Dielectric Enhancement of Charged Nanospheres Dispersed in an Electrolyte[†]

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Using a method introduced by Albano et al (Albano, A. M.; Bedeaux, D.; Vlieger, J. *Phys. A* **1979**, *99*, 293. Albano, A. M.; Bedeaux, D.; Vlieger, J. *Phys. A* **1980**, *102*, 105), we derive an exact analytic expression for the dipolar coefficient of a charged sphere in an electrolyte as a function of the frequency which is valid for all double layer thicknesses and is given both for low and for high zeta potentials. The expression is found to have the same form as the expression for a sphere surrounded by a multiple of shells of different complex conductivities. One shell can then be attributed to the double layer and another to a diffusion layer. Including a Stern layer in the model subsequently adds another shell with associated complex dielectric permittivity.

1. Introduction

The experimental and theoretical study of the behavior of charged colloidal particles in applied oscillating electric fields has a history of almost a century. For the early history, we refer to O'Konski,[1] who in 1960 presented a model for the strong dielectric enhancement observed in experiments at low frequencies using a surface conductivity. Subsequently, Dukhin[2] derived an expression for this parameter for the case of symmetric electrolytes in the thin double layer limit. His analysis was extended to nonsymmetric electrolytes by Hinch et al.[3] and by O'Brien.[4,5] A critical review and extension is given by Fixman.[6,7] See also refs 8 and 9 for further references. In 1981, DeLacey and White[10] numerically solved the fundamental set of equations governing the system. Their theory was improved by Mangelsdorf and White[11] so as to be valid at high frequencies. The concept of a Stern layer conductivity along the surface was introduced in order to improve the agreement between theory and experiment.[12,13]

In the present paper, we will present an analysis valid for arbitrary double layer thicknesses. Beyond the double layer, the asymptotic behavior (far from the particle) of the fields, densities, and ion fluxes is described by the linearized equations. The asymptotic solution can be extrapolated back through the double layer to the surface of the particle. This makes it possible to rigorously define "excess densities, ionic fluxes, and electromagnetic fields" describing the double layer.[14,15] This replaces the double layer by not previously derived boundary conditions. As shown in refs 14 and 15, the solution using these boundary conditions gives the exact amplitudes of the asymptotic fields. This results in an exact expression for the dipolar coefficient containing no free parameters other than the ζ-potential. Our results reduce to O'Brien's[4,5] in the thin double layer and in the large ζ-potential case. We find corrections to expressions given in ref 8, in which an expansion in the magnitude of the ζ potential is used.

In the second section, we review the standard equations needed in the further analysis. In the third section, we give the new boundary conditions containing the excess densities, fluxes, and electromagnetic fields. These are calculated for small ζ potentials, and for large ζ potentials in the fourth section, and we subsequently calculate the complex dipolar coefficient, both for small and large ζ potentials. The modifications due to a possible conductivity of the Stern layer are given. Our main result is the expression (92) for the dipolar coefficient of the particles which is found to have the same form as the expression for a sphere surrounded by a multiple of shells, representing respectively the Stern layer, the double layer, and the diffusion layer. In the last section, we compare the results of our theory with earlier results. Furthermore, we give examples of the behavior of the dipolar coefficient in some typical cases and discuss this in terms of the various contributions.

2. Governing Equations

2.1. Equilibrium Double Layer. The governing equations we present here are the same as those used in classical treatment of the problem (see, for instance, refs 2, 3, 8, and 10). The difference between the classical treatment and ours will arise in the next section on boundary conditions. We will consider spherical particles with a radius *a*. This radius may be larger than, comparable to, or smaller than the thickness of the double layer around the particle, which is given by the Debye length κ^{-1}.

The flux of ions around a (charged) particle can be described by the Nernst−Planck equation:

$$\mathbf{J}_i = n_i\mathbf{u} - D_i\left(n_i\frac{z_ie}{kT}\nabla\Psi + \nabla n_i\right) \tag{1}$$

The ions are carried along by the fluid and diffuse relative to the fluid under the influence of the electric and thermodynamic forces, via the gradient terms. Here n_i is the number of ions of type *i* and valence z_i per unit of volume, $i = +$ and $-$. Furthermore, $\mathbf{u}$ is the fluid velocity, $D_i = kT/f_i$ is the diffusion coefficient, where $f_i = 6\pi\eta a_i$ is the Stokes drag coefficient, η

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is the viscosity of the medium, a_i is the radius of the ion i, and Ψ is the electric potential. Conservation of ions gives

$$\frac{\partial n_i}{\partial t} + \nabla.\mathbf{J}_i = 0 \tag{2}$$

The charge density is related to the electric potential Ψ via Poisson's equation:

$$\Delta\Psi \equiv \nabla^2\Psi = \frac{-1}{\epsilon_1\epsilon_0}\sum_i z_i e n_i \tag{3}$$

where ϵ_1 is the relative dielectric permittivity of the solvent. Because of the electro-neutrality of the salt we have

$$\sum_i \nu_i z_i = 0 \tag{4}$$

where the $\nu_i's$ are the stoichiometric coefficients of the resulting ions.

In the absence of external applied electric field, the equilibrium charge densities are given by the Boltzmann distribution:

$$n_{i,\text{eq}}(\mathbf{r}) = \nu_i n_\infty \exp\left(\frac{-z_i e \Psi_{\text{eq}}(\mathbf{r})}{kT}\right) \tag{5}$$

where n_∞ is the salt concentration in the solution. The subscript eq stands for "equilibrium values in the absence of an external electric field". Substitution of the Boltzmann distribution in the Poisson equation results in the Poisson–Boltzmann equation:

$$\Delta\Psi_{\text{eq}}(\mathbf{r}) = \frac{-e n_\infty}{\epsilon_1\epsilon_0}\sum_i \nu_i z_i \exp\left(\frac{-z_i e \Psi_{\text{eq}}(\mathbf{r})}{kT}\right) \tag{6}$$

In the thin double layer approximation, the surface is in good approximation flat. In that case, this expression can be integrated, but we will not use this approximation. At low potentials ($\Psi \ll kT/e \simeq 26$ mV), this expression can be linearized and gives the Debye–Hückel approximation. In the case of spherical symmetry, the solution reads

$$\Psi_{\text{eq}}(r) = \frac{\zeta a}{r}\exp(-\kappa(r-a)) \tag{7}$$

where $\zeta = \Psi_{\text{eq}}(a)$ is the zeta potential and where the inverse Debye length κ is given by

$$\kappa^2 \equiv \frac{e^2 n_\infty}{\epsilon_1\epsilon_0 kT}\sum_i \nu_i z_i^2 \tag{8}$$

In the same low potential approximation, we have

$$n_{i,\text{eq}}(r) = \nu_i n_\infty\left\{1 - \frac{z_i e \zeta}{kT}\frac{a}{r}\exp[-\kappa(r-a)]\right\} \tag{9}$$

for the equilibrium ion densities.

2.2. Equations in the Presence of an External Electric Field. An oscillating electric field $E_0\exp(i\omega t)$ is applied which is directed along the z axis. The field strength is weak compared with the electric fields within the double layer. Typically, in dielectric spectroscopy measurements

$$E_0 < \frac{100\text{ V}}{1\text{ cm}} \ll \zeta\kappa \simeq \frac{26\text{ mV}}{10\text{ nm}} \tag{10}$$

The various equations can therefore be linearized around the

equilibrium values of the electric potential and the densities.[8−10] In view of the linearity, all variations of the various quantities around equilibrium are proportional to $\exp(i\omega t)$. This factor will for ease of notation therefore further be suppressed. We write

$$\Psi \equiv \Psi_{\text{eq}} + \delta\Psi$$
$$n_i \equiv n_{i,\text{eq}} + \delta n_i \tag{11}$$

The Nernst–Planck equation becomes to linear order

$$\mathbf{J}_i = n_i\mathbf{u} - \frac{D_i}{kT}n_{i,\text{eq}}\nabla\left(z_i e\delta\Psi + kT\frac{\delta n_i}{n_{i,\text{eq}}}\right) \tag{12}$$

The term between brackets is the first-order perturbation of the electrochemical potential. Substitution in the conservation law gives

$$\frac{\partial n_i}{\partial t} - \mathbf{u}.\nabla n_i = D_i\nabla.\left[n_{i,\text{eq}}\nabla\left(\frac{z_i e}{kT}\delta\Psi + \frac{\delta n_i}{n_{i,\text{eq}}}\right)\right] \tag{13}$$

where we used that the fluid is incompressible, $\nabla.\mathbf{u} = 0$. The Poisson equation becomes

$$\Delta\delta\Psi = \frac{-1}{\epsilon_1\epsilon_0}\sum_i z_i e\delta n_i \tag{14}$$

To simplify calculations, we work in the rest frame of the particle. This implies that

$$\mathbf{u} = 0 \quad\text{for}\quad r = a$$
$$\mathbf{u} = -\mathbf{u}_{\text{el}} \quad\text{for}\quad r \to \infty \tag{15}$$

where $\mathbf{u}_{\text{el}}$ is the electrophoretic velocity of the particle. The electrophoretic velocity due to the applied oscillating electric field is small compared to the velocities of the ions. Their relative size is of the order of the relative size of the ions and the particle. We may therefore neglect $\mathbf{u}.\nabla n_i$ in the calculation of the dipolar coefficient.

2.3. Solution Outside the Double Layer. The superscript $+$ is used to indicate the value of the asymptotic solution beyond the double layer. Beyond the double layer, the asymptotic behavior of the solution is found by replacing $n_{i,\text{eq}}$ by $\nu_i n_\infty$ in eq 13 and use eq 14. This results in

$$\Delta\delta n_i = \frac{i\omega}{D_i}\delta n_i + \frac{\nu_i z_i e^2 n_\infty}{\epsilon_0\epsilon_1 kT}\sum_j z_j\delta n_j \tag{16}$$

This equation can be written more conveniently in a matrix form

$$\Delta\begin{pmatrix}\delta n_+\\\delta n_-\end{pmatrix} = \begin{bmatrix}i\omega D_+^{-1} + \kappa_0^2\nu_+z_+^2 & \kappa_0^2\nu_+z_+z_-\\\kappa_0^2\nu_-z_-z_+ & i\omega D_-^{-1} + \kappa_0^2\nu_-z_-^2\end{bmatrix}\begin{pmatrix}\delta n_+\\\delta n_-\end{pmatrix} \tag{17}$$

with $\kappa_0^2 = e^2 n_\infty(\epsilon_0\epsilon_1 kT)^{-1}$. The eigenvectors, δn_n and δn_c, and eigenvalues, λ_n^2 and λ_c^2, of this matrix satisfy

$$\Delta\delta n_n = \lambda_n^2\delta n_n \quad\text{and}\quad \Delta\delta n_c = \lambda_c^2\delta n_c \tag{18}$$

For frequencies such that $\omega \ll D_\pm\kappa^2$, to which most experiments are restricted, the eigenvectors reduce to first order to

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$$\delta n_n = \delta n_+ - \delta n_- \left(\frac{z_+}{z_-}\right)\left[1 + \frac{i\omega}{\kappa^2}(D_+^{-1} - D_-^{-1})\right]$$

$$\delta n_c = \delta n_+ - \delta n_-\left[1 - \frac{i\omega}{\kappa^2}(D_+^{-1} - D_-^{-1})\right] \quad (19)$$

and the eigenvalues to

$$\lambda_n^2 = i\omega\left(\frac{z_+/D_- - z_-/D_+}{z_+ - z_-}\right) \equiv \frac{i\omega}{D_m}$$

$$\lambda_c^2 = \kappa^2 + i\omega\left(\frac{z_+/D_+ - z_-/D_-}{z_+ - z_-}\right) \quad (20)$$

D_m is the weighted harmonic average of the ionic diffusion coefficients. Expressions for larger values of the frequency may easily be given. Inverting this equation gives

$$\delta n_+ = \frac{1}{z_+ - z_-}\left[z_+ \delta n_c - z_- \delta n_n - \right.$$

$$\left. \frac{i\omega}{\kappa^2}(D_+^{-1} - D_-^{-1})\frac{2z_- z_+}{z_+ - z_-}(\delta n_c - \delta n_n)\right] \quad (21)$$

$$\delta n_- = (\delta n_c - \delta n_n)\frac{z_-}{z_+ - z_-}\left[1 - \frac{i\omega}{\kappa^2}(D_+^{-1} - D_-^{-1})\frac{z_+ + z_-}{z_+ - z_-}\right] \quad (22)$$

The resulting charge density is

$$\delta\rho = e(z_+\delta n_+ + z_-\delta n_-) = ez_+\delta n_c + \frac{ez_-}{z_+ - z_-}\left[z_+ + z_- - \right.$$

$$\left. \frac{i\omega}{\kappa^2}(D_+^{-1} - D_-^{-1})\left(\frac{2z_+^2 + z_+z_- + z_-^2}{z_+ - z_-}\right)\right](\delta n_c - \delta n_n) \quad (23)$$

The potential due to the external oscillating electric field is given by

$$\delta\Psi_0 = -E_0 r \cos\theta \quad (24)$$

The resulting variation of the ion densities and therefore of δn_n and δn_c will also be symmetric around the field direction and proportional to $\cos\theta$. The solution of eq 18 then becomes

$$\delta n_n = C_n\frac{1 + \lambda_n r}{r^2}\exp[-\lambda_n(r - a)]\cos\theta \quad (25)$$

$$\delta n_c = C_c\frac{1 + \lambda_c r}{r^2}\exp(-\lambda_c(r - a))\cos\theta \quad (26)$$

The first eigenvector is a diffusion mode and decays over a distance of the order $\sqrt{D_m/\omega}$. The second eigenvector δn_c decays over a typical Debye length due to the contribution κ^2 to the eigenvalue λ_c^2. Asymptotically, δn_c does not contribute to the solution, which therefore reduces to

$$\delta n_+^+ = -\frac{z_-\delta n_n}{z_+ - z_-}\left[1 - \frac{i\omega}{\kappa^2}(D_+^{-1} - D_-^{-1})\frac{2z_+}{z_+ - z_-}\right]$$

$$\delta n_-^+ = -\frac{z_-\delta n_n}{z_+ - z_-}\left[1 - \frac{i\omega}{\kappa^2}(D_+^{-1} - D_-^{-1})\frac{z_+ + z_-}{z_+ - z_-}\right] \quad (27)$$

The resulting charge density is

$$\delta\rho^+ = e(z_+\delta n_+^+ + z_-\delta n_-^+) = -\frac{ez_-\delta n_n}{z_+ - z_-}\left[z_+ + z_- - \right.$$

$$\left. \frac{i\omega}{\kappa^2}(D_+^{-1} - D_-^{-1})\left(\frac{2z_+^2 + z_+z_- + z_-^2}{z_+ - z_-}\right)\right] \quad (28)$$

For a symmetric electrolyte, $z_+ = -z_-$, the expression reduces to

$$\delta\rho^+ = -\frac{1}{2}\frac{i\omega}{\kappa^2}ez_+(D_+^{-1} - D_-^{-1})\delta n_n \quad (29)$$

For a symmetric electrolyte, the system is in good approximation electroneutral, as also found by Dukhin. For an asymmetric electrolyte, $z_+ \neq -z_-$, we find, as O'Brien[4,5] and Fixmann[6,7] do, that the charge density deviates from zero beyond the double layer.

The asymptotic solution of the Poisson equation beyond the double layer has the form

$$\delta\Psi^+ = \left(-E_0 r + \frac{P}{4\pi\epsilon_1\epsilon_0 r^2}\right)\cos\theta + A_n\delta n_n \quad (30)$$

The first term is the external electric field potential, the second term gives the dipole field, of strength P, far from the sphere, and the third term gives the contributions due to the ionic distribution around the sphere. We find from the Poisson equation

$$A_n = \frac{ez_-}{z_+ - z_-}\left[z_+ + z_- - \frac{i\omega}{\kappa^2}(D_+^{-1} - D_-^{-1})\right.$$

$$\left. \left(\frac{2z_+^2 + z_+z_- + z_-^2}{z_+ - z_-}\right)\right]\frac{1}{\epsilon_1\epsilon_0\lambda_n^2}$$

For a symmetric electrolyte, this expression reduces to

$$A_n = \frac{ez_+}{2\kappa^2}(D_+^{-1} - D_-^{-1})\frac{D_m}{\epsilon_1\epsilon_0} \quad (31)$$

The potential properly reduces to the external field potential when $r \to \infty$. For zero frequency, $\lambda_n = 0$. In that case, the second and the third term in the expression for the potential should be combined. This leads to a zero frequency polarizability which differs from the zero frequency limit of the finite frequency polarizability as was pointed out by O'Brien (see ref 4, page 213, and ref 8).

3. Boundary Conditions

3.1. Excess Quantities. Excess densities, fluxes, and fields are defined in terms of integrals over the full solution minus the extrapolated asymptotic solutions. We refer to refs 14 and 15 for a detailed discussion. The explicit expressions needed are given below. The analysis in refs 14 and 15 then gives the following boundary conditions for the extrapolated asymptotic fields at the surface of the particle:

$$i\omega\delta n_i^s(\theta) = -\nabla_\parallel \cdot \mathbf{J}_{i,\parallel}^s(\theta) - \mathbf{J}_{i,\perp}^+(a,\theta) \quad (32)$$

$$\epsilon_0\epsilon_2\left(\frac{\partial(\delta\Psi_2(r,\theta))}{\partial r}\right)_{r=a} - \epsilon_0\epsilon_1\left(\frac{\partial(\delta\Psi^+(r,\theta))}{\partial r}\right)_{r=a} = \delta\rho^s(\theta) \quad (33)$$

$$\epsilon_0 \delta\Psi^+(a,\theta) - \epsilon_0 \delta\Psi_2(a,\theta) = \delta P^s_\perp(\theta) \qquad (34)$$

The first condition expresses conservation of ions in the double layer. The second and the third are the usual conditions for the parallel electric and the normal displacement fields. The superscript s indicates the excess of the corresponding quantity in the double layer, and the subscripts $\parallel$ and $\perp$ indicate the components of a vector along and normal to the surface of the sphere, respectively, whereas the superscript $+$ indicates the value of the extrapolated asymptotic solution. Furthermore, $\delta\Psi_2$ is the variation of the electric potential, and ϵ_2 is the relative dielectric permittivity inside the sphere. $\delta\Psi_2$ is a solution of the Laplace equation and is for this case given by

$$\delta\Psi_2 = - E_2 r \cos\theta \qquad (35)$$

Below, we shall give definitions and derive explicit expressions for the excess quantities involved, and we will concentrate only on the case of low ζ potentials. The large ζ-potentials case will be reported in the fourth section. Calculations in that case can be performed in exactly the same way and are somewhat simplified due to cancellation of certain terms.

3.2. Excess Densities. The excess densities of the ions are found by integration through the double layer after subtracting the extrapolated asymptotic densities:[14,15]

$$n_i^s(\theta) \equiv \frac{1}{a^2} \int_a^\infty r^2[n_{i,eq}(r) - \nu_i n_\infty + \delta n_i(r,\theta) - \delta n_i^+(r,\theta)]\, dr \qquad (36)$$

For the contributions due to the external electric field, one has

$$\delta n_+^s(\theta) = \frac{1}{a^2} \int_a^\infty r^2[\delta n_+(r,\theta) - \delta n_+^+(r,\theta)]\, dr =$$

$$\frac{1}{a^2}\frac{z_+}{z_+ - z_-}\left[1 - \frac{i\omega}{\kappa^2}(D_+^{-1} - D_-^{-1})\frac{2z_-}{z_+ - z_-}\right]\int_a^\infty r^2 \delta n_c(r,\theta)\, dr$$

$$\delta n_-^s(\theta) = \frac{1}{a^2} \int_a^\infty r^2[\delta n_-(r,\theta) - \delta n_-^+(r,\theta)]\, dr =$$

$$\frac{1}{a^2}\frac{z_-}{z_+ - z_-}\left[1 - \frac{i\omega}{\kappa^2}(D_+^{-1} - D_-^{-1})\frac{z_+ + z_-}{z_+ - z_-}\right]\int_a^\infty r^2 \delta n_c(r,\theta)\, dr \qquad (37)$$

We here use that, for small ζ potentials, the solution across the double layer is given by the general expressions of δn_+ and δn_- in terms of δn_n and δn_c given in eqs 21 and 22. The first eigenvector δn_n decays over a distance of the order $\sqrt{D_m/\omega}$. This mode is therefore equal to its extrapolated asymptotic value δn_n^+ in the double layer and therefore does not contribute to the excess densities. This makes it possible to extrapolate this solution inside the double layer as practically constant. The second eigenvector δn_c decays over a typical Debye length. The extrapolated asymptotic solution δn_c^+ is therefore zero. Integration results in

$$\delta n_+^s(\theta) = \frac{z_+}{z_+ - z_-} C_c \frac{2 + \lambda_c a}{\lambda_c a^2}\left[1 - \frac{i\omega}{\kappa^2}(D_+^{-1} - \right.$$

$$\left. D_-^{-1})\frac{2z_-}{z_+ - z_-}\right]\cos\theta$$

$$\delta n_-^s(\theta) = \frac{z_-}{z_+ - z_-} C_c \frac{2 + \lambda_c a}{\lambda_c a^2}\left[1 - \frac{i\omega}{\kappa^2}(D_+^{-1} - \right.$$

$$\left. D_-^{-1})\frac{z_+ + z_-}{z_+ - z_-}\right]\cos\theta \qquad (38)$$

The resulting excess of the charge density of the double layer is

$$\delta\rho^s(\theta) = \frac{eC_c}{z_+ - z_-}\frac{2 + \lambda_c a}{\lambda_c a^2}\left[z_+^2 + z_-^2 - \frac{i\omega}{\kappa^2}(D_+^{-1} - \right.$$

$$\left. D_-^{-1})\frac{z_-(2z_+^2 + z_+ z_- + z_-^2)}{z_+ - z_-}\right]\cos\theta \qquad (39)$$

Remark: For the *equilibrium* contribution one finds for small ζ potentials

$$n_{i,eq}^s = \frac{1}{a^2}\int_a^\infty r^2(n_{i,eq}(r) - \nu_i n_\infty)\, dr =$$

$$-\frac{e\nu_i z_i n_\infty}{kTa^2}\int_a^\infty r^2 \Psi_{eq}(\mathbf{r})\, dr$$

$$= -\frac{e\nu_i n_\infty \zeta}{kTa}\int_a^\infty r \exp(-\kappa(r - a))\, dr$$

$$= -\nu_i n_\infty \left(\frac{ez_i\zeta}{kT}\right)\frac{1 + \kappa a}{a\kappa^2} \qquad (40)$$

In view of the cylindrical symmetry, none of the variables depends on φ. The resulting excess of the charge density of the double layer is

$$\rho_{eq}^s = -\frac{\zeta}{a}(1 + \kappa a)\epsilon_0 \epsilon_1 \qquad (41)$$

The equilibrium excess charge density of the double layer is, as expected, identical to minus the surface charge density, which can be deduced from the derivative of the equilibrium potential given in eq 7.

3.3. Excess Fluxes. For the excess diffusion fluxes along the curved surface of the sphere, we similarly have[14,15]

$$\mathbf{J}_{i,\parallel}^s(\theta) \equiv \frac{1}{a}\int_a^\infty r(\mathbf{J}_{i,\parallel}(r,\theta) - \mathbf{J}_{i,\parallel}^+(r,\theta))\, dr$$

$$= -\frac{D_i}{kT}\frac{1}{a}\int_a^\infty r\left[n_{i,eq}(r)\nabla_\parallel\left(z_i e \delta\Psi(r,\theta) + \right.\right.$$

$$\left.\left. kT\frac{\delta n_i(r,\theta)}{n_{i,eq}(r)}\right) - \nu_i n_\infty \nabla_\parallel\left(z_i e \delta\Psi^+(r,\theta) + kT\frac{\delta n_i^+(r,\theta)}{\nu_i n_\infty}\right)\right]\, dr \qquad (42)$$

where $\nabla_\parallel \equiv (1 - \mathbf{rr}/r^2)\nabla$ is the gradient operator parallel to the surface, and $\mathbf{1}$ is the unit matrix. The expressions inside the gradient are the electrochemical potentials. For these, it is common to make a local equilibrium assumption. We may therefore use that these terms vary slowly through the double layer and are therefore equal to their asymptotic values. We thus find

$$\mathbf{J}_{i,\parallel}^s(\theta) = -\frac{D_i}{kT}\frac{1}{a}\int_a^\infty r(n_{i,eq}(r) - $$

$$\nu_i n_\infty)\, dr\, \nabla_\parallel\left(z_i e \delta\Psi^+(a,\theta) + kT\frac{\delta n_i^+(a,\theta)}{\nu_i n_\infty}\right) \qquad (43)$$

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Using eq 9 for the equilibrium densities in the low ζ-potential case, we then obtain upon integration

$$\mathbf{J}_{i,\parallel}^{s}(\theta) = D_i \frac{ez_i\zeta}{kT\kappa}\nabla_{\parallel}\left(\frac{ez_i\nu_i n_{\infty}}{kT}\delta\Psi^{+}(a,\theta) + \delta n_i^{+}(a,\theta)\right) \quad (44)$$

The diffusion coefficients of the ions along the double layer may therefore be identified as

$$D_i^s = D_i \frac{ez_i\zeta}{kT\kappa} \quad (45)$$

The only component unequal to zero in this case is in the θ-direction and is given by

$$J_{i,\theta}^{s}(\theta) = D_i^s \frac{1}{a}\frac{\partial}{\partial\theta}\left(\frac{ez_i\nu_i n_{\infty}}{kT}\delta\Psi^{+}(a,\theta) + \delta n_i^{+}(a,\theta)\right) \quad (46)$$

For the electric flux along the surface this results in

$$\mathbf{I}_{\parallel}^{s}(\theta) = \sum_i ez_i \mathbf{J}_{i,\parallel}^{s}(\theta) = -\sum_i z_i eD_i^s\nabla_{\parallel}\left(\frac{ez_i\nu_i n_{\infty}}{kT}\delta\Psi^{+}(a,\theta) + \right.$$
$$\left. \delta n_i^{+}(a,\theta)\right) \quad (47)$$

The only component unequal to zero in this case is in the θ direction and is given by

$$I_{\theta}^{s}(\theta) = -\sum_i D_i^s\frac{z_i e}{a}\sin\theta\frac{\partial}{\partial\theta}\left(\frac{ez_i\nu_i n_{\infty}}{kT}\delta\Psi^{+}(a,\theta) + \delta n_i^{+}(a,\theta)\right) \quad (48)$$

As the diffusional force along the surface for the two ions is different for different ions, it is impossible to define an electric conductivity along the surface. The oscillating excess electric flux along the surface results in an oscillating excess charge density. Using charge conservation, we have

$$i\omega\delta\rho^{s}(\theta) = -\nabla_{\parallel}.\mathbf{I}_{\parallel}^{s}(\theta) - I_{\perp}^{+}(a,\theta) =$$
$$-\frac{1}{a\sin\theta}\frac{\partial}{\partial\theta}[\sin\theta I_{\theta}^{s}(\theta)] - I_{\perp}^{+}(a,\theta) \quad (49)$$

3.4. Excess Polarization Normal to the Surface. In the direction normal to the surface, the electric flux is given by

$$I_{\perp}(r,\theta) = \sum_i ez_i J_{i,\perp} = -\sum_i \frac{ez_i D_i}{kT}n_{i,eq}(r)\frac{\partial}{\partial r}\left(z_i e\delta\Psi(r,\theta) + \right.$$
$$\left. kT\frac{\delta n_i(r,\theta)}{n_{i,eq}(r)}\right) \quad (50)$$

Solving this equation for $\partial\delta\Psi(r,\theta)/\partial r$, we find

$$\frac{\partial}{\partial r}\delta\Psi(r,\theta) = -\frac{kT}{e^2}[\sum_i z_i^2 D_i n_{i,eq}(r)]^{-1} \quad (51)$$
$$\times\left[I_{\perp}(r,\theta) + e\sum_i z_i D_i n_{i,eq}(r)\frac{\partial}{\partial r}\frac{\delta n_i(r,\theta)}{n_{i,eq}(r)}\right] \quad (52)$$

The normal electric flux in this expression is corrected for the diffusive contribution due to the change of the ion density distribution due to the applied field. The remaining contribution

is due to the electric field alone and therefore given by the asymptotic behavior for $r \gg \lambda_n^{-1}$

$$I_{\perp,as}(r,\theta) = -\frac{e^2}{kT}[\sum_i \nu_i z_i^2 D_i n_{\infty}]\frac{\partial}{\partial r}\delta\Psi_{as}$$
$$= -\frac{e^2}{kT}[\sum_i \nu_i z_i^2 D_i n_{\infty}]\frac{\partial}{\partial r}\left(-E_0 r + \frac{P}{4\pi\epsilon_1\epsilon_0 r^2}\right)\cos\theta$$
$$= K_1\left(E_0 + \frac{P}{2\pi\epsilon_1\epsilon_0 r^3}\right)\cos\theta \quad (53)$$

where

$$K_1 \equiv \sum_i D_i\frac{e^2 z_i^2\nu_i n_{\infty}}{kT} \quad (54)$$

is the electric conductivity of the electrolyte. This gives

$$\delta E_{\perp}(r,\theta) = -\frac{\partial}{\partial r}\delta\Psi(r,\theta) = \frac{kT}{e^2}[\sum_i z_i^2 D_i n_{i,eq}(r)]^{-1}I_{\perp,as}(a,\theta) \quad (55)$$

The resulting excess electric field normal to the surface is[15]

$$\delta E_{\perp}^{s}(\theta) = \int_a^{\infty}[\delta E_{\perp}(r,\theta) - \delta E_{\perp}^{+}(r,\theta)]\,dr = \frac{kT}{e^2}I_{\perp,as}(a,\theta)$$
$$\times\int_a^{\infty}\{[\sum_i z_i^2 D_i n_{i,eq}(r)]^{-1} - [\sum_i \nu_i z_i^2 D_i n_{\infty}]^{-1}\}\,dr \quad (56)$$

Using the explicit solution given for $n_{i,eq}(r)$ above one may perform the integration and obtains

$$\delta E_{\perp}^{s}(\theta) = \left[\frac{\kappa a}{K_1^2}\exp(\kappa a)E_1(\kappa a)\sum_i\left(\frac{z_i e\zeta}{kT}\right)\frac{e^2 z_i^2\nu_i n_{\infty}}{kT\kappa}D_i\right]I_{\perp,as}(a,\theta)$$
$$= \left[\frac{\kappa a}{K_1}\exp(\kappa a)\,E_1(\kappa a)\sum_i\frac{e^2 z_i^2\nu_i n_{\infty}}{kT}D_i^s\right]E_{\perp,as}(a,\theta) \quad (57)$$

where the following function was introduced, see ref 21, page xxxii:

$$E_1(\kappa a) \equiv \int_a^{\infty}\exp(-\kappa r)\frac{dr}{r} \quad (58)$$

For the normal surface polarization, this gives

$$\delta P_{\perp}^{s}(\theta) = -\epsilon_0\delta E_{\perp}^{s}(\theta) \equiv \epsilon_0\epsilon_{\perp}^{s}E_{\perp,as}(a,\theta) \quad (59)$$

where $\epsilon_0\epsilon_{\perp}^{s}$ is a contribution to the double layer capacity per unit of surface area. (An extensive discussion of singular polarization densities at surfaces is given in a monograph by Bedeaux and Vlieger.[17] In this monograph, a susceptibility normal to the surface β is introduced which is related to $\epsilon_{\perp}^{s}$ by $\beta\epsilon_1 = \epsilon_{\perp}^{s}$.) We find

$$\epsilon_{\perp}^{s} = -\frac{\kappa a}{K_1}\exp(\kappa a)E_1(\kappa a)\sum_i\frac{e^2 z_i^2\nu_i n_{\infty}}{kT}D_i^s \quad (60)$$

If the diffusion coefficients of the ions are equal, in a symmetric

electrolyte, this contribution reduces to zero, similar to the so-called liquid-junction potential.

Remark: One may similarly calculate the *equilibrium* surface polarization. For $r = a$, the equilibrium solution satisfies the following boundary condition:

$$\epsilon_0 \Psi_{eq}^+(a) - \epsilon_0 \Psi_{2,eq}(a) = P_{\perp,eq}^s \qquad (61)$$

$$P_{\perp,eq}^s = -\epsilon_0 E_{\perp,eq}^s = -\epsilon_0 \int_a^\infty [E_{\perp,eq}(r) - E_{\perp,eq}^+(r)] \, dr$$

$$= -\epsilon_0 \int_a^\infty E_{\perp,eq}(r) \, dr = \epsilon_0 \int_a^\infty \frac{\partial}{\partial r} \Psi_{eq}(r) \, dr$$

$$= -\epsilon_0 \Psi_{eq}(a) = -\epsilon_0 \zeta \qquad (62)$$

The net equilibrium polarization normal to the surface of the double layer is therefore equal to $-\epsilon_0$ times the ζ potential; thus, we get

$$\Psi_{eq}^+(a) - \Psi_{2,eq}(a) = -\Psi_{2,eq}(a) = -\zeta \qquad (63)$$

as was to be expected. The usual double layer capacity per unit surface area, $(a^{-1} + \kappa)\epsilon_0\epsilon_1$, follows by taking the ratio of the charge density, eq 41, and the potential difference ($-\zeta$).

4. Polarizability of the Sphere

In a suspension of particles with a dipolar coefficient β, the complex conductivity $\tilde{K}(\phi,\omega)$ is given by Maxwell–Wagner[20]

$$\frac{\tilde{K}(\phi,\omega) - \tilde{K}_1}{\tilde{K}(\phi,\omega) + 2\tilde{K}_1} = \phi\beta \qquad (64)$$

where $\tilde{K}_1$ is the complex conductivity of the electrolyte. For small volume fractions, this reduces to

$$\tilde{K}(\phi,\omega) = \tilde{K}_1(1 + 3\phi\beta) \qquad (65)$$

4.1. Low ζ Potentials. The above analysis has now given the necessary boundary conditions, eqs 32–34 and 49, to calculate the amplitudes of the fields beyond the double layer. This results in the following expression for the polarization of the sphere surrounded by the ion cloud:

$$P =$$
$$4\pi\epsilon_0\epsilon_1 a^3 E_0 \frac{\tilde{K}_2 - \tilde{K}_1 + 2\tilde{K}_{\parallel}^s/a + \tilde{K}_{\perp}^s/a + 2\tilde{K}_{\parallel}^D/a + \tilde{K}_{\perp}^D/a}{\tilde{K}_2 + 2\tilde{K}_1 + 2\tilde{K}_{\parallel}^s/a - 2\tilde{K}_{\perp}^s/a + 2\tilde{K}_{\parallel}^D/a - 2\tilde{K}_{\perp}^D/a}$$
$$(66)$$

Here $\tilde{K}_2$ is the complex conductivity of the core material of the sphere. Writing the complex conductivities in their real and imaginary parts, we have

$$\tilde{K}_2 \equiv i\omega\epsilon_0\epsilon_2 \quad \text{and} \quad \tilde{K}_1 \equiv K_1 + i\omega\epsilon_0\epsilon_1 \qquad (67)$$

in the relevant frequency domain. Furthermore $\tilde{K}_{\parallel}^S$ and $\tilde{K}_{\perp}^s$ are the "excess" complex conductances of the double layer along and normal to the surface:

$$\tilde{K}_{\parallel}^s \equiv -\sum_i D_i^s \frac{e^2 z_i^2 \nu_i n_\infty}{kT} \quad \text{and} \quad \tilde{K}_{\perp}^s \equiv i\omega\epsilon_0\epsilon_2\epsilon_{\perp}^s \qquad (68)$$

The contributions $\tilde{K}_{\parallel}^D$ and $\tilde{K}_{\perp}^D$ are "excess" complex conductances due to the diffusion layer outside the double layer and

are given by

$$\tilde{K}_{\parallel}^D = -\frac{F}{G}\sum_i \frac{\nu_i}{N_i^s} D_i^s \operatorname{sign} z_i$$

$$\tilde{K}_{\perp}^D = -\frac{F}{G}\sum_i \frac{\nu_i}{N_i^s} a D_i \operatorname{sign} z_i \qquad (69)$$

where

$$F = A_n\left[J_1\left(\frac{2}{a}\tilde{K}_{\parallel}^s + \tilde{K}_2\right) + J_2\tilde{K}_1\right] + \frac{ez_-}{z_+ - z_-}\sum_i z_i N_i\left(J_1\frac{2D_i^s}{a} - J_2 D_i\right) \qquad (70)$$

and

$$G = \sum_i \frac{\nu_i}{N_i^s}\left(A_n - \frac{z_-}{z_+ - z_-}N_i\frac{kT}{ez_i\nu_i n_\infty}\right)\left(J_1\frac{2D_i^s}{a} - J_2 D_i\right)\operatorname{sign} z_i \qquad (71)$$

with

$$N_- = N_-^s = 1 - \frac{i\omega}{\kappa^2}\left(\frac{1}{D_+} - \frac{1}{D_-}\right)\frac{z_+ + z_-}{z_+ - z_-}$$

$$N_+ = 1 - \frac{i\omega}{\kappa^2}\left(\frac{1}{D_+} - \frac{1}{D_-}\right)\frac{2z_+}{z_+ - z_-}$$

$$N_+^s = 1 - \frac{i\omega}{\kappa^2}\left(\frac{1}{D_+} - \frac{1}{D_-}\right)\frac{2z_-}{z_+ - z_-} \qquad (72)$$

Finally

$$J_1 = 1 + \lambda_n a \quad \text{and} \quad J_2 = 2 + 2\lambda_n a + \lambda_n^2 a^2 \qquad (73)$$

One usually writes the polarization in the form

$$P = 4\pi\epsilon_0\epsilon_1 a^3 \beta E_0 \qquad (74)$$

where we have found

$$\beta = \frac{\tilde{K}_2 - \tilde{K}_1 + 2\tilde{K}_{\parallel}^s/a + \tilde{K}_{\perp}^s/a + 2\tilde{K}_{\parallel}^D/a + \tilde{K}_{\perp}^D/a}{\tilde{K}_2 + 2\tilde{K}_1 + 2\tilde{K}_{\parallel}^s/a - 2\tilde{K}_{\perp}^s/a + 2\tilde{K}_{\parallel}^D/a - 2\tilde{K}_{\perp}^D/a} \qquad (75)$$

for the dipolar coefficient. Together with the above formulas, this gives a general expression for the coefficient β for all values of κa of symmetric and asymmetric electrolytes. The expression for the dipolar coefficient is the same as the one found in a shell model with a double layer shell and a diffusion layer shell in the limit that both shells have a thickness small compared to a.[16]

It is interesting to see how the result simplifies in the thin double layer limit, $\kappa a \gg 1$. In that case, we find that

$$\tilde{K}_{\parallel}^s = \tilde{K}_{\perp}^s = \tilde{K}_{\parallel}^D = 0 \qquad (76)$$

as all these contributions are inversely proportional to κa. Only the contribution due to the difference between $\tilde{K}_2$ and $\tilde{K}_1$ in addition to the one from $\tilde{K}_{\perp}^D$ remain.

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Another special case is the symmetric electrolyte. In this case, the diffusion layer remains in good approximation electroneutral. This is the case originally considered by Dukhin.[2] The above formulas simplify somewhat but not enough to give them separately. An interesting special case is KCl, which is a symmetric electrolyte, $z_+ = -z_- = \nu_+ = \nu_- = 1$, with diffusion coefficients of the ions which are in good approximation equal. Setting $D_- = D_+ = D$, we find

$$K_1 = 2D\frac{e^2 n_\infty}{kT} \tag{77}$$

The excess complex conductances of the double layer along and normal to the surface are zero:

$$\tilde{K}_\parallel^s = 0 \quad \text{and} \quad \tilde{K}_\perp^s = i\omega\epsilon_0\epsilon_2\epsilon_\perp^s = 0 \tag{78}$$

whereas only the complex conductances due to the diffusion layer along the surface is unequal to zero:

$$\tilde{K}_\parallel^D = -2\frac{J_1}{J_2}\left(\frac{e\zeta}{kT}\right)^2\epsilon_0\epsilon_1\frac{D}{a}$$

$$\tilde{K}_\perp^D = 0 \tag{79}$$

4.2. High ζ Potentials. For higher ζ potentials, the expression for the excess ion densities in the double layer should be corrected. In this case, the counterion density in the double layer becomes very large compared to the coion density. The surface charge density q^s on the sphere is then in very good approximation compensated in the double layer by the counterions alone. We therefore have

$$n_{ctr,eq}^s = -\frac{q^s}{z_{ctr}e} \quad \text{and} \quad n_{co,eq}^s = 0 \tag{80}$$

No exact relation is known for the surface charge density in terms of the ζ potential. A good approximation for a symmetric electrolyte is provided by (see ref 18, page 109)

$$q^s = \frac{\epsilon_0\epsilon_1 kT}{e z_{ctr}}\kappa\left[2\sinh\left(\frac{e|z\zeta|}{2kT}\right) + \frac{4}{\kappa a}\tanh\left(\frac{e|z\zeta|}{4kT}\right)\right] \tag{81}$$

Both for symmetric and asymmetric electrolytes the values have been tabulated.[19]

As the expressions derived in the section on the boundary conditions contain the excess ion densities in the double layer, we may now give the expressions obtained for $e|z\zeta| \gg kT$. Along the lines sketched in this section, we then find from eq 43 the following diffusion coefficient for the counterions along the surface:

$$D_{ctr}^s = -\frac{D_{ctr}}{\nu_{ctr}n_\infty}\frac{1}{a}\int_a^{a+\kappa^{-1}} rn_{ctr,eq}(r)\,dr \tag{82}$$

whereas the diffusion coefficient along the surface for the coions is zero:

$$D_{co}^s = 0 \tag{83}$$

Using the Poisson–Boltzmann equation, this results in
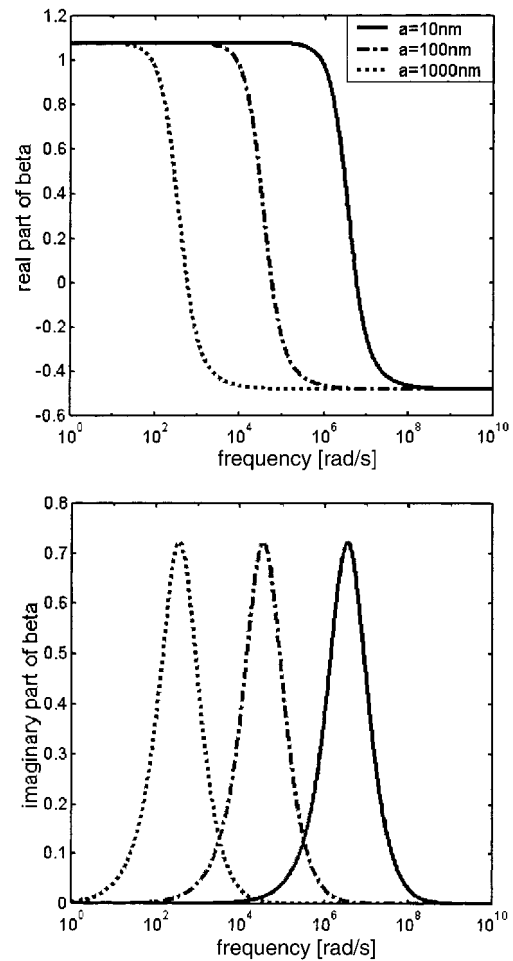
Figure 1. Real and imaginary parts of the dipolar coefficient β as a function of frequency for $e\zeta/kT = 0.5$, $\kappa a = 0.1$, and $a = 10$, 100, and 1000 nm.

$$\begin{aligned}
D_{ctr}^s &= \frac{D_{ctr}}{\nu_{ctr}n_\infty}\frac{\epsilon_0\epsilon_1}{ez_{ctr}}\frac{1}{a}\int_a^{a+\kappa^{-1}} r\Delta\Psi_{eq}(r)\,dr \\
&= \frac{D_{ctr}}{\nu_{ctr}n_\infty}\frac{\epsilon_0\epsilon_1}{ez_{ctr}}\frac{1}{a}\int_a^{a+\kappa^{-1}} \frac{\partial^2}{\partial r^2}(r\Psi_{eq}(r))\,dr \\
&= -\frac{D_{ctr}}{\nu_{ctr}n_\infty}\frac{\epsilon_0\epsilon_1}{ez_{ctr}}\frac{1}{a}\left[\Psi_{eq}(r) + r\frac{\partial}{\partial r}\Psi_{eq}(r)\right]_{r=a} \\
&= \frac{D_{ctr}}{ez_{ctr}\nu_{ctr}n_\infty}\left[q^s - \frac{\epsilon_0\epsilon_1}{a}\zeta\right]
\end{aligned} \tag{84}$$

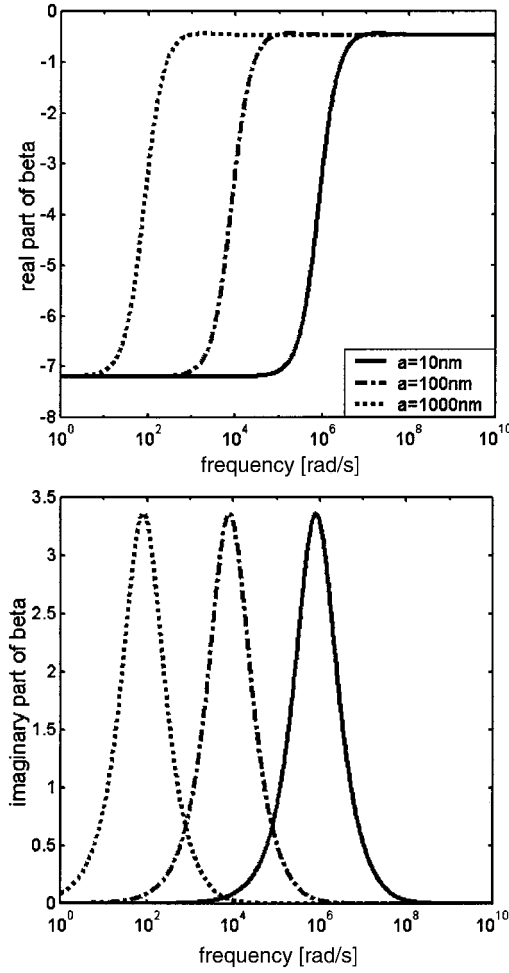The corresponding electric conductance along the surface is

$$\tilde{K}_\parallel^s = \frac{-ez_{ctr}D_{ctr}}{kT}\left[q^s - \frac{\epsilon_0\epsilon_1}{a}\zeta\right] \tag{85}$$

The capacity of the double layer may be analyzed in a similar manner and is now found to be zero

$$\epsilon_\perp^s = 0 \rightarrow \tilde{K}_\perp^s = 0 \tag{86}$$

For the contributions to the excess densities of the counter- and the coions due to the external electric field, we may now use

$$\delta n_{co}^s = 0 \tag{87}$$

Figure 2. Real and imaginary parts of the dipolar coefficient β as a function of frequency for $e\zeta/kT = 0.5$, $\kappa a = 0.4$, and $a = 10$, 100, and 1000 nm.

Substitution in the boundary conditions given in section 3 now results in

$$\tilde{K}_{\parallel}^{D} = 0 \quad \text{and} \quad \tilde{K}_{\perp}^{D} = a\frac{F}{H} \tag{88}$$

where F is again given by eq 70 and where

$$H = J_2\left(A_n - \frac{z_-}{z_+ - z_-}N_{co}\frac{kT}{ez_{co}\nu_{co}n_\infty}\right) \tag{89}$$
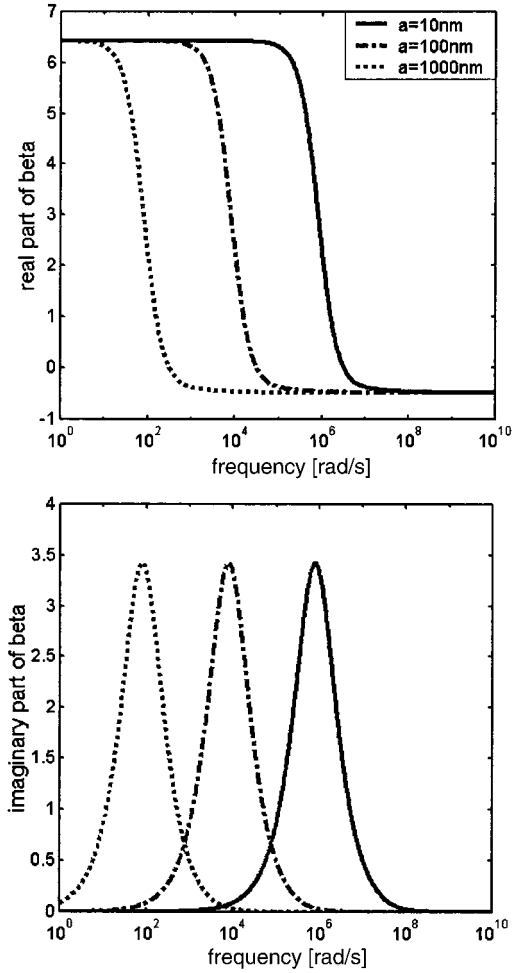
The expression for the dipolar coefficient β reduces to

$$\beta = \frac{\tilde{K}_2 - \tilde{K}_1 + 2\tilde{K}_{\parallel}^{s}/a + \tilde{K}_{\perp}^{D}/a}{\tilde{K}_2 + 2\tilde{K}_1 + 2\tilde{K}_{\parallel}^{s}/a - 2\tilde{K}_{\perp}^{D}/a} \tag{90}$$

O'Brien[4,5] finds the same expression without the contribution due to the diffusion layer. He uses for q^s the expression for a flat surface appropriate in the thin double layer case.

In the case of KCl, where $z_+ = -z_- = \nu_+ = \nu_- = 1$ and $D_- = D_+ = D$, we find

$$\tilde{K}_{\perp}^{D} = 2\frac{J_1}{J_2}\frac{eD}{kT}\left[\left|q^s\right| + \frac{\epsilon_0\epsilon_1}{a}\left|\zeta\right|\right]$$

$$\tilde{K}_{\parallel}^{s} = \frac{-eD}{kT}\left[\left|q^s\right| + \frac{\epsilon_0\epsilon_1}{a}\left|\zeta\right|\right] \tag{91}$$

Figure 3. Real and imaginary parts of the dipolar coefficient β as a function of frequency for $e\zeta/kT = 0.5$, $\kappa a = 0.5$, and $a = 10$, 100, and 1000 nm.

4.3. Contributions due to the Stern Layer. It is sometimes argued[11,12] that, if there is a Stern layer, the counterions bound in this layer are mobile. This adds another layer in the description with an electric conductance $K_{\parallel}^{St}$ along the surface (with a dimensionality of a Siemens) and may also contribute a capacitance normal to the surface which results in a term $K_{\perp}^{St}$. This leads to additional terms in the expression for the dipolar coefficient

$$\beta = \frac{\tilde{K}_2 - \tilde{K}_1 + 2\tilde{K}_{\parallel}^{St}/a + \tilde{K}_{\perp}^{St}/a + 2\tilde{K}_{\parallel}^{s}/a + \tilde{K}_{\perp}^{s}/a + 2\tilde{K}_{\parallel}^{D}/a + \tilde{K}_{\perp}^{D}/a}{\tilde{K}_2 + 2\tilde{K}_1 + 2\tilde{K}_{\parallel}^{St}/a - 2\tilde{K}_{\perp}^{St}/a + 2\tilde{K}_{\parallel}^{s}/a - 2\tilde{K}_{\perp}^{s}/a + 2\tilde{K}_{\parallel}^{D}/a - 2\tilde{K}_{\perp}^{D}/a} \tag{92}$$

Lacking a theory for the mobility in the Stern layer, the values are usually fitted to experiment.

5. Discussion and Conclusions

Using a method introduced by Albano et al.,[14,15] it was possible to derive an exact analytic expression for the dipolar coefficient of a charged sphere in an electrolyte. The expression is valid for all double layer thicknesses and was derived both for low ζ potentials and high ζ potentials. We limited the calculations to first order in ω, which is sufficient to almost all experiments, but expressions could easily be extended to higher orders.
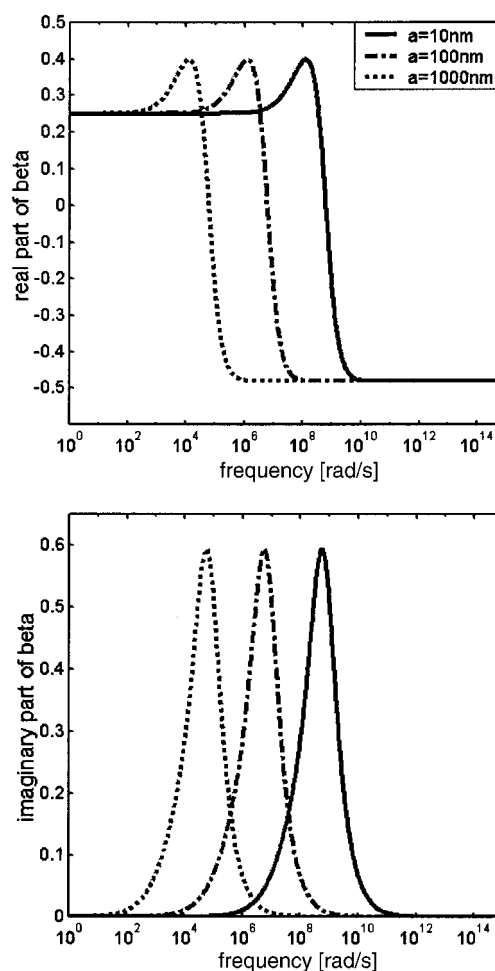
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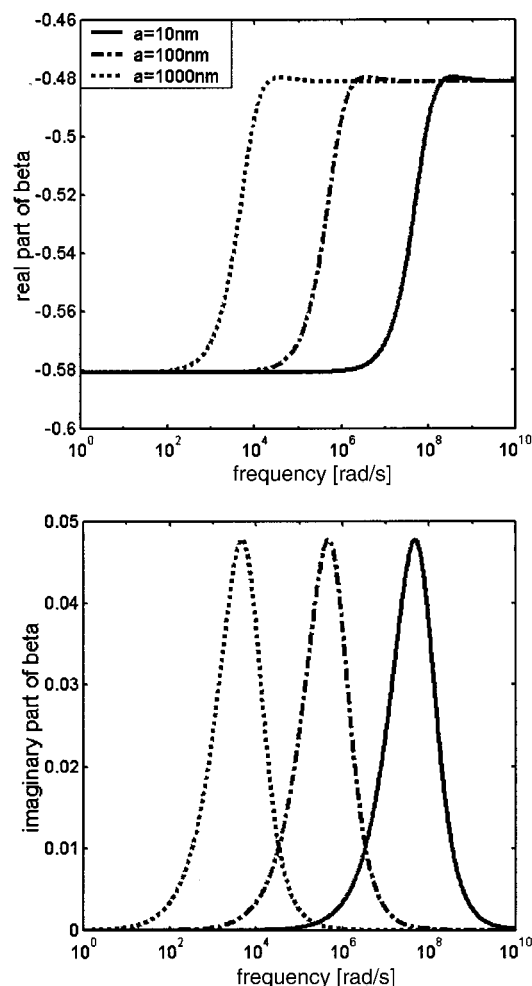
Figure 4. Real and imaginary parts of the dipolar coefficient β as a function of frequency for $e\zeta/kT = 0.5$, $\kappa a = 2.0$, and $a = 10$, 100, and 1000 nm.

Figure 5. Real and imaginary parts of the dipolar coefficient β as a function of frequency for $e\zeta/kT = 10$, $\kappa a = 0.1$, and $a = 10$, 100, and 1000 nm.

It is found that the expression has the same form as the expression found using a shell model[16] with one shell due to the double layer and another shell due to the diffusion layer beyond the double layer. It should be emphasized that, despite the formal analogy, we did not use that either the double layer or the diffusion layer were thin in comparison to the radius of the sphere in our derivation. The analogy with the shell model enables us to account for possible contributions due to the Stern layer[11,12] by treating it as an additional shell.

For the double layer and the diffusion layer, we find that both are characterized by a "conductance" along the surface, $\tilde{K}_{\parallel}^{s,D}$, and a "capacitance" normal to the surface, $\tilde{K}_{\perp}^{s,D}/i\omega$. We put both conductance and capacitance between quotes to indicate that they are in general complex, whereas the name is only appropriate for the real part. In both cases, the real parts are the dominant contribution. The usual discussions of this problem make the thin double layer approximation and use large ζ potentials. When we take the thin double layer limit in our expressions for large ζ potentials, we reproduce the usual contribution $\tilde{K}_{\parallel}^{s}$, due to conduction along the double layer found by Dukhin et al.[2] for the symmetric electrolyte and by O'Brien,[4,5] for the general case. In addition, we obtain a capacitive contribution, $\tilde{K}_{\perp}^{D}/i\omega$, due to the diffusion layer. Such a contribution was also found by Hinch et al.[3] but was neglected by Dukhin and O'Brien.[2,4,5,8] When we use a Stern layer contribution instead of a diffusion contribution, our expression reproduces the results of Mangelsdorf and

White.[11] As has been established, their theory, and therefore ours, compares favorably with experiment; see, e.g., refs 22 and 23. In a future article, we will investigate the relative importance of the Stern layer and the diffusion layer contributions in interpreting experimental data in more detail.

Using our expressions, one may easily generate dipolar coefficients for many different systems. We will restrict ourselves here to a few special cases which illustrate important properties of this coefficient. We do not consider Stern layer contributions. As electrolyte, we use a KCl solution in water which is symmetric and has ionic diffusion coefficients which are approximately equal, $D_+ = D_- \simeq 1.65 \times 10^{-9}$ m^2/s. Furthermore, we use $T = 300$ K, $\epsilon_1 = 78.54$ and $\epsilon_2 = 2$.

We first consider a case with a small ζ potential such that $e\zeta/kT = 0.5$. As shown in section 4, only the diffusion layer contribution $\tilde{K}_{\parallel}^{D}$ is unequal to zero.

In Figures 1−4, the real and imaginary parts of β are given for $\kappa a = 0.1$, 0.4, 0.5, and 2.0, respectively, and for radii a =10, 100, and 1000 nm. For sufficiently small values of κ, the conductivity K_1 of the electrolyte, which is proportional to κ^2, vanishes compared to $\tilde{K}_{\parallel}^{D}/a$ (which is inversely proportional to a^2). This gives a zero frequency limit of the real part of β equal to 1.0. Increasing κa leads to an increase of K_1 relative to the $\mathrm{Re}(\tilde{K}_{\parallel}^{D}/a)$. As K_1 and $\mathrm{Re}(\tilde{K}_{\parallel}^{D}/a)$ have an opposite sign, this leads to an decrease of the real part of the denominator and therefore to an increase of the real part of β. For small
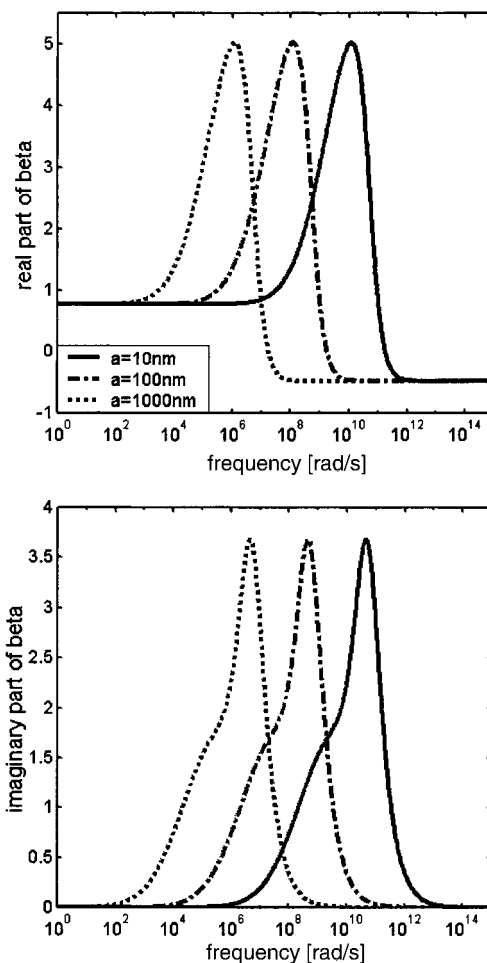
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Chassagne et al.
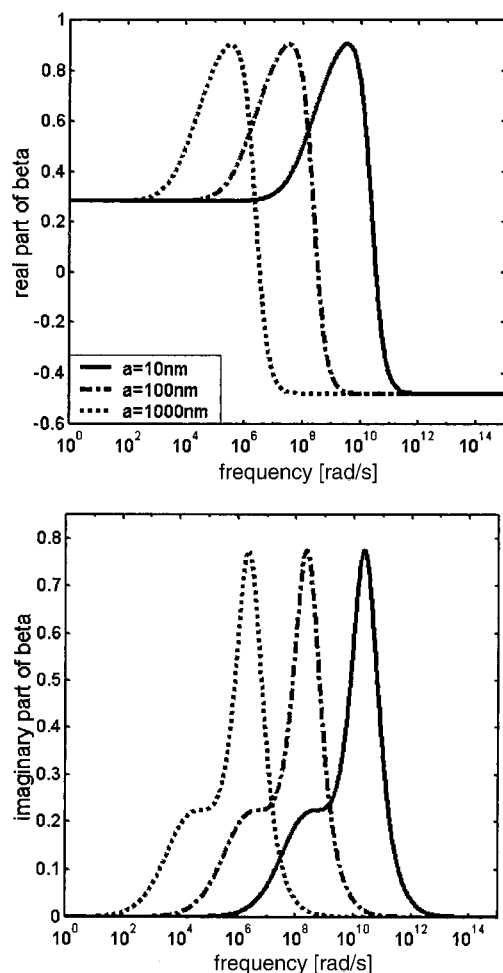
Figure 6. Real and imaginary parts of the dipolar coefficient β as a function of frequency for $e\zeta/kT = 10$, $\kappa a = 10$, and $a = 10$, 100, and 1000 nm.

Figure 7. Real and imaginary parts of the dipolar coefficient β as a function of frequency for $e\zeta/kT = 10$, $\kappa a = 100$, and $a = 10$, 100, and 1000 nm.

frequencies, the absolute value of the real part of β becomes larger than 1.0 as can be seen in Figures 2 and 3. A crossover to a negative value of the real part of β occurs for $\kappa a \simeq e|\zeta|/kT$. In the figures, this occurs between $\kappa a = 0.4$ and 0.5. For even larger values of κa, one may neglect $\tilde{K}_{\parallel}^{D}$, so that the polarization coefficient is determined by $\tilde{K}_1$ and $\tilde{K}_2$ alone. The typical behavior is given in Figure 4. For large frequencies, the polarization coefficient becomes real and reduces to $(\epsilon_2 - \epsilon_1)/(\epsilon_2 + 2\epsilon_1)$ as expected.

Next we consider a case with a large ζ potential such that $e\zeta/kT = 10$. As shown in section 5, the diffusion layer contribution $\tilde{K}_{\perp}^{D}$ and the double layer contribution $\tilde{K}_{\parallel}^{s}$ are now unequal to zero.

In Figures 5–7, the real and imaginary parts of β are given for $\kappa a = 0.1$, 10, and 100, respectively, and for radii $a = 10$, 100, and 1000 nm. For sufficiently small values of κ, the conductivity K_1 of the electrolyte may again be shown to vanish compared to $\tilde{K}_{\perp}^{D}/a$ and $\tilde{K}_{\parallel}^{s}/a$. In the zero frequency limit, one has $\tilde{K}_{\perp}^{D} = -\tilde{K}_{\parallel}^{s}$. This gives a zero frequency limit of the real part of β equal to 0.25 as can be seen in Figure 5. Increasing κa leads to an increase of K_1 relative to the contribution due to the other two terms which is of the opposite sign in the denominator. This leads to an decrease of the real part of the denominator and therefore to an increase of the low-frequency value of the real part of β. A crossover occurs when K_1 and $2\mathrm{Re}(\tilde{K}_{\parallel}^{s}/a)$ cancel each other after which the low-frequency value of the real part of β becomes negative. In the case

considered, this occurs for $\kappa a \simeq 1000$. For even larger values of κa, the polarization coefficient is again determined by $\tilde{K}_1$ and $\tilde{K}_2$ alone. For increasing frequencies, $\tilde{K}_{\perp}^{D}$ decreases. This decreases the real part of the denominator and leads to an increase of the real part of β. This effect increases with increasing values of κa as can clearly be seen in the figures. For sufficiently large frequencies, the polarization coefficient becomes $(\epsilon_2 - \epsilon_1)/(\epsilon_2 + 2\epsilon_1)$. The crossover to this behavior is also clearly visible in the figures.

A feature common to all figures is that increasing the radius of the spheres seems to shift the graphs toward lower frequencies. This shift is proportional to a^{-2}. One may verify this property by scaling all the frequencies in the general formula with a^{-2}. Using the fact that the sets of figures are always for the same value of κa, one may show that this property is in good approximation valid.

In conclusion, we find that the general expression we have found reproduces many known properties. The behavior as a function of the frequency can in a straightforward manner be understood in terms of the relative size of the various contributions. In particular, this leads to values of the real part of β larger than 1.0, both for small and for large values of the ζ potential. In earlier discussions,[11,13] it was necessary to introduce such large values of β and contributions due to the Stern layer to explain some features of the electrokinetic transport properties and dielectric response of spherical colloidal particles suspensions. We also find the characteristic peaks in the real part of β for large ζ potentials without the introduction of a Stern layer.

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