Computer Simulation of the Dynamics of a Polymer Chain Terminally Attached to a Rigid Flat Surface

THOMAS D. HAHN AND JEFFREY KOVAC*

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600

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Introduction

The properties of polymers near interfaces are of tremendous technological importance and therefore have been studied in great detail.[1] While there have been many experimental and theoretical studies of the equilibrium properties of polymers interacting with surfaces, the modification of the chain dynamics by the interface has received much less attention. The work reported in this note represents a modest first step toward understanding the effects of a surface on the motion of polymer chains. We have studied the dynamics of a single linear polymer terminally attached to a rigid plane surface by means of Monte Carlo computer simulation and compared the results to those obtained previously for isolated free chains in solution. This represents the case of a Rouse (or Gaussian) chain grafted to a reflecting boundary.

Our objective was to study the simplest effects of an interface on chain motions. In particular, we tested the applicability of the dynamic scaling hypothesis,[2] which relates the relaxation time of the chain to its dimensions, to this situation. Since the impenetrable surface will increase the equilibrium dimensions of a chain with excluded volume, the dynamic scaling hypothesis would predict an increase in the relaxation time for the tethered chain. In addition, there may be an additional, purely dynamical, effect of the surface on the chain motions. We find that, although the dynamic scaling hypothesis does hold for the tethered chains, there is additional chain-length-independent increase in the end-to-end vector relaxation time as compared to the free chain.

Model

The model chosen for this study was the face-centered cubic (FCC) lattice model developed by Downey, Crabb, and Kovac.[3] An FCC chain was permanently attached at one end to an impenetrable (or reflecting) infinite plane surface. The dynamics of the chain were simulated by using the Downey–Crabb–Kovac model with the additional restriction that no bead was allowed to intersect the surface. No hydrodynamic interactions are included. Simulations were done for chains with lengths of 24, 36, 48, 60, and 72 beads with and without excluded volume. The mean-square end-to-end distance, $\langle R^2 \rangle$, and the end-to-end vector autocorrelation, $C_R(t) = \langle \mathbf{R}(t)\cdot\mathbf{R}(0) \rangle$, function 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, τ_R, was estimated by fitting an unweighted least-squares line to the linear long-time region of a semilog plot of $C_R(t)$ vs t. The inverse of the slope of this line is the negative of the relaxation time. At least five runs were done for each chain length in order to estimate the error.

Results and Discussion

The results for the mean-square end-to-end distance of the terminally attached chains with and without excluded volume are listed in Table I. For comparison, the mean-square end-to-end distances of free FCC chains are also listed. The values for the free chains with excluded volume are taken from the work of Downey, Crabb, and Kovac[3] while the ideal chain values have been calculated from the exact relationship given by Domb and Fisher.[4] It is clear from the table that the surface has no effect on the dimensions of the ideal, random-walk chains but causes a modest increase in the dimensions of the chains with excluded volume. The fractional increase is approximately 1.17 and is essentially independent of chain length. We determined the scaling exponent 2ν for the terminally attached chains in both cases. 2ν for the ideal chains was 1.07, while for the chains with excluded volume, it was 1.23. These values are close to those found for free FCC chains.

Table I
Values of the Mean-Square End-to-End Distance, $\langle R^2 \rangle$, for Terminally Attached Chains and Free Chains with and without Excluded Volume[a]

	$\langle R^2 \rangle$			
	grafted chains		free chains	
$N-1$	excluded volume	no excluded volume	excluded volume	no excluded volume
23	45.6 (1.4)	26.4 (0.7)	39.3	27.6
35	77.2 (2.0)	41.3 (1.1)	65.6	42.0
47	108.4 (2.6)	54.9 (1.6)	98.8	56.4
59	146.6 (3.8)	71.3 (1.8)	121.1	70.8
71	182.5 (3.3)	89.7 (3.0)	154.5	85.2

[a] The free chain values with excluded volume are taken from ref 3. The free chain values without excluded volume were calculated from the formula of Domb and Fisher.[4] For the results obtained in this work, standard deviations are shown in parentheses.

Table II
End-to-End Vector Relaxation Times for Terminally Attached and Free Chains with and without Excluded Volume[a]

	τ_R			
	grafted chains		free chains	
$N-1$	excluded volume	no excluded volume	excluded volume	no excluded volume
23	810 (130)	275 (13)	249	84.1
35	2010 (290)	606 (51)	643	187
47	3630 (300)	1077 (87)	1190	316
59	6341 (1180)	1740 (150)	2030	533
71	9152 (1240)	2440 (500)		

[a] The values for free chains are taken from ref 3. For the results obtained in this work, standard deviations are shown in parentheses.

While the equilibrium dimensions for the ideal chain obtained here agree well with exact results, the ratio of the mean-square end-to-end distance of the grafted chain with excluded volume to the dimensions of the free excluded-volume chain is significantly larger than the results obtained from renormalization group calculations.[5] One obvious explanation of this difference is that the chains used in our study are rather short. We have observed that our lattice chains are expanded on the short range.[6] This expansion should be exacerbated by the presence of the reflecting boundary. This could easily account for the large increase in chain dimensions observed here. The renormalization group calculations, however, are carried out for infinite chains where any local chain expansion is irrelevant. We plan to examine this question in follow-up studies to this work by looking at longer chains.

End-to-end vector relaxation times, τ_R, for the terminally attached chains are listed in Table II along with values for the same quantity for free chains as determined by Downey, Crabb, and Kovac. The relaxation times increase by more than a factor of 3 in going from the free chain to

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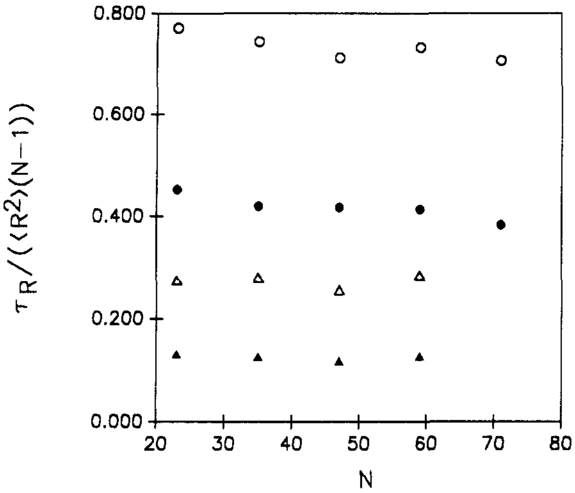

Figure 1. Plot of the ratio $\tau_R/(\langle R^2\rangle(N-1))$ vs chain length N for terminally attached chains (O) and free chains (Δ). Open symbols are the excluded-volume values, while filled symbols are the values for chains without excluded volume.

the terminally attached case. We determined the scaling exponent, α_R, giving the chain-length dependence of the relaxation time according to

$$\tau_R \sim (N-1)^{\alpha_R} \quad (1)$$

The values for α_R are 1.95 and 2.16 for the non-excluded-volume and excluded-volume cases, respectively. These compare fairly well with the values for free chains of 1.98 and 2.25 determined previously. Clearly the impenetrable surface does not have a significant effect on the chain length dependence of the relaxation times.

In order to test the validity of the dynamic scaling hypothesis, we constructed the ratio $\tau_R/[\langle R^2\rangle(N-1)]$ and plotted it as a function of chain length $N-1$ in Figure 1. As can be seen from the figure, this ratio is essentially independent of molecular weight for both the free chains and the terminally attached chains. The slight decrease in the ratio with increasing chain length is not statistically significant due to the fairly large scatter in the values of τ_R. The ratio is significantly larger for the terminally attached chains, however. This means that the impenetrable surface does have an influence on the chain dynamics beyond its effect on the overall conformation. This effect is independent of chain length, however. It is important to note that the inclusion of hydrodynamic interactions could significantly alter this conclusion.

To summarize, we find that terminally attached polymer chains with excluded volume are expanded compared to free chains, yet the static scaling exponent is unchanged. The end-to-end vector relaxation times of both ideal and excluded-volume chains increase significantly when the chains are attached to a surface. The dynamic scaling hypothesis applies to the grafted chains, but there is an additional chain-length-independent slowing of the motion of the terminally attached chain as compared to a free chain of the same length.

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References and Notes

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