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Hui Zhao

University of Nevada, Las Vegas, hui.zhao@unlv.edu

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Diffuse-charge dynamics of ionic liquids in electrochemical systems

Hui Zhao*

Department of Mechanical Engineering, University of Nevada Las Vegas, Las Vegas, Nevada 89154, USA

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We employ a continuum theory of solvent-free ionic liquids accounting for both short-range electrostatic correlations and steric effects (finite ion size) [Bazant *et al.*, *Phys. Rev. Lett.* **106**, 046102 (2011)] to study the response of a model microelectrochemical cell to a step voltage. The model problem consists of a 1-1 symmetric ionic liquid between two parallel blocking electrodes, neglecting any transverse transport phenomena. Matched asymptotic expansions in the limit of thin double layers are applied to analyze the resulting one-dimensional equations and study the overall charge-time relation in the weakly nonlinear regime. One important conclusion is that our simple scaling analysis suggests that the length scale $\sqrt{\lambda_D^* l_c^*}$ accurately characterizes the double-layer structure of ionic liquids with strong electrostatic correlations where l_c^* is the electrostatic correlation length (in contrast, the Debye screening length λ_D^* is the primary double-layer length for electrolytes) and the response time of $\lambda_D^{*3/2} L^* / (D^* l_c^{*1/2})$ (not $\lambda_D^* L^* / D^*$ that is the primary charging time of electrolytes) is the correct charging time scale of ionic liquids with strong electrostatic correlations where D^* is the diffusivity and L^* is the separation length of the cell. With these two new scales, data of both electric potential versus distance from the electrode and the total diffuse charge versus time collapse onto each individual master curve in the presence of strong electrostatic correlations. In addition, the dependence of the total diffuse charge on steric effects, short-range correlations, and driving voltages is thoroughly examined. The results from the asymptotic analysis are compared favorably with those from full numerical simulations. Finally, the absorption of excess salt by the double layer creates a depletion region outside the double layer. Such salt depletion may bring a correction to the leading order terms and break down the weakly nonlinear analysis. A criterion which justifies the weakly nonlinear analysis is verified with numerical simulations.

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I. INTRODUCTION

Room-temperature ionic liquids as a solvent-free liquid salt composed of cations and anions attract growing interest due to their unique and desirable physical and chemical properties [1–6]. For example, ionic liquids have low vapor pressure, high thermal stability, and a large potential window, making them ideal candidates for applications in electrochemistry [7,8]. They have been proposed as media for batteries [9–11], electrochemical capacitors [12–17], electrosynthesis [18,19], electrodeposition [20], solar cells [21,22], and electroactuators [23]. The application in electrochemical capacitors is particularly appealing since ionic liquids have a large (up to 5 V) electrochemical window within which Faradaic reactions are inappreciable [8]. Electrochemical capacitors storing electric energy can complement or replace batteries for energy storage and harvesting when high power delivery is necessary [17].

To design electrochemical capacitors, one needs to understand the structure of the double layer of ionic liquids near metal surfaces and charging/discharging dynamics of the corresponding double layer. It has been recognized that the classical Gouy-Chapman-Stern model for dilute electrolytes [24] cannot even qualitatively predict the dependence of the capacitance of ionic liquids on the driving voltage [8,25]. Such deficiency of the classical model was attributed to neglecting the constraint of ions' finite size [8,26]. Accounting for steric effects of ions in ionic liquids, Kornyshev [8] predicted bell or camel shapes of the capacitance versus voltage, which were later verified by both experiments and simulations, in

particular, at large driving voltages where steric effects are more prominent [27–37].

In ionic liquids, Coulomb short-range electrostatic correlations [38] are considerably strong [39,40]. Short-range correlations usually result in overscreening [38]: the first layer near the metal surface overcompensates the surface charge and leads to a second layer with opposite net charge, which again induces another oppositely charged layer, and so on until the charge neutrality reaches in the bulk. Recent studies have observed overscreening structures in ionic liquids [39]. However, the aforementioned model accounting for steric effects alone cannot capture short-range electrostatic correlations or predict overscreening. To account for electrostatic correlations, a simple Landau-Ginzburg-type continuum model was developed for solvent-free ionic liquids [41]. This continuum model includes both short-range electrostatic correlations and steric effects into the free energy via Cahn-Hilliard-gradient based expansions [42]. By minimizing the free energy, the governing differential equations of the electric potential and concentrations of cation and anion were derived. For detailed derivations and justification, we refer interested readers to Bazant *et al.* [41]. This continuum model captures both overscreening and steric effects. The predicted capacitance-voltage relation is consistent with computer simulations and experiments [41]. More importantly, this model is simple enough to be numerically tractable and lays the foundation for studying dynamics. However, we must stress that the approach adopted here is based on local density approximation [26] and neglect short-range ion correlations (the chemical potential only depends on local ion concentrations, not on neighboring concentrations). To account for the nonlocality effect, the density functional theory can be used [43]. The density functional

*hui.zhao@unlv.edu

theory ends up with coupled integral equations which may be difficult to be numerically solved for the dynamical problems. The objective here is to examine the impact of both overscreening and steric effects on diffuse-charge dynamics of ionic liquids. For mathematical convenience, we choose the Landau-Ginzburg-type local continuum model.

The standard transient electrochemical response of ionic liquids to a step voltage is typically studied under the framework of the circuit model where double layers act as capacitors in series with a bulk resistance [44,45]. The double layer is assumed to be in quasiequilibrium with the bulk which is neutral and remains a constant concentration. This approximation in terms of equivalent circuits for dilute and concentrated electrolytes was validated in the thin double layer limit by the asymptotic analysis of the Poisson-Nernst-Planck equations or modified equations accounting for steric effects [46,47]. The limitation of the nonlinear circuit model was rigorously delineated and discussed [46,47]. Similar work on responding to an ac voltage was also presented [48]. The influence of the diffuse double layer on the passage of Faradaic current was also theoretically investigated for steady-state voltammetry [49].

The charging dynamics for ionic liquids is more complicated compared to simple electrolytes. Due to short-range electrostatic correlations, there exists an additional length scale l_c^* , the correlation length. It is well known that the Debye length λ_D^* is the characteristic double-layer length for electrolytes [24]. It is also recognized that electrostatic correlations lead to overscreening and the double layer extends far beyond λ_D^* [39,41]. In short, for moderate or strong correlations, the Debye length is not the correct double-layer scale any more. A new scale which shall depend on both l_c^* and λ_D^* needs to be identified. Furthermore, the length scale l_c^* may introduce a new time scale to describe the diffuse-charge dynamics as well. The traditional RC time $\lambda_D^* L^* / D^*$ for electrolytes may not be applicable in the presence of electrostatic correlations either. A new time scale needs to be identified.

The paper is organized as follows. We begin with the general mathematical model accounting for both electrostatic correlations and steric effects. Then we nondimensionalize the problem, which can be solved numerically to compare against our asymptotic analysis. Next, under the limit of thin double layers, we can derive uniformly valid asymptotic expansions in the weakly nonlinear regime with proposed length and time scales. Finally, we discuss the criterion under which the weakly nonlinear analysis breaks down.

II. MATHEMATICAL MODEL

Here we consider a basic model problem [46–48,50]: a 1-1 symmetric ionic liquid with same-size anions and cations confined by two parallel planar, blocking electrodes, respectively, located at $x = \pm L^*$ (Fig. 1). The concentrations of cation and anion C_{\pm}^* are described by the modified Nernst-Planck equation accounting for steric effects [8,26,50–52]:

$$\frac{\partial C_{\pm}^*}{\partial t^*} = D_{\pm}^* \nabla \cdot \left(\nabla C_{\pm}^* \pm \frac{F_a}{RT} C_{\pm}^* \nabla \phi^* + \frac{\gamma C_{\pm}^* \nabla (C_{+}^* + C_{-}^*)}{1 - \gamma (C_{+}^* + C_{-}^*)} \right). \quad (1)$$

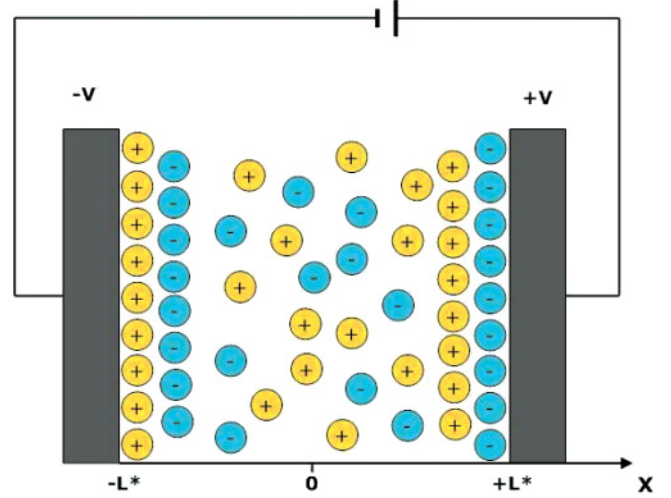


FIG. 1. (Color online) Schematic of the model problem and the coordinate system.

In the above, ϕ^* is the electric potential; D_{\pm}^* is ions' diffusivity (for simplicity we assume $D_{+}^* = D_{-}^*$); R is the ideal gas constant; F_a is the Faraday constant; T is the ambient temperature; γ is the minimum volume available in space for ions.

The electric potential satisfies a modified Poisson equation accounting for short-range electrostatic correlations [41]:

$$\epsilon_1 (l_c^{*2} \nabla^2 - 1) \nabla^2 \phi^* = F_a (C_{+}^* - C_{-}^*), \quad (2)$$

where ϵ_1 is the dielectric permittivity and l_c^* is the electrostatic correlation length [41].

Here we assume that electrodes are ideally polarizable without Faradaic reactions. Thus the ionic flux is set to be zero on electrodes:

$$\frac{\partial C_{\pm}^*}{\partial n} \pm \frac{F_a}{RT} C_{\pm}^* \frac{\partial \phi^*}{\partial n} + \frac{\gamma C_{\pm}^*}{1 - \gamma (C_{+}^* + C_{-}^*)} \frac{\partial (C_{+}^* + C_{-}^*)}{\partial n} = 0, \quad \text{at } x = \pm L^*. \quad (3)$$

By neglecting electrostatic correlations at the solid surface, the electric potential obeys the following boundary conditions:

$$\frac{\partial^3 \phi^*}{\partial n^3} = 0, \quad (4)$$

and

$$\phi^* = \pm V_0^*, \quad \text{at } x = \pm L^*. \quad (5)$$

When $t < 0$, there is no voltage imposed on electrodes ($\phi^* = 0$) and the ionic concentrations are uniform ($C_{\pm}^* = C_0^*$). When $t > 0$, a voltage difference $2V_0^*$ is applied between two electrodes. Counterions are attracted to the charged surface and coions are repelled from the surface. The condensed counterions form an electric double layer [24,53]. Once the double layer is well established, the electric field is fully screened by diffuse charge and the relaxation reaches the steady state.

To analyze this model problem, we first nondimensionalize Eqs. (1)–(5) using L^* ($\sim \mu\text{m}$) as the length scale, the thermal potential [RT/F_a (25 mV)] as the electric potential scale, and $\lambda_D^{*3/2} L^* / (D^* l_c^{1/2})$ ($\sim 10^{-6}$ s) as the time scale where

$\lambda_D = \sqrt{\frac{\epsilon_1 RT}{2F_a^2 C_0^*}}$ is the Debye screening length. To further simplify the equations, we introduce two reduced variables: the local salt concentration $C = (C_+^* + C_-^*)/2C_0^*$ and the local charge density $\rho = (C_+^* - C_-^*)/2C_0^*$. Throughout the paper, variables without superscript $*$ are dimensionless. Later on, we will show that $\lambda_D^{*3/2} L^*/(D^* l_c^{1/2})$ is the primary diffuse-charge time scale (τ_c) associated with ionic liquids in the case that the correlation length is larger than the Debye length ($l_c^* > \lambda_D^*$).

The dimensionless equations are

$$\frac{\partial C}{\partial t} = \frac{\epsilon}{\delta_c} \frac{\partial}{\partial x} \left(\frac{\partial C}{\partial x} + \rho \frac{\partial \phi}{\partial x} + \frac{\nu C}{1 - \nu C} \frac{\partial C}{\partial x} \right), \quad (6)$$

$$\frac{\partial \rho}{\partial t} = \frac{\epsilon}{\delta_c} \frac{\partial}{\partial x} \left(\frac{\partial \rho}{\partial x} + C \frac{\partial \phi}{\partial x} + \frac{\nu \rho}{1 - \nu C} \frac{\partial C}{\partial x} \right), \quad (7)$$

and

$$\left(\frac{1}{l_c^2} - \frac{\partial^2}{\partial x^2} \right) \frac{\partial^2 \phi}{\partial x^2} = -\frac{\rho}{\epsilon^2}. \quad (8)$$

In the above, $l_c = l_c^*/L^*$; $\epsilon = \sqrt{\lambda_D^* l_c^*/L^*}$; $\delta_c = l_c^*/\lambda_D^*$.

The boundary conditions at $x = \pm 1$ are

$$\frac{\partial C}{\partial x} + \rho \frac{\partial \phi}{\partial x} + \frac{\nu C}{1 - \nu C} \frac{\partial C}{\partial x} = 0, \quad (9)$$

$$\frac{\partial \rho}{\partial x} + C \frac{\partial \phi}{\partial x} + \frac{\nu \rho}{1 - \nu C} \frac{\partial C}{\partial x} = 0, \quad (10)$$

$$\phi = \pm V_0, \quad (11)$$

and

$$\frac{\partial^3 \phi}{\partial x^3} = 0. \quad (12)$$

The initial conditions are, respectively, $C(x, 0) = 1$, $\rho(x, 0) = 0$, and $\phi(x, 0) = V_0 x$. The total diffuse charge near the cathode can be defined as

$$q(t) = \int_{-1}^0 \rho(x, t) dx. \quad (13)$$

Finally, the dimensionless Faradaic current density is

$$j = \frac{\partial \rho}{\partial x} + C \frac{\partial \phi}{\partial x} + \frac{\nu \rho}{1 - \nu C} \frac{\partial C}{\partial x}. \quad (14)$$

There are four parameters which determine the solution: V_0 , the ratio of the driving voltage to the thermal voltage; ϵ , the dimensionless double-layer length scale; δ_c , the dimensionless correlation length normalized by the Debye length, denoting the importance of short-range electrostatic correlations; and $\nu = 2\gamma C_0^*$, the ratio of the bulk ion concentration to the maximum possible concentration, characterizing the ability of ionic liquids to compress [8,41].

The above equations are not analytically tractable. Thus we used the commercial finite element software COMSOL 3.5 (Comsol, Los Angle, USA) to numerically solve this model problem. To resolve the details of the electric double layer, nonuniform elements were used with a dense mesh concentrated next to electrodes. The element size gradually increases as the distance from the electrodes increases. The mesh was refined a few times to assure that the results are mesh independent. To verify the computational algorithm, both the computed total diffuse charge and full solutions of the electric

potential, charge density, and local salt concentration were compared against those obtained from the asymptotic analysis (see below).

III. ASYMPTOTIC ANALYSIS

We use matched asymptotic expansions in the limit of thin double layers $\epsilon = \sqrt{\lambda_D^* l_c^*/L^*} \ll 1$ [46–48]. Since the Debye length and the electrostatic correlation length of ionic liquids (λ_D^* is around Å and $l_c^* \sim \text{nm}$ [41]) are very small compared to the size of a typical microelectrochemical cell (μm), the asymptotic expansions around ϵ are appropriate.

Briefly, the solution can be expanded as a series of power ϵ :

$$\begin{pmatrix} \phi \\ \rho \\ C \end{pmatrix} = \begin{pmatrix} \phi^{(0)} \\ \rho^{(0)} \\ C^{(0)} \end{pmatrix} + \epsilon \begin{pmatrix} \phi^{(1)} \\ \rho^{(1)} \\ C^{(1)} \end{pmatrix} + O(\epsilon^2). \quad (15)$$

Equation (15) is then substituted into the governing equations (6)–(12) and different order terms of ϵ are collected to form a hierarchy of differential equations [54,55]. The solution converges in the limit of $\epsilon \rightarrow 0$ with all other parameters remaining fixed at any values. For a given ϵ , other parameters could be restricted by ϵ no matter how small ϵ is. In particular, there is an ϵ dependence on the driving voltage V_0 to guarantee accurate approximations. Following Bazant and co-workers [46–48,56], we define the regime where the asymptotic approximations are valid as the weakly nonlinear regime and denote the regime where the standard asymptotic analysis breaks down as the strongly nonlinear regime.

A. Bulk region

In the bulk region, we seek regular asymptotic expansions (denoted by a bar accent). The modified Poisson equation (8) indicates that the leading order of the charge density ρ is of the second order ($\bar{\rho}^{(0)} = \bar{\rho}^{(1)} = 0$).

In the bulk, the salt concentration can be written as

$$C(x, t) \sim \bar{C}(x, t) = \bar{C}^{(0)} + \epsilon \bar{C}^{(1)} + O(\epsilon^2). \quad (16)$$

Substituting Eq. (16) into Eq. (6) and recognizing $\bar{\rho}^{(0)} = 0$, at the leading order, we have $\bar{C}^{(0)} = 1$. In other words, the bulk concentration does not vary at the charging time scale (τ_c), but exhibits diffusive behavior at the diffusion time scale (L^{*2}/D^*).

The leading order electric potential can be readily derived:

$$\bar{\phi}^{(0)} = \bar{j}^{(0)}(t)x, \quad (17)$$

where the leading order current density has an initial condition: $\bar{j}^{(0)}(0) = V_0$. $\bar{j}^{(0)}(t)$ is unknown, which needs to be computed by matching the outer approximations with the singular inner approximations in the double layer. To further simplify the problem, we take advantage of the following symmetries:

$$\begin{aligned} C(-x, t) &= C(x, t), \\ \rho(-x, t) &= -\rho(x, t), \\ \phi(-x, t) &= -\phi(x, t), \end{aligned} \quad (18)$$

and only consider the double layer at the cathode side ($x = -1$).

B. Quasiequilibrium double layer

The singular perturbation in the modified Poisson equation (8) leads to a boundary layer with the width $O(\epsilon)$ in which the charge is not neutral at the zeroth order. To remove the singularity, we define a new inner coordinate $\tilde{x} = (1+x)/\epsilon$. Casting Eqs. (6)–(8) into this new inner coordinate, we have

$$\delta_c \epsilon \frac{\partial \tilde{C}}{\partial t} = \frac{\partial}{\partial \tilde{x}} \left(\frac{\partial \tilde{C}}{\partial \tilde{x}} + \tilde{\rho} \frac{\partial \tilde{\phi}}{\partial \tilde{x}} + \frac{\nu \tilde{C}}{1 - \nu \tilde{C}} \frac{\partial \tilde{C}}{\partial \tilde{x}} \right), \quad (19)$$

$$\delta_c \epsilon \frac{\partial \tilde{\rho}}{\partial t} = \frac{\partial}{\partial \tilde{x}} \left(\frac{\partial \tilde{\rho}}{\partial \tilde{x}} + \tilde{C} \frac{\partial \tilde{\phi}}{\partial \tilde{x}} + \frac{\nu \tilde{\rho}}{1 - \nu \tilde{C}} \frac{\partial \tilde{C}}{\partial \tilde{x}} \right), \quad (20)$$

and

$$\left(\frac{1}{\delta_c} - \frac{\partial^2}{\partial \tilde{x}^2} \right) \frac{\partial^2 \tilde{\phi}}{\partial \tilde{x}^2} = -\tilde{\rho}. \quad (21)$$

The singularity in the modified Poisson equation (21) is successfully removed in the inner coordinate system. Now regular asymptotic analysis can be performed (denoted by tilde accents). At the zeroth order, the time-dependent terms in Eqs. (19) and (20) drop out. In other words, the electric double layer is in quasiequilibrium. Accordingly, the zeroth order charge density and salt concentration can be integrated [8,26,47,50]:

$$\begin{aligned} \tilde{C}^{(0)} &= \frac{\cosh \tilde{\psi}^{(0)}}{1 + 2\nu \sinh^2(\tilde{\psi}^{(0)}/2)}, \\ \tilde{\rho}^{(0)} &= \frac{-\sinh \tilde{\psi}^{(0)}}{1 + 2\nu \sinh^2(\tilde{\psi}^{(0)}/2)}, \end{aligned} \quad (22)$$

where $\tilde{\psi}$ is the excess voltage relative to the bulk [$\tilde{\psi}(\tilde{x}, t) = \tilde{\phi}(\tilde{x}, t) - \tilde{\phi}(-1, t)$]. $\tilde{\psi}$ obeys the modified Poisson equation:

$$\left(\frac{1}{\delta_c} - \frac{\partial^2}{\partial \tilde{x}^2} \right) \frac{\partial^2 \tilde{\psi}^{(0)}}{\partial \tilde{x}^2} = \frac{\sinh \tilde{\psi}^{(0)}}{1 + 2\nu \sinh^2(\tilde{\psi}^{(0)}/2)}. \quad (23)$$

The boundary conditions are $\tilde{\psi}^{(0)}(\infty, t) = 0$ and $\tilde{\psi}^{(0)}(0, t) = \tilde{\zeta}(t)$ in which the ζ potential $\tilde{\zeta}$ changes as the diffuse layer charges.

van Dyke conditions are used to match the inner solution with the outer solution in space [54,55]:

$$\lim_{\tilde{x} \rightarrow \infty} \tilde{C}(\tilde{x}, t) = \lim_{x \rightarrow -1} \tilde{C}(x, t) \quad (24)$$

and

$$\frac{\partial \tilde{\psi}}{\partial \tilde{x}}(\infty, t) \sim \epsilon \frac{\partial \tilde{\phi}}{\partial x}(-1, t). \quad (25)$$

Equation (25) suggests that at the leading order,

$$\frac{\partial \tilde{\psi}^{(0)}}{\partial \tilde{x}}(\infty, t) = 0. \quad (26)$$

The problem is still not solvable since the time-dependent ζ potential is unknown. In fact, in the weakly nonlinear regime, the charging dynamics is controlled by the time-dependent ζ potential in response to the Faradaic current from the bulk.

C. Time-dependent matching

To close the aforementioned matching problem, we adopt Bazant's approach [46,47] and consider the total diffuse charge

$q(t)$. The leading order term of $q(t)$ is of the first order [$q(t) \sim \epsilon \tilde{q}(t)$] where

$$\tilde{q}(t) = \int_0^\infty \tilde{\rho}(\tilde{x}, t) d\tilde{x} \sim \tilde{q}^{(0)} + \epsilon \tilde{q}^{(1)} + O(\epsilon^2). \quad (27)$$

Taking a time derivative (27) and using Eq. (20) with the no flux boundary condition (10), we have

$$\begin{aligned} \frac{\partial \tilde{q}(t)}{\partial t} &= \lim_{\tilde{x} \rightarrow \infty} \frac{1}{\delta_c \epsilon} \left(\frac{\partial \tilde{\rho}}{\partial \tilde{x}} + \tilde{C} \frac{\partial \tilde{\phi}}{\partial \tilde{x}} + \frac{\nu \tilde{\rho}}{1 - \nu \tilde{C}} \frac{\partial \tilde{C}}{\partial \tilde{x}} \right) \\ &\sim \lim_{x \rightarrow -1} \frac{1}{\delta_c} \left(\frac{\partial \tilde{\rho}}{\partial x} + \tilde{C} \frac{\partial \tilde{\phi}}{\partial x} + \frac{\nu \tilde{\rho}}{1 - \nu \tilde{C}} \frac{\partial \tilde{C}}{\partial x} \right). \end{aligned} \quad (28)$$

In the above, we have matched the flux densities of inner and outer solutions. Substituting the inner and outer solutions, we have the following equation determining the leading order total diffuse charge:

$$\frac{\partial \tilde{q}^{(0)}(t)}{\partial t} = \frac{1}{\delta_c} \tilde{j}^{(0)}(t). \quad (29)$$

Equation (29) indicates that at the leading order, the double layer acts as a capacitor where the total charge density $\tilde{q}^{(0)}(t)$ changes due to the transient Faradaic current density $\tilde{j}^{(0)}(t)$ from the bulk.

D. Results and discussion

Before we start our asymptotic analysis, we first demonstrate that the length scale $\sqrt{\lambda_D^* J_c^*}$ rather than λ_D^* that is the double-layer length for electrolytes is the correct scale to characterize the double layer when $\delta_c > 1$. The above conclusion can be readily drawn from Eq. (21). When $\delta_c \gg 1$, the first term in Eq. (21) becomes insignificant and Eq. (21) can be simplified:

$$\frac{\partial^4 \tilde{\phi}}{\partial \tilde{x}^4} = \tilde{\rho}. \quad (30)$$

In other words, the electric potential does not explicitly depend on δ_c any more when $\delta_c \gg 1$. Figure 2 depicts the electric potentials and charge densities of equilibrium double layers for different δ_c when $\zeta = -20$ and $\nu = 0.5$. As expected, at large δ_c ($\delta_c > 20$), the results are indistinguishable, indicating that $\sqrt{\lambda_D^* J_c^*}$ is indeed the characteristic double-layer length for ionic liquids. When $\delta_c < 1$, the effect of electrostatic correlations is inappreciable, ions behave like point charges, and λ_D^* again is the correct double-layer length scale. In addition, Fig. 2(b) shows that the applied continuum model captures both electrostatic correlations (overscreening) and steric effects (ions' saturation).

Next, to study the diffuse-charge dynamics of ionic liquids, we integrate Eq. (21) and use Eqs. (4) and (26). At the leading order,

$$\frac{\partial \tilde{\psi}^{(0)}(0, t)}{\partial \tilde{x}} = \delta_c \tilde{q}^{(0)}(t), \quad (31)$$

which connects the total diffuse charge to the electric potential.

Then consider that the boundary condition (11) yields

$$\tilde{j}^{(0)}(t) = V_0 + \tilde{\psi}^{(0)}. \quad (32)$$

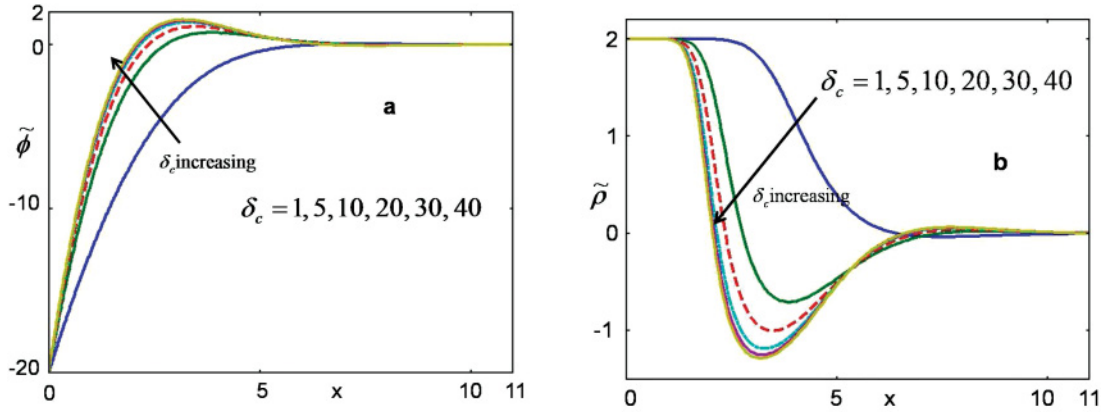


FIG. 2. (Color online) (a) Dimensionless electric potential; (b) dimensionless charge density as a function of dimensionless \bar{x} when $\zeta = -20$ and $\nu = 0.5$.

Equation (29) becomes

$$\frac{\partial \tilde{q}^{(0)}(t)}{\partial t} = \frac{1}{\delta_c} (V_0 + \tilde{\psi}^{(0)}). \quad (33)$$

Now, Eqs. (23), (31), and (33) can be solved simultaneously to understand the dynamics of the total diffuse charge of ionic liquids.

For low driving voltages ($V_0 \ll 1$), when $\delta_c > 1/2$, the above equations can be solved analytically [41]:

$$\tilde{q}^{(0)}(t) = \frac{\sqrt{2\delta_c + 1}V_0}{\sqrt{\delta_c(\delta_c + 1)}} (1 - e^{-(\delta_c + 1)/\sqrt{\delta_c(2\delta_c + 1)}t}). \quad (34)$$

For an arbitrary V_0 , numerical technique has to be resolved. To verify the accuracy of our numerical algorithm, we first compared the total diffuse charge from our simulations to those predicted by Eq. (34). Figure 3 plots the normalized

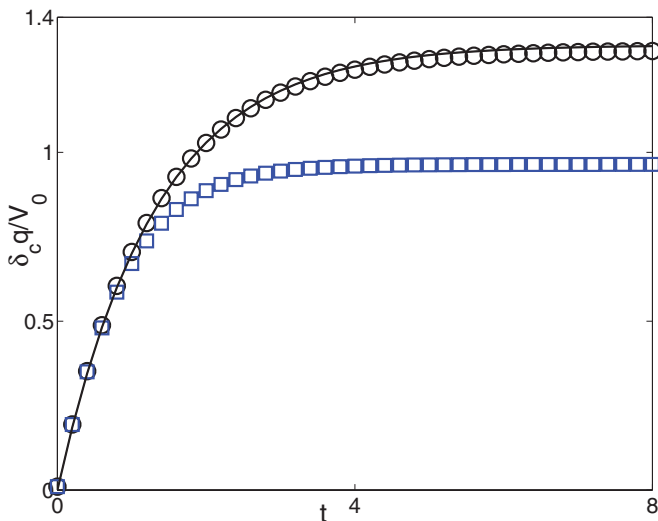


FIG. 3. (Color online) Normalized total diffuse charge $\delta_c \tilde{q}^{(0)}(t)/V_0$ as a function of time t (all variables are dimensionless). The solid line represents the predictions from the analytical expression (34). The circles and squares correspond, respectively, to the results of $V_0 = 1$ and $V_0 = 2$ computed by numerical simulations when $\epsilon = 0.03$, $\nu = 0.5$, and $\delta_c = 10$.

total diffuse charge $\delta_c \tilde{q}^{(0)}(t)/V_0$ as a function of time for two different V_0 . Since Eq. (34) is derived under the assumption $V_0 \ll 1$, it is not surprising that the computed total diffuse charge deviates from the theoretical prediction when $V_0 = 2$.

We can rewrite Eq. (33) as

$$\frac{\partial \delta_c \tilde{q}^{(0)}(t)}{\partial t} = (V_0 + \tilde{\psi}^{(0)}). \quad (35)$$

Interestingly, Eqs. (30), (31), and (35) are essentially the same if $\delta_c \tilde{q}^{(0)}(t)$ is considered as one single entity. Evidently, for strong electrostatic correlations ($\delta_c \gg 1$), without any further calculation, our simple scaling analysis indicates that in the weakly nonlinear regime the total diffuse charge $\tilde{q}^{(0)}$ is proportional to δ_c^{-1} assuming that all other parameters remain the same. Since the differential capacitance of the double layer is defined as

$$\tilde{C}^{(0)} = -\frac{d\tilde{q}^{(0)}}{d\tilde{\psi}^{(0)}}, \quad (36)$$

one can immediately conclude that in the case of $\delta_c \gg 1$ the differential capacitance is proportional to δ_c^{-1} as well. A similar conclusion was also reached by Bazant *et al.* [41] where they derived analytical expressions of the differential capacitance for small and moderate driving voltages with additional assumptions. Our analysis extended this scaling relation to all voltages. Notice that in Bazant's paper [41], the differential capacitance is predicted to be proportional to $\delta_c^{-1/2}$ at $\delta_c \gg 1$. But two scaling relations are consistent. The difference is attributed to the fact that different length scales are used to normalize the governing equations. In their work, the double layer length λ_D^* was chosen as the length scale. Here $\sqrt{\lambda_D^* l_c^*}$ is the length scale. Since $\sqrt{\lambda_D^* l_c^*} = \sqrt{\delta_c} \lambda_D^*$, after rescaling, our results are identical to theirs. Figure 4 shows that when $\delta_c > 20$, the curves of $\delta_c \tilde{q}^{(0)}(t)$ collapse onto a single master one, conforming the scaling relation $\tilde{q}^{(0)} \sim \delta_c^{-1}$.

The decrease of the differential capacitance or the total diffuse charge ($\tilde{q}^{(0)}$) with the increase of δ_c can be readily explained: the larger δ_c is, the more important the impact of overscreening. Overscreening causes the first layer of counterions near electrodes to overcompensate the imposed

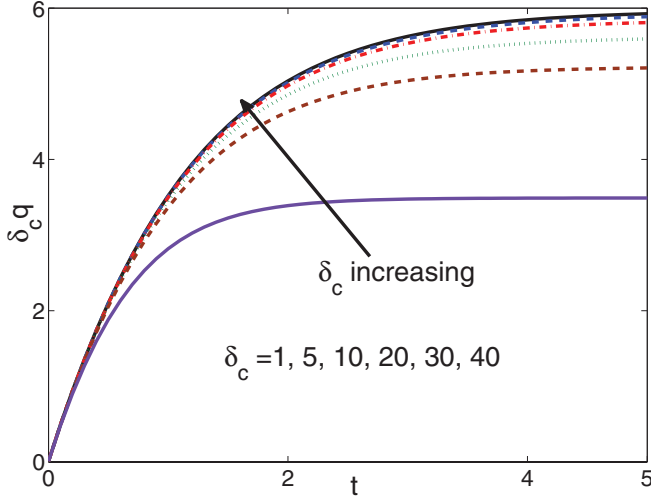


FIG. 4. (Color online) Dimensionless total diffuse charge $\delta_c \tilde{q}^{(0)}(t)$ as a function of dimensionless time t when $\epsilon = 0.01$, $\nu = 0.5$, and $V_0 = 5$.

surface charge and the second layer has to attract coions to compensate the net charge of the opposite sign from the combination of the first layer and the surface charge, which again overscreens and so on until the electroneutrality is recovered [33,38,39,41,57]. Owing to overscreening, a portion of counterions are compensated by coions existing in adjacent layers and accordingly the total net charge decreases as δ_c increases.

Next, we plot the normalized total diffuse charge as a function of time for different ν in Fig. 5. The solid, dashed, and dashed-dot lines correspond, respectively, to $\nu = 0.2$, $\nu = 0.5$, and $\nu = 0.8$. Since ν characterizes steric effects, the larger ν is, the fewer ions there are inside the double layer. Therefore the steady-state total diffuse charge decreases as ν increases. Moreover, the data of the initial rise of $\tilde{q}^{(0)}$ at different ν appear

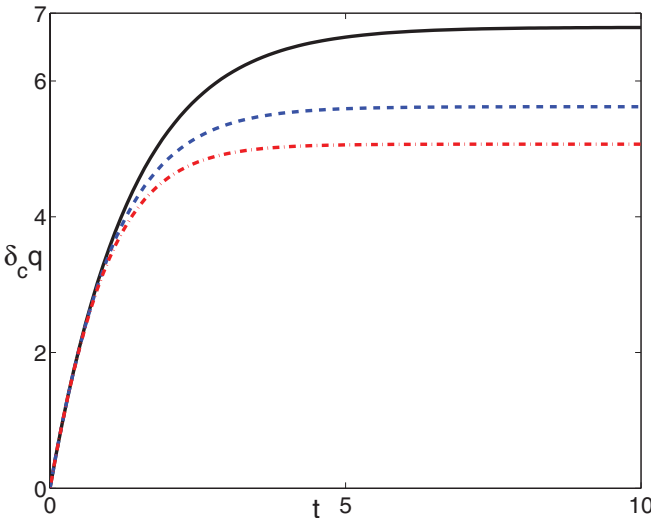


FIG. 5. (Color online) Dimensionless total diffuse charge $\delta_c \tilde{q}^{(0)}(t)$ as a function of dimensionless time t when $\epsilon = 0.01$, $\delta_c = 10$, and $V_0 = 5$. The solid, dashed, and dashed-dot lines correspond, respectively, to $\nu = 0.2$, $\nu = 0.5$, and $\nu = 0.8$.

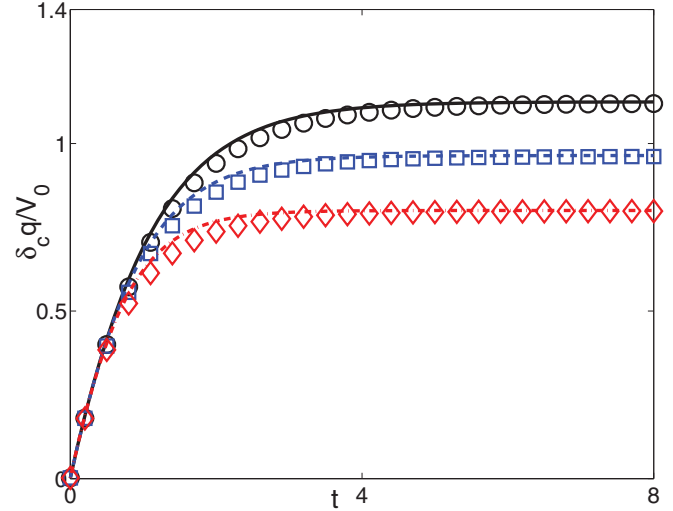


FIG. 6. (Color online) Normalized total diffuse charge $\delta_c \tilde{q}^{(0)}(t)/V_0$ as a function of time t (all variables are dimensionless) when $\epsilon = 0.01$, $\delta_c = 10$, and $\nu = 0.5$. The circles, squares, and diamonds correspond, respectively, to $V_0 = 5$, $V_0 = 10$, and $V_0 = 20$. The symbols and lines denote results from numerical simulations and asymptotic analysis, respectively.

to collapse onto each other. It can be explained: it takes time for ions' concentration to reach the saturation caused by steric effects.

Figure 6 depicts the normalized total diffuse charge $\delta_c \tilde{q}^{(0)}(t)/V_0$ as a function of time for different V_0 . In Fig. 6, we also plot the predictions by numerical simulations via solving the nonlinear equations (6)–(14). Good agreements between numerical simulations and the asymptotic analysis are obtained which, in turn, verify the accuracy of the numerical simulations. The decrease of the normalized diffuse charge $\delta_c \tilde{q}^{(0)}/V_0$ as the increase of V_0 is equivalent to the decrease of the differential capacitance which has been reported by many researchers conducting both experimental investigations and numerical simulations [8,25,27–37,41]. The dependance of the differential capacitance on the driving voltage V_0 is attributed to steric effects. Ion concentrations strongly depend on the driving voltage on electrodes: the higher the driving voltage is, the stronger the steric effects are. The saturation of ions induced by steric effects leads to a decrease of the capacitance.

Interestingly, Figs. 3–6 show that the charging time of various ν , δ_c ($\delta_c > 1$), and V_0 is of the order one, indicating that the time scale $\lambda_D^{*3/2} L^*/(D^* l_c^{1/2})$ is the primary diffuse-charge time scale for strong electrostatic correlations (large δ_c) in contrast to the famous RC time scale $\lambda_D^* L^*/D^*$ for electrolytes [46]. This observation can be understood by a simple scaling analysis of Eqs. (30), (31), and (35) where the coefficients in front of the time derivative are all equal to 1.

IV. UNIFORMLY VALID APPROXIMATIONS

The asymptotic analysis not only predicts the integral behavior of the total diffuse charge but also provides the full time-dependent spatial profiles of the electric potential,

charge density, and local salt concentration. One can add the outer and inner solutions and subtract the overlaps to construct the uniformly valid approximations [46,56]. Consider the symmetries (18). At the leading order, the full solutions become

$$\phi(x,t) \sim \bar{j}^{(0)}(t)x + \tilde{\psi}^{(0)}\left(\frac{1+x}{\epsilon}, t\right) - \tilde{\psi}^{(0)}\left(\frac{1-x}{\epsilon}, t\right), \quad (37)$$

$$\rho(x,t) \sim \tilde{\rho}^{(0)}\left(\frac{1+x}{\epsilon}, t\right) - \tilde{\rho}^{(0)}\left(\frac{1-x}{\epsilon}, t\right), \quad (38)$$

$$C(x,t) \sim \tilde{C}^{(0)}\left(\frac{1+x}{\epsilon}, t\right) + \tilde{C}^{(0)}\left(\frac{1-x}{\epsilon}, t\right) - 1. \quad (39)$$

Figure 7 plots the time-dependent ϕ , ρ , and C . The lines and symbols correspond, respectively, to the predictions from the asymptotic analysis and numerical simulations. The asymptotic approximations for ϕ and ρ are in good agreement with numerical simulations well into the nonlinear regime $V_0 = 20$.

On the contrary, the asymptotic approximation for the local salt concentration fairly agrees with numerical simulations in the bulk region and the thin layer near the cathode. But there are intermediate regions with depleted concentration extending far into the bulk which are not captured by the asymptotic analysis.

V. BREAKDOWN OF WEAKLY NONLINEAR ANALYSIS

It is recognized that the diffuse layer absorbs an excess amount of ions which is not captured by the asymptotic model [46,47]. The transport of the excess concentration is via diffusion of neutral solution from the bulk. Since in our weakly nonlinear analysis the diffusion is absent at the leading order. The impact of diffusion is considered to be a higher-order correction. To characterize the importance of the absorption of excess amount of ions by the double layer, similar to previous work on electrolytes [46–48,56], we introduce a new variable

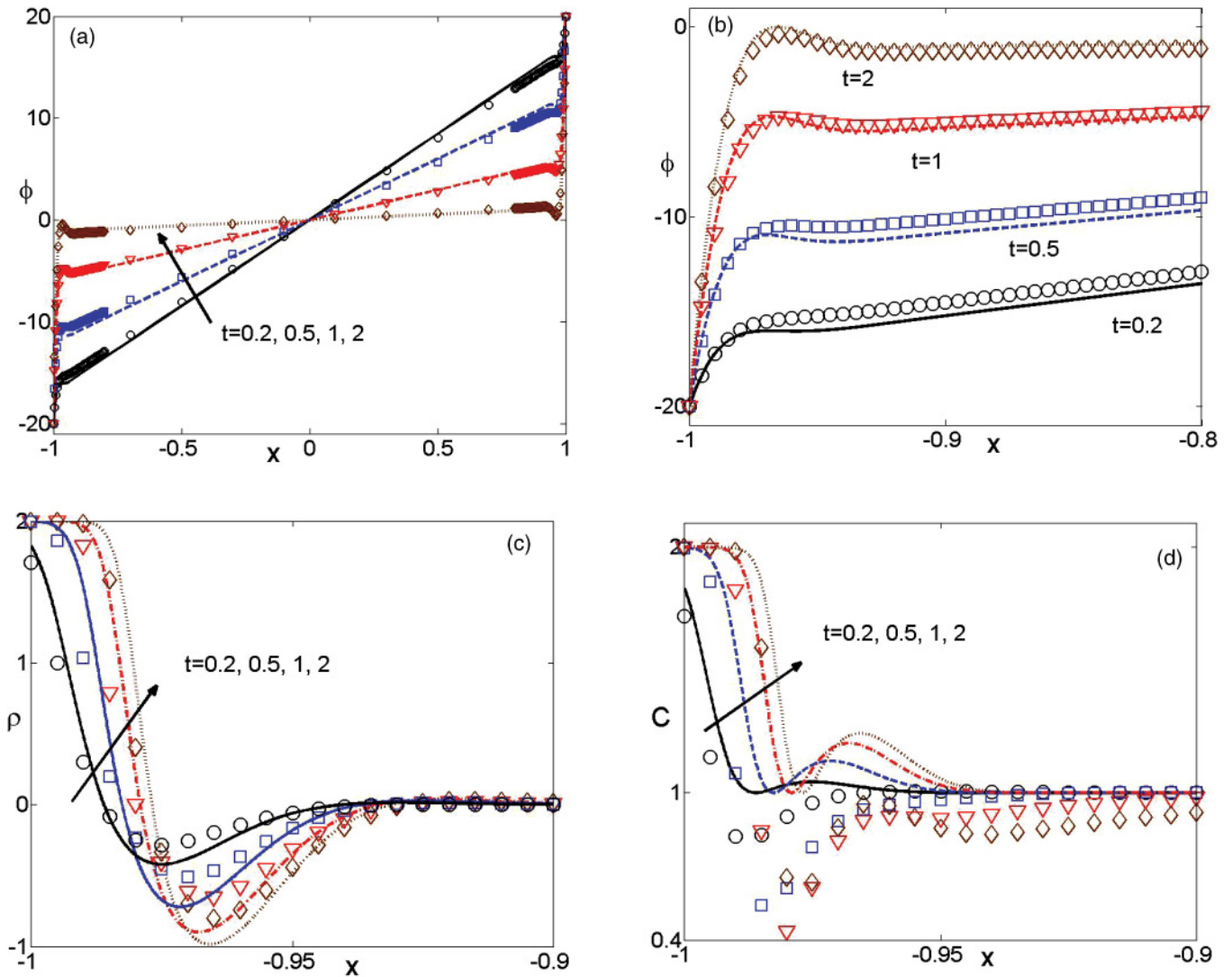


FIG. 7. (Color online) (a) The dimensionless electric potential in the whole electrochemical cell; (b) the dimensionless electric potential near the cathode; (c) the dimensionless charge density near the cathode; and (d) the dimensionless local salt concentration near the cathode at different time steps when $\nu = 0.5$, $V_0 = 20$, $\epsilon = 0.01$, and $\delta_c = 10$. The lines and symbols correspond, respectively, to the predictions from the asymptotic analysis and numerical simulations.

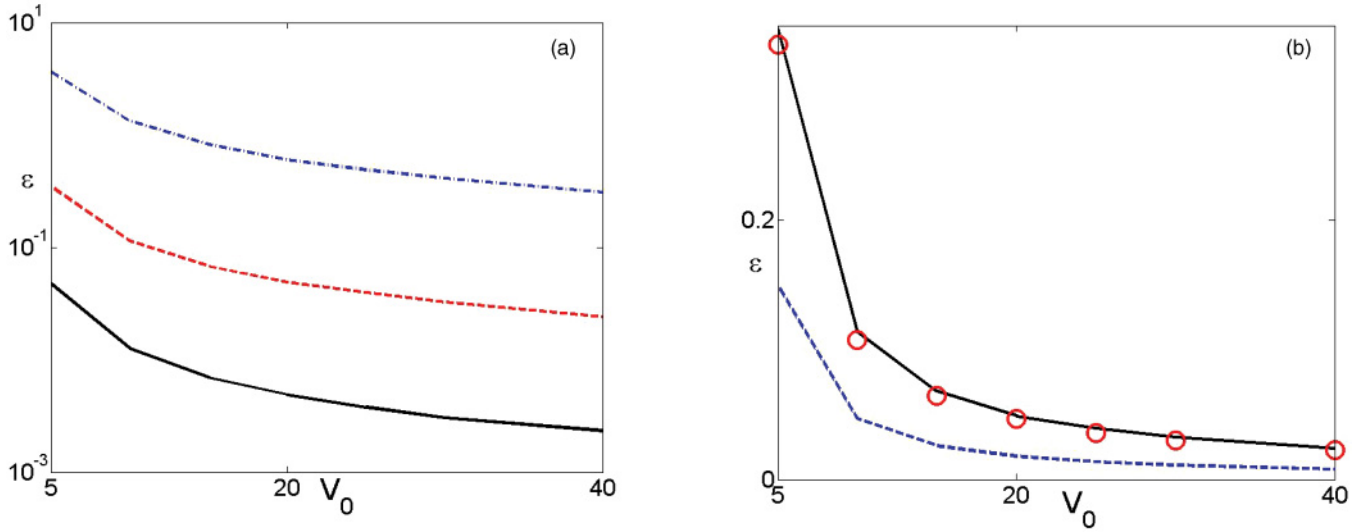


FIG. 8. (Color online) The curves on which $\sqrt{\epsilon}\tilde{w}^{(0)}(\infty) = 0.5$ in the parametric space of V_0 and ϵ : (a) for various ν in which the solid, dashed, and dashed-dot lines correspond, respectively, to $\nu = 0.2$, $\nu = 0.5$, and $\nu = 0.8$ when $\delta_c = 10$; (b) for various δ_c in which the symbols and solid and dashed lines correspond, respectively, to $\delta_c = 20$, $\delta_c = 10$, and $\delta_c = 1$ when $\nu = 0.5$.

$w(t) = \epsilon \tilde{w}(t)$ representing the excessive amount of salt in the double layer:

$$\begin{aligned} \tilde{w}(t) &= \int_0^\infty [\tilde{C}(\tilde{x}, t) - \tilde{C}^{(0)}(-1, t)] d\tilde{x} \\ &= \tilde{w}^{(0)}(t) + \epsilon \tilde{w}^{(1)}(t) + \dots \end{aligned} \quad (40)$$

An excess amount of salt $w(t)$ is adsorbed into the double layer from a diffusion zone, leading to a local maximum depletion of the salt concentration on the order of $\sqrt{\epsilon}\tilde{w}^{(0)}(\infty)$ which has been thoroughly discussed for electrolytes [46,47]. Such analysis can be easily extended to ionic liquids to show that the above criterion holds for ionic liquids as well. For the weakly nonlinear approximation to be valid, the fluctuation in the salt concentration outside the double layer is required to be only a small perturbation to the bulk value [$\sqrt{\epsilon}\tilde{w}^{(0)}(\infty) \ll 1$]. Since the analysis of the impact of diffusion of ionic liquids is essentially the same as that of electrolytes, we direct interested readers to [46,47] for detailed derivations and justification.

Figure 8 plots the curves on which $\sqrt{\epsilon}\tilde{w}^{(0)}(\infty) = 0.5$ in the parametric space of V_0 and ϵ for various values of ν and δ_c . The weakly nonlinear approximation holds when (V_0, ϵ) locates far below the critical curve where $\sqrt{\epsilon}\tilde{w}^{(0)}(\infty) \ll 1$. Figure 8 suggests that $\tilde{w}^{(0)}(\infty)$ depends on the driving voltage V_0 , steric effects ν , and short-range electrostatic correlations δ_c . In terms of V_0 , the larger V_0 is, the stronger absorption of excess salt into the double layer since a larger V_0 attracts more counterions from and repels more coions to the bulk, leading to a larger $\tilde{w}^{(0)}(\infty)$. Thus to make the weakly nonlinear analysis valid, ϵ has to be sufficiently small. With respect to ν , a larger ν implies a smaller difference between the ion concentrations inside the double layer and the bulk, indicating a smaller $\tilde{w}^{(0)}(\infty)$. In other words, for a fixed ϵ , the constraint on V_0 can be relaxed or the critical curve shifts to the right for an increase of ν . Due to overscreening, the oscillatory nature of the double layer of ionic liquids partially compensates each adjacent layer with excess oppositely charged ions and yields a smaller absorption

of salts. Accordingly, the curve in Fig. 8(b) shifts to the right as δ_c increases. Furthermore, since the double layer structure remains nearly the same at large δ_c , it is not surprising that all curves collapse when $\delta_c > 10$.

To examine the aforementioned criterion for the weakly nonlinear analysis, we plot the normalized total diffuse charge $\delta_c \tilde{q}^{(0)}(t)$ as a function of time for different $\sqrt{\epsilon}\tilde{w}^{(0)}(\infty)$ when $\delta_c = 10$ in Fig. 9. When the value of $\sqrt{\epsilon}\tilde{w}^{(0)}(\infty)$ is small, the match with numerical simulation is good. In the case of $\sqrt{\epsilon}\tilde{w}^{(0)}(\infty) = 0.46$, the agreement is improved over time. This is because at steady state, the local depletion of the salt concentration is around $\epsilon \tilde{w}^{(0)}(\infty)$ [46,47]. Though $\sqrt{\epsilon}\tilde{w}^{(0)}(\infty)$ is not small, $\epsilon \tilde{w}^{(0)}(\infty)$ can be still small and thus the weakly

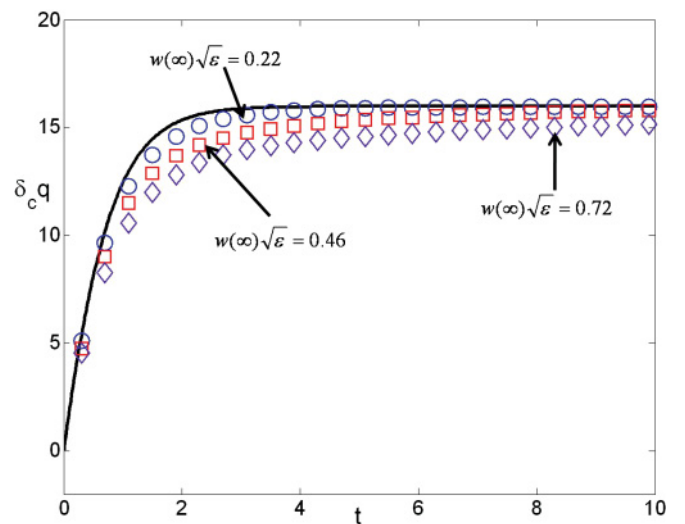


FIG. 9. (Color online) Dimensionless total diffuse charge $\delta_c \tilde{q}^{(0)}(t)$ as a function of dimensionless time t when $\delta_c = 10$, $\nu = 0.5$, and $V_0 = 20$. The solid line is the prediction from the asymptotic model. The symbols represent the predictions from numerical simulations for various values of $\sqrt{\epsilon}\tilde{w}^{(0)}(\infty)$.

nonlinear approximation is applicable for the final state. In summary, to accurately predict the charging dynamics at any time steps, the criterion $\sqrt{\epsilon}\tilde{w}^{(0)}(\infty) \ll 1$ needs to be enforced, while if only the final state is concerned, $\epsilon\tilde{w}^{(0)}(\infty) \ll 1$ is sufficient.

VI. CONCLUSIONS

We applied the recently developed Landau-Ginzburg-type continuum model accounting for both short-range electrostatic correlations and steric effects [41] to a model problem of the step charging of a parallel electrochemical cell. We performed an asymptotic analysis to study the diffuse-charge dynamics of ionic liquids to examine the influences of steric effects ν , short-range electrostatic correlations δ_c , and driving voltages V_0 in the weakly nonlinear regime. One original contribution is that at strong electrostatic correlations ($\delta_c \gg 1$), we discovered a new length scale ($\sqrt{\lambda_D^* l_c^*}$) and a time scale [$\lambda_D^{*3/2} L^* / (D^* l_c^{1/2})$], correctly capturing the underlying physics of ionic liquids under the action of an electric field. Numerical simulations verified these two scales by showing that not only all the curves of equilibrium double layers collapsed, but also the data of the

total diffuse charge $\delta_c \tilde{q}^{(0)}$ versus t fell onto a single master curve when $\delta_c \gg 1$.

We also examined the criterion justifying the nonlinear circuit model describing the overall current-voltage response. The criterion is related to the absorption of excess salt into the double layer. Our results suggested that both large ν and δ_c are beneficial to the applicability of the weakly nonlinear analysis.

When the absorption of excess salt into the double layer [$\sqrt{\epsilon}\tilde{w}^{(0)}(\infty)$] is small, we compared our asymptotic analysis to the full numerical simulations and found both good qualitative and quantitative agreements, in particular, for electric potential and charge density. The agreement on the local salt concentration is not as good due to the effect of the absorption even for small $\sqrt{\epsilon}\tilde{w}^{(0)}(\infty)$, but its impact on the total diffuse charge or the diffuse-charge dynamics is fairly modest.

Room-temperature ionic liquids can stand up to 5 V, which corresponds to $V_0 = 200$ in our analysis. For such a large driving voltage, the weakly nonlinear analysis likely breaks down and the strongly nonlinear analysis accounting for the bulk salt transport seems more appropriate [48], which is in order for future research consideration.

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