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Tutorial IV
Rouse model

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4 Rouse Model

The Rouse model is a model for the dynamics of a polymer chain in a solvent. In this model, the chain is represented by a sequence of effective monomers (called "beads"). The positions of the beads will be denoted by $(\vec{r}_0, \cdots, \vec{r}_n, \cdots, \vec{r}_N)$ where the index n is a continuous variable. Every bead is subject to the following forces :

- a force $\vec{F}^c$ resulting from the connectivity between successive beads. In the rouse model, the beads are linked by a harmonic spring force with force constant k. In the continuum limit, the force $\vec{F}^c_n$ on bead n is given by :

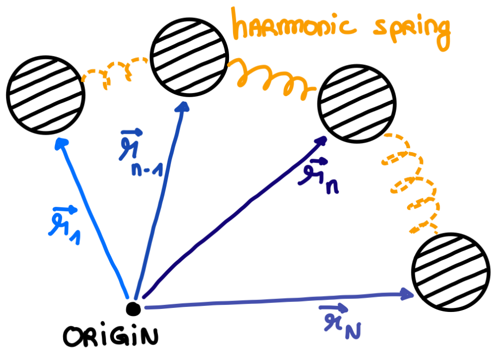
$$\vec{F}^c_n = k\frac{\partial^2 \vec{r}_n}{\partial n^2} \quad \text{with} \quad k = \frac{3k_BT}{b^2}, \tag{1}$$

  where b is the length of the bond between nearest-neighbor beads along the chain, k_B is the Boltzmann constant, and T is the temperature ;
- a friction force $-\zeta\partial\vec{r}_n/\partial t$ where ζ denotes the friction coefficient and
- a Gaussian white noise $\vec{F}^R_n$ characterized by :

$$\langle \vec{F}^R_n(t)\rangle = 0, \tag{2}$$

$$\langle F^R_{n,\alpha}(t)F^R_{m,\beta}(t')\rangle = 2\zeta k_BT\delta_{\alpha\beta}\delta(n-m)\delta(t-t'), \tag{3}$$

  where t is the time and α, β $(= x, y, z)$ are the cartesian coordinates.



A Brownian particle is submitted to a friction force $\vec{F}^n_{\text{vis}}$ and a random force $\vec{F}^R_n$ (Gaussian white noise, meaning that the two first moment allow to fully characterize it). Saying white noise is equivalent to say that all frequency are allowed in the spectrum. We can write the potential $U(\vec{r}^N) = \frac{k}{2}\sum_{n=2}^{N}(\vec{r}_n - \vec{r}_{n-1})^2$ with $k = 3k_BT/b^2$ where b is the average length of the spring. With those information we can write the equation of motion,

$$m\ddot{\vec{r}}_n = -\frac{\partial}{\partial\vec{r}_n}U(\vec{r}^N) - \zeta\dot{\vec{r}}_n + \vec{F}^R_n(t)$$

We indeed neglect inertia in the expression above. We can thus split in two sets this expression, inner beads $(n = 2, \cdots, N-1)$ and outer beads $n = 1$ or $n = N$.

- **Inner beads**,

$$\begin{aligned}\zeta\dot{\vec{r}}_n &= -\frac{k}{2}\left[2(\vec{r}_{n+1}-\vec{r}_n)(-1)+2(\vec{r}_n-\vec{r}_{n-1})\right]+\vec{F}_n^R(t)\\ &= k\left[(\vec{r}_{n+1}-\vec{r}_n)-(\vec{r}_n-\vec{r}_{n-1})\right]+\vec{F}_n^R(t)\\ &= k\left[\frac{\frac{\vec{r}_{n+1}-\vec{r}_n}{(n+1)-n}-\frac{\vec{r}_n-\vec{r}_{n-1}}{n-(n-1)}}{(n+1)-n}\right]+\vec{F}_n^R(t)\\ &\approx k\frac{\partial^2}{\partial n^2}\vec{r}_n+\vec{F}_n^R(t)\end{aligned}$$

- **End beads**,

$$\zeta\dot{\vec{r}}_1 = -\frac{k}{2}\left[2(\vec{r}_2-\vec{r}_1)(-1)\right]+\vec{F}_1^R$$

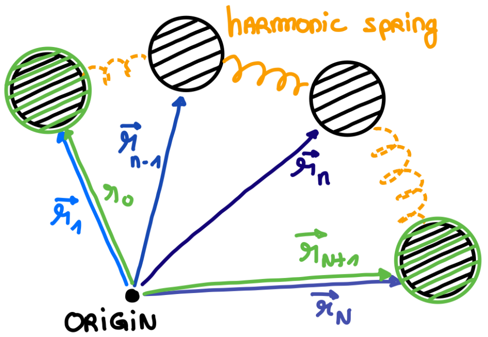
We can rewrite it using a little trick, let's suppose $\vec{r}_1=\vec{r}_0$ thus,

$$\zeta\dot{\vec{r}}_1 = k\left[(\vec{r}_2-\vec{r}_1)-(\vec{r}_1-\vec{r}_0)\right]+\vec{F}_1^R$$

and similarly, if $\vec{r}_N=\vec{r}_{N+1}$,

$$\zeta\dot{\vec{r}}_N = k\left[(\vec{r}_{N+1}-\vec{r}_N)-(\vec{r}_N-\vec{r}_{N-1})\right]+\vec{F}_N^R$$

In a sens, writing $\vec{r}_0$ and $\vec{r}_{N+1}$ is like writing a *fictious bead*



with all of that, this allows us to write boundary conditions,

$$\frac{\vec{r}_{n+1}-\vec{r}_n}{(n+1)-n}\approx\frac{\partial}{\partial n}\vec{r}_n$$

leading to the following boundary conditions,

$$\left.\frac{\partial}{\partial n}\vec{r}_n\right|_{n=0}=\left.\frac{\partial}{\partial n}\vec{r}_n\right|_{n=N}=0$$

this is not entirely mathematically correct to say so, but it is to give a good physical picture. In this model the *tension* in the chain is everywhere but at the ends.

1. The balance of these forces gives the following equation of motion for the Rouse model :

$$\zeta \frac{\partial \vec{r}_n(t)}{\partial t} = k \frac{\partial^2 \vec{r}_n(t)}{\partial n^2} + \vec{F}_n^R(t) \quad \text{with} \quad (n \in [0, N]). \tag{4}$$

This equation represents a *coarse-grained* description of the polymer dynamics :

(a) Explain the term "coarse-grained description" of the dynamics.

(b) When discussing the problem of Brownian motion in the course we distinguished between the "coarse-graining of Langevin" and the "coarse-graining of Einstein". Does Eq.(4) correspond to the "coarse-graining of Langevin" or to the "coarse-graining of Einstein". Justify your answer.

2. Now we introduce the "Rouse modes" which are defined by

$$\vec{X}_p(t) = \frac{1}{N} \int_0^N \mathrm{d}n \vec{r}_n(t) \cos \frac{p\pi n}{N} \quad \text{with} \quad p = 0, 1, 2, 3, \cdots. \tag{5}$$

Using this definition show that the equation of motion of the Rouse mode $\vec{X}_p(t)$ is given by :

$$\zeta_p \frac{\partial \vec{X}_p(t)}{\partial t} = -k_p \vec{X}_p(t) + \vec{F}_p^R(t) \tag{6}$$

where ζ_p is the friction coefficient of the mode p,

$$k_p = \frac{\zeta_p}{\zeta} \left(\frac{p\pi}{N}\right)^2 k \tag{7}$$

and

$$\vec{F}_p^R(t) = \frac{\zeta_p}{\zeta} \frac{1}{N} \int_0^N \mathrm{d}n \vec{F}_n^R(t) \cos \frac{p\pi n}{N}. \tag{8}$$

Remark : To derive Eqs.(6-8) start from $\zeta_p \partial \vec{X}_p / \partial t$ and use the following boundary conditions : $\partial \vec{r}_n / \partial n \big|_{n=0} = \partial \vec{r}_n / \partial n \big|_{n=N} = 0$.

$$\begin{aligned}
\zeta_p \frac{\partial \vec{X}_p}{\partial t} &= \zeta_p \frac{1}{N} \int_0^N \mathrm{d}n \frac{\partial \vec{r}_n(t)}{\partial t} \cos \frac{p\pi n}{N} \\
&= \frac{\zeta_p}{\zeta} \frac{1}{N} \left\{ k \int_0^N \mathrm{d}n \cos\left(\frac{p\pi n}{N}\right) \frac{\partial^2 \vec{r}_n}{\partial n^2} + \int_0^N \mathrm{d}n \cos\left(\frac{p\pi n}{N}\right) \vec{F}_n^R(t) \right\}
\end{aligned}$$

The red part is still a Gaussian process that we can call $\vec{F}_p^R(t)$ because a superposition of Gaussian remains Gaussian. The other integral is calculated using twice an integral by parts and leading to,

$$\begin{aligned}
\zeta_p \frac{\partial \vec{X}_p}{\partial t} &= -\frac{\zeta_p}{\zeta} \left(\frac{p\pi}{N}\right)^2 k \vec{X}_p(t) + \vec{F}_p^R(t) \\
&= -k_p \vec{X}_p(t) + \vec{F}_p^R(t)
\end{aligned}$$

3. The random force $\vec{F}_p^R$ on mode p is also a Gaussian white noise. Justify qualitatively this result.

   This is because a superposition of Gaussians remains Gaussian.

4. Therefore, $\vec{F}_p^R$ is fully determined by the first two moments $(p, q = 0, 1, 2, 3, \cdots)$,

$$\langle \vec{F}_p^R(t) \rangle = 0, \tag{9}$$

$$\langle F_{p,\alpha}^R(t) F_{q,\beta}^R(t') \rangle = 2\zeta_p k_B T \delta_{\alpha\beta} \delta_{pq} \delta(t - t') \quad \text{for} \quad p = 0, 1, 2, 3, \cdots. \tag{10}$$

   Show that

$$\zeta_p = \frac{2}{1 + \delta_{p0}} \zeta N = \begin{cases} \zeta N \text{ for } p = 0, \\ 2\zeta N \text{ for } p > 0. \end{cases} \tag{11}$$

   Remark : For this derivation insert Eq. (8) into the left-hand-side of Eq. (10) and use

$$\int_0^N \mathrm{d}n \cos \frac{p\pi n}{N} \cos \frac{q\pi n}{N} = \frac{1 + \delta_{p0}}{2} N \delta_{pq}. \tag{12}$$

$$\begin{aligned}
\langle F_{p,\alpha}^R(t) F_{q,\beta}^R(t') \rangle &= \left(\frac{\zeta_p}{\zeta}\right)\left(\frac{\zeta_q}{\zeta}\right) \frac{1}{N^2} \int_0^N \mathrm{d}n \int_0^m \mathrm{d}m \cos\left(\frac{p\pi n}{N}\right) \cos\left(\frac{q\pi m}{N}\right) \underbrace{\langle F_{n,\alpha}^R(t) F_{m,\beta}^R(t) \rangle}_{=2k_B T \zeta \delta_{\alpha\beta} \delta(n-m) \delta(t-t')} \\
&= \left(\frac{\zeta_p \zeta_q}{\zeta}\right) 2k_B T \delta_{\alpha\beta} \delta(t - t') \int_0^N \mathrm{d}n \int_0^N \mathrm{d}m \cos\left(\frac{p\pi n}{N}\right) \cos\left(\frac{q\pi m}{N}\right) \delta(n - m) \\
&= \left(\frac{\zeta_p \zeta_q}{\zeta}\right) 2k_B T \delta_{\alpha\beta} \delta(t - t') \int_0^N \mathrm{d}n \cos\left(\frac{p\pi n}{N}\right) \cos\left(\frac{q\pi n}{N}\right) \\
&= \left(\frac{\zeta_p \zeta_q}{\zeta}\right) 2k_B T \delta_{\alpha\beta} \delta(t - t') \left(\frac{1 + \delta_{p,0}}{2}\right) N \delta_{pq}
\end{aligned}$$

   To have an analogy with the Gaussian white noise Eq. (3), we have to enforce

$$\zeta_p = \frac{\zeta_p^2}{\zeta} \left(\frac{1 + \delta_{p0}}{2}\right) \frac{1}{N}$$

   Leading to,

$$\zeta_p = \frac{2}{1 + \delta_{p,0}} \zeta N$$

   And we can express now k_p,

$$k_p = \begin{cases} 0 \text{ for } p = 0 \\ \dfrac{6k_B T}{b^3} N \left(\dfrac{p\pi}{N}\right)^2 \text{ for } p \neq 0 \end{cases}$$

5. Use the results obtained above to show that Eq. (6) can be written as

$$(2\zeta N)\frac{\partial \vec{X}_p(t)}{\partial t} = -\left(\frac{6\pi^2 k_B T p^2}{N b^2}\right)\vec{X}_p(t) \quad \text{for} \quad p > 0, \tag{13}$$

$$(\zeta N)\frac{\partial \vec{X}_0(t)}{\partial t} = \vec{F}_0^R(t) \quad \text{for} \quad p = 0. \tag{14}$$

This is immediately seen.

6. Questions referring to the course :
   (a) To which stochastic process does Eq. (13) correspond ?

   This is a Ornstein–Uhlenbeck process.

   (b) To which stochastic process does Eq. (14) correspond ?

   This is a Wiener process.

7. We consider now the case $p = 0$:
   (a) Utilize the inverse transform

$$\vec{r}_n = \vec{X}_0 + 2\sum_{p=0}^{\infty} \vec{X}_o \cos\frac{p\pi n}{N} \tag{15}$$

   to show that the center of mass $\vec{R}$ of the polymer chain is given by $\vec{X}_0$, *i.e.*,

$$\vec{R} = \frac{1}{N}\int_0^N \mathrm{d}n \vec{r}_n = \vec{X}_0. \tag{16}$$

   We know that the center of mass is,

$$\vec{R}_{\mathrm{CM}} = \frac{\sum_{i=1}^N m_i \vec{r}_i}{\sum_{i=1}^N m_i} = \frac{1}{N}\sum_{i=1}^N \vec{r}_i$$

   and thus, setting $p = 0$ in Eq.(5) is immediately getting us the equivalence to center of mass.

   (b) Show that the mean-square displacement of the center of mass is diffusive, *i.e.*,

$$\langle[\vec{R}(t) - \vec{R}(0)]^2\rangle = 6Dt, \tag{17}$$

   and give the explicit expression for the diffusion coefficient D.