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LETTER TO THE EDITOR

The apparent mass in sedimentation profiles of charged suspensions

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Abstract. Recent experiments have revealed that the exponential decay in the sedimentation density profiles of charged colloidal suspensions is governed by an apparent mass that is smaller than the buoyant mass. A simple analytical density functional study is presented which describes the reduction of the apparent mass. In accordance with experiments, it is found that the mass reduction depends on the concentration of added salt as well as on the colloidal sedimentation height.

At the beginning of this century, Einstein [1] suggested extracting Boltzmann's constant k_B from the low-density wing of a colloidal sedimentation profile. In fact, Boltzmann's statistics predicts an exponentially decaying number density profile $\rho(z)$ of the colloidal particles

$$\rho(z) \propto \exp(-z/\ell_g). \quad (1)$$

Here z is the height coordinate parallel to the direction of the gravitational acceleration g and $\ell_g \equiv k_B T/m_0 g$ is the gravitational length where m_0 is the buoyant mass of a single colloidal particle and T is temperature. Hence k_B is obtained by the slope of a plot of $\ln \rho(z)$ versus z provided all the other parameters are known. Perrin [2] actually used this idea and determined k_B . Of course, by now, all these considerations are well-established in the present literature [3], but recently an interesting deviation from the ideal barometric law (1) was reported in depolarized-light scattering experiments by Piazza *et al* [4]. In strongly deionized charged colloidal suspensions they still found an exponential decay of the colloidal density profiles, but the associated decay length ℓ was larger than the gravitational length ℓ_g . This result can immediately be expressed in terms of an *apparent mass*, m , which is smaller than the buoyant mass, m_0 , i.e. $m/m_0 = \ell_g/\ell < 1$.

A first obvious explanation of the unexpected mass reduction is due to the intrinsic size and mass polydispersity of the colloidal sample. For a strongly polydisperse suspension, it is clear that the light particles dominate the wing, resulting in an apparent mass reduction. However, the samples used in the experiments were practically monodisperse and furthermore the mass reduction reported in the experiments depends on the amount of added salt. This gives a hint that the mass reduction is a pure *electrostatic* effect.

A full theoretical understanding of the mass reduction is still missing. However, there have been two complementary attempts based on density functional theory [5] of the primitive model of strongly asymmetric electrolytes involving the colloidal macroions and the microscopic counter- and coions. Firstly, Biben and Hansen [6] numerically

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solved the minimizing equations for the associated density functional in order to obtain the sedimentation profiles in a finite container. They observed an accumulation of counterions on the top of the container and conclude that the mass reduction could be generated by an electric condenser compensating at least partially the gravitational acceleration [7]. In this work, however, only one single parameter combination was examined for which no mass reduction was found, although a significant electric field was present. Secondly, Simonin [8] solved the same equations under the constraint of local charge neutrality which implies a vanishing local electric field. He could reproduce a ratio $m/m_0 \approx 1$ for a large amount of added salt in accordance with the experiments, but failed to describe the mass reduction for a strongly deionized system. The drawback of this work is that it excludes *a priori* a condenser effect and hence the local charge neutrality assumption is questionable.

The aim of this letter is to present a simple analytical theory for the mass reduction which is particularly designed for the low-density wing of the colloidal density profiles. The theoretical starting point is the same as in [6, 8]. However, no attempt is made to solve the minimizing equations for the density functional. Instead, the problem is viewed as a variational calculation and a simple *ansatz* involving exponential trial functions for the counterionic and macroionic densities is used. It is found that, apart from the charge asymmetry Z and the relative amount of added salt, the mass ratio depends crucially on a coupling parameter γ which describes the strength of Coulomb interaction between the ions relative to the gravitational field. While the two previous theoretical calculations correspond to either small γ [6] or to the limit $\gamma \rightarrow \infty$ [8], the present theory works over the whole range of γ . Comparing our results to the experimental data, the dependence of m/m_0 on the added salt concentration, c_s , and the sedimentation height, h , is qualitatively confirmed. However, the dependence on h is weak and the dependence on c_s is strong in our theory while these trends are opposite in the experimental data. For a strongly deionized sample it is furthermore pointed out that m/m_0 depends crucially on the residual salt concentration.

First, let us recall the free energy density functional \mathcal{F} per unit area which has to be minimized with respect to the macroionic number density profile $\rho_1(z)$ and with respect to the counter- and coion density profiles, $\rho_2(z)$ and $\rho_3(z)$ respectively [6]. Assuming that the gravity only couples to the colloidal particles but not to the microscopic ions, it reads as follows:

$$\begin{aligned} \mathcal{F}[\rho_1(z), \rho_2(z), \rho_3(z)] = & \sum_{v=1}^3 \int_0^\infty dz k_B T \rho_v(z) (\ln(\Lambda_v^3 \rho_v(z)) - 1) \\ & + \int_0^\infty dz m_0 g z \rho_1(z) + \frac{1}{2} \int d^2 r' \int_0^\infty dz \int_0^\infty dz' \frac{\rho_t(z) \rho_t(z')}{\epsilon \sqrt{r'^2 + (z - z')^2}}. \end{aligned} \quad (2)$$

Here, Λ_v are the (irrelevant) thermal de Broglie wavelengths of the ions, ϵ is the dielectric constant of the solvent and $\rho_t(z) \equiv Zq\rho_1(z) - q\rho_2(z) + q\rho_3(z)$ is the total charge density of the system. Here, $Z > 0$ is the polyvalency of the macroions in units of the counterion charge $q > 0$. For simplicity we assume that the counterions stemming from the macroions and the salt ions have the same valency. The functional \mathcal{F} has to be minimized under the constraint of fixed concentration c_s of added salt and of fixed overall colloidal density per unit area, i.e. $\int_0^\infty dz \rho_1(z) \equiv \sigma$. Here the bottom of the cell is at $z = 0$. The latter parameter, σ , is proportional to $h\Phi_0$ where h is the cell height and Φ_0 the averaged colloidal volume fraction. This quantity can be controlled in the experiments. The basic assumption for (2) is that the Coulomb interaction between the macroions and microscopic ions is dominant. For moderate colloidal volume fractions ($\Phi \lesssim 0.3$), excluded volume interactions between the macroions are irrelevant since they are completely masked by the Coulomb forces. The

excluded volume forces become relevant, however, for large Φ ($\Phi \gtrsim 0.3$) but are certainly unimportant in the low-density wing of the macroions which is of interest here. Furthermore any macroionic correlations beyond the mean-field level of description are ignored.

In the following we adopt a simple variational *ansatz* for the three density fields $\{\rho_1(z), \rho_2(z), \rho_3(z)\}$ with two scalar variational parameters. Motivated by the experimental data [4] where the macroionic density follows an exponential decay, we parametrize $\rho_1(z)$ as

$$\rho_1(z) = \frac{\sigma\alpha}{\ell_g} \exp(-\alpha z/\ell_g) \quad (3)$$

α being a variational parameter. As an advantage, this provides a direct access to the mass ratio since the minimal value of α is identical to m/m_0 . For the counterionic density, we again use an exponential *ansatz* with a single variational parameter β

$$\rho_2(z) = c_s + \frac{Z\sigma\beta}{\ell_g} \exp(-\beta z/\ell_g) \quad (4)$$

while the coionic density is assumed to be constant along the sample: $\rho_3(z) = c_s$. While we have always guaranteed *global* charge neutrality, we have abandoned the *local* charge neutrality condition. It is only for the special case $\alpha \equiv \beta$, that $\rho_r(z)$ vanishes. Inserting the density fields into the functional $\mathcal{F}[\rho_1(z), \rho_2(z), \rho_3(z)]$ and minimizing with respect to α and β , the mass ratio m/m_0 is given as the root of the following implicit equation in α :

$$Z\beta(\alpha) - \kappa I\left(\frac{Z\beta(\alpha)}{\kappa}\right) - \gamma + \frac{4\gamma\beta^2(\alpha)}{(\alpha + \beta(\alpha))^2} = 0. \quad (5)$$

Here $I(x) := \int_0^x dy(\ln(1+y))/y$ and the decay parameter β for the counterionic density profiles is related to α via $\beta(\alpha) = \alpha(2/\sqrt{1+(1-\alpha)/\gamma} - 1)$. Obviously, m/m_0 only depends on *three* dimensionless parameters, namely the charge asymmetry Z , the coupling parameter $\gamma := 4\pi Z^2\sigma\lambda_B\ell_g$, and the relative amount of added salt $\kappa := c_s\ell_g/\sigma$. Here, $\lambda_B = q^2/\epsilon\kappa_B T$ is the Bjerrum length of the counterions.

For some limiting cases explicit expressions for m/m_0 are available.

- (i) Strong Coulomb coupling, $\gamma \gg 1$. In this case, $\alpha \equiv m/m_0 = \beta[1 + ((1 - \beta)/\gamma) + O(1/\gamma^2)]$ where the decay constant β for the counterions is the root of $(Z + 1)\beta - 1 - \kappa I(Z\beta/\kappa) = 0$. For small concentrations of added salt ($\kappa \ll 1$), this yields $m/m_0 = [(1 + \frac{\kappa}{2} \ln^2(\kappa(1 + \frac{1}{2}))) / (Z + 1)] + O(1/\gamma)$ which again in the academic case of a completely deionized system ($\kappa \equiv 0$) reduces to $m/m_0 = 1/(Z + 1)$. The striking fact is that the correction to this limiting value is significant even for small κ . Hence any small residual salt concentration will shift m/m_0 to values which are much larger than $1/(Z + 1)$. On the other hand, for a large amount of added salt, $\kappa \gg 1$, we obtain $m/m_0 = 1 - (Z^2/4\kappa) + [((Z^3/9) + (Z^4/8))/\kappa^2] + O(\kappa^{-3}, \gamma^{-1})$. Hence there is no mass reduction in the limit of high salt concentration ($\kappa \gg 1$).
- (ii) Strong gravitational coupling $\gamma \ll 1$. In this case, the macroions and counterions decouple and one gets $m/m_0 = 1 - 3\gamma$ and $\beta \rightarrow 0$ for arbitrary κ . Hence, as expected, no mass reduction is obtained for strong gravity ($\gamma \equiv 0$).

Summarizing, a mass reduction is only possible if there is a sufficiently high Coulomb coupling *and* a small relative amount of added salt.

In general, the counterions are more delocalized than the macroions which gives rise to a *local electric field*, $E(z)$, along the z -axis which can be expressed as $E(z) = E_0(\exp(-\beta z/\ell_g) - \exp(-\alpha z/\ell_g))$, where the amplitude $E_0 = 8\pi Zq\sigma/\epsilon$ is the electric field of a condenser with completely separated macroion and counterion charges. Obviously,

due to global charge neutrality, $E(0) = E(z \rightarrow \infty) = 0$. The local electric field exhibits a maximum $E_m/E_0 = (1 - (\alpha/\beta))(\alpha/\beta)^{-1/d}$ at $z/\ell_g = \ln(\alpha/\beta)/(\alpha - \beta)$ where $d = 1 - \beta/\alpha$. For $\gamma \rightarrow \infty$, $\alpha \rightarrow \beta$, and hence E_m/E_0 vanishes. This is shown in figure 1 where we have plotted m/m_0 and E_m/E_0 over several decades of γ . Here we have varied ℓ_g and c_s such that κ remains fixed. Hence E_0 is independent of γ in this case. It can be seen that the mass reduction is accompanied by a decrease of E_m . This underlines the fact that the mass reduction is not induced by an electric field. On the contrary, for large couplings γ , the build-up of an internal electric field is energetically too costly, and the local-charge-neutrality condition is almost perfectly fulfilled. The physical reason of the mass reduction lies in the fact that the counterions gain entropy in being more delocalized and the macroions are ‘slaved’ to the counterions due to the strong Coulomb coupling. For small γ , on the other hand, an electric field is present, but there is no mass reduction in accordance with the findings of [6].

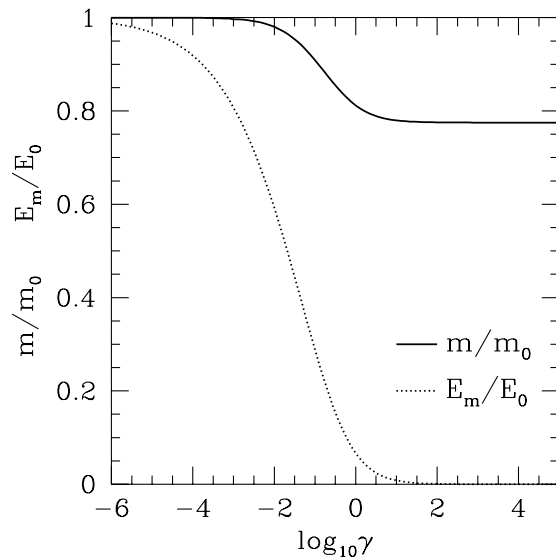


Figure 1. Plot of the mass ratio m/m_0 (solid line) and the reduced maximal electric field strength E_m/E_0 (dotted line) over several decades of the Coulomb coupling constant γ . Note the logarithmic scale in γ . Fixed parameters are $q = e$, $Z = 100$, $\lambda_B = 7.2 \text{ \AA}$, σ and $\kappa = 6 \times 10^4$, such that the γ -dependence corresponds to a change in ℓ_g and c_s .

We now relate our results to the experimental data. Working out the effective parameters, one can express γ as $3Z^2\lambda_B\ell_g^2\Phi(0)/R^3\alpha$ where $\Phi(0)$ is the colloidal volume fraction at which the density fields starts to exhibit the exponential decay and R is the radius of the colloidal particles. In the experiments, $\lambda_B = 7.2 \text{ \AA}$, $\ell_g = 0.0235 \text{ cm}$, $R = 73 \text{ nm}$, $q = e$. However, $\Phi(0)$ and α are not known *a priori* and also the effective macroion charge Z is not known exactly, but is of the order of a few hundreds. Let us first estimate the physically relevant range of γ for the experiments. Assuming $\alpha \approx 1$, $100 \lesssim Z \lesssim 1000$, and $0.02 \lesssim \Phi(0) \lesssim 0.1$ in accordance with the measurements, the possible range of γ is $6 \times 10^7 \lesssim \gamma \lesssim 3 \times 10^{10}$. In any case, $\gamma \gg 1$, such that the local charge neutrality condition is practically fulfilled. This in turn implies that the behaviour in the wings is completely decoupled from the other part of the sediment. This first of all shows that our analysis of the wings should apply. Secondly, the mass reduction in the wings should be

quite insensitive to the (large) sedimentation height h .

In figure 2, the physical domain for the mass ratio m/m_0 is shown as a hatched area versus concentration of added salt. The borderlines are obtained for $Z = 100$ and $\gamma = 6 \times 10^7$ (solid line) and for $Z = 1000$ and $\gamma = 3 \times 10^{10}$ (dashed line). Seven experimental data [4] are also shown as triangles. Care has to be taken for the so-called salt-free measurements. There is always a residual salt contribution which can be estimated to be of the order of 0.1 mMol l^{-1} [9]. The important conclusion is that all the experimental data fall reasonably well into the physical domain. However, for a quantitative comparison, one has to assume an strong dependence of the effective charge Z on c_s .

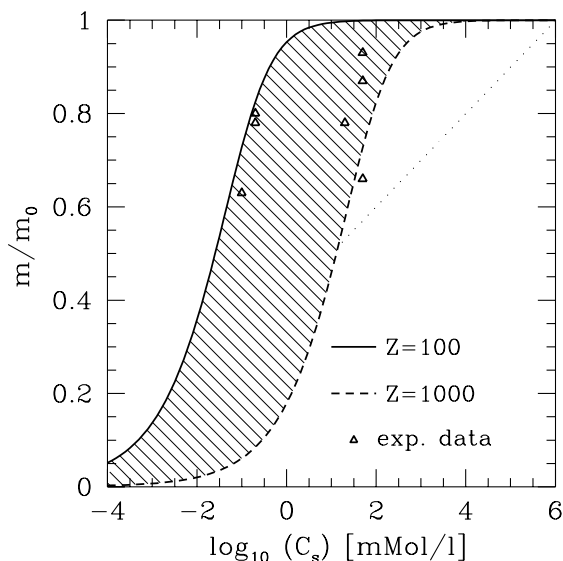


Figure 2. Mass ratio m/m_0 versus concentration c_s of added salt. The unit of the monovalent salt concentration is 1 mMol l^{-1} . Note the logarithmic scale for c_s . The solid curve is for $Z = 100$ and $\gamma = 6 \times 10^7$, the dashed curve for $Z = 1000$ and $\gamma = 3 \times 10^{10}$. The remaining parameters are from the experiment, $q = e$, $\ell_g = 0.0235 \text{ cm}$, $\lambda_B = 7.2 \text{ \AA}$. The physical region is indicated by the hatched area. The experimental data are shown by triangles. The residual salt concentration in the experiments was estimated to be 0.1 mMol l^{-1} .

Moreover, the experimental data for m/m_0 depend strongly on the sedimentation height h : an almost linear dependence between m/m_0 and h was reported [4], which was nearly independent of the salt concentration. In figure 3 we have plotted m/m_0 versus h (or equivalently versus σ or γ) for the experimental parameters and a *constant* macroion charge of $Z = 300$. In fact, m/m_0 decreases with h and there is an almost linear dependence but the slope depends strongly on the salt concentration. Provided Z is independent of c_s , the strong h -dependence together with the weak c_s -dependence of the experimental data cannot be explained by our theory which yields quite the opposite behaviour, namely a strong c_s -dependence and a weak h -dependence. Apparently, the only escape to reconcile both results is to assume a c_s -dependent effective charge Z as usually done in nonlinear screening theories [10].

In conclusion we have presented a simple analytical approach describing the mass reduction in sedimentation density profiles of charged suspensions which explains semi-quantitatively the experimental data provided a reasonable effective macroion charge is assumed. In more detail, however, the strong dependence of the mass reduction on the

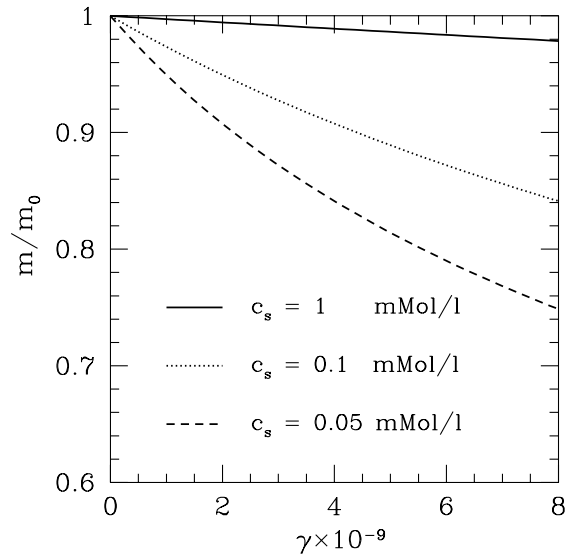


Figure 3. Plot of the mass ratio m/m_0 versus Coulomb coupling constant γ for different salt concentration: $c_s = 1$ mMol l^{-1} (solid line), $c_s = 0.1$ mMol l^{-1} (dotted line), $c_s = 0.05$ mMol l^{-1} (dashed line). Fixed parameters are $q = e$, $Z = 100$, $\ell_g = 0.0235$ cm, such that the γ -dependence corresponds to a change in the sedimentation height $h \propto \sigma$.

sedimentation height and the weak dependence on the salt concentration could only be explained with an effective charge that depends strongly on the added salt concentration.

We remark that the present approach can be extended to include more variational parameters for all density fields. It is particularly important to check the assumption of a constant coion profile throughout the suspension by using z -dependent *ansatz* for the coion profile. In this context it is worth mentioning that the coion profile calculated in [6] only exhibits a weak z -dependence. At the same time one can take into account the excluded-volume macroion–macroion interaction by assuming local excess-free-energy terms for hard spheres in the free energy density functional [6]. This, together with a more flexible density parametrization, should allow for a more detailed study of the whole colloidal density profile and may help to better explain the strong dependence of m/m_0 on the sedimentation height.

Finally we remark that for one-component-macroion model the density profile is given by the inverted equation of state [5]. Hence any interaction in such a model will certainly alter the exponential decay of the density profile to another functional form and therefore fails to extract the apparent mass.

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