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An Ohmic model for electrokinetic flows of binary asymmetric electrolytes

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ABSTRACT

The transport of electrolytes in electric fields is a ubiquitous phenomenon commonly harnessed in microfluidics. A classic leaky dielectric model for flow generated by electric fields accurately predicts electrohydrodynamic transport phenomenon but is valid for millimeter-scale and larger flows and at relatively low ionic strength. Here, we derive and use a modified version of this model to sub-millimeter scales more relevant to microfluidics, where diffusive transport of charged species becomes non-negligible. We formulate a general equation set, the modified Ohmic model, applicable to the transport of binary, asymmetric electrolytes. We leverage this model to describe a variety of microfluidic electrokinetic systems, including DC electroosmosis, alternating current electrokinetics (ACEK) and induced-charge electroosmosis (ICEO), thus highlighting some unifying principles of these flows.

1. Introduction

To our knowledge, British physicist William Gilbert first demonstrated the effects of electric forces on fluids *circa* 1600. In *De Magnete*, he described the deformation of a water droplet into a conical shape pointing toward a proximate piece of charged amber [1]. More than 200 years later, Reuss used a galvanic cell to drive fluid through a packed soil column, thereby generating electroosmotic flow (EOF) [2]. On one hand, a fair characterization of Gilbert's experiment is an exploration of what is now generally referred to as electrohydrodynamics (EHD), which corresponds to the general interaction between fluids and electric fields. EHD is sometimes associated with “macro” length scales (order 1 cm or greater) and submicromolar ion densities. On the other hand, Reuss highlighted a subset of EHD we can refer to as electrokinetics (EK). EK is typically characterized by the importance of electric double layers (EDLs). EDLs form at interfaces and can strongly affect the response of a liquid to an externally applied potential. Here, we concentrate on this subset of EHD, as EK describes most of EHD flows at the microscale.

Helmoltz and Von Smoluchowski together contributed to EK by including respectively early treatments of the EDL over charged surfaces and quantification of electroosmosis in applied electric fields [3,4]. Perrin later elegantly modeled the EDL as a distributed-charge capacitor [5]. The locations of the capacitor plates relative to the surface, the inner and outer planes, were later named after Helmoltz [6]. Continuing Perrin's work, Gouy and Chapman independently derived the ionic distribution of diffuse charges in the EDL using the Boltzman distribution for charges in solution [7,8]. In his derivation, Gouy noted the importance of a characteristic length of charge screening, λ_D, which now bears the name of Debye length.

Perhaps the most important contribution in the field of modern EHD came from J.R. Melcher. Inspired by G.I. Taylor's leaky dielectric model for droplet deformation in an electric field explaining Gilbert type droplet phenomena [9•], Melcher derived the so-called Ohmic model linking the interaction of ionic species and fluid flow with electric fields [10]. Ohmic model equations describe the interaction of electric fields with free charge density, bound charge density (dipoles), conductivity fields, and momentum transport. Taylor and Melcher together synthesized this work by stressing the importance of net charge regions within the fluid [11•]. This bulk charge occurs at electric heterogeneities in the medium (*e.g.*, gradients in conductivity or permittivity) in the form of monopole and dipole density gradients and can generate pressure and shear stresses (and inject vorticity) that drive flow and can destabilize its motion.

In his Ohmic model, Melcher assumed that the diffusive transport of charges remains negligible. This assumption is reasonable for

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centimeter-scale flows with relatively low conductivity but fails for EK microdevices where diffusion plays an important role in developing the conductivity field. Further, Melcher recognized that the imbalance between positive and negative charges that generates Coulomb forces is very small compared to the total number of charges. The latter is referred to as the electroneutrality assumption, and Melcher cautioned that it does not hold for length scales below 2.5 μm [10]. As we shall see, this lower limit is roughly 1 μm for EK microflows (lengths approaching the Debye length for achievable ion densities).

Here, we formulate a general equation set we term a "generalized Ohmic model," which is relevant to a wide range of microfluidic EK systems. We will leverage the model to discuss physics of the electric double layer and dynamics of charge transport in microflow devices. We demonstrate applications of this generalized Ohmic model to DC electroosmotic flows (EOF), alternating current electrokinetics (ACEK), induced-charge electroosmosis (ICEO), electrothermal flows (ETF), and electrokinetic instabilities (EKI). Our goal here is to summarize and help unify a physical understanding and formulate approximate equations used to study these phenomena. We strive to show that various disparate formulations are each special cases of the same equation set, and part of a more general EHD theory for coupling between electric fields and fluid flow.

2. Ohmic model for binary electrolytes

We here describe governing equations useful for modeling the flow of binary asymmetric electrolytes. We first write the conservation of momentum and describe forces acting on fluids in electric fields. We then write Gauss' law for free charge density and discuss various regimes for the electroneutrality approximation. Finally, we derive a general Ohmic model for EK flows that includes effects of currents generated by diffusion and electrolyte asymmetry. Our goal is to provide a roadmap for the modeling of general EK flows and to provide insight into the transport mechanisms involved in EK phenomena.

2.1. Momentum

We focus in the limit of low Reynolds number *Re* typically applicable to microfluidic devices [12]. We neglect the advection term in the incompressible Navier–Stokes equation for a fluid of density ρ, kinematic viscosity μ, and dielectric constant ε:

$$\nabla \cdot \mathbf{v} = 0 \tag{1}$$

$$\rho \frac{\partial \mathbf{v}}{\partial t} = -\nabla p + \mu \nabla^2 \mathbf{v} + \rho_e \mathbf{E} - \frac{1}{2}|\mathbf{E}|^2 \nabla \varepsilon \tag{2}$$

where $\mathbf{v}$ is the fluid velocity, p the pressure, $\mathbf{E}$ the local electric field, and $\rho_e \equiv F(z_+c_+ + z_-c_-)$ is the free charge density where F is Faraday's constant, c is the species molar concentration, and z its valence. The subscripts + and − denote the cation and anion of an asymmetric binary electrolyte. We retain the unsteady flow velocity term as inertial forces due to locally accelerating liquids may be important (*e.g.*, in devices with high-frequency forcing phenomena such time-varying electric fields). We omitted the magnetic induction term $\mathbf{j} \times \mathbf{B}$ where $\mathbf{j}$ is the current density and $\mathbf{B}$ the magnetic field, which is typically negligible for flows of aqueous non-magnetic solutions and in the absence of large magnetic fields. We also neglect the electrostriction term $\nabla(\frac{1}{2}|\mathbf{E}|^2 \rho \frac{\partial \varepsilon}{\partial \rho}|_T)$ which is small for incompressible flows [11•]. The electric force density then reduces to the last two terms of Eq. (2): respectively the force on the free charge density (or Coulomb force) and the force on electric dipoles within the fluid.

2.2. Scaling of Gauss' law and concept of electroneutrality

We present a scaling of Gauss' law and introduce the concept of electroneutrality. We decompose the electric field into the applied (external) field $\mathbf{E}_{ext}$ (defined by $\nabla \cdot (\varepsilon \mathbf{E}_{ext}) = 0$) and the internal field $\mathbf{E}_{\text{int}}$ generated by net (unbalanced) free charges, hence:

$$\nabla \cdot (\varepsilon \mathbf{E}_{\text{int}}) = \rho_e \tag{3}$$

Here ρ_e is the free charge density (*i.e.*, charge not bound within net neutral dipoles, whether it is stationary or not). Forces on dipole gradients are accounted for by the concept the dielectric constant ε, which is a scalar for isotropic materials. We non-dimensionalize Eq. (3) as

$$\frac{\varepsilon E_{\text{int}}}{\delta c_0 F} \nabla^* \cdot \mathbf{E}^*_{\text{int}} = \alpha \rho^*_e \tag{4}$$

where $\rho_e = F\Delta c_0 \rho^*_e$, $\mathbf{E}_{\text{int}} = E_{\text{int}} \mathbf{E}^*_{\text{int}}$, and E_{int} is the characteristic scale of internal field. We define a characteristic scale background concentration of ions c_0 (in moles per unit volume) of the form $c_0 = {}^1\!/_2(c_+ + c_-)$. We use this simple arithmetic average as most EK applications involve valences of ± 1 or ± 2. To measure the degree of charge imbalance, we define the non-dimensional parameter $\alpha \equiv \Delta c_0 / c_0$ where $\Delta c_0 = z_+c_+ + z_-c_-$ is the dimensional imbalance between cations and anions per unit volume. δ is a characteristic scale for the dimension of the flow region containing net free charge and is determined by the particular physics of the problem. Given a correct determination/estimation of δ, the starred terms are order unity, and so the two prefactors should be on the same order.

The question of electroneutrality can be phrased as follows: how much more or less positive charge z_+c_+ is there than negative charge z_-c_- in regions where E_{int} is order E_{ext}? In such regions, the internally generated field can cancel or double (depending on sign) the external field. We consider two examples.

A first example is the characteristic shielding length of charge in a classic EDL. Here, δ is determined by the local balance between diffusion and electromigration and scales as Debye (a.k.a. Gouy) screening length $\lambda_D \equiv \sqrt{\varepsilon kT / z^2 e^2 c_0}$ [13]. Substituting λ_D for δ in Eq. (4), we find α scales as $\phi_{\text{int}} e / kT$ where $\phi_{\text{int}} = E_{\text{int}} \delta$ is on the order of the zeta potential ζ of the diffuse layer [13]. Measured zeta potentials can be as high as order 10 times the thermal voltage kT/e [14]. Hence, our scaling shows α can be up to order 10. Electroneutrality is therefore not a valid assumption within an EDL.

As a second example, consider charge densities created by the coupling of electric fields with gradients in physicochemical properties of a solution. Examples include conductivity gradients in field amplified sample stacking [15], electrokinetic instabilities [16•,17] or permittivity, and conductivity gradients in electrothermal flows [18]. In these problems, δ is often limited by the interplay between advection and diffusion, and so order 10 μm (examples include the interface between two buffer streams mixing at an intersection [17] or the distances between microfabricated electrodes [19,20•]). Taking $\delta = 10$ μm and assuming an external electric field of order 10^4 V/m (and monovalent ion densities of order 1 mM), we see from Eq. (4) that E_{int} can cancel or double E_{ext} for $\alpha \sim 10^{-5} \ll 1$, an approximately neutral charge balance.

These scaling arguments are consistent with the concept and utility of electroneutrality: in equations describing conservation of species, we can assume $z_+c_+ \approx -z_-c_-$ in regions outside any EDLs. At the same time, we must take into account even the smallest (compared to c_0) imbalances between z_+c_+ and $-z_-c_-$ when we consider conservation of electric fields (Gauss' law).

The concept of electroneutrality is somewhat analogous to the Boussinesq approximation for buoyancy-driven flows associated with small density differences [21], for example, due to temperature gradients. Under the Boussinesq approximation, we can assume approximately