Relaxation of a tethered polymer using dynamic mean field calculation

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Relaxation of a tethered polymer using dynamic mean field calculation

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Since Fraaije’s original proposal, the dynamic mean field (DMF) technique, which is a dynamical extension of the self-consistent field calculation, has been used for many nonequilibrium phenomena in dense polymer systems. However, the validity of the local segment diffusion model used in the DMF has not been discussed extensively. In this note, we study the conformational relaxation of a single tethered polymer chain using the DMF, and show that the relaxation behavior does not contradict Rouse dynamics.

As schematically illustrated in Fig. 1, we consider a tethered polymer chain in a solvent subject to a steady uniform flow. We switch off the flow at time $t=0$, and calculate the relaxation of the chain using both DMF and the Rouse model. The characteristic length and time scales of this chain are $R_g = \sqrt{N}b^2/6$ and $\tau_R = b^2N^2\xi/6k_BT$, where $N$ is the number of segments in the chain, $b$ is the Kuhn statistical length, $k_B$ is the Boltzmann constant, $T$ the temperature, and $\xi$ is the friction constant of the Rouse segment in the solvent.

In DMF, the time evolution of the segment density at position $r$ and time $t$, denoted $\Phi(r,t)$, is given by

$$\frac{\partial}{\partial t} \Phi(r,t) = \frac{1}{\xi} \nabla \cdot [\Phi(r,t) \nabla \mu(r,t,\{\Phi\})],$$

where $\mu(r,t,\{\Phi\})$ is the chemical potential that is a functional of the segment density field. To evaluate $\mu(r,t,\{\Phi\})$, we employ path integral method.

Using the Rouse model, we can calculate the relaxation dynamics of the chain conformation analytically. Let $z(i,t)$ be the $z$ component of the mean position of the $i$th segment at time $t$. From the Langevin equation for the Rouse model, it can be shown that $z(i,t)$ satisfies

$$\frac{\partial}{\partial t} z(i,t) = \frac{3k_B T}{\xi b^2} \frac{\partial^2}{\partial t^2} z(i,t).$$

FIG. 1. Schematic representation of the simulation system.

FIG. 2. Semilogarithmic plot of the end-to-end distance as a function of the dimensionless time. The solid line is the result of the DMF simulation and the dashed line is the solution of the Rouse model.
Figure 2 shows the relaxation of the end-to-end distance $L(t)$ calculated using DMF, where $L(t)$ is defined by $L(t) = \langle z_N(t) \rangle - z_0$, and $z_0$ is the $z$ coordinate of the average position of the free end segment and the tethered point. In Fig. 2, one can confirm that the relaxation behavior obtained by the DMF method is a single exponential one, which is consistent with the long time behavior of the Rouse model on the time scale of the Rouse time $\tau_R$. Due to such an exponential behavior, we can define the longest relaxation time $\tau$ by $\log L \sim -t/\tau$. The value of $\tau$ obtained by the DMF simulation is $\tau = 0.77 \tau_R$, which is consistent with that for the Rouse model, $\tau = 0.81 \tau_R$.

To investigate the relaxation dynamics in more detail, we evaluated the amplitudes of the normal modes of the DMF data defined by

$$A(p, t) = \frac{2}{N} \int_0^N d\xi \langle z_i(t) \rangle \sin \frac{\pi p \xi}{2N},$$

where $\langle z_i(t) \rangle$ is the average position of the $i$th segment. Figure 3 shows the relaxation of the normal modes. The relaxation time for the mode with $p = 1$ obtained in the DMF simulation is $\tau = 0.76 \tau_R$, which again coincides with the corresponding value of the Rouse model, $\tau = 0.81 \tau_R$. On the other hand, the relaxation times of the $p = 3$ modes are $\tau = 0.71 \tau_R$ for the DMF simulation and $\tau = 0.31 \tau_R$ for the Rouse model, respectively. Such a large difference between these two models for the mode $p = 3$ indicates that the information on the density profile is not enough to reproduce the behavior of the higher modes of the Rouse model.

As a conclusion, the dynamics of the DMF is consistent with the Rouse dynamics only on the time scale of the longest relaxation time of the chain conformation. In order to achieve a quantitatively correct dynamics in shorter time scales, however, we have to introduce other auxiliary fields into the DMF simulation, such as the bond orientation distributions.

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Figure 3. Semilogarithmic plot of the normal mode as a function of the dimensionless time. The solid line is the result of the DMF simulation and the dashed line is the solution of the Rouse model for (a) $p = 1$ and (b) $p = 3$, respectively.