## Influence of Hydrodynamic Coupling on Pair Diffusion in a Quasi-One-Dimensional Colloid System

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The effect of hydrodynamic interaction on the separation dependence of the center of mass and relative pair diffusion coefficients of colloid particles in a quasi-one-dimensional system, including the influence of proximate walls, is calculated using the method of reflections. There is excellent agreement between the theoretical predictions and the experimental data. We show that the separation dependence of the relative pair diffusion coefficient has an oscillatory structure on the scale length of the correlation length in the system, and we directly relate that oscillatory structure to the pair correlation function of the system.

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Relatively little is known about the diffusion dynamics of a pair of interacting particles in a dense medium. In particular, the dependences of the relative and center of mass pair diffusion coefficients on the pair separation are not known, although it is expected that excluded volume and other interactions between the pair will influence those dependences. At the molecular level, this lack of information is a consequence of the unavailability of appropriate probes of pair motion. The situation is somewhat different for colloid systems with particles large enough to be imaged with a visible light microscope. In this Letter, we show, both theoretically and experimentally, that the relative pair diffusion coefficient in a quasi-one-dimensional (Q1D) fluid is a decaying oscillating function of the pair separation that approaches the single particle self-diffusion coefficient at large pair separation, while the center of mass pair diffusion coefficient is a smooth function of the pair separation. To our knowledge this is the first theoretical and experimental study of the properties of the pair diffusion coefficient in a dense Q1D fluid. Some properties of the pair diffusion dynamics in a quasi-two-dimensional fluid are reported in [1], but the oscillatory structure in the relative pair diffusion coefficient was not analyzed. Although the hydrodynamic interaction between colloid particles differs from, say, the Lennard-Jones type interaction between Ar atoms, we expect all the qualitative features of the pair diffusion coefficient to be the same in the two cases. We also expect the qualitative features of the pair diffusion coefficient to be the same in Q1D and true 1D systems. We note that the pair diffusion coefficients play an important role in some formulations of the kinetic theory of liquids [2]. We also note that diffusion in a Q1D channel is important in processes as diverse as transport through a zeolite [3] and transfer of species across biological membranes [4].

The fundamental dynamics of colloid particles has long been described by a combination of single particle Brownian motion and hydrodynamic coupling between the particles. To characterize the diffusion of a pair of particles in a Q1D channel, one commonly uses the center of mass  $(D^+)$  and relative  $(D^-)$  diffusion coefficients. However, we prefer to analyze the properties of  $D_{11}$  and  $D_{12}$  because of their close relation to the mobility of the pair of particles [see Eq. (1)]. Of these four diffusion coefficients, only two are independent and the relation among them is given in (1) below.

A recent experimental and theoretical study of the influence of hydrodynamic interactions on  $D_{12}$  of a pair of particles in a Q1D channel, by Cui, Diamant, and Lin [5], reveals that the interaction between particles is screened on the scale length of the channel width. The Cui-Diamant-Lin analysis of this system was based on the approximations that the particle radius is very small relative to both the channel width and the mean spacing between particles, and that the particle motion is restricted to be along the axis of the channel. With the approximations mentioned, the effect of one particle on the flow can be treated as if it exerts a point force on the liquid [6,7]. The general features of the dependence on particle separation of  $D_{12}$  at large particle separation are correctly accounted for. However, this analysis cannot capture effects that arise from the competition between excluded volume and hydrodynamic interactions; hence it does not explain the observed oscillations in the pair diffusion coefficients as a function of pair separation. That analysis, based on a point force hydrodynamic treatment, also cannot evaluate the single particle self-diffusion coefficient. In fact, the self-diffusion coefficient of each particle in a pair was taken to be known and equal to the experimentally observed single particle selfdiffusion coefficient. Furthermore, as the hydrodynamic interactions were parametrized by the single particle diffusion coefficient at infinite dilution, this analysis is density independent and is limited to the low colloid concentration domain.

In this Letter we use the so-called method of reflections to evaluate the diffusion coefficients of a dense Q1D colloid fluid. By inclusion of higher and higher order reflections we can, in principle, compute the influence on the diffusion coefficients of hydrodynamic interactions between particles and between the particle and the walls to arbitrary accuracy. We are also able to directly compute the self-diffusion coefficient and incorporate its density dependence into our analysis.

This Letter is concerned primarily with understanding the origin of the structure displayed in the pair diffusion coefficients as functions of the pair separation. We report a calculation of the influence of hydrodynamic coupling between pairs of colloid particles and the walls of a Q1D channel, and each other, on the pair diffusion coefficients. Similar to the Stokeslet analysis, this method exploits the fact that when the particle velocity is very small the hydrodynamic interactions between particles and between each particle and the walls can be described by the linear Navier-Stokes equation for incompressible stationary flow. The analysis has been shown to quantitatively predict the concentration dependence of the one particle diffusion coefficient in a Q1D system [8]. The exact triplet correlation function of a one-dimensional fluid of hard rods is used in our analysis, noting that the treatment of hydrodynamic interaction between pairs of particles inevitably requires integration over the two- and three-particle distribution functions. The separation dependence of the pair self-diffusion coefficient is predicted to have a decaying oscillatory form, as is found by the experiments reported in this Letter. We note that the pair diffusion coefficients reported here differ from those reported in [5] because in that Letter only nearest neighbor pairs were considered, whereas in this Letter all pairs are considered.

We have described elsewhere [8] the application of the method of reflections to the calculation of hydrodynamic interactions in a Q1D colloid system confined in a cylindrical capillary with radius  $R_0$  and length  $L \gg R_0$ , inside of which is a viscous fluid (viscosity  $\mu$ ) containing equal size solid spheres with radius *a*. The separation between a pair of spheres is denoted *r*. The viscous fluid would be at rest if unperturbed. We assume that the centers of the spheres are on the central axis of the capillary and that they can only move parallel to that axis. The reader is referred to [8] and references cited therein for details of the method.

The experimental studies were carried out using the same setup as in [5] in an open rectangular channel, but a different counting methodology was applied. The center of mass and relative diffusion coefficients in the Q1D colloid system are denoted  $D^+$  and  $D^-$  with  $D^{\pm} \equiv \langle [\Delta x_1(t) \pm \Delta x_2(t)]^2 \rangle / 4t$  with  $\Delta x_i(t)$  the displacement of particle *i* in time *t*. In the present analysis the average  $\langle \cdots \rangle$  is taken over all observed pairs whose separations fall in the range  $r \pm \delta r$ , whereas in [5] the average was taken only over

those nearest neighbors whose separations fell in this range. Note that

$$\frac{D^{+}(r) + D^{-}(r)}{2} = \frac{\langle 2(\Delta x_{1})^{2} + 2(\Delta x_{2})^{2} \rangle(r)}{8t} = D_{11}(r),$$
  
$$\frac{D^{+}(r) - D^{-}(r)}{2} = \frac{\langle 4\Delta x_{1}\Delta x_{2} \rangle(r)}{8t} = D_{12}(r).$$
 (1)

The use of a cylindrical capillary to calculate the hydrodynamic interactions is an approximation. We argue that this model is appropriate because the tangential velocity of the viscous fluid in the square open channel must be zero at the walls, and there must be some surface with zero tangential fluid velocity that connects the lips, and thereby defines the effective fourth wall of the channel. Although crude, the model does capture the essential feature that the tangential velocity of the liquid in contact with the walls is zero.

To evaluate the hydrodynamic interactions, imagine that the only external force acting on the system,  $F_1 = 6\pi\mu a U_1$ , is applied on particle 1 along the capillary axis. Thus for single particle diffusion in a solution, the important results previously obtained [8] are

$$\frac{U_{1f}}{U_1} = 1 - \frac{1}{\pi} \int_0^\infty A d\alpha - \frac{\eta}{\sigma} \int_{-\infty}^\infty g_2(x) \left[ \frac{3\beta}{2(\frac{x}{R_0})^2} - \frac{3\beta^3}{2(\frac{x}{R_0})^4} - \frac{1}{\pi} \int_0^\infty B \alpha \sin\left(\alpha \frac{x}{R_0}\right) d\alpha \right] \left[ \frac{5\beta^3}{2(\frac{x}{R_0})^2} - \frac{4\beta^5}{(\frac{x}{R_0})^4} - \frac{2}{\pi} \int_0^\infty C \sin\left(\alpha \frac{x}{R_0}\right) d\alpha \right] dx$$

$$= 1 + \chi_w + \frac{2\eta}{\sigma} \int_0^\infty g_2(x) \chi_p(x) dx, \qquad (2)$$

$$\frac{U_{2f}(r)}{U_{1}} = \frac{3\beta}{2(\frac{r}{R_{0}})} - \frac{\beta^{3}}{\frac{r}{R_{0}}} - \frac{1}{\pi} \int_{0}^{\infty} A \cos\left(\alpha \frac{r}{R_{0}}\right) d\alpha$$
$$- \frac{\eta}{\sigma} \int_{-\infty}^{\infty} \frac{g_{3}(0, r, x)}{g_{2}(r)} \left[\frac{3\beta x}{2(\frac{x}{R_{0}})^{2}|x|} - \frac{3\beta^{3} x}{2(\frac{x}{R_{0}})^{4}|x|}\right]$$
$$- \frac{1}{\pi} \int_{0}^{\infty} B\alpha \sin\left(\alpha \frac{x}{R_{0}}\right) d\alpha \left[\frac{5\beta^{3}}{2(\frac{x-r}{R_{0}})^{2}} \frac{x-r}{|x-r|}\right]$$
$$- \frac{4\beta^{5}}{(\frac{x-r}{R_{0}})^{4}} \frac{x-r}{|x-r|} - \frac{2}{\pi} \int_{0}^{\infty} C \sin\left(\alpha \frac{x-r}{R_{0}}\right) d\alpha dx,$$
(3)

with  $g_2(x)$  and  $g_3(0, r, x)$  the pair and triplet correlation functions of the liquid, respectively,  $\eta$  the particle packing fraction, and  $U_{1f}$  and  $U_{2f}$  the velocities of particle 1 and particle 2 along the axis of the confining cylindrical capillary that result from the hydrodynamic interaction with other particles and the wall. The function  $\chi_w$  represents the effects of the wall, and the function  $\chi_p(r)$  represents the effects of interactions between particles with separation *r*. The other terms in (1) and (2) are

$$\begin{split} A &= (\beta^3 \alpha^2 + 3\beta) \frac{K_0(\alpha)}{I_0(\alpha)} - \frac{3\beta}{2I_0^2(\alpha)} \\ &+ \frac{\frac{3\beta \alpha I_0'^2(\alpha)}{2I_0^2(\alpha)} - \beta^3 \alpha^2 \frac{I_0'(\alpha)}{I_0(\alpha)} + \frac{\beta^5 \alpha^3}{6}}{\alpha I_0'^2(\alpha) + 2I_0(\alpha)I_0'(\alpha) - \alpha I_0^2(\alpha)}, \\ B &= \left(\frac{\beta^3 \alpha^2}{2} + 3\beta\right) \frac{K_0(\alpha)}{I_0(\alpha)} - \frac{3\beta}{2I_0^2(\alpha)} \\ &+ \frac{\frac{3\beta \alpha I_0'^2(\alpha)}{2I_0^2(\alpha)} - \frac{\beta^3 \alpha^2}{2} \frac{I_0'(\alpha)}{I_0(\alpha)}}{\alpha I_0'^2(\alpha) + 2I_0(\alpha)I_0'(\alpha) - \alpha I_0^2(\alpha)}, \\ C &= \left(\frac{5}{2}\beta^3 \alpha + \frac{2}{3}\beta^5 \alpha^3\right) \frac{K_0(\alpha)}{I_0(\alpha)} - \frac{5\beta^3 \alpha}{4I_0^2(\alpha)} \\ &+ \frac{\frac{5\beta^3 \alpha^2 I_0'^2(\alpha)}{4I_0^2(\alpha)} - \frac{2\beta^5 \alpha^3}{3} \frac{I_0'(\alpha)}{I_0(\alpha)} + \frac{\beta^7 \alpha^4}{12}}{\alpha I_0'^2(\alpha) + 2I_0(\alpha)I_0'(\alpha) - \alpha I_0^2(\alpha)}, \end{split}$$

where  $\beta = a/R_0$ ,  $K_0(\alpha)$  is the modified Bessel function of the second kind of order 0, and  $I_0(\alpha)$  is the modified Bessel function of the first kind of order 0.

Using the relationship between the mobilities of particles 1 and 2 along the capillary axis and the diffusion coefficients, we have

$$\mu_{11} = \frac{1}{6\pi\mu a} \frac{U_{1f}}{U_1} \Rightarrow D_{11} = \frac{U_{1f}}{U_1} D_0,$$

$$\mu_{12} = \frac{1}{6\pi\mu a} \frac{U_{2f}}{U_1} \Rightarrow D_{12} = \frac{U_{2f}}{U_1} D_0,$$
(4)

where  $D_0$  is the infinite dilution single particle selfdiffusion coefficient in an unconfined (3D) system.

To calculate the diffusion coefficients of a given pair, we note that  $D_{11}(r)$  differs from the single particle diffusion coefficient  $D_s$  because we consider two particles, one at the origin and one at r, in which case the probability density for finding another particle at x is changed from  $(\eta/\sigma)g_2(x)$  to  $(\eta/\sigma)[g_3(0, r, x)/g_2(r)]$ . For a onedimensional fluid of hard rods, the superposition approximation to the triple correlation function is exact, so that  $g_3(0, r, x) = g_2(0, r)g_2(r, x)g_2(0, x)$ . Thus we claim that

$$\frac{D_{11}(r,\eta)}{D_0} = 1 + \chi_w + \chi_p(r) + \frac{\eta}{\sigma} \int_{-\infty}^{\infty} g_2(|x|)g_2(|r - x|)\chi_p(|x|)dx.$$
(5)

From our earlier study of the concentration dependence of the single particle diffusion coefficient in the Q1D channel, we know that  $\chi_w$  is dependent only on the parameter  $a/R_0$ , and  $\chi_p(r)$  is dependent only on x and  $a/R_0$ .

We have carried out experimental and theoretical evaluations of pair diffusion coefficients for several values of the packing fraction and the ratio of the particle radius to the capillary radius. Figure 1 shows  $D_{11}(r, \eta)$ ,  $D_{12}(r, \eta)$ , and  $D^{\pm}(r, \eta)$  for the cases  $\eta = 0.61$ ,  $a/R_0 = 0.15$  and  $\eta =$ 0.39,  $a/R_0 = 0.15$ . All of the diffusion coefficients have been normalized so that  $D_{11}(r, \eta)$  and  $D^{\pm}(r, \eta)$  approach unity when the separation between the particles of the pair is infinite. Figure 1 shows that there is only a minor discrepancy between theory and experiment at very small separations which, we claim, can be removed by taking higher order reflections into account. To our knowledge, these are the first theoretical and experimental results pertinent to the spatial dependence of the pair selfdiffusion coefficient as a function of pair separation.

We now consider the shape of  $D_{11}(r, \eta)$  as a function of r. This structure has an uncanny resemblance to the structure of the Q1D pair correlation function, which suggests the following argument. If we define  $f(r, \eta) \equiv 1 - D_{11}(r, \eta)/D_S(\eta)$ , we can write

$$\frac{D_{S}(\eta)}{D_{0}}f(r,\eta) = \chi_{p}(r) + \frac{\eta}{\sigma} \int_{-\infty}^{\infty} g_{2}(|x|)[g_{2}(|r-x|) - 1]\chi_{p}(|x|)dx.$$
(6)

Figure 2 displays  $\chi_p(\rho)$  for a typical value of  $a/R_0 = 0.3$ , with  $\rho = x/\sigma$  the scaled separation. With the approximations  $\chi_p(\rho) \approx 0$  for  $|\rho| \ge 2$  and  $g_2(\rho)\chi_p(\rho) = M\Theta(|\rho| - 1)\delta(|\rho| - 1)$ , with  $\Theta$  the unit step function, the last equation takes the form

$$\frac{D_{S}(\eta)}{D_{0}}f(\rho,\eta) \approx M\eta \int_{-\infty}^{\infty} \delta(|\rho|-1)[g_{2}(|\rho-x|)-1]dx$$
$$= M\eta[g_{2}(\rho-1)+g_{2}(\rho+1)-2]$$
(7)



FIG. 1 (color online). Comparison between theory and experiment at  $a/R_0 = 0.15$  and (a)  $\eta = 0.61$ , (b)  $\eta = 0.39$ . The solid lines are theoretical results, and the circles are the experimental observations.



FIG. 2.  $\chi_p$  as a function of scaled separation  $\rho = r/\sigma$  at  $a/R_0 = 0.3$ .

for  $\rho > 2$ . We expect that, because of the character of the pair correlation function at small separation,  $|g_2(\rho - 1) - 1| \gg |g_2(\rho + 1) - 1|$  and then, as neither  $D_S(\eta)/D_0$  nor  $M\eta$  are dependent on  $\rho$ , we have

$$f(\rho) \equiv 1 - \frac{D_{11}(\rho, \eta)}{D_S(\eta)} \propto g_2(\rho - 1) - 1$$
(8)

for  $\rho > 2$ . We show in Fig. 3 the validity of Eq. (8) for colloid packing fractions  $\eta = 0.7$  and  $\eta = 0.5$  respectively; very good agreement is found in both cases. The small phase shift that appears in both cases, we argue, arises from the  $\delta$ -function approximation we make. And from the figures, we see that the higher  $a/R_0$  is, the better the approximation is, which is confirmed as we have observed that the peak in the function  $\chi_p$  gets narrower when  $a/R_0$  is bigger.

With the above argument, we predict that for softer particles or binary mixtures the peaks in the function  $D_{11}(r, \eta)$  and the relative diffusion coefficient will shift to larger separation as compared to those for their hard particles counterparts, as a result of the change in the pair correlation function.

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FIG. 3. Comparison between  $g_2(\rho - 1) - 1$  and  $f(\rho)$  at  $a/R_0 = 0.4$  or  $a/R_0 = 0.15$  and (a)  $\eta = 0.7$ , (b)  $\eta = 0.5$ . All  $f(\rho)$  are rescaled so that they are suitable to be put into one figure.

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