Dielectric enhancement due to electrochemical double layer: Thin double layer approximation

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The dielectric constant and conductivity of a dilute ensemble of immobile, spherical particles with fixed surface (zeta) potential Φ_o, immersed in an electrolytic solution, is obtained in the thin double layer approximation $\delta \ll a$, δ being the thickness of the double layer, and a the radius of the particles. Equations of motion for coions and counter-ions are solved by the method of matched asymptotics. The equations of motions, linearized in the applied electric field E_o and with coefficients that are functions of the unperturbed potential (zeroth order in E_o), are solved to second order in (δ/a). The term giving enhancement in the real part of the effective dielectric constant of the ensemble ε_e', is second order in δ/a; but the series converges if $(\delta/a)t^2/(1-t^2) \ll 1$, where $t = \tanh(e\Phi_o/k_BT)$, e being the ionic charge, k_B the Boltzmann constant, and T the absolute temperature. The static value of ϵ_e', to this order, is $\epsilon_e' \sim 36 f\epsilon' t^2/(1-t^2)^2$, where f is the volume fraction of particles, ϵ' the real part of the dielectric constant of the solution. When $\Phi_o \rightarrow \infty$, therefore, $t \rightarrow 1$, ϵ_e' diverges as $\epsilon_e' \sim 9/4 f\epsilon' \exp(e\Phi_o/k_BT)$. The present treatment is free from the approximations of previous analytical results. When applicable, the theory agrees well with experiments over three decades in frequency, with one adjustable parameter Φ_o. Comparison with other theories are made.

I. INTRODUCTION

A charged particle, like a clay particle, immersed in an electrolytic solution acquires a charge cloud, known as an electrochemical double layer. Polarization of the double layer in an external electric field has been invoked, for the last 20 years as the mechanism responsible for large (~1000) values of low frequency dielectric constant of rocks containing clay particles, as well as other colloidal and biological systems.

In this paper, we give a rigorous analysis of the phenomenon, and obtain excellent agreement with experiments. This analysis is free from incorrect assumptions of previous theories, and provides insight that numerical solutions cannot.

Schwan[1] and co-workers (in 1962) observed that a suspension of polystyrene particles (of ~ 0.1 μm diam) in KCl solution has a dielectric constant of well over 10^3 at frequencies below 1 kHz. This is remarkable considering that the dielectric constant of the solution is about 80 and that of the polystyrene is about 2. They also found that (i) the dielectric constant is proportional to the particle size; (ii) the characteristic time is proportional to the square of the particle radius, and (iii) both the dielectric constant and the characteristic time are independent of salinity at high salinity. Neither the Maxwell–Wagner effect[2–5] nor the electrophoretic effect[1] were capable of explaining these high values, or the size dependences. Accordingly, an explanation was sought in the polarization of the interfacial ions.

Schwarz[4] explained these experimental results remarkably well by a model of interfacial charges which cannot exchange with those in the bulk of the solution. This model has been criticized in the literature for being *ad hoc*.[6–10]

In the more recent treatments,[7–11] the tightly bound double layer is abandoned in favor of the Guoy–Chapman model.[12] The Guoy–Chapman or the diffuse double layer assumes that the charge distribution is given by the Boltzmann distribution in terms of the potential. The potential is given, self-consistently, in terms of these charges by Poisson's equation. The first step of the problem involves solving these equations to a suitable approximation.

Next, to obtain the dielectric and conductivity response, an external field E_0 is applied. Our starting premises are the same as these recent investigations,[7–11] but our procedure is different from the previous techniques.

We obtain here analytical result in the limit that the double layer thickness δ is small compared to the radius a of the charged particle (with a surface zeta-potential Φ_0) using matched asymptotic expansions.[13,14] The technique is described briefly below. The existence of a boundary layer naturally separates the space into overlapping inner and outer regions (see Fig. 1). Solutions are developed in power series in (δ/a) in each region, and are matched between the regions order by order. Far from the particle, the screening cloud shields the charge, the potential becomes small, the terms which

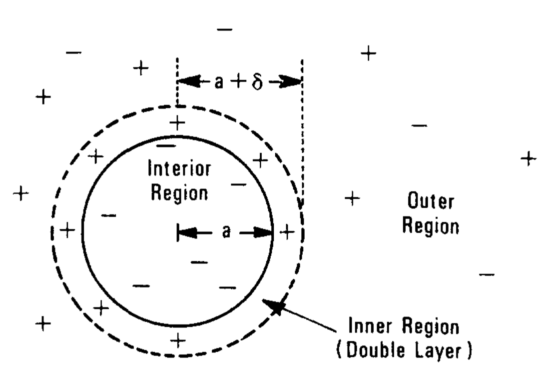

FIG. 1. A negatively charged particle immersed in electrolyte attracts positively charged counterions and repels negatively charged coions in a double layer of thickness δ.

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are exponentially small, can be neglected in comparison with algebraic terms and the equations become simpler. If r is the distance from the center of a particle, for $r \sim a+\delta$, i.e., in the boundary layer region, the potential changes rapidly and the governing equations assume different forms. To simplify them, the rapid variations, with distance, are emphasized by a coordinate-stretching-transformation to a new variable $X=(r-a)/\delta$. Then the asymptotic form of the inner solution in the outer region ($X \to \infty$) is matched, order by order in δ/a, to the asymptotic form of the outer solution in the inner region ($r \to a$). We have used this method previously to obtain the potential and charge distribution for the unperturbed $E_0=0$ case.[15] Excellent agreement with numerical results is found with the solution containing terms just up to first-order in (δ/a).

When an external field $E_0 e^{-i\omega t}$ is applied, the currents acquire nonzero values $\mathbf{j}_\pm$ and the potential changes to $\Phi+\phi$, and the charge densities become $N_\pm+n_\pm$. All the field induced quantities are functions of E_0, and are denoted by the lower scripts. Since we are interested in the linear response only, we obtain charges, potential and currents linear in E_0. The equations for $n_\pm$ and ϕ are described in Sec. II. In Sec. III, we give solutions of $n_\pm^{(0)}$, $\phi^{(0)}$ zeroth order in δ/a by heuristic arguments. The rigorous derivation is given in Appendix A. It turns out that the dielectric constant becomes large when the induced dipole moment and the induced potential develop an out-of-phase component. The first nonzero out-of-phase component comes from terms second order in (δ/a). The solutions to first-order in (δ/a) are given in Sec. IV and are used in Sec. V to obtain solutions to order $(\delta/a)^2$. For the simplicity of presentation we take $D_+=D_-$ but we give the final general solution when $D_+\neq D_-$. Also in Sec. V, the dielectric constant and conductivity of an ensemble of such particles are considered. Comparison with experimental data of Schwan[1] is made. In Sec. VI, a summary of the derivation is given. In Sec. VII, our results are compared with other theories. Appendix B contains some mathematical details.

Our perturbative approach lends to a new understanding of the mechanism that gives rise to the dielectric enhancement. This mechanism is vastly different from that proposed by Schwarz and also from the Maxwell–Wagner effect. Schwarz's or Maxwell–Wagner effect arises principally from induced charges on the surface. In our case the enhancement depends critically on a neutral induced diffusion cloud that extends far beyond the original double layer. In the unperturbed double layer, charges fall off exponentially as $\exp[-(r-a)/\delta]$. The induced cloud falls off rather slowly, as

$$\exp[-\lambda(r-a)], \quad \lambda \sim \sqrt{\omega} ,$$

and the enhancement disappears when ω becomes large so that $a\lambda \ll 1$. These points are discussed in Secs. VI and VII.

II. MODEL AND POTENTIAL IN THE PRESENCE OF AN EXTERNAL FIELD

As pointed in the Introduction, we adopt the model which is accepted in the recent studies.[7–11] A dilute ensemble of particles immersed in an electrolytic solution, with potential given by the Poisson–Boltzmann equations. The charge density and the potential around a charged particle in the absence of an external field are already obtained analytically in Ref. 15. Henceforth, we will refer to such a solution as the unperturbed solution.

In the presence of a quasistatic external electric field $E_0\exp(-i\omega t)$, the charge densities and potential are perturbed from the equilibrium values. Hence,

$$N_\pm^t = N_\pm + n_\pm , \tag{2.1}$$

$$\Psi^t = \Psi + \psi , \tag{2.2}$$

where $N_\pm^t$, $N_\pm$, and $n_\pm$ are the total charge densities, unperturbed charge densities, and perturbed charge densities respectively, and Ψ^t, Ψ, and ψ are the total potential, unperturbed potential, and perturbed potential, respectively. Here Ψ's and ψ are normalized potentials, related to the actual potential Φ through $\Psi=(e/k_BT)\Phi$. The total ionic currents are

$$\mathbf{j}_\pm^t = D_\pm(-\nabla N_\pm^t \mp N_\pm^t \nabla\Psi^t) . \tag{2.3}$$

The first term in the above corresponds to diffusion current while the second term is the consequence of conduction current. Assuming that the perturbing electric field is small, $n_\pm$ and ψ can be assumed to be linearly proportional to E_0, when $E_0^2 \ll E_0$. Substituting Eqs. (2.1) and (2.2) into Eq. (2.3), and using the fact that the ionic currents are *zero* in the *absence* of the external field, the perturbed currents that are linearly proportional to E_0 are

$$\mathbf{j}_\pm \sim D_\pm(-\nabla n_\pm \mp N_\pm \nabla\psi \mp n_\pm \nabla\Psi) + O(E_0^2) , \quad E_0 \to 0 . \tag{2.4}$$

The total charge densities, potential, and currents have to satisfy the Poisson's equation, i.e.,

$$\nabla^2\Psi^t = -\frac{N_+^t - N_-^t}{2N_0\delta^2} , \tag{2.5}$$

where $\delta=[\epsilon' k_BT/(e^2 2N_0)]^{1/2}$ is the Debye length ϵ' the real part of the dielectric constant of the ionic solution and N_0, the equilibrium ionic densities in the absence of the charged particles. Also, from the continuity equations,

$$\nabla\cdot\mathbf{j}_\pm = i\omega n_\pm . \tag{2.6}$$

Linearizing Eqs. (2.5) and (2.6) with Eqs. (2.1), (2.2), and (2.4), we have the pertinent equations

$$\nabla^2\psi = -\frac{n_+ - n_-}{2N_0\delta^2} , \tag{2.7}$$

and

$$D_\pm\nabla\cdot(-\nabla n_\pm \mp N_\pm\nabla\psi \mp n_\pm\nabla\Psi) = i\omega n_\pm . \tag{2.8}$$

Equations (2.7) and (2.8) constitute three coupled differential equations from which the three unknowns, $n_\pm$ and ψ can be solved. The appropriate boundary conditions are

$$\mathbf{j}_\pm\cdot\hat{r}\big|_{r=a} = 0 , \tag{2.9}$$

where a is the radius of the particle. This implies that the ions do not penetrate the insulating particle. The

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continuity of potential implies that

$$\psi(a^+)=\psi(a^-) \;, \tag{2.10}$$

and the continuity of displacement current gives rise to

$$\epsilon' \frac{\partial\psi}{\partial r}\bigg|_{a^+} = \epsilon_p \frac{\partial\psi}{\partial r}\bigg|_{a^-} \;, \tag{2.11}$$

where ϵ_p is the dielectric constant of the insulating particle. The potential for $r<a$ is given by the solution of Laplace's equation

$$\nabla^2\psi=0 \;, \quad r<a \;. \tag{2.12}$$

In the outer region, we require that as $r\to\infty$,

$$\psi \sim -e_0 r\cos\theta \;,$$

where

$$e_0=E_0 e/k_B T \;, \tag{2.13}$$

i.e., only the applied field exists when one is very far from the particle. The boundary conditions for the ionic densities at infinity are

$$n_\pm \to 0 \;, \quad \text{as } r\to\infty \;. \tag{2.14}$$

Because of the nature of the applied field, and the boundary condition (2.13), it follows that

$$n_\pm(\mathbf{r})=n_\pm(r)\cos\theta \;, \quad \psi(\mathbf{r})=\psi(r)\cos\theta \;. \tag{2.15}$$

At this stage, Eqs. (2.7) and (2.8) with the boundary conditions still seem formidable. However, they can be made tractable by expanding the quantities in power series of (δ/a):

$$n_\pm \sim n_\pm^{(0)}+(\delta/a)\,n_\pm^{(1)}+(\delta/a)^2 n_\pm^{(2)}+\cdots \;, \tag{2.16a}$$

$$\psi \sim \psi^{(0)}+(\delta/a)\,\psi^{(1)}+(\delta/a)^2\psi^{(2)}+\cdots \;, \tag{2.16b}$$

$$N_\pm \sim N_\pm^{(0)}+(\delta/a)\,N_\pm^{(1)}+\cdots \;, \tag{2.16c}$$

$$\Psi \sim \Psi^{(0)}+(\delta/a)\,\Psi^{(1)}+\cdots \;. \tag{2.16d}$$

The series (2.16c) and (2.16d) are already obtained in Ref. 15. We divide the space outside the sphere into an outer and inner region. The outer region is the region where $(r-a)\gg\delta$, i.e., where sufficient Debye shielding occurs. The inner region is the region where $(r-a)\sim O(\delta)$, i.e., in the double layer itself. Next, we seek the solutions of the terms in the perturbation series (2.16a) and (2.16b) in the outer and inner regions. The solutions in the outer and inner regions are asymptotically matched to each other in the overlapping region through the technique of matched asymptotic expansions.[13,14] This technique gives analytic solutions under the thin double layer approximation, i.e., $\delta\ll a$.

III. THE ZEROTH ORDER SOLUTION

When $\delta/a\to 0$, the charged particle is completely shielded by Debye shielding and the insulating particle looks like a neutral particle when one is outside the double layer. Hence, the zeroth order solution resembles the solution of an insulating particle in the presence of a conductive medium. In the outer region, we may write

$$\psi_{\text{out}} \sim \psi_{\text{out}}^{(0)} = -e_0 r\cos\theta - \tfrac{1}{2}e_0(a^3/r^2)\cos\theta \;, \quad \delta/a\to 0 \;, \tag{3.1}$$

a well-known solution for an insulating particle in a conductive medium. It can be easily shown that in such a problem, the diffusion current is zero outside the particle, or

$$n_{\pm\text{out}} \sim n_{\pm\text{out}}^{(0)}=0 \;, \quad \delta/a\to 0 \;. \tag{3.2}$$

It is also easily shown that the inner solutions that match to Eqs. (3.1) and (3.2), are

$$\psi_{\text{inn}}^{(0)} = -\tfrac{3}{2}e_0 a\cos\theta \sim \lim_{r\to a}\psi_{\text{out}}^{(0)} \;, \tag{3.3}$$

$$n_{\pm\text{inn}}^{(0)}=0 \;. \tag{3.4}$$

The interior solution for the potential inside the particle is given by

$$\psi_{\text{int}}^{(0)} = -\tfrac{3}{2}e_0 r\cos\theta \tag{3.5}$$

from the continuity of potential. The rigorous derivation of these results are given in Appendix A.

IV. THE FIRST ORDER SOLUTION

The zeroth order solution does not give rise to the enhancement of the dielectric constant of the ensemble. To give rise to enhancement, the solution has to be such that

$$\psi = -e_0 r\cos\theta + (Pe_0/r^2)\,a^3\cos\theta \;, \tag{4.1}$$

where $P=P'+iP''$ is complex. Complex P implies that the dipolar potential in Eq. (4.1), i.e., the second term, will drive a displacement current that is out of phase with the mainstream current, which is the conduction current. Hence $P''\neq 0$ implies that there is an increase of displacement current in the system of the ensemble of particles.

For the simplicity of presentation, we consider the case $D_+=D_-=D$ where the essential physics of the problem is entailed. The final result for the general case where $D_+\neq D_-$ will be presented in Eq. (5.14). When P in Eq. (4.1) differs from $-\frac{1}{2}$, as in Eq. (3.1), there will be a nonzero normal component of the current. Therefore we proceed to find the order of the nonvanishing component of the normal current at the particle surface.

A. Inner region

We note that the electric field at the surface of the particle is purely tangential to zeroth order [see Eq. (3.3)]. To emphasize the inner region, we perform the coordinate stretching transformation,

$$r-a=\delta X \;. \tag{4.2}$$

This implies that the gradient operator is approximately

$$\nabla=\text{grad}\sim \hat{X}\frac{1}{\delta}\frac{\partial}{\partial X}+\hat{\theta}\frac{1}{a}\frac{\partial}{\partial\theta}-\hat{\theta}\frac{\delta X}{a^2}\frac{\partial}{\partial\theta} \;, \quad \delta\to 0 \;. \tag{4.3}$$

Using Eqs. (3.3), (3.4), and (4.3) in Eq. (2.4), we find that

$$\mathbf{j}_{\pm\text{inn}}^{(0)} = \mp\hat{\theta}\,DN_\pm^{(0)}\frac{\partial}{a\,\partial\theta}\psi^{(0)} = \mp\hat{\theta}\,DN_\pm^{(0)}\tfrac{3}{2}e_0\sin\theta \;, \tag{4.4}$$

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$N_\pm^{(0)}$ is derived in Ref. 15, and is given by

$$N_\pm^{(0)}(X) = N_0\left(\frac{1 \mp t\,e^{-X}}{1 \pm t\,e^{-X}}\right)^2 , \quad t = \tanh(\Psi_0/4) . \tag{4.5}$$

Here Ψ_0 is the potential at the surface of the particle. Thus the zeroth-order potential in the inner region drives a purely circumferential zeroth-order current. The current varies rapidly with X or $r-a$. In the inner region, a divergent operator can be written approximately as

$$\nabla = \mathrm{div} \sim \hat{X}\,\frac{1}{\delta}\frac{\partial}{\partial X} + \left(\hat{X}\,\frac{2}{a} + \hat{\theta}\,\frac{1}{a\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\right) - \frac{\delta X}{a^2}\left(\hat{X}\,2 + \hat{\theta}\,\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\right) + O(\delta^2) . \tag{4.6}$$

Applying the continuity equation (2.6) in the inner region with Eqs. (3.4) and (4.6), we can show that the first nonvanishing normal component of the current is of the order (δ/a). If we assume that

$$\mathrm{j}_{\pm\mathrm{inn}} \sim \mathrm{j}_{\pm\mathrm{inn}}^{(0)} + (\delta/a)\,\mathrm{j}_{\pm\mathrm{inn}}^{(1)} + (\delta/a)^2\,\mathrm{j}_{\pm\mathrm{inn}}^{(2)} , \tag{4.7}$$

we can show from the continuity equation

$$\frac{\partial}{\partial X} j_{\pm X}^{(1)} + \frac{1}{\sin\theta}\cdot\frac{\partial}{\partial\theta}\sin\theta\, j_{\pm\theta}^{(0)} = 0 . \tag{4.8}$$

Integrating Eq. (4.8) with the substitution of Eqs. (4.4) and (4.5), we have

$$j_{\pm X}^{(1)} = \pm\, 3\,e_0 D N_0\cos\theta\left[X \mp \frac{4t}{1\pm t} \pm \frac{4t\,e^{-X}}{1\pm t\,e^{-X}}\right] \sim \pm\, 3 e_0 D N_0 \cos\theta\left[X \mp \frac{4t}{1\pm t}\right], \quad X \to \infty . \tag{4.9}$$

Since $t = \tanh(\Psi_0/4)$, we notice that if the particle is highly charged or $|\Psi_0| \gg 1$, then $|t| \to 1$ implying that $j_{\pm X}^{(1)}$ can differ greatly in magnitudes when one is far away from the surface of the particle.

The wide difference in amplitudes of $j_{+X}^{(1)}$ and $j_{-X}^{(1)}$ implies that these ionic currents cannot be carried away from the inner region into the outer region by conduction current alone, since conduction gives rise to ionic currents which are equal and opposite. These normal ionic currents, which are induced by the change in the circumferential ionic currents [see Eq. (4.8)], can only be convected away from the surface by conduction and diffusion. Hence, we expect a diffusion cloud of ions in the outer region which is induced by the inequality in amplitudes of $j_{\pm X}^{(1)}$.

B. Outer region

To obtain an expression for the diffusion cloud or $n_\pm$ in the outer region, we need to solve Eqs. (2.7) and (2.8). Using the fact that

$$N_\pm \sim N_0 + \mathrm{est} , \quad \Psi \sim \mathrm{est} , \quad r - a \gg \delta , \tag{4.10}$$

where est stands for exponentially small term of order $\exp[-(r-a)/\delta]$. Equation (2.8) with the use of Eq. (2.7) can be written as

$$\nabla^2 n_\pm^{(1)} + (i\omega/D)\,n_\pm^{(1)} \mp (1/2\delta^2)\left[n_+^{(1)} - n_-^{(1)}\right] = 0 , \tag{4.11}$$

which is a set of coupled-mode equations. The solution can be easily obtained by taking sums and differences of

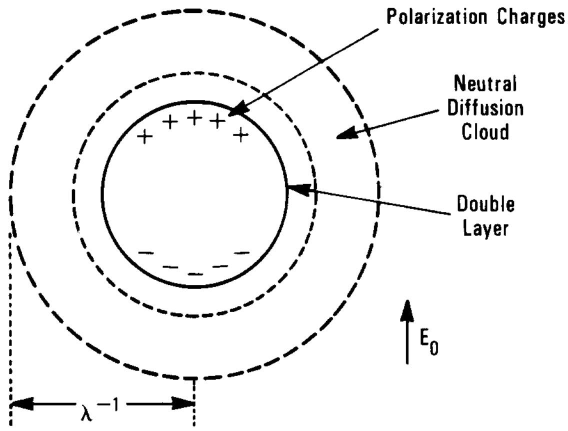

FIG. 2. In the presence of an electric field E_0 the charge distribution in the double layer changes and polarization charges develop within the particle. The most important effect is that a cloud of charges consisting of equal positive and negative charges develops. This neutral cloud has a characteristic thickness of $1/\lambda$. For enhancement, the inequality $a\lambda \ll 1$ has to be satisfies.

the above equations,

$$n_\pm^{(1)} = N_0 C^{(1)}\,\frac{a^3 e^{-\lambda(r-a)}}{r^2}\,\frac{(1+\lambda r)}{(1+\lambda a)}\cos\theta , \tag{4.12}$$

where $\lambda = (1-i)\sqrt{\omega/2D}$. In Eq. (4.12), we have neglected exponentially growing solutions, and solutions which are exponentially small (est) in the outer region. The potential can be derived by solving Laplace's equation (2.7), giving

$$\psi^{(1)} = P^{(1)}\,e_0\,(a^3/r^2)\cos\theta . \tag{4.13}$$

We have assumed the right-hand side of Eq. (2.7) to be zero due to Eq. (4.12).

The diffusion cloud with $n_+^{(1)} = n_-^{(1)}$ given by Eq. (4.12), is neutral and has a size $\sim 1/\lambda$, see Fig. 2. We will find that in Sec. IV, $n_+^{(2)} = n_-^{(2)}$ also. Despite its neutrality, this cloud plays a crucial role in introducing an out-of-phase term in the dipole moment of the particle. A new length scale $1/\lambda$ emerges of this analysis. For enhancement the inequality $\lambda a \ll 1$ has to be satisfied. The amplitudes $P^{(1)}$ and $C^{(1)}$, are obtained by matching the radial currents driven by Eqs. (4.12) and (4.13) to the normal currents given by Eq. (4.9). The radial currents from Eq. (2.4) with the approximation Eqs. (4.12) and (4.13) are

$$j_{\pm r}^{(1)} = D N_0 \cos\theta\left\{2C^{(1)}\,\frac{a^3 e^{-\lambda(r-a)}}{r^3}\left(\frac{1+\lambda r + \dfrac{\lambda^2 r^2}{2}}{1+\lambda a}\right) \pm \frac{2P^{(1)} e_0 a^3}{r^3}\right\}. \tag{4.14}$$

In the inner region $r - a \sim \delta$, the outer currents Eq. (4.14) take the following form:

$$j_{\pm r} \sim j_{\pm r}^{(0)} + (\delta/a)\,j_{\pm r}^{(1)} \sim \pm\,(\delta/a)\,D N_0\cos\theta\left\{3e_0 X \pm 2C^{(1)}\alpha + 2P^{(1)} e_0\right\} , \tag{4.15}$$

where

$$\alpha = \left(1 + \lambda a + \frac{\lambda^2 a^2}{2}\right)\Big/(1+\lambda a) . \tag{4.16}$$

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It can be shown that α is the ratio of the radial component to the circumferential component of the diffusive ionic currents near the surface of the particle. Comparing Eqs. (4.15) and (4.9), we deduce that

$$P^{(1)}=\frac{6t^2}{1-t^2}, \quad C^{(1)}=-\frac{6e_0 t}{(1-t^2)\alpha} . \tag{4.17}$$

The potential is given by

$$\psi\sim\psi^{(0)}+\left(\frac{\delta}{a}\right)\psi^{(1)}=-e_0 r\cos\theta+\frac{e_0 a^3\cos\theta}{r^2}\left[-\frac{1}{2}+\frac{6t^2}{1-t^2}\left(\frac{\delta}{a}\right)\right]. \tag{4.18}$$

Since the induced dipole moment $P^{(1)}$ is still pure real, there is no dielectric enhancement up to order (δ/a). This is very much like the O'Konski's[16] result, i.e., the presence of conduction current alone in the double layer does not give rise to dielectric enhancement.

V. HIGHER ORDER THEORY

In the previous section, we have derived the potential up to order $\psi^{(1)}$, but $P^{(1)}$ still does not contain an out-of-phase term. An out-of-phase term for P, appears in the second order solution $\psi^{(2)}$. Previously, we obtained $\psi^{(1)}$ from $j_{\pm X}^{(1)}$ in the double layer. By the similar token, $\psi^{(2)}$ is obtained from $j_{\pm X}^{(2)}$ in the double layer. From the continuity equation, and using the perturbation series Eqs. (2.16) and (4.7) in the inner region, we can show that

$$\frac{1}{a}\frac{\partial}{\partial X}j_{\pm X}^{(2)}=i\omega n_\pm^{(1)}-\frac{1}{a\sin\theta}\frac{\partial}{\partial\theta}\sin\theta(j_{\pm\theta}^{(1)}-Xj_{\pm\theta}^{(0)})-\frac{X}{a}j_{\pm X}^{(1)} , \tag{5.1}$$

where

$$j_{\pm\theta}^{(1)}=D\frac{\partial}{a\,\partial\theta}\{-n_\pm^{(1)}\mp[N_\pm^{(1)}\psi^{(0)}+N_\pm^{(0)}(\psi^{(1)}-X\psi^{(0)})]\} , \tag{5.2}$$

and from Ref. 15,

$$N_\pm^{(1)}=\mp N_\pm^{(0)}\frac{2te^{-X}}{(1-t^2e^{-2X})}[t^2(1-e^{-2X})-2X] , \tag{5.3}$$

$j_{\pm\theta}^{(0)}$ and $j_{\pm X}^{(1)}$ are given in Eqs. (4.4) and (4.9), respectively.

To derive $j_{\pm X}^{(2)}$, we need to know $\psi^{(1)}$ and $n_\pm^{(1)}$ in the double layer region. We have anticipated this earlier, for when we evaluate the outer solution of $n_\pm^{(1)}$ and $\psi^{(1)}$ in Eqs. (4.12) and (4.13), near the surface of the particle, we have nonzero values

$$n_{\pm\mathrm{out}}\sim(\delta/a)\,n_{\pm\mathrm{out}}^{(1)}\sim\delta N_0 C^{(1)}\cos\theta , \quad r\to a , \tag{5.4a}$$

$$\psi_{\mathrm{out}}\sim\psi_{\mathrm{out}}^{(0)}+(\delta/a)\,\psi_{\mathrm{out}}^{(1)}\sim[-\tfrac{3}{2}e_0+(\delta/a)P^{(1)}e_0]\,a\cos\theta, \quad r\to a . \tag{5.4b}$$

In other words, Eqs. (4.12) and (4.13) imply nonzero $n_\pm^{(1)}$ and $\psi^{(1)}$ quite easily in the inner region that will match asymptotically to the outer solutions (5.4a) and (5.4b). The derivation is given in Appendix B:

$$n_\pm^{(1)}=\mp N_\pm^{(0)}a\left[C_3^{(1)}\frac{e^{-X}}{1-t^2e^{-2X}}-C^{(1)}\left(\frac{t(1+2X)e^{-X}}{1-t^2e^{-2X}}\pm1\right)\right]\cos\theta, \tag{5.5a}$$

$$\psi^{(1)}=\left[C_3^{(1)}\frac{e^{-X}}{1-t^2e^{-2X}}-C^{(1)}\frac{t(1+2X)e^{-X}}{1-t^2e^{-2X}}+P^{(1)}e_0\right]a\cos\theta. \tag{5.5b}$$

The unknown $C_3^{(1)}$ can be determined by the boundary condition (2.11), i.e., the displacement current produced by Eq. (5.5b) is equal to the displacement current produced by Eq. (3.5) at $r=a$ or $X=0$, giving

$$-\tfrac{3}{2}e_0\frac{\epsilon_p}{\epsilon'}=-C_3^{(1)}\frac{1+t^2}{(1-t^2)^2}-C^{(1)}\frac{t(1-3t^2)}{(1-t^2)^2} . \tag{5.6}$$

Hence, with $n_\pm^{(1)}$ and $\psi^{(1)}$ known in the inner region, we can determine $j_{\pm X}^{(2)}$ from Eq. (5.1),

$$\begin{aligned}j_{\pm X}^{(2)}(X,\theta)&=i\omega N_0 a\left\{C^{(1)}X\mp\frac{1}{(1\pm t)^2}[C_3^{(1)}+t(1\pm 2t)C^{(1)}]\right\}\cos\theta\\&\mp\frac{DN_0}{a}\cos\theta\left[6e_0X^2+2X\left(P^{(1)}e_0\pm C^{(1)}\mp\frac{12e_0t}{1\pm t}\right)\right.\\&\left.-24e_0\ln(1\pm t)\mp\frac{8t}{1\pm t}(P^{(1)}e_0\pm C^{(1)})\pm12e_0t\right], \quad X\to\infty .\end{aligned} \tag{5.7}$$

These normal currents $j_{\pm X}^{(2)}(X,\theta)$ will induce a potential and diffusion cloud $\psi^{(2)}$ and $n_\pm^{(2)}$ in the outer region. The potential to second order in the outer region can be shown to be

$$\begin{aligned}\psi&\sim\psi^{(0)}+\left(\frac{\delta}{a}\right)\psi^{(1)}+\left(\frac{\delta}{a}\right)^2\psi^{(2)}\\&=\left[-\frac{r^3}{a^3}-\frac{1}{2}+\frac{\delta}{a}P^{(1)}+\left(\frac{\delta}{a}\right)^2P^{(2)}\right]\frac{a^3e_0}{r^2}\cos\theta .\end{aligned} \tag{5.8}$$

The ionic densities are

$$\begin{aligned}n_\pm&\sim\frac{\delta}{a}n_\pm^{(1)}+\left(\frac{\delta}{a}\right)^2n_\pm^{(2)}\\&=\delta N_0\frac{a^2e^{-\lambda(r-a)}}{r^2}\left(\frac{1+\lambda r}{1+\lambda a}\right)\left[C^{(1)}+\frac{\delta}{a}C^{(2)}\right] .\end{aligned} \tag{5.9}$$

Next, using Eqs. (5.8) and (5.9) we can show that the outer radial currents at the surface of the particle are

$$\begin{aligned}j_{\pm r}&\sim DN_0\cos\theta\left\{\pm\frac{\delta}{a}[3e_0X+2P^{(1)}e_0\pm2C^{(1)}\alpha]\right.\\&\mp\left(\frac{\delta}{a}\right)^2\left[6e_0X^2+6X\left(P^{(1)}e_0+C^{(1)}\alpha\pm\tfrac{1}{6}C^{(1)}\frac{\lambda^3a^3}{1+\lambda a}\right)\right.\\&\left.\left.-2P^{(2)}e_0\mp2C^{(2)}\alpha\right]\right\}, \quad r\to a .\end{aligned} \tag{5.10}$$

Matching Eq. (5.10) with the inner solution obtainable from Eqs. (5.7) and (4.9):

$$j_{\pm X}\sim\left(\frac{\delta}{a}\right)j_{\pm X}^{(1)}+\left(\frac{\delta}{a}\right)^2j_{\pm X}^{(2)} , \tag{5.11}$$

we deduce that

$$\begin{aligned}P^{(2)}e_0\pm C^{(2)}\alpha&=12e_0\ln(1\pm t)\pm\frac{4t}{1\pm t}[P^{(1)}e_0\pm C^{(1)}]\mp6e_0t\\&-\frac{i\omega a^2}{2D}\frac{1}{(1\pm t)^2}[C_3^{(1)}+t(1\pm2t)C^{(1)}] .\end{aligned} \tag{5.12}$$

From the above, we can determine $P^{(2)}$ and $C^{(2)}$. Hence, in the outer region, we determined P as defined in Eq. (4.1) to second order, giving

$$\begin{aligned}P&\sim-\frac{1}{2}+\left(\frac{\delta}{a}\right)\frac{6t^2}{1-t^2}\\&+\left(\frac{\delta}{a}\right)^2\left[-\frac{3}{4}\frac{i\omega}{D}\frac{\epsilon_p}{\epsilon'}a^2+6\ln(1-t^2)-\frac{24t^2}{(1-t^2)^2}\left(t^2+\frac{1}{\alpha}\right)\right].\end{aligned} \tag{5.13}$$

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We note that $P^{(2)}$ and hence P now has an out of phase term. The first out of phase term in Eq. (5.13) can be associated with the Maxwell–Wagner effect,[2,3] which is usually small.[5] Since $1/\alpha$ is complex, the second out of phase term is magnified by $t^2/(1-t^2)^2$ which can be large when $|t| \to 1$ or $|\Psi_0| \gg 1$.

We have gone through the analysis with $D_+ \neq D_-$ and the result for P is

$$\begin{aligned} P \sim & -\frac{1}{2} + \left(\frac{\delta}{a}\right)\frac{6t}{1-t^2}\left(t + \frac{D_- - D_+}{D_s}\right) \\ & + \left(\frac{\delta}{a}\right)^2 \left\{ -\frac{3}{2}\frac{i\omega}{D_s}\frac{\epsilon_p}{\epsilon'} a^2 + \frac{12}{D_s}\left[D_+ \ln(1+t) + D_- \ln(1-t)\right] \right. \\ & - \frac{24t^2}{(1-t^2)^2}\left[t\left(t + \frac{D_- - D_+}{D_s}\right) + \frac{4D_+D_-}{D_s^2}\left(\frac{1-\alpha}{\alpha}\right) \right. \\ & \left. \left. + 1 + t\,\frac{D_- - D_+}{D_s}\right] + 6t\,\frac{D_- - D_+}{D_s} \right\} , \end{aligned} \quad (5.14)$$

where $D_s = D_+ + D_-$. In the above, α is as defined in Eq. (4.16), but in Eq. (5.14)

$$\lambda = (1-i)\sqrt{\frac{\omega D_s}{4D_+D_-}} \; . \quad (5.14a)$$

We note that if D_+ or D_- equals zero, $\lambda \to \infty$, or from Eq. (4.16), $\alpha \to \infty$. In this case, the complex terms, other than the Maxwell–Wagner term, vanish in Eq. (5.14), and the dielectric enhancement disappears. Hence, in a simpler jellium model of immobile coions and free moving counterions, the enhancement disappears. To be more explicit in the double layer, the population of coions are negligible particularly for large Ψ_0. Since we are interested in the polarization of double layer, the dominance of counter-ions in the double layer may suggest wrongly that a simpler model could be used. In this simpler model the coions would be distributed in a continuum or a jellium immobile background and counter-ions would respond to the external field. However, our results show that for the enhancement we need both the ions to be mobile. In Schwarz's model, co ions are completely neglected but the enhancement comes from the neglect of normal current in the double layer.

From Maxwell's mixing formula,[2] the effective complex dielectric constant of an ensemble of spherical particles randomly distributed in a background medium of ϵ is given by

$$\epsilon_e \cong \epsilon(1 + 3fP) \; , \quad f \to 0 \; , \quad (5.15)$$

where f is the fractional volume of the particles. For a conducting background medium,

$$\epsilon = \epsilon' + (i\sigma/\omega) \; . \quad (5.16)$$

For an ionic solution, the conductivity can be written as

$$\sigma = \epsilon'(D/\delta^2) \; . \quad (5.17)$$

We can show from Eqs. (5.13) and (5.15) that when $t \to 1$, $\omega \to 0$,

$$\epsilon_e' = \mathrm{Re}(\epsilon_e) \sim 36 f \epsilon' [t^2/(1-t^2)^2] \; . \quad (5.18)$$

Hence the dielectric constant is greatly enhanced at low frequencies.

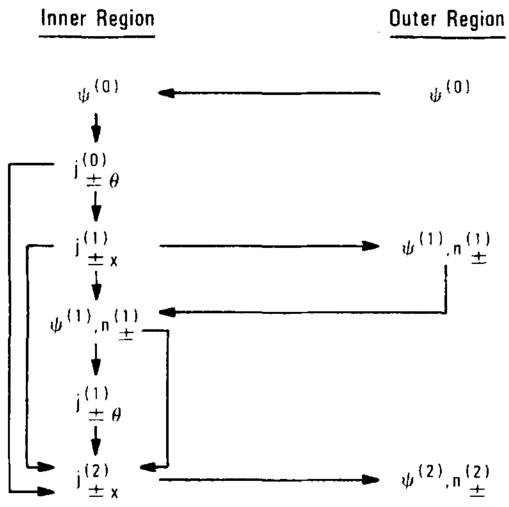

FIG. 3. The sequence showing the derivation of the potential in the outer region $\psi^{(2)}$. This potential gives the induced dipole moment $P^{(2)}$ which is responsible for enhancement. Because of the coordinate stretching, terms of different order are connected to each other in the inner region.

A point is in order concerning the range of validity of the solution (5.13). The perturbation series in Eq. (5.13) will be a good approximation only if $(\delta/a)[t^2/(1-t^2)] \ll 1$. When

$$\Psi_0 \gg 1 \; , \quad t = \tanh\Psi_0/4 \to 1 - 2\exp(-\psi_0/2)$$

and we require

$$(\delta/a)\, e^{\Psi_0/2} \ll 1 \quad (5.19)$$

for the convergence of the perturbation series (5.13). This is a stronger condition than $\delta/a \ll 1$. It seems that Fixman[9] has anticipated such a small parameter.

VI. DISCUSSION OF THE DERIVATION

Although the expressions for the perturbed quantities are long, only one term in each expression leads to the enhancement in ϵ_e'. The enhancement comes from the last term $24t^2/(1-t^2)^2\alpha$ in Eq. (5.13). The complex nature comes from α being complex and the denominator is small, since $t \to 1$. This term in Eq. (5.13) can be traced back to the last term in the expression (5.5a) for $n_\pm^{(1)}$. This term in Eq. (5.5a) corresponds to departure from equilibrium, as discussed below. Then in Eq. (5.2) for $j_{\pm\theta}^{(1)}$, only term which is important is $\partial n_\pm^{(1)}/\partial\theta$, and similarly in Eq. (5.1) for $j_{\pm x}^{(2)}$ only term that is important is $j_{\pm\theta}^{(1)}$.

We discuss the physical significance of the mathematical terms below. Figure 3 shows the mathcing sequences between the inner and the outer solutions. It also shows how certain terms induce other terms in this perturbative derivation. First, we note that the zeroth order potential $\psi^{(0)}$, which exists both in the inner and the outer regions, drives a circumferential current $j_{\pm\theta}^{(0)}$, which is greatly enhanced for one type of ions in the inner region. This is because $j_{\pm\theta}^{(0)}$ arises from a conduction process. Since the conductivities of the ions are proportional to the ionic populations, the conductivity for the counterions is greatly enhanced

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[see Eq. (4.4)]. This inequality in the circumferential currents induces unequal normal currents $j_{\pm X}^{(1)}$ leaving the double layer [see Eq. (4.9)]. This imbalance in normal currents cannot be taken up by the conduction process alone, since the conduction currents are equal and opposite. Therefore, a diffusion cloud is set up in the outer region, given by $n_{\pm}^{(1)}$. The potential which drives the normal conduction current $j_{\pm X}^{(1)}$ is $\psi^{(1)}$. The equation for the potential is Laplacian, because of the charge neutrality, $n_{+}^{(1)}=n_{-}^{(1)}$, in the far zone. Thus $\psi^{(1)}$ essentially comes from the enhancement of the counterion conductivity in the double layer. So far the results are similar to those of O'Konski's model.[16] In the O'Konski's model, the particle has a surface conductance, the potential obeys Laplace's equation, and diffusion currents are neglected. This model fails to predict dielectric enhancement, since $\psi^{(1)}$ is pure real. The key ingredient for the enhancement—the diffusion cloud—is missing from O'Konski's model. The importance of the diffusion cloud has also been noted by Dukhin and Shilov,[7,8] and by Fixman.[9] Next consider how the charge distribution in the double layer is modified by the diffusion cloud.

The existence of the diffusion cloud in the outer region, in which the density varies much slowly with distance than in the double layer, alters the ambient ionic densities in the outer region. The counterions and coions in the double layer match with the ambient density as $X\to\infty$, i.e.,

$$N_{\pm}^{(0)} \sim N_0 , \quad \text{when } X\to\infty , \tag{6.1}$$

in the absence of electric field. When the electric field is applied, the alteration of this ambient density from N_0 to $N_0+n_{\pm}^{(1)}$ in the outer region changes the structure of the ionic density in the inner region. This effect is reflected in the last term in Eq. (5.5a), $N_{\pm}^{(0)}(X)C^{(1)}a \times\cos\theta$, which grows rapidly as $N_{\pm}^{(0)}(X)$ within the double layer. However, the perturbed charges $n_{\pm}^{(1)}$ in the double layer can only be held in their places by the polarization charges induced by $\psi_{\text{int}}^{(0)}$ inside the particle (see Fig. 2). In other words, $n_{+}^{(1)}-n_{-}^{(1)}$ integrated over the thickness of the double layer should be equal to the polarization charges inside the sphere. Hence, the first two terms in Eq. (5.5a) are necessary to maintain this charge balance. Equation (5.6) states that the total perturbed charges in the double layer equals the polarization charges inside the sphere.

Next we discuss why only the last two terms in Eqs. (5.5a) and (5.5b) are important as discussed above. An ensemble of ions in statistical equilibrium satisfies the Boltzmann distribution,

$$N_{\pm}+n_{\pm}=N_0\, e^{\mp(\Psi+\psi)} , \tag{6.2a}$$

which implies

$$n_{\pm}\sim\mp N_{\pm}\psi . \tag{6.2b}$$

We notice that the first two terms in Eqs. (5.5a) and (5.5b) are in statistical equilibrium, i.e., they satisfy Eq. (6.2b). In passing, we should mention that Fixman[9] has defined a velocity potential $p_{\pm}=(n_{\pm}/N_{\pm}\pm\psi)$. From Eqs. (5.5a) and (5.5b), we find that $p_{\pm}$ is a constant across the double layer. This confirms his supposition that tangential gradient of p is constant across the thin double layer.

In summary, $n_{\pm}^{(1)}$ in the inner region is a "spill over" effect from $n_{\pm}^{(1)}$ in the outer region, which in turn come from $j_{\pm\theta}^{(0)}$ via $j_{\pm X}^{(1)}$. We can say that $n_{\pm}^{(1)}$ are all due to the enhancement of $j_{\pm\theta}^{(0)}$ in the double layer because of the enhancement of the counterion population.

Next consider the second-order current $j_{\pm X}^{(2)}$ and the terms that give rise to the out-of-phase dipole moment. The terms in statistical equilibrium do not give rise to a total current, the diffusion current cancels the conduction current. The last terms of Eqs. (5.5a) and (5.5b) are not in statistical equilibrium with each other, i.e., they do not satisfy Eq. (6.2b). These two terms give rise to $j_{\pm\theta}^{(1)}$ [see Eq. (5.2)]. Due to the enhancement of $n_{\pm}^{(1)}$ in the double layer, $j_{\pm\theta}^{(1)}$ is much larger in the double layer than outside the double layer for the counter-ions. This gives rise to $j_{\pm X}^{(2)}$ in accordance with the continuity Eq. (5.1). The term proportional to $j_{\pm\theta}^{(1)}$ is the most important term in Eq. (5.1). The first term on the right-hand side of Eq. (5.1) accounts for the Maxwell–Wagner effect, and the other terms are corrections due to the curvature of the sphere. Thus, $j_{\pm X}^{(2)}$ is derived from $n_{\pm}^{(1)}$, $j_{\pm\theta}^{(1)}$, and $j_{\pm X}^{(1)}$ in the double layer, as indicated in Fig. 3. However, due to the fact that $n_{\pm}^{(1)}$ has an out-of-phase term with the applied field, $j_{\pm X}^{(2)}$ has an out-of-phase term. Hence $\psi^{(2)}$ or $P^{(2)}$ has an out-of-phase term, which enhances the displacement current in the system.

The ratio of the radial component of the diffusion current to the value of the diffusion cloud in the matching region between the inner and outer regions is proportional to

$$\lim_{r\to a}\frac{(\partial n_{\pm}^{(1)}/\partial r)}{n_{\pm}^{(1)}}\sim-\frac{2}{a}\,\frac{\left(1+\lambda a+\dfrac{\lambda^2a^2}{2}\right)}{(1+\lambda a)}=-\frac{2}{a}\,\alpha . \tag{6.3}$$

Since α is complex, the diffusion cloud near the double layer always has an out-of-phase term compared to the radial diffusion currents. The radial diffusion currents are in phase with the applied electric field since it is caused by $j_{\pm\theta}^{(0)}$. Hence, $n_{\pm}^{(1)}$ are out-of-phase with the applied field.

The above description follows the mathematical derivation which is an iterative scheme to derive the perturbation series. We like to summarize the result in a more physical perspective, explaining the source of the out-of-phase dipole moment. In summary, the existence of the double layer greatly enhances the counterion current in the double layer region in the presence of an externally applied field. This strong counter-ion ion current piles up charges at the polar ends of the particle, which discharge into the bulk solution through a diffusion process in addition to a conduction process. At low frequencies, a large diffusion cloud of size $\lambda^{-1} =\sqrt{2D/\omega}$ is set up. The diffusion current in the diffusion cloud is out of phase with the applied field. This out-of-phase diffusion current has a "back-up" effect on the circumferential current in the double layer, causing the circumferential current to be out-of-phase. Hence, the charges piled up at the ends of the sphere have an out-of-phase component, giving rise to the out-

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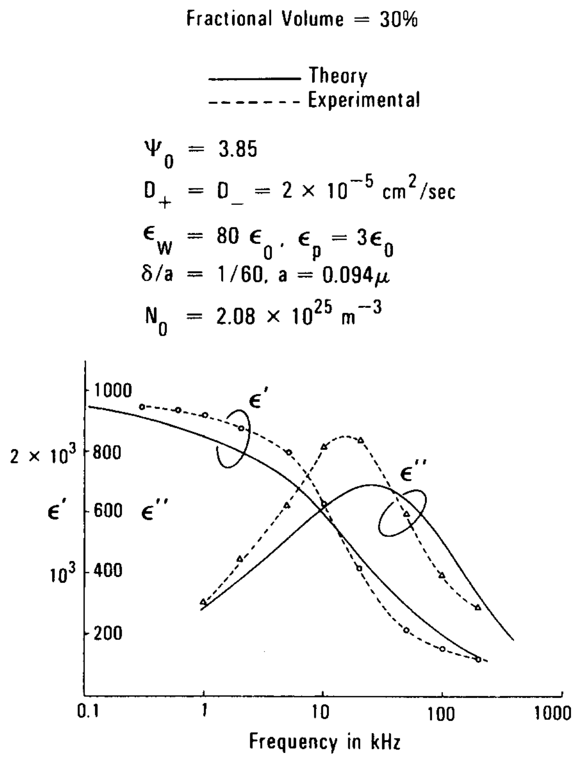

FIG. 4. The comparison of theroetical and experimental values of the real and imaginary parts of the dielectric constant of polystyrene particles suspended in electrolyte solution.

of-phase dipole moment. On the other hand, when the frequencies are high, the rapid oscillation of circumferential current in the double layer does not allow the buildup of a large diffusion cloud outside the double layer. In fact, the diffusion cloud is smaller both in extent, and in amplitude. Hence the out-of-phase component of the circumferential current in the double layer is small, resulting in little or no enhancement.

VII. DISCUSSION OF THE RESULTS

In this section we compare our theory with experiment. The limitations of the present model and analysis are pointed out and possible remedies are suggested. Brief comments on other theories are also made.

In Fig. 4 we compare our theory with the experimental data of Schwan *et al.*[1] We use the experimental values of $\epsilon' = 80\epsilon_0$ (ϵ_0 is the dielectric constant of vacuum),

$$N_0 = 2.08\times 10^{25}\ \mathrm{m}^{-3}\ ,$$

$$a = 0.094\ \mu\mathrm{m}\ ,\quad \delta/a = 1/60\ ,$$

$$D_+ = D_- = 2.0\times 10^{-5}\ \mathrm{cm}^{-2}/\mathrm{s}\ ,\quad f = 30\%\ .$$

The diffusion coefficients are typical of NaCl solution.[17] The only quantity that was not measured is Ψ_0. Taking $\Psi_0 = 3.85$, for an agreement with the static value of ϵ_e', we find excellent agreement with experiment over three decades in frequency. This surface potential corresponds to a surface charge density which is three times smaller than that used by Fixman.[9] The inequality $\delta \ll a\exp(-|\Psi_0|/2)$ is satisfied. In Fig. 4, we also plot the imaginary part of ϵ after subtracting the dc contribution, i.e., $\epsilon'' = [\sigma_e(\omega) - \sigma_e(0)]/\omega$.

Our analysis gives a broad frequency dependence which closely resembles the experiment. This dependence on ω is much broader than the frequency dependence of Debye equation,

$$\epsilon \sim 1/1 - i\omega\tau\ , \tag{7.1}$$

where τ is a characteristic time. Previously, Schwarz[4] attempted to fit the experiment of Schwan[1] by introducing a distribution of τ. In our study we find

$$\epsilon \sim \frac{1}{1 + \sqrt{-2i\omega\tau} - i\omega\tau}\ , \tag{7.2}$$

where $\tau = a^2/2D$. Equation (7.2) has a more gradual transition. This essentially is due to the fact that Eq. (7.1) corresponds to a one-dimensional diffusion process, whereas Eq. (7.2) corresponds to a complicated diffisuion process. In Schwarz's model where Eq. (7.1) ensues, the diffusion process is purely circumferential. This broader than Debye frequency dependence has been seen in many other experiments and are usually fitted to an empirical formula given by Cole and Cole[18] $\epsilon \sim 1/[1 - (i\omega\tau)^\alpha]$, where α is a constant. As far as we know, this is the first time we found a real physical explanation for such a broader than Debye type behavior. Furthermore, Eq. (7.2) has a form different than the usual Cole–Cole[18] form, although they resemble each other at low frequencies.

The dependence of τ on the size of the particle is in agreement with the experimental results of Schwan *et al.*[1] Schwarz's[4] theory gives $\tau = 2D_s/a^2$, where D_s is the surface diffusion coefficient of the charges (that cannot leave the surface). In other words, Schwarz's τ is the time needed for the charges to diffuse along the surface over the size of the particle. In our calculation D is the *bulk* diffusion coefficient.

For a fixed value of Ψ_0, the static ($\omega\tau \ll 1$) value of ϵ_e' is independent of the radius of the particle a. The experimental data shows that the static value of ϵ_e' varies linearly with a. The numerical solution of Delacey and White[11] also shows that ϵ_e' depends on a. This can be due to the following reasons. First, our analysis breaks down when the inequality $\delta \ll at^2/(1-t^2)$ does not hold. It is possible that when this inequality is not satisfied, $\epsilon_e'(\omega=0)$ varies greatly with particle size, but $\epsilon_e'(\omega=0)$ saturates to a size-independent value in the regime where it holds. We are currently studying this conjecture numerically as well as analytically. Our preliminary numerical results still show an enhancement when the inequality is not satisfied. Fixman's[9] result also shows that ϵ_e' is independent of size for $a \gg \delta\exp(\Psi_0/2)$, but depends on size when this inequality does not hold.

Second, in the experiments of Schwan Ψ_0 was not measured independently. If, indeed, the charge density in the material (polystyrene) were constant, the total charge Q and hence Ψ_0 would have changed with the radius a. From the unperturbed solution, it is easy to show that the surface charge density is given by[15]

$$e\Sigma_0 = 2e\delta N_0 e^{\Psi_0/2}\ . \tag{7.3}$$

Combining Eq. (6.1) with Eq. (5.17) gives

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$$\epsilon_e'(\omega=0) \sim \tfrac{9}{8} f \frac{\Sigma_0^2 e^2}{k_B T N_0} . \quad (7.4)$$

This should be compared with Schwarz's result

$$\epsilon_e'(\text{Schwarz}) \sim \tfrac{9}{4} f \frac{\Sigma_0 e^2 a}{k_B T} . \quad (7.5)$$

If the bulk charge density rather than the surface charge density Σ_0 were held constant our and Schwarz's theory would both give $\epsilon_e'(\omega=0) \sim a^2$. More experiments are needed to verify this prediction. The $1/T$ dependence in Eq. (7.4) agrees with experiment.[1,19]

There is a great difference between our and Schwarz's mechanisms for enhancement. Schwarz's model is essentially an amplification of the Maxwell–Wagner effect. The Maxwell–Wagner effect is due to the polarization charges inside the spherical particle. These polarization charges attract ionic charges on the outside of the spherical particle. The polarization charges are in phase with the applied electric field, but the conduction current that feeds the ionic charges outside the particle is out of phase with the applied field, enhancing the displacement current around the particle. In Schwarz's model, the polarization charges are augmented by double layer charges, with a much higher density, and like the polarization charges, do not exchange with the conduction current outside. This large amount of double layer charges augments the polarization charges, and makes the enhancement clearly noticeable. Like Maxwell–Wagner effect, the Schwarz's effect does not involve a diffusion cloud outside the particle. However, in our model the enhancement depends on the presence of a diffusion cloud outside the particle. The diffusion cloud in turn, arises from the enhanced population of the counter-ions in the double layer, giving rise to predominately counter-ionic normal current, which cannot be convected away from the double layer by a conduction process alone. This diffusion cloud carries diffusion currents circumferentially as well as radially, and is out of phase with the applied field in general. The diffusion cloud greatly enhances the perturbed counterion density in the double layer which increases the circumferential diffusion current in the double layer. This out-of-phase diffusion current in the double layer induces an out-of-phase dipole field outside the particle which is responsible for the enhancement. At high frequencies, the diffusion cloud does not have the chance to build up in amplitude and in size. The amplitude of the cloud is proportional to $1/\alpha$. Hence, at high frequencies, it disappears and there is no dielectric enhancement.

In the limit when $t \to 1$, Eq. (5.17) gives $\epsilon_e' \sim (9/4)\epsilon' f e^{\Psi_0}$. This is in agreement with Dukhin and Shilov's[7] and Fixman's[9] result in the similar limit. However, the analysis of Dukhin and Shilov is different from ours. They invoke a complicated effective boundary condition, which is obtained by heuristic arguments. They use $\delta/a \ll 1$ condition, but do not use a systematic perturbation analysis. Our perturbative approach, which provides correctly an asymptotic expression for the dipole moment P up to order δ^2/a^2, offers clearer insight. Our asymptotic series for P is a new result and is not derivable from Dukhin and Shilov's result. Their heuristic derivation gives rise to enhancement but the physical mechanism of the problem is obscured in the effective boundary condition.

We have neglected, as Schwarz and Fixman, the solvent flow and the motion of the charged particles. The motion of the particles cannot be essential for dielectric enhancement, because, many rocks containing immobile clay particles show this enhancement.[19] Second, a rough estimate[7] shows that the drift velocity of particle is lower than the ionic velocity by an order of magnitude. The solvent flow can be important and will be considered elsewhere.[20]

The present paper employs the Guoy–Chapman model. It is well known that in many circumstances this model is inadequate, and the Stern model is more appropriate.[12] In the Stern model, the layer adjacent to the solid surface is strongly bound and the rest of the interface is diffuse, as in the Guoy–Chapman model. In these cases Schwarz's model resembles the reality more closely. The present paper treats the currents normal to the surface correctly but Schwarz neglects them altogether. We have shown elsewhere that inclusion of conduction currents can reduce Schwarz's enhancement.[10] But the conduction current is subtly balanced by diffusion current. The diffusion currents cannot be treated properly in Schwarz's or Schurr's thin double layer model. A correct description of polarization for Stern type model will be valuable.

Equation (5.15) holds only as $f \to 0$, but we and all other previous investigators have used it for $f = 0.3$. Since the enhancement depends on the presence of the diffusion cloud, the large size of the diffusion cloud makes the interaction between particles important whereas the mixing formula used in Eq. (5.15) has ignored this interaction. We are currently investigating the effect of interaction between the particles. Elsewhere we have developed methods to go beyond the low concentration limit for the case $\delta \equiv 0$. Extending these to $\delta \neq 0$ is being investigated.

Finally, analytical results beyond the regime of validity of our results will be very useful.

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APPENDIX A: RIGOROUS SOLUTION FOR $(\delta/a)^0$ CASE

We present here a more rigorous derivation of the result of Sec. III. With the gradient operator approximated by Eq. (4.3) in the inner region, we can show from Eq. (2.4) that

$$\mathrm{j}_\pm \sim \left(\frac{\delta}{a}\right)^{-1} \mathrm{j}_\pm^{(-1)} + \mathrm{j}_\pm^{(0)} + \left(\frac{\delta}{a}\right) \mathrm{j}_\pm^{(1)} + \left(\frac{\delta}{a}\right)^2 \mathrm{j}_\pm^{(2)} + O\left(\frac{\delta^3}{a^3}\right) . \quad \text{(A1)}$$

Since $\mathrm{j}_\pm$ has to be bounded, as $\delta/a \to 0$, it follows that

$$\mathrm{j}_\pm^{(-1)}(X) = 0 , \quad \text{all } X . \quad \text{(A2)}$$

By collecting terms of the same order in Eq. (2.4), it follows that

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$$j_{\pm X}^{(-1)}(X)=0=\frac{D_\pm}{a}\left[-\frac{\partial n_\pm^{(0)}}{\partial X}\mp\left(N_\pm^{(0)}\frac{\partial}{\partial X}\psi^{(0)}+n_\pm^{(0)}\frac{\partial}{\partial X}\Psi^{(0)}\right)\right] . \tag{A3}$$

The above differential equation is easily integrated after multiplying it by an integrating factor $\exp(\pm\Psi^{(0)})$:

$$n_\pm^{(0)}=\mp N_\pm^{(0)}(\psi^{(0)}+C_1^{(0)}\mp C_2^{(0)}) , \tag{A4}$$

where $C_{1,2}^{(0)}$ are integration constants. The potential has to satisfy Poisson's equation (2.7). Approximating the Laplacian operator by

$$\nabla^2\sim\frac{1}{\delta^2}\frac{\partial^2}{\partial X^2} ,\quad \frac{\delta}{a}\to 0 , \tag{A5}$$

we find that

$$\frac{\partial^2}{\partial X^2}\psi^{(0)}=-\frac{1}{2N_0}(n_+^{(0)}-n_-^{(0)}) . \tag{A6}$$

Substituting Eq. (A4) into Eq. (A6) with $N_\pm^{(0)}$ given by Eq. (4.5), gives

$$\frac{\partial^2}{\partial X^2}\psi^{(0)}=\cosh\Psi^{(0)}(\psi^{(0)}+C_1^{(0)})+C_2^{(0)}\sinh\Psi^{(0)} . \tag{A7}$$

The above differential equation can be solved exactly, giving

$$\psi^{(0)}=C_3^{(0)}\frac{(1-t^2)e^{-X}}{1-t^2e^{-2X}}+C_1^{(0)}-C_2^{(0)}\frac{t(1+2X)e^{-X}}{1-t^2e^{-2X}} . \tag{A8}$$

We have rejected exponentially growing solutions in Eq. (A8). Combining Eq. (A8) with Eq. (A4) gives

$$n_\pm^{(0)}=\mp N_\pm^{(0)}\left[C_3^{(0)}\frac{(1-t^2)e^{-X}}{1-t^2e^{-2X}}-C_2^{(0)}\left(\frac{t(1+2X)e^{-X}}{1-t^2e^{-2X}}\pm 1\right)\right] . \tag{A9}$$

The zeroth order potential in the interior region is given by

$$\psi_{\rm int}\sim\psi_{\rm int}^{(0)}=B^{(0)}r\cos\theta\ (r<a) . \tag{A10}$$

The continuity of displacement current at the surface of the particle implies that

$$\epsilon_p B^{(0)}\cos\theta=\epsilon'\frac{1}{\delta}\frac{\partial}{\partial X}\psi^{(0)}\Big|_{X=0} . \tag{A11}$$

The above equation cannot be satisfied when $\delta\to 0$. Hence,

$$\frac{\partial}{\partial X}\psi^{(0)}\Big|_{X=0}=0 ,\quad \delta\to 0 , \tag{A12}$$

or

$$-C_3^{(0)}\left(\frac{1+t^2}{1-t^2}\right)-C_2^{(0)}\frac{t(1-3t^2)}{(1-t^2)^2}=0 . \tag{A13}$$

The outer solution for $n_\pm^{(0)}$ is derived similar to Eq. (4.12) of the main text, i.e.,

$$n_\pm\sim n_\pm^{(0)}=N_0\hat{C}_2^{(0)}\frac{a^3\exp[-\lambda(r-a)]}{r^2}\left(\frac{1+\lambda r}{1+\lambda a}\right)\cos\theta . \tag{A14}$$

Since by the matching criterion,

$$\lim_{r\to a}n_{\pm\rm out}^{(0)}\sim\lim_{X\to\infty}n_{\rm inn}^{(0)} , \tag{A15}$$

we deduce that

$$\hat{C}_2^{(0)}a\cos\theta=C_2^{(0)} . \tag{A16}$$

The potential in the outer region is easily derived to be

$$\psi\sim\psi^{(0)}=(\hat{C}_1^{(0)}/r^2)a^3\cos\theta-e_0 r\cos\theta , \tag{A17}$$

and by using the matching criterion on Eqs. (A8) and (A17), we have

$$[-e_0+\hat{C}_1^{(0)}]a\cos\theta=C_1^{(0)} . \tag{A18}$$

The radial current due to $n_\pm^{(0)}$ and $\psi^{(0)}$ in the outer region can be derived similar to Eq. (4.14). The normal current of the outer solution when $r\to a$ can be derived similar to Eq. (4.15) giving

$$j_{\pm r}\sim j_{\pm r}^{(0)}\sim\pm DN_0\cos\theta[2\hat{C}_1^{(0)}+e_0\pm\hat{C}_2^{(0)}\alpha] ,\quad r\to a . \tag{A19}$$

By the matching criterion,

$$\lim_{r\to a}j_{\pm r}^{(0)}\sim j_{\pm X}^{(0)}=0 . \tag{A20}$$

Hence

$$2\hat{C}_1^{(0)}+e_0\pm\hat{C}_2^{(0)}\alpha=0 . \tag{A21}$$

The above is only possible if

$$\hat{C}_2^{(0)}=0 ,\quad \hat{C}_1^{(0)}=\tfrac{1}{2}e_0 . \tag{A22}$$

From Eqs. (A18), (A16), and (A13), we deduce that

$$C_1^{(0)}=-\tfrac{3}{2}e_0 a\cos\theta ,\quad C_2^{(0)}=0 ,$$
$$C_3^{(0)}=0 . \tag{A23}$$

These results are the same as the simple result of Sec. III.

APPENDIX B: DERIVATION OF EQS. (5.5)

In this Appendix, we derive the solutions (5.5a) and (5.5b). The derivation is very similar to the result of Appendix A.

Using the approximation for the divergence operator in Eq. (4.6), the continuity Eq. (2.6), and the fact from Eq. (A2) that $j_{\pm X}^{(-1)}=0$, we can show that

$$\frac{\partial}{\partial X}j_{\pm X}^{(0)}=0 . \tag{B1}$$

Since $j_{\pm X}^{(0)}(X=0)=0$, by the boundary condition, we have

$$j_{\pm X}^{(0)}(X)=0 ,\quad \text{all } X . \tag{B2}$$

From Sec. III, and Appendix A, we know that $n_\pm^{(0)}=0$, and $\partial/\partial X\,\psi^{(0)}=0$ in the inner region. Using this fact, we deduce that

$$j_{\pm X}^{(0)}(X)=\frac{D}{a}\left[-\frac{\partial}{\partial X}n_\pm^{(1)}\mp\left(N_\pm^{(0)}\frac{\partial}{\partial X}\psi^{(1)}+n_\pm^{(1)}\frac{\partial}{\partial X}\Psi^{(0)}\right)\right] , \tag{B3}$$
$$=0 .$$

The above diffential equation is identical to Eq. (A3) in Appendix A. Furthermore, the potential has to satisfy Laplace's equation, i.e.,

$$\frac{\partial^2}{\partial X^2}\psi^{(1)}=-\frac{1}{2N_0}[n_+^{(1)}-n_+^{(1)}] . \tag{B4}$$

Hence,

$$\frac{\partial^2}{\partial X^2}\psi^{(1)}=\cosh\Psi^{(0)}(\psi^{(1)}+C_1^{(1)})+C_2^{(1)}\sinh\Psi^{(0)} . \tag{B5}$$

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Equations (B3) and (B5) are identical to Eqs. (A3) and (A7). Consequently, the expressions in Eqs. (5.5a) and (5.5b) are similar to Eqs. (A8) and (A9).

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