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Electrophoretic motion of a charged particle in a charged cavity

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ABSTRACT

A theoretical investigation of the electrophoresis of a dielectric colloidal sphere located at an arbitrary position inside a charged spherical cavity filled with an ionic fluid is presented. The applied electric field is perpendicular to the line through the centers of the particle and cavity, and the electric double layers adjacent to the solid surfaces are assumed to be much thinner than the particle radius and any gap width between the surfaces. The general solutions to the Laplace and Stokes equations governing the electric potential and fluid velocity fields, respectively, are established from the superposition of their basic solutions in the two spherical coordinate systems about the two centers, and the boundary conditions are satisfied by a multipole collocation method. Results for the translational and angular velocities of the confined particle are obtained for various cases. When the particle is positioned at the center of the cavity, these results are in excellent agreement with the available analytical solution. The effects of the cavity wall on the electrokinetic motion of the particle are interesting, complicated, and significant. In general, the electrophoretic translational/rotational mobility of the particle decreases/increases with increases in the particle-to-cavity radius ratio and the relative distance between the particle and cavity centers (the direction of rotation is opposite to that of a corresponding settling particle), but there exist some exceptions. The direct and recirculating cavity-induced electroosmotic flows can strengthen or weaken the electrophoretic translation and rotation of the particle and even reverse their directions, depending on the cavity-to-particle zeta potential ratio and geometric parameters. The effect of the cavity wall on the electrokinetic translation of a particle perpendicular to the line connecting their centers is slightly weaker than that parallel to this line.

1. Introduction

Electrophoresis, which refers to the migration of a charged colloidal particle in an ionic fluid caused by an external electric field, has been widely applied to the particle characterization and separation in many physicochemical and biomedical systems. The imposed electric field interacts with the particle's surface charge and drives the particle to undergo electrophoretic motion in one direction and the fluid in the surrounding, oppositely charged double layer to move relative to the particle by electroosmosis in the other directions simultaneously. The electrophoretic velocity of a dielectric particle of arbitrary shape in an unbounded fluid is given by the Smoluchowski equation [1,2],

$$\mathbf{U}_0 = \frac{\varepsilon \zeta_{\mathrm{p}}}{\eta} \mathbf{E}_\infty, \tag{1}$$

provided that the thickness of the electric double layer is much smaller than the local radii of curvature of the particle. In Eq. (1), the constants η, ε, ζ_{p}, and $\mathbf{E}_\infty$ are the fluid viscosity, fluid permittivity, particle zeta potential, and applied electric field, respectively.

In practical applications of electrophoresis, colloidal particles are not isolated and will move in the presence of confining boundaries, such as electrodes [3,4], capillaries or orifices [5,6], gels or membranes [7,8], interstices of porous composites [9,10], microchannels [11–13], and spherical cavities for the Gyricon display [14,15]. Also, the Debye screening length (thickness of the electric double layer) usually has the order of several to tens nanometers, which is much less than the typical particle and boundary sizes. Therefore, the boundary effects on electrophoresis of colloidal spheres with thin double layers are essential and have been studied for various cases of boundaries, including a conducting [16–19] or insulating [19–21] plane wall, two parallel plane walls [22–25], a circular cylindrical pore [26–28], a circular orifice or disk [29], and a concentric spherical cavity [30,31].

The model of a charged sphere undergoing electrophoresis within a nonconcentric spherical cavity can be applied for the

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relevant movement of colloidal particles in media or microchannels constituted by connecting spherical pores. Recently, the electrophoretic migration of a dielectric spherical particle positioned arbitrarily within a charged spherical cavity along the line connecting their centers was examined for the case of thin double layers through the use of a combined analytical–numerical method with a boundary collocation technique, and accurate results of the particle mobility were obtained (there was no particle rotation owing to the axial symmetry in the charge and fluid flows) [32]. The object of the present article is to investigate the complementary electrophoretic motion of a spherical particle inside a spherical cavity subject to an applied electric field perpendicular to the line of their centers. The Laplace and Stokes equations will be solved for the electric potential and fluid velocity distributions (which are not axially symmetric), respectively, by using the boundary collocation method and the translational and rotational velocities of the confined particle are obtained with good convergence. Because the governing equations for the general problem of electrophoretic motion of a spherical particle within a spherical cavity in an arbitrary direction are linear, its solution can result from the vectorial addition of the solutions for its two subproblems: migration along the line connecting the particle and cavity centers, which was dealt with previously [32], and motion perpendicular to this line, which is managed in the current work.

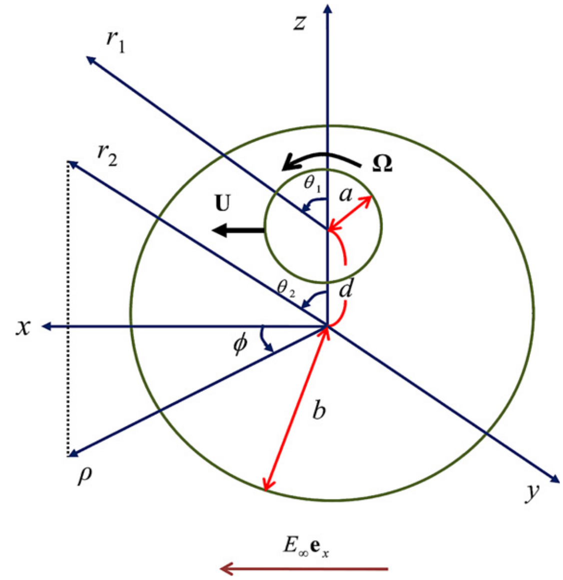

Fig. 1. Geometrical sketch for the electrokinetic motion of a colloidal sphere in a spherical cavity caused by an applied electric field perpendicular to the line connecting the particle and cavity centers.

2. Analysis

Consider the quasi-steady electrophoresis of a dielectric spherical particle of radius a and zeta potential ζ_p at an arbitrary position inside a spherical cavity of radius b and zeta potential ζ_w filled with an electrolytic solution, as illustrated in Fig. 1. Here (x, y, z), (ρ, ϕ, z), and (r_2, θ_2, ϕ) are the Cartesian, circular cylindrical, and spherical coordinate systems, respectively, with the origin at the cavity center, and (r_1, θ_1, ϕ) represent the spherical coordinates originating from the particle center located away from the cavity center in the z direction at a distance d. The imposed electric field (field in the absence of the particle) is uniform and equals $E_\infty \mathbf{e}_x$, where $\mathbf{e}_x$ is the unit vector in the x direction and E_∞ is a constant. The electric double layers adjacent to the particle surface and cavity wall are assumed to be very thin in comparison with the particle radius and any spacing between the particle and cavity surfaces. To obtain the translational and rotational velocities of the particle within the cavity, the electric potential and velocity fields in the fluid outside the thin double layers need to be determined first.

2.1. Electric potential distribution

The fluid outside the double layers is of constant conductivity, electric neutrality, and uniform composition. Hence, the electric potential distribution ψ is governed by Laplace's equation,

$$\nabla^2 \psi = 0. \tag{2}$$

Because the particle is nonconductive, the boundary condition for ψ at its surface is

$$\frac{\partial \psi}{\partial r_1} = 0 \quad \text{at } r_1 = a. \tag{3}$$

The electric potential distribution over the cavity wall gives rise to the applied electric field $E_\infty \mathbf{e}_x$ when the particle is absent. Thus, a legitimate choice of the boundary condition there is [31,33,34]

$$\psi = -E_\infty r_2 \sin\theta_2 \cos\phi \quad \text{at } r_2 = b, \tag{4}$$

where $\psi = 0$ is set on the plane $x = 0$ without loss in generality. On the other hand, one may take the electric potential gradient at the cavity wall equal to the applied electric field, and replace the Dirichlet boundary condition in Eq. (4) by the Neumann approach [30,35],

$$\frac{\partial \psi}{\partial r_2} = -E_\infty \sin\theta_2 \cos\phi \quad \text{at } r_2 = b. \tag{5}$$

However, the tangential component of the electric potential gradient at the cavity wall is not specified by this boundary condition. The Neumann condition in Eq. (5) is considered here only for a comparison, perceiving that it is less correct than the Dirichlet condition in Eq. (4).

The general solution to Eq. (2) satisfying the requirement that the electric potential is finite for any position in the fluid phase can be written as

$$\psi = E_\infty \sum_{m=1}^{\infty} [S_{1m} r_1^{-m-1} P_m^1(\mu_1) + S_{2m} r_2^m P_m^1(\mu_2)] \cos\phi, \tag{6}$$

where P_m^1 is the associated Legendre function of the first kind of order m and degree one, μ_i with $i = 1$ and 2 is used to denote $\cos\theta_i$ for brevity, and S_{im} are the unknown constants to be determined using the boundary conditions at the particle and cavity surfaces. In the establishment of Eq. (6), the general solutions to the linear Laplace equation in two different spherical coordinate systems are superimposed [36]. The solution for ψ contains only the first-order harmonics $P_m^1(\mu_i)\cos\phi$ due to the axial symmetry of the two-sphere geometry.

Substituting Eq. (6) into Eqs. (3)–(5), we obtain

$$\sum_{m=1}^{\infty} \{(m+1) S_{1m} a^{-m-2} P_m^1(\mu_1) - S_{2m} [\delta_m^{(1)}(\rho, z)]_{r_1=a}\} = 0, \tag{7}$$

$$\sum_{m=1}^{\infty} \{S_{1m} [r_1^{-m-1} P_m^1(\mu_1)]_{r_2=b} + S_{2m} b^m P_m^1(\mu_2)\} = -b(1-\mu_2^2)^{1/2}, \tag{8}$$

$$\sum_{m=1}^{\infty} \{S_{1m} [\delta_m^{(2)}(\rho, z)]_{r_2=b} + m S_{2m} b^{m-1} P_m^1(\mu_2)\} = -(1-\mu_2^2)^{1/2}, \tag{9}$$

where the functions $\delta_m^{(1)}$ and $\delta_m^{(2)}$ are defined by Eqs. (A.1) and (A.2) in the Appendix. To use Eqs. (7)–(9), which are independent of the