Behavior of Starlike Polymers between Walls

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Received March 15, 1990; Revised Manuscript Received July 25, 1990

ABSTRACT: The behavior of four-armed star polymers between walls is studied via off-lattice Monte Carlo simulations. The molecules consist of a central bead with four arms of five beads each protruding from it. Simulation results for density profiles and global properties are reported for a volume fraction of 0.3 and a wall separation of 16 bead diameters. The behavior of these molecules is found to be similar to that of linear polymers between walls: the end sites are enhanced at the wall relative to the middle sites, the molecules near the wall are flattened against the wall, and the solvation force is an oscillatory function of wall separation. In the middle of the pore the fluid is uniform. The distribution of sites about the center of mass is sharply peaked near the wall but smooth in the middle of the pore.

1. Introduction

In recent years there has been considerable interest in the behavior of polymers confined between surfaces,[1-16] a problem that is of practical and theoretical importance. One stimulus for this increased interest is the recent experimental measurements of forces between surfaces that contain polymer between them.[14-16] It is of interest to see if the phenomena observed in experiments can be explained by simple models for polymers. Computer simulation is an attractive route to this information because for a given model the results may be considered exact. Consequently, there have been a number of computer simulation studies[1-10] of polymers between surfaces. Most of this work, including our own,[4,8,9] has been on linear polymers, and considerable insight into the behavior of chains near surfaces has been gained. In this paper, we study the effect of polymer branching on the solvation force. It has been suggested[14] that the presence of branches will change the nature of solvation forces between the walls and that the oscillatory forces that accompany linear chains will disappear if the chains are branched. In their experimental investigation of polybutadiene[14] and various branched alkanes[15] using the surface forces apparatus, Israelachvili et al.[14,15] observed no oscillations in the force as a function of wall separation but rather a monotonic decay, which they attributed to branching in the chains. This is a plausible explanation because it is likely that branched chains might not be able to pack as efficiently as linear chains. Although other experiments[16] have suggested that the monotonic force law observed by Israelachvili et al.[14,15] might not be an equilibrium effect but rather a viscous drag effect, it is still interesting to investigate the effect of branching on solvation forces. It is not obvious what effect branching of the chains would have on the force law.

In this paper we study the effect of branching on the solvation force by investigating the configurational properties of starlike polymers between surfaces via off-lattice Monte Carlo simulation and by comparing them with our previous linear chain results.[9] Star polymers have received considerable attention in recent years, and there have been a number of theoretical,[17-22] experimental,[23-26] and computer simulation[27,32] studies. Much of this work has focused on the conformational properties and on nonequilibrium properties such as self-diffusion coefficients and intrinsic viscosities. Lattice simulations[27-29,32] and off-lattice simulations[30,31] have concentrated on single star properties for stars with fairly long arms; these simulations are in good agreement with the Daoud–Cotton scaling relationships[17] and the Miyake–Freed renormalization group analysis.[18] The only works, to our knowledge, that address the properties of star polymers between walls are those of Chee and Whittington[21] and Soteros and Whittington.[22] These authors studied the properties of a single uniform star on a lattice in the limit where the arms are infinitely long. The main result of their work[21,22] is that in three dimensions the limiting entropy per bond is independent of the number of arms but that this is not the case in two dimensions. In the absence of a microscopic theory for stars between walls, we feel that a computer simulation will offer valuable insight into the behavior of confined star polymers. We model each molecule as a four-armed star; each link on the star is modeled as a hard sphere. There are 21 beads/molecule, a central bead and four arms containing five beads each. The surfaces are modeled as hard walls impenetrable to the centers of the beads on the molecule. Our model allows us to eliminate enthalpic effects and concentrate instead on the entropic effects of polymer confinement.

Computational considerations force us to work with a relatively small number of beads per molecule. We choose 21 beads/molecule in order to facilitate comparison with our earlier linear 20-mer simulations using the same bead–bead potential. Since the arms of the stars are only five beads long it is possible that we might not observe phenomena that might be present in stars with very long arms. We must therefore be careful in extending the conclusions drawn from this work to "real" star polymers. We believe, however, that our molecules are large enough to investigate the effect of branching on the force law, since a monotonic (as opposed to oscillatory) variation of force with wall separation has been observed for fluids composed of relatively small molecules such as 2-methylundecane.[15]

We fix the reduced bead density, $n\rho\sigma^3$ (n is the number of beads per molecule, ρ is the number density of molecules, and σ is the bead diameter), in the simulation cell to be 0.573 (a volume fraction of 0.3), which roughly corresponds to that of polyethylene ($n\rho\sigma^3 \approx 0.6$) at ambient conditions (obtained by dividing the van der Waals volume by the experimental value for the molar volume).[33] A reduced bead density of around 0.6–0.65 is believed to be fairly typical of a polymer melt.[10] We might add that simulation of hard systems at higher densities is extremely difficult.

The simulations are performed by using a modified version of the algorithm used in an earlier paper.[9] The simulation cell has walls that are 16σ apart, where σ is the

0024-9297/91/2224-0709$02.50/0

hard-sphere diameter. We report site density profiles, center of mass profiles, and the radius of gyration and distribution of sites about the center of mass as a function of the distance from the walls. From the density profile we obtain, using a superposition approximation,[34] the force as a function of the separation of the walls. A comparison with the simulations of linear chains shows that there is little qualitative difference in the behavior of linear and star polymers between walls, at least for the short-armed stars studied here. As observed in linear polymers, in star polymers the molecules near the wall are flattened against the wall, the concentration of end sites near the wall is greater than that of middle sites, and the force between the walls is an oscillatory function of wall separation. Quantitative differences arise from the fact that entropic restrictions are greater in starlike molecules than they are in linear chains.

In section 2 we present our simulation results, and in section 3 we present our conclusions.

2. Monte Carlo Simulations

Simulation Method. Monte Carlo simulations are performed in the canonical ensemble. The simulation cell is bounded on two sides by hard walls (in the z direction) that are impenetrable to the centers of the beads (or sites) on each molecule. Normal periodic boundary conditions are employed in the other (x and y) directions. The system consists of 40 molecules each containing 21 sites. The walls are 16σ apart, and the periodic length is 9.57σ. The volume fraction, η ($=v_0\rho$, where, v_0 is the volume of each molecule and ρ is the number density of molecules), is fixed at 0.3.

The simulation algorithm is similar to that used earlier[4,8,9] and is not described here in much detail. Successive configurations are generated by moving a molecule; the move is accepted if it is free of overlap and rejected otherwise. To move the molecules, we use the "translation-jiggling" move of Dickman and Hall.[4] The maximum allowable displacement is adjusted so that about 30–35% of the attempted moves are accepted.

The simulation proceeds in three phases: initial configuration generation, equilibration, and averaging.

Initial configurations are generated by a growth algorithm. First 40 hard spheres are randomly placed in the cell, and the arms of the star are then grown from these spheres. Each attempt to add a bead to a randomly chosen molecule is followed by an attempt to move another randomly chosen molecule. The process requires approximately 30 000 such attempts. The system is equilibrated to ensure that the results are independent of the initial configuration. Symmetry of the density profile about the center of the pore is used to determine if the system is relaxed. In the averaging part of the simulation, properties are monitored as a function of the distance from the wall. For all but one property, a total of 74 million moves are attempted (in sets of 2 million moves), of which 20 million moves are discarded to account for equilibration. The exception is the distribution of sites about the center of mass in the direction perpendicular to the wall for centers of mass near the wall; this is monitored for 26 million moves. The variation of the averages of each of these runs is used to determine the standard deviation errors in the simulations. The errors in the total density profiles, individual site density profiles, and distribution of sites are small, about 2%. Errors in the radius of gyration profiles are higher, about 5–7%. The errors in the center of mass profile are about 10–15%.

Simulations are performed on a Cray Y-MP with a CPU time per attempted move of approximately 0.002 s.

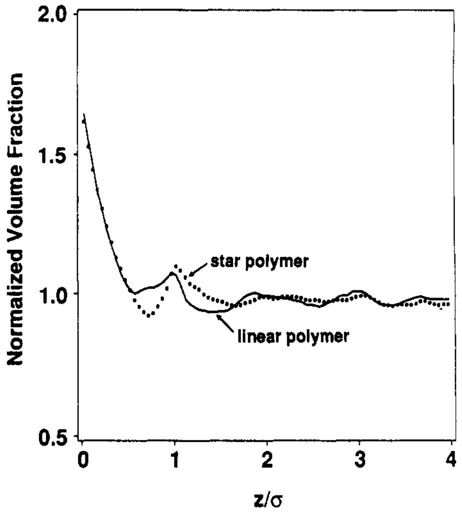

Figure 1. Comparison of the total site density profile in a star polymer fluid with that in a linear polymer fluid.

Simulation Results. At the volume fraction we study, $\eta = 0.3$, packing effects dominate the total density profile. The beads pile up against the wall as observed in studies of linear chains.[4,6,9] Figure 1 compares the total site density profile in the star polymer fluid to that in a linear polymer fluid (with 20 beads/molecule) at the same volume fraction. The ordinate in the figure is the total site density normalized to the average value in the cell. The profile is oscillatory, with a period of oscillation of about 1 bead diameter. As noted in our earlier paper,[9] there is a cusp at a distance of σ that is a consequence of the fixed bond lengths employed in the molecular model. In the middle of the pore the profile is flat, suggesting that the fluid is uniform. In both the linear and the star polymers, the effect of the wall on the density profile is short–ranged, less than 2 bead diameters. This is in agreement with the observations of Bitsanis and Hadziioannou (BH)[10] in their study of linear polymers between walls. In fact the effect of the wall on other segment-scale properties (such as the end-bead density profile) has a range of the order of the bead diameter, also in agreement with the simulations of Bitsanis and Hadziioannou.[10]

We find that, as in linear polymers, the solvation force is an oscillatory function of wall separation with a period of 1 bead diameter. We calculate the solvation force by invoking a superposition approximation due to Van Megen and Snook.[34] The density profile in a small pore at the same chemical potential as the fluid at a single wall is approximated as

$$\rho_h(z) = \rho_1(z) + \rho_1(h - z) - \rho_b \qquad (1)$$

where $\rho_h(z)$ is the density profile in a pore of width h, $\rho_1(z)$ is the density profile at a single wall, and ρ_b is the bulk density. We shall see that the pore under consideration is large enough that the fluid in the middle does not feel the walls so that Figure 1 can be viewed as a plot of $\rho_1(z)$. It has been shown[9] that the solvation force as a function of the wall separation is given (to a multiplicative constant) by

$$F(h) \propto \rho_1(h) - \rho_b \qquad (2)$$

Figure 1 then also represents the solvation force as a function of wall separation. Clearly, this solvation force is an oscillatory function of wall separation.

Entropic restrictions are more severe on the middle sites[36] than on the end sites. Figure 2 compares the end- and middle-site profiles in the star polymer to that in a

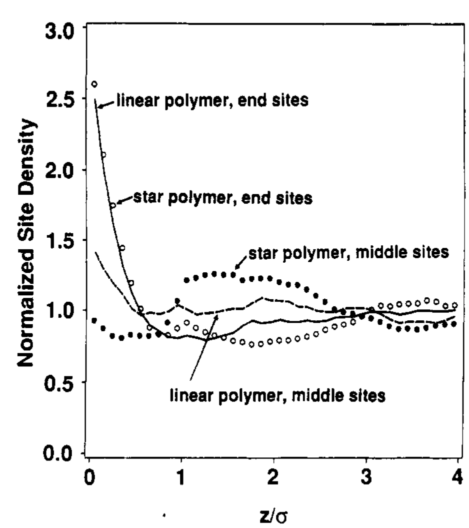

Figure 2. Comparison of the density profiles of middle beads and end beads in a star polymer fluid with those in a linear polymer fluid.

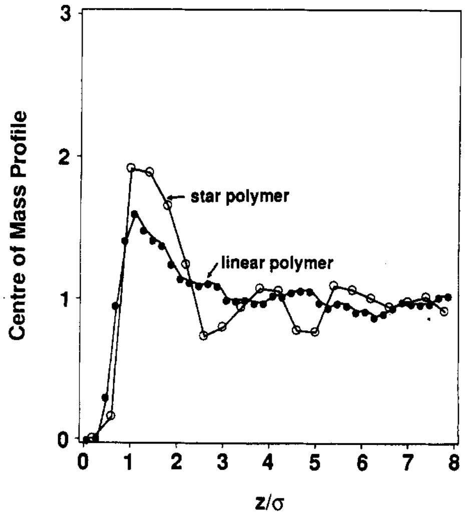

Figure 3. Comparison of the center of mass profile in a star polymer fluid with that in a linear polymer fluid.

linear polymer. The profiles are normalized to the average value in the cell. As in the linear polymers,[1,2,6,9] the end sites are enhanced at the wall relative to the middle sites. In fact there is little difference in the profiles of the end sites in the linear and star polymer. The middle-site profile shows that, in the star, the entropic restrictions near the wall are more severe than in linear chains. The density of middle sites at distances of 1–2σ is higher than that in the bulk, because packing effects force the molecules to the wall; the entropic restrictions on the middle sites on the other hand prevent them from going next to the wall. This results in the middle sites occupying the region between 1σ and 2σ from the wall.

The global properties such as the center of mass profile and the components of the mean-square radius of gyration (as a function of the position of the center of mass) are qualitatively similar to those observed in linear chains. Figure 3 compares the center of mass profile in the star polymer to that in the linear polymer normalized in each case to the average value in the cell. Both the profiles are marked by a sharp peak at a distance of approximately $z_{\mathrm{cm}} \approx \sigma$. In their simulations, Bitsanis and Hadziioannou[10] (BH) observed a peak in the center of mass profile at $z_{\mathrm{cm}} \approx R_{\mathrm{G}}\sqrt{3}$, where R_{G} is the root-mean-radius of gyration of the unperturbed chain. The R_{G} for the linear polymer is 5.65,[9] and that for the star polymer is 1.93 (see below).

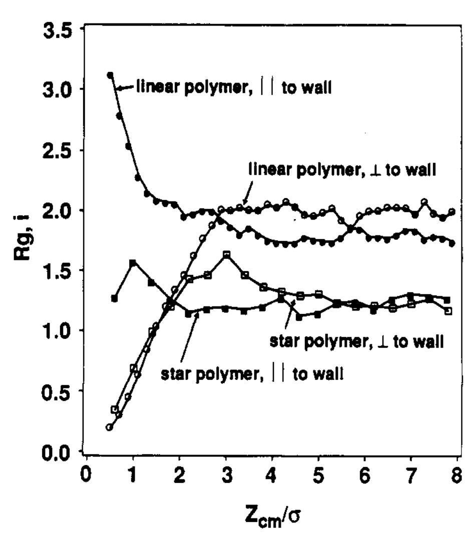

Figure 4. Comparison of the components of the mean-square radius of gyration (as a function of center of mass position) in the star polymer fluid with those in a linear polymer fluid.

Therefore, for the peaks in Figure 3 to be consistent with the BH simulations, they would have to be located at 1.37σ for the linear polymer and 1.11σ for the star polymer. In Figure 3, the peak in the profile for the linear polymer seems to be closer to σ than 1.37σ, but the error in the simulation data (about 10%) prevents us from drawing concrete conclusions. We estimate the peak in the profile for the star polymer to be between σ and 1.2σ, which is in agreement with the BH predictions for *linear* chains. Figure 4 compares the components of the mean-square radius of gyration[37] as a function of the center of mass position in star and linear polymers. Again, the profiles for the star polymer have a similar shape to those of the linear polymer but are reduced in amplitude because the star molecules are much smaller in size than the linear molecules. The molecules near the wall are flattened against the wall, as evidenced by the fact that the component of the mean-square radius of gyration in the direction perpendicular to the wall is much smaller than the component in the direction parallel to the wall. Far from the wall the fluid is uniform. From the bulklike region in Figure 4 we determine the unperturbed root-mean-square radius of gyration of the stars, R_{G}, to be 1.93 ± 0.03 at this density. The transition from the dilute to the semidilute regime occurs at a volume fraction $\eta^* \approx \pi n/6d^3$) where d is the diameter of the star. For a self-avoiding star with a small number of arms, $d \approx 1.99 R_{\mathrm{G}}^*$,[30] where R_{G}^* is the radius of gyration of the stars at $\eta = \eta^*$. Since we do not know R_{G}^*, we use the value obtained from our simulations at $\eta \approx 0.3$. This results in an estimate of $\eta^* \approx 0.19$, which is well below the volume fraction of our system. Therefore, there is probably considerable interpenetration of the stars in our simulation.

We also monitor the distribution of sites about the center of mass in the directions parallel, x, and perpendicular z, to the wall; these distributions are denoted $f(x)$ and $f(z)$, respectively. In the middle of the pore the distribution of sites parallel and perpendicular to the wall are almost identical, so we plot the average of $f(x)$ and $f(z)$. Figure 5a compares the distribution of sites about the center of mass in the star polymer and the linear polymer for centers of mass in the middle of the pore. In both the linear and the star polymers, the distribution of sites is smooth. The star polymer is on the average smaller in size than the linear polymer; this results in a site distribution that is of much shorter range than in the linear polymer. The distribution of sites in the star polymer also has a higher

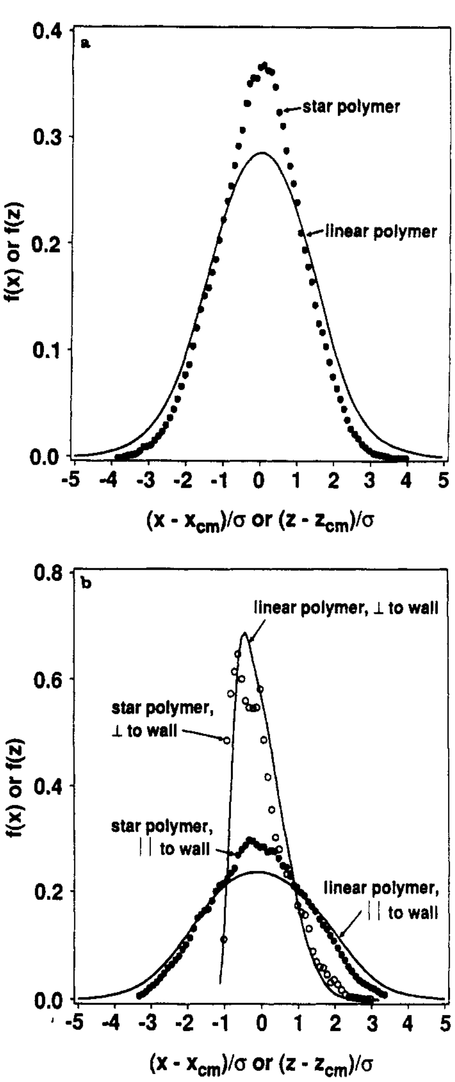

Figure 5. Comparison of the distribution of sites about the center of mass in the star polymer fluid with that in the linear polymer fluid: (a) for centers of mass in the middle of the pore, (b) for centers of mass near the wall ($0 < z_{\mathrm{cm}} < 1$).

peak than that in the linear polymer because there are more sites in the close proximity of the center of mass. Figure 5b compares the distribution of sites about the center of mass in the star polymer to that in the linear polymer for centers of mass near the wall ($0 < z_{\mathrm{cm}} < 1$). In this figure $f(z)$ and $f(x)$ are plotted against $(z - z_{\mathrm{cm}})/\sigma$ and $(x - x_{\mathrm{cm}})/\sigma$, respectively. The wall is located to the left of the curves representing $f(z)$. The distribution of sites in the direction parallel to the wall is symmetric (in both star and linear polymers) while the distribution of sites in the direction perpendicular to the wall is asymmetric and sharply peaked. In the star polymer, the distribution of sites in the direction perpendicular to the wall shows two peaks at approximately $(z - z_{\mathrm{cm}})/\sigma = -1$ and $(z - z_{\mathrm{cm}})/\sigma = 0$. The first peak corresponds to the position of the wall and can be attributed to the enhanced density of end sites at the wall (see Figure 2). The second peak corresponds to the position of the center of mass and can be attributed to the fact that there are many sites in the close proximity of the center of mass. This suggests that the star molecules near the wall might take on "spiderlike" configurations, with the tips of their "arms" lying against the wall.

3. Conclusions

Monte Carlo simulations are performed to obtain equilibrium properties of four-armed star polymers between walls. We find, at least for the short-armed stars studied here, that the behavior of star polymers is qualitatively similar to that of linear chains at similar liquidlike densities.

Near the wall the molecules are flattened against the wall; in the middle of the pore the fluid is essentially uniform. The end sites are enhanced at the wall relative to the middle sites. The distribution of sites about the center of mass is sharply peaked and asymmetric near the wall but smooth and bell-shaped in the middle of the pore.

We find that the solvation forces are oscillatory with wall separation. Physically, oscillatory forces arise because, as the walls are moved in, it is more favorable for some of the molecules to be squeezed out from between the walls than for the existing molecules to be compressed further. This also causes the period of the oscillations to be on the length scale of the bead diameter. A monotonic variation of the force with wall separation would occur if it were too difficult to squeeze a molecule out from between the walls resulting in a compression of the system instead. In this study, we find that the force law is oscillatory for star polymers, similar to what was observed in linear polymers.[9] Even the simple hard-core bead–bead potentials we use are expected to adequately describe the qualitative behavior of the system because at the high density studied packing effects (governed by the repulsive part of the potential) dominate fluid structure. Therefore, these simulations appear to support the claim[16] that the monotonic force law observed by Israelachvili et al.[14] is not an equilibrium effect due to branching in the chains. It does not, however, rule out the possibility of a transition from the linear-chain-like behavior reported here to a qualitatively different behavior as the arms of the star become longer and more numerous.

Acknowledgment. This study was supported by the Gas Research Institute under Grant No. 5082-260-724. We gratefully acknowledge the North Carolina Supercomputer Center for time on the Cray Y-MP computer.

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(36) We refer to the central bead and the four beads attached to it collectively as "middle sites".

(37) We define the ith component ($i = x, y, z$) of the mean-square radius of gyration, R_{Gi}^2 to be

$$R_{G,i}^2 = \left\langle \frac{1}{n} \sum_{j=1}^{n} (r_{j,i} - r_{\mathrm{cm},i})^2 \right\rangle$$