Abstract

This thesis presents a numerical study supplemented with theoretical analysis of electrokinetic transport beyond the classical mean-field theory. The interfacial transport is illustrated in the context of electrophoresis of dielectric rigid and polarizable particles, diffusiophoresis of rigid particles in non-Newtonian media and the electric power generation in conical nanopores by temperature or salinity gradients. A modified Poisson-Nernst-Planck (PNP) model is introduced, which includes finite ion size effect through ionic volume exclusion and variation of viscosity of suspension medium. The nonlocal electrostatic correlation leads to a fourth-order modified Poisson equation and accounts the viscosity variation due to ionic volume exclusion. The full set of nonlinear governing equations is solved through a pressure-correction based finite-volume method without imposing any restriction on the Debye length, surface charge density and strength of the applied electric field. One of the notable features of the present study is the development of semi-analytical solutions for simplified models derived under linearized or weak-field approximation, which may serve as a benchmark for experimental studies. This thesis also aims to develop comprehensive mathematical models and electrokinetic strategies for power generation driven by salinity and temperature gradients, highlighting their potential for electric energy conversion applications.

Chapter 1 provides an introductory overview. In **Chapter 2**, we consider a modified electrokinetic model to analyze nonlinear electrophoresis by taking into account the finite ion size effects and ion–ion electrostatic correlations. In this approach, the mean-field-based model is extended to capture the many-body phenomena by considering the non-local electrostatic contribution in the ion free energy functional and the ion–ion hydrodynamic steric interactions are incorporated through the volume exclusion effect in the electrochemical potential. The viscosity of the medium is considered to vary with the local ionic volume fraction. Stronger correlations for multivalent counterions create ion layering, charge density oscillation and mobility reversal. Such phenomena are captured by the present continuum model. The ion crowding attenuates the growth of the electrophoretic mobility with the electric field. At a higher range of the imposed electric field, the ion concentration in the electric double layer enhances, which modifies both the overscreening and ion crowding processes. In **Chapter 3**, the modified electrokinetic model adopted in Chapter 2 is employed to investigate the nonlinear electrophoresis of a polarizable charged particle in monovalent and multivalent electrolytes. At a moderate applied field, in which the voltage drop across the Debye layer becomes higher than the thermal potential, the impact of the dielectric particle polarization becomes significant, resulting in an induced surface charge, which has opposite polarity on the two sides of the particle. The steric effect due to the finite size of ions and correlation among ions modifies the ion distribution in the electric double layer and consequently modifies the polarization of the particle. By considering the modified electrokinetic model for a dielectric particle, we provide an intricate analysis and justification of several experimentally observed phenomena. The valence asymmetric electrolyte generates a nonuniform induced surface charge density, which modifies the electric force on the particle. We have validated our numerical algorithm with existing experimental results of polarizable particles and thin-layer analysis of conducting particles. At a higher imposed electric field, the overscreening of the surface charge due to the correlations among multivalent counterions attenuates, leading to the suppression of mobility reversal.

Thermoelectric transport driven by an imposed temperature gradient in an ionized liquid through a charged hydrophobic conical nanopore is studied in **Chapter 4** in the context of waste-heat-to-electricity conversion. A modified electrokinetic model is employed that accounts for hydrodynamic steric interactions of finite-sized ions and viscosity variations with local ionic volume fraction, extending its validity to higher surface charge densities where the ionic volume fraction can reach approximately 0.1. Based on the modified model, the effects of surface charge density and membrane slip length on the thermoelectric field are analyzed, accounting for temperature-dependent viscosity, dielectric permittivity and ionic diffusivity over a wide range of bulk ionic concentrations. The impact of an additional imposed pressure gradient for enhancing thermoelectric transport is also analyzed in this chapter. Analogous to the thermoelectric study presented in Chapter 4, **Chapter 5** focuses on salinity-gradient-based energy harvesting (blue energy) in bipolar nanopores, relevant to microfluidic and healthcare applications. Numerical analysis shows that a mixture of mono- and multivalent electrolytes in a bipolar pore can enhance the output voltage and energy conversion efficiency, despite the known attenuation caused by divalent counterions. To capture short-range ion–ion correlations of multivalent, finite-sized ions, a modified continuum electrokinetic framework is adopted. The model is numerically solved and validated against existing studies, reproducing experimentally observed phenomena such as surface-charge overscreening and ionic layering. Enhanced output voltage and conversion efficiency are obtained in bipolar pores, further amplified with valence-asymmetric salts, yielding a maximum osmotic power of up to 116 pW under an 800-fold concentration ratio. The influence of ion selectivity in geometrically asymmetric pore is studied. We have illustrated the dependency of the output voltage and maximum power on the electrokinetic parameters in a bipolar conical pore.

Chapter 6 examines the diffusiophoresis of a uniformly charged rigid colloid in non-Newtonian viscoplastic fluids described by Casson, Herschel–Bulkley, and Bingham models. The nonlinear governing equations are solved numerically using a pressure-correction-based finite-volume method, and a semi-analytical mobility expression is derived in the thin electric double layer and zero-yield-stress limit. The results show that shear-thinning behavior enhances diffusiophoretic velocity, while yield stress suppresses particle motion. A reversal of diffusiophoresis with increasing surface charge is observed in shear-thinning fluids, but this effect is suppressed under diffusion-dominated conditions, higher yield stress, multivalent electrolytes, or shear-thickening behavior. Overall, mobility decreases monotonically with increasing flow consistency index.

Chapter 7 summarizes the main findings of this thesis and outlines future research directions.

Keywords: Electrophoresis; Dielectric polarization; Diffusiophoresis; Non-Newtonian fluid; Thermoosmosis; Thermophoresis; Ion steric interaction; Electrostatic correlation; Mobility reversal; Power generation; Thin layer analysis.