

Electrophoretic Motion of a Charged Particle in a Cavity

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Abstract- The electrophoretic motion of a charged spherical particle located at an arbitrary position within a charged spherical cavity along the line connecting their centers is studied theoretically for the case of thin electric double layers. To solve the electrostatic and hydrodynamic governing equations, the general solutions are constructed using the two spherical coordinate systems based on the particle and cavity, and the boundary conditions are satisfied by a collocation technique. Numerical results for the electrophoretic velocity of the particle are presented for various values of the zeta potential ratio, radius ratio, and relative center-to-center distance between the particle and cavity. In the particular case of a concentric cavity, these results agree excellently with the available exact solution. The contributions from the electroosmotic flow occurring along the cavity wall and from the wall-corrected electrophoretic driving force to the particle velocity are equivalently important and can be superimposed due to the linearity of the problem. The normalized migration velocity of the particle decreases with increases in the particle-to-cavity radius ratio and its relative distance from the cavity center and increases with an increase in the cavity-to-particle zeta potential ratio. The boundary effects on the electrokinetic migration of the particle are significant and interesting.

Keywords: Electrophoresis, electroosmosis, colloidal sphere, boundary effect, spherical pore.

1. Introduction

A charged solid surface in contact with an electrolyte solution is surrounded by a diffuse cloud of ions carrying a total charge equal and opposite in sign to that of the solid surface. This distribution of fixed charge and adjacent diffuse ions is known as an electric double layer. When a charged colloidal particle is subjected to an external electric field, a force is exerted on both parts of the double layer. The suspended 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 analysis and separation in a variety of physicochemical and biomedical systems (Masliyah and Brattacharjee 2006).

The electrophoretic velocity U_0 of a dielectric particle of arbitrary shape and thin double layer (relative to the local radii of curvature of the particle) in an unbounded ionic solution is related to the uniformly imposed electric field E_∞ by the well-known Smoluchowski equation (Anderson 1989),

$$U_0 = \frac{\varepsilon \zeta_p}{\eta} E_\infty \quad (1)$$

where η and ε are the viscosity and permittivity, respectively, of the fluid, and ζ_p is the zeta potential associated with the particle surface. Since the thickness of the double layer usually ranges from several to tens of nanometers, which is much smaller than the typical particle size, Eq. 1 has been used widely in practice.

On the other hand, the interaction between the ions in the mobile portion of the double layer adjoining a charged solid surface with the zeta potential ζ_w and an external electric field generates a

tangential velocity for the fluid within the diffuse layer. This electroosmotic velocity at each point on the outer edge of the thin diffuse layer, which appears as a slip velocity relative to the frame of the solid surface, is given by the classic Helmholtz equation,

$$\mathbf{v}_s = -\frac{\zeta_w}{\eta} \mathbf{E}_s \quad (2)$$

where \mathbf{E}_s is the component of the local electric field tangential to the dielectric solid surface.

In real situations of electrophoresis in microfluidic and other practical applications, colloidal particles are not isolated and will move near solid boundaries (Smith et al. 2000; Kang and Li 2009). The purpose of this article is to obtain a semi-analytical solution for the axisymmetric electrophoresis of a dielectric sphere in a nonconcentric spherical cavity with thin double layers. The electrostatic and hydrodynamic equations governing the system are solved by using the boundary collocation method, and the wall-corrected electrophoretic mobility of the particle is obtained with good convergence for various cases. Some interesting features of the boundary effect on the electrokinetic migration of the particle are revealed from the results.

2. Analysis

We consider the axisymmetric electrophoretic motion of a dielectric spherical particle of radius a and zeta potential ζ_p in an electrolyte solution within a spherical cavity (pore) of radius b and zeta potential ζ_w , as shown in Fig. 1, at the quasi-steady state. Here, (ρ, ϕ, z) and (r_2, θ_2, ϕ) represent the circular cylindrical and spherical coordinate systems, respectively, with the origin at the center of the cavity. The center of the particle is located on the z axis away from the cavity center at a distance d . A uniform electric field $E_\infty \mathbf{e}_z$ is imposed to the fluid, where \mathbf{e}_z is the unit vector in the z direction. The thickness of the electric double layers adjoining the particle and cavity surfaces is assumed to be much smaller than the particle radius and the spacing between the solid surfaces. Our objective is to obtain the correction to Eq. 1 for the particle velocity due to the presence of the cavity wall.

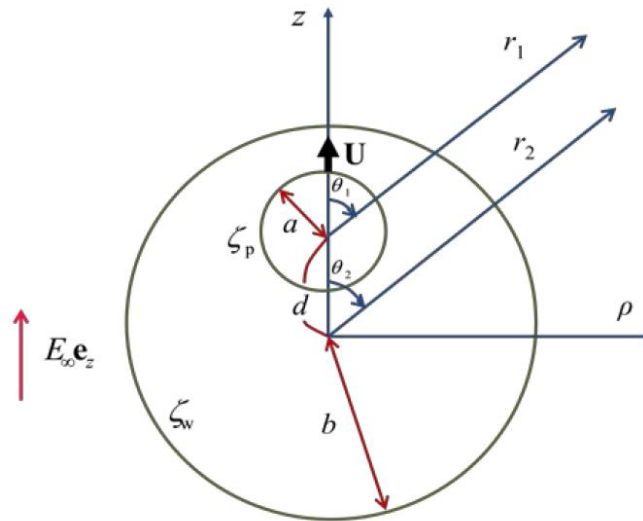


Fig. 1 Geometrical sketch for the axisymmetric electrokinetic migration of a spherical particle in a spherical cavity.

The fluid outside the thin double layers is of uniform composition, electric neutrality, and constant conductivity; hence, the electric potential distribution $\psi(r, \theta)$ is governed by the Laplace equation from charge conservation,

$$\nabla^2 \psi = 0 \quad (3)$$

Since the particle is non-conducting, the boundary condition for ψ at its surface (or more precisely, the outer edge of the double layer) is

$$r_1 = a: \quad \frac{\partial \psi}{\partial r_1} = 0, \quad (4)$$

where (r_1, θ_1, ϕ) are the spherical coordinates based on the center of the particle.

$$r_2 = b: \quad \psi = -E_\infty r_2 \cos \theta_2 \quad (5)$$

in the Dirichlet approach (Keh and Hsieh 2007).

The general solution of the electric potential distribution can be expressed as

$$\psi = E_\infty \sum_{m=0}^{\infty} [S_{1m} r_1^{-m-1} P_m(\cos \theta_1) + S_{2m} r_2^m P_m(\cos \theta_2)] \quad (6)$$

where P_m is the Legendre polynomial of order m , and the unknown constants S_{1m} and S_{2m} need to be determined using the boundary conditions at the particle surface and cavity wall.

With knowledge of the solution for the electric potential field, we can now proceed to find the fluid velocity distribution. Owing to the low Reynolds number, the fluid motion outside the thin double layers is governed by the Stokes equations,

$$\begin{aligned} \eta \nabla^2 \mathbf{v} - \nabla p &= \mathbf{0}, \\ \nabla \cdot \mathbf{v} &= 0, \end{aligned}$$

where \mathbf{v} is the fluid velocity field and p is the dynamic pressure distribution.

The boundary conditions for the fluid velocity require that

$$r_1 = a: \quad \mathbf{v} = U \mathbf{e}_z + \frac{\mathcal{E}_p}{\eta} \frac{\partial \psi}{r_1 \partial \theta_1} \mathbf{e}_{\theta_1}, \quad (8)$$

$$r_2 = b: \quad \mathbf{v} = \frac{\mathcal{E}_w}{\eta} \frac{\partial \psi}{r_2 \partial \theta_2} \mathbf{e}_{\theta_2}. \quad (9)$$

Here, U is the migration velocity of the particle to be determined, \mathbf{e}_{θ_1} and \mathbf{e}_{θ_2} are the unit vectors along the θ_1 and θ_2 coordinates, respectively, and the expression for ψ has already been given by Eq. 6. There is no rotation of the particle due to the axial symmetry of the system.

Since the particle is freely suspended in the surrounding fluid, the net force on the particle must vanish.

$$F = 4\pi\eta D_2 = 0 \quad (10)$$

Obtaining the general solution of Eq. 7 (Keh and Lee 2010) and the electric potential distribution ψ , we can use the boundary collocation method to determine the electrokinetic migration velocity U of the confined particle.

3. Results and Discussion

The numerical solutions for the electrokinetic migration of a spherical particle within a spherical cavity caused by an imposed electric field along the line through the particle and cavity centers can be obtained by using the boundary collocation method. The details of the collocation scheme used for this work were given by Keh and Lee (2010), in which very good accuracy and convergence behavior have been achieved.

The results for the electrokinetic migration velocity of a charged spherical particle in a charged spherical cavity normalized by its electrophoretic velocity in an unbounded fluid, U/U_0 , versus the radius ratio a/b for various values of the zeta potential ratio ζ_w/ζ_p and normalized center-to-center distance $d/(b-a)$ are presented in Fig. 2. For constant values of a/b and $d/(b-a)$, as expected, the value of U/U_0 increases monotonically with an increase in ζ_w/ζ_p . When the value of ζ_w/ζ_p is positive, the presence of the cavity can greatly enhance the electrophoretic migration of the particle, and this great enhancement is attributed to the electroosmotic flow recirculation arising from the interaction between the applied electric field and the charged cavity wall. As long as the value of ζ_w/ζ_p is greater than -1 , the value of U/U_0 is positive. When the value of ζ_w/ζ_p is smaller than about -1 , however, the value of U/U_0 may become negative, meaning that the velocity of the particle reverses its direction due to the relatively strong effect of the cavity-induced electroosmotic flow in the opposite direction. For a specified value of ζ_w/ζ_p , the magnitude of U/U_0 in general decreases with an increase in a/b or $d/(b-a)$.

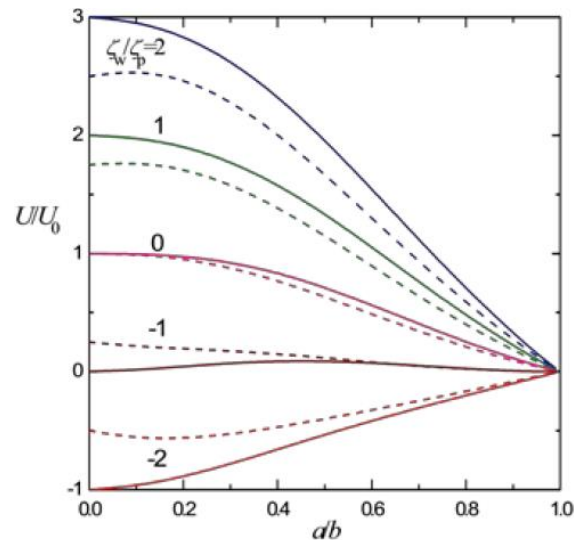


Fig.2 Plots of the normalized electrokinetic migration velocity U/U_0 of a charged sphere in a charged spherical cavity versus the radius ratio a/b with the zeta potential ratio ζ_w/ζ_p as a parameter. The solid and dashed curves denote the case of $d/(b-a) = 0$ and $d/(b-a) = 0.5$, respectively.

4. Conclusions

A semi-analytical investigation of the electrophoretic motion of a charged spherical particle arbitrarily positioned within a charged spherical cavity along the line of their centers using a boundary collocation method is presented in the limit of thin electric double layers. The Laplace and Stokes equations are solved for the electric potential and velocity fields, respectively, in the fluid phase, and numerical results for the electrokinetic migration velocity of the particle are obtained for various values of the relative particle radius, distance between the particle and cavity centers, and zeta potential of the cavity wall. The electroosmotic flow induced by the interaction between the applied electric field and the thin double layer adjoining the cavity wall can lead to a significant enhancement/reduction of the electrophoretic migration of the particle if the ratio of their zeta potentials is positive/negative. When the particle is situated closer to the cavity wall or becomes larger, the wall effect of hydrodynamic retardation increases and the electrophoresis of the particle slows down. The boundary effects on the electrophoresis can be significant in appropriate situations.

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