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Simulation of a Confined Polymer in Solution Using the Dissipative Particle Dynamics Method[1]

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The dynamics of a bead-and-spring polymer chain suspended in a sea of solvent particles are examined by dissipative particle dynamics (DPD) simulations. The solvent is treated as a structured medium, comprised of particles subject to both solvent–solvent and solvent–polymer interactions and to stochastic Brownian forces. Thus hydrodynamic interactions among the beads of the polymer evolve naturally from the dynamics of the solvent particles. DPD simulations are about two orders of magnitude faster than comparable molecular dynamics simulations. Here we report the results of an investigation into the effects of confining the dissolved polymer chain between two closely spaced parallel walls. Confinement changes the polymer configuration statistics and produces markedly different relaxation times for chain motion parallel and perpendicular to the surface. This effect may be partly responsible for the gap width-dependent rheological properties observed in nanoscale rheometry.

KEY WORDS: dissipative particle dynamics; confined polymer chains; molecular dynamics simulations.

1. INTRODUCTION

The rheological properties of dilute solutions of polymers are of interest for a variety of industrial applications; automotive lubrication and oil recovery are two of many. To enable molecular design of polymers targeted at specific applications, it is necessary to understand the link between microscopic fluid characteristics (i.e., polymer molecular structure) and

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macroscopic (i.e., rheological) fluid properties. In both oil recovery and lubrication, the rheology of polymer chains confined in very small spaces is of particular importance. It also has an important bearing in analytical techniques such as size exclusion chromatography. Here we apply the dissipative particle dynamics method [1, 2] to investigate dynamic and conformational properties of polymer chains confined between parallel walls where the wall spacing is of the order of macromolecular dimensions. Discussion of the extensive earlier theoretical and computational work on such systems may be found in the recent monograph by Fleer *et al.* [3] and in the compendia edited by Sanchez [4] and by Roe [5].

In principle, any model fluid system can be simulated rigorously at a microscopic level in large-scale computer simulations (i.e., molecular dynamics simulations). For polymer solutions and melts, however, the time scale separation between the fast solvent relaxation and the slow polymer dynamics makes ordinary molecular dynamics simulations a cumbersome, time-consuming, and costly tool, generally requiring dedicated weeks or months of supercomputer time for a single simulation. A computationally more efficient way of investigating microscopic behavior and rheological properties of polymer chains in a solvent is offered by the dissipative particle dynamics (DPD) simulation technique, introduced by Hoogerbrugge and Koelman [1]. The simulation method is motivated by the highly efficient lattice-gas automata methods for simulation of complex fluid flow, but generalized for application to the continuum, with mass confined to discrete particles. The time-stepping procedure is similar to the basic MD scheme but avoids explicit calculation of the Newtonian forces among the particles. The motion of the particles involves both stochastic and dissipative terms that guarantee evolution of the system toward equilibrium and long time consistency with the Navier–Stokes equations.

Because ineffectual high-frequency motion is eliminated, the particles move relatively large distances in any one time step. As a result, the method probes long-time behavior two orders of magnitude more efficiently than ordinary molecular dynamics. The collision rules in the DPD method imply a soft repulsive intermolecular potential that is not explicitly specified. Modifications that allow for attractive interactions are also available. It is easy to introduce bead-and-spring-type polymer chains into the basic simulation scheme, which results in a suitable model for a dilute polymer solution. Schlijper *et al.* [2] have examined static and dynamic scaling relationships for this DPD polymer solution model. For athermal solutions at rest, they have shown that the dependence of both radius of gyration and relaxation times on molecular weight follow the classical Zimm model [6] closely. The small-scale hydrodynamics of solvent flow, including hydrodynamic interactions with the polymer and solvent interactions with the confining walls, are modeled explicitly, but the solvent is completely characterized in terms of macroscopic parameters such as viscosity and density. The basic DPD model is fully described in Ref. 1 and details of the DPD polymer model are given in Ref. 2.

2. SIMULATION DETAILS

Dilute polymer solutions were modeled by placing a polymer chain of N beads connected by $N-1$ Fraenkel springs [2] in a sea of solvent particles. The repulsive-force terms for bead–bead and bead–solvent interactions are identical to those for solvent–solvent interactions, effectively yielding an athermal solution. The particles are confined in a three-dimensional simulation box of finite size, and periodic boundary conditions are applied to produce image boxes that mimic the behavior of an infinitely large system.

Confining walls are modeled by filling a layer at an edge of the simulation box with solvent particles at four times the bulk density. These "wall" particles are allowed to equilibrate and are then frozen in place so that they may interact with the surrounding "free" solvent particles but cannot move. The high density of particles in the frozen wall produces large repulsions that exclude polymer and solvent particles from the wall region. Although only a single wall is defined within the simulation box, the periodic boundary condition produces a parallel image wall, thereby confining the solvent and polymer particles between two impenetrable parallel glassy surfaces. The thickness of the wall is set equal to the maximum particle–particle interaction radius r_c, so that mobile particles in adjacent boxes

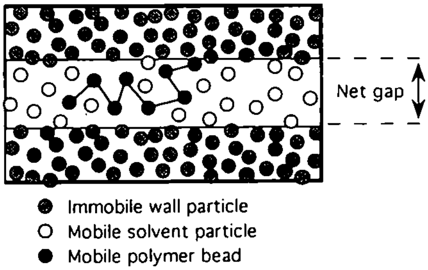

Fig. 1. Schematic diagram of periodic simulation box. The polymer chain, suspended in a sea of solvent particles, is confined in a gap between a dense wall of "frozen" particles and a parallel-image wall from the adjacent simulation box. Actual particle densities in the simulations are higher than illustrated here.

cannot interact across the thickness of the wall. The spacing between the walls is varied, but the net particle density kept constant and equal to 3 particles per unit volume, r_c^3. A two-dimensional schematic picture of the simulation environment is shown in Fig. 1.

Static and dynamic properties of the polymer chain were determined by analyzing the position autocorrelation function defined by

$$C(t)=\frac{1}{N}\sum_{i=1}^{N}\langle[\mathbf{r}_i(t)-\mathbf{R}_{\mathrm{cm}}(t)]\cdot[\mathbf{r}_i(0)-\mathbf{R}_{\mathrm{cm}}(0)]\rangle \tag{1}$$

where $\mathbf{r}_i(t)$ is the position of bead i of the N-bead chain and $\mathbf{R}_{\mathrm{cm}}(t)$ is the center of mass of the chain. The mean value of $C(t)$ at $t=0$ yields the mean square radius of gyration of the polymer chain. In the unperturbed bulk, the decay of $C(t)$ has been shown to proceed exponentially according to a spectrum of relaxation times that characterize the chain dynamics [2]. The wall confinement employed in this study induces anisotropic chain configurations. Therefore, $C(t)$ may be rigorously decomposed into components parallel and perpendicular to the confining wall, which we take to be in the XY plane:

$$C_{\parallel}(t)=\frac{1}{N}\sum_{i=1}^{N}\langle[x_i(t)-X_{\mathrm{cm}}(t)][x_i(0)-X_{\mathrm{cm}}(0)]$$

$$+[y_i(t)-Y_{\mathrm{cm}}(t)][y_i(0)-Y_{\mathrm{cm}}(0)]\rangle \tag{2a}$$

$$C_{\perp}(t)=\frac{1}{N}\sum_{i=1}^{N}\langle[z_i(t)-Z_{\mathrm{cm}}(t)][z_i(0)-Z_{\mathrm{cm}}(0)]\rangle \tag{2b}$$

These quantities are obtained from the simulation data to determine direction-dependent dynamical properties. At $t=0$, Eqs. (2a) and (2b) define the mean square radii of gyration parallel and perpendicular to the confining surfaces. For purposes of compact presentation, "r_g" is used as shorthand to indicate $\langle r_g^2\rangle^{1/2}$ and is appended with appropriate symbols when indicating the contributions parallel and perpendicular to the confining walls.

3. RESULTS

It is well-known that periodic boundary conditions affect the results of studies in condensed phases. The general understanding is that dynamical properties are affected more strongly than static configurational properties [7] and that these effects are more pronounced in two dimensions than in three. Since the confining walls have the effect of varying the dimensionality of the simulation, we conducted a study of a bulk (wall free) two-dimensional system involving a single 10-bead polymer chain plus solvent. The total density of particles was kept constant as the periodic dimensions were increased by the addition of an appropriate number of solvent particles. The correlation function was analyzed according to the method described in Ref. 2 using a functional form motivated by the classic Zimm model for chain relaxation dynamics. For bulk chains in three dimensions, this functional form fit the data essentially quantitatively. The fits in two dimensions are slightly poorer but still quite good. The results of these studies are shown in Fig. 2. For clarity, only the relaxation time τ_1 associated with the dominant (lowest) eigenvalue is shown. The abscissa is reduced by the radius of gyration for these two-dimensional chains (about $1.5r_c$).

As anticipated, both the radius of gyration and the dominant relaxation times are relatively independent of box length for larger box sizes ($L > 4r_g$) but are perturbed for smaller boxes. The effect on $C(t)$, as evidenced by the dominant relaxation time τ_1, is particularly striking. A less dramatic effect would be expected for three-dimensional chains under confined conditions. We have therefore performed all calculations with the periodic box length in the unconfined directions chosen to be at least $4r_g$. We believe this to be a conservative choice. However, it means that for longer chains a large number of solvent and wall particles must be

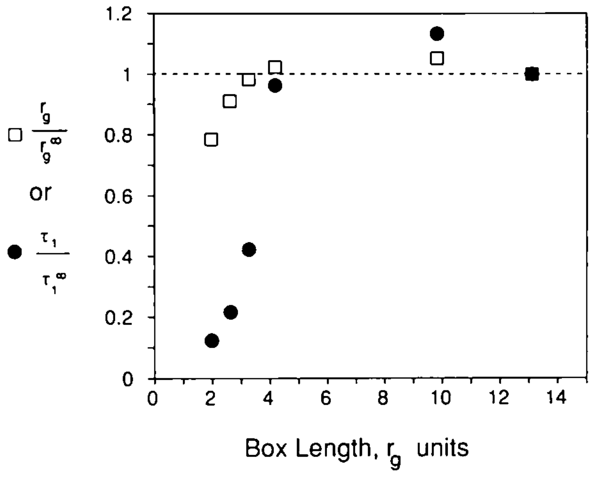

Fig. 2. Effect of periodic box length on radius of gyration and principal relaxation time for bulk two-dimensional (2-D) simulations of a 10-bead chain suspended in solvent. The box has dimensions $L \times L$ and the total density is kept fixed by adding solvent particles as the box is expanded.

included, thus slowing the simulation significantly. In this preliminary report, we focus our attention on the results for 5- and 10-bead chains (in solvent), with a few preliminary results for chains of length 20 where available.

Figure 3 shows how the parallel and perpendicular components of the radius of gyration vary with the gap between the confining walls. What is actually shown is the ratio of each quantity to the bulk radii of gyration. The prefactors $(3/2)^{1/2}$ and $3^{1/2}$ ensure that these ratios approach unity as the walls are further separated and the polymer increasingly sees an unperturbed bulk-like environment. The gap size is given in units of the unperturbed radius of gyration of the chains. The scaling behavior is seen to be excellent and perhaps even surprising for chains as short as these. Note the very small effect of confinement on $r_g^{\|}$, which is consistent with an ideal-chain analysis. A slight increase in this quantity near a wall has been indicated in other work on somewhat different systems [8].

Figure 4 shows typical results for $C(t)$, the global time correlation function, as well as its decomposition into components involving displacements parallel and perpendicular to the wall. The polymer is of length 10 beads and the net gap between the walls is $6.4r_c$ ($\approx 4.0r_g$). These correlation functions are unnormalized, so that $C(0)=r_g^2$, $C^{\perp}(0)=(r_g^{\perp})^2$ and $C^{\|}(0)=(r_g^{\|})^2$. The decomposition $C(t)=C^{\perp}(t)+C^{\|}(t)$ is rigorous at all

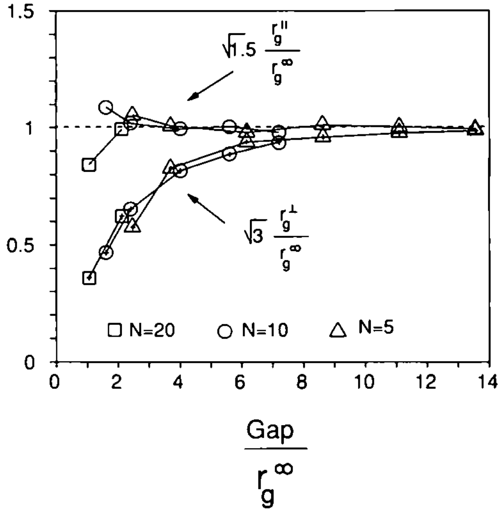

Fig. 3. Variation of parallel and perpendicular components of r_g with gap dimension for 3-D simulations of 5-, 10-, and 20-bead chains.

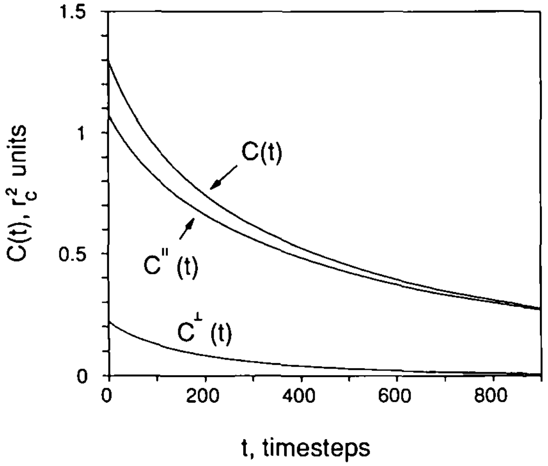

Fig. 4. Decay of the 3-D position autocorrelation function $C(t)$ with time for a 10-bead chain confined in a gap of dimension $3r_c$. The parallel and perpendicular components of $C(t)$ decay according to widely different relaxation times.

times. These functions were separately fit to the Zimm functional form using the procedure described in Ref. 2. This procedure, which yields a different spectrum of relaxation times for each function, loses more than a little of its theoretical foundation, since there is no rigorous decoupling of the perpendicular and parallel dynamics and, indeed, only a single set

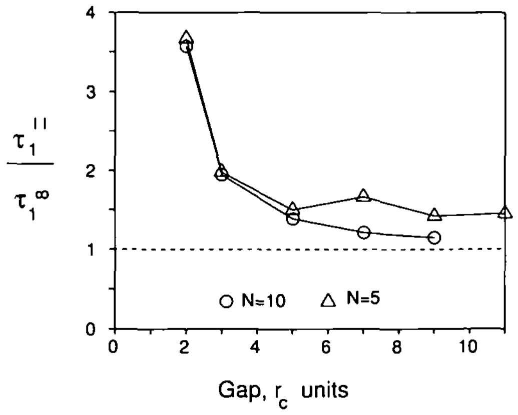

Fig. 5. Variation of principal relaxation time for parallel component of $C(t)$ with gap dimension in 3-D simulations of 5- and 10-bead chains.

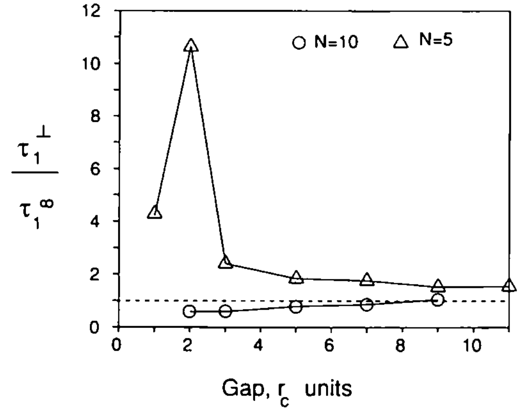

Fig. 6. Variation of principal relaxation time for perpendicular component of $C(t)$ with gap dimension in 3-D simulations of 5- and 10-bead chains.

of normal modes in the confined molecules. In fact, the fits to this quasi-Zimm form are somewhat poorer than were observed in the three-dimensional bulk simulations. However, the spectrum of relaxation times gives at least a hint of what might be occurring. For instance, $\tau_1^{\parallel}$ for the $C^{\parallel}(t)$ is always very similar to that for $C(t)$ itself and becomes increasingly similar as the gap is narrowed. This suggests that the global motion of the chain associated with this eigenmode may well be confined largely to movement parallel to the walls. In contrast, the relaxation time for $C^{\perp}(t)$ for substantially confined cases is roughly comparable to the second or third relaxation time for the global $C(t)$. This may indicate a much more local character to the relaxation mechanism, probably involving isolation of subchains by the wall.

Figures 5 and 6 show how τ_1 varies with gap size for relaxation in the parallel and perpendicular directions, respectively. Note that the gap between confining surfaces is given here in units of r_c rather than r_g. The dominant relaxation time for parallel motion, $\tau_1^{\parallel}$, scales well for chains of length 5 and 10 when the gap size is small. It remains to be seen whether the minor differences for larger gaps are significant. More striking is the behavior for perpendicular motion shown in Fig. 6. The data for chains of length 10 show a small but persistent decrease with decreasing gap size, while the relaxation times for chains of length 5 show a generally increasing trend. Whether this is truly a consequence chain length alone or whether the roughness of our surfaces also contributes to this phenomenon remains unclear.

4. CONCLUSIONS

Dissipative particle dynamics allows one to study the configurational and dynamical behavior of confined chains in the presence of solvent with workstation-level computational resources. The observed scaling of the radius of gyration with gap size is consistent with observations made on single-chain systems. A decomposition of the position autocorrelation function into components parallel and perpendicular to the confining walls shows a striking dissimilarity in the dominant relaxation times and suggests that different modes may be involved.

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