

Dynamic double layer effects on ac-induced dipoles of dielectric nanocolloids

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Normal and tangential surface ionic currents around low-permittivity nanocolloids with surface charges are shown to produce three different conductive mechanisms for ac-induced dipoles, all involving dynamic space charge accumulation at the double layer/bulk interface with a conductivity jump. However, the distinct capacitor dimensions and diffusive contributions produce three disparate crossover frequencies at which the induced dipole reverses direction relative to the bulk field. A highly conducting collapsed diffuse layer, with bulk ion mobility, renders the particle conductive and produces an ionic strength independent crossover frequency for weak electrolytes. A precipitous drop in crossover frequency occurs at high ionic strengths when charging occurs only at the poles through field focusing around the insulated colloid. A peculiar maximum in crossover frequency exists between these two asymptotes for colloids smaller than a critical size when normal charging of the diffuse layer occurs over the entire surface. The crossover frequency data for latex nanocolloids of various sizes in different electrolytes of wide ranging ionic strengths are collapsed by explicit theoretical predictions without empirical parameters. © 2010 American Institute of Physics.

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I. INTRODUCTION

Electric-field-induced polarization of a dielectric particle plays an essential role in colloid self-assembly, electrorheology, ac impedance spectroscopy, and dielectrophoresis.^{1,2} Conductive surface polarization by space charges such as electrons or ions, in addition to interfacial molecular dielectric polarization, is speculated to produce various relaxation times of particle induced dipole dynamics. The classical Maxwell–Wagner (MW) theory³ accounts for conductive polarization mechanism by combining the electric displacement jump at the surface due to some accumulated interfacial space charge q , $[\epsilon \partial \phi / \partial n] = -q$, with the accumulation of q at the interface by a jump in the normal current $[\sigma \partial \phi / \partial n] = i\omega q$, due to a conductivity jump at the interface, to produce a complex displacement jump across the interface, $[\tilde{\epsilon} \partial \phi / \partial n] = 0$ with a complex permittivity $\tilde{\epsilon} = \epsilon - i\sigma/\omega$ in the frequency domain.

When the Laplace equation is solved on two sides for a sphere of size a in a uniform far field E_∞ with this complex displacement jump and potential continuity, $[\phi] = 0$, a dipole potential of $\phi = E_\infty a f_{CM} (a/r)^2 \cos \theta$ is obtained with the complex Clausius–Mossotti (CM) factor f_{CM} , whose real part vanishes at the crossover frequency (in hertz) given by, $\omega_{CO} = (1/2\pi)[(\sigma_P - \sigma_M)(\sigma_P + 2\sigma_M)/(\epsilon_M - \epsilon_P)(2\epsilon_M + \epsilon_P)]^{1/2}$, the critical frequency when the induced dipole changes direction with respect to the external field. (Subscripts M and P represent the medium and the particle, respectively). As both the boundary conditions and the Laplace equations are invariant to rescaling by the size of the sphere, this ω_{CO} is independent of particle size a , monotonically decreases with

medium ionic strength (as measured by the bulk conductivity $\sigma_M = 2F^2 z^2 DC_\infty / RT$ for an electrolyte concentration of C_∞), and ceases to exist when the particle becomes less conductive than the medium.

These predictions are found to be inconsistent with measured data for latex spheres in electrolytes,⁴ which exhibit size-dependent ω_{CO} that can be nonmonotonic with respect to σ_M , even though polystyrene is much less conductive than the medium. Stern layer conductance due to adsorbed ions can render the particle more conducting than the medium⁵ and a modified MW theory can introduce size dependence.^{4,6–10} However, the necessary Stern layer conductance is empirically estimated, as the mobility of the bound ions is unknown. Theories have been advanced^{6–13} to account for surface currents by tangential ionic flux carried by mobile ions in the diffuse double layer. In Ref. 11, we reported a theory for low-conductivity fluids whose Debye layer is larger than the particle and whose conductivity is comparable to the bulk. For such conditions, we found the Stern layer adsorption dynamics to be important as a charge accumulation mechanism for the Debye layer charging. Here, we connect the Stern layer adsorption and conduction more explicitly by scrutinizing a highly concentrated polarized layer, which we believe to be the classical Stern layer. More importantly, we extend the theory to intermediate and high-conductivity conditions where conductivity jump across the thin Debye layer now replaces the Stern layer adsorption to provide the required charge accumulation dynamics. The charge convection by electro-osmotic flow is again neglected for thin layers, as the relevant Péclet number is much less than unity. An averaging theory (without empirical parameters) over the thin double layer is then introduced to capture all the mechanisms affecting ac polarization: conductivity gradient between the layer and the bulk (which accumulates space charge) due to surface charge attraction, tangential diffusion/current, and normal electric displacement.

II. THEORY

A. Large Debye layer asymptote

The thickness of the charged layer of counterions adjacent to a charged surface is not necessarily the Debye screening length, $\lambda = \sqrt{\epsilon RT / 2C_\infty z^2 F^2}$, which is from a linearized version of the Poisson–Boltzmann (PB) equation for symmetric electrolytes with valency z , when the zeta potential is small ($\zeta F / RT \ll 1$). An earlier analysis of the full nonlinear PB theory¹⁴ reproduced in Ref. 15 shows that the zeta potential ζ scales as $E_S \lambda$ when it is small but as $(RT/F) \ln(E_S \lambda F / 2RT)^2$ when it is large. Thus the thickness of the counterions is λ only for intermediate and strong electrolytes. For weak electrolytes with large differences in counterion and coion concentrations, omitting the coion concentration allows an analysis of the nonlinear PB equation^{14,15} to produce a collapsed diffuse double layer with a nonlinear screening length $\lambda_S = \alpha RT / FE_S$, where α is a unit order empirical constant taken to be 4 here, to be no more than 5 nm for most surface charge densities. This thickness is independent of ionic strength and is fixed for a given particle. Hence, for electrolyte concentrations and medium conductivity below the critical bulk electrolyte concentration $C_\infty^C = \epsilon_M RT / (2F^2 z^2 \lambda_S^2)$ (3 mM for univalent electrolytes at $E_S = 2.0 \times 10^7$ V/m) or medium conductance $\sigma_M^c = \epsilon_M D / \lambda_S^2$ (about 0.14 S/m for the same conditions), the relevant polarized layer thickness is λ_S . For weak electrolytes with ionic strength below these values, the total counterions within this layer represent almost the total surface charge and hence, there is a little space charge outside PB equilibrium. Also, the conductivity within the collapsed layer is larger than the medium by a large Boltzmann factor of $\exp(\zeta F / RT)$ assuming that the mobile ions in the collapsed layer retain the bulk mobility. Due to the high-conductivity and small dimension of the collapsed layer with respect to the bulk value and particle size, the bulk field lines are focused into this layer.⁶ Because of this field focusing effect, the tangential ion flux within it is dominated by electromigration with little contribution from convection by electro-osmotic flow or from diffusion. The thinness of the layer also implies that the dielectric displacement jump $[\epsilon \partial \phi / \partial n]$ at the particle-medium surface can be extrapolated by λ_S to the diffuse layer interface. One can hence use the standard practice of relating the disturbance potential field across an insulated sphere with a conducting shell to that of a conducting sphere to obtain effective particle conductivity.⁵ However,

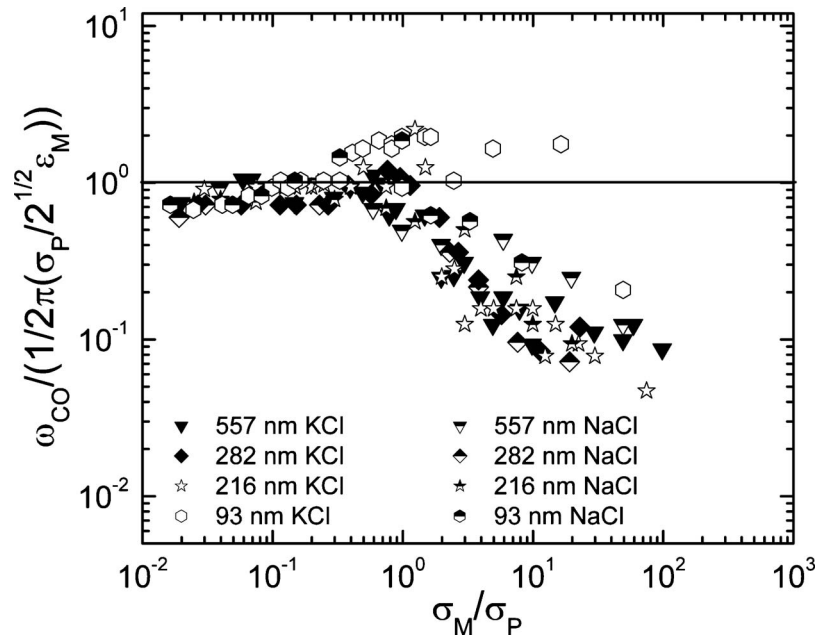


FIG. 1. The collapse of low-conductivity data of latex particles by the collapsed layer theory ($E_s=2.0 \times 10^7$ V/m and $D=5 \times 10^{-9}$ m²/s). Open symbols correspond to colloids smaller than 220 nm.

the shell conductivity is based on mobile ions here and this quasisteady averaging for a purely conducting shell without tangential diffusion produces an effective particle conductivity of $\sigma_P = 2K_s/a \gg \sigma_M$ for a dielectric sphere with a surface conductance $K_s = D\epsilon_M(E_s F/RT)$. This effective particle conductivity can then be used in the standard MW theory.

As the collapsed layer thickness and conductivity are independent of the medium conductivity, the resulting $\omega_{CO} = (1/2\sqrt{2}\pi)(\sigma_P/\epsilon_M)$, for weak electrolytes is independent of ionic strength or solvent, provided that it has a higher permittivity than the particle. With a surface field of $E_s = 2.0 \times 10^7$ V/m corresponding to a surface charge density of $1.4 \mu\text{C}/\text{cm}^2$, consistent with a measured surface charge density of around $2.0 \mu\text{C}/\text{cm}^2$ (Ref. 4) for latex colloids and a generic ion diffusivity of $D=5 \times 10^{-9}$ m²/s, we are able to collapse all data of Green and Morgan⁴ in Fig. 1 below σ_M^C . Positive deviation from the theory for colloids smaller than 220 nm (open symbols) occurs near σ_M^C . A precipitous drop occurs for $\sigma_M > \sigma_P$ for all particles when the MW theory fails.

B. Thin Debye layer asymptote

Beyond C_{∞}^C , the collapsed layer disappears and is replaced by an ionic strength dependent Debye diffuse layer of thickness λ , with $(\lambda/a) \ll 1$. The particle now becomes nonconducting without the collapsed layer. The thin diffuse layer remains sufficiently thick to allow tangential field penetration into the diffuse layer. The conductivity difference between this layer and the bulk is small as $\zeta F/RT \ll 1$, but this small difference needs to be resolved in the analysis as it is this conductivity gradient that allows dynamic space charge accumulation. Conductivity jump across the Debye layer, which is still necessary for charge accumulation, is often absent from thick-layer theories that expand from the PB equilibrium.^{11,13} Also, with a small conductivity increase in the layer relative to the bulk, field focusing effects of the highly conducting collapsed layer disappear and tangential diffusion must now be included. Because the colloid is now an insulator, the field lines that penetrate the diffuse layer do not approach the colloid surface. The displacement jump at the particle surface hence becomes irrelevant. The pertinent displacement jump is that across the diffuse layer, which is related to the local diffuse layer charge accumulation, determined by various mobile ion currents.

The leading order solution ϕ_{eq} satisfies the surface field condition due to the surface charge and is the classical PB equilibrium distribution near the surface with a polarized diffuse layer containing nonhomogeneous ion distributions. This leading inner solution screens the surface charge such that the far field sees an insulated sphere and hence produces a potential $\phi_0 = -((a/r)^2/2 + (r/a))E_\infty a \cos \theta \sin(\omega t)$ in the outer region outside the Debye layer. The nonequilibrium correction $\hat{\phi}$ to ϕ_0 in the outer medium occurs due to ion accumulation in the diffuse layer. Let $\langle \rho \rangle$ be the layer-averaged perturbation charge density (deviation from the PB equilibrium), then a layer-averaged charge balance can be derived by integrating the Nernst–Planck ion flux equation over the diffuse layer of thickness λ ,

$$\frac{\partial \langle \rho \rangle}{\partial t} = \sigma_{DL} \frac{\partial^2 \phi_0}{\partial s^2} + D \frac{\partial^2 \langle \rho \rangle}{\partial s^2} - J(n=\lambda)/\lambda. \quad (1)$$

The only nonlinear term in the Nernst–Planck equation is the electromigration term and the expansion about PB equilibrium ϕ_{eq} , which is independent of the tangential coordinate s , produces the conduction term in Eq. (1) whose conductivity σ_{DL} represents the layer-averaged conductivity of the PB equilibrium distribution. The normal charging flux from the homogeneous bulk involves only electromigration $J(n=\lambda) \sim -\sigma_M(\partial\phi_0/\partial n)_D$, where the subscript D denotes the outer boundary of the diffuse layer and is supplied by the outer field and the new field due to the deviation charge at the outer boundary of the diffuse layer, $\phi = \phi_0 + \hat{\phi}$. On the other hand, displacement jump across the double layer, across both the surface charge and the space charge in the Debye layer, is determined by deviation charge density. With the field negligible inside the particle, this displacement jump stipulates that $\epsilon_M(\partial\phi/\partial n)_D = -\lambda\langle\rho\rangle$. The field at the outer boundary of the diffuse layer can be approximated by an expansion from the particle surface $(\partial\phi/\partial n)_D \sim (\partial^2\phi_0/\partial n^2)_s\lambda + (\partial\hat{\phi}/\partial n)_s$, where subscript s denotes the particle surface. Eliminating the deviation charge density, we obtain an effective electrostatic condition for the deviation potential in the frequency space,

$$\left(\sigma_M + i\omega\epsilon_M - D\epsilon_M \frac{\partial^2}{\partial s^2} \right) \left(\lambda \frac{\partial^2 \phi_0}{\partial n^2} + \frac{\partial \hat{\phi}}{\partial n} \right) = -\lambda \sigma_{DL} \left(\frac{\partial^2 \phi_0}{\partial s^2} \right). \quad (2)$$

Since the dielectric dipole (having a CM factor of $-1/2$) produced by the zero order outer solution ϕ_0 is always out of phase with the applied field, it is the in-phase dipole component of nonequilibrium potential $\hat{\phi}$ that determines the dipole intensity and orientation.

Using boundary condition (2), we solve the Laplace equation for $\hat{\phi}$ with a zero far field and find the corresponding dipole coefficient. Together with $-1/2$ from ϕ_0 , we obtain the dipole intensity in terms of the classical CM factor

$$f_{\text{CM}} = -\frac{1}{2} + \frac{3}{2} \left(\frac{\lambda}{a} \right) \left(\frac{\left(\frac{\sigma_{DL}}{\sigma_n} \right) - 1 - \frac{i\omega\lambda^2}{D} - 2 \left(\frac{\lambda}{a} \right)^2}{\frac{i\omega\lambda^2}{D} + 1 + 2 \left(\frac{\lambda}{a} \right)^2} \right). \quad (3)$$

The real (in-phase) part yields the crossover to leading order in (λ/a) for electrolyte concentrations near C_∞^c , $\omega_{CO} = (\sqrt{3}/2\pi)(D/\lambda^2)((\lambda/a)((\sigma_{DL}/\sigma_m) - 1) - 1)^{1/2}$. At moderate electrolyte conductivities considered here, the zeta potential can be sufficiently high that $(\lambda/a)(\sigma_{DL}/\sigma_m) \gg 1$ or tangential conduction dominates. In this case, the conductivity given by the PB equilibrium theory⁶ is $(\sigma_{DL}/\sigma_M) = \cosh(\zeta F/RT) \sim (1/2)(E_s \lambda F/RT)^2$ and one concludes that

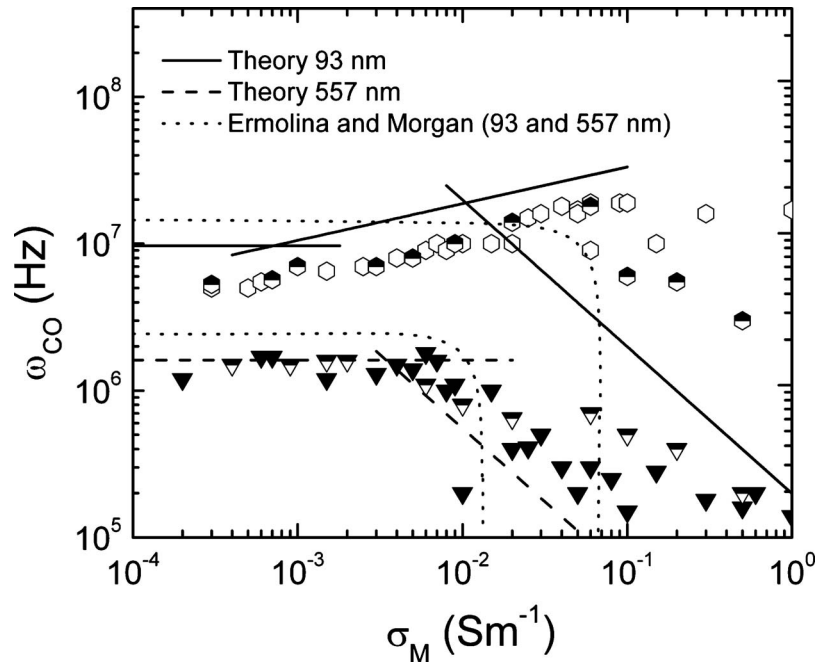


FIG. 2. The crossover data for two different latex particle sizes compared to the three theories for different medium conductivities. Same symbols as Fig. 1 are used. Also shown is Ermolona and Morgan's theory, which uses the Maxwell–Wagner expression but included in the particle conductivity contributions from the Stern layer conduction and diffuse layer conduction and convection $\sigma_p = (2K_S/a) + (2K_{diff}/a)$. The Stern layer conductance $K_S = 2\sigma_s\mu/a = 2E_s\epsilon_s\mu/a$ was estimated to be 0.92 nS and the diffuse layer conductance is $K_{diff} = ([4F^2cz^2D(1+3m/z^2)]/(RT/\lambda))(\cosh(zF\zeta/2RT) - 1)$ with the electro-osmotic contribution captured by $m = (RT/F)^2(2\epsilon_M/3\eta D)$. The zeta potential ζ is related to the surface field E_s .

$$\omega_{CO} = \frac{\sqrt{6}}{4\pi} \left(\frac{D}{\lambda^2} \right) \left(\frac{\lambda}{a} \right)^{1/2} \left(\frac{\lambda E_s F}{RT} \right). \quad (4)$$

As λ scales as $\sigma_M^{-1/2}$, ω_{CO} varies as $\sigma_M^{3/4}$ and its curious rise with respect to ionic strength is captured. In Fig. 2, we are able to favorably compare the collapsed diffuse layer theory to the ω_{CO} data in Ref. 4 for 93 and 557 nm latex nanocolloids below σ_M^c for the same values of E_s and D as used in Fig. 1. The distinct rise is absent for the larger particle (>220 nm as seen in Fig. 1) since Eq. (4) predicts ω_{CO} that is lower than the constant asymptote at low conductivities. Physically, the tangential flux through the thin Debye layer is not sufficient to distort the charge accumulation over the entire particle surface for these large particles. In contrast, an earlier theory,¹⁰ which does not properly capture charge accumulation with normal conductivity and displacement jumps across the double layer and the full tangential flux along it, is shown in Fig. 2 to produce negligible rise in the crossover even for the smaller particle.

C. Polar charging asymptote

Even for very small particles, the tangential flux in the diffuse layer disappears for very strong electrolytes, when λ approaches atomic scales. The penetrating outer field can again reach the particle surface and produce a dielectric polarization with a CM factor of $-1/2$. That a crossover frequency still exists means that a new conductive polarization mechanism due to current penetration to the surface appears. The outer field $-\nabla\phi_0$ has the largest normal component at the poles and we expect that the poles are the last locations where the surface charging can survive for strong electrolytes. The tangential field line gets focused as they exit the pole like the induced dipoles of carbon nanotubes¹⁶ and penetrates the double layer interface where the conductivity

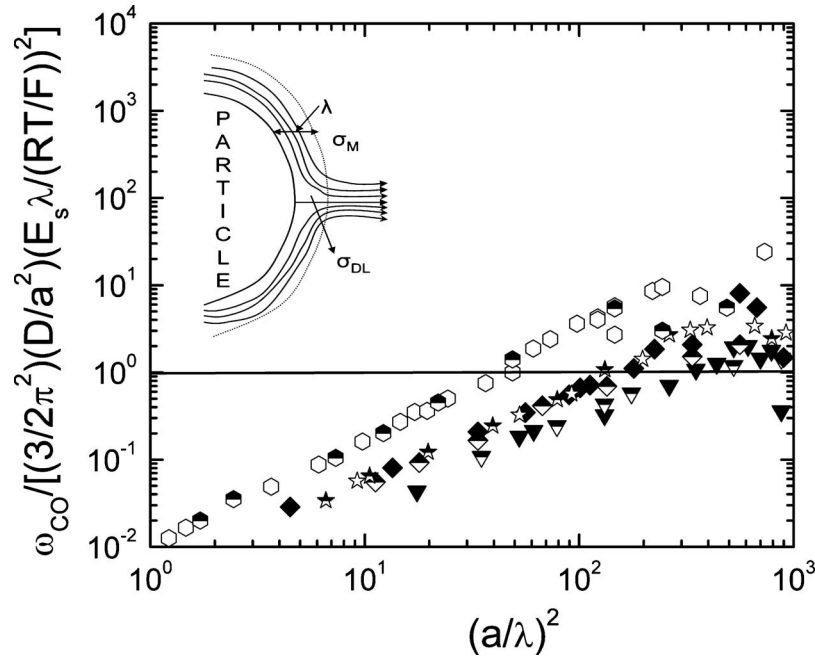


FIG. 3. Collapse of crossover data below 0.1 S/m by the high-conductivity theory. Same symbols as in Fig. 1. Field focusing around an insulated sphere driving an intense charge accumulation at the polar double layer interface due to conductivity gradients.

jump occurs (see Fig. 3). Hence a dipole is produced that has a much higher strength than classical MW dipole. The discharging time is fast and hence the polar capacitor is in-phase with the applied field.

A local Cartesian expansion at the pole simplifies the local two-dimensional Debye–Huckel equation. Extending the one-dimensional theory of González *et al.*¹⁷ to two dimensions and to include curvature, the Debye–Huckel equation is converted to a linear Poisson equation for the local perturbation charge density at PB equilibrium,

$$\frac{\partial^2 \rho}{\partial z^2} + \frac{2}{a} \frac{\partial \rho}{\partial z} + \frac{\partial^2 \rho}{\partial s^2} + \frac{1}{s} \frac{\partial \rho}{\partial s} = \frac{\rho}{\lambda^2} \quad (5)$$

with s being the tangential coordinate and z the normal coordinate. For the localized polar charging with vanishing ρ at $s, z \rightarrow \infty$, the solution of Eq. (5) is in the form of $\rho = A(t) \exp(-z/\lambda) K_0(s\sqrt{2/a\lambda})$ with the geometric mean length scale arising from the curvature at the pole and with a modified Bessel function.

Coefficient A is determined from the accumulation of space charge at the pole due to the conductivity gradient at diffuse layer interface. Due to the conductivity jump across the outer double layer interface, the leading outer potential $\phi_0 = -((a/r)^2/2 + (r/a))E_\infty a \cos \theta \sin(\omega t)$ produces a jump in the radial flux density at the double layer interface $D(r=a+\lambda)$ of the right pole ($\theta=0$): $\lambda(\sigma_{DL} - \sigma_M)(\partial E/\partial r) \sin(\omega t)|_{r=\lambda+a} = 3(\sigma_{DL} - \sigma_M)(\lambda/a)E_\infty \sin(\omega t)$. The flux tube that conducts ion into the pole is of radius $(a\lambda/2)^{1/2}$ and hence the total charge accumulation rate at this interface due to conductivity gradient is $3(\sigma_{DL} - \sigma_M)(\lambda/a)E_\infty \sin(\omega t)(\pi\lambda a/2)$. On the other hand, the total accumulated charge q in the polar region can be estimated by the volume integral of Eq. (5) in s and z from $0 \rightarrow \infty$ to yield $A(t)\pi\lambda^3(a/\lambda)$. Taking the time derivative of this quantity and relating it to the former accumulation rate, we obtain an equation for the space charge accumulation rate at the pole: $dA/dt = (3/2)(\sigma_{DL} - \sigma_M)(\lambda/a)E_\infty \sin(\omega t)/\lambda$. With the boundary condition that the charge density vanishes exactly at the beginning of each half cycle, this equation can be integrated over each half cycle to produce $A(t) = G \sin^2(\omega t/2)$ for $0 < t < \pi/\omega$ and $A(t) =$

$-G \cos^2(\omega t/2)$ for $\pi/\omega < t < 2\pi/\omega$, where $G = (3/2)(\sigma_{DL} - \sigma_M)(\lambda/a)(2/\omega)(E_\infty/\lambda)$ and with an inner discharging boundary layer in time of width (λ^2/D) separating the regions. Fourier sine transforming $A(t)$, converting it to the total polar charge $q = A\pi\lambda^2 a$ and relating to the dipole potential at the pole ($q/(2\pi\epsilon_M a) = f_{CM} E_\infty a$), yields an equivalent CM factor of $(3/\pi\omega)(D/a^2) \times (\sigma_{DL}/\sigma_M - 1)$. When this is balanced with the dielectric CM factor of $(-1/2)$, we obtain the crossover of this polar region (in hertz) as

$$\omega_{CO} = \left(\frac{3}{\pi^2}\right) \left(\frac{D}{a^2}\right) \left(\frac{\sigma_{DL}}{\sigma_M} - 1\right) \sim \left(\frac{3}{2\pi^2}\right) \left(\frac{D}{a^2}\right) \left(\frac{E_s \lambda F}{RT}\right)^2, \quad (6)$$

where the approximation is taken for small zeta potential in the high medium conductivity regime. The resulting crossover scales as σ_M^{-1} and is seen to be in quantitative agreement with the high-conductivity data in both Figs. 2 and 3. This peculiar polar charging mechanism at high conductivities is not captured by any earlier theory, one of which is shown in Fig. 2.

III. CONCLUSION

In this paper we present the dielectrophoretic crossover frequency spectrum for a latex colloid across different conducting buffers by exploring the multitude of physical phenomenon associated with charging of the double layer. The double layer charging dynamics clearly establishes the conductivity gradient responsible for the dielectrophoretic crossover frequency seen in otherwise insulated latex colloids. This phenomenon we believe can be exploited to design the next generation of point of care microfluidic chips based on molecular manipulation,¹⁸ rapid concentration of biomolecules,¹⁸ and biomolecule dielectrophoretic spectroscopic analysis.¹⁵

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