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Computer simulation of rheological phenomena in dense colloidal suspensions with dissipative particle dynamics

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Abstract. The rheological properties of colloidal suspensions of spheres and rods have been studied using dissipative particle dynamics (DPD). We have measured the viscosity as a function of shear rate and volume fraction of the suspended particles. The viscosity of a 30 vol% suspension of spheres displays characteristic shear-thinning behaviour as a function of shear rate. The values for the low- and high-shear viscosity are in good agreement with experimental data. For higher particulate densities, good results are obtained for the high-shear viscosity, although the viscosity at low shear rates shows a dependence on the size of the suspended spheres. Dilute suspensions of rods show an intrinsic viscosity which is in excellent agreement with theoretical results. For concentrated rod suspensions, the viscosity increases with the third power of the volume fraction. We find the same scaling behaviour as Doi and Edwards for the semidilute regime, although the explanation is unclear. The DPD simulation technique therefore emerges as a useful tool for studying the rheology of particulate suspensions.

The design of colloidal suspensions with the desired rheological properties is a key issue for industrial research. To study the effects of non-spherical or polydisperse particles and colloidal interactions on suspension rheology, computer simulations offer a powerful alternative to experiments. Simulation techniques used to date are based on a continuum model for the solvent, such as Brownian and Stokesian dynamics. To calculate many-body hydrodynamic interactions, however, it would be computationally more efficient to employ a particle-based simulation of the solvent. Inspired by this idea, Hoogerbrugge and Koelman [1] proposed a novel particle-based method to simulate complex fluid systems, called dissipative particle dynamics (DPD). In DPD, the system is updated in discrete time steps δt consisting of an instantaneous collision followed by a free propagation substep of duration δt . In the collision phase the momenta are simultaneously updated according to the stochastic rule

$$\mathbf{p}_i(t + \delta t) = \mathbf{p}_i(t) + \sum_j \Omega_{ij} \mathbf{e}_{ij} \quad (1)$$

where \mathbf{e}_{ij} is the unit vector pointing from particle j to particle i . The change in momentum Ω_{ij} can be written as

$$\Omega_{ij} = W(|\mathbf{r}_i - \mathbf{r}_j|) \{ \Pi_{ij} - \omega(\mathbf{p}_i - \mathbf{p}_j) \cdot \mathbf{e}_{ij} \}. \quad (2)$$

$W(r)$ is a dimensionless ‘weight’ function which is zero beyond the interaction range $r_c = 1$. The first stochastic term within the braces on the right-hand side of equation (2) causes the system to heat up, while the second dissipative term tends to relax any relative motion. Both terms acting together have the effect of a thermostat. The fluid particles in DPD should

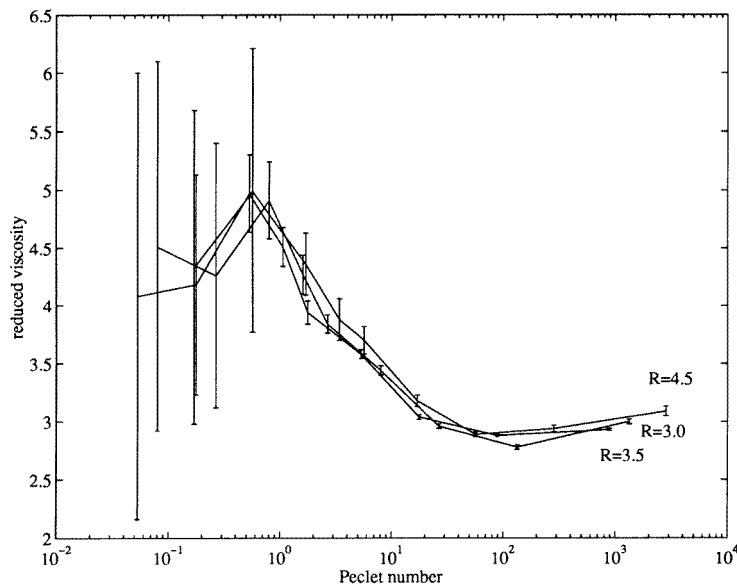


Figure 1. Reduced viscosity of a 30% suspension of spheres as a function of Peclet number, for spheres with radii $R = 4.5$, 3.5 and 3.0 .

not be seen as representations of molecules but are more abstract mesoscopic ‘carriers of momentum’. It has been shown that the DPD method is capable of simulating dispersed systems, such as colloidal suspensions [2] and polymer solutions [3]. In the present work we have performed simulations of the rheology of suspensions of spheres and rods, to validate further the DPD simulation method. Large solid objects, such as suspended particulates, can be modelled by a local ‘freezing’ of the fluid particles. Therefore these solid objects do not have perfectly smooth surfaces. In order to measure the viscosity of a suspension, a macroscopic steady shear flow regime is imposed on the fluid using Lees–Edwards [4] sliding periodic boundary conditions. The stress tensor is then calculated at each time step, from which the shear viscosity η of the suspension is obtained from $\eta = -\sigma_{xy}/\dot{\gamma}$, where σ_{xy} is the xy component of the stress tensor, and $\dot{\gamma}$ represents the imposed shear rate.

For suspensions of spheres, Koelman and Hoogerbrugge [2] obtained viscosities from DPD simulations which are in excellent agreement with experimental data of van der Werff and de Kruif [5]. They present results only for high Peclet numbers. The Peclet number is the ratio of the shear rate $\dot{\gamma}$ to the diffusion rate D_0/a^2 (where D_0 is the diffusion coefficient and a is the radius of the colloidal spheres) and is defined as $Pe = \dot{\gamma}a^2/D_0 = 6\pi\eta_s a^3\dot{\gamma}/k_B T$, where η_s is the solvent viscosity. van der Werff and de Kruif [5] obtained experimental results not only for the high-shear viscosity $\eta(\infty)$, but also for the low-shear viscosity $\eta(0)$. In the present work, we have performed simulations of suspensions of spheres for volume fractions $\phi = 0.3$ – 0.4 to calculate both $\eta(\infty)$ and $\eta(0)$ and compared the results with the available experimental data [5]. To generate a 30% suspension of spheres, 45 spheres with radius 3.5 were randomly positioned within a 3D simulation box of size $30 \times 30 \times 30$, with length unit $r_c = 1$. To check finite size effects, we also created suspensions containing 21 spheres of radius 4.5 and 68 spheres of radius 3.053. These suspensions were subject to dimensionless steady shear rates, varying from

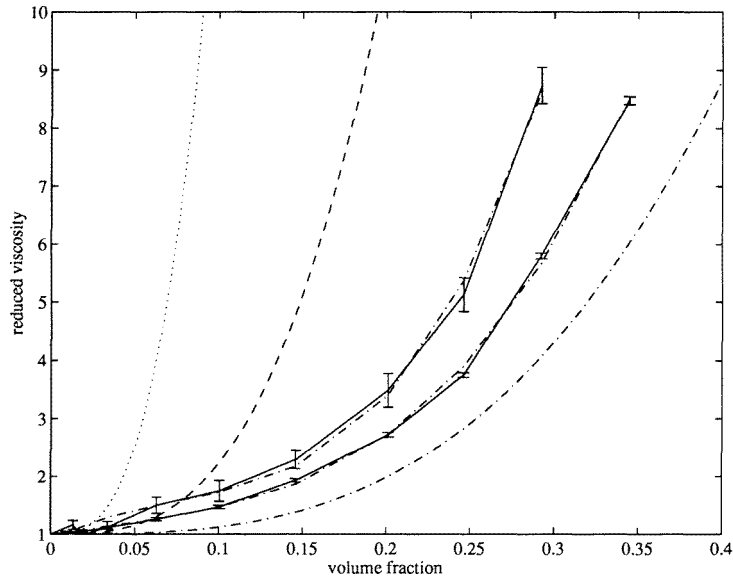


Figure 2. Reduced viscosity of suspensions of prolate ellipsoids with aspect ratio $f = 5$ as a function of solid volume fraction, at steady shear rates $\dot{\gamma}$ of 0.0003 (lower curve) and 0.0003 (higher curve). The error bars represent RMS fluctuations. The polynomial fits are indicated as chain curves. As a guide to the eye, the Doi-Edwards [8] expression has been drawn for $\beta = 10^2$ (dotted curve), 10^3 (broken curve) and 10^4 (chain curve).

3×10^{-6} to 0.05, thus covering four orders of magnitude. The shear stress was measured at each time step, and the viscosity was then calculated as an average over all the steps. The reduced viscosity is calculated as the suspension viscosity divided by the solvent viscosity, which was found to be constant as a function of shear rate, at a value of 0.0362. Our calculated viscosities are shown in figure 1 as a function of the Peclet number, using $3k_B T = 0.0033$. This figure shows that the viscosity follows a typical shear-thinning curve. The viscosity does not depend significantly on the sphere size. Averaged over the various sphere sizes, we find that, at low Peclet numbers ($Pe < 1$), $\eta(0)$ is fairly constant at a value of 4.5, corresponding to the first Newtonian plateau. A shear-thinning regime is observed at higher shear rates ($1 < Pe < 10$) followed by a second Newtonian plateau, where $\eta(\infty)$ is constant at a value of 3.0. The actual values for the low- and high-shear viscosities are in good agreement with the experimental results (3.77 and 2.99, respectively [5]). At higher particulate densities, the low-shear viscosity depends on the size of the suspended spheres. The reason is that the solvent particles have a finite and, at this volume fraction, not negligible size compared with the colloidal particles. In principle this problem can be resolved by significantly increasing the size of the simulation box.

We have also performed DPD simulations for rod-like particles. For dilute suspensions of rods, the viscosity can be written as an expansion up to first order in the rod volume fraction ϕ as $\eta_R = \eta/\eta_s = 1 + [\eta]\phi$, where η_R is the *reduced* viscosity. We shall compare our results for the *intrinsic* viscosity $[\eta]$ with available theoretical results. Doi and Edwards [8] have argued that entanglement interactions between rods become important in the semidilute regime, and that the viscosity increases with the third power of the rod volume fraction ϕ . For rods with a low aspect ratio ($f = 5$ in our simulations), it can be shown that

the semidilute regime does not exist [9]. The dilute regime is directly followed by the concentrated regime, where log-jamming effects are expected to become important. Our simulated viscosity curves as a function of ϕ are shown in figure 2. In order to describe the viscosity as a function of volume fraction over the whole range of concentrations, we have to include linear [6] and quadratic [7] expansions in the dilute regime as well as the third-power dependence in the concentrated regime. Therefore we have fitted our data to a third-degree polynomial function. The results are presented in figure 2 and show a good fit to the viscosity curves for both shear rates. We find a linear coefficient of 5.67, which can be interpreted as the intrinsic viscosity. This result is in excellent agreement with the theoretical prediction of 5.78 for this aspect ratio [6]. In the concentrated regime the cubic term dominates. This is in agreement with the Doi–Edwards scaling law, extrapolated into the concentrated regime, although the explanation for this agreement is unclear.

In conclusion, we have shown that the DPD simulation technique produces realistic rheological behaviour for particulate suspensions. For sphere suspensions up to 30%, both the low- and the high-shear viscosities are in good agreement with experimental data. For denser suspensions at low shear rates, the size of the simulation box should be significantly increased to prevent finite size effects. Dilute suspensions of rods show intrinsic viscosities which are in excellent agreement with theoretical expansions in the volume fraction. Therefore DPD should be regarded as a valuable tool for simulating the flow behaviour of complex particulate fluids.

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