do $v_{ratchet} = 0$.

8.1 Multiple Diffusing Cohesins on Chromatin

In this case one considers the density of cohesins ρ. On equation that one can write for uniform binding of cohesins reads:

$$\frac{d\rho}{dt} = k_{on}\frac{N_{off}}{L} - k_{off}\rho + D\frac{d^2\rho}{dx^2} \tag{8.6}$$

where N_{off} is the number of off cohesins that can rebind at any time and L the system size. Steady state is

$$\rho_{ss} = \frac{k_{on}}{k_{off}}\frac{N_{off}}{L} = \frac{Nk_{on}}{k_{on}+k_{off}}\frac{1}{L} \tag{8.7}$$

since $N_{off} = Nk_{off}/(k_{on}+k_{off})$ and N being the total number of cohesins. In this case the density is of course constant everywhere.

Another equation that one can write is one in which the cohesins always rebind in the same site (loading side). In this case the equation is

$$\frac{d\rho}{dt} = k_{on}N_{off}\delta(x) - k_{off}\rho + D\frac{d^2\rho}{dx^2} \tag{8.8}$$

and in this case the steady state

$$\rho_{ss}(x) = Ae^{-\sqrt{\frac{k_{off}}{D}}|x|} \tag{8.9}$$

This behaviour can be understood as a steady state difference of density of cohesins, i.e. a difference of pressure as $pV = nRT$ or $p = RT\rho$.

To measure the force on any one cohesin induced by this pressure difference one can use the overdamped form $f = \gamma dl/dt$ where l is the distance along the fibre, i.e. the 1D position, and dl/dt being the speed due to the force. Since the force can also be computed as $dp/dx\sigma = Ak_BT\sigma e^{-\alpha x}(-\alpha)$ (with $\alpha = \sqrt{k_{off}/D}$) one can finally relate the distance travelled l with the pressure p and compute what is the speed of any cohesin at a given l. The result is something along the line:

to check

$$\gamma\frac{dl}{dt} = k_{on}\sigma N_{off}e^{-\alpha l/2}\gamma \tag{8.10}$$

and finally the prediction of loop length l

$$\frac{l}{2} = \frac{2}{\alpha}\log\left[1 + \frac{\alpha}{2}N_{off}k_{on}\sigma t\right]. \tag{8.11}$$

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