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The structure of a model two-component colloidal mixture in the vicinity of a charged wall is studied in the framework of the Derjaguin–Landau–Verweg–Overbeek potential and the hypernetted-chain approximation for the particle–particle and wall–particle direct correlation functions as the closure for the bulk and wall–particle Ornstein–Zernike equations. It is found that for strongly repulsive walls the structure of the inhomogeneous mixture near the wall only depends on the bulk parameters. For neutral and attractive walls, a monolayer of colloidal particles adjacent to the wall is formed. Depending on the charge asymmetry between the two colloidal species, the composition of this monolayer indicates a preferential electrostatic adsorption of the more highly charged species. For large charge asymmetry between the two species, a distinct segregation effect is predicted.

I. INTRODUCTION

The investigation of the structure of colloidal dispersions has benefitted from the application of techniques such as light and neutron scattering.[1–6] The fundamental understanding of the properties thus studied has been assisted by the corresponding development of theoretical models and approaches,[7–11] mostly borrowed from the theory of simple liquids.[12,13] As a result, the experimentally determined static structure factors of rather clean and well characterized model experimental systems have been compared quite successfully with the predictions of fairly simple theoretical models and approximations. Thus, we can say that the basic features of the static structure of dilute suspensions of highly charged particles are well understood on the basis of the Derjaguin–Landau–Verweg–Overbeek (DLVO) model for the pair interactions, at least for monodisperse suspensions in the bulk. The extension of this line of work to polydisperse suspensions is still the subject of research.[14–17] On the other hand, the experimental research on the structural properties of inhomogeneous colloidal dispersions is still in a more primitive stage. However, the first attempts to directly measure the interaction force between colloidal particles and charged surfaces,[18] and the structure of the suspension that this force induces in the vicinity of such a surface[19] have recently been reported. This prompted the recent proposal of theoretical models and approximations to describe the structure of a monodisperse suspension of highly charged colloidal particles near charged walls.[20,21] These developments were based on the DLVO level of description[22] of the particle–particle and wall–particle interactions, and on the use of simple but well established approximations borrowed from the equilibrium theory of inhomogeneous fluids. As a result, the local concentration profile of a suspension near a charged surface has been calculated, and some features have

been observed which seem rather specific to colloids, or at least to their DLVO model. Thus, it has been predicted[21(a)] that highly repulsive surfaces expel the colloidal particles from an adjacent slab of thickness d (which depends on the strength of the wall–particle repulsion), but that the concentration profile for distances beyond d only depends on the bulk properties of the suspension (formed by highly charged particles). In addition, for neutral or attractive surfaces, a distinct colloidal monolayer adjacent to the wall has been predicted.[21(b)] The important role of electrostatic interactions, in many practical problems, such as in colloid deposition, which involve charged colloidal particles near charged surfaces, call for the further development of these theoretical studies. The present paper reports the results of our theoretical calculation of the local concentration profile of a bidisperse colloidal suspension of highly charged particles in the vicinity of a charged wall. This work is an extension of previous research[21] involving monodisperse suspensions, and is also based on the DLVO model and the hypernetted-chain/hypernetted-chain (HNC/HNC) approximation.

The salient features of the results presented here include a similar effect to that observed in inhomogeneous monodisperse suspensions in front of highly repulsive walls. Thus, we find that the structure of the mixture only depends on the bulk conditions, provided that a slab adjacent to the wall is produced, where no colloidal particles are allowed by the wall–particle repulsion. For weakly repulsive, neutral, and attractive walls, the effect of electrostatic trapping of a colloidal monolayer is also observed in mixtures. There is, however, an additional feature concerning the composition of this monolayer. Thus, it is found that the more highly charged species adsorbs preferentially onto the wall, indicating an electrostatic segregation mechanism.

The following section describes the DLVO model of the interactions, on which our study is based, as well as the HNC/HNC approximation scheme employed in our calculations. Section III reports our results and discusses their main features, one of which is explained in more detail in Sec. IV. The last section summarizes the main conclusions of this work.

II. BASIC EQUATIONS

In this work the wall–particle and particle–particle interactions are modeled according to the DLVO potential, and the local concentration profile is determined from the Ornstein–Zernike equation for wall–particle correlations. Let us consider a polydisperse suspension of charged spherical particles in an aqueous solution of temperature T. The species i has a diameter σ_i, charge Q_i, and bulk concentration n_i. Then, according to this model, the pair potential between any two particles of species i and j is given by

$$u_{ij}(r) = \begin{cases} \dfrac{Q_i Q_j}{\epsilon(1 + \kappa\sigma_i/2)(1 + \kappa\sigma_j/2)} \dfrac{e^{-\kappa(r-\sigma_{ij})}}{r}, & r > \sigma_{ij} \\ \infty, & r\sigma_{ij} \end{cases}$$

(1)

where $\sigma_{ij} = (\sigma_i + \sigma_j)/2$, ϵ being the dielectric constant of the solvent and κ the inverse Debye screening length, given by

$$\kappa^2 \equiv \frac{4\pi}{\epsilon k_B T} \sum_{\lambda=1}^{s} n_\lambda^0 q_\lambda^2,$$

(2)

where k_B is Boltzmann's constant, and n_λ^0 and q_λ are the bulk concentration and electric charge of the small ions of species λ in the solution. The pair potential of Eq. (1) corresponds to the multispecies extension of the hard-sphere plus electrostatic terms of the well-known DLVO potential. Thus, our model does not include van der Waals forces, ordinarily involved in the DLVO model. Whereas this attractive component is highly relevant to the problem of colloid stability, in our case we shall only deal with stable suspensions of highly charged particles, in which case the van der Waals forces do not contribute to the static properties.

For the interaction between the wall and the particles of specie i we use the exponential potential

$$u_{wi}(x') = \begin{cases} \dfrac{4\pi\sigma_{el}Q_i}{\epsilon\kappa(1 + \kappa\sigma_i/2)} e^{-\kappa x'}, & x' > \sigma_i/2 \\ \infty, & x' < \sigma_i/2 \end{cases}, \quad (3)$$

where σ_{el} is the surface charge density on the wall.

Since we are interested only in the effects of polydispersity in the electric charge, we shall assume for simplicity that the diameters of all the species are equal to some common diameter σ, that is $\sigma_i = \sigma$, and for convenience we shall make the transformation $x' = x + \sigma/2$. As in previous work,[21] we shall not make much emphasis on the detailed form of the DLVO model in Eqs. (1) and (3), but instead, we will only refer to their dimensionless form,

$$\beta u_{ij}(r) = \begin{cases} K_i K_j \dfrac{e^{-z(r/\sigma - 1)}}{(r/\sigma)}, & r/\sigma > 1 \\ \infty, & r/\sigma < 1 \end{cases}$$

(4)

and

$$\beta u_{wi}(x) = \begin{cases} K_w K_i e^{-z(x/\sigma)}, & x > 0 \\ \infty, & x < 0 \end{cases}, \quad (5)$$

where $\beta = 1/k_B T$ and

$$K_i = \frac{Q_i}{\sqrt{\epsilon k_B T\sigma}(1 + \kappa\sigma/2)},$$

(6)

$$K_w = \frac{4\pi\sigma_{el}}{\kappa}\sqrt{\frac{\sigma}{\epsilon k_B T}},$$

(7)

and

$$z = \kappa\sigma.$$

(8)

From this point on we shall only refer to this dimensionless form of the potentials, employing typical values for K_i, K_w, and z, corresponding to parameters Q_i, σ, κ, σ_{el}, etc., which are typical of experimentally realizable conditions. We shall also refer to the partial volume fractions $\phi_i = \pi n_i \sigma^3/6$.

In this paper we calculate the wall–particle total correlation function $h_{wi}(x)$, which is related to the local concentration $n_{wi}(x)$ of colloidal particles of specie i at a distance $(x + \sigma/2)$ from the wall, and to the one-particle distribution function $g_{wi}(x)$, by

$$n_{wi}(x) = n_i g_{wi}(x) = n_i[1 + h_{wi}(x)].$$

(9)

We determine h_{wi} by solving the wall–particle Ornstein–Zernike equations

$$h_{wi}(x) = C_{wi}(x) + 2\pi \sum_{j=1}^{N} n_j \int_{-\infty}^{\infty} dt\, h_{wj}(t)$$

$$\times \int_{|x-t|}^{\infty} ds\, s\, C_{ij}(s), \quad (10)$$

where $C_{wi}(x)$ is the wall–particle direct correlation function for species $i(=1,2,...,N)$, and $C_{ij}(r)$ is the bulk particle-particle direct correlation function between species i and j. This is the straightforward extension to mixtures of the basic equation employed in previous work on monodisperse suspensions,[21] and can also be derived in the same manner from the work of Henderson *et al.*[23] In order to solve this equation for $h_{wi}(x)$ we need to define specific approximations for the direct correlation functions $C_{wi}(x)$ and the $C_{ij}(r)$. In this paper we base our discussion on the HNC closure relation for $C_{wi}(x)$, namely,

$$C_{wi}(x) = -\beta u_{wi}(x) + h_{wi}(x) - \ln[1 + h_{wi}(x)].$$

(11)

which allows us to solve Eq. (10) for $h_{wi}(x)$ once the bulk direct correlation functions $C_{ij}(r)$ have been provided. Here we approximate $C_{ij}(r)$ by the solution of the bulk Ornstein–Zernike integral equations,

$$h_{ij}(r) = C_{ij}(r) + \sum_{k=1}^{N} n_k \int h_{ik}(|\mathbf{r} - \mathbf{r}'|)C_{kj}(r')d^3r',$$

(12)

where $g_{ij}(r) = 1 + h_{ij}(r)$ is the radial distribution function, also complemented by the HNC closure,

$$C_{ij}(r) = -\beta u_{ij}(r) + h_{ij}(r) - \ln[1 + h_{ij}(r)].$$

(13)

The resulting approximation for $h_{wi}(x)$ corresponds to what in the literature on inhomogeneous fluids is referred to as the HNC/HNC approximation.

III. RESULTS

In this section we report some illustrative results for the local concentration profiles represented by the wall–particle distribution functions $g_{wi}(x)$, calculated according to the HNC/HNC scheme just discussed. Figures 1–3 present the results corresponding to a dilute binary colloidal mixture of highly charged particles, with fixed bulk parameters $K_1^2 = 900$, $K_2^2 = 196$, $z = 0.15$, and $\phi_1 = \phi_2 = 2.1 \times 10^{-4}$. These dimensionless parameters correspond to the values $\sigma = 79.7$ nm, $Q_1 = 341e^-$, $Q_2 = 159e^-$, $n_1 = n_2 = 7.9 \times 10^{11}$ cm^{-3}, and $T = 300$ K, with a charge of $1e^-$ for the counterions. The sequence of Figs. 1–3 corre-

FIG. 2. Wall–particle distribution function $g_{wi}(x)$ calculated from the HNC/HNC approximation for a suspension with the same bulk parameters as in Fig. 1, but with (a) $K_w = 5$, and (b) $K_w = 3.5$.
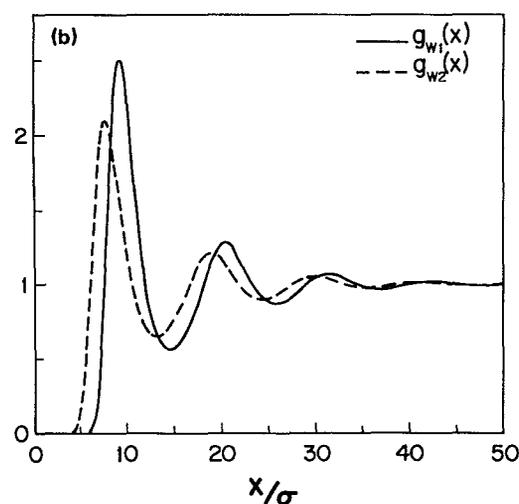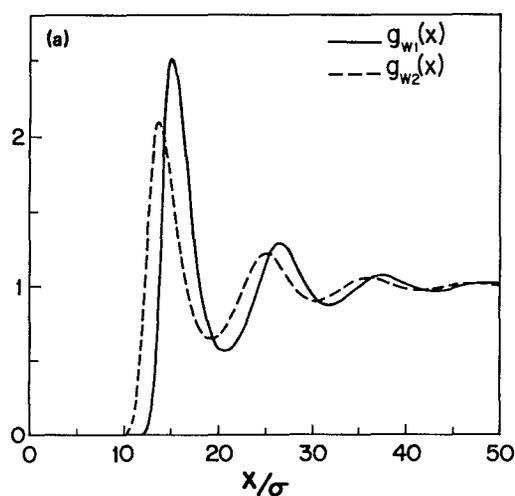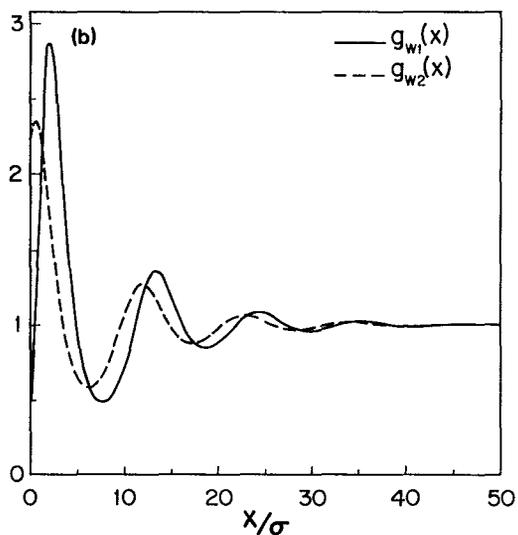
FIG. 1. Wall–particle distribution functions $g_{wi}(x)$ calculated from the HNC/HNC approximation for a binary suspension with bulk parameters $K_1 = 30$, $K_2 = 14$, $z = 0.15$, and $\phi_1 = \phi_2 = 2.1 \times 10^{-4}$, when (a) $K_w = 25$, and (b) $K_w = 10$.

sponds to a process in which the intensity of the wall–particle repulsion is lowered by varying the dimensionless surface charge density parameter K_w from $K_w = 25$ (which corresponds to $\sigma_{el} = 4.96 \times 10^{10} e^-$ m^{-2}) to $K_w = 0$. This process starts with a highly repulsive wall and ends with a neutral wall. Let us first compare the results in Figs. 1(a) and 1(b). In both cases, the repulsive forces between the wall and the particles are so strong that the particles of both species are expelled from a region adjacent to the wall. The width of this empty slab is clearly dependent on the strength of the wall–particle repulsion, and increases when K_w increases. Other than that, the shape of the local concentration profiles in these two figures happen to be the same, i.e., the width and the relative spacing of the successive oscillations of $g_{wi}(x)$ are not affected when K_w changes, as long as it is kept above a certain threshold value K_w^*. Thus, the profiles in Fig. 1(a) are found to superimpose almost exactly on top of the profiles in Fig. 1(b) upon an adequate horizontal displacement. This effect, first discovered in similar calculations involving
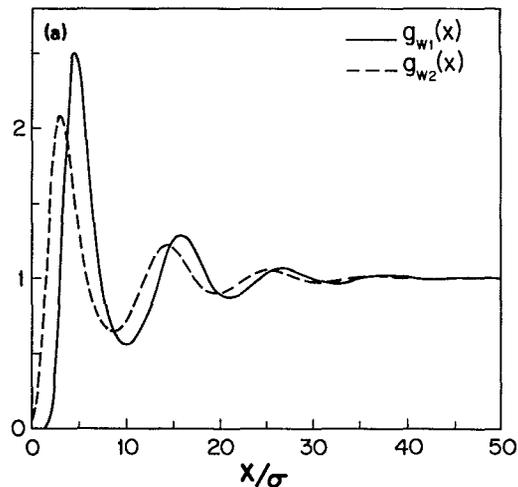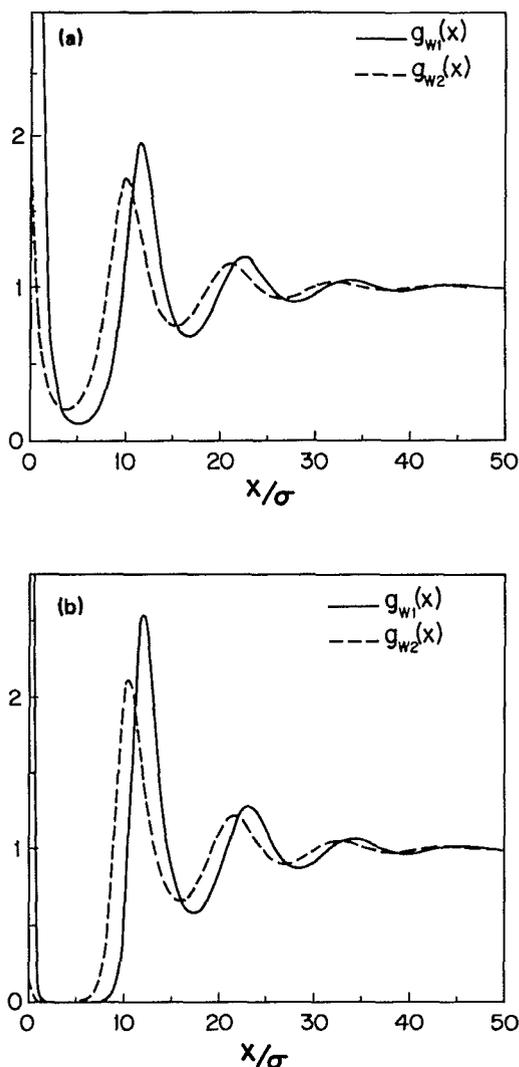
FIG. 3. Wall–particle distribution function $g_{wi}(x)$ calculated from the HNC/HNC approximation for a suspension with the same bulk parameters as in Fig. 1, but with (a) $K_w = 2$, and (b) $K_w = 0$.

monodisperse suspensions,[21(a)] indicates that the structure of the inhomogeneous mixture in front of highly repulsive walls only depends on the bulk parameters of the mixture (K_1, K_2, z, ϕ_1, and ϕ_2 in our model), and not on the wall–particle interactions, which only determines, for fixed bulk parameters, the width of the depletion slab. Let us point out that this particular feature may be rather specific to the DLVO model of the wall–particle interactions employed here [see Eq. (5)], in which a single parameter, namely, K_w, determines the strength of both wall–particle potentials $u_{w1}(x)$ and $u_{w2}(x)$ (for given bulk parameters). Thus, increasing K_w increases these potentials in a proportional manner. Nevertheless, as long as the wall–particle electrostatic interaction depends linearly on the surface charge density or surface potential, as in our particular DLVO model, the general picture just described should also be expected for other models of the wall–particle forces.

The regime discussed above corresponds to highly re-

pulsive walls, and is characterized by the appearance of the region adjacent to the wall for which both, $g_{w1}(x)$ and $g_{w2}(x)$ attain vanishingly small values. The threshold value K_w^* may then be defined as the largest value of K_w for which the contact values $g_{w1}(0 +)$ and $g_{w2}(0 +)$ of these two distribution functions remain negligibly small (e.g., $\leqslant 10^{-2}$). Clearly, this threshold value is a property of the bulk parameters. For the specific conditions of the model suspension in our illustration, we find that $K_w^* \approx 5$. Figure 2(a) corresponds to these conditions. As the charge on the wall is decreased still further, i.e., as K_w decreases below this threshold value, the shape of the distribution functions now become dependent on the surface charge density parameter K_w. Figure 2(b) illustrates this regime, corresponding to weakly repulsive walls. As can be observed from this figure, now the first maximum of both distribution functions have moved towards the wall, and the second and successive maxima have also moved to the left, changing their heights. At the same time, the first valley of both distribution functions is being depressed down to smaller values, and the contact value of the more highly charged species grows significantly faster compared to the contact value of the other species. This is better illustrated comparing Fig. 2(b) with Figs. 3(a) and 3(b).

As can be observed from this comparison, the contact value of the less highly charged species not only does not increase any further as K_w is lowered from $K_w = 2$ to $K_w = 0$, but it decreases to a rather small value [for $K_w = 2$, $g_{w2}(0 +) = 2.10$, and for $K_w = 0$, $g_{w2}(0 +) = 0.23$, while the respective values of $g_{w1}(0 +)$ are 31.2 and 207.0]. This indicates that as the wall is being discharged, the local composition of the mixture near the wall shows a preferential adsorption of the more highly charged species. Notice also that as this occurs, the formation of a distinct monolayer of electrostatically absorbed particles onto the wall has been completed [Fig. 3(b)]. This is indicated by the region where $g_{w1}(x)$ and $g_{w2}(x)$ attain vanishingly small values between the cusps at contact and the second maximum. The formation of this monolayer had already been observed and discussed in results similar to these but dealing with monodisperse suspensions. Clearly, some of the features observed for mixtures are completely analogous. For example, one can compare the structure of the nonadsorbed particles ($g_{wi}(x)$ for $x > 2\sigma$), with the structure of the mixture near highly repulsive walls, such as in Figs. 1(a) and 1(b). From such a comparison we find that the shape of $g_{wi}(x)$ in both cases may superimpose almost exactly upon an adequate horizontal shift. As in the monodisperse case, if one decreases K_w to still lower (negative) values, to consider attractive walls, the same pattern is observed as for monodisperse suspensions. Thus, although we do not illustrate this graphically, we find that as K_w decreases below 0, the only effect observed in $g_{wi}(x)$ is that the width of the monolayer decreases, and the subsequent region with $g_{wi}(x) \approx 0$ becomes still wider, thus pushing to the right the other, nonadsorbed particles without change in the shape of their structure.

Thus, we find mostly the same features already observed in monodisperse suspensions.[21] The most important difference in then the evolution of the local composition of the

mixture near the wall. As we saw, as the monolayer is being formed, a tendency of the more highly charged species to adsorb preferentially onto the wall is clearly observed. This is also understandable as the result of the same physical mechanism by which the monolayer itself is formed. Thus, the more highly charged particles experience more strongly the imbalance of the electrostatic forces originating from the absence of charge on the wall when $K_w \rightarrow 0$.

IV. THE ADSORBED MONOLAYER AS AN EFFECTIVE REPULSIVE WALL

The trapped monolayer is formed due to the electrostatic repulsion exerted by the unconfined particles on the adsorbed particles. Since this pressure is not counter balanced by a similarly strong wall–particle repulsion, the particles in the vicinity of the wall are pushed against the hard wall so strongly that they become electrostatically bound. It is important to remark that no other kind of forces (van der Walls, steric, etc.) have been taken into account, and therefore, this phenomenon is only of electrostatic nature. Let us also remark that the concentration profile has been calculated from an equilibrium theory. Thus, this profile only describes the equilibrium states which under experimental conditions may be expected to establish only after a probably long equilibration time. How long this relaxation time may be, in order to reach equilibrium, must be determined by kinetic considerations which are beyond the present discussion.

Let us discuss in more detail the features of the static structure when the adsorbed monolayer appears. Once the monolayer is formed, it in turn acts as an effective surface charge density which produces the effect of a highly repulsive wall on the unconfined particles. Let us calculate such an effective potential by defining a surface number density of adsorbed particles of the species i, ν_i, as

$$\nu_i = n_i \int_0^\Delta g_{wi}(x)dx, \tag{14}$$

where Δ is the "width" of the monolayer, i.e., it is the distance from the wall to the point where the total density

$$n_w(x) = \sum_i n_{wi}(x) \tag{15}$$

first decreases down to, say, 10^{-2} times the total bulk density $n_w(\infty)(=\Sigma_i n_i)$. For the conditions in Fig. 3(b), $\Delta \approx 2.1\sigma$. The surface number densities ν_i are better expressed in dimensionless form by defining the surface fraction coverage of the monolayer by particles of species i,

$$\sigma_i^{(m)} \equiv \frac{\pi}{4}\nu_i\sigma^2. \tag{16}$$

For example, for $K_w = 0$, using the results for $g_{wi}(x)$ in Fig. 3(b), we find that $\sigma_1^{(m)} = 7.91 \times 10^{-3}$ and $\sigma_2^{(m)} = 1.99 \times 10^{-5}$, i.e., the adsorbed particles of species 1 cover 0.8% of the wall surface, where a species 2 covers only 0.002%.

Once this average surface densities ν_i are determined, the effective potential for the interaction between the mono-

layer and one of the unconfined particles of species i, $u_i^{\text{eff}}(x)$, may be obtained from

$$u_i^{\text{eff}}(\mathbf{r}) = \sum_j \int u_{ij}(|\mathbf{r} - \mathbf{r}'|)n_j^{(m)}(\mathbf{r}')d^3\mathbf{r}', \tag{17}$$

where $u_{ij}(r)$ is the pair potential between a particle of species i and a particle of species j, and with $n_j^{(m)}(\mathbf{r}')$ being the local concentration of the adsorbed particles of species j in the monolayer, i.e.,

$$n_j^{(m)}(\mathbf{r}') = \nu_j\delta(x') \tag{18}$$

(here the finite width Δ of the monolayer has been neglected). Thus, using Eq. (18) and the form for u_{ij} in Eq. (4), the integral in Eq. (17) can be evaluated using polar coordinates, with the following result

$$\beta u_i^{\text{eff}}(x) = \frac{8e^zK_i}{z}\sum_j \sigma_j^{(m)}K_j e^{-z(x/\sigma)}, \tag{19}$$

which may also be written as

$$\beta u_i^{\text{eff}}(x) = K_w^{\text{eff}}K_i e^{-z(x/\sigma)}, \tag{20}$$

with

$$K_w^{\text{eff}} = \frac{8e^z}{z}\sum_j \sigma_j^{(m)}K_j. \tag{21}$$

For example, for the conditions of Fig. 3(b), corresponding to an uncharged wall, we find that the adsorbed monolayer mimic the effect of a charged surface, with an effective surface charge parameter $K_w^{\text{eff}} = 14.7$. Just as it was done before in the monodisperse case,[21(b)] we may compare the structure of the suspension near the uncharged wall [Fig. 3(b)] with the structure of the same suspension near a repulsive wall, with a surface charge parameter $K_w = K_w^{\text{eff}} = 14.7$. Such a comparison is presented in Fig. 4, in which the result in Fig. 3(b) are reproduced (in solid lines) and compared
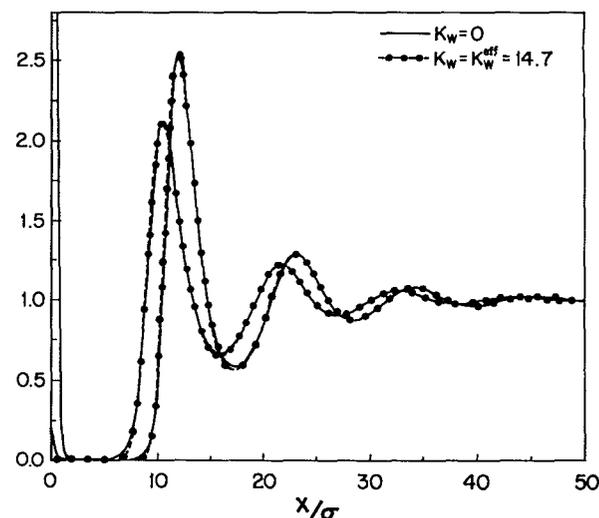
FIG. 4. Comparison of the wall–particle distribution functions $g_{wi}(x)$ for the system in Fig. 3(b) (solid line) with the corresponding $g_{wi}(x)$ for the same bulk parameters, but with $K_w = K_w^{\text{eff}} = 14.7$ (dashed line with circles).

with the calculations for $K_w = 14.7$. As we can see from this comparison, the interpretation of the adsorbed monolayer as the source of an effective field on the other, nonconfined particles, has a full degree of quantitative accuracy, to such an extent that it is difficult to distinguish the two curves $g_{wi}(x)$ for $x > \Delta$ in the scale of the figure.

V. CONCLUDING REMARKS

In this paper we have shown that all of the features of the structure of a monodisperse suspension of highly charged particles near a charged (o uncharged) wall, predicted by inhomogeneous-liquid theories, are also apparent in the corresponding results for colloidal binary mixtures. Thus, for highly repulsive walls, the shape of the local concentration profiles are found to depend only on the bulk parameters of the mixture, as long as the surface charge parameter K_w exceeds a certain threshold value K_w^*. The actual value of $K_w (> K_w^*)$ only fixes the thickness of the depletion slab, i.e., the region adjacent to the wall which the huge wall–particle repulsion renders inaccessible to the colloidal particles. In a similar manner as in the monodisperse case, we have also found that when K_w decreases below K_w^*, the particles may now come into contact with the wall. For low enough wall–particle repulsions, some of the particles are pushed against the wall by the unbalanced electrostatic pressure exerted by the rest of the particles. This produces eventually the formation of a well-defined monolayer of electrostatically trapped particles. In the case of mixtures, we saw in this paper that this monolayer is constituted mainly of particles of the species with the largest electric charge, this being the main new feature originating from the electric asymmetry of the colloidal species. Here we also showed that the role of the adsorbed monolayer as the source of an effective field is, as in the monodisperse case, an interesting concept which finds an accurate quantitative description in the comparison explained in Fig. 4. Although our model does not consider Van der Waals interactions, this is not a major problem concerning particle–particle interactions, since we have restricted ourselves to highly charged particles, i.e., we have in mind a highly electrostatically stable suspension. This may be however, a severe limitation concerning wall–particle interactions, since in this last case the colloidal particles are in contact with the wall. As it was stressed in Ref. 21(b), Van der Waals and other forms of short-ranged interactions, like chemical bonds, will play an important role under experimental conditions. These interactions will modify the strength of the adsorption of the confined macroparticles, and will introduce irreversiblity effects in the adsorption process. Still, due to the importance of electrostatic interactions in suspensions of highly charged particles, the description of their effects, even under the idealized conditions considered in this work, will be useful in developing a more fundamental understanding of rather practical processes such as colloid deposition on surfaces.

As a final remark, let us emphasize that in spite of the rather abundant studies of inhomogeneous fluids near walls, to our knowledge no similar findings have been reported before in the literature. This is problably due to the rather marginal interest that the hard-sphere plus repulsive Yukawa model has in the context of the theory of atomic liquids, from which the theoretical approaches employed here derive. Thus, already from a purely statistical mechanical point of view, our results represent an interesting addition to the theoretical understanding of the properties of inhomogeneous fluids. Nevertheless, our original main motivation for considering this rather simple model was its relevance, and potential practical usefulness, in understanding the current and future results of the experimental studies of specific colloidal suspensions, in the presence of the external fields.

ACKNOWLEDGMENTS

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