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# Electrophoresis of a charge-regulated sphere at an arbitrary position in a charged spherical cavity

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ABSTRACT

The electrophoresis of a charge-regulated spherical particle at an arbitrary position in a charged spherical cavity is modeled under conditions of low surface potential ($<25$ mV) and weak applied electric field ($<25$ kV/m). The charged cavity allows us to simulate the effect of electroosmotic flow, and the charge-regulated nature of the particle permits us to model various types of surface. The problem studied previously is reanalyzed based on a more rigorous electric force formula. In particular, the influences of various types of charged conditions on the electrophoretic behavior of a particle and the roles of all the relevant forces acting on the particle are examined in detail. Several new results are found. For instance, the mobility of a particle has a local minimum as the thickness of a double layer varies, which is not seen in the cases where the surface of a particle is maintained at a constant potential and at a constant charge density.

## 1. Introduction

Boundary effect is one of the key factors that are of practical significance in electrophoresis operation. This effect can influence the electrophoretic behavior of a particle both qualitatively and quantitatively [1–3]. Among various types of boundary assumed in theoretical analyses, the spherical cavity proposed by Zydney [4] is simple in structure but is capable of modeling the boundary effect appropriately under certain conditions [5–7]. The geometry of a sphere in a spherical cavity has been adopted by many researchers for studies of boundary effects on the electrophoretic behavior of a particle [4–10].

In a study of the electrophoresis of a charge-regulated particle in a spherical cavity, Yu et al. [6] found that if both the surface of a particle and that of a cavity are kept at constant potential, then the mobility of the particle may have a local minimum as its position in the cavity varies. A similar result was also observed in Hsu et al. [9]. This behavior was explained by charge reversal as a particle is sufficiently close to a cavity. In these studies, the evaluation of the electric force acting on a particle was based on the total potential, which includes the equilibrium potential and the potential that arises from the applied electric field. Although this approach has been adopted by many investigators, we showed recently that for a non-totally-symmetric geometry, it is more realistic to exclude the driving force contributed by the equilibrium potential [11,12]. In an attempt to provide more a rigorous explanation for the electrophoretic behavior of a particle near a boundary, the problem considered by Yu et al. [6] is reanalyzed in this study. In particular, the influence of various types of charged conditions on the electrophoretic behavior of a particle and the roles of all the relevant forces acting on a particle are examined in detail.

## 2. Materials and methods

Let us consider the problem illustrated in Fig. 1, where a nonconductive spherical particle of radius $a$ is at an arbitrary position in a nonconductive spherical cavity of radius $b$. The surface of the particle bears an acidic function group AH, which is capable of undergoing the dissociation reaction expressed by

$$\mathrm{AH} \Leftrightarrow \mathrm{A}^- + \mathrm{H}^+. \tag{1}$$

The equilibrium constant of this reaction, $K_a$, is expressed by

$$K_a = \frac{[\mathrm{A}^-]_s(\mathrm{H}^+)_s}{[\mathrm{AH}]_s}, \tag{2}$$

where $[\mathrm{A}^-]_s$ and $[\mathrm{AH}]_s$ are the number densities of $\mathrm{A}^-$ and AH on the particle surface, respectively, and $(\mathrm{H}^+)_s$ is the surface concentration of $\mathrm{H}^+$. The cavity is filled with an incompressible Newtonian fluid of constant physical properties containing electrolytes.

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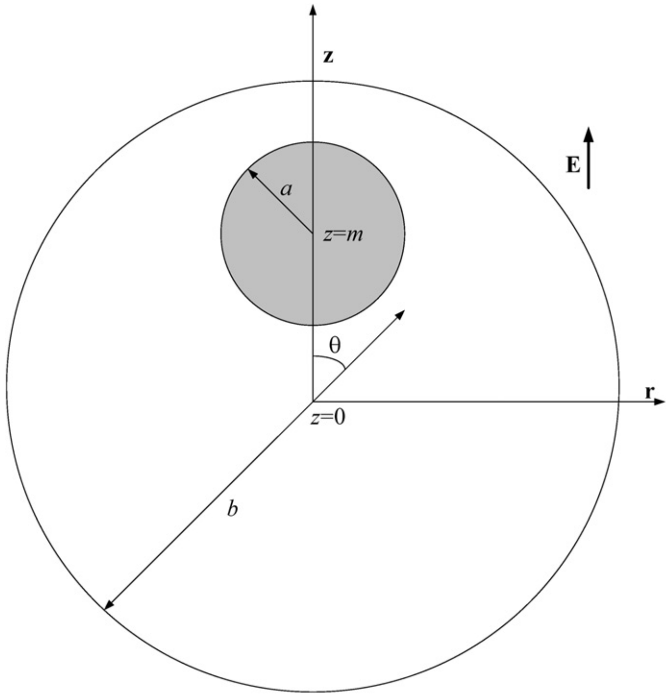

**Fig. 1.** The electrophoresis of a charged, nonconductive spherical particle of radius $a$at an arbitrary position in a spherical cavity of radius $b$, where ($r$, $\theta$, $z$) are the cylindrical coordinates with the origin at the center of the cavity, **E** is an applied uniform electric field in the $z$-direction, and the center of the sphere is at $z = m$.

The cylindrical coordinates $(r, \theta, z)$ are adopted with the origin located at the center of the cavity. The center of the particle is at $z = m$. A uniform electric field **E** pointed in the $z$-direction with strength $E$ is applied. Because the system is symmetric about $\theta$, only the $(r, z)$ domain needs to be considered. Assuming steady state, the governing equations of the present problem can be summarized as follows [13]:

$$\nabla^2 \Psi = -\frac{\rho_e}{\varepsilon} = -\sum_j \frac{z_j e n_j}{\varepsilon}, \tag{3}$$

$$\nabla \cdot \mathbf{u} = 0, \tag{4}$$

$$\eta \nabla^2 \mathbf{u} - \nabla p = -\rho_e \mathbf{E}. \tag{5}$$

Here, $\Psi$, $\nabla^2$, $\varepsilon$, $\rho_e$, $n_j$, $z_j$, and $e$ are the electrical potential, the Laplacian, the dielectric constant of the liquid phase, the space charge density, the bulk number concentration and the valence of ionic species $j$, and the elementary charge, respectively. $\mathbf{u}$, $\eta$, and $p$ are the fluid velocity, the viscosity, and the pressure, respectively.

Suppose that **E** is a weak electric field relative to that established by the particle and/or the cavity, and the surface potential of the particle and/or that of the cavity is low. The former is reasonable if $E$ is lower than ca. 25 kV/m, and the latter is satisfied if the surface potential is lower than ca. 25 mV [11]. Under these conditions, Eq. (3) can be replaced by [14]

$$\nabla^2 \Psi_1 = \kappa^2 \Psi_1, \tag{6}$$

$$\nabla^2 \Psi_2 = 0, \tag{7}$$

where $\Psi = \Psi_1 + \Psi_2$, $\Psi_1$ is the electrical potential in the absence of $E$ or the equilibrium potential, and $\Psi_2$ is the electrical potential outside the particle arising from **E**, $\mathbf{E} = -\nabla \Psi_2$.

$$\kappa = \left[\sum_j n_j^0 (e z_j)^2 / \varepsilon k_B T\right]^{1/2}$$

is the reciprocal Debye length, $n_j^0$, $k_B$, and $T$ being the bulk number concentration of ionic species $j$, the Boltzmann constant, and the absolute temperature. The boundary conditions associated with Eqs. (6) and (7) are assumed to be

$$\mathbf{n} \cdot \nabla \Psi_1 = -\frac{\sigma_p}{\varepsilon} \quad \text{and} \quad \mathbf{n} \cdot \nabla \Psi_2 = 0 \quad \text{on the particle surface}, \tag{8}$$

$$\Psi_1 = \zeta_w \quad \text{and} \quad \mathbf{n} \cdot \nabla \Psi_2 = -E_z \cos\theta \quad \text{on the cavity surface}, \tag{9}$$

where $\sigma_p$ is the surface charge density of the particle, $\zeta_w$ is the surface potential of the cavity, $\mathbf{n}$ is the unit normal vector pointing to the liquid phase, and $E_z$ is the $z$-component of **E**.

Assuming Boltzmann distribution for the spatial variation of the molar concentration of $H^+$, it can be shown that [3]

$$\sigma_p = -\frac{e N_s}{1 + \frac{C^0_{H^+}}{K_a} \exp(-\frac{e\zeta_p}{k_B T})}, \tag{10}$$

where $N_s$ is the density of the acidic functional groups on the particle surface, $\zeta_p$ is the surface potential of the particle, and $C^0_{H^+}$ is the bulk concentration of $H^+$. If $\zeta_p$ is low, this expression can be approximated by

$$\sigma_p \cong \frac{-e N_s}{\{1 + C^0_{H^+}/K_a\}} - \frac{(e^2 N_s / k_B T)\{C^0_{H^+}/K_a\}}{\{1 + C^0_{H^+}/K_a\}^2} \zeta_p. \tag{11}$$

Suppose that both the surface of the particle and that of the cavity are no-slip. Then the boundary conditions associated with Eqs. (4) and (5) are

$$\mathbf{u} = U \mathbf{e}_z \quad \text{on the particle surface}, \tag{12}$$

$$u = 0 \quad \text{on the cavity surface}. \tag{13}$$

Here, $U$ is the $z$-component of the particle velocity and $\mathbf{e}_z$ is the unit vector in the $z$-direction.

For the present case, the forces acting on the particle include the electric force $\mathbf{F}_E$ and the hydrodynamic force $\mathbf{F}_D$. If we let $F_E$ and $F_D$ be the $z$-components of these forces, then $F_E + F_D = 0$ at steady state. $F_E$ and $F_D$ can be evaluated by [1–3,14–17]

$$F_E = \iint_S \sigma_p E_z \, dS, \tag{14}$$

$$F_D = \iint_S \eta \frac{\partial (\mathbf{u} \cdot \mathbf{t})}{\partial n} t_z \, dS + \iint_S -p n_z \, dS, \tag{15}$$

where $S$ is the surface of the particle, $\mathbf{t}$ the unit tangent vector on $S, n$ the magnitude of $\mathbf{n}$, and $t_z$ and $n_z$ are the $z$-components of $\mathbf{t}$ and $\mathbf{n}$, respectively. For a simpler treatment, the problem under consideration is decomposed into two subproblems [18]. In the first subproblem the particle translates with a constant velocity $U$ in the absence of **E**, and in the second subproblem **E** is applied but the particle is held fixed. In the first subproblem the particle experiences a conventional drag force $F_{D,1} = -UD$, where $D$ is the drag coefficient. In the second subproblem the particle experiences both an electric force $F_E$ and a hydrodynamic force $F_{D,2}$, which arises from the movement of the ionic species in the double layer surrounding the particle. The force balance $F_E + F_D = 0$ yields

$$U = \frac{F_E + F_{D,2}}{D}. \tag{16}$$

For convenience, the following scaled symbols are defined: $P$ $(= 100m/(b-a)\%)$ is the scaled position of the particle; $\kappa a$ is the scaled thickness of the double layer; $\lambda$ $(= a/b)$ is the scaled size of the cavity; $A = e^2 N_s a / \varepsilon k_B T$ is a parameter measuring the density of the acidic functional groups on the particle surface; $B = C^0_{H^+}/K_a$ is a parameter measuring the bulk concentration of $H^+$ (or pH); $U^* = U/U_{ref}$ is the scaled electrophoretic mobility,