Summary for the Zimm model

Ryoichi Yamamoto

1. The Langevin equation

Using the mobility tensor $\mathbf{H}_{nm}$ to take into account the hydrodynamic interactions (HI) between particles m and n, the Langevin equation for the motions of bead n is now modified to be

$$\frac{d\mathbf{R}_n}{dt} = \sum_{m=0}^{N} \mathbf{H}_{nm} \bullet \left(\frac{3k_BT}{b^2} \left(\mathbf{R}_{m+1} - 2\mathbf{R}_m + \mathbf{R}_{m-1} \right) \right) + \mathbf{g}_n(t), \tag{1}$$

where

$$\left\langle \mathbf{g}_n(t) \right\rangle = \mathbf{0}, \quad \left\langle \mathbf{g}_n(t)\mathbf{g}_m(t') \right\rangle = 2k_BT\delta(t-t')\mathbf{H}_{nm}. \tag{2}$$

If $\mathbf{H}_{nm}$ is chosen to be neglecting HI, i.e.,

$$\mathbf{H}_{nn} = \frac{1}{6\pi\eta_s a}\mathbf{I}, \quad \mathbf{H}_{nm} = 0 \qquad (n \neq m), \tag{3}$$

it recovers the Langevin equation used in the previous case of Rouse model

$$\frac{d\mathbf{R}_n}{dt} = \frac{3k_BT}{6\pi\eta_s ab^2} \left(\mathbf{R}_{n+1} - 2\mathbf{R}_n + \mathbf{R}_{n-1} \right) + \mathbf{g}_n(t). \tag{4}$$

While HI can be correctly captured, at the lowest order in respect to the inter particle distance $R_{nm} = \sqrt{\mathbf{R}_{nm}^2} = \sqrt{\left(\mathbf{R}_m - \mathbf{R}_n\right)^2}$, with the Oseen tensor, i.e.,

$$\mathbf{H}_{nn} = \frac{1}{6\pi\eta_s a}\mathbf{I}, \quad \mathbf{H}_{nm} = \frac{1}{8\pi\eta_s R_{nm}} \left[\mathbf{I} + \frac{\mathbf{R}_{nm}\mathbf{R}_{nm}}{R_{nm}^2} \right] \qquad (n \neq m), \tag{5}$$

the Langevin equation becomes intractable due to too complicated couplings between $\mathbf{R}_n$ and $\mathbf{R}_m$ depending on instantaneous forms of the polymer chain.

2. Pre-averaging of HI

A drastic simplification is introduced in the Zimm model by replacing the original Oseen tensor with its pre-averaged form

$$\begin{aligned} \mathbf{H}_{nm} \approx \left\langle \mathbf{H}_{nm} \right\rangle_{eq} &= \frac{1}{8\pi\eta_s} \left\langle \frac{1}{R_{nm}} \right\rangle_{eq} \left[\mathbf{I} + \left\langle \frac{\mathbf{R}_{nm}\mathbf{R}_{nm}}{R_{nm}^2} \right\rangle_{eq} \right] = \frac{1}{8\pi\eta_s} \left\langle \frac{1}{R_{nm}} \right\rangle_{eq} \left[\mathbf{I} + \frac{\mathbf{I}}{3} \right], \\ &= \frac{\mathbf{I}}{6\pi\eta_s} \left\langle \frac{1}{R_{nm}} \right\rangle_{eq} = \frac{\mathbf{I}}{6\pi\eta_s} \left(\frac{\pi}{6} |n-m| b^2 \right)^{-1/2} \equiv h(n-m)\mathbf{I} \end{aligned} \tag{6}$$

thus the Langevin equation becomes

$$\frac{d\mathbf{R}_n}{dt} = \frac{3k_BT}{b^2}\sum_{m=0}^{N} h(n-m)\left(\mathbf{R}_{m+1} - 2\mathbf{R}_m - \mathbf{R}_{m-1}\right) + \mathbf{g}_n(t). \tag{7}$$

Using the discrete cosine transformation

$$\mathbf{X}_p(t) = \frac{1}{N+1}\sum_{n=0}^{N} \mathbf{R}_n(t)\cos\left[\frac{p\pi}{N+1}\left(n+\frac{1}{2}\right)\right] \tag{8}$$

and the inverse transformation

$$\mathbf{R}_n(t) = \mathbf{X}_0(t) + 2\sum_{p=1}^{N} \mathbf{X}_p(t)\cos\left[\frac{p\pi}{N+1}\left(n+\frac{1}{2}\right)\right], \tag{9}$$

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

$$\frac{d\mathbf{X}_p}{dt} = -\sum_{q=1}^{N} h_{pq}\frac{3k_BT}{b^2}4\sin^2\left(\frac{q\pi}{2(N+1)}\right)\mathbf{X}_q + \mathbf{g}_p, \tag{10}$$

where

$$\left\langle \mathbf{g}_p(t)\right\rangle = \mathbf{0},\ \left\langle \mathbf{g}_p(t)\mathbf{g}_q(t')\right\rangle = k_BT\frac{h_{pq}\delta(t-t')}{(N+1)}\mathbf{I}, \tag{11}$$

and

$$\begin{aligned} \boxed{h_{pq}} &= \frac{2}{N+1}\sum_{n=0}^{N}\sum_{m=0}^{N} h(n-m)\cos\left[\frac{p\pi}{N+1}\left(n+\frac{1}{2}\right)\right]\cos\left[\frac{q\pi}{N+1}\left(m+\frac{1}{2}\right)\right] \\ &\boxed{\approx \left(\frac{N+1}{3\pi^3 p}\right)^{\frac{1}{2}}\frac{1}{\eta_s b}\delta_{pq}} \end{aligned} \tag{12}$$

Finally, the Langevin equation becomes independent

$$\frac{d\mathbf{X}_p}{dt} = -\frac{k_p}{\zeta_p}\mathbf{X}_p + \mathbf{g}_p, \tag{13}$$

where $k_p = \frac{6\pi^2 k_BT}{(N+1)b^2}p^2,\ \zeta_p = \left(12\pi^3(N+1)b^2 p\right)^{\frac{1}{2}}\eta_s,$ (14)

$$\left\langle \mathbf{g}_p(t)\right\rangle = \mathbf{0},\ \left\langle \mathbf{g}_p(t)\mathbf{g}_q(t')\right\rangle = k_BT\frac{h_{pq}\delta(t-t')}{(N+1)}\delta_{pq}\mathbf{I}. \tag{15}$$

3. The dynamics of Zimm model

Similarly to the Rouse model, the time correlation function for the p-th normal mode is determined to be

$$\left\langle \mathbf{X}_p(t)\cdot\mathbf{X}_p(0)\right\rangle = \left\langle \mathbf{X}_p^2\right\rangle \exp\left[-\left(\frac{t}{\tau_p}\right)\right] \tag{16}$$

where

$$\left\langle \mathbf{X}_p^2\right\rangle \approx \frac{b^2(N+1)}{2\pi^2 p^2} \tag{17}$$

represents the magnitude of the fluctuations and

$$\boxed{\tau_p = \frac{\zeta_p}{k_p} \approx \frac{3\pi\eta_s b^3}{k_BT}\left(\frac{N+1}{3\pi p}\right)^{\frac{3}{2}}} \tag{18}$$

represents the relaxation times of the p-th normal mode.

The diffusion constant for the center of mass of the chain can then be calculated as

$$\begin{aligned}\boxed{D_G} &= \frac{1}{6t}\left\langle \left(\mathbf{X}_0(t)-\mathbf{X}_0(0)\right)^2 \right\rangle = \left\langle \int_0^t dt' \int_0^t dt'' \mathbf{g}_0(t')\, \mathbf{g}_0(t'') \right\rangle \\ &= \frac{k_B T}{2}\frac{h_{00}}{N+1} = \frac{k_B T}{(N+1)^2}\sum_{n=0}^{N}\sum_{m=0}^{N} h_{nm}(n-m) \\ &\approx \frac{k_B T}{6\pi\eta_s b}\left(\frac{6}{\pi}\right)^{\frac{1}{2}}\frac{1}{(N+1)^2}\int_0^N dn \int_0^N dm |n-m|^{-1/2} \\ &\boxed{= \frac{8}{3}\frac{k_B T}{6\pi\eta_s b}\left(\frac{6}{\pi(N+1)}\right)^{\frac{1}{2}} \propto N^{-1/2}}.\end{aligned} \tag{19}$$

4. Beads (segments) motions

The mean square displacements $\phi_n(t)$ of the individual beads (segments) is given by

$$\begin{aligned}\phi_n(t) &\equiv \left\langle \left(\mathbf{R}_n(t)-\mathbf{R}_n(0)\right)^2 \right\rangle \\ &= \left\langle \left(\mathbf{X}_0(t)-\mathbf{X}_0(0)\right)^2 \right\rangle + 4\sum_{p=1}^{N}\left\langle \left(\mathbf{X}_p(t)-\mathbf{X}_p(0)\right)^2 \right\rangle \cos^2\left[\frac{p\pi}{N+1}\left(n+\frac{1}{2}\right)\right] \\ &= 6D_G t + 4\sum_{p=1}^{N}\left\langle \mathbf{X}_p^2 \right\rangle \left[1-\exp\left[-\left(\frac{t}{\tau_p}\right)\right]\right]\end{aligned} \tag{20}$$

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

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

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

$$\begin{aligned}\boxed{\phi_n(t)} &= 4\sum_{p=1}^{N}\left\langle \mathbf{X}_p^2 \right\rangle \left[1-\exp\left[-\left(\frac{t}{\tau_p}\right)\right]\right] \\ &\approx \frac{2b^2}{\pi^2}(N+1)\int_0^\infty dp \frac{1}{p^2}\left[1-\exp\left(-t\frac{k_B T}{3\pi\eta_s b^3}\left(\frac{3\pi p}{N+1}\right)^{\frac{3}{2}}\right)\right]. \\ &= \Gamma\left(\frac{1}{3}\right)\frac{2(N+1)b^2}{\pi^2}\left(t\frac{k_B T}{3\pi\eta_s b^3}\left(\frac{3\pi}{N+1}\right)^{\frac{3}{2}}\right)^{\frac{2}{3}} \boxed{\propto t^{2/3}}\end{aligned} \tag{21}$$

5. Stress correlation function

The Zimm model predicts the stress relaxation function of the from

$$G(t) = \frac{ck_BT}{N}\sum_{p=1}^{N}\exp\left[-\frac{2k_p}{\zeta_p}t\right] = \frac{ck_BT}{N}\sum_{p=1}^{N}\exp\left[-2\left(\frac{t}{\tau_p}\right)\right]$$

$$= \frac{ck_BT}{N}\sum_{p=1}^{N}\exp\left[-\frac{k_BT}{6\pi\eta_s b^3}\left(\frac{3\pi p}{N+1}\right)^{\frac{3}{2}}t\right]. \quad (22)$$

The shear viscosity is thus calculated as

$$\eta = \int_0^\infty G(t)dt \approx \frac{ck_BT}{N+1}\sum_{p=1}^{N}\frac{\tau_p}{2}$$

$$= c\eta_s b^3\left(\frac{N+1}{3\pi}\right)^{1/2}\sum_{p=1}^{N}\frac{1}{p^{3/2}} \approx c\eta_s b^3\left(\frac{N+1}{3\pi}\right)^{1/2}\sum_{p=1}^{\infty}\frac{1}{p^{3/2}} \quad (23)$$

$$= 2.612c\eta_s b^3\left(\frac{N+1}{3\pi}\right)^{1/2} \quad \propto N^{1/2}$$

Appendix A.

Because the distribution of R_{nm} is Gaussian with the variance $|n-m|b^2$,

$$\left\langle \frac{1}{R_{nm}} \right\rangle_{eq} = \int_0^\infty dr 4\pi r^2 \left(\frac{3}{2\pi|n-m|b^2} \right)^{2/3} \exp\left(-\frac{3r^2}{2\pi|n-m|b^2} \right) \frac{1}{r} = \left(\frac{\pi}{6}|n-m|b^2 \right)^{-1/2}.$$

Appendix B.

$$\begin{aligned}
h_{pq} &= \frac{2}{N+1} \sum_{n=0}^{N} \sum_{m=0}^{N} h(n-m) \cos\left[\frac{p\pi}{N+1}\left(n+\frac{1}{2} \right) \right] \cos\left[\frac{q\pi}{N+1}\left(m+\frac{1}{2} \right) \right] \\
&= \frac{2}{N+1} \sum_{n=0}^{N} \cos\left[\frac{p\pi}{N+1}\left(n+\frac{1}{2} \right) \right] \sum_{l=n-N}^{n} h(l) \cos\left[\frac{q\pi}{N+1}\left(n-l+\frac{1}{2} \right) \right] \\
&= \frac{2}{N+1} \frac{1}{6\pi\eta_s b} \left(\frac{6}{\pi} \right)^{1/2} \sum_{n=0}^{N} \cos\left[\frac{p\pi}{N+1}\left(n+\frac{1}{2} \right) \right] \cos\left[\frac{q\pi}{N+1}\left(n+\frac{1}{2} \right) \right] \sum_{l=n-N}^{n} \cos\left(\frac{q\pi l}{N+1} \right) \frac{1}{\sqrt{l}} \\
&\quad + \frac{2}{N+1} \frac{1}{6\pi\eta_s b} \left(\frac{6}{\pi} \right)^{1/2} \sum_{n=0}^{N} \cos\left[\frac{p\pi}{N+1}\left(n+\frac{1}{2} \right) \right] \sin\left[\frac{q\pi}{N+1}\left(n+\frac{1}{2} \right) \right] \sum_{l=n-N}^{n} \sin\left(\frac{q\pi l}{N+1} \right) \frac{1}{\sqrt{l}} \\
&\approx \frac{2}{N+1} \frac{1}{6\pi\eta_s b} \left(\frac{6}{\pi} \right)^{1/2} \sum_{n=0}^{N} \cos\left[\frac{p\pi}{N+1}\left(n+\frac{1}{2} \right) \right] \cos\left[\frac{q\pi}{N+1}\left(n+\frac{1}{2} \right) \right] \sqrt{\frac{2(N+1)}{q}} \\
&= \left(\frac{N+1}{3\pi^3 p} \right)^{\frac{1}{2}} \frac{1}{\eta_s b} \delta_{pq}
\end{aligned}$$

Here, we used

$$\sum_{l=n-N}^{n} \cos\left(\frac{q\pi l}{N+1} \right) \frac{1}{\sqrt{l}} \approx \int_{-\infty}^{\infty} dl \cos\left(\frac{q\pi l}{N+1} \right) \frac{1}{\sqrt{l}} = 4\int_0^\infty dx \cos\left(\frac{q\pi x^2}{N+1} \right) = \sqrt{\frac{2(N+1)}{q}}.$$

$$\sum_{l=n-N}^{n} \sin\left(\frac{q\pi l}{N+1} \right) \frac{1}{\sqrt{l}} \approx \int_{-\infty}^{\infty} dl \sin\left(\frac{q\pi l}{N+1} \right) \frac{1}{\sqrt{l}} = 0$$