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Low-Frequency Dielectric Dispersion in Colloidal Suspensions of Uncharged Insulating Particles

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The standard electrokinetic equations for a spherical uncharged insulating particle suspended in a binary electrolyte solution with an applied ac electric field are analytically solved in the general case when both the ion diffusion coefficients and valences have arbitrary values. It is shown that under these conditions, the field-induced ion density profiles extend at low frequencies at far larger distances from the particle than in the case when both diffusion coefficients have the same value. The corresponding induced charge density modifies the dipolar coefficient, leading to an additional low-frequency dielectric dispersion.

Introduction

The theory of the frequency response of suspensions of uncharged spherical particles goes back to the works of Maxwell[1] and Wagner.[2] It was later extended by O'Konski[3] to the case of particles bearing a surface conductivity. Finally, ion diffusion effects in the surrounding electrolyte solution were taken into account in ref 4. All these treatments agree in that the system undergoes just one high-frequency dispersion, which is usually in the 1 MHz to 10 MHz range. Moreover, this frequency range is essentially independent of the size of the suspended particles.

The situation is totally different when the suspended particles are charged. Theoretical[5−11] and numerical[12−14] treatments developed in the last 40 years, as well as numerous experimental studies,[15−24] show that the suspension undergoes an additional dispersion at low frequencies, usually in the 100 Hz to 100 kHz range. In contrast with the high-frequency dispersion, the characteristic time of the LFDD is proportional to the square of the radius of the suspended particles.

In this work we present rigorous analytical results that show that the LFDD is also to be expected in suspensions of uncharged particles when the diffusion coefficients of the two types of ions are different. Though this situation was generally considered in the formalisms of the LFDD of suspensions of charged particles, it was apparently omitted when the particles are uncharged. For charged particles, the effect of the difference of the diffusion coefficients on the dielectric properties of the suspension is obscured by the presence of the usual LFDD. However, for uncharged particles, it leads to the appearance of a LFDD in a frequency range where no dispersion process is classically expected.

Theory

We consider an uncharged suspended particle represented by an insulating sphere of radius R and absolute permittivity ϵ_i.

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The surrounding electrolyte solution is characterized by its absolute permittivity ϵ_e, the valences of its ions $z^\pm$, their diffusion coefficients $D^\pm$, and their equilibrium number concentrations $C_0^\pm$. We consider that there are only two types of ions in the solution and that there is no ion recombination. We assume, as is usually done in the framework of the standard model, that the ion diffusion coefficients and the electrolyte solution permittivity have constant values everywhere outside the surface of the particle.

When a macroscopic electric field $E(t) = E e^{i\omega t}$ is applied to the system, the ion concentrations $C^\pm(\vec{r})$ and the electric potential $\Phi(\vec{r})$ are determined by the following equation system.

Equations for the ion flows:

$$\vec{j}^\pm = -D^\pm \nabla C^\pm \mp C^\pm z^\pm e D^\pm \nabla\Phi/(kT) \tag{1}$$

Continuity equations:

$$\nabla \cdot \vec{j}^\pm = -\partial C^\pm/\partial t \tag{2}$$

Poisson equation:

$$\nabla^2 \Phi = -(z^+ C^+ - z^- C^-)e/\epsilon_e \tag{3}$$

To first order in the applied field, there is no field-induced liquid flow because there is no equilibrium volume charge surrounding the particle. Therefore, neither the fluid velocity term in eq 1 nor the Navier−Stokes equation need to be included.

Referring the ion concentrations to their equilibrium values,

$$C^\pm = C_0^\pm + \delta C^\pm$$

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and keeping only linear terms in E, eqs (1)–(3) transform into the following system:

$$\nabla^2 \delta C^+ = \left(\frac{C_0^+ z^+ z^+ e^2}{\epsilon_e kT} + \frac{i\omega}{D^+}\right)\delta C^+ - \frac{C_0^+ z^+ z^- e^2}{\epsilon_e kT}\delta C^-$$

$$\nabla^2 \delta C^- = -\frac{C_0^- z^- z^+ e^2}{\epsilon_e kT}\delta C^+ + \left(\frac{C_0^- z^- z^- e^2}{\epsilon_e kT} + \frac{i\omega}{D^-}\right)\delta C^-$$

$$\nabla^2 \Phi = -(z^+ \delta C^+ - z^- \delta C^-)e/\epsilon_e$$

that can be solved leading to

$$\frac{\Phi}{E\cos\theta} = \left(\frac{K_d R^3}{r^2} - r\right) + (A + \beta)K_u H(\rho,r)e^{\rho(R-r)} +$$
$$(B + 1)K_v H(\sigma,r)e^{\sigma(R-r)} \quad (4)$$

$$\frac{\delta C^\pm}{E\cos\theta} = Nz^\mp(1 \mp z^\pm\beta)K_u H(\rho,r)e^{\rho(R-r)} +$$
$$Nz^\mp(\alpha \mp z^\pm)K_v H(\sigma,r)e^{\sigma(R-r)} \quad (5)$$

where

$$\alpha = \frac{d - a - \sqrt{(d-a)^2 + 4bc}}{2c}$$

$$\beta = \frac{a - d + \sqrt{(d-a)^2 + 4bc}}{2b}$$

$$\rho^2 = \frac{a + d - \sqrt{(d-a)^2 + 4bc}}{2}$$

$$\sigma^2 = \frac{a + d + \sqrt{(d-a)^2 + 4bc}}{2}$$

$$a = \frac{i\omega}{D_{ef}} \qquad b = \Delta z^+ z^- a \qquad c = \Delta a \qquad d = Qa + \kappa^2$$

$$\Delta = \frac{D^- - D^+}{D^+ z^+ + D^- z^-} \qquad D_{ef} = \frac{D^+ D^-(z^+ + z^-)}{D^+ z^+ + D^- z^-}$$

$$Q = \frac{D^+ z^- + D^- z^+}{D^+ z^+ + D^- z^-}$$

$$\kappa = \sqrt{\frac{z^+ z^-(z^+ + z^-)e^2 N}{kT\epsilon_e}} \qquad N = C_0^+/z^- = C_0^-/z^+$$

$$A = \frac{a(\Delta - Q\beta)}{\rho^2} \qquad B = \frac{a(\Delta\alpha - Q)}{\sigma^2}$$

$$H(x,r) = \frac{1 + xr}{x^2 r^2}$$

This solution has already be presented in ref 25, as part of the calculation of the far-fields around a charged suspended particle.

The unknown coefficients K_d, K_u, and K_v, can be obtained using the usual boundary conditions. The first is obtained from the continuity of both the electric potential and the radial component of the displacement:

$$\Phi_i(R) = \Phi(R)$$

$$\epsilon_i \frac{\partial \Phi_i}{\partial r}\bigg|_{r=R} = \epsilon_e \frac{\partial \Phi}{\partial r}\bigg|_{r=R}$$

These expressions together with the linear dependence of the potential inside the particle on $r\cos\theta$, lead to

$$\epsilon_i \frac{\Phi(R)}{R} = \epsilon_e \frac{\partial \Phi}{\partial r}\bigg|_{r=R}$$

The other two conditions express the assumption that the ions from the electrolyte solution cannot penetrate inside the particle:

$$-\frac{\partial \delta C^\pm}{\partial r}\bigg|_{r=R} \mp \frac{C_0^\pm z^\pm e}{kT}\frac{\partial \Phi}{\partial r}\bigg|_{r=R} = 0$$

The results so obtained are

$$K_d =$$
$$\frac{\epsilon_i(B - A\alpha)RG_1 G_2 - \{\epsilon_e RG_1 G_2(\alpha\beta - 1) + \epsilon_i[(B+1)H_2 G_1 - \alpha(A+\beta)H_1 G_2]\}}{\epsilon_i(B - A\alpha)RG_1 G_2 + 2\{\epsilon_e RG_1 G_2(\alpha\beta - 1) + \epsilon_i[(B+1)H_2 G_1 - \alpha(A+\beta)H_1 G_2]\}}$$
$$(6)$$

$$K_u =$$
$$\frac{-3\epsilon_i\alpha RG_2}{\epsilon_i(B - A\alpha)RG_1 G_2 + 2\{\epsilon_e RG_1 G_2(\alpha\beta - 1) + \epsilon_i[(B+1)H_2 G_1 - \alpha(A+\beta)H_1 G_2]\}}$$
$$(7)$$

$$K_v =$$
$$\frac{3\epsilon_i RG_1}{\epsilon_i(B - A\alpha)RG_1 G_2 + 2\{\epsilon_e RG_1 G_2(\alpha\beta - 1) + \epsilon_i[(B+1)H_2 G_1 - \alpha(A+\beta)H_1 G_2]\}}$$
$$(8)$$

where

$$H_1 = H(\rho,R) \qquad H_2 = H(\sigma,R) \qquad G_1 = G(\rho,R)$$
$$G_2 = G(\sigma,R)$$

$$G(x,R) = \frac{\partial[H(x,r)e^{x(R-r)}]}{\partial r}\bigg|_{r=R} = -\frac{2 + 2Rx + R^2 x^2}{R^3 x^2}$$

For $D^+ = D^- = D$, these expressions simplify to

$$\frac{\Phi}{E\cos\theta} = \left(\frac{K_d R^3}{r^2} - r\right) + \frac{\kappa^2}{\sigma^2}K_v H(\sigma,r)e^{\sigma(R-r)} \quad (9)$$

$$\frac{\delta C^\pm}{E\cos\theta} = \mp Nz^\mp z^\pm K_v H(\sigma,r)e^{\sigma(R-r)} \quad (10)$$

$$K_d = \frac{\epsilon_i BRG_2 - [-\epsilon_e RG_2 + \epsilon_i(B+1)H_2]}{\epsilon_i BRG_2 + 2[-\epsilon_e RG_2 + \epsilon_i(B+1)H_2]} \quad (11)$$

$$K_v = \frac{3\epsilon_i R}{\epsilon_i BRG_2 + 2[-\epsilon_e RG_2 + \epsilon_i(B+1)H_2]} \quad (12)$$

$$\sigma^2 = \kappa^2 + \frac{i\omega}{D} \qquad B = -\frac{i\omega}{D\sigma^2} \quad (13)$$

These results reduce to those presented in ref 4 in the simplest case: $z^+ = z^- = 1$.

The main difference between the solutions corresponding to $D^+ = D^-$, eqs 9 and 10, and $D^+ \neq D^-$, eqs 4 and 5, is that in the first case the field-induced ion concentration profiles extend to a distance of the order of $1/\kappa$ from the surface of the particle, eq 10. On the contrary, in the second case, they extend much further away at low frequencies, leading to volume charge densities at distances on the order of the radius of the particle.

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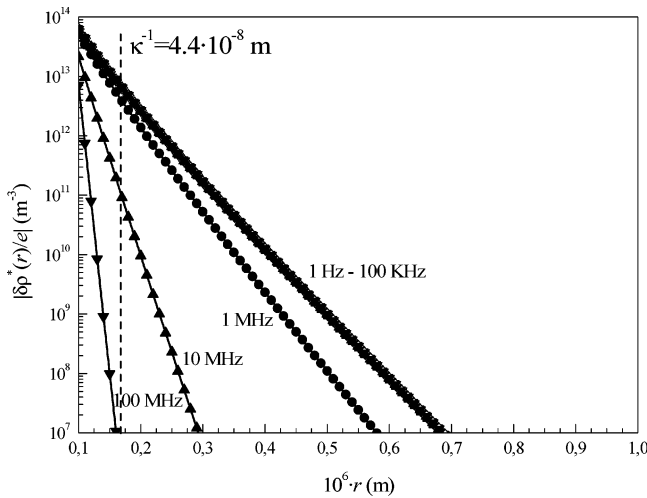
Figure 1. Modulus of the field-induced charge density profiles around an uncharged spherical particle calculated using eqs 10 and 12 for the indicated frequencies and for $D^+ = D^- = 6.8 \times 10^{-9}$ m²/s. Other constants used: $z^+ = 1$, $z^- = 2$, $\epsilon_i = 2\epsilon_0$, $\epsilon_e = 80\epsilon_0$, $N = 10^{22}$ m⁻³, $T = 300$ K, $R = 10^{-7}$ m, $k_e = 2.52 \times 10^3$ S/m, $\kappa R = 2.29$.
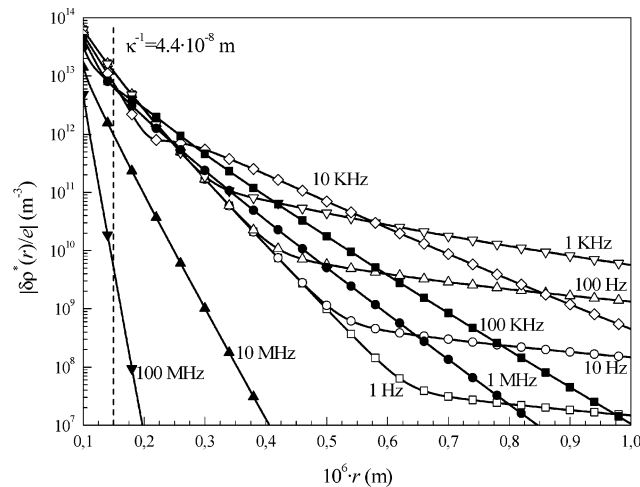

Figure 2. Modulus of the field-induced charge density profiles around an uncharged spherical particle calculated using eqs 5, 7, and 8, for the indicated frequencies and for $D^+ = 2 \times 10^{-8}$ and $D^- = 2 \times 10^{-10}$ m²/s. Remaining constants as in Figure 1.

These densities are at the origin of the appearance of an additional low-frequency dispersion in the system.

Discussion

The dielectric behavior of colloidal suspensions of uncharged particles predicted by eqs 4 and 6 is better analyzed considering an extreme case when the diffusion coefficients widely differ and when the size of the particle is comparable to the Debye screening length. Figures 1 and 2 show the modulus of the field-induced charge density profiles, $\delta\rho^* = e(z^+\delta C^+ - z^-\delta C^-)/(E\cos\theta)$, calculated using eqs 10 and 5, respectively. To be able to use (9)−(13), deduced for $D^+ = D^- = D$, in a case when $D^+ \neq D^-$, it is essential to set in eq 13 the value $D = (z^+D^+ + z^-D^-)/(z^+ + z^-)$ rather than $D = D_{ef}$.

Figure 1 shows that when the two diffusion coefficients have the same value, the field-induced charge density profile around the particle has approximately an exponential shape that is frequency independent up to the Maxwell−Wagner relaxation frequency ($f_{MW} \approx 3.5$ MHz). It then rapidly decreases at higher frequencies, as expected. A totally different behavior is represented in Figure 2, which corresponds to the general case when
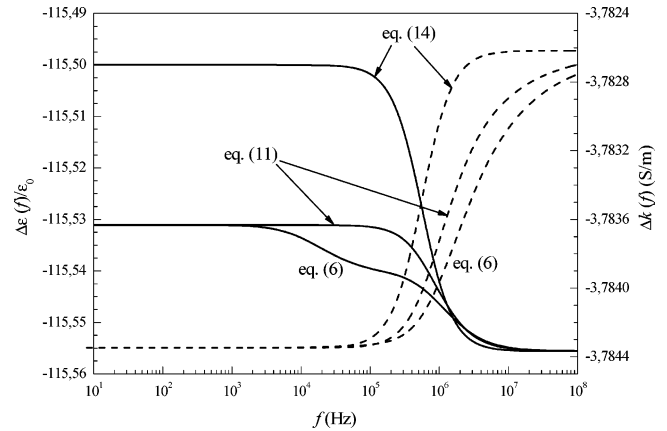
Figure 3. Theoretical permittivity (full lines) and conductivity (dashed lines) increment spectra for colloidal suspensions of uncharged insulating particles calculated using the classical expression (14) ($D^+ = D^- = 6.8 \times 10^{-9}$), eq 11 ($D^+ = 2 \times 10^{-8}$ and $D^- = 2 \times 10^{-10}$ m²/s), and eq 6. Remaining constants as in Figure 1.

the two diffusion coefficients have different values. The lowest frequency profile is almost the same as in Figure 1, except for the long-reaching tail that appears at very low charge concentrations. This tail is ever more important at higher frequencies whereas the charge density increases instead of remaining constant as in Figure 1. This increment stops at around 10 kHz, and the charge density profiles remain approximately constant and then rapidly decrease at very high frequencies, just as in Figure 1.

This behavior clearly shows that a difference in the diffusion coefficient values of the two types of ions leads to the appearance of an additional low-frequency dispersion. It is due to the small charge densities that build up far away from the surface of the particle, at distances on the order of its radius rather than the reciprocal Debye length. This large distance has two main consequences: it requires a long time to build up so that the dispersion phenomenon appears at low frequencies, and it leads to significant contributions to the dipolar coefficient despite the small value of the charge densities involved.

Figure 3 shows the permittivity and conductivity increments calculated using the usual expressions:[26]

$$\Delta\epsilon = \frac{\epsilon - \epsilon_e}{p} = 3\epsilon_e\left[K_d' + \frac{k_e}{\omega\epsilon_e}K_d''\right]$$

$$\Delta k = \frac{k - k_e}{p} = 3k_e\left[K_d' - \frac{\omega\epsilon_e}{k_e}K_d''\right]$$

where p is the volume fraction of suspended particles and k_e is the conductivity of the electrolyte solution:

$$k_e = \frac{Nz^+z^-e^2(z^+D^+ + z^-D^-)}{kT}$$

The different curves correspond to eqs 6 and 11 and the classical expression obtained from the solution of the Laplace equation, fully neglecting all diffusion related effects:[26]

$$K_d = \frac{\epsilon_i - \epsilon_e}{\epsilon_i + 2\epsilon_e} - \frac{\dfrac{3\epsilon_i}{2(\epsilon_i + 2\epsilon_e)}}{1 + i\omega\dfrac{\epsilon_i + 2\epsilon_e}{2k_e}} \tag{14}$$

As can be seen, diffusion effects are all important in the extreme
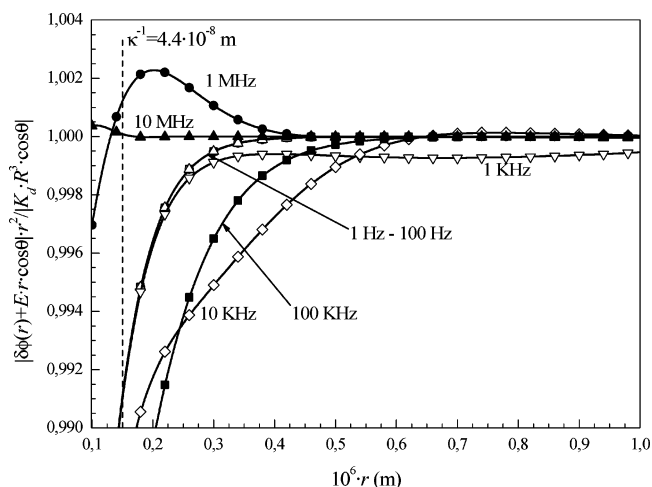
Figure 4. Modulus of the electric potential (minus the applied field term) profile around an uncharged spherical particle divided by the modulus of just the dipolar potential, eqs 4 and 6, calculated for the indicated frequencies and for $D^+ = 2 \times 10^{-8}$ and $D^- = 2 \times 10^{-10}$ m^2/s. Remaining constants as in Figure 1.
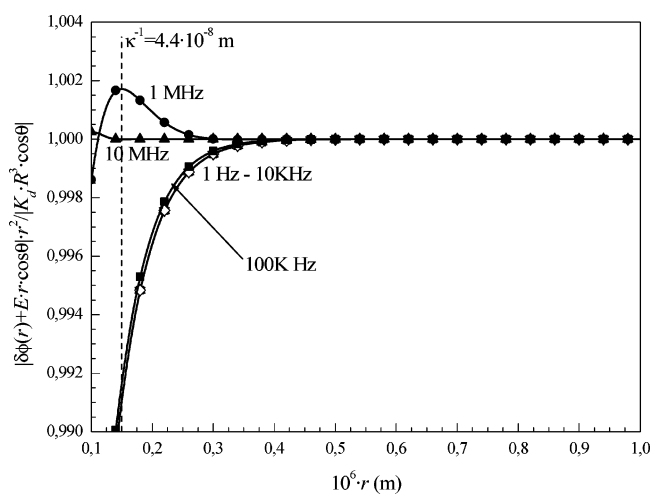
Figure 5. Modulus of the electric potential (minus the applied field term) profile around an uncharged spherical particle divided by the modulus of just the dipolar potential, eqs 9 and 11, calculated for the indicated frequencies and for $D^+ = D^- = 6.8 \times 10^{-9}$ m^2/s. Remaining constants as in Figure 1.

case chosen, reducing the dispersion amplitude to less than half its classical value. Moreover, the difference of the two diffusion coefficients introduces an additional low-frequency dispersion totally ignored in the existing theories, eqs 14 and 11. Although the total amplitude of the dispersion is very small (as expected for low-permittivity insulating particles suspended in a high-permittivity conducting medium), it should be noted that the amplitude of the new dispersion term can be of the same order of magnitude as that of the high-frequency term, Figure 3.

As a concluding remark, it is worth noting that the results obtained draw attention to a possible difficulty of numerical calculations dealing with the dielectric and electrokinetic properties of suspensions. Such calculations typically integrate the concentration and potential profiles starting at distances of

the order of 20 Debye lengths[12] from the surface of the particle, where it is assumed that the system is electroneutral so that asymptotic expressions apply. The above results show that this assumption could be unjustified when the diffusion coefficients differ, because the charge density profiles could then extend to much longer distances. The small values of these charge densities are misleading, as can be seen in Figures 4 and 5, where the modulus of the potential minus the term corresponding to the applied field, eqs 4 and 9, is divided by the modulus of the dipolar potential calculated using eqs 6 and 11. Figure 5 shows that both potentials reduce to the same value a few Debye lengths from the surface of the particle when $D^+ = D^-$. On the contrary, according to Figure 4, which corresponds to $D^+ \neq D^-$, a distance of 10 particle radii is still not sufficient to numerically determine the dipolar coefficient at a frequency of 1 kHz. Further study is required to establish whether these conclusions, valid for uncharged particles, also apply to charged ones.

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