Influence of hydrodynamics on many-particle diffusion in 2D colloidal suspensions

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Abstract. – We study many-particle diffusion in 2D colloidal suspensions with full hydrodynamic interactions through a novel mesoscopic simulation technique. We focus on the behaviour of the effective scaled tracer and collective diffusion coefficients \(D_T(\rho)/D_0\) and \(D_C(\rho)/D_0\), where \(D_0\) is the single-particle diffusion coefficient, as a function of the density of the colloids \(\rho\). At low Schmidt numbers \(Sc = O(1)\), we find that hydrodynamics has essentially no effect on the behaviour of \(D_T(\rho)/D_0\). At larger \(Sc\), \(D_T(\rho)/D_0\) is enhanced at all densities, although the differences compared to the case without hydrodynamics are minor. The collective diffusion coefficient, on the other hand, is much more strongly coupled to hydrodynamical conservation laws and is distinctly different from the purely dissipative case.

Introduction – The dynamics of Brownian particles in confined geometries, and in two dimensions (2D) in particular, is an important theoretical problem with applications in surface science and colloidal systems \cite{1}. Examples of fundamental questions that have been addressed recently are the form of effective interactions between macroions in a colloidal suspension \cite{2,3} and the effects of hydrodynamic interactions (HI) on the diffusive properties of colloidal particles \cite{4,5,6,7}.

So far, most studies have focused on self-diffusion of particles in 2D. In the ideal case of no external potential and without HI, the density dependent self-diffusion coefficients of 2D hard disk particles have been recently determined using numerical simulations \cite{8,9} and various theoretical approximations \cite{9,10,11}. While the single-particle limit in the ideal case is trivial, no exact analytic results exist for finite densities. In this regime complicated many-body effects manifest themselves through memory effects in the motion of tagged colloidal particles.

The situation is even more complicated when the HI mediated by the solvent in a colloidal suspension are taken into account. Recent work on the self-diffusion of colloidal particles in 2D and quasi-2D \cite{4,5,6,7} indicate that HI do indeed influence self-diffusion. In many cases...
it has been found that diffusion is enhanced [4, 5, 6, 7] by the HIs. Nevertheless, it is possible that the nature and magnitude of these subtle effects in a given system depend on the relative importance of the HIs and other interactions.

While the self-diffusion properties of 2D colloidal systems are relatively well understood, much less is known about collective diffusion in 2D colloidal suspensions. Nevertheless, collective diffusion plays a crucial role in processes such as spreading and phase separation, as it describes the decay rate of density fluctuations in a system. While the case without HIs has been considered recently [9, 12], the theoretical understanding of 2D situations with HIs is very limited. This is, in part, due to theoretical difficulties when dealing with collective transport in 2D liquids. Furthermore, realistic numerical simulations of collective diffusion in two-phase colloidal systems with full hydrodynamics have turned out to be a considerable methodological challenge.

In this letter, our purpose is to employ a recently proposed mesoscopic simulation method [13–14] to shed light on some of the fundamental issues of many-particle diffusion in 2D colloids. To this end, we consider an ensemble of colloidal particles that interact mutually with a short-range repulsive potential and long-range HIs. The main issue we want to address here is the influence of hydrodynamics in the diffusive dynamics of this system, as the extent of HIs is varied in a controlled fashion by tuning the Schmidt number of the system (see below). In particular, we are interested in the behaviour of the effective collective diffusion coefficient as a function of the density of the colloidal particles and the impact of the HIs on this dependence.

Schmidt number – An important quantity measuring the properties of a fluid in equilibrium is the dimensionless Schmidt number $Sc$, defined as the ratio of momentum diffusivity to mass diffusivity:

$$Sc = \frac{\nu}{D}. \tag{1}$$

Here $\nu = \eta / \rho_s$ is the kinematic viscosity of the fluid, $\eta$ being the viscosity, $\rho_s$ the density of the fluid and $D$ the tracer diffusion coefficient of the fluid particles. In a real fluid such as water $Sc = \mathcal{O}(10^3)$. Theoretical arguments, too, often include the assumption that hydrodynamic fluctuations have reached a steady state on the timescale of the motion of the colloidal particles. The situation can be quite different in computer simulations. In molecular dynamics (MD) simulations the Schmidt number is typically large. Unfortunately, MD is computationally too intensive for simulations of colloidal suspensions with explicit solvent, especially at high densities. Mesoscopic simulation techniques such as dissipative particle dynamics (DPD) reduce the computational cost. On the other hand, in recent DPD simulations $Sc = \mathcal{O}(1)$ [15]. It is not quite clear how a Schmidt number several magnitudes smaller than those measured in realistic systems influences the properties of, e.g., colloidal suspensions. In our opinion, the understanding of the influence of $Sc$ on colloidal dynamics is necessary. It is also crucial to develop new approaches to bridge the various scales in colloidal systems and, consequently, to allow a direct comparison between physical model studies and experiments.

Model and methods – The model system we consider here comprises an ensemble of disks immersed in a 2D liquid. The dynamics of the system is simulated using a novel mesoscopic technique introduced by Malevanets and Kapral (MK) [13–14]. The MK method is essentially a hybrid MD model, where the colloid is treated microscopically and the solvent obeys coarse-grained dynamics. The interaction potential between two solvent particles is zero, while the solvent-colloid and colloid-colloid interactions can be chosen at will. For the purposes of the coarse-grained solvent dynamics, the time is partitioned into segments $\tau$, and the system itself is divided into so-called collision volumes or cells. During one collision step $\tau$, the system obeys Newton’s equations of motion, i.e. the time evolution is taken care of by
The effective interactions between two solvent molecules occur at each τ: a collision event takes place, and the velocities of the solvent particles are transformed according to \( \mathbf{v}_i(t + \tau) = \mathbf{V} + \mathbf{\omega} \cdot [\mathbf{v}_i(t) - \mathbf{V}] \). Here \( \mathbf{v}_i \) is the velocity of particle \( i \), \( \mathbf{V} \) is the average velocity of all the particles in the cell the particle \( i \) belongs to and \( \mathbf{\omega} \) is a random rotation matrix over an angle \( \alpha \) chosen separately for each cell. It can be shown [13] that this multiparticle collision dynamics conserves the momentum and energy in each collision volume. Furthermore, it gives a correct description of the hydrodynamics of the velocity field. The method also reduces computing times significantly, as the tedious calculation of solvent-solvent forces can be omitted.

The interactions between the colloid particles are strongly repulsive and of short range. The interaction potentials are of the form

\[
V(r) = \begin{cases} 
\epsilon \left( \frac{\sigma}{r} \right)^n, & r \leq r_c \equiv 2.5\sigma; \\
0, & r > r_c,
\end{cases}
\]

where \( r \) is the separation between two particles. Here we set \( n = 12 \), which allows a direct comparison with previous calculations on a smooth surface without hydrodynamics [9]. The colloid-colloid interaction parameters were chosen to be \( \sigma_{cc} = 2\sigma \) and \( \epsilon_{cc} = \epsilon \), while the colloid-solvent parameters are given by \( \sigma_{cs} = \sigma \) or zero(\(^1\)) and \( \epsilon_{cc} = \epsilon \). The colloidal particles have a mass of \( m_c = 5\sigma \) and the solvent mass is set to \( m_s = m \) or \( m_s = 0.5m \). The parameters \( \sigma \), \( \epsilon \) and \( m \) now define our system of units, and hence our unit of time is given by \( \tau_{L,J} = \sigma(m/\epsilon)^{1/2} \).

The simulations were performed at a temperature \( k_B T = 2 \) and for the solvent density we used \( \rho_s = 1 \). \(^2\) The equations of motion were integrated using the velocity Verlet algorithm with a time step \( \Delta t = 0.005 \). The linear size of our simulation box was set to either \( L = 200 \) or \( L = 100 \). Periodic boundary conditions were employed in all simulations. Within our statistical accuracy, the scaled diffusion coefficients did not change with system size. However, we did not carry out a systematic finite-size scaling analysis.

The choice of the parameters that determine the collision dynamics fixes the properties of the coarse grained solvent, and in particular the Schmidt number. The value of \( Sc \) is affected \( e.g. \) by the choice of the collision step \( \tau \), the linear size of the collision volume \( \ell_c \) and the collision rule, \( i.e. \) the choice of the random rotation matrix \( \mathbf{\omega} \). We have used different sets of parameters in the simulations. These sets lead to different Schmidt numbers and kinematic viscosities. A list of the three different parameter sets is shown in Table I.

### Table I - A summary of the three different parameter sets used. See text for details.

| \( Sc \) | \( \nu [\sigma^2 \tau_{L,J}] \) | \( \tau [\tau_{L,J}] \) | \( \ell_c [\sigma] \) | \( \alpha \) | \( m_s [m] \) | \( L [\sigma] \) |
|---|---|---|---|---|---|---|
| 1  | 0.82(1) | 0.5  | 2  | \( \pm 90^\circ \) | 1  | 200  |
| 20 | 3.70(2) | 0.1  | 2  | \( \pm 125^\circ \) | 0.5 | 100  |
| 100| 9.11(2) | 0.1  | 2  | \( \pm 170^\circ \) | 1  | 100  |

\(^1\)In the case where the direct solvent-colloid interaction is absent, the colloidal particles participate in the collision events [10]. In other words, the solvent-colloid interaction is described indirectly through collisions. As a consequence the calculations speed up significantly. We have verified explicitly that the results obtained from simulations without solvent-colloid interactions are in quantitative agreement with those computed including the interaction directly, see fig. 1(b).

\(^2\)The solvent and colloidal densities have been defined as \( \rho_s \equiv N_s(A/\sigma^2) \) and \( \rho \equiv N/(A/\sigma_c^2) \), respectively. Here \( A \) is the area of the system, \( N_s \) the number of solvent particles and \( N \) the number of colloidal particles.
Results and discussion – Perhaps the simplest transport coefficient is the tracer diffusion coefficient $D_T$, which describes the motion of a tagged tracer particle as $D_T = \lim_{t \to \infty} D_T(t)$, where

$$\frac{1}{d} \int_0^t dt' \left\langle \frac{1}{N} \sum_{i=1}^N \mathbf{v}_i(t') \cdot \mathbf{v}_i(0) \right\rangle,$$

among $N$ identical particles. Here $d = 2$ is the dimension of the system and $\mathbf{v}_i(t)$ is the velocity of particle $i$ at time $t$. The quantity $\phi(t) = \left\langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \right\rangle$ is the velocity autocorrelation function. In evaluating the diffusion coefficients we employ the memory expansion method [18].

For colloidal systems with HIs, it has been known since the 1970s that there are long-time tails in the velocity autocorrelation functions. These have been observed in MD [19] and lattice-Boltzmann [20] computer simulations, and will lead to a divergence of the tracer diffusion coefficient in 2D [19,21]. In this case, the diffusion coefficients $D_T(t)$ can be considered to be time-dependent, effective quantities. When tracer diffusion in concentrated suspensions is investigated experimentally, it is common to single out the effects of the HIs by concentrating on the so-called short-time diffusion coefficients [22,4,5,7]. These are measured at times much shorter than $\tau_1$, the time it takes the tracer particles to diffuse the average distance between the suspended colloidal particles. For this definition to be meaningful, such times should be significantly larger than the time $\tau_B$ it takes for the velocities of the colloidal particles to relax. In our case, for concentrated solutions and small values of $Sc$ in particular, the time interval between $\tau_B$ and $\tau_1$ becomes very narrow. Hence, this definition for short-time diffusion coefficients cannot be used.

We consider $D_T(\rho, t)$ normalised by the single-particle diffusion coefficient $D_0(t) \equiv D_T(\rho \to 0, t)$. As shown in fig. 1(a), in the limit of large times, the quantities $D_T(\rho, t)/D_0(t)$ seem to converge to a finite limit. Although the slow logarithmic divergences are present in our data (data not shown), the amplitudes of the tails at late simulation times are very small and partially masked by statistical fluctuations. In practice we have first determined $D_0$ at a time $t_{\text{eff}}$, where the tracer particle has diffused approximately $\ell$ times its own diameter, where $\ell = 25, 5, 2$ for $Sc = 1, 20, 100$, respectively. The effective diffusion coefficients $D_T(\rho)$ at finite densities have then been determined at the corresponding time intervals.

In fig. 1(b) we show a summary of our results for the scaled $D_T(\rho)/D_0$ as a function of the density of the disks $\rho$. For comparison we also present our earlier MD results for the purely dissipative case [7]. Remarkably, it is clear that at low values of $Sc$ hydrodynamics has virtually no influence on tracer diffusion. As $Sc$ is tuned to larger values, we find an enhancement of $D_T(\rho)/D_0$ which is largest at intermediate densities. This sheds some light on the issues addressed in ref. [5]. The authors study the influence of HIs on self-diffusion, and find that in quasi-2D systems with long-range interactions between the colloidal particles, the scaled diffusion coefficients are enhanced. The larger the particle density, the stronger the enhancement [5]. Our data indicate that even for short-range interactions of the form $V(r) \sim 1/r^n$ with $n = 12$, the HIs may enhance self-diffusion. Although the mechanism leading to enhancement may be complex in a many-particle diffusion process, we expect that it is related to the formation of vortices, which have been shown to enhance self-diffusion in simple liquids [19]. Further, although direct comparison with experiments is not possible due to a different magnitude and range of interactions, we may note that this result is in agreement with previous findings [5,7].

Another important transport coefficient characterizing collective density fluctuations is the...
collective diffusion coefficient $D_C(t)$, which can be defined through a Green-Kubo relation:

$$D_C(t) = \xi D_{cm}(t) = \xi \lim_{t' \to t} \frac{1}{2dNt'} \langle |R(t')|^2 \rangle.$$  \hfill (4)

Here $\xi = \langle N \rangle / [(\langle N^2 \rangle - \langle N \rangle^2)]$ is the thermodynamic factor (proportional to the inverse of the isothermal compressibility $\kappa_T$) and $R(t) = \sum_{i=1}^{N}[\mathbf{r}_i(t) - \mathbf{r}_i(0)]$ is the center of mass (CM) displacement \cite{23}. The thermodynamic factor $\xi$, which is a static quantity, is not affected by hydrodynamics within our accuracy. To estimate $\xi$ we have used the Boublik approximation \cite{24} which is in excellent agreement with MD simulations for most densities \cite{9}.

In fig. 2(a) we show the scaled CM mobility as a function of density in the present system\cite{3}. It is now a decreasing function of $\rho$, and decreases much more rapidly than $D_T(\rho)/D_0$ shown in fig. 1(b). It is also remarkable that, unlike self-diffusion, $D_{cm}(\rho)/D_0$ is not sensitive to $Sc$: while the self-diffusion of individual particles is influenced by $Sc$, the effects on individual particles are largely independent of each other, and thus cancel out in the CM mobility.

In fig. 2(b) we show the scaled collective diffusion coefficient that displays a minimum at small values of density. This minimum is due to the rapid initial decay of $D_{cm}(\rho)/D_0$. It is in striking contrast to the dissipative case (see fig. 2(b)) which is entirely determined by $\xi$. We argue that this behaviour is generic in colloidal suspensions governed by hydrodynamics, since then CM mobility is not constant, but competes with $\xi$. However, the actual form of $D_C(\rho)/D_0$ may vary from one system to another, depending on the details of interactions and the impact of the HIs.

\cite{3}The CM mobilities $D_{cm}(\rho)$ have been determined from $D_{cm}(\rho, t)$ in the same manner as the effective self-diffusion coefficients $D_T(\rho)$ have been obtained from $D_T(\rho, t)$.

Fig. 1 – (a) Scaled effective tracer diffusion coefficients $D_T(\rho, t)/D_0(t)$ as a function of $t$ for $Sc \approx 1$. These data have been obtained from simulations without colloid-solvent interactions. The colloidal densities from top to bottom are 0.1232, 0.2464 and 0.3697. (b) Scaled effective tracer diffusion coefficients $D_T(\rho)/D_0$ as a function of $\rho$ for $Sc \approx 1$ (open circles), $Sc \approx 20$ (open triangles) and $Sc \approx 100$ (open boxes). For reference, results without HIs \cite{9} are also presented (solid circles).
**Fig. 2** – (a) Scaled CM mobility $D_{cm}(\rho)/D_0$ as a function of $\rho$ for $Sc \approx 1$. The inset shows the thermodynamic factor $\xi$ from the Boublik approximation [21]. (b) Scaled effective collective diffusion coefficients $D_{C}(\rho)/D_0$ as a function of $\rho$. Open circles are results with $Sc \approx 1$, obtained from simulations without colloid-solvent interactions. Open diamonds are results from simulations where the colloid-solvent interactions are present. Squares, in turn, are from computations where $Sc \approx 100$. For reference, the solid line is $D_{C}(\rho)/D_0$ in the case where HIs have not been taken into account [9].

**Concluding remarks** – We have presented a detailed numerical study of the effects of hydrodynamics on both self- and collective diffusion of 2D repulsive colloidal particles. This has been achieved by using a novel hybrid mesoscopic scheme for two-component liquids. We have found that the effective tracer diffusion coefficient $D_T(\rho)/D_0$ is enhanced by HIs, an effect which becomes more pronounced with an increasing Schmidt number. A more dramatic change has been found in the behaviour of the effective collective diffusion coefficient $D_{C}(\rho)/D_0$, which is completely changed by hydrodynamics. This is due to the dynamic term which now competes directly with the thermodynamic factor, leading to non-monotonic behaviour in contrast with the case of purely dissipative dynamics. It is an interesting question how these results are affected when changing from a 2D to a confined 3D geometry as in thin films, and how effective interactions obtained from experiments [3] would be manifested in the collective diffusion. Work in this direction is in progress.

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