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Electrokinetic multiphase hydrodynamics

Yunfan Huang ; Moran Wang  



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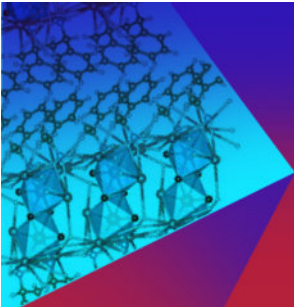
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ABSTRACT

Electrokinetic phenomena around charged interfaces in electrolyte solutions represent a fundamental coupling between interfacial chemical physics and electro-mechanics. While the electrified solid–liquid interface has been extensively studied, its multiphase counterpart involving immiscible liquid–liquid interfaces presents unique challenges due to the interacting behaviors of ion transport within the Debye layer and solvent mixing layer. Electrokinetic multiphase hydrodynamics (EKmHD), dating back to the early 20th century, has regained prominence since the 2010s, supported by advanced methods spanning microfluidics, spectroscopy, molecular dynamics, phase-field-based modeling, coarse-grained analysis, and high-performance computing. After briefly sketching fundamental mechanisms, this review establishes a unified framework of experimental, theoretical, and numerical issues to consolidate the quantitative methodology of EKmHD, which is essential to uncover the underlying interfacial transport mechanisms. The systematic synthesis will not only advance predictive modeling methods for liquid–liquid electrokinetics but also propel the technological developments in multiphase-system-based energy conversion, bio-medical devices, and smart fluidics.

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I. INTRODUCTION

Electrified interfaces between immiscible liquids exhibit electrokinetic (EK) phenomena that govern multiphase transport in both natural and engineered systems, which includes the interfacial physico-chemical charging mechanisms and electro-chemo-mechanical transport processes. Unlike rigid solid–liquid boundaries, the diffuse and soft nature of liquid–liquid interfaces introduces comparable physical scales, including the Debye screening length and solvent mixing layer thickness, and more possibilities on the interfacial and interphase ion transport behaviors. The intrinsic cross-scale and multiphysical characters make electrokinetic multiphase hydrodynamics (EKmHD) a quintessential interdisciplinary field, bridging colloidal science, electrochemical engineering, and soft matter physics. In fact, the EKmHD of electrified oil–water interfaces (especially the interface between two immiscible electrolyte solutions, ITIES) serves as a novel paradigm connecting electrochemists studying ion transfer kinetics, fluid dynamicists analyzing multiphase flow patterns, and material scientists engineering functional interfaces.

The historical foundations of EKmHD trace their origins to seminal investigations of electrification and EK phenomena in liquid–liquid

systems, notably the pioneering experiments on droplet electrophoresis, electrocapillarity, and two-liquid streaming potential in the early 20th century^{1,2} and relevant electrification and EK theories around the 1950s.^{3–7} While the rapid evolution has yielded significant advances, it has simultaneously engendered persistent epistemological divides. This methodological oversimplification is exemplified in the characterization of droplet electrophoresis, where phenomena intrinsic to soft liquid–liquid interfaces are frequently interpreted through the rigid solid–liquid EK theories. In particular, a critical analysis reveals unresolved issues in electrophoretic characterization of conductive dielectric droplets, especially on those limitations persisting in theoretical modeling and experimental validation despite its widespread use for interfacial charge measurement. This serves as an important motivation for this review.

Since the early 2010s, the resurgence of EKmHD reflects two synergistic trends, both bridging the long-standing gaps between colloidal science and EK multiphase flow engineering. One is the technological demands from emerging applications spanning nanobubble stability in nucleation and mineral flotation,⁸ brain-inspired bionic neural computing,⁹ electrospinning, electropatterning, and electro-demulsification;^{10,11} dielectric liquid micropumping, digital microfluidics, and droplet self-propelling;^{12–14} ion-tuned wettability and two-phase displacement control;^{15,16} evaporation-based energy conversion and harvesting;^{17,18} and self-potential geophysical measurement and biochemical/environmental signal detection.^{19–22} The other is the methodological breakthroughs integrating advanced spectroscopy and microfluidic experiments,^{23,24} scanning electrochemical microscopy and electrochemical atom syringes by defining the ITIES,^{25,26} particle-based simulations such as molecular dynamics,^{27,28} and multiscale asymptotic modelling, and diffuse-interface-model-based numerical simulations.^{29–31}

Therefore, current frontiers of EKmHD research can be defined through the key challenges and the corresponding critical gaps are correspondingly addressed in this review, including (1) *methodology transfer* adapting solid–liquid EK experimental techniques to soft liquid–liquid interfaces, which requires the experimental-theoretical synthesis for interfacial property quantification; (2) *multiphase charge regulation* reconciling adsorption-dominated and partition-dominated charging mechanisms, which requires the unified physical descriptions bridging complex interfacial charging and EK transport; and (3) *scale bridging* connecting solvent mixing layer thickness, Debye screening layer thickness and viscous scale, which requires the integration of diffuse-interface simulations with asymptotic matching techniques. For the historical development in a more general sense, there are several previous reviews or monographs, which summarize the fundamental physical models and essential transport mechanisms.^{32–35}

As shown in Fig. 1, this review will begin with the general research paradigms of EK, then focus on analyzing the uniqueness introduced by the ITIES system and the interdisciplinary nature of EK multiphase flow (Sec. II). Then, we will overview and analyze the experimental measurement methods for interfacial charging (Sec. III), followed by an in-depth exploration of the details of various research methods including physical and theoretical modeling, as well as the corresponding analytical and numerical solutions for applications at the micro- and nanoscales (Secs. IV and V). We will focus on how these research methods address the differences in EK transport at

solid–liquid and liquid–liquid interfaces, and the challenges that these specific approaches may bring. Additionally, this article will pay special attention to new understandings and possibilities led by recent technological changes, thereby outlining potential future directions (Sec. VI). As a self-contained review, the fundamental principles of EK and the general methods in experimental measurement, physical modeling, theoretical analysis, and numerical simulation are included in the [supplementary material](#) file.

II. OVERVIEW OF ESSENTIAL PHYSICS IN EKMHD

Electrokinetic multiphase hydrodynamics, as a branch of electrokinetics, requires adherence to its general physical picture and research method. Electrokinetic phenomena originate from the fluid layer with net charge near charged interfaces within electrolyte solutions. As mentioned earlier, this endows it with two fundamental characteristics distinct from pure fluid viscous flow: interfacial multiphysical transport and scale disparity.

On one hand, the formation of the interfacial net charge layer and the coupling of non-equilibrium ion transport and fluid flow within it are the core mechanisms of various electrokinetic flow phenomena. Considering that the former involves interfacial physicochemical actions, while the latter involves the coupling of flow and mass transfer in electrolyte solutions with electric fields, electrokinetics exhibits prominent multiphysical characteristics. From the perspectives of interfacial physicochemistry and electromechanics, important conceptual models involved in interfacial charging and the essential mechanisms of interfacial electrokinetic flow have been expounded in Sec. S1 to highlight the ionic double layer polarization phenomenon that requires particular attention in electrokinetic multiphase flow. In particular, a comprehensive research perspective is thus emphasized which combines the physical picture of interfacial charging with electrokinetic flow and integrates research methods of theoretical simulation solutions with physical experimental measurements.³²

On the other hand, the range of surface and interfacial interactions involved in interfacial charging typically occurs at the nanoscale, while interfacial flow transfers momentum through viscosity at the micro- or millimeter scale. This endows electrokinetics with prominent cross-scale characteristics and modeling demands, which is also a natural consequence of the nonlinear features of multiphysical transport at charged interfaces. The interfacial charging model needs to elucidate the nanoscale spontaneous charging mechanisms within the electrical double layer (EDL), establishing quantitative correlations between interfacial charging and ionic distribution and chemical environmental parameters such as solution concentration and pH. This is closely related to the physicochemical actions of ions at the nanoscale interface and the diffusion and electromigration transport behaviors near the interface. The interfacial flow transport model needs to analyze the coupling transport mechanisms of electrokinetic flow near the EDL under given interfacial charging conditions and to establish a theory of multiphysical transport coupling between interfacial fluid flow and ion transport under different charged interface characteristics. Therefore, how to upscale the coupled transport within the thin net charge layer of the EDL into an asymptotic-matching-based coarse-grained effective boundary condition through cross-scale modeling is usually the key to clarifying the physical picture and enhancing solution efficiency.³⁶

By analogy with the solid–liquid interface electrokinetics, the model systems involved in the liquid–liquid interface electrokinetics

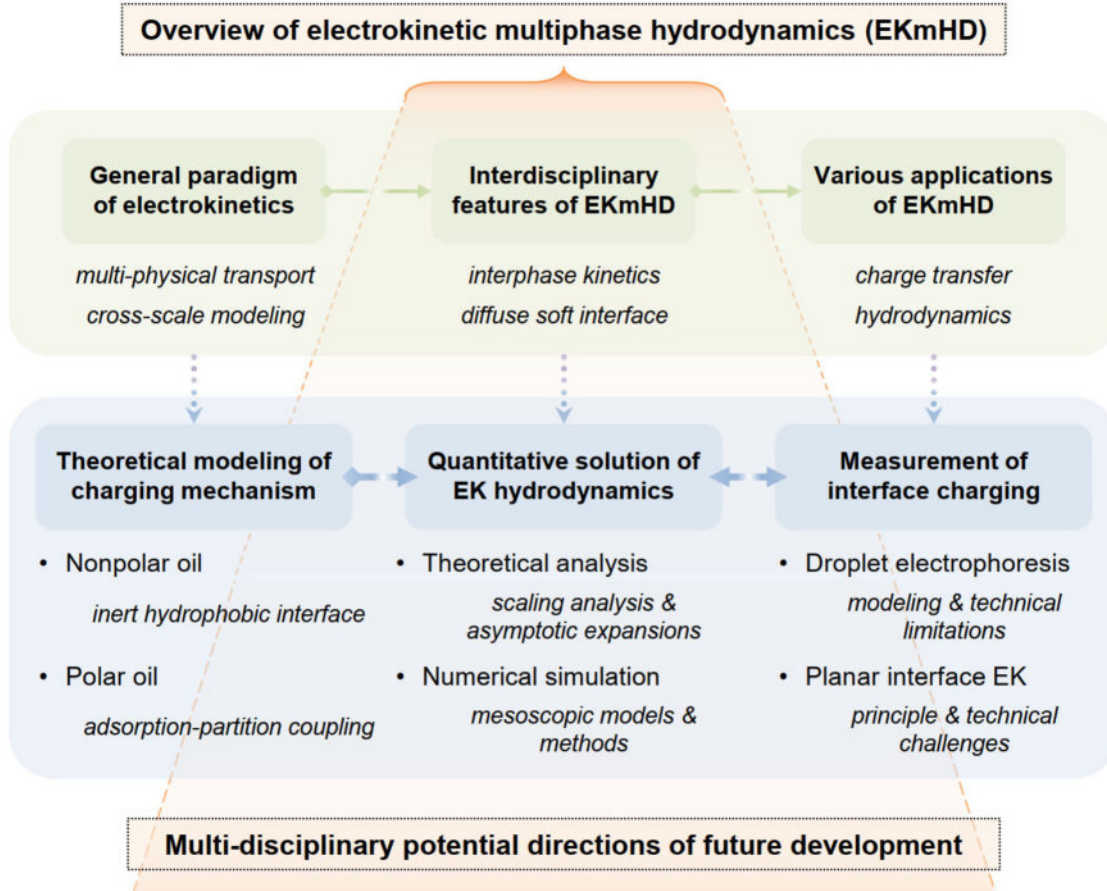


FIG. 1. Logic framework of this review on EKmHD.

can be summarized into two basic forms as shown in Figs. 2(a) and 2(b), namely, the electrokinetic multiphase flow systems with multi-interface hydrodynamic interaction coupling and the electrokinetic multiphase flow systems with surface and interfacial interaction coupling. The former mainly involves electrokinetic multiphase flows containing independent liquid-liquid interfaces or those constrained by solid walls, while the latter mainly involves electrokinetic multiphase flows coupled with thin film disjoining pressure or wetting dynamics. In particular, the model systems include free-space electrokinetic multiphase flows without solid wall constraints, such as electrophoresis and diffusiophoresis of droplets [as shown in Fig. 2(d)], and multi-interface hydrodynamically coupled systems including two-liquid electroosmotic flow, two-liquid streaming potential, two-liquid electroconvective instability, and electrokinetic flows on slippery surfaces [as shown in Figs. 2(c) and 2(e)–2(g)]. It also includes surface and interfacial interaction-coupled systems such as ion-tuned interfacial property coupling with two-phase displacement and electric field-driven electrokinetic two-phase displacement [as shown in Fig. 2(h)].

Through the case of solid-liquid interfaces, this section will meticulously analyze the physical picture behind electrokinetic flow phenomena, thereby laying the groundwork for the elucidation of electrokinetic multiphase flow. Specifically, in Sec. II A, the research logic

basis and quantitative solution methods of electrokinetics that bridge the nanoscale of interfacial interactions and the micro-/millimeter scale of viscous flow will be presented. In Sec. II B, we will focus on the unique physical characteristics and transport mechanisms of electrokinetic flows at oil-water interfaces. It will begin by analyzing the key physical processes and theoretical descriptions, and then provide a brief analysis of the transport mechanisms of electrokinetic multiphase flows from two perspectives: the transport mechanisms of interfacial physicochemistry and electromechanics, and the research perspectives of physicochemical hydrodynamics.

A. Quantitative description

Considering that the Debye length characterizes the effective range of the electric field near a charged interface, it represents the characteristic thickness of the diffuse layer within the interfacial net charge layer and can also be regarded as the characteristic length scale of electrokinetic phenomena. Given that transport in the nanoscale thin layer of interfacial interactions significantly affects the millimeter-scale viscous flow, the core of electrokinetics modeling lies in the analysis of the coupled transport behavior of charges and fluids within the EDL. This implies that establishing the connection between

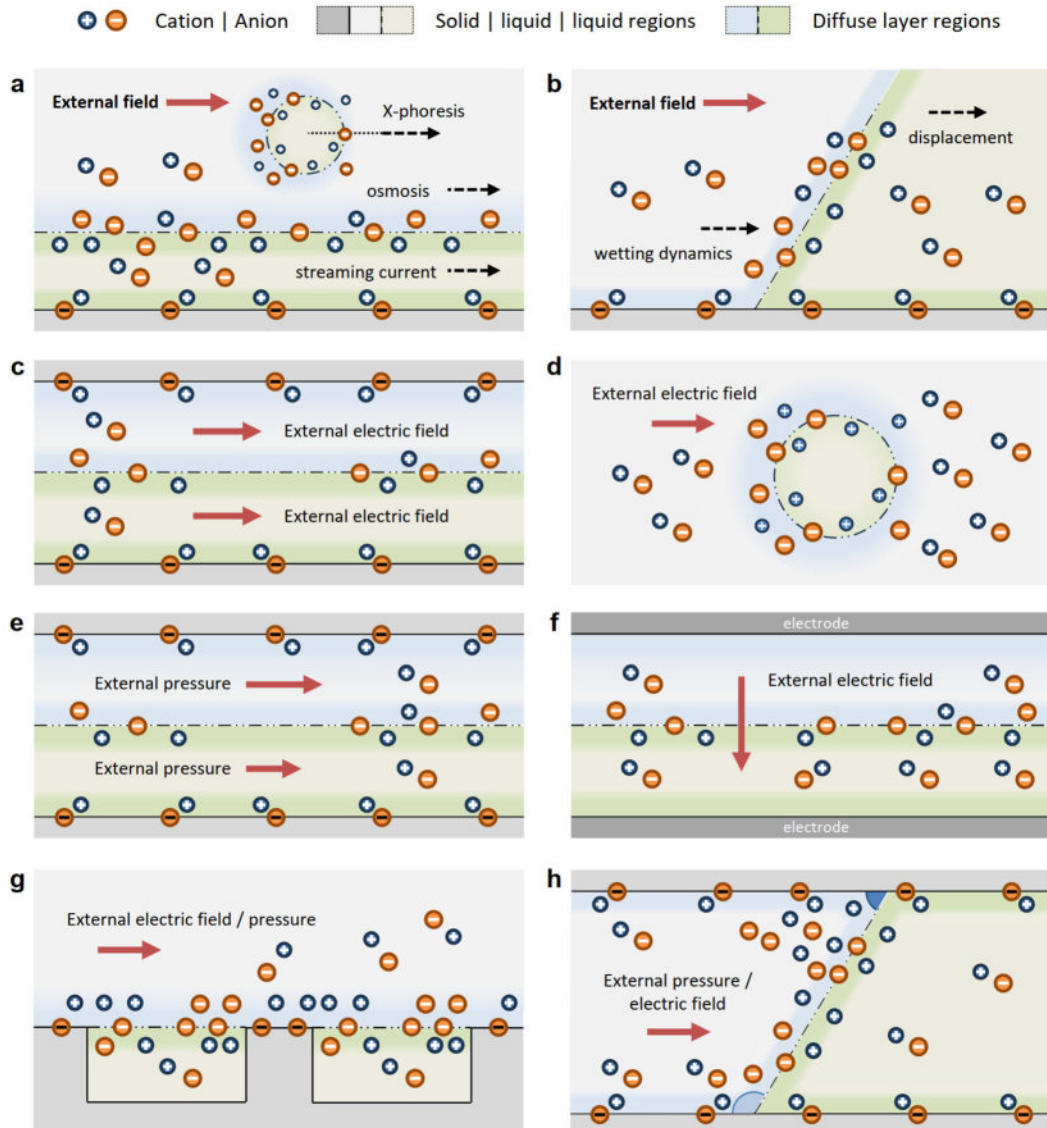


FIG. 2. Electrokinetic multiphase flow: basic and specific forms. (a) Hydrodynamic interaction coupling; (b) nanoscale interaction coupling; (c) two-liquid electroosmosis; (d) droplet electrophoresis; (e) two-liquid streaming potential; (f) two-liquid electroconvection; (g) liquid-infused surface electrokinetics; and (h) ion-tuned wettability and electrokinetic displacement.

spontaneous interfacial cross-scale charging and interfacial flow transport, and effectively capturing this connection, is key to quantitative modeling. To achieve this, it is necessary to first clarify the mechanisms of their mutual influence.

For an equilibrium EDL, given the effective surface charge density at the charged interface, the normal ion equilibrium distribution in the electrolyte solution near the interface can be determined using the electrostatic Poisson equation and the equilibrium Nernst-Planck equation (i.e., the Boltzmann distribution law). The effective surface charge is closely related to the interfacial excess energy (i.e., surface tension), which is also the main source of the electrocapillary effect. Under the influence of a tangential electric field, ions within the net charge layer

will migrate tangentially and drag the fluid flow. In complete theoretical modeling and direct numerical simulations, boundary conditions for the electric potential and flow field are often proposed at the so-called slip plane. Here, the slip plane refers to the interface between the mobile region and the stagnant region, located within the diffuse layer and near the boundary between the diffuse and compact layers, and can generally be approximated as coinciding with each other. The electric potential at the slip plane is called the ζ potential. The slip velocity at the outer edge of the net charge layer is closely related to and usually proportional to the ζ potential, specifically correlated through Smoluchowski theory, which is also commonly used as a simplified effective boundary in macroscopic upscaling coarse-grained models of

electrokinetic flow.³⁷ Generally, in strong electrolyte solutions, the Debye length λ_D , which serves as a screening scale, does not exceed the nanometer range, and the system's characteristic scale a is typically much larger than the EDL thickness λ_D . If the above equilibrium charge distribution can be approximately maintained during transport, and considering that the dimensionless thickness of the net charge layer λ_D/a is much less than 1, the system flow can be divided into an inner flow region with strong shear and multiphysical coupling within the net charge layer and an outer flow region with weak shear dominated by flow outside, analogous to boundary layer theory. Thus, the electrokinetic flow behavior within the local EDL is analyzed first in the inner flow region to obtain the relationship between the interfacial charge and the effective slip velocity at the outer edge of the EDL. This relationship is then used as a boundary condition to solve for the viscous flow in the outer flow region. This macroscopic effective interfacial condition based on matched asymptotic expansion is very common in the field of physicochemical hydrodynamics and typically leads to a linear characteristic between the flow characteristics and the spontaneous interface charging.^{38,39}

In the discussions mentioned above, electrokinetic flow exhibits a linear dependence on spontaneous interfacial charging and the applied static electric field. This linear flow characteristic is based on the assumptions of a thin EDL and a flat interface, as well as small and uniform spontaneous interfacial charge density, weak external fields, and no induced charging. When $\lambda_D/a \gg 1$, significant ion relaxation effects occur in the external flow system, and the original concept of interfacial slip velocity no longer holds, instead, an effective slip velocity must be defined to locally correct and approximate the description, though this concept typically loses its clear physical meaning. When the interfacial charge density is large and there are additional factors such as geometric structural heterogeneity or prescribed inhomogeneous charging,^{40–42} ion concentration polarization and charge relaxation effects will occur, inducing electrokinetic flow behavior under weak non-equilibrium conditions. Moreover, if the solid side is a polarizable metal sphere or a high dielectric constant dielectric sphere, the induced charging by the external electric field will interact with the physicochemical spontaneous charging. In this case, the interfacial induced charge will be related to the strength of the external electric field, and the resulting electrokinetic flow may exhibit a nonlinear dependence on the external electric field strength.^{43,44} Furthermore, the above scenarios can be combined with different types of interfaces to form more complex asymmetric nonlinear electrokinetic flow behaviors.^{45,46} Up to this point, the spontaneous charging density of the interface is usually predefined. In the case of a thin EDL, the spontaneous interfacial charging and electrokinetic flow can still be correlated from the microscopic nanometer scale to the macroscopic millimeter scale through perturbation expansion methods. In these scenarios, the ion distribution within the EDL may deviate from equilibrium, leading to nonlinear effects or even instability in fluid flow. However, the interaction between interfacial charging and electrokinetic flow remains a one-way weak coupling in the context of interfacial physicochemical kinetics.

In fact, there are also scenarios where there is a strong two-way coupling between interfacial charging and electrokinetic flow transport. In such cases, the physicochemical kinetics at the interface will lead to local regulation of the interfacial charging state, thereby allowing a non-zero normal ion flux at the interface. At this time, interfacial

charging (physical adsorption or chemical reaction) will be deeply coupled with ion transport and fluid flow behavior, and it is necessary to add a description of the physicochemical kinetics of interfacial adsorption to capture the non-equilibrium EDL transport behavior in the sense of interfacial charge regulation. For example, when there is a concentration gradient of potential-determining ions (including pH gradients) at the system interface, it will cause the solid wall to spontaneously generate inhomogeneous surface charges; even changes in the concentration of supporting electrolyte ions can cause local charge regulation on the solid wall. Therefore, the concentration gradient of general solute ions will trigger the spontaneous heterogeneous charging of the solid wall. If the diffusion process still dominates (i.e., mass transfer control), it will degenerate into electrokinetic flow behavior with the aforementioned heterogeneous charging. However, the interfacial charging state at each moment must be defined in real-time by the local chemical environment of the system interface. Thus, the coupling behavior of ion concentration polarization and inhomogeneous spontaneous charging at the surface usually triggers strong nonlinear flow behavior,^{47,48} but it is still possible to solve it using perturbation expansion methods.^{29,49} Conversely, if the diffusion process no longer dominates (i.e., reaction control), it is often necessary to introduce characteristic scales for interfacial adsorption or chemical reactions, which may even lead to precipitation or dissolution of the solid wall. This is also an important mechanism for the self-propelling behavior of reactive particles at the interface.^{50,51} At this time, due to the complex coupling behavior of ion transport and fluid flow, direct numerical simulation methods are often required to achieve quantitative solutions. As a special case of the latter, if the interface allows the passage of ions and has strong ion selectivity, the ion flux induced by the external electric field normal to the surface will also cause significant normal ion concentration polarization and nonlinear flow, leading to the formation of ion enrichment-depletion layers and even electroconvective instability.^{52,53} Additionally, if there is an overlap of the EDL in the system, the interaction between the charged interfaces on both sides of the channel or water film will regulate the interfacial charge and the three-phase contact angle, which are no longer arbitrarily given and uniformly constant independent parameters, thereby significantly affecting the flow behavior. This means that at this time, the constant potential or charge density boundary conditions will fail, and the heterogeneity of the width of the narrow channel with overlapping diffuse layers will also cause spontaneous inhomogeneous charging of the solid wall, which has an important impact on the quantitative modeling of electrokinetics in nanochannels or thin film wetting dynamics.^{15,54}

As a multiphysical transport phenomenon with scale disparity, the study of electrokinetics strongly relies on the interaction and joint development between the perspectives of macroscopic viscous flow at the micrometer scale (electrokinetics) and microscopic interfacial interactions at the nanoscale (electrification). In fact, the general analytical framework for interfacial electrokinetic transport mechanisms is similar to the previously mentioned matched asymptotic expansion approach. This involves first obtaining the electric potential distribution and the non-equilibrium transport behavior of ions within the diffuse layer, and then calculating the total tangential shear stress of the diffuse layer to derive the asymptotic matching effective interfacial conditions for velocity and stress at the outer edge of the diffuse layer. The physical quantities that require asymptotic matching conditions

generally include electric potential, concentration, and its flux, velocity, and stress. Consequently, a clearer physical picture of the interfacial electrokinetic effects can be established, which can be used for further analysis of the viscous flow behavior in the outer flow region. This implies that, on one hand, there is a need to progressively analyze and focus from macro to micro, refining key issues, that is, constructing quantitative models of electrokinetics and charging mechanisms to study electrokinetic flow model systems and guide the measurement of interfacial charging to summarize the charging mechanism. On the other hand, there is also a need to emphasize comprehensive application from micro to macro, achieving quantitative prediction, that is, extracting detailed charging mechanisms from experimental data and linking microscopic interfacial charging with macroscopic electrokinetic viscous flow, guiding the theoretical modeling and application research of electrokinetic flow systems. This self-referential characteristic, where the experimental measurement of interfacial charging properties closely depends on the modeling of interfacial charging and electrokinetic flow mechanisms, means that the study of electrokinetics typically requires an overall consideration of multiphysical features and cross-scale modeling. This is also the research challenge of electrolyte solution interface systems as complex systems, and thus usually demands the research methods that combine theoretical simulation solutions with physical experimental measurements.

B. Two-liquid interface electrokinetics

Unlike solid–liquid interfaces, liquid–liquid interfaces are typical multiphase soft interfaces. Considering that the core of electrokinetics stems from the multiphysical non-equilibrium transport behavior at the interface, focusing on the characteristics of liquid–liquid interfaces in terms of equilibrium interfacial physical quantities and ion distribution, as well as non-equilibrium interfacial flow and ion transport, the basic features of charged liquid–liquid interface systems can be specifically summarized as follows:

- Continuous transition of properties and fields. The solvent properties and field quantities change continuously across the nanoscale solvent mixing layer.
- Interphase partition and adsorption of ions. Ions exhibit partition and adsorption behavior in the nanoscale diffuse layers on both sides of the interface.
- Interface deformation and stress coupling. The interface can deform normally or flow tangentially under shear stress or an external field.
- Interfacial charge convection and polarization. Interface ions can slip and accumulate along the interface or transport across the interface under an external field.

The multiphase soft interface characteristic of electrokinetic multiphase flow brings additional theoretical levels to the description of its multiphysical coupled transport behavior, which can be specifically divided into the following three intercoupled key elements:

- Continuum electrostatics. The charged multi-component liquid–liquid interface, acting as a deformable non-uniform continuum containing free charges, requires descriptions from multiphase electrostatics and electromechanics for its evolution.
- Multiphase flow and wetting. Modeling of multiphase interfacial flow determines the selection of the interfacial mass transfer (ion

transport) description scheme, including the dynamics of liquid–liquid two-phase interfaces and three-phase contact lines.

- Interphase charging and ion transfer. The partition and adsorption of ions at the charged liquid–liquid interface necessitate a full consideration of interfacial physicochemical kinetics, including spontaneous equilibrium charging at the interface and interfacial ion transport.

In terms of interfacial physicochemical behavior, the spontaneous charging behavior at oil–water interfaces is particularly sensitive to the properties of both the oil phase and the ions, indicating that the mechanisms of interfacial charging are crucial in the study of electrokinetic multiphase flow behaviors. For cases where the oil phase has low polarity and the system contains only common, simple inorganic ions, the dielectric constant of the oil phase is approximately 1/10 that of the aqueous phase, and the free energy barrier for ion transfer from the aqueous to the oil phase is typically on the order of $100k_B T$.⁵⁵ This implies that the diffusion of ions into the oil phase is weak, resulting in very low ion concentrations within the oil phase; thus, the contribution of ion partition to interfacial charging is quite minimal. However, for cases where the oil phase has a relatively high polarity or the system contains organic ions, the contribution from the ion distribution on the oil side may not be negligible, which actually corresponds to the typical ITIES system. Consequently, this gives rise to issues such as the impact of trace ions dissolved in the oil phase on the interfacial stress matching, the influence of complex charging mechanisms on the polarization state of both sides of the interface, and the effect of interfacial ion transport on non-equilibrium electrokinetic flow, all of which depend on effective descriptions of the complex interfacial charging mechanisms and ion transport behaviors.

In terms of electromechanical behavior, the mobility of liquid–liquid interfaces means that their electrokinetic flow behavior typically no longer exhibits a linear characteristic based on interfacial slip velocity, but rather often shows a dependency on the matching of interfacial shear stress and the electrical properties (such as conductivity and permittivity) of the fluids on both sides.^{56,57} This dependency is also associated with new features of non-equilibrium interfacial ion transport, such as the heterogeneity of charging and ion concentration polarization caused by the mobility and ion adsorbability of the liquid–liquid interface, and the coupling of transport on both sides due to the polarizability and permeability of the interface, as well as the synergistic effects of multi-interface electrokinetics in interfacial flow behavior. Therefore, to understand the nonlinear and non-equilibrium multiphysical coupling transport behavior at the liquid–liquid interface between interfacial charging, ion transport, and fluid flow, it is necessary to establish reliable models for both interfacial charging behavior and electrokinetic flow behavior to capture the key physical mechanisms, and at the same time, to use appropriate upscaling coarse-grained methods to obtain asymptotic-matching-based effective interfacial conditions to achieve quantitative prediction of multiphysical cross-scale transport behavior.

Moreover, apart from the mercury–electrolyte solution interface, immiscible liquid–liquid interfaces are generally not strictly flat geometric surfaces but feature a solvent mixing layer of sub-nanometer thickness.⁵⁸ From the perspective of particle dynamics, the solvent mixing layer is formed by surface fluctuation dissipation and molecular thermal motion, with its thickness related to the system temperature, the chemical potential properties of the locally homogeneous

mixture of the two-phase solvents, and the excess energy of the inhomogeneously mixed interface of the two-phase solvents. This is somewhat analogous to the atomic-scale roughness on solid–liquid interfaces, but liquid–liquid interfaces also possess their own mobility and the characteristic of allowing solute slip, which is quite distinct from solid–liquid interfaces. In the physicochemical hydrodynamic studies of multiphase flow and transport phenomena, the interface with finite thickness of the solvent mixing layer is often equivalently reduced to a zero-thickness geometric interface through a sharp interface limit, known as the Gibbs dividing surface, with discontinuous distribution of material properties and physical fields on both sides. This is described and solved using a macroscopic theory with interfacial conditions based on the sharp interface model.⁵⁹

However, for charged liquid–liquid interfaces, not only does the interface itself have a sub-nanometer thickness with continuously varying properties and field quantities in the solvent mixing layer (interface phase), but the diffuse layers on both sides of the interface also have nanoscale thicknesses. Moreover, solute ions exhibit adsorption and permeation behaviors near the mobile liquid–liquid interface. In cases where the thickness of the solvent mixing layer is comparable to that of the electrical double layer, the additional potential jump induced by the capacitive charging of the interface phase, as well as the additional velocity and shear stress jumps brought about by the shear rate and concentration gradients, may not be negligible. Therefore, it is necessary to use quantitative numerical simulations based on diffuse interface models to provide corrections to the interfacial connection conditions for macroscopic sharp interface theories.³¹ This implies that, in addition to the combination of microscopic interfacial charging with macroscopic electrokinetic flow in terms of physical picture and the combination of theoretical simulation solutions with physical experimental measurements in terms of research methods, electrokinetic multiphase hydrodynamics also requires a combined approach of quantitative descriptions of diffuse and sharp interfaces, as well as modeling techniques that combine direct numerical simulations of diffuse interfaces with asymptotic-matching-based effective interfacial conditions. It should be noted that there is a need to distinguish between the finite-thickness solvent mixing layer where physical quantities are continuously distributed in diffuse interface models, the interfacial conditions on both sides of the liquid–liquid geometric interface in sharp interface models, and the effective interfacial conditions between the outer edges of the two diffuse layers in matched asymptotic expansion methods. This also reflects the cross-scale physics and modeling characteristics of electrokinetic multiphase flow at charged liquid–liquid interfaces. Here, two examples are given to briefly illustrate the essential mechanisms in EKmHD.

Example I: Double-sided electrokinetic transport coupling and induced-charge diffusio-osmosis effect. The semipermeable membrane is an important starting point for understanding micro- and nanoscale interfacial transport, with a history tracing back to the early 20th century when scholars such as Donnan studied the possible mechanisms of electrophysiological effects in biological membranes.⁶⁰ To some extent, artificial elastic semipermeable membranes between the same solutions and immiscible interfaces between different solutions (i.e., ITIES systems) can both serve as artificial model systems for biological membranes. The latter also possesses the properties of ion-selective permeability and specific adsorbability, and thus can be used to further analogize the behavior of mobile ion channels embedded in

biological membranes. The diffusio-osmotic transport mechanisms related to semipermeable membranes are very common in the fields of colloid and interface science and membrane science.^{38,61} Among them, the normal interfacial interaction and the tangential concentration gradient-induced osmotic pressure gradient are the core mechanisms of semipermeable membrane concentration differences, triggering solution transport across the membrane.

In contrast, for the ITIES system, which originated from the field of electrochemistry at liquid–liquid interfaces, its diffusio-osmotic effect remains unclear to this day. More generally, the diffusio-osmotic effect induced at the interface between electrolyte solutions and conductive liquids under the influence of an external field was first observed in a series of studies by Frumkin and Levich^{5,62} and was specifically mentioned and systematically discussed in Levich's monograph,³⁹ focusing on the electromigration behavior of mercury droplets in electrolyte solutions under an external electric field. This series of studies particularly focused on how an external electric field could induce an inhomogeneous charge distribution at the interface, potentially triggering electrocapillary effects under thin electrical double layer conditions. The resulting gradient in interfacial tension would directly affect the distribution of interfacial stress and the stress-matching behavior on both sides, particularly leading to a significant increase in slip velocity. However, despite the theory's predictions aligning well quantitatively with experimental results, this physical picture has not received sufficient attention from the academic community and has even been questioned⁶³ due to its seemingly oversimplified use of the Helmholtz double layer model for the electric double layer and its equilibrium thermodynamic treatment of the electrokinetic transport within.

It was not until recent years that the electrokinetic flow behavior near the interface between electrolyte solutions and conductive liquid strips was reexamined in a retrospective article.⁶⁴ For cases where the conductive liquid is a liquid metal, the study pointed out that due to the very weak electroosmotic effect near the metal interface, the electrocapillary theoretical treatment method used by Frumkin and Levich can capture the dominant diffusio-osmotic behavior. Unlike semipermeable membranes with given concentration gradients, the diffusio-osmotic effect is caused by the inhomogeneous charging of the liquid metal interface induced by the external electric field and the tangential concentration gradient of the nearby electrical double layer. This effect triggers interfacial Marangoni stress (equivalent electrocapillary effect) through the tangential gradient of the normal osmotic pressure, which in turn can induce flow behavior within the conductive liquid strip.⁶¹ It is worth noting that liquid metal strips, due to their inability to accommodate electric field forces within, will significantly increase the effect of osmotic slip. This conclusion can be extended from liquid metals to more general conductive dielectric liquid interfaces (i.e., ITIES systems) under steady-state conditions. It is pointed out that for the ideal polarizable interface formed between a general conductive liquid strip and an electrolyte solution, under steady-state conditions, the osmotic slip velocity will increase due to the cancelation of the diffusio-osmosis effect and the electric field force within the conductive liquid.⁶⁴ However, when the liquid–liquid interface is highly charged, the electroosmotic and diffusio-osmotic effects within the electrolyte solution in the strip may no longer be balanced. Instead, they can trigger a streaming potential effect and introduce a net electric field force within the strip, which may weaken the increase in osmotic slip velocity.

The aforementioned studies reflect that there are essential differences in electrokinetic flow behavior between conductive dielectric liquids and liquid metals. In fact, in terms of conductive dielectric properties, the solute ions within the conductive dielectric liquid strip have relatively finite mobility, and the diffusio-osmosis effect triggered by their interaction with the solvent background cannot be ignored. This effect has been briefly mentioned in Levich's book in the emulsion system and has been treated with a method similar to the electrocapillary effect, but its accuracy and equivalence to the diffusio-osmotic perspective still lack verification and validation.³⁹ In addition to the diffusio-osmotic effect, since conductive dielectric liquids can also accommodate a finite electric field, the electroosmotic effect may no longer be negligible, and the possibilities of interfacial stress matching relationships will thereby become richer.⁶⁴ In terms of interfacial charging characteristics, unlike liquid metals that typically form a double net charge layer through external field induction or chemical reactions, the ITIES system may also form a triple net charge layer through the adsorption of ions at the interface, thereby inducing inhomogeneous charging behavior directly on the liquid-liquid interface. At this time, the interphase ion transfer and the coupling of electrokinetic transport on both sides of the interface will become more complex, and there will be a certain degree of ambiguity between the diffusio-osmosis caused by the tangential gradient of the bulk concentration and the Marangoni flow (electrocapillary effect) triggered by the tangential gradient of the interfacial excess concentration.^{38,65}

Example II: Asymptotic-matching-based effective interfacial conditions and diffuse-interface phase field model. The theoretical solution of electrokinetic flow primarily relies on sharp interface models. In its early development, regular perturbation methods under the weak external field limit were predominantly used, yielding semi-analytical and semi-numerical solutions that facilitate indirect analysis of parameterized curve results.⁶³ In contrast, the singular perturbation asymptotic expansion method, based on the assumption of a thin electrical double layer, can directly provide effective interfacial transport matching conditions from the interface conditions of sharp interface models through upscaling coarse-grained methods.³⁹ This approach not only offers a clearer physical picture of ion transport and fluid flow near the interface but also extends its applicability to studies of electrokinetic transport behavior under strong electric fields. Unlike solid-liquid interfaces, which saw a transition from regular to singular perturbation in the 1980s,^{38,66} charged liquid-liquid interface electrokinetic flow systems have only recently, in the past decade or so, begun to see applications of singular perturbation theoretical methods, represented by studies on bubble/droplet electrophoresis/diffusiophoresis. Since most liquid-liquid electrokinetic flow systems can satisfy the thin double layer assumption, the singular perturbation method has been widely applied in liquid-liquid interface electrokinetics in recent years, obtaining asymptotic matching effective interfacial conditions for the solution and characteristic mechanism study of electrokinetic flow.^{57,67,68} Notably, two studies among them are particularly remarkable,^{29,49} with the following two main similarities observed in this series of studies. However, it should be noted that both adopted macroscopic sharp interface models. When the thickness of the interfacial solvent mixing layer is not negligible compared with the double layer thickness, their theoretical formulations and results still require corrections to the interfacial conditions based on quantitative numerical simulation results from diffuse interface models.³¹

On one hand, both studies focus on the flow behavior of weakly conductive dielectrics under an electric field and, for the first time, systematically consider the analysis of spontaneous charging mechanisms such as interfacial partition and adsorption, as well as mechanisms of charge diffusion and convective transport. In terms of research subjects, the behavior of weakly conductive dielectrics inducing charging and flow under an electric field traditionally falls under the category of electromechanical hydrodynamics, where the classical electrohydrodynamics theory based on the leaky dielectrics model is relatively mature.^{69,70} Both papers introduce the interfacial charging mechanisms, as well as charge diffusion (and possible weak electrolyte ionization behavior) and convective effects within the net charge layer, into the modeling of weakly conductive dielectrics, and employ singular perturbation coarse-grained upscaling represented by the method of matched asymptotic expansions, ultimately arriving at the Taylor-Melcher leaky dielectrics model. The impact of this approach is far-reaching, signifying, to a certain extent, a paradigm shift in the study of weakly conductive dielectrics from classical electrohydrodynamics to the research paradigm of electrokinetic multiphase hydrodynamics.

On the other hand, both studies have focused on the typical ITIES system, paying attention to the mechanism of the ratio of electrical conductivity on both sides of the partially non-polarizable interface and its impact on electrokinetic flow at the liquid-liquid interface. They have also, for the first time, provided a more systematic explanation based on the interfacial kinetics picture of spontaneous interfacial charging. In terms of research subjects, the impact of interfacial physicochemical kinetics and mass transfer on fluid flow traditionally falls under physico-chemical hydrodynamics. In recent years, the physico-chemical hydrodynamics of liquid-liquid two-phase interface systems has gradually become a more active research field, such as self-propelled droplets and chemo-hydrodynamic patterns and instabilities at the interface.^{46,53,71,72} The ITIES interface exhibits selective permeability to different ions, and the ion transport on both sides of the interface may show strong coupling behavior, making the ITIES droplets exhibiting properties similar to vesicles to a certain extent, but with softer interfaces.⁶⁸ This provides new possibilities for constructing artificial systems that simulate the behavior of biological membrane systems based on physico-chemical hydrodynamics,^{73,74} and also brings this system back into the field of view of colloid science.

III. EXPERIMENTAL MEASUREMENT OF TWO-LIQUID INTERFACE CHARGING

Accurate measurement of the charging properties at liquid-liquid interfaces provides key fundamental parameters for the quantitative modeling of electrokinetic multiphase flow systems and is crucial for connecting theoretical prediction with the real physical world. We will focus on how the charging densities at the interfacial phase and within diffuse layers vary with local chemical environmental parameters such as solute ion concentration and pH of the electrolyte solution. The main differences between various measurement methods lie in the theoretical model formulations for different experimental setups and geometrical configurations, as well as the corresponding calibration of additional independent parameters specific to the particular configuration of the physical process. These two aspects are also the main sources of limitations on the accuracy and applicability of experimental measurement methods, which implies the importance of cross-validation of experimental results from different and independent experimental configurations. In recent years, there have been several

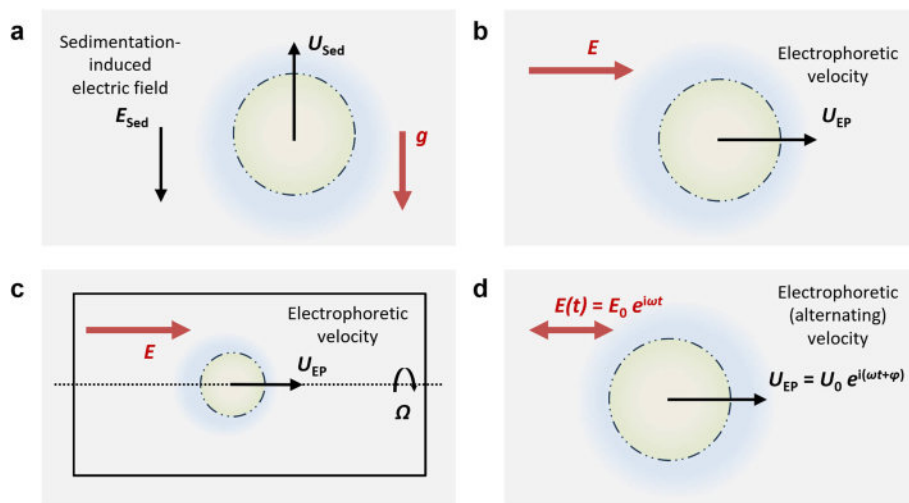


FIG. 3. Droplet-based electrokinetic measurement of two-liquid interface charging. (a) Sedimentation potential; (b) DC electrophoresis in free space; (c) DC electrophoresis in confined space; and (d) electroacoustics, i.e., AC electrophoresis.

reviews on experimental measurement methods of interfacial charging focused primarily on solid–liquid interfaces.^{23,34,75} An overview of general experimental measurement methods for interfacial charge density has been given in Sec. S2.

This section will highlight the importance of electrokinetics-based measurements, pointing out the current bottlenecks and possible future directions of these methods. From the perspective of the geometric configuration and modeling complexity of electrokinetic multiphase flow systems, they can be divided into two types: droplet-based and plane-based methods, as shown in Figs. 3 and 4. Particularly, since the beginning of this century, microfluidic chip technology has been widely used in the study of interfacial electrokinetic phenomena.⁷⁶ The planar interface in two-liquid parallel streaming potential systems, compared with the curved interface in droplet electrophoresis, offers significant advantages in terms of the simplicity of theoretical modeling, fundamental mechanisms, and experimental operations. Therefore, microfluidic-based two-liquid parallel streaming potential is expected to provide an alternative approach for electrokinetic measurements of the charging properties at liquid–liquid interfaces.²⁴

A. Fundamentals of electromechanics

Considering that we focus on the electrokinetic flow behavior of liquid–liquid interface systems as an application, this section will particularly focus on introducing the theoretical models of two *macroscopic electromechanical methods*, which will be closely related to liquid–liquid interface electrokinetics. These include methods based on interfacial tension as quasi-static measurements and electrokinetic methods as dynamic measurements. It should be noted that this section will focus on fundamental principles and technical issues of the experimental measurement; for the analytical solution methods of electrokinetics-based measurement, see Sec. V B.

Interfacial-tension-based methods primarily rely on the variation of two-liquid interfacial tension with chemical environmental parameters or applied voltage, combined with interfacial thermodynamic relationships and models of interfacial charge distribution to deduce the interfacial charging patterns. Specifically, these include two methods: the interfacial tension method and the electrocapillarity method. Both utilize the fundamental principle that interfacial adsorption of solution ions can reduce interfacial tension, thereby allowing the direct inference of interfacial charge density from the distribution of interfacial

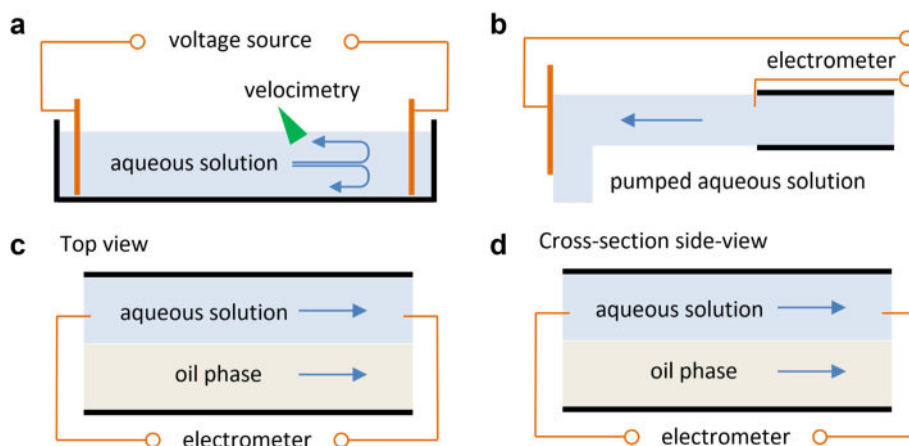


FIG. 4. Plane-based electrokinetic measurement of two-liquid interface charging. Two-liquid (a) electro-osmosis; (b)–(d) streaming potential, including (b) jet flow, (c) bypass, and (d) stack configurations.

ion concentrations. The difference between the two lies in the distinct approaches used to regulate the amount of interfacial ion adsorption. The interfacial tension method achieves this by altering the bulk ion concentration (variation in chemical potential), while the electrocapilarity method does so by applying a normal electric field (variation in electric potential). Since, compared with solid-liquid interfaces, the interfacial tension of liquid-liquid interfaces is more easily measurable, this represents a unique method specific to liquid-liquid interfaces for more directly obtaining interfacial charge quantities. However, because liquid-liquid interfacial tension is not sensitive to the adsorption of simple inorganic ions without external electric field, quantitative measurements demand high resolution and precision from experimental instruments.

For interfacial tension method without external voltage, where the differential and integral forms of the interfacial thermodynamic relations are expressed as follows:²³

$$d\gamma = - \sum_i \Gamma_i d\mu_i, \quad \Gamma_i = \int_0^\infty [c_i^\infty - c_i(z)] dz,$$

$$\Delta\gamma = -k_B T \sum_i \Gamma_i - \int_0^\infty \frac{\epsilon}{2} \left(\frac{d\phi}{dz} \right)^2 dz.$$

Here, c_i represents the molar concentration of component i . The variation in interfacial tension is composed of two parts: the excess chemical energy and the electrostatic energy included in the electrochemical potential $d\mu_i$. In this context, the interfacial adsorption amount Γ_i of component i and the electrostatic energy both depend on the specific distribution of the interfacial potential $\phi(z)$. Specifically, the former is also associated with the interfacial additional potential $W_i(z)$, which reflects the influence of charging mechanisms near the interface, such as image forces, structural forces, intermolecular interactions, dehydration effects, hydrogen bonding, amphiphilic structures, and chemical reactions.

Electrokinetics-based methods primarily rely on the interfacial flow resistance coefficient and particle mobility under constant or alternating voltage, including methods such as droplet electrophoresis, droplet sedimentation potential, two-liquid electroosmotic flow, two-liquid streaming potential, and droplet electroacoustics. Their fundamental principle is that the flow characteristic quantities have a certain dependency on the interfacial charge density q_s , or a more commonly encountered physical quantity, the ζ potential, which is often positively correlated with q_s . When the thickness of the EDL is much smaller than the flow scale ($\lambda_D \ll a$) and the interfacial charging is not large ($\zeta \ll V_T$), the two are approximately proportional to each other, where a is the characteristic scale of the system, and $V_T \equiv k_B T/e$ is the thermal voltage. The general theoretical formulas for the three fundamental types of electrokinetic phenomena at the solid-liquid interface are provided here.^{23,77}

$$\zeta_{EO} = -\frac{\eta}{\epsilon} \left(\frac{u_\infty}{E_\parallel} \right)_{\nabla p=0} F(\kappa h, \zeta/V_T).$$

$$\zeta_{StP} = -\frac{\eta K_\infty}{\epsilon} \left(\frac{\nabla \phi}{\nabla p} \right)_{I=0} \frac{1}{G(\kappa h, \zeta/V_T, \Omega^2 \eta \kappa^2 / K_\infty)},$$

$$\zeta_{EP} = \frac{\eta 3u_\infty}{\epsilon 2E_\infty} \frac{1}{H(\kappa R, \zeta/V_T, \lambda_+/\lambda_-)},$$

Here, $\kappa = 1/\lambda_D$, where the particle radius R and channel width h represent the characteristic scale a of the corresponding system, and the

definitions of the remaining physical quantities can be found in Masliyah's monograph.⁷⁷ It is noteworthy that most of the discussions here on the basic modeling issues of the solid-liquid interface electrokinetics are still qualitatively applicable in the liquid-liquid interface electrokinetics.

When the interfacial charge is small ($\zeta \ll V_T$) and there is a significant difference between the system's characteristic scale and the Debye length of the solution (i.e., $\kappa a \gg 1$ or $\kappa a \ll 1$), F , G , and H can be reduced to known constants. This implies that the electroosmotic/electrophoretic mobility or streaming potential is proportional to the ζ potential, corresponding to the leading-order theoretical solution of the electrokinetic system. For example, in particle electrophoresis, the fundamental principle is that the particle velocity increases with the increase in the effective interfacial slip velocity, and the effective slip velocity at the outer edge of the double layer is proportional to the interfacial ζ potential when $\zeta \approx V_T$. Another example is the solid-liquid streaming potential, under a given hydrostatic pressure difference between upstream and downstream reservoirs, the net charge within the double layer accumulates downstream due to convective action and open-circuit conditions, and the resulting potential difference (i.e., streaming potential) is proportional to the interfacial ζ potential when $\zeta \approx V_T$.

However, when the system's characteristic scale is comparable to the solution's Debye length, i.e., $\kappa a \sim 1$, or under high ζ potential conditions where ζ/V_T holds, both solid particle electrophoresis and solid-liquid streaming potential may exhibit non-monotonic characteristics (as shown in Fig. 5). In fact, due to the non-negligible screening of the external electric field by surface conduction within the double layer at this time, and the difficulty in maintaining the center symmetry of the double layer leading to double layer relaxation phenomena, ion non-equilibrium transport and concentration polarization effects become very pronounced, and the simplified conclusions of the aforementioned leading-order theory no longer hold. Here, the measurement results of electrophoretic mobility and streaming potential may not correspond to a unique interfacial ζ potential, requiring cross-referencing or combination with other measurement schemes to

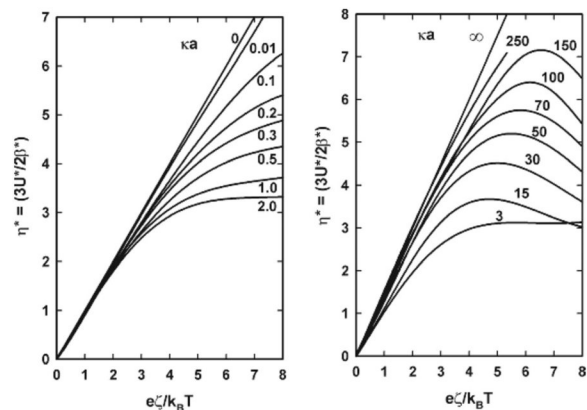


FIG. 5. Non-monotonic dependence of dimensionless electrophoretic mobility on ζ potential of solid particle.^{32,78} Here, $\kappa a \equiv R/\lambda_D$ is the dimensionless double layer thickness, $e\zeta/k_B T \equiv \zeta/V_T$ is the dimensionless surface charge density, and $\eta^* \equiv M^* = (3\eta e/2\epsilon k_B T)(u_\infty/E_\infty)$ is the dimensionless electrophoretic mobility.⁷⁷ Reproduced with permission from Jacob and Masliyah, *Electrokinetic and Colloid Transport Phenomena* (John Wiley & Sons, Inc., New Jersey, 2006). Copyright 2006 John Wiley & Sons, Inc.

determine the true ζ potential. In fact, the above discussion also implies a systematic scale requirement for ζ potential electrokinetic measurement methods based on leading-order theory. From Fig. 5, it can be seen that the applicable range of the leading-order theory for particle electrophoresis is approximately $\kappa R \notin (0.025, 250)$ and $\zeta/V_T \lesssim 3$, and the specific applicable range for streaming potential is similar. Specifically, in cases where the number density of particles is relatively high during electrophoretic measurements, the overlap of double layers will trigger electrophoretic behavior different from that of single particles,⁷⁷ which also imposes additional requirements on the scope of applicability of the system measurement principles.

In fact, interfacial electromechanical hydrodynamic phenomena also encompass *dielectrophoresis*,⁷⁹ *alternating-current electroosmosis*,⁷⁹ *electrothermal flow*,⁷⁹ *induced-charge electrokinetics*,⁴⁴ and *electroconvection*.^{52,80} However, these are typically confined to specific colloid transport systems with particular interfacial properties and external field conditions. They lack easily measurable physical quantities or simple theoretical models, and thus are commonly employed for driving fluid flow or particle movement in microfluidic systems rather than for quantitative measurements of interfacial charging.

Considering that electrokinetics-based methods are closely related to practical application scenarios related to electrokinetic multiphase flow, and that existing measurement schemes for solid–liquid interfaces are relatively mature, while the requirements for the resolution and accuracy of experimental instruments in quantitative measurements are moderate and offer advantages compared with interfacial-tension-based methods, we will focus on these methods in the main text.

B. Droplet-based EK methods

The droplet-based experimental methods for liquid–liquid interface electrokinetic measurements include two methods: sedimentation

potential and electrophoresis. The latter can be further divided into electrophoresis under a constant electric field in free conditions (i.e., free DC electrophoresis), electrophoresis under a constant electric field in constrained conditions (i.e., confined DC electrophoresis), and electrophoresis under an alternating electric field (i.e., AC electrophoresis or electroacoustics). Since these methods can directly utilize the measurement devices from solid–liquid particle electrophoresis, they are widely used in the measurement of charging properties at liquid–liquid interfaces.

Among the four typical droplet electrophoresis methods shown in Table I, the sedimentation potential method and confined direct current (DC) electrophoresis are less commonly used for measuring the charging at liquid–liquid interfaces. On one hand, the sedimentation potential method is largely based on simplified models for solid particles that neglect the relaxation of EDL charges, which is not applicable to droplets or bubbles where the relaxation effect causing interfacial tension gradients is critical.³⁹ Currently, there is still a lack of quantitative modeling with good repeatability and accuracy, making it difficult to use for measuring interfacial charging. On the other hand, since the density of gases is generally much lower than that of aqueous solutions, electrophoretic measurements of bubbles often cannot avoid the influence of buoyancy. Therefore, Sherwood *et al.* proposed a rotating cylindrical constraint DC electrophoresis measurement scheme to stabilize bubbles,⁸² which has subsequently been commercialized and widely used for measuring charging at gas–liquid interfaces. However, Sherwood's theory assumes a no-slip condition at the bubble/droplet surface due to the enrichment of surfactants,³⁹ which is hard to meet under pure oil–water interface conditions. Moreover, since bubbles are compressible and more deformable, the measurement results may also depend on droplet size, electric field conditions, and the rotation speed of the chamber,^{90,91} none of which are considered in Sherwood's theory. It is evident that accurate quantitative modeling of confined DC

TABLE I. Comparisons between droplet-based EK measurement methods for two-liquid interface charge density.

	Sedimentation potential	Free DC electrophoresis	Confined DC electrophoresis	Electroacoustics (AC electrophoresis)
Representative theory	Solid particle ^{39,77}	Solid particle ⁷⁸ or droplet ^{5,7,81}	Gas bubble ⁸²	Solid particle ^{33,83} or droplet ⁸⁴
Representative experiment	Gas bubble ⁸⁵	Droplet ⁸⁶	Gas bubble ⁸⁷	Droplet ^{87–89}
Fundamental principle	Sedimentation-induced electric field leading to sedimentation equilibrium	Constant electric field actuation of droplet electrophoresis	Rotating cylinder as a constraint of bubble/droplet electrophoresis	AC electric field actuation of particle/droplet vibration
Accuracy of modeling	Simplified models based on solid particles, and the theory is still far from complete	Early measurements were based on early droplet electrophoresis theories, while recent studies often directly apply theories from solid particle electrophoresis	Specialized theories based on rotating cylinder constraints for bubble electrophoresis, demanding complex apparatus and usually limited to bubble applications	Still debate on whether droplet behavior is similar to that of solid particles, and theory from solid particle studies is often applied
Comments on the application	Less commonly used in the measurement of interface charge density	Widely applied	Mainly for measurement of gas–liquid interface charge density	Widely applied

electrophoresis still faces significant challenges and cannot be directly applied to the measurement of charging at liquid–liquid interfaces.

Free direct current (DC) electrophoresis and electroacoustics (alternating current (AC) electrophoresis) under weak electric field have been widely applied among the aforementioned methods. Below, we will focus on their transport mechanisms and experimental evidence under weak electric fields, where the spontaneous charging due to ion partition and adsorption dominates over charging induced by the external electric field. The following discussion will show that droplet electrophoresis is still in the preliminary stages of theoretical exploration and experimental verification, and quantitative measurements of interfacial charging at liquid–liquid interfaces based on this principle still face significant theoretical and technical challenges.

At the modeling level, current approaches are often based on solid particle or early droplet theories, with insufficient consideration given to the characteristics of electrokinetic flows at liquid–liquid interfaces.^{33,88,92} Specifically, considering the characteristics of conductive dielectric droplet electrophoresis, their mobility should lie between that of liquid metals and perfect dielectrics, with the specific magnitude depending on the interfacial matching relationship between viscous and Maxwell stresses. The specific experimental correlation formula should be related to the polarizability of the charged interface, the amount of charge, the viscosity of the droplet, and the dielectric and conductive characteristics.^{56,81} In fact, both in terms of theoretical solutions and numerical simulations, there is currently a lack of reasonable and effective theoretical descriptions and quantitative predictions for droplet electrophoresis behavior.^{29,34,93} The theoretical analysis of single droplet electrophoresis (see Sec. V B) reveals that, as a widely applied method for measuring the charging properties at liquid–liquid interfaces, the understanding of key mechanisms, the formulation of parametric relationships, and the prediction of quantitative behavior remain unclear. Particularly, the theoretical analysis and numerical simulations are significantly complicated by the inhomogeneous interfacial charging and ion concentration polarization behaviors of charged two-liquid interface electrokinetics.

In addition, droplet electrophoresis methods also have inherent technical limitations, with the core difficulty lying in the preparation of

a pure and stable emulsion system composed of monodisperse droplets. Potential issues include: (1) difficulty in removing impurities, the droplet dispersion process is highly susceptible to introducing soluble gases, organic solvents, and other impurities, thus requiring additional treatment steps,⁹² which increases the complexity of the experimental process, reduces repeatability, and further adds uncertainty to the theoretical modeling of interfacial continuity and stress conditions. (2) Difficulty in achieving uniform size, the emulsion system composed of dispersed droplets generally cannot ensure the uniformity of droplet size (i.e., monodispersity), but instead exhibits a certain particle size distribution. The use of theoretical models based on a single droplet size can only yield an equivalent interfacial charge density in terms of average droplet size, which introduces further errors into the already inhomogeneously charged droplet electrophoresis and makes it difficult for subsequent quantitative modeling and prediction.⁹⁴ (3) limited parameter range, to ensure the stability of the droplet dispersion system, the interfacial charge of the droplets cannot be too low, which imposes significant restrictions on the range of chemical environmental parameters and makes it difficult to obtain accurate isoelectric point data (i.e., the chemical environmental parameters corresponding to zero interfacial charge).⁸⁷ Some previous studies have used surfactants to suppress droplet coalescence, but the measured values at this time are no longer the intrinsic interfacial charge quantities.⁸⁹

C. Plane-based EK methods

The plane-based experimental methods for liquid–liquid interface electrokinetic measurements include two major types: two-liquid electroosmosis and two-liquid streaming potential. The latter encompasses various subtypes such as jet-type, bypass-type, and stack-type. For the planar interface methods shown in Table II, the definition of a planar liquid–liquid interface necessitates the suppression of various flow instabilities at the liquid–liquid interface,⁹⁵ with Kelvin–Helmholtz, Yih, and Marangoni instabilities being predominant.^{96,97} However, current research on electrokinetic measurement has not sufficiently considered the impact of flow instabilities at the liquid–liquid interface.^{2,37,98,99} As the system scale diminishes, the dominant force in

TABLE II. Comparisons between plane-based EK measurement methods for two-liquid interface charge density.

	Electro-osmosis	Streaming potential—jet	Streaming potential—bypass	Streaming potential—stack
Representative theory	Mobile interface ³⁷	Immobile interface ³⁷	Mobile interface ²⁴	...
Representative experiment	Gas–liquid interface ^{99,102–104}	Gas–liquid/two-liquid interface ²	Two-liquid interface ²⁴	Two-liquid interphase mass transfer ⁹⁸
Electrode setup	Metallic plate–plate	Metallic wire–plate	Ag/AgCl electrode with salt bridge	Metallic plate–plate
Measurement method	Velocity field–PIV	Pressure–Hg column; potential–electrode/electrometer	Pressure–pump; potential–electrode/electrometer	
Stability of interface	Relatively good	Poor	Relatively good	Relatively good
Accuracy of modeling	Simple	Complex formulation of boundary conditions	Simple and straightforward	Simple
Comments on technique	Large measurement errors of the flow field	A relatively simple measurement setup	Challenging <i>in situ</i> pressure potential measurement	

flow phenomena transits from volumetric forces to surface/interface forces. A notable consequence of this transition is the reduction of instability factors such as inertial effects and the enhancement of stabilizing factors like surface tension, which aid in suppressing the development of perturbations and thereby diminishing the instability of the liquid–liquid interface. The two-liquid parallel electroosmotic system was among the first electrokinetic multiphase flow systems realized in microfluidic systems. Lee *et al.* successively established a PIV experimental platform and conducted quantitative theoretical modeling for a two-liquid parallel electroosmotic system with a gas–liquid interface, yet the influence of particle charging on the measurement results of the electroosmotic flow profile was not fully addressed.^{99,100} This approach was subsequently extended to microfluidic systems for the quantitative regulation of the mass flux ratio in two-phase liquid–liquid flow systems, but its quantitative theoretical modeling did not account for the spontaneous charging of the liquid–liquid interface.¹⁰¹

Compared with droplet electrophoresis methods, planar interface methods have their unique advantages. First, their electrokinetic modeling is simpler, more straightforward, and more accurate, largely avoiding the influence of charge relaxation within the EDL.¹⁰⁵ Second, the feasible domain of environmental parameters for the measurement system is larger, allowing for independent control of the chemical environmental parameters on either side of the liquid–liquid interface. Third, the preparation process of the measurement system is not limited by the droplet dispersion step, thus avoiding the influence factors such as impurities, polydispersity, and stability. In addition, these methods will inevitably face corresponding technical challenges, which mainly stem from the interface flow instability due to the deformability and mobility of the liquid–liquid interface, as well as the unique characteristic of being difficult to completely exclude the influence of the solid wall. Below is a brief discussion of possible solutions and new opportunities in recent years.

However, planar interface methods require the development of new measurement devices, and the existing methods also face various technical and modeling limitations. Therefore, these methods are currently less frequently used for measuring the charging properties at liquid–liquid interfaces, and the reliable experimental results are still limited. In addition, the measurement device for the planar liquid–liquid interface inevitably introduces the influence of solid–liquid interface electrokinetics. In early studies, the impact of solid wall charging on electrokinetic multiphase flows was often neglected without discussion,¹² or it was directly assumed to be negligible based on polymer coatings.²⁴ For the surface charge of tracer particles used for flow visualization, their electrophoretic behavior was considered to have a negligible effect on the flow field near the interface.^{99,102} This implies that existing research still fails to accurately identify the significance of this influence. In fact, to accurately measure the streaming potential of oil–water two-phase flow in microfluidic systems, it is required that the chip material can effectively avoid swelling due to oil absorption, and the chip structure design needs to be optimized to achieve high-precision *in situ* measurements of hydrostatic pressure, potential, or flow field.

Inspired by microfluidic systems used for liquid–liquid extraction,¹⁰⁶ Alizadeh *et al.* recently proposed the idea of measuring the charge at the liquid–liquid interface based on planar streaming potential in microfluidic systems.²⁴ Specifically, a Y–Y-shaped microchannel was used to form a relatively flat and stable liquid–liquid interface, and

a polymer coating was applied to suppress interference from the solid–liquid interface. The experimental setup was first verified by re-examining the charge at the water–silicon surface interface, and then the charge at the decane–KCl solution interface without surfactants was studied. It was confirmed that the decane–KCl solution interface is negatively charged and increases with increasing pH, which can be explained by the charging mechanism of hydroxide ion adsorption. This study provides a simple and flexible experimental scheme for the research of charging mechanisms at the double diffuse layer of liquid–liquid interfaces and offers insights for quantitative macroscopic interface modeling in important scenarios such as droplet electrophoresis. However, the novel development presents different results (even with scale differences) on the surface charge densities compared with the droplet electrophoresis, thereby requiring further efforts to clarify whether the droplet electrophoresis modeling and the streaming potential setup should be improved, the latter of which will be shortly discussed in the following.

Overall, the use of metal electrodes in conjunction with pure PDMS or PDMS-resin/silicon-based chip materials (such as silica, elemental silicon, glass, etc.) is simpler in design and packaging, and thus is widely adopted in current research. In contrast, the work involving metal electrodes with homogeneous silicon-based microfluidic chip packaging is relatively rare and requires further refinement of the system construction plan in terms of etching and packaging strategies, in combination with specific *in situ* pressure and potential measurement techniques. For *in situ* pressure measurement, it is necessary to convert hydrostatic pressure signals into other easily measurable optoelectronic signals, including optical wavelength schemes such as reflection/refraction/interference, piezoelectric schemes such as piezoresistivity/piezoelectric charge/capacitance, pressure-sensitive schemes such as effective resistance/optical intensity, and mechanical schemes such as interface displacement/gas column volume.¹⁰⁷ In the case of *in situ* potential measurement, not only is it necessary to achieve electromagnetic shielding and vibration damping of the measurement unit in experimental operation techniques, but also to ensure the consistency of the substrate material on one side of the solid wall, which can be specifically divided into two schemes where the chip/channel is on the same side or on different sides.^{108,109}

In recent years, there have been emerging scenarios such as the streaming potential on liquid-infused surfaces with strips,¹¹⁰ two-liquid electroosmosis on superhydrophobic surfaces,¹¹¹ and streaming potential in microfluidic systems with multiple flow regimes (such as slug flow, bubbly flow, parallel flow).¹¹² These developments offer new ideas for the design of expandable measurement schemes from solid–liquid to liquid–liquid interfaces, with theoretical modeling discussed in Sec. V B. However, these schemes also face technical challenges such as the stable construction of liquid–liquid interfaces.^{113,114} For instance, for two-liquid parallel flows, methods such as selective modification of solid wall surfaces and channel guiding structure design may be required to alleviate these issues.^{106,115}

IV. QUANTITATIVE MODELING OF TWO-LIQUID INTERFACE CHARGING

The accurate depiction of electrokinetic multiphase flows relies on the quantitative prediction of charging behavior at oil–water interfaces and the three-phase contact angle of oil–brine–solid walls. An accurate analysis of the charging mechanisms at liquid–liquid interfaces also lays the foundation for the non-equilibrium kinetics in the

quantitative modeling of electrokinetic multiphase flows. The analysis of interfacial charging mechanisms mainly includes two aspects: capturing the specific electrification mechanisms and resolving the charge distribution structures at the interface. Here, we focus on the case of spontaneous charging, specifically discussing the latest progress and limitations in modeling the charging mechanisms of nonpolar and polar oils, in order of their similarity to charging at solid–liquid interfaces.

Oil phases can be categorized into polar and nonpolar oils based on their interfacial charging and bulk dielectric and conductive characteristics.³⁵ The former contains hydrophilic polar groups, with a dielectric constant lower than that of water but not negligible; the latter typically exhibits hydrophobic characteristics, with a dielectric constant much lower than water. According to the current consensus,^{15,23} polar oils are primarily dominated by adsorption-induced charging, including hydrolysis of carboxyl or amino groups and chemical reactions with electrolyte ions. Their surfaces exhibit hydrophilic properties and can dissociate free charges. This includes small organic molecules with polarizable groups containing oxygen or nitrogen atoms.²³ In contrast, nonpolar oils, with their lower dielectric constants and negligible bulk partition effects, are mainly dominated by adsorption-induced charging. Their surfaces are hydrophobic, typically inert and weakly polarizable, thus allowing a certain degree of free charge exchange and structural reorientation among water molecules near the interface. This includes many hydrocarbon organic compounds and long-chain molecules with polar groups.¹¹⁶ It should be noted that the hydrophobicity mentioned here is not entirely the same as the concept of wettability in terms of the three-phase contact angle, for more details see Israelachvili's monograph.¹¹⁷

However, existing studies have primarily focused on typical geological conditions involving crude oil and simple ionic solutions, often employing modeling techniques from solid–liquid interfaces, thus typically neglecting partitioning effects.¹¹⁸ Nevertheless, considering that the dielectric constant of polar oils may not be low and that they often dissolve various organic impurity ions, their complex interfacial physicochemical behaviors near the interface, including partitioning, may have a non-negligible impact on the charging at liquid–liquid interfaces. This aspect has received little attention in recent years, and early electrochemical research on ITIES systems may aid in enhancing our understanding of these partitioning behaviors. On the other hand, inert hydrophobic organic interfaces are widely used in micro- and nanofluidics¹¹⁹ and are prevalent in biological systems such as biomembranes.¹²⁰ However, the charging mechanisms of nonpolar oils, as typical inert hydrophobic materials, remain controversial. The rapid advancement of sophisticated simulation and experimental techniques in recent years has provided possibilities for further elucidating their charging mechanisms.

A. General formulations of models

In general, the modeling methods of interfacial charging and wettability mechanisms are outlined in Sec. S3, in which the generalized electrical layer (GEL) and modified Poisson–Boltzmann (MPB) methods are emphasized. To capture the quantitative influence of complex factors in actual conditions, the relevant formulations of those two models are given here under the condition of a single-sided double layer,³² which can be easily extended to the double-sided double layer cases and utilized to analyze the effect of temperature and impurities.³¹

The primary advantage of the GEL model lies in its clear physical meaning. Through assumptions of layered charge distribution near the interface and electrochemical constitutive relations between layers, it achieves quantitative modeling of interfacial charging based on simple assumptions regarding charge layers and physicochemical kinetics. However, its drawbacks are also quite evident, namely, it makes intuitive *a priori* assumptions about the distribution structure of interfacial ions, thus making it difficult to analyze the complex interactive behaviors of solute ions near the interface. In terms of model formulation, the GEL model mainly includes the EDL model, the ETL model, and the electrical quadruple layer (EQL) model, as shown in Fig. 6. The EDL model can be further divided into the single-site single reaction model (equivalent to the Stern adsorption isotherm)^{92,103} and the single-site model with image force correction.¹²¹ The ETL model primarily considers the specific adsorption effects of some ions,¹²² while the EQL model further incorporates the effect of the hydrodynamically stagnant buffer charge layer.¹²³

Here we present a brief example of the GEL model. Considering the general case of a triple layer model, the compact layer can be characterized using a *surface complexation* model or an *adsorption isotherm* model to depict the adsorption-induced charging mechanism.^{15,127} The diffuse layer is then correlated with the bulk neutral solution through the Boltzmann distribution and the electrostatic Poisson equation.^{15,128} Specifically, the surface charge densities and electrical potentials at (or within) the 0-plane, β -plane, and d -plane (diffuse layer) are denoted as (σ_0, φ_0) , $(\sigma_\beta, \varphi_\beta)$, and (σ_d, φ_d) , respectively. The interactions between the layers are described using a capacitive model

$$\varphi_0 - \varphi_\beta = \frac{\sigma_0}{C_1}, \quad \varphi_d - \varphi_\beta = \frac{\sigma_d}{C_2}.$$

The entire system satisfies the condition of electrical neutrality

$$\sigma_0 + \sigma_\beta + \sigma_d = 0.$$

Adopting the single-site single-reaction surface complexation model $>S + M^+ \leftrightarrow SM^+$, assuming that M^+ is located at the 0-plane, then

$$K_m = \frac{\Gamma_S c_{M^+}^\infty}{\Gamma_{SM^+}} \exp\left(-\frac{e\varphi_\beta}{k_B T}\right).$$

Given that the number of $>S$ groups at the interface is constant, we have

$$\Gamma_0 = \Gamma_S + \Gamma_{SM^+}.$$

Combining the definitions of σ_0 and σ_β , we have

$$\sigma_0 = e\Gamma_{SM^+}, \quad \sigma_\beta = 0.$$

The aforementioned seven equations implicitly provide a constraint between σ_d and φ_d . By associating the interfacial ion concentration with the bulk neutral solution through the Boltzmann distribution and the electrostatic Poisson equation, the electrostatic equilibrium equation can be obtained (also known as the Grahame equation)

$$\sigma_d = -\text{sign}(\varphi_d) \sqrt{2N_A \epsilon k_B T \sum_i c_i^\infty \left[\exp\left(-\frac{z_i \varphi_d}{k_B T}\right) - 1 \right]}.$$

By simultaneously solving the above two series of constraints (one electrostatics and the other physico-chemistry), we obtain σ_d and

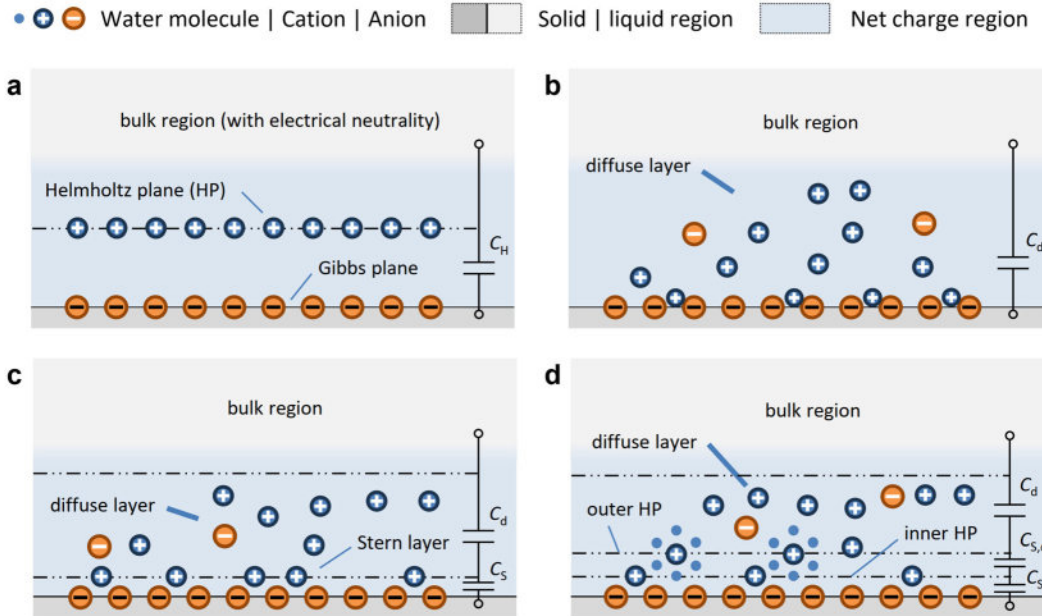


FIG. 6. Electrical double layer models at solid-liquid interfaces. (a) Helmholtz model. (b) Gouy-Chapman model.^{124,125} (c) Stern model.¹²⁶ (d) Grahame model.⁴

$\varphi_d \simeq \zeta$ for an individual independent EDL.^{15,128} Here, c_i^∞ represents the molar concentration of component i in the neutral regions of the electrolyte solution, and z_i is the charge number of that component. It should be noted that in the surface complexation model chosen here, the charge quantity on the β -plane is zero, and thus, the electrical triple layer (ETL) model essentially reduces to a narrow-sense electrical double layer (EDL) model. In addition to the surface complexation model, adsorption isotherm models can also be used for modeling specific adsorption-induced charging mechanisms, such as the Stern adsorption isotherm model, which provides the interfacial adsorbed ion density as follows:

$$\frac{\Gamma_s}{\Gamma_{s,\max}} = \frac{x_s^\infty \exp[-(e\varphi_s + \Delta g_{a,s})/k_B T]}{1 + x_s^\infty \exp[-(e\varphi_s + \Delta g_{a,s})/k_B T]}$$

Here, it is assumed that the saturated adsorption density of the charged component is $\Gamma_{s,\max}$, and the adsorption reaction corresponds to the effective adsorption free energy $\Delta g_{a,s}$, where x_s^∞ is the mole fraction of the adsorbed component s in the neutral region of the electrolyte solution. It can be seen that the GEL model divides the net charge into the compact layer and the diffuse layer and describes them using lumped parameters. The flexibility of this model mainly lies in the description of various specific adsorption mechanisms. This model is typically used for nonpolar oil interfaces where simple adsorption-induced charging is predominant.

Compared with the GEL model, the MPB model can capture various specific charging mechanisms, including partition and adsorption, and more accurately depict the distribution structure of solute ions near the interface by introducing the single-particle effective interaction potential or multi-particle correlation effects of solute ions under the mean-field assumption. The accuracy of the MPB model strongly depends on the profile assumption of the effective interaction potential

of solute ions or the correction form of multi-particle correlation effects. On the one hand, this indeed significantly increases the degrees of freedom for describing interfacial solute-solvent interactions compared with the GEL model. On the other hand, it still leaves behind issues such as the determination of the details of interaction potentials and the interpretation of the rationality of the simplification of single-particle effective potentials. This requires a foundation in the many-body electrostatic interactions of ionic plasmas, specifically analyzing the effective correlation effects between solute ions or the solvent polarization effects induced by solute ions, to provide benchmark results for the refinement of descriptions of single-particle potentials or to directly give multi-particle correlation corrections.

Here, we present a brief example of the MPB model. The electric potential and solute ion concentration distribution can be obtained by solving the electrostatic Poisson equation in conjunction with the interfacial additional potential determined by the interfacial charging mechanism model and the electrostatic boundary conditions. The interfacial additional potential W_i for solute ion i can be provided by mean field free energy functional theory or particle simulation, while the electrostatic boundary conditions can include schemes such as the inert interface assumption with zero surface charge density or the adsorption isotherm model with a given surface adsorbed ion density. Below, taking the inert electrostatic boundary condition as an example, a typical physical model for the charging of an ideally polarizable interface is presented²³

$$-\nabla \cdot (\epsilon \nabla \varphi) = \rho_e(y) \equiv \sum_i z_i e n_i(y),$$

$$n_i(y) = n_i^\infty \exp[-z_i e \varphi(y)/k_B T - W_i(y)].$$

Here, a simple step potential model is adopted, where the interfacial additional potential W_i takes the form of a piecewise function with an interaction range of y_i^* for component i , that is

$$W_i = \alpha_i \theta(y - y_i^*), \quad \sigma_0 \equiv -\frac{d\varphi}{dz} = 0.$$

Then, the specific adsorption charge density at the interface can be further solved as $\sigma_\beta = \int_0^{y^*} \rho_e(y) dy$, assuming $y_i^* \equiv y^*$. It can be seen that the MPB model uses the interfacial additional potential to modify the Boltzmann distribution law, and its flexibility mainly lies in embedding various partition and adsorption effects, as well as ion correlation effects, into a unified form. This model is typically used for gas–water interfaces and polar oil interfaces where interfacial partition-induced charging and complex interfacial interactions cannot be ignored.

In addition, with the continuous enhancement of computational capabilities, particle-based simulation methods with high spatiotemporal resolution, represented by molecular dynamics (MD) simulations, have made significant progress. These methods have been successively applied to predict interfacial physicochemical properties such as interfacial charging^{129–131} and wetting mechanisms,^{132,133} as well as to capture electrokinetic phenomena such as droplet electrophoresis.^{134–136} However, due to the limited affordable spatiotemporal scales, relatively high ion concentrations, the still immature simulation methods for interfacial chemical reactions, and the excessive number of adjustable microscopic parameters in inter-particle potentials and chemical reactions, the computational results and mechanism analyses of interfacial charging or electrophoresis obtained from MD simulations need to be treated with caution.^{129,134,135} Some works even may use inconsistent macroscopic concepts.¹³¹

B. Case I: Non-polar oil

The charging mechanism of nonpolar oils is a fundamental issue in the field of interfacial science. For instance, in phenomena such as the arrangement of surface water molecules/hydrated ions,⁸⁹ the hydrophobic effect related to oil solubility and hydrodynamic slip,¹³⁷ and hydrophobic interactions with self-assembly behaviors,¹²⁰ the distribution of ions near the interface plays a crucial role.¹³⁸ In fact, the issue of water molecules and related ion distribution near nonpolar oil interfaces has been preliminarily reviewed by renowned scholars from perspectives such as the transfer free energy and the mean-field effective description of inhomogeneous refractive index, as well as molecular mechanism models for interfacial physicochemical properties.^{139,140} Around 2008, there was a surge of interest in the charging behavior of inert hydrophobic organic interfaces in the fields of interfacial physical chemistry and colloid electrokinetics, leading to the publication of special issues and reviews.^{119,141,142} In recent years, with the development of particle simulation and machine learning technologies, this fundamental issue has once again attracted the attention of the academic community.^{143–145}

Regarding the sign of the charge at nonpolar oil interfaces, there is currently a widespread consensus in the academic community that they carry a negative charge. Specifically, there are two prevailing views on the charging of hydrophobic interfaces: one suggests a negative charge, supported by droplet electrophoresis experiments, acid-base titration experiments, some molecular dynamics simulations, and ESI-MS characterization experiments; the other suggests a positive charge, with evidence including interfacial tension measurements of oil in concentrated salt solutions, some molecular dynamics simulations, and interfacial SFG spectroscopic characterizations. Additionally, water droplet electrophoresis experiments indicate that the oil-side surface

carries a positive charge (regardless of the original pH of the water droplet), which is consistent with the former mechanism, but the aforementioned phenomena may also originate from contact charging due to the historical dependence of pipette tips¹⁴⁶ or inaccurate electrophoretic modeling.¹⁴⁷ Overall, considering that interfacial tension measurements are still relatively scarce, the detection depth in spectral characterizations is uncertain, the limitations of molecular dynamics simulations are still significant, and the contact charging mechanism is stochastic, the academic community generally supports the widespread consensus that inert hydrophobic interfaces carry a negative charge.^{24,92} This is not only supported by numerous electrokinetic experiments represented by droplet electrophoresis,^{87,88,92,94,148} but similar behaviors are also observed in other inert hydrophobic interfaces, including organic solid and gas surfaces.^{87,102,149,150}

However, for the specific charging mechanisms of nonpolar oils, there is still no unified understanding,^{148,151} such as hydroxide ion adsorption or proton exclusion,⁹² specific adsorption of simple anions,¹⁵² and the influence of impurities.^{94,153} It is worth noting that for different types of solid–liquid–gas inert hydrophobic interfaces, a large number of electrokinetic experiments represented by droplet electrophoresis indicate that the effective interfacial potential exhibits a similar qualitative dependence on pH, and the isoelectric point is very close to the maximum effective interfacial potential. Therefore, particles including water molecules, hydroxide ions, and hydrated protons are likely the universal causes of charging. Here, we focus on the distribution structure of water molecules and related ions near nonpolar oil interfaces, and the two mainstream charging mechanisms mentioned in the literature are summarized below, which show a progressive relationship.

Mechanism I: Specific adsorption of hydroxide ions. This perspective posits that the negative charge of nonpolar oils directly stems from the specific adsorption of hydroxide ions at their interfaces. This adsorption is attributed to various physical interactions between the ions and the inert hydrophobic surface (such as image forces, dispersion forces, solvation forces, and hydrogen bonding), and is associated with a reduction in the fluctuation of the dipole moments of water molecules near the ions.¹⁵⁴ The view is primarily based on the microscopic observation of dielectric behavior near the interface, which differs from that of the bulk. Early spectroscopic characterizations and molecular dynamics simulations have both captured the oriented arrangement of interfacial water molecules resembling a hydrogen bond network.¹³⁹ These experimental and simulation evidence partially explains the contradiction in the constant dielectric model, where solute ions should be repelled by the hydrophobic surface, leading to the formation of an ion depletion layer.¹⁵⁵ Consequently, the mechanism of specific hydroxide ion adsorption was widely accepted in the early studies of charging at inert hydrophobic interfaces and used to establish various theoretical models.^{92,121,123} However, the main drawback of this view is the lack of clarity regarding the cause of specific hydroxide ion adsorption. If it is merely due to electrostatics-related physical adsorption, it becomes difficult to distinguish from common simple anions.¹⁵² Additionally, results from spectroscopic characterizations are often unreliable due to the inaccurate positioning relative to the Gibbs dividing surface.^{23,129} Early molecular dynamics simulation studies mostly failed to reflect the true charging mechanisms at the interface and could only approximate the macroscopic electrodynamic phenomena. For instance, some simulation studies added only a

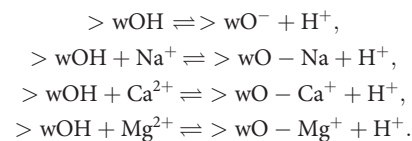
single hydroxide ion instead of an ion pair, which does not allow for the determination of specific adsorption behavior of protons and results in abnormally high ion concentrations around the surface.¹⁵⁶ Other simulations that do not include ions or charge transfer and focus solely on the electromigration of droplets can demonstrate the existence of dielectrophoresis and the significant role of the electric dipole dielectric effect of water molecules, but they struggle to establish a connection with real interfacial systems.^{28,134,135}

Mechanism II: Negatively charged hydrogen bonding network. This perspective partially inherits the mechanism explanation of the oriented arrangement of water molecules at the interface from the aforementioned view and involves the formation of a complex hydrogen bonding network. Specifically, it is believed that nonpolar oil interfaces preferentially adsorb a small number of hydrogen ions, which then electrostatically attract oppositely charged hydroxide ions and enrich them through a hydrogen bonding network to form a negatively charged hydroxide ion layer. This ultimately results in the compact layer being composed of hydrogen ions near the Gibbs dividing surface and the adjacent negatively charged hydrogen bonding network layer.^{87,148} This view is primarily based on new findings from molecular dynamics simulation techniques in recent years. The overlapping oscillatory distribution characteristic of hydrogen ions and hydroxide ions is easily understood from the density curve results near the inert wall obtained from traditional molecular dynamics simulations,¹⁵⁷ while the specific adsorption behavior of hydroxide ions is explained by their hydrogen bonding interactions.¹¹⁷ It is worth noting that, unlike simulation results that only add hydroxide ions, existing simulations that add hydrated hydrogen ions and hydroxide ions simultaneously or individually have found that the Gibbs dividing surface layer is more likely to adsorb hydrogen ions, thus becoming positively charged.^{155,158,159} This finding contradicts the conclusion of negatively charged interfaces observed in numerous droplet/bubble electrophoresis experiments which once sparked intense controversy. It was not until larger-scale simulations indicated that both hydrated hydrogen ions and hydroxide ions tend to adsorb to the interface, with both showing an oscillatory distribution characteristic and the adsorption density of hydroxide ions being greater.^{129,130} It should be noted that the aforementioned molecular dynamics simulations of inert hydrophobic interface charging can be divided into simulations with and without ions. The former simulates charge transfer through particle interactions and induced rigid motions (such as proton hopping), while the latter simulates charge transfer through the movement of electron clouds (such as electron hopping). In simulations with ions, often only one type of ion is added due to computational constraints, and the pH is either strongly acidic or strongly basic, making it difficult to rigorously extend the conclusions to neutral pH conditions. In simulations without ions, gas–water and oil–water interfaces are modeled as electron-polarizable and non-polarizable interfaces, respectively, showing differences in charging mechanisms and net charge distributions. Notably, the charging conditions near oil–water interfaces may be

completely opposite in different studies, which should be treated with caution. Additionally, considering that the relaxation time of electrons is generally much shorter than that of ions, although the two may show similar net charge distributions, there are essential differences in the characteristic time scales of the corresponding charging mechanisms.

The distribution structure of water molecules and related ions at the interface layer of nonpolar oils remains a frontier issue, and interface charging models can be inspired by the charging mechanisms derived from the aforementioned microscopic experimental characterizations and simulation results. It is worth noting that the charging mechanisms and quantitative modeling of inert hydrophobic interfaces, represented by nonpolar oil–water interfaces, are still not well-established. The current theoretical models largely draw from the charging mechanism descriptions of solid–liquid interfaces based on simple adsorption, employing GEL or MPB models to depict their physical mechanisms.

The GEL model is commonly used to describe the charging of nonpolar oil interfaces,⁹² general charging of inert hydrophobic interfaces,¹²³ and the interfacial adsorption of ionic surfactants.¹⁰³ Correspondingly, the MPB model is frequently used for the theoretical modeling of the dependence of interfacial tension on ion concentration, more so for gas–water interfaces¹⁶⁰ and less for oil–water interfaces.¹⁶¹ This is primarily because the potential of mean force for solute ions within the mixing layer at the gas–water interface is more complex, hence the charging at such interfaces is commonly described using the MPB model. In recent years, this model has been extensively used in the modeling of charging and interfacial tension at gas–water interfaces,^{161,162} as well as in the modeling of disjoining pressure of liquid films in air.^{163–165} Particularly, Schechter *et al.* explained the electrification of the gas–water interface through the difference in partition coefficients between protons and hydroxide ions, which can also be considered a degenerate case of the mean force field correction.¹⁶⁶ For clarity, here, we only provide the surface complexation reactions in an ETL model with weak adsorption sites and dehydration-related specific adsorption¹²²



Here, $> \text{wOH}$ represents the weak adsorption site for hydroxide ions OH^- near the inert interface.

It is worth noting that in various scenarios such as ion-tuned interfacial tension, electrocapillarity, droplet electrophoresis, and ion-mediated electrokinetic flows, the existing models for the charging of nonpolar oil interfaces currently show significant discrepancies compared with experimental results of effective interfacial potential,^{121–123,162} and there is still controversy regarding the saturated adsorption site density of hydroxide ions as shown in Table III. This primarily stems from the

TABLE III. Saturated adsorption density of hydroxide ions on inert hydrophobic interfaces.

	Marinova <i>et al.</i> ⁹²	Karraker and Radke ¹⁶⁰	Manciu <i>et al.</i> ¹⁶⁷	Creux <i>et al.</i> ⁸⁷	Leroy <i>et al.</i> ¹²¹
Hydrophobic phase	Xylene	Air	Air	Non-polar oil, air	Air
$\Gamma_{\text{OH}^-,\text{max}}$ (nm^{-2})	1/17	1/65	1/200	1/3	0.363–0.398

unclear understanding of the specific mechanisms of its adsorption behavior. Moreover, as analyzed above, mechanism models based on the hydrogen bond network structure of the interfacial layer and the differences in adsorption energy at hydrophobic interfaces still need to be established, which will provide a fundamental reference for the electrostatic interactions in the wettability model of nonpolar oils.

C. Case II: Polar oil

For the adsorption-induced charging mechanisms of polar oils, modeling is more commonly seen in the geological field and is based on single-sided adsorption-induced charging mechanisms, primarily using the more established multi-site electrical triple layer (ETL) model with dehydration-related specific adsorption.¹⁶⁸ The charging mechanisms include two types of actions: physical adsorption and chemical adsorption reactions. The former can be further divided into the effects of hydroxide/hydrated proton, halide/alkali metal ions, multivalent ions, and organic (impurity) ions. The latter mainly refers to the combination or ion exchange reactions between silicate/carboxylate/ammonium ions and hydroxide/hydrogen/high-valency metal/carbonate (hydrogen) ions. However, as previously mentioned, polar oil–water interfaces often exhibit behaviors characteristic of ITIES systems, where the partition effects of solute ions near the interface are often as non-negligible as specific adsorption. Below, the existing research on theoretical models is outlined on the order of GEL and MPB models.

Figure 7 summarizes the typical GEL models of spontaneous charging at oil–water interfaces due to imbalanced partition and specific adsorption. Compared with solid–liquid interfaces, the presence of a solvent mixing layer at liquid–liquid interfaces allows for a greater variety of possible ion distribution forms and induces a double-sided

charging coupling behavior between the two diffuse layers. The Verwey–Niessen model^{3,169} and the Verwey–van den Tempel model^{172,173} both consider the differences in partition coefficients of different ions, providing a double-sided diffuse layer similar to the Gouy–Chapman model, with the latter also accounting for the contributions of specifically adsorbed ions. These models allow for additional partitioning effects beyond hydration energy. For instance, Ohshima studied the charging at ion-selective membranes with a given bulk charge density and found that under certain conditions, the simple partition-based Donnan model can degenerate into a simple adsorption-based EDL model.^{176,177} However, for cases involving double diffuse layers with specific adsorbed ions or chemical reactions,^{178,179} the equivalence between the two remains unknown. The Gavach–Samec model^{170,171} further considers the interface potential jump contributed by solvent dipoles within the solvent mixing layer and allows for ions that penetrate the solvent mixing layer or form interfacial cation–anion pairs, which may provide additional effective contributions to the interface capacitance. The Krylov–Kakiuchi model¹⁷⁵ further takes into account the interfacial adsorbed ions and the double-sided Stern layers related to the finite volume effect of solute ions.

The GEL model is widely applied in the wettability modeling of polar oils, incorporating various interfacial effects to account for deviations from experimental data, such as multiple ion exchange and temperature dependence effects.^{168,180,181} It should be pointed out that, due to the extensive variations in the components of crude oil according to their sources, these wettability models are primarily significant in engineering applications. It is noteworthy that recent studies, when considering specific adsorption and possible contributions from the compact layer, have approximated the diffuse layer as a gel layer,⁸⁶ which is quite similar to the Donnan model of the diffuse layer from

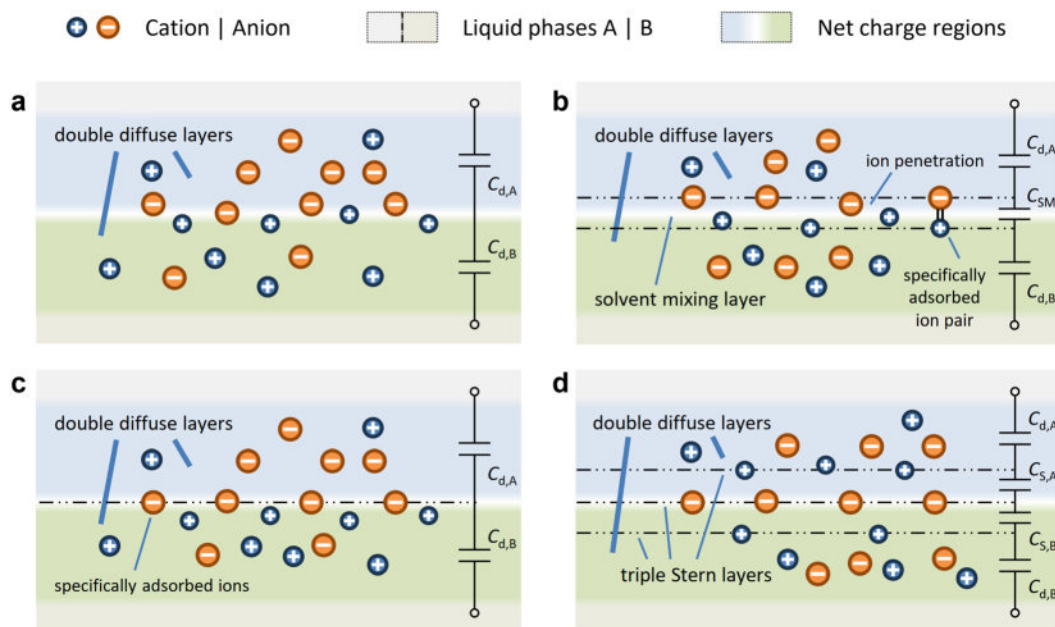


FIG. 7. Double diffuse layer models at two-liquid interfaces. (a) Verwey–Niessen model.⁴¹⁷⁰ (b) Gavach–Samec model.^{170,171} (c) Verwey–van den Tempel model.^{172,173} (d) Krylov–Kakiuchi model.^{174,175}

earlier times¹⁸² but differs from the Donnan model across an ion-selective membrane. In fact, there have historically been two forms of Donnan models: one used to describe the partitioning of ions between the bulk phase and the diffuse layer approximated as a surface phase, such as the adsorption-induced Donnan model mentioned in the monograph by Davies and Rideal,¹⁸² the other used to describe the partitioning of ions between two bulk phases, such as the Donnan potential and surface potential of a charged membrane used by Ohshima and Ohki.¹⁷⁷ The former is only found in early EDL models and was later extended to the field of geophysical chemistry and incorporated into related computational software; the latter was extended to describe the gel layer on the surface of solid particles to approximately capture cellular behaviors,^{183–185} referred to as soft particles. When referring to the Donnan model in this article, the latter is implied by default.

From the aforementioned GEL model, it is straightforward to derive the corresponding expression for the MPB model. Here, the single-particle interaction potential or multi-particle correlation effects serve as a simplified mean-field description of the complex interactions between solute ions and the solvent background near the interface, and can be used to describe effects such as the partial penetration of solute ions into the solvent mixing layer,^{174,186} effective adsorption (e.g., dehydration) or solvent polarization effects,^{187,188} image potential effects near the dielectric discontinuity,^{189,190} and finite volume and weak correlation effects between solute ions.^{43,191} It should be noted that the description of ion partition is based on the electrochemical potential equilibrium between two bulk phases that allow for material exchange, and the corresponding transfer free energy should be incorporated into the ion concentration equilibrium distribution to characterize the distribution potential across the two-liquid interface.^{176,177} Recent modeling work by Bier *et al.* has shown that to capture the variation of liquid–liquid interfacial tension with salinity, it must be treated as a double-sided diffuse layer and consider the differences in ion partition coefficients,¹⁹² which to some extent illustrates the necessity of incorporating ion partition behavior into the charging mechanisms at liquid–liquid interfaces.

In terms of model construction, one can either consider the particle statistical model based on the particle correlation functions to handle the interaction between solute ion plasmas and solvent electric dipole molecules;^{174,189,193} or one can adopt the system free energy functional model under the mean-field picture, considering electrostatic interactions, to portray the equilibrium free energy of the interfacial system as the sum of contributions such as electrostatic potential, chemical potential, and image correlation potential.^{194,195} Among these, the Ginzburg–Landau free energy form has been widely applied,^{196,197} which models the immiscible solvent interface as a dielectric background with inhomogeneous permittivity and correlates the permittivity with the local electric field-induced solvent polarization effects. This provides a powerful theoretical tool for explaining the complex interactions between solute ions and solvent molecules, as well as the correlation effects between solute ions, such as electro-induced phase separation,^{198,199} and the adsorption of ionic surfactants.^{196,197}

To this end, two core issues in the modeling of charging mechanisms at polar oil–water interfaces can be summarized. On one hand, the influence of partition behavior needs to be further clarified. For oil phases with high polarity (such as crude oil), ions near the oil–water

interface may exhibit significant double-sided partition behavior, which is markedly different from the charging mechanisms at solid–liquid interfaces. However, many current studies still employ models similar to or even more simplified than those used for solid–liquid interface charging, particularly the EDL model based on simple adsorption.^{86,122} While these may meet the requirements for engineering problems, their applicability in terms of physical picture for liquid–liquid interfaces remains unclear, necessitating a careful re-evaluation of the applicability of different models under oil–water interface conditions.^{174,200} On the other hand, there is still a lack of effective models for partition-adsorption coupling behavior. For ITIES systems represented by polar oils, partition-adsorption coupling is the most common form of ion distribution. However, existing interfacial charging models in various fields typically only describe the cases of simple adsorption or simple partition. For those with more complex solute–solvent interaction mechanisms within and around the solvent mixing layer, such as systems where weak electrolyte ionization and physicochemical interactions beyond dehydration effects play significant roles, the current understanding remains unclear. Considering that the quantitative description of interfacial charging mechanisms is the foundation for further studies on electrokinetic flows at liquid–liquid interfaces, the aforementioned limitations greatly restrict the reliability of subsequent studies on electrokinetic multiphase flows. Therefore, it is essential to extract the core ideas of existing mechanism models to connect and unify them.^{3,174,192,193,201} It is worth noting that the MPB model provides the possibility for a unified description of adsorption- and partition-induced interface charging, and it has the advantage of being easily incorporated into descriptions of interfacial electrokinetic flows and ion transport, thus serving as a key bridge to connect interfacial charging mechanisms with electrokinetic flow modeling. This has been applied to simple case studies of electrokinetic multiphase flows by Rotenberg *et al.*³⁰ and Huang and Wang.³¹

V. QUANTITATIVE PREDICTION OF TWO-LIQUID ELECTROKINETIC TRANSPORT

To quantitatively capture the typical characteristics and flow mechanisms of electrokinetic multiphase flows in typical application scenarios, it is necessary to establish the methods including theoretical analysis and numerical simulations, to obtain the solution, where the accurate analysis of transport behavior at liquid–liquid interfaces is essential. This includes interfacial physicochemical ion transport kinetics and ion transport coupled with multiphase interface electrokinetic flow. The former mainly refers to the analysis of interfacial ion transport kinetics, including the charging mechanisms of ion partition and adsorption and the ion transport kinetics dependent on the interfacial polarizability. The latter mainly refers to the analysis of the electromechanical and physicochemical multiphysical transport around the charged liquid–liquid interface, as well as the adsorption equilibrium and dynamic evolution around the three-phase contact lines. This section will introduce existing theoretical analysis and numerical simulation studies on electrokinetic multiphase flows, and summarize the state of the art and limitations. Here, we will take droplet electrophoresis and streaming potential as examples to describe the theoretical analysis schemes for macroscopic theoretical models of electrokinetic multiphase flows, and then briefly introduce numerical simulation methods based on mesoscopic numerical models. Specifically, regarding the macroscopic theory and numerical simulation of metallic droplets, one can also refer to other reviews.^{202,203}

According to the description of the phase interface, typical physical models for liquid–liquid multiphase flows can be categorized into mixture models,^{204,205} phase interface evolution models, and particle-based models, as shown in Fig. 8. Sharp interface models treat the interface as a zero-thickness geometrical surface, with the provision of interfacial conditions for various physical fields. They are often used for theoretical analysis to obtain formal theories and intuitive physical pictures. However, macroscopic equations typically only yield theoretical, approximate solutions under specific limiting conditions, and the applicability of these interfacial conditions often relies on verification through mesoscopic numerical simulations. Diffuse interface models, on the other hand, allow the interface to diffuse into a finite-thickness thin layer, requiring the implementation of phase separation and interfacial tension. They have a solid thermodynamic physical foundation and are easily coupled with complex interfacial kinetic behaviors. Although it is more difficult to obtain theoretical approximate solutions and macroscopic formal theories, they are suitable for numerical simulations studying the complex mass transfer mechanisms at multiphase interfaces. However, with the further development of numerical models and algorithms, the differences between the two branches of interface capturing models—sharp-like and diffuse-like interface models—are gradually diminishing, as both exhibit certain characteristics of charged diffuse interfaces. In addition, since particle-based models also inherently possess certain diffuse interface characteristics, they can also be considered as a type of diffuse interface model to some extent. Therefore, unless specifically indicated otherwise in the following text, interface capturing models and particle-based models will be collectively referred to as diffuse interface models. It should be noted that diffuse interface models often only represent a numerically determined finite thickness and do not necessarily represent the actual physical thickness. In practical simulations, it is

essential to ensure that this thickness is much less than the minimum characteristic scale of the key interfacial transport process, which is particularly important for problems such as electrokinetic multiphase flows where there are small interfacial characteristic lengths.

To this end, based on the different perspectives of interfacial transport description, the theoretical models of electrokinetic multiphase flows can be divided into two categories: macroscopic theoretical models based on sharp interface descriptions and mesoscopic numerical models based on diffuse interface descriptions. The former focuses on phenomenological descriptions and includes models such as the electrohydrodynamic model,^{206,207} electrokinetic models with adsorption-induced charging,^{29,56,57} and electrokinetic models with partition-induced charging,^{49,68} which are typically used for theoretical analysis and occasionally for numerical simulations. The latter emphasizes mechanism analysis and includes models such as the phase field model,³⁰ pseudo-potential model,⁹³ and coloring model,²⁰¹ depending on the type of mesoscopic numerical method, which are primarily used for numerical simulations. For simplicity, we refer to these as macroscopic and mesoscopic models, respectively. Their fundamental physical pictures have been mentioned in Sec. II, and this section will further introduce their theoretical analysis and numerical simulation methods as quantitative computational approaches. Noting that the quantitative simulation analyzing the key parameters is quite limited,³⁵ the results from the analytical and experimental studies can be found in the previous reviews or milestone studies.^{34,81} In particular, the transport mechanism of two-liquid systems under strong electric field has been widely studied within the scope of electrohydrodynamics,^{70,208,209} where the simultaneous charging of two-liquid interface are typically ignored and the effective interfacial transport is proved to share the similar form with the well-known Taylor–Melcher leaky dielectric model.^{29,49,207,210}

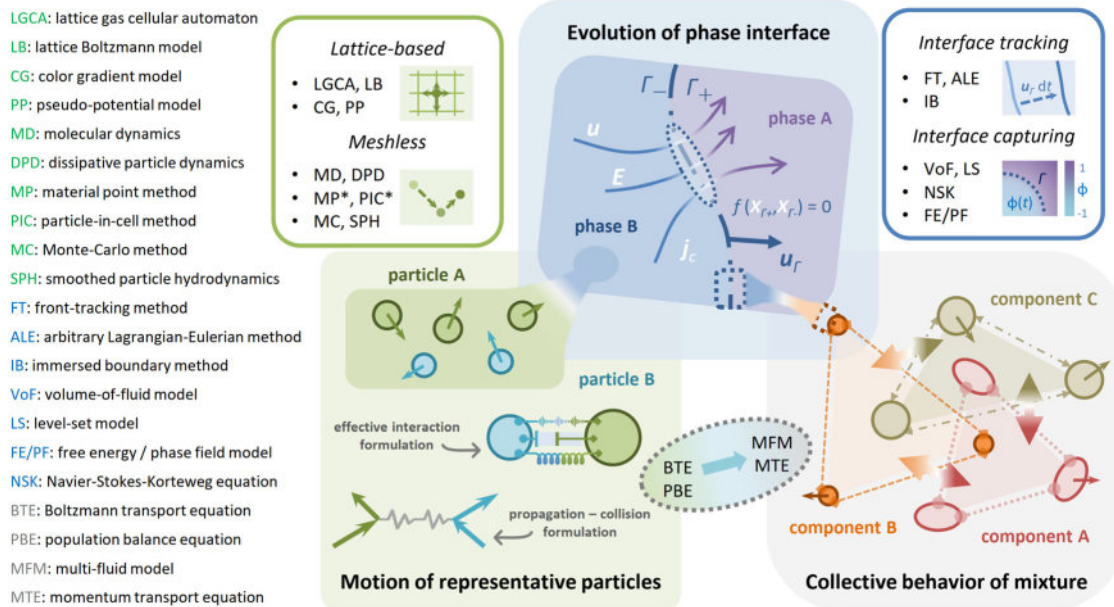


FIG. 8. Categories of physical models of multiphase flow. The perspectives could be classified into the evolution of the phase interface, the motion of representative particles, and the collective behavior of the mixture. It should be noted that, strictly speaking, the MP and PIC methods belong to Lagrangian–Eulerian methods and are not strictly meshless methods. Here, they are classified as meshless methods primarily because the information is stored in Lagrangian particles, whose motion is not constrained to a mesh.

Currently, there are relatively few studies on the theoretical analysis and numerical simulation of electrokinetic multiphase flows, largely due to the complexities introduced by the charging with solute ions, which include multiphysical, nonlinear, and cross-scale challenges. Specifically, multiphysics refers to the spontaneous charging at liquid–liquid interfaces and the coupled transport behavior between ions and fluids, which are typically difficult to simplify directly. Nonlinearity refers to the nonlinear transport phenomena, including the electric body force and the relaxation of interfacial charges, which pose challenges in theoretical analysis and numerical stability. Cross-scale refers to the scale disparity often present between the thickness of the solvent mixing layer, the thickness of the EDL, and the characteristic scale of flow in the system, leading to high computational costs. It is worth noting that with the increasing research interest in the fields of physico-chemical two-phase hydrodynamics and electromechanical two-phase hydrodynamics, as well as advancements in numerical simulation techniques, related research methods can be progressively extended to the study of electrokinetic multiphase hydrodynamics.

A. Analytical methods

The macroscopic models for electrokinetic multiphase flows have been briefly mentioned in Sec. II. It is evident that these models generally exhibit nonlinear characteristics, and the system geometry typically lacks high symmetry. In practice, for general electrokinetic flow problems, the main challenge in theoretical treatment often lies in the strong nonlinear transport behaviors triggered by a high surface ζ potential ($\zeta/V_T \gg 1$), a strong external electric field ($\beta_E \gg 1$), or a thick EDL ($\lambda_D/a \equiv 1/\kappa a \gg 1$), where ζ is the surface ζ potential, $V_T \equiv k_B T/e$ is the thermal voltage, $\beta_E \equiv Ea/V_T$ is the external field strength, λ_D is the Debye length, and a is the characteristic scale of the system. In the approximate solution methods based on small parameter asymptotic analysis, different leading-order theoretical forms and scopes of applicability will be obtained depending on the selected parameters. This implies that the macroscopic theoretical analysis often requires capturing the major physical process. On the basis of appropriate scaling assumptions for a specific dimensionless governing parameter, a combination of scaling analysis, dimensional analysis, and asymptotic analysis methods is employed for the solution. Among these, perturbation asymptotic analysis has received increasing attention in recent years due to its clear physical meaning and explicit result formulation.

Below, having reviewed the development of theoretical analysis of dielectric particle electrophoresis and summarized the general characteristics of various perturbation methods in electrokinetics, we will then provide a historical overview of droplet electrophoresis theory and introduce novel theoretical treatments on multi-interface electrokinetic flow that have emerged in recent years.^{211–213} Specifically, for the theoretical results of electrokinetic multiphase flow discussed in this section, which are often difficult to validate through experiments, it is necessary to establish mesoscopic numerical models to conduct numerical simulations to assess their applicability. This is the main focus of Sec. V B.

1. Scaling analysis and perturbation

Here, we briefly review the development of theoretical analysis for particle electrophoresis, summarizing the general characteristics of

various perturbation methods in electrokinetic problems. See Sec. S4 for the details of the historical development of asymptotic methods for solid–liquid interface electrokinetics.^{65,214,215}

The earliest theoretical models for particle electrophoresis were proposed in the early 20th century, including the Helmholtz–Smoluchowski model ($\kappa R \gg 1$) and the Debye–Hückel–Onsager model ($\kappa R \ll 1$). These models made linearized approximations of geometric boundaries and the electrostatic Poisson equation for the two limiting cases of thin and thick EDLs, respectively, and were only applicable to situations where charge convection relaxation could be neglected and the surface ζ potential was much less than the thermal voltage, i.e., $\zeta/V_T \ll 1$. It is worth noting that these two models have, to some extent, guided subsequent theoretical developments. Specifically, the Henry–Overbeek–Booth and O’Brien–White methods (referred to as the HOB and OBW methods, respectively) represent the early stages of classical treatment methods and theoretical development in electrophoresis. In a sense, they are similar in approach to the Debye–Hückel–Onsager theory, where the linearization treatment of the OBW method directly triggered the vigorous development of numerical solution methods for particle electrophoresis. The Frumkin–Levich–Dukhin method (FLD method), on the other hand, grasped the underlying physics in the charge relaxation effect under the condition of a thin double layer. This method was first proposed by Frumkin and Levich when solving for the electrophoresis of metallic droplets, combining the planar double layer model with electrocapillary theory. The FLD method largely inherits the theoretical assumptions of the Helmholtz–Smoluchowski model and has profoundly influenced a series of subsequent developments in colloid particle transport theory, especially as extended to the study of nonlinear non-equilibrium colloid transport phenomena by Dukhin and co-workers continues to influence the field to this day.^{38,45,52,216}

It is worth mentioning that Dukhin and Lyklema reviewed the importance of surface conduction theory based on recent experimental results around the turn of the century.^{217–219} By analogy with the electroviscous theory in electro-osmosis and streaming potential, they argued that for dielectric particles with a high surface charge density, the surface conduction contributed by the counterions enriched within the surface Stern layer and the diffuse layer is non-negligible. Although this view is essentially the same as the theories of Dukhin and Derjaguin and later Zukoski and Saville, it has attracted attention in the academic community. However, this conclusion is only strictly applicable under the condition of a thin double layer. Therefore, some recent works are questionable since they often fail to fully consider the charge relaxation effects induced by the finite thickness of the EDL.^{121,220} In recent years, Bazant, Yariv, and Schnitzer have extended the matched asymptotic expansion method to cases involving transient induced charging, strong external fields, and high surface charge densities.²²¹ Under these conditions, ion transport within the double layer is in a state of strong non-equilibrium,²¹⁶ often inducing diffusive boundary layers and nonlinear electrokinetic flow behaviors. These include nonlinear flows induced by the finite volume effect of ions due to high surface charge density,^{43,191,222,223} nonlinear electrokinetic flows or corrections induced by strong external electric fields at the surfaces of dielectric or metallic particles,^{45,224–228} and electroviscosity and non-equilibrium diffusive boundary layers induced at high Péclet numbers.^{105,229–232}

Based on the different small parameter perturbation strategies adopted, the perturbation approximate solution methods can be

divided into two categories: regular perturbation expansion based on the parameters of surface charge density ζ/V_T and/or external electric field magnitude β_E , and singular perturbation expansion based on the charge distribution scale λ_D/a with regional matching. For the scheme that takes ζ/V_T as the small parameter (i.e., the aforementioned HOB method), corresponding to the limit case of sufficiently small interfacial charge density, its leading-order approximate theory is the linearized Poisson–Boltzmann equation and the linear superposition form of the intrinsic electric field within the double layer and the induced potential by the external electric field. However, it is typically only applicable to cases where $\zeta/V_T \lesssim 1$ and $\beta_E \lesssim 1$. For the scheme that takes β_E as the small parameter (i.e., the aforementioned OBW method), corresponding to the limit case of not too strong external field strength, its leading-order approximate theory is a set of linear differential equations for the perturbations of physical fields (such as $\delta\phi$, $\delta\mu_i(c_i)$, $\delta\mathbf{u}$, δp , etc.), but it is typically only applicable to cases where $\beta_E \ll 1$. For the scheme that takes λ_D/a as the small parameter (i.e., the aforementioned FLD method), corresponding to the limit case of the thin double layer approximation, its leading-order approximate theory is the effective interfacial conditions for physical quantities near the charged interface (such as ϕ_s , c_s , \mathbf{j}_s , \mathbf{u}_s , $\boldsymbol{\tau}_s$, etc.), but it is typically only applicable to cases where $\lambda_D/a \ll 1$.

From the perspective of applicability, the regular perturbation expansion method based on the small parameter β_E (and possibly the additional small parameter ζ/V_T) is suitable for cases where the external electric field is not too strong and the induced polarization effect remains linear. Its advantage lies in the general form that can be extended to any spontaneous interfacial charge density and double layer thickness, but it typically requires numerical computation and is difficult to obtain a universal analytical solution form. Moreover, it is challenging to consider nonlinear polarization under strong external fields and the nonlinear dependence of effective mobility on the electric field. On the other hand, the singular perturbation expansion method based on the small parameter λ_D/R with regional matching is applicable to thin double-layer scenarios. Its advantage is that it can be extended to any spontaneous interfacial charge density and strong external field-induced polarization. Under leading-order conditions, it can provide a clearer physical picture and a more universal analytical solution form, but it is difficult to consider the charge relaxation behavior for any double layer thickness. Therefore, in practical applications, it is often necessary to select an appropriate method based on the characteristics of the problem and the main requirements, conduct a comprehensive evaluation in combination with existing theoretical analysis and experimental or simulation results, and attempt to obtain more widely applicable approximate solutions under more general parameter conditions.^{63,233,234}

From the perspective of application scenarios, the HOB and OBW methods were very commonly used in early colloid and interface science research, while the HOB and FLD methods have gradually been extended to studies in the field of physicochemical hydrodynamics. Among them, the leading-order theoretical form of the HOB method is typically concise and straightforward, making it easy to apply. However, its higher-order theory, similar to the OBW method, usually does not have a closed-form solution and is highly limited in its applicability to moderate external electric field strength β_E . Therefore, it is rarely seen in the interpretation of experimental results in practical applications. In contrast, the FLD method, based on the

assumption of a thin double layer, can reflect a clear physical picture through its effective interfacial conditions, and this assumption is not excessive for many liquid–liquid interface systems. Nevertheless, there is still a lack of numerical and physical experimental assessments of the accuracy of this model in electrokinetic multiphase flow studies.

2. Droplet electrophoresis

Similar to particle electrophoresis, the theory of droplet electrophoresis also features different perturbation methods. For the regular perturbation expansion based on small parameters ζ/V_T and/or β_X , the corresponding development of HOB and OBW methods is similar to that of particle electrophoresis. In the early stages, the HOB method was primarily adapted to the conductive dielectric droplet by Booth based on Henry's linear superposition method used for particle electrophoresis,⁶ and then extended to the dielectric and metallic droplets.^{7,235,236} This method focuses on mobile interface and ion partition effects (which can also be extended to induced polarization effects), and can effectively incorporate the charge relaxation effects due to diffusion and electromigration.³² Later on, the OBW method was introduced as a standard approach using linear perturbation under weak external electric fields, with related work mainly inheriting the treatment from O'Brien and White's semi-analytical and semi-numerical solutions for dielectric particle electrophoresis. In specific, Ohshima, Healy, and White provided semi-analytical and semi-numerical results for metallic droplet electrophoresis under weak external fields with polarization field corrections, and conducted a quantitative assessment of the Frumkin–Levich theory,^{63,234} although the applicability of these two theories may be quite different.⁵⁶ Baygents and Saville provided semi-analytical and semi-numerical results for the diffusiophoresis of dielectric droplets and bubbles based on weak-field perturbation theory, but did not specify the applicable parameter range or provide a closed-form theoretical solution.^{81,237}

In recent years, the HOB method is further modified into a degenerate form of the perturbation method based on the parameter β_X . Due to its simplicity, this method has been used for the approximate solution calculations of electrophoresis and diffusiophoresis of a series of dielectric and metallic droplets, and for studies on the influence of charge distribution characteristics on droplet electrophoresis, as well as the similarity between droplet electrophoresis and the electrophoresis of soft particles with hydrodynamic slip interfaces. For example, Pascall and Squires focused on the differences between liquid metals and conductive dielectric liquids, incorporating the induced polarization field and its influence on the interfacial potential of liquid–liquid interfaces through linear superposition under weak external fields, revisiting the electrokinetic flow behavior of the aforementioned two types of polarizable interfaces under weak fields. However, the restrictive applicable conditions on the magnitude of spontaneous and induced surface potentials are still too strong, and the related discussions are mainly limited to the assumptions of interfacial polarizability and the electrochemical potential of conductive dielectrics. This makes it difficult to directly apply to understanding the electrokinetic behavior of liquid metals such as Ga and Ge, where interfacial chemical reaction charging is essential,²³⁸ as well as situations where the surface charge density of conductive dielectric droplets is large enough that the internal electric field force cannot be ignored.^{29,49,81}

Moreover, the HOB methods have been also applied to studies such as the electrophoresis of gas bubbles,²³⁹ the interfacial flow of

fixed dielectric droplets,²⁴⁰ and the electrophoresis of water droplets with net charge,¹⁴⁷ while the OBW method has been extended in studies of droplet diffusiophoresis^{241–244} and droplet deformation.^{245,246} However, for the macroscopic theoretical analysis of adsorption-induced interface charging, only the Ohshima–Healy–White and Baygents–Saville methods^{63,81} have provided comprehensive semi-analytical and semi-numerical solutions, but they lack a closed-form approximate analytical form and are rarely seen in the interpretation of experimental results. For macroscopic solutions considering adsorption or partition-induced charging mechanisms, there is still a lack of sufficient evaluation of model accuracy based on physical experiments or numerical simulations.^{29,49,68}

For the FLD method based on the singular asymptotic expansion with spatial decomposition and matched asymptotic expansion using the small parameter λ_D/R , the early representative figures in the field of liquid–liquid interface electrokinetic flows were primarily Frumkin and Levich. During the 1940s to 1960s, they successively proposed the electrophoresis theory of mercury droplets and were pioneers in introducing the singular perturbation method into the study of electrokinetic flows. This theory originated from observations of the induced polarization behavior of metallic particles and droplets and employed modeling that combined an effective boundary layer approximation of the Helmholtz thin double layer with Lippmann’s theory. It considered the interfacial Maxwell stress gradient resulting from the redistribution of interfacial charges triggered by external field-induced polarization, and the correction coefficient obtained for small external field strength β_E was dependent on both the interfacial charge density and the dimensionless surface conductivity.²⁴⁷ This method was later extended by Levich to studies on the sedimentation potential and velocity of metallic droplets, the electrophoresis of metallic droplets with non-polarizable surfaces, and the electrophoresis of conductive dielectric droplets with double diffuse layers.³⁹

In recent years, the FLD method has been widely applied to the solution of droplet electrophoresis and diffusiophoresis under strong external electric fields or concentration gradients, as well as to the theoretical connection between classical electrohydrodynamics and electrokinetics under conditions of complex charging mechanisms and moderate external fields. Specifically, Baygents *et al.* incorporated the effects of interfacial linear adsorption kinetics on spontaneous adsorption-induced interface charging and interphase ion transport, noting that it could degenerate into the classical leaky dielectric model, but there exists a diffusive boundary layer due to the excess interfacial normal ion flux, as shown in Fig. 9(a).²⁴⁸ Schnitzer and Yariv have, in recent years, extended existing weak-field perturbation theories to strong external electric fields, focusing on the influence of ion transport within the EDL on the electrophoretic behavior of metallic droplets with spontaneous adsorption-induced interface charging under moderate external fields. They found that their results were similar to Levich’s predictions but differed from Ohshima’s predictions.^{56,249} They subsequently also investigated the nonlinear dependence of gas bubble electrophoresis on interfacial charge density under weak fields and on electric field strength under strong fields.⁵⁷ Ma *et al.*, under the assumptions of ideally polarizable and partially non-polarizable interfaces, respectively, provided the effective interfacial conditions for interfacial ion transport and potential distribution of droplets and vesicles under strong external fields.⁶⁸ However, the assumption of strong convection in the outer region in their study may lead to

theoretical failure in certain situations, such as interface instability under strong external fields.⁴⁹

In practice, singular perturbation concerning the thickness of the double layer can be jointly implemented with regular perturbation concerning the strength of the external field (or at least in an equivalent sense). For instance, Levine and O’Brien added the induced polarization field to Booth’s classical theory, obtaining results similar to Frumkin–Levich’s theory under the assumption of a thin double layer, and provided a condition for the validity of the boundary layer approximation treatment for charge conservation at the interface—namely, that the spontaneous surface charge density is very low and the drag coefficients of each ionic component are comparable.²³⁶ Furthermore, Ohshima, Healy, and White, using the theoretical form of linear perturbation of a weak external electric field, further provided a theoretical approximate solution for metallic droplet electrophoresis under the thin double layer assumption through the method of matched asymptotic expansion. This conclusion was later further simplified by Ohshima in subsequent articles, yielding an approximate solution with an error within 1%.^{63,234} Additionally, Yang and Stone studied the diffusiophoretic behavior of dielectric droplets, provided effective interfacial boundary conditions, and confirmed the correlation between the direction of droplet diffusiophoresis and the interfacial Maxwell shear stress.⁶⁷ Moreover, this method has also been successively applied by Sherwood in the analysis of gas bubble electrophoresis, although the perturbation approximation assumptions used in the latter’s article are unclear and difficult to analyze.⁸² It is worth noting that Schnitzer pointed out in his theoretical article on gas bubble electrophoresis that the order of implementation of regular and singular perturbations may have a significant impact on the validity and scope of the results, which may correspond to specific different experimental procedures and conditions.⁵⁷

Herein, theoretical studies on the electrophoresis of conductive dielectric droplets are compared.^{6,7,29,39,49,64,81} Booth, as well as Jordan and Taylor, almost concurrently investigated the electrophoretic behavior of dielectric droplets, obtaining results for various internal charge distribution scenarios. A typical correction coefficient for electrophoretic mobility due to interfacial slip is given by $[3\eta_{ex}(1 - \lambda) + 2\eta_{in}(1 - 2\lambda)]/(2\eta_{ex} + 3\eta_{in})$.^{6,7} However, the λ in these two studies carries different physical meanings, which are closely related to the different assumptions made about the polarizability of the liquid–liquid interface in the studies by Booth and Jordan. Booth assumed the interface to be completely non-polarizable, with λ being related to the conductivity ratio of the internal and external fluids; Jordan did not explicitly state the assumptions about interface polarizability and the definition of λ , but it can be inferred that the interface is partially polarizable and λ should be related to the permittivity ratio of the internal and external fluids. Schnitzer *et al.*, based on the assumption of a thermodynamically polarizable interface, incorporated the effects of spontaneous adsorption-induced charging through linear adsorption kinetics and assumed the existence of interphase ion transport and inhomogeneous charging.²⁹ They successfully provided the asymptotic matching conditions for the inner and outer solutions under moderate external fields and pointed out that double-sided adsorption in the case of symmetric electrolytes may lead to conductivity no longer being a well-defined material property. Mori *et al.*, also based on the assumption of a thermodynamically polarizable interface, incorporated the effects of spontaneous partition-induced charging through the partition coefficient and assumed the existence of

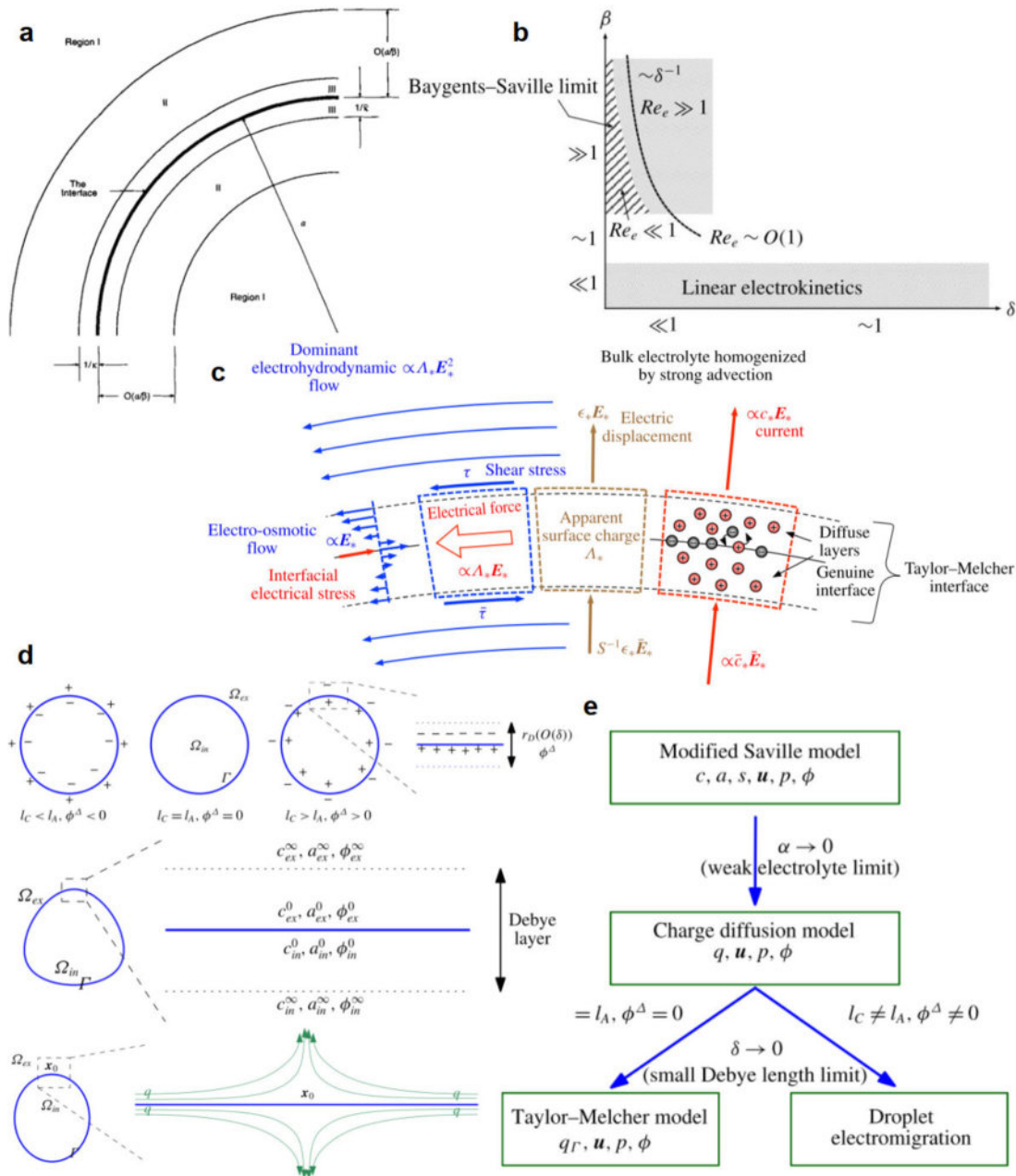


FIG. 9. Typical theoretical frameworks on conductive dielectric droplet electrophoresis. (a) Baygents and Saville's physical picture.²⁴⁸ Reproduced with permission from Baygents and Saville, AIP Conf. Proc. **197**, 7–17 (1990). Copyright 1990 AIP publishing. (b) and (c) Schnitzer and Yariv's physical picture.²⁹ Reproduced with permission from Schnitzer and Yariv, J. Fluid Mech. **773**, 1–33 (2015). Copyright 2015 Cambridge University Press. (d) and (e) Mori and Young's physical picture.⁴⁹ Reproduced with permission from Mori and Young, J. Fluid Mech. **855**, 67–130 (2018). Copyright 2018 Cambridge University Press. Both pictures focus on the interfacial regions around a charged two-liquid interface under an external field. Here, $\delta \equiv \lambda_D/a$ is the characteristic thickness of the electrical double layer, $\beta \equiv \beta_E := E_\infty a/V_T$ is the characteristic strength of the external electric field, $\alpha \equiv c/s$ is the characteristic strength of weak electrolyte ionization, and $\phi^\Delta \equiv \phi_{in,\infty} - \phi_{ex,\infty}$ is the interphase distribution potential induced by spontaneous imbalanced ion partition.

interphase ion transport. They found that the theory of electrokinetic multiphase flows degenerates into the classical leaky dielectric model under weak electrolyte conditions. They also provided effective interfacial conditions that include the convection of interfacial charges and

possible conditions for the existence of geometrical singularities and interfacial instabilities.

Here, a brief comparative discussion is provided for the two milestone articles by Schnitzer and Yariv²⁹ and Mori and Young.⁴⁹ The

former assumes a spontaneous adsorption-induced charging mechanism in strong electrolyte solutions, where, at the leading order, the charge is completely shielded by the diffuse layer. The latter assumes a spontaneous partition-induced charging mechanism in weak electrolyte solutions, where even at the leading order, there still exists a space charge layer beyond the diffuse layer. This suggests that the ion distribution state in the case of partition-induced charging may be more susceptible to the influence of induced charges from the external field compared with adsorption-induced charging, which may be a key reason for the significantly different scales of electrophoretic mobility observed. However, as pointed out in Bazant's commentary article, the direct matching of inner and outer solutions by Schnitzer may rely on assumptions of a single symmetric electrolyte and the Walden rule. In more general conditions, the violation of these assumptions may lead to the failure of direct matching and the emergence of a space charge transition layer, which could result in different behaviors in spontaneous adsorption-induced charging and two-liquid electrokinetic flow.²¹⁰

3. Multi-interface configurations

The theoretical analysis methods for electrokinetic multiphase flows with solid wall constraints in multi-interface configurations typically depend on specific geometric conditions and flow setups. Here, we primarily focus on the analytical solution methods for typical systems. Theoretical studies widely used in electrokinetic convection and interface instability, such as linear stability analysis and scaling analysis, will not be the focus of this article. Examples include two-liquid parallel flow instability,^{12,250} interface instability in liquid films and bridges,^{251,252} instability in electrokinetic displacement,²⁵³ interface instability of elastic semi-permeable membranes,^{254,255} electrochemical and flow instability at non-polarizable interfaces,^{256,257} and oscillation effects in gas bubble rising dynamics.^{258,259}

Two-liquid parallel electro-osmosis and streaming potential, as the simplest quasi-one-dimensional electrokinetic flow phenomena, typically rely on the linear characteristics of the problem for their solutions. Therefore, they often utilize the Debye-Hückel assumption to simplify the original problem into a linear Poisson-Boltzmann equation for solution.²⁶⁰ In recent years, Huang *et al.* incorporated the potential jump effect induced by the finite thickness of the solvent mixing layer into the macroscopic interfacial conditions of two-liquid parallel electroosmosis flow. They provided a semi-empirical correction based on diffuse interface numerical simulations, which is expected to offer a fundamental strategy for coarse-grained upscaling from diffuse interface models to sharp interface models in the numerical simulation of electrokinetic multiphase flows based on macroscopic theories.³¹ Additionally, this work extensively employed non-dimensionalization techniques, thereby effectively identifying the physical significance of key governing parameters, which will aid in the understanding of the physical mechanisms and the development of quantitative control methods for two-liquid electroosmosis flow. Particularly, Ganchenko and Demekhin transformed the two-liquid electroosmosis flow into a single steady-state Ginzburg-Landau equation through variable substitution, thereby obtaining an analytical solution that is not dependent on the assumption of low surface charge density.²⁵⁰

For electrokinetic flow problems with complex geometries and mixed boundary conditions, the most common approach is based on the thin double layer approximation, applying the Smoluchowski slip velocity boundary condition to the outer region flow, which is the

traditional boundary layer method in electrokinetic flows. For example, in the study of gas bubble electrophoresis within a rotating cylindrical tube, Sherwood, assuming a no-slip condition at the gas-liquid interface and using the boundary layer method, provided a quantitative expression for the electrophoretic mobility of the gas bubble.⁸² For electrokinetic flow phenomena over inhomogeneously slipping surfaces, Squires utilized the Lorentz reciprocal theorem to simplify it into two linear flow problems under simplified boundary conditions for solution,²¹² a method widely used in the Stokesian flow regime with linear flow characteristics.²¹¹ For electroosmosis or streaming potential at liquid-infused surfaces, where fluid flow is coupled with charge transport, the transport coefficients are typically studied using the linear constitutive relations of non-equilibrium thermodynamics,^{110,212,261} and the effective slip length will have tensor forms in anisotropic surface conditions.¹¹¹ Particularly, for cases of inhomogeneous charging, inhomogeneous slip, or finite curvature, the surface conduction effect induced by inhomogeneous electroosmosis is typically non-negligible when the surface charge density is high, requiring a surface conduction correction considering the slip-induced convection effect,^{64,121} while the physical mechanism and theoretical treatment of ion concentration polarization on both sides are still not well understood.

The thin-film flow near a rigid wall typically involves complex effects such as hydrodynamic coupling across multiple interfaces and coupling of surface and interfacial interactions. Depending on the complexity of the problem at hand, two strategies are commonly employed, i.e., scaling law correction or governing equation modification.²¹¹ For instance, in the case of streaming potential around a bubble moving inside a capillary, if the characteristic size of the bubble is significantly smaller or larger than the capillary radius, then typically only one region, either the finite-curvature segment or the planar liquid film segment, will dominate. In such scenarios, conventional computational approaches can be applied; that is, first solving for the flow field distribution of the two-liquid flow, followed by calculating the upstream and downstream streaming potentials through the balance of convective and conductive currents.^{112,262,263} However, when the characteristic size of the bubble is comparable to the capillary radius, the flow behaviors in the finite-curvature and planar liquid film segments become deeply coupled, making the direct solution of the flow field exceedingly complex. In these cases, scaling analysis and dimensional analysis are initially utilized to propose possible scaling law behaviors of the bubble interface flow. Subsequently, numerical solutions are employed to quantitatively confirm the relevant scaling laws and to determine the specific dimensionless pre-exponential factors, thereby also providing the scaling laws and quantitative pre-exponential parameters for the streaming potential.^{264,265}

However, for electrophoresis of bubbles or droplets within a capillary, the fluid flow is induced by ion transport driven by an external electric field, leading to a strongly coupled behavior between the ion transport and fluid flow. To establish a quantitative correlation between bubble mobility and ion concentration, Takhistov employed a long liquid film approximation and accounted for the relative slip at the gas-liquid and solid-liquid interfaces, thereby obtaining a Bretherton film equation modified by interfacial charging effects. This film approximation leverages the disparity in scaling along different directions to significantly simplify the governing equations and can also couple with more complex nanoscale interfacial interactions.²¹³

The study based on this equation examined the limiting cases under high and low concentration conditions, finding that the former behaves similarly to an uncharged bubble, while the latter, due to a reduced screening effect, results in a continuous decrease in the film thickness between the oppositely charged gas–liquid and solid–liquid interfaces down to the nanoscale.²⁶⁶ This approach has also been applied to studies on the interfacial stability and wetting dynamics of electrolyte solution films.^{267,268}

B. Numerical methods

The multiphysical, nonlinear, and cross-scale characteristics of electrokinetic multiphase flows pose numerous challenges for numerical simulation methods. These challenges include the accuracy of physical modeling for multiphysical transport at the interface layer, the numerical stability of multiphysical nonlinear coupling at the interface, and the resolution accuracy and computational cost associated with the thin diffuse layer at the interface. Although meshing techniques have made significant progress, the movement of charged liquid–liquid interfaces leads to a large sweeping area of the interfacial diffuse layer to be resolved during the system evolution. This places high demands on the computational accuracy, stability, and cost of adaptive refinement multigrid techniques.³¹ This section will focus on the accurate capture of the multiphysical transport characteristics at the interface layer, which is a necessary condition for the numerical model to effectively describe and accurately solve the processes of electrokinetic multiphase flows.

For numerical simulation methods based on sharp interface models, they typically rely on the interface conditions with discontinuous physical quantities in macroscopic theories, or require matching asymptotic expansion methods to provide reasonable effective boundary conditions. This implies that it is difficult to capture the interfacial non-equilibrium transport behavior under general conditions, and it is challenging to bottom-up account for the solvent mixing effects and complex kinetic transport behaviors at the liquid–liquid interface. In contrast, diffuse interface models adopt a continuous distribution of material properties and physical field quantities across the interface, thus potentially incorporating the interaction between solute ions and solvent background fluid through a bottom-up approach by correlating the interfacial physicochemical properties with the solvent phase fraction. This is essential for capturing complex charging mechanisms and strong non-equilibrium transport conditions in electrokinetic multiphase flow behaviors and also aids in providing effective modification correlations for sharp interface models. Therefore, this section mainly focuses on the study of numerical simulation methods based on diffuse interface models for electrokinetic multiphase flows. Particular attention will be given to the analysis of interfacial charge distribution and transport behavior in electrical matching conditions, as well as the limitations of current numerical simulation studies.

1. Physical models in simulation

Electrokinetic multiphase flows are typical multiphysical multiphase transport problems, whose numerical simulation methods can be categorized into three types based on the underlying multiphase interface models: the lattice Boltzmann method (LB method or LBM), the volume-of-fluid-model-based finite volume method (VoF-FVM), and the finite element method (FE method or FEM), which has been

briefly introduced in Sec. S5. It is worth noting that several particle-based microscopic or mesoscopic numerical models have been applied to the simulation of electrokinetic multiphase flows, such as molecular dynamics (MD),^{269–272} dissipative particle dynamics (DPD),^{273,274} and smoothed particle hydrodynamics (SPH).²⁷⁵ Compared with these particle simulation methods, PF-FE (phase-field-model-based finite element) and LB methods can solve the systems with computational domain sizes closer to actual system dimensions, thus enabling them to be used for electrokinetic multiphase flows. Moreover, PF-FE and LB methods have smaller momentum calculation errors near solid interfaces compared with the SPH method and do not require dealing with the calibration of potential functions, which may introduce additional errors and artificial assumptions, as is the case with MD and DPD methods.

The VoF-FVM encompasses original, algebraic, and geometric methods and is widely utilized for mass transfer across liquid–liquid interfaces, being available in open-source or commercial software such as OpenFOAM and ANSYS Fluent. The original method directly discretizes the VoF model using the finite volume method to discretize the conservative equations, where interfacial tension is typically described by a continuous surface force model.^{276,277} Yet under unstructured mesh conditions, the interface is prone to strong phase diffusion and struggles to capture sharp interfaces. In contrast, geometric and algebraic methods (also known as pseudo-VoF methods) have been specifically improved. The former explicitly reconstructs the interface, while the latter employs strategies such as constructing special surface interpolations and adding artificial convection terms (to inhibit phase diffusion) to control phase evolution, both of which share similarities in their implementation processes.^{278,279} The related studies primarily focus on the construction of transport formats for multiphase interfacial transport of uncharged components. The single-scalar form eliminates interfacial discontinuities through variable substitution and redefinition, whereas the double-scalar form requires explicit reconstruction through the analysis of interfacial conservation equations. This model has been extended to compressible media.^{278–280} However, the single-scalar form exhibits poor interfacial conservation properties, and the double-scalar form incurs high reconstruction costs. Currently, VoF methods are seldom used in electrokinetic multiphase flow studies. Even when applied, simplifications of varying degrees are made to interfacial motion or charge transport behavior, which may significantly impact the results. For example, it is assumed that the droplet interface can deform and slip but that the interfacial potential is uniformly distributed.²⁸¹ Additionally, a few numerical simulation studies on two-liquid electrohydrodynamics have employed the VoF-FVM method, considering ion diffusion behavior and systematically discussing the influence of interfacial ion polarizability.^{282–284} However, these studies are not suitable for cases where charge relaxation is non-negligible and interfacial charging is inhomogeneous under broader parametric conditions, thus making it difficult to intuitively verify phenomena such as droplet electrophoresis theory and two-liquid streaming potential under general conditions.

The majority of current numerical simulation research on electrokinetic multiphase flows focuses on PF-FE methods and LB methods. The FE method employs the finite element method as a solver, facilitating adaptive mesh refinement iterations. It describes interface evolution based on level set or phase field models, with a solid foundation for diffuse interfaces, and is available in commercial software such

as COMSOL. The level set model has relatively poor conservation properties, with the interface thickness being numerically prescribed and lacking a robust thermodynamically physical foundation. In contrast, the phase field model has a better equilibrium/non-equilibrium thermodynamic physical basis, but typically requires a larger computational effort to resolve the interface. Since multiphase flow transport is usually convection-dominated, it is necessary to modify traditional finite element formats with artificial upwind diffusion to enhance stability. In addition, the finite element method requires implicit iteration to solve the fully coupled multiphysical field equations across the entire domain, which typically demands a high amount of memory. The LB method uses distribution functions with a mesoscopic foundation, evolving according to the mesoscopic Boltzmann equation. It is available in commercial or open-source software such as PowerFLOW, OpenLB, and Palabos, though more often it involves self-coded programs. This method has the advantages of a quasiparticle picture that naturally captures complex interfaces, a mesoscopic foundation that easily couples with multiphysical fields, and local explicit iterations that are conducive to parallel computing. However, for multiphysical multiphase flow processes, the increased number of required distribution functions leads to relatively higher memory costs. Compared with VoF-FVM, although FVM has better flux conservation properties, PF-FE and LB methods do not require special treatment of interface meshes and possess a better thermodynamic and mesoscopic foundation. They are more flexible and concise in handling the complex multiphysical coupling processes of mass transfer at charged interfaces. Here, we focus on explaining the phase field model and LB model involved in PF-FE and LB methods, both of which serve as diffuse interface mesoscopic numerical models and are relatively more suitable for the quantitative and accurate description of electrokinetic multiphase behaviors. A brief introduction to the basic ideas of how the phase field model and LB model describe multiphase interfacial flows with mass transfer is given in Sec. S5.

To describe the adsorption and partition behavior of ions near the liquid–liquid interface, it is not only necessary to apply the Nernst–Planck equation to describe the ion flux (including diffusion) within the diffuse layer, but also to characterize the interaction between solute ions and solvent molecules on both sides, as well as the production or consumption rate of interfacial solute ions, corresponding to the charging mechanisms and ion transport behaviors of interfaces with different polarizability characteristics. Different treatment schemes for

the equilibrium distribution and non-equilibrium transport of interfacial ions delineate different types of mesoscopic numerical models. Among the models shown in Table IV, the pseudo-potential model provides a direct characterization by explicitly constructing the interaction between two-phase solvent molecules and solute ions.⁹³ Both the phase field and coloring models add corresponding modified free energy constraints and reaction source terms near the interface to the Nernst–Planck equation or Maxwell–Stefan equations, depending on whether the interface is prone to be polarizable or not. The difference between the phase field and coloring models is that the former explicitly constructs a free energy form containing concentration gradients and reflecting the characteristics of components across the interface,^{30,31} while the latter specifies corresponding activity coefficient fitting expressions for the distribution of interfacial solutes in equilibrium,²⁰¹ but this has not yet been extended to the electrokinetic transport characterization at multiphase interfaces. It is worth noting that Huang *et al.*, by introducing the reference chemical potential $\mu_i^0(\phi)$ of ion i and the potential energy distribution $\Delta g_i(\phi)$ near the solvent mixing layer, provided a unified quantitative effective description of the specific physicochemical interactions between solute ions and solvent (including two charging mechanisms of imbalanced partition and specific adsorption), and reduced the complexity of analyzing the nonlinear multiphysical interactions in the interfacial solvent mixing layer in the original phase field model. Therefore, it is an important approach to characterize the charging mechanism (ion equilibrium distribution) and physicochemical kinetics (ion non-equilibrium transport) of thermodynamically polarizable interfaces.^{30,31} In particular, the saturated adsorption density of hydroxide ions on inert hydrophobic interfaces in numerical modeling is shown in Table III, which shows significant discrepancies.

In fact, the practice of embedding the interaction potential between particles and the solvent background or solid interfaces into particle transport equations is not uncommon. In recent years, this approach has been adopted in some studies of neutral-component transport in single-phase micro- and nano-flows, and its extensive application in transport modeling of colloidal particle systems and electrolyte solution systems is well-established, albeit typically confined to systems with a singular solvent background. In the context of liquid–liquid multiphase interfaces, modified interaction potentials have been introduced to model the interfacial transport behavior of neutral components.²⁰¹ Similarly, in the modeling of the equilibrium charging

TABLE IV. Comparisons of mesoscopic models for two-liquid interface electrokinetic transport.

	Phase field	Pseudo potential	Color gradient
Representative scholars	Rotenberg <i>et al.</i> ³⁰ and Huang and Wang ³¹	Rivas <i>et al.</i> ⁹³	Riaud <i>et al.</i> (mass transfer) ²⁰¹
Characteristics	Mean-field free energy formulation	Microscopic inter-particle forces	Prescribed ionic distribution
Charging mechanism	Simple partition; partition–adsorption coupling	Phenomenological conservation; simple partition	Adaptive to the prescribed distribution
Applications	Ionic distribution; two-liquid electro-osmosis	Droplet electrophoresis; ionic distribution, droplet deformation	Interphase mass transfer

mechanisms in ITIES systems, complex interaction potentials have been incorporated into the Poisson–Boltzmann equation, yet this has been restricted to modeling the equilibrium ion distribution structure near the interface.^{196,197,285} Electrokinetic transport systems at charged liquid–liquid interfaces still lack mesoscopic perspective-based diffuse interface modeling.³⁰ The work by Huang *et al.* considers both the partition of ions on either side of the interface and their adsorption behavior toward the interface, further introducing the non-equilibrium transport of charged components near (partially non-polarizable) liquid–liquid interfaces. This description can be regarded as a regular perturbation form of the more complete Poisson–Maxwell–Stefan equations under weak external field conditions. Such an approach can conveniently be extended to research on various complex micro- and nano-scale liquid–liquid interface electrokinetic transport mechanisms, such as inhomogeneous interface charging, confined interfacial interactions, electrochemical non-equilibrium transport, and strong external field effects.³¹

2. Mesoscopic simulation studies

Despite the aforementioned breakthroughs in the physical models of electrokinetic multiphase flows in recent years, simulation studies targeted at specific systems remain largely confined to scenarios such as the deformation and motion of dielectric or leaky dielectric droplets^{286–290} and electrowetting.^{291–293} Nevertheless, only a fraction of these studies have taken into account the effects of ion diffusion behavior,^{30,93,290,294,295} with representative numerical simulation studies illustrated in Fig. 10. For the most common phenomenon of droplet electrophoresis, there is still a lack of quantitatively accurate simulations. The accuracy of various simplified approximation methods awaits evaluation, making it difficult to intuitively verify droplet electrophoresis theories under general conditions. Below, in conjunction with existing numerical simulation research, we discuss and analyze the potential challenges faced.

On one hand, it is challenging to simultaneously depict multiple physical behaviors such as spontaneous charging and non-equilibrium ion transport at liquid–liquid interfaces, especially descriptions of spontaneous adsorption-induced charging and ion transport along the interface are currently very scarce. For charged liquid–liquid interfaces, there are two noteworthy, distinct features. First, the thickness of the two-phase solvent mixing layer may be comparable to that of the diffuse layer, which can regulate the capacitive charging of the diffuse layer and the viscous shear stress; thus, the diffuse interface effects may significantly influence the charging and electrokinetic behavior within the diffuse layer. Second, in addition to adsorption-induced charging similar to that at solid–liquid interfaces, immiscible electrolyte solution interfaces also produce ion partition effects within the two-phase solvent, which is similar to the partition-induced charging behavior of so-called soft particles due to the presence of polyelectrolyte gel layers, but obviously the net charge layer at the liquid–liquid interface will produce a shear strain rate under Maxwell’s shear stress leading to flow, which is quite different from the behavior of solids resisting shear through elastic deformation. Despite the potentially critical role of solvent mixing and ion partitioning behavior in the charging and electrokinetics at liquid–liquid interfaces, current research still rarely focuses on these aspects. This may stem from the lack of a unified description of the two charging mechanisms in current diffuse interface models, or due to the difficulty in the literature review brought about by the

interdisciplinary characteristics of electrokinetic multiphase hydrodynamics.

In the numerical simulation of electrohydrodynamics, studies have compared different interfacial charging mechanisms, often employing a qualitative description of the motion of spontaneously charged droplets based on interfacial charge conservation models.^{288,296,297} However, due to the absence of shear stress from electrokinetic transport within the diffuse layer, the induced droplet motion still falls within the classical electrohydrodynamics. There remains an essential difference from droplet electrophoresis within the scope of electrokinetic multiphase flows, which exhibits electrophoretic retardation effects, making it difficult to quantitatively and accurately describe the interfacial spontaneous charging kinetics. For cases of induced charging at partially non-polarizable or thermodynamically polarizable interfaces, Liu *et al.* and Luo *et al.* proposed LB numerical simulation schemes based on phase field models, yet these did not adequately consider the effects of spontaneous charging, as shown in Fig. 10(a).^{284,290} Regarding the spontaneous adsorption-induced charging at thermodynamically polarizable interfaces, some research has directly prescribed the potential distribution within the electrolyte solution based on electrochemical equilibrium assumptions and assumed the oil phase as a dielectric liquid, assigning the effective interfacial potential directly onto the isosurface of the phase parameter, as shown in Fig. 10(b).^{294,295} However, these approaches can only qualitatively capture droplet electrophoresis behavior and struggle to provide accurate quantitative predictive results, nor can they capture the tangential polarization of charge along the interface under an external field. For droplets with partition-induced charging, only a few studies have provided corresponding phase field or pseudo-potential model descriptions, as shown in Figs. 10(c) and 10(d),^{30,93} and there is still a lack of quantitative verification and mechanism studies on the influence of partition-induced charging mechanisms on the characteristics of electrokinetic flows.

In the aforementioned studies, the interfacial charging mechanisms (involving interfacial physicochemistry) and electrokinetic flows (involving electromechanical hydrodynamics) have been treated in a decoupled manner, thus making it difficult to discuss the complex coupling charging mechanisms, including partition and adsorption based on real material properties and charging mechanisms. Notably, Huang *et al.* recently adopted a quasi-equilibrium thermodynamic perspective to provide a unified descriptive framework for partition- and adsorption-induced charging.³¹ This approach considered the actual additional free energy parameters from solute–solvent interactions in practical ITIES systems and preliminarily discussed the novel electrokinetic behaviors triggered by the distinct charging characteristics of liquid–liquid interfaces through two-liquid parallel electroosmotic flows in microchannels, as shown in Fig. 10(e). Additionally, some phase field models have employed the Maxwell–Stefan equations, suitable for multiphysical multicomponent non-dilute solutions, and combined them with activity coefficients and source terms that reflect the characteristics of interfacial ion adsorption and partition, related to the additional interfacial free energy.²⁰¹ These studies also provide inspiration for further modifications of LB models. For instance, phase field and coloring models can easily be integrated with mean field modifications to describe various charging mechanisms such as imbalanced partition and specific adsorption, suitable for depicting the electrokinetic behavior of liquid–liquid interfaces that tend to be non-polarizable or polarizable. In contrast, the existing pseudo-potential

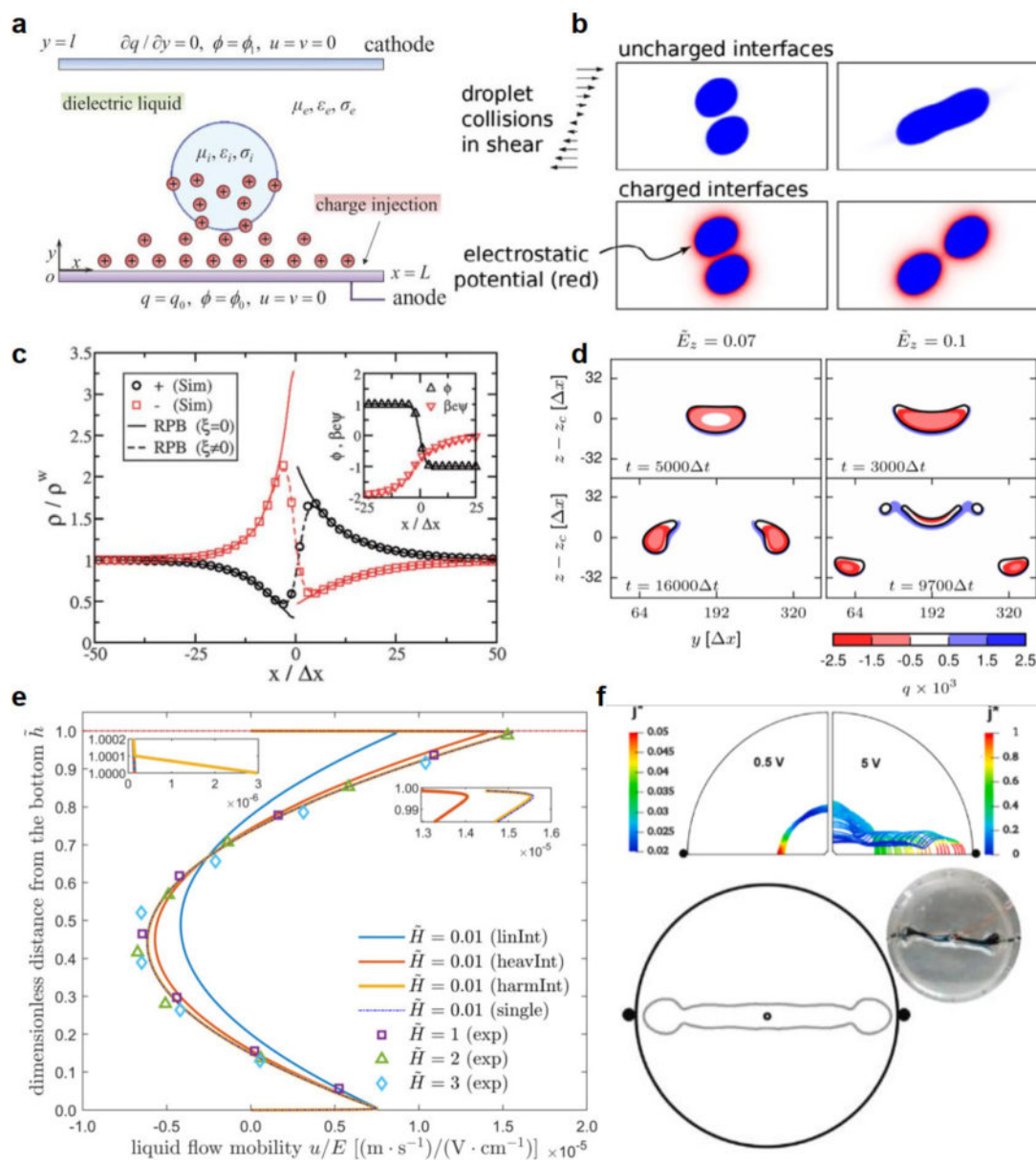


FIG. 10. Typical numerical methods on two-liquid electrokinetics. (a) Lattice Boltzmann (LB) modeling of two-phase electrohydrodynamic flows under unipolar charge injection.^{284,290} Reproduced with permission from Luo *et al.*, *Phys. Rev. E* **105**, 065304 (2022). Copyright 2022 American Physical Society. (b) LB simulations of charged droplet collisions in shear flow.²⁹⁴ Reproduced with permission from Shardt *et al.*, *Chem. Eng. J.* **302**, 314–322 (2016). Copyright 2016 Elsevier. (c) Distribution of ions at an oil–water interface as a function of their affinity for both solvents.³⁰ Reproduced with permission from Rotenberg *et al.*, *Faraday Discuss.* **144**, 223–243 (2010). Copyright 2010 the Royal Society of Chemistry. (d) Electrohydrodynamic deformation of droplets with a nonzero electric charge.⁹³ Reproduced with permission from Rivas *et al.*, *J. Chem. Phys.* **148**, 144101 (2018). Copyright 2018 AIP publishing. (e) Two-liquid parallel electroosmosis under large viscosity and permittivity ratios.³¹ Reproduced with permission from Huang and Wang *Phys. Rev. Fluids* **9**, 103701 (2024). Copyright 2024 American Physical Society. (f) Electrochemically generated Marangoni flow around a metal droplet in a basic electrolyte solution.²³⁸ Reproduced with permission from Karimi-Sibaki *et al.*, *Electrochem. Commun.* **155**, 107567 (2023). Copyright 2023 Authors, licensed under a Creative Commons Attribution (CC BY) license.

models are mainly applicable for bottom-up descriptions of imbalanced partition-induced charging and are only suitable for describing the electrokinetic behavior of systems with interfaces that tend to be non-polarizable. To extend them to specific adsorption-induced

charging behaviors, improvements in the design of pseudo-potentials by analogy with phase field models are required.

On the other hand, capturing the cross-scale nonlinear coupling between the deformation and movement of liquid–liquid interfaces

and ion transport is challenging. The computational cost for multi-physics processes with scale disparity across orders of magnitude remains high, and there is a lack of effective coarse-grained descriptions for nonlinear transport or cross-scale simulation schemes. Currently, only a few simulation studies have fully considered both interface motion and charge non-equilibrium transport,^{93,284,288,290,296,297} and simulations of droplet electrophoresis (rather than electrophoresis within the realm of electrohydrodynamics) are still limited to qualitative capturing of phenomena and lack quantitative verification.⁹³ As previously noted, interface deformation and nonlinear multiphysical transport are the main sources of difficulty in numerical simulations. To address this, numerous studies have simulated simple electrokinetic multiphase flow systems by assuming fixed interface positions and quasi-equilibrium states of adsorbed ions, but these methods are difficult to generalize to more general cases.^{298–300} Some research has incorporated the perfect conductor approximation along with electrocapillary effects to study the electrochemical Marangoni flow effects during the electrowetting process of metallic droplets, but it is challenging to directly extend these findings to the electrowetting mechanism studies of conductive dielectric droplets, as shown in Fig. 10(f).²³⁸

In practice, for multiscale systems with scale disparity, the common approach is to employ multiscale expansions based on spatiotemporal decomposition. This involves solving for effective interface conditions in the inner flow regions near the diffuse layers and then coupling these with the outer flow regions to significantly reduce computational costs. The unique challenge in electrokinetic multiphase flows is the strong nonlinearity of the potential and ion distributions near the diffuse layers, and the singular influence of the diffuse layer thickness as a perturbation parameter. Therefore, special singular perturbation methods, such as matched asymptotic expansions, are required. Some work has been attempted in this area, but the applicability to general scenarios remains unknown, and there are still few numerical solution applications based on such macroscopic effective theories.^{29,49,56,57,67,68}

In addition, for the wetting dynamics behavior of strong electrolyte solution interfaces, the current work focuses on the description of ion-induced dynamic changes in wettability. Apart from the quasi-equilibrium phenomenological linear³⁰¹ and nonlinear models¹⁶ for transient responses (see Sec. IV C), related numerical simulation methods predominantly adopt the instantaneous response of local wettability to concentration, with insufficient consideration of the relaxation effects brought about by ion non-equilibrium transport observed in experiments.^{16,301,302} At present, only a few studies have conducted modeling on interfacial adsorption kinetics, carrying out qualitative simulation research by artificially controlling the rate of wettability change at different time steps.³⁰³ However, these studies still have significant limitations in terms of simulation accuracy and mechanism understanding, and the current research is mainly limited to the local, simple scenario of single droplet wetting dynamics. The impact mechanism of ion transport-induced wettability changes on multiphase displacement within porous media remains unclear.^{16,301}

VI. SUMMARY AND PERSPECTIVES

Electrokinetic multiphase hydrodynamics (EKmHD) at liquid–liquid interfaces has emerged as a quintessential interdisciplinary domain, bridging nonequilibrium thermodynamics, colloidal science,

electrochemistry, and microfluidic engineering. Its defining feature, i.e., multiphase soft diffuse interfaces coupled with ion transfer dynamics, introduces unique multiscale challenges that demand integrated experimental-theoretical frameworks, which underscores the capacity to transcend conventional cross-disciplinary overlaps. This establishes novel paradigms for interfacial transport analysis and positioning EKmHD to address fundamental questions in electrochemical energy conversion and programmable soft matter design, while driving innovations in microfluidic diagnostics and colloidal assembly. Compared with the previous reviews integrating the physical models and transport mechanism,³⁵ this review focuses on the fundamental physics and advanced methodologies of EKmHD, which complement each other.

Two interdependent methodological challenges articulated in EKmHD are stressed throughout this review, with the former pertaining to experimental quantification of interfacial charges and the latter addressing multiscale modeling of nonlinear electro-chemo-mechanical coupling transport. For the former, overcoming limitations in droplet electrophoresis and streaming potential measurements requires synergistic innovations. Microfluidic platforms integrating *in situ* potentiometry could reconcile interfacial stability concerns,²⁴ while enabling simultaneous mapping of ζ -potentials, pressure gradients, and velocity fields. Such systems must address scale-dependent charge heterogeneity through advanced interfacial instability control and purity processing protocols, which is a critical gap in current electrophoretic analyses. The latter challenge demands rigorous unification of molecular-scale charging mechanisms with continuum transport models. Polar/nonpolar oil systems exemplify this dichotomy, i.e., nonpolar interfaces governed by adsorption kinetics vs polar systems (with large organic ions) dominated by partition-dominated charging.^{30,31} Bridging these requires hybrid methodologies combining first-principles molecular dynamics and precise spectroscopic measurement of charge redistribution with phase-field simulations of hydrodynamic coupling.³¹ Recent advances in asymptotic expansion techniques^{29,57} and lattice Boltzmann implementations²⁹⁰ demonstrate promising pathways to overcome scale-separation barriers in predictive modeling.

Cross-disciplinary convergence will be catalytic. Single-molecule spectroscopic techniques from biophysics could resolve interfacial charge transfer dynamics, while active matter principles may inspire novel interfacial patterning strategies.^{9,304} The combination of machine learning and multiphase flow simulation is emerging, which demands efforts of both societies of computational physics and statistical physics if interfacial nonlinear charge transport is further incorporated.^{305,306} Concurrently, multiscale simulations must embed nonequilibrium thermodynamic constraints to achieve predictive capability across diverse flow regimes, particularly Onsager-type couplings including interfacial reactions and bulk transport.⁶¹ Realizing this potential necessitates sustained efforts in three aspects, including experimental platforms achieving subnanometer-resolution under flow conditions, theoretical frameworks unifying equilibrium interfacial thermodynamics with far-from-equilibrium transport physics, and computational architectures bridging molecular charge dynamics to macroscopic predictions.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) present the contents which may help readers understand the main text well, but are not significant

enough to be involved in the main text, including: some fundamental principles of electrokinetics (Sec. S1); general methods in experimental measurements of liquid–liquid interfacial charges (Sec. S2); methods of physical modeling (Sec. S3), theoretical analysis (Sec. S4), and numerical simulation (Sec. S5) for EKmHD.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Yunfan Huang: Investigation (equal); Validation (equal); Writing – original draft (equal). **Moran Wang:** Conceptualization (equal); Resources (equal); Supervision (equal); Writing – review & editing (equal).

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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