Influence of cell-model boundary conditions on the conductivity and electrophoretic mobility of concentrated suspensions

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Abstract

In the last few years, different theoretical models and analytical approximations have been developed addressing the problem of the electrical conductivity of a concentrated colloidal suspension. Most of them are based on the cell model concept, and coincide in using Kuwabara's hydrodynamic boundary conditions, but there are different possible approaches to the electrostatic boundary conditions. We will call them Levine–Neale's (LN, they are Neumann type, that is they specify the gradient of the electrical potential at the boundary), and Shilov–Zharkikh's (SZ, Dirichlet type). The important point in our paper is that we show by direct numerical calculation that both approaches lead to identical evaluations of the conductivity of the suspensions if each of them is associated to its corresponding evaluation of the macroscopic electric field. The same agreement between the two calculations is reached for the case of electrophoretic mobility. Interestingly, there is no way to reach such identity if two possible choices are considered for the boundary conditions imposed to the field-induced perturbations in ionic concentrations on the cell boundary \( r=b \), \( \delta n_i(r=b) \). It is demonstrated that the conditions \( \delta n_i(b)=0 \) lead to consistently larger conductivities and mobilities. A qualitative explanation is offered to this fact, based on the plausibility of counter-ion diffusion fluxes favoring both the electrical conduction and the motion of the particles.

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1. Introduction

It is a well known fact that the different electrokinetic phenomena, including static and dynamic electrophoresis, dielectric spectroscopy of suspensions, dc and ac conductivity, etc., are extremely sensitive to the properties of the particle/liquid interface [1]. In the case of dilute suspensions, the effects of the concentration of solids are negligible or can be accounted for by means of terms linearly dependent on the volume fraction (concentration expressed in volume of solids by volume of suspension) \( \phi \) of dispersed material, and the problem can be solved based on the case of a single particle in an unbounded electrolyte [2–4].

In this paper, we will focus on the evaluation of the static (dc) conductivity of a suspension. If this is dilute, Dukhin and Derjaguin [5] first derived a simple conductivity formula in the case of the so-called “thin double layer” or, more properly, “large \( \kappa a \)” limit, that is, when the particle radius \( a \) is much larger than the electrical double layer thickness \( \kappa^{-1} (\kappa a > 1) \). Dukhin and Derjaguin’s analysis was subsequently extended to include arbitrary values of \( \kappa a \) or of the zeta potential, \( \zeta \) [6–8] or complex systems such as suspensions of porous or composite particles [9,10].

While the problem can be considered as rigorously solved for dilute suspensions, there is an increasing interest in studying concentrated systems, not only because they are potentially more useful from the technological point of view, but also because this opens the field to new theoretical elaborations.

The fundamental problem of accounting for hydrodynamic particle–particle interactions in concentrated suspensions is usually faced by means of cell models [11,12], which have been applied to a large variety of electrokinetic phenomena, including electrophoresis, sedimentation, electroacoustic and others [13–20].

Note that, since the particle/liquid interface is usually charged, electrostatic interactions between particles must be considered in addition to hydrodynamic ones. Again, different approaches have been proposed, and several authors have developed formulas for the dc conductivity of concentrated suspensions [16,21,22]. All these contributions were based on the so-called Levine–Neale (LN) boundary conditions [13], that will be described below. After Dukhin et al. [23] pointed out some inconsistencies in LN conditions, a series of papers [24–29] have used boundary conditions according to the now called Shilov–Zharkikh cell model [30].

In this paper we intend to describe both types of boundary conditions, and to discuss the existence of differences between the two corresponding ways of calculating the dc conductivity and the electroosmotic mobility of concentrated suspensions of spheres. The paper is organized as follows: in the Next section, a brief summary will be given of the basic equations governing the problem of calculating the conductivity \( K \) of a suspension of spheres. Then we will discuss the boundary conditions (both hydrodynamic and electrostatic) allowing to obtain the expression of \( K \) and of the electroosmotic mobility, \( \mu_e \), of the particles. Finally, in the Results and discussion paragraphs we will analyze the implications of the choice of boundary conditions on the numerically evaluated conductivity and mobility data.

2. Basic equations

Before proceeding with the calculation of the conductivity of a concentrated suspension, it may be useful to briefly review the basic equations of the full theory. A more extensive mathematical treatment can be found in previous papers [16,25,26].

In the following, use will be made of a reference frame fixed to the particle, with origin at its centre, \( r \) denoting the position of any point with respect to that frame. The velocity \( \mathbf{v}(r) \) of the liquid will be governed by Navier–Stokes equations for an incompressible, viscous fluid with viscosity \( \eta \), subjected to an electrical body force because of the double layer charge:

\[
\eta \nabla^2 \mathbf{v}(r) - \nabla p(r) - \rho_{el}(r) \nabla \Psi(r) = 0, \tag{1}
\]

\[
\nabla \cdot \mathbf{v}(r) = 0, \tag{2}
\]

where \( \Psi(r) \) is the electric potential at position \( r \), the pressure \( p(r) \), and \( \rho_{el}(r) \) is the volume charge density,

\[
\rho_{el}(r) = \sum_{i=1}^{N} z_i e n_i(r). \tag{3}
\]

In Eq. (3), we have assumed that the dispersion medium contains \( N \) ionic species with charges \( e z_i \) and number concentrations \( n_i(r) \) \( (i=1,2,\ldots,N) \).

The relationship between charge density and potential is given by Poisson’s equation,

\[
\nabla^2 \Psi(r) = -\frac{\rho_{el}(r)}{\epsilon_m}, \tag{4}
\]

where \( \epsilon_m \) is the permittivity of the liquid medium, which we assume constant.

The velocity of ions includes convective, electrical, and diffusive contributions:

\[
\mathbf{v}_i(r) = \mathbf{v}(r) - \frac{1}{k_i} \nabla \mu_i(r) \quad (i = 1, \ldots, N), \tag{5}
\]

where \( k_i \) is the drag coefficient of type \( i \) ions, related to their diffusion coefficient, \( D_i \), as follows

\[
k_i = \frac{k_B T}{D_i} \quad (i = 1, \ldots, N), \tag{6}
\]

where \( k_B \) is the Boltzmann constant, and \( T \) the absolute temperature.
In Eq. (5), \( \mu_i(r) \) is the electrochemical potential of the \( i \)th ion:
\[
\mu_i(r) = \mu_i^0 + z_i e \Phi(r) + k_B T \ln n_i(r) \quad (i = 1, \ldots, N),
\]
where \( \mu_i^0 \) is its standard chemical potential. The conservation of the number of each ionic species leads to:
\[
\nabla \cdot [n_i(r) v_i(r)] = 0 \quad (i = 1, \ldots, N).
\]

3. Boundary conditions

According to Kuwabara’s cell model \[12\], hydrodynamic interactions between particles can be accounted for by solving the problem of a single spherical particle (radius \( a \)) surrounded by a spherical liquid shell, concentric with it and with radius \( b \), such that the particle/cell volume ratio \( a^3/b^3 \) is equal to the volume fraction of solids in the whole suspension, \( \phi \):

\[
\phi = \left( \frac{a}{b} \right)^3.
\]

A crucial aspect of the problem is the proper choice of boundary conditions, both in the inner (\( r = |r| = a \)) and outer (\( r = b \)) cell surfaces. The former is effectively the solid/liquid separation, so-called slip plane: both the ions and the liquid located beneath that surface are considered immobile, strongly attached to the particle. The fact that the liquid cannot slip on the particle will be expressed as:

\[
v(r = a) = 0.
\]

Additionally, since the particle is non-conducting, the velocity of ions in the normal direction to the surface is zero:

\[
v_i \hat{r} \big|_{r=a} = 0 \quad (i = 1, \ldots, N),
\]

where \( \hat{r} \) is the outward normal to the surface.

In the outer surface of the cell (\( r = b \)), we will follow Kuwabara’s boundary conditions. In the radial direction, the velocity of the liquid will be the radial component of its value far from the particle:

\[
v_i \big|_{r=b} = -v_c \cos \theta = -u_c E^* \cos \theta,
\]

where \( v_c \) is the electrophoretic velocity, and \( E^* \) is the electric field responsible for the particle motion, that will be evaluated later. \( \theta \) is the angle between the direction of the field and that of the position vector, \( r \). In addition, the flow is free of vorticity on that surface:

\[
\nabla \times v_i \big|_{r=b} = 0.
\]

If \( \Psi^0(r) \) is the equilibrium (i.e., in the absence of any applied field) potential distribution, its value on \( r = a \) is the zeta potential, \( \zeta \):

\[
\Psi^0(r = a) = \zeta,
\]

and the discontinuity of the normal electric displacement yields:

\[
\epsilon_m \frac{d\Psi^0}{dr} \bigg|_{r=a} = -\sigma
\]

where \( \sigma \) is the surface charge density of the particles. The condition that the cell is electroneutral leads finally to:

\[
\frac{d\Psi^0}{dr} \bigg|_{r=b} = 0.
\]

The key problem now is the specification of the electrostatic boundary conditions in the presence of the field. First, it is convenient to write the non-equilibrium quantities in terms of their equilibrium values plus a field-dependent perturbation:

\[
n_i(r) = n_i^0(r) + \delta n_i(r), \quad (i = 1, \ldots, N)
\]

\[
\mu_i(r) = \mu_i^0(r) + \delta \mu_i(r), \quad (i = 1, \ldots, N)
\]

\[
\Psi^0(r) = \Psi^0(r) + \delta \Psi(r).
\]

In the linear theory of electrokinetic phenomena it is admitted that the applied field strength is low enough for the perturbations to be linear in the field, and, furthermore, quadratic and higher terms will be dropped.

Following Ohshima \[16,31\], spherical symmetry considerations permit us to introduce the radial functions \( h(r) \), \( \phi_i(r) \), and \( \Xi(r) \) as follows:

\[
v(r) = \left\{ \begin{array}{c} -\frac{2}{r} h(r) E^* \cos \theta, \\ \frac{1}{r} \frac{d}{dr} [r h(r)] E^* \sin \theta, \\ 0 \end{array} \right\},
\]

\[
\delta \mu_i(r) = -z_i e \phi_i(r) E^* \cos \theta, \quad (i = 1, \ldots, N),
\]

\[
\delta \Psi(r) = -\Xi(r) E^* \cos \theta,
\]

where \( E^* \) is a field yet to be defined in terms of the macroscopic electric field.

The boundary conditions described so far yield:

\[
h(a) = \left. \frac{dh}{dr} \right|_{r=a} = 0,
\]

\[
L[h(r)] \big|_{r=b} = 0,
\]

\[
h(b) = \frac{u_c b}{2},
\]

\[
\left. \frac{d\phi_i}{dr} \right|_{r=a} = 0 \quad (i = 1, \ldots, N),
\]

where \( L \) is a differential operator:

\[
L = \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{2}{r^2}.
\]
and the ordinary differential equations verified by \( h, \phi_i \), and \( \Xi \) are detailed in refs. [16,31].

Let us now consider the boundary conditions associated to \( \delta \Psi \) and \( \Xi \), that will also give us clues on how to define the field \( E^* \) in Eqs. (20)–(22). Specifying the values of \( \delta \Psi \) on the cell boundary \( r=b \) is essential and, as Dukhin et al. [23] pointed out, it displays the connection between the macroscopic, or experimentally measured field, and the local electrical properties.

One possible choice of boundary condition is that of Levine–Neale (LN), (a Neumann type condition):

\[
\text{LN} : (\nabla \delta \Psi) \frac{d \hat{r}}{dr} |_{r=b} = -E^*\hat{r} = -E^*\cos\theta, \tag{28}
\]
or

\[
\text{LN} : \frac{d \Xi(r)}{dr} |_{r=b} = 1. \tag{29}
\]

Shilov et al. [30] propose a Dirichlet-type condition (SZ hereafter):

\[
\text{SZ} : \frac{\delta \Psi(r)}{r=b} = -E^*r |_{r=b} = -E^*b \cos\theta, \tag{30}
\]
and in terms of \( \Xi \):

\[
\text{SZ} : \Xi(b) = b. \tag{31}
\]

Some condition must be imposed on the ionic perturbations \( \delta n_i(r) \) at \( r=b \). Following Lee et al. [32,33], the number density of each ionic species must be equal to the corresponding equilibrium ionic density. Therefore:

\[
\begin{align*}
\delta n_i(r) |_{r=b} &= 0, \\
\delta \mu_i(r) |_{r=b} &= z_i e \delta \Psi(r) |_{r=b}, \\
\phi_i(b) &= \Xi(b), \quad (i = 1, \ldots, N).
\end{align*} \tag{32}
\]

Ding and Keh [29] suggest that an alternative condition on ionic perturbations can be

\[
\begin{align*}
\frac{\partial \delta n_i(r)}{\partial r} |_{r=b} &= 0, \\
\frac{d \phi_i}{dr} |_{r=b} &= \frac{d \Xi}{dr} |_{r=b}, \quad (i = 1, \ldots, N).
\end{align*} \tag{33}
\]

In addition, we must impose the constraint that in the steady state the net force acting on the cell must vanish. This condition can be expressed as [31]:

\[
\eta \frac{d}{dr} [rLh(r)] |_{r=b} = \rho^0_i(b) \Xi(b), \tag{34}
\]

where \( \rho^0_i(b) \) is the equilibrium charge density at \( r=b \). Note that neglecting double layer overlap is equivalent to set \( \rho^0_i(b)=0 \) in Eq. (34). Our target now is to find an expression for the conductivity \( K \) of the suspension, considering the different choices for boundary conditions. This will be done in the next section.

4. DC conductivity of the suspension

The electrical conductivity, \( K \), of the suspension is defined in terms of the volume averages of the current density \( \langle j \rangle \) and the electric field, \( \langle E \rangle \):

\[
\langle j \rangle = K \langle E \rangle, \tag{35}
\]

where the integration is extended to the total volume of the cell. The average field, \( \langle E \rangle \), will be:

\[
\langle E \rangle = -\frac{1}{V} \int V^* \nabla \Psi(r) dV = -\frac{1}{V} \int V^* \nabla \delta \Psi(r) dV, \tag{36}
\]

where use has been made of the fact that the volume average of the gradient of the equilibrium electric potential is zero [7].

Using Eqs. (5) and (18):

\[
j(r) = \rho^0_i(r)v(r) - \sum_{i=1}^{N} z_i e \eta^0_i(r) r \nabla \delta \mu_i(r), \tag{37}
\]

Noting that \( \nabla \cdot (r j) = 0, \) and using the divergence theorem,

\[
\langle j \rangle = -\frac{1}{V} \int \sum_{i=1}^{N} z_i e \int \left( r \left( -n^0_i v + n^0_i \nabla \delta \mu_i \right) \right) dS, \tag{38}
\]

where \( S \) is the outer spherical surface of the cell.

Using Eq. (21), and calling

\[
C_i = -\frac{b^2}{3} r \partial^2 \phi_i |_{r=b}, \tag{39}
\]

one obtains

\[
\langle j \rangle = -\frac{1}{V} \sum_{i=1}^{N} \frac{z_i e \eta^0_i(r)}{\lambda_i} \left( \frac{3 C_i}{b^2} - \phi_i(b) \right) \frac{4}{3} \pi b^3 E^* \]

\[ + \frac{1}{V} \sum_{i=1}^{N} \int_S (rv) \hat{r} dS. \tag{40}
\]

Now, taking into account Eqs. (20) and (25):

\[
\int_S (rv) \hat{r} dS = -\frac{4}{3} \pi b^3 u_e E^*, \tag{41}
\]

Also, Eq. (22) leads to [34]:

\[
\langle E \rangle = \frac{\Xi(b)}{b} E^*, \tag{42}
\]

and, finally, substituting (Eqs. (9), (41), (42)) in (40) and using (35):

\[
K = \frac{\sum \frac{z_i^2 e^2 e^2 \delta^2}{C_i}}{\sum \frac{z_i^2 e^2 e^2 \delta^2}{C_i}} - \frac{\eta^0_i(n^0_i)}{h(n^0_i)} \exp \left( -\frac{z_i e \Psi^0_i(b)}{h(n^0_i)} \right) \tag{43}
\]

where we have expressed \( n_i^0(b) \) in terms of the potential at \( b \) using the Boltzmann factor:

\[
n_i^0(b) = n_i^0 \exp \left( -\frac{z_i e \Psi(b)}{k_B T} \right),
\]

(44)

\( n_i^0 \) being the bulk concentration of the \( i \)-th ionic species, and the following expression has been used to evaluate the conductivity of the medium, \( K_m \):

\[
K_m = \sum_{i=1}^{\mathcal{N}} \frac{z_i^2 e^2 n_i^0}{\lambda_i}.
\]

(45)

If, in addition, we use the conditions (Eq. (32)) for the ionic perturbations,

\[
\frac{K}{K_m} = \frac{\sum_{i=1}^{\mathcal{N}} \frac{z_i^2 e^2 n_i^0}{\lambda_i} \left[ 1 - \frac{3 \phi}{2} \left( \frac{1}{\Xi(b)} \right) - 2 \left( \frac{1}{\Xi(b)} \right) (z_i e \Psi) \right] \exp \left( -\frac{z_i e \Psi(b)}{k_B T} \right)}{\sum_{i=1}^{\mathcal{N}} \frac{z_i^2 e^2 n_i^0}{\lambda_i}},
\]

(46)

whereas if the conditions chosen for \( \delta n_i (r=b) \) are those given by Eq. (33), the suitable equation for conductivity is (Eq. (43)) with the additional constraints that \( d\phi_i/dr|_{r=b}, (i=1, \ldots, \mathcal{N}) \).

Note that if the perturbations in Eqs. (20)–(22) were expressed in terms of \( \langle E \rangle \) (that is, if \( E^* = \langle E \rangle \)), then Eq. (42) would yield \( \Xi(b)=b \), which is precisely Eq. (31), corresponding to SZ boundary condition.

Thus we reach the important conclusion that if Shilov–Zharkikh boundary condition (Eq. (31)) is used, then the field \( E^* \) is necessarily equal to the macroscopic (average) one \( \langle E \rangle \), and \( \Xi(b)=b \). If, on the other hand the Levine–Neale boundary condition (Eq. (28)) is chosen, the field \( E^* \) (that Ohshima calls applied external field, see Ref. [34]) is related to the average one as \( E^* = \langle E \rangle b / \Xi(b) \), and, in addition, \( d\Xi/dr|_{r=b} = 1 \). Mixing these conditions leads to unphysical results, whereas, properly used, Levine–Neale and Shilov–Zharkikh conditions should lead to identical evaluations of \( K \).

5. Results and discussion

5.1. Choice of electrostatic boundary conditions

A numerical technique based on the method used by DeLacey and White [4] for solving the problem of ac conductivity was used to numerically evaluate the conductivity of the suspensions. This method has turned out to be very efficient in the integration of the electrokinetic equations in the static case [26,27]. We will first consider how the choice of the cell boundary condition for \( \delta \Psi(r) \) influences the calculation of \( K \).

Fig. 1 shows that LN and SZ boundary conditions (with \( \delta n_i (b)=0 \)) lead to identical results whatever the value of zeta potential (Fig. 1a), \( \kappa a \) (Fig. 1b) and volume fraction (Fig. 1c). Note that for the volume fraction involved, increasing \( \zeta \) (Fig. 1a) can provoke a very important raise in \( K \), a clear consequence of the large surface conductivity contribution of such highly charged double layers.

As to the effect of \( \kappa a \), the results in Fig. 1b indicate that increasing this quantity provokes a fall in \( (K-K_m)/K_m \) because the influence of the medium conductivity progressively hides that of the surface conductivity. In fact, it must be recalled here that the net effect of the double layer conductivity is controlled by the Dukhin number \( Du \) [1],
relating the surface conductivity $K^a$ to that of the medium, and to the particle radius:

$$Du = \frac{K^a}{K_m a}.$$  \hfill (47)

Note that $Du$ (and, as a consequence, the contribution of the particles to the conductivity $K$) is more important the larger the $\zeta$, the lower the $K_m$ and the smaller the size.

Finally, Fig. 1c is also self-explaning: increasing the volume fraction of particles with low zeta potential leads to a reduction of the conductivity of the suspension as compared to that of the solution, whereas performing the same operation if $\zeta$ is high yields a higher conductivity the larger the volume fraction.

5.2. Boundary condition for ionic concentrations

As mentioned, we have in principle two options in establishing a boundary condition for the ionic perturbation, as specified by Eqs. (32) ($\partial n_i(b) = 0$) and (33) ($\partial n_i / \partial r|_{r=b} = 0$). Both are compatible with (and independent of) the previously discussed conditions for $\delta \Psi$.

Fig. 2 shows our estimations of $(K - K_m)/K_m$ as a function of the dimensionless zeta potential for different $\kappa a$ values and a fixed volume fraction, $\phi = 0.5$. Three features are immediately clear: i) using $\partial n_i / \partial r|_{r=b} = 0$ leads to lower conductivity increments; ii) the differences between the results obtained with this condition and with $\partial n_i(b) = 0$ increase with zeta potential; iii) the relative differences between the two approaches change with $\kappa a$. In order to stress the latter point, in Fig. 3 we have plotted $K/K_m$ as a function of $\kappa a$ at constant zeta and volume fraction.

Items i) and ii) above can be explained by considering that forcing $\partial n_i = 0$ at $r = b$, instead of $\partial n_i / \partial r|_{r=b} = 0$, opens the possibility of the existence of diffusion fluxes of ions (mainly counter-ions, much more abundant at high $|\zeta|$) at the cell boundary. The increased flow of counter-ions will yield a higher surface conductivity and hence a larger $K$ of the suspension, as compared to the case of no concentration gradients. Clearly, as the zeta potential increases, the effects associated to double layer polarization will be more intense [35,36], and the differences between the cases $\partial n_i(b) = 0$ and $\partial n_i / \partial r|_{r=b} = 0$ are consistently more significant. At low $|\zeta|$, the counter-ion excess concentration is equally low and so will be the eventual diffusion fluxes.

The effect of $\kappa a$ (Figs. 2a–c and 3) appears to confirm our arguments: the two ways of calculation of $K$ differ mainly in the medium $\kappa a$ regime, where double-layer polarization effects are known to be more significant for electrokinetics [5]. At low $\kappa a$ the double layer is so extended that the effect of the external field on it is very small (the volume charge density is very low throughout the ionic atmosphere). On the contrary, at high $\kappa a$, the Dukhin number is so small that again double layer polarization effects are unimportant. In the region in between these two extremes, the effects of changes in the fluxes of counter-ions in the double layer will be significant, and the arguments above explained, concerning the differences between $\partial n_i = 0$ and $\partial n_i / \partial r = 0$, effectively apply. Note (Fig. 3) that at very high $\kappa a$ the conductivity ratio tends to its Maxwell value, as it is only controlled by volume fraction and not by particle charge.

5.3. Addendum. Electrophoretic mobility

According to Eq. (25), the electrophoretic mobility, $u_e$, is equal to $2h(b)/b$, so that having solved the velocity function $h(r)$ at $r = b$, $u_e$ is immediately obtained. Fig. 4 shows some
representative results calculated with LN and SZ boundary conditions for $dW$, and with $dn_i=0$ and $dn_i/dr|_{r=b}=0$ for the ionic concentration perturbations. It is important to point out that, in this case, not only different choices for $dn_i$ but also different electrostatic boundary conditions for $dW$ largely affect the estimation of $ue$. While the effect of $dn_i$ boundary conditions might be expected, the fact that $dW(b)$ choice influences the mobility and not the conductivity is, at first glance, striking.

In previous papers from different authors [19,26], calculations based on LN and SZ boundary conditions can be brought to coincidence at low $|f|$ values, if the former are multiplied by the Maxwell factor $(1/C_0)/(1+\phi/2)$. This is done in Fig. 5 for the same set of data as in Fig. 4: note that, indeed, both types of calculation tend to coincide in that region of zeta potentials. When $\zeta$ is above $\sim 50$ mV at room temperature the divergence between them is noticeable, and the Maxwell factor is clearly insufficient.

Our previous analysis of the conductivity can help us in elucidating the source of such differences: in the case of $K$, both approaches use the same field, $\langle E \rangle$, to define the conductivity in terms of $j$. But when it is the electrophoretic mobility that is calculated, the SZ model would write, for the velocity of electrophoresis:

$$v_e^{SZ} = u_e^{SZ} E^b, \quad (48)$$

whereas, according to Levine–Neale approach,

$$v_e = u_e^{LN} E^*, \quad (49)$$

and both fields are related (Eq. (42)):

$$E^* = b / \Xi(b), \quad (50)$$

so that $u_e^{SZ}$ should be compared with $(u_e^{LN} b / \Xi(b))$. However, it is advisable to define any kinetic coefficients in terms of model-independent fields; in the case of electrophoresis, this can be done by referring to the macroscopic, average electric field, $<E>$, so that Eq. (48) would be the
requested model-independent relationship. A detailed discussion on this subject is given by Dukhin et al. [23]. Fig. 6 demonstrates that in this case, a perfect agreement between SZ and LN evaluations of the mobility can again be found: one can use either of them to calculate \( u_e \), but, since they have different definitions of the field, a connection factor is needed to bring them to coincidence.

The difference between the choices \( \delta n_i(b) = 0 \) and \( \frac{\partial \delta n_i}{\partial r} |_{r=b} = 0 \), that was evident in conductivity calculations, still persists: the electrophoretic mobility is consistently larger in the former case, the more so the larger \( |\zeta| \). Looking at the problem for the reference frame fixed in the particle, this means that the liquid moves faster past the steady particle. Again, a qualitative explanation can be given to this fact, based on the plausible existence of non-zero diffusion fluxes of counter-ions if the condition \( \delta n_i(b) = 0 \) is chosen. These fluxes will drag liquid with them, increasing its velocity with respect to the particle. Turning to the laboratory frame, the electrophoretic velocity will be larger, as observed.

6. Conclusions

It is of utmost importance in modern colloid science to improve on our knowledge of the electrokinetics of concentrated suspensions, a challenging fundamental problem, and a field of many technological applications. We have discussed in this contribution the usefulness of cell models, considering the essential point of choosing boundary conditions for both the electrostatic potential and the ionic concentrations. In the case of the potential, Dirichlet and Neumann conditions lead to identical results for the conductivity and the electrophoretic mobility of concentrated suspensions of spheres if the field responsible for the perturbations is suitably chosen in each case. Concerning the perturbations in ionic concentrations, the differences are apparent in both conductivity and mobility. Experimental data will perhaps be the definitive check for the validity of Dirichlet or Neumann’s conditions.

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