

# Influence of Double-Layer Overlap on the Electrophoretic Mobility and DC Conductivity of a Concentrated Suspension of Spherical Particles

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In this paper, the specific effect of the overlapping of electrical double layers on the electrophoretic mobility and the electrical (DC) conductivity of concentrated suspensions of spherical colloidal particles is considered. Previous work has dealt with the study of such physical quantities for general conditions, including arbitrary zeta potentials, particle volume fractions, double-layer thicknesses (overlapping of double layers was allowed), and ionic properties of the solution. However, the large number of variables involved screened to some extent the specific role and, in many cases, the extraordinary magnitude of the overlapping contribution by itself. This is the reason that we are concerned here with the analysis of the latter effect in more detail. Thus, we present an extensive set of numerical data of both the electrophoretic mobility and the electrical conductivity versus the zeta potential and particle volume fraction for different electrolyte concentrations, specially in the region where overlapping effects are more relevant. Numerical results corresponding to the same theoretical conditions but where the overlapping correction is neglected are also shown for comparison. The treatment is based on the use of a cell model to account for hydrodynamic and electrical interactions between particles. The results show that neglecting double-layer overlapping corrections leads in most cases to an important underestimation of the true values of both the electrophoretic mobility and the electrical conductivity. The differences between both treatments are more pronounced the larger the double layer thickness and/or particle volume fraction are. Concerning DC conductivity, the overlap of double layers might help in interpreting discrepancies generally found between experimental data and standard theoretical values, even in suspensions with particle volume fractions that are typically considered to be dilute.

## 1. Introduction

Considerable effort is being devoted to the development and improvement of theoretical electrokinetic models for such phenomena as electrophoresis, sedimentation, electrical conductivity, electroacoustic phenomena, and so forth in concentrated colloidal suspensions.<sup>1–7</sup> The fundamental problem of accounting for hydrodynamic particle–particle interactions is usually faced by means of cell models.<sup>8,9</sup> When particles are charged, additional electrical boundary conditions have to be implemented to solve the problem completely. Concerning electrophoresis, Levine and Neale<sup>1</sup> developed a mobility expression for spherical particles with low zeta potentials and arbitrary double-layer thicknesses on the basis of the Kuwabara cell model,<sup>9</sup> including the possibility of the overlapping of adjacent double layers. Kozak and Davies<sup>10,11</sup> extended the model of Levine and Neale and derived a mobility expression that is valid for arbitrary zeta potentials with nonoverlapping double layers. More recently, Ohshima<sup>12</sup> presented a general mobility equation for a swarm of identical spherical particles in concentrated suspensions that fulfilled the limiting cases of Levine and Neale and Kozak and Davies. Ohshima also developed a general expression for the electrical conductivity of a concentrated suspension that is valid for low zeta potentials and nonoverlapping double layers.<sup>4</sup> Shortly after, Lee et al.<sup>13</sup> analyzed the electrophoresis of concentrated suspensions for arbitrary surface

potentials taking double-layer polarization and overlapping of adjacent cells into account and also using the Kuwabara cell model. Their study, although more general than the above-mentioned ones, is also based on the Levine–Neale electrical boundary conditions. Hsu et al.<sup>14</sup> have recently studied the electrophoresis of concentrated suspensions of spherical particles (Kuwabara's cell model and Levine–Neale's conditions), extending previous approaches with the inclusion of a general condition on the particle surface permitting the exchange of ions between the surface and the surrounding medium. The effects of overlapping of nearby double layers and appreciable double-layer polarization are included in their model. Lin et al.<sup>15</sup> extended the study of Lee et al.<sup>13</sup> to the case where the strength of the applied electric field is arbitrary.

Most of the relevant studies on electrokinetic phenomena in concentrated suspensions, electrophoresis and electrical conductivity in particular, are based on Levine–Neale's boundary conditions. In a recent series of papers,<sup>16–20</sup> a new set of boundary conditions have been checked according to the Shilov–Zharkikh cell model<sup>21</sup> following the suggestion of Dukhin et al.,<sup>22</sup> who described some inconsistencies in the Levine–Neale model. Following Levine and Neale's boundary conditions and another set of conditions somewhat similar to those of Shilov–Zharkikh's model, Ding and Keh<sup>23</sup> analyzed the electrophoresis and the electric conductivity of concentrated suspensions according to Happel and Kuwabara's cell models and derived analytical expressions for the electrophoretic mobility and conductivity, correct to  $O(\zeta)$  and  $O(\zeta^2)$  ( $\zeta$  is the

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zeta potential), respectively, assuming double-layer overlapping. A comparison with Ohshima's predictions<sup>4</sup> (Levine–Neale model and nonoverlapping double layers) was also shown. In a recent paper,<sup>17</sup> we presented an analytical expression for the electrophoretic mobility, which is valid for low zeta potentials and arbitrary double-layer thickness, according to Kuwabara's cell model and Shilov–Zharkikh's boundary conditions. Likewise, we also derived a general expression for the electrical conductivity of concentrated suspensions that is valid for arbitrary zeta potentials and nonoverlapping double layers and extended the latter theoretical approaches to include the effect of surface conductance in the inner region of the double layer via a dynamic Stern layer (DSL hereafter) on the electrophoretic mobility and electrical conductivity of concentrated suspensions.<sup>17</sup>

Very recently, a generalization of the theories of the electrophoretic mobility and electrical conductivity in concentrated suspensions, valid for arbitrary zeta potentials, particle volume fractions, surface conductance values (through a DSL model), and double layer thicknesses (double-layer overlapping is allowed), has been developed by us.<sup>18</sup> Because several contributions (surface charge, ionic strength, hydrodynamic and electrostatic interactions between particles) superimpose in a complex way to yield the overall response, quantitative knowledge of the importance of overlapping effects has probably been masked in previous works by those different factors. Thus, as will be shown in the present paper, sound reasons can be found to justify the present study concerning the specific issue of the overlap between double layers of nearby particles. For simplicity, a dynamic Stern layer will not be considered in this study.

The paper is set out as follows: In the next section, the governing equations and appropriate boundary conditions for a general theory of static electrophoresis and electrical conductivity will be shown. In section 3, electrophoretic mobility and electrical conductivity expressions, with and without correction for the overlapping of adjacent double layers, will be presented. Finally, in section 4, the role of double-layer overlap will be discussed.

## 2. Basic Equations and Boundary Conditions

Before analyzing the specific role of the overlap in the electrokinetic properties, it is useful to review briefly the basic electrokinetic equations and boundary conditions of the theories of electrophoresis and electrical conductivity in concentrated suspensions. A more extensive mathematical treatment can be found in refs 4, 12, 17, and 18. Only the Kuwabara cell model<sup>9</sup> has been used to take hydrodynamic particle–particle interactions into account. As previously mentioned, other possible cell models such as that proposed by Happel<sup>8</sup> can be used, as Ding and Keh pointed out,<sup>23</sup> but the basic characteristics of the results of both the electrophoretic mobility and the electrical conductivity are rather similar. (See a comparison between results from both cell models in ref 23.) According to Kuwabara's model, each spherical particle is enclosed by a concentric spherical shell of electrolyte solution of outer radius  $b$  such that the particle/cell volume ratio in the unit cell is equal to the particle volume fraction throughout the whole suspension:

$$\phi = \left(\frac{a}{b}\right)^3 \quad (1)$$

$a$  is the radius of the spherical particle. We will call the “slip plane” to the surface of the particle or, more properly, to that of the electrokinetic unit the particle plus a thin stagnant layer of liquid. This is the plane outside which the continuum

equations of hydrodynamics are assumed to be valid. Let us first consider a charged spherical particle of radius  $a$  immersed in an electrolyte solution of relative permittivity  $\epsilon_{rs}$  and viscosity  $\eta$  composed of  $N$  ionic species of valences  $z_i$ , bulk number concentrations  $n_i^\infty$ , and drag coefficients  $\lambda_i$  ( $i = 1, \dots, N$ ). In the presence of a static electric field  $E$  (it will be considered to be the modulus of the uniform macroscopically measured electric field  $\langle \mathbf{E} \rangle$ ), the particle moves with a uniform velocity  $\mathbf{v}_e$ , the electrophoretic velocity. The axes of a spherical coordinate system ( $r, \theta, \varphi$ ) are fixed at the center of the particle. The electrophoretic mobility  $u_e$  is defined by  $\mathbf{v}_e = u_e \langle \mathbf{E} \rangle$ . The polar axis ( $\theta = 0$ ) is chosen parallel to the electric field. The electric potential at  $r = a$  or equivalently at the slip plane when no electric field is applied to the system is the zeta potential  $\zeta$ . The solution of the problem requires us to know at every point  $\mathbf{r}$  of the system relevant quantities such as the electric potential  $\Psi(\mathbf{r})$ , the number density of each type of ion  $n_i(\mathbf{r})$ , the drift velocity  $\mathbf{v}_i(\mathbf{r})$  of each ionic species ( $i = 1, \dots, N$ ), the fluid velocity  $\mathbf{v}(\mathbf{r})$ , and the pressure  $p(\mathbf{r})$ . The fundamental equations connecting them are<sup>24–26</sup>

$$\nabla^2 \Psi(\mathbf{r}) = - \frac{\rho_{el}(\mathbf{r})}{\epsilon_{rs} \epsilon_0} \quad (2)$$

$$\rho_{el}(\mathbf{r}) = \sum_{i=1}^N z_i e n_i(\mathbf{r}) \quad (3)$$

$$\eta \nabla^2 \mathbf{v}(\mathbf{r}) - \nabla p(\mathbf{r}) - \rho_{el} \nabla \Psi(\mathbf{r}) = 0 \quad (4)$$

$$\nabla \cdot \mathbf{v}(\mathbf{r}) = 0 \quad (5)$$

$$\mathbf{v}_i = \mathbf{v} - \frac{1}{\lambda_i} \nabla \mu_i \quad (i = 1, \dots, N) \quad (6)$$

$$\mu_i(\mathbf{r}) = \mu_i^\infty + z_i e \Psi(\mathbf{r}) + k_B T \ln n_i(\mathbf{r}) \quad (i = 1, \dots, N) \quad (7)$$

$$\nabla \cdot [n_i(\mathbf{r}) \mathbf{v}_i(\mathbf{r})] = 0 \quad (i = 1, \dots, N) \quad (8)$$

where  $e$  is the elementary electric charge,  $k_B$  is Boltzmann's constant,  $T$  is the absolute temperature, and  $\mu_i^\infty$  is the standard chemical potential of the  $i$ th ionic species. Equation 2 is Poisson's equation, where  $\epsilon_0$  is the permittivity of a vacuum and  $\rho_{el}(\mathbf{r})$  is the electric charge density given by eq 3. Equations 4 and 5 are the Navier–Stokes equations that are appropriate for a steady incompressible fluid flow at low Reynolds number in the presence of an electrical body force. Equation 6 means that the ionic flow is provoked by the liquid flow and the gradient of the electrochemical potential defined in eq 7, and it can be related to the balance of the hydrodynamic drag and the electrostatic and thermodynamic forces acting on each ionic species. Equation 8 is the continuity equation expressing the conservation of the number of each ionic species in the system.

The drag coefficient  $\lambda_i$  is related to the limiting conductance  $\Lambda_i^0$  of the  $i$ th ionic species by<sup>24</sup>

$$\lambda_i = \frac{N_A e^2 |z_i|}{\Lambda_i^0} \quad (i = 1, \dots, N) \quad (9)$$

where  $N_A$  is Avogadro's number. At equilibrium, that is, when no electric field is applied, the distribution of electrolyte ions obeys the Boltzmann distribution, and the equilibrium electric potential  $\Psi^{(0)}$  satisfies the Poisson–Boltzmann equation.<sup>24</sup>

The boundary conditions at the slipping plane and at the outer surface of the cell for the equilibrium electrical potential are given by

$$\Psi^{(0)}(a) = \zeta \quad (10)$$

$$\left. \frac{d\Psi^{(0)}}{dr} \right|_{r=a} = -\frac{\sigma}{\epsilon_{rs}\epsilon_0} \quad (11)$$

$$\left. \frac{d\Psi^{(0)}}{dr} \right|_{r=b} = 0 \quad (12)$$

where  $\sigma$  is the surface-charge density of the particle.

The boundary conditions for the liquid velocity  $\mathbf{v}$  and the velocity of each ionic species at the particle surface are expressed as

$$\mathbf{v} = 0 \quad \text{at } r = a \quad (13)$$

$$\mathbf{v}_i \cdot \hat{\mathbf{r}} = 0 \quad \text{at } r = a \quad (i = 1, \dots, N) \quad (14)$$

Equation 13 expresses that, relative to the particle, the liquid is at rest at the slipping plane, and eq 14 implies that no ion fluxes are allowed to cross the slipping plane if a DSL is absent, as is the case in the present study ( $\hat{\mathbf{r}}$  is the unit normal directed outward from the particle surface). According to the Kuwabara cell model, the liquid velocity at the outer surface of the unit cell must satisfy<sup>4</sup>

$$v_r = -v_e \cos \theta = -u_e E \cos \theta \quad \text{at } r = b \quad (15)$$

$$\boldsymbol{\omega} = \nabla \times \mathbf{v} = \mathbf{0} \quad \text{at } r = b \quad (16)$$

which mean, respectively, that there is no normal perturbation velocity at the outer surface of the cell<sup>8,23</sup> that is different from that due to the particle electrophoretic velocity (recall that the coordinate system is taken to travel with the particle) and that the vorticity is equal to zero at the outer surface of the cell.

Now, we will assume that the electrical double layer around the particle is only slightly distorted by the electric field (the external field must be low enough for this condition to be valid; it is most often fulfilled in practical situations) so that a linear perturbation scheme for the above-mentioned quantities can be used. This means that each quantity  $X$  will be expressed as<sup>24–26</sup>

$$X(\mathbf{r}) = X^{(0)}(r) + \delta X(\mathbf{r}) \quad (17)$$

where  $X$  can be  $n_i$ ,  $\Psi$ , or  $\mu_i$  and the superscript  $(0)$  refers to equilibrium.

In terms of the perturbation quantities, the condition that the ionic species cannot penetrate the particle surface in eq 14 transforms into

$$\nabla \delta \mu_i \cdot \hat{\mathbf{r}} = 0 \quad \text{at } r = a \quad (i = 1, \dots, N) \quad (18)$$

According to the Shilov–Zharkikh cell model,<sup>21</sup> the boundary condition for the perturbed electric potential at the outer surface of the unit cell is expressed by

$$\delta \Psi|_{r=b} = -\langle \mathbf{E} \rangle \cdot \mathbf{r}|_{r=b} = -Eb \cos \theta \quad (19)$$

showing the connection between the macroscopic, experimentally measured electric field and local electrical properties, as stated by Dukhin et al.<sup>22</sup> Following Lee et al.,<sup>13,27</sup> the number density of each ionic species at  $r = b$  must be equal to the corresponding equilibrium ionic density. Therefore

$$\delta \mu_i|_{r=b} = -z_i e \langle \mathbf{E} \rangle \cdot \mathbf{r}|_{r=b} = -z_i e E b \cos \theta \quad (i=1, \dots, N) \quad (20)$$

where eq 19 has been used.

Following Ohshima's formalism,<sup>12</sup> spherical symmetry considerations permit us to introduce the radial functions  $h(r)$ ,  $\phi_i(r)$ , and  $Y(r)$  and write

$$\mathbf{v}(\mathbf{r}) = (v_r, v_\theta, v_\varphi) = \left( -\frac{2}{r} h E \cos \theta, \frac{1}{r} \frac{d}{dr} (r h) E \sin \theta, 0 \right) \quad (21)$$

$$\delta \mu_i(\mathbf{r}) = -z_i e \phi_i(r) E \cos \theta \quad (i = 1, \dots, N) \quad (22)$$

$$\delta \Psi = -Y(r) E \cos \theta \quad (23)$$

This leads to the following set of ordinary differential equations:<sup>12</sup>

$$L(Lh) = -\frac{e}{\eta r} \frac{dy}{dr} \sum_{i=1}^N n_i^\infty z_i^2 \exp(-z_i y) \phi_i(r) \quad \text{with } y = \frac{e\Psi^{(0)}}{k_B T} \quad (24)$$

$$L\phi_i(r) = \frac{dy}{dr} \left( z_i \frac{d\phi_i}{dr} - \frac{2\lambda_i}{e} \frac{h(r)}{r} \right) \quad (i = 1, \dots, N) \quad (25)$$

$$LY(r) = \frac{1}{\epsilon_{rs} \epsilon_0 k_B T} \sum_{i=1}^N z_i^2 e^2 n_i^{(0)}(r) [Y(r) - \phi_i(r)] \quad (26)$$

$L$  is a differential operator defined by

$$L \equiv \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{2}{r^2} \quad (27)$$

and the boundary conditions for the quantities  $h(r)$ ,  $\phi_i(r)$ , and  $Y(r)$ <sup>12,17</sup> are

$$h(a) = \frac{dh}{dr}(a) = 0 \quad (28)$$

$$Lh(b) = 0 \quad (29)$$

$$h(b) = \frac{u_e b}{2} \quad (30)$$

$$\left. \frac{d\phi_i}{dr} \right|_{r=a} = 0 \quad (i = 1, \dots, N) \quad (31)$$

$$\phi_i(b) = b \quad (i = 1, \dots, N) \quad (32)$$

$$Y(b) = b \quad (33)$$

In addition to the latter boundary conditions, we must impose the constraint that in the stationary state the net force acting on the particle or the unit cell must be zero. This condition can be expressed as<sup>12</sup>

$$\eta \left. \frac{d}{dr} [rL h(r)] \right|_{r=b} - \rho_{el}^{(0)}(b) Y(b) = 0 \quad (34)$$

where  $\rho_{el}^{(0)}(b)$  is the equilibrium electric charge density at  $r = b$ . Note that neglecting double-layer overlapping is equivalent to setting  $\rho_{el}^{(0)}(b) = 0$  in eq 34:

$$\left. \frac{d}{dr} [rL h(r)] \right|_{r=b} = 0 \quad (35)$$

At this point, it is necessary to remark that in true overlapping conditions  $\rho_{\text{el}}^{(0)}(b)$  cannot be dismissed without introducing serious errors into the numerical procedure. We will confront this important fact in the next section.

A numerical method similar to that proposed by DeLacey and White in their theory of the dielectric response and conductivity of a dilute colloidal suspension in time-dependent fields<sup>26</sup> has been applied to solve the above-mentioned set of ordinary differential equations. The numerical results will be shown and discussed in section 4.

### 3. Electrophoretic Mobility and Electrical Conductivity of the Suspension

**3.1. Electrophoretic Mobility.** The electrophoretic mobility and the electrical conductivity of a concentrated suspension can be expressed in terms of the far-field behavior of functions  $h(r)$  and  $\phi_i(r)$  ( $i = 1, \dots, N$ ) in the vicinity of the outer surface of a representative cell. Because the unperturbed electrical potential has zero slope at the outer surface of the cell (see eq 12), the right-hand sides of eqs 23 and 24 can be set equal to zero when  $r$  approaches  $b$ :

$$L\phi_i(r)|_{r \rightarrow b} = 0 \quad (i = 1, \dots, N) \quad (36)$$

$$L[Lh(r)]|_{r \rightarrow b} = 0 \quad (37)$$

By solving these equations, the asymptotic forms of the functions  $h(r)$  and  $\phi_i(r)$  in the immediacy of the outer surface of the cell take the form

$$\phi_i(r) \approx \frac{C_i}{r^2} + C_{N+i}r \quad (i = 1, \dots, N) \quad (38)$$

$$h(r) \approx C_{2N+1}r + \frac{C_{2N+2}}{r^2} + C_{2N+3} + C_{2N+4}r^3 \quad (39)$$

The latter solutions must verify the boundary conditions expressed by eqs 29, 30, and 32–35. This permits the number of independent constants  $C_j$  ( $j = 1, \dots, 2N + 4$ ) to be reduced. The exact value of each of the remaining constants will be obtained once the full system of differential equations is numerically solved, and the general solutions satisfy the boundary conditions at the slipping plane. (See eqs 28 and 31.) Let us see now how the quantities of interest for our study are uniquely expressed in terms of these constants.

With the help of eqs 1 and 30, a general expression for the electrophoretic mobility  $u_e$ , after the numerical procedure, can be obtained. This turns out to be

$$u_e = 2 \left[ C_{2N+1} + \frac{\phi}{a^3} C_{2N+2} + \frac{a^2 \phi^{-2/3}}{5\eta} \sum_{i=1}^N z_i e n_i^\infty \exp \left( - \frac{z_i e \Psi^{(0)}(b)}{k_B T} \right) \right] \quad (40)$$

where the last term between the square brackets is related to the overlap between double layers. In conditions of negligible overlapping, we have

$$\exp \left( - \frac{z_i e \Psi^{(0)}(b)}{k_B T} \right) \approx 1 \quad (i = 1, \dots, N) \quad (41)$$

and then eq 40 transforms into

$$u_e = 2 \left[ C_{2N+1} + \frac{\phi}{a^3} C_{2N+2} \right] \quad (42)$$

It is worth pointing out that if eq 42 is used in conditions of true overlapping (i.e., out of its range of validity) then the final values of its coefficients once the numerical procedure has been concluded would not coincide with their analogues in eq 40. Recall that eq 42 is used in connection with the simplified boundary condition of zero net force acting on the cell in the absence of overlapping, as shown in eq 35. Obviously, the modification of boundary conditions at the outer surface of the cell (eq 35 instead of eq 34) implies a different quantitative behavior for the far-field asymptotic solution of function  $h(r)$ . As a consequence, different values for the coefficients are found.

Our aim is to study the differences between the full treatment and the simpler one developed for nonoverlapping conditions, when the latter is used beyond its natural region of validity. (Words such as “full” and “simple” treatments will refer to our models with and without overlapping hereafter.) The results will show that tremendous errors can be involved in many ordinary cases if overlapping is not correctly dealt with. Unfortunately, there is no way of exactly separating the overlapping contribution from the overall response in situations where remarkable double-layer polarization and hydrodynamic interference are also present. The first step is simply to calculate the corresponding properties for every condition using both the full and the simple theories. The differences that are eventually found could be ascribed to the additional overlapping correction in the general treatment (last term in eq 40), which is absent in the simple treatment. But doing so would drive us to misleading conclusions. The latter argument would be meaningful if the final values of the coefficients  $C_{2N+1}$  and  $C_{2N+2}$  in eq 41 obtained by numerically solving the simple theory were equal to those in eq 40 calculated with the full treatment. In this situation, the differences between both mobility formulas might be fully assigned to the extra-overlapping correction term in eq 40. But this is not the case; in fact, the values of the same coefficients obtained with the two approaches turn out to be quite different, as was previously mentioned.

What we can always do is to carry out a formal comparison between the results of the two theories, trying to find qualitative physical reasons explaining their differences. Furthermore, the discrepancies or coincidences that arise from this comparison will tell us whether the simpler, easily convergent, and less computer-time-consuming theory can be used.

**3.2. DC Conductivity.** Regarding the electrical conductivity,  $K^*$ , of the suspension, recall that is usually defined in terms of the volume averages of the local electric current density and electric field in the suspension

$$\langle \mathbf{i} \rangle = \frac{1}{V} \int_V \mathbf{i}(\mathbf{r}) \, dV = K^* \langle \mathbf{E} \rangle \quad (43)$$

The macroscopic electric field  $\langle \mathbf{E} \rangle$  (i.e., minus the average of the gradient of the electrical potential  $\Psi(\mathbf{r})$  at each position of the system with total volume  $V$ ) is given by

$$\langle \mathbf{E} \rangle = - \frac{1}{V} \int_V \nabla \Psi(\mathbf{r}) \, dV = - \frac{1}{V} \int_V \nabla \delta \Psi(\mathbf{r}) \, dV \quad (44)$$

where the fact that a value of zero for the volume average of the gradient of the equilibrium electric potential has been used.



In a previous paper,<sup>18</sup> we derived a general expression for the conductivity of a concentrated suspension that is valid for arbitrary conditions of zeta potential, surface conductance, double-layer thickness  $\kappa^{-1}$ , and so forth. Here, the parameter  $\kappa$ , also known as the reciprocal Debye length, is defined by<sup>28</sup>

$$\kappa = \left[ \sum_{i=1}^N \frac{n_i^{\infty} z_i^2 e^2}{\epsilon_{rs} \epsilon_0 k_B T} \right]^{1/2} \quad (45)$$

See ref 18 for a fuller treatment. The following general conductivity expression was obtained:

$$\frac{K^*}{K^{\infty}} = \frac{\sum_{i=1}^N \left[ \frac{z_i^2 e^2 n_i^{\infty}}{\lambda_i} \left( 1 - \frac{3\phi}{a^3} C_i \right) - u_e(z_i e n_i^{\infty}) \right] \exp \left( - \frac{z_i e \Psi^{(0)}(b)}{k_B T} \right)}{\sum_{i=1}^N \frac{z_i^2 e^2 n_i^{\infty}}{\lambda_i}} \quad (46)$$

$K^{\infty}$  is the conductivity of the supporting electrolyte solution. The coefficients  $C_i$  ( $i = 1, \dots, N$ ) in eq 46, originally defined by Ohshima<sup>4</sup> as

$$C_i = - \frac{b^2}{3} \left( r \frac{d\phi_i}{dr} - \phi_i \right)_{r=b} \quad (i = 1, \dots, N) \quad (47)$$

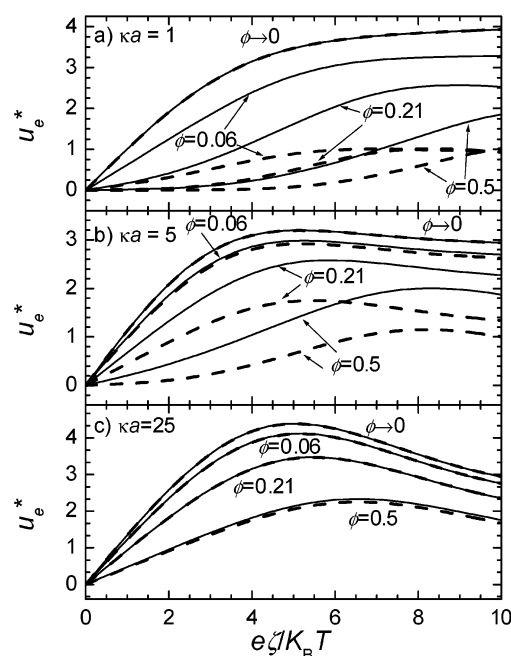
coincide with those in our eq 38 for the far-field asymptotic behavior of functions  $\phi_i$  ( $i = 1, \dots, N$ ). Recall that the electrophoretic mobility  $u_e$  in eq 46 has been calculated in eq 40 in terms of the coefficients of the asymptotic form of function  $h(r)$ . In conditions where double layers of neighboring particles do not overlap (see eq 41), eq 46 transforms into

$$\frac{K^*}{K^{\infty}} = \left\{ 1 - \frac{3\phi \sum_{i=1}^N \frac{z_i^2 n_i^{\infty} C_i}{\lambda_i}}{a^3 \sum_{i=1}^N \frac{z_i^2 n_i^{\infty}}{\lambda_i}} \right\} \quad (48)$$

Because of electroneutrality, the summation term multiplying the electrophoretic mobility in eq 46 vanishes.

As previously mentioned, we recently derived<sup>18</sup> the general conductivity expression in eq 46, which is valid for arbitrary  $\zeta$  values. Only Shilov–Zharkikh's conditions were used, the most promising ones if attention is paid to the comparison between theoretical and experimental results.<sup>23</sup> In the following section, we will investigate the consequences of overlapping on the electrophoretic mobility and the electrical conductivity for the conditions established before and compare with the case where the overlapping correction is neglected.

Let us finally mention that, similarly to the case of electrophoresis, the values of the asymptotic coefficients  $C_i$  of functions  $\phi_i$  ( $i = 1, \dots, N$ ) in eq 48—the simpler theory—do not coincide with those to be used in the full expression (eq 46). However, the fact that  $\Psi^{(0)}(b)$  is not zero in overlapping conditions yields a large, and in some cases, very significant positive contribution to the conductivity, which is basically linked to the electrophoretic mobility term in eq 46. This is the term responsible for the majority of discrepancies found between the conductivity



**Figure 1.** Scaled electrophoretic mobility of a spherical colloidal particle ( $a = 100$  nm) in a KCl solution at 25 °C as a function of the scaled zeta potential for different particle-volume fractions at fixed  $\kappa a$ . (—) General theory (overlapping-corrected data); (---) simple theory (overlapping not taken into account).

predictions of the full and simple theories under conditions of remarkable overlapping.

## 4. Results and Discussion

**4.1. Electrophoretic Mobility.** Let us now specially analyze the predictions of the two mobility equations (see eqs 40 and 42) for conditions such as thick double layers (low  $\kappa a$  values) or high volume fraction, both leading to maximum deviations from values where the overlapping correction is neglected. Figure 1 shows some numerical data on the scaled electrophoretic mobility as a function of the dimensionless zeta potential for different particle volume fractions at different fixed  $\kappa a$  values. The scaled electrophoretic mobility  $u_e^*$  is commonly defined as

$$u_e^* = \frac{3\eta e}{2\epsilon_{rs} \epsilon_0 k_B T} u_e \quad (49)$$

Figure 1 displays three cases corresponding to a low  $\kappa a$  value where maximum deviations can be observed, an intermediate value, and a high-enough value where the overlapping correction is clearly not significant.

First, under practically all of the conditions considered, the maxima in the mobility–zeta potential relationships predicted by classical theories of electrophoresis can be observed.<sup>18,24,29</sup> Recall the physical origin of these maxima: the application of an electric field (from left to right, say) to a dispersed colloid particle alters the ionic distribution around the particle. At low zeta potential (i.e., when the surface conductivity  $\kappa^s$  (conductivity due to ions in the electric double layer) of the particle is low), the accumulation of cations (anions) on the left (right) side of the particle gives rise to the formation of a dipole that favors the particle's motion. When the zeta potential increases, ions find a tangential path along the surface, and the dipole strength decreases and even changes direction. In the latter case, it will reduce the particle velocity. Thus, whereas the increase

in surface charge should raise the velocity, the dipole will tend to decrease it. Eventually, the latter effect will dominate the former, and the mobility will decrease when  $\zeta$  is increased. Hence, the presence of the maximum.

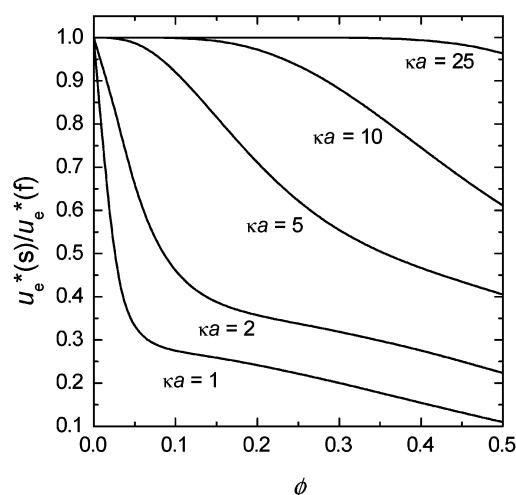
Let us now discuss the discrepancies between the two approaches considered in this paper for the calculation of the electrophoretic mobility. These are most important when  $\kappa a = 1$  for every volume fraction. First, remarkable differences can be observed even at volume fractions that are not too far from those being considered as typically dilute. At fixed  $\kappa a$ , increasing volume fraction leads to higher hydrodynamic interactions between particles and, if  $\kappa a$  is low, inevitably to overlapping. Because of the existing coupling between hydrodynamic and electrochemical functions, as expressed in the fundamental equation set (see eqs 2–8), there is not a simple explanation for the effects that arise from that coupling when  $\kappa a$  is low or, in other words, when significant overlapping exists.

As observed, the full electrophoretic mobility (solid lines) monotonically decreases as volume fraction increases at fixed  $\zeta$  and  $\kappa a$ . For low  $\zeta$  and arbitrary  $\kappa a$  values, this behavior has also been found elsewhere.<sup>23</sup> It has also been found for arbitrary  $\zeta$  and high  $\kappa a$  (insignificant overlapping).<sup>17</sup> Note that in the  $\kappa a = 25$  case of Figure 1 the overlapping is practically negligible. In this situation, the main reduction of the electrophoretic mobility as volume fraction rises can be ascribed to the increase of pure hydrodynamic interactions between particles.

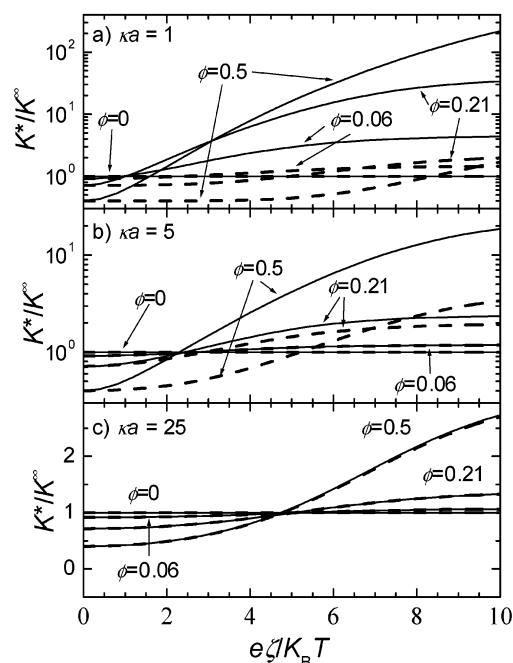
When present, overlapping can play a fundamental role in explaining the electrophoretic mobility of particles in concentrated suspensions. The calculation based upon the simple model ignoring overlapping may be seriously in error, as Figure 1 shows. The main point in connection with this Figure is that the simple theory underestimates the true mobility if overlapping is likely to occur. Recall that in that theory it was assumed that  $\rho_{\text{el}}^{(0)}(b) = 0$ ; however, in both the simple and the full treatments, the boundary conditions for the potential (eqs 10–12) are identical, and the equilibrium potential distribution should obey the Poisson–Boltzmann equation. This means that in the presence of overlapping the condition  $\rho_{\text{el}}^{(0)}(b) = 0$  that is used in the simple model could be more likely fulfilled if  $\zeta$  is low. Hence, we can say that setting  $\rho_{\text{el}}^{(0)}(b) = 0$  as one does in the simple treatment is roughly equivalent to using the full theory with a lower zeta potential. Note that at low  $\zeta$  the mobility increases with zeta potential in all cases shown in Figure 1; as a consequence, under such conditions, lowering  $\zeta$  must lead to decreasing mobilities. This explains why the simple theory underestimates the mobility. Clearly, the simple treatment is less in error the lower the volume fraction and the higher  $\kappa a$ , a fact that is easily explained by simple geometrical considerations.

For obvious practical reasons, it may be useful to find the approximate  $\phi$  and  $\kappa a$  ranges in which overlapping is important and should not be neglected. Figure 2 can help us in this: we have plotted the ratio between reduced mobilities calculated with and without overlapping for several  $\kappa a$  values as a function of volume fraction. Note how for  $\kappa a = 1$  and even  $\kappa a = 5$  the simple theory cannot be safely applied to any volume fraction, no matter how small. Furthermore, as they should be, the differences are more significant for larger volume fractions and thicker double layers.

**4.2. Electrical Conductivity.** The electrical conductivity of the suspension, normalized by that of the solution, is represented in Figure 3 as a function of the scaled zeta potential for different particle volume fractions at three fixed  $\kappa a$  values.



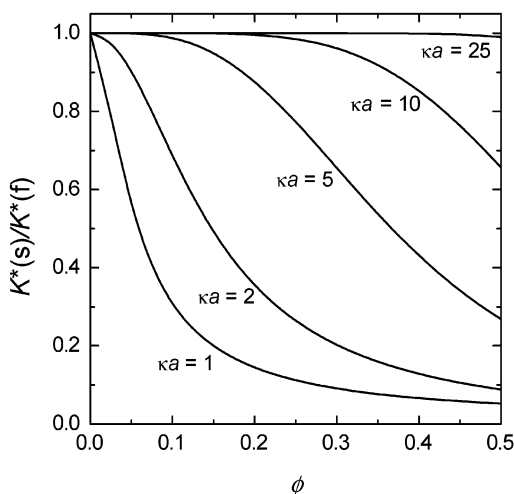
**Figure 2.** Ratio of the simple and full calculations of the electrophoretic mobility of spherical particles as a function of the volume fraction of solids, for several  $\kappa a$  values. Particle radius: 100 nm; zeta potential: 100 mV; electrolyte: KCl.



**Figure 3.** Ratio of the electrical conductivity of a colloidal suspension of spherical particles ( $a = 100$  nm) in a KCl solution at 25 °C to that of the solution as a function of the scaled zeta potential for different particle-volume fractions at fixed  $\kappa a$ . (—) General theory (overlapping-corrected data); (---) simple theory (overlapping not taken into account).

The first conclusion that we can extract from the comparison between approximate and full overlapping-corrected data is the remarkable underestimation of true conductivity values in a broad region of  $\zeta$  potentials when the simple theoretical approach is used, especially for low  $\kappa a$  and high particle volume fraction. Even at moderately low volume fractions the reduction can be quite important, mainly if  $\zeta$  is high. The agreement between both calculations in the  $\kappa a = 25$  case, for which overlapping conditions are not likely, is also worth mentioning.

Let us consider how our explanation for the differences between simple and full calculations of the electrophoretic mobility applies to the case of conductivity. Clearly, for all conditions, increasing  $\zeta$  yields larger conductivity ratios: the contribution of surface conductivity to the overall value of  $K^*$



**Figure 4.** Ratio of the simple and full calculations of the electrical conductivity of a colloidal suspension of spherical particles as a function of the volume fraction of solids for several  $\kappa a$  values. Particle radius, 100 nm; zeta potential, 100 mV; electrolyte, KCl.

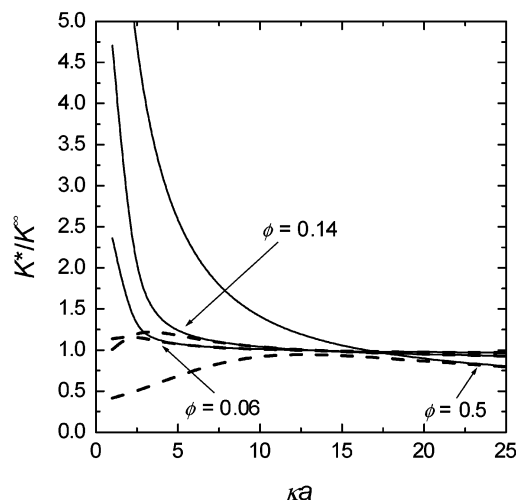
is more significant for a more highly charged interface. Note further that the overlapping correction is quantitatively more important for higher  $\zeta$  values. This fact is primarily related to the last term in the numerator of eq 46, which we reproduce here for convenience:

$$-u_e \sum_{i=1}^N z_i e n_i^\infty \exp\left(-\frac{z_i e \Psi^{(0)}(b)}{k_B T}\right) \quad (50)$$

It always represents a positive contribution to the conductivity. As an example, if we consider positively charged particles, then their mobility  $u_e$  will be positive, and the summation will be negative because of the large contribution of negative counterions at the cell surface, where the equilibrium potential  $\Psi^{(0)}(b)$  will be nonzero if overlapping occurs.

Recall that, as mentioned before, treating the situation of overlapping double layers with the simple theory is roughly equivalent to lowering the zeta potential. We can thus explain that the simpler theory yields lower suspension conductivity. This explains that the isoconductivity (i.e.,  $K^* = K^\infty$ ) is reached for higher  $\zeta$  the higher the volume fraction if overlapping is neglected (dashed lines in Figure 3). This is a consequence of the fact that the simple treatment in some way assigns a lower “effective”  $\zeta$  to particles in more concentrated suspensions, where overlapping will be more important. Ding and Keh<sup>23</sup> have recently analyzed the conductivity of concentrated suspensions. They derived a closed-form conductivity equation correct to  $O(\zeta^2)$  and compared experimental conductivity data with their theoretical predictions (the overlapping was allowed). They also compared their data with other theoretical results from existing theories neglecting overlapping. It is well known that theoretical conductivity predictions underestimate experimental conductivity results. They concluded that when conductivity is corrected for overlapping a better agreement between theory and experiment is found<sup>23</sup> because larger conductivity values can now be predicted for the same experimental conditions. This behavior is confirmed by our theory, which is valid for arbitrary  $\zeta$  values.

As with the case of electrophoretic mobility, a plot of the ratio between data obtained with both theories is useful in illustrating the role of  $\kappa a$  in their predictions for the conductivity. Figure 4 shows that for very low  $\kappa a$ , even for very dilute suspensions, the simplified theory underestimates  $K^*$ , although



**Figure 5.** Ratio between suspension ( $K^*$ ) and dispersion medium ( $K^\infty$ ) conductivities as a function of  $\kappa a$  with (—) and without (---) accounting for double-layer overlapping. Calculations are performed for  $\phi = 0.06$ , 0.14, and 0.5; the reduced zeta potential equals 4; and  $\kappa a$  is changed by varying the KCl concentration in the medium.

its separation with respect to the full treatment increases of course with volume fraction, that is, with overlapping. The range of  $\phi$  values for which the simple theory is applicable increases as  $\kappa a$  is raised, and the differences between the two methods of calculation are essentially inappreciable when  $\kappa a > \sim 25$ .

Figure 5 can help in explaining the trends observed in Figure 4 by plotting separately the values of  $K^*/K^\infty$  versus  $\kappa a$  for several volume fractions and constant  $\zeta$  ( $\zeta = 4$ ).

Note how if overlapping is included in the calculations the conductivity ratio  $K^*/K^\infty$  monotonically decreases with  $\kappa a$ , mostly because of the fact that the role of surface conductivity as compared to that of bulk conductivity (i.e., the value of the Dukhin number,  $Du = \kappa^\sigma/aK^\infty$ , where  $\kappa^\sigma$  is the surface conductivity) is less significant upon increasing the ionic strength. This correct prediction is not, however, found if the simple theory is used (except of course for moderate-to-high  $\kappa a$  values,  $\kappa a \geq 20$ , say). For the latter model,  $K^*/K^\infty$  increases with  $\kappa a$ : as the latter quantity grows, the extent of overlapping must be lower, and the “effective” zeta potential implicitly used in the simple theory will not be so much reduced with respect to the true one. In some way, using the simplified model with increasing  $\kappa a$  is equivalent to calculating with higher  $\zeta$  potentials, hence the rise in  $K^*/K^\infty$  when  $\kappa a$  is increased up to  $\kappa a > 20$ , when the simple theory roughly begins to be correct and the expected trend is recovered.

## 5. Conclusions

In this paper, electrophoresis and DC conductivity in concentrated suspensions have been dealt with for arbitrary conditions of zeta potential, particle volume fraction, double-layer thickness (overlapping of double layers is allowed), and ionic properties of the supporting electrolyte solution. Special interest has been paid to the study of the role that overlapping between double layers of neighboring particles plays in the latter electrokinetic properties. A comparative study has been systematically presented showing numerical data stemming from a theory that neglects overlapping and full overlapping-corrected data according to a more general treatment. The significant underestimation of the values of the different electrokinetic properties under conditions of relevant overlapping, when the simple theory is used, is pointed out in this paper. The effects are more pronounced the larger the double-layer thickness and

particle volume fraction are, but because of the complex and coupled nature of the processes involved, especially under conditions of considerable double-layer overlapping and hydrodynamic interference between particles, a full understanding of the exact role of each of them is a difficult task. The overall conclusion is that the overlapping correction cannot be neglected in a great number of typical situations, from nearly dilute suspensions (if  $\kappa a$  is low) to highly concentrated ones (at moderately high  $\kappa a$ ). It has also been found that using the simple theory under conditions of overlapping is somewhat equivalent to working with the full model but using a volume-fraction-dependent  $\zeta$  potential that is effectively lower the larger the degree of overlap.

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