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The mobility and diffusivity of a knotted polymer : Topological deformation effect

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一、Abstract

The effect of topological deformation on the mobility and diffusivity of a polymer chain in a good solvent is investigated by off-lattice dynamic Monte Carlo simulations. The topological deformation of the polymer is expressed through the knotted structure. The Nernst-Einstein relation is obeyed and thus the diffusivity is proportional to the mobility. As the crossing number of the knotted polymer, which characterizes the extent of the deformation, is increased, the mobility declines. A scaling analysis confirmed by simulations indicates that the deformation yields an extra contribution to the resistance $\propto N$ associated with a linear chain, $\alpha N^{-3/5}p^{8/5}$, where N is the chain length and p is the length-to-diameter ratio associated with a maximum inflated knot. The mobility of the polymer chain is further reduced due to the confinement in a cylindrical tube. Nevertheless, the confinement only slightly increases the friction coefficients $\propto$ and the internal friction constant α. Our numerical results for the Rouse model are qualitatively different from those anticipated on the basis of scaling arguments for the Zimm model.

二、Introduction

When a weak external force F is applied to a polymer in the dilute polymer solution, the field will cause a uniform motion of the center of mass of the polymer with a constant velocity U which is proportional to the force F. This would correspond physically to sedimentation or to electrophoresis[2]. According to the Nernst-Einstein relation or fluctuation-dissipation theorem, the mobility $M=U/F$ is proportional to the self diffusion constant, $D_G=MkT$, where kT denotes the thermal energy. The mobility and self-diffusivity associated with a linear polymer are closely related to the dynamics of a polymer in dilute solution and have been well studied in the past decades.[1-3] In the Rouse model, the hydrodynamic interaction is neglected and the self diffusion constant is inversely proportional to the chain length N, $D_G=T/(N\propto_s)$, where $\propto_s$ is the solvent-monomer friction coefficient. On the other hand, in the Zimm model, the hydrodynamic interaction is taken into account and the diffusivity is given by $D_G \sim (kT/(N^{\nu}\propto_s))$. In a good solvent, $\nu=3/5$.

There are two types of barriers opposing the migration process of a polymer[1,2]. One is associated with the hydrodynamic friction; the other is associated with the changes in chain conformation: "internal barrier." In other words, consideration of the hydrodynamic friction term only gives the upper bound for self diffusion constant.[1,2] It has been shown that for a linear chain in a liquid medium, internal barriers are negligible for uniform translational properties.[2] In the first Rouse mode, if N is large enough, any fraction of the chain moves essentially as if it were in uniform translation. However, the internal barrier may become significant when the topological deformation is imposed upon a polymer through a knotted structure. In ad-

dition, the confinement of a knotted polymer within a cylindrical tube may enhance the deformation effect furthermore. It is the purpose of this paper to investigate the effect of the topological deformation on the mobility and diffusivity.

三、Model and Simulation Details

The knotted polymers studied in this work are up to nine crossings: 3_1, 4_1, 5_1, 5_2, 6_1, 6_2, 6_3, 7_1, 7_2, 8_1, 8_2, 9_1. They are modeled as beads connected by stiff springs. The interactions between the nonbonded beads are through the standard Lennard-Jones potentials.

$$U_{nb} = 4\pounds\left[\left(\frac{\pm}{r}\right)^{12} - \left(\frac{\pm}{r}\right)^{6}\right], \qquad (1)$$

where ε and ó are the energy and size parameters, respectively. The interactions between bonded beads are represented by a cut-off harmonic spring potential as

$$U_b = \frac{1}{2}k\pm^2\left(\frac{r}{\pm} - 1.2\right)^2, \quad 1.4 \geq \frac{r}{\pm} > 1.0. \quad (2)$$

The potential is infinite elsewhere. We have chosen kó²/ε=400.

The systems studied contain a single polymer chain with chain length N ranging from 42 to 82. In the present study, the reduced temperature T^*=10 is chosen. It is high enough so that the system is in the good solvent regime.

The interactions between the chain and the tube wall are purely excluded volume. The new configurations resulting from this move are accepted according to the standard Metropolis acceptance criterion.[4-11] Runs for the different chain length and at different tube radius (free space and 3.5) are first equilibrated for 1 million steps/monomer. Then each bead of the knot is subjected to an external force f. In this work, fó/kT=0.5 is adopted for calculating the mobility. Measurements for migration speed along the axial direction are taken for over 5000 realizations in our simulations.

The mean position of the center of mass along the axial directions in a tube and in free space are given by

$$\left\langle r_{Z,CM} \right\rangle = \left\langle z_{CM}(t) - z_{CM}(0) \right\rangle. \qquad (3)$$

and

$$< r^2 >=< \left\langle x_{CM}(t) - x_{CM}(0) \right\rangle^2 + \left\langle y_{CM}(t) - y_{CM}(0) \right\rangle^2 + \left\langle z_{CM}(t) - z_{CM}(0) \right\rangle^2 > \qquad (4)$$

where (x_{CM},y_{CM},z_{CM}) are the coordinates of the center of mass of the chain. The angular brackets <> denote the average of all realizations. The migration velocity of a knot polymer caused by externally applied forces is then evaluated by

$$U = \frac{\left\langle r_{Z,CM} \right\rangle}{t} \qquad (5)$$

Since the z-direction trajectory is almost linear, the velocity can then be evaluated directly by dividing the z-direction displacement by the elapsed time. The self-diffusion constant of a knotted polymer is calculated through the Einstein relation,

$$D_G = \frac{\left\langle r^2 \right\rangle}{2dt} \qquad (6)$$

where d is the dimensionality of the system. Time is measured in units of Monte Carlo steps per monomer (MCS/monomer), one MCS/monomer means that on average every monomer has attempted to move once.

四、Results and Discussion

The mobility can be determined by M=U/(Nf). When fó/kT is small enough, the disturbance of the polymer configuration due to externally applied forces is essentially the same as that caused by the thermal fluctuation at equilibrium (f=0) according to the fluctuation-dissipation theorem. As a consequence, one anticipates that the mobility is independent of the external force. Figure 1 demonstrates the linear relationship between the velocity and the applied force. The excellent agreement between the data and the straight line with zero intercept indicates that the range of the applied forces in our simulation, fa/kT e- 0.6, is alv
gime.

To further examine the validity of the dynamic Monte Carlo approach adopted in this paper, we evaluate the self-diffusivity and the mobility of the knotted polymers of various types. Figure 2 shows that the diffu-

sivity and the mobility can be well fitted by a straight line with a slope 1. This result indicates that the Nernst-Einstein relation, D_G=MkT is obeyed and the validity of the dynamic Monte Carlo approach is justified for weak external forces.

The variation of the mobility with the topological invariant p, which characterizes the extent of the topological deformation, is shown in Fig. 3 for N=42, 60, and 82 with the dimensionless tube radius R_t/σ =3.5 and ∞ . It is clearly demonstrated that the mobility decreases with the chain length for a given type of knot. It is well-known that the mobility (or diffusivity) of a linear Rouse chain (p=0) in an unbounded domain is simply $(æ_sN)^{-1}$. For simplicity, we assume that the confinement resistance is approximately proportional to the number of beads. Therefore, the mobility of a Rouse chain confined in a tube can still be described by $(æN)^{-1}$, where $æ=æ_s+æ_w$ with $æ_w$ denoting the bead-wall friction coefficient. These results are confirmed in our simulation by varying the length of linear chains and will also be shown in the later analysis for knotted chains (p>0). For a given chain length, the mobility of a knotted polymer declines with increasing p. As the chain length is increased, however, the degree of the mobility reduction becomes less substantial. Because of the additional resistance caused by the tube wall, the mobility of a knotted polymer confined in a tube is less than that in an unbounded domain.

The migration velocity of the polymer chain is evaluated from the mean velocity of every bead[1]

$$< U >= \frac{1}{N}\sum_n \sum_m \left\langle P\mathbf{H}_{nm}\cdot\left(-kT\frac{\partial \ln P}{\partial \mathbf{r}_m}+\frac{\mathbf{F}}{N}\right)\right\rangle_{eq} \quad (7)$$

where P is the steady state distribution function and can be obtained by solving the Smoluchowski equation. $\mathbf{H}_{nm}$ is the mobility tensor and is often approximated by the Oseen tensor if the hydrodynamic interactions are taken into account. $\mathbf{r}_m$ is the position of m-th bead. In the Rouse model, $\mathbf{H}_{nm}$ is simply $\mathbf{H}_{nm}=ä_{nm}/æ_s$. The term kT $\mathbf{r}_m$ denotes the driving force due to the deformation of the polymer[1]. When this term is neglected, an upper bound corresponding to the linear Rouse chain is obtained. This term is also referred to as the internal friction effects and is shown to be weak, particularly for long chains[2]. For a knotted polymer, however, this term becomes much important than that for a linear chain. In the Rouse model the equation of motion for the m-th bead is given by

$$\frac{\partial \mathbf{r}_m}{\partial t}=¸_s\left[f+\frac{3kT}{a^2}\frac{\partial^2 \mathbf{r}_m}{\partial m^2}\right] \quad (8)$$

The second term represent the internal barrier associated with the changes in chain conformation driven by the thermal motion. This term simply consists of a characteristic work times a characteristic deformation and then divided by the square of a characteristic bond size. By expressing the knot polymer in terms of the R-size tube, we assume a characteristic work fa, a characteristic deformation proportional to L_R/N, and a characteristic bond size D_R. As a consequence, one obtains the total resistivity

$$M^{-1}=¸_s(N+\sim N^{¬}p^{8/5}) \quad (9)$$

The second term denotes the effect of topological deformation on the mobility and yields a next order correction. A linear chain (p=0) gives no contribution. For a finite value of p, the internal friction effect becomes insignificant as $N\rightarrow\infty$.

Now we can examine the scaling law by our simulation results. Rearranging Eq. (9) gives a straight line for M^{-1}/N versus $p^{8/5}$ with an intercept $æ_s$ and a N-dependent slope. In other words, all lines of different chain lengths should converge to the same intercept. Figure 4 depicts the agreement between the scaling law and the simulation data with a common intercept for knotted polymers in an unbounded domain. In addition, all three lines corresponding to three different chain lengths can be well represented by the internal friction constant, á ▪ 0.458.

For knotted polymers confined in a tube, the bead-wall friction gives additional contribution to the resistance. We expect that the scaling law, Eq. (9), is still valid with $æ_s$ replaced by æ As illustrated in Fig. 5(a), simulation data of different chain lengths can be well represented by three lines with a common intercept æ=363 kTô/ó[2]. Again, all three lines can be well described by an

lines can be well described by an internal friction constant, which increases only a little bit, á ▪ 0.513. Figure 5(b) shows that the data for polymers of different chain lengths confined in a tube can crumple into a straight line following Eq.(9). Those consequences indicate that the scaling law, Eq.(9), is applicable to both unbounded domains and confined tubes. Nevertheless, the bead-wall friction is not as significant as the internal friction associated with topological deformations.

五、References

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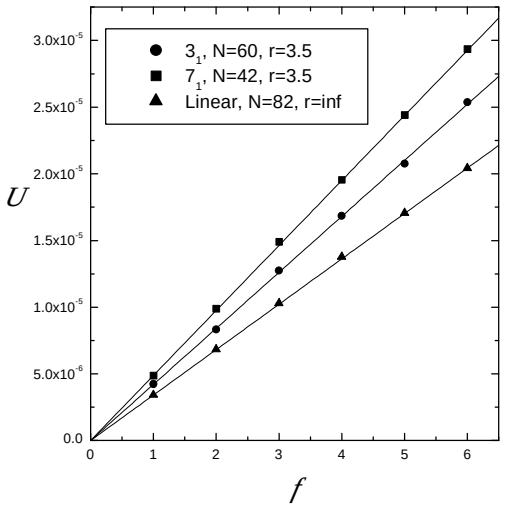

Figure 1. The variation of the migration velocity with the external force under various conditions.

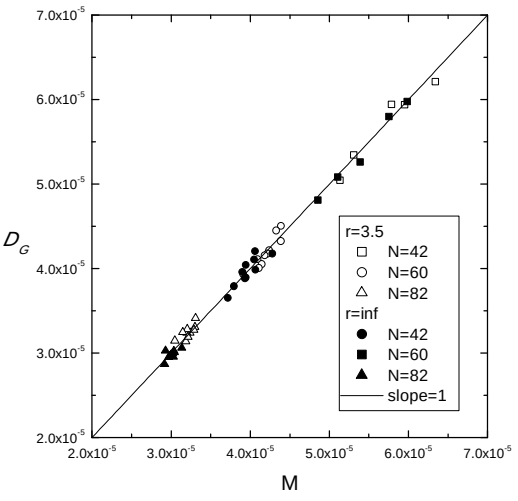

Figure 2. The diffusivity is plotted against the mobility for various chain length and various types of knot.

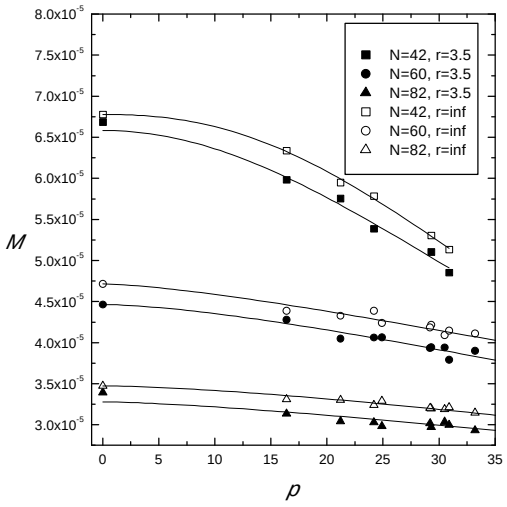

Figure 3. The variation of the mobility with the topological invariant.

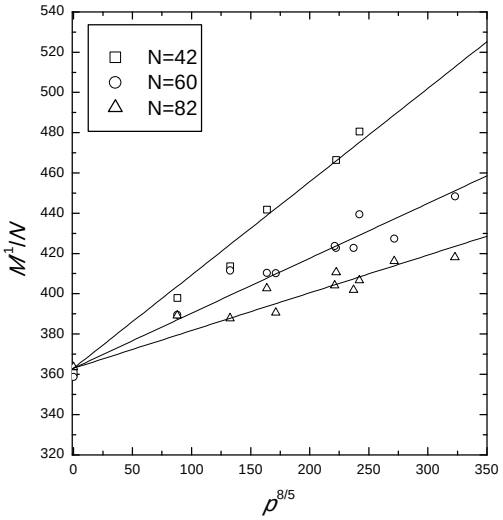

Figure 5(a). The variation of the resistivity per bead for different chain length with tube diameter equals 3.5.

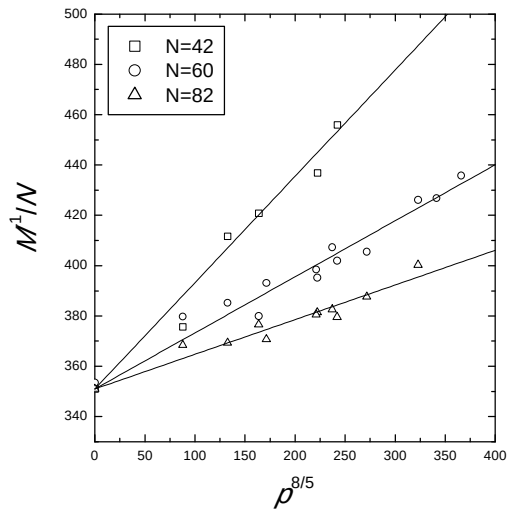

Figure 4. The variation of the resistivity per bead for different chain lengths of infinite tube diameter.

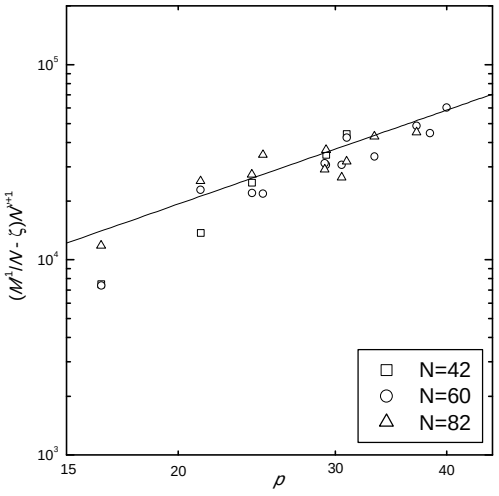

Figure 5(b). The variation of scaled mobility with p on a log-log plot for tube diameter equaling 3.5.