

## Colloidal Interactions in Partially Quenched Suspensions of Charged Particles

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We report measurements of the effective pair potential between charged colloidal particles in a bidimensional matrix of fixed obstacles. A binary mixture of polystyrene spheres in water is confined between two glass plates. The larger particles are trapped by the plates in a disordered configuration with respect to which the smaller species of particles equilibrates. The structures of both the mobile and the fixed species are measured by videomicroscopy. The pair potential, obtained by deconvoluting the structural information via the Ornstein-Zernike equation, exhibits two attractive components. [S0031-9007(98)06744-1]

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Recent measurements of the direct interaction between charged colloidal particles in suspension, such as polystyrene spheres in water, have provided evidence of an attractive effective pair potential between the particles under conditions of confinement [1–3]. The physical properties of such systems have been extensively studied in the homogeneous three-dimensional (3D) space. In this case, the assumption of a repulsive screened Coulomb pair potential, as the one derived by Derjaguin, Landau, Verwey, and Overbeek [4], provides a functional form for the interparticle potential in terms of which the experimental observations have been reasonably well described [5,6]. However, for the same kind of systems but now confined between two parallel glass plates, direct and indirect determinations of the effective interparticle potential show an attractive component, rather than repulsive, at intermediate distances [1–3]. This observation is quite interesting and raises the question about the physical origin of such effective attractive interaction, and also whether this interaction is further modified under different conditions of confinement, for instance, in an arbitrary geometry such as a disordered porous medium. The answer to these questions is quite important because the accurate determination of colloidal interactions is essential in order to understand on a fundamental basis colloidal properties such as their stability, structure, dynamics, thermodynamics, and so on. Here we address the latter question, namely, the question about the sensitivity of the effective colloidal interactions on the local environment. In this Letter, we report indirect measurements of the effective interaction between charged colloidal particles in suspension when it is permeating a bidimensional porous matrix. We measure both the structure of the colloidal suspension and the porous matrix. Then, the effective pair potential is determined by deconvoluting the information contained in the structural properties of the system, by using the multicomponent Ornstein-Zernike (O-Z) integral equation and a closure relation. This deconvoluting method was employed to determine the effective interaction potential

between polystyrene spheres in water, confined between two parallel glass plates in such a way that the system becomes an effective two-dimensional colloidal suspension [2]. As mentioned before, the result in that case is an attractive interaction potential between charged colloidal particles. Essentially the same potential was also observed by different indirect [1] and direct [3] measurements on similar systems.

Let us now describe our system. It consists of a binary mixture of polystyrene spheres of diameters  $\sigma_1$  and  $\sigma_2$ , with  $\sigma_2 > \sigma_1$ , suspended in water. The suspension is confined between two glass plates in such a way that the separation between the inner surfaces of the plates coincides with  $\sigma_2$ . Thus, the dynamics of species 2 is quenched, i.e., the particles of species 2 are frozen in a given configuration forming in this way a two-dimensional (2D) (porous) matrix of fixed particles. The particles of species 1 then form an effective 2D colloidal fluid which equilibrates in the field of the fixed particles of species 2. The particles of species 1 are fluorescent polystyrene spheres of a diameter of  $0.5 \mu\text{m}$ , and the particles of species 2 are nonfluorescent polystyrene spheres of a diameter of  $2 \mu\text{m}$ . Under these confining conditions, the most important contribution to the solution's ionic strength comes from the ions released from the glass plates (surface charge density of  $\sim 10^6 \mu\text{m}^{-2}$ ) [7]. Thus, the Debye length is  $\sim 10\text{--}20 \text{ nm}$ , and the effective diameters are only slightly larger than their physical values. Further details of the sample preparations can be found elsewhere [8,9]. Figure 1 shows a typical image of a small area of one of our systems as it is seen through an optical microscope using both transmitted and fluorescence illumination and a  $100\times$  objective. The differences in size and in color of both species allow us to clearly identify the particles of the different species and to determine accurately their positions using digital videomicroscopy. In practice, the positions of the particles of the two species are determined separately. For species 1, we use only fluorescence

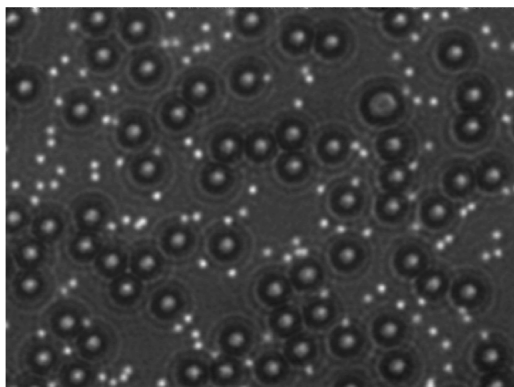


FIG. 1. Image of a small area of a sample with reduced concentrations of fixed particles  $n_2^* = 0.25$  and mobile particles  $n_1^* \approx 0.02$ . The bright and shadowed particles are the mobile and fixed particles, respectively. The scale of the picture is  $60 \mu\text{m}$  along the  $x$  direction.

illumination (the fixed particles are not seen). For the larger particles, we use only transmitted light and we focus the top of the fixed particles so that only they are clearly imaged.

For the first part of our work, we determine the effect of the porous matrix on the structure of the colloidal fluid, characterized by the radial distribution function  $g_{11}(r)$  of the diffusing particles along the plane parallel to the plates. We measured  $g_{11}(r)$  for different concentrations of fixed particles. In order to minimize the effect of the interactions between the mobile particles themselves on  $g_{11}(r)$ , we kept the average particle concentration of species 1,  $n_1$  ( $\equiv N_1/A$ , where  $N_1$  is the average number of particles of species 1 in the area  $A$ ), very low. In all our samples the dimensionless reduced concentration  $n_1^* \equiv n_1\sigma_1^2$  was  $\approx 0.02$  [10]. The measurement of  $g_{11}(r)$  in the field of the fixed particles constitutes, by itself, an important contribution of this work. Additionally, our model system allows us to characterize the structure of the porous matrix where the colloidal suspension is absorbed, as well as the correlation between mobile particles and the matrix. Those quantities are described here by the 2D radial correlation function of the fixed particles  $g_{22}(r)$  and by the cross-correlation function (mobile particles-matrix)  $g_{12}(r)$ , respectively. It is important to stress here that the precise characterization of the physical properties of liquid systems absorbed in a porous medium is an interesting area of research in its own right, which is important in processes such as catalysis, oil recovery, and others [11,12]. Let us mention that theoretical approaches based on integral equation methods have been developed [13–15], as well as computer simulation methods that have been employed [16,17], to study the structure, the thermodynamic and dynamic properties, of mobile liquids in equilibrium with a rigid matrix of obstacle particles. Thus, our systems constitute a particular experimental realization of those theoretical model systems.

Although, in our case the presence of the confining glass plates plays the role of an extra external field. In principle, if in our samples the interparticle potentials were known, one could use those theoretical approaches and/or computer simulation methods to calculate the structure of the colloidal liquid and compare with our experimental measurements. However, the pair potentials are precisely the important quantities we would like to determine from our experiments. Let us now discuss our results.

Figure 2 shows the radial distribution function  $g_{11}(r)$  of the colloidal suspension for various values of the fixed particle's reduced concentration  $n_2^* \equiv n_2\sigma_2^2$ , keeping constant  $n_1^* \approx 0.02$  [10]. Here one can see the effect of the porous matrix on the structure of the colloidal fluid. In the limit of very low concentrations of fixed particles ( $n_2^* \approx 0$ ), the system corresponds to a monodisperse quasi-bidimensional suspension. Here the few large particles present in the system serve only as spacers and allow us to control accurately the distance between the plates. Since the colloidal suspension is rather dilute, one could expect the system to not be highly structured. In fact, that is what we obtain, the measured  $g_{11}(r)$  exhibits only a low first peak (solid line) at around  $r = 1.5\sigma_1$ , followed by minor oscillations that fade away rather quickly. As discussed elsewhere [2], the apparent unphysical result  $g_{11}(r) > 0$  for  $r < \sigma_1$  is only an artifact of the quasi-bidimensionality of the system and has no relevance here. At finite values of  $n_2^*$ ,  $g_{11}(r)$  reveals an increase in the structure of the colloidal fluid. As one can see here, the height of the first peak of  $g_{11}(r)$  increases quite appreciably as  $n_2^*$  increases and, interestingly, its position is almost independent of  $n_2^*$ . One can also notice in Fig. 2 that the first peak of  $g_{11}(r)$  decays more slowly for larger values of  $n_2^*$  and that there is an abrupt change in the slope that, also interestingly, happens at the same place (about  $r = 2.2\sigma$ ) in all the samples. This behavior of  $g_{11}(r)$  is notoriously different from what is observed in

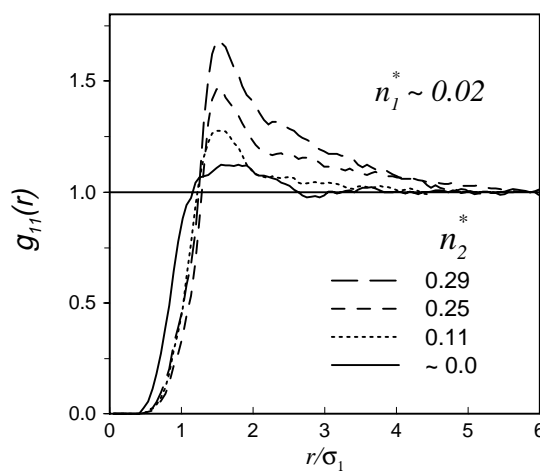


FIG. 2. Radial distribution function of the mobile particles at various concentrations of the fixed particles.

homogeneous suspensions, i.e., when instead of increasing the number of frozen particles, one varies  $n_1^*$  keeping  $n_2^* \approx 0$ . Then, the system is an effective 2D system that can be considered homogeneous along the plane parallel to the plates [2,8]. There, as the particle concentration increases, the radial distribution function develops a higher first maximum, followed by a minimum, a lower secondary maximum, and so on. The positions of the maxima and minima depend on concentration and there are not abrupt changes in the slope of the radial distribution function. Thus, the presence of fixed obstacles or porous matrix enhances the correlation between the mobile particles, but there is not any development of secondary maxima or minima, as is the case for homogeneous systems. Here the correlations become stronger and of longer range, but  $g_{11}(r)$  has basically only one peak that decays slower for larger values of  $n_2^*$  and exhibits a marked change in the slope. The curves of  $g_{11}(r)$  shown in Fig. 2 represent the average of about  $1.4 \times 10^4$  different configurations of the mobile particles digitized at four different configurations of the fixed particles as the one shown in Fig. 1. Therefore,  $g_{11}(r)$  in Fig. 2 is also an average over the structure of the matrix.

The cross-correlation functions between fixed and mobile particles,  $g_{12}(r)$ , are shown in Fig. 3(a). An interest-

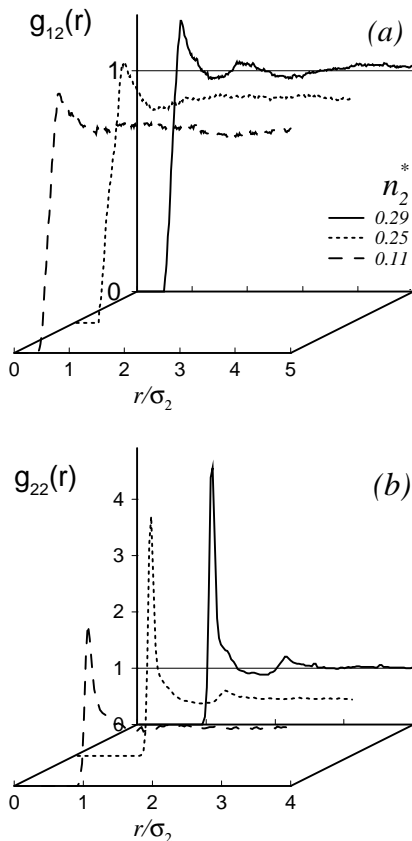


FIG. 3. Cross-correlation function (a) and fixed particle's radial distribution function (b) for the systems in Fig. 2.

ing feature to be noticed here is the existence of a low first maximum of  $g_{12}(r)$  with height and position varying very little with  $n_2^*$ . Another important effect of increasing the number of fixed particles is the development of long range correlations between the particles of species 1 and 2, exhibited in the presence of more evident oscillations of  $g_{12}(r)$  at longer distances as  $n_2^*$  increases. The curves for  $g_{12}(r)$  in Fig. 3(a) are also the average of cross-correlation functions measured at four different configurations of the fixed particles as in the case of  $g_{11}(r)$ . For the particles of species 2, we can also determine the corresponding radial distribution function,  $g_{22}(r)$ , as a practical way to characterize the structure of the porous matrix. Thus, in Fig. 3(b) we show  $g_{22}(r)$  for the same systems. In all of these samples,  $g_{22}(r)$  has a very high first maximum close to contact. For the larger values of  $n_2^*$ , one can observe the development of a minimum and a secondary maximum. This shape of  $g_{22}(r)$  resembles a system of hard disks, although in our systems the first peak is higher than that corresponding to a hard disk system at the same particle concentration. The curves of  $g_{22}(r)$  were determined from  $1-2 \times 10^3$  different configurations.

The radial distribution functions of the colloidal suspension in Fig. 2 show clearly that the presence of the fixed particles increases the correlation between the mobile particles. The question is whether the observed behavior of  $g_{11}(r)$  is due only to the fact that the large particles cage the mobile particles within the porous so that they remain close together for longer times than in the homogeneous case ( $n_2^* \approx 0$ ), or if the presence of the matrix also induces changes on the effective interaction between the mobile particles. To answer this question let us determine the effective pair potential between the mobile colloidal particles. This potential can be extracted from the detailed structural information of the system contained in  $g_{ij}(r)$ , by deconvoluting this information via the 2D Ornstein-Zernike integral equation. For a two-component system, the O-Z equation is a set of coupled integral equations for the total correlation functions  $h_{ij}(r) = g_{ij}(r) - 1$  and the direct correlation functions  $c_{ij}(r)$  between particles of species  $i$  and  $j$  ( $i, j = 1, 2$ ). For symmetry, one assumes  $h_{ji}(r) = h_{ij}(r)$  and  $c_{ji}(r) = c_{ij}(r)$ . Usually, the O-Z equation is employed to calculate  $g_{ij}(r)$  for a given system, assuming the pair potentials  $u_{ij}(r)$  are known between the different species. In those equations both sets of functions  $h_{ij}(r)$  and  $c_{ij}(r)$  are unknown and an additional set of relations or closure relations is required to be able to solve the equations. The closure relations more frequently used are the mean spherical, the Percus-Yevick, and the hypernetted chain (HNC) approximations [18]. Thus, if the pair potentials are known, one can use the O-Z equation and one of these closure relations to obtain the pair correlation functions  $g_{ij}(r)$ . Here we follow the inverse process. We Fourier transform the O-Z equation to obtain a set of four coupled linear equations involving  $c_{ij}(k)$

and  $h_{ij}(k)$ , the Fourier transforms of  $c_{ij}(r)$  and  $h_{ij}(r)$ , respectively. Since we measured  $h_{ij}(r)$ , we solve the set of equations for  $c_{ij}(k)$ , which are then transformed back to the real space to get the measured direct correlation functions  $c_{ij}(r)$ . The pair potential between the mobile particles  $u_{11}(r)$  is obtained from  $c_{11}(r)$  using one of the closure relations. Here we use the HNC approximation, but the results from the other closure relations are qualitatively similar. The results of this deconvoluting method of measuring the pair potential are presented in Fig. 4.

The curve in Fig. 4(a) corresponds to the sample where  $n_2^* \approx 0$ . Here  $u_{11}(r)$  shows a well defined attractive component at about  $1.5\sigma_1$ , which is the attractive interaction observed previously [2]. At finite values of  $n_2^*$ ,  $u_{11}(r)$  also exhibits this attractive component at  $r \approx 1.5\sigma_1$ . As one can see, its position remains basically independent of  $n_2^*$  and it becomes only slightly deeper as  $n_2^*$  increases. At large concentrations of fixed particles there is an additional feature of the pair potential, namely, the attractiveness of the mobile particles becomes of larger range. One can observe the development of a second attractive component of  $u_{11}(r)$  at larger distances, as seen in Fig. 4(c). This second component widens out towards smaller distances and merges with the first attractive well [see Fig. 4(d)]. Thus, one could say that the effective pair potential between the particles of the colloidal fluid exhibits two well defined attractive components under the particular confinement studied here. The first attractive component, the minimum at  $r \approx 1.5\sigma_1$ , can be attributed to the effect of the confining by the glass plates. As shown in Fig. 4 this component changes very little as  $n_2^*$

is varied. The second attractive component arises as an extra effect of the fixed particles, which then not only serve as obstacle particles reducing [19] and molding the space available to the colloidal fluid, but their interaction with the mobile particles introduces a strong modification of the effective pair potential  $u_{11}(r)$ .

The specific features reported here, for the structure and the effective interparticle potential between the particles of a colloidal fluid permeating a matrix of obstacles, correspond to our particular system where charged polystyrene spheres are used for both the mobile and the fixed particles. We expect, however, that this simple model system captures the general trends of those physical quantities, at least for systems of charged particles.

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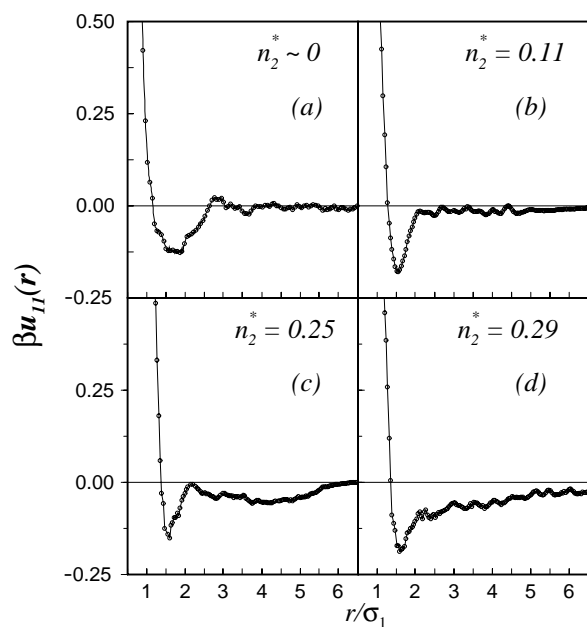


FIG. 4. Effective pair potential between mobile particles absorbed in matrices of different porosities.

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