

Self-Diffusion of Interacting Colloids Far from Equilibrium

Xia Qiu,^(1,2) H. Daniel Ou-Yang,^(1,2) D. J. Pine,^(2,3) and P. M. Chaikin^(2,4)

⁽¹⁾ *Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104*

⁽²⁾ *Exxon Research and Engineering Laboratory, Annandale, New Jersey 08802*

⁽³⁾ *Department of Physics, Haverford College, Haverford, Pennsylvania 19041*

⁽⁴⁾ *Department of Physics, Princeton University, Princeton, New Jersey 08534*

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Forced Rayleigh scattering is used to measure the self-diffusion of charged polyball suspensions driven far from equilibrium by an oscillating shear flow. Aside from the usual enhancement of the diffusion due to Taylor dispersion, we observe an additional isotropic contribution which increases linearly with the shear rate. This anomalous contribution is absent in noninteracting samples and increases monotonically with the interparticle interaction strength.

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Charge-stabilized monodisperse suspensions of polystyrene spheres (polyballs) are useful model systems for the study of the static equilibrium properties of both solids and liquids.¹⁻³ They also provide a unique way of studying the structure and dynamics of systems far from equilibrium. The particle spacings are on the scale of 10^3 to 10^4 Å so that the energy density and elastic constants are 10^9 to 10^{12} smaller than conventional condensed atomic or molecular systems. Thus, it is possible to perform experiments where the applied stresses are comparable to the energy density, whereas in conventional systems experimentally accessible stresses are orders of magnitude smaller than the energy density. As a result, new phenomena such as shear-induced melting⁴ and laser-induced freezing⁵ have been observed in polyball systems. The effect of high shear rate on the properties of simple liquids has been the subject of many theoretical and computational studies. These studies predict interesting new types of ordered states with stringlike and crystallinelike correlations.^{6,7} Polyball systems are a convenient way to experimentally test these ideas and gain insight into the highly sheared liquid state.

In this Letter we report on experiments on the self-diffusion of polyballs in the liquid state driven far from equilibrium by a strong imposed oscillating shear flow. The shear flow destroys the symmetry of the diffusion equation so that the diffusion is anisotropic. We have measured the diffusion coefficient in two of the three relevant directions, both in the plane perpendicular to the shear gradient. In the direction parallel to the velocity field ($D_{s\parallel}$) there is a strong convective term which results from particles diffusing along the velocity gradient, and being carried down stream by the more rapid flow (Taylor dispersion⁸). Our experiments are in quantitative agreement with an exact solution of the convective diffusion equation for $D_{s\parallel}$ in the absence of interactions. For diffusion perpendicular to the velocity field ($D_{s\perp}$), we observe no effect of shear for noninteracting particles. However, we find that once the Taylor dispersion has

been accounted for, there is an additional isotropic enhancement of the diffusion with shear for particles which interact electrostatically. The enhancement is linear with the shear rate and increases with increasing interaction strength.

The technique we employ for these studies is forced Rayleigh scattering.⁹ Briefly, 0.073- μm -diam polyballs are impregnated with a photochromic dye, spiropirane, which changes its absorption in the visible when illuminated with uv light. The dyed samples are deionized and diluted to a volume fraction of 0.3% in aqueous suspension. Light from a uv laser is split and recombined on the sample producing an interference pattern with intense fringes periodically spaced by $7\mu\text{m}$. The uv is flashed on the sample for 1 msec, labeling the particles, and producing dark fringes in the regions where the uv was intense. The photoexcited dyed particles form a thick diffraction grating (the dyed spheres are in sheets with a depth much greater than their separation) which is probed by the scattering of light from a He-Ne laser and by detecting the light with a photomultiplier. Both writing and reading laser beams penetrate the thickness of the sample cell. The diffracted light intensity decays as the modulation of the absorption grating diminishes because of diffusion of the labeled particles from the dark region into the light regions. Thus, diffusion is measured in the direction perpendicular to the grating. The forced Rayleigh technique has previously been used for equilibrium self-diffusion measurements on polyballs and many other systems.⁹⁻¹¹

The sample cell consists of a rectangular quartz cuvette 4 cm \times 1 cm \times 0.5 mm fitted with inlet and outlet tubes at either end. The oscillating shear flow is induced by our connecting the inlet tube to a syringe which is driven periodically by a modified speaker. The outlet tube is connected to a chamber containing air and a pressure transducer for measurement of the instantaneous total liquid displacement through the sample cell. For a steady flow, we would have Poiseuille flow in this

geometry. For finite oscillation frequency, the velocity profile is readily calculated from the solution to the Navier-Stokes equation.¹² We have performed several experiments including flow visualization with a Kalliroscope to assure that the flow in the experimental region (~ 1 cm from the inlet and outlet tubes) is not turbulent, as expected from the moderate Reynolds number (~ 500) for the largest-amplitude drive.

At a particular time in the oscillation cycle, when the velocity is zero and the displacement is maximum, a shutter in front of the uv laser is momentarily opened and the particles are labeled with the usual periodic grating. We have used two orientations of this grating as illustrated in the inset of Fig. 1, with the fringes either parallel or perpendicular to the velocity field. The diffusion coefficients measured in these two configurations are $D_{s\perp}$ and $D_{s\parallel}$, respectively.

Consider the case of $D_{s\parallel}$: As the oscillation cycle progresses, the thick fringes are distorted by the shear flow and approximately follow the displacement of fluid elements [Fig. 1, inset (a)]. The dyed particles in the center of the cell are displaced by ~ 0.1 – 10 mm relative to the dyed particles near the surface, a distance much greater than the fringe spacing, $l=7\ \mu\text{m}$. When the relative displacement from cell center to cell surface becomes greater than the fringe spacing, the diffracted intensity falls nearly to zero. In the absence of diffusion, the particles should return to their original positions and reform the thick diffraction grating at each full cycle. Thus, the intensity of the diffracted spot should vary periodically. If the particles diffuse, then the amplitude of the oscillating intensity will also decay with an envelope given by $\exp(-2D_{s\parallel}q^2t)$, where q is $2\pi/l$. The

measured intensity as a function of time is shown in Fig. 1 for a rms shear rate of $100\ \text{sec}^{-1}$. We emphasize that for the data in this figure, particles in layers separated by an average interparticle spacing, $r_{12}\sim 0.45\ \mu\text{m}$, have been sheared over ~ 15 other particles and back in one cycle, yet they return essentially to perfect registry. This, of course, is the usual but nonintuitive result for reversible Poiseuille flow, which holds even at our highest Reynolds number of 500. The reestablishment of the original pattern after its dispersion by the inhomogeneous (flow) field is reminiscent of a spin-echo experiment in magnetic resonance.

In the case of the $D_{s\perp}$ measurement, the velocity field carries the particles along the fringes, and we find no oscillation in the diffracted intensity for low shear rates. However, as the amplitude of the oscillation is increased, particles in the center of the cell are displaced outside the area of the probe beam spot (~ 0.5 mm diameter), and the diffraction intensity is lost [Fig. 1, inset (b)]. Thus for large shear rates oscillations are also seen for this geometry. The envelope of the diffracted intensity decays by diffusion as $\exp(-2D_{s\perp}q^2t)$.

The relevant dimensionless number which characterizes the importance of the convection and diffusion in our experiment is the Peclet number $Pe = r_{12}^2\dot{\gamma}/D_s \leq 35$, where $\dot{\gamma}$ is the shear rate. We are in the limit where the motion of the particles is governed to a much larger extent by convection rather than diffusion. In the time it takes a polyball to diffuse an interparticle spacing r_{12} , a particle a distance r_{12} above or below the constant velocity plane has been convected $\leq 35r_{12}$. Another important ratio is the shear rate relative to an oscillation period, $\dot{\gamma}/\omega \leq 10$. This implies that a near-neighbor particle traverses many times r_{12} in a cycle. Thus, we are measuring effects similar to what might be expected for steady shear.

For the case $D_{s\parallel}$ we expect a strong contribution to the measured diffusion constant from convection—Taylor dispersion. A dyed particle in a dark fringe can diffuse along the velocity gradient and be convectively displaced a large distance along the velocity direction. Referring to the coordinate system in the inset in Fig. 1, a particle diffusing Δz along the gradient gets swept downstream a distance $\Delta x = \Delta z\dot{\gamma}t$ in time t . The mean squared displacement along x is then

$$\langle(\Delta x)^2\rangle_{\text{eff}} = \langle(\Delta x)^2\rangle + \langle(\Delta z)^2\rangle(\dot{\gamma}t)^2.$$

If we average over an oscillation period, the effective diffusion along x becomes $D_{x\text{eff}} = D_x + D_z(\dot{\gamma}_{\text{av}}/\omega)^2/2$. Thus there is a contribution of diffusion along the gradient to the effective diffusion along the velocity. Analytically, this can be seen from the exact solution to the convective diffusion equation:

$$\partial\phi/\partial t + (\mathbf{v}\cdot\nabla)\phi = D\nabla^2\phi, \quad (1)$$

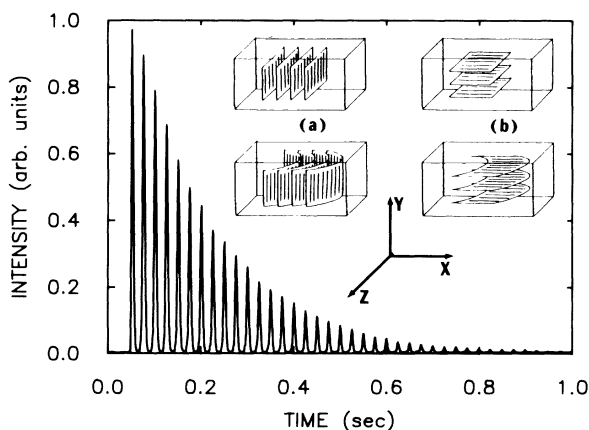


FIG. 1. Intensity of the light diffracted from particles initially labeled in a spatially modulated grating and undergoing oscillating shear. The decay of the envelope measures the self-diffusion. Insets: The labeled fringes and their distortion under flow for configurations used to measure (a) $D_{s\parallel}$ and (b) $D_{s\perp}$.

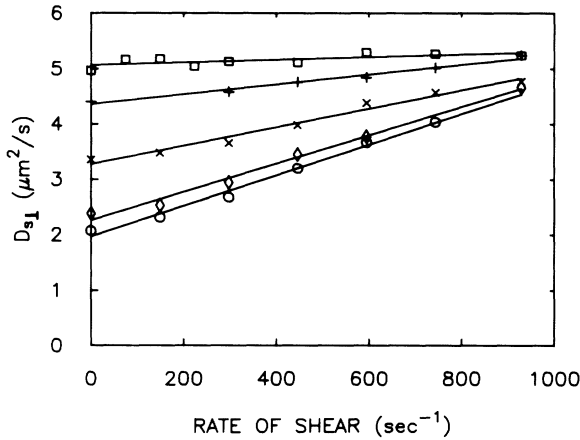


FIG. 2. Self-diffusion in the perpendicular direction with no convective component, $D_{s\perp}$, as a function of shear rate for samples with differing interparticle interactions. The more strongly interacting samples have lower values of $D_{s\perp}(\dot{\gamma}=0)$ and larger values of the slope, b^2 [Eq. (3)].

which, for an oscillating Couette flow, gives

$$D_{s\parallel} = D_s (1 + \dot{\gamma}_{av}^2 / 2\omega^2), \quad (2)$$

if we assume that the nonconvective diffusion coefficients under shear are isotropic and independent of $\dot{\gamma}$. For Poiseuille flow we take the additional spatial average $\langle \dot{\gamma}^2 \rangle$ for $\dot{\gamma}_{av}^2$, and the data for $\langle \dot{\gamma}^2 \rangle \leq (200 \text{ sec}^{-1})^2$ are well described ($\pm 5\%$) by Eq. (2) without any free parameters. Thus, in the absence of interactions, the convective diffusion equation accounts for the enhancement of diffusion due to shear.

Our most interesting result is from the study of $D_{s\perp}$ shown in Fig. 2. In this case we are measuring the effect of the shear flow on the diffusion coefficient in the direction where the velocity and the velocity gradient have no components and therefore there is no contribution from convection. We gauge the strength of the interactions by the value of the self-diffusion at zero shear rate. For weakly interacting particles ($D_s \approx D_0 = k_B T / 6\pi\eta R$), we see that there is very little dependence of $D_{s\perp}$ on the shear rate. This leads to two conclusions: Hydrodynamic effects have a negligible effect on the diffusion and we are nowhere in a regime where the flow involves turbulent mixing. For interacting samples, we find that $D_{s\perp}$ increases approximately linearly with the shear rate. That is

$$D_{s\perp}(\dot{\gamma}) = D_s(\dot{\gamma}=0) + b^2 \dot{\gamma}, \quad (3)$$

where b is a constant with dimensions of length that is a strong function of the interactions between the particles. The linear dependence implies that for Poiseuille flow we simply replace $\dot{\gamma}$ by $\langle \dot{\gamma} \rangle$. The dependence of b on the strength of the interaction is illustrated in Fig. 3 where b^2 is plotted as a function of $D_s(\dot{\gamma}=0)^{-1}$.

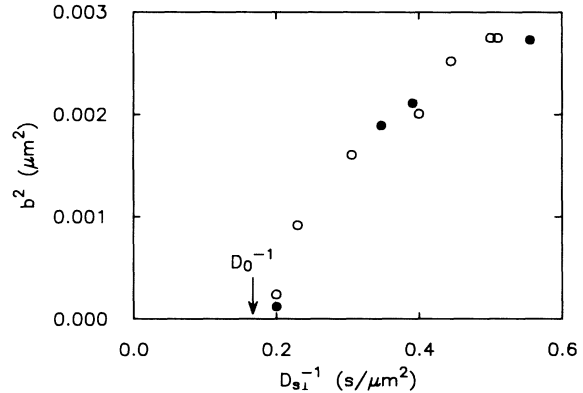


FIG. 3. The coefficient b^2 of the isotropic linear enhancement of the self-diffusion as a function of the unsheared diffusion coefficient $D_{s\perp}$ from the data of Fig. 2 and similar studies. Filled circles: frequency = 20 Hz; open circles: frequency = 40 Hz.

We have also measured $D_{s\parallel}(\dot{\gamma})$ for different interaction strengths, with the general result that $D_{s\parallel}(\dot{\gamma}) \approx D_{s\perp}(\dot{\gamma})(1 + \dot{\gamma}^2 / 2\omega^2)$. This is illustrated in Fig. 4, where $D_{s\perp}(\dot{\gamma})$ is given by Eq. (3) with $D_{s\perp}(\dot{\gamma}=0) = 2.3 \mu\text{m}^2/\text{sec}$ and $b^2 = 0.0021 \mu\text{m}^2$. This suggests that the effective diffusion changes isotropically under shear except for the convective diffusion term which is always present for $D_{s\parallel}$.

The form of Eq. (3) suggests a simple interpretation of our data. The rate at which particles in neighboring sheets encounter one another is $\dot{\gamma}$. If at each encounter there is a random displacement of rms magnitude b , then there is an additional isotropic diffusion contribution $b^2 \dot{\gamma}$. Intuitively, the random displacement should grow as the interparticle forces grow, which is qualitatively the dependence we find. It is interesting that the same

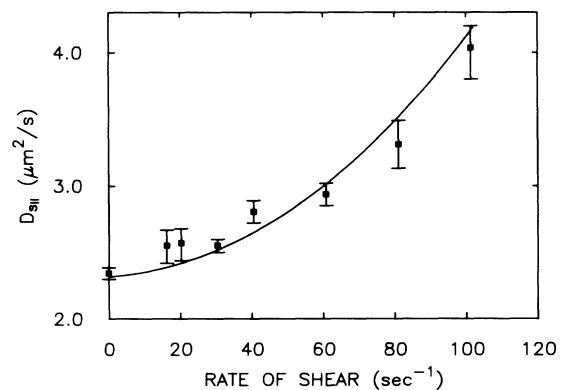


FIG. 4. Self-diffusion with convective contributions, $D_{s\parallel}$, vs shear rate for an interacting suspension. The largest dependence is the quadratic increase from Taylor dispersion, but there is also a linear term resulting from the isotropic increase resulting from the interactions.

forces which "cage" particles and slow down their equilibrium motion appear to increase the random motion as the particles are convected past one another. As a first guess one might expect b to be of the order of the Debye screening length, $\lambda = (4\pi n e^2 / \epsilon k T)^{-1/2}$. For our most interacting samples we estimate $\lambda \sim 1500 \text{ \AA}$ and $b \sim 550 \text{ \AA}$ from our measurements. On the other hand, for our least interacting samples $\lambda \sim 500 \text{ \AA}$ and $b < 50 \text{ \AA}$. Thus the dependence is in the correct direction but the values do not scale simply. We therefore lack at present a reliable way of ascertaining the interaction length b or effective cross section b^2 for the polyballs.

Although we know of no calculations or simulations of the diffusion coefficient of sheared fluids, it is interesting to compare our results with the simulations of the shear rate dependence of a related transport coefficient, the viscosity. For simple hard-sphere or Lennard-Jones fluids, the viscosity is found to decrease with $\dot{\gamma}$ but it is controversial whether the initial dependence is $\dot{\gamma}$ or $\dot{\gamma}^{1/2}$.^{6,7} The shear rate dependence is very large for volume fractions just below the liquid-solid transition and decreases rapidly as the system is diluted. If we make the natural assumption that an enhancement of the self-diffusion is associated with the reduction in viscosity, then our results are in qualitative agreement with the simulations. We find an initial linear dependence on $\dot{\gamma}$ with a coefficient which is largest as one approaches the solid phase. On the other hand, we see no evidence in our measurements of the shear-induced ordering that occurs in the simulations. The difference between our experiments and the computations lies in the soft-core nature of our interactions and the Brownian dynamics in our colloid.

In conclusion, we have measured the self-diffusion of polyballs as a function of shear rate. We find quantitative agreement with the solution to the convective diffusion equation in all regimes. The effect of hydrodynamic interactions is negligible in the region we have studied while there is a sizable isotropic linear shear rate

dependent contribution to the self-diffusion which increases with the strength of the electrostatic interparticle interactions. Further theoretical work is required to understand this unusual observation.

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³The polyballs interact through a screened Coulomb potential. The screening length can be conveniently varied by addition of small amounts of acid or salt to control the density of screening ions.

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