

Sedimentation of binary mixtures of like- and oppositely charged colloids: the primitive model or effective pair potentials?

Marjolein Dijkstra¹, Jos Zwanikken² and René van Roij²

¹ Soft Condensed Matter, Debye Institute, Utrecht University, Princetonplein 5, 3584 CC Utrecht, The Netherlands

² Institute for Theoretical Physics, Utrecht University, Leuvenlaan 4, 3584 CE Utrecht, The Netherlands

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Abstract

We study the sedimentation equilibrium of low salt suspensions of binary mixtures of charged colloids, both by Monte Carlo simulations of an effective colloids-only system and by Poisson–Boltzmann theory of a colloid–ion mixture. We show that the theoretically predicted lifting and layering effect, which involves the entropy of the screening ions and a spontaneous macroscopic electric field (Zwanikken and van Roij 2005 *Europhys. Lett.* **71** 480), can also be understood on the basis of an effective colloid-only system with pairwise screened-Coulomb interactions. We consider, by theory and by simulation, both repelling like-charged colloids and attracting oppositely charged colloids, and we find a re-entrant lifting and layering phenomenon when the charge ratio of the colloids varies from large positive through zero to large negative values.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Suspensions of charged colloids are multicomponent mixtures of mesoscopic (colloidal) particles and microscopic cations, anions, and solvent molecules. Due to the large size asymmetry and charge asymmetry between the colloids on the one hand and the microscopic species on the other, it is often difficult to treat all species on an equal footing in descriptions of for example the thermodynamic equilibrium properties of these systems. Given the asymmetry it is natural, and often practical, to view colloidal suspensions as ‘colloids-only’ systems described by effective colloidal interactions in which the presence of the microscopic particles appear only through medium properties such as the dielectric constant ϵ and the Debye screening length κ^{-1} . For bulk systems in equilibrium one can in fact prove (by formally integrating out all the microscopic degrees of freedom in the partition function in a fixed colloid configuration) that such a course-grained description yields the exact thermodynamics; the problem is of course to actually perform the integration explicitly. Within linear screening

theory it is possible to integrate out the ionic degrees of freedom explicitly, and the resulting effective colloid pair interactions are of the screened-Coulomb form $\propto \exp(-\kappa r)/r$, with r the centre-to-centre distance between the colloidal pair [1]. Descriptions of suspensions of charged colloids on the basis of this effective pair potential have often been used over the years; see e.g. [2, 3] for a few examples related to crystallization of charged colloids, and [4] for a sedimentation study.

However, in recent studies of sedimentation equilibrium of charged colloids at extremely low salinity this effective ‘colloids-only’ view was *not* taken. Instead the experiments [5–8], theory [9–14], and simulations [15] of sedimentation equilibrium were essentially all analysed within the so-called primitive model, in which the colloids and ions are treated as charged massive hard spheres and charged massless point particles, respectively, while the solvent is treated as a continuum with dielectric constant ϵ . These studies have shown the existence of a spontaneously formed macroscopic electric field that lifts the colloids to much higher altitudes than to be expected on the basis of their mass. This electric field is the result of the competition between entropy (favouring a homogeneous fluid), electrostatics (favouring local neutrality), and gravitational energy (favouring the colloids at the bottom, but not the cations or anions because they are essentially massless) [13]. At high salt concentrations local neutrality can easily be fulfilled at low entropic cost because of the large number of ions, and hence the competition is the usual one between colloid entropy and gravity, giving rise to a barometric distribution at low packing fractions. At low salinity the situation is more complicated, since fulfilling local neutrality would imply, when the colloids are all close to the bottom because of gravity, that a large fraction of the counterions must also be close to the bottom. Such a state has a low ion entropy, because the ion distribution is far from homogeneous. It turns out, according to theories of for example [9, 13], that the state with the lowest grand potential spontaneously sacrifices local neutrality at the bottom and at the meniscus, such that an electric field is generated that lifts the colloids upwards at the expense of gravitational energy, such that the colloids and the counterions can be rather homogeneously distributed over the available volume, thereby increasing their entropy. For colloids with buoyant mass m and charge Ze the generated electric field strength was shown to be $E \simeq mg/Ze$ at low enough salt concentrations, such that the upward electric force ZeE and the downward gravitational force mg essentially cancel each other, leading to almost homogeneously distributed colloids. Here g is the gravitational acceleration, and e the proton charge. This lift mechanism involving a macroscopic electric field was confirmed by primitive model simulations of colloids and explicit ions [15], and by a direct measurement of the potential difference between the bottom and the meniscus [7]. Moreover, quantitative agreement was found between the measured density profiles and the theoretically calculated ones in [8], while the measured profiles of [6, 7] agree with the theory of [14] which involves the electric field mechanism combined with charge regularization.

It is at first sight not at all obvious that these phenomena, which involve charge separation and macroscopic electric fields, can be described within the framework of the effective colloids-only picture. After all, in this picture the presence of anions and cations is only accounted for in the screening length κ^{-1} that determines the range of the effective pairwise interactions. However, the theoretical study of [13] showed that hydrostatic equilibrium between the external gravity field and the internal (osmotic) pressure of the effective colloids-only system (described by the simple and crude Donnan equation of state in [13]), actually predicts the existence of the electric field and the lift effect at low salinity, despite the underlying local density (and hence local neutrality) approximation. The predicted density profile is linear with height [13], not unlike those predicted by a density functional treatment of an effective colloids-only system with screened-Coulomb interactions [4]. Recently other accurate osmotic equations of state were employed and revealed the lift effect [16, 17], and in fact [17] shows that the colloid

density profile that was experimentally measured and quantitatively described in terms of the primitive model in [8] can *also* be described quantitatively by a colloids-only theory with screened-Coulomb interactions. The inconsistency of a theory based on local charge neutrality that predicts an electric field without explaining its sources does not, apparently, lead to erroneous predictions for the density profile, at least not for monodisperse suspensions at the parameters considered.

The question we address in this paper is whether the ‘colloids-only’ picture can also account for the very recently predicted layering and segregation phenomena in equilibrium sediments of *binary* mixtures of charged colloids at low salinity [18–20]. These studies are actually direct extensions of the primitive model discussed before, but now with two (or more) colloidal components with different charges and masses. Not only was the lifting effect recovered in [18–20], but in addition segregation into layers was found, such that the two colloidal species order with height according to mass-per-charge: the colloids with the lowest mass-per-charge are found at higher altitudes. This implies the possibility of an inversion phenomenon, whereby sufficiently highly charged heavy colloids float on top of lighter colloids with a lower charge [18–20]. In terms of the electric field this phenomenon can be understood, at least qualitatively, by first considering a pure system of colloidal species with mass m_1 and charge Z_1e , such that the electric field strength is $E \simeq m_1g/Z_1e$ according to [13]. Adding a trace amount of colloids with mass m_2 and charge Z_2e does not change the field strength E , and hence the upward force Z_2eE on the colloids of species 2 exceeds the downward force m_2g provided $m_2/Z_2 < m_1/Z_1$. In other words, if the mass-per-charge of the tracer species 2 is smaller than that of species 1, the former will float on top of the latter, even if $m_2 > m_1$. In the case that both colloidal species are present in substantial amounts, the segregation into layers was found with electric field strengths $E_i \approx m_i g/Z_i e$ in the layer with species i [19]. This implies a finite, nonzero charge density in the crossover regime from one layer to another, as observed in [19]. The question we address in this paper is whether hydrostatic equilibrium (based on a local density and neutrality assumption) in a colloids-only system with screened-Coulomb interactions can catch this layering phenomenon.

There is, in addition, a second motivation for our present study. It stems from recent experimental progress in preparing binary mixtures with *oppositely* charged colloids that do not aggregate but form equilibrium crystals [3]. It is of fundamental interest to investigate the consequence of opposite charges in the equilibrium sediment, in particular when there is a substantial mass difference between the two colloidal species: to what extent does the lighter species then lift the heavier one, and to what extent does segregation into layers take place? We therefore present not only results for colloidal mixtures with the same charge sign ($Z_1 Z_2 > 0$), but also with a different sign ($Z_1 Z_2 < 0$). Sedimentation in this latter parameter regime has, to the best of our knowledge, not been studied at all yet. We compare the results of computer simulations of the effective colloids-only system with theoretical calculations based on the Poisson–Boltzmann theory of [19].

This paper is organized as follows. In section 2 we present the model of the suspension, and discuss it viewed as either a mixture of colloids and ions as in [19] or as an effective colloids-only system that we simulate. In section 3 we present the resulting equilibrium density profiles, and section 4 is devoted to a discussion.

2. One model and two theories

In this section we introduce the details and the notation of our model of a binary mixture of charged colloids that we use in this paper, and discuss two alternative ways of describing the equilibrium density profiles in sedimentation equilibrium.

We denote the (fixed) colloidal charges, radii, and buoyant masses by $Z_i e$, a_i , and m_i for the two species $i = 1, 2$, and assume that the charge is homogeneously distributed on the colloidal surface. The solvent is a continuum with dielectric constant ϵ at temperature T , and the solvent volume is $V = AH$ with A the (thermodynamically large) area in the horizontal plane and H the vertical height between the bottom of the sample (at height $x = 0$) and the meniscus (at height $x = H$). The gravitational force points in the negative vertical direction, such that the potential energy of a colloid of species i at height x is given by $m_i g x$, with g the gravitational acceleration. It is convenient to introduce the so-called gravitational length $L_i = k_B T / m_i g$, which is the characteristic length scale of the barometric density distribution that holds in the dilute limit.

The density profiles and the number of colloidal particles in the sample are denoted by $\rho_i(x)$ and N_i , respectively, for species $i = 1, 2$. We will also use the packing fraction profile $\eta_i(x) = (4\pi/3)a_i^3 \rho_i(x)$, and we characterize the density of the suspension by the overall packing fractions $\bar{\eta}_i = (4\pi/3)a_i^3 N_i / V = (1/H) \int_0^H dx \eta_i(x)$. The average height of species i , or its centre-of-mass, is defined as

$$h_i = \frac{\int_0^H dx \rho_i(x) x}{\int_0^H dx \rho_i(x)}, \quad (1)$$

which can be seen as a rough indication of the nature of the colloidal profile.

The suspension is imagined to be in osmotic contact with a reservoir of massless, monovalent cations and anions of charge $\pm e$, with a total ion density $2\rho_s$, such that the Debye screening length (in the reservoir) is $\kappa^{-1} = (8\pi\lambda_B\rho_s)^{-1/2}$, where $\lambda_B = e^2/\epsilon k_B T$ is the Bjerrum length of the medium. Here k_B denotes the Boltzmann constant.

In the present calculations we restrict attention to spheres of equal radius, and we denote the (common) diameter of the spheres by $2a_1 = 2a_2 \equiv \sigma$.

2.1. Poisson–Boltzmann theory for the colloid–ion mixture

It was shown in [19] that this system can be described by five coupled nonlinear equations for the following five unknown profiles: the colloid densities $\rho_1(x)$ and $\rho_2(x)$, the two ion densities $\rho_{\pm}(x)$ for the cations (+) and anions (−), and the electrostatic potential $\psi(x)$ or its dimensionless form $\phi(x) = e\psi(x)/k_B T$. Two relations are given by the Boltzmann distributions $\rho_{\pm}(x) = \rho_s \exp[\mp\phi(x)]$ for the ions, while the other three relations are a Boltzmann distribution for the colloidal densities and the Poisson equation for the potential, namely

$$\begin{aligned} \rho_i(x) &= c_i \exp\left(-\frac{x}{L_i} - Z_i \phi(x)\right) \quad (i = 1, 2); \\ \phi''(x) &= \kappa^2 \sinh \phi(x) - 4\pi\lambda_B (Z_1 \rho_1(x) + Z_2 \rho_2(x)), \end{aligned} \quad (2)$$

where a prime denotes a derivative with respect to x , and where c_i represent normalization constants such that $A \int_0^H dx \rho_i(x) = N_i$. We impose boundary conditions $\phi'(0) = \phi'(H) = 0$, which corresponds to a globally charge neutral system without any external electric field. This set of five equations follows directly from the minimum condition on a grand potential functional that only involves ideal-gas contributions for all four species, a potential energy of the colloids due to their mass, and a Coulomb energy treated at a mean-field level [19]. It is straightforward to solve this set numerically on an x -grid; for details see [19]. From the solution for $\phi(x)$ the magnitude of the electric field follows as $(k_B T/e)\phi'(x)$.

We note that these five equations are independent of the hard-core radii a_i of the colloids, i.e. the short-range part of the (direct) correlations are not taken into account. As a consequence

this level of approximation is not capable of describing packing effects properly. The radii a_i are therefore only used to convert $\rho_i(x)$ to $\eta_i(x)$. Despite this shortcoming the present theory agrees quantitatively with the primitive model simulations of [18, 21].

2.2. The colloids-only theory

The Poisson–Boltzmann theory for the colloid–ion mixture differs, at least at first sight, substantially from a description of charged colloids based on the idea that colloids interact with each other through effective interactions that depend on the solvent properties such as the dielectric constant ϵ , the Debye screening length κ^{-1} , and the temperature T . Standard linear screening theory [1] predicts that two colloids with charges $Z_i e$ and $Z_j e$ and radii a_i and a_j , separated by a distance r , interact with the pair potential $V_{ij}(r)$ given by

$$\frac{V_{ij}(r)}{k_B T} = Z_i Z_j \lambda_B \left(\frac{\exp(\kappa a_i)}{1 + \kappa a_i} \right) \left(\frac{\exp(\kappa a_j)}{1 + \kappa a_j} \right) \frac{\exp(-\kappa r)}{r}, \quad (3)$$

with the Boltzmann constant k_B and the Bjerrum length $\lambda_B = e^2/\epsilon k_B T$ as already introduced above. Here we ignore the attractive dispersion forces. Within this effective ‘colloids-only’ description the presence of salt ions (with a concentration $2\rho_s$ in the reservoir) is entirely included through the screening length κ^{-1} . We assume throughout that the screening length in the colloidal interactions is independent of the colloid concentration. Ignoring the counterion contribution to κ will turn out to be entirely justified for all cases we study in this paper: the ratio $y(x) \equiv \sum_{i=1}^2 Z_i \rho_i(x)/2\rho_s$ is always such that $|y(x)| \ll 1$, i.e. the background electrolyte dominates the screening. Typically we find $|y(x)| \simeq 0.01$ – 0.2 , and since the effective screening parameter can be written as $\kappa^{-1}(1 + y^2)^{-1/4}$ according to the Donnan-like theory of for example [22, 23], provided the packing fraction is not too high, we find with $(1 + y^2)^{-1/4} \simeq 1 - y^2/4$ that the effective screening length differs from the reservoir value κ^{-1} by at most one per cent.

The effective ‘colloids-only’ description based on equation (3) has proved to be very successful in describing many facets of colloid science; for example, in the case of monodisperse suspensions it explains freezing into fcc and bcc crystals at sufficiently high densities [2], and it was recently used to describe crystal structures of oppositely charged colloids successfully [3].

In this paper we use equation (3) in Monte Carlo simulations in a box of dimensions $K \times K \times H$, with $K^2 = A$ the horizontal area. In all cases the vertical box height was taken to be $H = 109\sigma$, and the lateral width $K = 10\sigma$. We checked that K was large enough to exclude finite size effects. We employed periodic boundary conditions in the horizontal directions; in the vertical direction the system is bounded by hard walls that exclude the centre of colloids at heights $x < 0$ and $x > H$.

3. Results

3.1. Heavy colloids

We first consider binary mixtures of equal-sized colloids with a diameter $\sigma = 1950$ nm, a Bjerrum length $\lambda_B = 10.4$ nm, and screening constant such that $\kappa\sigma = 1.2$. This corresponds to a salt concentration $\rho_s = 2.4$ nM in the reservoir. In addition, we fix the colloidal charge of species 1 to $Z_1 = 76$, and the gravitational length of species 1 to $L_1 = 2.5\sigma$. These numerical values, which correspond to the experimental system of [8], give rise to an effective contact potential between the colloids of species 1 given by $V_{11}(\sigma) = 12 k_B T$. The mass of species 2 is taken to be larger than that of species 1, by a factor of 2, such that $L_2 = 1.25\sigma$.

In figure 1 we plot the colloidal density profiles for three equimolar suspensions, with average packing fractions $\bar{\eta}_1 = \bar{\eta}_2 = 0.005$, for three values of the charge of species 2 given by (a) $Z_2 = 300$, (b) $Z_2 = 0$, and (c) $Z_2 = -300$. The box height is in all cases $H = 109\sigma$. Case (a), for which $Z_2L_2 > Z_1L_1$, shows a layer of the heavier species 2 floating on top of a layer of primarily species 1, both from the theory based on equations (2) [18, 19], and from the colloids-only simulations using equation (3). The agreement between the theory and the simulations is quantitatively reasonable though not perfect. In particular the packing effects shown by the simulations at length scales of the order of a few σ close to the hard walls of the container are not reproduced by the theory, and the lifting effect for species 2 as predicted by the theory is quite a bit stronger than that found in the simulations. Nevertheless it is a striking observation that the colloids-only picture is capable of describing the layering phenomenon without invoking explicitly a selfconsistent electric field. Case (b), where $Z_2 = 0$ such that it represents a mixture of charged and uncharged colloids, shows a clear lifting effect for species 1, both from the theory and the simulations. The theoretical prediction for species 2 is a barometric distribution, which is bound to fail quantitatively in comparison with the simulations given the high packing fraction up to 0.5 at the bottom, which causes hard-sphere-like density oscillations of species 1 close to the bottom in the simulations. Case (c) is for oppositely charged colloids, and shows again a lifting and layering effect, whereby a layer of the heavier species 2 floats onto a rather dense layer at $x \lesssim 15\sigma$, both in the simulations and in the theory. Ignoring the density oscillations on a length scale of a few σ in this bottom layer, the densities take the almost constant values $\eta_1(x) \simeq 0.035$ and $\eta_2(x) \simeq 0.018$, i.e. there is no large systematic decay and the ratio of the two densities does *not* correspond to $|Z_1/Z_2|$. In fact, the agreement between theory and simulations in (c) is much less satisfactory than in the cases (a) and (b): not only are the packing effects in the bottom layer not captured by the theory (as before), but also the ‘smoothed’ simulated profiles differ substantially from the theoretically predicted ones. We expect this to be caused by the strong correlations that build up between attracting pairs of oppositely charged colloids, with a contact potential of $V_{12}(\sigma) = -47.5 k_B T$, and between the repelling pairs of species 2 with a contact potential $V_{22}(\sigma) = 187 k_B T$. These correlations are not at all included in the theory. We checked explicitly that the bottom phase in the simulations is fluid and not crystalline.

An interesting observation that can be made on the basis of figure 1 is that species 2 floats onto a relatively dense layer (with an almost constant composition) if $Z_2 = \pm 300$, while species 1 floats onto a denser layer if $Z_2 = 0$. We can quantify this re-entrant layering effect by studying the average height h_i as defined in equation (1) as a function of Z_2 , keeping Z_1 and all the other parameters fixed. The result is shown in figure 2, and confirms the re-entrant phenomenon. It shows overall agreement between theory and simulation for all Z_2/Z_1 , although the agreement is substantially better for like-charged colloids ($Z_2 > 0$) than for opposite colloids ($Z_2 < 0$). For $Z_2/Z_1 \gtrsim 2$ the theory overestimates the lifting effect for the heavier particles and underestimates it for the lighter particles, in comparison with the simulations. For $Z_2/Z_1 \lesssim -1$ the theory predicts an essentially barometric distribution for the lighter species (with a lower absolute charge), whereas the simulations still show a considerable lift effect for species 1 in this regime, probably because they are correlated due to the attractions of the highly charged heavier colloids that float on top of them; this effect is poorly caught within the present theory. Note that for the equimolar case considered here the theory predicts $h_1 = h_2$ for $Z_1L_1 = Z_2L_2$ (i.e. for $Z_2/Z_1 = 2$ here) and for $Z_1 \simeq -Z_2$ (since then $\phi(x) \simeq 0$). On the basis of the numerical results of figure 2 these seem to be reasonable estimates for the crossover regimes.

We also studied the effect of the screening length on the mean height of the colloids. The result is shown, for the parameters of figure 1(a), in figure 3. Here the theory is found to be not

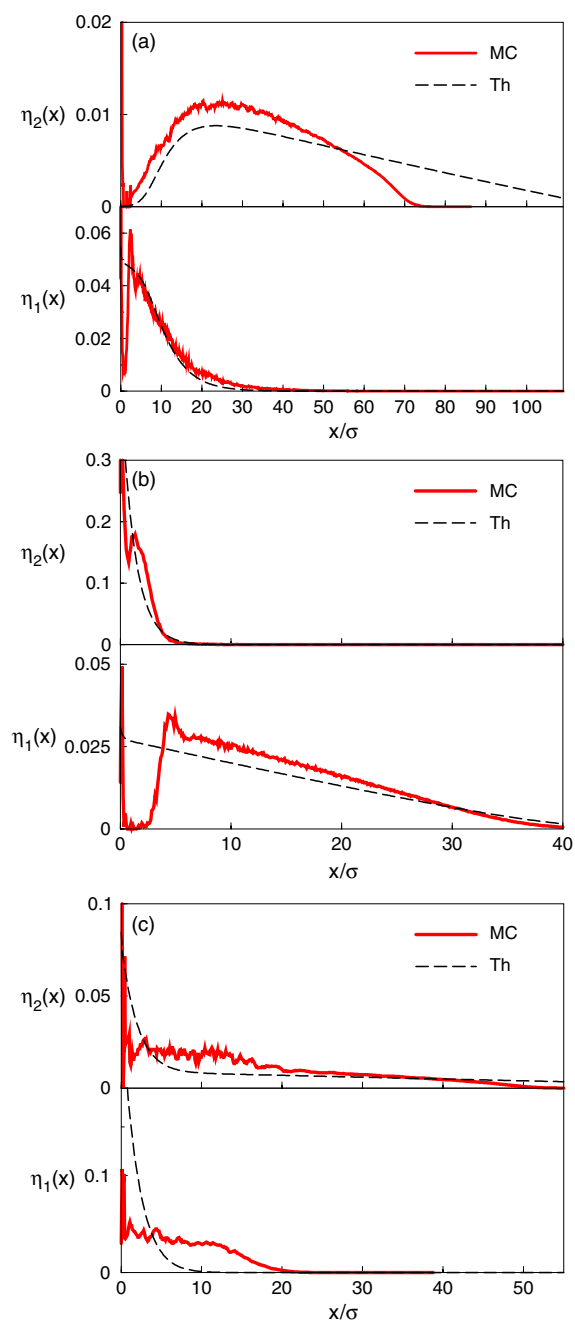


Figure 1. Simulated (full curves) and theoretically calculated (dashed curves) equilibrium sedimentation profiles for a binary mixture of lighter (species 1) and heavier (species 2) colloidal particles with charges $Z_1 = 76$ and various charges Z_2 given by (a) $Z_2 = 300$, (b) $Z_2 = 0$, and (c) $Z_2 = -300$, as a function of altitude x in a sample of height $H = 109\sigma$. The common diameter of the colloids is $\sigma = 1950$ nm, the mass ratio is $m_2/m_1 = 2$, the gravitational lengths are $L_1 = k_B T/m_1 g = 2.5\sigma$ and $L_2 = 1.25\sigma$, the total packing fractions are $\bar{\eta}_1 = \bar{\eta}_2 = 0.005$, the Bjerrum length is $\lambda_B = 10.4$ nm, and the screening parameter is $\kappa\sigma = 1.2$.

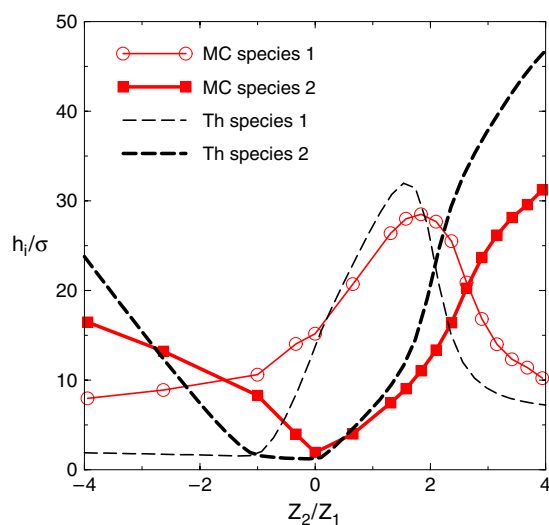


Figure 2. Simulated (full curves) and theoretically predicted (dashed curves) mean heights h_i of light (open circles, species 1) and heavy (solid squares, species 2) colloids as a function of the charge ratio Z_2/Z_1 for fixed $Z_1 = 76$. All other parameters are identical to those of figure 1.

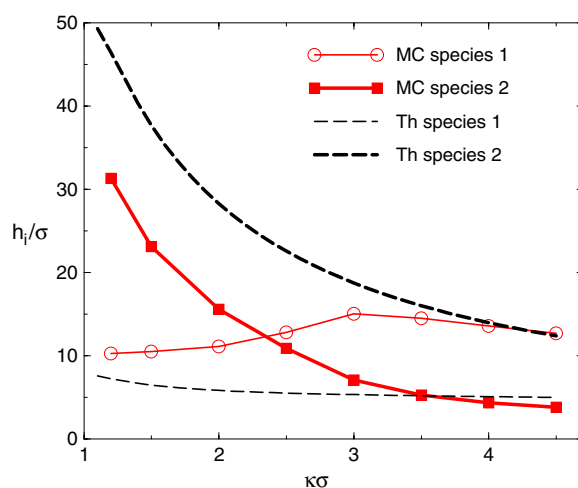


Figure 3. Simulated (full curves) and theoretically predicted (dashed curves) mean heights h_i of light (open circles, species 1) and heavy (solid squares, species 2) colloids as a function of the screening parameter $\kappa\sigma$ for fixed $Z_1 = 76$ and $Z_2 = 300$. All other parameters are identical to those of figure 1.

at all in agreement with the simulations, except perhaps for the decreasing mean height of the heavier species 2 with increasing $\kappa\sigma$. The crossover where $h_1 = h_2$ is found to be at $\kappa\sigma \simeq 2.4$ in the simulations, whereas the theory cannot locate a crossover at all for any reasonable $\kappa\sigma$. Moreover, the theory cannot catch the phenomenon of increasing h_1 with increasing $\kappa\sigma$ for $\kappa\sigma \lesssim 3$. One could argue that the theory breaks down, not only quantitatively but even qualitatively, when $\kappa\sigma \gtrsim 2$.

3.2. Lighter colloids

For the sake of comparison we repeated the study reported above to the case where both colloidal species are ten times lighter, such that $L_1 = 25\sigma$ and $L_2 = 12.5\sigma$. We left all the other parameters identical to those of figures 1–3.

In figure 4 we consider the three density profiles for the three charges (a) $Z_2 = 300$, (b) $Z_2 = 0$, and (c) $Z_2 = -300$, and find reasonably good agreement between theory and simulation for cases (a) and (b), and now in fact also for case (c). As in the case of the heavier colloids the theory still fails to describe the oscillating character of the profiles close to the bottom and the meniscus, but in all cases it can account for a ‘smoothed’ version of the simulated profiles. We note that case (a) does not show a significant layering effect, in the sense that the density profiles of both species span the whole sample from bottom to meniscus. This can be understood from the theory of [19] if one realizes that both $Z_1L_1, Z_2L_2 \gg H$, i.e. both species would prefer to be lifted to much higher altitudes than the present system size $H = 109\sigma$ allows. Unlike the layering effect, the lift effect remains clearly visible for this relatively small H . In figures 4(b) and (c) the layering effect does exist, although it is perhaps a bit weaker than in the case of the heavier colloids discussed above. We can again conclude that the lifting (and layering) effect can be accounted for within a colloids-only picture, and that there is a re-entrant phenomenon with varying Z_2 from 300 through 0 to -300 such that the heavier species is lifted provided that $|Z_2|$ is large enough. This effect is quantified in figure 5, which is the analogue of figure 2 and shows the mean height h_i as a function of Z_2/Z_1 at fixed Z_1 . The agreement between theory and simulation is more quantitative for these lighter colloids, at least for like-charged colloids. This is in line with our earlier notions that the differences between theory and simulation are probably due to correlations, which are weaker for lighter colloids since the system is then more homogeneous and hence more dilute at the bottom. The analogue of figure 3 is shown in figure 6, and shows the same poor agreement between theory and simulation as figure 3: the theory breaks down completely for $\kappa\sigma \gtrsim 1.5$, where it cannot even predict the correct ordering of the species with height.

4. Conclusions

We have studied the equilibrium sediment of binary mixtures of charged colloids in suspension, viewed both as a colloid–ion mixture within a Poisson–Boltzmann theory and as an effective colloids-only system with pairwise screened-Coulomb interactions in Monte Carlo simulations. The main conclusion is that the layering effect, whereby colloids order with height according to charge-per-mass as predicted by the Poisson–Boltzmann theory [18, 19], can also be obtained within the effective colloids-only system. This result is not obvious, since the theoretical ion–colloid description invokes the ion-entropy and a selfconsistent electric field that pushes the colloids upwards against gravity, while the ions only occur very indirectly in the screening constant of the effective system. Nevertheless, these results suggest that both pictures are, at least qualitatively, different sides of the same coin. The inconsistency of the colloids-only system, where local electric neutrality is assumed whereas the (Donnan) potential varies with height and thus requires a non-vanishing local charge density at least somewhere in the system, is apparently no serious problem for describing the phenomenology quantitatively.

It is of interest to try to understand the layering mechanism within the colloids-only picture qualitatively. For like-charged colloids one may argue that the colloids with the highest charge repel each other most strongly, such that they expand to relatively high altitudes, leaving the lower charged (and possibly lighter) colloids behind at lower altitudes. For oppositely charged colloids the situation is more subtle: the attraction between the most expanded highest charged

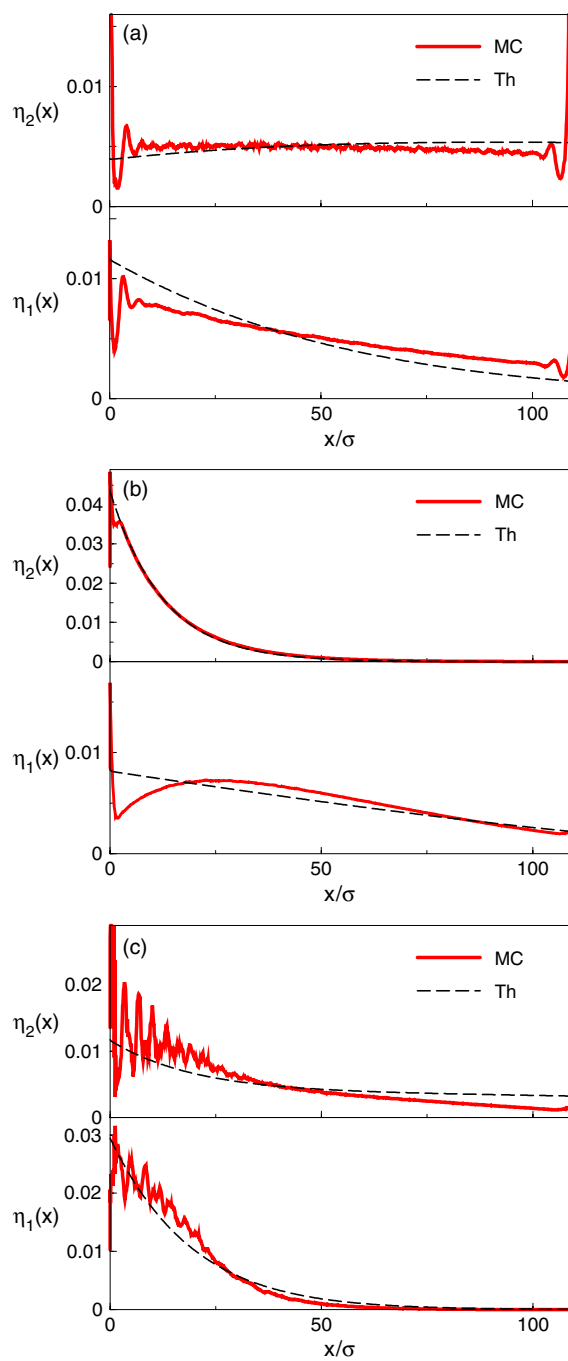


Figure 4. Same as figure 1, but for ten times lighter colloids with gravitational lengths $L_1 = 25\sigma$ and $L_2 = 12.5\sigma$.

colloids and the less expanded lower charged colloids is such that the tendency to layering is reduced. This effect depends, probably, sensitively on composition and charge, and has not been investigated here in any detail.

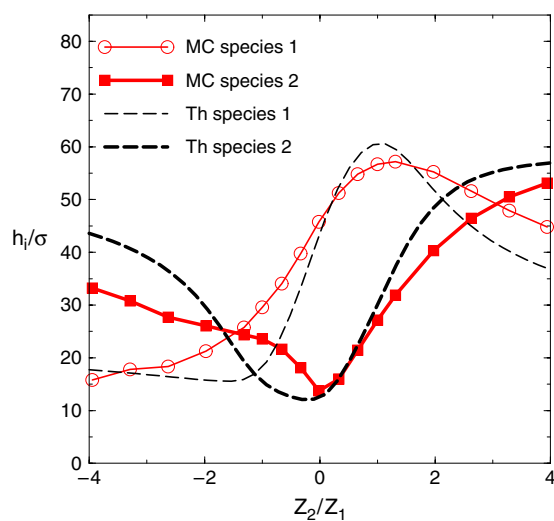


Figure 5. Same as figure 2, but for ten times lighter colloids with gravitational lengths $L_1 = 25\sigma$ and $L_2 = 12.5\sigma$.

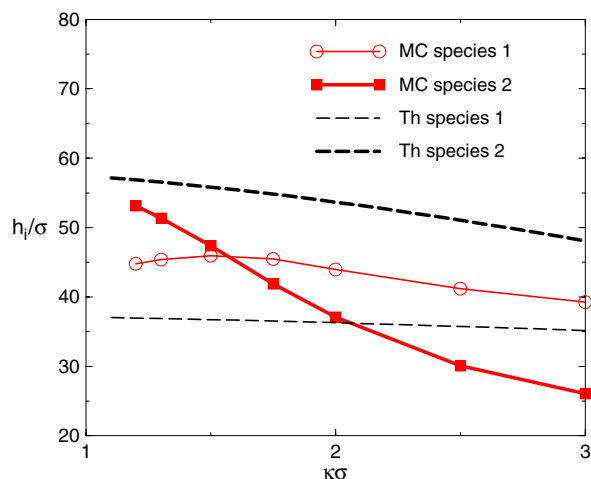


Figure 6. Same as figure 3, but for ten times lighter colloids with gravitational lengths $L_1 = 25\sigma$ and $L_2 = 12.5\sigma$.

At a quantitative level we can conclude that the theory does not catch the oscillatory character of the density profiles that were found close to the bottom and meniscus in the simulations. This effect requires a better account of the short-range correlations, and will be addressed in future work. The theory is, all in all, in better agreement with the simulations for repelling like-charged colloids than for attracting oppositely charged colloids. This can probably also be traced back to the poor level of our theoretical treatment of the short-ranged correlations, which are more pronounced in the presence of attractions. Given the recent exciting new experimental developments in the study of oppositely charged colloids exhibiting equilibrium behaviour (as opposed to irreversible aggregation phenomena) [3], there is good reason to attempt to improve the theory. Moreover, the theory is also shown to

break down completely for $\kappa\sigma \gtrsim 1.5$ –2 (for the present choice of parameters), where short-ranged correlations become more important once more. Despite these shortcomings, our main conclusion should be that the layering phenomenon at low salt concentration, say at $\kappa\sigma \lesssim 1$ –2, is a real effect that can be understood from a colloid–ion mixture perspective as well as from a colloids-only perspective. We hope that these findings stimulate experimental study of these phenomena.

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