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Brownian-dynamics simulation studies of a charge-stabilized colloidal suspension under shear flow

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We have carried out Brownian-dynamics simulations of a charged colloidal suspension under oscillatory shear flow with both Couette and Poiseuille velocity profiles. We show that in the "steady-shear" limit, for both of the velocity profiles, the enhancement of the self-diffusion coefficient in directions transverse to the flow shows a crossover from a $\dot{\gamma}^2$ dependence to a $\dot{\gamma}^{1/2}$ dependence as the shear rate $\dot{\gamma}$ increases. The magnitude of the enhancement is a function of the interparticle interaction strength. There is a layering tendency in the direction of the velocity gradient for Couette flow, while such a tendency is not that prominent for Poiseuille flow.

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Charge-stabilized monodisperse suspensions of polystyrene spheres [1] are good model systems for the study of both the structural and dynamical properties of solids and liquids in equilibrium states as well as in states driven far from equilibrium [2]. The macrosize of the colloidal particles (radius $R\sim$ 500 Å) and their large interparticle separation a_s result in a density relaxation time τ that is orders of magnitude larger than that of conventional liquids. Typically, $\tau\sim D_0/a_s^2\sim 10^{-3}$ sec. Here $a_s=n_p^{-1/3}$, n_p being the polystyrene sphere concentration; and D_0 is the self-diffusion coefficient in the noninteracting limit, $D_0=k_BT/6\pi\eta R$, η being the viscosity of the solvent. As a consequence, it is possible by readily available means to apply shear rates ($\dot{\gamma}$) in the laboratory which are comparable to $1/\tau$, and interesting flow behavior under shear can be observed [3].

Recently, Qiu *et al.* [4] performed forced Rayleigh scattering experiments to measure the self-diffusion coefficients of polystyrene spheres in aqueous suspension under an oscillatory Poiseuille shear flow. They measured the self-diffusion coefficients in directions both transverse and parallel to the flow. They found that the self-diffusion coefficients in all the directions increase linearly with $\dot{\gamma}$ (apart from the usual Taylor enhancement in the flow direction [5]). The slope of the linear enhancement increases monotonically with the interparticle interaction strength and is absent in the noninteracting limit. They did not find any evidence of ordering induced by the shear flow in their experiment.

Subsequently, Brownian-dynamics simulation studies [6] were carried out on a polystyrene sphere suspension in the presence of an oscillatory Couette flow, where the particles were assumed to interact with each other by means of the Derjaguin-Landau-Verwey-Overbeek (DLVO) potential [1]. Contrary to the experiments [4], the increases in the self-diffusion coefficients in the transverse directions varied as $\dot{\gamma}^{1/2}$. In addition, a tendency towards layering in the velocity gradient direction was observed, which resulted in a value of the self-diffusion coefficient smaller in this gradient direction than in the direction normal to the shear plane (the plane containing the velocity and the velocity gradient directions).

Given that the velocity profile used in the laboratory experiment is different from the one used in the computer simulations, an important question arises whether the difference in the $\dot{\gamma}$ dependence of the self-diffusion coefficients is due to the difference in the velocity profiles. Furthermore, the mode-coupling calculations of Kirkpatrick [8] for atomic fluids predict that the shear viscosity as a function of $\dot{\gamma}$ shows a crossover from a $\dot{\gamma}^2$ dependence in the low $\dot{\gamma}$ regime to a $\dot{\gamma}^{1/2}$ dependence in high $\dot{\gamma}$ regime. It is interesting to ask if such a crossover takes place for colloids too, although no such crossover for the self-diffusion coefficient [7] as a function of the shear rate has been reported in Ref. [4] or in Ref. [6].

In this paper we present the results of Brownian-dynamics simulation studies of a polystyrene sphere system (similar to that in [6]) subjected to Couette and to Poiseuille shear flow. Our motivation was (1) to check whether the different velocity profiles lead to different results and (2) to see whether the above-mentioned crossover is present in colloids. Some of our key results are given in Figs. 1 and 2, for the flow geometry as in the inset of Fig. 1(a). They are supportive of a crossover in the $\tilde{\gamma}$ ($\tilde{\gamma}\equiv\dot{\gamma}\tau$, a dimensionless shear rate variable) dependence of the fractional change in the transverse

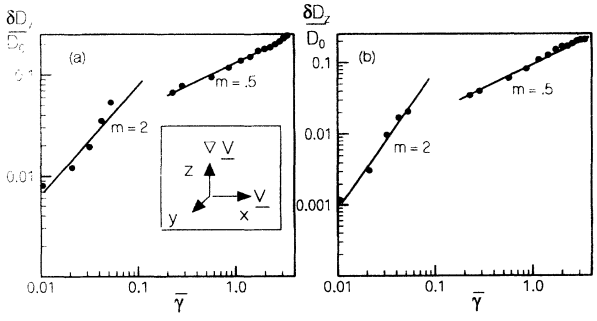

FIG. 1. Log-log plot of $\delta D_y/D_0$ (a) and $\delta D_y/D_0$ (b) as functions of $\tilde{\gamma}$ for Couette flow. In both the cases the best fit lines with assumed slopes of 2 and 0.5 are also shown. The flow geometry is indicated in (a).

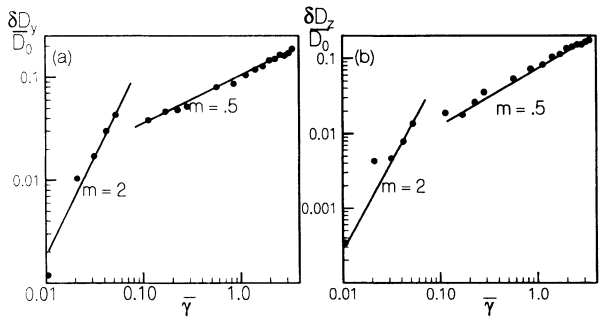

FIG. 2. Log-log plot of $\delta D_y/D_0$ (a) and $\delta D_y/D_0$ (b) as functions of $\bar{\gamma}$ for Poiseuille flow. In both the cases the best fit lines with assumed slopes of 2 and 0.5 are also shown.

self-diffusion coefficients, $\delta D_y/D_0 \equiv [D_y(\bar{\gamma}) - D_y(\bar{\gamma}=0)]/D_0$, and $\delta D_z/D_0 \equiv [D_z(\bar{\gamma}) - D_z(\bar{\gamma}=0)]/D_0$ from a $\bar{\gamma}^2$ dependence for low $\bar{\gamma}$ ($\bar{\gamma}<0.1$) to a $\bar{\gamma}^{1/2}$ dependence for higher $\bar{\gamma}$ ($\bar{\gamma}>0.1$), for both the velocity profiles. We also find a pronounced layering effect in the case of Couette flow but not in the case of Poisseuille flow.

The system we considered was an aqueous suspension of polystyrene spheres of radius $R=0.038$ μm. The volume fraction, ϕ ($=4\pi R^3 n_p/3$) was 0.003 as in the experiments [4]. The interaction between two polystyrene spheres separated by a distance r was taken to be of the DLVO form [1]:

$$V(r) = (Z^* e)^2 \exp(2R/\lambda)(1+R/\lambda)^{-2} \exp(-r/\lambda)/\epsilon r, \tag{1}$$

where ϵ ($=78$) is the dielectric constant of the medium, $Z^* e$ ($Z^*=200$ as in [6]) is the effective surface charge of the polystyrene spheres (e being the electronic charge), and λ is the Debye screening length given by

$$\lambda^{-2} = \frac{4\pi}{\epsilon k_B T}\left((n_p Z^*) e^2 + \sum_\alpha n_\alpha (z_\alpha e)^2 \right). \tag{2}$$

Here n_α is the number density of the impurity ions of type α with charge z_α. We neglected the hydrodynamic interactions between the polystyrene spheres, because it has been suggested [4] that this is not important for ϕ and $\bar{\gamma}$ values we considered. Our simulations were carried out using the Brownian-dynamics algorithm due to Ermak and Yeh [9]. Here, in the absence of shear, the position of a polystyrene sphere $\vec{r}(t+\delta t)$ at time $t+\delta t$ is updated from its position $\vec{r}(t)$ as

$$\vec{r}(t+\delta t) = \vec{r}(t) + \frac{D_0}{k_B T}\vec{F}(t)\,\delta t + \vec{X}, \tag{3}$$

where $\vec{F}(t)$ is the force acting on the given polystyrene sphere due to all other polystyrene spheres in the system at time t via Eq. (1). The components of $\vec{X}$ are random displacements sampled from a Gaussian distribution with zero mean and variance $2D_0\delta t$. In the presence of the shear flow, with the geometry illustrated in Fig. 1(a), we add an extra contribution due to the shear to the right hand side of Eq. (3) as in Ref. [6]:

$$\delta\vec{r}_{\text{shear}} = \frac{\pi\dot{\gamma}}{2} z \sin(\omega t)\,\delta t\,\hat{x} \quad \text{(Couette)};$$

$$= \frac{\pi\dot{\gamma}}{L}(L^2/4 - z^2)\sin(\omega t)\,\delta t\,\hat{x} \quad \text{(Poiseuille)}.$$

Here ω is the shear frequency and L ($=N^{1/3}$ in units of a_s, where N is the number of particles in the simulation box) is the length of the simulation box. Since we were interested mainly in the "steady shear" limit we chose $\omega \ll \dot{\gamma}$. We took $\omega/2\pi = 5$ Hz for $\bar{\gamma}>0.23$ and $\omega/2\pi = 0.25$ Hz for $\bar{\gamma}<0.23$. We, however, verified that different physical quantities calculated do not depend on ω for a given $\dot{\gamma}$. The integration time step δt should be much smaller than the density relaxation time τ ($=5.7\times10^{-3}$ sec), but much larger than the velocity relaxation time ($\sim 10^{-10}$ sec, given by $m/6\pi\eta R$, where m is the mass of a polystyrene sphere) of the system. We used $\delta t = 0.004\tau$ such that the system remains stable under the highest $\bar{\gamma}$ for the smallest λ we studied (as monitored by steady values of the potential energy per particle and the radial distribution function).

The bulk of our simulations were done on $N=500$ particles in a cubic box with periodic boundary conditions in all three directions. In case of Couette flow, we assumed that the top of the box is moving relative to the bottom; so if a particle exited from the top, it was reintroduced at the bottom with a shift equal to $\pi\dot{\gamma}L\sin(\omega t)\delta t/2$, which is the shear displacement at the top of the box [6]. We extensively studied the case of $\lambda/a_s = 0.471$ for both velocity profiles and different shear rates up to $\bar{\gamma}=3.42$. For a given $\bar{\gamma}$, the steady state configuration of the previously studied $\bar{\gamma}$ was taken as the initial configuration. The cutoff of the DLVO potential was kept at $2.5a_s$. We used the minimum image convention and constructed the Verlet neighbor list (updated every ten steps) to calculate the force on a given particle due to all other particles. Typically the first 10 000 steps were discarded in order to allow the system to reach the steady state.

In the steady state, we calculated the anisotropic structure factors and the self-diffusion coefficients in directions transverse to the flow as follows. The anisotropic structure factors were calculated directly using the following definitions: $S(q_y) = \frac{1}{N}\langle \Sigma_{i,j=1}^N \exp[iq_y(y_i - y_j)]\rangle$ and $S(q_z) = \frac{1}{N}\langle \Sigma_{i,j=1}^N \exp[iq_z(z_i - z_j)]\rangle$ for $(q_y, q_z) = (2\pi/L)(n_y, n_z)$. Here N is the number of particles in the system and the angular bracket denotes averaging over a large number of steady state configurations $\{x_i, y_i, z_i\}$. We also calculated the mean squared displacements: $M_y(t) \equiv \frac{1}{N}\Sigma_{i=1}^N [y_i(t) - y_i(0)]^2$ and $M_z(t) \equiv \frac{1}{N}\Sigma_{i=1}^N [z_i(t) - z_i(0)]^2$ for a given choice of initial configurations $\{x_i(0), y_i(0), z_i(0)\}$. These two quantities were averaged over 15 (for high $\bar{\gamma}$) to 20 (for low $\bar{\gamma}$) initial configurations, chosen at time intervals $\simeq 5\tau$ (the interparticle diffusion time) up to a time of 0.6 sec (for high $\bar{\gamma}$) and 0.75 sec (for low $\bar{\gamma}$). These were finally averaged over two (for high $\bar{\gamma}$) and four (for low $\bar{\gamma}$) independent runs. A number N_0 of initial data for M_y and M_z were discarded and the rest were partitioned into segments of time width $\Delta \geq 5\tau$. The slopes of M_y and M_z versus t were calculated for each segment yielding two distributions. The means were assumed to give $2D_y$ and $2D_z$, and the variances, error bounds on $2D_y$ and

TABLE I. Best fit exponents for different $\tilde{\gamma}$ regimes and for different velocity profiles.

Couette				Poiseuille			
for $\delta D_y/D_0$ region of $\tilde{\gamma}$	α_y	for $\delta D_z/D_0$ region of $\tilde{\gamma}$	α_z	for $\delta D_y/D_0$ region of $\tilde{\gamma}$	α_y	for $\delta D_z/D_0$ region of $\tilde{\gamma}$	α_z
$\tilde{\gamma}<0.11$	1.96	$\tilde{\gamma}<0.11$	1.66	$\tilde{\gamma}<0.11$	1.70	$\tilde{\gamma}<0.11$	1.86
$\tilde{\gamma}>0.11$	0.57	$\tilde{\gamma}>0.17$	0.59	$\tilde{\gamma}>0.11$	0.56	$\tilde{\gamma}>0.11$	0.59

$2D_z$. This led to our data for $\delta D_y/D_0$ and $\delta D_z/D_0$ shown in Figs. 1 and 2.

We fitted our data for the self-diffusion coefficients using $\delta D_y/D_0 = A_y \tilde{\gamma}^{\alpha_y}$ and $\delta D_z/D_0 = A_z \tilde{\gamma}^{\alpha_z}$ with separate fitting parameters (A_y, α_y) and (A_z, α_z) in the low and the high $\tilde{\gamma}$ regimes. The corresponding exponents, given in Table I, are close to 2 and 0.5; if they are set to these values, the best fits are as shown in Figs. 1 and 2. Thus our results clearly indicate a crossover in the $\tilde{\gamma}$ dependence of $\delta D_{y,z}/D_0$, from a $\tilde{\gamma}^2$ dependence for low $\tilde{\gamma}$ to a $\tilde{\gamma}^{1/2}$ dependence for high $\tilde{\gamma}$, for both velocity profiles with crossover at $\tilde{\gamma} \sim 0.1$, in agreement with the calculations of shear viscosity in sheared atomic fluids [8] as well as with recent calculations of self-diffusion coefficients in sheared polystyrene sphere systems using mode-coupling theory [10].

We note that for large $\tilde{\gamma}$ regime our error bounds on D_y/D_0 and D_z/D_0, estimated as indicated above, varied from 5% to 12%. The changes in D_y/D_0 and D_z/D_0 with $\tilde{\gamma}$ in this region are sizable compared to these error bounds. Hence one can regard the $\tilde{\gamma}^{1/2}$ dependence of $\delta D_{y,z}/D_0$ independently of the velocity profile, as conclusively established. However, for low $\tilde{\gamma}$, $\delta D_{y,z}/D_0$ are themselves very small, and if we take our error bounds on $D_{y,z}/D_0$ (typically 8%) seriously, we cannot make any conclusive statements regarding the $\tilde{\gamma}$ dependence of $\delta D_{y,z}/D_0$. The same would be true of presently available experimental data as well. Nevertheless, we do believe that the trends clearly visible in Figs. 1 and 2 indicating the $\tilde{\gamma}^2$ dependence of $\delta D_{y,z}/D_0$ for the low $\tilde{\gamma}$ regime are to be taken seriously. We have checked this in two ways. (1) For a given system size (500 particles), we found that averaging over four instead of two independent runs reduced typical error bounds from 10% to 8%, whereas the mean changed at the most by 2–3%. (2) We carried out the simulations for 864 particles under Couette flow for low $\tilde{\gamma}$ and calculated $M_{y,z}(t)$ up to 1 sec, averaging over two independent runs. We found that errors once again reduced to 8% from 10% (for 500 particles) and the mean values showed a slight downward shift $\leq 3\%$.

Next we draw attention to Fig. 3, where we show S_{my} and S_{mz}, being respectively the first peak heights in $S(q_y)$ and $S(q_z)$, as functions of $\tilde{\gamma}$ in the large $\tilde{\gamma}$ regime for both the velocity profiles. The anisotropic structure factors were calculated by averaging over typically 200 configurations sampled every 25 Brownian-dynamics steps. The enhancement of S_{mz} compared to S_{my} indicates that there is a tendency to form layers parallel to the x-y plane as a result of the shear flow. This tendency is clearly pronounced in the case of Couette flow. In the low $\tilde{\gamma}$, we find that S_{mz} is insensitive to system size ($108 \geq N \leq 864$) but in the high $\tilde{\gamma}$, S_{mz} grows with system size perhaps indicating a layering transition [11]. One would then expect that the diffusion between the layers would be suppressed relative to that within the layers implying that $D_z < D_y$. This is indeed the case with our data, in agreement with the findings of the earlier simulations [6]. We find that in the Poiseuille case too, D_y is larger than D_z for all $\tilde{\gamma}$, but with smaller differences, consistent with the smaller increase in S_{mz}.

It has been reported [4] that the enhancement in the self-diffusion coefficient depends on the interaction strength between the particles, the enhancement being altogether absent in the noninteracting case. Accordingly, we have studied the dependence of A_y and A_z on the Debye screening length, but only in the high shear regime where our error bounds on $\delta D_{y,z}$ are reasonable. For each λ/a_s, we determined A_y and A_z by fixing the exponents $\alpha_{y,z}$ at 0.5. We find that $A_y \sim (\lambda/a_s)^{0.51}$ and $A_z \sim (\lambda/a_s)^{0.56}$ [Figs. 4(a) and 4(b)]. It would be worthwhile to understand this dependence analytically.

In conclusion, we have presented in this paper results from extensive Brownian dynamics simulation studies of a polystyrene sphere system subjected to Couette and to Poiseuille shear flow. Our results are in agreement with the earlier simulations [6] in the large $\dot{\gamma}$ regime; however, for low

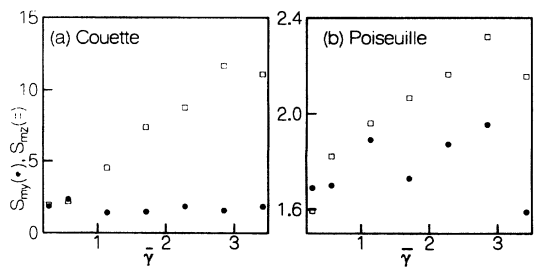

FIG. 3. First peak heights of the transverse structure factors, S_{my} and S_{mz}, as functions of $\tilde{\gamma}$ for Couette flow (a) and Poiseuille flow (b). Note the difference in the scale of the vertical axis in the two cases.

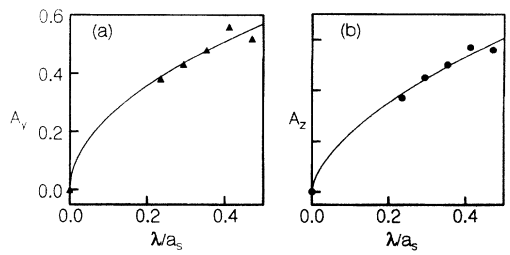

FIG. 4. A_y (a) and A_z (b) as functions of λ/a_s. The points are obtained from the simulation data and the solid lines are the best fits (see text).

$\dot{\gamma}$ our results are very different. They suggest that the shear induced enhancement in the transverse diffusion constants of colloidal suspensions also exhibits a *crossover* analogous to that found by Kirkpatrick [8] for the shear viscosity of atomic fluids, as predicted in a recent calculation by Indrani and Ramaswamy [10]. The magnitude of the enhancement depends on the Debye screening length as found in the experiment. Its dependence on the shear rate does not seem to depend on the geometry of the velocity profile. However, the structural ordering induced by the shear flow is dependent on the geometry of the velocity profile. This may have bearing on shear induced ordering investigated recently [12]. Our results on the $\dot{\gamma}$ dependence of the self-diffusion coefficients do not agree with that found in the laboratory experiments [4] in any regime of $\dot{\gamma}$. The discrepancy between experiment and simulations is not due to the difference in the velocity profile, and needs to be resolved. Perhaps it is due to the neglect of the hydrodynamic interactions in the simulations; this needs to be looked into. Finally, it would be very interesting if the crossover between the low $\dot{\gamma}$ and high $\dot{\gamma}$ regimes seen in our simulation can be observed experimentally, even though this would call for very accurate measurements of the diffusion coefficients.

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