Structure and Dynamics of Wall-Confined Colloids

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The confinement of a dispersion of colloidal particles can lead to interesting static and dynamic features not observed in bulk systems. The aim of this work is to assess the influence of the complicated many-body hydrodynamic interactions (HI) on the particle dynamics by calculating various dynamical properties and pointing to interesting hydrodynamic effects. To analyze the influence of HI on the dynamics of wall-confined charged and neutral colloidal particles, we have employed a Stokesian Dynamics (SD) simulation technique [1]. This powerful method can be applied to a variety of colloidal systems where HI effects need to be accounted for with good accuracy. To keep the numerical effort manageable, we have only considered the lateral diffusion of interacting colloidal particles within the midplane between the two parallel plates, separated by a fixed distance $h = 2\sigma$. Here, σ is the diameter of the particles. In the case of charged particles, we have used an effective pair potential of Yukawa type with a screening parameter depending on the plate separation [2].

The SD evolution equation for the trajectories of N identical spherical Brownian particles immersed in an incompressible fluid of shear viscosity η follows from a two-fold time integration (i.e. coarse-graining) of the many-particle Langevin equation. To describe the hydrodynamic influence of the two confining planes, we have used a superposition of the image force description for colloids in the presence of a single plane with stick boundary conditions [3,4]. In our SD simulations, typically $N = 200$ particles were equilibrated in a square replicated periodically. After equilibration, several thousand configurations were generated for calculating various properties.

To assess the importance of HI on the dynamics, we have analyzed the mean squared displacement (MSD) $W(t)$ of the particles, as well as real-space van Hove functions and the hydrodynamic function $H(q)$. We have further investigated static properties like the radial distribution functions, $g(r)$, and the static structure factor, $S(q)$, in two dimensions [4].

In Fig. 1, we present self-diffusion SD results for effective charge numbers $Z^* = 10^2$ and $Z^* = 10^3$, respectively, at plate separation $h = 2\sigma$ and area fraction $C = N\pi a^2/A = 0.063$. We distinguish the case, labeled as full HI, where HI are accounted for (including the effect of the walls) from the case where particle-particle HI is neglected and where only particle-wall HI are accounted for (labeled as p-w HI). The MSD with full HI acting among the particles, and the particles and the walls, is compared with the corresponding result where particle-particle HI are disregarded. Consider first the system of less charged particles with $Z^* = 10^2$. As seen, inclusion of p-p HI gives rise to a hydrodynamic reduction of the MSD as observed also for neutral particles. In contrast, strongly charged particles with $Z^* = 10^3$ behave qualitatively different: far-field HI prevailing in systems of strongly repulsive particles support the diffusion of a particle out of its dynamic cage of neighboring particles. This leads to a hydrodynamic enhancement of $W(t)$ at intermediate and long times. Hard-sphere-like systems are most strongly

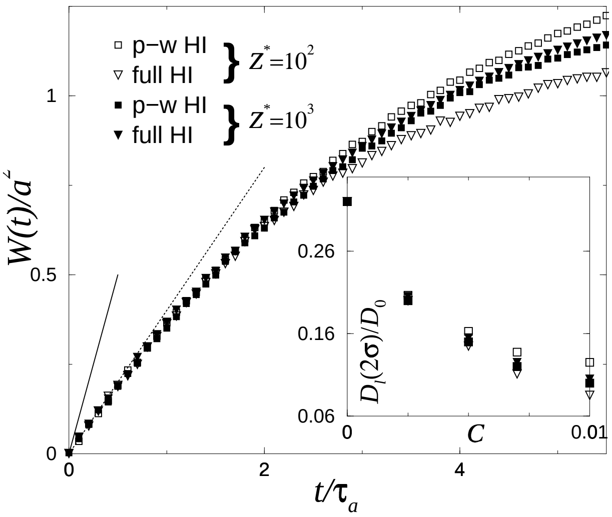

Figure 1: Lateral MSD $W(t)$ for a monolayer of charged spheres vs. reduced time for full HI and p-w HI only. Here $\tau_a = a^2/D_0$, where a is the particle radius and D_0 the bulk self-diffusion coefficient of an isolated sphere. Two charge numbers are considered: $Z^* = 10^2$ and 10^3. Solid line segment indicates the slope, D_0, of the MSD for a free particle in the bulk fluid; the dotted line is the slope, $D_0(2\sigma)$, of the MSD for an isolated particle in the midplane between two walls separated by $h = 2\sigma$. Inset: long-time self-diffusion coefficient $D_l(2\sigma)/D_0$ vs. area fraction C. Shown are hard sphere results with full HI (open triangles) and with p-w HI (open squares), in comparison with results for charged particles of $Z^* = 10^2$ with full HI (filled squares) and p-w HI (filled triangles).

affected by near-field HI, since the position r_m of the principal peak of $g(r)$ is close to the contact distance σ. Near-field HI always causes thus a slowing down of the particle motion. For $Z^* = 10^2$, the principal peak of $g(r)$ appears at a value significantly smaller than the geometrical mean interparticle distance, explaining thus the observed hydrodynamic reduction of $W(t)$. The long-time self-diffusion coefficient in the case where HI are completely neglected is significantly larger than when full HI are considered, since there is no retarding hydrodynamic influence of the confining walls.

We mention that hydrodynamic enhancement of the long-time self-diffusion coefficient, D_l, which is the long-time slope of the MSD, was theoretically predicted for three-dimensional charged-stabilized suspensions in [5], and experimentally verified subsequently [6].

SD results for $D_l(h = 2\sigma)$ vs. area fraction are shown in the inset of Fig. 1 for the opposite cases of neutral hard spheres, and highly charged particles with $Z^* = 10^3$, for full HI and p-w HI. Inclusion of particle-particle HI leads to a visible increase (decrease) of D_l for highly charged (neutral) wall-confined colloidal spheres.

SD results for the self and distinct van Hove functions $G_s(r,t)$ and $G_d(r,t)$ with $Z^* = 10^3$ are included in Fig. 2. It is remarkable that self-motion (i.e. $G_s(r,t)$) is most strongly affected by p-w HI, whereas dynamic pair correlations (i.e. $G_d(r,t)$) are dominated by p-p HI.

Results for the two-dimensional hydrodynamic function $H(q)$ are shown in Fig. 3 for hard spheres and charged particles with $Z^* = 10^3$ (inset). The undulations in $H(q)$ grow larger for increasing C in case of hard spheres. The local maximum of $H(q)$ at wave-number $q = q_m$

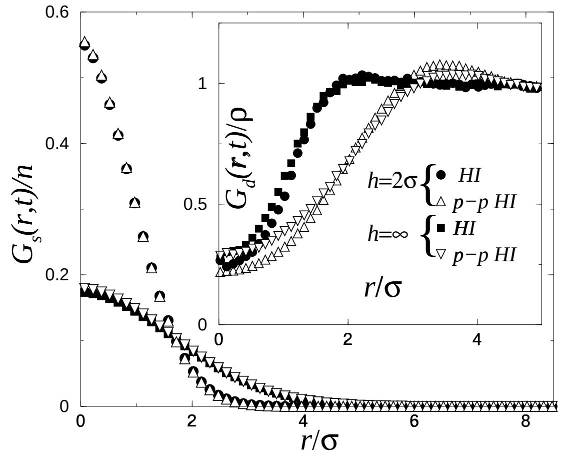

Figure 2: Reduced self and distinct (inset) van Hove functions, $G_s(r,t)/n$ and $G_d(r,t)/n$ for charged particles with $Z^* = 10^3$, area fraction $C = 0.063$, $t = 3.5\tau_a$ and $h = 2\sigma$.

is smaller than one and decreases with increasing C, with q_m shifted to slightly larger values of q. This behavior of $H(q)$ is similar to the one observed for the hydrodynamic function of three-dimensional suspensions of colloidal hard spheres. The q-dependence of $H(q)$ for charged systems is qualitatively different since $H(q_m)$ is now larger than one and increases monotonically with C. A monotonic increase in $H(q_m)$ for increasing concentration is further observed in three-dimensional charge-stabilized suspensions. As discussed in full detail in [7], $H(q_m)$ refers to particle pairs separated by the next-neighbor shell radius r_m and moving in opposite directions. Hard spheres are dominated by near-field HI since $r_m = \sigma$, which results in a reduction of the antagonistic motion of a particle pair due to the laminar friction in the thin coating of solvent sticking to the surfaces of both particles. Therefore, $H(q_m) < 1$ in case of hard spheres. The dynamics of charged particles, on the other hand, is dominated by far-field HI which favors the antagonistic motion of particle pairs separated by $r_m \geq 2\sigma$ due to a cumulative solvent back-flow effect. This leads for charged spheres at small C to values $H(q_m) > 1$. There is a striking difference in the small-q behavior of $H(q)$ between three-dimensional and quasi-two-dimensional colloids. Whereas $H(q \approx 0) < 1$ in the three-dimensional case, the SD results of Fig. 3 reveal a strong increase of $H(q)$ at small q, suggesting $H(q)$ to diverge as $q \to 0$. The unbounded increase of $H(q)$ for $q \to 0$ is due to the lateral confinement with no off-plane motion of the particles. By using a point force approximation for the mobility tensor, we find an expression for $H(q)$ with a first-order pole at $q = 0$ [8]. This divergence of $H(q)$ is a characteristic feature of two-dimensional systems. It depends not on the pair potential acting between the colloids. As a result, the two-dimensional dynamic structure factor $S(q,t)$ decays as $S(q,t)/S(q) \approx \exp[-(3CD_0(h)/\sigma)qt]$ for q and t small. In Fig. 3, we have included the graphs of the asymptotic term of $H(q)$ (of the form $1+3C/q\sigma$). The small-q part of the SD $H(q)$ is well described by this singular form even in the presence of the walls. The hydrodynamic influence of the walls on $H(q)$ becomes manifest only at intermediate values of q, where it gives rise to a small increase in $H(q)$.

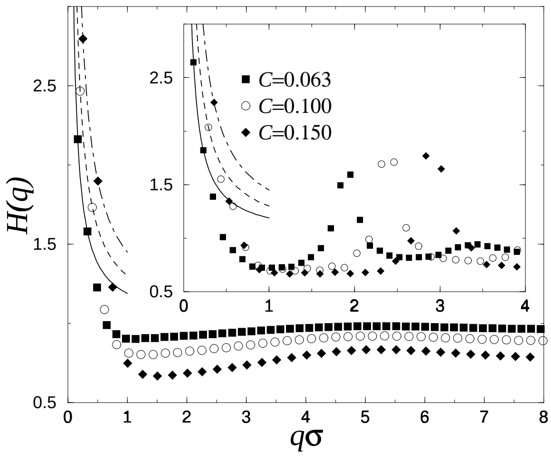

Figure 3: Hydrodynamic function at plate separation $h = 2\sigma$ for hard spheres and charged particles (shown in the inset) with $Z^* = 10^3$. Further shown is the asymptotic part, $1 + 3C/q$, of $H(q)$ for $C = 0.063$ (solid line), $C = 0.1$ (dashed line) and $C = 0.15$ (dashed-dotted line).

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