The dielectric response of a colloidal spheroid

C. Chassagne a,*, D. Bedeaux b

a Department of Environmental Fluid Mechanics, TU Delft, Stevinweg 1, 2628 CN Delft, The Netherlands
b Department of Physical Chemistry, NTNU, 7491 Trondheim, Norway

ARTICLE INFO

Article history:
Received 25 January 2008
Accepted 28 June 2008

Keywords:
Colloidal spheroids
Dielectric spectroscopy
Complex conductivity
Electrokinetics
Dipolar coefficient
Double layer polarization
Zeta potential

1. Introduction and main result

The equations governing the behavior of a dielectric sphere in an oscillating electric field have been solved numerically. The most widely used numerical code is due to DeLacey and White [1], whose code was later extended by Mangelsdorf and White [2]. In certain cases (for thick double layers or/and for high frequencies), the numerical analysis can be time consuming or sometimes impossible, but some recent studies are making progress on this topic [3].

The analytical formula we propose for the dipolar coefficient arising from a dielectric sphere in an electrolyte solution gives fast solutions for the whole range of conditions investigated. We found that this analytical formula agrees with the numerical simulations for all frequencies, zeta potentials and \( \kappa a \gg 1 \) where \( \kappa \) is the inverse of the Debye length and \( a \) is the radius of the sphere. The form of the analytical formula makes it possible to compare the weight of the different contributions and therefore easily predict the particle’s response upon a change in parameters. Since electrokinetic measurements are often used as a quality-control tool [4–6], ready-to-use formulae are useful and we will give simple expressions that correctly approximate the numerical simulations in the cases generally found in experiments.

More importantly, we will show that the form of the analytical formula gives the possibility to extend our results to spheroidal particles. We define \( 2a_p \) as the length along the axis of revolution of the spheroid and \( 2a_n \), the maximum cross-sectional diameter normal to the axis of symmetry. We also define \( a = \min(a_p, a_n) \). For a sphere we get \( a = a_p = a_n \). The analytical formula we propose for the frequency-dependent dipolar coefficient for a dielectric spheroid in an electrolyte solution in an oscillating (AC) electric field is valid for all frequencies, zeta potentials and \( \kappa a \gg 1 \). So far, the only analytical or numerical expressions available for the dipolar coefficients of spheroids are for zero frequency (DC electric fields) and \( \kappa a \gg 1 \) [4–7]. We found the dipolar coefficient to be in the general case:

\[
\rho_i = \left( \tilde{K}_2 - \tilde{K}_1 + 3(1 - L_i) \left[ \tilde{K}_i + \tilde{K}_U + \tilde{K}_\text{extra} \right] + 3L_i \left[ \tilde{K}_\perp + \tilde{K}_\text{extra} \right] \right) \\
\left/ \left( 3\tilde{K}_1 + 3L_i (\tilde{K}_2 - \tilde{K}_1) + 9L_i (1 - L_i) \left[ \tilde{K}_i (a/r_0)^3 + \tilde{K}_U (a/r_1)^3 \right] + \tilde{K}_\text{extra} - \tilde{K}_\perp - \tilde{K}_\text{extra} \right) \right.,
\]

where \( i = n \text{ and } p \) indicate the direction normal and along the axis of symmetry of the spheroid, respectively. \( \tilde{K}_i, \tilde{K}_2, \tilde{K}_1, \tilde{K}_\perp, \tilde{K}_U \) are given by Eqs. (42), (48), (65), \( r_0 \) and \( r_1 \) are given by Eqs. (57), (68), \( L_i \) are the depolarization factors given by Eqs. (A.6)–(A.8) using \( m = a_p/a_n \) in the case of spheroids. The formulae for \( L_i \) can also be written for a more general type of ellipsoid, using \( i = p, n_1 \text{ and } n_2 \) as the principal axes of this ellipsoid. The appropriate formulae for \( L_i \) are given for example in [10]. However, the most encountered case in the experiments is the one of spheroids (\( n_1 = n_2 = n \)).
As we already stated in [11], the form of the analytical solution enables us to include extra conductances, like Stern layer conductances but also core material conductances if the particle consist of layers of material of different (complex) conductivities, like bioparticles [12,13]. These extra conductances can be decomposed in the general case in a contribution along the particle's surface (\(K_{\text{extra}}\)) and normal to it (\(K_{\text{extra}}^{\perp}\)) and can be included in the expression of \(\beta\) as shown above.

The value of the dipolar coefficient can be used to interpret dielectrophoretic and electrorotation measurements which requires the knowledge of \(\beta\) as a function of the frequency of the applied electric field [5,6,12,13]. It can also be used to calculate the complex conductivity increment of the colloidal suspension \(K = K + i\omega\varepsilon_0\varepsilon\) (\(\omega\) being the frequency of the applied electric field and \(\varepsilon_0\) the dielectric permittivity of vacuum) found in dielectric spectroscopy measurements [1,4,11]. In the case of randomly oriented particles and a low volume fraction \(\varphi\) of the spheroids, the complex conductivity increment of the suspension is given by:

\[
\tilde{K} = \tilde{K}_1[1 + \phi(\beta_0^2 + 2\beta_1)],
\]

where \(\tilde{K}_1\) the complex conductivity of the electrolyte (see Eq. (42)).

1.1. Outline of the paper

In the next section, we will present the set of electrokinetic equations and boundary conditions required to find the dipolar coefficient arising from a dielectric sphere in an electrolyte solution. This set of equations will be the base of the numerical simulations used in the fourth section. We will limit our analysis to monovalent and symmetric electrolytes of type like KCl in water for simplicity. No extra layer conductances are considered. The fluid motion (electrophoretic mobility of the particle) is neglected in this section.

In Section 3, the analytical derivations are presented and briefly compared to the derivations made in [11] where we also neglected fluid flow.

The comparison between the numerical and analytical theories (without considering fluid flow), is done in Section 4, for a wide range of zeta potentials, frequencies and ionic strengths. The assumptions made in the analytical derivation are critically assessed.

The results of the comparison in the case where we consider fluid flow, which is the general case, will be presented in Section 5, also for a wide range of zeta potentials, frequencies and ionic strengths. The numerical code we used here is a slightly modified version of the code we obtained from prof. A. Delgado (Department of Applied Physics, University of Granada, Spain). This code is based on the code of DeLacey and White [11] and includes fluid flow. The analytical expression found in Section 3 is then corrected so as to include the effect of fluid flow, in terms of the particle's electrophoretic mobility.

In Section 5, the analytical derivations (including fluid flow) are presented and compared to the numerical simulations. The analytical solutions of Hinch [14] and O’Brien [15] are also presented and discussed.

The expression for \(\beta\) is then extended to the case of spheroids (prolate and oblate). This is discussed in Section 6, with the help of Appendix A. The analytical solutions are compared to the ones of O’Brien and Ward [7]. A conclusion is given in the last section.

2. Theory

In this section, the equations needed to solve the problem are derived, making the following simplifying assumptions:

(i) The electrolyte considered is monovalent and symmetric (like, for instance, KCl).

The derivation can however be extended for any type of electrolyte [11].

(ii) The fluid is assumed to be at rest with respect to the sphere. This means in particular that we neglect the electrophoretic mobility of the particle. One of the numerical codes we used (NUM), which is discussed at the end of this section is based on the equations of this section. Keeping the fluid at rest will enable us to test, thanks to NUM, the important hypothesis on which the analytical derivation is based (see Section 4). The inclusion of the electrophoretic mobility of the particle will be given in the third section.

We refer to [1,2,11] for a more complete set of equations. The ions (labeled + and −) have equal ionic diffusion coefficients \(D_+ = D_− = D\) (m²/s) and valence \(z_+ = −z_− = 1\). The colloidal sphere with radius \(a\) (m) is submitted to a (weak) electric field of amplitude \(E_0\) (V/m) and of radial frequency \(\omega\) (rad/s). We take: \(E_0 = E_0 \exp(i\omega t)\), with \(i = \sqrt{−1}\). The origin of the coordinate system we use is the center of the sphere, with \(\theta\) the angle with the direction of the electric field (\(E_2\)) and \(r\) the distance from the center of the sphere. No Stern layer conductances are considered.

The relevant variables are:

\[
\Psi_{\text{tot}} = \Psi_{\text{eq}} + \delta\Psi,
\]

\[
n_{r,\text{tot}} = n_{r,\text{eq}} + \delta n_r,
\]

\[
n_{−,\text{tot}} = n_{−,\text{eq}} + \delta n_−,
\]

where \(\Psi_{\text{eq}}(r)\) and \(n_{r,\text{eq}}(r)\), \(n_{−,\text{eq}}(r)\) are respectively the equilibrium potential \((V)\) and the ionic density of positively/negatively charged ions \((m^−3)\) in absence of applied electric field, \(\delta\Psi(r,\theta)\) and \(\delta n_r(r,\theta)\) the small perturbation in the potential \((V)\) and the small perturbations in the ionic density of positively/negatively charged ions \((m^−3)\) due to the applied electric field.

Using the symmetry of the system [16], we introduce the variables \(\Psi(r, n_r)\) and \(n_r\) such that:

\[
\delta\Psi = (\psi − r)E_0 \cos \theta \exp(i\omega t),
\]

\[
\delta n_r = n_r E_0 \cos \theta \exp(i\omega t),
\]

We also introduce the variables [11]:

\[
n_{n,\text{tot}} = n_{r,\text{tot}} + n_{−,\text{tot}} = n_{n,\text{eq}} + \delta n_n,
\]

\[
n_{c,\text{tot}} = n_{r,\text{tot}} − n_{−,\text{tot}} = n_{c,\text{eq}} + \delta n_c,
\]

We define similarly:

\[
\delta n_n = n_n E_0 \cos \theta \exp(i\omega t),
\]

\[
\delta n_c = n_c E_0 \cos \theta \exp(i\omega t).\]

The Poisson equation relates \(\Psi_{\text{tot}}\) to \(n_c\) by:

\[
\Delta\Psi_{\text{tot}} = \frac{−e}{\varepsilon_0\varepsilon_1} n_c\text{tot},
\]

where \(e\) (C) is the absolute value of the electron charge, \(\varepsilon_1\) the relative dielectric permittivity of the solvent and \(\varepsilon_0\) (F/m) the dielectric permittivity of vacuum. The electrochemical potential \(\tilde{\mu}_1,\text{tot}(r,\theta)\) is \(\mu_1,\text{eq}(r) + \delta\tilde{\mu}_1,\text{tot}(r,\theta)\) of ion \(i (i = +, −)\) is defined by:

\[
\tilde{\mu}_1,\text{tot} = z_i e \Psi_{\text{tot}} + \mu_0^i + kT \ln\left(\frac{n_{i,\text{tot}}}{n_0}\right),
\]

where \(\mu_0^i (J)\) and \(n_0 (m^−3)\) are the reference chemical potential and density, \(k (J/K)\) Boltzmann’s constant and \(T \) (K) the temperature.
The ionic fluxes \( \mathbf{J}_i \) are given by the Nernst–Planck equation:

\[
\mathbf{J}_i = -D_n_i \nabla n_i \mu_i, \quad (9)
\]

The conservation of ions can be expressed as:

\[
\frac{\partial n_i}{\partial t} + \nabla \cdot \mathbf{J}_i = 0. \quad (10)
\]

### 2.1. The equilibrium state

In the absence of an applied electric field the Poisson equation relates \( \psi_{eq} \) to \( n_{eq} \) by:

\[
\Delta \psi_{eq} = -\frac{e}{\varepsilon_0 \varepsilon_1} n_{eq}. \quad (11)
\]

Using the fact that the electrochemical potential is constant in the system (as there are no ionic fluxes in the absence of applied electric field: \( \mathbf{J}_i(r, \theta) = 0 \), we have \( \mu_i, eq(r, \theta) = \mu_i, eq(\infty) \). This leads to the Boltzmann distribution: \( n_{eq, eq} = n_\infty \exp(-e \varepsilon_i \psi_{eq}(r)/kT) \) (\( i = +, - \)) and therefore:

\[
n_{eq, eq} = 2n_\infty \cosh\left(\frac{\varepsilon_i \psi_{eq}}{kT}\right) \quad \text{and} \quad n_{eq, eq} = -2n_\infty \sinh\left(\frac{\varepsilon_i \psi_{eq}}{kT}\right). \quad (12)
\]

We get the Poisson–Boltzmann relation:

\[
\Delta \left( \frac{\varepsilon_i \psi_{eq}}{kT} \right) = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r \frac{\partial \varepsilon_i \psi_{eq}}{kT} \right) = \kappa^2 \sinh\left(\frac{\varepsilon_i \psi_{eq}}{kT}\right). \quad (13)
\]

where \( \kappa = [2e^2 n_\infty/(\varepsilon_0 \varepsilon_1 kT)]^{1/2} \) is the inverse of the Debye length in the (symmetric) electrolyte.

#### 2.1.1. Boundary conditions and asymptotic solution

We assume in this article that the slip (or shear) plane, where the zeta potential \( \zeta \) is defined, coincides with the surface of the particle and simultaneously with the beginning of the diffuse part of the double layer (since no Stern layer is considered in this study): \( \psi_{eq}(t = a) = \zeta \).

Far from the particle and its double layer (where \( \sinh(\psi_{eq}) \approx \psi_{eq} \)), and taking into account the boundary condition \( \psi_{eq}(r \to \infty) = 0 \), the potential has the asymptotic expression:

\[
\psi_{eq}^+ = \psi_0 + \frac{a}{\kappa} \exp(\kappa a - \kappa r), \quad (14)
\]

where \( \psi_0 \) is an unknown coefficient which depends on \( \zeta \) and \( \kappa \) and that can be found by numerical integration in the general case. For low zeta potentials \( (e\zeta/kT \ll 1) \), it can be shown that \( \psi_0 = \zeta \), using Eq. (13) and the fact that \( \sinh(x) \approx x \) for \( x \ll 1 \). Analytical formulae are available for the high zeta potential case, but under some restrictions regarding the ionic strength and valence of the electrolyte. The expression for the electrophoretic surface charge density \( -\varepsilon_0 \varepsilon_1 (\partial \psi_{eq}/\partial r)_{r=a} \) in terms of the zeta potential has for instance been tabulated [17] in these special cases.

#### 2.2. In the presence of an applied electric field

In the presence of an applied electric field, the Poisson equation links \( \delta \Psi(r, \theta) \) to \( \delta n_i(r, \theta) \) by:

\[
\Delta \delta \Psi = -\frac{e}{\varepsilon_0 \varepsilon_1} \delta n_i. \quad (15)
\]

The conservation of ions equation can be written to linear order as:

\[
i_0 \delta n_i = D \nabla \left[ n_{eq} \frac{\varepsilon_i e}{kT} \delta \Psi + \frac{\delta n_{eq}}{n_{eq}} \right]. \quad (16)
\]

Using the fact that \( \nabla n_{eq} = -n_{eq} \nabla (e\varepsilon_i \psi_{eq}/kT) \), we get:

\[
i_0 \delta n_i = \Delta \delta n_i + \frac{e\varepsilon_i}{kT} n_{eq} \nabla \delta \Psi + \frac{\delta n_{eq}}{n_{eq}} \delta \Psi + n_{eq} \frac{\varepsilon_i e}{kT} \delta \Psi.
\]

Using Eq. (14) and the operator \( L \) that is defined on any function \( f \) by:

\[
L f = \frac{1}{r^2} \left( \frac{d^2 f}{dr^2} - \frac{2f}{r^2} \right),
\]

the Poisson equation reduces to:

\[
L \psi = -\frac{e}{\varepsilon_0 \varepsilon_1} n_c. \quad (19)
\]

And the conservation of ions (rewritten as two equations, in terms of \( n_a \) and \( n_c \)) gives:

\[
L n_a = i_0 \frac{n_a}{D} + e \frac{d n_c}{d r} \left[ \frac{e (d \psi_{eq}/dr) - 1}{kT} n_{eq} - \frac{d n_{eq}}{d r} \right] + e^2 n_{eq} n_c - n_a \frac{d n_{eq}}{d r} \quad (20)
\]

where we used the fact that \( \psi_{eq} \) only depends on \( r \).

#### 2.2.1. Boundary conditions

The boundary conditions at the surface of the particle for the electric potentials are:

\[
\varepsilon_0 \varepsilon_2 \left( \frac{\partial (\delta \psi)}{\partial r} \right)_{r=a} = \varepsilon_0 \varepsilon_1 \left( \frac{\delta \psi}{\partial r} \right)_{r=a},
\]

\[
\delta \psi_{eq}(r) = \delta \psi(a). \quad (21)
\]

\( \delta \psi_2 \) is the potential inside the sphere of relative dielectric permittivity \( \varepsilon_2 \ll \varepsilon_1 \) and is a solution of the Laplace equation \( \Delta \delta \Psi = 0 \) since the sphere is assumed to be not conducting. This gives:

\[
\delta \psi_2 = -r E_2 \cos \theta \exp(\text{iot}). \quad (22)
\]

\( E_2 \) (the electric field inside the sphere) is a coefficient that can be eliminated using Eqs. (21). We get:

\[
E_2 = \left( 1 - \frac{\psi(a)}{a} \right) E_0.
\]

\[
\left( \frac{d \psi}{dr} \right)_{r=a} = \frac{\varepsilon_2}{\varepsilon_1} \frac{\psi(a)}{a} + \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1}. \quad (23)
\]

The no-flux conditions provide the last boundary conditions:

\[
(i_0 \cdot \mathbf{e}_i)_{r=a} = 0. \quad (24)
\]

which for the symmetric electrolyte considered here leads to:

\[
\frac{e \varepsilon_i}{kT} \left( \frac{d \psi}{dr} - 1 \right) n_{eq} + \frac{d n_{eq}}{dr} + n_{eq} \frac{e \varepsilon_i}{kT} = 0 \quad \text{in} \ r = a,
\]

\[
\frac{e \varepsilon_i}{kT} \left( \frac{d \psi}{dr} - 1 \right) n_{eq} + \frac{d n_{eq}}{dr} + n_{eq} \frac{e \varepsilon_i}{kT} = 0 \quad \text{in} \ r = a. \quad (25)
\]
2.2.2. Asymptotic behavior

Beyond the double layer (for $r > a + \kappa^{-1}$), the variables $\Psi_{eq}, d\Psi_{eq}/dr$, and $n_{eq}$ tend to zero and $n_{eq}$ tends to $2n_{eq}$. Equations (20) then reduce to (we use the superscript + to indicate that the variables are considered beyond the double layer):

\begin{equation}
\begin{align*}
L_n^+ &= \frac{i\omega}{D} n_n^+ , \\
L_t^+ &= \left( k^2 + \frac{i\omega}{D} \right) n_t^+ ,
\end{align*}
\end{equation}

which can be solved analytically for all frequencies by [11]:

\begin{equation}
\begin{align*}
\frac{n_n^+}{\kappa_n} &= \frac{C_0 + \frac{1 + \lambda_n}{r^2} \exp[-\lambda_n(r - a)]}{1 - \frac{1}{\kappa_n r^2} \exp[-\lambda_n(r - a)]}, \\
\frac{n_t^+}{\kappa_t} &= \frac{C_0 + \frac{1 + \lambda_t}{r^2} \exp[-\lambda_t(r - a)]}{1 - \frac{1}{\kappa_t r^2} \exp[-\lambda_t(r - a)]},
\end{align*}
\end{equation}

where $C_0$ and $C_t$ are constants that have to be determined.

Far from the double layer $n_n^+ \cong 0$ (since $\lambda_n r \gg 1$) and Eq. (19) can be solved analytically by:

\begin{equation}
\Psi^+ = \beta \frac{a^3}{r^2},
\end{equation}

where $\beta$ is the dipolar coefficient to be found. Note that $\lambda_n r \gg 1$ comes from the hypothesis that we are far from the double layer ($\kappa r \gg \kappa a + 1$). For small $\kappa a$ it is therefore important to start the numerical integration far enough from the double layer to ensure that $\Psi_{eq}/kT \ll 1$ where the asymptotic functions are evaluated.

2.3. Numerical procedures

The general set of electrokinetic equations (including fluid flow) were solved numerically by DeLacey and White [1] using a fifth grad Nordsieck method in a FORTRAN program. Their work was extended later by Mangelsdorf and White (see [2,18]) who in particular included the acceleration term in the Navier–Stokes equation. The solutions of DeLacey and White and Mangelsdorf and White are virtually identical. They start only to deviate from each other for frequencies above $3 \times 10^3$ Hz ($a = 100$ nm, $c\epsilon/kT = 4$) for $\kappa a \ll 1$ [18].

A numerical code based on DeLacey and White’s was graciously provided to us by prof. A. Delgado of the Department of Applied Physics of the University of Granada (Spain) and modified for the special cases considered in this study:

- The program was modified to allow the diffusion coefficients of the co- and counter-ions to be strictly equal ($D_+ = D_-$). It was checked to give the same results as in the limit $D_+ \approx D_-$. 
- In order to keep the fluid at rest relative to the sphere (when necessary), the viscosity in the complex set of electrokinetic equations was taken virtually infinite ($10^{10}$ Pa.s). It was verified that in that case the mobility of the sphere calculated by the program was in extremely good approximation zero. The ionic diffusion constants however were defined separately and taken to be roughly the ionic diffusion coefficient of $K^+$ and $Cl^-$ in water ($D_+ = D_- = 2.0 \times 10^{-9}$ m$^2$/s).

A second numerical code called NUM was made based on the set of equations presented in this section. The program was solved using either the Nordsieck or the Euler method (both methods gave the same results). This program was also checked to give the same results as the program based on DeLacey and White's and modified for a large viscosity. The advantage of using NUM is that this program could be used in cases where the modified program proved difficult (or impossible) to run, especially for low $\kappa a$, low zeta potentials and high frequencies. Moreover NUM, using the same variables as in the theoretical analysis, made the comparison between numerical and analytical results easier.

3. Analytical theory

In this section we will present the boundary conditions, the derivation of which will result in the analytical solution, given in Eq. (45).

In a previous article [11], we introduced an analytical analysis, based on the concept of excess quantities in the sense of Gibbs [19,20]. The standard boundary conditions (21) and (24) are now replaced by new ones that use the excess quantities $\delta n_i^\pm$ and $\delta J_i^\pm$. Following Gibbs’ approach, excess densities $\delta n_i^\pm$ and fluxes $\delta J_i^\pm$ are defined in terms of integrals over the actual variables ($n_i, J_i$) minus the values of the variables beyond the double layer. We introduce a length $r_0 > a$, the value of which will be discussed in Section 4, and define:

\begin{equation}
\begin{align*}
\delta n_i^\pm(r, \theta) &= \frac{1}{a^2} \int_0^{r_0} \int_0^{\pi} \left[ \delta n_i(r, \theta) - \delta n_i(r_0, \theta) \right] dr , \\
\delta J_i^\pm(r, \theta) &= \frac{1}{a} \int_0^{r_0} \int_0^{\pi} \left[ \delta J_i(r, \theta) - \delta J_i(r_0, \theta) \right] dr.
\end{align*}
\end{equation}

These integrals characterize the excess of the variables in the double layer. We refer to [11] for more details about the form of $\delta n_i^\pm$ and $\delta J_i^\pm$, and the general expression of the boundary conditions based on the excess quantities. We will here present these boundary conditions only for a symmetric electrolyte. The first boundary condition, can be written for the symmetric electrolyte as:

\begin{equation}
\delta \Psi^+(a, \theta) = \delta \Psi_2(a, \theta)
\end{equation}

with $\delta \Psi^+(r, \theta) = (-r + \beta a^3/r^2) E_0 \cos \theta \exp(i\omega t)$ and $\delta \Psi_2(r, \theta) = -r E_0 \cos \theta \exp(i\omega t)$ (see Eqs. (22) and (28)). The second boundary condition reads:

\begin{equation}
\begin{align*}
\epsilon_0 \epsilon_2 \frac{\partial \delta \Psi^+}{\partial r}(r = a) &= -\epsilon_0 \epsilon_1 \left( \frac{\partial \delta \Psi^+}{\partial r} \right)(r = a) = \delta \rho^S,
\end{align*}
\end{equation}

with $\delta \rho^S = \epsilon_0 \epsilon_2 \delta n_2^S$. These two first boundary conditions lead to:

\begin{equation}
E_2 = E_0(1 - \beta),
\end{equation}

\begin{equation}
\delta \rho^S(\theta) = \left[ \epsilon_0 \epsilon_2 (\beta - 1) + \epsilon_0 \epsilon_1 (1 + 2\beta) \right] E_0 \cos \theta \exp(i\omega t).
\end{equation}

The third boundary condition is:

\begin{equation}
\begin{align*}
\iota \omega \delta n_2^S(\theta) &= -\nabla \cdot J_{22}^\pm(\theta) - J_{21}^\pm(\theta) ,
\end{align*}
\end{equation}

which leads to, using the definitions $J_n = J_+ + J_-$ and $J_c = J_+ - J_-$:

\begin{equation}
\begin{align*}
\iota \omega \delta n_2^S(\theta) &= -\epsilon_0 \epsilon_2 \nabla \cdot J_{22}^\pm(\theta) - \epsilon_0 \epsilon_1 \nabla \cdot J_{21}^\pm(\theta) ,
\end{align*}
\end{equation}

where:

\begin{equation}
\begin{align*}
J_{22}^\pm(\theta) &= -D_\parallel \frac{\partial}{\partial r} \left[ \frac{\epsilon_0 \epsilon_2 e n_2^\pm}{kT} \frac{\partial \delta \Psi^+(r, \theta) + \delta n_2^+(r, \theta)}{r} \right]_{r = a} , \\
J_{21}^\pm(\theta) &= -K_1(1 + 2\beta) E_0 \cos \theta \exp(i\omega t) , \\
J_{22}^\pm(\theta) &= -K_1 \frac{kT}{2 \epsilon_0 a} C_n J_2 E_0 \cos \theta \exp(i\omega t).
\end{align*}
\end{equation}
We defined the conductivity of the electrolyte \( K_1 = \varepsilon_0 \varepsilon_1 \kappa^2 D \) and \( J_2 = 2 + 2 \lambda_0 a + \lambda_0^4 a^2 \). We furthermore find, using Eq. (29):

\[
\mathbf{J}^\ell_{||} = \frac{-D}{\alpha^2 kT} \int_a^{r_0} \left[ \nabla \delta \mu_i r_i \right] \left[ \nabla \bar{\delta \mu}_i (r_0) \right] dr \\
\approx \frac{-D}{\alpha^2 kT} \int_a^{r_0} \left[ \nabla \delta \mu_i (r_0) \right] \left[ \nabla \bar{\delta \mu}_i (r_0) \right] dr \\
\approx \frac{-D}{\alpha^2} \nabla \left[ \frac{z e^r}{kT} \delta \psi^+ + \frac{\delta n^+_0}{2n_\infty} \right] \int_a^{r_0} \left[ n_i - n_{\infty} \right] dr. \tag{36} \]

In doing so, we assumed that \( \nabla \delta \mu_i \) varies slowly in the double layer and is in good approximation equal to the value \( \nabla \delta \mu_i (r_0) \) and that \( n_i (r_0) \approx n_{\infty} \).

Evaluating \( \nabla \delta \mu_i \) from the values gotten from the numerical simulations, it could be seen that for any \( \zeta \) and for \( k \alpha > 2 \), \( \nabla \delta \mu_i \) is indeed roughly constant through the double layer. This is not true for \( k \alpha < 2 \) where the variation of \( \nabla \delta \mu_i \) starts to be larger than 30\% in the double layer. This is illustrated in Fig. 1 where the real part of \( \nabla \delta \mu_i \) and \( \nabla \delta \mu_i \) are displayed as function of the distance from the sphere for \( k \alpha = 1 \) and \( k \alpha = 100 \) (\( k \varepsilon_1 / kT = 4 \), \( \omega = 10 \) rad/s). The imaginary parts are not given in these examples; they are of the order of \( 10^{-5} \) times the real parts or smaller.

As will be shown in Section 4, \( r_0 \) can be chosen in such a way that we get a good estimate of \( \mathbf{J}^\ell_{||} \) for all \( k \alpha > 10 \). From this investigation it also follows that a better approximation of \( \mathbf{J}^\ell_{||} \) for \( k \alpha > 10 \) is

\[
\mathbf{J}^\ell_{||} \approx \frac{-D}{\alpha^2} \nabla \left[ \frac{z e^r}{kT} \delta \psi^+ + \frac{\delta n^+_0}{2n_\infty} \right] \int_a^{r_0} \left[ n_i - n_{\infty} \right] dr. \tag{37} \]

which is the approximation we used in [11]. The dipolar coefficient values obtained using Eq. (36) differ only of a few percents for \( k \alpha > 10 \) from the ones obtained using Eq. (37), however. In the following, we will use Eq. (36).

Using the definition \( J_1 = 1 + \lambda_0 a \), we get:

\[
-e \nabla \cdot \mathbf{J}^\ell_{||} (\theta) = K_1 \left[ 2 \left( 1 + a^2 \beta / r_0^2 \right) n_{\infty} + \frac{kT}{\varepsilon_0} C_0 J_1 I_{eq} \right] \times \exp \left( -\lambda_0 (r_0 - a) \right) E_0 \cos \theta \exp(i \omega t),
\]

\[
-e \nabla \cdot \mathbf{J}^\ell_{||,p} (\theta) = K_1 \left[ 2 \left( 1 + a^2 \beta / r_0^2 \right) I_{c, eq} + \frac{kT}{\varepsilon_0} C_0 J_1 I_{c, eq} \right] \times \exp \left( -\lambda_0 (r_0 - a) \right) E_0 \cos \theta \exp(i \omega t), \tag{38} \]

where:

\[
I_{eq} = -\frac{1}{2a^2 n_\infty} \int_a^{r_0} \left[ n_i - 2n_\infty \right] dr
\]

\[
= -\frac{1}{2a^2} \int_a^{r_0} \left[ \cosh \left( \frac{e \psi_{eq}}{kT} \right) - 1 \right] dr, \tag{39} \]

\[
I_{c, eq} = -\frac{1}{2a^2 n_\infty} \int_a^{r_0} \left[ n_{c, eq} - 2n_\infty \right] dr = \frac{1}{2a^2} \int_a^{r_0} \left[ \sinh \left( \frac{e \psi_{eq}}{kT} \right) \right] dr. \tag{40} \]

From Eqs. (32) and (34) we find, using \( \delta \rho^5 = \varepsilon \delta n^5_{s} \):

\[
 Fig. 1. Real part of dimensionless \( \nabla \delta \mu_{i} \) (full and dashed lines) and \( \nabla \delta \mu_{i} \) (dash-dotted and dotted lines) are displayed as function of \( \kappa (r - a) \) for \( \varepsilon_1 / kT = 4 \), \( \omega = 10 \) rad/s. (A) \( k \alpha = 1 \) and (B) \( k \alpha = 100 \). When \( k \alpha = 100 \), the curves corresponding to \( \nabla \delta \mu_{i} \) and \( \nabla \delta \mu_{i} \) are nearly exactly superposed.
\]

\[
\hat{\kappa}_2 = i \hat{\kappa}_2 + i \omega \varepsilon_0 \varepsilon_1,
\]

\[
\hat{\kappa}_1 = \hat{\kappa}_1 + i \omega \varepsilon_0 \varepsilon_1 = \varepsilon_0 \varepsilon_1 (\kappa^2 D + i \omega). \tag{42} \]

\( \hat{\kappa}_2 \) is the complex conductivity of the core material of the sphere and \( \hat{\kappa}_1 \) the complex conductivity of the bulk electrolyte.

We have 4 equations and 5 unknown: \( C_0, E_2, \beta, \delta n^5, \delta n^5_s \) and we need therefore a fifth equation. In [11], this equation was provided by the relation \( \delta n^5 = 0 \) in the low-zeta potential case, and by the relation \( |\delta n^5_s| = |\delta n^5| \) in the high potential case. We now introduce a parameter \( \gamma \) by:

\[
\delta n^5_s = \gamma \delta n^5. \tag{43} \]
From Eq. (34) we then get:
\[ \frac{kT}{\epsilon n_{\infty}} C_n \exp(-\lambda_n(r_0 - a)) = -2\beta \left( l_{\infty, eq} - \gamma \mu_{\infty, eq} a \right)^2 r_0^2 + \gamma + 2(l_{\infty, eq} - \gamma \mu_{\infty, eq}) - \gamma. \]
\[ J_1(l_{\infty, eq} - \gamma \mu_{\infty, eq}) - 2J_2(2a)^2 \exp(\lambda_n(r_0 - a)). \] (44)
Inserting the value of \( C_n \) in Eq. (41), we finally find:
\[ \beta = \frac{\tilde{K}_2 - \tilde{K}_1 + 2\tilde{K}_1 + \tilde{K}_\perp}{K_2 + 2K_1 + 2K_\parallel - 2K_\perp} \] (45)
with:
\[ \tilde{K}_1 = -K_1 l_{\infty, eq} + \frac{K_1 l_{\infty, eq}[l_{\infty, eq} - \gamma \mu_{\infty, eq}]}{(l_{\infty, eq} - \gamma \mu_{\infty, eq}) - J_2(2J_1)(a/r_0)^2 \exp(\lambda_n(r_0 - a))}, \]
\[ \tilde{K}_\perp = \frac{(l_{\infty, eq} - \gamma \mu_{\infty, eq}) - J_2(2J_1)(a/r_0)^2 \exp(\lambda_n(r_0 - a))}{(l_{\infty, eq} - \gamma \mu_{\infty, eq}) - J_2(2J_1)(a/r_0)^2 \exp(\lambda_n(r_0 - a))}. \] (46)
The subscripts \( \parallel \) and \( \perp \) are introduced to indicate that the corresponding complex conductivity mainly originates from the contribution of flux of ions along or perpendicular to the surface of the particle. The difference is more subtle, however. For example, the right term (containing \( J_2 \)) in the denominator of Eqs. (46) originates from the flux of ions perpendicular to the surface, whereas the left term comes from the contribution of ions along the surface. It is interesting to notice that for frequencies such that \( \omega \ll Dk^2 \) (which means that \( K_1 \simeq K_2 \) and \( |K_2| \ll |K_1| \) the expression for \( \beta \) can be simplified into:
\[ \beta = 1/2((1 + 2l_{\infty, eq})(a/r_0)^2 \exp(-\lambda_n(r_0 - a)) + (2J_1/J_2) \times \left[ -l_{\infty, eq} + 2(l_{\infty, eq} - l_{\infty, eq}) \right]/\left[ (l_{\infty, eq} - \gamma \mu_{\infty, eq}) - J_2(2J_1)(a/r_0)^2 \exp(\lambda_n(r_0 - a)) \right] \]
\[ \exp(-\lambda_n(r_0 - a)) + (2J_1/J_2)l_{\infty, eq} \times (l_{\infty, eq} - l_{\infty, eq})(a/r_0)^2 \] (47)
and that the terms containing \( \gamma \) cancel out. From the numerical results, we found that a good estimate of \( \gamma \) for all frequencies, zeta potentials and \( k\alpha \) is: \( \gamma = l_{\infty, eq}/l_{\infty, eq} \). Equations (46) then reduce to:
\[ \tilde{K}_\parallel = -K_1 l_{\infty, eq} + \frac{2J_1 K_1 l_{\infty, eq}[l_{\infty, eq} - l_{\infty, eq}]}{J_2(2J_1)(a/r_0)^2 \exp(\lambda_n(r_0 - a))}, \]
\[ \tilde{K}_\perp = \frac{2J_1 K_1 l_{\infty, eq} \exp(\lambda_n(r_0 - a))}{J_2(2J_1)(a/r_0)^2 \exp(\lambda_n(r_0 - a))}. \] (48)

3.1. Special case: \( k\alpha > 10 \)
As we already mentioned, Eq. (37) is a better approximation than Eq. (36) for \( k\alpha > 10 \). We refer to [11] for this case. Using Eq. (37), Eq. (45) reduces to:
\[ \beta = \frac{\tilde{K}_2 - \tilde{K}_1 + 2\tilde{K}_1 + \tilde{K}_\perp}{K_2 + 2K_1 + 2K_\parallel - 2K_\perp} \] (49)
with:
\[ \tilde{K}_\parallel = -K_1 l_{\infty, eq} - K_1 l_{\infty, eq}[l_{\infty, eq} - l_{\infty, eq}], \]
\[ \tilde{K}_\perp = K_1(2J_1/J_2)l_{\infty, eq}. \] (50)

3.1.1. Low zeta potentials
For low zeta potentials, we find for \( k\alpha > 10 \) to first order in zeta (with \( l_{\infty, eq} = 0 \) and \( l_{\infty, eq} = (\epsilon\zeta/kT)/(k\alpha) \)):
\[ \beta = \frac{\tilde{K}_2 - \tilde{K}_1 - 4J_1/J_2)K_1(\epsilon\zeta/kT)^2/(k\alpha)^2}{K_2 + 2K_1 - 4J_1/J_2)K_1(\epsilon\zeta/kT)^2/(k\alpha)^2}. \] (51)
Moreover, we find \( C_n \) and \( C_c \) to first order in \( \zeta \) and for \( \omega \ll k^2D \):
\[ C_n = a + \frac{\epsilon\zeta}{e} - \frac{2\beta - 1}{e} \]
\[ C_c = a + \frac{\epsilon\zeta}{e} + \frac{1 + 2\beta + \epsilon\zeta(\beta - 1)/\epsilon_1}{2 + \kappa\alpha} \] (52)

3.1.2. High zeta potentials
For high zeta potentials and for \( k\alpha > 10 \) (which is the case most commonly found in experiments), we made the assumption in [11] that the counterions dominate in the double layer, so we have:
\[ l_{\infty, eq} = -l_{\infty, eq} \quad \text{and} \quad \delta n^z = -\delta n^z \quad \text{if} \quad \zeta > 0, \]
\[ l_{\infty, eq} = +l_{\infty, eq} \quad \text{and} \quad \delta n^z = +\delta n^z \quad \text{if} \quad \zeta < 0. \] (53)
\( l_{\infty, eq} \) can be evaluated using
\[ l_{\infty, eq} = \frac{\epsilon\zeta}{2\kappa\alpha} \int_a^{\infty} r\Delta \Psi_{eq} dr = \frac{1}{(k\alpha)^2} \left[ -\frac{\epsilon\zeta}{kT} - \frac{\partial}{\partial r} \left( \frac{\epsilon\Psi_{eq}}{kT} \right) \right]_{r=a} \] (54)
Using the expression for the electrosurface charge density \( \epsilon\zeta/(r\Delta \Psi_{eq}/dr)\) in terms of the zeta potential tabulated for all zeta potentials and \( k\alpha \gtrsim 0.5 \) in [17], we find:
\[ q^* = 2 \sinh \left( \frac{\epsilon\zeta}{2kT} \right) + \frac{4}{k\alpha} \tan \left( \frac{\epsilon\zeta}{4kT} \right) - \frac{1}{k\alpha} \frac{\epsilon\zeta}{kT} \] (55)
\( l_{\infty, eq} \) found by numerical integration of Eq. (40) and found by Eq. (55) differs less than 1% for \( k\alpha > 0.5 \) and less than 0.1% for \( k\alpha > 10 \). Using Eqs. (53) we then find that \( l_{\infty, eq} = -|q^*|/k\alpha \).
We can also evaluate \( C_n \) (but not \( C_c \)) in the high zeta potential case:
\[ C_n = a - \frac{\epsilon\zeta}{e} - \frac{2\beta - 1}{e} \] (56)
The difference between the values obtained from Eqs. (45) and (49) using Eqs. (53) and (55) for the example \( \epsilon\zeta/kT = 4 \) and \( k\alpha = 50 \) for all frequencies is less than 10%. This difference is mainly due to the fact that the assumption \( |l_{\infty, eq}| = |l_{\infty, eq}| \) is not correct for \( |l_{\infty, eq}|/|l_{\infty, eq}| = 0.75 \). For \( \epsilon\zeta/kT = 4 \) and \( k\alpha = 100 \) and for all frequencies, the difference between Eqs. (45) and (49) is less than 5%.

4. Comparison without fluid flow
In this section we will use the abbreviations:
NUM: numerical simulations based on the equations presented in Section 2;
THEO: semi-analytical formula (45).
In our previous article [11] we reported the discrepancies between the numerical solutions and our analytical theory, which was supposed to be appropriate for all zeta, ionic strengths and frequencies. We already stated in Section 2 why the deviations occurred: they have to do with the fact that our assumption of constant electrochemical potential through the double layer is not correct for low \( k\alpha \) as shown by the numerical simulations. After analyzing the differences between NUM and THEO for all zeta potentials and \( k\alpha \) we found that the best fit between NUM and THEO for any zeta potential and any \( k\alpha \) was obtained by choosing:
\[ r_0 = a + \delta_0 k^{-1}. \]
\[ \delta_0 = 1 + \frac{2}{k\alpha} \exp(-\epsilon\zeta/(2kT)). \] (57)
In NUM, the asymptotic functions were evaluated at a distance $r_{\text{start}} = a + 10k^{-1}$ (which is also the distance used in the numerical code based on DeLacey and White's), unless stated otherwise. From these values the solution was derived, using the Nordsieck method.

Other values of $r_{\text{start}}$ have been tried and the influence of $r_{\text{start}}$ on NUM will be discussed below. It was found that $\beta_{\text{NUM}}$ and $C_{\text{NUM}}$ are in good approximation constant for all $r_{\text{start}} > a + 10k^{-1}$. The values of $C_{\text{NUM}}^2$ depend on the values of $r_{\text{start}}$ but are so small that it does not affect the values of $\beta_{\text{NUM}}$ and $C_{\text{NUM}}$; we found for all $r_{\text{start}}$ that $n_i(t_{\text{start}}) < 10^{-10} n_i(t_{\text{start}})$. The Euler method gave for $\beta$ and $C_0$ results which agree with the Nordsieck method within 1%. The results for $C_0$ are not presented, but when $\beta_{\text{THEO}}$ and $\beta_{\text{NUM}}$ agree, so do $C_{\text{THEO}}^2$ and $C_{\text{NUM}}^2$.

$I_{n,\text{eq}}$ and $I_{c,\text{eq}}$ were evaluated numerically. We used $a = 100$ nm, $\varepsilon_1 = 78.55$, $\varepsilon_2 = 2$, $T = 298$ K and $D = 2.0 \times 10^{-9}$ m$^2$/s. The characteristic frequencies for the system are $\omega_k = Dk^2 = 2.0 \times 10^5 \sqrt{\varepsilon_k a}^2$ rad/s and $\omega_a = D/a^2 = 2.0 \times 10^5 \sqrt{\varepsilon_a}$. 

4.1. Comparison between NUM and THEO for all $\kappa a$

(i) For frequencies such that $\omega < \omega_k < \omega_a$ (which implies that $\kappa a < 1$, which is a case not usually found in experiments) we find that for any zeta potentials $K_{\parallel} = -K_{1\,\text{eq}} \gg K_{\perp} \approx 0$ and THEO reduces to

$$\beta_{\text{THEO}} \approx -1/2 - I_{n,\text{eq}}. \quad (58)$$

Note that $I_{n,\text{eq}}$ is extremely sensitive to $\varepsilon c/kT$. For $\kappa a = 0.1$ and $\varepsilon c/kT = 0.1$ for example, we find $I_{n,\text{eq}} \approx 7 \times 10^{-3}$ and $\beta_{\text{THEO}} \approx -0.49 (= \beta_{\text{NUM}})$. For $\varepsilon c/kT = 2$, we find $I_{n,\text{eq}} \approx -3$ and $\beta_{\text{THEO}} \approx 2.5$ ($\beta_{\text{NUM}} = 2.91$). For $\varepsilon c/kT = 4$, we find $I_{n,\text{eq}} \approx -17$ and $\beta_{\text{THEO}} \approx -16.5$ ($\beta_{\text{NUM}} = -12.3$).

(ii) For frequencies such that $\omega < \omega_k < \omega_a$ (which implies that $\kappa a > 1$ and which is the case most commonly found in the experiments), we find that for any zeta potentials $K_{\parallel} \approx -K_{2\,\text{eq}} + I_{c,\text{eq}} - I_{n,\text{eq}}^2$ and $K_{\perp} \approx K_{1\,\text{eq}}$. For high zeta potentials we have in good approximation $I_{n,\text{eq}}^2 \approx I_{c,\text{eq}}$ and THEO reduces to

$$\beta_{\text{THEO}} \approx 1 + I_{n,\text{eq}}. \quad (59)$$

Note that $\beta_{\text{THEO}}$ goes through zero for $I_{n,\text{eq}} = -1$. We checked that for $\kappa a > 1$ (Re$[\beta_{\text{NUM}}]$ also goes through zero (from positive to negative values) when $I_{n,\text{eq}} = -1$). This occurs for all potentials $\varepsilon c/kT > 2$. For lower potentials, Re$[\beta]$ also goes through zero but for $\kappa a < 1$.

(iii) For $\omega > \max[\omega_k, \omega_a]$ both NUM and THEO reduces to $(\varepsilon_2 - \varepsilon_1)/(\varepsilon_2 + 2\varepsilon_1)$ which reflects the pure dielectric behavior of the dipolar coefficient at high frequencies.

4.2. Comparison between NUM and THEO for all $\zeta$

NUM and THEO have been compared for (dimensionless) zeta potentials $\varepsilon c/kT$ ranging from 0 to 6 and the main conclusions are:

(i) For potentials such that $\varepsilon c/kT \ll 0.1$, NUM and THEO overlap for all zeta’s, frequencies and $\kappa a$ and are equal to $(K_{\perp} - K_{\parallel})/(K_{\parallel} + 2K_{\perp})$.

(ii) For potentials such that $\varepsilon c/kT < 1$ and $\kappa a > 1$, NUM overlaps THEO with an error of less than 1% for any frequency.

(iii) For intermediate potentials such that $\varepsilon c/kT \approx 1$ THEO gives a good estimate of the magnitude and behavior of the dipolar coefficient. This is illustrated in Fig. 2A. From this figure, we also see that Eq. (49) (which differs from THEO only a few percents for $\kappa a > 10$) is an even better estimate of NUM for higher $\kappa a$. For comparison, we also plotted the results according to the theories of Hincht et al. [14] and O’Brien [15] in Fig. 2B. Their formulations are given for example in Eqs. (4.4), (4.5) in [15]. The theory of Hincht is valid for $\kappa a \gg 1$ and at low frequencies such that $\omega < \omega_a$ whereas the theory of O’Brien is valid for $\kappa a \gg 1$ and at high frequencies such that $\omega \gg \omega_a$. Both theories were here modified to neglect the ionic drag by taking $m = 0$. We refer to [11] for a discussion about the differences between THEO and the theories of Hincht et al. and O’Brien. The discrepancies between the analytical theories of Hincht et al. and O’Brien and NUM arise from the evaluation of $I_{n,\text{eq}}$. Both Hincht and O’Brien used $I_{n,\text{eq}} \approx -\varepsilon c/kT$ in their derivation. For example, for $\varepsilon c/kT = 1$ and $\kappa a = 10$ we find $-\varepsilon c/kT = -0.10$ which leads using Eq. (59) to $\beta_{\text{THEO}} = -0.37$ (which is close to the value found from Hincht et al.’s formula, see Fig. 2B) whereas evaluating $I_{n,\text{eq}}$ numerically we find $I_{n,\text{eq}} = -2.24 \times 10^{-3}$ which leads to $\beta_{\text{THEO}} = -0.47$.

(iv) For potentials such that $\varepsilon c/kT > 1$, THEO and NUM agree in magnitude and behavior. For $\omega_a \gg \omega_k (\kappa a > 1)$ the difference between NUM and THEO is only a few percents. Both the theories of Hincht et al. and O’Brien can be used (in their respective range of validity) when $\varepsilon c/kT > 1$ since we then have in good approximation $I_{n,\text{eq}} \approx -\varepsilon c/kT \approx 1$.

In Fig. 3, the influence of $r_{\text{start}}$ on NUM is shown for $r_{\text{start}} = a + 10k^{-1}$ and $r_{\text{start}} = a + 30k^{-1}$. We observe that Eq. (49) agrees perfectly with NUM evaluated at $r_{\text{start}} = a + 30k^{-1}$. For smaller values of $\kappa a$ it was often impossible to take $r_{\text{start}} > a + 10k^{-1}$ but when the computation was possible the differences between the $\beta_{\text{NUM}}$ found for various $r_{\text{start}} \gg a + 10k^{-1}$ was a few percents only.

5. Inclusion of the electrophoretic mobility

It was assumed in the previous sections that the fluid was at rest in the frame of reference moving with the particle. The analytical equations will now be corrected to include the fluid velocity $u$ (m/s). First we note that in the absence of applied electric field: $u_{\text{eq}} = 0$. We have therefore:

$$u_{\text{test}} = u_{\text{eq}} + \delta u = \delta u \equiv u. \quad (60)$$

The fluid is supposed incompressible: $\nabla \cdot u = 0$. The ionic fluxes now become:

$$J_i = n_i u_{\text{eq}} - n_i D \nabla \left[ \frac{\varepsilon c}{kT} \delta \Psi + \frac{\delta n_{\text{eq}}}{n_{\text{eq}}} \right]. \quad (61)$$

Far from the double layer, we get the same asymptotic variables as in Section 2.2.2, considering the fact that $\nabla \cdot J_i = 0 = \nabla \cdot [n_i \mathbf{u} - \mathbf{u} \cdot \nabla \mathbf{u}]$ since $\mathbf{u} = 0$, where $J_i$ is the flux found in Section 3. The excess fluxes $J_i^{\pm}(\theta)$ and the fluxes beyond the double layer $J_i^{\pm}(\alpha, \theta)$ now become:

$$J_i^{\pm}(\theta) = J_i^{\pm}(\alpha, \theta) + \frac{q_{\text{eq}}}{\alpha} \int_a^\infty r |n_i u_{\text{eq}} - n_{\infty} u_{\text{eq}}^\uparrow| \, dr, \quad (62)$$

where $J_i^{\pm}(\theta)$ and $J_i^{\pm}(\alpha, \theta)$ are the fluxes found in Section 3. We have the boundary condition $\mathbf{u}(r = 0) = 0$ and therefore $u_{\text{eq}}$ will vary from $\mathbf{u} = \mathbf{u}^\uparrow$ beyond the double layer to $\mathbf{u} = 0$ in $r = 0$. The dependence of $u_{\text{eq}}$ on $r$ makes it difficult to give a simple approximation of the integral in Eq. (62). The general expression of $u_{\text{eq}}(r)$ is however available. We refer to [8] for this general expression. Similarly to what we did to estimate $J_i^{\pm}(\theta)$ by assuming...
Fig. 2. Real and imaginary part of the dipolar coefficient $\beta$ as a function of frequency for $\epsilon \zeta / kT = 1$ and $\kappa a = 10$ (squares), $\kappa a = 20$ (diamonds), $\kappa a = 50$ (circles) as calculated by NUM. (A) THEO (full line), Eq. (49) (dashed line). (B) Hinch et al.’s theory (dashed line) and O’Brien’s theory (full line). All theories are modified so as to neglect the effect of fluid flow.

Fig. 3. Real and imaginary part of the dipolar coefficient $\beta$ as a function of frequency for $\epsilon \zeta / kT = 4$ and $\kappa a = 100$ as calculated by THEO (full line) and Eq. (49) (dashed line). NUM (diamonds) was calculated with the asymptotic functions evaluated at $r_{start} = a + 10\kappa^{-1}$. NUM (squares) with the asymptotic functions evaluated at $r_{start} = a + 30\kappa^{-1}$. Equation (49) (dashed line) is almost indistinguishable from the squares. All theories are modified so as to neglect the effect of fluid flow.
\[ V \delta \tilde{\mu}_1 \simeq V \delta \tilde{\mu}_1^+ (r_0) \text{ in the double layer, we calculated the integral using } u_i \simeq u_i^+ (r_1). \text{ We took } u^+ \text{ to be given by:} \]

\[ u^+ = -U \left[ 1 - \beta \left( \frac{a}{r_1} \right)^3 \right] E_0, \quad U = \frac{2 \varepsilon_0 \varepsilon_1 \xi}{3 \eta}. \] (63)

The value of \( r_1 \) will be discussed in the next section. By including the effect of fluid flow, Eq. (45) has to be corrected into:

\[ \beta = \frac{K_2 - K_1 + 2[K_1 + K_U] + K_\perp}{K_2 + 2K_1 + 2[K_1(a/r_0)^2 + K_U(a/r_1)^2] - 2K_\perp}. \] (64)

This is now the full expression of the dipolar coefficient arising from a dielectric sphere in an electrolyte solution, with:

\[ \tilde{K}_U = K_m \frac{\varepsilon_c}{kT} I_{c,eq} \]

\[ \times \left[ \frac{I_{c,eq} - \gamma I_{c,eq} - 1/4}{I_{c,eq} - J_2/(2J_1)(r_0/a)^3 \exp(\lambda_o(r_0 - a))} - 1 \right]. \] (65)

where

\[ m = \frac{2 \varepsilon_0 \varepsilon_1 (kT)^2}{3 \eta \varepsilon_a^2}. \] (66)

is the factor used both by Hinch et al. and O'Brien to correct their expression of \( \beta \) for the ionic drag [15]. In their case, as we discussed in [11], \( 1 + 3m \) multiplies both \( \tilde{K}_1 \) and \( \tilde{K}_\perp \) in the numerator and in the denominator. We did not include this correction as it did not improve the agreement between the analytical and the numerical results. Using \( \gamma = I_{c,eq}/I_{c,eq} \) we get:

\[ \tilde{K}_U = K_m \frac{\varepsilon_c}{kT} I_{c,eq} \left[ \frac{J_1}{2J_2(r_0/a)^3 \exp(\lambda_o(r_0 - a))} - 1 \right]. \] (67)

6. Comparison with fluid flow

Equation (64) was compared to the results of the numerical simulations with fluid flow. To this purpose, we used the Delaeye and White based program (using the Nordieck method) and set the viscosity to be the viscosity of water \( \eta = 0.89 \times 10^{-3} \text{ Pa.s}. \) We will use the abbreviations:

- \( \text{DLWF: numerical simulations using the code based on Delaeye and White's allowing fluid flow; } \)
- \( \text{THEOF: semi-analytical formula (64) for } \beta_{\text{THEOF}} \text{ and Eq. (63) for } u_i^+. \text{THEOF for } \)

We started the integration at \( r_{\text{start}} = a + 10 \kappa^{-1}. \) Other values of \( r_{\text{start}} \) could not be tested due to numerical problems. Again, we use \( \gamma = I_{c,eq}/I_{c,eq}. \) \( I_{c,eq} \) and \( I_{c,eq} \) were evaluated numerically. We used \( a = 100 \text{ nm}, \, \varepsilon_1 = 78.55, \, \varepsilon_2 = 2, \, T = 298 \text{ K and } D = 2.0 \times 10^{-7} \text{ m}^2/\text{s}. \) The characteristic frequencies for the system are \( \omega_k = \omega_0 = \omega_0 = 2 \times 10^{10} \text{ rad/s and } \omega_0 = \omega_0 = 2 \times 10^{10} \text{ rad/s}. \)

After analyzing the differences between DLWF and THEOF for all zeta potentials and \( \kappa \alpha \) we found that the best fit between DLWF and THEOF for any zeta potential and any \( \kappa \alpha \) was obtained by choosing:

\[ r_1 = a + \delta_1 \kappa^{-1}, \quad \delta_1 = \frac{2.5}{1 + 2 \exp(-\kappa \alpha)}. \] (68)

\( \delta_1 \) is also the value found by Ohshima [8] who proposed a simple analytical formula for the mobility of a colloidal sphere for low zeta potentials in static (DC) fields. Ohshima's formula agrees within less than 1% with Henry's formula for all \( \kappa \alpha \) and \( \varepsilon_\eta/kT < 1. \)

6.1. Comparison between DLWF and THEOF for all \( \kappa \alpha \)

(i) For frequencies such that \( \omega < \omega_k < \omega_0 \) (which implies that \( \kappa \alpha < 1 \)) we find that for any zeta potentials \( \tilde{K}_U \simeq -K_m \varepsilon_c, \text{THEOF reduces to } \beta_{\text{THEOF}} \simeq -1/2 - m I_{c,eq} (\varepsilon_\eta/kT). \) For \( \kappa \alpha \ll 1, \) any zeta potential, we have \( a/r_1 \ll 1. \) We therefore find:

\[ u_i^+ = -\frac{2 \varepsilon_0 \varepsilon_1 \xi}{3 \eta} E_0. \] (70)

which is the Hückel limit for a particle with a large double layer. Note that the minus sign comes from the fact that \( u_i^+ \) represents minus the electrophoretic mobility of the particle. This is illustrated in Fig. 4A.

(ii) For frequencies such that \( \omega < \omega_k < \omega_0 \) (which implies that \( \kappa \alpha > 1 \)), we find that for any zeta potentials \( \tilde{K}_U \simeq -3m I_{c,eq} (\varepsilon_\eta/4kT) \) and THEOF reduces to:

\[ \beta_{\text{THEOF}} \simeq 1 + \frac{I_{c,eq} - 3m I_{c,eq} (\varepsilon_\eta/2kT)}{2 + 4I_{c,eq} - 3m I_{c,eq} (\varepsilon_\eta/2kT)}. \] (71)

For \( \kappa \alpha \gg 1 \) we get \( \beta_{\text{THEOF}} \simeq -1/2 \) for any zeta potential. We therefore find:

\[ u_i^+ = -\frac{\varepsilon_0 \varepsilon_1 \xi}{\eta} E_0. \] (72)

which is the Smoluchowski limit for a particle with a thin double layer. Again, the minus sign comes from the fact that \( u_i^+ \) represents minus the electrophoretic mobility of the particle. This is illustrated in Fig. 4C. We find that DLWF shows the same trend but we were unable to run the numerical simulations for \( \kappa \alpha > 200. \) Better estimations of \( u_i^+ \text{DLWF} \) than ours exist for \( \kappa \alpha \gg 1. \) In Fig. 4A we plotted for instance the values according to the formula of O'Brien and Hunter (see [21], Eq. (67)). However, using this better estimation of \( u_i^+ \text{DLWF} \) in Eq. (64) did not lead to an improvement of the agreement between \( \beta_{\text{DLWF and THEOF. Moreover O'Brien and Hunter's formula does not give good estimates of } u_i^+ \text{DLWF for } \varepsilon_\eta/kT < 3. \) For higher frequencies, we find that the agreement between \( u_i^+ \text{DLWF and THEOF and } \beta_{\text{DLWF and THEOF is very good (Figs. 4C and 4D).} \)

6.2. Comparison between DLWF and THEOF for all \( \zeta \)

(i) For potentials such that \( \varepsilon_\eta/kT \ll 0.1, \) DLWF and THEOF overlap for all zeta's, frequencies and \( \kappa \alpha \) and are equal to \( (K_2 - K_1)/(K_2 + 2K_1). \)

(ii) For potentials such that \( \varepsilon_\eta/kT < 1, \) we find in good approximation that \( \beta_{\text{DLWF and THEOF}} \simeq -1/2 \) for the whole range of frequencies and \( \kappa \alpha \) and therefore:

\[ u_i^+ = \frac{2 \varepsilon_0 \varepsilon_1 \xi}{3 \eta} \left[ 1 + \frac{1}{2(1 + \delta_1 \kappa^{-1})^2} \right] E_0. \] (73)

This expression is to be compared with the expression found by Ohshima [8] (Eq. (27), p. 25) who proposed a simple analytical formula for the mobility of a colloidal sphere for low zeta potentials in static (DC) fields. We observe that the formula still applies for (AC) frequencies. Ohshima's formula agrees within less than 1% with Henry's formula for all \( \kappa \alpha \) and \( \varepsilon_\eta/kT < 1. \) (Note that the minus sign difference between the two formula comes from the fact that \( u_i^+ \) represents minus the electrophoretic mobility of the particle.) For \( \kappa \alpha \gg 1, \) \( u_i^+ \text{THEOF} \) reduces to the Hückel formula (with a minus sign):

\[ u_i^+ = -(2\varepsilon_0 \varepsilon_1 \xi)/(3\eta). \]
Fig. 4. (A and C) Real part of normalized mobility $|u^+|/(\varepsilon_0 \varepsilon_1 \kappa)$ as a function of $\kappa a$. (B and D) real part of $(\beta + 1/2)$ as a function of $\kappa a$. DLWF (symbols), THEOF (full line), O’Brien and Hunter’s theory for the electrophoretic mobility (valid at high $\kappa a$) (dashed lines). For (A) and (B) we evaluated $\beta$ and $u^+$ at frequencies such that $\omega \ll \min[\omega a, \omega \kappa]$. The values of $\beta$ and $u^+$ are constant is that region and Im($\beta$) and Im($u^+$) negligible compared to Re($\beta$) and Re($u^+$). For (C) and (D) we used $\omega = 10^6$ rad/s.

(iii) For potentials such that $e\zeta/kT \geq 1$, $\beta_{DLWF}$ and $\beta_{THEOF}$ agree in magnitude and behavior for all frequencies and $\kappa a$. When $\omega_\kappa > \omega_\kappa (\kappa a \geq 1)$ the difference between $\beta_{DLWF}$ and $\beta_{THEOF}$ is of only a few percents.

In Fig. 5 it is shown how $\beta_{DLWF}$ and $\beta_{THEOF}$ agree for all $\kappa a \geq 1$, frequencies and $e\zeta/kT = 4$. Both the theories of Hinch et al. and O’Brien were included in the figures. As was already found in [2] those theories are in agreement with $\beta_{DLWF}$ for $\kappa a \gg 1$ only. This is due to the fact that both Hinch and O’Brien’s lack a term equivalent to $a/r_1$ in their expressions. For small $\kappa a$ we have $a/r_1 \ll 1$ and this leads the very high values of $\beta_{THEOF}$ observed for small $\kappa a$ at low frequencies. For $\kappa a \gg 1$, $a/r_1 \approx 1$ and $\beta_{THEOF}$ reduces to Eq. (71) for low frequencies with $3m_{\text{eq}}(e\zeta/2kT)$ in both the numerator and denominator of $\beta_{THEOF}$. O’Brien and Hinch et al. find a somehow similar contribution. For $e\zeta/kT < 2$, however, similar deviations as the ones described in Section 4 occur and neither Hinch et al.’s nor O’Brien’s theory correctly predict $\beta_{DLWF}$ for any $\kappa a$.

7. Generalization to ellipsoids

Extending the results obtained for spheres to spheroidal (or ellipsoidal) particles is quite straightforward. We show in Appendix A how to derive the expression of the dipolar coefficient of spheroids (prolate and oblate). We hereby make the assumption that the particle can be modeled by a succession of confocal (spheroidal) shells of different complex conductivities. We then obtain the general formula (1) given in Section 1, which is valid for all frequencies, $\kappa a \geq 1$ and zeta potentials. As stated in the introduction and Appendix A, we have now defined $a = \min[a_p, a_n]$, where $2a_p$ is the length along the axis of revolution of the spheroid and $2a_n$ the maximum cross-sectional diameter normal to the axis of symmetry.

The only analytical formula for ellipsoids existing so far is due to O’Brien and Ward [7].3 Their theory is valid for $\kappa a \gg 1$ and DC

---

3 We note two misprints in the article of O’Brien and Ward: the $\pi$ in their Eq. (4.9) should be deleted and there is a minus sign missing in front of Eq. (4.14).
Fig. 5. Real and imaginary part of the dipolar coefficient $\beta$ as a function of frequency for $\varepsilon\eta/kT = 4$ and $\kappa a = 1$ (1), $\kappa a = 10$ (2) and $\kappa a = 50$ (3), as calculated by: THEOF (C), O'Brien's theory (O), Hinch et al.'s theory (H), DLWF (symbols).

In order to avoid confusion with the symbols used in this article, we will use the symbol $K_W^{\parallel}$ for the variable defined as $\beta$ in their article (Eq. (2.5) in [7]) and $K_1^{\parallel}$ for their symbol $K_1$ (Eq. (4.15) in [7]). In the case of a symmetric electrolyte:

$$K_1^{\parallel} = 2(1 + 3m)[\exp(e|\eta|/2kT) - 1]/\kappa a.$$  (74)

O'Brien and Ward used spheroidal coordinates to express their dipolar coefficient. In order to compare to the notations used in
this article, we give here Eq. (4.14), p. 408 of [7] as a function of the depolarization factor $L^{\text{OBL}}_p$:

$$f^0(K^W) = \frac{-1 + 3K^W \sinh(\xi_0)K^W}{3(1 - L^{\text{OBL}}_p) - 9L^{\text{OBL}}_pK^W \sinh(\xi_0)K^W/2}. \quad (75)$$

$$L^{\text{OBL}}_p = -\cos^2(\xi_0)Q_1 = 1 - \sinh(\xi_0)\cos^2(\xi_0)Q_1'. \quad (76)$$

The expressions for $K^W$ given in Eqs. (76) and (A.8) are equivalent. Similar expressions can be obtained for $K^O$ and $L^O$ and the corresponding $f^0(\beta)$, $f^1(\beta)$ (Eqs. (4.9), (4.11), (4.17), p. 408 of [7]). More general forms of the depolarization factors can be found in [22].

If we use the same assumptions as O'Brien and Ward, this implies in our notation that: $K_1 = K^W \times K_1$, $K_1 = K_1$, $K_\perp = K_U = K_2 = 0$ and $\alpha/r_0 = 1$. Equation (1) then reduces to:

$$\beta_W = \frac{-1 + 3(1 - L^{\text{OBL}}_p)K^W}{3(1 - L^{\text{OBL}}_p) + 9L^{\text{OBL}}_p(1 - L^{\text{OBL}}_p)K^W}. \quad (77)$$

Comparing Eqs. (75) and (77) we note that in order to get an equivalence $K^W$ needs to satisfy the relation: $\sinh(\xi_0)K^W/2 = 1 - L^{\text{OBL}}_p$. Similar relations are obtained for the other parameters in Eqs. (4.9), (4.11), (4.17), p. 408 of [7]. We also have a minus sign difference between $f^0(K^W)$ and $\beta$ which stems from the definitions of these variables (see Eqs. (4) and (28) in this article and Eq. (4.3) in [7]).

In Fig. 6A we plotted $f^0$ as a function of $K^W$ and in Fig. 6B as a function of the aspect ratio $(\alpha_p/\alpha_n)$. We find that even if the values found from the numerical evaluations of O'Brien and Ward are close to those found from Eq. (77), the relation $\sinh(\xi_0)K^W/2 = 1 - L^{\text{OBL}}_p$ is not satisfied. This means that the relation found by O'Brien and Ward deviates from the Clausius–Mossotti form we find for $\beta_W$ (which originates from the assumption of confocal spheroids). We also find a deviation from a Clausius–Mossotti type of equation for $K^W \approx 0$ (which occurs for $\kappa a > 100$ when $\epsilon(\zeta)/\kappa T = 4$ for example) we find that both $(-f^0)$ and $\beta_W$ reduce to $-1/3(1 - L^{\text{OBL}}_p)$. This is illustrated in Fig. 6A. For $K^W \gg 1$ (which occurs for very high $\epsilon(\zeta)/\kappa T$) we find that both $(-f^0)$ and $\beta_W$ reduce to $1/(3L^{\text{OBL}}_p)$.

We refer to [7] for the procedure used by O'Brien and Ward to calculate their full expression of the dipolar coefficient $\beta$. We used their approximate formulation (4.9)-(4.18) and derived $\beta$ from Eq. (4.7).

In our case we calculate $\beta = (\beta_p + 2\beta_n)/3$ using Eq. (1) without extra conductances, which gives:

$$\beta_i = \frac{K_2 - K_1 + 3(1 - L_i)(K_1 + K_U) + 3L_iK_\perp}{2K_1 + 3L_i(K_2 - K_1) + 9L_i(1 - L_i)(K_1(a/r_0)^3 + K_U(a/r_1)^3 - K_\perp)} \quad (i = n, p). \quad (78)$$

We will use the abbreviations:

THEOW: O'Brien and Ward’s approximate formulæ [7]:

THEOFE: semi-analytical formula (78) with $\beta = (\beta_p + 2\beta_n)/3$.

We use $\gamma = \ell_\text{eq}/\ell_\text{eq}$, $\ell_\text{eq}$ and $\ell_\text{eq}$ were evaluated numerically. Moreover $\alpha = 100$ nm (we calculated $\alpha_p$ and $\alpha_n$ accordingly), $\eta = 0.89 \times 10^{-3}$ Pas, $\xi_1 = 78$, $\xi_2 = 2$, $T = 298$ K and $D = 2.0 \times 10^{-9}$ m$^2$/s. The characteristic frequencies for the system are $\omega_p = D\kappa^2 = 2.0 \times 10^5$ rad/s and $\omega_n = D/a^2 = 2.0 \times 10^5$ rad/s.

7.1. Comparison between THEOW and THEOFE

In Fig. 7A we plotted THEOW and THEOFE for $\kappa a \geq 1$, $\omega < \min(\omega_p, \omega_n)$ and $\epsilon\xi/kT = 4$. We also included the values found from DLWF for spheres. The theory of O'Brien and Ward is valid for high $\kappa a$ and it is therefore not surprising that it does not correctly reproduce the value found from DLWF for $\kappa a = 2$. We also note that O'Brien and Ward did not include terms corresponding to $K_U$ and $K_\perp$ in their derivation. A term corresponding to $K_\perp$ was also found by Hinch in the case of spheres. If we would remove this term from the formula of Hinch, the solutions found from O'Brien's theory for spheres [15] (which does not take into account $K_\perp$ neither) and the modified formula of Hinch would overlap at low frequencies. This would lead to a substantial error, as can be seen in Fig. 5: for low frequencies and $\kappa a > 10$, Hinch’s theory predicts DLWF within a reasonable accuracy, whereas O’Brien’s theory does not.

(i) For spheres ($a_p = a_n = a$) and $\kappa a > 10$ both THEOW and THEOFE agree with DLWF and overlap in fairly good accuracy. 

Please cite this article in press as: C. Chassagne, D. Bedeaux, J. Colloid Interface Sci. (2008), doi:10.1016/j.jcis.2008.06.055
In the case of oblate spheroids \( (\omega \ll 1) \) for \( J_{\text{OW}} \) and \( J_{\text{OF}} \) also overlap in quite good accuracy. For \( \omega \ll 1 \) we find in good approximation \( L_p \approx 1 \) which leads to:

\[
\beta_p^{\text{OBL}} = -1/\left[ 3(1 - L_p) \right] \to -\infty, \quad (81)
\]

\[
\beta_n^{\text{OBL}} = -1/3 + \left[ \tilde{K}_1 + \tilde{K}_U \right]/K_1. \quad (82)
\]

The fact that \( \beta_p^{\text{OBL}} \) goes to infinity for \( \omega \ll 1 \) is linked to the difficulty in evaluating \( \beta_p^{\text{OBL}} \) numerically and is discussed by O’Brien and Ward, p. 407 of [7].

For \( \kappa a \gg 1 \) we get \( \beta_n^{\text{OBL}} \approx -1/3 \). We checked that both \( J_{\text{OW}} \) and \( J_{\text{OF}} \) give the same results in this limit. (iv) In Fig. 7B we plotted \( J_{\text{OF}} \) and \( J_{\text{DF}} \) for \( \kappa a \gg 1 \), \( \omega = 10^6 \) rad/s and \( e\epsilon_0/kT = 4 \). In that case we have in good approximation \( \tilde{K}_1 \ord{\kappa a} \), \( \tilde{K}_2 \ord{\kappa a} \), and \( \tilde{K}_L \ord{\kappa a} \). For \( \kappa a \gg 1 \) we find:

\[
\beta_1 \simeq \frac{K_2 - K_1 + 3(1 - L_1)K_1e_{\text{eq}}[1 - 3m(e\epsilon_0/kT)]}{3K_1 + 3L_1(K_2 - K_1) + 9L_1(1 - L_1)K_1e_{\text{eq}}[1 - 3m(e\epsilon_0/kT)]}. \quad (83)
\]

8. Conclusion

The behavior of the dipolar coefficient arising from a dielectric sphere immersed in an electrolyte solution has been investigated for a wide range of zeta potentials, ionic strengths and frequencies. From this study, it can be concluded that the values found from the newly derived analytical theory (see Eq. (64) for the general expression) overlap with a good accuracy the ones found using the numerical code based on Delaney and White’s for the whole very broad range of frequencies, ionic strengths and zeta potentials investigated.

The results for spheroidal particles were also presented and compared to the analytical formula of O’Brien and Ward [7] in the range where their results were applicable (\( \kappa a \approx 1 \) and \( \omega \approx 0 \)).

The most general formula we obtain is given by Eq. (1) in the introduction. This formula is valid for all frequencies, \( \kappa a \approx 1 \) and zeta potentials. As explained in the preceding section, however, caution should be taken in some limiting cases: for oblate spheroids with a very small aspect ratio \( a_p/a_n \), one can get the situation that \( \kappa a_p \) is small whereas \( \kappa a_n \) is large and the definition of \( \kappa a \equiv \min[\kappa a_p, \kappa a_n] \) should be reconsidered. It then remains to be tested if the theory we propose still gives a reasonable approximation of \( \beta \).

Acknowledgments

We would like to thank Prof. A. Delgado of the Department of Applied Physics of the University of Granada (Spain) for his kind hospitality and fruitful discussions. We are especially grateful to him and his collaborators for making the numerical code based on Delaney and White’s available.

Appendix A

Let us consider two confocal spheroids with symmetry axes \( b_0 \) and \( b_1 \) and axis normal to the symmetry axis \( a_0 \), \( a_1 \) (see Fig. 8). The volume corresponding to the spheroid \( i \) (\( i = 0, 1 \)) is

\[
V_i = \frac{4}{3} \pi a_i^3 b_i. \quad \text{(A.1)}
\]

The volume fraction of the inner spheroid in the outer spheroid is

\[
\varphi \equiv \frac{V_0}{V_1} = \frac{a_0^2/b_0}{a_1^2/b_1} = 1 - x. \quad \text{(A.2)}
\]
It should be emphasized that it is not assumed that \( x \) is much smaller than 1.

The complex frequency dependent conductivities in the inner spheroid (“shell A”), in the region between the two spheroids (“shell B”) and outside the outer spheroid (“region C”) are \( K_A, K_B \) and \( K_C \), respectively. In order to calculate the dielectric response of the spheroid made of the superposition of shells \( A \) and \( B \), one may attribute to the spheroid an equivalent complex conductivity \( \tilde{K}_{AB} \) given by:

\[
\frac{\tilde{K}_{AB} - \tilde{K}_B}{\tilde{K}_B + 3L_i(\tilde{K}_{AB} - \tilde{K}_B)} = \phi \frac{\tilde{K}_A - \tilde{K}_B}{\tilde{K}_B + 3L_i(\tilde{K}_A - \tilde{K}_B)},
\]

where \( L_i \) are the depolarization factors. \( i = p \) indicates the direction along and \( i = n \) indicates the direction normal to the symmetry axis of the spheroid. The dipolar coefficient is obtained from:

\[
\beta_i = \frac{K_A - K_B}{3K_C + L_i(K_A - K_C)}.
\]

From Eqs. (A.3) and (A.4) we get:

\[
\beta_i = \frac{K_A - K_B + x(\tilde{K}_B - \tilde{K}_A)(\tilde{K}_B(1-L_i) + \tilde{K}_C L_i)/\tilde{K}_B}{3\tilde{K}_C + 3L_i(\tilde{K}_A - \tilde{K}_C) + x(\tilde{K}_B - \tilde{K}_A)3(1-L_i)L_i(\tilde{K}_B - \tilde{K}_C)}/\tilde{K}_B.
\]

For \( m = b_0/a_0 (= b_1/a_1) > 1 \), which is the case of prolate spheroids, the depolarization factor \( L_i \) are given by

\[
L_{p}^{\text{PRO}} = 1 - 2L_n^{\text{PRO}} = \frac{1}{1 - m^2} + \frac{m}{(m^2 - 1)^{3/2}} \ln(m + (m^2 - 1)^{1/2}).
\]

For \( m = b_0/a_0 (= b_1/a_1) = 1 \), which is the case of spheres, the depolarization factor \( L_i \) is given by

\[
L_p = 1 - 2L_n = 1/3.
\]

For \( m = b_0/a_0 (= b_1/a_1) < 1 \), which is the case of oblate spheroids, the depolarization factor \( L_i \) is given by

\[
L_{p}^{\text{OBL}} = 1 - 2L_n^{\text{OBL}} = \frac{1}{1 - m^2} - \frac{m}{(1 - m^2)^{3/2}} \arccos(m).
\]

By identification of Eq. (A.5) taking \( L_p = L_n = 1/3 \) with Eq. (49), which is the expression for \( \beta \) we obtained for spheres for \( \kappa a > 10 \), we find that:

\[
\tilde{K}_A = \tilde{K}_B,
\]

\[
\tilde{K}_C = \tilde{K}_A,
\]

\[
\tilde{K}_C = x(\tilde{K}_B - \tilde{K}_A)/3,
\]

\[
\tilde{K}_{OBL} = x(\tilde{K}_B - \tilde{K}_A)/3(\tilde{K}_B).
\]

Using the general form of Eq. (A.5) this identification leads to:

\[
\beta_i = \frac{2\tilde{K}_B - 1 + (1-L_i)\tilde{K}_A + 3L_i\tilde{K}_C}{3\tilde{K}_C + 3L_i(\tilde{K}_B - \tilde{K}_C) + 9L_i(1-L_i)\tilde{K}_C/\tilde{K}_B}.
\]

However, we have found that Eq. (49) had to be corrected in order to be valid for \( \kappa a < 10 \) and in order to account for fluid flow. These corrections lead to the inclusion of \( \tilde{K}_U \) and the correcting factors \( (a/r_0)^3 \) and \( (a/r_1)^3 \) in the denominator of \( \beta \) and resulted into Eq. (A.5). From including these corrections in Eq. (A.10) we get:

\[
\beta_i = \frac{2\tilde{K}_B - 1 + (1-L_i)\tilde{K}_A + 3L_i\tilde{K}_C}{3\tilde{K}_C + 3L_i(\tilde{K}_B - \tilde{K}_C) + 9L_i(1-L_i)\tilde{K}_C/\tilde{K}_B}.
\]

We define \( a = \min(a_p, a_o) \), where \( 2a_p \) is the maximum cross-sectional diameter normal to the axis of symmetry. We have \( m = a_p/a_n \).

References