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Non-linear screening in concentrated colloidal suspensions

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Abstract. In a charge-stabilized colloidal solution, the large colloidal particles are surrounded by microions that are up to four orders of magnitude smaller than the colloidal particles. Because of this size asymmetry, it is desirable to obtain an effective one-component description of the mixture where the colloidal particle plus its ionic atmosphere is treated as one, dressed particle. The effective pair potential between these dressed particles is a screened Coulomb potential. The screening depends, of course, on the density distribution of the small ions around and between the big colloidal particles. If the colloidal charge and the concentration of the ions is not too high, this distribution can be approximately determined from the linearized Poisson–Boltzmann equation, and the resulting effective pair potentials are Yukawa potentials. In concentrated suspensions, however, the full, non-linear Poisson–Boltzmann equation must be solved to determine the density distribution of the small ions. In this article, we suggest a way to obtain effective pair potentials for this case. We solve the non-linear Poisson–Boltzmann equation around a colloidal particle that is displaced a certain distance from the centre of its Wigner–Seitz cell. From the resulting density profile of the ions, we determine the total force acting on the shifted particle as a function of the displacement. From this function one can then estimate the non-linearly screened pair forces, and, thus, the effective pair potentials.

Introduction

Many important macromolecules, such as proteins, are soluble in water because they become charged [1]. The resulting macroions are surrounded by small ions which are released from the surface of the molecule and which then screen the Coulomb forces between the macroions. Since the structure, function, correlations, and rheology of the suspension all depend entirely on interparticle forces, a detailed understanding of the suspension is not possible without an accurate description of these screened forces.

A model system that lends itself well to the study of these screened Coulomb interactions is formed by monodisperse polystyrene latex spheres in aqueous solution [2]. It is a typical example of a charge-stabilized colloidal suspension, which we want to focus on in the present paper. Such aqueous latex suspensions are made up of highly charged, spherical macroions (the latex spheres), having a diameter ranging from some tens of nm to several hundreds of nm, and an ionic atmosphere surrounding each macroion. These ions, with a diameter of a few Å only, stem from a dissociation of ionizable groups at the surface of the colloidal particle, or from salt added to the solution. Due to the ionic atmosphere, the colloidal particles are prevented from coagulating, thereby stabilizing the suspension against flocculation (charge stabilization).

Such charge-stabilized colloidal suspensions can also be regarded as a realization of an asymmetric electrolyte, a term that highlights the extreme size and charge asymmetry between the individual ion species of the suspension. This asymmetry is in fact one of the reasons for

the ongoing theoretical interest in these systems, as it renders a number of standard theoretical methods (for instance, the usual liquid-state integral equation theory) useless and calls for new and alternative approaches.

One way out of the rather involved problems posed by the size and charge asymmetry in charged colloidal suspensions is the formal contraction of the initial multicomponent system into an effective one-component description. The idea is to consider the ionic atmosphere, strongly accumulated near the colloid surface, together with the macroion itself as a new entity, i.e. a (fictitious) quasiparticle, which might be called a *dressed* macroion. Instead of the real multicomponent suspension, one then has to consider a system made up of one species only, namely the dressed macroions, with new, *effective* interactions between them.

The question of how to find such effective forces is not new, but has been the subject of numerous research efforts, the first of which was published as early as 1941. It is the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [3] which is still generally accepted as the basic theory of interactions between spherical macroions. It predicts a repulsive Yukawa-like effective potential which is derived from the linearized Poisson–Boltzmann (PB) equation (*linear screening*). However, the linear approximation is only valid if the mean-field electrostatic potential is small, i.e. in the limit of small counterion densities and macroion charges.

This article addresses the question of how to find such effective interparticle forces in charge-stabilized colloidal suspensions when this linear approximation fails, i.e. in a parameter regime where the full, non-linear PB equation instead of its linearized form is required to find sufficiently accurate mean-field potentials. The screening of the Coulomb forces by the ionic atmosphere is then referred to as *non-linear screening*. The direct way to come to such PB-based effective pair potentials is clear: in principle, one has to solve the multicentred PB equation for the microions in the external field of the fixed macroions. Doing that for every possible configuration of macroions, one would end up with the effective total potential energy as a function of the positions of all macroions which one had to approximate by a sum of pairwise additive pair potentials. Undoubtedly, a difficult, not to say impossible, task.

Our idea is to consider just one specific configuration of macroions, namely a slightly distorted fcc configuration. For this configuration, we will solve the non-linear PB equation for one macroion in its Wigner–Seitz (WS) cell. From the calculated density profiles we can then determine the total force acting on the macroion by integrating the stress tensor in an appropriate way. It is clear that this force is directed towards the centre of the WS cell so as to restore the perfect fcc symmetry. This total force can then be decomposed into pair forces between the dressed colloidal particles in neighbouring WS cells. The non-linearly screened pair forces thus determined are finally compared with pair forces from standard DLVO theory.

Let us briefly mention some of the important papers in this field [1, 4]. Several authors have attempted to extend the useful domain of effective Yukawa interactions by replacing the bare macroion charge by a smaller effective (renormalized) charge Z^* [5–7] which takes account of the non-linear screening. For regions far from the surface of the colloid, one can then still resort, even in the case of highly charged macroions, to a Debye–Hückel-like approach by using Z^* instead of the real charge Z . For small colloidal charges, the Z^* thus determined has recently been shown to reproduce results from primitive model calculations quite nicely [8]. Experimentally, this concept has been used many times to describe interaction-dependent properties of colloidal suspensions such as phase behaviour [9], the structure of binary mixtures [10], the diffusive dynamics [11], and electrokinetic phenomena [12].

An idea similar to ours has been proposed by Belloni and co-workers in reference [13] where the eccentric PB cell model as a natural extension of the standard PB cell model is discussed. From the older papers, we mention that of Beresford-Smith, Chan, and Mitchell

who suggested modifications of the DLVO pair potential so as to account for the effect of the colloidal concentration [14], and those of Senatore and Blum [15] and Nägele, Klein, and Medina-Noyola [16] who studied, at very large volume fractions, the effect of the finite size of the microions on the macroion–macroion structure factor. In reference [7], Belloni calculated the structure factors for a mixture of charged hard spheres (primitive model) using the mean-spherical approximation, and derived from it different expressions for the effective potential depending on the volume fraction of the colloidal particle and the finite size of the small ions.

Starting with section 1, where we define more precisely what is meant by ‘effective potentials’, we describe in section 2 how the non-linear PB equation can be formally introduced into the problem. Section 3 then explains our idea, and discusses, in particular, the important role of the boundary conditions, while in section 4 the density profiles obtained from the non-linear PB equations are presented. Section 5 explains how these profiles can be used to determine forces and how these forces are related to the effective pair forces that we want to determine. We conclude in section 6 with a short summary.

1. The model

We study a suspension of identical spherical macroions, each bearing a charge of $+Ze$. The density of the macroparticles is $n_p = N_p/V$ which is the inverse of the volume per particle denoted by V_{WS} (in the crystalline phase this is the volume of the WS cell). Also present are N_m counterions, each bearing a charge of $-e$. Their density is $n_m = N_m/V$. For simplicity, we restrict ourselves to the salt-free case. The solvent (water) is assumed to be a continuum of dielectric constant ϵ (primitive model), while the microions are considered to be pointlike particles. The total number of negative microions equals the number of macroionic charges, i.e. $N_p Z = N_m$. This model is characterized by a total Hamiltonian consisting of Hamiltonians for both macroions and microions, H_p and H_m , and the microion–macroion interaction term, H_{pm} :

$$H = H_p + H_{pm} + H_m. \quad (1)$$

The Helmholtz free energy F derived from this model Hamiltonian may be written as

$$\begin{aligned} \exp(-\beta F) &= \text{Tr}_p \text{Tr}_m \exp(-\beta H) \\ &= \text{Tr}_p \exp(-\beta H_p) \text{Tr}_m \exp(-\beta(H_{pm} + H_m)) \\ &= \text{Tr}_p \exp(-\beta H_p^{eff}) \end{aligned} \quad (2)$$

where Tr_p and Tr_m denote phase-space integrals over the macroion and microion phase space. $\beta = 1/k_B T$ is the inverse temperature. The effective Hamiltonian H_p^{eff} introduced in this equation is the sum of the direct Hamiltonian H_p and a free energy F_m , which reads

$$\beta F_m(\{\vec{R}_i\}) = -\ln(\text{Tr}_m \exp(-\beta(H_{pm} + H_m))). \quad (3)$$

It depends on the positions of all N_p macroions which we denote by $\{\vec{R}_i\}$, and can be interpreted as the free energy of an inhomogeneous fluid of microions in the external field of the macroions. We see that by introducing an effective Hamiltonian the multicomponent system is now reduced to an effective one-component system. The particles of this new system are at $\{\vec{R}_i\}$; the forces between them can be derived from the total potential energy

$$V_p^{eff}(\{\vec{R}_i\}) = V_p(\{\vec{R}_i\}) + F_m(\{\vec{R}_i\}) \quad (4)$$

which is the sum of the direct potential energy between the bare macroions and the free-energy contribution of the microionic fluid between them[†].

[†] This section is a condensed version of a more detailed presentation of the subject in reference [19].

With the preceding paragraph we can define more precisely what we aim to find in the following. It is the effective pair potential v^{eff} between the dressed macroions whose form we want to determine such that for all realistic configurations $\{\vec{R}_i\}$ the sum of v^{eff} over all interparticle distances $R_{ij} = |\vec{R}_i - \vec{R}_j|$ gives the best approximation possible to the total potential energy of equation (4):

$$V_p^{eff}(\{\vec{R}_i\}) \approx \sum_{i < j} v^{eff}(R_{ij}). \quad (5)$$

To that end, we first need to find V_p^{eff} for any given configuration $\{\vec{R}_i\}$ of macroions. This quantity is based on the free energy $F_m(\{\vec{R}_i\})$ of the microionic fluid which one can approximately determine from a density functional approach as we will discuss now.

2. The non-linear Poisson–Boltzmann equation

The inhomogeneous distribution of the microions in the external field of the macroions at $\{\vec{R}_i\}$ is characterized by the equilibrium density profile $\rho(\vec{r})$. In a mean-field approach, neglecting all microion–microion correlations, this density distribution can be obtained from the solution to the PB equation:

$$\nabla^2 \Phi(\vec{r}) = 4\pi \lambda_B \rho(\vec{r}) \quad (6)$$

where $\Phi = e\beta\Psi$ is the normalized mean-field electrostatic potential and $\lambda_B = e^2/(\epsilon k_B T)$ is the Bjerrum length. This equation is different from the ordinary Poisson equation, since the density itself depends on the potential, namely through the Boltzmann factor:

$$\rho(\vec{r}) = n_m e^{-\Phi(\vec{r})} \quad (7)$$

which makes equation (6) a complicated non-linear differential equation. In most cases, it can only be handled numerically once the boundary conditions are specified. For our case at hand, these boundaries are given by the spherical surfaces of all macroions where either the potential or the electric field is fixed.

On the other hand, one can show that the solution $\rho(\vec{r})$ to the PB equation minimizes the functional

$$\mathcal{F}[n(\vec{r})] = \int d\vec{r}' \left[\frac{\epsilon}{8\pi} E^2(\vec{r}') + n(\vec{r}') k_B T (\log\{\Lambda^3 n(\vec{r}')\} - 1) \right] \quad (8)$$

which is a free-energy functional of the total electric field, E , and the variational counterion density $n(\vec{r})$. Λ is the thermal de Broglie wavelength. The first term is the Coulomb energy for the macroions surrounded by a charge density $n(\vec{r})$ of counterions, while the second term—which is the local free-energy density of the ideal gas—takes into account the entropic contribution of the discrete microions to the free energy. Inserting now the PB profile $\rho(\vec{r})$ (for a given configuration of macroions, specified by $\{\vec{R}_i\}$) into equation (8), we can determine the free energy $F_m(\{\vec{R}_i\})$ of the microionic fluid:

$$F_m(\{\vec{R}_i\}) = \mathcal{F}[\rho(\vec{r})] \quad (9)$$

and thus from equation (4) the total potential V_p^{eff} of the configuration.

Numerically solving the multicentred non-linear PB equation is an extremely involved and daunting task, and only a few studies are known where such PB profiles have been used to actually calculate forces [17, 18]. Because of these difficulties, it is customary to linearize the PB equation by expanding equation (7) to first order, which changes equation (6) into

$$\nabla^2 \Phi = 4\pi \lambda_B n_m (1 - \Phi). \quad (10)$$

As shown explicitly by van Roij *et al* [19], this expansion of the Boltzmann factor leads to a density distribution $\rho(\vec{r})$ that is the sum

$$\rho(\vec{r}) = \sum_j \rho_{SM}(\vec{r} - \vec{R}_j) \quad (11)$$

over spherically symmetric microion-charge distributions ρ_{SM} ('orbitals') around single macroions. Placing this sum again into equation (8), one can show that $F_m(\{\vec{R}_i\})$ can be expressed by a sum of pairwise additive potentials [19] and, with equation (4), one then finds the effective pair potential to be given by the well-known DLVO pair potential

$$v^{eff}(R) = \left(Z \frac{e^{\kappa a}}{1 + \kappa a} \right)^2 \frac{e^2}{\epsilon} \frac{e^{-\kappa R}}{R} \quad R > 2a \quad (12)$$

with a being the radius of the colloidal sphere and $\kappa = (4\pi\lambda_B n_m)^{1/2}$ the inverse screening length.

We here want to go beyond this linear screening theory and consider colloidal suspensions where the linear PB equation is insufficient. The expansion in equation (10) is justifiable only if $|\Phi| < 1$ which ceases to be valid if the mean counterionic density becomes too large. Since $n_m = Zn_p$, this happens either for a highly concentrated suspension (large n_p), or for high charges Z of the macroions. If $|\Phi|$ becomes too large for the exponential factor to be linearized, the full non-linear PB equation, equation (6), must be used to determine the profile $\rho(\vec{r})$. The non-linearity also prevents $\rho(\vec{r})$ from being obtainable from a superposition of single macroion orbitals ρ_{SM} , as in equation (11). We see from equation (9) that, in principle, the PB equation must be solved for every possible configuration $\{\vec{R}_i\}$. Even if this enormous task could be completed, one would still be faced with the problem of how to determine from equations (9) and (4) the effective potential in the sense of equation (5).

From that, it becomes clear that drastic approximations have to be made in order to introduce effects of non-linear screening into effective pair potentials. One such approximative scheme has been introduced by Alexander *et al* [5] who calculated the PB profile for one specific configuration of macroions only, namely the fcc configuration of the crystalline phase, and fitted it to a superposition of effective orbitals:

$$\rho^{fcc}(\vec{r}) \approx \sum_j \rho_{SM}^{Z_{eff}}(\vec{r} - \vec{R}_j). \quad (13)$$

Note that the l.h.s. of this equation is a density profile based on the full *non-linear* PB equation, while the assumption of additivity of orbitals of the r.h.s. is based on the *linear* PB equation. However, by introducing a new effective charge Z_{eff} that replaces the bare charge Z of the macroion, the r.h.s. is modified so that it approximately equals the l.h.s. Inserting equation (13) in equation (8), we then find the same DLVO pair potential as in equation (12), except that the real charge Z is now replaced by Z_{eff} . Taken together, one may say that the effective charges of Alexander *et al* serve to introduce non-linear PB behaviour in a pair potential that is formally derived from the linear PB equation.

3. The eccentric cell model

We suggest another way to find pair potentials that are based on the non-linear PB equation. Like Alexander *et al*, we also calculate PB density distributions in the crystalline fcc phase, i.e. we start from the assumption that all macroions are initially located near fcc lattice sites. However, in contrast to the Alexander model case, we do not require each macroion to occupy the centre position of its cell, but displace each of them the same small distance X from their centre positions. This is, of course, not a configuration of macroions where the total free energy

V_p^{eff} is minimal; it will certainly change when X is altered. This then indicates a possible way to calculate forces: we change X in a systematic manner, calculate for each configuration the PB profiles, and determine V_p^{eff} as a function of X . Its derivative will then be a force which, in a second step, can be decomposed into the effective pair forces.

Figure 1 sketches our model. It shows a macroion (radius a) shifted a distance X from the centre of its WS cell which is assumed to have a spherical shape. The radius R of the WS sphere is chosen such that its volume equals $V_{WS} = 1/n_p$. The volume of the WS sphere outside the colloidal particle is filled with $N_m/N_p = Z$ counterions, so the sphere is electrically neutral. We determine the counterion density profile inside this WS sphere only. The four spheres of figure 1 surrounding the central WS sphere are a reminder of the fact that the other macroions and counterions of the suspension are still present; they enter the calculation of the density distribution via appropriately chosen boundary conditions for the PB equation.

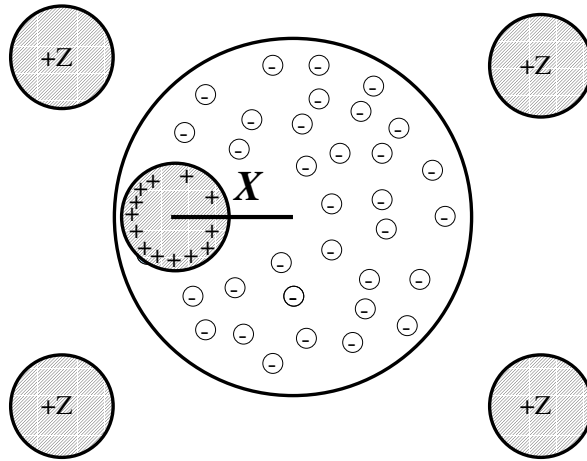


Figure 1. The eccentric cell model: the positively charged macroion (charge Z , hatched circles) inside its spherical Wigner–Seitz (WS) cell is shifted a distance X from the centre. In the cell, there are also Z negatively charged, small counterions. The macroions outside the cell are drawn as a reminder of the fact that the cell is surrounded by other WS cells. They are taken into account by appropriately chosen boundary conditions applied to the Poisson–Boltzmann equation, whose solution gives the counterion density distribution inside the central cell.

The importance of the role of the boundary conditions at the WS cell boundary in our problem cannot be overemphasized; their choice determines the final results. This is, of course, intended, since we are not only interested in the interaction of a macroion with its own cloud of counterions, but also in its interaction with all $N_p + N_m$ ions of the colloidal suspension. The boundary condition at the WS cell boundary marks the point where we couple the remaining ions of the suspension to the problem of finding the density profile for the Z counterions in the WS cell. Hence, the net force acting on the macroion inside this cell can be regarded as the accumulated force of *all* the neighbouring ions acting on the centre macroion. To distinguish it in the following from the pair forces, let us call this net cumulative force the ‘cavity force’, to indicate that it is the force of the entire spherical cavity surrounding the macroion acting on that macroion. From the above paragraph, the cavity force is then the derivative of V_p^{eff} with respect to X :

$$F_c(X) = \frac{d}{dX} V_p^{eff}(X). \quad (14)$$

The boundary condition at the WS cell boundary is impossible to determine correctly

without knowledge of the full solution of the multicentred PB equation. Our way out of this difficulty is just to assume a boundary condition (in fact, the simplest possible) and to investigate in the end what macroionic configuration of the neighbouring macroions must be assumed in order for this condition to be realized. We take the normal component of the electric field to be zero everywhere at the WS cell boundary. Further on, it becomes evident that this corresponds to a situation where all neighbouring macroions are shifted the same distance X in their WS cells.

4. The counterion density profile in a spherical cavity

We numerically solve the PB equation, equations (6) and (7), for the eccentric cell model. Since there is still a rotational symmetry about the line joining the centre of the WS sphere and the centre of the colloidal particle, equation (6) is a differential equation in two spatial variables. In our numerical scheme we use bispherical coordinates [20] because they are symmetry adapted to the geometric situation of the eccentric cell model. This coordinate system was also used in similar studies of double-layer forces [21–23].

Like spherical coordinates, bispherical coordinates have two angular coordinates θ and ψ and a third coordinate η that has the character of a radius, i.e., the coordinate surfaces of the η -coordinate are again simple spheres[†]. However, unlike in the case of the spherical coordinates, these spheres are not concentric with each other, but their centre positions are a function of η . Figure 2 reveals why this coordinate system lends itself to our problem: Both the surface of the spherical WS cell and the surface of the macroion correspond to one η -coordinate surface. In the (η, θ) system, this means that the region external to the macroion is a *rectangular* domain which is defined by η_0 (surface of macroion) and η_1 (surface of WS cell) and $\theta = 0$ and $\theta = \pi$. Clearly, in such a rectangle the two-dimensional PB equation is easier to solve numerically than in the more complicated region of figure 2(a). Another reason why the coordinate system must by symmetry adapted comes from the typical form of the density profiles. They have very steep slopes near the colloid surface, so care must be exercised to have an sufficiently fine grid in this region. A coordinate that is not adapted to the symmetry, like for instance the usual cartesian coordinate system, would invariably lead to material grid errors near the curved surface of the colloidal sphere.

We have to specify the boundary conditions on all four sides of this rectangle. They are

$$\begin{aligned} E_\eta(\eta_0, \theta) &= Z\lambda_B/a^2 \\ E_\eta(\eta_1, \theta) &= 0 \\ E_\theta(\eta, 0) &= 0 \\ E_\theta(\eta, \pi) &= 0. \end{aligned} \tag{15}$$

Here E_η and E_θ are the electric fields in the η - and θ -directions. The last two boundary conditions follow from symmetry considerations, the second one has been discussed already, and the first is just the constant-charge boundary condition at the macroionic surface commonly used for colloidal particles. One recognizes from equation (15) that we are dealing with a von Neumann boundary value problem.

As pointed out above, the solution to the PB equation is also the density distribution that minimizes the free-energy functional of equation (8). Since we can also write down the functional derivative of the free-energy functional with respect to the variational density $n(\vec{r})$, one may ask whether one can determine the equilibrium density distribution by direct minimization of this functional. That, indeed, is the idea of our numerical scheme for finding

[†] A good introduction to bispherical coordinates applied to a similar problem can be found in reference [21].

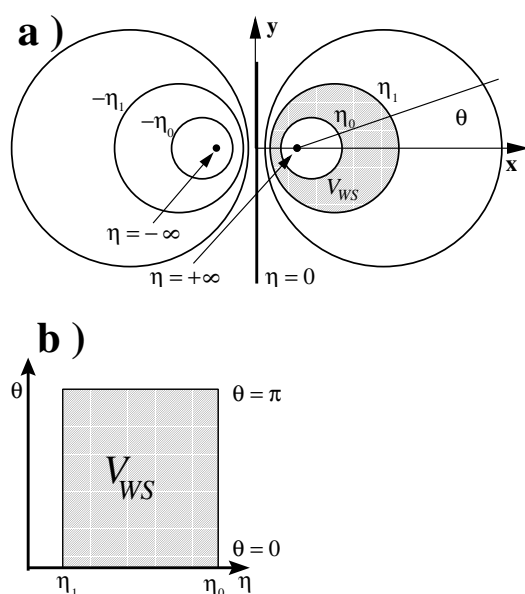


Figure 2. The hatched area in (a) represents a cut through the spherical Wigner–Seitz cell (volume V_{WS}) with the off-centre colloidal particle inside (eccentric cell model, figure 1). In the bispherical coordinate system, this hatched area becomes a rectangle (b). In the (x, y) plane, the η -coordinate surfaces are spheres whose radii are proportional to the inverse of η . The centre positions of these spheres are a function of η , so in the (x, y) plane, $\eta = -\infty$ and $\eta = +\infty$ are points on the x -axis, while $\eta = 0$ corresponds to the entire (y, z) plane.

the solution to the PB equation: starting from an initial trial density distribution, we (i) solve the Poisson equation, (ii) calculate the potential and electric field distributions, and from it, (iii) the free energy, equation (8), and its derivative, and use (iv) simulated annealing techniques to produce from these two quantities a new density distribution that corresponds to a lower energy. This iteration cycle is repeated until the free energy does not change any more; the variational density distribution $n(\vec{r})$ is then equal to the equilibrium density profile $\rho(\vec{r})$. To solve the Poisson equation, we have expressed the Laplacian in equation (6) in terms of bispherical coordinates [20] and solved the resulting differential equation using a publicly available computer code [24].

A good choice of the grid in the domain of bispherical coordinates (η, θ) is of crucial importance for the accuracy of the calculated profiles. A simple uniform grid proves to be sufficient only for relatively small macroionic charges ($Z < 500$). For higher charges, we have used a non-uniform grid in the (η, θ) plane which, after each iteration cycle, has been readjusted to the gradient of the density profile so as to ensure that the number of node points corresponds to the steepness of the profile. The total number of node points has been varied from 1000 up to 4000 until a sufficient accuracy has been achieved.

Figure 3 displays a typical counterion density distribution calculated from the PB equation in the way just described. The volume of the WS cell corresponds to a volume fraction of the colloidal suspension of $\phi = 0.05$ ($\phi = 4\pi n_p a^3/3 = a^3/R^3$). The macroion is displaced a distance of $X = 0.38R$. Its charge is $Z = 500$, its radius $a = 0.368R$. From the data of figure 3, we have produced in figure 4 density profiles along certain θ -directions, now plotted as functions of the radial distance from the centre of the colloidal sphere. Both figures reveal that the main feature of the density distribution is the thick layer of counterions located very

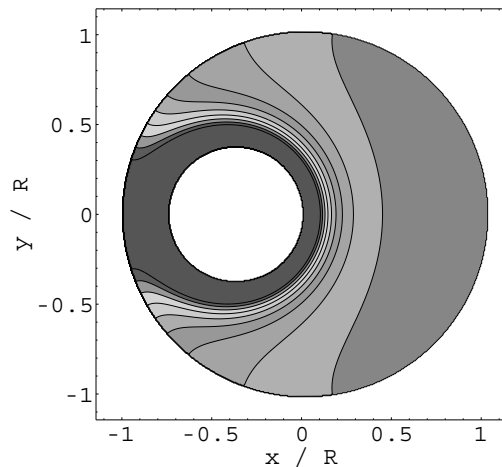


Figure 3. The density distribution of counterions calculated from the mean-field Poisson–Boltzmann equation around a colloidal macroion ($Z = 500$) that is shifted a small distance from the centre of its WS cell. The radius R of the cell corresponds to a colloidal volume fraction of $\phi = 0.05$ ($R = 1357 \text{ \AA}$). The density is large near to the colloid surface and falls off rapidly further away. For the absolute values for the density, see figure 4.

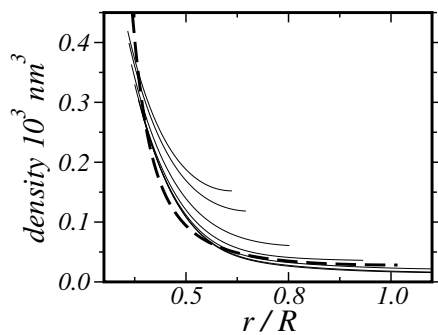


Figure 4. The thick dashed curve gives the counterionic density profile if the macroion is centred, while the thin lines represent cuts through the distribution of figure 3 (from bottom to top, the angle θ varies from 0 to π in steps of $\pi/6$). The densities are plotted as functions of the radial distance r from the centre of the colloidal particle.

near to the surface of the macroion. The profile represents a kind of compromise: a balance between the tendency of the entropy to spread the counterions over as large a region as possible and the tendency of the electrostatic energy to bring the ions near to the surface of the colloid. Near the colloid surface this competition is won by the electrostatic contribution, but, for larger distances from this surface, the resulting layer of counterions around the macroion is capable of screening the macroionic charges so efficiently that entropy has a better chance to counterbalance the electrostatic interaction.

In addition, we observe from figure 3 that and how the eccentricity affects the distribution. Due to the presence of the confining cell boundary, the density of counterions to the left of the colloid particle is substantially higher than that to the right to it. This asymmetry has a twofold effect: first, with the centre of negative charge being different from the centre of positive charge, the whole cell has an effective dipole moment and there will be electric field lines in the θ -direction at the cell boundary (in the η -direction, the field, of course, vanishes). And, secondly, the osmotic pressure will also have an (η, θ) dependence. Both will contribute to the electric stress tensor, and will lead to a net force directed towards the centre of the WS cell.

We can check the reliability of our numerical scheme if we consider the concentric case

where $X = 0$. The PB equation, expressed in terms of spherical coordinates, then depends only on the radius and can be easily solved with standard numerical procedures described, for instance, in reference [5]. The dashed curve in figure 4 shows the resulting profile. We have explicitly checked that the density distributions calculated in bispherical coordinates with our simulated annealing techniques collapse onto this curve if X approaches zero.

5. From cavity forces to pair forces

We can calculate the force acting on the macroion in the WS cell by integrating the stress tensor

$$\vec{T} = \left(\Pi + \frac{\epsilon}{8\pi} E^2 \right) \vec{I} - \frac{\epsilon}{4\pi} \vec{E} \vec{E} \quad (16)$$

over a suitable surface. Here $\vec{E} = E_\theta \vec{e}_\theta + E_\eta \vec{e}_\eta = -\vec{\nabla} \Psi$ is the electric field and Π is the local osmotic pressure which, in the PB theory, is related to the density by $kT\rho(\eta, \theta)$. We can choose any convenient surface S that encloses the macroion and perform the following surface integration to get the cavity force:

$$\vec{F}_c = \int_S \vec{T} \cdot \vec{n} \, dS \quad (17)$$

where \vec{n} is a unit vector directed normal to the surface S . For convenience, we integrate over the surface of the WS cell ($\eta = \eta_1$) where E_η is zero. For symmetry reasons, the force will be directed along the line joining the centre of the WS sphere and the centre of the macroion (the x -axis), so $\vec{F}_c = F_c \vec{e}_x$. From equation (17), we thus obtain

$$F_c = 2\pi \int_0^\pi \left(k_B T \rho(\eta_1, \theta) + \frac{\epsilon}{8\pi} E_\theta^2(\eta_1, \theta) \right) (\vec{e}_\eta \cdot \vec{e}_x) \frac{(a \sinh \eta_0)^2 \sin \theta}{(\cos \eta_1 - \cos \theta)^2} \, d\theta \quad (18)$$

which we rewrite to find an expression for the dimensionless force, $f = \beta F_c 4\pi \lambda_B$:

$$f = \pi \int_0^\pi \left(\rho(\eta_1, \theta) 8\pi \lambda_B + (e\beta E_\theta(\eta_1, \theta))^2 \right) A(\eta_1, \theta) \, d\theta \quad (19)$$

where

$$A(\eta, \theta) = (a \sinh \eta_0)^2 \frac{\sin \theta (1 - \cos \theta \cos \eta)}{(\cos \eta - \cos \theta)^3}. \quad (20)$$

Figure 5 shows the cavity forces calculated from the density profiles using equation (19). We considered a colloidal suspension of a volume fraction of $\phi = 0.01$, with the colloidal charges ranging from $Z = 200$ to $Z = 2000$. For this volume fraction, the WS cell has a

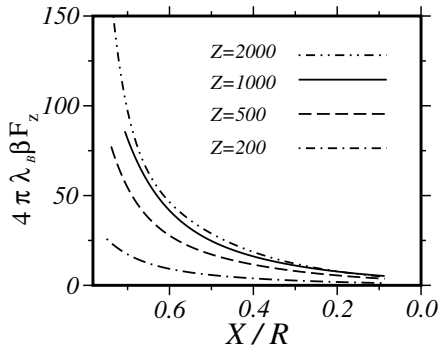


Figure 5. Cavity forces calculated from density distributions of the counterions by integration of the stress tensor, as functions of the shift X of the colloidal particle in its cell. Force curves for several charges of the macroion are shown.

radius of $R = 2320 \text{ \AA}$. The radius of the colloid is $a = 500 \text{ \AA}$. Figure 5 gives the force curves as functions of the displacement X divided by R . For each curve, we calculated 20 density distributions for varying X and fitted the data to a sum of two simple exponential functions. We carefully checked that our results are free from grid errors. A further check of the calculation can be performed by calculating the total energy $V_p^{eff}(X)$ as a function of X . Numerically differentiating this function with respect to the variable X must then lead to the same forces as one obtains from equation (19) (see equation (14)).

As pointed out above, we want to use these cavity forces to estimate the effective pair forces between the dressed colloidal particles, or, alternatively, to determine the effective pair potentials from the total energy of the configuration. We follow equation (5), which for our case at hand may be written in the form

$$V_p^{eff}(X) \approx \sum_j v^{eff}(|\vec{R}_j - X\vec{e}_x|). \quad (21)$$

Our calculations so far provide us with the function $V_p^{eff}(X)$ on the l.h.s. of this equation. Is it possible to estimate from it the effective pair potential inside the sum of the r.h.s. of the equation? For this, we have to make a number of approximations. The first is that we assume the sum in equation (21) to be confined to the twelve nearest neighbours of the central macroion in a fcc crystal, which is justifiable as we expect screened potentials to be short ranged. These neighbours are located somewhere inside their own (spherical) WS cell, not necessarily in a central position. Their exact position must be found from the boundary condition, $E_n(\eta_1, \theta) = 0$, equation (15), since we justified these boundary conditions by claiming that here the electric field contributions of neighbouring dressed macroions cancel each other. If a neighbouring WS cell touches the surface of the central WS cell at (θ, ϕ) (spherical coordinates, figure 6), the condition of vanishing normal electric field at the touching point (θ, ϕ) requires the colloidal particle in this neighbouring cell to be located at

$$\vec{r}(\theta) = \begin{pmatrix} 2R \cos \theta + X \cos 2\theta \\ -2R \sin \theta - X \sin 2\theta \end{pmatrix}. \quad (22)$$

After some algebra, the relative distance between this colloid and the central one is found to be

$$r(X, \theta) = 2(R + X \cos \theta). \quad (23)$$

In the fcc configuration of neighbouring WS cells, there are twelve WS cells touching the central cell at certain positions. For convenience, we assume that these touching points are equally distributed over the surface of the central WS cell. This assumption is consistent with

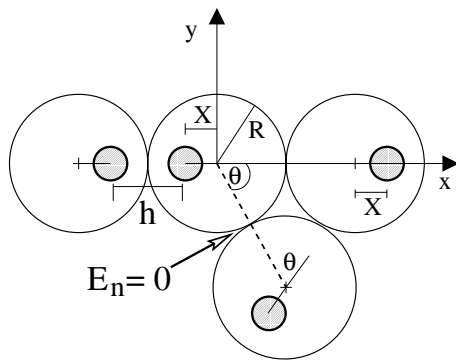


Figure 6. The central WS cell is surrounded by spherical WS cells of the neighbouring colloidal particles. Their positions in their cells are determined by the boundary condition for the normal component of the electric field ($E_n = 0$). This boundary condition can only be realized if every colloidal particle is shifted the same distance X in its cell.

the assumption of a spherical cell. Then the probability $P(\theta, \phi)$ of finding a touching point at (θ, ϕ) is just $12/(4\pi R^2)$.

With equation (23) and $P(\theta, \phi)$ to hand, we can approximate equation (21) by the following integral:

$$V_p^{eff}(X) \approx 2\pi R^2 \int_0^\pi v^{eff}(r(X, \theta)) P(\theta) \sin \theta d\theta \quad (24)$$

where the function $r(X, \theta)$ from equation (23) embodies the boundary condition at the cell boundary. This integral can now be brought into the form

$$V_p^{eff}(X) = \frac{12}{4X} \int_{2(R-X)}^\infty v^{eff}(r') dr' \quad (25)$$

where it is assumed that the pair potential is zero at and beyond $2(R+X)$. Replacing $2(R-X)$ by h , and differentiating equation (25) twice, one finally arrives at

$$F_c(h) - XF'_c(h) = -6v^{eff'}(h) \quad (26)$$

where we used $V_p^{eff'}(h) = -F_c(h)/2$. The prime here denotes derivatives with respect to h .

Equation (26) now gives the desired connection between the pair force and the cavity force, both as functions of h which is the shortest distance between two neighbouring colloidal spheres (see figure 6). We also realize now that our choice of the boundary condition at the cell boundary implies, as claimed above, that all neighbouring macroions are shifted the same distance X in their WS cells. Figure 7 shows the pair force extracted from the data of figure 5 for $Z = 2000$ using equation (26). It is compared with the cavity force curve from figure 5 and the pair forces derived from the DLVO potential of equation (12). For the latter, we had to determine the effective charges Z^* from the one-dimensional spherical PB equation following the renormalization concept of Alexander *et al* that we described above[†]. Note that all three force curves are plotted against the distance h now. This graph is typical of other force curves for smaller macroionic charges. As expected, the cavity force is considerably larger than the pair force for almost all distances because it is the cumulative force of all twelve neighbours on the central colloidal particle. We furthermore observe that our PB derived pair forces have a qualitatively different distance dependence when compared with the standard DLVO forces.

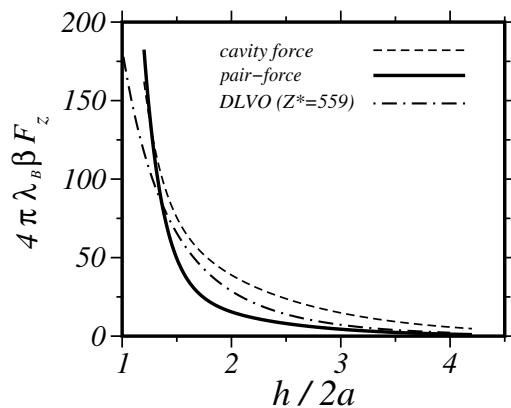


Figure 7. The cavity force of figure 5 for $Z = 2000$ (dashed curve) is compared with the pair force (solid line) which has been extracted from the cavity force by means of equation (26). The latter can be compared with the DLVO pair force, derived from equation (12), where an effective charge of $Z^* = 559$ is used.

[†] At this point we have to take a spherical WS cell that is slightly larger than the radius corresponding to $\phi = 0.01$ ($R = 2320 \text{ \AA}$). This is because we have implicitly assumed that the WS cells of neighbouring colloidal particles only touch each other but do not overlap as they would normally do. If one expands the crystal so that $R = 2320 \text{ \AA}$ spheres in a fcc configuration only touch, the real volume fraction to compare with is $\phi = 0.74 \times 0.01$ which results in a sphere radius of $R = 2566 \text{ \AA}$. The effect of this alteration on the effective charges is however quite small.

This is confirmed by figure 8 where the pair forces are plotted for the four different macroionic charges of figure 5. The four thick lines are (from bottom to top) the pair forces for $Z = 200, 500, 1000,$ and 2000 . They are compared with the renormalized DLVO forces (dashed lines). All forces are now multiplied by h and plotted on a logarithmic scale so that the DLVO forces become straight lines for larger distances. In figure 8, we firstly perceive that the gross features of all four curves calculated from equation (26) are the same, with a linear behaviour in an intermediate regime ($2 < h/2a < 3.5$) and non-linear behaviour for large and small distances. The second observation is that the sequence of curves converges for increasing charges towards a limiting curve, much as one finds for the DLVO forces. We know that this is due to counterion condensation which is reflected in the saturation behaviour of the effective charges. So, we see that this property is not affected by the way in which we derive the effective pair forces.

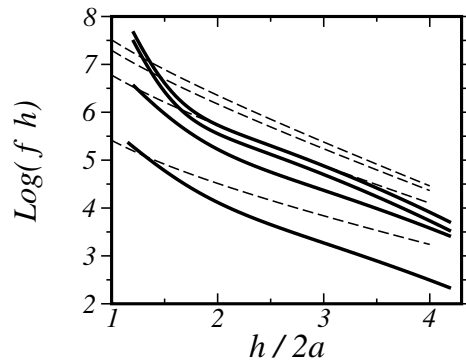


Figure 8. Comparison between DLVO pair forces, equation (12) (dashed lines), and pair forces obtained from the cavity forces of figure 5 (thick solid lines). For the latter, the four curves correspond to the following charges (from bottom to top): $Z = 200, Z = 500, Z = 1000,$ and $Z = 2000$, while the four DLVO curves are based on the following effective charges: $Z^* = 191, Z^* = 383, Z^* = 500, Z^* = 559$.

6. Summary and outline

For sufficiently diluted colloidal suspensions, or for suspensions of colloids bearing not too many charges, the effective potential between the dressed quasi-particles is a screened Yukawa potential which can be derived from the linear Poisson–Boltzmann equation. For more highly charged colloids or highly concentrated suspensions, this linearization ceases to be valid and one has to resort to the full non-linear Poisson–Boltzmann equation instead. The question then is that of whether it is still possible to obtain an effective interaction between the particles of an effective one-component system. In this article we suggest a way in which such non-linearly screened pair forces can be determined.

We have seen that the direct method, even on a mean-field level, is not practicable for realistic systems: one had to determine the free energy of the microionic fluid for every possible configuration $\{\vec{R}_i\}$ of the colloidal particle in order to find $V_p^{eff}(\{\vec{R}_i\})$ and, from it, effective potentials. We, here, consider only one specific configuration instead, in which every macroion is shifted (in a highly correlated way) a distance X from its fcc lattice point, in such a way that the normal component of the electric field can be assumed to vanish at the surface of the WS cell. With this boundary condition we have solved the two-dimensional Poisson–Boltzmann equation for the counterions of one macroion shifted a distance X from

the centre of its spherical WS cell. Integrating the stress tensor over the cell surface, we can then determine a force acting on the macroion. We have shown how this cavity force, which in itself is an interesting quantity, can be used to extract effective pair forces. Finally, we have compared the forces thus determined with the forces derived from standard DLVO theory using renormalized charges, and found a qualitatively different distance dependence.

We do not claim that our method is the best possible. We do, however, think that it improves on the established charge renormalization theory of Alexander *et al* where forces are obtained from a fairly ‘*ad hoc*’ introduction of the effective charges into the DLVO forces. In this effective charge concept, a configuration of macroions is considered (perfect fcc symmetry) where the net forces on the macroions are identical to zero, so it is unclear why this configuration can provide useful information on effective interparticle forces. In contrast to that, we here come to forces through the investigation of a distortion from perfect symmetry where integration of the stress tensor really results in non-vanishing net forces. The natural extension of this work is to consider two colloids in a cell where the presence of all the other macroions in the solution is again taken into account by the appropriate choice of the boundary conditions. Here, again, the question will be that of how to choose these boundary conditions. Work in this direction is in progress.

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