Notes

Equilibrium and Dynamic Properties of a Polymer Chain in a Reflecting Wedge

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Introduction

In a recent paper Hahn and Kovac[1] studied the equilibrium and dynamic properties of a single polymer chain terminally attached to an infinite reflecting boundary using a Monte Carlo method. The equilibrium properties of the chain were in reasonable agreement with renormalization group (RG) calculations.[2] The end-to-end vector relaxation times for the tethered chain adhered to the dynamic scaling hypothesis for all chain lengths studied, although the reflecting boundary did induce a chain length independent slowing of the chain motion.

Recent renormalization group calculations of the equilibrium properties of chains interacting with more than one surface[3] have stimulated us to study the equilibrium and dynamic properties of a single chain terminally attached to the junction of two perpendicular reflecting surfaces, a chain in a wedge. There were two reasons for undertaking this study. First, we wanted to provide simulation data of the equilibrium dimensions of the chain in order to compare with the RG calculations. Second, we were interested in seeing whether the dynamic scaling relation would hold in this more confined situation. The general question of the effects of interfaces on the motions of polymer chains has been little studied. The motion of the chain in a wedge is the logical extension of our earlier paper on the effects of a single surface on the chain dynamics.

We find that the equilibrium properties of the chain are in reasonable agreement with the RG calculations just as in the single-wall case. The dynamics, however, are somewhat different. We find that short chains do not follow the dynamic scaling hypothesis exactly. The second confining wall slows the chain motions. As the chain becomes longer, the effect of the wall decreases, and for sufficiently long chains the dynamic scaling relation does again provide a link between the equilibrium and dynamic properties of the chain.

Model

The model chosen for this study was the face-centered cubic (fcc) lattice model developed by Downey, Crabb, and Kovac.[4] An fcc chain was permanently attached to the intersection of two perpendicular impenetrable (reflecting) walls. The dynamics of the chain were simulated using the Downey–Crabb–Kovac model with the additional restriction that no bead was allowed to intersect either surface. Simulations of the equilibrium properties were done for chains of lengths 35–215 bonds with excluded volume. Because of the very long simulation runs needed to study the end-to-end vector relaxation, dynamic properties were only studied for chains of lengths 35–107 bonds. (One chain length without excluded volume was run in order to verify that the simulation algorithm corresponded to reflecting boundary conditions.) No hydrodynamic interactions were included. The mean-square end-to-end distance $\langle R^2 \rangle$ and the end-to-end vector autocorrelation function, $C(t) = \langle \mathbf{R}(t)\cdot\mathbf{R}(0) \rangle$, were calculated for each simulation run. As usual, the ensemble averages were approximated as time averages over a simulation run begun from a fully equilibrated conformation. The end-to-end vector relaxation time was estimated by fitting an unweighted least-squares line to the linear long time portion of a semilog plot of $C(t)$ vs t. Generally, at least 10 runs were done for each chain length in order to estimate the error.

Table I
Values of the Mean-Square End-to-End Distance $\langle R^2 \rangle$ for Free and Grafted Chains as a Function of Chain Length, $N-1$

$N-1$	$\langle R^2 \rangle_f$	$\langle R^2 \rangle_g$	γ_{R^2}[a]
35	65.9	116	1.78
53	110	186	1.71
71	154	263	1.70
107	243	426	1.75
143	350	594	1.70
179	470	818	1.74
199	530	922	1.74
215	574	1010	1.76

[a] $\gamma_{R^2} = \langle R^2 \rangle_g / \langle R^2 \rangle_f$.

Results and Discussion

The results for the mean-square end-to-end distances of the terminally attached chains with excluded volume, $\langle R^2 \rangle_g$, are collected in Table I along with the results for free chains, $\langle R^2 \rangle_f$, of the same length. In the final column the ratio $\gamma_{R^2} = \langle R^2 \rangle_g / \langle R^2 \rangle_f$ has been computed. The average of this for all chain lengths is 1.74 ± 0.04. There appears to be no systematic variation with chain lengths. We calculated this ratio for a chain of length $N = 72$ without excluded volume and found a value of $\gamma_{R^2} = 1.0$. This verifies that our simulation indeed represents the case of reflecting walls. While not an exact comparison, recent renormalization group calculations for a chain in a 90° wedge formed by two repulsive walls give a ratio of 1.61,[5] which is quite close to our value.

We also calculated the scaling exponent 2ν by making double-logarithmic plots of $\langle R^2 \rangle$ vs $(N-1)$ and determining the slope of an unweighted least-squares line. This slope corresponds to the exponent in the scaling relation

$$\langle R^2 \rangle \sim (N-1)^{2\nu} \tag{1}$$

The value of the exponent 2ν is 1.19 for the grafted chains and 1.17 for the free chains. These values are in excellent agreement with the expected value of 1.2.

The values of the end-to-end vector relaxation times, τ_R, are listed in Table II. For a chain grafted to a single-plane reflecting surface Hahn and Kovac found that the

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Table II
Values of the End-to-End Vector Relaxation Time τ_R and the Dynamic Scaling Ratio S_N as a Function of Chain Length, $N-1$

$N-1$	τ_R	$S_N = \tau_R/\langle R^2\rangle(N-1)$
35	1160	0.287
53	2740	0.277
71	5170	0.272
107	12500	0.270

relaxation time obeyed the dynamic scaling relation

$$\tau_R \sim \langle R^2\rangle(N-1) \quad (2)$$

To test this hypothesis for the two-wall case, we computed the ratio $S_N = \tau_R/\langle R^2\rangle(N-1)$. These values are also listed in Table II and plotted as a function of N^{-1} in Figure 1. Clearly the dynamic scaling ratio is not constant at short chain lengths but appears to approach a constant value at the longest chain lengths studied. A quadratic extrapolation to infinite chain length provides a limiting value for the ratio of $S_\infty = 0.268$. It is clear that the confining walls do slow the relaxation time in addition to their effect on the chain conformation, but this effect disappears as the chains become very long. This differs from the single-wall case where the ratio S_N was essentially independent of chain length even for the shortest chain lengths studied.

For the simple case of self-avoiding chains confined by reflecting walls it appears that the major effect of the walls on the chain dynamics is predicted by the dynamic scaling hypothesis, although there are corrections for short chains confined by two walls. We are currently extending our algorithms to study both attractive walls and self-attracting chains where quite different effects might well be observed.

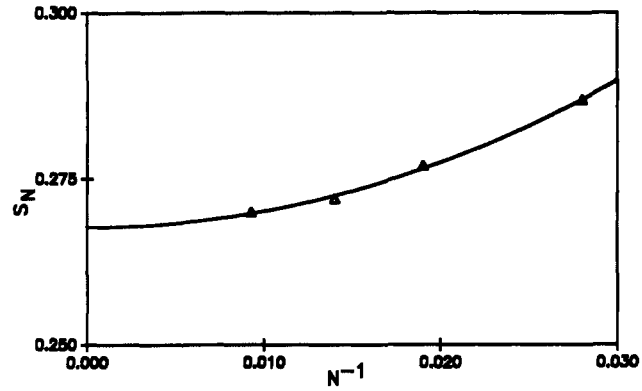

Figure 1. Plot of the ratio $S_N = \tau_R/\langle R^2\rangle(N-1)$ as a function of inverse chain length, N^{-1}. The line is a quadratic extrapolation to $N^{-1} = 0$.

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References and Notes

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