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High-frequency dielectric relaxation of spherical colloidal particles

Reghan J. Hill,* D. A. Saville and W. B. Russel

Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08542, USA. E-mail: reghan.hill@mcgill.ca and dsaville@princeton.edu

The high-frequency limit of the conductivity and dielectric constant increment spectra for dilute suspensions of spherical colloidal particles is obtained from numerical solutions of the standard electrokinetic model. Our numerical method allows frequencies beyond 1 GHz to be reached, allowing Maxwell–Wagner relaxation to be observed. Contrary to previous thinking, the conductivity increment passes through a maximum as the momentum diffusion length becomes comparable to and then smaller than the double-layer thickness. Therefore, at sufficiently high frequencies, fluid inertia within the double layer causes the phase of the double-layer relaxation to further lag the applied electric field. As expected from elementary scaling, these 'exact' calculations show that a maximum in the conductivity increment can be observed with an aqueous electrolyte at a frequency of 10 MHz when the double-layer thickness is *ca.* 300 nm. With thinner double layers, inertial effects become important inside the double layer at even higher frequencies.

I. Introduction

Dielectric relaxation spectroscopy is a powerful diagnostic tool that is particularly sensitive to the surface charge of colloidal particles dispersed in an electrolyte. In practice, an oscillatory electric field is applied to a suspension of charged colloidal particles, and the complex conductivity of the suspension is measured. For dilute suspensions, the particle contribution to the effective conductivity and dielectric constant can be interpreted with theory describing the response of a single particle in an unbounded electrolyte. The fluctuating electric field probes dynamical processes with characteristic time scales much shorter than can be detected with electrophoresis, for example. With the advent of electroacoustic techniques,[10] it has become increasingly important to understand the high-frequency behavior, which is addressed here.

The standard electrokinetic model serves as the foundation for interpreting electrokinetic measurements.[6,13] Previous exact numerical solutions of the model equations for electrophoresis,[11] dielectric relaxation[2,8] and the dynamic mobility[7] deal with steady and relatively low-frequency fields ($\lesssim 1$ MHz). In this work, we examine the high-frequency characteristics of the standard model at frequencies from 1 kHz to well beyond 1 GHz. This has been elusive because: (i) the effects of fluid inertia inside the double layer have been neglected in the existing 'high-frequency' asymptotic theory[9]; and (ii) numerical instabilities have been encountered at high frequencies when solving the full equations.[8] Our numerical method, originally developed for particles with polymer coatings,[4,5] also works well at high frequencies for the simpler problem addressed here.[14]

The conductivity and dielectric increments for bare particles were calculated by DeLacey and White[2] without the effects of fluid inertia. Later, Mangelsdorf and White included the inertial effects and presented the dipole coefficient (polarizability)[8] and the dynamic mobility.[7] However, numerical solutions of the governing electrokinetic equations have not been reported at frequencies beyond *ca.* 1 MHz, so the high-frequency limit has not been examined in detail. Note that Ennis and White[3] performed an asymptotic analysis for high frequencies, but

the utility of their approach is limited when the surface potential is not small.

We will refer to the limit in which the double layer is occupied by inviscid flow as the *high-frequency* limit. Frequencies where the fluid beyond the particle radius is 'inviscid', but the region within the double layer is viscous, will be referred to as *moderately high*. This is the 'high-frequency' limit treated analytically by O'Brien[9] for particles with thin double layers. Our calculations reveal both the lower and the upper frequency limits of O'Brien's theory.

The viscous penetration depth, $\delta = (2\pi\nu/\omega)^{1/2}$, denotes the characteristic distance from the particle surface over which momentum diffuses during a period of oscillation. As the frequency increases, δ eventually becomes smaller than the double-layer thickness, κ^{-1}, so the dimensionless angular frequency, $\Omega = \omega\kappa^{-2}/\nu$, becomes greater than one. Here, ω is the angular frequency of the applied electric field and $\nu = \eta/\rho_s$ is the kinematic viscosity. At radial distances beyond δ, the fluid is effectively inviscid, because viscous stresses become weak compared to inertial stresses.

Consideration must also be given to the time scale for ion diffusion. We will therefore refer to dimensionless frequencies, $\Omega_j = \omega\kappa^{-2}/D_j$, which denote the ratio of the characteristic time for diffusion of the jth ion species over the double layer thickness to the inverse angular frequency. The diffusivity of the jth ion species, D_j, is typically related to the ion mobility, *via* the Stokes–Einstein relationship, and calculated from limiting conductances. Note that the polarizability is a complex quantity, with the real and imaginary parts reflecting the components of the dipole moment that oscillate, respectively, in and out of phase with the applied electric field. The out-of-phase component mostly represents double-layer relaxation by ion diffusion, but, at sufficiently high frequencies, momentum diffusion gives rise to a convective ion flux that lags the applied electric field. When $\Omega_j \ll 1$, the imaginary part of the double-layer polarization is weak, since there is sufficient time for diffusion to maintain quasi-steady dynamics. When $\Omega_j \gg 1$, however, the magnitude of the polarization is small, because there is insufficient time for electro-migration to deform the double layer. Therefore, the imaginary part of

the polarizability reaches a maximum when $\Omega_j \sim 1$, with the real part decreasing monotonically with increasing frequency.

The numerical method used in this work provides 'exact' solutions of the governing electrokinetic equations at both moderately high frequencies and asymptotically high frequencies where Maxwell–Wagner electrokinetic relaxation sets in.[1] Furthermore, our results extend those obtained by Mangelsdorf and White to thicker double layers, thus providing results for the mobility and dielectric relaxation of colloidal particles dispersed in low-dielectric solvents. Since ion concentrations in such solvents are very low, the double layer is often much thicker than in aqueous electrolytes.

Before presenting the results, we briefly relate the conductivity and dielectric constant increments to the dipole strength or polarizability. For illustrative purposes, results are presented for colloidal particles with a radius of 100 nm, with surface potentials up to *ca.* 200 mV, in an aqueous KCl electrolyte. Ionic strengths giving double-layer thicknesses up to 10 times the particle radius are considered, at frequencies from *ca.* 1 kHz to well beyond 1 GHz.

II.   Theory

As usual, the electrostatic potential and ion densities are calculated *via* numerical solutions of the governing electrokinetic equations.[2,11] Our numerical solution of the standard electrokinetic model is different from the well-known method of DeLacey and White, however. Consequently, we are able to obtain solutions at much higher frequencies. Details of the electrokinetic model and the numerical method are described, with respect to polymer-coated colloidal particles, by Hill *et al.*[4,5] The following describes how the dielectric response is obtained from the solution of the governing electrokinetic transport equations.

Under the oscillatory conditions of interest here, the conductivity and dielectric constant increments can be obtained from knowledge of only the far-field decay of the perturbed electrostatic potential, which takes the form

$$\psi' \sim -E' \cdot r' + D'E' \cdot \hat{r}/r'^2 \quad \text{as } r' \to \infty, \tag{1}$$

where ψ' is the electrostatic potential, ψ, scaled with $k_B T/e$, r' is the radial distance, r, scaled with the Debye length, κ^{-1}, E' is the electric field strength, E, scaled with $\kappa k_B T/e$, and D' is the polarizability, D, scaled with κ^{-3}.

It is convenient to define another dimensionless polarizability

$$\mathscr{P} = D'/(\kappa a)^3, \tag{2}$$

where a is the particle radius, so the macroscopic current density, in a dilute suspension, may be written as[2]

$$I' = (1 - i\hat{\omega})(1 + 3\phi\mathscr{P})E' + \mathcal{O}(n_p^2), \tag{3}$$

where $\phi = n_p(4/3)\pi a^3$ is the particle volume fraction and $\hat{\omega} = \omega \varepsilon_s \varepsilon_o / \sigma_\infty$. As usual, ω is the angular frequency of the applied electric field and $\varepsilon_s \varepsilon_o$ is the dielectric permittivity of the solvent. Note that I' is the current density, I, scaled with $\sigma_\infty k_B T \kappa/e$, where

$$\sigma_\infty = \sum_{j=1}^{N} z_j^2 n_j^\infty D_j e^2/(k_B T) \tag{4}$$

is the conductivity of the bulk electrolyte (in the absence of particles). Moreover, z_j and n_j^∞ are the valencies and bulk number densities, respectively, of the N ion species.

The complex conductivity of a colloidal dispersion can be written as

$$I'/E' = \sigma_e - i\hat{\omega}\varepsilon_e, \tag{5}$$

where σ_e and ε_e are, respectively, defined as the *effective* conductivity and *effective* dielectric constant, which are scaled here with σ_∞ and ε_s, respectively; both are real quantities that are experimentally obtained from the *amplitude* and *phase* of the measured current.

It follows from eqns. (3) and (5) that the $\mathcal{O}(\phi)$ particle contribution to the effective conductivity and dielectric constant, the so-called *conductivity* and *dielectric constant increments*, can be expressed in terms of the real and imaginary parts of the polarizability, giving

$$\Delta\sigma = [\sigma_e - 1]/\phi$$
$$= 3[\mathscr{R}(\mathscr{P}) + \hat{\omega}\mathscr{I}(\mathscr{P})] \tag{6}$$

and

$$\Delta\varepsilon = [\varepsilon_e - 1]/\phi$$
$$= 3[\mathscr{R}(\mathscr{P}) - \hat{\omega}^{-1}\mathscr{I}(\mathscr{P})], \tag{7}$$

respectively. While these are the quantities to which theory is typically compared with experiment, the way in which the real and imaginary parts of the polarizability are combined can make the increments more difficult to interpret than the polarizability.

Readers familiar with the conventions and notation adopted by DeLacey and White[2] may note the following *equivalences*, where the left- and right-hand sides of the $\equiv$ symbols are expressed in our notation and that of DeLacey and White, respectively. First, because we have expressed dielectric permittivities as the product of a dielectric constant and the permittivity of a vacuum, we have $\varepsilon_o \varepsilon_s \equiv \varepsilon_0/(4\pi)$, from which it follows naturally that $\Delta\varepsilon\varepsilon_s\varepsilon_o \equiv \Delta\varepsilon'/(4\pi)$ and $\Delta\sigma \equiv \Delta K_{eff}/K^{(\infty)} = [\Delta K + \omega\Delta\varepsilon''/(4\pi)]/K^{(\infty)}$. As DeLacey and White point out, the experimentally measured contribution to the 'effective' conductivity increment comprises a conductivity increment that they denote ΔK, and the imaginary part of the dielectric permittivity increment, $\Delta\varepsilon''$. Clearly, we have avoided explicit reference to ΔK and $\Delta\varepsilon''$, because these quantities are combined in the experimentally measured quantity $\Delta\sigma \equiv \Delta K_{eff}/K^{(\infty)}$.

Note that eqn. (3) does not include the contribution of added counter-ions and non-specific adsorption,[13] which is independent of the frequency and only affects the conductivity increment. Because the dipole contribution to the conductivity increment increases with frequency, the effect of added counter-ions and non-specific adsorption is most significant at low frequencies. Accordingly, we have compared the added counter-ion and non-specific adsorption correction with the low-frequency polarization contribution over a wide range of ionic strengths and surface potentials.[5] The effect of added counter-ions and non-specific adsorption increases with decreasing ionic strength and increasing surface charge. For typical colloids, however, the correction is significant only at ionic strengths less than *ca.* 1 mM.

At high frequencies, the imaginary part of the dipole moment polarizes the solvent in the far-field and, therefore, contributes to the component of the macroscopic current density that is in phase with the applied electric field. Thus, unlike at low frequencies, the imaginary part of the polarizability dominates the conductivity increment at high frequencies. Since the dipole moment relaxes much more quickly when the double layer is thin, the high-frequency conductivity increment increases with decreasing double-layer thickness.

At low frequencies, the imaginary part of the polarizability is small because the relaxation is fast compared to the forcing frequency. Thus, at low frequencies, the double-layer contribution to the conductivity increment reflects directly the magnitude of the polarizability, whereas the contribution to the dielectric constant increment reflects the relaxation (dynamics) of the polarization. It follows that the low-frequency dielectric

constant increment is large when the double layer is thick, whereas the high-frequency conductivity increment is large when the double layer is thin. Of course, increasing the surface charge density and, hence, the surface potential, increases the magnitude of the polarizability and accentuates these effects.

III. Results

The following computational results are for the system whose characteristics are listed in Table 1. Recall that $\zeta' = \psi'(r' = \kappa a)$ denotes the surface potential (scaled with $k_B T/e$), which reflects the (negative) surface charge density, the ionic strength of the bulk electrolyte, and the surface curvature.[4,12] Because the particle velocity, as obtained from knowledge of the dynamic mobility, has a small effect on the polarizability, the results can be assumed to be independent of the particle density. For reference, the calculations were performed with neutrally buoyant particles. In the examples discussed here, the low-frequency limits of the computational results are marked by the onset of numerical instability, because ion density perturbations propagate far beyond the equilibrium double layer. Therefore, at low frequencies, DeLacey and White's numerical method is preferable, since they calculated (well-behaved) perturbations to the far-field analytical solution of the momentum and ion transport equations. Here, 'far-field' refers to distances beyond the double layer where the equilibrium electrostatic potential and perturbations to the bulk ion densities are exponentially small.

It is important to note that the spectra observed here reflect mostly the double-layer thickness and frequency, rather than the particle size. Because the particle radius for all the results is 100 nm, plotting the spectra *versus* $\omega a^2/(2\pi\nu)$ emphasizes the effect of changing the ionic strength. With an ionic strength of 1 mM, the Debye thickness is *ca.* 9 nm. Note also that the dimensional frequency, $\omega/(2\pi)$, can be conveniently obtained by multiplying the abscissae by $\nu/a^2 \approx 8.9 \times 10^7 \sim 10^8$ Hz.

Contrary to previous thinking,[2] Fig. 1 shows that the conductivity increment exhibits a maximum at moderately high frequencies. This is because fluid inertia becomes important inside the double layer. DeLacey and White's computations did not include the inertia of the fluid,[2] so they did not observe the maximum. While Mangelsdorf and White[8] did include the effects of fluid inertia, they did not identify a maximum because: (i) they presented their results in the form of the complex polarizability; and (ii) their computational method was apparently restricted to lower frequencies ($\lesssim 1$ MHz) than can be achieved using our numerical method.

Here, the conductivity increment decreases at asymptotically high frequencies because the convective ion flux due to fluid inertia within the double layer attenuates the flux due to electro-migration. Such a maximum could be observed at experimentally achievable frequencies when the ionic strength is low. With $\kappa a = 0.1$ and 1, for example, the corresponding ionic strengths are *ca.* 10^{-4} and 10^{-2} mM, respectively, when $a = 100$ nm. While the former cannot usually be obtained with an aqueous electrolyte, the latter is typically achieved by dispersing colloids in distilled water, without added salt.

Table 1 Dimensional parameters for the results shown in Figs. 1–5

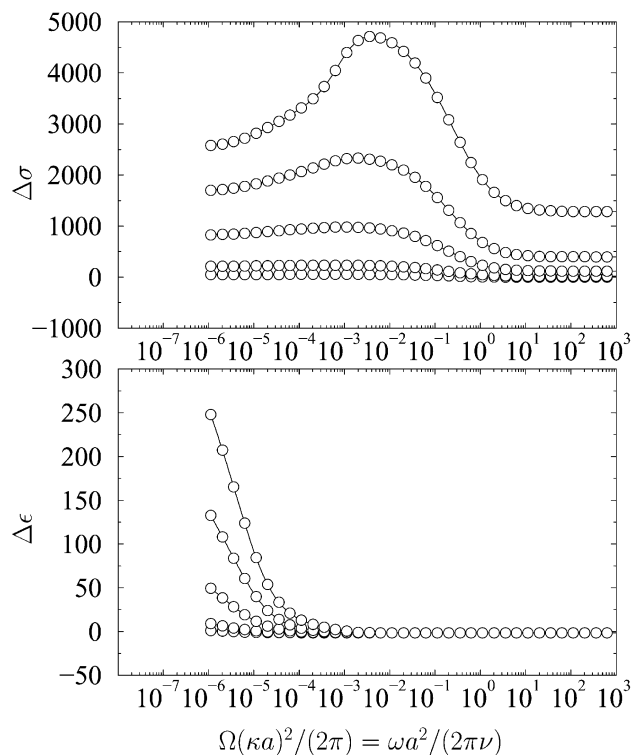|		
Particle radius	a	100 nm
Particle dielectric constant	ε_p	2.0
Solvent dielectric constant	ε_s	78.5
Solvent viscosity	η	8.90×10^{-4} kg m^{-1} s^{-1}
Solvent density	ρ_s	997 kg m^{-3}
Temperature	T	298 K
Electrolyte	KCl	
K$^+$ diffusion coefficient	D_1	1.96×10^{-9} m^2 s^{-1}
Cl$^-$ diffusion coefficient	D_2	2.03×10^{-9} m^2 s^{-1}

Fig. 1 The dimensionless conductivity, $\Delta\sigma$, and dielectric constant, $\Delta\varepsilon$, increments as functions of the frequency, $\omega/(2\pi)$, scaled with ν/a^2: $\kappa a = 0.1$; $\zeta' = -1, -2, -4, -6, -8$ (magnitude increasing upwards). Dimensional parameters are listed in Table 1.

Note that the distinguishing features of the real and imaginary parts of the polarizability spectra shown in Fig. 2 do not necessarily coincide with characteristics of the conductivity and dielectric constant increment spectra. This is because the
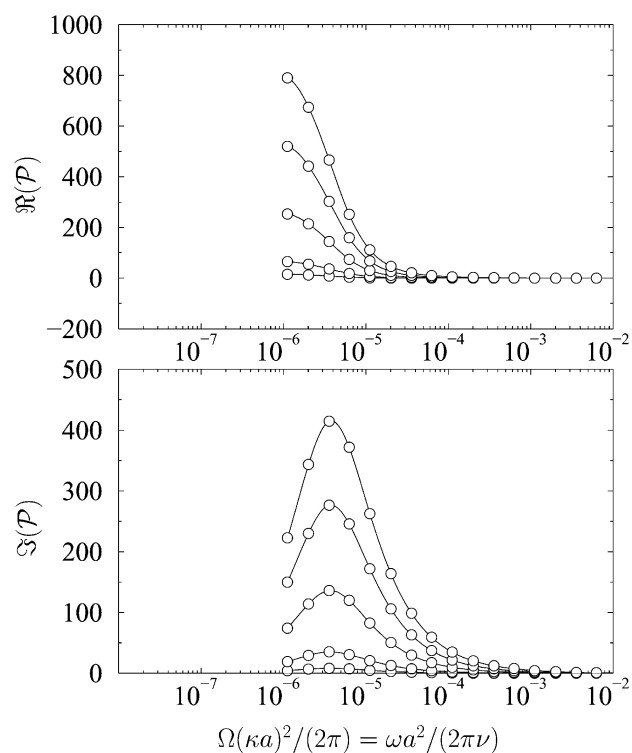

Fig. 2 The dimensionless real and imaginary parts of the polarizability as functions of the frequency, $\omega/(2\pi)$, scaled with ν/a^2: $\kappa a = 0.1$; $\zeta' = -1, -2, -4, -6, -8$ (magnitude increasing upwards). Dimensional parameters are listed in Table 1.
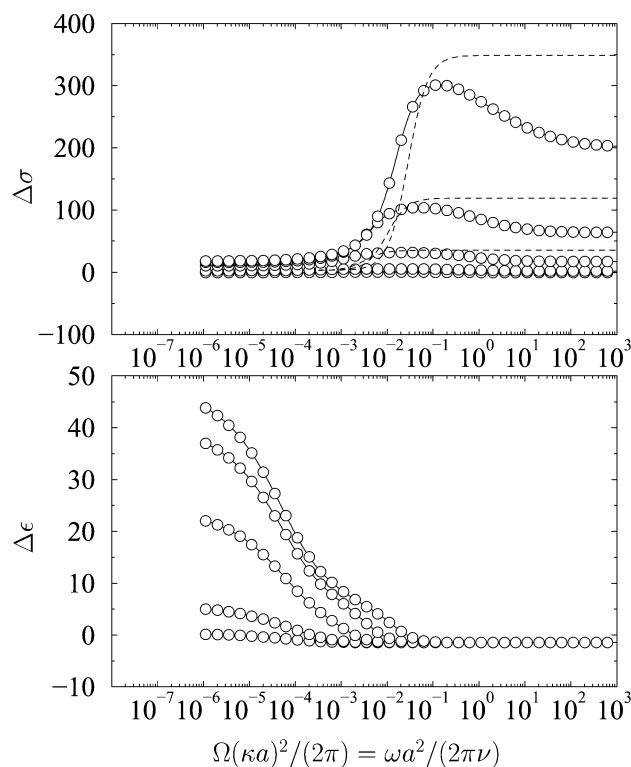
Fig. 3 As in Fig. 1, but with $\kappa a = 1$. The dashed curves are O'Brien's theory[9] for thin double layers, 'high' frequencies and high surface potentials.

Fig. 4 As in Fig. 3, but with $\kappa a = 10$.

polarizability depends mostly on the diffusive time scale, κ^{-2}/D_j, whereas the conductivity and dielectric constant increments also take into account the characteristic relaxation time of the bulk electrolyte, as suggested by the appearance of the dimensionless frequency $\hat{\omega} = \omega \varepsilon_s \varepsilon_o / \sigma_\infty$ in eqns. (6) and (7). For the spectra shown in Figs. 1 and 2 with $\kappa a = 0.1$, κ^{-2}/D_j corresponds to a frequency of *ca.* 2 kHz or, as shown in the figures, $\omega a^2 / (2\pi\nu) \approx 2 \times 10^{-5}$.

Some evidence for a maximum in the conductivity increment can be found in experiments performed in our laboratory[15] with 'bare' polymer latex particles with $a \approx 78$ nm, $\kappa a \approx 2.57$ and $\zeta' \approx -6.3$. These indicate a maximum in the conductivity increment when $\omega / (2\pi)$ is between 20 and 40 MHz. Unfortunately, because the maximum occurs near the upper frequency limit of the device, the maximum cannot be distinguished unambiguously from a plateau. From Fig. 3, the maximum is seen to occur when $\Omega / (2\pi) \sim 0.04$ ($\kappa a = 1$), where, recall, $\Omega = \omega \kappa^{-2} / \nu$. If the frequency at the maximum depends only on the double-layer thickness and the kinematic viscosity of the electrolyte, with $\kappa a \approx 2.57$ and $a \approx 78$ nm, the maximum should occur when $\omega / (2\pi) \sim 0.04(2.57)^2 \nu / a^2 \approx 40$ MHz. While this is indeed close to the experimentally observed maximum, a more convincing comparison requires data with larger Ω. This could be achieved, in the same frequency range, by further decreasing the ionic strength and, hence, increasing the double-layer thickness.

At experimentally accessible frequencies, O'Brien's theory[9] is accurate at high frequencies when $\kappa a \gg 1$, as has already been shown by Mangelsdorf and White.[8] However, in the true high-frequency limit, *i.e.*, when $\Omega \gg 1$, inertial rather than viscous stresses dominate the dynamics inside the double layer. At all values of κa, the conductivity increment reaches a maximum when $\Omega \sim 0.1$. Note that the amplitude of the peak, relative to the high-frequency plateau, increases with $|\zeta'|$. When the double layer is assumed viscous, such as in O'Brien's theory, the conductivity increment increases monotonically to a limiting plateau, which is higher than when inertial effects
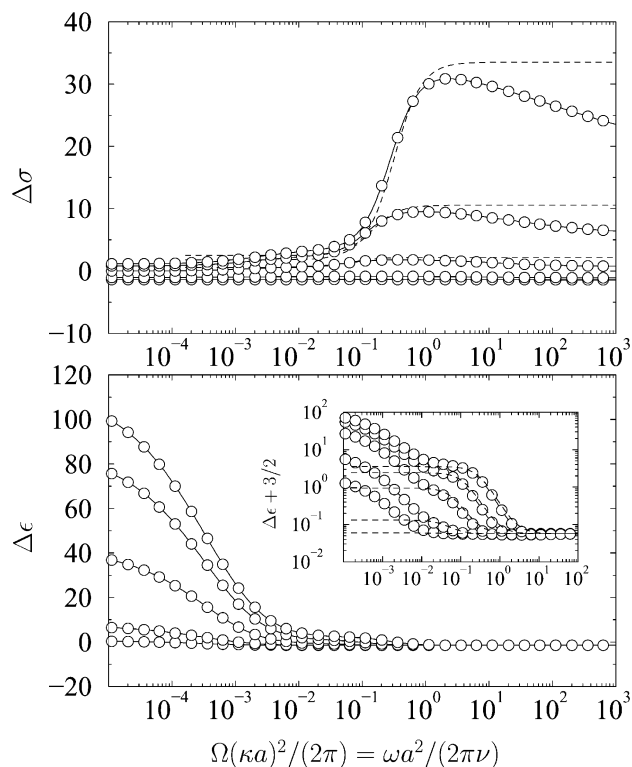
are accounted for. This is shown clearly in Figs. 4 and 5 with $\kappa a = 10$ and 50, respectively. Note that the maximum value of the conductivity increment tends to coincide with the departure of O'Brien's theory from the 'exact' calculations. As discussed above, this is because, with increasing frequency, fluid inertia gives rise to a convective ion flux that increases the phase lag of the double-layer relaxation.
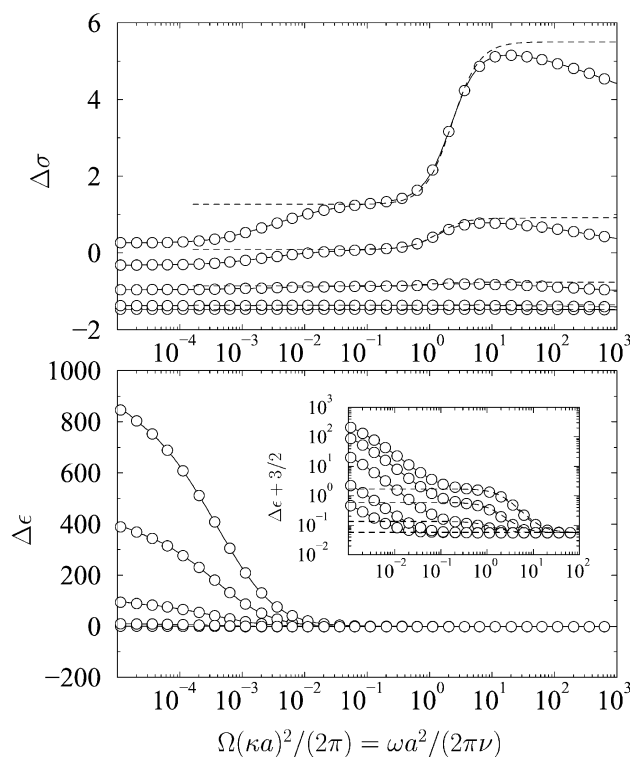
Fig. 5 As in Fig. 3, but with $\kappa a = 50$.

Finally, as shown in the insets of Figs. 4 and 5 with doubly logarithmic axes, O'Brien's prediction of the dielectric-constant increment at high frequencies is much closer to the full calculations. However, the high-frequency dielectric constant increment is dominated by the real (quasi-steady) part of the polarizability, and simply reflects the dielectric contrast of the particle and the solvent. This is captured by the well-known Maxwell–Wagner theory for the polarizability of a dielectric sphere embedded in a non-conducting dielectric continuum.[1,12] Therefore, the high-frequency behavior of the dielectric constant increment does not reflect dynamics of the double layer. Rather, the double-layer dynamics at high frequencies only affects the conductivity increment, as illustrated by the difference between O'Brien's theory and the 'exact' calculations.

IV. Summary

We have examined the dielectric relaxation of hydrodynamically smooth, spherical colloids at frequencies well beyond those previously reported, using 'exact' numerical solutions of the standard electrokinetic model. The conductivity and dielectric constant increments in the true high-frequency limit are most notably affected by fluid inertia within the diffuse double layer. Consequently, the calculations clearly reveal lower and upper bounds on the range of frequencies at which O'Brien's asymptotic theory for thin double layers is accurate. The upper frequencies at which O'Brien's theory breaks down, however, are mostly beyond those achieved in typical dielectric relaxation spectroscopy experiments. At very low ionic strengths, the calculations show that a maximum in the conductivity increment could be observed at frequencies between 10 and 100 MHz. In contrast to previous computational approaches, our method appears to be successful when the double-layer thickness is greater than the particle radius. Therefore, it may be useful for examining the electrokinetics of colloidal particles dispersed in low-dielectric fluids.

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14 A computer program that implements our numerical method for 'bare' and polymer-coated colloids is available from the authors.
15 Unpublished results of experiments performed by A. D. Hollingsworth.