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Importance of core electrostatic properties on the electrophoresis of a soft particle

Simanta De[*] and Somnath Bhattacharyya[†]
Department of Mathematics, Indian Institute of Technology Kharagpur, Kharagpur-721302, India

Partha P. Gopmandal[‡]
Department of Mathematics, National Institute of Technology Patna, Patna-800005, India

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The impact of the volumetric charged density of the dielectric rigid core on the electrophoresis of a soft particle is analyzed numerically. The volume charge density of the inner core of a soft particle can arise for a dendrimer structure or bacteriophage MS2. We consider the electrokinetic model based on the conservation principles, thus no conditions for Debye length or applied electric field is imposed. The fluid flow equations are coupled with the ion transport equations and the equation for the electric field. The occurrence of the induced nonuniform surface charge density on the outer surface of the inner core leads to a situation different from the existing analysis of a soft particle electrophoresis. The impact of this induced surface charge density together with the double-layer polarization and relaxation due to ion convection and electromigration is analyzed. The dielectric permittivity and the charge density of the core have a significant impact on the particle electrophoresis when the Debye length is in the order of the particle size. We find that by varying the ionic concentration of the electrolyte, the particle can exhibit reversal in its electrophoretic velocity. The role of the polymer layer softness parameter is addressed in the present analysis.

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I. INTRODUCTION

The theoretical analysis of the electrokinetics of charged soft particles, comprising a rigid inner core coated with a soft (permeable) polyelectrolyte layer (PEL), is important in order to characterize the electrokinetic properties of viruses, bacteria, humic substances, and polysaccharides. The functional groups in the polyelectrolyte layer ionize when the particle is suspended in an aqueous medium. A complete dissociation of functional groups in PEL produces a fixed charge density in the PEL. Under an applied electric field, the charged particle experiences a Columbic force and translates with the electrophoretic velocity. The electrophoretic velocity arises from the balance of the resultant electric force and drag exerted by the surrounding fluid medium.

The previous theoretical studies (Ohshima [1–3], Duval and Gaboriaud [4]) on determining the electrophoretic mobility of a soft particle consider the core to possess either a constant surface charge density or constant surface potential. However, several studies on biological entities in the paradigm of soft particles suggests that the inner core may possess a finite dielectric constant with a finite volume charge density (McDaniel *et al.* [5]). Viruses can be considered as bionanoparticles consisting of a viral genome surrounded by protein capsids. Several authors, i.e., Šiber and Podgornik [6], Šiber *et al.* [7], considered charged genome molecules (DNA or RNA) to analyze the electrostatic interactions of the virus systems. Virus genome molecules may carry a negative charge due to dissociation of phosphate groups on RNA and DNA bases (Šiber *et al.* [7]). Nguyen *et al.* [8] investigated the contribution from the RNA core on interfacial interactions of the bacteriophage MS2 viruses.

The theoretical studies by Phan *et al.* [9] and McDaniel *et al.* [5], intended to analyze the electrostatics of bacteriophage MS2 virus, considered soft particles consisting of a dielectric hard inner core which possess a fixed volume charge density. These studies are limited to determining the electric potential distribution under the Debye-Hückel approximation. Gopmandal *et al.* [10] determined the mobility of a weakly charged soft particle as a function of the volume charge density of the dielectric rigid core by modifying the analytic expression of Ohshima [3] under a weak-field assumption. This study shows that the electrophoretic mobility depends on the volume charge density of the inner core when the Debye length is in the order of the particle size. At a thin Debye length the core charge density have a negligible influence on the electrophoresis of the soft particle. Moussa *et al.* [11] cited several studies on the electrokinetics of a specific class of soft colloids with nonuniform distribution of internal cationic and peripheral anionic charges. Through a combined experimental and theoretical analysis they have demonstrated the reversal in mobility and the point of zero mobility.

Unlike a perfect conductor, the dielectric materials do not have mobile charges that can freely move under an applied electric field. Under an applied electric field the dielectric core polarizes and a nonuniform surface charge density results. This might have a significant influence on the electrophoresis of a soft particle. The seminal work by O'Brien and White [12] has shown that under a weak field assumption, the particle electrophoretic velocity is independent of its dielectric properties. However, the nonlinear analysis under a thin Debye layer assumption of Yariv and Davis [13] and Schnitzer and Yariv [14,15] show that the dielectric permittivity influence its electrophoresis when the electric field is strong enough to induce a potential drop across the particle in the order of the thermal potential. Recently, Bhattacharyya and De [16] have analyzed the impact of the dielectric permittivity constant on the electrophoresis of a charged colloid for a

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[*] simanta.de@gmail.com

[†] Corresponding author: somnath@maths.iitkgp.ernet.in

[‡] partha@nitp.ac.in

finite Debye length. Figliuzzi *et al.* [17] made a numerical study on nonlinear electrophoresis of ideally polarizable bare particles under high applied electric fields and found that the surface conduction significantly decreases the electrophoretic mobility.

The theoretical analysis of Li *et al.* [18] on gel-electrophoresis under the Debye-Hückel approximation of a soft particle shows that the dielectric constant of the core can significantly influence the mobility. Based on the Poisson-Nernst-Planck formulation, the polarization of a soft particle and induced dipole moment coefficient for a soft particle with uncharged dielectric core was analyzed by Dingari and Buie [19]. Recently, Bhattacharyya and De [20] have studied the nonlinear electrophoresis of a soft particle with a polarizable uncharged rigid core.

The polarization of a double layer and its impact on the soft particle electrophoresis also becomes an important aspect when the double-layer thickness is comparable with the particle size. The polarization of a double layer creates a retardation effect on the electrophoresis and its characteristics are governed by the interaction of advection-diffusion-electromigration of ions. The impact of double-layer polarization (DLP) and the relaxation for soft particles with constant core charge density has been studied by several authors, namely, Saville [21], Hill *et al.* [22,23], Hill and Saville [24], López-Viota *et al.* [25], Huang *et al.* [26], and Tseng *et al.* [27]. All those studies, and the references therein, analyzed the DLP based on a first-order perturbation analysis of the nonlinear Poisson-Boltzman equation under a weak applied field assumption. It has been established in all those previous theoretical works that in the thin Debye layer limit, it is the properties of the polyelectrolyte layer (PEL) rather than the inner core that dominates the soft particle electrophoresis. The importance of the DLP and relaxation for a soft particle in electrophoresis was demonstrated in a review article by Cametti [28] and Barbati and Kirby [29]. There they have concluded that when the thickness of the Debye layer induced by the charged inner core is in the order of the PEL thickness, the nonlinear DLP and relaxation effects are significant and a computational approach must be adopted to analyze the electrokinetics. Recently, Hill [30] considered the electrophoresis of a soft particle with a charge regulated inhomogeneous polyelectrolyte layer grafted on a metallic core of constant surface charge density through a first-order perturbation of the governing electrokinetic equations.

Raafatnia *et al.* [31] have shown that the mobility of a soft particle undergoes a transition from a net-charge-dominated regime at low ionic strengths to a PEL-dominated regime at high ionic strengths. The mobility reversal in a monovalent electrolyte solution of a soft particle with negatively charged inner core grafted with a positively charged PEL is demonstrated through a molecular dynamic simulation by Raafatnia *et al.* [31,32]. In those studies the electrophoresis of a net-neutral soft particle was analyzed in a monovalent electrolyte. It may be noted that the mechanism for electrophoretic mobility reversal of a charged dielectric particle in a concentrated multivalent electrolyte as reported by several authors, e.g., Stout and Khair [33], is different from the present context. For the charged soft particle the mobility switches over from a net-charge-dominated regime at low ionic strengths to a shell-dominated regime at high ionic strengths (Raafatnia *et al.* [32]).

The present study deals with the electrophoresis of a soft particle that consists of a dielectric inner core possessing a volumetric charge density, which is coated with a homogeneous polyelectrolyte layer. The ion impermeable inner core can be considered as the limiting case of a hyperbranched structure encapsulated by an outer shell surface. The inner core can possess a volumetric charge density that is found in bacteriophage MS2 or dendrimers. The volume charge density of the core is found to be half of the charge density of the surface layer in a bacteriophage MS2 (Phan *et al.* [9]). The dielectric core polarizes under an applied electric field and a nonuniform surface charge density develops at the outer surface of the core. This surface charge density depends on the permittivity and the volumetric charge density of the core along with other factors. Our objective is to illustrate the dependence of the particle electrophoresis on the electrostatic property of the core. The previous study on analyzing the impact of core charge density on the soft particle electrophoresis (Gopmandal *et al.* [10]) was based on the Debye-Hückel approximation, in which the double-layer relaxation and polarization effects are neglected under a weak applied field and low charge density conditions. A spherical symmetry was assumed in that study (Gopmandal *et al.* [10]), thus the variables were considered to vary only in the radial direction. The impact of the electric polarization of the dielectric core also becomes negligible under a weak applied electric field assumption. Bhattacharyya and De [20] studied the nonlinear electrophoresis of a soft particle by considering an uncharged inner core. Consequently, the occurrence of mobility reversal and zero electrophoretic velocity by varying the ionic concentration of electrolyte is absent in the study by Bhattacharyya and De [20]. These studies show that the impact of core is significant for low to moderate range of Debye length with highly permeable PEL. We have considered the electrophoresis for a wide range of Debye length, softness parameter of the PEL, core-to-electrolyte permittivity ratio, and volumetric charge density of the core and PEL. We find velocity reversal and zero velocity by regulating the volume charge density of the particle.

In the present study, we have considered a homogeneous soft layer of definite thickness with a step change in charge density within the layer. A more realistic approach would have been the consideration of diffuse soft particles (Duval and Ohshima [34]), which considers an inhomogeneous polymer segment distribution. Since the aim of the present study is to illustrate the core electrostatic property on the soft-particle electrophoresis, we have restricted our attention to the simpler description of a soft particle. However, the analysis based on the present model for the soft particle is also valid for a diffuse soft particle.

II. MATHEMATICAL MODEL

We consider the electrophoresis of a soft spherical particle of radius b consisting of a dielectric charged rigid core of radius a coated with a homogeneous polyelectrolyte layer, which is assumed to have a definite thickness $(b - a)$ with a uniform segment density distribution and a fixed charge density ρ_f. The PEL is considered to be of continuum media

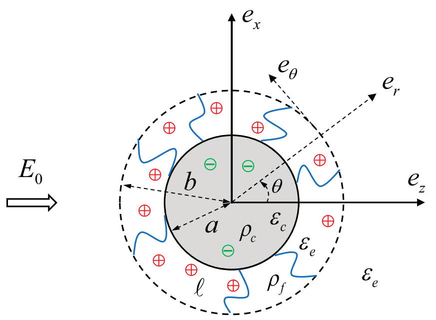

FIG. 1. Schematic description of the soft particle in electrophoresis under an applied electric field.

and the hydrodynamics is governed by the Brinkman equation. The Brinkman screening length of the homogeneous PEL, which is related to the polymer segment density distribution, is assumed to be ℓ and the fixed charge density of the PEL ions is $\rho_f = \pm\mathcal{Z}en_f^*$, where n_f^* is the ionic number concentration of the immobile PEL ions, $\mathcal{Z}$ is the valence, and e is the protonic charge. A detailed physical description and the correspondence between ℓ and ρ_f with the polymer concentration is provided by Hill *et al.* [35] and Dingari and Buie [19]. The charged nonconducting dielectric rigid core bears a constant volumetric charged density ρ_c with dielectric permittivity ε_c. In response to an applied electric field E_0, the particle translates with the electrophoretic velocity U_E (*a priori* unknown) in an electrolyte medium of constant dielectric permittivity ε_e.

The equations governing the electrokinetics are based on the conservation principles of mass, momentum, and ion flux along with the Poisson equation for an electric field. The Brinkman equations describe the fluid flow within the soft layer and Stokes equations govern the fluid transport outside the soft particle. The ion transport is governed by the Nernst-Planck equation. The nondimensional form of the governing equations in a spherical polar coordinate system (r,θ,ψ) with the initial line $(\theta = 0)$ along the direction of the imposed electric field E_0 (Fig. 1) can be expressed under an axisymmetric assumption as

$$\nabla\cdot\boldsymbol{u} = 0,\quad (r>\gamma), \tag{1}$$

$$\nabla p - \nabla^2\boldsymbol{u} + \beta^2\boldsymbol{u}[H(r-\gamma) - H(r-1)] + \frac{(\kappa b)^2}{2}\rho_e\nabla\phi = 0,\quad (r>\gamma), \tag{2}$$

$$Pe_i(\boldsymbol{u}\cdot\nabla n_i) - [\nabla^2 n_i \pm \nabla\cdot(n_i\nabla\phi)] = 0,\quad (r>\gamma). \tag{3}$$

Here $\boldsymbol{u}$ is velocity vector, p is pressure, ϕ is the electric potential, $\rho_e = (n_1 - n_2)$ is the charge density with n_i as the ionic concentration of ith ionic species with valence $z_i = \pm\mathcal{Z}$, and $H(r)$ is the Heaviside step function. Here $\kappa = \sqrt{2\mathcal{Z}en_0/\varepsilon_e\phi_0}$ is the inverse of the EDL thickness. For the sake of simplicity the electrolyte is assumed to be symmetric electrolyte. However, as the present model is based on the Nernst-Planck equation, there is no restriction on the number of ionic species and their valences. We scale the dimensional variables as follows: the length scale as the radius of the soft sphere b, the thermal potential $\phi_0 = k_BT/\mathcal{Z}e$ is the potential scale, $U_0 = \varepsilon_e\phi_0^2/b\mu$ is the velocity scale, $\varepsilon_e\phi_0^2/b^2$ is the pressure scale, the bulk ionic number n_0 is the scale for ionic concentration, and $\Lambda = E_0b/\phi_0$ is the scaled external electric field with ϕ_0/b as the characteristic electric field. Here e is the elementary electric charge, k_B is the Boltzmann constant, T is the absolute temperature, and μ is the dynamic viscosity. We defined the nondimensional polymer layer thickness as $e_p = (1-\gamma)$, where $\gamma = a/b$ is the nondimensional core radius. The nondimensional parameter $\beta = b/\ell$ provides a measure of the hydrodynamic penetration length of the soft layer. Here D_i for $i = 1,2$ are the diffusivity of ions with that the nondimensional parameter, $Pe_i = \varepsilon_e\phi_0^2/\mu D_i$, measures the ratio of advective to diffusion transport of ions.

The electric potential in the liquid and the soft layer satisfies the following Poisson equation. The nondimensional quantity $Q_f = \pm n_f(\kappa b)^2/2$ measures the scaled fixed charge density of the soft shell and Q_c is the scaled volumetric charge density of the core, and both are scaled by $\varepsilon_e\phi_0/b^2$:

$$\nabla^2\phi = -\frac{(\kappa b)^2}{2}\rho_e - Q_f[H(r-\gamma) - H(r-1)],\quad (r>\gamma). \tag{4}$$

The electric potential inside the solid core is governed by

$$\nabla^2\phi_c = -\frac{Q_c}{\varepsilon_r},\quad (0<r<\gamma). \tag{5}$$

A nonslip boundary condition and no normal flux of ions are imposed on the surface of the solid core $(r=\gamma)$:

$$\boldsymbol{u} = \boldsymbol{0},\ (\nabla n_i \pm n_i\nabla\phi)\cdot\boldsymbol{e_r} = 0. \tag{6}$$

The jump in the electric displacement on the surface of the dielectric hard core $(r=\gamma)$ governs

$$\frac{\partial\phi}{\partial r} = \varepsilon_r\frac{\partial\phi_c}{\partial r},\ \phi_c = \phi, \tag{7}$$

and the later condition is governed by the continuity of electric potential. Here $\varepsilon_r = \varepsilon_c/\varepsilon_e$ is the particle-to-electrolyte dielectric permittivity ratio. Far from the particle $(r = R)$,

$$\boldsymbol{u} = -U_E\boldsymbol{e_z},\ \phi = -\Lambda r\cos\theta,\ n_i = 1. \tag{8}$$

Here $\mathbf{e_r}$ and $\mathbf{e_z}$ are the unit vectors along the radial and axial direction, respectively. A symmetry condition is imposed along the axis of symmetry, i.e., $\theta = 0$ and π.

The problem can be considered to be steady. However, we adopt a time-marching procedure to obtain the steady-state solution with the initial condition being governed by the equilibrium condition with the particle initially at rest. The electrophoretic velocity of the particle (U_E) is obtained by solving the balance of the drag and electric forces experienced by the particle iteratively. The iteration process starts with an initial assumption for electrophoretic velocity based on the mobility expression obtained by Gopmandal *et al.* [10]. Based on this electrophoretic velocity, the governing electrokinetic Eqs. (1)–(5) along with the prescribed boundary conditions are solved by a control volume approach in a staggered grid arrangement. The electric force and drag force experienced by the particle are then obtained through the expression as provided in Bhattacharyya and De [20]. The iteration process continues till the balance of forces is established.

A nonuniform grid distribution is considered to compute the governing electrokinetic equations. A dense grid is considered

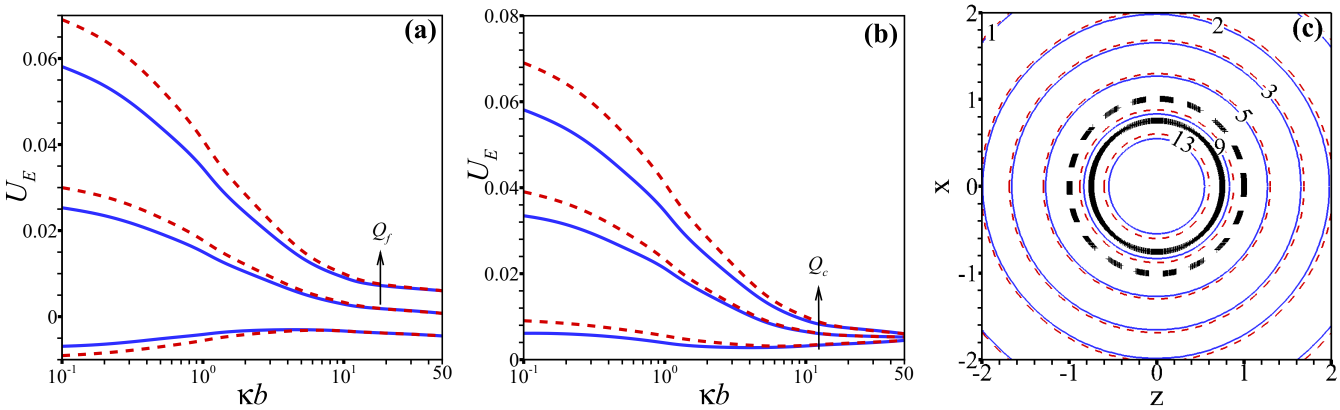

FIG. 2. Variation of electrophoretic velocity at $\ell = 3$ nm, $a = 10.3$ nm, $b = 13.6$ nm, $E_0 = 10^4$ Vm^{-1}, with κb when (a) $\rho_c = 5 \times 10^6$ C/m^3 for different $\rho_f (= -5 \times 10^6, 0, 5 \times 10^6$ C/m$^3)$; (b) $\rho_f = 5 \times 10^6$ C/m^3 for different $\rho_c (= -5 \times 10^6, 0, 5 \times 10^6$ C/m$^3)$. Dashed lines are results of Gopmandal *et al.* [10]; (c) Potential distribution inside and around the particle when $\rho_f = 5 \times 10^6$ C/m^3 and $\rho_c = 5 \times 10^6$ C/m^3, $\kappa b = 1$ and $\varepsilon_r = 1$. Dashed thin lines are results of Phan *et al.* [9]; solid and dashed thick lines are the surface of the solid core and soft particle, respectively.

within and around the soft layer. Grid spacing is increased as we move away from the particle. The outer radius R of the computational domain is taken to be large enough so that a further extension of R produces a negligible difference on the drag and electric force. In general, R is taken to be bigger than $20b$; however, it varies with the electrokinetic parameters. A grid independency test was conducted to choose the optimal grid size. We have tested our code by comparing with the existing results on soft particle electrophoresis. A discussion on the comparisons is provided in the next section.

III. RESULTS AND DISCUSSION

In the present computation we have taken $\phi_0 = 0.02568$ V, $\mu = 10^{-3}$ Pa · s, $\rho = 10^3$ kg/m^3, $\varepsilon_e = 695.39 \times 10^{-12}$ C/Vm, $D_1 = 1.33 \times 10^{-9}$ m^2/s, and $D_2 = 2.03 \times 10^{-9}$ m^2/s. We first present results for weak applied field, i.e., $\Lambda = E_0 a/\phi_0 = 0.005$. The applied field is moderate when the potential drop across the particle is in the order of the thermal potential, i.e., $\Lambda \sim O(0.5)$. The scaling of variables shows that for a fixed Λ the applied field can be increased by the same rate at which the particle size is lowered and the shell pore size is increased. Subsequently, the results for $\Lambda \sim O(0.5)$ is presented when particle of size $b = 100$ nm is considered. The results are presented for a wide range of ε_r in which the core can be considered either as nonmetallic [$\varepsilon_r \sim O(1)$] or metallic one ($\varepsilon_r \gg 1$). Zhang and Li [36] provided a table for relative dielectric constants of dielectric materials. This table shows that ε_r can be considered to vary between 0.1 to 100. Phan *et al.* [9] and McDaniel *et al.* [5] have considered the ε_r within this indicated range to determine the electric potential distribution of a soft particle with a charged core.

A. Numerical results for weak applied field, $\Lambda \ll 1$

The electrophoresis of the bacteriophage MS2 (Nguyen *et al.* [8], Phan *et al.* [9]) under a weak applied field is presented in Figs. 2(a)–2(c). Here $a = 10.3$ nm, $b = 13.6$ nm, with ρ_f and ρ_c are varied between -5×10^6 to 5×10^6 C/m^3 under a weak applied field, i.e., $\Lambda \ll 1$. Figures 2(a) and 2(b) present the computed electrophoretic velocity along with the semianalytic solutions as obtained by Gopmandal *et al.* [10]. Here we have considered the core-to-electrolyte permittivity ratio $\varepsilon_r = 1$, i.e., the dielectric constant of the core is close to that of the solvent. The present computed solutions are in good agreement with the theoretical analysis of Gopmandal *et al.* [10] when $\kappa b \geqslant 10$, however, it over-estimates the present results when $\kappa b \sim O(1)$. The theoretical analysis of Gopmandal *et al.* [10] is based on the Debye-Hückel approximation, in which the double-layer relaxation effect is neglected. In Fig. 2(c) we have compared the electric potential distribution with the analytic solution based on the linear analysis as obtained by Phan *et al.* [9]. The electric potential is found to vary only in the radial directions under the weak applied electric field and it agrees well with the analytical solution as obtained by Phan *et al.* [9]. The electric potential distribution is found to be unperturbed due to the variation of ε_r at this weak applied field, i.e., $\Lambda = 0.005 (\ll 1)$. At this low applied electric field, the electric potential on the surface of the core becomes constant and it is 11.5 for $\rho_f = 5 \times 10^6$ C/m^3 and $\rho_c = 5 \times 10^6$ C/m^3 at $\kappa b = 1$.

B. Effect of Debye layer thickness and comparisons with existing results

We have considered the particle size in the order of 100 nm and the screening length of the soft layer 30 nm. The electrolyte concentration is varied between 10^{-4} and 23.3 mM, i.e., κ^{-1} to vary between 2 nm to 1 μm. We now consider the electrophoresis for moderate range of applied field, i.e., $\Lambda \sim O(1)$. Figure 3(a) shows the distribution of the surface potential on the rigid core for weak and moderate value of E_0. The volumetric charge density of the soft layer is considered to be $\rho_f = 2.7 \times 10^4$ C/m^3 ($Q_f = 15$) and the volumetric charge density of the core is varied between $\rho_c = -2.7 \times 10^4$ C/m^3 ($Q_c = -15$) and $\rho_c = 2.7 \times 10^4$ C/m^3 ($Q_c = 15$) for thick Debye layer case ($\kappa b \leqslant 10$) and the soft layer is considered to be $\rho_f = 9 \times 10^4$ C/m^3 ($Q_f = 50$) and the volumetric charge density of the core is varied between $\rho_c = -9 \times 10^4$ C/m^3 ($Q_c = -50$) and $\rho_c = 9 \times 10^4$ C/m^3 ($Q_c =$

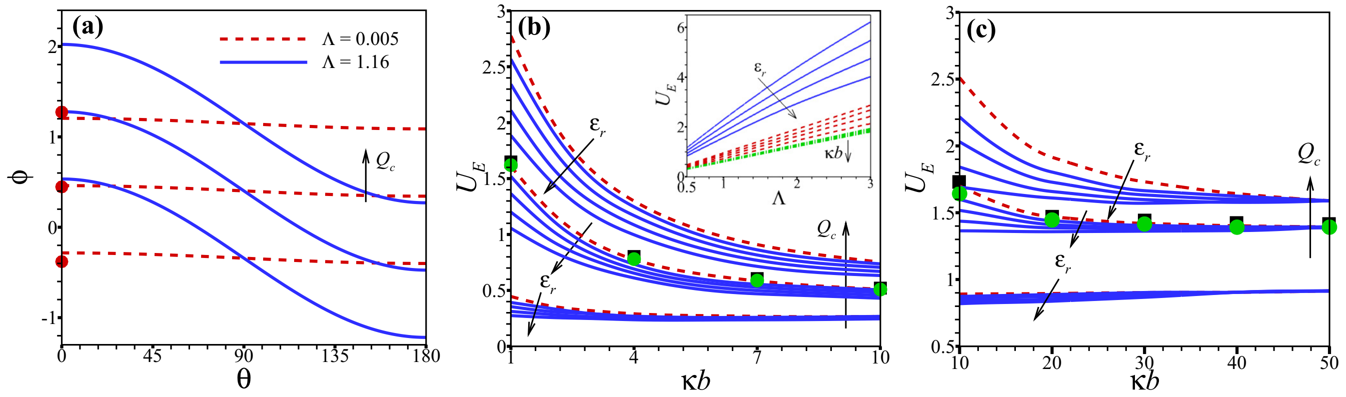

FIG. 3. (a) Potential distribution on the surface of solid core ($r = \gamma$,θ is the polar angle (in deg) from the positive z axis) at $\varepsilon_r = 1$ when $\kappa b = 10$, $Q_f = 50$, $Q_c = -50,0,50$. Symbols are results of Phan *et al.* [9]; variation of electrophoretic velocity with κb at $\Lambda = 1.16$, $\beta = 3.3$, $e_p = 0.25$ for different $\varepsilon_r(= 0.1,1,10,100)$ when (b) $Q_f = 15$, $Q_c = -15,0,15$. Inset figure shows the variation of U_E with Λ when $\beta = 3.3$, $Q_c = 15$, $Q_f = 15$ at different $\kappa b(= 1,5,10)$ and $\varepsilon_r(= 0.1,1,10,100)$; (c) $Q_c = -50,0,50$, $Q_f = 50$. Circular symbols, computational result for $\varepsilon_r = 0$; square symbol, the result of Ohshima [3] for $\varepsilon_r = 0$; dashed lines are results of Gopmandal *et al.* [10].

50) for thin Debye layer case ($\kappa b \geqslant 10$). The surface potential on the rigid core is constant when a weak electric field is considered, i.e., $\Lambda = 0.005$. However, the induced surface potential due to electric polarization of the core becomes nonuniform when a moderate value of the applied electric field is considered, i.e., $\Lambda = 1.16$. The electric potential depends on the particle dielectric permittivity ratio when $\Lambda \sim O(1)$. The existing theoretical analysis on dielectric rigid colloids shows that the dielectric permittivity has an impact for nonweak applied field (Yariv and Davis [13]).

In Figs. 3(b) and 3(c) we have compared our computed solutions for electrophoretic velocity for low-to-high values of Debye length at different choice of the core-to-electrolyte permittivity ratio with the results due to Gopmandal *et al.* [10]. At a given value of the Debye length (κb), the core and PEL charge density are considered in that range for which the core surface charge density remains below $4\phi_0$, for which the ion-ion interactions becomes negligible. It may be noted that in the present formulation, the surface potential of the core reduces as the ionic concentration of the electrolyte is raised. The semianalytic results of Gopmandal *et al.* [10] is based on the analytic expression for mobility due to Ohshima [3], in which the DLP effect is neglected under a weak applied field and weak charge density of the soft particle conditions. Comparisons show that the existing solutions as obtained by Gopmandal *et al.* [10] based on the linear analysis overestimate the present computational solution when the charge density of the particle is large and the Debye layer is thicker. It further deviates as the core-to-electrolyte permittivity ratio (ε_r) is raised. Our results are in good agreement with the results due to Gopmandal *et al.* [10] when the DLP effect is negligible, i.e., Debye layer is thin ($\kappa b > 10$). Figures 3(b) and 3(c) also show that a good agreement occurs when the net-charge density of the soft particle is low. We find a good agreement of our computed solution with Ohshima [3] for the case of an uncharged nonpolarizable rigid core (i.e., $\varepsilon_r = 0, Q_c = 0$) when the Debye layer is thin (i.e., $\kappa b > 10$). It may be noted that an induced surface charge density develops on the surface of the core due to the electric polarization even when the core volumetric charge density is zero ($Q_c = 0$). The electric polarization of an uncharged conducting bare spherical colloid does not alter its electrokinetic propulsion. However, in the present case, the presence of the immobile PEL ions creates an imbalance in electric force on the nonuniform surface charge density of the dielectric rigid core. We find that the solid polarization of the uncharged core have a negligible effect for thin Debye layers and the electrophoretic velocity is governed by the PEL charge density. However, for a charged dielectric core, the impact of the core charge density is not negligible even at a thin Debye layer. The results in Figs. 3(b) and 3(c) show that the mobility is high at a low ionic strength (thick Debye layer) as the shielding effect is low. At high electrolyte concentration, a dense layer of counterions on the outer surface lowers the mobility of the particle. The impact of the electrostatic property, i.e., volumetric charge density and permittivity of the core on the particle electrophoretic velocity gradually reduces as the ionic concentration of the electrolyte increases and it approaches a constant value at a large value of κb. The magnitude of the electrophoretic velocity decreases as the core-to-electrolyte permittivity ratio is raised and it approaches saturation at a large ε_r, i.e., the core becomes conducting. The inset in Fig. 3(b) shows a nonlinear variation of the electrophoretic velocity with the applied electric field for $\Lambda \geqslant 0.5$. The dependence of U_E on Λ depends on the Debye length as well as the core permittivity.

C. Influence of dielectric permittivity, core charge density, and layer softness

The deformation of the counterion cloud around the soft particle at different values of the core-to-electrolyte permittivity ratio is illustrated in Figs. 4(a)–4(c). Here we have considered the Debye length and Brinkman screening lengths to be equal to the particle size. The induced surface charge density of the core and the PEL fixed charges attracts counterions. At low ionic strength of the electrolyte, the loosely attracted counterions undergo electroosmosis (EOF) due to the applied electric field. The EOF of the mobile counterions within the PEL also becomes strong for this high

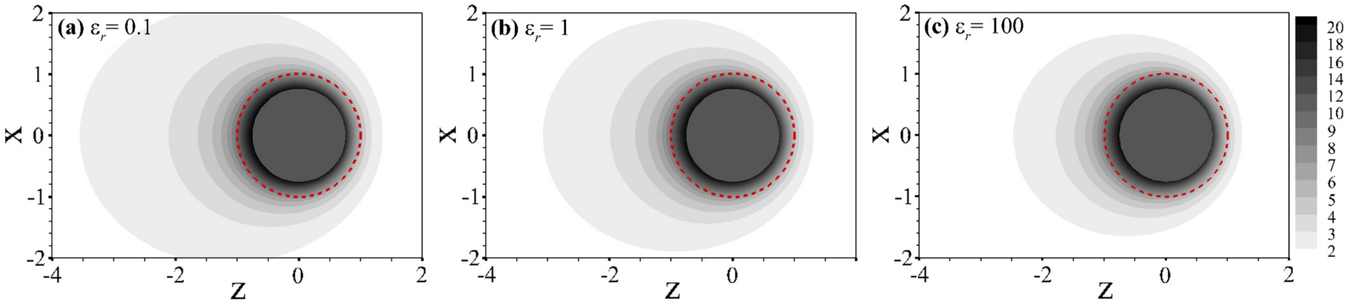

FIG. 4. Distribution of counterions at different $\varepsilon_r(= 0.1,1,100)$ for $Q_f = 15$, $Q_c = 15$, $\kappa b = 1$, $\beta = 1$, $\Lambda = 1.16$, $e_p = 0.25$. Dashed line represent the surface of the soft particle.

permeable layer. The motion of the particle under the applied electric also pushes the counterions downstream along $z < 0$.

Figure 5(a) shows the ratio between the electrophoretic drag and the drag experienced by a neutral particle translating with the velocity U_E, i.e., $F_D^H = 6\pi\mu U_E b\Omega^H$, where Ω^H is defined by Eq. (32b) in Masliyah *et al.* [37]. This provides a measure of the impact of the diffuse layer on the electrokinetics of the particle. The electrohydrodynamic pressure field created by the mobile counterions creates a retardation effect on the migration of the particle. The drag ratio rises with the rise of the positive charge density of the core. When the core is oppositely charged to that of the PEL, the counterions shielding the core charge are repelled by the PEL ions being of same sign. In this case, the role of the electrohydrodynamic pressure field created by the mobile ions is reduced. For this, we find that the drag factor reduces and approaches 1 as the negative charge density of the core increases. It is evident that the impact of the core volume charge density becomes low as the Debye length is decreased.

Figure 5(b) shows that as the PEL becomes denser (increase of β) the particle electrophoretic velocity decreases. As the PEL becomes denser the diffusion-dominated mechanisms, such as counterion condensation, enhances, which lowers the effective charge density of the PEL and, hence, creates a reduction in mobility. The soft particle behaves like a rigid colloid at large values of β and the particle electrophoretic velocity approaches a constant value at a large β. The Debye-Hückel parameter (κb) and the parameter β have a similar role on the EOF of the mobile counterions inside the PEL. The surface charge density of the core is screened by the counterions and this screening effect grows with the increase of β as the EOF of the mobile counterions attenuate. The screening effect also grows with the increase of κb. However, unlike the case of large κb in which U_E becomes independent of the electrostatic property of the core, here at large β (denser PEL) both ε_r and Q_C influences U_E. The impact of β on U_E enhances with the increase of the core charge density when the charge density of the core and shell have the same sign. However, the shell permeability (β) has relatively little influence when the core is charged oppositely to that of the shell. A possible explanation for this trend in U_E due to the variation of β is outlined in the next subsection.

D. Mobility reversal and net-zero-charged particle

We have seen in Figs. 3(a) and 3(b) that for low to moderate range of Debye length, both the core and the PEL charge density have a contribution in determining the electrophoresis of the soft particle. The impact of the core charge density diminishes as the Debye layer becomes thinner than the PEL thickness and the electrophoresis is dominated by the shell property. This form of variation of the electrophoretic velocity with the Debye length may result in reversal in velocity direction when the core and PEL are oppositely

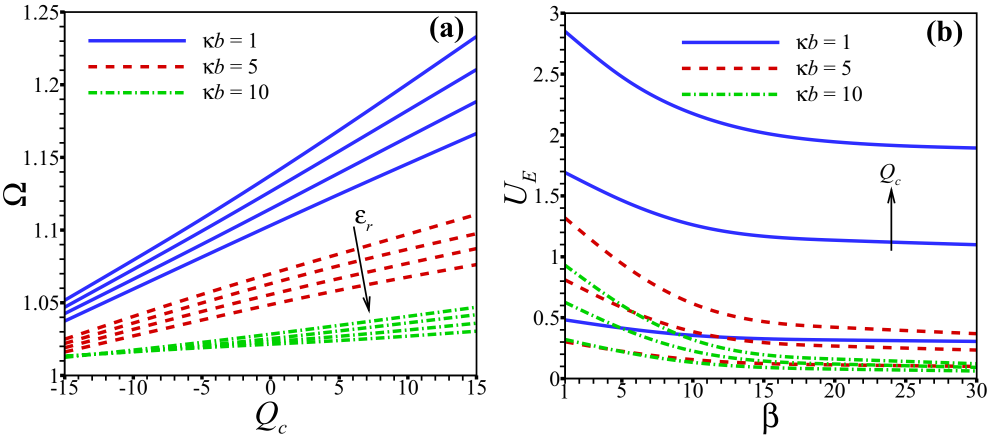

FIG. 5. Variation of the (a) ratio of the drag forces on a charged and uncharged particle migrating at the same velocity with Q_c when $Q_f = 15$, $\kappa b = 1,5,10$, $\varepsilon_r = 0.1,1,10,100$; (b) electrophoretic velocity with β when $Q_c = -15,0,15$, $Q_f = 15$, $\kappa b = 1,5,10$, and $\varepsilon_r = 1$. Here $\Lambda = 1.16$, $e_p = 0.25$.

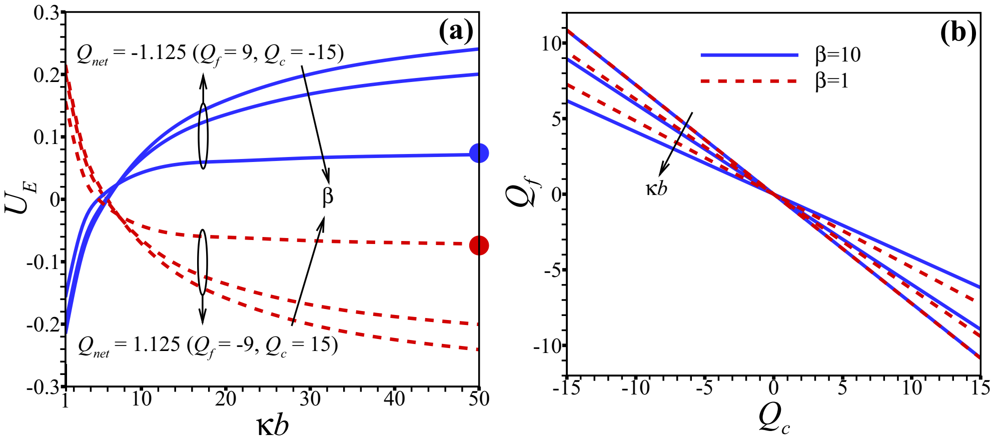

FIG. 6. Variation of the (a) electrophoretic velocity with κb when the net-fixed charge density of the soft particle is $Q_{\text{net}} = 1.125$ (i.e., $Q_f = -9$, $Q_c = 15$) or $Q_{\text{net}} = -1.125$ (i.e., $Q_f = 9$, $Q_c = -15$) for different $\beta(= 1,3,10)$. Symbols represent mobility of a porous sphere as obtained by Hermans and Fujita [38] at $\beta = 10$; (b) critical value of charge density to achieve zero mobility of a soft particle at $\kappa b = 1,5,10$ when $\beta = 1,10$. Here $e_p = 0.25$, $\Lambda = 1.16$, and $\varepsilon_r = 1$.

charged. To illustrate this phenomena, we consider the effect of the variation of the Debye length on the velocity of a soft particle with a net-positive (or -negative) charge. The net-charge density of the soft particle is defined as $Q_{\text{net}} = (1-\gamma^3)Q_f + \gamma^3 Q_c$. Figure 6(a) shows that the particle with net-positive (or -negative) charge undergoes a transition from positive (negative) velocity to negative (positive) velocity as the Debye length becomes smaller than the PEL thickness, i.e., $\kappa b \cdot e_p > 1$. The velocity increases with the decrease of Debye length and approaches a constant value as the Debye length becomes smaller, i.e., larger κb. A similar result has already been reported by Raafatnia *et al.* [31] through the molecular dynamic simulation of the electrophoresis of a soft particle with a constant surface charge density of the core. At a high ionic concentration, the direction of the velocity is primarily determined by the charge density of the PEL and the soft particle behaves like a full porous particle. Figure 6(a) shows that at $\kappa b = 50$ and $\beta = 10$, the electrophoretic velocity approaches the corresponding electrophoretic velocity of a polyelectrolyte particle as obtained by Hermans and Fujita [38] with a charge density that is the same as the charge density of the PEL. However, the corresponding electrophoretic velocity (Hermans and Fujita [38]) of a polyelectrolyte particle with a charge density the same as the PEL charge density overestimates our computed results when the lower values of β are considered. Previous studies (Bhattacharyya and Gopmandal [39], Gopmandal and Bhattacharyya [40]) on polyelectrolyte electrophoresis have shown that the solutions based on Hermans and Fujita [38] overestimates the computed solutions for a lower range of β in which the double layer polarization and relaxation effects are important. At lower range of β, i.e., when the PEL is highly permeable, the effect of the core charge density is not negligible even at $\kappa b = 50$. We find from Fig. 6(a) that the softness parameter of the shell have relatively little influence on the particle electrophoresis for the lower range of κb. However, in the higher range of κb in which the particle electrophoresis is dominated by the shell property, an increase in shell softness (i.e., decrease of β) produces a large increment in the magnitude of the velocity. In the present case the core possesses an opposite charge to that of the shell. At low ionic concentration or thick Debye length, the ions counter to core surface charge are repelled by the PEL charges being of the same sign as that of the counterions and, hence, the accumulation of mobile ions within the PEL become less. Since the accumulation of mobile ions are low for low ionic concentration, the shell permeability does not have a large influence on the electrophoresis. At a higher ionic strength (thin Debye layer) the electrolytes outside the particle is uninfluenced by the core surface charge density and the ions counter to the PEL charges penetrates the PEL. The contribution of these mobile counterions to the particle electrophoresis depends on the shell permeability. For this, we find that the dependence of U_E on β is pronounced when the ionic concentration is large, i.e., higher κb. The EOF induced by the mobile counterions is strong at lower values of β, whereas the PEL charge neutralization due to counterion condensation effect grows as the PEL becomes denser (higher β). For this, we find an increased magnitude in U_E as β assumes smaller values. It may be noted that in electrophoresis the variation of electric force (or drag) experienced by the particle due to the variation of κb follow a similar trend to that of the electrophoretic velocity. This implies that the soft particle bearing a net-positive (negative) charge with oppositely charged core and shell experiences a negative (positive) electric force when Debye length becomes lower than the thickness of the soft layer (i.e., $\kappa b \cdot e_p > 1$). As the PEL becomes more dense (increase in β) the enhanced counterion condensation effect creates a reduction in the electric force exerted on the particle.

The trapping of soft particles is important in different practical contexts. In Fig. 6(b) we have presented an estimate of the volume charge density of the core and PEL for which the particle has zero velocity at different choices of Debye length. Beyond these critical charge densities the particle will exhibit a velocity reversal. These critical values, however, depend on the screening length of the PEL, i.e., β. The zero mobility may occur when the core and shell are oppositely charged. With the increase of ionic concentration of the electrolyte, the

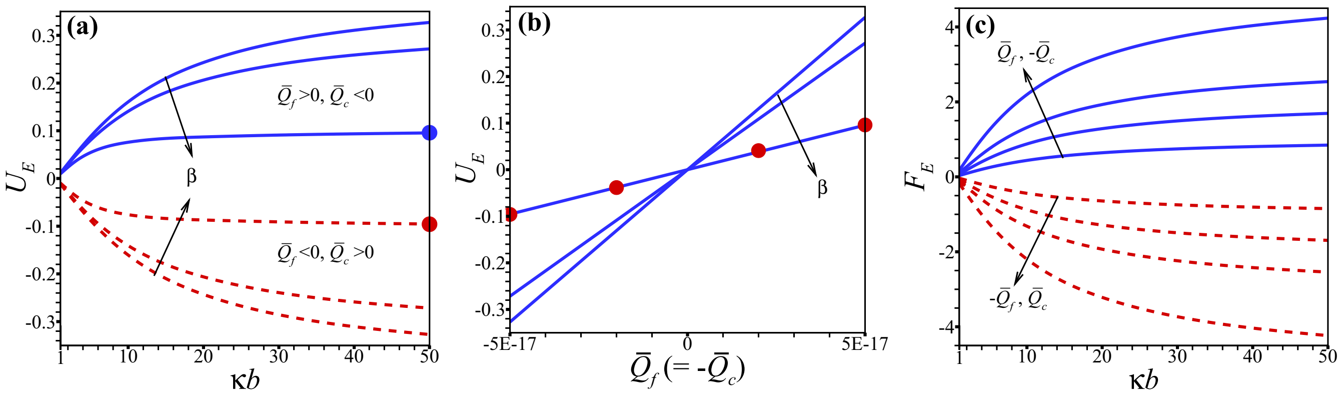

FIG. 7. Variation of the electrophoretic velocity (U_E) for a net-zero-charged soft particle when $\varepsilon_r = 100$, $\beta = 1,3,10$, $a = 75\,\text{nm}$, $b = 100\,\text{nm}$ ($e_p = 0.25$), and $\Lambda = 1.16$ with the (a) Debye length (κb) when $\bar{Q}_c = -\bar{Q}_f = \pm 5 \times 10^{-17}C$ and (b) with $\bar{Q}_f$ (or $-\bar{Q}_c$) at $\kappa b = 50$; (c) variation of the electrostatic force with κb for a net-zero-charged soft particle, i.e., $\bar{Q}_c = -\bar{Q}_f = \pm 10^{-16}C$, $\pm 2 \times 10^{-16}C$, $\pm 3 \times 10^{-16}C$, $\pm 5 \times 10^{-16}C$ at $\beta = 3$. Symbols, result of bare polyelectrolyte as obtained by Hermans and Fujita [38] at $\beta = 10$.

critical value of the shell charge density decreases, whereas the critical value of the core charge density rises. Results show that a net nonzero charged soft particle can have zero mobility and, subsequently, a mobility reversal occurs for that range of Debye length for which the core charge density can influence the ion distribution in the electrolyte medium, i.e., $\kappa b \cdot e_p \sim O(1)$. For a thin Debye layer ($\kappa b \gg 1$), electrophoresis is governed by the PEL charge density.

In Figs. 7(a)–7(c) we consider the electrophoresis of a soft particle with zero net charge. We consider the net-zero-charged soft colloid ($Q_{\text{net}} = 0$) by considering either the net fixed volume charge of the core ($\bar{Q}_c$) as positive and net fixed charge of the PEL, i.e., $\bar{Q}_f$ as negative or viceversa. For Q_{net} to be zero, the $\bar{Q}_f = -\bar{Q}_c$. The core-to-electrolyte permittivity ratio is taken to be $\varepsilon_r = 100$. At this ε_r the core behaves like a conducting metal. The electrophoretic velocity is close to zero for large Debye length, it grows and approaches a constant as the ionic concentration of the electrolyte rises. The net-zero-charged soft particle has a nonzero mobility at high salt concentration, the sign of which is determined by the grafted-polyelectrolytes charge. We find that at a thin Debye length the soft particle electrophoretic velocity approaches the corresponding bare polyelectrolyte electrophoretic velocity when the permeability of the shell is low [Fig. 7(b)]. The impact of the core grows as the shell becomes more permeable. Our computed solutions for the electrophoretic velocity of a bare polyelectrolyte at $\kappa b = 50$ overestimates the corresponding electrophoretic velocity of the soft particle for lower range of β(=1, 3.3). Based on this result and other existing analysis (Raafatnia *et al.* [32]) we may state that at a sufficiently thin Debye length, which depends on the permeability of the shell and particle charge density, the soft particle behaves like a full porous particle and its propulsion velocity approaches the electrophoretic velocity of a bare polyelectrolyte of charge density, which is the same as that of the PEL. The electrophoretic velocity at the thin Debye length varies linearly as the net charge of the shell is increased [Fig. 7(b)] by keeping the net charge of the soft particle as zero. The contribution of the core electric charge is insignificant when a thin Debye length ($\kappa b = 50$) is considered. We find from Fig. 7(c) that the electric force (drag force) rises with the increase of κb and approaches a constant value at large κb.

IV. CONCLUSIONS

We have analyzed numerically the electrophoresis of a soft particle in which the rigid core is considered to be polarizable and possesses a constant volumetric charge density. A computer simulation of the governing equations based on the first principles of electrokinetics provides a clear understanding of the underlying physics and guidelines to control the biocolloids. Our computed solutions are in agreement with the previous semianalytic solutions for a weakly charged particle and lower values of the core-to-electrolyte permittivity ratio when a thin Debye length is considered.

We have demonstrated through the present study that the impact of the core electrostatic property on the soft particle electrophoresis depends not only on the ionic concentration of the electrolyte (Debye length) but also on the permeability (hydrodynamic pore length) of the shell. The impact is strong when the Debye length is comparable to the shell thickness. The electrophoresis of the particle is governed by the core and shell electrostatic properties for a moderate range of Debye length; it is dominated by the shell property when the Debye length becomes smaller than the shell thicknesses. This phenomena may lead to a reversal in electrophoretic velocity direction when the shell has an opposite charge than that of the core. Our results shows that the soft particle approaches to a full porous particle (bare polyelectrolyte) when the Debye length becomes sufficiently thin. The combination of the core and shell charge density to obtain zero velocity of a soft particle with nonzero charge density is estimated at different values of the Debye length. This may provide a guideline for trapping a soft particle through electrophoresis.

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