Short-Time Dynamics in Quasi-Two-Dimensional Colloidal Suspensions

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The short-time dynamic properties of colloidal particles in quasi-two-dimensional geometries are studied by digital video microscopy. We demonstrate experimentally that the effective-two-dimensional physical quantities such as the dynamic structure factor, the hydrodynamic function, and the hydrodynamic diffusion coefficients are related in exactly the same manner as their three-dimensional counterparts.

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The motion of colloidal species in confined geometries, e.g., porous media, capillaries, microfluidic devices, and rock fractures, is of great interest in various areas of science and technology [1–11]. In the bulk, the dynamic properties depend on the interparticle interactions, both direct and hydrodynamic [12,13]. Under confinement, the particles also interact with the confining walls, and, therefore, the description of the dynamics has to incorporate also the particularities of the confining geometry. Thus, while in homogeneous three-dimensional (3D) colloidal systems there are well defined relationships between the different physical quantities describing the dynamical properties, under confinement the complexity introduced by the geometry makes uncertain whether any relationship could be established.

In this Letter, we demonstrate experimentally that, in quasi-two-dimensional (Q2D) systems, the quantities describing the short-time dynamics of the confined colloids maintain a relationship with exactly the same structure as their 3D counterparts. In Q2D systems, a colloidal suspension is confined between two parallel flat walls, separated by a distance only slightly larger than the particle's diameter. The reduced gap between the plates allows only small excursions of the particles in the perpendicular direction (z), and their main motion is then along the plane (x, y) parallel to the walls. Thus, the systems are regarded as effectively two-dimensional (2D), and the dynamic quantities, such as the mean squared displacement, the dynamic correlation function, and the hydrodynamic diffusion coefficients, are measured as if the system was actually two-dimensional. Those effective-2D quantities carry, nevertheless, implicitly the effect of the direct and hydrodynamic particle-walls interactions.

In homogeneous 3D colloidal systems, the dynamical properties are described by a set of physical quantities with a well defined interrelationship [12,13]. In such a case, the general quantity describing the dynamic properties is the dynamic structure factor $F_{3D}(k, t)$, which is the k-Fourier component of the time correlation function of the fluctuations, of wavelength $\lambda = 2\pi/k$, of the local particle concentration. This quantity can be expressed in terms of other quantities describing the effects of the direct and hydrodynamic interactions on the collective and self-diffusion motions at different time scales. For instance, at short times, within the diffusion regime, $F_{3D}(k, t)$ decays exponentially, i.e.,

$$F_{3D}(k, t) = S_{3D}(k) \exp[-k^2 H_{3D}(k) t / S_{3D}(k)]. \quad (1)$$

Here $S_{3D}(k) \equiv F_{3D}(k, 0)$ is the static structure factor, a quantity depending only on the direct interparticle interactions, and $H_{3D}(k)$ is the hydrodynamic function, a quantity describing the collective hydrodynamic interactions between the particles. The hydrodynamic function can be expressed in terms of the configuration average of the diffusion tensors $\boldsymbol{D}_{lj}^{3D}(\boldsymbol{r}^N)$, which are N-particle correlation functions describing the hydrodynamic coupling between particles l and j in the presence of the other $N - 2$ particles in the system, i.e.,

$$H_{3D}(k) = \left\langle \frac{1}{N} \sum_{l,j=1}^{N} \hat{\boldsymbol{k}} \cdot \boldsymbol{D}_{lj}^{3D}(\boldsymbol{r}^N) \cdot \hat{\boldsymbol{k}} \exp(i\boldsymbol{k} \cdot [\boldsymbol{r}_l - \boldsymbol{r}_j]) \right\rangle, \quad (2)$$

with the components of the diffusion tensor given by [14]

$$D_{lj}^{\alpha\beta}(\boldsymbol{r}^N) \equiv \frac{\langle \Delta x_l^{\alpha}(t) \Delta x_j^{\beta}(t) \rangle}{2t}. \quad (3)$$

Here $\Delta x_l^{\alpha}(t)$ is the displacement of the particle l in the direction α at time t, and the angle brackets in Eqs. (2) and (3) mean an equilibrium ensemble average. In principle, Eqs. (1)–(3) can also be established for strictly two- and one-dimensional systems. As we show below, those relations also remain valid for the effective-2D quantities measured in Q2D systems.

Quasi-two-dimensional colloidal suspensions are prepared following a standard procedure [8,15]. Briefly, monodisperse water suspensions of polystyrene spheres carrying negatively charged sulfate end groups on the surface are extensively dialyzed against nanopure water to eliminate the surfactant added by the manufacturer (Duke Scientific). In a clean atmosphere of nitrogen gas, the suspension of particles of diameter $\sigma = 2.05 \pm 0.06\ \mu$m is mixed with a small amount of larger particles of diameter $h = 2.92 \pm 0.09\ \mu$m. A small volume of the mixture ($\approx 1\ \mu$l) is confined between two clean glass plates (a slide and a cover slip), which are uniformly pressed one against the other until the separation between the plates is h. Thus, the larger particles scattered across the sample serve as spacers with an average distance of $\sim 100\ \mu$m. The system is then sealed with epoxy resin, and the species of mobile particles is allowed to equilibrate in this confined geometry at room temperature ($27.7 \pm 0.1\ ^\circ$C). The samples are observed from a top view (perpendicular to the walls plane) using an optical microscope, and the motion of the particles is recorded using standard video equipment. The field of view is $\sim 80 \times 60\ \mu\mathrm{m}^2$ (640×480 pixels) with $\sigma = 16.8$ pixels. From the analysis of the images, the 2D trajectories $\boldsymbol{r}_j(t)$ of the particles are determined with a time resolution $\Delta t = 1/30$ s. From $\boldsymbol{r}_j(t)$, various effective-2D physical quantities describing self- and collective dynamics along the plane of motion are obtained. All the results presented here were obtained from the analysis of 10^4–10^5 total video frames taken in short runs of 120 consecutive images at intervals of a few minutes between runs [8].

In real space, the collective motion is described by the effective-2D van Hove function $G(r, t)$, defined as the time correlation of the fluctuations of the local particle concentration, i.e., $G(r, t) \equiv N^{-1}\langle n(\mathbf{r}', t = 0) n(\mathbf{r}'', t)\rangle$, where $n(\mathbf{r}, t) = \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_j(t))$ is the 2D local concentration of particles at the 2D position $\mathbf{r}$ and time t, with $r \equiv |\mathbf{r}'' - \mathbf{r}'|$. At time $t = 0$ and $r > 0$, $G(r, 0) = n^* g(r)$, $n^* \equiv n\sigma^2$ is the reduced concentration, with n being the average number of particles per unit area, and $g(r)$ is the effective-2D pair correlation function. In analogy to 3D, we define here the effective-2D dynamic structure factor $F(k, t)$ as the 2D-Fourier transform of $G(r, t)$ and the effective-2D hydrodynamic function $H(k)$ as the initial slope of $F(k, t)$ in analogy to Eq. (1). Measurements of $F(k, t)$ and $H(k)$ as described above were reported in a previous work [8]. Those results are compared here with the results for the hydrodynamic function obtained from measurement of the diffusion coefficients as described below.

The components of the effective-2D hydrodynamic diffusion tensors can be determined in a laboratory-fixed reference system using Eq. (3). In the case where $l = j$ and $\alpha = \beta$, we have $D_{ll}^{\alpha\alpha} \equiv D_s$ for $l = 1, 2, \ldots, N$ and $\alpha = x, y$, with D_s being the short-time self-diffusion coefficient, a quantity describing single particle diffusion in a N-particle system. In the case $l \neq j$, the diffusion coefficients $D_{lj}^{\alpha,\beta}$ characterize the hydrodynamic coupling between particles l and j by cross-correlating the fluctuations of their positions along the Cartesian coordinates. It is usually more convenient to describe the coupled motion of a pair of particles in terms of the dynamics of their relative position $\boldsymbol{r} = \boldsymbol{r}_l - \boldsymbol{r}_j$ and of their center of mass $\boldsymbol{c} = \boldsymbol{r}_l + \boldsymbol{r}_j$ (the collective mode). Changes in the collective and relative variables can be decomposed in components along the parallel ($\|$) and the perpendicular ($\perp$) directions to the line connecting the particles centers at time $t = 0$, i.e., $\Delta\boldsymbol{c}(t) \equiv (\Delta c_{\|}(t), \Delta c_{\perp}(t))$ and $\Delta\boldsymbol{r}(t) \equiv (\Delta r_{\|}(t), \Delta r_{\perp}(t))$. Then the hydrodynamic coupling of a pair of particles is characterized by collective and relative diffusion coefficients denoted here as $D_{c,\|}$, $D_{c,\perp}$, $D_{r,\|}$, and $D_{r,\perp}$ and defined as $D_{m,p} \equiv \langle \Delta m_p(t) \Delta m_p(t)\rangle / 2t$, where $m = r, c$ and $p = \|, \perp$. Both sets of diffusion coefficients, $D_{lj}^{\alpha,\beta}$ and $D_{m,p}$, are related one to the other by a simple rotation. Here we measure and present results for $D_{m,p}$ in order to compare with results reported recently [11]. The coefficients are determined as follows. We select a pair of particles at a distance r within a small range $\delta r = 0.05\sigma$. From short-time trajectories of both particles, the autocorrelation of $\Delta m_p(t)$ is determined. The time should be short enough to ensure that changes in r are within δr and that the correlation is linear with time. In our systems, this is accomplished for times $\sim 5\Delta t$. The diffusion coefficient $D_{m,p}$ is then given by the initial slope of the correlation function. This procedure is applied to every pair of particles in the field of view, obtaining in this way the diffusion coefficient as a function of the interparticle distance r. This measurement is repeated at different times and the results are averaged to yield smooth curves with very small experimental uncertainties (within the symbol size of the figures below).

Figure 1 shows the hydrodynamic diffusion coefficients vs the interparticle distance r for $\phi_a = 0.23$ (a) and 0.42 (b), where $\phi_a \equiv \frac{\pi}{4} n^*$ is the particle area fraction. Circles correspond to the collective mode in the parallel (solid symbols) and perpendicular (open symbols) directions, whereas the relative mode is represented by triangles. The insets show the corresponding measured effective-2D radial distribution functions for both systems (open circles), compared with Monte Carlo (MC) computer simulations of 2D hard-disk systems at the same area fractions (lines). This comparison shows that the interparticle repulsive interaction is screened by the ionic species dissociated from the glass walls and the particle behavior resembles a system of hard spheres. Thus, the diffusion coefficients in Fig. 1 contain only the effect of the hydrodynamic coupling between particles and that of the excluded volume interaction, except at distances close to contact where the particles also feel the screened electrostatic interaction. The hydrodynamic diffusion coefficients for a pair of isolated hard spheres in a homogeneous unbounded fluid has interesting features, which we summarize here in order to compare with the results in confined systems [14,16]. In that case, the hydrodynamic coupling is long ranged with the leading term being r^{-1}; both collective diffusion modes (parallel and perpendicular)

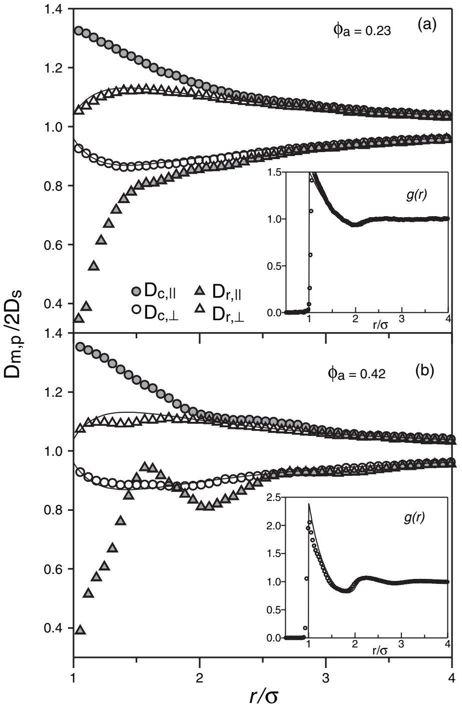

FIG. 1. Normalized diffusion coefficients vs interparticle distance r. The insets show the experimental radial distribution function (open circles) compared to MC simulations of hard disks (solid lines).

are enhanced, while both relative motions are suppressed; there is symmetry around the asymptotic value between the parallel modes and between the perpendicular modes. In Q2D systems, we found that the hydrodynamic interactions are also long ranged but decay faster; our results are consistent with r^{-2} (see below). Here the perpendicular modes are anomalous. They have the opposite behavior of their 3D counterparts; i.e., the collective diffusion is suppressed while the relative motion is enhanced; the symmetry between the perpendicular modes is maintained but not between the parallel modes. As is shown here, only the relative parallel coefficient depends strongly on the particle concentration. The shape of the collective parallel coefficient $D_{c,\|}$ shows also some structure, but it is less dependent on particle concentration. The perpendicular modes are symmetric and fit well to a function of the form $D_{m,\perp}/2D_s = 1 \pm a(r^{-2} - br^{-3})$ for $m = r$ and c, respectively. From the analysis of the systems studied here, we found a and b to be almost independent of particle concentration. The solid lines in Fig. 1 are the functions $D_{m,\perp}/2D_s = 1 \pm \frac{4}{5}(r^{-2} - 0.95r^{-3})$. Thus, $D_{r,\|}$ depends more strongly on the interparticle direct interactions than the other modes.

Figure 2 shows the behavior of the normalized diffusion coefficients at long interparticle separations for various particle concentrations. As one can see here, for $r > 3\sigma$, which is the range of the pair correlation functions (see insets in Fig. 1), the decay of the 4 modes (symbols) becomes independent of particle concentration and the symmetry between the parallel and between the perpendicular modes is recovered. The solid lines are the functions $\pm\frac{4}{5}r^{-2}$, which fit well the experimental data at long r. The asymptotic r^{-2} decay of $D_{m,p}$ was reported, and rationalized in terms of a *mass dipole* contribution to the flow field, by Cui *et al.* [11]. The anomalous behavior of the perpendicular modes was also reported by those authors. However, they did not observe the symmetry between $D_{c,\perp}$ and $D_{r,\perp}$ with respect to $2D_s$ being reported here.

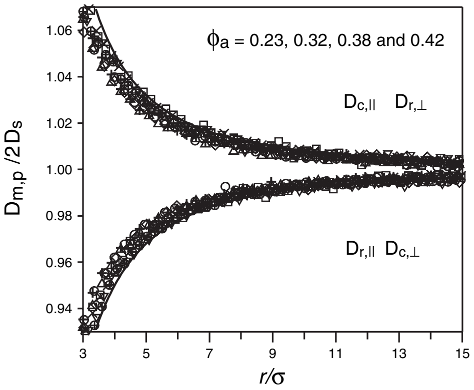

FIG. 2. Asymptotic behavior of the hydrodynamic modes (symbols). The solid lines are the functions $\pm\frac{4}{5}r^{-2}$.

Let us now focus on the main objective of this work, i.e., on the relationship between the physical quantities describing the dynamic properties of colloidal particles in Q2D systems. As mention above, here we are concerned with the quantities describing the short-time dynamics and, in particular, those describing the hydrodynamic interactions, such as the two-body hydrodynamic correlation described by $\boldsymbol{D}_{lj}$ and the collective hydrodynamic coupling described by the effective-2D hydrodynamic function $H(k)$, which, in analogy with Eq. (1), is defined as the initial slope of the effective-2D dynamic structure factor, i.e., $H(k) = -S(k)k^{-2}\ln[F(k,t)/S(k)]$. Let us stress here the fact that the latter is just a definition since no formal expression for the actual hydrodynamic function for Q2D systems has been derived yet. Thus, one could equally well use the 2D version of Eq. (2) as the definition of the hydrodynamic function $H'(k)$. Then the question here is whether these two quantities describe the same physics, at least qualitatively. In other words, the question is whether Eq. (2) is indeed the microscopic expression for the initial slope of $F(k,t)$ in terms of (effective-2D) two-body hydrodynamic correlations. In order to answer this question, we evaluate the 2D version of Eq. (2), substituting the tensors $\boldsymbol{D}_{lj}^{3D}$ by the measured effective-2D $\boldsymbol{D}_{lj}$. The Cartesian components of the diffusion tensors are obtained from $D_{m,p}$ by a simple rotation. The final expression, after some straightforward algebra, is

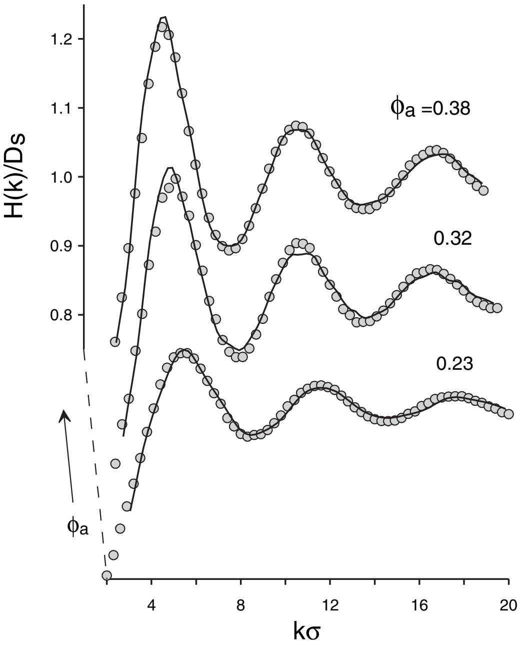

FIG. 3. Effective-2D hydrodynamic function $H(k)$ vs k, obtained from measurements of the initial slope of the dynamic structure factor [8] (lines) and from measurements of the diffusion tensors according to Eq. (4) (symbols).

$$H'(k) = D_s\left[1 + \frac{2\phi_a}{D_s\sigma^2}\int drrg(r)f(k,r)\right], \qquad (4)$$

where $g(r)$ is the effective-2D radial distribution function and $f(k,r) \equiv J_0(kr)[D_{c,\parallel} - D_{r,\parallel}] + J_1(kr)(kr)^{-1} \times [D_{c,\perp} - D_{c,\parallel} + D_{r,\parallel} - D_{r,\perp}]$, with $J_0(kr)$ and $J_1(kr)$ being the Bessel functions of order 0 and 1, respectively.

Figure 3 shows $H'(k)$ obtained from the evaluation of Eq. (4) for 3 high concentration systems (symbols). We also plot $H(k)$ for the same systems (solid lines), obtained from the initial slope of $F(k,t)$ as reported in Ref. [8]. As one can see here, there is an excellent agreement between both quantities. Let us stress that this remarkable coincidence between both measurements could not be anticipated since (i) both quantities are obtained following very different routes; in one case the collective correlation function is measured, whereas in the other case one measures the dynamic correlation between pairs of particles; and (ii) the behavior of the effective-2D diffusion coefficients is qualitative and quantitatively different from that of their 3D counterparts. This result validates the 2D version of Eq. (2) as the microscopic expression for the effective-2D hydrodynamic function and allows us to define unambiguously this physical quantity describing the effect of the hydrodynamic interactions in the short-time colloidal dynamics.

The main result of the present work is the experimental demonstration that the effective-2D quantities used to describe the dynamical properties of colloidal particles in Q2D geometries at short times satisfy exactly the same relationship as their 3D counterparts. In other words, we demonstrate that the short-time collective dynamics [i.e., $F(k,t)$] can be recovered from measurements of two-body hydrodynamic correlations, exactly in the same way as it can be done in homogeneous 3D systems. This result poses the problem of its formal derivation, but it is beyond the aim of the present work. Nevertheless, let us note that this might be a property of confined systems which are homogeneous and isotropic along the unbounded dimensions, and, thus, it should also be true for other geometries such as quasi-one-dimensional systems (for instance, particles in a cylindrical capillary). Finally, let us note that our measurements of the diffusion coefficients exhibit feature some in agreement and others in disagreement with those reported by other authors [11]. This issue is interesting and will be discussed in more detail elsewhere.

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