

## Static properties of confined colloidal suspensions

M. D. Carbajal-Tinoco, F. Castro-Román, and J. L. Arauz-Lara

*Instituto de Física "Manuel Sandoval Vallarta,"*

*Universidad Autónoma de San Luis Potosí, Alvaro Obregón 64, 78000 San Luis Potosí, San Luis Potosí, México*

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The static structure of aqueous suspensions of polystyrene spheres, confined between two parallel glass plates, is measured by means of digital video microscopy. The concentration of colloidal particles is varied in a wide range within the liquid phase. The effective interparticle pair potential between the colloidal particles in this geometry is obtained from the measured static properties of the system via the two-dimensional version of the Ornstein-Zernike equation. The effective pair potential obtained in this way is found to be of short range with a well defined attractive component, features that are qualitatively reproduced in the whole range of concentrations studied.

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The study of nonhomogeneous colloidal fluids is an area of intense research due to its scientific and technological relevance. In particular, the structural properties, static and dynamic, of colloidal suspensions in the presence of external fields or in the presence of restricting boundaries is an exciting field of research. This is in part due to the development of experimental techniques, such as digital video microscopy (DVM) [1], which allows the direct visual observation and quantification of the phenomena occurring in suspensions of particles with sizes in the range from tenths to a few micrometers [2–5]. Since the structural and other relevant properties of these systems depend strongly on the nature of the interactions between macroparticles, one important step towards a complete microscopic understanding of those properties is the characterization of the effective interactions between particles and between particles and the boundaries. For instance, in the case of three-dimensional homogeneous colloidal suspensions, submicrometer size charge-stabilized polystyrene spheres in water or sterically stabilized silica particles in organic solvents have served as a model of systems with different interparticle pair potentials. For these systems, extensive and careful experimental studies of their static structural properties have been performed over the past two decades [6,7]. The experimental results are accurately described theoretically [6–8] and by computer simulation methods [8,9] by assuming a hard-sphere pair potential for the sterically stabilized particles. For the charged particles, where the repulsive interactions are dominant at low ionic strength, the pair potential is assumed to be given essentially by the repulsive term of the well known Derjaguin-Landau-Verwey-Overbeek [10] (DLVO) pair potential, i.e., by the second term of the expression

$$u(x) = \frac{-A}{12} \left[ \frac{1}{x^2 - 1} + \frac{1}{x^2} + 2 \ln \left( \frac{x^2 - 1}{x^2} \right) \right] + \frac{Q^2}{\sigma \epsilon (1 + z/2)^2} \frac{e^{-z(x-1)}}{x}, \quad (1)$$

where  $x = r/\sigma$  is the distance between particles normalized with the particle's diameter  $\sigma$ ,  $A$  is the Hamaker

constant,  $Q$  is the effective particle's charge, and  $z = \kappa\sigma$  is the screening constant, with  $\kappa$  being the inverse of the Debye screening length.

It is now desirable to develop a microscopic understanding of the structural properties of colloidal systems in confined geometries and of the effective interaction between particles, as they are now understood in the case of homogeneous three-dimensional suspensions. This requires extensive and careful experimental studies and the development of appropriate theoretical and computer simulation approaches to describe the quantities of interest. Steps in this direction have been reported in the literature. Thus, by using also aqueous suspensions of polystyrene spheres as the experimental model system, the structure of a colloidal suspension near a flat surface has been determined with the DVM technique [2]. The same technique has also been employed to measure the "two-dimensional" radial distribution function of dilute suspensions of polystyrene spheres confined between two parallel glass plates in such a way that the colloidal particles are restricted to move in an effectively two-dimensional space [4]. Similar cases have also been studied theoretically and by computer simulation methods. For instance, the structure of a suspension of interacting colloidal particles in the presence of a repulsive (or attractive) flat wall or confined between two of them has been calculated theoretically using the Ornstein-Zernike equation adapted to consider these inhomogeneous systems [11–14] and by means of computer simulation [13,14]. On the other hand, concerning the determination of the effective pair potential between particles in restricted geometries, interesting experimental methods have been proposed [4,5]; they are discussed below.

Here we report measurements of the static structure, using the DVM technique, of suspensions of colloidal particles confined between two parallel walls for a broad range of particle concentrations. We discuss also a general method to determine the effective interparticle pair potential, based on the two-dimensional version of the Ornstein-Zernike (OZ) equation. The system studied consists of fluorescent sulphonate polystyrene spheres of diameter  $\sigma = 0.5 \mu\text{m}$ , monodisperse to within 3% (Duke Scientific), suspended in deionized water and confined

between two parallel glass plates. The sample cell, similar to that used by Crocker and Grier [5], is made of a clean glass slide and a cover slip glued together with an epoxy resin (Epo-Tek 302). The two glass plates are pressed against each other and then the epoxy resin is dropped around two edges of the cover slip. The other two edges are connected to three-dimensional reservoirs containing a mixed bed of ion exchange resin (Serdolit MB, from Serva). The reservoirs are filled with the colloidal suspension, which is then introduced into the space between the plates by capillarity. Although this method of constructing the cell does not allow us to control very accurately the distance  $d$  between the plates, it allows us to produce cells with a separation  $d$  less than  $1 \mu\text{m}$  ( $\approx 1.5\sigma$ ), thus restricting the spheres to move only in a plane. The sample is allowed to equilibrate for several days at a constant temperature of  $23^\circ\text{C}$  (in contact with a circulating bath). The sample is then observed through a fluorescence microscope (Zeiss axioskop), using a  $100\times$  oil immersion objective (numerical aperture of 1.3). The motion of the fluorescent particles is recorded by a charge coupled device video camera (Hitachi KP-161, which is attached to the microscope and connected to a video recorder, Hi8 Sony EV-100). The images are then digitalized, using a frame grabber with a resolution of  $640 \times 480 \text{ pixel}^2$  (data translation), every 3 sec for the calculation of the static properties.

The position of the particles is determined from the digitalized images and the two-dimensional radial distribution function is calculated by means of standard procedures [15]. In Fig. 1 we plot  $g(r)$  for various values of the reduced concentration  $n^* = n\sigma^2$ , where  $n = N/S$  is the average concentration of particles observed in one frame of area  $S = 640 \times 480 \text{ pixel}^2 \approx 4250\sigma^2$  ( $\sigma = 8.5 \text{ pixels}$ ) and  $N$  is the number of particles per frame. In order to get good statistics for  $g(r)$  several frames were analyzed; about 700 for the dilute suspensions ( $N \approx 200$ ) and about 50 for the most concentrated sample ( $N \approx 2000$ ). Neither variation on  $g(r)$  nor aggregation between particles was observed after several days (1–2 weeks). In Fig. 1(a) the radial distribution functions of five dilute samples are shown. One can observe in this figure that  $g(r)$  presents the same characteristic features for the different systems: a well defined first peak, essentially at the same position, with no particular trend of its height as  $n^*$  is varied. This indicates that the static structure is basically independent of  $n^*$  in this concentration regime. This is consistent with the results reported by Kepler and Fraden [4], who measured  $g(r)$  in dilute suspensions of polystyrene spheres of diameter  $\sigma = 1.27 \mu\text{m}$  (with the same technique, DVM, and geometry), in a range of concentrations similar to the systems in Fig. 1(a). Other interesting features observed in this figure are some effects of the dimensionality of the system on its static structure. The apparent unphysical result  $g(r) > 0$  for  $r < \sigma$ , for the samples with  $n^* = 0.03, 0.065,$  and  $0.066$ , is due to that effect. For these samples the distance  $d$  between the inner surfaces of the plates ranges between  $3\sigma$  and  $6\sigma$ , while for the samples with  $n^* = 0.023$  and  $0.057$ , where the contact value  $g(\sigma) = 0$ ,  $d \approx 1.5\sigma$ . The variation in the height and in the width of the first peak

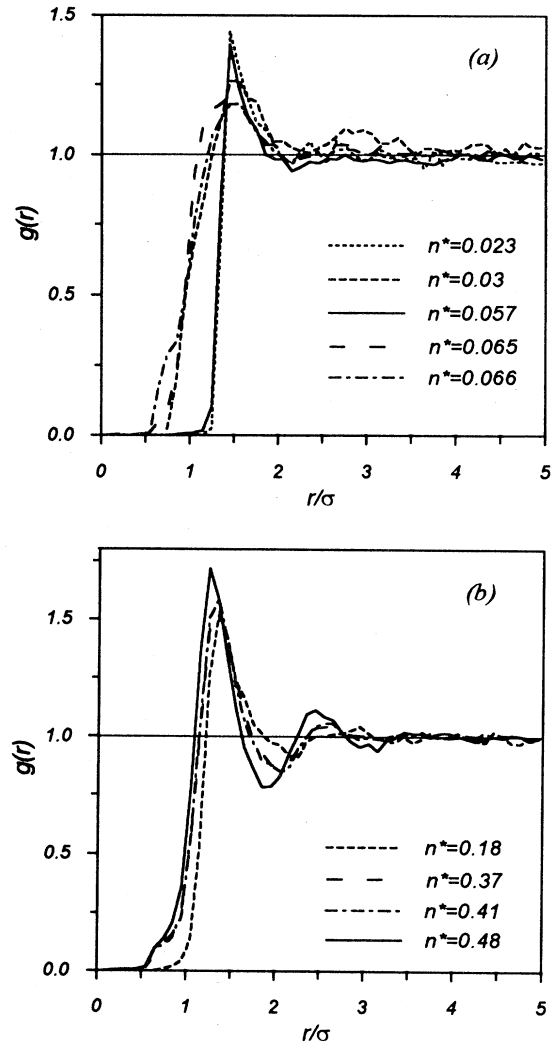


FIG. 1. Radial distribution function  $g(r)$  of quasi-two-dimensional colloidal suspensions (a) in the dilute regime of concentrations and (b) in the concentrated regime but still in the liquid phase.

of  $g(r)$  is another effect of the system's dimensionality. For more concentrated samples, the system's structure increases due to the higher total coupling between particles. This can be observed in Fig. 1(b), where we plot the radial distribution function corresponding to four concentrated samples (but still far from the order-disorder transition). We observe in this figure that the height of the first peak of  $g(r)$  increases, and its position shifts towards lower values, as  $n^*$  is increased. We also observe the development of a minimum and a secondary peak of  $g(r)$ . This behavior of the radial distribution function with  $n^*$  of our quasi-two-dimensional system is similar to the behavior of  $g(r)$  for three-dimensional systems.

The interaction between particles in a restricted geometry, as is the case studied here, is modified to some extent by the presence of the confining boundaries. The characterization of the effective direct interactions between the colloidal particles is then one of the issues that

should be addressed in order to get a more fundamental understanding of the system. The pair potential between polystyrene spheres in water, confined in precisely the same geometry considered in this work, has been studied using also the DVM technique. Crocker and Grier [5] measured the interaction between isolated pairs of polystyrene spheres of diameter  $0.65 \mu\text{m}$  in distilled water with the glass plates separated a distance  $d \approx 5\sigma$ . Their results suggest a repulsive interaction between particles, in agreement with the repulsive term of the DLVO pair potential, but with a higher screening constant than expected from the contribution of the counterions alone. This extra screening of the interaction between particles is due to the small ions dissociated from the glass surfaces, whose contribution becomes more important as the sample's volume is reduced, i.e., as  $d$  decreases. On the other hand, Kepler and Fraden [4] proposed a different method to determine the effective pair potential from the measured radial distribution function in dilute suspensions of polystyrene spheres, just referred to above. In their samples  $d \approx 1.5\sigma - 5\sigma$ . They obtain an effective pair potential by an iteration method, based on the Brownian dynamics algorithm, to calculate  $g(r)$  for a modified Lennard-Jones pair potential, by using as the initial input for  $u(r)$  the pair potential obtained from the measured  $g(r)$  through the low concentration approximation [16,17], i.e.,

$$g(r) = e^{-\beta u(r)}, \quad (2)$$

where  $\beta = 1/k_B T$ , with  $k_B$  the Boltzmann constant and  $T$  the absolute temperature. In this way, they find an attractive pair potential, with a deeper minimum than that expected from the attractive part of the DLVO expression. Both results suggest that the presence of the glass plates not only affects the structural properties of the system, as a result of restricting one dimension, but it might also modify the particle-particle interaction [compared with Eq. (1), which is valid for homogeneous three-dimensional systems] by inducing additional effects (distortion of the spherical ionic cloud around the colloidal particles, additional van der Waals forces, etc.) that might depend on the particle concentration and on the system's dimensionality ( $d/\sigma$ ). Therefore, a more general method to determine the effective pair potential should be developed to consider a broader range of concentrations, including the high concentration regime where those additional effects may be stronger. Here we investigate an alternative procedure that allows for the determination of the effective  $u(r)$  in systems with arbitrary concentration within the liquid phase.

For two-dimensional systems, the radial distribution function can be calculated, if the pair potential is known, using the two-dimensional version of the Ornstein-Zernike equation [16],

$$h(r) = c(r) + n \int d^2 r' c(r') h(|\mathbf{r} - \mathbf{r}'|), \quad (3)$$

together with an appropriate closure relation. In Eq. (3),  $h(r) = g(r) - 1$  is the total correlation function and

$c(r)$  is the direct correlation function. Although Eq. (3) does not relate one to one the radial distribution function with the pair potential, one might attempt to invert the procedure to get  $u(r)$  from the experimental values for  $g(r)$ . Thus, by taking the Fourier-Bessel (FB) transform [18,19] of Eq. (3), we obtain an expression for  $C(k\sigma)$ , the FB transform of  $c(r/\sigma)$ , in terms of the FB transform of the measured total correlation function, i.e.,

$$C(k\sigma) = \frac{H(k\sigma)}{1 + n^* H(k\sigma)}. \quad (4)$$

Then this equation can be transformed back to the real space to get the "experimental" direct correlation function  $c(r/\sigma)$ . The effective pair potential may now be obtained using a closure relation such as the hypernetted chain (HNC) approximation, the mean spherical approximation (MSA), or the Percus-Yevick (PY) approximation, which are different ways to approximate  $c(r)$  in terms of  $u(r)$  and  $g(r)$  [16], i.e.,

$$c(r) = -\beta u(r) + h(r) - \ln g(r) \quad (\text{HNC}), \quad (5)$$

$$c(r) = -\beta u(r), \quad r > \sigma \quad (\text{MSA}), \quad (6)$$

and

$$c(r) = (1 - e^{-\beta u(r)})[1 + h(r)] \quad (\text{PY}). \quad (7)$$

In Fig. 2(a) we plot  $\beta u(r)$  for the most dilute sample ( $n^* = 0.023$ ), calculated using Eq. (3) and these three closure relations. Thus we see that the three closure relations lead to very similar results for the pair potential and that they reproduce very well the main features of the pair potential [closed circles in Fig. 2(a)] obtained directly from the measured radial distribution function and the low concentration approximation Eq. (2). This equation is exact for very dilute systems, i.e., in the concentration regime where  $g(r)$  is independent of the concentration, which is the case of the samples considered in Fig. 1(a). Similar results are obtained for the other dilute samples in that figure. Thus we see that for the dilute systems studied here, both Eqs. (3) and (2) lead to an attractive pair potential between the colloidal particles in the confining geometry considered here. These results are in qualitative and quantitative agreement with the pair potential reported in Ref. [4]. For higher concentrations, where Eq. (2) is no longer valid, we expect that the OZ equation, together with a closure relation, should provide a pair potential containing at least the main physical features of the actual effective interactions between the colloidal particles. In Fig. 2(b) we show the results for  $\beta u(r)$ , corresponding to the most concentrated sample studied in this work ( $n^* = 0.48$ ). We see that in this case the three closure relations also lead to pair potentials with the same physical characteristics, although with some quantitative differences between them, and that they are qualitatively similar to the pair potential of the dilute system presented in Fig. 2(a). It is in fact the case for all the samples studied in this work. This can be seen in Fig. 2(c) where we show the pair potentials

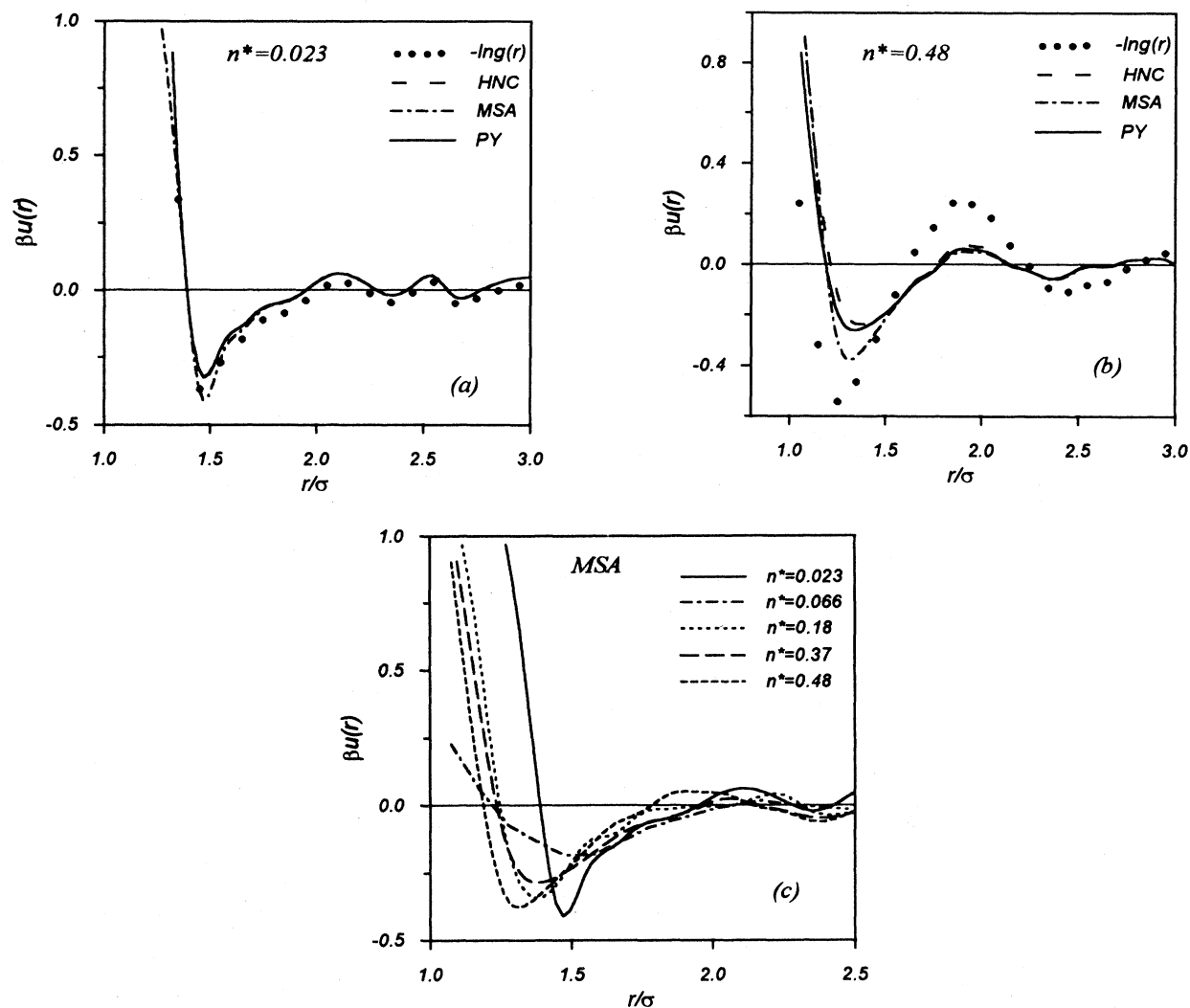


FIG. 2. Effective pair potential between the colloidal particles. (a) Comparison of the results obtained from the Ornstein-Zernike equation and the three closure relations HNC, MSA, and PY (lines), compared with the results from the low concentration approximation (closed circles), for the most dilute sample considered in this work ( $n^* = 0.023$ ). (b) The same comparison as in (a), but for the most concentrated sample ( $n^* = 0.48$ ). (c) Results from the OZ equation and the MSA approximation for five different samples, covering a wide range of concentrations. Here we can observe that the pair potential presents the same characteristic features in the whole range of concentrations studied.

for five different samples, covering a wide range of concentrations, calculated within the MSA. The other two closure relations lead to the same general picture shown in Fig. 2(c). We present the MSA results because they are in better quantitative agreement with the results of the low concentration approximation in the case of dilute systems. Thus Fig. 2(c) shows that the analysis of the effective pair potential through the two-dimensional Ornstein-Zernike equation reproduces quite consistently an effective pair potential with the same physical features in a wide range of concentrations. The quantitative differences, in the position and depth of the minimum, may be explained in terms of the effects of the system's dimensionality on its static structure used as input in Eq. (3).

As mentioned before, the effective pair potential, whose main features are summarized in Fig. 2, includes

contributions from different sources, in addition to those already contained in Eq. (1). Those additional effects may arise from transient double layer deformation due to close encounters of the particles [20], van der Waals interactions between the particles and the plates, image charges, multipole interactions, etc., which may depend on particle concentration, ionic strength, and the separation between plates. Thus a careful theoretical calculation of those effects, for the particular geometry considered here, is needed in order to assess the regimes where they are important and the extent of their relative contribution to the effective  $u(r)$ . This potential should, however, reduce to Eq. (1), the DLVO pair potential, for the appropriate limiting cases.

In this work we have presented experimental results for the static structure of aqueous suspensions of

polystyrene spheres, restricted to move in an effectively two-dimensional space by confining the suspension between two parallel glass plates. We measured the radial distribution function of the colloidal particles, for a wide range of particle concentration, by means of digital video microscopy. Our results show that the local static structure of the system increases for higher concentrations. This is expected since the total coupling between particles increases for more concentrated samples. Another interesting feature of our results is the effect of the system's dimensionality on its static structure (see Fig. 1). With respect to the other issue discussed here, the determination of the effective pair potential between the colloidal particles, we analyzed a general method based on the Ornstein-Zernike equation, using the measured static structure as input. The pair potential derived in this way exhibits a well defined attractive component, in the whole range of concentrations considered in this work, with a much deeper minimum than predicted by Eq. (1). A fit to this equation of the effective  $u(r)$ , obtained from Eq. (2) for the dilute samples in Fig. 1(a), or the MSA  $u(r)$  results for the more concentrated samples, leads to a value for the constant  $A$  at least one order of magnitude larger than the Hamaker constant expected between two polystyrene plates in water [10] and a Debye

screening length not larger than  $0.05 \mu\text{m}$  (a small fraction of the particle's diameter). The fitting to Eq. (1) was carried out by fixing the value of the effective charge  $Q$  to obtain the values of  $\kappa$  and  $A$ .  $Q$  was varied (decreased) for more than one order of magnitude, starting from its tritratable value of about  $5 \times 10^4 e$ , while the value of  $A$  ( $\kappa$ ) was found to increase (decrease) less than a factor of 2. Our results of a much larger value for  $A$  than expected is in agreement with the results reported in Ref. [4], while our results for  $\kappa$  are smaller than those reported in Refs. [4,5]. Thus the results in Fig. 2 suggest that the confining walls not only restrict the particles motion to a plane but they might modify their interactions with respect to the homogeneous three-dimensional case [Eq. (1)]. This calls for the exact derivation of the pair potential between colloidal particles in confined geometries, in a way similar to how the DLVO expression was obtained.

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