# Sedimentation–diffusion equilibrium of binary mixtures of charged colloids including volume effects

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**Abstract**
We describe the sedimentation–diffusion equilibrium of binary mixtures of charged colloids in the presence of small ions and for non-dilute conditions, by extending the work of Biben and Hansen (1994 *J. Phys.: Condens. Matter* **6** A345). For a monocomponent system, they included a Carnahan–Starling hard-sphere correction and a pressure term due to the small ions. We extend this approach to mixtures of spheres of unequal size, and implement the fact that the effective buoyant mass of a particle is based on the difference in mass density between the particle itself and the local average mass density, and not on the difference with the mass density of the pure liquid.

Without the three volume effects (hard-sphere repulsion, ion pressure, buoyant particle mass based on local, average, mass density), the lighter particle (buoyant mass $m_L$, charge $z_L$) only levitates from the bottom (with a maximum in concentration displaced upwards) when $z_L/m_L > z_H/m_H$ (with H indicating the heavier particle). With these volume effects included the fractionation is much sharper and occurs even for $z_L/m_L \ll z_H/m_H$.

For certain parameter settings we find a bimodal distribution of the heavier particles with most of them in the bottom region, but with a small fraction forming a thin layer higher up in the column. This second layer is not found when the buoyant particle mass is based on the mass density difference with the pure liquid and/or when the ion pressure is neglected, suggesting that it is due to a subtle interplay between these two contributions.

## 1. Introduction

In a gravitational or centrifugal field, charged colloidal particles will distribute themselves to form a sedimentation–diffusion equilibrium (SDE) profile. Because of their charge, particles not only remain levitated because of translational entropy, but because of the electrostatic repulsion between them as well [1–17].

Mean-field theory exists to describe the SDE-profile of charged colloids for a monodisperse system, either by assuming charge neutrality at each height in the column [3, 5, 6, 8, 9, 11, 12, 14–16], or by making use of the full Poisson–Boltzmann (PB) equation (in the direction of the applied force) [2, 7, 17]. Both approaches are in good agreement with molecular dynamics [10] and Monte Carlo simulations [13]. In most cases these theories are restricted to the dilute limit of systems containing only one type of colloid. However, Biben and Hansen [2] considered the non-dilute case, accounting for the non-ideality on the Carnahan–Starling level. They also added a pressure contribution resulting from the small ions, assuming these to be infinitely small and without mass. The hard-sphere contribution was also considered in [3, 5, 6]. Systems containing more than one type of colloid are considered in [13] and [17], but only in the dilute limit.

In the present paper we extend the approach of [2] to multicomponent systems with several types of particles of non-zero volume, by using the Boublik–Mansoori–Carnahan–Starling–Leland (BMCSL) excess function [18–21]. From the BMCSL function we can also derive the contribution to the chemical potential of a colloid due to the (infinitely small) ions, leading to the ion pressure term already given in [2]. We implement the fact that the buoyant mass of a particle is given by the product of its volume and the difference between the particle mass density and the average (local) mass density, rather than on the difference with the mass density of the pure liquid [22–29]. This leads to a third volume contribution to the driving force on a colloid, in addition to those stemming from hard-sphere repulsion and ion pressure.

We present the theory and results of calculations for monodisperse systems, bidisperse systems with particles of equal size, and bidisperse systems with particles of unequal size but of the same mass density and surface charge density (as if consisting of the same material). In all cases the colloids are spherical and have a fixed charge. We neglect the possibility that the charge on the colloids is reduced with increasing particle concentration [3, 14].

In the appendix we present the expressions required to model the (time-dependent) evolution of SD-profiles towards the (equilibrium) SDE-profile, by extending expressions from the literature for multicomponent sedimentation of uncharged, non-colloidal, particles to the case of charged colloids [25–28]. At the same time, the appendix is an extension of the work of Dufrêche *et al* [5, 6], who considered monodisperse charged colloids, mainly in the dilute limit.

## 2. Theory

We consider the general case of $i$ types of incompressible particles (colloids, ions, etc) suspended in a continuous liquid phase. The particles have a charge $z_i$, volume $v_i$, mass $m_i$, mass density $\rho_i = m_i/v_i$ ($\rho_L$ is that of the pure liquid, or solvent) and a local volume fraction $\phi_i$. The total particle volume fraction, $\phi$, is given by $\phi = \Sigma \phi_i$, and the average, local, mass density is

$$\rho_t = \sum_i \phi_i \rho_i + (1 - \phi) \rho_L \qquad (1)$$

where $i$ runs over all particles. By 'local' we mean that the corresponding property is height dependent (such as $\rho_t$, $\phi_i$ and $\phi$). Indeed, we consider a one-dimensional geometry solely defined by $h$, the height above the bottom of the cell (axial coordinate). Radial gradients are neglected—that is, we assume a mean field in the non-axial directions. Related to that, within each slice d$h$ the ions and colloids are considered to be smeared-out, and inhomogeneous distributions such as a diffuse layer of ions around a larger colloid are not considered. This approximation becomes the more accurate the more these electrostatic double layers overlap, thus at a high value for the ratio of Debye length to interparticle distance.

The gravitational acceleration, $g$, is assumed constant, as if in gravity, or in a centrifugal field far away from the centre (compared to the distance over which the SDE-profile is established). However, the theory is easily modified to describe sedimentation in a divergent centrifugal field [11, 14].

When equilibrium is reached and the SDE-profile therefore established, the net force on each of the particle types has become zero; gravity, electrostatics and entropic forces are now in balance at each height and for each particle type. The force, $f$, is (minus) the derivative with height of the total potential, $\mu_i$, which at equilibrium is constant throughout the system [24], and includes not only the standard and composition-dependent terms, but also the contributions from gravity, electrostatics and hydrostatic pressure.

## 2.1. Maxwell–Stefan theory

A very elegant starting point to describe the multicomponent transport of particles (ions, molecules, colloids, etc) due to combinations of external fields and gradients in chemical potential and temperature is the Maxwell–Stefan (MS) theory [29–32]. MS theory describes the molecular fluxes—in our case, of the solvent, ions and colloids—as a balance between the friction of a certain particle with the different particles/molecules in its local environment (described in terms of binary diffusion coefficients), and the total of the driving forces that act on it. Neglecting temperature gradients, the (negative of) the driving force, $f_i$, is given by

$$-f_i = \frac{d\mu_i^{\text{chem}}}{dh} + \frac{\phi_i - \omega_i}{c_i}\frac{dP}{dh} - m_i\left(F_i - \sum_j \omega_j F_j\right) \tag{2}$$

where $c_i$ is the number density of particle type $i$, $\phi_i$ the volume fraction, $\phi_i = c_i \cdot v_i$, $\omega_i$ the mass fraction, $\omega_i = \phi_i \cdot \rho_i/\rho_t$, $P$ the pressure and $F_i$ the external body force per unit mass of particle $i$, while the sum over $j$ runs over all colloidal species and the solvent. Equation (2) follows, for instance, from equation (2.3.10) in [31] after dividing both sides by $c_i$, by $kT$, replacing $\rho_i$ in [31] (where it is a mass density per total volume) by $c_i \cdot m_i$, considering the $h$-direction only, and by taking the negatives of both sides. The chemical potential, $\mu^{\text{chem}}$, has a standard contribution, $\mu_0$, an ideal term, $\ln \phi_i$, and an excess (non-ideal) contribution, $\mu_i^{\text{ex}}$. As the standard contribution is constant, we can leave out gradients in $\mu_0$, while the non-ideal term will be discussed in the next section.

The body force in equation (2), $F_i$, has a gravitational and an electrostatic component,

$$F_i = -g + \frac{z_i}{m_i}E \tag{3}$$

where the axial field strength $E = -dy/dh$, with $y$ the dimensionless electrostatic potential, and $g = g^\dagger/kT$ with $g^\dagger = 9.81$ m s$^{-2}$ (note that we use $g$ as a positive number). Mechanical equilibrium implies (equation (2.3.6) in [31])

$$\frac{dP}{dh} = \rho_t \sum_j \omega_j F_j \tag{4}$$

with the sum over $j$ again running over all particles and the liquid (a sum that runs over $i$ only includes colloids and ions). Equation (4) results in

$$\frac{dP}{dh} = -\rho_t g + E \cdot \sum_j z_j c_j. \tag{5}$$

Making the appropriate substitutions, and inserting equation (5), modifies equation (2) into [29]

$$-f_i = \frac{d\ln\phi_i}{dh} - z_i E + v_i\frac{dP}{dh} + m_i g. \tag{6}$$

When combined with Poisson's equation, equation (22), to be discussed below, equations (5) and (6) can be solved self-consistently at equilibrium, when $f_i = 0$ (see the appendix for non-equilibrium calculations). However, when we assume charge neutrality in each slice $dh$ at height $h$ in the column (which is a very good approximation for our problem), the second term of equation (5) becomes zero, after which equation (6) can be simplified to

$$-f_i = \frac{d \ln \phi_i}{dh} - z_i E + m_i^b g, \tag{7}$$

with the buoyant mass

$$m_i^b = v_i (\rho_i - \rho_t), \tag{8}$$

defined relative to the local average mass density, $\rho_t$, given by equation (1). Equations (7) and (8) show that the effective gravitational contribution to the driving force is based on the difference in density between the particle and the colloidal solution (or sol), $\rho_i - \rho_t$, not on the difference with the pure liquid (solvent), $\rho_i - \rho_L$. This result can also be obtained from a thermodynamic analysis [22–24] or from mechanical equilibrium [25], and is routinely used in the ultracentrifugation literature [22, 24] and to describe multicomponent (non-colloidal) particle transport in sedimentation and liquid fluidized beds [25–28].

The classical barometric profile for the change of pressure with the height of, for instance, the earth's atmosphere can be derived from these equations. Taking a single type of uncharged particle (or molecule) of mass $m$ and volume $v$ in a surrounding weightless fluid (vacuum), we can combine equations (7) and (8) using additionally that $z = E = 0$, $f = 0$, $g$ is constant, $m = v \cdot \rho$ and $\rho_t = \phi \cdot \rho$. As deviations from the classical barometric profile only occur for densities where the excess, hard-sphere term—to be discussed further on—becomes important as well, we add to equation (7)

$$-f^{ex} = \frac{d\mu^{ex}}{dh} = \frac{8 - 2\phi}{(1 - \phi)^4} \frac{d\phi}{dh} \tag{9}$$

which is based on the Carnahan–Starling expression, given by equation (19). After integration we obtain the following explicit expression for the height, $h$, as a function of the volume fraction, $\phi$:

$$h = -\frac{1}{mg} \left[ \ln \frac{\phi}{\phi_0} \frac{1 - \phi_0}{1 - \phi} + \frac{1}{6} \left( \frac{13 - 4\phi}{(1 - \phi)^4} - \frac{13 - 4\phi_0}{(1 - \phi_0)^4} \right) \right] \tag{10}$$

with $\phi_0$ the volume fraction at $h = 0$ (note that $g = g^\dagger/kT$ with $g^\dagger = +9.81$ m s$^{-2}$). An explicit expression for $\phi(h)$ follows when we linearize the $\phi$-containing terms around $\phi = 0$ (except for the $\ln \phi$-term), resulting in

$$\phi = \tfrac{1}{9} \text{LW} (9\phi_0 \cdot \exp(9\phi_0 - mgh)) \tag{11}$$

where LW is the 'LambertW'-function given by $\text{LW}(x) \cdot \exp(\text{LW}(x)) = x$. Equation (11) simplifies to the classical barometric profile for $\phi_0 \to 0$, resulting in

$$\phi = \phi_0 \exp(-mgh). \tag{12}$$

Equation (12) is valid for $\phi$ up to $\sim 1$ vol% which, for an assumed volume per molecule of 34 Å$^3$ (diameter 4 Å) corresponds to a limiting pressure of $\sim 10$ bar (equation (11) can be used up to $\sim 5$ vol%). Thus, the classical, exponential, barometric profile of equation (12) well describes the earth's atmosphere. However, in the colloidal regime deviations cannot not be neglected. Note that to obtain this result one cannot simply combine equation (5) with (1) and the ideal-gas equation of state, $\Pi = \phi/v$, because the osmotic pressure $\Pi$ only equals the hydrostatic pressure $P$ for $\phi$ close to zero; for example, for ideal, volumeless, molecules.

Integration of the force, equation (6), with respect to the height results in ($f = -d\mu/dh$, and $f = 0$ at any $h$)

$$\mu_i = \mu_{\text{ref}} + \ln \phi_i + z_i y + v_i P + m_i g h \tag{13}$$

where the fourth term on the right-hand side is the insertion energy required to create a volume $v_i$ against the local (hydrostatic) pressure, $P$, given by (5), and the last term is the gravity potential. Equation (13) together with equation (5) will be used in the calculations. For a dilute system, where $\rho_t \sim \rho_L$, inserting equation (5) (after assuming electroneutrality) results in the classical expression [3, 11, 14]

$$\mu_i = \mu_{\text{ref}} + \ln \phi_i + z_i y + m_i^{\text{b},0} g h \tag{14}$$

where the buoyant mass in the limit of infinite dilution, $m_i^{\text{b},0}$, is given by

$$m_i^{\text{b},0} = v_i (\rho_i - \rho_L). \tag{15}$$

In the case when all particles have the same mass density, $\rho_i$ (e.g., for a monocomponent system), then $m_i^{\text{b}}$ relates to $m_i^{\text{b},0}$ according to

$$m_i^{\text{b}} = (1 - \phi) \, m_i^{\text{b},0}. \tag{16}$$

## 2.2. Hard-sphere contribution

It is from this point onwards that we will assume that all particles are spherical; their volume $v_i$ relates to their size, $\sigma_i$, according to $v_i = \pi/6 \cdot \sigma_i^3$. A hard-sphere contribution to the total potential is implemented based on the Carnahan–Starling equation of state, which is very accurate [2, 33] for uncharged, non-interacting, spheres. Tacitly we will assume that it can also be used in mixtures of charged spheres, although in this case the positions of the particles are more strongly correlated.

For mixtures of spheres of unequal sizes, the BMCSL [18–21] equation of state can be used, which results for the excess contribution to the chemical potential in

$$\mu_i^{\text{ex}} = -\left(1 + \frac{2\xi_2^3 \sigma_i^3}{\phi^3} - \frac{3\xi_2^2 \sigma_i^2}{\phi^2}\right) \ln (1 - \phi) + \frac{3\xi_2 \sigma_i + 3\xi_1 \sigma_i^2 + \xi_0 \sigma_i^3}{1 - \phi} + \frac{3\xi_2 \sigma_i^2}{(1 - \phi)^2} \left(\frac{\xi_2}{\phi} + \xi_1 \sigma_i\right)$$
$$- \xi_2^3 \sigma_i^3 \frac{\phi^2 - 5\phi + 2}{\phi^2 (1 - \phi)^3} \tag{17}$$

which is a more concise form of the expression given for $\mu_i^{\text{ex}}$ by Lue *et al* [20]. In equation (17) the $\xi_\alpha$ have their usual meaning,

$$\xi_\alpha = \frac{\pi}{6} \sum_i \frac{\phi_i}{v_i} \sigma_i^\alpha, \tag{18}$$

while we have replaced $\xi_3$ by $\phi$. When all particles have the same size, equation (17) simplifies to the well-known Carnahan–Starling excess function [34, 35]

$$\mu_i^{\text{CS}} = \frac{\phi \left(8 - 9\phi + 3\phi^2\right)}{(1 - \phi)^3}. \tag{19}$$

Interestingly, when one or several of the species are infinitely small (denoted by $k$ in the following) further simplifications are possible. First of all, the excess potential, $\mu^{\text{ex}}$ of these small '$k$'-particles is given simply by

$$\mu_k^{\text{ex}} = -\ln (1 - \phi). \tag{20}$$

To obtain the excess potential for the colloids with volume we leave out the $k$-particles from the summations required to calculate $\xi_\alpha$ using equation (18), and use either equation (17),

or equation (19) when only one size remains. An additional term, due to the $k$-particles, must be added to the potential of the colloids, $\mu_i^{ex}$, given by

$$\mu_i^* = \frac{v_i c_k}{1 - \phi} \tag{21}$$

with $c_k$ the total number concentration of all of the infinitely small particles. Equations (19)–(21) were already used by Biben and Hansen for one type of charged colloid ([2], equations (5) and (9)).

### 2.3. Electrostatics

In each slice $dh$ at height $h$ in the column, the electrostatic potential, $y$, is obtained from Poisson's law (Gauss' differential law) which is [36]

$$\varepsilon_0 \frac{d}{dh} \left( \varepsilon_{eff} \frac{dy}{dh} \right) = -\frac{e^2}{kT} \sum_j z_j c_j \tag{22}$$

where we have included the fact that due to the ions and colloids the effective local permittivity, $\varepsilon_{eff}$, differs from that of the pure liquid, $\varepsilon_L$ (these are relative permittivities; $\varepsilon_0$ is that of vacuum). This is partly caused by a different permittivity within the colloid (or ion), $\varepsilon_i$, and partly by polarization of the surrounding medium. It must be noted that, for small ions, the effect, however, is generally small [37]. One simple option to include the permittivity reduction is to take $\varepsilon_{eff}$ as a volume-average of the permittivities of the different phases [38]. In that case the additional contribution to the potential of a colloid of volume $v_i$, due to polarization, is [39, 40]

$$\mu_i^{pol} = \frac{v_i \varepsilon_0 (\varepsilon_i - \varepsilon_L) kT}{2e^2} E^2. \tag{23}$$

Poisson's law, equation (22), requires boundary conditions at the bottom and top of the system (typically $dy/dh = 0$).

### 2.4. Mass conservation

Finally, we need to conserve particle mass, for each colloidal species, according to

$$\frac{1}{H} \int_0^H \phi_i \, dh = \phi_{i,0}. \tag{24}$$

### 2.5. Simplified approach

The above set of equations can be solved for any set of colloids and (small) ions. However, a simplified approach will be taken next, by making the following assumptions.

First of all, we will assume that the small ions have no volume or mass, and furthermore fix the chemical potential of the small ions, as if the supernatant phase above the SDE-profile (devoid of colloids) is very large and of a certain ionic strength $c_\infty$ $(m^{-3})$. There we will also set the electrostatic potential, $y$, to zero. In this case the chemical potential of the ions is given by

$$\mu_{ion} = \ln c_\infty = \ln c_i + z_i y - \ln (1 - \phi) \tag{25}$$

with the last term stemming from equation (20). From equation (25) a modified Boltzmann relation follows,

$$c_i = c_\infty (1 - \phi) e^{-z_i y}. \tag{26}$$

Note that all ion concentrations, $c$, are defined relative to the total volume, which also contains a volume fraction, $\phi$, of colloids. The ion 'solvent' concentration, $c^* = c/(1 - \phi)$, is the ion concentration defined per unit solvent volume (without the colloidal particles) [2].

Substituting equation (26) (for the small ions) in equation (22) results in a modified Poisson–Boltzmann equation, given by [39, 40]

$$\varepsilon_0 \frac{\mathrm{d}}{\mathrm{d}h} \varepsilon_{\text{eff}} \frac{\mathrm{d}y}{\mathrm{d}h} = -\frac{e^2}{kT} \left( \sum_i z_i c_i - 2c_\infty (1 - \phi) \sinh y \right) \tag{27}$$

where the summation now only runs over the colloids (not the ions) and we have furthermore assumed that all small ions are monovalent. As a consequence of fixing $\mu_{\text{ion}}$, we only need to consider mass balances for the colloids, not for the ions.

The contribution from the cations and anions to the potential of the colloids, $i$, is given by equation (21), which results, together with equation (26), in

$$\mu_i^* = v_i \frac{c_{k,+} + c_{k,-}}{1 - \phi} \overset{-2v_i c_\infty}{=} 2v_i c_\infty (\cosh y - 1) \tag{28}$$

where we have subtracted a constant term, $2v_i c_\infty$. This is the ion pressure term of [39–41], given by the excess number of small ions that is expelled from A to B when a colloid of volume $v_i$ moves from B to A.

Next we will assume that local charge neutrality at a scale much smaller than the SDE-profile (which is of the order of centimetres) is a very good approximation for our system,

$$\sum_i z_i c_i - 2c_\infty (1 - \phi) \sinh y = 0, \tag{29}$$

which requires, see equation (27), that the axial field strength gradient is (close to) zero. As a result of using equation (29), the second term of equation (5) becomes zero. Also, because $E$ is so small in our system (of the order of perhaps 25 mV cm$^{-1}$), we can safely neglect the polarization contribution to the potential, equation (23).

In summary, the three volume-dependent contributions to the total potential, $\mu_i$, of the colloids are the following.

(I) A *gravity contribution* which in our analysis is computed by using equations (5) and (13), and not assuming that $\rho_t \sim \rho_L$ which would lead to equation (14). In terms of forces, it corresponds to using $m_i^{\text{b}}$ in equation (7) instead of $m_i^{\text{b},0}$.

(II) A *hard-sphere contribution* described by equation (17), or when all colloids have the same size by equation (19).

(III) *Ion exclusion*, leading to the '$1 - \phi$' term in equation (29), and to an additional contribution to the potential of each of the colloids, given by equation (28).

### 2.6. Comparison with the Biben and Hansen [2] approach

Contributions II and III were already presented in [2] (equation (9a′)) for a single type of colloid in the presence of infinitely small anions and cations (of zero mass). To show the similarity, we add to equation (7) the hard-sphere contribution of equation (9) and the small ion term of equation (21), and obtain for the force on the colloid (1) of volume $v$, buoyant mass $m^{\text{b}}$, and charge $z$, in the presence of anions (2) and cations (3)

$$-f = \frac{\phi'}{\phi} + 2\frac{4 - \phi}{(1 - \phi)^4} \phi' - zE + m^{\text{b}}g + v \left( c_2^{*\prime} + c_3^{*\prime} \right) = 0 \tag{30}$$
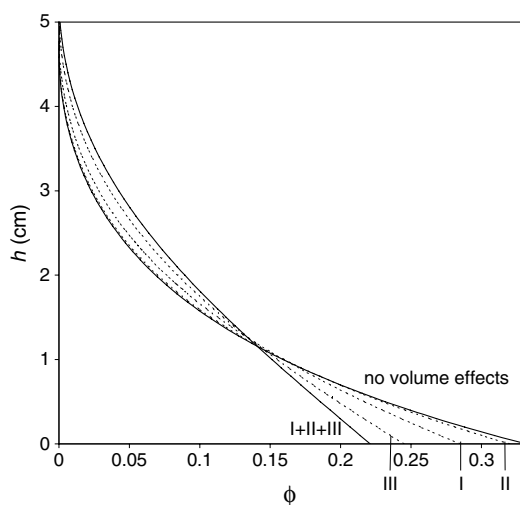
**Figure 1.** Volume contributions to the sedimentation–diffusion profile of charged colloids. I, II, and III refer to the three volume contributions discussed in the text (parameter of section 1).

where the superscript $'$ denotes the first derivative with height, and where $c_i^*$ is the ion 'solvent' concentration, given by $c_i/(1-\phi)$. For the small ions

$$c_i^{*\prime} - z_i E c_i^* = 0 \tag{31}$$

which can be obtained after adding equation (20) to equation (14), assuming for the ions $m^{b,0} = 0$, and differentiating with respect to height. Implementing equation (31) in equation (30) results in

$$\phi' = \left(1 + 2\phi\frac{(4-\phi)}{(1-\phi)^4}\right)^{-1} \left\{\left[v\left(c_2^* - c_3^*\right) + z\right]E - m^b g\right\}\phi \tag{32}$$

which equals equation (9a$'$) in [2] (neglecting a misplaced bracket there) when we assume $m^b = m^{b,0}$.

## 3. Results and discussion

### 3.1. Monodisperse system

For a single type of colloid, the three volume contributions all lead to an inflated SDE-profile when compared with the case of volumeless colloids. The calculation parameters are a particle size of $\sigma = 40$ nm ($v \sim 33\,500$ nm$^3$), liquid mass density $\rho_L = 0.8$ g ml$^{-1}$, colloid mass density $\rho_{\text{colloid}} = 1.6$ g ml$^{-1}$ and charge $z = 100$, similar to the silica in ethanol system of [11]. The rotational acceleration is set to $100g$, which corresponds to $\sim 115$ rad s$^{-1} \sim 1100$ rotations min$^{-1}$ at 7 cm from the centre of the rotor (like in [11]). The total particle volume in the test-tube per unit cross-sectional surface area is $\phi_0 \cdot H = 0.4$ cm. This corresponds, for instance, to a column height of $H = 20$ cm and an initial particle volume fraction of $\phi_0 = 0.02$. The ionic strength is $c_\infty = 0.1$ mM ($6 \times 10^{-5}$ nm$^{-3}$).

In this case the hard-sphere contribution is not very important, but the other two terms are. In figure 1 we show results for each of the three contributions implemented individually (curves I, II and III), and simultaneously (curve 'I + II + III'). The trend is as expected: near the bottom, excluded volume is higher, making the $h(\phi)$-profile steeper, i.e., the change of $\phi$ with $h$ is less pronounced.
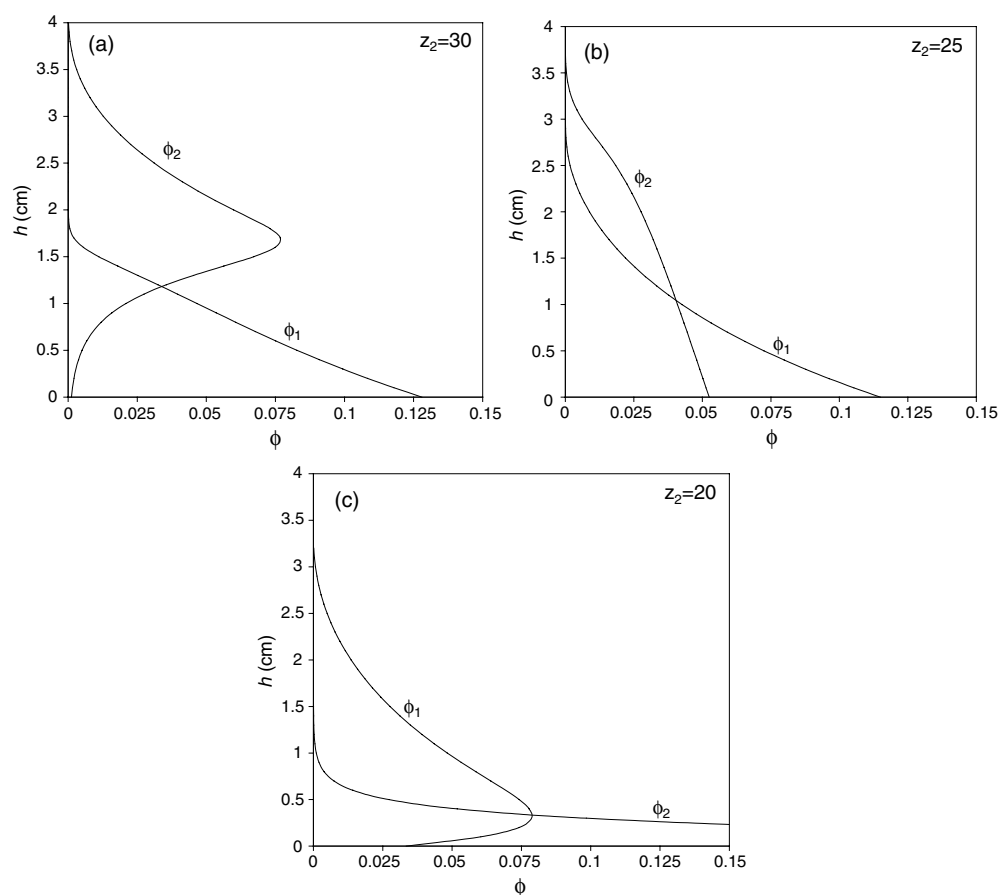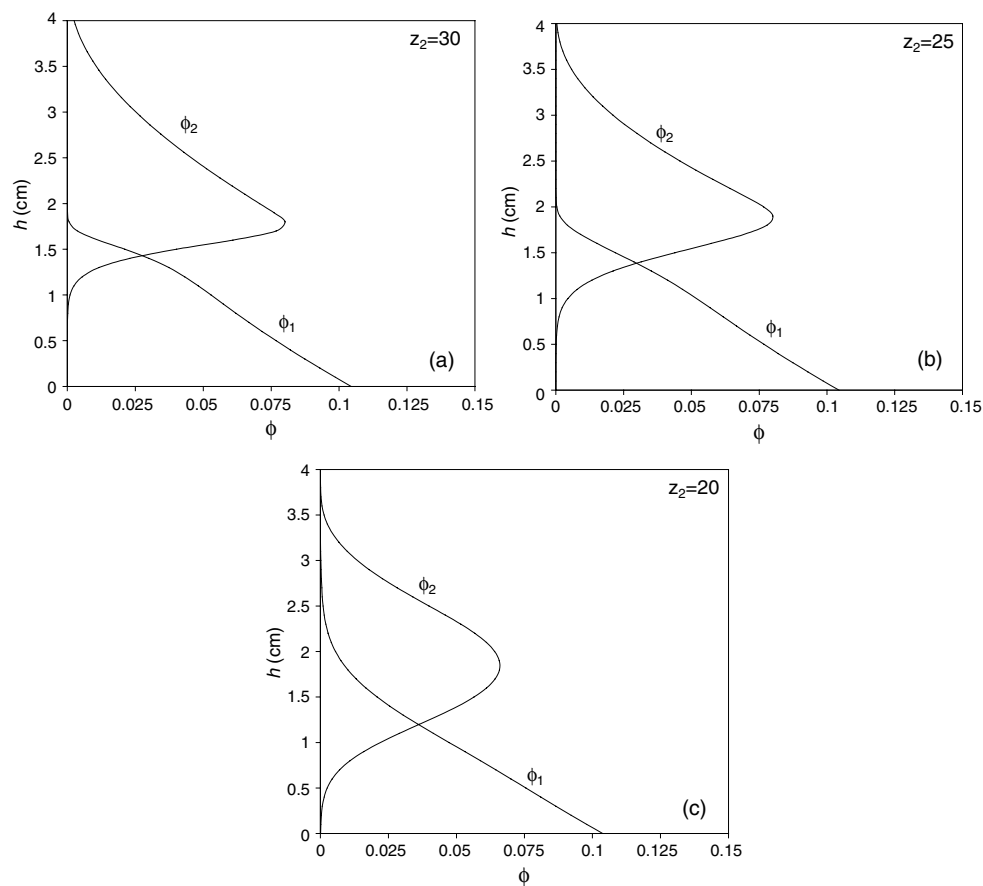
**Figure 2.** Density profiles without volume effects. Only when the charge of the lighter particle is $z_2 = 30$ is the maximum in $\phi_2$ displaced upwards (parameters of section 2).

### 3.2. Bidisperse system. Equally sized spheres

In the monodisperse case, volume contributions result in an inflation of the SDE-profile. The particle density, however, remains a decreasing function with height. However, for bidisperse systems an individual particle density profile can have a maximum at a non-zero height (above the bottom of the test-tube), resulting in stratification (fractionation, layering, segregation, etc) of the two particle types, as also discussed in [17].

The properties of the materials used in the calculation are as follows. Particle 1 is that of section 1 ($\sigma = 40$ nm, $\rho_1 = 1.6$ g ml$^{-1}$, $z_1 = 100$), while particle 2 is four times lighter (with respect to the liquid, $\rho_2 = 1.0$ g ml$^{-1}$) but of the same size. The total particle volume is $\phi_{i,0} \cdot H = 0.1$ cm which corresponds, for instance, to a column height of 5 cm and adding 2 vol% of both types of particles, thus: $\phi_{1,0} = \phi_{2,0} = 0.02$ ($c_\infty = 0.1$ mM).

For $z_2 = 30$, 25, and 20, figure 2 shows results for a calculation without volume effects, while figure 3 shows the corresponding results when volume effects are included. As long as $z_2 > 25$, and hence, $z_2/m_2 > z_1/m_1$, where $m$ is $m^{b,0}$ given by equation (15), fractionation is possible even without volume effects, with the lighter particle levitated above the heavier one [17]. Indeed, for $z_2 = 30$, figures 2(a) and 3(a) are, on first impression, not very different.

**Figure 3.** Density profiles with volume effects included. The maximum in $\phi_2$ is displaced upwards for all values of $z_2$ (parameters of section 2).

However, it must be noted that the fractionation is much more pronounced with volume effects included: whereas the fraction of type 2 particles at the bottom, $\phi_{2,b}/\phi_b$, a measure of the separation efficiency, is around 1% without volume effects, it is a factor of $\sim 6 \times 10^5$ smaller when volume effects are included.

When reducing $z_2$ to 25, the calculation without volume effects predicts monotonically decaying particle density profiles, see figure 2(b). However, with volume effects included, the decrease of charge has only a minor effect, with the density profiles only slightly smoother but stratification still observed. Reducing $z_2$ further to $z_2 = 20$ has a dramatic effect, see figure 2(c), namely that the '2' particle is now predicted to be at the bottom of the test-tube completely with particle densities up to unrealistically high values of $\sim 60$ vol%. Instead, when volume effects are included, see figure 3(c), we still find particle type '2' levitated above the heavier type '1'. When $z_2$ is reduced to even lower values (with volume effects still considered), the maximum in $\phi_2$ remains displaced from the bottom, even down to $z_2 = 5$. Only for $z_2 = 0$ are both profiles monotonically decaying (not shown). Clearly, neglecting volume effects can lead to dramatic errors in the predicted SDE-profile for $z_2/m_2 < z_1/m_1$.

An interesting phenomenon in bidisperse systems with particle fractionation is the presence of a local minimum in particle number density at the height where the two layers
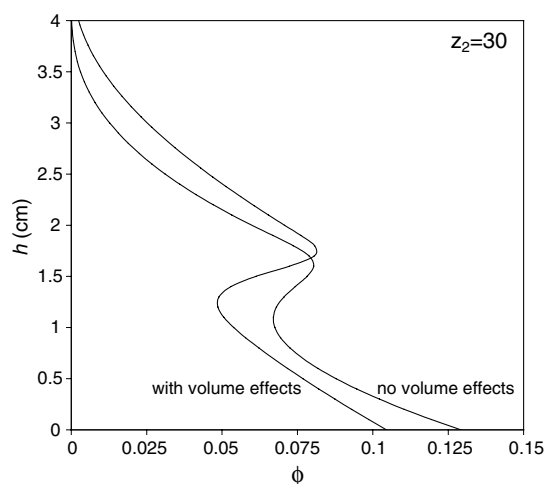
**Figure 4.** Total colloid volume density profile, showing the local minimum at the intersection between the lower layer (predominantly particle type 1) and the upper layer (predominantly type 2) (parameters of section 2).

intersect. Number density is proportional to volume density (volume fraction, $\phi$) when all particles have the same volume (as in this section). The minimum is not exclusive to models that include volume effects, and therefore in figure 4 we plot the total volume density profile, $\phi = \phi_1 + \phi_2$, for $z_2 = 30$, in which case fractionation is predicted for both models.

It must be noted that this minimum in particle number density in no way implies a corresponding minimum in the mass density, $\rho_t$, of the system. At equilibrium, the mass density is always a monotonically increasing function towards the bottom.

### 3.3. Binary mixtures of spheres of unequal size but of the same mass density

Next we consider binary mixtures of spheres of unequal size but of the same material, $\rho_1 = \rho_2$ (=1.6 g ml$^{-1}$), and with a charge, $z_i$, linearly scaling with the surface area, hence with $\sigma_i^2$. The size ratio is sr $= \sigma_1/\sigma_2$ with the average size $\sigma_{av} = \frac{1}{2} \cdot (\sigma_1 + \sigma_2) = 40$ nm for which the charge is set to $z_{av} = \frac{1}{2} \cdot (z_1 + z_2) = 100$ ($c_\infty = 1$ mM, $\phi_{i,0} \cdot H = 0.1$ cm).

Figure 5(a) shows the total particle volume fraction $\phi$ and local mixing ratio, $\alpha = \phi_1/\phi$ as functions of height, $h$, and size ratio, sr $= \sigma_1/\sigma_2$. Interestingly, the total particle volume density profile $\phi(h)$ does not depend much on the size ratio, sr. Only for the highest value of sr $= 1.4$ do we find a deviation from the very gradual increase of $\phi$ with decreasing $h$ found for the lower values of sr. However, the mixing ratio $\alpha$ responds very strongly to a slight difference in size. Already at a size ratio of sr $= 1.1$ an almost complete fractionation is found between the larger particles (at the bottom) and the smaller ones (displaced from the bottom), with a quite sharp transition zone. Clearly, the volume density profile is not a very sensitive property to detect an 'underlying' particle fractionation [17].

For mixtures of particles of the same mass density, $\rho$, the total colloid volume density profile $\phi(h)$ does not have a local minimum such as in figure 4 because $\phi$ is proportional to the system mass density $\rho_t$ (because the colloid mass density $\rho$ is the same for all colloids), and $\rho_t(h)$ must be a continuously decreasing function with $h$, as mentioned earlier. However, the colloid number density profile, $n(h)$, still shows a minimum for the binary mixture, but only at the highest value of the size ratio considered, sr $= 1.4$; see figure 5(b).

### 3.4. Non-monotonic particle density profiles

In sections 2 and 3 we have shown that the total particle number density, besides having a maximum at the bottom of the column, can have a second maximum higher up in the column.
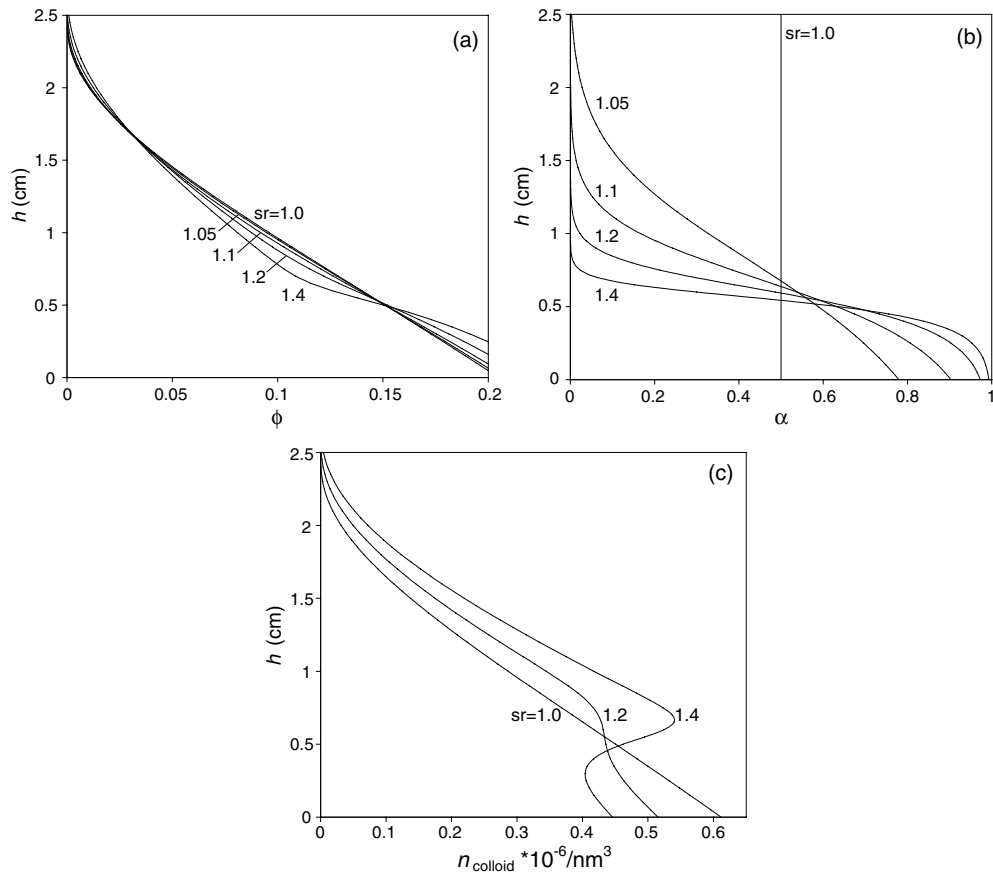
**Figure 5.** Sedimentation–diffusion profile for binary mixture of particles of equal mass density and surface charge density, but of different size, $\sigma_i$ (parameters of section 3). The size ratio is sr $= \sigma_1/\sigma_2$ and charge $z$ scales with $\sigma^2$. The average charge is $z_{av} = 100$ and the average diameter is $\sigma_{av} = 40$ nm. (a) Total colloid volume density, $\phi$. (b) Mixing ratio, $\alpha = \phi_1/\phi$. (c) Total number density.

Interestingly, we also encountered a range of conditions where the number density profile of an *individual* particle type can have more than one maximum; see figure 6, which shows individual volume fraction profiles as a function of height. These observations were made for the parameter setting of section 2 except that $z_2 = 15$ (not $z_2 = 25$) and values for $H \cdot \phi_{i,0}$ are different. (Case A: $\phi_{1,b} = 0.22$, $\phi_{2,b} = 10^{-10}$, $H \cdot \phi_{1,0} = 0.336\,61$, $H \cdot \phi_{2,0} = 0.335\,32$; case B: $\phi_{1,b} = 0.225$, $\phi_{2,b} = 10^{-10}$, $H \cdot \phi_{1,0} = 0.331\,19$, $H \cdot \phi_{2,0} = 0.457\,76$.) In each of these cases, particles of type 1 fill the bottom region, and particle type 2 is levitated upwards with a single maximum. For certain parameter settings, we very unexpectedly find a second, local, maximum in $\phi_1$ developing in the upper edge of the layer of type 2 particles.

The occurrence of this bimodal profile in $\phi_1$ does not depend on the hard-sphere repulsion: without the contribution of equation (19), it is actually more pronounced. However, after leaving out either the ion pressure term, or assuming $m_i^b = m_i^{b,0}$ and using equation (15) instead of equation (8), the phenomenon disappeared. This suggests that it is due to a subtle balance between the ion pressure (related via electroneutrality to the charge on the colloids) and the contribution of the particles to the pressure, $P$, which leads to equation (8) for $m_i^b$.
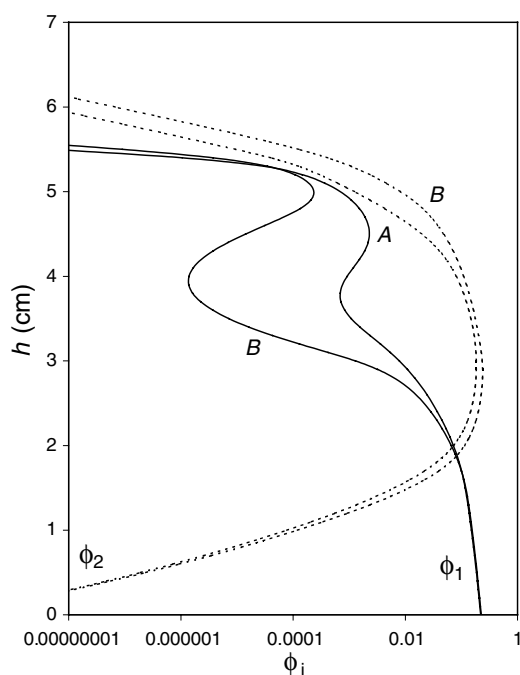
**Figure 6.** Volume fraction profiles of heavier and lighter particles, $\phi_1$ and $\phi_2$ for case A and B (see section 4).

A bimodal profile of an individual particle type has also been reported in [42] where the SDE-profile of bidisperse, uncharged, colloids is considered. In [42] the particles have the same mass density but particles of type 2 are larger. For the smaller particle the effective mass is assumed constant (not influenced by the presence of other particles), whereas the effective mass of the larger particles is corrected for the mass density increase of the surrounding fluid due to the presence of the small particles. Especially at a large size ratio, the larger particle is predicted to have a sharp peak in its distribution at some height above the bottom, where the distribution profile of the smaller particles has a local dip. The mass density profile $\rho_t(h)$ (in this case given by $\rho_t = \phi \cdot \rho_p + (1 - \phi) \cdot \rho_L$ with $\phi = \phi_1 + \phi_2$) is not monotonically decreasing with height, but has a distinct local maximum at the location of the peak in the concentration of the large particles.

However, this calculation is based on an unphysical form of the effective particle mass by only taking into account the effect of the small particles on the large ones, instead of considering that all particles influence the effective mass of all others (including those of their own kind). The predicted non-monotonic profile of $\rho_t(h)$ is a result of this choice, but it is physically impossible: the system would immediately gain potential energy by simply exchanging densely filled, thus heavy, layers (of high $\phi$, thus high $\rho_t$) higher up in the column with layers of lower $\rho_t$ lower in the column; i.e., the predicted profiles are mechanically unstable. For some tested parameter settings of figure 1 of [42] we recalculated the SDE-profiles, and always found the larger particles to be completely at the bottom of the system, with the density profile of the small particles having a single maximum just above the layer of larger particles.

## 4. Conclusion

We calculate the sedimentation–equilibrium profile of bidisperse mixtures of charged colloids in the presence of added salt. We implement three volume contributions to the potential of the

colloids. Without volume effects the number density with height profile is a monotonically decaying function for both particle types when $z_L/m_L \leqslant z_H/m_H$. However, for this condition, when we include volume effects a very pronounced fractionation of the two types of colloids is predicted, with the lighter, or smaller, particle depleted from the lower region almost completely. When the particles fractionate and form two layers, the possibility of a local minimum in colloid number density is predicted. For a binary mixture of particles of the same material (identical mass density and surface charge density) even at a size difference as small as 10% an almost complete fractionation is predicted, though the overall colloid volume density profile is hardly affected.

Conditions are found in which the lighter particle, type 2, has a maximum in density displaced from the bottom, with particle 1 having a global maximum in particle density at the bottom of the column and a second, local, maximum above the layer of particle type 2. To our knowledge such a bimodal profile has not been observed experimentally; further study would be promising because of its potential use in fractionation.

## Acknowledgments

## Appendix. Non-equilibrium in mixtures of charged colloids

For multicomponent flow of spherical particles (ions, as well as colloids) through a liquid a suitable force balance on each particle, $i$, in the mixture is

$$\frac{3\pi \sigma_i \eta \left(\mathbf{v}_i - \mathbf{v}_L\right)}{kT h_i} = f_i = -\frac{d\mu_i}{dh} \tag{A.1}$$

with $\mathbf{v}_i$ the particle velocity, $\mathbf{v}_L$ the liquid velocity, $\sigma_i$ the particle diameter, and $\eta$ the Newtonian viscosity of the liquid (solvent). Equation (A.1) shows on the left-hand side friction with the liquid, and on the right-hand side the driving forces. The total potential, $\mu_i$, contains all contributions discussed in the main text, including gravity, electrostatics, pressure and entropy. Equation (A.1) is an extension to the non-dilute case of the theory according to [5] and [6], and is a form of the Maxwell–Stefan equations [30–32], though with two modifications (compare with equations (2.3.10) and (2.3.17) in [31]): only friction with the liquid is considered (thus $x_j$ is set to 1), and the binary diffusion coefficients, $D_{ij}$, are replaced by $D_i \cdot h_i$ with $D_i$ the self-diffusion coefficient [5]

$$D_i = \frac{kT}{3\pi \sigma_i \eta} \tag{A.2}$$

and $h_i$ an empirical hydrodynamic hindrance function, for polydisperse mixtures of spheres, and for a Reynolds number $Re < 0.2$, given by [26–28]

$$h_i = \left(1 - \left(1 + \frac{(\phi^{-\frac{1}{3}} - 1)}{\phi} \frac{\sum_j \sigma_j \phi_j}{d_i}\right)^{-3}\right)^{n-2} \tag{A.3}$$

which, when all particles have the same size, simplifies to [25–28]

$$h_i = (1 - \phi)^{n-2} \tag{A.4}$$

with typically $n = 4.65$. The hindrance function is based on work on non-colloidal particles, where only external forces are important (gravity, centrifugation) and entropy and hard-sphere contributions are neglected. It is unknown to what extent this approach can be used for particles in the colloidal range where these latter forces become important (although it is valid in the dilute limit, for example, when all species are infinitely small, because then $h_i = 1$ according to equation (A.3), and the self-diffusion coefficient, $D$, is uncorrected).

This set of equations must be supplemented by particle mass conservation,

$$\frac{d\phi_i}{dt} = -\frac{d}{dh}\phi_i \mathbf{v}_i, \tag{A.5}$$

overall mass conservation (for batch sedimentation of incompressible particles)

$$\sum_i \phi_i \mathbf{v}_i + (1 - \phi)\, \mathbf{v}_L = 0, \tag{A.6}$$

and boundary conditions for equation (A.5), namely a zero particle flux, $\phi_i \cdot \mathbf{v}_i = 0$, at the bottom and top of the system.

To describe the electrostatic interactions, we can use the modified Poisson–Boltzmann equation, equation (27), in which case we need to consider fluxes and balances for all colloids and ions. However, we could assume local charge neutrality, $\Sigma z_i c_i = 0$, which is complementary to the zero-current condition [5]

$$\sum_i z_i c_i \mathbf{v}_i = 0. \tag{A.7}$$

Because of equation (A.7), the number of particle balances, equation (A.5), that need to be considered is reduced by one. Indeed, for a binary system (e.g., one type of colloid in the counterions-only case), only the colloid needs to be considered because equation (A.7) implies that in this case colloid and counterion have the same velocity [5].

Taking the simplified approach of the main text (for the SDE-profile) in which the ions are point charges of zero mass, and of a fixed potential $\mu_{ion}$ (corresponding to a certain supernatant ionic strength, $c_\infty$, see equation (25)), using local electroneutrality, equation (29), and equation (28) for the contribution to the potential of the colloids due to ion pressure, we find that the flux $(=\phi_i \cdot \mathbf{v}_i)$ of colloid $i$ in a multicomponent mixture is given by

$$\mathbf{v}_i - \mathbf{v}_L = -D_i h_i \left( \frac{1}{\phi_i}\frac{d\phi_i}{dh} - z_i E + m_i^b g - 2v_i c_\infty \sinh y \cdot E + \frac{d\mu_i^{ex}}{dh} \right) \tag{A.8}$$

where the final term follows from partial differentiating equation (17) (excluding small ions from the summations in $\xi_\alpha$). In case all colloids have the same size, this term is given by

$$\frac{d\mu_i^{ex}}{dh} = \frac{8 - 2\phi}{(1 - \phi)^4}\frac{d\phi}{dh}. \tag{A.9}$$

Two limiting situations of the above theory are the following.

(i) In the limit of uncharged, non-colloidal, particles, the force ($f_i = -d\mu_i/dh$) has only a buoyant gravitational contribution,

$$-f_i = \frac{d\mu_i}{dh} = m_i^b g, \tag{A.10}$$

which, when combined with equations (1), (8), (A.1), (A.4) and (A.6), results for a one-component system in the classical Richardson–Zaki expression for batch sedimentation [25, 28, 43],

$$\mathbf{v}_i = -\frac{(\rho_i - \rho_L)\,\sigma_i^2}{18\eta} g^\dagger (1 - \phi)^n. \tag{A.11}$$

(ii) Neglecting gravity, in the dilute limit, $\phi \to 0$, translational entropy, $\ln \phi_i$, is the only contribution to $\mu$, $h_i$ becomes zero, equation (A.8) reduces to Fick's first law (molar flux $J_i = c_i \cdot v_i$), and equation (A.5) to Fick's second law of diffusion.

## References

[1] Piazza R, Bellini T and Degiorgio V 1993 *Phys. Rev. Lett.* **71** 4267
[2] Biben T and Hansen J-P 1994 *J. Phys.: Condens. Matter* **6** A345
[3] Simonin J P 1995 *J. Phys. Chem.* **99** 1577
[4] Löwen H 1998 *J. Phys.: Condens. Matter* **10** L479
[5] Dufrêche J F, Simonin J P and Turq P 1999 *J. Mol. Liq.* **79** 137
[6] Dufrêche J F, Simonin J P and Turq P 2000 *J. Physique IV France* **10** 109
[7] Téllez G and Biben T 2000 *Eur. Phys. J.* E **2** 137
[8] Philipse A P and Koenderink G H 2003 *Adv. Colloid Interface Sci.* **100–102** 613
[9] van Roij R 2003 *J. Phys.: Condens. Matter* **15** S3569
[10] Hynninen A P, van Roij R and Dijkstra M 2004 *Europhys. Lett.* **65** 719
[11] Raşa M and Philipse A P 2004 *Nature* **429** 857
[12] Philipse A P 2004 *J. Phys.: Condens. Matter* **16** S4051
[13] Esztermann A and Löwen H 2004 *Europhys. Lett.* **68** 120
[14] Biesheuvel P M 2004 *J. Phys.: Condens. Matter* **16** L499
[15] Rasa M, Erne B H, Zoetekouw B, van Roij R and Philipse A P 2005 *J. Phys.: Condens. Matter* **17** 2293
[16] Royall C P, van Roij R and van Blaaderen A 2005 *J. Phys.: Condens. Matter* **17** 2315
[17] Zwanikken J W and van Roij R 2005 *Europhys. Lett.* **71** 480
[18] Boublik T 1970 *J. Chem. Phys.* **53** 471
[19] Mansoori G A, Carnahan N F, Starling K E and Leland T W 1971 *J. Chem. Phys.* **54** 1523
[20] Lue L, Zoeller N and Blankschtein D 1999 *Langmuir* **15** 3726
[21] Oversteegen S M and Roth R 2005 *J. Chem. Phys.* **122** 214502
[22] Williams J W, van Holde K E, Baldwin R L and Fujita H 1958 *Chem. Rev.* **58** 715
[23] Vrij A 1980 *J. Chem. Phys.* **72** 3735
[24] van Holde K E 1985 *Physical Biochemistry* (Englewood Cliffs, NJ: Prentice-Hall) pp 112–4
[25] Masliyah J H 1979 *Chem. Eng. Sci.* **34** 1166
[26] Patwardhan V S and Tien C 1985 *Chem. Eng. Sci.* **40** 1051
[27] Biesheuvel P M, Verweij H and Breedveld V 2001 *AIChE J.* **47** 45
[28] Biesheuvel P M, Verweij H and Breedveld V 2001 *AIChE J.* **47** 1969
[29] Wesselingh J A and Krishna R 1990 *Mass Transfer* (New York: Ellis Horwood) p 77
[30] Krishna R and Wesselingh J A 1997 *Chem. Eng. Sci.* **52** 861
[31] Taylor R and Krishna R 1993 *Multicomponent Mass Transfer* (New York: Wiley)
[32] Fornasiero F, Prausnitz J M and Radke C J 2005 *Macromolecules* **38** 1364
[33] Vrij A and Tuinier R 2005 Structure of concentrated colloidal dispersions *Fundamentals of Interface and Colloid Science* vol 4, ed J Lyklema (Amsterdam: Elsevier) section 5.4
[34] Carnahan N F and Starling K E 1969 *J. Chem. Phys.* **51** 635
[35] Vliegenthart G A and Lekkerkerker H N W 1999 *J. Chem. Phys.* **111** 4153
[36] Reitz J R, Milford F J and Christy R W 1979 *Foundations of Electromagnetic Theory* 3rd edn (Reading, MA: Addison-Wesley)
[37] Lyklema J 2005 *Fundamentals of Interface and Colloid Science* vol 1 (New York: Elsevier) section 5.3e
[38] Böttcher C J F 1952 *Theory of Electric Polarisation* (Amsterdam: Elsevier) chapter 7
[39] Biesheuvel P M 2005 *Eur. Phys. J.* E **16** 353
[40] Biesheuvel P M, van der Veen M and Norde W 2005 *J. Phys. Chem.* B **109** 4172
[41] Biesheuvel P M and Wittemann A 2005 *J. Phys. Chem.* B **109** 4209
[42] Biben T and Hansen J-P 1993 *Mol. Phys.* **80** 853
[43] Richardson J F and Zaki W N 1954 *Trans. Inst. Chem. Eng.* **32** 35