

Diffusiophoretic Mobility Reversal of Charged Colloidal Particles: Roles of Electrostatic Correlations and Ion Steric Interactions

Bapan Mondal* and Somnath Bhattacharyya

Department of Mathematics, Indian Institute of Technology Kharagpur, West Bengal-721302, India

*Email: bapanmondal2602@gmail.com

1. INTRODUCTION & OBJECTIVE

Diffusiophoresis of nanoparticles in ionic concentration gradients has attracted significant interest due to its applications in targeted drug delivery, manipulation of living cells, and the determination of electrostatic properties of colloids [1, 2]. The diffusiophoresis of a colloid is governed by two mechanisms: electrophoresis and chemiphoresis [3]. Experiments show mobility reversals at higher salt concentrations, caused by overscreening, where ion-ion electrostatic correlations create alternating layers of counterions and coions that overcompensate the surface charge, as predicted by several authors beyond mean-field Debye screening [4, 5].

This study examines the diffusiophoresis mobility reversal of a charged colloidal particle using a continuum model that includes ion-ion correlations and finite-size steric interactions. The medium's viscosity depends on the ionic volume fraction. A first-order perturbation model is developed which reveals that ion steric interactions weaken surface charge screening, enhancing both electrophoresis and chemiphoresis. The diffusion potential in the far-field also increases due to ion size effects. Electrostatic correlations cause surface charge overscreening and expand the electric double layer in multivalent electrolytes.

2. MATHEMATICAL DESCRIPTION

We consider the diffusiophoresis of a spherical charged colloid of radius a possessing a uniform surface charge density σ which is subjected to an applied electrolyte concentration gradient $\nabla^* C_0$.

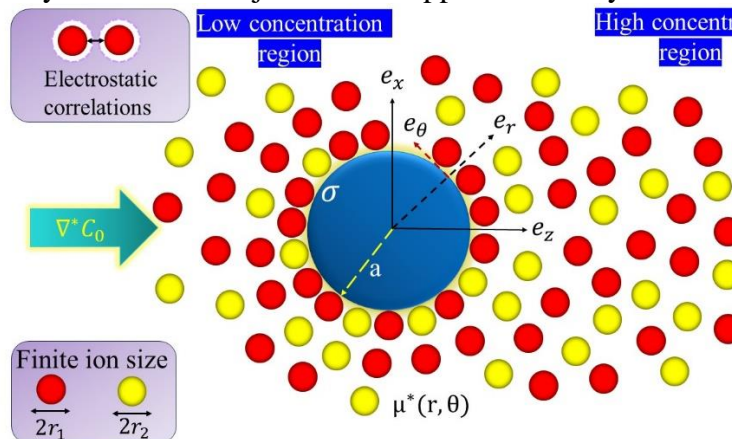


Figure 1. Geometric sketch for the diffusiophoresis of a charged colloidal particle

The motion of the incompressible Newtonian electrolyte is governed by

$$Re[\mathbf{u} \cdot \nabla \mathbf{u}] + \nabla p - \mu \nabla^2 \mathbf{u} - \nabla \mu \cdot [\nabla \mathbf{u} + (\nabla \mathbf{u})^T] + \frac{(\kappa a)^2}{2} \rho_e = 0, \quad \nabla \cdot \mathbf{u} = 0 \quad (1)$$

Here $Re = \rho U_0 a / \eta^\infty$, $\kappa = \sqrt{2eI_\infty / \epsilon_e \phi_0}$, and $\rho_e = \sum_i z_i n_i$ are respectively the Reynolds number, inverse electrical double layer (EDL) thickness and space charge density. The transport of i^{th} ionic species is governed by [6]

$$Pe_i[\mathbf{u} \cdot \nabla n_i] = D_i(n_i \nabla^2 \mu_i + \nabla n_i \cdot \nabla \mu_i) + n_i \nabla D_i \cdot \nabla \mu_i, \quad \mu_i = z_i \phi + \ln n_i + \mu_i^{ex} \quad (2)$$

Here $Pe_i = aU_0/D_i^\infty$, D_i , and μ_i are respectively the Péclet number, diffusivity, and electrochemical potential of i^{th} ionic species. The excess electrochemical potential μ_i^{ex} is modeled through Carnahan-Starling equation [6]. Note that the viscosity of the suspension and as a result the diffusivity of the ions are modeled through Batchelor-Green equation [4]. The induced electric potential (ϕ) is governed by [4, 5]

$$\delta_c^2 \nabla^4 \phi - (\kappa a)^2 \nabla^2 \phi = \frac{(\kappa a)^4}{2} \rho_e, \quad \delta_c = 0.35(Z^2 \kappa l_B)^{\frac{2}{3}} \left(\frac{ea}{2\pi Z^3 \epsilon_e \phi_0 l_B^2 |\sigma|} \right)^{\frac{1}{8}} \quad (3)$$

Here $\delta_c = \kappa l_c$ is the non-dimensional correlation length scaled by the EDL thickness. The Bjerrum $l_B = e/4\pi\epsilon_e\phi_0$ and Z is the magnitude of the counterion valency. The boundary conditions at the particle surface are [6]

$$\mathbf{e}_r \cdot \delta_c \nabla(\nabla^2 \phi) = 0, \quad \mathbf{e}_r \cdot \nabla \phi = -\sigma, \quad \mathbf{u} = \mathbf{0}, \quad \mathbf{e}_r \cdot \mathbf{N}_i = 0 \quad (4)$$

Here $\mathbf{N}_i = n_i \mathbf{v}_i = n_i(\mathbf{u} - D_i \nabla \mu_i)$ is the flux of i^{th} ionic species. Far from the particle the boundary conditions are specified as [6]

$$\mathbf{u} = -U_D \mathbf{e}_z, \quad \nabla \phi = -\beta \alpha \mathbf{e}_z, \quad \nabla^2 \phi = 0, \quad n_i = \frac{n_i^\infty}{I_\infty} (1 + \alpha \cos \theta) \quad (5)$$

Here U_D is the scaled diffusiophoretic velocity and $\alpha = a|\nabla^* C_0|/C_0$ is the scaled applied concentration gradient. $\beta = \beta^{id} + \beta^{ex}$ is the diffusion field [6] such that $\beta^{id} = (\sum_i z_i D_i n_i^\infty) / (\sum_i z_i^2 D_i n_i^\infty)$ and $\beta^{ex} = (\sum_i z_i D_i H_i^\infty) / (z_i^2 D_i n_i^\infty)$ where $H_i^\infty = \sum_j n_j \frac{\partial \mu_i^{ex}}{\partial n_j} |_{n_j=n_j^\infty}$.

A simplified model is formulated using a linear perturbation technique, where the perturbation parameter is α [3]. The approach is based on the assumption of a low Reynolds number, allowing the neglect of the inertia term in the Navier-Stokes equation (1). This leads to a transformation of the governing equations into a set of boundary value problems, which are subsequently solved using the finite difference method.

3. RESULTS & HIGHLIGHTS OF IMPORTANT POINTS

Our results show that ion steric interactions reduce surface charge screening and enhance the diffusion field, leading to increased chemiphoresis and electrophoresis. Electrostatic correlations reduce mobility when electrophoresis and chemiphoresis are cooperative, and enhance it when opposing, with our mean-field continuum model predicting the experimentally observed mobility reversal. We find that the reversal in particle mobility becomes prominent for a higher range of surface charge density for which the ionic correlations manifest.

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