

Pair diffusion in quasi-one- and quasi-two-dimensional binary colloid suspensions

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The authors report the results of measurements of the center of mass and relative pair diffusion coefficients in quasi-one-dimensional (q1D) and quasi-two-dimensional (q2D) binary colloid suspensions. The new results extend the findings of similar studies of one-component quasi-one-dimensional and quasi-two-dimensional colloid suspensions. Our principal new finding is that the presence of the smaller diameter component can destroy the oscillatory structure of the separation dependence of the q2D relative pair diffusion coefficient of the large particles even though the oscillatory character of the large particle equilibrium pair correlation function remains prominent, and that no such effect occurs with the q1D suspension. An interpretation of these results is proposed. © 2007 American Institute of Physics. [DOI: 10.1063/1.2719191]

I. INTRODUCTION

Consider a one-component colloid suspension. Except when the colloid particle density is very small, the Brownian motions of the particles are correlated via flows that those motions induce in the host liquid, i.e., by hydrodynamic interaction. Calculation of that hydrodynamic interaction requires solution of the Navier-Stokes equation with appropriate boundary conditions at the surfaces of the colloid particles and at the boundaries of the volume containing the suspension. In the quasi-one-dimensional (q1D) and quasi-two-dimensional (q2D) colloid systems of interest to us, as well as in typical three-dimensional (3D) systems, the fluid velocity and pressure are sufficiently small that the Reynolds number is very small and the Navier-Stokes equation can be simplified by linearization to the Stokes equation. When the Stokes equation is solved with the point force approximation, i.e., treating the colloid particles as point sources of force, one finds that in an unconfined 3D suspension the hydrodynamic interaction between particles decays with particle separation as $1/r$ and that the particles drag one another in the same direction.¹ The long range of the hydrodynamic interaction leads to very strong many body effects and a pronounced dependence of the transport coefficients of the suspension on the colloid particle density.

The long-range character of hydrodynamic interactions in an unconfined liquid is considerably modified when the extension of the containing volume is greatly constrained in

one or more dimensions. When the point force Stokeslet approximation is used it is found that in both q1D and q2D suspensions the decay of the hydrodynamic interactions with particle separation has very different functional forms than that in 3D. Specifically, in q2D (Refs. 2–5) the interaction falls off as $1/r^2$ and in q1D (Ref. 6) it is screened on the length scale of the channel width. In both q2D and q1D the many body effects on the transport coefficients are thereby considerably changed from that in 3D. When the nonzero size of the colloid particle must be accounted for, solutions to the Stokes equation in q1D and q2D systems can be developed by the method of reflections.¹ Although the inclusion of effects associated with the nonzero size of the colloid particle can be very important, many of the qualitative features of the influence of hydrodynamic interaction between particles on, say, the relative and center of mass pair diffusion coefficients, are unaltered, so the point force approximation results remain useful for organizing interpretations of experimental data.⁷

The properties of a colloid suspension in q1D, q2D, and 3D are modified in several ways by the addition of a second colloid component with smaller diameter. For example, when a binary mixture of large and small colloid particles is viewed as a pseudo-one-component system of the large particles by averaging over the configuration space of the small particles, it is found that the smaller colloid component generates an effective interaction (the depletion interaction) between the large particles.^{8–11} More important for the purposes of this paper, the structural and dynamical heterogeneity at high particle density that is exhibited by a q2D one-component colloid suspension is modified by the

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addition of a second, smaller, colloid component.^{12,13} Indeed, the addition of only a very small amount of a smaller colloid to a large colloid suspension has a dramatic effect on the sizes of the locally ordered domains in the liquid, greatly reduces the extent of three-particle correlations, and alters the particle displacement dynamics.¹⁴

An analysis of the colloid-colloid hydrodynamic interactions in a binary mixture of particles with different diameters is much more complex than is the analysis of hydrodynamic interactions in a one-component colloid suspension. Although the pseudo-one-component system with depletion interaction representation provides a convenient language with which to accurately describe the equilibrium properties of a binary colloid suspension it is not at all clear that this mean field representation accurately describes the effects of hydrodynamic coupling on diffusion in a binary suspension. If the colloid diameter ratio is small enough it is reasonable to expect the smaller particles to rapidly adjust to the motions of the larger particles, thereby generating a direct (i.e., a nonhydrodynamic) effective interaction, namely, the depletion interaction. And, at equilibrium, an attractive depletion interaction generally causes some small shifts in the positions and the amplitudes of the peaks in the large particle pair correlation function that can be expected to generate a corresponding signature in the small separation dependence of the relative pair diffusion coefficient. But the hydrodynamic interaction between colloid particles is sensitive to the flow boundary conditions at the surfaces of the colloid particles, hence also to the difference in particle size in a binary suspension. Indeed, it is not obvious that the Stokeslet point force approximation applied to all particles in a binary suspension can be the basis for a qualitatively valid description of particle-particle hydrodynamic interaction, nor how that interaction, via the combination of boundary condition effects associated with the nonzero particle size and the proximate walls, depends on the system dimensionality.

A useful tool for examining the influence of suspension composition on particle dynamics is measurement of the mean square displacements of the colloid particles, and thereby the self-diffusion coefficient and the center of mass and relative pair diffusion coefficients; the latter provide more information than the former concerning the influence of hydrodynamic interaction on the properties of the suspension. Recent studies of the pair separation dependence of the center-of-mass and relative pair diffusion coefficients in q2D and q1D one-component colloid suspensions have revealed interesting features associated with hydrodynamic interaction and the excluded volume interaction between particles.²⁻⁷ This paper reports an extension of those studies. We describe the results of measurements of the center-of-mass and relative pair diffusion coefficients in q2D and q1D binary colloid suspensions. Our goal is elucidation of how the hydrodynamic interaction between the larger colloid particles in a binary suspension is affected by the addition of a second colloid component with smaller diameter. Our principal new finding is that the presence of the smaller diameter component can destroy the oscillatory structure of the separation dependence of the q2D relative pair diffusion coefficient of the large particles even though the oscillatory character of

the large particle equilibrium pair correlation function remains prominent, and that no such effect occurs with the q1D suspension. An interpretation of these results is proposed.

II. EXPERIMENTAL DETAILS

We consider, first, studies of q2D colloid suspensions. The experimental procedure we have used is described in detail in previous publications from this laboratory.^{6,12} The binary colloid systems we have studied consist of uncharged spheres of two different diameters (σ_L and σ_S), suspended in water, confined between two glass plates separated by a small distance, $w=1.1\sigma_L$. The large colloid particles are silica spheres with diameter $\sigma_L=1.58\pm 0.04\ \mu\text{m}$. The small colloid particles are polystyrene spheres with hydroxyl end groups (PS/R-OH, Bangs Laboratory), with diameter $\sigma_S=0.34\pm 0.01\ \mu\text{m}$.

A schematic diagram of the q2D cell used is shown in Fig. 1. The small spacing between the parallel plates constrains the motions of the centers of the larger colloid particles to be q2D, but the motions of the small particles are fully 3D. The experiments reported in this paper cover a range of large sphere in-plane densities ($\eta_L=N_L\pi\sigma_L^2/4A$ for N_L particles in area A) from about 0.25 to 0.75, each with four small sphere volume fractions $\phi_S=0.0, 0.005, 0.05,$ and 0.10 .

Digital video microscope measurements were made using an Olympus BH2 microscope with a $2.5\times$ video eyepiece and a $100\times$, numerical aperture 1.25, oil immersion objective. The small colloid particles are not resolved in the images; they contribute to the background. The images were recorded by a Hitachi charge-coupled device video camera at 30 frames per second and transferred to an S-VHS tape in a Sanyo GVR-S955 VCR. The analog data were converted to digital data by feeding the former through a CG-7 frame grabber using Scion IMAGE 1.62C software.

The first step in analysis is locating the sphere centers using the procedure described by Crocker and Grier;¹⁵ this procedure can locate the center of a particle with precision of ± 0.1 pixel (1 pixel= $0.16\ \mu\text{m}$). The concentration of large spheres was measured by calculating the real area density, dividing the area occupied by spheres in the plane of view by the total plane of view area. The small sphere density was determined by the initial preparation of the mixture.

The q1D studies used particles of two sizes restricted to a $3\ \mu\text{m}$ wide, $3\ \mu\text{m}$ deep polydimethylsiloxane channel. A schematic diagram of the q1D cell used is shown in Fig. 1. The large sphere line densities ($N_L\sigma_L/L$) of our systems ranged from 0.08 to 0.69. The q1D experiments were restricted to a much smaller range of small particle densities than were the q2D experiments, specifically only $\phi_S=0.0, 0.001, 0.005,$ and 0.01 . At densities higher than 0.01 the small particles begin to cloud the image and resolving the large spheres becomes difficult. Because the number of colloid particles in the channel in each image is much smaller than in an image of the q2D system, each density measure-

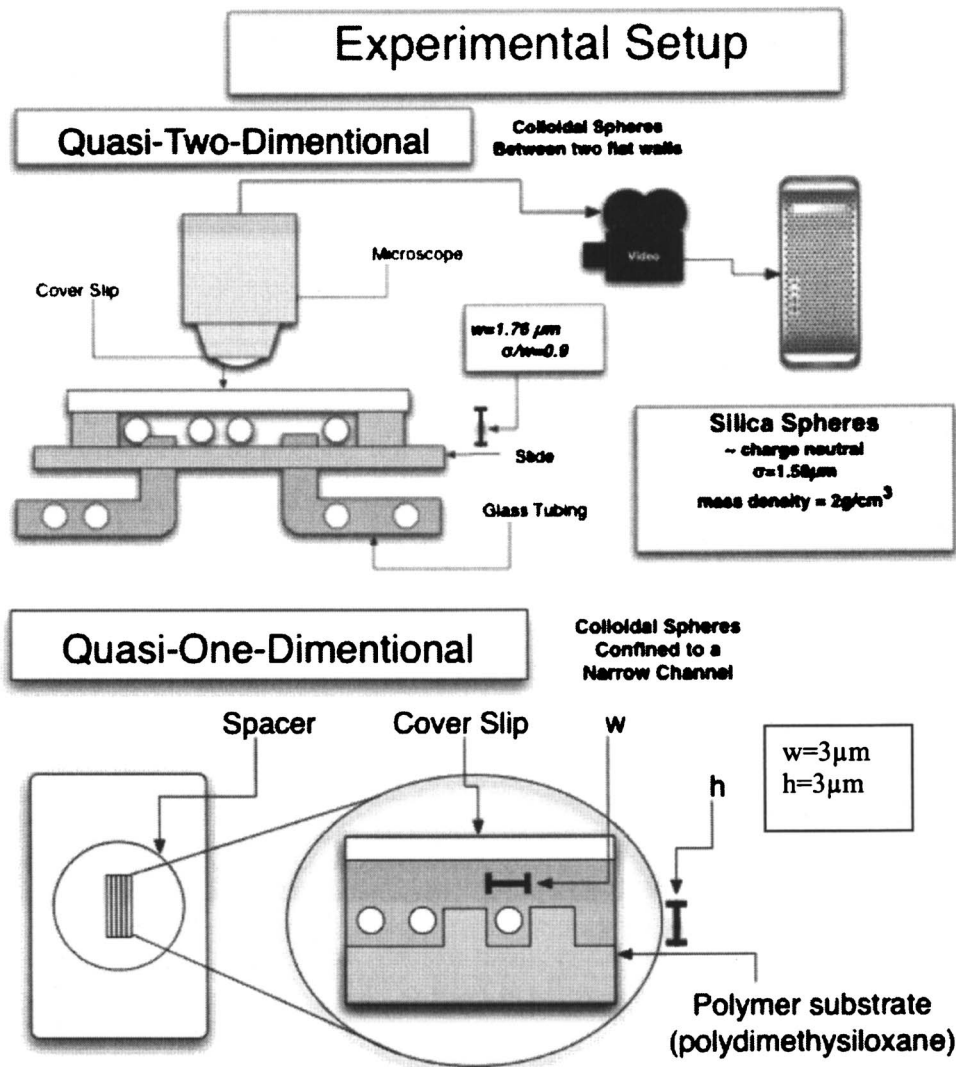


FIG. 1. Schematics of the q2D and q1D experimental setups.

ment reported represents a summation of the data from between 5 and 50 movies. The typical movie consists of a sequence 5000 frames long.

It is convenient to characterize the motion of pairs of colloid particles with four diffusion coefficients, describing center of mass and relative motion along the line of centers of the two particles (longitudinal, L) and perpendicular (transverse, T) to that line. These diffusion coefficients are obtained from the observed displacements of the particles in the x and y directions using the conventional relations,

$$D_L^\pm = \frac{\langle [x_1(t) \pm x_2(t)]^2 \rangle}{4t} = D_S \pm D_L^{12},$$

$$D_T^\pm = \frac{\langle [y_1(t) \pm y_2(t)]^2 \rangle}{4t} = D_S \pm D_T^{12}. \quad (1)$$

In Eq. (1), the plus and minus signs refer to the collective and relative motions of the particles, respectively, D_S is the self-diffusion coefficient, and D_L^{12} and D_T^{12} are the contributions to D_L^\pm and D_T^\pm attributable to the hydrodynamic interaction between particles. Note that D_L^{12} and D_T^{12} approach zero and D_L^\pm and D_T^\pm approach D_S as the particle separation becomes large, and that D_S differs from D_0 , the self-diffusion

coefficient at infinite dilution in a 3D system, by virtue of boundary conditions at the cell walls and the nonzero concentration of colloid particles. All of the diffusion coefficients reported in this paper are characteristic of the initial evolution of the particle trajectory, the regime in which $\langle x(t)^2 \rangle \propto t$. The time intervals used for the analysis were short compared to the time required for either a large or a small colloid to diffuse a distance equal to its diameter.

The raw data obtained from the video images consist of the x and y coordinates of the centers of the colloid particles relative to the experimental cell, the time, and the particle identity. The longitudinal and transverse pair diffusion coefficients were calculated from the simple relations

$$x_2^\pm = (x_2(t_2) \pm x_1(t_2)),$$

$$D_L^\pm = \left\langle \frac{((x_2^\pm - x_1^\pm)x_1^- + (y_2^\pm - y_1^\pm)y_1^-)^2}{4((x_1^-)^2 + (y_1^-)^2)} \right\rangle,$$

$$D_T^\pm = \left\langle \frac{((x_2^\pm - x_1^\pm)y_1^- + (y_2^\pm - y_1^\pm)x_1^-)^2}{4((x_1^-)^2 + (y_1^-)^2)} \right\rangle. \quad (2)$$

The average indicated in Eq. (2) is taken over all particles in the field of view. Of course, for particles in the q1D systems

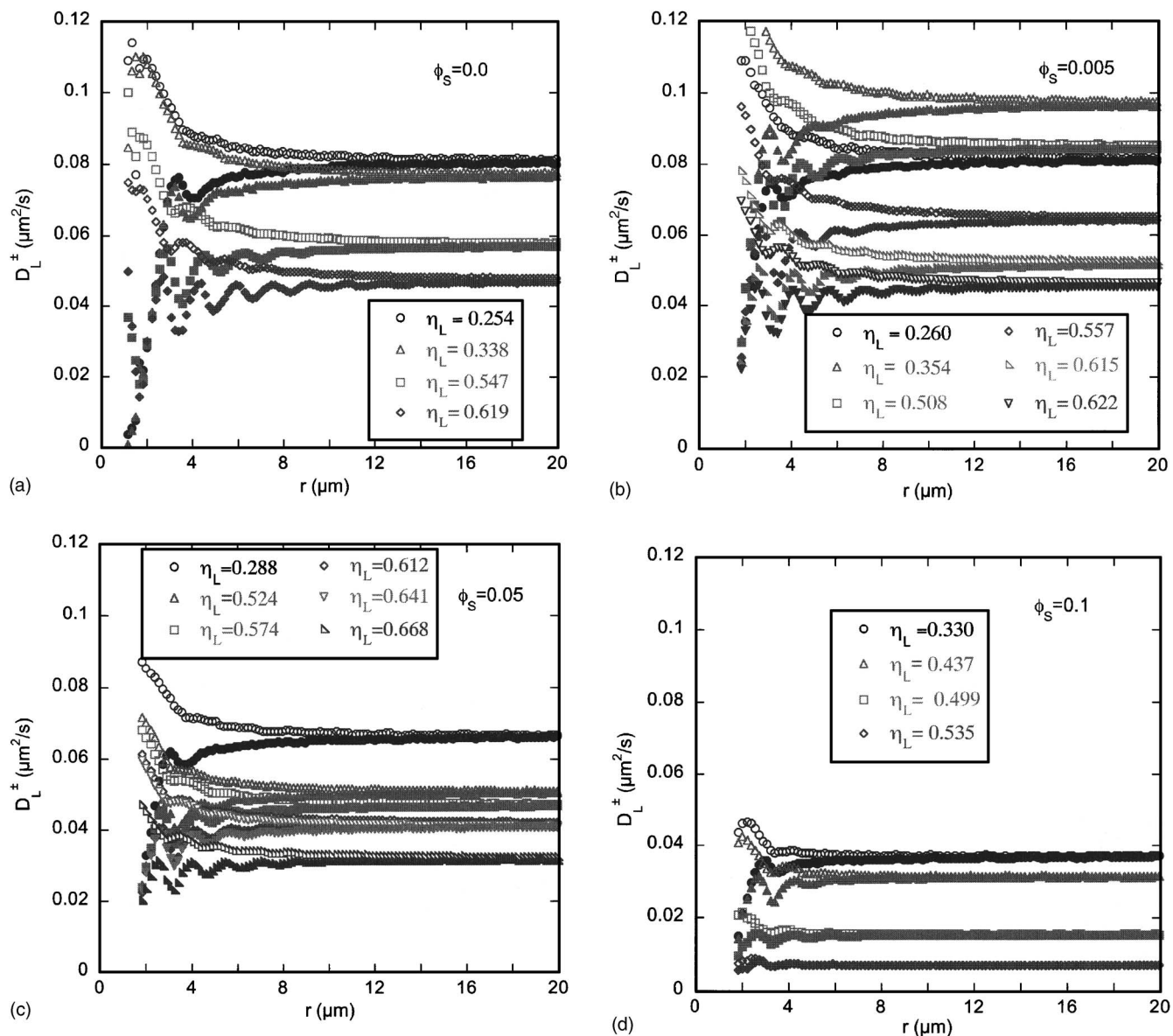


FIG. 2. Longitudinal collective and relative pair diffusion coefficients for the q2D liquid at various area fraction η_L with four different ϕ_s : (a) $\phi_s=0.0$, (b) $\phi_s=0.005$, (c) $\phi_s=0.05$, and (d) $\phi_s=0.10$. Open and filled symbols correspond, respectively, to collective and relative coefficients.

it is clear that the transverse pair diffusion coefficient should be zero. For some of the discussion of our results it is convenient to use

$$\Delta_{12} \equiv \frac{D^+ - D^-}{D_0} \frac{w}{\sigma_L}, \quad (3)$$

which is the difference between D^+ and D^- normalized by the self-diffusion coefficient at infinite dilution in a 3D system and the ratio of the q2D cell thickness or q1D channel width w to the large particle diameter.

III. EXPERIMENTAL RESULTS

We begin with the results of the q2D experiments. At $\phi_s=0$, an analysis of the hydrodynamic interaction between particles that are confined between two flat walls has shown that, at large particle separation r , $D_L^\pm = \pm \lambda/r^2$ and $D_T^\pm = \mp \lambda/r^2$, with $\lambda=0.36$, for all concentrations, whereas at small r the concentration effect is present and directly asso-

ciated with the equilibrium pair correlation function of the q2D liquid.²⁻⁴ The value of the pair diffusion coefficient at any specified pair separation is for all pairs of particles with that separation regardless of whether or not there are other particles between them. We display in Figs. 2(a)–2(d) and 3(a)–3(d) the pair separation dependences of D_L^\pm and D_T^\pm for several large colloid packing densities, organized with respect to the small particle volume fractions. As expected when the longitudinal hydrodynamic coupling is positive and the transverse hydrodynamic coupling is negative, $D_L^+ > D_L^-$ but $D_T^- > D_T^+$ in all the systems examined. We show in Figs. 4(a)–4(c) Δ_{L12} and Δ_{T12} as a function of pair separation for the q2D systems. It is interesting that addition of a very small amount of small colloid, $\phi_s=0.005$, somewhat enhances the structure in both Δ_{L12} and Δ_{T12} , whereas larger concentrations of the small colloid diminish that structure. Indeed, when $\phi_s=0.10$ the structure in Δ_{L12} and Δ_{T12} is sensibly destroyed.

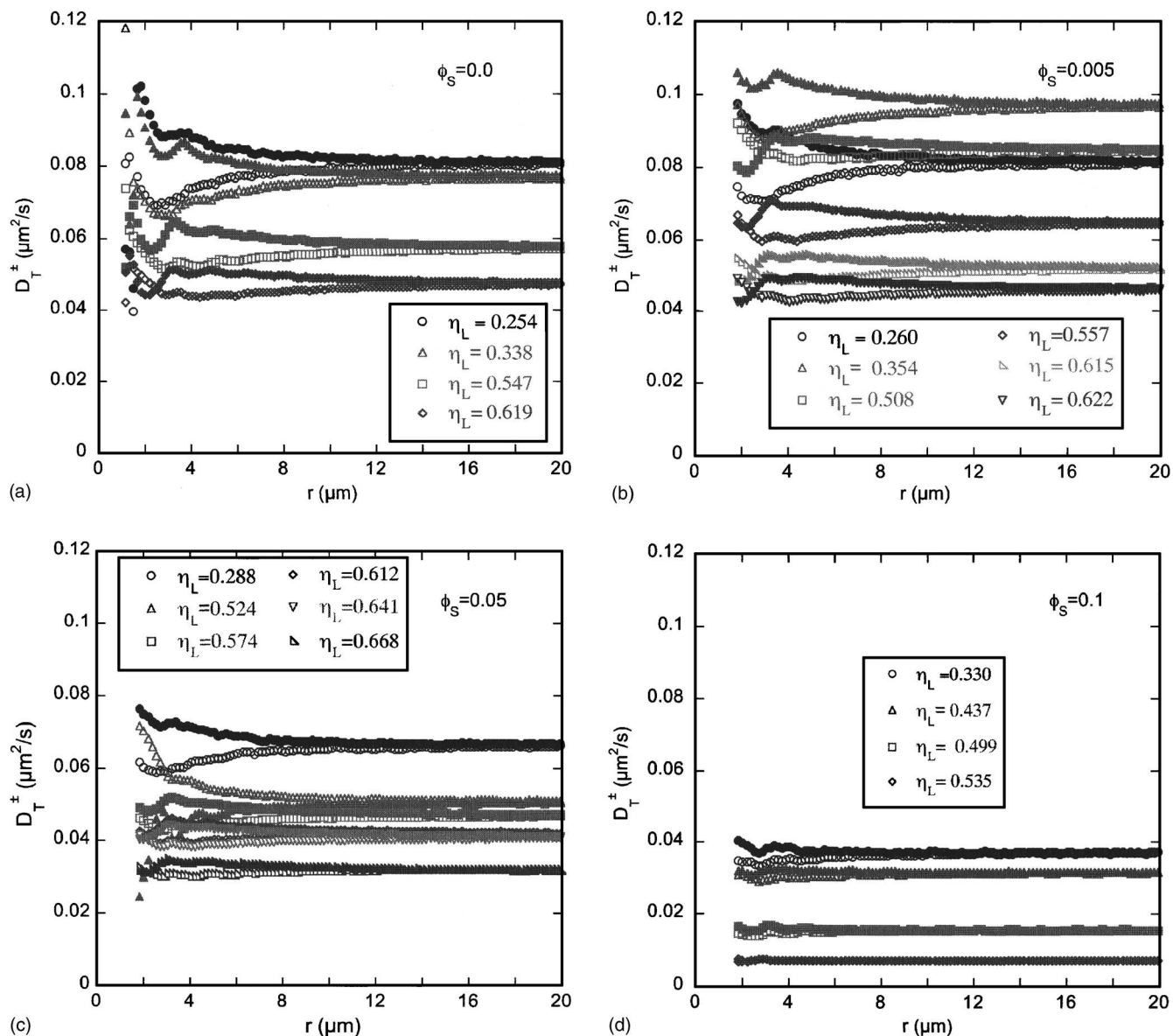


FIG. 3. Transverse collective and relative pair diffusion coefficients for the q2D liquid at various η_L with four different ϕ_s : (a) $\phi_s=0.00$, (b) $\phi_s=0.005$, (c) $\phi_s=0.05$, and (d) $\phi_s=0.10$. Open and filled symbols correspond, respectively, to collective and relative coefficients. Note the sign reversal of the transverse coupling.

We show in Fig. 5 the density dependence of the self-diffusion coefficient of the large colloid particles in the q2D systems. For the case of very small but nonzero ϕ_s , specifically $\phi_s=0.005$, the increase of D_S with increase of η_L at small η_L was noted in our earlier report.¹³ Otherwise, the general trend of the data shows that the self-diffusion coefficient decreases with increasing η_L and with increasing ϕ_s , and these data give no hint of the changes in the relative pair diffusion coefficient that accompany the addition of the small colloid to the large colloid suspension.

We now consider the results of the q1D experiments. An analysis of the hydrodynamic interaction between particles and particles and walls that includes the effects associated with the nonzero size of the particles has been reported for the case of a one-component q1D colloid suspension.⁷ That analysis showed that structure in the relative longitudinal pair diffusion coefficient is directly related to the equilibrium

structure function of the q1D liquid. We show in Figs. 6(a)–6(d) the center of mass and relative longitudinal pair diffusion coefficients for several q1D binary mixtures. These figures are organized with respect to the small particle volume fractions. In Figs. 6(a)–6(d) the small particle volume fractions are $\phi_s=0.0, 0.001, 0.005$, and 0.01 , respectively, and each panel shows the center of mass and relative longitudinal pair diffusion coefficients of the large particles for large particle densities ranging from about 0.08 to about 0.69, noting that the large particle densities are similar but not exactly the same for different values of ϕ_s . In Fig. 6, the value of the pair diffusion coefficient at any specified pair separation is for all pairs of particles with that separation regardless of whether or not there are other particles between them. As expected, the center of mass diffusion coefficient shows little structure other than an increase with decreasing pair separation, whereas the relative pair diffusion coefficient

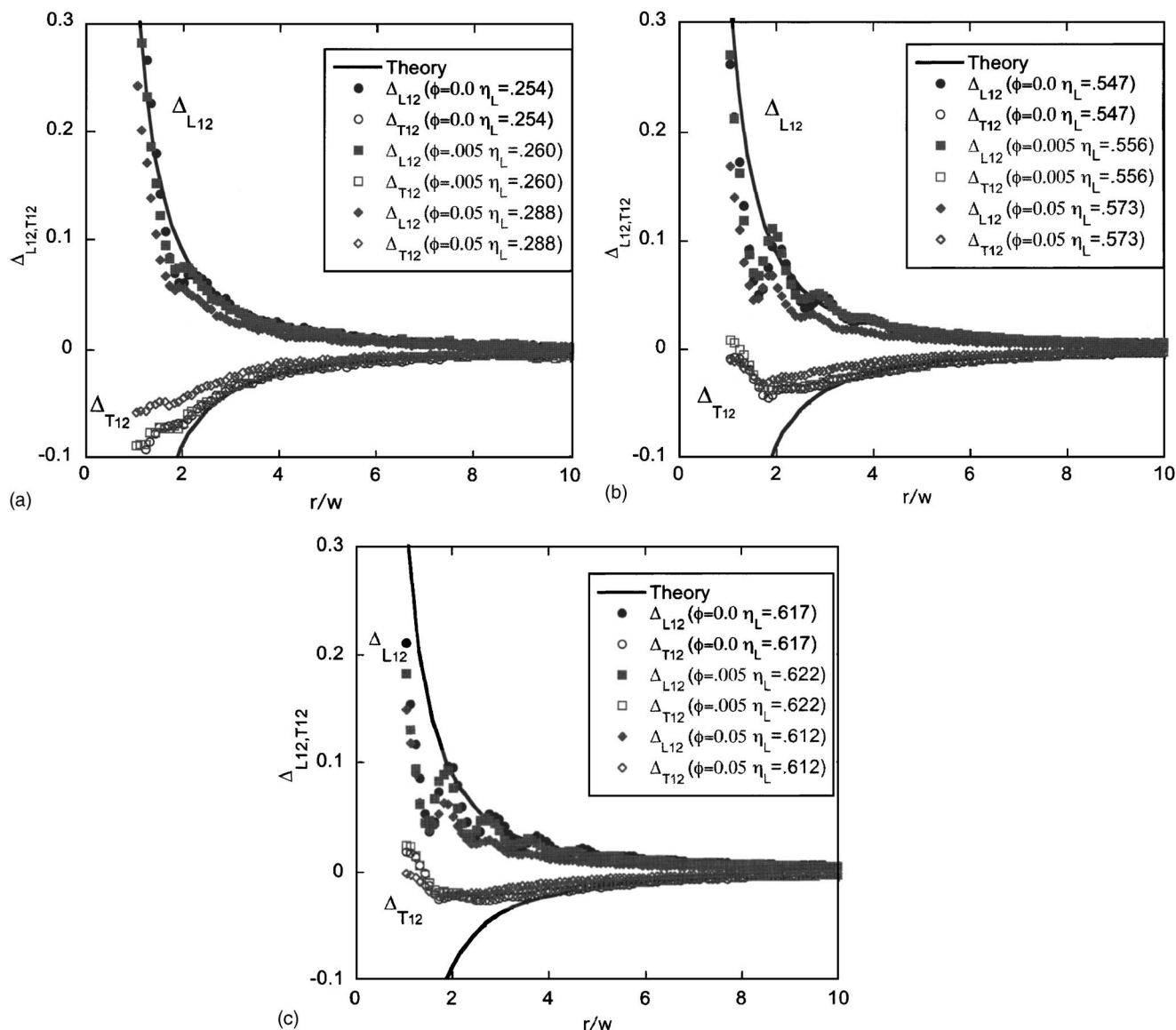


FIG. 4. Comparison of the q2D normalized pair diffusion coefficients Δ_{L12} and Δ_{T12} with similar values of η_L for different values of ϕ_s .

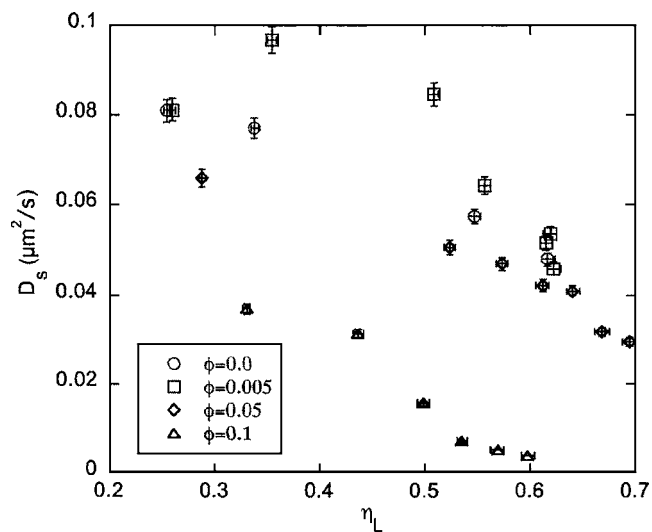


FIG. 5. The η_L dependence of the q2D self-diffusion coefficient for different values of ϕ_s .

displays structure that becomes more marked as the large particle density increases and that arises from the spatial correlations induced by the nonzero size of the particles.

As displayed in Fig. 6, the influence of the small colloid particle concentration on the pair relative diffusion coefficient of the large colloid particles appears small. That inference is made much clearer in a plot of Δ_{L12} versus pair separation, shown in Fig. 7. It is then clearly seen that, unlike the q2D case, addition of the small colloid particles to the large colloid particle suspension has little influence on the separation dependence of the pair diffusion coefficient. The large particle partial structure functions in these binary colloid suspensions, and the corresponding pair correlation functions, also display a very weak dependence on ϕ_s .

We show in Fig. 8 the density dependence of the self-diffusion coefficient of the large colloid particles, obtained from the large separation asymptotes of D_L^+ and D_L^- . The anomalous behavior at small ϕ_s observed for the q2D sus-

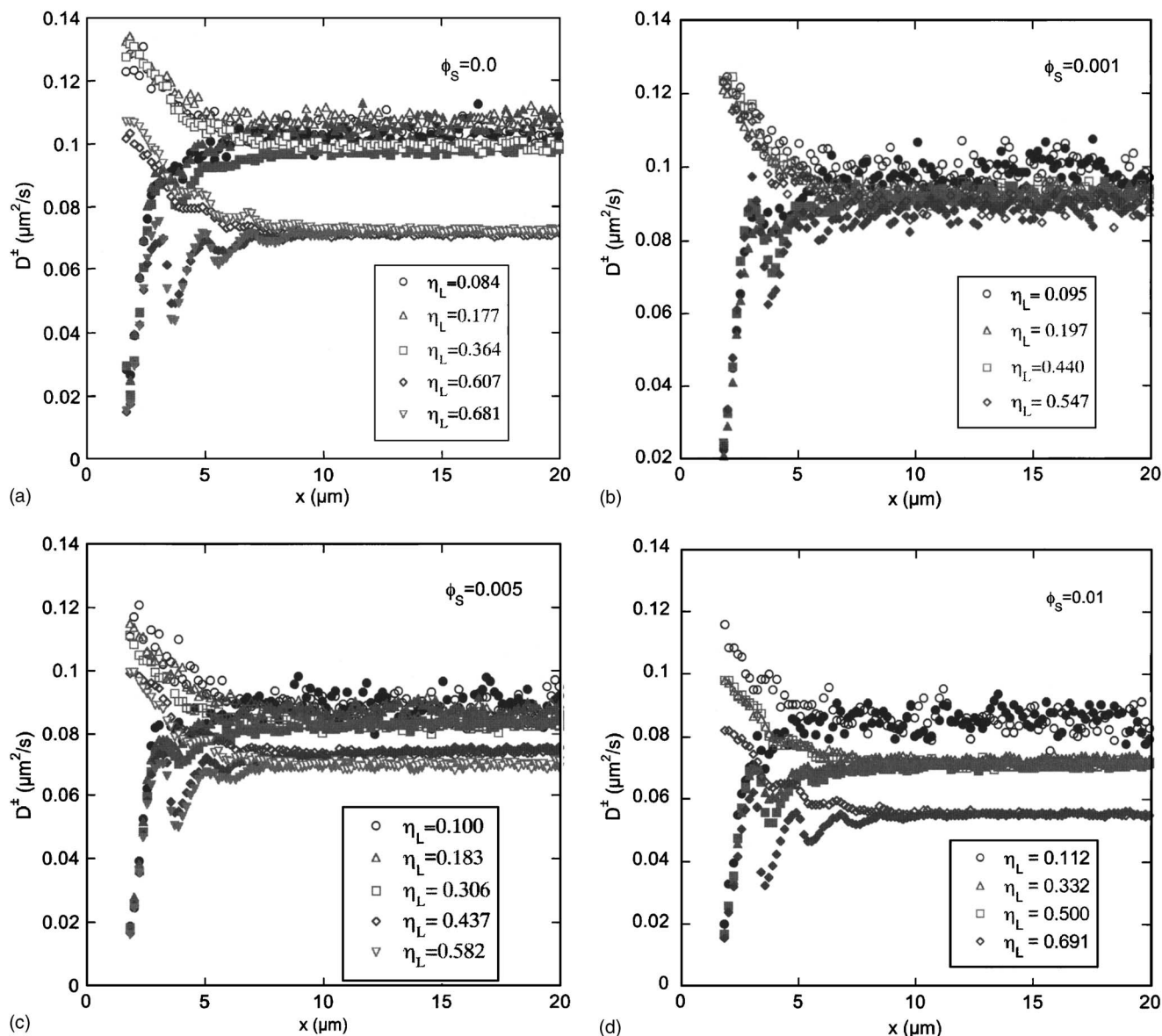


FIG. 6. Collective and relative pair diffusion coefficients for the q1D liquid at various η_L with four different ϕ_s : (a) $\phi_s=0.00$, (b) $\phi_s=0.001$, (c) $\phi_s=0.005$, and (d) $\phi_s=0.010$. Open and filled symbols correspond, respectively, to collective and relative coefficients.

pensions is not apparent in q1D suspensions. Overall, the self-diffusion coefficient decreases with increasing η_L and with increasing ϕ_s .

IV. DISCUSSION

Our previous analyses of hydrodynamic interactions in one-component q1D and q2D colloid suspensions led to the following conclusions.

- (1) In q1D, the hydrodynamic interaction between particles is screened on the length scale of the channel width, and the separation dependence of the relative pair diffusion coefficient has an oscillatory structure directly related to the oscillatory structure of the pair correlation function.
- (2) The influence of hydrodynamic coupling on the q1D relative pair diffusion coefficient is well described

when calculations of the interaction based on the method of reflections are combined with the pair and triplet correlation functions of the fluid.

- (3) In q2D, despite the long range of the interaction between particles, which falls off as $1/r^2$, the particle concentration influences Δ_{L12} and Δ_{T12} only if the separation between particles is small, in which domain the pair correlation function exhibits oscillatory structure.
- (4) In q2D, three body effects do not modify the colloid-colloid interaction at large particle separations.
- (5) In q2D, the effects of the hydrodynamic coupling for longitudinal and transverse displacements of the pair of particles are different; the longitudinal motions are positively correlated, i.e., the motion of one particle tends to drag the other in the same direction, but the transverse motions are negatively correlated, i.e., the motion of one particle generates an antidrag motion on the other particle.

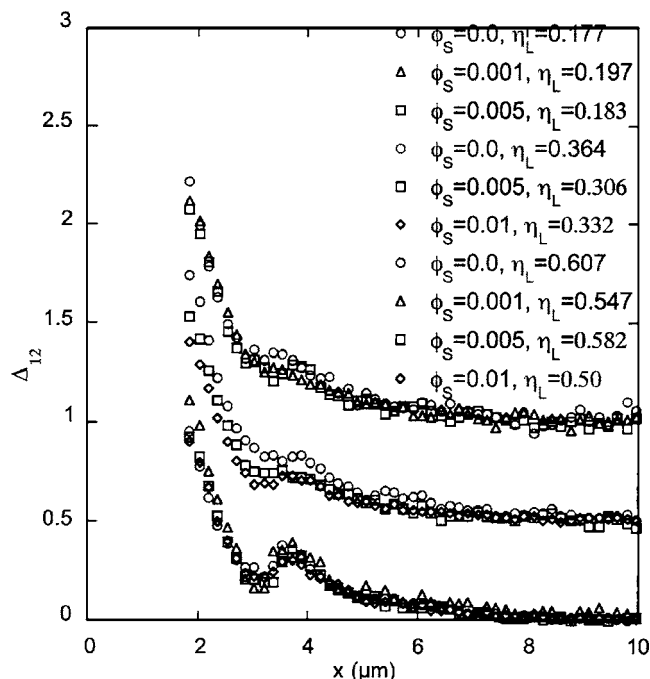


FIG. 7. Comparison of the q1D normalized pair diffusion coefficient Δ_{12} for similar values of η_L and different values of ϕ_S . For clarity, the data for different values of η_L are each shifted vertically by 0.5.

- (6) In q2D, the envelopes of the deviations from asymptotic behavior of Δ_{L12} and Δ_{T12} vary with pair separation as $\pm\lambda/r^2$, hence are symmetric with respect to their equal asymptotic values. This prediction is found to be accurate at large pair separation, but it fails at small pair separation.

The effects on the pair diffusion coefficient of adding a smaller diameter second colloid component to a suspension are somewhat different in q2D and q1D. An overview of the q2D pair diffusion coefficient data reported in this paper shows that in the binary colloid suspensions, as in the one-component suspension, there is negative transverse coupling

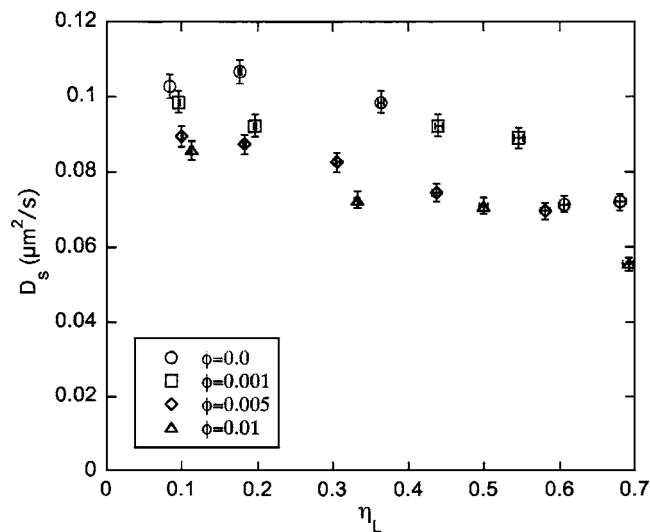


FIG. 8. The η_L dependence of the q1D self-diffusion coefficient for different values of ϕ_S .

and the envelopes of Δ_{L12} and Δ_{T12} have the forms $\pm\lambda/r^2$. And, as in the one-component case, at small pair separation these envelopes are not symmetric with respect to the asymptote. Moreover, the effect of the smaller colloid is not as simple as expected for a pseudo-one-component suspension. As shown in Fig. 4, addition of a small amount of the smaller colloid slightly enhances the oscillations in the small separation dependence of Δ_{L12} and Δ_{T12} , but with further addition of smaller colloid the oscillations are diminished and when $\phi_S=0.10$ they are only barely visible. When examined from the point of view of the self-diffusion coefficient (see Fig. 5), addition of a very small amount of the smaller colloid ($\phi_S=0.005$) generates an increase of D_S but further increases in the smaller colloid density generate a monotone decrease of D_S . Aside from the case with $\phi_S=0.005$, the influence of the smaller colloid on the one particle transport is broadly consistent with an effective medium picture, but the influence of the smaller colloid on the small separation dependence of the relative pair diffusion is not consistent with an effective medium picture.

In contrast, the influence of the smaller colloid on the one particle transport in a q1D suspension is broadly consistent with an effective medium picture for both small and large pair separations, and for the overall density dependence of D_S . We trace this difference to a qualitative structural difference between q1D and q2D systems. There is no evidence for structural and/or dynamical heterogeneity in either one-component or binary q1D suspensions, unlike the situation for q2D suspensions.

Our picture of how the structure in the small separation dependence of the relative pair diffusion in q1D and q2D suspensions arises is derived from considerations appropriate to a one-component colloid suspension. We suggest that it is necessary to augment those considerations with an explicit accounting for the difference in colloid diameters in a binary suspension.⁸⁻¹¹ If the effect of hydrodynamic interaction is described with the method of reflection analysis, the boundary conditions at the surfaces of the different particles will generate flows with different amplitudes and phases from those in a system with the same density of uniform diameter particles. Since these reflected flows are coherent, interferences can occur. The range of the hydrodynamic interaction in q2D is great enough that coupling of such flow interferences with averaging over the positions of the smaller particles could reduce the effects on the pair diffusion associated with the excluded volume and local packing in a one-component system. The range of the hydrodynamic interaction in q1D is small enough that interaction of flow interferences with excluded volume effects is unlikely to alter the influence of the latter on the pair diffusion.

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- ¹J. Happel and H. Brenner, *Low Reynolds Number Hydrodynamics*, 2nd ed. (Kluwer Academic, Dordrecht, 1983).
- ²B. Cui, H. Diamant, B. Lin, and S. A. Rice, Phys. Rev. Lett. **92**, 258301 (2004).
- ³H. Diamant, B. Cui, B. Lin, and S. A. Rice, J. Phys.: Condens. Matter **17**, S2787 (2005).
- ⁴H. Diamant, B. Cui, B. Lin, and S. A. Rice, J. Phys.: Condens. Matter **17**, S4047 (2005).
- ⁵J. Santana-Solano, A. Ramirez-Saito, and J. L. Arauz-Lara, Phys. Rev. Lett. **95**, 198301 (2005).
- ⁶B. Cui, H. Diamant, and B. Lin, Phys. Rev. Lett. **89**, 188302 (2002).
- ⁷X. Xu, B. Lin, S. A. Rice, and H. Diamant, Phys. Rev. Lett. **95**, 158301 (2005).
- ⁸B. Götzelmann, R. Evans, and S. Dietrich, Phys. Rev. E **57**, 6785 (1998).
- ⁹J. M. Méndez-Alcaraz, Phys. Rev. E **61**, 4095 (2000).
- ¹⁰B. Götzelmann, R. Roth, S. Dietrich, M. Dijkstra, and R. Evans, Europhys. Lett. **47**, 398 (1999).
- ¹¹R. Dickman, P. Attard, and V. Simonian, J. Chem. Phys. **107**, 205 (1997).
- ¹²B. Cui, B. Lin, and S. A. Rice, J. Chem. Phys. **119**, 2386 (2003).
- ¹³H. M. Ho, B. Cui, S. Repel, B. Lin, and S. A. Rice, J. Chem. Phys. **121**, 8627 (2004).
- ¹⁴H. M. Ho, B. Lin, and S. A. Rice, J. Chem. Phys. **125**, 184715 (2006).
- ¹⁵J. C. Crocker and D. G. Grier, J. Clin. **179**, 198 (1996).