Summary for the Rouse model

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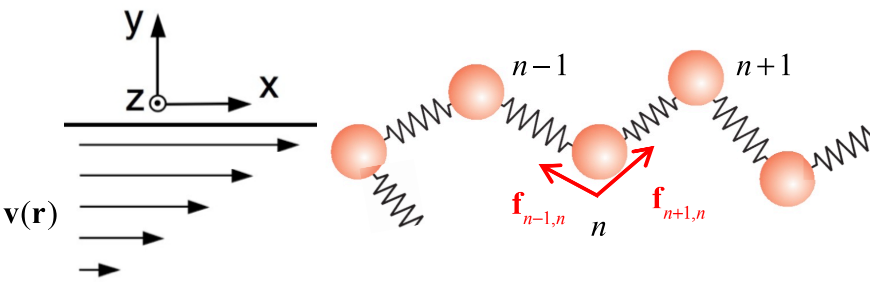
1. The Langevin equation

Let us consider the dynamics of a polymeric molecule, which is modeled as a non-interacting chain composed of $N+1$ spherical beads ($n=0,1,2,\cdots,N$) and N springs connecting between consecutive beads, in a solvent with steady flow field $\mathbf{v}(\mathbf{r})$.



Bead and spring model in solvent.

Using the physical variables and the parameters defined below,

$\mathbf{R}_n(t)$	Position of bead n at time t
$\mathbf{V}_n(t)$	Velocity of bead n at time t
$\mathbf{g}_n(t),\mathbf{g}'_n(t)$	Thermal (random) force acting on bead n at time t
$\mathbf{f}_{m,n}(t)$	Force acting on bead n due to adjacent bead m at time t
m	Mass of a bead
$\zeta = 6\pi\eta a$	Friction constant of a bead (radius a) in solvent (viscosity η)
T	Temperature
$3k_BT/b^2$	Spring constant between adjacent beads
$D_b = k_BT/\zeta$	Diffusion constant of beads
b	Average separation between adjacent beads
c	Number density of polymer molecules

the equation of motion for bead n is given by

$$m\frac{d\mathbf{V}_n}{dt} = \zeta\left(\mathbf{V}_n - \mathbf{v}(\mathbf{R}_n)\right) + \mathbf{f}_{n-1,n} + \mathbf{f}_{n+1,n} + \mathbf{g}'_n . \tag{1}$$

Then the use of $\frac{d\mathbf{V}_n}{dt}=0$ (over damped assumption), $\mathbf{V}_n = \frac{d\mathbf{R}_n}{dt}$, $\mathbf{f}_{m,n} = \frac{3k_BT}{b^2}\left(\mathbf{R}_m - \mathbf{R}_n\right)$, and a specially uniform velocity gradient $\kappa \equiv \frac{\partial \mathbf{v}}{\partial \mathbf{r}}$, yields the Langevin equation of the form

$$\frac{d\mathbf{R}_n}{dt} = -\frac{3k_BT}{\zeta b^2}\left(\mathbf{R}_{n+1} - 2\mathbf{R}_n + \mathbf{R}_{n-1}\right) + \kappa\bullet\mathbf{R}_n + \mathbf{g}_n(t), \tag{2}$$

where $\mathbf{R}_{-1} = \mathbf{R}_0$ and $\mathbf{R}_{N+1} = \mathbf{R}_N$ are used to take care of boundary conditions at the both ends of the chain, and the thermal force should satisfy the condition

$$\left\langle \mathbf{g}_n(t) \right\rangle = \mathbf{0}, \qquad \left\langle \mathbf{g}_n(t)\mathbf{g}_m(t') \right\rangle = 2\frac{k_B T}{\zeta}\delta_{nm}\delta(t-t')\mathbf{I}, \tag{3}$$

to reproduce the equilibrium fluctuations correctly.

2. Normal mode

By introducing the discrete cosine transformation

$$\mathbf{X}_p(t) = \frac{1}{N+1}\sum_{n=0}^{N}\mathbf{R}_n(t)\cos\left[\frac{p\pi}{N+1}\left(n+\frac{1}{2}\right)\right] \tag{4}$$

and the inverse transformation

$$\mathbf{R}_n(t) = \mathbf{X}_0(t) + 2\sum_{p=1}^{N}\mathbf{X}_p(t)\cos\left[\frac{p\pi}{N+1}\left(n+\frac{1}{2}\right)\right], \tag{5}$$

the Langevin equation for the p-th normal mode can be obtained as

$$\frac{d\mathbf{X}_p}{dt} = -\frac{k_p}{\zeta_p}\mathbf{X}_p + \kappa\bullet\mathbf{X}_p + \mathbf{g}_p, \tag{6}$$

where $k_p = \dfrac{6k_B T(N+1)}{b^2}\left[4\sin^2\left(\dfrac{p\pi}{2(N+1)}\right)\right]$, $\zeta_p = (N+1)\zeta(2-\delta_{0p})$,

$$\left\langle \mathbf{g}_p(t) \right\rangle = \mathbf{0}, \ \left\langle \mathbf{g}_p(t)\mathbf{g}_q(t') \right\rangle = 2\frac{k_B T}{\zeta}\frac{\delta_{pq}\delta(t-t')}{(N+1)(2-\delta_{0p})}\mathbf{I}. \tag{7}$$

When flow does not exist $\kappa = \mathbf{0}$, the 0-th mode can be obtained as

$$\mathbf{X}_0(t) = \mathbf{X}_0(0) + \int_0^t \mathbf{g}_0(t')\,dt'. \tag{8}$$

Because the center of mass of the chain is given by $\mathbf{X}_0(t) = \dfrac{1}{N+1}\sum_{n=0}^{N}\mathbf{R}_n(t)$, the diffusion constant for the center of mass of the chain can then be calculated

$$\boxed{D_G \equiv D_R} = \frac{1}{6t}\left\langle \left(\mathbf{X}_0(t) - \mathbf{X}_0(0)\right)^2 \right\rangle = \frac{1}{6t}\left\langle \int_0^t dt' \int_0^t dt'' \mathbf{g}_0(t')\bullet\mathbf{g}_0(t'') \right\rangle$$
$$= \frac{k_B T}{\zeta_0} \boxed{= \frac{k_B T}{\zeta(N+1)} \quad \propto N^{-1}}. \tag{9}$$

The time correlation function for the p-th normal mode is determined to be

$$\left\langle \mathbf{X}_p(t)\cdot\mathbf{X}_p(0) \right\rangle = \left\langle \mathbf{X}_p^2 \right\rangle \exp\left[-\left(\frac{t}{\tau_p}\right)\right], \tag{10}$$

where

$$\left\langle \mathbf{X}_p^2 \right\rangle = \frac{b^2}{8(N+1)\sin^2\left(\dfrac{p\pi}{2(N+1)}\right)} \quad \left(\approx \frac{b^2(N+1)}{2\pi^2 p^2} \quad \text{for } p \ll N\right) \tag{11}$$

represents the magnitude of the fluctuations and

$$\tau_p = \frac{\zeta_p}{k_p} = \frac{\zeta b^2}{3k_B T}\left[4\sin^2\left(\frac{p\pi}{2(N+1)}\right)\right]^{-1} \quad \left(\approx \frac{\zeta b^2 (N+1)^2}{3\pi^2 k_B T p^2} \quad \text{for } p \ll N\right) \tag{12}$$

represents the relaxation times of the p-th normal mode for $p \geq 1$.

3. Beads (segments) motions

Using the definition of the inverse cosine transformation the mean square displacements $\phi_n(t)$ of the individual beads (segments) is given by

$$\begin{aligned}
\phi_n(t) &\equiv \frac{1}{N+1}\sum_{n=0}^{N}\left\langle\left(\mathbf{R}_n(t)-\mathbf{R}_n(0)\right)^2\right\rangle \\
&= \left\langle\left(\mathbf{X}_0(t)-\mathbf{X}_0(0)\right)^2\right\rangle \\
&\quad + 4\sum_{p=1}^{N}\left\langle\left(\mathbf{X}_p(t)-\mathbf{X}_p(0)\right)^2\right\rangle \frac{1}{N+1}\sum_{n=0}^{N}\cos^2\left[\frac{p\pi}{N+1}\left(n+\frac{1}{2}\right)\right] \\
&= 6D_G t + 4\sum_{p=1}^{N}\left\langle\left(\mathbf{X}_p(t)\right)^2 - 2\mathbf{X}_p(t)\bullet\mathbf{X}_p(0) + \left(\mathbf{X}_p(0)\right)^2\right\rangle \frac{1}{2} \\
&= 6D_G t + 4\sum_{p=1}^{N}\left\langle\mathbf{X}_p^2\right\rangle\left[1-\exp\left[-\left(\frac{t}{\tau_p}\right)\right]\right]
\end{aligned} \tag{13}$$

The first term dominates for $t \gg \tau_{p=1}$, thus

$$\phi_n(t) \approx 6D_G t .$$

However, the second term dominates for $\tau_{p=N} \ll t \ll \tau_{p=1}$, thus

$$\begin{aligned}
\phi_n(t) &= 4\sum_{p=1}^{N}\left\langle\mathbf{X}_p^2\right\rangle\left[1-\exp\left[-\left(\frac{t}{\tau_p}\right)\right]\right] \\
&\approx \frac{2b^2}{\pi^2}(N+1)\int_0^\infty dp\frac{1}{p^2}\left[1-\exp\left[-\left(\frac{tp^2}{\tau_{p=1}}\right)\right]\right] \\
&= \frac{2b^2}{\pi^2}(N+1)\int_0^\infty dp\frac{1}{\tau_{p=1}}\int_0^t dt'\exp\left[-\left(\frac{t'p^2}{\tau_{p=1}}\right)\right] \\
&= \frac{2b^2}{\pi^2}(N+1)\frac{1}{\tau_{p=1}}\int_0^t dt'\int_0^\infty dp\exp\left[-\left(\frac{t'p^2}{\tau_{p=1}}\right)\right] \\
&= \frac{2b^2}{\pi^2}\frac{(N+1)}{\tau_{p=1}}\frac{1}{2}\sqrt{\pi\tau_{p=1}}\int_0^t dt'\frac{1}{\sqrt{t'}} \\
&= \frac{2b^2}{\pi^2}\frac{(N+1)}{\tau_{p=1}}\frac{1}{2}\sqrt{\pi\tau_{p=1}}\left(2t^{1/2}-0\right) \\
&= \left(\frac{12k_B T b^2}{\pi\zeta}\right)^{1/2} t^{1/2}
\end{aligned} \tag{14}$$

4. Stress relaxation function

When we consider a simple shear flow $\kappa = \begin{pmatrix} 0 & \dot{\gamma} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$, substitution of this into the Langevin equation for the *p*-th normal mode yields

$$\frac{d\left\langle X_p^x X_p^y \right\rangle}{dt} = -\frac{2k_p}{\zeta_p}\left\langle X_p^x X_p^y \right\rangle + \dot{\gamma}\left\langle \left(X_p^y\right)^2 \right\rangle . \tag{15}$$

Because flow exists only in *x*-direction, we can estimate the fluctuation in *y*-direction $\left\langle \left(X_p^y\right)^2 \right\rangle \approx \left\langle \mathbf{X}_p^2 \right\rangle / 3 = k_B T / k_p$ to close the above differential equation. We then finally obtain

$$\left\langle X_p^x X_p^y \right\rangle = \int_{-\infty}^{t} dt' \frac{k_B T}{k_p} \exp\left[-\frac{2k_p}{\zeta_p}(t-t')\right]\dot{\gamma}(t') . \tag{16}$$

From the expression for the macroscopic stress we already obtained, it can be reformulated with the normal modes using the inverse cosine transformation as shown below.

$$\begin{aligned} \sigma_{xy} &= \frac{c}{N}\frac{3k_B T}{b^2}\sum_{n=1}^{N}\left\langle \left(R_n^x - R_{n-1}^x\right)\left(R_n^y - R_{n-1}^y\right)\right\rangle \\ &= \frac{c}{N}\sum_{p=1}^{N} k_p \left\langle X_p^x X_p^y \right\rangle \\ &= \frac{ck_B T}{N}\int_{-\infty}^{t} dt' \sum_{p=1}^{N} \exp\left[-\frac{2k_p}{\zeta_p}(t-t')\right]\dot{\gamma}(t') \end{aligned} \tag{17}$$

Comparing the last equation with the Maxwell's superposition principle

$$\sigma_{xy} = \int_{-\infty}^{t} dt' G(t-t')\dot{\gamma}(t') , \tag{18}$$

the stress relaxation function for the Rouse model is finally determined as

$$\begin{aligned} \boxed{G(t)} &= \frac{ck_B T}{N+1}\sum_{p=1}^{N}\exp\left[-\frac{2k_p}{\zeta_p}t\right] = \frac{ck_B T}{N+1}\sum_{p=1}^{N}\exp\left[-2\left(\frac{t}{\tau_p}\right)\right] \\ &\boxed{= \frac{ck_B T}{N+1}\sum_{p=1}^{N}\exp\left[-24\sin^2\left(\frac{p\pi}{2(N+1)}\right)\left(\frac{t}{\tau_b}\right)\right]} \\ &\approx \frac{ck_B T}{N+1}\int_{p=0}^{\infty}\exp\left[-\left(\frac{\sqrt{6}p\pi}{N+1}\sqrt{\frac{t}{\tau_b}}\right)^2\right] = \frac{ck_B T}{\sqrt{24\pi}}\sqrt{\frac{\tau_b}{t}}, \qquad (\tau_{p=N} \ll t \ll \tau_{p=1}) \end{aligned} \tag{19}$$

where $\tau_b = \dfrac{\zeta b^2}{k_B T}$ represents a unit time according to the bead motion *i.e.*, the diffusion time of a bead particle over the unit length b. From the mechanical definition of the shear viscosity upon application of a step shear flow ($\dot{\gamma}(t) = 0$ for $t < 0$ and $\dot{\gamma}(t) = \dot{\gamma}$ for $t \geq 0$),

$$
\begin{aligned}
\boxed{\eta} &\equiv \lim_{t\to\infty}\frac{\sigma_{xy}(t)}{\dot{\gamma}(t)} = \int_0^\infty G(t)\,dt \approx \frac{ck_BT}{N+1}\sum_{p=1}^{N}\frac{\tau_p}{2} = \frac{ck_BT}{N+1}\frac{\tau_1}{2}\sum_{p=1}^{N}\frac{1}{p^2} \\
&\approx \frac{ck_BT}{N+1}\frac{\tau_1}{2}\sum_{p=1}^{\infty}\frac{1}{p^2} = \frac{ck_BT}{N+1}\frac{\tau_1}{2}\frac{\pi^2}{6} \\
&\boxed{= \frac{c\zeta b^2}{36}(N+1) \quad \propto N}
\end{aligned} \tag{20}
$$

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Appendix A.

Riemann zeta function $\zeta(s) = \sum_{p=1}^{\infty}\frac{1}{p^s}$ is a function of a complex variable s that converges when the real part of s is greater than 1. $\zeta(2)$ and $\zeta(3/2)$ appear in the Rouse and the Zimm models, respectively.

Specific values:

$$
\begin{aligned}
\zeta(1) &= \infty \\
\zeta(3/2) &= 2.612\cdots \\
\zeta(2) &= \pi^2/6 = 1.6449\cdots \\
\zeta(3) &= 1.20205\cdots \\
\zeta(4) &= \pi^4/90 = 1.0823\cdots \\
&\vdots
\end{aligned}
$$