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Two spheres translating in tandem through a colloidal suspension

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Using laser tweezers, two colloidal particles are held parallel to a uniformly flowing suspension of similarly sized bath particles at an effective volume fraction $\phi_{\text{eff}} = 0.41$. The local deformation in the bath suspension is imaged by confocal microscopy, and concurrently, the drag forces exerted on both the leading and the trailing probe particle are measured as a function of probe separation and velocity. The bath structure changes in response to the velocity and separation of the probes. A depleted region between probes is observed at sufficiently high velocities. Both probes experience the same drag force and the drag force increases with probe separation. The results indicate that bath-probe and probe-probe hydrodynamic interactions contribute microstructure and drag force and that drag exerted by direct bath-probe collisions is reduced compared to an isolated probe.

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I. INTRODUCTION

The flow field and interparticle forces imparted on two spheres as they translate through a Newtonian fluid has been theoretically addressed for nearly a century [1, 2]. Recent interest in the microrheology of complex fluids has led to calculations and theory that model the forces acting on two spheres translate through a dense suspension. Theoretical work by Dzubiella studied the nonequilibrium structure surrounding two probe particles translating through a suspension of equally sized bath particles as a function of probe particle velocity and configuration [3]. They determined that the forces experienced by the probes would be unequal, and dependent upon their configuration. Further work by Khair and Brady used an analytical approach to examine the problem of two probes moving along their line of centers through a colloidal suspension [4]. They also found that the particles would experience unequal forces. Yet, there is a lack of complementary experimental work to verify these theoretical and computational results.

Previous experimental measurements using laser tweezers focused on the drag force and resulting micro structural deformation surrounding a single probe particle driven through a suspension of similarly-sized bath particles [5, 6]. These experiments identified several nonequilibrium structural features of the bath, including the buildup of a boundary layer of bath particles on the upstream face of the probe, and a bath particle depleted wake behind the probe. Both of these features had been predicted previously in calculations by Squires and Brady [7]. However, the experimental work showed differences from the theoretical predictions in a few key ways. Notably, a decrease in the drag force relative to the Stokes drag occurred over a higher range of velocities. Also, the angular distribution of bath particles at contacting the probe in the experimental studies was strongly influenced by the presence of hydrodynamic interactions, in better agreement with later analysis by Khair and Brady [8]. Additional experimental work focused on the out-ofequilibrium forces between two probe particles translating perpendicularly to their line of centers in a bath suspension, in the form of an attraction between the probe particles [9].

While drag forces in complex media are important for microrheological applications, the out-of-equilibrium interactions between particles are also of interest for their potential to produce self-assembly.[10] The equilibrium interactions between colloidal particles are well understood, particularly in dilute suspensions; these include effects such as the well characterized "depletion" interaction, and associated self-assembly phenomena [11, 12]. Equilibrium studies have also been extended to more concentrated suspensions, with sometimes surprising results. For example, Crocker and coworkers found that depletants could induce repulsive interactions between two spheres.[13] Similar repulsive interactions were reported for colloids near a planar surface in the presence of polyelectrolyte depletants [14]. Extending the understanding of colloidal interactions to non-equilibrium cases remains as a challenging but interesting problem.

In this work, we study two probe particles moving *parallel* to their line of centers through a colloidal suspension containing bath particles of similar size. We identify several previously unreported structural features that are distinct from the single probe case, including variations in the structure of both the probe particle wake and the boundary layer. We propose that these differences are primarily caused by hydrodynamic interactions between the bath particles. Furthermore, we determine that the probes experience equal forces, in contrast to recent theoretical predictions.

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II. EXPERIMENTAL

А. Sample preparation

The experiments employ two different types of colloidal particles. The probe particles are carboxylated melamine, with a diameter $2a_p = 3.0 \,\mu\text{m}$, which have been fluorescently labeled with fluorescein isoth-The bath particle suspension iocyanate (FITC) [9]. consists of polymethyl methacrylate (PMMA) particles $(2a_b = 1.53 \,\mu\mathrm{m})$, that are stabilized by a grafted layer of poly(hydroxystearic acid), and fluorescently labeled with Nile red. The sample preparation has been described in detail previously; we summarize it here briefly [9]. The bath particles are suspended in a mixture of 65.6% cyclohexyl bromide and 34.4% decalin, which ensures that they are both density matched and refractive index matched with the surrounding fluid; the solvent mixture has a viscosity of approximately 2 cP. We control the quality of the density matching by centrifuging suspension samples continuously for approximately five minutes at 6000 RPM, checking for sedimentation or creaming, and adjusting the suspending solution composition accordingly. In order to screen electrostatic interactions, we add a small amount of the organic salt tetrabutyl ammonium chloride, at a final concentration of 0.81 mM. The suspensions are injected into a custom built sample chamber, and sealed using a sugar based adhesive containing a mixture of glucose, dextrose and water. An additional layer of UV cured optical adhesive is deposited over the sugar (NOA 81, Norland Products, Cranbury NJ) [15].

We determine the effective bath particle diameter by obtaining confocal images of the quiescent suspension, and using them to generate a radial distribution function [6, 9]. We then fit these data to a repulsive Yukawa potential model; we obtain the model parameters using Monte Carlo simulations. For these experiments, we determined an effective bath particle radius, $a_{b,\text{eff}} = 0.97 \,\mu\text{m}$, resulting in an effective volume fraction of $\phi_{\text{eff}} = 0.41$. The ratio of the effective bath particle radius to the actual radius is $a_{b,\text{eff}}/a_b = 1.27$.

в. Optical trapping and force measurements

Our optical trapping apparatus has been described in detail previously; we briefly outline it here. The trapping laser is a 4W neodymium: yttrium-aluminum-garnet (ND:YAG) laser (vacuum wavelength $\lambda = 1064$ nm). The laser is aligned into an inverted microscope (Zeiss, Axiovert 200), and the beam is sent through a high numerical aperture immersion objective (NA=1.3 Zeiss Approchromat 63x oil). A set of guide optics precedes the microscope, and these are used to steer and collimate the beam, and ensure that it overfills the back aperture of the objective. A computer controlled Acousto-Optic Deflector (AOD, AA.DTS.XY-400, AA Optoelectronics)

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FIG. 1: Schematic of the experimental configuration. Both probes are held using a time shared optical trap. U indicates the velocity of the flow, and a_p and a_b correspond to the radii of the probe and the bath particle, respectively. The centerto-center distance between the probes is r.

is used to generate multiple optical traps by time sharing.

Two time shared optical traps capture individual melamine probe particles. A motorized microscope stage translates the probe particles parallel to their line of centers through the quiescent suspension at velocities ranging from U = 7- 280 μ m per second. Local heating of the sample is minimized due to rapid conduction within the sample, and the low absorption of the sample at the optical trapping wavelength.

Probe particles are held at separations ranging from 5.2 - 41 μ m. The configuration of the particles is shown in Figure 1. All probe particle separations refer to the center-to-center distance, unless otherwise specified. To determine the force experienced by the probe particles, we find the displacement of each probe particle from its equilibrium position in the optical trap. The drag force is $F_z = k_{ot} \Delta z$, where Δz is the displacement of the probes from their equilibrium position, and k_{ot} is the optical trap constant, with values ranging from $1.41 \cdot 10^{-6} - 2.27 \cdot$ $10^{-5} N/m$. The drag force on both the trailing and the leading particle is calculated as a function of interparticle separation and speed.

C. Confocal microscopy

To image the suspension microstructure, we use con-The confocal system is a Nipkow focal microscopy. scanning disk confocal head (QLC-100, Yokogawa Electric). Images are recorded with a 10-bit digital intensified charge coupled device (ccd) camera (XR/Mega 10, Stanford Photonics). Images are recorded at 30 frames per second in bursts of 1000-3000 images.

The location of the bath particles in each image is found using well established tracking methods [16]. We are able to track particles up to a speed of approximately 50 μ m/s. At higher speeds, the particles appear as streaks due to limitations induced by the frame rate of the imaging camera. As described previously, the particle locations are used to calculate two dimensional plots of the time averaged bath particle density distribution [9]. The x and y coordinates for each individual bath particle in each frame are combined into a two dimensional histogram with one pixel binning. The histograms are normalized by the total number of frames that are obtained for each individual experimental condition.

III. RESULTS AND DISCUSSION

A. Bath suspension structure

Confocal microscopy images of the bath microstructure are organized into two dimensional histograms of the bath particle density. These data are shown in Figure 2. Two values of Peclet number ($Pe_D = 116$ and $Pe_D = 460$), and six probe particle configurations are plotted, for a total of twelve experimental conditions. Since the probe and bath particle diameters are similar,

the "direct" Peclet number is used to non-dimensionalize the velocity [6, 9, 17],

$$Pe_D = \frac{U(a_b + a_p)}{D_b},\tag{1}$$

where $D_b = \frac{kT}{6\pi a_b \eta_s}$ is the diffusivity of a single bath particle. Eqn 1 characterizes two competing time scales: the time scale for probe particles to advect a bath diameter $(a_p + a_b)/U$ and the timescale to diffuse the length scale of the probe particle, $(a_p + a_b)^2/D_b$. Asymmetric structure of the bath suspension around the probe particles is expected to occur when $\text{Pe}_D \gg 1$. The key characteristics of this non-equilibrium structure for a single probe particle are the development of a boundary layer of bath particles on the upstream face of the probe and a trailing wake depleted of bath particles [6, 7, 18].

In the two-probe case of $Pe_D = 116$, structural features similar to those previously found in the single probe case are observed [5, 6]. A concentrated layer of bath particles forms a boundary region on the upstream face of the leading probe, while a bath particle depleted wake is visible behind the probes. At small probe separations, a void space is present between the probes, indicating that bath particles are excluded from entering the interstitial space. However, at large separations, a compressed layer of bath particles enters the space in between the probe particles, as seen at the interprobe separation distance of $r = 9.5a_b$. At relatively large separations, bath particles freely flow into the space between the probes, suggesting that we have reentered the single probe regime, as the microstructure behind both probes appears to heal completely.

At $Pe_D = 460$, further changes in the structure occur. Both the wake structure and the boundary layer around the probes are preserved. However, bath particles are unable to diffuse within the interparticle space at this large Peclet number value, suggesting that microstructural deformations cannot be healed as readily by bath particle diffusion. This agrees with the predictions of Khair and Brady; they, too, found that the bath particle density between the probe particles decreases as the value of Pe_D increases.

One particularly intriguing feature is the anomalous structure of the wake region at the higher Peclet number value. In both the single probe and perpendicular case, the wake region behind the probe particles was entirely devoid of bath particles. Yet, in the present case, the center of the wake structure contains a detectable density of bath particles. Based upon our previous experimental observations, and theory, this behavior is unexpected. It is possible that in this configuration, the flow surrounding the leading probe particle causes bath particles to be injected into streamlines that would then move more closely to the trailing probe particle, and then detach closer to a value of 0° . The affinity of the bath particles for the probe may also be further enhanced due to lubrication forces.

At Peclet values of $Pe_D > 790$, bath particles can no longer be individually tracked to generate the probability distributions. Instead, averaged confocal images provide an average of the bath structure as seen in Figure 3. At this higher Peclet value, the bath structure is unable to heal until the largest probe separation of 54 a_b , at which point both probes display behavior that is similar to what is typically seen in the single probe case. Furthermore, there is no indication of healing from the center of the wake structure, as there is at the lower Peclet values.

To quantify the microstructure surrounding the probes further, the angular density of the bath particles around the probe particles is calculated. The angular distribution $g(r, \theta)$ is

$$g(r,\theta) = \frac{N(r+dr,\theta+d\theta)}{C},$$
(2)

where N is the number of particles that are found within a thickness of r + dr, over an angle of $\theta + d\theta$, and C is the far field value of the particle density. We note that $\theta = 0$ corresponds to the tail region, while $\theta = \pi$ corresponds to the center of the upstream region, as shown in Figure 1.

The angular distribution data are summarized in Figure 4, for the same Peclet number and distance values shown in Figure 2. The top and bottom curves in each graph correspond to the leading and trailing probe, respectively. The contact distribution curve for the trailing probe has been shifted up for clarity. The angle $\theta = \pi$ is the upstream face of both probes. Likewise, $\theta = 0$ and 2π are the downstream faces. Both probes exhibit a wake structure, with $g(2; \theta)$ exhibiting a minimum, in most cases going to zero, at $\theta = 0$ and 2π . The leading probe has a high density of bath particles on its upstream face, $\theta = \pi$. The structure of the suspension for the trailing probe depends more strongly on the probe separation and Peclet number.



FIG. 2: (Color online) Two dimensional histograms of the bath particle suspension density. Columns indicate the probe separations in terms of the bath particle hydrodynamic radius and the rows represent the Peclet number, as defined in equation 1. Dark colors are indicative of regions depleted of bath particles; conversely, bright regions have a greater than average bath particle density. The bright circle at the center of each depleted region indicates the position of the probe particle.



FIG. 3: (Color online) Averaged confocal images of structure taken at $Pe_D = 2255$. Probe separations of (a) 6.8 a_b , (b) 7.5 a_b , (c) 9.0 a_b , (d) 9.5 a_b , (e) 28 a_b , and (f) 54 a_b are shown.

Consider in more detail the contact distribution for $Pe_D = 116$. At small probe separations $(r = 6.8a_b)$, the trailing probe exhibits a boundary layer structure of

its downstream face that is similar to the single probe case. The boundary layer detaches from the probe at a value of $\theta = \pi/4$, consistent with the value found in prior experimental and theoretical work when hydrodynamic interactions are significant in the probe-bath interaction [6, 8]. At the intermediate probe particle separation of 9.5 a_b , the boundary layer for the trailing probe appears to detach from this probe at a lower angle, $\theta = \pi/8$, and a small buildup of bath particles occurs at $\theta = 0$ and 2π . There is a small layer of bath particles in the interstitial region behind the probes. Finally, at the large probe particle separation of 54 a_b , both the leading and the trailing probes exhibit the same angular density structure similar to the single-probe case. These observations hold at the larger Pe_D value, although the angular distribution at the intermediate probe separation $r = 9.5a_b$ indicates that bath particles are absent from the inter-probe region. This observation is underscored by the correlating structure in the two-dimensional histogram plots shown in Figure 2.

B. Force measurements

The forces experienced by both the leading and the trailing probes are shown in Figure 5. The drag force increases with increasing velocity. The force on each probe also increases as the their separation grows larger, and across all separations both the leading and the trailing probes experience the same drag. The identical forces

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FIG. 4: The bath particle density at contact, $g(r, \theta)$, surrounding the probe particles, at probe particle separations of 6.8 a_b , 9.5 a_b , and 54 a_b . The upper and lower curves correspond to the trailing probe and the leading probe, respectively.

on leading and trailing particles and their dependence on separation are consistent with the reversibility of a creeping flow and the calculations of Stimson and Jeffery [1], who considered the Stokes drag on two identical particles translating along their line of centers in a quiescent Newtonian fluid. They show that the drag force on each particle may be written as

$$F_d = 6\pi \eta_s a_p \lambda U \tag{3}$$

where λ is a correction factor that varies depending on the separation distance between the two probes,

$$\lambda = \frac{4}{3}\sinh\alpha\sum_{n=1}^{\infty}\frac{n(n+1)}{(2n-1)(2n+3)}\left\{1 - \frac{4\sinh^2[(n+1)\alpha] - (2n+1)^2\sinh^2\alpha}{2\sinh[(2n+1)\alpha] + (2n+1)\sinh2\alpha}\right\}$$
(4)

with $\alpha = \cosh^{-1}(r/2a_p)$.

The drag forces shown in Fig 5 are replotted in Fig 6 as the measured force scaled by Stimson and Jeffery's result, $F/6\pi\eta_s a_p\lambda U$. The scaled force can also be interpreted as a measure of the suspension microviscosity $\eta_{\mu} = F/6\pi a_p$ scaled by the solvent viscosity, η_{μ}/η_s . All of the scaled drag forces are slightly above 1, reflecting the higher viscosity of the suspension, and are independent of probe separation. The drag force is also constant over the range of Peclet numbers measured.

There are two unusual features of the two-probe tandem drag force. The normalized drag (or microviscosity) in Figure 6 does not exhibit velocity thinning, which was previously observed for single probe particles translating through the suspension, also shown the figure for comparison. The normalized force curve for the single probe steadily decreases as a function of Pe_D and approaches the value measured for two probes as the Peclet number exceeds $Pe_D > 10^3$. Second, the observation that both probe particles experience a similar drag force is also unexpected based on the theoretical work by Khair and Brady, who predicted that a trailing probe would experience a lower drag force [4]. The leading probe should screen the trailing probe from collisions with the bath particles, resulting in a lower drag. The experimental results suggest that direct collisions between the probes and bath particles have a smaller influence on the total drag force, which we attribute to the hydrodynamic interactions between the probe particles. As previously noted, hydrodynamic interactions between the probes and bath



FIG. 5: (Color online) Drag forces on probes in the z direction. Closed and open symbols correspond to the leading and trailing particle, respectively. As indicated in the legend, circles, squares, triangles, diamonds, inverted triangles, and flattened diamonds correspond to center-to-center distances of 6.8 a_b , 7.4 a_b , 9.1 a_b , 9.5 a_b , 28 a_b , and 54 a_b , respectively. The open black triangles without error bars correspond to the drag force for a single probe in a suspension of volume fraction $\phi_{\text{eff}} = 0.37$

particles also affect the structure of the wake that follows the probes as they translate through suspensions. In the presence of hydrodynamic interactions, the wake structure behind both probes is smaller, which would lead to a larger degree of collisions, even for the "trailing" probe.

The discrepancy between the experimental results and the predictions of Khair and Brady can also be attributed to the fact their force predictions were calculated using the "entropic" collision forces that the probes experience with bath particles, which scale as $\phi kT/a$ [4]. However, scaling the hydrodynamic drag as $6\pi\eta_s a_p\lambda U$, the ratio of hydrodynamic to entropic forces is then $\lambda \text{Pe}/\phi \sim \text{Pe} \gg$ 1. Therefore, it is unsurprising that the hydrodynamic contribution dominates at high values of Peclet number.

Overall, two probes translating through a bath suspension in tandem exhibit drag forces that are consistent with Stokes drag in a viscous fluid. The effect of direct collisions by the bath particles appears to be lower compared to a single probe. Although one might expect the suspension to exhibit a shear thinning behavior due to the perturbed microstructure, the limited contact bath particles have with the probes reduces the amount of strain built up in the suspension [19]. This suggests that the two-point experiment recovers the steady shear viscosity of the bath suspension while eliminating the contribution of direct bath-probe collisions.



FIG. 6: (Color online) Normalized drag forces for the leading probe. As indicated in the legend, circles, squares, triangles, diamonds, inverted triangles, and flattened diamonds correspond to center-to-center distances of 6.8 a_b , 7.4 a_b , 9.1 a_b , 9.5 a_b , 28 a_b , and 54 a_b , respectively.

IV. CONCLUSIONS

We studied two equally sized probe particles at identical velocities as they translate through a suspension containing similarly sized bath particles. The line joining the centers between the probe particles was parallel to the flow direction. We performed measurements as a function of both probe particle separation and Peclet number. Histograms of the bath suspension density show the microstructural deformation surrounding the probes, which exhibit several interesting features. At low values of Pe_D , bath particles enter the interstitial space between the probe particles. This behavior is purely hydrodynamic; if hydrodynamic interactions were not present, the bath particles would flow over and behind the probes. Furthermore, we find that the wake behind the probes is not completely devoid of bath particles. Despite these structural differences, the leading and the trailing probe particles experience the same drag force. Both the microstructure and drag force obtained in the experiments differ from those expected from recent calculations and theory and highlight the need for to consider bath-probe and probe-probe hydrodynamic interactions in future work.

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