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Attraction between two similar particles in an electrolyte: effects of Stern layer absorption

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ABSTRACT

When Debye length is comparable or larger than the distance between two identical particles, the overlapping among the particles double-layers can play an important role in their interactions. This paper presents a theoretical analysis of the interaction among two identical particles with overlapped double-layers. We particularly focus on the effect of a Stern electrostatic condition from linearization of the adsorption isotherm near the isoelectric (neutrality) point in order to capture how polyvalent ion condensation affects and reverses the surface charge. The stationary potential problem is solved within the framework of an asymptotic lubrication approach for a mean-field Poisson-Boltzmann model. Both spherical and cylindrical particles are analyzed. The results are finally discussed in the context of Debye-Hückel (D-H) limit and beyond it.

Key words: like-charge attraction, Stern layers, Poisson-Boltzmann problem, interacting double-layers.

INTRODUCTION

Recent AFM studies have shown that, in the presence of a polyvalent counter-ion, two similarly charged or identical surfaces can develop a short-range attractive force at a distance comparable to the Debye screening length λ (Zohar et al. 2006, Besteman et al. 2004). This observation is most likely related to earlier reports on attraction between identical colloids in an electrolyte, although the role of poly-valency is not as well established for colloids (Han and Grier 1999). It is also related to the condensation of likecharged molecules like DNAs (Gelbart et al. 2000). Such attraction has raised some debate during the past ten years since, for two identical objects it is necessarily repulsive according to the classical Poisson-Boltzmann (PB) mean-field theory (Neu 1999). Some supplementary polarisability effects could be important to consider. Such effects are associated with dipolar interactions among charges, which, in

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general, are much weaker than electro-static effects, but can be important to take into account at high ionic concentrations and for confined configurations (Boström et al. 2001). These polarisability effects can be described by a dispersion potential associated with a Hamaker cubic decay, and their implication have been computed for the interaction among two planes (Boström et al. 2001) and two cylinders (Boström et al. 2002). Improving theoretical description beyond the usual point-like charge description has been another quest to improve the standard PB description. Taking into account finite size steric effects (Borukhov et al. 1997, Kilic et al. 2007a, b) at high voltages also leads to modified mean-field PB equations, and could be part of the explanation for attraction or ion specific interactions at nano-scales.

Nevertheless, for moderate concentrations and potentials, the attraction is experimentally observed, and the observed exponential attraction is still left unexplained (Zohar et al. 2006, Besteman et al. 2004).

For this reason, theories for like-charge attraction phenomena have sought mechanisms beyond the classical mean-field description. Some contributions have investigated the inclusion of spatial correlation of charge fluctuations (Lukatsky and Safran 1999, Netz and Orland 2000, Lau and Pincus 2002, Lau 2008). In a previous contribution by Plouraboué and Chang (2009), we realized that including a Stern layer for the mean-field boundary condition is compatible with previous field-theoretical analysis of the role of fluctuations on mean-field description (Lau and Pincus 2002, Lau 2008). Those results have been obtained for two identical surfaces whereas previous studies by Chan et al. (2006) have investigated the effect of Stern layers for dissimilar surfaces. In this framework, we obtained an implicit analytic solution for the mean-field potential and compute the attraction among two planar surfaces for which the far field behavior leads to an exponential attraction.

In this contribution, we derive an asymptotic computation of the potential among two spherical or cylindrical identical particles. As opposed to the situation where the particle distance is large compared to the Debye length for which the DLVO approximation holds (Sader et al. 1995), we focus here on the possible non-linear interaction among the particles double-layers.

PROBLEM UNDER STUDY

Governing Equation

We very briefly discuss here the stationary electro-kinetic problem that one has to solve for the electric potential ϕ' (*Cf* for example Karniadakis et al. (2004) for more details). We consider an electrolyte solution composed of Z-charged positive/negative ions. Boltzmann equilibrium associated with the concentration/potential leads to the non-linear mean-field PB relation:

$$\nabla^2 \phi' = 2 \frac{Z F C_\infty}{\epsilon_0 \epsilon_p} \sinh\left(\frac{Z F \phi'}{R_g T}\right), \tag{1}$$

where F is the Faraday constant, ϵ_p the solution relative permittivity, ϵ_0 the dielectric permittivity of vacuum, R_g the perfect gas constant, T the temperature and C_∞ a reference concentration in the far-field region. These parameters are usually used to define the Debye length $\lambda = \sqrt{\epsilon_0 \epsilon_p R_g T / 2 Z^2 F^2 C_\infty}$.

Particle Shape and Boundary Conditions

Let us now discuss the surface shape $h'(r')$ of the particles sketched on Figure 1. This figure represents a section of either a cylindrical or a spherical particle. In the first case, the problem under study is translationally invariant along the direction perpendicular to the figure plane, aligned along the cylinder main axis. In the second case, the problem under study is rotationally invariant along the z' axis. In both cases the particle shape in the section follows a circle. From elementary trigonometry identities one gets:

$$\left(a - (h' - h_m)\right)^2 + r'^2 = a^2, \tag{2}$$

so that,

$$h'(r') = h_m + a - \sqrt{a^2 - r'^2}. \tag{3}$$

This problem can be associated with different boundary conditions at the particles surfaces. We mainly focus on the influence of a Stern layer at the particles surfaces:

$$\partial_n \phi'(\pm h'(r')) = K\phi'(\pm h'(r')) \tag{4}$$

We consider an iso-electric point situation for which the reference potential is taken to be zero, so that the right-hand side of (4) is a linear function of ϕ'. This very usual phenomenelogical boundary condition can be justified from a more fundamental point of view from realizing that fluctuations associated with the adsorption of ions at the solid surface produce some punctual effective interaction at the surface, which can be exactly mapped with a Stern layer boundary condition (Plouraboué and Chang 2009).

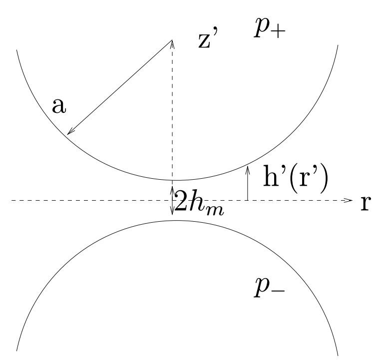

Fig. 1 – Slide view of the two indentical particles under study.

We compare the obtained results for Stern-Layer with other boundary conditions such as an applied surface field at each particles:

$$-\partial_n \phi'(\pm h(r')) = \mp E'_{p\pm}\,, \tag{5}$$

where $E'_{p\pm}$ stands for the Electric field prescribed either at the top $p+$ or the bottom $p-$ particle. From using Gauss's theorem, one realizes that prescribing the field is equivalent to prescribe a surface charge at the particle surfaces. Another widely used boundary condition is to prescribe the electrical potential at the particle surface:

$$\phi'(\pm h(r')) = \phi'_{p\pm}\,. \tag{6}$$

In the following we will compare these three boundary conditions in the D-H approximation.

Asymptotic Formulation

Dimensionless formulation

Let us first discuss some physics associated with the problem for choosing an interesting dimensionless formulation. First, the distance among the particles involves one characteristic length, which is the minimum distance h_m. As discussed in the Introduction, non-trivial effects for particles interactions arise when this distance is of the same order or shorter than the Debye length λ. Furthermore, difficulties in quantifying this interaction are associated with the importance of non-linear effects in the double-layer. Numerical estimation can be used, but needs an accurate description of rapid potential variations inside double layers, which can be computationally challenging. The use of some refined methods using bi-spherical coordinates discretized with finite volume (Lima et al. 2007) or spectral collocation (Carnie et al. 1994, Stankovich and Carnie 1996) methods can lead to accurate results with moderate computational cost. Such computations, nevertheless needs the elaboration of rather involved numerical formulations. Furthermore, the validation of these numerical methods is an useful and necessary step. We will see in the following how developping an alternative theoretical approximation associated with lubrication asymptotic approach can provide a simple one-dimensional integral for the interaction force, which is, then, useful for numerical validations. Finally, some more complex configurations (different than two spheres or two cylinders) for confined slender-body shapes might also be of interest in nano-scale context. For such complex confined geometries (maybe associated with the electrical interaction of rough surfaces), the elaboration of a simplified asymptotic lubrication approach should also be of interest in the limit for which double-layer effects matters, i.e. when the distance h_m is of the same order as the Debye lenght. From realizing that the Debye length λ generally lies between nanometer to sub-micron scale, it can be seen that many interesting situations are associated with particle radius a larger than Debye length $a \gg \lambda$. In the limit $h_m \ll a$, an asymptotic "lubrication" analysis of the problem can be sough for. More specifically, in this limit, most of the potential variation holds along the transverse direction between two particles whose typical length is h_m rather than in the longitudinal direction, roughly parallel to the particles surfaces, for which the potential variations holds along a typical length-scale $\sqrt{ah_m}$. This discussion suggests the following dimensionless formulation of transverse coordinates z, h and the longitudinal one r:

$$z' = h_m z\,, \qquad h' = h_m h\,, \qquad r' = \sqrt{h_m a} r \tag{7}$$

Those coordinates associated with rapid variation of the potential inside a central region are "inner" coordinates and are used in section Asymptotic expansion: inner region.

Another choice could have been taken from simply considering the potential variations far from the confined region, for which the only relevant length-scale is the particle radius. In this case, "outer" dimensionless coordinates can be defined with upper-case notations:

$$z' = aZ\,, \qquad r' = aR\,, \qquad h' = aH \tag{8}$$

that will be subsequently used in section Outer region.

Asymptotic expansion: inner region

Introducing the small parameter $\epsilon = h_m/a$, one can, then, re-write the shape equation (3):

$$h(r) = \frac{1}{\epsilon} + 1 - \frac{1}{\epsilon}(1 - \epsilon r^2)^{1/2} \simeq 1 + \frac{r^2}{2} + \epsilon \frac{r^4}{8} \tag{9}$$

This behavior suggests the following asymptotic sequence for the shape:

$$h = h_0 + \epsilon h_1 , \qquad h_0(r) = 1 + \frac{r^2}{2} , \qquad h_1(r) = \frac{r^4}{8} \tag{10}$$

The normal vector **n** to the particle surfaces can also be computed:

$$\mathbf{n} \simeq -\begin{pmatrix} 0 \\ 1 \end{pmatrix} + \sqrt{\epsilon}\begin{pmatrix} y \\ 0 \end{pmatrix} + \epsilon \begin{pmatrix} 0 \\ 1 \end{pmatrix} \frac{y^2}{2} + \cdots \tag{11}$$

Using the usual dimensionless formulation for the potential $\phi = ZF\phi'/R_gT$, the normal derivative of the dimensionless potential on the upper particle reads:

$$\partial_n \phi = \nabla \phi . \mathbf{n} \simeq -\partial_z \phi + \epsilon \left(\partial_y \phi y + \partial_z \phi \frac{y^2}{2} \right) \tag{12}$$

A similar result with opposite sign for the first term holds for the lower particle. Dimensionless PB problem (1) reads:

$$\left(\partial_z^2 + \epsilon \nabla_{//}^2\right) \phi = 2 \left(\frac{h_m}{\lambda}\right)^2 \sinh \phi , \tag{13}$$

where $\nabla_{//}^2$ is the Laplacian contribution orthogonal to the ($\mathbf{e_z}$, $\mathbf{e_r}$), section which is different for cylindrical or spherical particles. We will not need to specify it further, since we are just going to compute the leading order contribution to the following asymptotic sequence in the inner region suggested by (10):

$$\phi = \phi_0 + \epsilon \phi_1 . \tag{14}$$

Introducing this sequence in the governing equation (13) leads to the leading order:

$$\partial_z^2 \phi_0 = \beta_m \sinh \phi_0 , \tag{15}$$

where $\beta_m = 2(h_m/\lambda)^2$. From (12) the associated Boundary conditions, with prescribed electric fields (5), reads at the leading order:

$$\partial_z \phi_0(\pm h_0) = \pm E_{p\pm} , \tag{16}$$

where we have used dimensionless electric fields $E_{p\pm} = ZFE'_{p\pm}/R_gTh_m$. For prescribed potentials (6), the leading order boundary conditions reads:

$$\phi_0(\pm h_0) = \phi_{p\pm} \tag{17}$$

And finally the Stern layer boundary condition reads at leading order:

$$\partial_z \phi_0(\pm h_0) = \mp \mu \beta_m \phi_0(\pm h_0) , \tag{18}$$

where we have introduced a parameter μ that stands for dimensionless pre-factor between the potential and its gradient at the particle surface boundary condition.

Outer region

Using dimensionless formulation, (8) PB problems (1) reads:

$$\epsilon^2 \nabla^2 \Phi = \beta_m \sinh \Phi \,. \tag{19}$$

The inner problem suggests the following asymptotic sequence for the potential in the outer region:

$$\Phi = \Phi_0 + \epsilon \Phi_1 \tag{20}$$

Injecting this sequence in the outer governing equation (19) leads to the following leading order problem:

$$\sinh \Phi_0 = 0 \,, \tag{21}$$

whose solution is $\Phi_0 = 0$, so that the matching condition at leading order is just $\lim_{y\to\infty} \phi_0(0, y) = 0$.

RESULTS

Since the outer region solution is trivial, we now focus on the inner region solution that is going to provide the interesting potential variations for particle interactions.

DEBYE-HÜCKEL APPROXIMATION

We examine here the linearized limit of small dimensionless potential $\phi \ll 1$. Let us first consider prescribed electrical fields at the particles surfaces. In this case, the solution of the linearized limit of (15) with boundary conditions (16) reads:

$$\phi_0 = \frac{1}{2}\left(\frac{E_+ \cosh \sqrt{\beta_m} z}{\sinh \sqrt{\beta_m}\, h_0} + \frac{E_- \sinh \sqrt{\beta_m} z}{\cosh \sqrt{\beta_m} h_0}\right) \tag{22}$$

where we have introduced notation $E_+ = E_{p+} + E_{p-}$ and $E_- = E_{p+} - E_{p-}$. The case of symmetrical particles corresponds to $E_- = 0$, since the corresponding fields at each particle are identical and of opposite sign. We then recover in this case that $\partial_z \phi_0(r, z = 0) = 0$. Let us now write-down the solution associated with the boundary conditions (17):

$$\phi_0 = \frac{1}{2}\left(\frac{\phi_+ \cosh \sqrt{\beta_m}\, z}{\cosh \sqrt{\beta_m}\, h_0} + \frac{\phi_- \sinh \sqrt{\beta_m}\, z}{\sinh \sqrt{\beta_m}\, h_0}\right) , \tag{23}$$

where we have introduced notation $\phi_+ = \phi_{p+} + \phi_{p-}$, and $\phi_- = \phi_{p+} - \phi_{p-}$. One can also see that, in this case, symmetrical particles are associated with $\phi_- = 0$, so that the resulting field will also fulfills $\partial_z \phi_0(r, z = 0) = 0$. Finally, let us now discuss the D-H limit solution associated with boundary conditions (18). Since the boundary conditions specify two independant linear equations with an associated non-zero determinant, one coud think, in a first step, that the only possible solution is the trivial one $\phi_0 = 0$. Nevertheless, there is a special value of β_m for which the determinant of the linear system associated with boundary conditions becomes singular (Plouraboué and Chang 2009), i.e., $\beta_{mc} = 1/2 \ln(\mu + 1)/(\mu - 1)$. Up to this parameter, some non-trivial solution can emerge from the trivial one from a pitch-fork bifurcation through non-linear effects as shown in Figure 2.

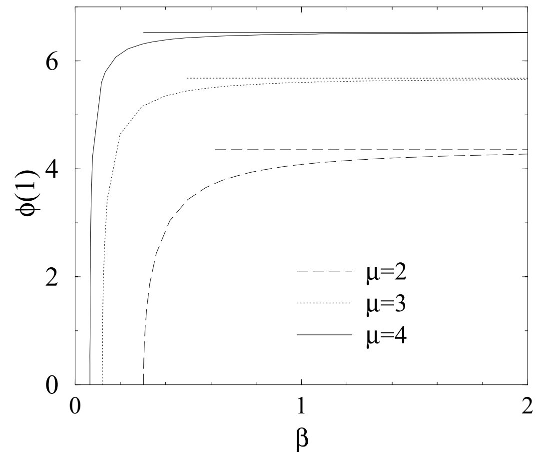

Fig. 2 – Surface potential of an anti-symmetric solution $\phi(1)$ at $\zeta = 1$ *versus* dimensionless parameter β. The dotted lines display an asymptotic value which can be computed (*Cf* see Plouraboué and Chang (2009) for more details on this point).

NON-LINEAR PB PROBLEM

It is now interesting to realize that the leading order problem (15) associated with boundary conditions (16), (17) or (18) can be expressed in a single variable $\zeta = z/h_0(r)$ independently of any other explicit dependance on the longitudinal variable r. Hence, one can, then, map the leading order PB problem between two identical particle onto the same problem between two parallel planes. Hence, we recover here the solution previously studied in (Plouraboué and Chang 2009) for Stern layer boundary conditions. Let us now recall here the main steps of the solution. A first integral of (15) using the variable change $\zeta = z/h_0(r)$ for $\phi_0(\zeta)$ is:

$$\frac{1}{2}(\partial_\zeta \phi_0)^2 = \beta(r)\,(\cosh \phi_0) + d \tag{24}$$

where d depends on the value prescribed at the particle, and $\beta(r) = 2(h_m h_0(r)/\lambda)^2$. Introducing notation $d' = d/\beta$, one finds that this constant depends upon the applied boundary condition. For prescribed electric field (16), one finds:

$$d'(r) = \frac{d}{\beta(r)} = \frac{1}{2}E_{p+}^2 - \cosh\phi_0(1) = \frac{1}{2}E_{p-}^2 - \cosh\phi_0(-1), \tag{25}$$

whilst, in the case of prescribed potentials (17):

$$d'(r) = \frac{d}{\beta(r)} = \frac{1}{2}[\partial_\zeta \phi_0(1)]^2 - \cosh \phi_{p+} = \frac{1}{2}[\partial_\zeta \phi_0(-1)]^2 - \cosh \phi_{p-}. \tag{26}$$

Finally, in the case of Stern layer boundary conditions (18), this constant is:

$$d'(r) = \frac{d}{\beta(r)} = \frac{1}{2}[\mu\phi_0(1)]^2 - \cosh \phi_0(1) = \frac{1}{2}[\mu\phi_0(-1)]^2 - \cosh \phi_0(-1) \tag{27}$$

Hence, in each case, the function $d'(r)$ either depends on the potential solution at the particle surface or on its gradient. In the case of Stern layer boundary condition (18), the anti-symmetrical solution associated with parameter $\mu > 1$ is always attractive (Plouraboué and Chang 2009). This is, thus, the solution onto which we will focus on. A symmetrical solution also exists for parameter $\mu < 1$, but this case is not considered in this study. Let us now briefly recall here the main steps for finding an implicit solution to the PB non-linear problem. We use Boltzmann transformation:

$$\psi_0 = e^{-\phi_0/2} \tag{28}$$

so that (24) reads:

$$\frac{1}{2}(\partial_\zeta \phi_0)^2 = 2e^{\phi_0}(\partial_\zeta \psi_0)^2 = \frac{1}{2}\left(\psi_0^2 + \frac{1}{\psi_0^2}\right) + d' \tag{29}$$

then, the problem on the new variable ψ_0 becomes:

$$\partial_\zeta \psi_0 = \pm\frac{1}{2}\sqrt{\psi_0^4 + 2d'\psi_0^2 + 1} = \pm\frac{1}{2}\sqrt{(\psi_0^2 - \alpha_-)(\psi_0^2 - \alpha_+)}\,, \tag{30}$$

with:

$$\alpha_\pm = -d' \pm \sqrt{d'^2 - 1}, \tag{31}$$

The first integral (30) can be solved formally by a supplementary integration from separating ζ and ψ_0 (dividing by the right hand side). The solution of this integral form is associated with an elliptic integral, so that,

$$\pm\frac{\sqrt{\beta(r)}}{2}\zeta + c = -\sqrt{\alpha_-}F\left(\psi_0\sqrt{\alpha_+}, \alpha_-\right), \tag{32}$$

up to a constant c to be specified. Evaluating (32) at the upper and lower particle boundary $\zeta = z/h_0 = \pm 1$ leads to the following implicit condition for the potential value $\psi_0(\pm 1)$:

$$\sqrt{\beta(r)} = -\sqrt{\alpha_-}\left[F\left(\psi_0(1)\sqrt{\alpha_+}, \alpha_-\right) - F\left(\psi_0(-1)\sqrt{\alpha_+}, \alpha_-\right)\right], \tag{33}$$

Now, collecting relation (28) and (33) with one of the boundary condition associated with the $d'(r)$ value (25), (27) gives a system of two transcendental equations for $\phi_0(\pm 1)$ that can be solved numerically (Plouraboué and Chang 2009) for each $\beta(r)$. Figure 2 shows the result of this numerical computation. It is interesting to note that, for value of β smaller than a critical value that depends on μ $\beta < \beta_c(\mu)$, the resulting surface potential is zero and, thus, the solution will be zero everywhere else in between the two particles (*Cf* Plouraboué and Chang (2009) for the expression of $\beta < \beta_c(\mu)$). In these regions, the local interaction will obviously be zero at leading order.

COMPUTATION OF THE FORCE

LOCAL PRESSURE CONTRIBUTION

We now compute the force between the particle. From using Green's theorem it is possible to show that the particle/particle interaction can be computed from evaluating the Maxwell stress tensor contraction with the normal surface of any closed surface around one particle (Neu 1999). Since, at infinity, the matching condition gives vanishing field perturbations, any closed far-field surface around one of the two particles, which intersects the mean-plane, has no contribution to the force. Hence, the only contribution on the force is the scalar product of the stress tensor on the normal to the $z = 0$ mean-plane.

Let us now compute the force from considering the asymptotic expansion of the Maxwell stress tensor. For dimensionless formulation $\sigma' = \sigma \epsilon_p (RT/ZF)^2/\lambda^2$, this tensor reads:

$$\sigma = \frac{1}{\beta(r)} \begin{pmatrix} -\frac{1}{2}(\partial_\zeta \phi)^2 + \frac{\epsilon}{2}(\partial_r \phi)^2 & \sqrt{\epsilon}\partial_r \phi \partial_\zeta \phi \\ \sqrt{\epsilon}\partial_r \phi \partial_\zeta \phi & -\frac{1}{2}(\partial_\zeta \phi)^2 - \frac{\epsilon}{2}(\partial_r \phi)^2 \end{pmatrix} \tag{34}$$

So that, one can write:

$$\sigma = \frac{1}{\beta(r)} \left(-\frac{1}{2}(\partial_\zeta \phi)^2 \mathbf{I} + \sqrt{\epsilon}\partial_r \phi \partial_\zeta \phi \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \epsilon (\partial_r \phi)^2 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + .. \right) \tag{35}$$

Using (11), one can have that the contribution of the stress tensor to the mean-plane being:

$$\mathbf{e}_z.\sigma.\mathbf{e}_z = \frac{1}{\beta(r)} \left(-\frac{1}{2}(\partial_z \phi)^2 - \frac{\epsilon}{2}(\partial_r \phi)^2 + .. \right) \tag{36}$$

Now using (14) one finds,

$$\mathbf{e}_z.\sigma.\mathbf{e}_z = \frac{1}{\beta(r)} \left(-\frac{1}{2}(\partial_z \phi_0)^2 - \epsilon \left(\frac{1}{2}(\partial_r \phi_0)^2 + \partial_z \phi_0 \partial_z \phi_1 \right) + .. \right) \tag{37}$$

which is the contribution of the Maxwell stress. The dimensionless osmotic contribution p_0 associated with a far-field zero reference potential is:

$$p_0 = \cosh \phi - 1 = \cosh \phi_0 - 1 + O(\epsilon) \tag{38}$$

Finally, to the leading order, one can find the total local pressure at $\zeta = 0$

$$p(r) = \left(-\frac{1}{2\beta(r)} [\partial_\zeta \phi_0(r, 0)]^2 + \cosh \phi_0(r, 0) - 1 \right) + O(\epsilon) \,. \tag{39}$$

As previously indicated, it is interesting to note that, in the case of an anti-symmetrical solution for which $\phi_0(r, 0) = 0$, this pressure is always negative and, thus, attractive. For any symmetrical solution for which, on the contrary, $\partial_z \phi_0(r, 0) = 0$ and $\phi_0(r, 0) \neq 0$, we observe that this pressure is positive, so that the interaction is repulsive, because the osmotic contribution is always positive. Finally, it is interesting to note from (24) that this force is simply related to the constant d':

$$p(r) = -d'(r) - 1 + O(\epsilon) \tag{40}$$

This shows that solving for the potential at the particle surface $\phi_0(r, \zeta = \pm 1)$ is enough to compute the total force from using (25) or (27) to deduce constant d' for a given value of $\beta(r)$, that is to say a given value of r. Let us now explicitly estimate this force for spherical or cylindrical particles.

TOTAL FORCE

The total force formulation is the integral of the local force over the horizontal plane $z = 0$. We define two distinct dimensionless forces in the case of spherical or cylindrical particles. For spherical particles, we scale the force to the square of the sphere radius $F_s = a\lambda\epsilon_p(RT/ZF)^2/\lambda^2 F'$. For cylindrical particles, we rather consider the product of radius a to the cylinder length L : $F_c = \sqrt{a\lambda}L\epsilon_p(RT/ZF)^2/\lambda^2 F'$. The integration, nevertheless, differs between spherical or cylindrical particles. In the case of two spheres, one finds:

$$F_s = 2\pi \int_0^{\infty} p(r) r dr. \tag{41}$$

In the following, we will also use an equivalent formulation, using parameter h rather than r. Both being dimensionless and related by (10), (41) can be rewritten:

$$F_s = 2\pi \int_{\frac{h_m}{\lambda}}^{\infty} p(h_0) dh_0. \tag{42}$$

In the case of two cylinders, the total force per unit length is:

$$\frac{F_c}{L} = 2\left(\frac{h_m}{\lambda}\right)^{1/2} \int_0^{\infty} p(r) dr \tag{43}$$

Relation (41) and (43) associated with expression (39) and (40) gives an one-dimensional integral formulation for the force given the local potential solution. At this stage, it is important to stress that it is a drastic simplification upon the initial three-dimensional non-linear problem (1). Furthermore, it is also interesting to mention here that such lubrication formulation provides very robust approximation for the force, even if the ϵ parameter is not small (even of order one).

The potential solution should be solved numerically for each gap distance r. This potential could be computed from solving numerically an one dimensional Poisson-Boltzmann problem, with, for exemple, a collocation method as in (Carnie et al. 1994, Stankovich and Carnie 1996). One could alternatively find the only necessary constant d' in (40) from using the potential value at one boundary in equation (27). The latter can be determined by solving the transcendental equation (33). In the subsequent analysis of the force, we did both: the former, with a moderate numerical cost, and the latter, without a negligeable time cost. We found no distinct differences in the results between the two methods.

Let us now first evaluate the forces in the D-H limit.

Force in the Debye-Hückel approximation

Even if it is known that the Debye-Hückel limit is a very rough approximation, it can be useful for code validation or comparison with experiments to get explicit analytical expression for the force.

• In the case of prescribed fields, the evaluation of (39) in the $\phi_0 \ll 1$ limit, using solution (22), leads to:

$$p(r) = \frac{1}{8}\left(\frac{\lambda}{h_m}\right)^2 \frac{E_+^2 \cosh^2 h_0 - E_-^2 \sinh^2(h_0)}{\cosh^2(h_0)\sinh^2(h_0)}, \tag{44}$$

One can see that, in the case of symmetrical boundary conditions $E_- = 0$, this pressure is positive leading to repulsion. In the fully non-symmetrical case, then, $E_+ = 0$, and this pressure is negative leading, as expected to an attraction among the particles. For sphere, one finds:

$$F_s = \left(\frac{\lambda}{h_m}\right)\frac{\pi}{4}(E_+^2 I_{s1} - E_-^2 I_{s2}) \tag{45}$$

where,

$$I_{s1} = \int_0^\infty \frac{r dr}{\sinh^2(1+r^2/2)} = \frac{2}{e^2+1} \simeq 0.23840$$
$$I_{s2} = \int_0^\infty \frac{r dr}{\cosh^2(1+r^2/2)} = \frac{2}{e^2-1} \simeq 0.31303 \tag{46}$$

For cylinders, one finds:

$$\frac{F_c}{L} = \left(\frac{\lambda}{h_m}\right)^{3/2} \frac{1}{4}(E_+^2 I_{c1} - E_-^2 I_{c2}) \tag{47}$$

where:

$$I_{c1} = \int_0^\infty \frac{dr}{\sinh^2(1+r^2/2)} \simeq 0.5895922$$
$$I_{c2} = \int_0^\infty \frac{dr}{\cosh^2(1+r^2/2)} \simeq 0.40108449 \tag{48}$$

• Let us now consider the case with prescribed potentials. From linearization of (39) in the $\phi_0 \ll 1$ limit, the solution (23) leads to the following local pressure

$$p = \left(\frac{\lambda}{h_m}\right)^2 \frac{1}{8} \frac{\phi_+^2 \sinh^2(h_0) - \phi_-^2 \cosh^2(h_0)}{\cosh^2(h_0)\sinh^2(h_0)}, \tag{49}$$

As expected, this pressure is again always repulsive for symmetrical boundary conditions $\phi_- = 0$, and might be attractive for fully anti-symmetric conditions $\phi_+ = 0$. For two spheres, one finds the total force:

$$F_s = \frac{\lambda}{h_m} \frac{\pi}{4} (\phi_+^2 I_{s2} - \phi_-^2 I_{s1}), \tag{50}$$

Whilst, for two cylinders:

$$\frac{F_c}{L} = \left(\frac{\lambda}{h_m}\right)^{3/2} \frac{1}{4}(\phi_+^2 I_{c2} - \phi_-^2 I_{c1}). \tag{51}$$

Hence, in the Debye-Hückel approximation, the force can only be attractive for prescribed non-symmetrical fields. We do not discuss here the D-H limit for the Stern layer boundary condition, since the solution is only specified up to a multiplicative constant in this regime. Therefore, the absolute value of the force is not define.

One needs to go to the non-linear PB problem to find a definite answer to this question.

FORCE FOR STERN-LAYER BOUNDARY CONDITION

In this case, a numerical computation has been carried out from the solution found for the potential field at the surface, which permits to deduce the $d'(r)$ from (27) and the local pressure from (40).

• The numerical integration is, then, performed in the spherical case from formulation (42) with a simple trapezoidal rule. The result obtained is plotted on Figure 3a where one can observe a saturation of the Force when the gap is smaller than the critical ratio β_c, for which the local pressure tends to zero.

• A different behavior for the total force is found in the case of two cylinders, for which the formulation (43), associated with an integration along variable r, is chosen to obtain again a simple direct integration. Depending on the value of parameter μ, the total force can either display a localized minimum close to $h_m/\lambda \simeq \sqrt{\beta_c/2}$, or can decay with the minimum gap as represented on Figure 3b.

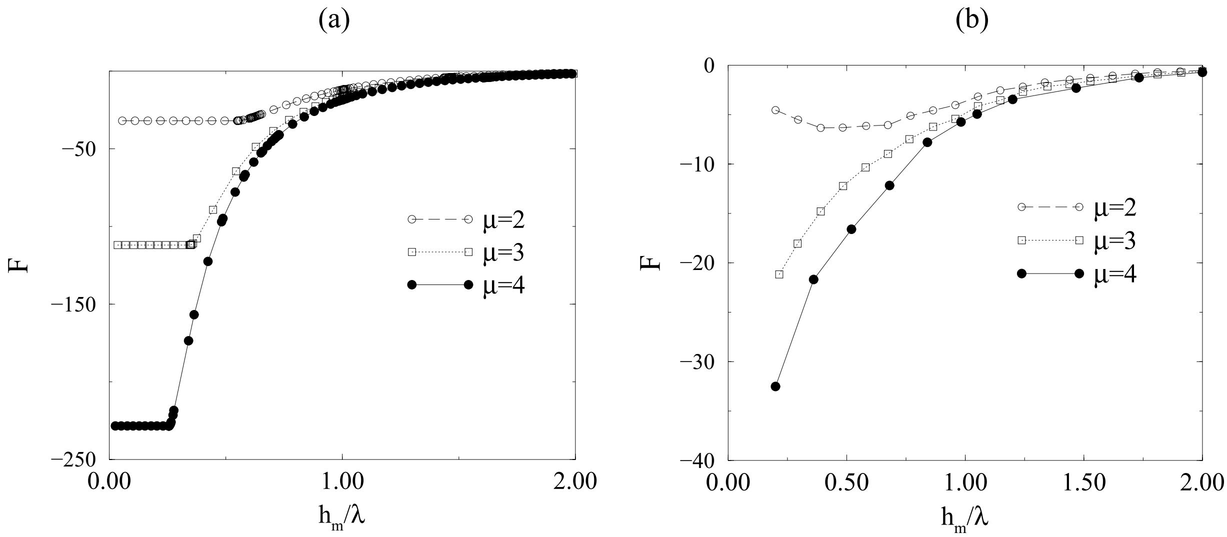

Fig. 3 – Dimensionless Force computed *versus* the minimum-gap to Debye layer ratio for a different value of the mixed boundary condition parameter μ. (a) Between two spheres, (b) between two cylinders.

DISCUSSION

Let us discuss here the main results that have been obtained. We found in the D-H limit that, for any imposed electric field or potential at the particle surface, the only possible attractive regime exists for non-symmetrical boundary conditions as expected from previous works (Neu 1999). On the quantitative point of view for any imposed electric field or potential, we found in the D-H limit that the (attractive or repulsive) force display a divergent behavior with the minimum distance h_m, which is $(\lambda/h_m)^2$ for a sphere or a $(\lambda/h_m)^{3/2}$ for a cylinder.

These results differ from the one obtained for Stern layer boundary conditions at the iso-electric point. For two spheres, the force decreases up to a critical ratio of h_m/λ, which is related to the parameter β_c below which the local pressure tends to zero. The total force, then, decays to zero for very small h_m/λ values due to the fact that, at small separation among the two spheres, the only admissible solution is a zero potential, which leads to zero interaction. This is obviously the leading-order behavior of the force, up to some $O(\epsilon)$ correction.

This behavior is similar for two cylinders for which a local minimum can be observed for a small value of the Stern layer parameter μ. Both behaviors are very different from those obtained for prescribed electric field and potential.

In any case, two important remarks have to be added to better grasp the validity range of the presented results in the Stern layer case.

First, it is interesting to note that our computation is not valid for very small value of $h_m/\lambda \ll 1$. It is important to realize that the most substantial part of potential variations is mostly concentrated in the thin region of width $\sqrt{ah_m}$, whereas it is very small outside this region. Since there is no interaction for distances smaller than β_c, for there is no local pressure, a critical in-plane distance r_c is associated with the critical parameter β_c, such that $\sqrt{\beta_c/2} = h_m/\lambda(1 + r_c^2/2)$ for any interaction to occur. If r_c exceeds $\sqrt{ah_m}$, our leading order estimate will not give an accurate answer to the resulting very small interaction that will be associated to the problem. This gives a lower bond for the ratio h_m/λ, which has to be larger than $h_m/\lambda > 2\beta_c\epsilon$ for our analysis to be valid.

For smaller value of the h_m/λ, one should, then, consider the influence of $O(\epsilon)$ corrections to the force, which might change the final picture.

CONCLUSION

We compute the electro-osmotic interaction among two particles when the gap h_m is smaller than the Debye length λ. We have shown that, in the confined regime for which $h_m \ll a$ and $h_m < \lambda$, the problem can be mapped onto an one dimensional planar formulation in a reduced parameter $z/h_0(r)$, which encapsulate any radial shape of the particles. We analyzed the influence of a Stern layer boundary condition at the iso-electric point on the interaction, and found distinct new and interesting behavior for the particle interaction. Further extension of this work to non iso-electric point situations could be considered in the future.

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RESUMO

Quando o comprimento de Debye é comparável ou maior do que as distâncias entre duas partículas idênticas, a interseção entre as duplas camadas pode desempenhar papel importante na interação entre elas. Este artigo apresenta uma análise teórica da interação entre duas partículas idênticas as quais apresentam interseção entre as camadas duplas. Nós particularmente focamos a análise sobre o efeito da condição eletrostática de Stern a partir da linearização da isoterma de adsorção perto do ponto isoelétrico para capturar como a condensação do íon polivalente afeta e reverte a densidade de carga superficial. O problema que governa o potencial estacionário é resolvido no contexto de uma teoria assintótica de lubrificação para o modelo de Poisson-Boltzmann. O modelo é analisado para partículas cilíndricas e esféricas. Os resultados são finalmente discutidos no contexto do limite de Debye-Hückel e além dele.

Palavras-chave: atração entre partículas, camadas de Stern, problema de Poisson-Boltzmann, interação entre duplas camadas.

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