Proceedings of the ASME 2010 3rd Joint US-European Fluids Engineering Summer Meeting and
8th International Conference on Nanochannels, Microchannels, and Minichannels
FEDSM-ICNMM2010
August 1-5, 2010, Montreal, Canada

FEDSM-ICNMM2010-30163

EFFECTS OF NON-LINEARITY OF THE MOMENTUM CONSERVATION EQUATION DURING ELECTROKINETIC TRANSPORT IN NANO AND MICROCHANNELS

Subir Bhattacharjee[*]
Department of Mechanical Engineering
University of Alberta
Edmonton, Alberta, T6G 2G8, Canada.
Email: Subir.B@ualberta.ca

Noor Al Quddus
Department of Mechanical Engineering
Bangladesh University of Engineering & Technology
Dhaka, 1000, Bangladesh.
Email: nquddus@me.buet.ac.bd

ABSTRACT

Electrokinetic transport phenomena, such as electroosmosis, streaming potential, electrophoresis, and sedimentation potential, are central to many micro- and nano-channel flows. During continuum modeling of such phenomena, incorporation of the electrical body force term can make the fluid momentum conservation equation highly non-linear. This non-linearity is often ignored in small-scale electrokinetic flow modeling because of our implicit reliance on the linearity of the Stokes equations for low Reynolds number flows. In this paper, ramifications of this non-linear Stokes equation in electrokinetic flows will be described with examples of our recent studies on pressure driven flows through porous media for electrokinetic power generation, electroosmotic flow of charged entities in nanochannels, and flow of DNA through self-assembled porous media under pulsed electric fields.

INTRODUCTION

The rigorous analysis of various electrokinetic transport phenomena requires a coupled solution of the governing equations for fluid flow (Navier-Stokes and continuity), electrostatics (Poisson), and ion transport (ion mass conservation equations with the ionic fluxes described through the Nernst-Planck equations). As the term electrokinetic suggests, the fluid motion in these types of processes are partially or entirely engendered by the interaction between electric charges and fields. Most surfaces acquire electric charges when immersed into a polar fluid containing ions. An external electric field applied parallel to the charged surface induces a relative motion between the surface and the fluid. Two types of relative motion between the charged surface and the electrolyte can be caused by this imposed field. If the surface is fixed in space with the fluid flowing parallel to the surface, we obtain *electroosmotic flow* (EOF). If the charged surface moves relative to the stationary electrolyte, we obtain *electrophoresis* (EP).

This paper will mainly focus on EOF and EP. Classical electrokinetic theory [1, 2] took practically identical approaches to analyze both phenomena. For a thin electrical double layer and low surface potential, the solutions for electroosmotic velocity past a plane charged surface and electrophoretic mobility of a charged particle in a stationary fluid are identical and are expressed by the same mathematical relationship known as the Helmholtz-Smoluchowski equation. At a more general level of analysis, complexity of the coupled equations in their native forms led to methods of solving these equations employing perturbation approach. The electrophoretic mobility, η, of a charged spherical particle of radius, a, in an unbounded electrolyte solution, subjected to an external electric field, $\mathbf{E}_\infty$, is generally expressed as [1],

$$\eta = \frac{U_p}{\mathbf{E}_\infty} = \frac{2\varepsilon\psi_p}{3\mu} f(\kappa a) \tag{1}$$

where U_p is the particle velocity, ψ_p is the particle surface po-

---

[*] Address all correspondence to this author.

Copyright © 2010 by ASME

tential, μ is the viscosity, ε is the dielectric permittivity of the medium, and κ is the inverse Debye length. The function $f(\kappa a)$, generally referred to as Henry's function, ranges between 1 for $\kappa a \to 0$ and 1.5 for $\kappa a \to \infty$. The limiting forms of Eq. (1) for $\kappa a \to 0$ and 1 for $\kappa a \to \infty$ are generally referred to as the Debye-Hückel [2] and Smoluchowski [3] results, respectively.

In deriving Eq. (1), Henry assumed the electric field near the particle to arise from a superposition of the applied field onto the field due to the equilibrium electric double layer around the particle. However, as the particle moves through the ionic solution due to electromigration and convection, the double layer surrounding the particle tends to distort. Overbeek [4] and Booth [5] used perturbation calculations to account for the effect of the distorted double layer by expressing the electrophoretic mobility as power series of particle surface potential or surface charge. Following the same trend, Wiersema *et al.* [6] used an iterative technique to obtain the mobility of the particle over a wider range of particle surface potentials and double layer thicknesses. O'Brien and White [7] provided a numerical solution for high particle surface potentials based on the perturbation approach. The solutions based on higher order perturbations [5–7] include the effects of hydrodynamic retardation and convective relaxation of the electric double layer, which were not accounted for in Henry's [1] original expression. Teubner [8] took a different approach by neglecting convective effect in the Nernst-Planck equations, and derived the same results as others.

All previous mobility calculations, particularly those based on perturbation analysis, made a critical assumption about the system. These studies assumed that the steady motion of a charged particle with velocity, U_p, in a quiescent fluid yields the same stress at the interface as caused by the fluid with a uniform far field velocity $-U_p$ flowing past a stationary particle. Such an assumption is common in creeping flow, owing to the linearity of the Stokes equation. Utilizing this assumption, the electrophoresis problem has usually been formulated on a particle fixed reference frame, whereby the governing equations were solved assuming the particle to be stationary. In this context, the objective of this paper is to investigate the validity of such an assumption when solving the general equations of electrophoresis. In other words, we investigate whether the solutions for electrophoretic mobility obtained assuming the particle fixed reference frame correctly represent the electrophoretic mobility of the particle.

To address the above question, this paper revisits the general formulation of the electrophoresis problem in a globally fixed (with particle moving) and a particle fixed reference frame. The governing equations are written by sequentially relaxing various assumptions that are commonly made regarding the coupling of the fluid flow with the ion transport equations. Numerical solution of the equations in the globally fixed reference frame was obtained employing an arbitrary Lagrangian-Eulerian (ALE) framework, whereas in the particle fixed reference frame, the problem was solved by a straightforward finite element algorithm. We observe that including the retardation and relaxation effects of the double layer in a globally fixed reference frame results in a deviation of the electrophoretic mobility compared to the values predicted on the basis of a particle fixed reference frame. This result has considerable impact on interpretation of experimental results of electrophoresis in micro-capillaries, or motion of charged particles in porous media.

THEORETICAL CONSIDERATIONS

Governing Equations for Electrophoresis

In electrokinetic problems, the Naiver-Stokes equation modified by an electrical body force term, $\rho_f \mathbf{E}$, and continuity equation provide pressure and fluid flow fields. [9, 10]

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p + \mu \nabla \cdot \left(\nabla \mathbf{u} + \nabla \mathbf{u}^{\mathbf{T}} \right) + \rho_f \mathbf{E} \tag{2}$$

$$\nabla \cdot \mathbf{u} = 0 \tag{3}$$

where ρ and μ are the fluid density and viscosity, respectively, p is the pressure, $\mathbf{u}$ is the fluid velocity, ρ_f is the space charge density, $\mathbf{E}\,(= -\nabla\psi)$ is the electric field, with ψ being the electrical potential. The potential distribution is obtained by solving Poisson equation,

$$-\varepsilon \nabla^2 \psi = \rho_f = e \sum z_i n_i \tag{4}$$

where ε is the dielectric permittivity of the medium, e is the elementary charge, n_i is the ionic concentration of the i^{th} species, and z_i is the valence of the i^{th} ionic species. The ion conservation equation gives ionic concentration n_i,

$$\frac{\partial n_i}{\partial t} = -\nabla \cdot J_i \tag{5}$$

The ionic fluxes, J_i, are given by the Nernst-Planck equations,

$$J_i = \mathbf{u} n_i - D_i \nabla n_i - \frac{z_i e}{kT} n_i \nabla \psi \tag{6}$$

where D_i is the diffusion coefficient of the i^{th} ionic species, k is the Boltzmann constant, and T is the temperature.

The above equations provide the basic description of the physics of electrophoresis or electroosmotic flow, and are independent of the coordinate frame chosen. The boundary conditions of these equations, however, are written differently depending on the coordinate reference frame used. In all subsequent

Copyright © 2010 by ASME

analysis, the particle is considered to be non-conducting, impermeable, and having a constant surface charge, q_p.

The boundary conditions defined in a stationary global reference frame are presented first. In this case, the particle is moving with an electrophoretic velocity U_p at steady state. Consequently, the boundary conditions on the particle surface are:

$$\begin{aligned} \mathbf{u} &= U_p \\ -\varepsilon \nabla \psi \cdot \mathbf{n} &= q_p \\ J_i \cdot \mathbf{n} &= 0 \end{aligned} \tag{7}$$

where **n** is the outward unit normal. Equilibrium potential distribution for an isolated stationary particle is obtained with a constant surface potential (ψ_p) boundary condition and the corresponding surface charge, q_p, is employed as a boundary condition in Eq. (7).

In the globally fixed reference frame, far from the particle, the fluid is stationary with no stress, the electric field equals the external (applied) field, $\mathbf{E}_\infty$, and the ionic concentrations approach their bulk values $n_{i\infty}$.

$$\begin{aligned} -p\mathbf{I} + \mu(\nabla \mathbf{u} + \nabla \mathbf{u}^T) &= 0 \\ -\nabla \psi \cdot \mathbf{n} &= \mathbf{E}_\infty \\ n_i &= n_{i\infty} \end{aligned} \tag{8}$$

Strictly speaking, the first condition in the above equation should be that the fluid is stationary far from the particle, or $\mathbf{u} = 0$. However, this is valid only at infinite distance from the particle. In numerical calculations where a finite computational domain needs to be considered, one generally employs a weaker boundary condition, which imposes zero hydrodynamic stress at a sufficiently large distance from the particle, as has been done here.

In a particle fixed reference frame, one formulates the boundary conditions on the particle surface as

$$\begin{aligned} \mathbf{u} &= 0 \\ -\varepsilon \nabla \psi \cdot \mathbf{n} &= q_p \\ J_i \cdot \mathbf{n} &= 0 \end{aligned} \tag{9}$$

whereas the far field conditions are

$$\begin{aligned} -p\mathbf{I} + \mu(\nabla \mathbf{u} + \nabla \mathbf{u}^T) &= 0 \\ -\nabla \psi \cdot \mathbf{n} &= \mathbf{E}_\infty \\ n_i &= n_{i\infty} \end{aligned} \tag{10}$$

Note that the only difference between the governing equations for electrophoresis formulated in a globally fixed or a particle fixed reference frame will be the fluid velocity condition imposed on the particle surface. The remaining boundary conditions are identical in both formulations.

Influence of Coordinate System on Convective Effects

The key influence of the coordinate reference frame on the governing equations for electrophoresis are manifested through the convective flux term, $\mathbf{u}n_i$, in the Nernst-Planck equations (Eq. 6). Considering the convection term for ionic species i, after incorporating Eq. 6 in Eq. 5, we find

$$\nabla \cdot (\mathbf{u}n_i) = n_i(\nabla \cdot \mathbf{u}) + \mathbf{u} \cdot (\nabla n_i) = \mathbf{u} \cdot (\nabla n_i) \tag{11}$$

where the final form arises due to the continuity, Eq. (3). When formulated in a particle fixed reference frame, since the particle surface is assumed stationary, this convective term will be zero at the particle surface even though $\nabla n_i \neq 0$. In contrast, when we consider a finite particle velocity in a globally stationary reference frame, the convection term is not necessarily zero at the particle surface.

The approximate forms of the governing equations, particularly those employed in perturbation analysis, can be generally classified as: (i) Poisson-Boltzmann Navier-Stokes (PB-NS), where the convection terms in the Nernst-Planck equations are completely neglected, and (ii) the Poisson-Nernst-Planck Navier-Stokes (PNP-NS), where the convective effects are considered. In the PB-NS formulation, the electric body force term, $\rho_f \mathbf{E}$, in the NS equations does not depend on the fluid velocity, and therefore, the NS equation still remains linear. Furthermore, if one linearizes the Poisson-Boltzmann equation assuming low potentials, even the electrostatics can be treated as a linear equation. This was done in Henry's solution, and hence, at this linearized PB-NS level, there was no consequence of altering the coordinate framework from a globally fixed to a particle fixed reference. In the PNP-NS framework, however, the ion concentration distributions are obtained by considering convection, and consequently, all the governing equations become non-linear. In this case, one cannot expect that the solution of the coupled PNP-NS equations will be independent of the coordinate frame chosen.

Let us consider a linear differential operator $\mathscr{L}$ applied to a velocity field **u**,

$$\mathscr{L}(\mathbf{u}) = \mathscr{G}(w) \tag{12}$$

where $\mathscr{G}(w)$ is a function. If we substitute $\mathbf{u} = \mathbf{v} + v'$, where **v** is another velocity field and v' is a constant,

$$\begin{aligned} \mathscr{L}\left(\mathbf{v} + v'\right) &= \mathscr{G}(w) \\ \Rightarrow \mathscr{L}(\mathbf{v}) + \mathscr{L}\left(v'\right) &= \mathscr{G}(w) \\ \Rightarrow \mathscr{L}(\mathbf{v}) &= \mathscr{G}(w) \end{aligned} \tag{13}$$

Copyright © 2010 by ASME

If the source term $\mathscr{G}(w)$ is constant or independent of $\mathbf{u}$, then we can say that $\mathscr{L}(\mathbf{u}) = \mathscr{L}(\mathbf{v})$. This is condition of linear superposition. Use of a Poisson-Boltzmann type expression for potential distribution that does not depend on convection or velocity $\mathbf{u}$ with Stokes equation is an example of such case. However, if $\mathscr{G}(w)$ depends on $\mathbf{u}$, then $\mathscr{L}(\mathbf{u}) \neq \mathscr{L}(\mathbf{v})$. Which implies that use of Poisson equation with ionic transport equation restricts the Stokes type velocity boundary transfer from the particle surface to the far field.

We now describe how this discrepancy can influence the electrophoretic mobility predictions under different levels of approximation. It is straightforward to deduce from the foregoing discussion that if one does not consider convective relaxation of the double layer, and solves the electrophoresis problem at the Poisson-Boltzmann level, there will be no discrepancy between the mobility obtained from solving the equations under either particle fixed or globally fixed reference frames. This is owing to the neglect of the convective term altogether in the Poisson-Nernst-Planck equations. However, for any solution of the governing equations that explicitly consider convection, one can expect a discrepancy arising from the choice of the coordinate framework.

Mobility Calculation

Forces acting on the particle are calculated by integrating the stress tensors over the particle surface. The forces that contribute to the motion of the particle include the hydrodynamic force, F_h, and the electrical force, F_e. Integration of the total hydrodynamic stress tensor over the particle surface gives the total hydrodynamic force, F_h, as

$$F_h = \int_S \left[-p\,\overline{\overline{\mathbf{I}}} + \mu\left(\nabla\mathbf{u} + \nabla\mathbf{u}^{\mathbf{T}}\right)\right] \cdot \mathbf{n}\, dS \tag{14}$$

where $\overline{\overline{\mathbf{I}}}$ is the identity tensor and S indicates the surface of the particle. Electrostatic contribution, F_e, composed of electrostatic attraction and relaxation effect is given by,

$$F_e = \int_S \varepsilon \left[\mathbf{EE} - \frac{1}{2}\mathbf{E}\cdot\mathbf{E}\,\overline{\overline{\mathbf{I}}}\right] \cdot \mathbf{n}\, dS \tag{15}$$

Upon the application of the external electric field, the particle accelerates and attains a steady velocity almost instantaneously. In an unsteady force field, the motion of the accelerating particle is calculated by,

$$m_p \frac{\partial U_p}{\partial t} = F_h + F_e \tag{16}$$

where m_p is the particle mass. In steady motion, as the particle attains a steady velocity, the mobility is determined by equating the hydrodynamic and electrical forces.

Particle Motion in ALE Kinematics

The key reason for incorporating a particle fixed reference frame in solving the governing equations for electrophoresis is the manner in which such a formulation enables facile computation of the forces, and consequently, the mobility. Calculation of mobility in a globally fixed reference frame inevitably requires solution of a transient problem, which necessitates a Lagrangian approach lo track the particle. In this paper, we implement the Arbitrary Lagrangian Eulerian (ALE) method [11, 12] to solve electrophoretic mobility of a charged particle in the globally fixed reference frame. In ALE kinematic approach, the motion of the particle is calculated with respect to its initial configuration as in Lagrangian fashion and the deformation or motion is transformed to the Eulerian spatial frame to solve the continuum equations. In ALE kinematics, the two frames of reference are connected by the mapping,

$$r(R,Z,t),\ z(R,Z,t)\ (R,Z) \in \Omega_f,\ (r,z) \in \Omega_m,\ t \in R^+ \tag{17}$$

where the upper case letters correspond to the Lagrangian reference frame, Ω_f, the lower case letters represent the moving mesh Eulerian frame, Ω_m, and t represents time. All governing equations are non-dimensionalized. kT/ze is considered as the scaling parameter for potential and the particle radius, a, is chosen as the length scale. Other scaling parameters are derived from these two, and given in Table 1. In ALE kinematics, the non-dimensionalized governing equations take the form,

$$\begin{aligned} &Re^* \frac{\partial \mathbf{u}^*}{\partial \tau} + Re^* \left(\mathbf{u}^* - \phi_{\mathbf{m}}\right) \cdot \nabla^* \mathbf{u}^* = \\ &-\nabla^* p^* + \nabla^* \cdot \left(\nabla^* \mathbf{u}^* + \nabla^* \mathbf{u}^{*\mathbf{T}}\right) - 0.5\,(\kappa a)^2 \left(n_p^* - n_n^*\right) \nabla^* \Psi \end{aligned} \tag{18}$$

$$\nabla^* \cdot \mathbf{u}^* = 0 \tag{19}$$

$$-\nabla^{*2}\Psi = 0.5\ (\kappa a)^2 \left(n_p^* - n_n^*\right) \tag{20}$$

$$\frac{\partial n_i^*}{\partial \tau} = -\nabla^* \cdot \left[\left(\mathbf{u}^* - \phi_{\mathbf{m}}\right) n_i^* - \frac{1}{Pe^*}\nabla^* n_i^* - \frac{1}{Pe^*} z_i n_i^* \nabla^* \Psi\right] \tag{21}$$

Copyright © 2010 by ASME

TABLE 1. NON-DIMENSIONAL PARAMETERS USED IN FORMULATION OF THE SCALED POISSON-NERNST-PLANCK NAVIER-STOKES ARBITRARY LAGRANGIAN EULERIAN (PNP-NS-ALE) MODEL

	Variable	Scaling
Potential	Ψ	$\frac{ze}{kT}\psi$
Electric Field	β	$\frac{aze}{kT}E$
Surface Charge	q^*	$\frac{aze}{\varepsilon kT}q$
Concentration	n_i^*	$\frac{n_i}{n_{i\infty}}$
Stress	σ^*	$\frac{1}{\varepsilon}\left(\frac{aze}{kT}\right)^2\sigma$
Velocity	u^*	$\frac{\mu a}{\varepsilon}\left(\frac{ze}{kT}\right)^2u$
Mobility	η^*	$\frac{\mu}{\varepsilon\psi}\eta$
Time	τ	$\frac{\varepsilon}{\mu a^2}\left(\frac{kT}{ze}\right)^2t$
Force	F_b^*	$\frac{1}{\varepsilon}\left(\frac{ze}{kT}\right)^2F_b$
Reynolds Number	Re^*	$\frac{\varepsilon\rho}{\mu^2}\left(\frac{kT}{ze}\right)^2$
Peclet Number	Pe^*	$\frac{\varepsilon}{\mu D}\left(\frac{kT}{ze}\right)^2$
∇ operator	∇^*	$a\nabla$

where $\phi_{\mathbf{m}}$ is the mesh velocity. Mesh adjacent to the particle surface moves with the particle velocity. Outer boundaries of the domain are kept stationary. The mesh velocities of the computational domain are gradually smoothed out from the particle surface to the outer boundaries. Mesh velocity, $\phi_{\mathbf{m}}$, are obtained by solving two elliptic equations for mesh velocities.

$$\nabla^2\phi_{mr} = 0 \tag{22}$$

$$\nabla^2\phi_{mz} = 0 \tag{23}$$

$$dr = r - R = \int_0^t \phi_{mr}dt \tag{24}$$

$$dz = z - Z = \int_0^t \phi_{mz}dt \tag{25}$$

where dr and dz are the mesh displacements, and ϕ_{mr} and ϕ_{mz} are mesh velocities in r and z directions, respectively.

Numerical Solution Methodology

A finite element model containing the set of equations described in the previous sections has been developed. An axisymmetric model is considered for the current analysis. A detail of the analysis technique is described in our previous work [12]. Due to the nonlinearity of the ionic concentration distribution near the particle, specially for higher κa, a very fine mesh was used. Mesh sensitivity analysis was performed to obtain an optimum number of elements for the desired accuracy.

The model was developed and solved by using COMSOL3.3 and COMSOL Script 1.1 environment. Quad core AMD Opteron processor $4 \times 2.80GHz$ speed with $32GB$ RAM machines were used to obtain the solution having number of element between 25,000 to 40,000.

RESULTS AND DISCUSSION

In this section, we present solutions of the electrophoretic mobility of a particle obtained in a particle fixed and a globally fixed reference frame at different levels of approximation of the governing equations. All numerical solutions are compared against Henry's solution.

PB-NS Model

The solution of the Poisson-Boltzmann equation coupled with the Navier-Stokes and continuity equations was obtained in both the particle fixed and globally fixed reference frames. Figure 1 shows the electrophoretic mobility predicted using these two models. In all calculations, the scaled particle surface potential was $\Psi_p = -1.0$, which is considered to be sufficiently low to render the assumption of linearity in Henry's solution valid. Our numerical solutions in both the references frames are identical (open and solid circles), and both predictions virtually superimpose with Henry's predictions (solid line). This comparison also establishes the accuracy of the ALE formulation in the globally fixed reference frame. Furthermore, it is established that at the PB-NS level, the electrophoretic mobility prediction is independent of the coordinate reference frame chosen.

Copyright © 2010 by ASME

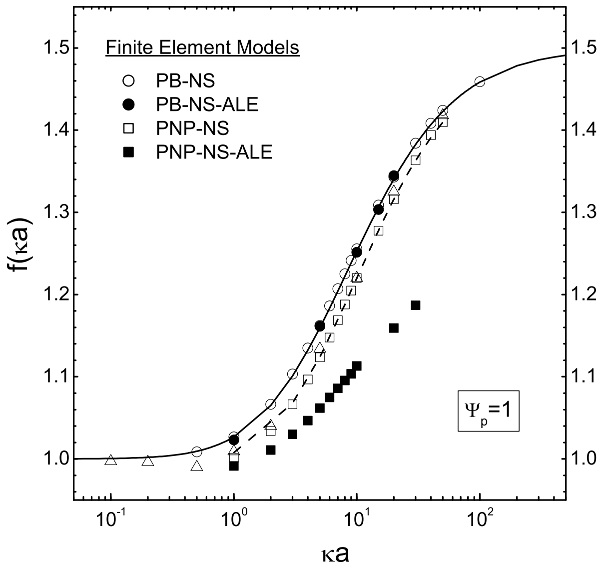

FIGURE 1. COMPARISON OF ELECTROPHORETIC MOBILITY OF A CHARGED SPHERICAL PARTICLE SUBJECTED TO AN EXTERNAL FIELD. ELECTROPHORETIC MOBILITY IS CALCULATED FOR A POSITIVELY CHARGED PARTICLE, $\psi_p = 1$. PB-NS MODEL CONSIDERS EQUILIBRIUM POTENTIAL DISTRIBUTION AROUND THE PARTICLE SHOWS VERY GOOD AGREEMENT WITH HENRY'S SOLUTION. THE RESULTS OBTAINED FROM PNP-NS MODEL IS CONSISTENT WITH THE NUMERICAL RESULTS OF WIERSEMA [6]. BOTH THE MODELS ARE SOLVED USING PARTICLE-FIXED CONFIGURATION, AS DOES THE COMPARED ONES. OUR PNP-NS-ALE MODEL SHOWS THAT THE ELECTROPHORETIC MOBILITY IS OVER-PREDICTED IN A PARTICLE FIXED REFERENCE FRAME.

PNP-NS Model

In this case, we obtain the solution of the Poisson, Nernst-Planck, and Navier-Stokes equations in the particle fixed and globally fixed reference frames. The coupled solution of these equations, along with the inclusion of the convective effects in the Nernst-Planck equations, results in consideration of the convective relaxation effects. The numerical predictions are compared with two well-known perturbation solutions of electrophoretic mobility, namely, the results of Wiersema *et al.* (triangle) and O'Brien and White (inverted triangle). It is evident from Figure 1 that in a particle fixed reference frame, the electrophoretic mobility predicted by our numerical method (open squares) is identical to the predictions of the above mentioned perturbation approaches. However, our ALE kinematics based predictions of the electrophoretic mobility in the globally fixed reference frame (solid squares) are considerably lower. In the range $1 < \kappa a < 50$, where we obtained our numerical results, we observe a systematically lower mobility in the globally fixed reference frame. The deviation between the PNP-NS level predictions of the mobility in the two reference frames appear to increase with κa.

Comparison with Existing Solutions

Electrophoretic mobility calculated from the four models are compared with the existing analytical and numerical results for a positively charged particle ($\Psi_p = 1$), as shown in Figure. 1. Results shown in solid line is Henry's solution [1] where the scaled mobility is varying from 1.0 to 1.5 as κa goes from 0 to ∞. Both the PB-NS and PB-NS-ALE models that have similar assumptions like Henry's solution fall on top of the solid line. Numerical solution obtained by Wiersema *et al* [6] and O'Brien [7] using perturbation technique are also plotted. Their results show that Henry's solution overestimated the scaled mobility as it does not account for ionic relaxation effect. Our PNP-NS model that is also solved in particle fixed configuration is in good agreement with their results. However, the calculated scaled mobility by the current PNP-NS-ALE model is lower than other models, specially in the higher κa range.

CONCLUDING REMARKS

It was demonstrated that prediction of the electrophoretic mobility at the complete Poisson-Nernst-Planck Navier-Stokes level differ when the governing equations are solved in a globally fixed and a particle fixed reference frame. This difference arises from the fact that the non-linear governing equations in the particle fixed and globally fixed reference frames do not provide an identical description of the physics of electrophoresis. The convective relaxation of the double layer and the hydrodynamic retardation effects appear to be more dominant in the globally fixed reference frame. In light of these observations, one might wonder what would be the implications of these results in the Debye-Hückel ($\kappa a \to 0$) and Smoluchowski limits ($\kappa a \to \infty$). Clearly, the influence of the coordinate system choice will not be relevant at the Debye-Huckel limit, where ionic transport is not considered, and the governing electrostatic equation is the linear Laplace equation. In the Smoluchowski limit, the double layer is infinitesimally thin, and hence, $\nabla n_i \to \infty$. Consequently, the finite velocity at the particle surface will be immaterial in defining ionic convection. Thus, the Smoluchowski limit is also unaffected by the choice of the reference frame.

However, for all intermediate values of κa, the discrepancy in the mobility prediction will be encountered depending on the choice of the coordinate reference frame. The problem is definitely worth further exploration in context of electrophoresis of charged particles in charged confining media (such as capillaries and porous media). In such systems, imposing an external electric field to engender electrophoresis of the charged particles concurrently sets up an electroosmotic flow of the electrolyte. Analysis of these types of problems should be attempted with caution.

Acknowledgment

Financial Support from Natural Sciences and Engineering Research Council (NSERC) of Canada is gratefully acknowledged.

REFERENCES

[1] Henry, D. C., 1931. "The cataphoresis of suspended particles part i - the equation of cataphoresis". *Proc. Roy. Soc. Lond. A,* ***133***(821), pp. 106–129.

[2] Hückel, E., 1924. "Die kataphorese der kugel". *Phys. Z.,* ***25***, pp. 204–210.

[3] v. Smoluchowski, M., 1903. "Contribution à la théorie de l'endosmose électrique et de queeques phenomènes corréslatifs". *Bull. Int. Acad. Sci. Cracovie,* ***8***, pp. 182–200.

[4] Overbeek, J. T., 1943. "Theorie der elektrophorese". *Kolloid-Beih,* ***54***, pp. 287–364.

[5] Booth, F., 1950. "The cataphoresis of spherical, solid non-conducting particles in a symmetrical electrolyte". *Proc. Roy. Soc. Lond. A,* ***203***(1075), pp. 514–533.

[6] Wiersema, P. H., Loeb, A. L., and Overbeek, J. T., 1966. "Calculation of electrophoretic mobility of a spherical colloid particle". *J. Colloid Interface Sci.,* ***22***(1), pp. 78–.

[7] Obrien, R. W., and White, L. R., 1978. "Electrophoretic mobility of a spherical colloidal particle". *J. Chem. Soc. Faraday Trans. II,* ***74***, pp. 1607–1626.

[8] Teubner, M., 1982. "The motion of charged colloidal particles in electric-fields". *J. Chem. Phys.,* ***76***(11), pp. 5564–5573.

[9] Russel, W. B., Saville, D. A., and Schowalter, W. R., 1989. *Colloidal Dispersions*. Cambridge University Press, Cambridge.

[10] Masliyah, J. H., and Bhattacharjee, S., 2006. *Electrokinetic and Colloid Transport Phenomena*. John Wiley & Sons, New York.

[11] Donea, J., Huerta, A., Ponthot, J.-P., and Rodriguez-Ferran, A., 2004. "Chapter 14: Arbitrary lagrangian-eulerian methods". In *Encyclopedia of Computational Mechanics*, E. Stien, R. de Borst, and J. R. Hughes, eds., Vol. 1:Fundamentals. John Wiley and Sons, New York.

[12] Quddus, N. A., Moussa, W. A., and Bhattacharjee, S., 2008. "Motion of a spherical particle in a cylindrical channel using arbitrary lagrangian-eulerian method". *J. Colloid Interface Sci.,* ***317***(2), pp. 620–630.

Copyright © 2010 by ASME