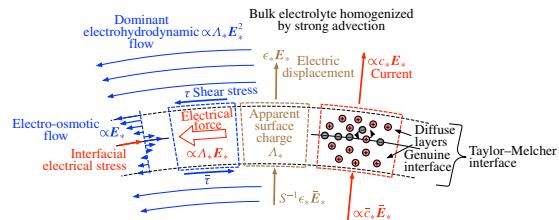# Focus on **Fluids**

Electrokinetics meets electrohydrodynamics

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Despite studying the same subject – electrically induced flow – the fields of electrokinetics (EK) and electrohydrodynamics (EHD) have developed separately, for different types of fluids and interfaces. In colloids or porous media, EK phenomena derive from the electro-osmotic slip of a liquid electrolyte across the neutral electric double layer on a solid surface. On the other hand, EHD phenomena involve poorly conducting neutral fluids and solids, whose interfaces acquire net charge in response to electric fields. Over the past decade, combined theories of EK and EHD have emerged for fluid/solid interfaces, and now Schnitzer & Yariv (*J. Fluid Mech.*, vol. 773, 2015, pp. 1–33) have taken a major step towards unifying EK and EHD for fluid/fluid interfaces. Following previous work by Baygents and Saville, they derive the classical Taylor–Melcher model of droplet EHD as the large-field thin-double-layer limit of the electrokinetic equations, thus elucidating the ubiquitous 'leaky dielectric' approximation. Future work could consider the secondary electro-osmotic flow and electrophoretic motion of the drop (neglected here as small perturbations) and allow for more general EK models.

Key words: drops and bubbles, electrohydrodynamic effects

1. Introduction

The field of electrokinetics (EK) began two centuries ago with Reuss' discovery of electrophoresis of clay particles. In colloid science (Lyklema 1995) and, more recently, in microfluidics (Bruus 2008), EK studies have focused on charged fluids (liquid electrolytes) that form neutral dipolar interfaces called electric double layers (EDLs). Helmholtz first described the EDL as a thin capacitor with mobile ions screening the surface charge and predicted the electro-osmotic slip velocity, and Smoluchowski derived the associated force-free electrophoretic motion of a solid particle.

In contrast, the field of electrohydrodynamics (EHD) considers charged monopolar interfaces and neutral fluids of constant permittivity and (small) conductivity (Melcher & Taylor 1969; Saville 1997). This 'leaky dielectric' approximation has been applied
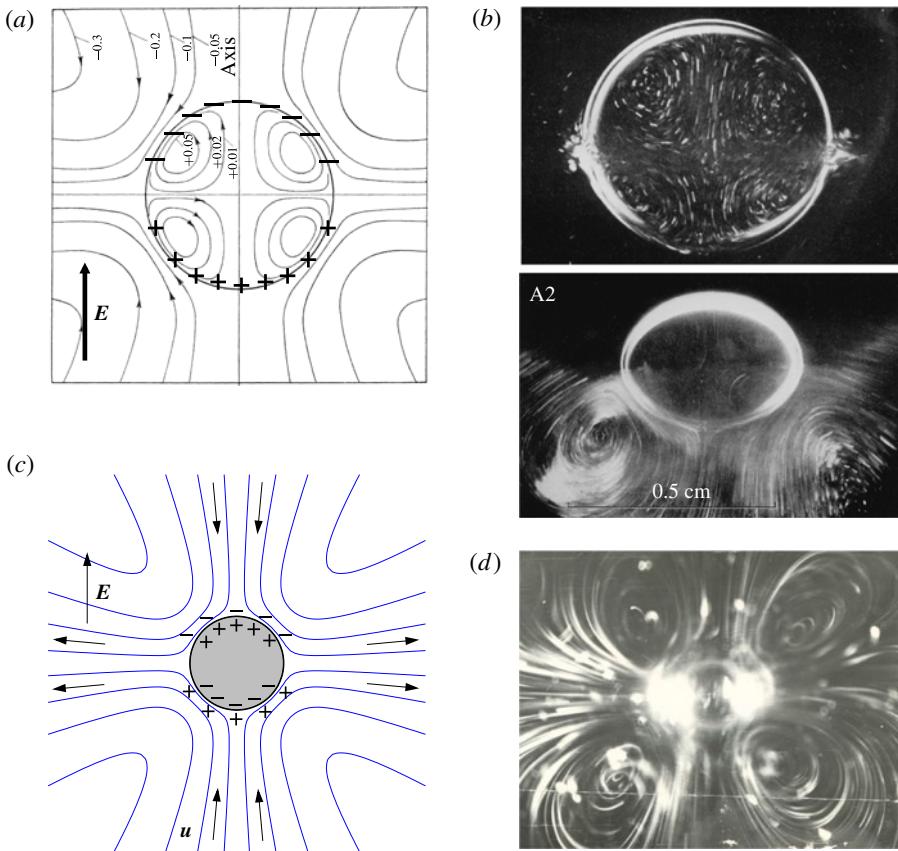
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FIGURE 1. (*a*) Predicted EHD flow around an oil droplet in a uniform electric field (with induced interfacial charges added) and (*b*) experimental visualization from Taylor (1966) (with permission). (*c*) Predicted EK flow of a liquid electrolyte around a solid metal sphere (with induced double-layer charges) (Squires & Bazant 2004) and (*d*) flow visualization around a tin particle by V. A. Murtsovkin (photo courtesy of A. S. Dukhin) from the experiments of Gamayunov, Mantrov & Murtsovkin (1992). In spite of the different charge distributions, the external flows in (*a*) and (*c*) have the same scaling and are identical for spherical shapes, as noted by Squires & Bazant (2004).

to dielectrophoresis and electrorotation of solid particles (Jones 1995) and interfacial flows (Melcher 1981). Although mobile charges are responsible for conductivity, diffuse charge imbalances and double layers are neglected, and motion is forced by the electric field acting on the interfacial polarization charge.

Taylor (1966) pioneered the study of EHD for drops by predicting and visualizing the quadrupolar flow that affects their shape, whose direction depends on the electrical properties of both fluids. As shown in figure 1, Taylor's EHD flow outside the drop resembles the quadrupolar flow of induced-charge electro-osmosis (ICEO) around metal particles (Gamayunov *et al.* 1992; Bazant & Squires 2010), including the possibility of reverse flow. This suggests the need for a unified theory of EK and EHD phenomena. For solid/fluid interfaces, the classical theory of EHD has recently been extended to electrolytes by including ICEO flows (Squires & Bazant 2006; Miloh 2008), and now Schnitzer & Yariv (2015) have achieved a similar unification for fluid/fluid interfaces.

2. Overview

In order to describe EHD phenomena in electrolytes, an EK model must allow for net interfacial charge that is not fully screened by the EDLs. Baygents & Saville (1991) introduced such a model for specific adsorption of ions with fast reaction kinetics, analogous to the charge regulation of solid surfaces (Lyklema 1995). The local concentration of ion i in each liquid is thus proportional to its interfacial concentration via equilibrium constants K_i and $\bar{K}_i$. Schnitzer & Yariv (2015) adopted the same microscale EK model in the simplest (but relevant) case of a symmetric binary salt dissolved in both liquids.

Baygents & Saville (1991) also introduced the asymptotic limit in which their EK model should reduce to the leaky dielectric model of EHD, although they were unable to complete the mathematical procedure. Since liquid drops tend to have larger sizes than the solid particles or pores considered in electrokinetics, the ratio δ of the Debye screening length (defined in the outer electrolyte) to the drop length scale is small, so the interfacial EDL is thin and amenable to boundary layer analysis. At the same time, the electric fields in EHD are typically larger than in EK, due to the low liquid conductivity. In particular, the ratio β of the drop voltage (background electric field times its size) to the thermal voltage ($k_B T/e = 26$ mV at room temperature) is large, but not so large as to trigger nonlinear screening effects, i.e. $\delta\beta \ll 1$.

The distinguished limit, $1 \ll \delta \ll \beta^{-1}$, can be analysed by matched asymptotic expansions in order to derive the effective leading-order EHD model. Baygents & Saville (1991) analysed the inner and outer regions of $O(\delta)$ and $O(1)$ thickness respectively, but were unable to match them, which they attributed to an intermediate region of $O(\beta^{-1})$ thickness. Their analysis also includes many dimensionless parameters, not only the ratios M and S of viscosity and permittivity respectively, between the inner and outer fluid, but also the ratios of diffusivities and adsorption equilibrium constants for each ion.

Schnitzer & Yariv (2015) succeeded in matching the inner and outer regions (without any intermediate region) and showed that the Baygents–Saville EK model indeed reduces to the Melcher–Taylor EHD model in the appropriate limit, with some interesting caveats. Their key insight was to recognize that the ionic diffusivity ratios are not independent parameters, but all proportional to the viscosity ratio, M, according to the Einstein–Smoluchowski relation. As a result, the effective conductivity ratio R that enters the leading-order EHD model is also proportional to M, times the ratio of ion concentrations set by the adsorption equilibria: $R = M\sqrt{K^+ K^-/\bar{K}^+ \bar{K}^-}$.

The leading-order $O(\beta^2)$ quadrupolar EHD flow is driven by a small $O(\delta\beta)$ net charge induced in the 'triple layer' consisting of the charged interface of adsorbed ions and the diffuse screening clouds, as shown in the figure by the title. Unlike the leaky dielectric model of Melcher & Taylor (1969), there is no leading-order convection of interfacial charge, as assumed (without justification) by Taylor (1966). The clear signature of EK is a weak $O(\beta)$ electro-osmotic flow proportional to the $O(1)$ total charge that leads to slow electrophoretic motion of the drop, as observed (but not explained) by Taylor (1966).

3. Future

It would be interesting to analyse other distinguished limits of the model for drops. As suggested by figure 1, it should be possible to recover leading-order ICEO

flow around a solid dielectric sphere (Squires & Bazant 2004) for very viscous drops, $M \gg 1$, that maintain finite conductivity $R^{-1} = O(1)$ in the limit of weak ion adsorption, $K^{\pm}, \bar{K}^{\pm} \to 0$. Ion adsorption could also be added to the authors' analyses of bubbles (Schnitzer, Frankel & Yariv 2014) and perfectly conducting (Schnitzer, Frankel & Yariv 2013) or polarizable (Schnitzer & Yariv 2013) liquid metal drops, which unify EK and electrocapillary phenomena.

Besides drops, there are other important applications. For example, the model could predict how EK phenomena are enhanced by ion adsorption at superhydrophobic surfaces (Bahga, Vinogradova & Bazant 2010) or influence Taylor cones and jets (Melcher & Taylor 1969). The analysis could also be extended to ionic liquids (Storey & Bazant 2012), vesicles (Schwalbe, Vlahovska & Miksis 2011) and membranes (Lacoste *et al.* 2009).

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