Collective Dynamics in Quasibidimensional Colloidal Suspensions

H. Acuña-Campa, M. D. Carbajal-Tinoco,* J. L. Arauz-Lara, and M. Medina-Noyola

Instituto de Física "Manuel Sandoval Vallarta," Universidad Autónoma de San Luis Potosí,
Alvaro Obregón 64, 78000 San Luis Potosí, S.L.P., México

We report the direct measurement by video microscopy of the Van Hove function of quasi-two-dimensional colloidal suspensions. Under these conditions of confinement, the effective interparticle potential exhibits an intermediate range attractive component. This is obtained by deconvoluting the measured pair correlation function using an inverse Monte Carlo method. The experimental dynamic behavior is well represented by a Brownian dynamics simulation, performed using the experimental pair potential and an effective quasi-two-dimensional short-time diffusion coefficient. [S0031-9007(98)06595-8]

PACS numbers: 82.70.Dd, 05.40.+j

The study of colloidal suspensions under conditions of severe confinement is a topic of considerable current interest. This is due to the practical importance of such systems, and to the many fundamental questions that these systems present to the field of colloid physics. To illustrate the latter, let us mention the recent measurements of the effective pairwise forces between charged spherical particles of aqueous suspensions confined between two glass plates [1–3]. These measurements suggest that two charged particles under those conditions of confinement attract, rather than repel, each other at intermediate distances. So far, there is not a plausible explanation of such an attractive component of the measured effective pair potential, $u^{ef}(r)$. Because of the fundamental relevance of this observed feature, it is worthwhile to characterize in still more detail the properties of these effective forces, through the measurement of other properties that depend on them. This is what we do in this work by analyzing the Van Hove function of the system.

For this, it is instructive to recall what was the situation with respect to the same system (an aqueous suspension of highly charged colloidal particles) in the absence of confinement, i.e., in the three-dimensional bulk. In this case, the direct measurement of the forces between two particles was performed rather recently [3,4]. However, the indirect determination of these forces had been made many years before. Thus, in a first step, the static structure factor of the suspension, measured by static light scattering, was employed to determine the effective pairwise forces by adjusting the experimental data using computer simulations and approximate liquid state theories [5–7]. Then, this experimentally extracted pair potential was employed to do Brownian dynamics simulations of the main dynamic properties of the suspension, and the predictions were compared with dynamic light scattering results [5–7]. The agreement was a further evidence of the accuracy of this indirect experimental determination of the effective pair potential, for which a theory was already available, namely, that developed by Derjaguin, Landau, Verwey, and Overbeek (DLVO) [8]. In contrast, in our

present case, no theory analogous to the DLVO theory is available. However, the effective pair potential has been determined indirectly [1,2], by measuring the radial distribution function $g(r)$ by digital video microscopy (DVM) and extracting the effective forces using liquid-state theory approximations. The first contribution of this work consists in refining this indirect determination by employing Monte Carlo (MC) computer simulations to deconvolute the effective pair potential $u^{ef}(r)$ from $g(r)$. In a second step, we use this experimental pair potential in an idealized Brownian dynamics (BD) experiment to simulate the most detailed dynamic property of the system, namely, the Van Hove function $G(r, t)$. We then compare these results with the actual measurements by video microscopy of $G(r, t)$ on the real system. This direct measurement of the real $G(r, t)$ in this type of system is another relevant contribution of this work.

In the present conditions, our aim is to see only to what extent the dynamics of the idealized computer simulated system resembles the dynamics of the real system. The main reason for not expecting full agreement has to do with still another fundamental complication that appears when a colloidal suspension is severely confined. Highly charged colloidal particles in bulk aqueous suspensions are strongly structured even at very low volume fractions. Thus, hydrodynamic interactions can be neglected [9]. Under such conditions, the dynamic properties of the suspension depend on, besides on the effective forces, only one single additional parameter, namely, the short-time diffusion coefficient D^S. This parameter can be experimentally determined by measuring the self-diffusion behavior in the short-time regime, i.e., at times $t \ll \tau_I$, where τ_I is the mean collision time. Furthermore, for highly charged particles in the 3D bulk, D^S does not depend on concentration [9], and, hence, it is identical to its infinite-dilution value D_0, which can be determined by its Stokes-Einstein value, i.e., $D^S = D^0 \equiv k_B T / \zeta^0$. In contrast, in our present case we do not know of an accurate expresion for D^0, which now should also depend on the separation of

the confining plates. Furthermore, there is no reason to assume that the short-time self-diffusion coefficient D^S is independent of concentration. The very presence of attractive interactions between the particles, and the strong screening due to counterion dissociation from the plates, may lead to important contributions from hydrodynamic interactions. However, for a given system, one may attempt to experimentally measure D^S, and this value can be used in an idealized Brownian dynamics simulation experiment [5,10], expecting that the only effect of hydrodynamic interactions is to set the value of D^S, but other than that, the real system behaves as if it were free from those dissipative forces, just as in the idealized computer simulation experiment. There are good reasons to expect this, since such an assumption has proved to be quite useful, at least in the case of highly concentrated monodisperse hard sphere suspensions [11].

Thus, the purpose of the work described in this Letter is to test the capability of the effective pair potential determined from the MC deconvolution to reproduce, when employed in an idealized Brownian dynamics simulation, the main features of the experimentally determined Van Hove function of the system. At the same time, however, we also test the conjecture that the experimentally determined D^S embodies the most important effects of the complex hydrodynamic interactions of the real system.

Let us first briefly describe the experimental system studied here. This is a quasi-two-dimensional aqueous suspension of polystyrene spheres of diameter $\sigma = 0.5\ \mu$m. The suspension is confined between two glass plates. A very small amount of larger polystyrene spheres (diameter 1 or 2 μm) added in the suspension serve as spacers between the plates and allows us to accurately control their separation. Further details on the preparation of this system are provided in Ref. [12]. The sample is observed using an optical microscope with a CCD camera attached to it, and the motion of the particles is recorded for its analysis. Several runs of 750 consecutive frames are digitized and the particles' positions determined [12] with a time resolution of $1/30$ s. Static and dynamic properties such as $g(r)$ and $G(r,t)$ are then determined. These properties reveal the space and time correlations between the colloidal particles induced by the interactions of the particles between them and with their surroundings. The most fundamental quantity describing those correlations is the Van Hove function [13]. For homogeneous and isotropic systems $G(r,t)$ is written as $G(r,t) = \frac{1}{n}\langle n(\mathbf{r},t)n(0,0)\rangle = \frac{1}{N}\sum_{i,j=1}^{N}\langle\delta[\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_j(t)]\rangle$, where $n(\mathbf{r},t) = \sum_{i=1}^{N}\delta[\mathbf{r} - \mathbf{r}_i(t)]$ is the local particle concentration at time t and at position $\mathbf{r}$ ($r = |\mathbf{r}|$) in a system with N particles in an area A, $\mathbf{r}_i(t)$ the position of particle i at time t, $n = N/A$ is the average particle concentration, and the angular parentheses indicate an equilibrium ensemble average. The Van Hove function can be separated in itself ($i = j$) $G_s(r,t)$ and

distinct ($i \neq j$) $G_d(r,t)$ parts, i.e., $G(r,t) = G_s(r,t) + G_d(r,t)$, where these functions describe single particle dynamics and the time correlation between the positions of different particles, respectively. At time $t = 0$, we have $G_s(r,0) = \delta(r)$ and $G_d(r,0) = ng(r)$, where $g(r)$ is the radial distribution function.

Let us point out that this $G(r,t)$ is in reality the projection, as viewed from the direction normal to the plates. Thus, it is an effective $G(r,t)$, measured as if the system were strictly two dimensional, and we do not record the coordinate z of each particle. As we comment later, this fact turns out to be of little relevance. In order to obtain the experimental effective pair potential $u^{ef}(r)$, we carry out MC simulations for a series of trial pair potentials $u(r)$ until the resulting $g(r)$ is fine-tuned to concide with the experimental data for this property. The trial functions are functional forms which initially model the pair potential obtained from the deconvolution of $g(r)$ via the two-dimensional (2D) Orstein-Zernike (OZ) equation and the hypernetted chain approximation (HNC) [2,13]. Figure 1 shows the corresponding data for $g(r)$ and $u^{ef}(r)$ for three samples studied. We should stress at this point that the MC simulations correspond also to a strictly 2D system with the same dimensionless number concentration $n^* = n\sigma^2$. From the results in Fig. 1, we can see that the experimental $g(r)$ (open circles) for each sample is accurately reproduced by the MC simulations (solid lines). In Fig. 1 the effective pair potentials obtained from the MC inverse method (solid lines on right column) and those obtained from OZ-HNC (open circles) are also shown, which happen to coincide quite remarkably for the range of concentrations considered here. Let
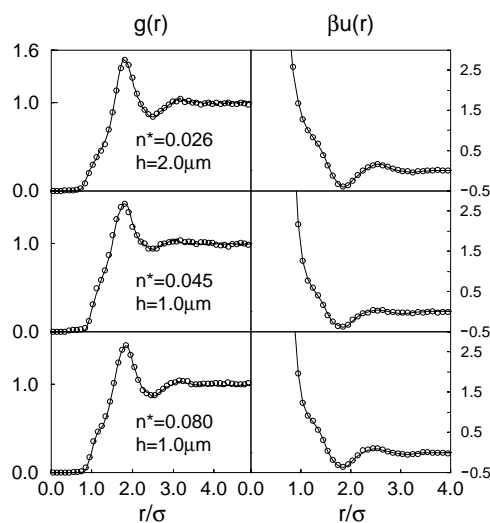

FIG. 1. Left column: Measured $g(r)$ for three different systems (open circles); n^* is the reduced particle concentration and h the plates separation. The solid lines represent 2D-MC simulation results. Right column: Experimental effective pair potential determined by deconvoluting $g(r)$ using OZ-HNC (open circles) and 2D-MC (solid lines).

us also mention that the MC results for $g(r)$ are quite sensitive to the input $u(r)$, i.e., in order to reproduce accurately the features of the experimental data, the pair potential used in the simulated experiment must contain exactly all the features displayed in Fig. 1.

The Van Hove function at $t = 0$, $G(r,0)$, consists of a delta function representing self-correlations, and a second component given by the radial distribution function representing the correlations between distinct particles. Thus, Fig. 1 shows basically the case $t = 0$. Figure 2 shows the measured Van Hove function for the three samples (open circles) at five different later times. Here, we can look separately at the time evolution of both components $G_s(r,t)$ and $G_d(r,t)$. For instance, at a given time, going from the left to the right column, i.e., from the less confined system (larger separation between the plates and lower particle concentration) to the most confined system studied here (smaller plates separation and higher particle concentration), one can see that $G_s(r,t)$ [the part of $G(r,t)$ at small values of r] spreads out faster for the less confined system and it slows down as the confinement increases, i.e., the particles are less mobile as the confinement increases. If we go now from top to bottom, we find, as also reported elsewhere [12], that the time evolution of the self-part is well described by a Gaussian function with zero mean and dispersion $\sqrt{W(t)}$, where $W(t) \equiv \langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \rangle /4$ is the mean squared displacement of the particles along the plane of motion parallel to the glass plates [12]. Thus, the self-component of the Van Hove function is initially a narrow and sharp function and it spreads out with time as a result of particles' self-diffusion.

On the other hand, the structure of the distinct part (the oscillating part) given initially by $ng(r)$ is smeared out with time and, as in the case of the self-part, its time

evolution is slower for more confined systems. As seen in Fig. 2, the lifetime of $G_d(r,t)$ for our samples is only a few times the experimental time step $\Delta t = 1/30$ s. One can also observe that for $t \gtrsim 5/30$ s the only component still evolving is $G_s(r,t)$. One should notice that although the dynamics of the distinct part is somewhat fast for our experimental time resolution, we still capture some interesting details of its time evolution.

To compare with these experimental data of $G(r,t)$, we performed a strictly 2D Brownian dynamics computer experiment. The results for $G(r,t)$ are shown in Fig. 2 (solid lines). In the BD experiments we employed the previously determined MC pair potentials and the effective 2D short-time-diffusion coefficients D^S. The latter was determined in the following way. As a first step, we used for D^S the initial slope of the experimental $W(t)$, which contains the effect of hydrodynamic and direct interactions between the particles and between the particles and the confining walls. In practice, a more accurate determination of D^S was achieved by requiring the BD results to reproduce the experimental data for $W(t)$ at all times, which we found to be possible. Figure 3 shows the quality of the fit of the experimental data by the BD results for this dynamic quantity describing self-diffusion. The actual values for D^S obtained from this fit and employed in the simulations are only slightly higher than the very initial slope of $W(t)$. This indicates that due to the attractive interaction between the particles, the actual short-time regime ($t < \tau_I$) happens to be restricted to a time scale shorter than our experimental time resolution of $1/30$ s.

Here, we should stress the fact that with only two experimental inputs, namely, $u^{ef}(r)$ and D^S, the BD simulation exhibits remarkably well the general features of the measured $G(r,t)$, as illustrated in Fig. 2. One should notice, however, that the dynamics of the simulated $G_d(r,t)$ is somewhat slower that the experimental data. In our
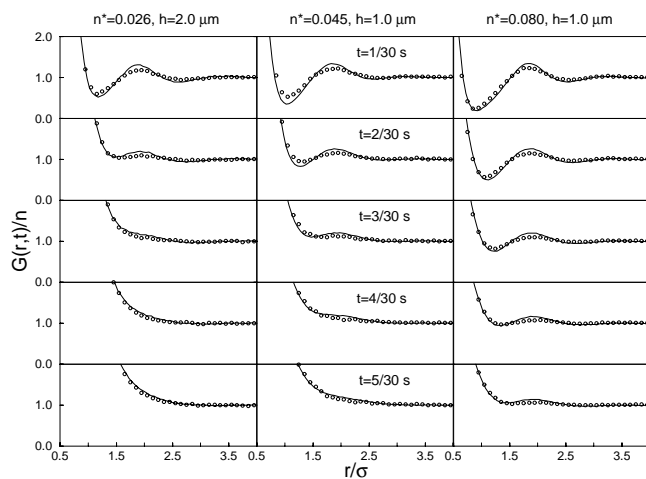
FIG. 2. The Van Hove function, at five different times, of the three samples in Fig. 1. The open circles are the experimental data from DVM and the solid lines the results from 2D-BD simulations.
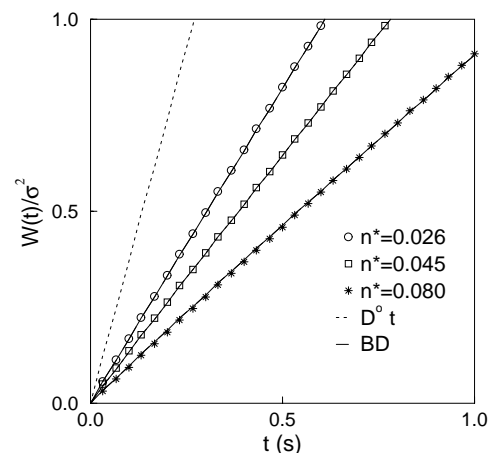
FIG. 3. Measured (symbols) and simulated (solid lines) mean squared displacement for the samples in Fig. 1. For comparison, we plot $W(t) = D^0 t$ for a freely diffusing particle in 3D.

simulations many effects present in the real systems are taken into account in a simplified manner throughout $u^{ef}(r)$ and D^S. However, one obvious effect is not considered which might be the source of the discrepancies. The real systems are quasi-two-dimensional, while our BD simulations are strictly 2D. In order to check this, we performed BD simulations for a quasi-two-dimensional geometry corresponding to the experimental systems. In the experiment we observe the particles from a top view. Since the plates separation is larger than σ, we observe an apparent overlapping, i.e., $g(r) > 0$ for $r < \sigma$ (see Fig. 1). Thus, the 2D simulation requires a soft potential inside the hard core in order to reproduce this feature of $g(r)$. On the other hand, the quasi-two-dimensional simulation reproduces that feature of the effective 2D $g(r)$ without the need of a soft potential at short distances ($r < \sigma$). This is the main difference found, which, however, does not change in any appreciable way the results for the dynamic properties. In particular, the retardation of the computer-simulated $G(r, t)$, with respect to its experimental counterpart, remains the same as in Fig. 2. Thus, other effects such as the hydrodynamic interactions, which are only partially accounted for through the value of D^S, must be responsible for the quantitative discrepancies observed. Such effects may then be important, and, hence, should be studied in more detail. However, the overall agreement between the simulated and the experimental $G(r, t)$ in Fig. 2 constitute an additional evidence of the overall accuracy of $u^{ef}(r)$, determined in Fig. 1, as the true effective pair potential describing the direct interactions between the particles in the confined colloidal system.

---

*Present Address: Departamento de Física, Centro de Investigación y de Estudios Avanzados del IPN, Apdo. Postal 14-740, 07000 México D.F., Mexico.

[1] G. M. Kepler and S. Fraden, Phys. Rev. Lett. **73**, 356 (1994).

[2] M. D. Carbajal-Tinoco, F. Castro-Román, and J. L. Arauz-Lara, Phys. Rev. E **53**, 3745 (1996).

[3] J. C. Crocker and D. G. Grier, Phys. Rev. Lett. **77**, 1897 (1996).

[4] J. C. Crocker and D. G. Grier, Phys. Rev. Lett. **73**, 352 (1994).

[5] W. van Megen and S. M. Underwood, J. Chem. Phys. **88**, 7841 (1988), and references therein.

[6] G. Nägele, M. Medina-Noyola, R. Klein, and J. L. Arauz-Lara, Physica (Amsterdam) **149A**, 123 (1988).

[7] (a) R. Krauze, G. Nägele, D. Karrer, J. Schneider, R. Klein, and R. Weber, Physica (Amsterdam) **153A**, 400 (1988); (b) R. Krause, J. L. Arauz-Lara, G. Nägele, H. Ruiz-Estrada, M. Medina-Noyola, R. Weber, and R. Klein, Physica (Amsterdam) **178A**, 241 (1991).

[8] E. J. W. Verwey and J. T. G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948).

[9] P. N. Pusey, in *Liquids, Freezing and Glass Transition,* edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (Elsevier, Amsterdam, 1991), p. 763.

[10] D. L. Ermak and J. A. McCammon, J. Chem. Phys. **69**, 1352 (1978).

[11] M. Medina-Noyola, Phys. Rev. Lett. **60**, 2705 (1988).

[12] M. D. Carbajal-Tinoco, G. Cruz de León, and J. L. Arauz-Lara, Phys. Rev. E **56**, 6962 (1997).

[13] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, New York, 1986), 2nd ed.