Relaxation of a Single Knotted Ring Polymer

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ブラウン動力学シミュレーション法を用いて, 結び目をもつ孤立環状高分子の緩和率を調べた研究 (J. Phys. Soc. Jpn. **77** (2008) 034001) の結果について紹介する. 環状高分子は高分子鎖に沿った並進対称性を持っているため, その緩和率は波数で分類される. 波数 q の緩和率 λ_q は, 各セグメントの座標のフーリエ成分の時間相関関数から評価される. 三葉結び目をもつ環状分子では, 各鎖長ごとに最も遅い緩和率を与える波数が, 鎖長が長くなるにつれ, $q=2$ から $q=1$ に変化した. この変化は, 鎖長が長くなるにつれ結び目部分が局在することに対応すると考えられる.

The results of a Brownian dynamics study on the relaxation of a single knotted ring polymer (J. Phys. Soc. Jpn. **77** (2008) 034001) are presented. Relaxation rates of a ring polymer are classified by a wave number, because it has the translational symmetry along the polymer. The relaxation rate λ_q for the wave number q is estimated from the long-time behavior of the time correlation function of the Fourier component of the segment positions relative to the center of mass. In the case of a single ring polymer with the trefoil knot, the wave number q of the slowest relaxation rate λ_q for each N changes from $q=2$ to $q=1$ as N increases. This change is considered to correspond to the knot locaization where the knotted part of a ring polymer becomes localized to a part of the polymer as the polymer length increases.

1 Introduction

The topological effects caused by the entanglement of polymers on the properties of polymer systems have attracted much interest.[1] A single knotted ring polymer is one of the self-entangled systems and can be considered as an ideal system for the study of topological effects. The relaxation of a single linear polymer has been studied systematically in terms of the relaxation modes and rates.[2] The relaxation modes are chosen so that their equilibrium time correlation functions satisfy $\langle X_p(t)X_q(0)\rangle \propto \delta_{p,q}\exp(-\lambda_p t)$, where X_p and λ_p denote the pth relaxation mode and its relaxation rate, respectively. For a single linear polymer with N segments, the relaxation modes are similar to the Rouse modes and the pth slowest relaxation rate behaves as $\lambda_p \propto (p/N)^{2\nu+1}$.[2] Here $\nu \simeq 0.588$ is the exponent for the power law dependence of the size of the linear polymer on N.[1] In the following, we present the results of a study of effects of the topological constraints on the relaxation of ring polymers,[3] where an analysis similar to that which has been done for linear single polymers has been carried out.

2 Model and Relaxation Rates

Brownian dynamics simulations of a knotted ring polymer in good solvent are performed by using a bead-spring model. The dynamics of the ith segment of a single ring polymer with N segments is described by the overdamped Langevin equation for $\boldsymbol{r}_i$, which denotes the position of the ith segment, with Gaussian white random forces.

For a single ring polymer each relaxation mode is associated with a wave number q because of its translational invariance along the polymer chain. The slowest relaxation rate λ_q for each wave number $q = 1, 2, \ldots, \lfloor N/2 \rfloor$ is estimated by the least square fit of $\hat{C}_q(t) = \frac{1}{3}\langle \hat{\boldsymbol{R}}_q(t)\cdot\hat{\boldsymbol{R}}_{-q}(0)\rangle$ to the double exponential decay. Here, $\hat{\boldsymbol{R}}_q$ is defined by $\hat{\boldsymbol{R}}_q = \frac{1}{\sqrt{N}}\sum_{j=1}^{N}\boldsymbol{r}_j\exp(\mathrm{i}\frac{2\pi}{N}qj)$.

3 Results of Simulations

Figure 1 shows log-log plots of λ_q versus q/N for single ring polymers with the trivial and trefoil knots. The solid and open symbols represent λ_q for $q=1$ and $q>1$, respectively.

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For single ring polymers with the trivial knot, the data points for $q=1$ and those for $q>1$ fall on two different straight lines at small values of q/N, which leads to the power law behaviors $\lambda_q \simeq A_1 (1/N)^{x_1}$ for $q=1$ and $\lambda_q \simeq A_{>1} (q/N)^{x_{>1}}$ for $q>1$. The estimated parameters are given by $A_1 \simeq 24.0$, $x_1 \simeq 2.10$, $A_{>1} \simeq 50.2$, and $x_{>1} \simeq 2.17$. The exponents x_1 and $x_{>1}$ are similar to that for single linear polymers $2\nu+1 \simeq 2.18$.[1] The separation of the power law dependences is considered to be due to the topological constraints, since no such separation appears for ideal single ring polymers, which have no excluded volume interaction.

In the case of the trefoil knot, the data points for $q=1$ and those for $q=2$ and 3 fall on two different straight lines at small values of q/N, which suggests the power law behaviors $\lambda_q \simeq A_1 (1/N)^{x_1}$ for $q=1$ and $\lambda_q \simeq A_{2,3} (q/N)^{x_{2,3}}$ for $q=2$ and 3. The parameters are estimated as $A_1 \simeq 591$, $x_1 \simeq 2.61$, $A_{2,3} \simeq 7.74$, and $x_{2,3} \simeq 2.02$. The separation of the power law behaviors, which is considered to be due to the topological constraints, leads to the crossover behavior that the wave number $q = q_{\min}$, which gives the slowest relaxation rate for each N, changes from $q_{\min}=2$ for small N to $q_{\min}=1$ for large N.

4 Conclusion

In the distribution of λ_q for single ring polymers with the trivial and trefoil knots, the topological effect appears as the separation of the power low dependences of λ_q on q/N for each q. For the trefoil knot, the wave number $q_{\min}$ of the slowest relaxation rate for each N changes from $q_{\min}=2$ to $q_{\min}=1$ as N increases. According to the linearization approximation,[1, 2] the relaxation rate λ_q is proportional to $\hat{C}_q(0)^{-1}$, which is found to hold qualitatively. Because $\hat{C}_q(0)$ roughly represents the mean square of the end-to-end distance of a partial chain with $N/(2q)$ segments, the crossover behavior of $q_{\min}$ is considered to correspond to the change in the structure of a single ring polymer due to the localization of the knotted part, where the number of the segments of the partial chain which has the longest end-to-end distance changes form $N/4$ to $N/2$ as N increases.

References

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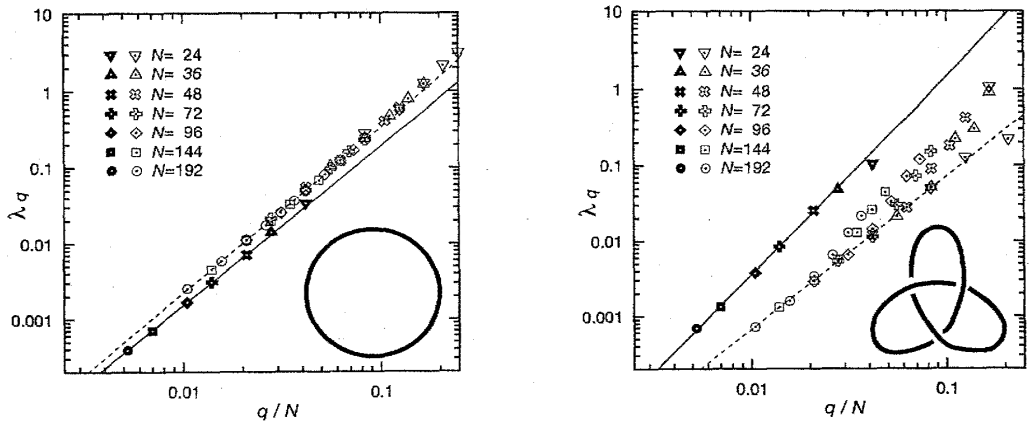

Figure 1: q/N-dependences of λ_q for single ring polymers with trivial knot (left) and trefoil knot (right).[3]