

Shear-induced enhancement of self-diffusion in interacting colloidal suspensions

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We set up the generalized Langevin equations describing coupled single-particle and collective motion in a suspension of interacting colloidal particles in a shear flow and use these to show that the measured self-diffusion coefficients in these systems should be strongly dependent on shear rate $\dot{\epsilon}$. Three regimes are found: (i) an initial $\text{const} + \dot{\epsilon}^2$, followed by (ii) a large regime of $\dot{\epsilon}^{1/2}$ behavior, crossing over to an asymptotic power-law approach (iii) $D_0 - \text{const} \times \dot{\epsilon}^{-1/2}$ to the Stokes-Einstein value D_0 . The shear dependence is *isotropic* up to very large shear rates and increases with the interparticle interaction strength. Our results provide a straightforward explanation of recent experiments and simulations on sheared colloids.

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I. INTRODUCTION

The large natural time scales ($\tau \sim \text{ms}$) and (in the crystalline state) weak elastic constants ($G \sim 10 \text{ dyn/cm}^2$) in colloidal suspensions of latex spheres (“polyballs”) [1] make it easy to drive them far from equilibrium [2] by the application of shear rates $\dot{\epsilon} \sim \tau^{-1}$ and stresses $\sim G$. Shear-enhanced diffusion, a novel nonequilibrium phenomenon encountered in these systems, has been studied in forced Rayleigh scattering experiments [3] and nonequilibrium Brownian dynamics simulations [4,5], but a theoretical explanation has been lacking. This paper presents a theory of this effect.

Before presenting our results, we summarize the findings of [3–5]. The systems were subjected to a shear flow with velocity field

$$\mathbf{v}(\mathbf{r}) = \dot{\epsilon}(y) \cos(\dot{\epsilon}_0 t) y \hat{\mathbf{x}}. \quad (1)$$

The flow was taken to be oscillatory for convenience. All properties of interest can be understood by looking at the case of steady flow, to which we will restrict all further remarks. In the laboratory experiment [3], the shear rate $\dot{\epsilon}(y)$ in (1) varied linearly with y , corresponding to plane Poiseuille flow. The authors measured the self-diffusion coefficients D_i , $i = x, z$, along x and z . The Brownian simulations of [4] used the plane Couette flow geometry, $\dot{\epsilon} = \text{const}$, while [5] considered both Couette and Poiseuille flows. Both simulations measured D_y and D_z .

All these studies found an excess diffusivity ΔD_i , relative to that in the absence of shear, that went to zero in the noninteracting (large concentration of ionic impurities) limit. The authors of [3] fitted their data to $\Delta D_i \propto |\dot{\epsilon}|$ (where $\dot{\epsilon}$ is an average measure of the shear rate, say, the central velocity divided by the capillary diameter), while the simulations, in seeming disagreement, found an $\dot{\epsilon}^{1/2}$ behavior for the excess diffusivity at intermediate shear rates. In addition, [5] found a quadratic growth for $\dot{\epsilon}$ much lower than that explored by [3,4], while [4] noted a saturation for very large $\dot{\epsilon}$.

We emphasize that this enhancement of diffusion by shear is not the well-known Taylor dispersion [6]. The latter is a purely kinematic effect, which acts only *along* the flow direction, and which occurs even for a single Brownian particle in a shear flow. Briefly, since the equation of motion for such a particle is $\dot{x} = \dot{\epsilon}y(t) + f_x(t)$ and $\dot{y} = f_y(t)$ with f_x and f_y being independent white noise sources, we see that the mean-square *velocity* along x grows as the mean-square *displacement* along y , giving $x^2 \sim \dot{\epsilon}^2 t^3$.

We adopt a continuum, coarse-grained approach, in which the detailed particle configurations and microscopic pair potential are replaced by concentration fields and a direct pair correlation function. The dynamics of the concentration and momentum density fields of the particles are described by generalized Langevin equations including a coupling to a background shear flow. These we solve in a mode-coupling approximation [7] without hydrodynamic interaction (HI). Despite this apparent limitation, they should describe not only the simulations but the experiments as well, since the latter are in the dilute, large-screening-length regime [3] in which the HI can be absorbed into a redefined “bare” friction [8]. We return at the end of the paper to a discussion of the approximations made in our treatment.

The rest of this paper is organized as follows. In the next section, we state our results and give a qualitative,

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physical explanation of the phenomenon. In Sec. III, we present our model in detail, and discuss in Sec. IV the mode-coupling approach used to solve the model. We close in Sec. V with a discussion of our results, the approximations made in obtaining them, and what remains to be explained.

II. RESULTS AND A QUALITATIVE EXPLANATION

A. Results

Our findings are simply summarized in Figs. 1 and 2. Figure 1 shows the enhancement of self-diffusion arising *only* from interaction effects (i.e., Taylor dispersion has been subtracted out of the diffusivity along x). We have used an effective hard-sphere description [9] of the colloid for two different packing fractions. We find three regimes in the dependence of the self-diffusion coefficient D_i on shear rate: (i) an initial quadratic growth, followed by (ii) a substantial range of $\dot{\epsilon}^{1/2}$, crossing over to (iii) a power-law approach $D_i = D_0 - \text{const} \times \dot{\epsilon}^{-1/2}$ to the Stokes-law value D_0 . This behavior holds for diffusion in all three directions, and we find that the effect is *isotropic* until we reach very large shear rates. This direction independence of the enhancement is in agreement with [3,4]. As is perhaps clearer from Fig. 2, which shows the self-energy (i.e., the fractional excess friction as a function of shear rate for effective hard-sphere packing fractions 0.1, 0.3, and 0.46), the effect of shear on self-diffusion is greater for more strongly interacting colloids (again confirming this observation in [3,4]). While our detailed quantitative results are obtained from a numerical evaluation of the mode-coupling integral, analytical asymptotic arguments

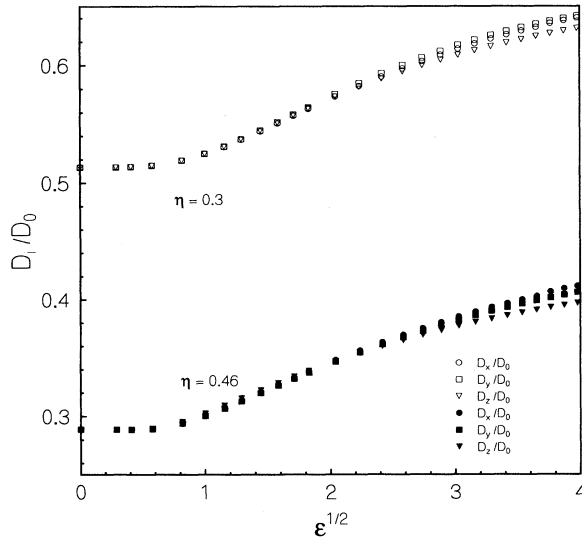


FIG. 1. Self-diffusion coefficients D_i/D_0 under shear (for $i = x, y, z$), vs $\epsilon^{1/2}$, for three packing fractions $\eta = 0.1$, $\eta = 0.3$, and $\eta = 0.46$. The initial ϵ^2 growth followed by $\epsilon^{1/2}$ are clearly seen, and there is some evidence for the onset of saturation.

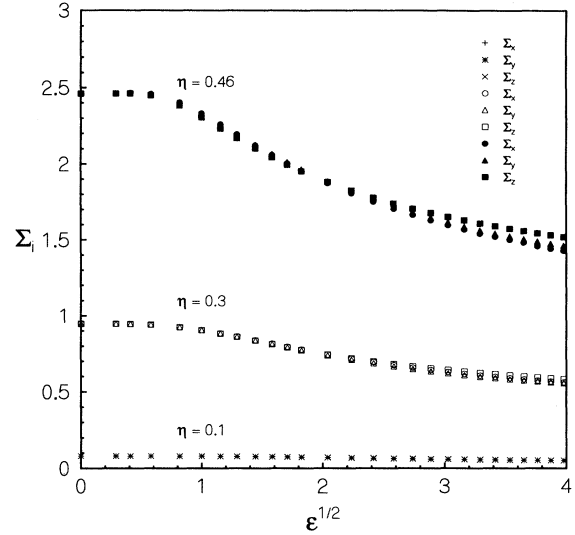


FIG. 2. The self-energies $\Sigma_i(\epsilon)$ for ($i = x, y, z$) plotted against $\epsilon^{1/2}$, at two different packing fractions, $\eta = 0.3$ and $\eta = 0.46$. The initial quadratic reduction in Σ_i can be seen, followed by an intermediate region of $\epsilon^{1/2}$ behavior, tending toward saturation at higher values of shear.

for small and large $\dot{\epsilon}$ give, respectively, regimes (I) and (III), and (II) can be explained as a crossover.

We are thus able to account completely for the behavior observed in the simulations [5,4]. Moreover, a closer look at the data of [3] reveals that the apparent linear behavior is in fact a roughly quadratic growth crossing over to sublinear behavior at larger shear rates, in agreement with our predictions and with [5]. There are, however, not enough data in [3] to make a good quantitative comparison.

B. Qualitative arguments

The physical mechanism underlying our theory is relatively simple. At temperature T , in the absence of shear, the self-diffusion coefficient of the colloidal particles is equal to T/Γ where the friction coefficient Γ has two contributions: a “bare” part Γ_0 , from the solvent, and a correction $\Delta\Gamma$, from the interactions with the other particles [10]. The important contribution to $\Delta\Gamma$ in a strongly interacting suspension is from concentration fluctuations with wave number $q \sim q_0$ not far from the peak of the static structure factor. Even away from equilibrium, e.g., in a shear flow, the relation between friction coefficient and diffusivity can be used if the former is always taken, by convention, to refer to the decay rate of the velocity autocorrelation function (VACF) and not necessarily to the inverse of a mobility. With this caution [11], we can argue that the effect of a shear flow (1) on the picture outlined above, qualitatively, is to eliminate the contribution to $\Delta\Gamma$ from all modes with relaxation rates smaller than $\dot{\epsilon}$, i.e., from all modes that are sheared before they relax. The effective friction thus decreases as $\dot{\epsilon}$ increases. Further, no nonanalytic behavior is expected for $\dot{\epsilon} \rightarrow 0$

since the major contribution to $\Delta\Gamma$ is from the wave number region around q_0 , *not* from $q \rightarrow 0$ (the nonanalytic contribution from the hydrodynamic long-time tails [12], although present in principle, being negligible in quantitative terms [13]). Lastly, it is reasonable to suppose that, at very large $\dot{\epsilon}$, all modes are cut out, and Γ flattens out to its bare value Γ_0 after passing through some kind of crossover region. This, since the diffusivity will do the inverse of what Γ does, explains qualitatively the shapes of the curves in Fig. 1.

III. THE MODEL

Our detailed calculation begins with the continuity equation for the self-number density $n_s(\mathbf{r}, t)$ and a Langevin equation for the self-momentum density $\mathbf{g}_s(\mathbf{r}, t)$ (or self-velocity field $\mathbf{v}_s = \mathbf{g}_s/mn_s$) of a *tagged particle* of mass m in a colloidal suspension in a shear flow [14] of the form (1), with $\dot{\epsilon}(y) = \text{const}$ and $\dot{\epsilon}_0 = 0$.

$$\frac{\partial n_s}{\partial t} + \nabla \cdot (n_s \mathbf{v}_s) = 0, \quad (2)$$

$$\frac{\partial \mathbf{g}_s}{\partial t} + \gamma_0(\mathbf{v}_s - \dot{\epsilon}y\hat{\mathbf{x}}) + n_s \nabla \frac{\delta F}{\delta n_s} = \mathbf{f}(\mathbf{r}, t). \quad (3)$$

These equations are the generalization, to the case of a sheared suspension, of those presented in [15] and [8]. Their physical content is clear. (2) merely says that the tagged particle never disappears. In (3), the second term on the left attempts to dissipate any difference between the velocities of the particle and the solvent. Observe that this term contains the bare damping constant γ_0 , which should be taken as equal to $\Gamma_0 \langle n_s \rangle$, where the interpretation of the mean self-density $\langle n_s \rangle$ in the preceding expression is as in [15]. Brownian dynamics corresponds to the case $m = 0$, so that the VACF in the absence of interactions is δ correlated in time, with the same *value* of the bare diffusivity. The fact that the solvent velocity field has been taken to be exactly as in (1) means that the hydrodynamic interaction has been ignored. The third term is simply the density of thermodynamic force, F being the free-energy functional for the tagged-particle density field, including ideal-gas entropy and interaction with the *collective* density [15]:

$$\frac{\delta \beta F}{\delta n_s(\mathbf{r}, t)} = \ln n_s(\mathbf{r}, t) - \int d^3 r' c(|\mathbf{r} - \mathbf{r}'|) \delta n(\mathbf{r}', t), \quad (4)$$

where $\delta n(\mathbf{r}, t)$ is the deviation of the collective number density field $n(\mathbf{r}, t)$ from its uniform quiescent value n_0 , and $c(r)$ is the *equilibrium* direct pair correlation function. The right-hand side of (3) is the usual δ -correlated Gaussian thermal noise source with variance proportional to γ_0 times the temperature $T = \beta^{-1}$. In addition, the Fourier transform $n_{\mathbf{q}}$ of the collective density obeys, in the presence of shear, the (linearized) equation

$$\frac{\partial n_{\mathbf{q}}(t)}{\partial t} - \dot{\epsilon}q_x \frac{\partial n_{\mathbf{q}}}{\partial q_y} + \tau_q^{-1} n_{\mathbf{q}} = \zeta_{\mathbf{q}}(t), \quad (5)$$

where $\tau_q^{-1} = D_0 q^2 / S_0(q)$, $S_0(q) = [1 - n_0 c(q)]^{-1}$ is the equilibrium static structure factor of the suspension, and $\zeta_{\mathbf{q}}$ is a Gaussian thermal noise source with variance proportional to $D_0 q^2$, where $D_0 = T/\Gamma_0$ is the bare self-diffusivity. If we linearize (2) and (3) and consider time scales $\gg m/\Gamma_0$ or, equivalently, pass to the limit of no inertia, which is appropriate for the Brownian dynamics simulations, then (3) simply becomes a constitutive relation: $n_s \mathbf{v}_s = -(T/\Gamma_0) \nabla n_s + \dot{\epsilon}y \hat{\mathbf{x}}$. In this approximation, (2) reduces to the sheared fluctuating-diffusion equation, with a diffusivity D_0 :

$$\frac{\partial n_{s\mathbf{q}}(t)}{\partial t} - \dot{\epsilon}q_x \frac{\partial n_{s\mathbf{q}}}{\partial q_y} + D_0 q^2 n_{s\mathbf{q}} = \zeta_{\mathbf{q}}(t). \quad (6)$$

IV. MODE-COUPPLING ANALYSIS UNDER SHEAR

To extract the excess diffusivity, let

$$\mathbf{u}_s(\mathbf{r}, t) = \mathbf{v}_s(\mathbf{r}, t) - \dot{\epsilon}y \hat{\mathbf{x}} \quad (7)$$

be the self-velocity field relative to the local background shear flow, and let

$$C_{ui}(\mathbf{k}, z; \dot{\epsilon}) = \int_0^\infty dt e^{izt} \int d^3 r e^{-i\mathbf{k}\cdot\mathbf{r}} \langle u_{si}(\mathbf{0}, 0) u_{si}(\mathbf{r}, t) \rangle \quad (8)$$

(with no sum over repeated indices implied) be the diagonal part of its correlation function, Fourier transformed in space and Laplace transformed in time. $C_{ui}(\mathbf{k}, z; \dot{\epsilon})$ is the natural correlation function to consider, since it has the effect of Taylor dispersion subtracted out. Thus the effect of shear on diffusion with interactions is obtained by calculating

$$D_i(\dot{\epsilon}) = \lim_{z \rightarrow 0} \lim_{k \rightarrow 0} C_{ui}(\mathbf{k}, z; \dot{\epsilon}) \quad (9)$$

where the limit exists because Taylor dispersion has been removed. It is natural to define a self-energy $\Sigma_i(\mathbf{k}, z; \dot{\epsilon})$ by

$$C_{ui}(\mathbf{k}, z; \dot{\epsilon}) = \frac{T}{z + \Gamma_0 [1 + \Sigma_i(\mathbf{k}, z; \dot{\epsilon})]}. \quad (10)$$

Then

$$\frac{D_i(\dot{\epsilon})}{D_0} = \frac{1}{1 + \Sigma_i(\dot{\epsilon})} \quad (11)$$

where $\Sigma_i(\dot{\epsilon}) = \Sigma_i(\mathbf{k} = 0, z = 0; \dot{\epsilon})$. The nonlinearity in Eq. (3) contains one power each of n_s and n , as can be seen from (4). The contribution of this nonlinearity to the VACF, and hence to Σ_i , will thus be of the form $\langle n_s(0) n(0) n_s(t) n(t) \rangle$ which, in a Gaussian decoupling approximation, will be the product of a self-density and a collective-density correlation function. Explicitly, starting from (2) and (3), one can obtain

$$\Sigma_i(\dot{\epsilon}) = \int \frac{d^3q}{(2\pi)^3} \int_0^\infty dt (q_i^2 + \dot{\epsilon} t q_x q_y \delta_{iy}) c(q) \times c(|\mathbf{q} + \dot{\epsilon} t q_x \hat{\mathbf{y}}|) C_s(\mathbf{q}, t; \dot{\epsilon}) C_c(\mathbf{q}, t; \dot{\epsilon}) \quad (12)$$

where $c(q)$ is the direct pair correlation function at equilibrium, and C_s and C_c are the bare correlation functions of the self-density (n_s) and the collective density (n), respectively, in the presence of shear

$$C_s(\mathbf{q}, t; \dot{\epsilon}) = e^{-t(D_0 q^2 - \dot{\epsilon} q_x \frac{\partial}{\partial q_y})} \quad (13)$$

and

$$C_c(\mathbf{q}, t; \dot{\epsilon}) = e^{-t\left(\frac{D_0 q^2}{S_0(q)} - \dot{\epsilon} q_x \frac{\partial}{\partial q_y}\right)} n_0 S(\mathbf{q}; \dot{\epsilon}) \quad (14)$$

In deriving Eq. (12) the peculiar nature of translation invariance in a shear flow, viz., that $\langle \delta n(\mathbf{q}, t) \delta n(\mathbf{q}', 0) \rangle \propto C_c(\mathbf{q}, t; \dot{\epsilon}) \delta(\mathbf{q} + \mathbf{q}' + \dot{\epsilon} t q_x \hat{\mathbf{y}})$ (likewise for n_s) has been taken into account. Equations (13) and (14) are obtained in a straightforward manner from (5) and (6) by multiplying by the appropriate density and taking correlations at equal time. We evaluate the sheared static structure factor [16] $S(\mathbf{q}; \dot{\epsilon})$ as follows. First multiply (5) by $n_{-\mathbf{q}}$ and average over the noise. This leads to

$$\left(2\tau_q^{-1} - \dot{\epsilon} q_x \frac{\partial}{\partial q_y} \right) S(\mathbf{q}; \dot{\epsilon}) = 2D_0 q^2 \quad (15)$$

where τ_q^{-1} has been defined above. Equation (15) is then integrated directly, leading to

$$S(\mathbf{q}; \dot{\epsilon}) = \int_0^\infty d\lambda e^{-\lambda\left(\frac{D_0 q^2}{S_0(q)} - \frac{1}{2}\dot{\epsilon} q_x \frac{\partial}{\partial q_y}\right)} D_0 q^2 \quad (16)$$

The exponential decay factors appearing in (13), (14), and (16) can be evaluated exactly, by introducing an additional ‘‘time’’ variable α and using the identity [17]

$$e^{-\tau\left(h(\mathbf{q}) - b \frac{\partial}{\partial q_y}\right)} = e^{-\int_0^\tau d\alpha h(\tilde{\mathbf{q}})} e^{b\tau \frac{\partial}{\partial q_y}} \quad (17)$$

for any function $h(\mathbf{q})$ and constant b , where $(\tilde{\mathbf{q}} = \mathbf{q} + b\alpha \hat{\mathbf{y}})$ is a shifted wave vector. We can integrate (12) numerically, using Eqs. (13) – (17) to obtain an explicit expression for the shear-dependent diffusivity. In doing the numerical integration, we scale all lengths by the mean interparticle distance σ , and all times by $\tau_0 = \sigma^2/6D_0$, the time that a noninteracting particle takes to diffuse a distance σ . Then the dimensionless shear rate to consider is $\epsilon = \dot{\epsilon}\tau_0$.

Apart from this direct numerical calculation, several general remarks can be made about the structure of $\Sigma_i(\dot{\epsilon})$. First, since C_s and C_c decay faster in time for $\dot{\epsilon} \neq 0$ than for $\dot{\epsilon} = 0$, we expect that $\Sigma_i(\dot{\epsilon} \neq 0) < \Sigma_i(\dot{\epsilon} = 0)$. Secondly, $\Sigma_i(\dot{\epsilon})$ is analytic for $\dot{\epsilon} \rightarrow 0$: $\Sigma_i(\dot{\epsilon}) - \Sigma_i(0) \sim -\dot{\epsilon}^2$ for $\dot{\epsilon} \rightarrow 0$ since the dominant contribution to Σ_i comes from nonzero wave numbers $q \sim q_0$ where the integrand [controlled by a combination of $S_0(q)$, the vertex $|c(q)|^2 q^2$, and the self-relaxation time $1/D_0 q^2$] is largest. The hydrodynamic density modes near $q = 0$ are suppressed both by phase-space factors and the vanishing of the vertex. Thirdly, we can do a rough asymptotic analysis on (12) for $\dot{\epsilon} \rightarrow \infty$. In this case, from (16), $S(\mathbf{q}; \dot{\epsilon}) \rightarrow$

1, and C_s as well as C_c decay as $e^{-D_0 q^2(t + \dot{\epsilon}^2 t^3)}$ for most directions of \mathbf{q} . We must therefore evaluate an integral of the form $\int_0^\infty dt \int_0^\infty dq q^4 [c(q)]^2 e^{-q^2(t + \dot{\epsilon}^2 t^3)} \equiv I(\dot{\epsilon})$. This can be rewritten

$$I(\dot{\epsilon}) = \int_0^\infty dq q^2 [c(q)]^2 H(\dot{\epsilon}/q^2) \quad (18)$$

where

$$H(x) \rightarrow \begin{cases} 1, & x \rightarrow 0 \\ \text{const} \times x^{-2/3}, & x \rightarrow \infty \end{cases} \quad (19)$$

is a scaling function whose asymptotic properties are all that concern us. Since H vanishes for large values of its argument, the dominant contribution to the integral for $\dot{\epsilon} \rightarrow \infty$ is from *large* q ($\sim \dot{\epsilon}^{1/2}$), so that $H \simeq 1$, and $I(\dot{\epsilon}) \sim \int_{\dot{\epsilon}^{1/2}}^\infty dq q^2 [c(q)]^2$. The behavior of the diffusivity for large shear rates is thus determined by the approach of $c(q)$ to zero for large q . For hard spheres [18] $c(q) \sim q^{-2}$ for $q \rightarrow \infty$. Even for the Yukawa potential this behavior, though not *asymptotic* [19], seems to hold, by visual inspection, for wave numbers beyond the peak. If we therefore assume this form for the large- q behavior, we see that (18) and (19) lead to $\Sigma_i(\dot{\epsilon}) \sim \dot{\epsilon}^{-1/2}$, at least for shear rates such that the corresponding wave numbers are in the q^{-2} regime. Correspondingly, for large $\dot{\epsilon}$, $D_i(\dot{\epsilon})$ will in general display a fair region of $\dot{\epsilon}^{1/2}$ growth before saturating to a constant. These observations are consistent with our detailed calculation, whose results are summarized in Figs. 1 and 2.

We use as inputs to our numerical calculation the Percus-Yevick [20] expressions for $c(q)$ and $S_0(q)$ for hard spheres [9]. The general structure of the result is unlikely to be modified by a more accurate model for the density correlations; we have commented on this after Eq. (19). We have evaluated (12) for three different densities, corresponding to packing fractions $\eta = 0.1$, $\eta = 0.3$, and $\eta = 0.46$, where the peak heights of $S_0(q)$ are, respectively, about 1.1, 1.5, and 2.6. At these packing fractions, the unsheared self-energies are about 0.08, 0.9, and 2.5, respectively, corresponding to the zero-shear-rate diffusivities of 0.9, 0.5, and 0.3 of the bare Stokes-Einstein value. An increase in packing fraction from 0.1 to 0.46 results in an increase of slope of about 30% in the diffusivity curves, indicating the strong dependence of the enhancement on the interaction strength. Also note that the enhancement in the self-diffusion is isotropic, up to large shear rates. Numerical difficulties prevent us from going beyond $\epsilon \simeq 15$.

V. DISCUSSION

The overall shape of our curve for D_i/D_0 (at $\eta = 0.46$) compares well with that of [4] at similar values of zero-shear-rate diffusivities. However, our results are quantitatively different, the reason for which can also be understood within our calculation: we obtain the enhancement ΔD in a description where the tagged particle moves through a medium of *freely diffusing* particles. The relaxation rate of the modes that the tagged particle confronts,

and which produces the friction it experiences, is the bare D_0q^2 . Shear will affect the process when $\dot{\epsilon} \sim D_0q_0^2$. In the experimental system (or in a self-consistent description) the relevant rate is $D_s(\dot{\epsilon} = 0)q^2 < D_0q^2$. Shear effects should set in at an $\dot{\epsilon}$ which is lower than that given by our “non-self-consistent” calculation. We can thus account for the discrepancy mentioned above. We suggest that the relation between suitably nondimensionalized self-diffusivity $[D_s(\dot{\epsilon})/D_s(\dot{\epsilon} = 0)]$ and shear rate ($\epsilon = \dot{\epsilon}\tau$, where τ is the *observed* interparticle diffusion time rather than that in the absence of interactions), should be roughly universal as speculated in [4].

It should be noted that a related calculation by Kirkpatrick [21] of the non-Newtonian viscosity of a sheared one-component hard-sphere liquid found, numerically, a const $-\dot{\epsilon}^{1/2}$ shear-thinning behavior, although no analytical arguments were offered for this. We suggest that this too is a crossover from quadratic to inverse square-root behavior, as an asymptotic analysis like ours will doubtlessly reveal.

Although we have given a convincing explanation of the enhancement of diffusion by shear, there are some points to which we would like to draw the reader's attention. First, the simulations of [4] and [5] see an *enhancement* of the structure factor height for wave vectors along the gradient direction. The present (and generally used [16]) linearized treatment of the effect of shear on collective density fluctuations cannot account for this. Secondly, we (and the simulators [4,5]) have used all along a noise source whose strength and statistics are identical to those known to hold at equilibrium. While this is doubtlessly acceptable at low shear rates, it must surely break down in real colloids as a result of hydrodynamic or even inertial effects. This brings us to a third point, namely, the neglect of the hydrodynamic interaction. We have argued that the shear dependence seen in

the experiments of [3] must arise from direct interparticle interactions and not from hydrodynamics, since the systems they look at are very dilute, and the effect is absent when the interactions are eliminated by strong screening. However, we cannot rule out the possibility that the hydrodynamic interaction and the strong liquidlike correlations in the polyball configurations combine to give an effect that is greater than the sum of its parts. Stokesian dynamics simulations [22] find a purely hydrodynamic contribution to the diffusivity of sheared suspensions at large shear rates, scaling as $\dot{\epsilon}a^2$ where a is the radius of the colloidal particle. This is clear evidence for a nonthermal source of noise for strongly sheared suspensions. Moreover, this last contribution, linear in the shear rate, could be present in a minor way in the experiments of [3].

Note added in proof. A considerable while after this paper was submitted for publication, we became aware of independent work by O. Bychuk and B. O'Shaughnessey [Bull. Am. Phys. Soc. **40**, 460 (1995)] which appears to be along lines that are similar to the present paper.

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