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Boundary effects on electrophoresis of a colloidal cylinder with a nonuniform zeta potential distribution

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Abstract

The electrophoretic motion of a long dielectric circular cylinder with a general angular distribution of its surface potential under a transversely imposed electric field in the vicinity of a large plane wall parallel to its axis is analyzed. The thickness of the electric double layers adjacent to the solid surfaces is assumed to be much smaller than the particle radius and the gap width between the surfaces, but the applied electric field can be either perpendicular or parallel to the plane wall. The presence of the confining wall causes three basic effects on the particle velocity: (1) the local electric field on the particle surface is enhanced or reduced by the wall; (2) the wall increases viscous retardation of the moving particle; (3) an electroosmotic flow of the suspending fluid may exist due to the interaction between the charged wall and the tangentially imposed electric field. Through the use of cylindrical bipolar coordinates, the Laplace and Stokes equations are solved analytically for the two-dimensional electric potential and velocity fields, respectively, in the fluid phase, and explicit formulas for the quasisteady electrophoretic and angular velocities of the cylindrical particle are obtained. To apply these formulas, one has only to calculate the multipole moments of the zeta potential distribution at the particle surface. It is found that the existence of a plane wall near a nonuniformly charged particle can cause its translation or rotation which does not occur in an unbounded fluid with the same applied electric field.

Keywords: Electrophoresis; Nonuniform zeta potential distribution; Circular cylindrical particle; Plane wall; Boundary effect

1. Introduction

A charged particle suspended in an electrolyte solution is surrounded by a diffuse cloud of ions carrying a total charge equal and opposite in sign to that of the particle. This distribution of fixed charge and diffuse ions is known as an electric double layer. When an electric field is imposed on the particle, a force is exerted on both parts of the double layer. The particle is attracted toward the electrode of its opposite sign, while the ions in the diffuse layer migrate in the other direction. This particle motion is termed electrophoresis and has long been applied to the particle characterization or separation in a variety of colloidal and biological systems.

The electrophoretic velocity $\mathbf{U}$ of an isolated particle is related to the applied electric field $\mathbf{E}_\infty$ by the Smoluchowski equation [1–3],

$$\mathbf{U} = \frac{\varepsilon \zeta_\mathrm{p}}{\eta} \mathbf{E}_\infty. \tag{1}$$

Here, η and ε represent the viscosity and permittivity, respectively, of the solution surrounding the particle, and ζ_p is the zeta potential associated with the particle surface. This formula is valid on the basis of several assumptions: (i) the local radii of curvature of the particle are much larger than the thickness of its electric double layer; (ii) the ambient fluid is unbounded; (iii) the zeta potential is uniform on the length scale of the particle. The first restriction also implies that the double layer remains approximately in equilibrium despite the migration of the particle and diffuse ions. Even though many colloidal particles undergoing electrophoresis fulfill this condition, electrophoresis of particles with thick or distorted double layers does occur in certain cases so that relevant corrections to the Smoluchowski prediction in Eq. (1) are necessary and have been obtained [4–8].

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In practical applications of electrophoresis, colloidal particles are not isolated and will move in the presence of neighboring boundaries [9–11]. Therefore, the boundary effects on electrophoresis are of great importance and have been studied extensively in the past for various cases of uniformly charged colloidal spheres and boundaries in the limit of thin electric double layers. Using a method of reflections, Keh and Anderson [12] analyzed the electrophoretic motions of a dielectric sphere normal to a large conducting plane, parallel to a large dielectric plane, along the axis of a long circular tube, and along the central plane between two large parallel plates. Through an exact representation in spherical bipolar coordinates or a lubrication theory, semianalytical solutions for the electrophoretic velocity of a colloidal sphere in the vicinity of an infinite plane wall have also been obtained in two principal cases: the migration perpendicular to a conducting plane [13–15] and the movement parallel to an insulating wall [16,17]. Subsequently, the boundary effects on electrophoresis of a charged sphere were investigated for geometries like migration along the axis of a circular orifice or disk [18], movement in a circular cylindrical pore at an axial [19] or eccentric [20,21] position, and motion in between two parallel plane walls [22–24]. The boundary effects on electrophoresis have also been theoretically examined for the cases of spherical particles with thick or distorted double layers [24–28] and of nonspherical particles [29–31].

On the other hand, many colloidal particles have heterogeneous surface structures or chemistry and are nonuniformly charged. For instance, elementary clay particles are flat disks with edges having a different charge density or zeta potential from the faces. Distributions of surface charge or potential for particles can also result from aggregation of different species of colloids. Even if a particle is homogeneously charged on its surface, an applied electric field could cause rearrangement of these charges if they are mobile [32]. A distribution of zeta potential on particle surfaces has been found to lead to colloidal instability, even the average zeta potential should be sufficiently high to keep the suspension stable [33,34]. The electrophoretic motion of a dielectric sphere with nonuniform zeta potential and thin electric double layer was first analyzed thoroughly by Anderson [35], although it had also been discussed to some extent earlier [36]. It was found that, in terms of the multipole moments of the zeta potential, the electrophoretic mobility depends not only on the monopole moment (area-averaged zeta potential) but also on the quadrupole moment, and the dipole moment contributes to particle rotation which tends to align the particle with the electric field. This analysis was later extended to the cases of a nonuniformly charged spherical particle with a double layer of finite thickness [37–40] and a nonuniformly charged nonspherical particle [41–45]. Recently, that particles can have random charge nonuniformity has also been demonstrated experimentally [46,47].

The electrophoretic motion of nonuniformly charged particles in the proximity of confining walls could also be encountered in some real situations. For example, the translation and rotation of each of an array of nonuniformly charged bichromal spheres in its own elastomer-made and solvent-filled cavity controlled by imposing a voltage of either positive or negative polarity have been applied to a technology of electric paper displays [48,49]. Also, an electrophoretic positioning process has been employed in electronic applications for assembling very small individual devices, such as an InGaAs light-emitting diode or a nanowire, which is nonuniformly charged and must have all electric contacts available on one surface, onto the contact electrodes of a silicon circuit by biasing the contacts to control the placement of these devices with the precision required [50,51]. Recently, the electrophoresis of a dielectric spherical particle in a concentric spherical cavity with nonuniform zeta potential distributions at the solid surfaces has been investigated and analytical expressions for the translational and angular velocities of the particle in terms of the monopole, dipole, and quadrupole moments of the zeta potentials were obtained [52].

The objective of this paper is to determine the electrophoretic velocity of a long dielectric circular cylinder with an a nonuniform zeta potential distribution in the angular direction near a large plane wall parallel to its axis in transversely applied electric fields. The electric double layers are assumed to be thin compared with the radius of the cylindrical particle and with the surface-to-surface spacing between the particle and the wall. A cylindrical bipolar coordinate system is used to solve the quasisteady problem. In the next section, the electrophoresis of a circular cylinder caused by an imposed electric field in the direction perpendicular to its axis and to a conducting plane wall is examined. The analytical solution for the wall-corrected electrophoretic velocity of the particle is obtained in Eqs. (20a) and (20b). The analysis of a complementary problem to that treated in Section 2, the electrophoretic motion of a circular cylinder driven by an applied electric field in the direction perpendicular to its axis and parallel to a dielectric plane wall, is presented in Section 3. The general expressions for the electrophoretic velocity of the particle in this case are given in Eqs. (28a)–(28c).

2. Electrophoresis in an applied electric field perpendicular to a conducting plane wall

In this section we consider the quasisteady electrophoretic motion of a long circular cylindrical particle of radius a caused by a uniform electric field $\mathbf{E}_\infty = E_\infty \mathbf{e}_x$ imposed normal to its axis and to a large conducting plane wall located at a distance d from the axis, as illustrated in Fig. 1a, where $\mathbf{e}_x$ together with $\mathbf{e}_y$ and $\mathbf{e}_z$ are the principal unit vectors in the Cartesian coordinate system (x, y, z) with a right-handed screw. The zeta potential ζ_p on the surface of the particle at $r = a$ can be a general function of the azimuth angle θ, where (r, θ, z) are circular cylindrical coordinates. The thickness of the electric double layers surrounding the particle and adjacent to the plane wall is assumed to be much smaller than the radius of the cylinder and the spacing between the solid surfaces. Gravitational and end effects are neglected. Our purpose is to determine the electrophoretic velocity of the nonuniformly charged cylindrical particle in the presence of the plane wall.

For convenience in satisfying the boundary conditions at the solid surfaces, an orthogonal curvilinear coordinate system (ξ, ψ, z) known as cylindrical bipolar coordinates and shown in Fig. 2 is utilized to solve the problem. This coordinate system