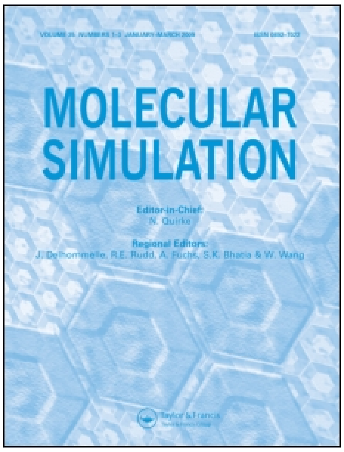

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SIMULATION OF POLYMER SOLUTIONS BY DISSIPATIVE PARTICLE DYNAMICS

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Dissipative Particle Dynamics (DPD) is employed to model the dynamics and rheology of polymer solutions, and suspensions of spherical particles with adsorbed polymers. Static and dynamic scaling relationships for the variation of radius of gyration and relaxation time with polymer chain length are reviewed, demonstrating that the DPD polymer solution model correctly represents the effects of hydrodynamic interaction and excluded volume. Rheological simulations for both polymer solutions and polymer-sphere suspensions predict Newtonian viscosities at low shear rate followed by shear-thinning behavior as a reduced shear rate of unity is approached. Both the Newtonian viscosity and the extent of shear-thinning are greatly enhanced in the case of good solvents, compared to the viscosity curves for polymers and polymer-spheres structures dissolved in theta solvents and poor solvents.

Keywords: Polymer solution; DPD; suspensions

INTRODUCTION

The original development of Dissipative Particle Dynamics (DPD) as a technique for hydrodynamic simulations [1], and later modifications [2] establishing DPD as a stochastic particle dynamics method, have led to promising new applications of DPD for modeling the rheology of polymeric liquids and other complex fluids. Schlijper *et al.* [3] introduced a mesoscopic bead-and-spring model for polymer solutions by linking DPD particles together with entropy springs. Thermodynamic interactions between the

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polymer and the solvent are represented by simple modifications of the DPD interparticle forces. Here we review the static and dynamic scaling behavior predicted by this DPD polymer solution model, and present new predictions for the rheology of solutions of linear polymers in steady shear flow. The DPD polymer solution model is then combined with a DPD model for suspended particles to simulate the rheological behavior of suspended spherical particles with adsorbed polymer chains. These simulations, motivated by the need to understand the behavior of practical systems where suspended particles are stabilized by dispersant polymers, illustrate the utility of DPD for modeling the rheology of complex fluids.

DPD POLYMER MODEL

The DPD simulation is performed on a collection of N particles of equal mass m placed in a 3-D simulation box, which is replicated in space by means of periodic boundary conditions. Particle i has a position $\boldsymbol{r}_i$ and momentum $\boldsymbol{p}_i$, which are calculated at each time step according to Newton's law of motion. DPD particles interact pairwise according to a set of short-range interparticle forces that include a repulsive conservative force $\boldsymbol{F}^c_{ij}$, a dissipative force $\boldsymbol{F}^d_{ij}$, and a random force $\boldsymbol{F}^r_{ij}$ acting symmetrically between every pair of particles i and j. Each forces acts along the unit vector $\boldsymbol{e}_{ij}$ connecting the interacting particles. For particles separated by a distance greater than the interaction radius r_c, the interaction forces vanish. The coefficients of the conservative force and the dissipative force are Π_0 and ω, respectively, and the variance of the random force is σ. Mathematical details of these forces, and of the DPD algorithm are given in Kong *et al.* [4].

A "bead-and-spring" model for polymer chains is constructed by linking a series of DPD particles together with spring forces $\boldsymbol{F}^s_{ij}$ acting between adjacent beads of the polymer structure. Both linear and branched polymers can be constructed by this method, but here we consider only linear polymer chains. The beads of the polymer chain are of mesoscopic size, representing a collection of monomer units, and the springs represent entropic forces along the polymer chain backbone. Thus the DPD polymer model is similar to the classical Rouse-Zimm theory for polymer dynamics (see Schlijper *et al.* [3]). However, an important difference between the DPD model and most other kinetic theories of polymer solutions is that the solvent is represented explicitly in DPD by means of the unconnected DPD particles in the simulation box. In classical kinetic theories [5], the solvent is regarded as a continuum that acts on the polymer beads through Stokesian drag forces. Thus DPD can model the small-scale hydrodynamics of solvent-polymer interactions directly, whereas other models must introduce these interactions through a hydrodynamic interaction tensor.

Another useful feature of the explicit solvent model in DPD is that thermodynamic interactions between the polymer and the solvent can be represented. This is accomplished by modifying the coefficient Π_0 of the conservative force by the factor $(1+\xi)$ to model interactions between polymer beads and solvent particles. The resultant polymer-solvent force coefficient $\Pi_0(1+\xi)$ is less repulsive than the like-particle coefficient Π_0 when $\xi < 1$, thereby representing good solvents. Conversely, when $\xi > 1$, polymer-solvent forces are more repulsive than like-particle forces, representing poor solvents. Kong *et al.* [4] and Groot and Warren [6] have shown that the DPD solvent quality parameter ξ is closely related to the interaction parameter χ in the classical Flory-Huggins theory. Complete details of the DPD polymer model are given in Schlijper *et al.* [3] and Kong *et al.* [4].

STATIC AND DYNAMIC SCALING RELATIONSHIPS

Kong *et al.* [4] examined the scaling of radius of gyration R_g and principle relaxation time τ_1 with chain length for linear DPD polymer chains in solvents of varying quality. Their results show that a chain collapse transition occurs near the point $\xi = 0$, and that both R_g and τ_1 scale ideally with chain length raised to constant exponents. Logarithmic plots of the variation of R_g and τ_1 with chain length are shown in Figures 1 and 2. The static and dynamic scaling exponents v and α are determined as functions of solvent quality ξ by measuring the slopes of straight lines fit to the data in these figures. The predicted scaling exponents are given in Table I.

The static scaling exponent v varies from values near 0.3 for poor solvents ($\xi \geq +0.1$) to values near 0.6 for good solvents ($\xi \leq -0.1$). These values are in very good agreement with the accepted values of $v = 1/3$ for poor solvents and $v = 0.6$ for good solvents, see de Gennes [7]. In particular, the scaling exponent $v = 0.6$ for good solvents indicates that the effects of excluded volume are properly represented by the DPD model.

For polymer solutions with complete hydrodynamic interaction, simple hydrodynamic arguments [7] show that the ratio α/v should be equal to 3. The values of α/v for the DPD simulations, given in Table I, are close to 3 for all values of solvent quality ξ, indicating the presence of strong hydrodynamic interaction. Hydrodynamic interactions in the DPD model emerge naturally from the predicted small-scale hydrodynamics of solvent

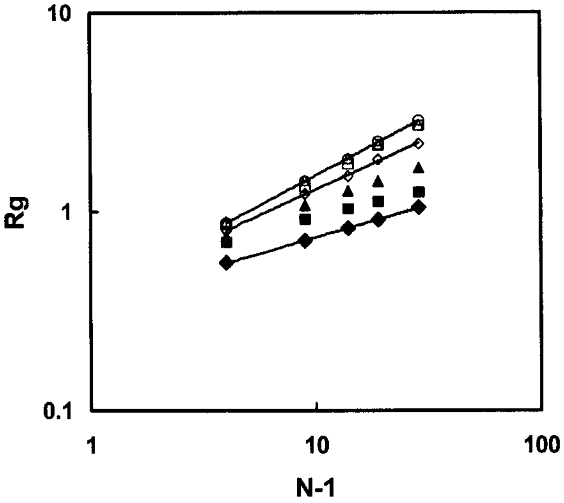

FIGURE 1 Variation of radius of gyration R_g with polymer chain length, as measured by the number of springs $N-1$. Straight lines indicate scaling according to the relationship $R_g \sim (N-1)^{v}$, where the constant v is the static scaling exponent. Simulation data are taken from Kong *et al.* [4]. Symbols represent different values of the solvent quality parameter: ◆ $\xi = +0.3$; ■ $\xi = +0.1$; ▲ $\xi = +0.05$; ◇ $\xi = 0$; □ $\xi = -0.1$; △ $\xi = -0.2$; ○ $\xi = -0.3$.

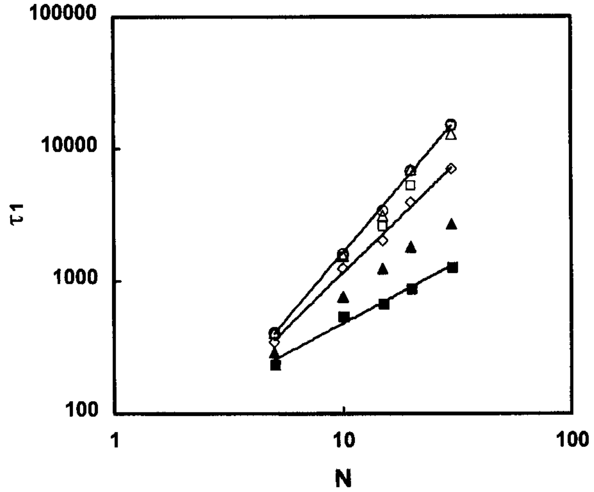

FIGURE 2 Variation of principle relaxation time τ_1 with polymer chain length, as measured by the number of beads N. Straight lines indicate scaling according to the relationship $\tau_1 \sim N^{\alpha}$, where the constant α is the dynamic scaling exponent. Simulation data are taken from Kong *et al.* [4]. Symbols represent different values of the solvent quality parameter: ■ $\xi = +0.1$; ▲ $\xi = +0.05$; ◇ $\xi = 0$; □ $\xi = -0.1$; △ $\xi = -0.2$; ○ $\xi = -0.3$.

TABLE I Values of the static and dynamic scaling exponents determined from the slopes of the curves shown in Figures 1 and 2. The static scaling exponent v is determined from the relationship $R_g \sim (N-1)^v$ and the dynamic scaling exponent α is determined from $\tau_1 \sim N^\alpha$. The ratio α/v predicted by the DPD model is nearly equal to 3 for all values of the solvent quality parameter ξ

ξ	v	α	α/v
−0.3	0.61	2.0	3.3
−0.2	0.58	2.0	3.3
−0.1	0.59	2.0	3.3
0	0.52	1.7	3.2
+0.05	0.40	1.3	3.1
+0.1	0.30	0.9	3.0

flow within the polymer coil, thus external hydrodynamic interaction tensors such as the Oseen tensor [5], are not required in the DPD model.

RHEOLOGY

Dilute Solutions of Linear Polymers

Steady shear flow can be modeled in DPD simulations by utilizing Lees-Edwards boundary conditions [8]. In this method, particles leaving the periodic box through the faces perpendicular to the velocity gradient are reinserted at an offset position, reflecting the shear strain evolved during the time step. Shear flow simulations were performed at different shear rates for 10-bead DPD polymer chains in a sea of solvent particles. The polymer beads were linked by FENE springs (see [5]) with an equilibrium length of 0.86 r_c and a maximum extensibility of 2 r_c. All simulations were performed in the dilute concentration regime where polymer chains contribute linearly to the shear stress. The contribution of the polymer chains to the total stress is evaluated by Kramers Equation [5], in which the nonisotropic stresses are calculated from the sum of the products of the spring connector vector and spring force for all of the segments of the polymer chain.

The predicted variation of intrinsic viscosity $[\eta]$ with reduced shear rate $\gamma\tau_1$ is shown in Figure 3 for solvents of different quality. In this figure γ is shear rate, τ_1 is the principle relaxation time for the $\xi = 0$ case. The intrinsic viscosity, defined as $[\eta] \equiv (\eta - \eta_s)/c\eta_s$ where η is total viscosity, η_s is the viscosity of the solvent alone, and c is polymer concentration, is expressed here in units of volume/polymer chain, *i.e.*, r_c^3/chain. The curve for the good solvent ($\xi = -0.3$) case exhibits a region of constant, Newtonian viscosity

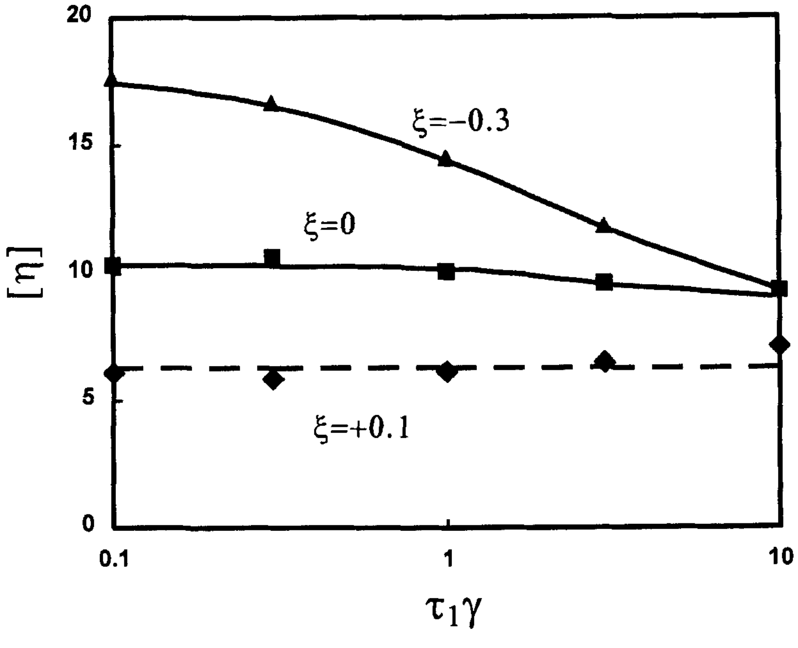

FIGURE 3 Intrinsic viscosity $[\eta]$ of 10-bead polymer chain with FENE spring connectors plotted as a function of scaled shear rate $\tau_1\ \gamma$ for various values of the solvent quality parameter ξ. Intrinsic viscosity $[\eta]$ is given in units of inverse concentration: 1/(number of chains/r_c^3) and τ_1 is the principle relaxation time for the case $\xi = 0$.

at low shear rates followed by substantial reductions in viscosity (shear-thinning) with increasing γ in the region $\gamma\tau_1 > 1$. The near-theta solution $\xi = 0$ exhibits a lower value for $[\eta]$ in the low shear rate regime, followed by only slight shear-thinning of viscosity as $\gamma\tau_1 > 1$. These trends reflect the fact that the polymer coil is much less expanded in the near-theta solvent than in a good solvent. The final viscosity curve in Figure 3 is for the case of a poor solvent, $\xi = +0.1$. In this case, $[\eta]$ is less than that of the $\xi = 0$ case, and no shear-thinning is observed. These predictions are consistent with a completely collapsed polymer chain that is unable to deform in response to the shear flow.

Suspended Spherical Particles

The use of DPD to model the rheology of suspended spheres was first introduced by Hoogerbrugge and Koelman [9], who formed suspended spheres by "freezing" DPD particles together within spherical domains to form "objects" free to rotate and translate within the surrounding fluid.

Boek and coworkers [10] have subsequently used DPD to study the rheology of dense colloidal suspensions. The method of Hoogerbrugge and Koelman is used here to model a dilute system of spherical particles of radius $1.2\,r_c$ suspended in a solvent of free DPD particles. The overall particle density is 3 DPD particles per unit volume r_c^3, and the suspended spheres have the same density as the solvent, thus each sphere is comprised of 22 frozen DPD particles. Figure 4 shows the predicted viscosity of the suspension as a function of volume fraction spheres. The rheological behavior of dilute suspensions of spherical particles should follow the Einstein relationship $\eta = \eta_s\,(1 + 2.5\,\varphi)$, see [11], where φ is the volume fraction spheres. At small φ, the DPD predictions are in excellent agreement with this expression. At higher particle volume fractions, the DPD simulations predict suspension viscosity values that are higher than those predicted by the Einstein equation, reflecting the effects of sphere–sphere interactions that occur at finite concentrations.

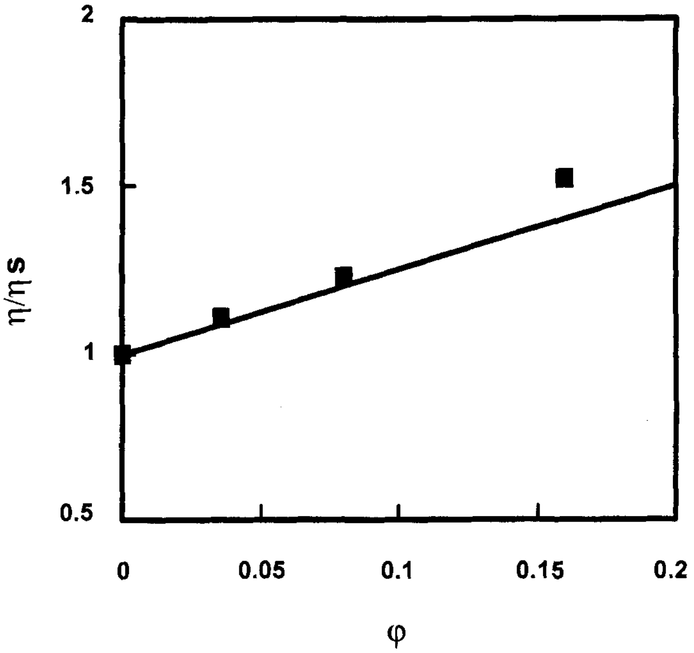

FIGURE 4 Variation of specific viscosity η/η_s with volume fraction of particles φ for a suspension of spherical particles. Here η is the viscosity of the suspension and η_s is the viscosity of the solvent alone. The predictions of the DPD simulation, solid squares, are compared to the results of the Einstein equation: $\eta/\eta_s = 1 + 2.5\,\varphi$ (solid line).

Suspended Spherical Particles with Attached Polymer Chains

Having validated the DPD predictions for the rheological behavior of dilute suspensions of spherical particles, we now consider a more complex suspended structure consisting of spheres with short polymer chains attached to the sphere surfaces. This model system pertains to many systems of practical interest where dispersant polymers are adsorbed to the surfaces of suspended particles to stabilize the suspension. In our simulations, eleven 5-bead FENE chains (see above for details of FENE chain model) are attached endwise to the surface of the spherical particles described above. Figure 5 shows the predicted intrinsic viscosity as a function of shear rate for two values of the solvent quality parameter ξ. Like the linear polymer chains, a high value for low-shear rate viscosity is predicted for the good solvent case ($\xi = -0.3$), followed by a regime of marked shear thinning as dimensionless shear rate approaches unity. The near-theta solvent case $\xi = 0$, exhibits a much smaller low-shear rate viscosity followed by only modest shear thinning. The difference between the good solvent viscosity curve

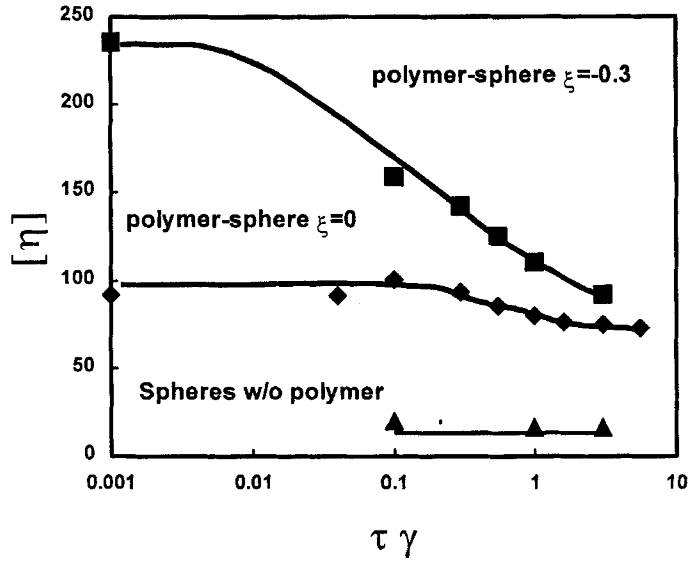

FIGURE 5 Intrinsic viscosity $[\eta]$ of suspension of structures consisting of a sphere of radius $1.2r_c$ with 11 5-bead FENE polymer chains attached randomly to the surface of the sphere. Intrinsic viscosity is plotted as a function of scaled shear rate $\tau\gamma$ for the good solvent case $\xi = -0.3$ and the near-theta solvent case $\xi = 0$. Intrinsic viscosity $[\eta]$ is given in units of inverse concentration: 1/(number of structures/r_c^3) and τ is the principle relaxation time for the case $\xi = 0$. Results for a suspension of spheres of radius $1.2\,r_c$ without attached polymers are shown for comparison.

and the near-theta solvent viscosity curve is attributable to the greater expansion of the polymer chains into the solvent for the good solvent case. The viscosity curves for suspended spheres in both good and near-theta solvents lie considerably above the viscosity curve for suspended spheres without polymers, indicating that the attached polymer chains play a dominant role in the rheology of these polymer-sphere systems. Also, the shear-thinning behavior exhibited by the polymer-sphere systems is entirely absent from the viscosity curve for suspended spheres without polymers.

CONCLUSIONS

Dissipative Particle Dynamics can be readily adapted to mesoscopic simulation of polymer solutions by means of a Rouse/Zimm-like polymer model where DPD particles are linked together by entropic springs. Unlike conventional kinetic theories of polymer solutions, the DPD polymer solution model represents the solvent explicitly through the unconnected DPD particles, and simple modifications of the conservative forces can be employed to represent thermodynamic interactions between the polymer and solvent. Studies of the static and dynamic scaling relationships for the DPD polymer model show that the static scaling exponent v varies from about 1/3 for poor solvents to 1/2 for theta solvents to 0.6 for good solvents, in close agreement with the known behavior of physical systems. The static scaling exponent of 0.6 for good solvents confirms that the DPD solvent quality model correctly represents the effect of excluded volume in such systems. The dynamic scaling exponent α is nearly equal to $3v$ for all values of solvent quality, indicating strong hydrodynamic interaction among the beads of the polymer chain. In the DPD model, hydrodynamic interaction is a natural consequence of the small-scale flow of the solvent particles, and special hydrodynamic interaction tensors are not required to model this phenomena.

The rheology of polymer solutions in homogeneous steady shear flow can be represented through the use of Lees-Edwards boundary conditions. Rheological predictions for a 10-bead linear polymer chain with FENE spring connectors show a Newtonian viscosity at low shear rate, followed by a shear-thinning regime as dimensionless shear rate $\tau_1\gamma$ approaches unity. Both the Newtonian viscosity and the extent of shear-thinning are predicted to be greater for good solvents than for theta solvents and poor solvents. Similar trends are observed for the predicted rheological behavior of a suspension of spherical particles with adsorbed polymer chains, illustrating the ready adaptability of DPD for modeling the rheology of complex fluids.

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