

Asymptotic Analysis of Diffuse-Layer Effects on Time-Dependent Interfacial Kinetics

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We investigate the subtle effects of diffuse charge on interfacial kinetics by solving the governing equations for ion transport (Nernst-Planck) with realistic boundary conditions representing reaction kinetics (Butler-Volmer) and compact-layer capacitance (Stern) in the asymptotic limit $\epsilon = \lambda_D/L \rightarrow 0$, where λ_D is the Debye screening length and L is the distance between the working and counter electrodes. Using the methods of singular perturbation theory, we derive the leading-order steady-state response to a nonzero applied current in the case of the oxidation of a neutral species into cations, without any supporting electrolyte. In certain parameter regimes, the theory predicts a reaction-limited current smaller than the classical diffusion-limited current. We also analyze the impedance of the electrochemical cell when a small AC current modulation is added to an applied DC current. At sufficiently high AC frequencies, the Maxwell displacement current is found to exceed the Faradaic conduction current, and experimentally observed “negative impedances” (out of phase AC voltage responses) are predicted close to the reaction-limited current. Overall, we demonstrate that the dynamics of diffuse charge plays a fundamental role in nonequilibrium surface reactions when the transport of one of the reacting species is coupled to the total interfacial response of the compact and diffuse layers.

I. INTRODUCTION

The influence of diffuse-layer structure on electrochemical surface reactions has been studied for many years since the pioneering work of Frumkin [1]. The double layer is typically modeled as a stationary outer “diffuse layer” (or “Debye layer”) of charged species in transport equilibrium and an inner “compact layer” (or “Stern layer”) where the electroactive species can react at an effective electrostatic potential Φ_r (reaction plane) which is different from the electrode potential Φ_e by an amount $\Delta\Phi_S = \Phi_e - \Phi_r$, the Stern-layer voltage. In such models the only effect of the diffuse layer on interfacial kinetics is to modify the activation energy and effectively rescale the interfacial concentration of the reacting species [2–15]. Within this theoretical approach, two types of models have been used: Either (i) the diffuse layer is treated as a continuum retaining the essential features of the mean concentration and electric field profiles [2–10] or (ii) the interfacial double layer is treated as an idealized set of nested layers (e.g. the inner and outer Helmholtz planes) consisting of discrete molecular and/or ionic species [11–16]. When diffuse-charge effects are incorporated into either type of model, the diffuse layer is assumed to have a stationary, equilibrium distribution of charges. The dynamical effect of the diffuse layer on charge transfer kinetics has only rarely been considered since it was first mentioned by Levich forty years ago [17,18].

The present study is motivated by the idea that the dynamical charging of the diffuse layer could also have an important effect on surface reaction kinetics in weak electrolytes (whose Debye screening length significantly exceeds the effective width of the compact layer). In this work, we adopt the classical Nernst-Planck “mean-field” continuum model for ion transport, without considering the possible steric effects due to finite ion sizes [19]. We do, however, allow for the compact Stern layer to have a different permittivity ϵ_S from the bulk solvent ϵ_b as described in Ref. [20], and we also consider nonlinear reaction kinetics given by the Butler-Volmer equation without any approximations (e.g. linearization).

Unlike previous studies, we focus here on dynamical, non-equilibrium effects of the diffuse-layer charging on the effective kinetic parameters measured by impedance spectroscopy. There have been few attempts in the literature aimed at characterizing the dynamics of the diffuse layer and its interplay with surface reactions, and existing studies have been mostly numerical in various approximations [10,17,21,22]. Here we illustrate the power of asymptotic analysis to provide analytical predictions of the statics and dynamics of realistic interfacial double layers in response to both DC and AC currents. Asymptotic analysis has rarely been applied to electrochemical systems, and previous studies have only focused on static cases with oversimplified boundary conditions [6,7,23–26]. Recently, more realistic boundary conditions have been proposed to model the interplay between the diffuse and compact layers, and asymptotic analysis has provided insight into the static response of a binary cell near the classical diffusion-limited and reaction-limited currents [20]. In this work, the same realistic equations and boundary conditions are used to model the AC+DC response of a three-species electrochemical cell (composed of a binary electrolyte plus a neutral solute molecule). To

our knowledge, this is the first asymptotic analysis of a time-dependent, nonequilibrium electrochemical system.

The article is organized as follows. In section II, we describe the electrochemical system and present the model equations for ion transport and surface reactions. In section III leading-order asymptotic approximations of steady solutions to these equations are derived in the case of a DC applied current. Finally, in section IV the asymptotic analysis is generalized to a time-dependent case by deriving the linear response to a small AC modulation added to a nonzero DC current. The full details of the time-dependent analysis will be presented elsewhere, but here we focus on the prediction of the negative impedance which has been observed in experiments and invoked as interpretation of the occurrence of oscillatory instabilities in electrochemical systems [27–30].

II. DESCRIPTION OF THE MODEL EQUATIONS

A. Transport Equations

For simplicity, we consider an electrochemical cell with a planar geometry, possessing one electrode at $X = 0$ (working electrode) and another at $X = L$ (counter electrode), and hence we ignore the possible effect of convection on ion transport. (Note that we use upper-case letters to denote quantities with dimensions to distinguish them from the corresponding dimensionless quantities introduced below, which are denoted by lower-case letters.) In order to limit our study to a small number of species, we analyze the case of a cation C which reacts at the electrodes to produce a neutral molecule N according to the electrochemical reaction



in the presence of an anion A , which aids in charge neutralization. For analytical convenience, we also assume that the electrolyte is symmetric, $z_C = -z_A = z$.

The continuum fields representing the state of the solution are the cation, anion and neutral molecule concentrations (moles/volume) $C_C(X, t)$, $C_A(X, t)$ and $C_N(X, t)$, respectively, and the electrostatic potential $\Phi(X, t)$. (Note that we use a lower case t for dimensional time, to distinguish it from the absolute temperature T .) Although we allow for time-dependent electric fields and currents, it can be shown that magnetic effects are negligible at the time scales under consideration so the electric field is given by $E = -\partial_X \Phi$. In the dilute solution approximation, the average concentrations evolve according to the Nernst-Planck equations describing diffusion and electromigration

$$\partial_t C_C = D \partial_X^2 C_C + \mu \partial_X (C_C \partial_X \Phi) \quad (2a)$$

$$\partial_t C_A = D \partial_X^2 C_A - \mu \partial_X (C_A \partial_X \Phi) \quad (2b)$$

$$\partial_t C_N = D \partial_X^2 C_N \quad (2c)$$

where the diffusion coefficients and electrostatic mobilities of all species are assumed to be constant and equal to D and μ , respectively. The electrostatic potential is given by Poisson's equation

$$-\epsilon_b \partial_X^2 \Phi = zF(C_C - C_A) \quad (3)$$

where ϵ_b is the permittivity of the bulk solvent (assumed to be constant outside the compact layer) and F is the Faraday constant.

The Faradaic current density due to the electromigration (conduction) of charged species is given by

$$J_F = -zF [D \partial_X (C_C - C_A) + \mu (C_C + C_A) \partial_X \Phi]. \quad (4)$$

Although we consider time-varying electric fields which are too small to generate significant magnetic fields, we will show that they can be large enough to produce a non-negligible Maxwell displacement current. Therefore, the total current density is given by

$$J(t) = J_F(X, t) - \epsilon_b \partial_t \partial_X \Phi(X, t) \quad (5)$$

which is the sum of the conduction and displacement current densities. Note that J is uniform across the cell since $\partial_X J = 0$, and therefore J is the experimentally controlled (or measured) current in a time-dependent situation, not J_F .

B. Boundary Conditions

At each electrode, $X = 0$ and $X = L$, there are three boundary conditions on the ionic fluxes expressing mass conservation in the electrochemical surface reaction (1)

$$D\partial_X C_C + \mu C_C \partial_X \Phi = -J_F/zF \quad (6a)$$

$$D\partial_X C_A - \mu C_A \partial_X \Phi = 0 \quad (6b)$$

$$D\partial_X C_N = J_F/zF \quad (6c)$$

(We adopt the sign convention that a cathodic current is negative.) In the mean-field approximation, the Faradaic current J_F at each electrode (which contributes to the surface reaction, unlike the displacement current) is related to the local concentrations and potential through the Butler-Volmer kinetic equation (applied at $X = 0$ and $X = L$)

$$J_F = -K_O C_C \exp(-\alpha_O z F \Delta\Phi_S/RT) + K_R C_N \exp(\alpha_R z F \Delta\Phi_S/RT) \quad (7)$$

where K_O and K_R are the oxidation and reduction kinetic rate constants, respectively, C_C and C_N are the interfacial concentrations, α_O and α_R are the transfer coefficients (which are set equal to 1/2 below) and $\Delta\Phi_S = \Phi_e - \Phi_r$ is the voltage drop across Stern's compact layer mentioned above. Following Frumkin [1], we imagine applying (7) at the outer Helmholtz plane, or any other convenient molecular distance which acts as the edge of the continuum region. Note we do not apply the Butler-Volmer equation across the entire interface (including both the compact and diffuse layers) as is frequently done.

No other boundary conditions are typically mentioned in electrochemistry textbooks because none are needed when the common assumption of electroneutrality is made [31]. In this work, however, since we treat diffuse charge explicitly we need another boundary condition on the potential. Ignorance of this boundary condition is typically hidden in the "zeta-potential" ζ (the potential drop across the diffuse layer $\Delta\Phi_D$) or equivalently the total charge in the diffuse layer. In colloidal science these quantities can be assumed to be constant properties of a surface, but in electrochemistry, the zeta potential of an electrode should be determined self-consistently from the microscopic electrochemical boundary conditions. We will see that the zeta potential of a working electrode can vary widely with electrochemical conditions, especially in time-dependent situations.

A general expression for the missing boundary condition has recently been proposed based on the Grahame model of the interface, which contains the Stern model as a special case [20]. Here we adopt the Stern model, which postulates a constant capacitance C_S for the compact layer

$$\Delta\Phi_S = \begin{cases} -\epsilon_S \partial_X \Phi / C_S & \text{at } X = 0 \\ \epsilon_S \partial_X \Phi / C_S & \text{at } X = L \end{cases} \quad (8)$$

where ϵ_S is an effective permittivity for the Stern layer. Note that we do not consider, in this model, any chemical adsorption effect. In this work, we model experiments in which the current $J(t)$ is prescribed and the voltage difference between the working electrode and the reference electrode $\Delta\Phi_{tot} = \Phi_e - \Phi_{ref}$ is determined by solving the equations. Note that

$$\lambda_S = \epsilon_S / C_S \quad (9)$$

defines an effective width for the Stern layer. We do not claim that λ_S corresponds to any well-defined molecular distance, but only that it captures the combined effect of the compact layer capacitance and permittivity. In our numerical calculations below, we assume that the permittivity of the Stern layer is $\epsilon_S = 10\epsilon_o$, compared with the value $\epsilon_b = 80\epsilon_o$ for a water solvent, consistent with previous studies [32]. From the equation $\lambda_S = \epsilon_S / C_S$ and the literature data on $C_S \sim 80\mu\text{F}\cdot\text{cm}^{-2}$ [32] an estimate of $\lambda_S \sim 1\text{\AA}$ can be computed. We also assume that λ_S is independent of the local ionic concentrations.

C. Dimensionless Equations and Boundary Conditions

The first step in any asymptotic analysis is to scale all quantities appropriately and identify the relevant dimensionless groups. Here we scale length to the electrode separation L , time to the diffusion time across the cell L^2/D , potential to the thermal voltage zFD/RT , concentrations to the mean anion concentration C^*

$$C^* = \frac{1}{L} \int_0^L C_A(X) dX \quad (10)$$

and current to the classical diffusion-limited current of Nernst

$$J_{DL} = \frac{4zFDC^*}{L}. \quad (11)$$

The dimensionless variables at these scales are

$$x = X/L, \quad \tau = tD/L^2, \quad j = J/J_L, \quad c_i = C_i/C^* \quad (i = C, A, N), \quad \phi = zF\Phi/RT. \quad (12)$$

We also introduce the mean concentration of charged species $c(x, t)$ and the charge density $\rho(x, t)$

$$c = \frac{1}{2}(c_C + c_A) \quad (13a)$$

$$\rho = \frac{1}{2}(c_C - c_A) \quad (13b)$$

In terms of these variables, the Nernst-Planck and Poisson equations take the dimensionless forms (using the Einstein relation $\mu = zFD/RT$)

$$\partial_\tau c = \partial_x^2 c + \partial_x(\rho \partial_x \phi) \quad (14a)$$

$$\partial_\tau \rho = \partial_x^2 \rho + \partial_x(c \partial_x \phi) \quad (14b)$$

$$\partial_\tau c_N = \partial_x^2 c_N \quad (14c)$$

$$-\epsilon^2 \partial_x^2 \phi = \rho \quad (14d)$$

where the dimensionless group $\epsilon = \lambda_D/L$ indicates that the natural scale for charge screening is the Debye length λ_D given by

$$\lambda_D^2 = \frac{\epsilon_b RT}{2F^2 C^*} \quad (15)$$

rather than the electrode separation L . In this work we consider the typical case in which ϵ is much smaller than unity (for a cell of typical length $L = 1\text{cm}$ and $\lambda_D < 100\text{nm}$, $\epsilon < 10^{-5}$), which is the basis for our asymptotic analysis. Since ϵ multiplies the highest derivative in the equations, it is a singular perturbation which must be treated using the methods of boundary layer theory [33]. Note that the expression for the dimensionless current (which is uniform across the cell since $\partial j/\partial x = 0$)

$$j(t) = j_F(x, t) + j_d(x, t) \quad (16)$$

where

$$j_F = -\frac{1}{2}(\partial_x \rho + c \partial_x \phi) \quad (17a)$$

$$j_d = -\frac{1}{2}\epsilon^2 \partial_\tau \partial_x \phi(x, t) \quad (17b)$$

involves the perturbation parameter multiplying the displacement current density j_d , which indicates that it only becomes important at high frequencies (and/or small length scales).

The flux boundary conditions at $x = 0$ and $x = 1$ take the dimensionless forms

$$\partial_x c + \rho \partial_x \phi = -2j_F \quad (18a)$$

$$\partial_x \rho + c \partial_x \phi = -2j_F \quad (18b)$$

$$\partial_x c_N = 4j_F \quad (18c)$$

where the dimensionless Faradaic current at each electrode is given by

$$j_F = -k_O(c + \rho) \exp(-\alpha_O \Delta \phi_S) + k_R c_N \exp(\alpha_R \Delta \phi_S) \quad (19)$$

where $k_O = K_O L/4D$ and $k_R = K_R L/4D$ are the dimensionless kinetic constants and $\Delta \phi_S = zF\Delta \Phi_S/RT$. The dimensionless Stern boundary conditions

$$\Delta \phi_S = \begin{cases} -\delta \epsilon \partial_x \phi & \text{at } x = 0 \\ \delta \epsilon \partial_x \phi & \text{at } x = 1 \end{cases} \quad (20)$$

involve a second dimensionless group $\delta = \lambda_S/\lambda_D$, which is the ratio of the effective widths of the compact and diffuse parts of the interfacial double layer. The Gouy-Chapman model (with no compact layer) corresponds to the limit $\delta = 0$ while the Helmholtz model (with no diffuse layer) corresponds to the limit $\delta \rightarrow \infty$. In this work, we consider the full range of values for δ , but always require $\epsilon \ll 1$.

It is ubiquitous in electrochemistry to assume that the total charge in the cell

$$q(t) = \int_0^1 \rho(x, t) dx \quad (21)$$

is identically zero, but this ‘‘macroscopic intuition’’ (which is valid in the limit $\epsilon \rightarrow 0$) is flawed whenever diffuse charge is being treated explicitly ($\epsilon > 0$), as we do here, because there is a total charge (of order ϵ) in the diffuse layers which exists to satisfy the nonlinear and asymmetric reaction conditions at the electrodes [20].

The fact that $q(t)$ can vary in time does not contradict the conservation of law for charge because dq/dt is related by (14b) to the Faradaic currents at the electrodes

$$\partial_\tau q = \int_0^1 \partial_\tau \rho(x, t) dx = 2 [j_F(0, \tau) - j_F(1, \tau)] \quad (22)$$

rather than the total currents (which are equal). Since the total current $j = j_F + j_d$ is uniform across the cell, any changes in the total charge of the cell are caused by temporary differences between the displacement currents at the two electrodes.

III. STEADY STATE RESPONSE TO A DC CURRENT

A. The Smyrl-Newman Equation

In this section, we derive leading-order steady-state solutions of (14) and (18)–(20) in response to a constant applied DC current density j , which are valid after transients have died away, following the analysis of Ref. [20]. Integrating the steady Nernst-Planck equations once, we arrive at a system of ordinary differential equations

$$\partial_x c + \rho \partial_x \phi = -2j \quad (23a)$$

$$\partial_x \rho + c \partial_x \phi = -2j \quad (23b)$$

$$\partial_x c_N = 4j \quad (23c)$$

$$-\epsilon^2 \partial_x^2 \phi = \rho \quad (23d)$$

By subtracting the first two equations we obtain

$$\partial_x (c - \rho) = (c - \rho) \partial_x \phi \quad (24)$$

which is easily integrated to show that (in steady-state) the anions are in Boltzmann thermal equilibrium throughout the cell

$$c_A = c - \rho \propto \exp(\phi) = \exp(-z_A F \Phi / RT) \quad (25)$$

since they do not react at the electrodes.

Our analysis begins by combining the three coupled equations (23a), (23b) and (23d) into a single equation for the potential, which is decoupled from the fourth equation (23c) for the neutral species concentration (except through the boundary conditions). Substituting (23d) into (23a) and integrating we obtain

$$c(x) = c_o - 2jx + \frac{\epsilon^2}{2} (\partial_x \phi)^2 \quad (26)$$

where c_o is an integration constant to be determined by the boundary conditions. If we substitute this expression and (23d) into (23b) we obtain a third order nonlinear equation for the potential [20]

$$\epsilon^2 \left[\partial_x^3 \phi - \frac{1}{2} (\partial_x \phi)^3 \right] + (2jx - c_o) \partial_x \phi = 2j \quad (27)$$

A similar equation was first derived by Smyrl and Newman for the electric field of a rotating disk electrode near the diffusion-limited current [7]. Once this equation is solved for the potential ϕ , the concentration c and charge density ρ are computed from (26) and (23d), respectively.

The Smyrl-Newman equation (27) cannot be solved analytically in terms of elementary functions, but due to the singular perturbations (terms involving ϵ), it is even difficult to solve numerically. Both of these difficulties can be conveniently resolved with asymptotic analysis [6,7,33]. The idea is to construct a uniformly valid approximation for all x (in the limit $\epsilon \rightarrow 0$) by adding the leading order solution to the “outer problem” in the neutral bulk region $\epsilon \ll x \ll 1 - \epsilon$ to the leading order solutions to the “inner problems” in the charged diffuse layers $0 \leq x \ll \epsilon$ and $1 - \epsilon \ll x \leq 1$ and subtracting the overlapping parts through asymptotic matching, which is valid well below the diffusion-limited current $|j| = 1$. As emphasized by Newman [6], the asymptotic approach used here reduces to the familiar Gouy-Chapman (Poisson-Boltzmann) theory of the diffuse layer in the special case $\delta = 0$, but it is more easily generalized to the time-dependent case. We also study for the first time the novel nonlinear effects of the coupled Stern and Butler-Volmer boundary conditions when $\delta > 0$, which include the possibility of a reaction-limited current.

B. Leading Order Solution of the Outer Problem

In the outer region, we set $\epsilon = 0$ in (27) to derive the leading order approximations

$$\partial_x \phi = 2j/(2jx - c_o) + O(\epsilon) \quad (28a)$$

$$c(x) = c_o - 2jx + O(\epsilon) \quad (28b)$$

$$\rho(x) = O(\epsilon^2) \quad (28c)$$

from (26) and (23d), where the integration constant c_o can be evaluated using the conservation of anions over the cell $\int_0^1 c_A(x, t) dx = 1$ at zeroth order in ϵ .

$$c_o = 1 + j \quad (29)$$

since $q(t) = O(\epsilon)$. Note that the outer region is neutral ($\rho = 0$) at leading order, as is commonly assumed in electrochemistry. The bulk potential profile at leading order is obtained by a simple integration

$$\phi(x) - \phi_e = -\Delta\phi_i + \log[(c_o - 2jx)/c_o] + O(\epsilon) \quad (30)$$

where $\Delta\phi_i = \phi_e - \phi(0)$ is the total (leading-order) potential drop across the interface consisting of contributions from the diffuse (Debye) and compact (Stern) layers

$$\Delta\phi_i = \Delta\phi_D + \Delta\phi_S \quad (31)$$

which must be calculated by asymptotic matching with the inner problem. (Note again that $\Delta\phi_D$ is the familiar zeta potential.) The equation for the neutral species concentration is also easily integrated, writing the conservation over the cell of the *sum* of the cation and neutral species numbers at zeroth order in ϵ .

$$c_N = \gamma - 2j(1 - 2x) + O(\epsilon). \quad (32)$$

Typical bulk concentration, electric field and potential profiles are shown in Fig. 1. (We set $\gamma = 1$ in all the numerical results presented here.) The potential profile ϕ is slightly curved (logarithmic dependence on x), and the electric field $\partial_x \phi$ is not constant since the migration term is a nonlinear function of the concentration c (which varies linearly in the bulk when $j \neq 0$). The profiles of ϕ and $\partial_x \phi$ corresponding to opposite values of j (e.g. 0.4 and -0.4) are not symmetric across x -axis because the product of the reduction of cations is neutral. On the other hand, the profiles of c and c_N are symmetric when the current is reversed.

C. Leading Order Solution of the Inner Problem

The leading order approximation for the diffuse layer potential at the $x = 0$ electrode is obtained by changing variables to the inner coordinate $y = x/\epsilon$ in (27)

$$-\partial_y^3 \phi + \frac{1}{2} (\partial_y \phi)^3 + c_o \partial_y \phi = O(\epsilon). \quad (33)$$

where we ignore the $O(\epsilon)$ terms. Multiplying by $2\partial_y^2\phi$ and integrating (using the matching conditions $\partial_y\phi, \partial_y^2\phi \rightarrow 0$ as $y \rightarrow \infty$) we obtain

$$\partial_y^2\phi = -\partial_y\phi\sqrt{c_o + (\partial_y\phi)^2/4} \quad (34)$$

which is a first-order separable equation for $\partial_y\phi$. The next integration can be performed with an hyperbolic substitution $\partial_y\phi = \pm 2\sqrt{c_o}\text{csch}(u)$ (where $\text{csch}(u) = 1/\sinh(u)$), which yields the trivial equation $\partial_y u = \sqrt{c_o}$, whose solution is $u = \sqrt{c_o}(y + K)$ for some constant K . Therefore, the electric field in the diffuse layer is

$$\partial_y\phi = \pm 2\sqrt{c_o}\text{csch}(\sqrt{c_o}(y + K)) + O(\epsilon) \quad (35)$$

where K is related to the Stern-layer voltage through the boundary condition at $y = 0$

$$\Delta\phi_S = \mp 2\delta\sqrt{c_o}\text{csch}(\sqrt{c_o}K). \quad (36)$$

The upper sign refers to potentials below the potential of zero charge (“p.z.c.”) with $\Delta\phi_D, \Delta\phi_S < 0$, and the lower sign to potentials above p.z.c.

Transforming to the inner coordinate in (26) and (23d)

$$c = c_o + \frac{1}{2}(\partial_y\phi)^2 + O(\epsilon) \quad (37a)$$

$$\rho = -\partial_y^2\phi + O(\epsilon) \quad (37b)$$

and substituting (35) for the electric field, we obtain the leading order concentration and charge density profiles

$$c = c_o [1 + 2\text{csch}^2(\sqrt{c_o}(y + K))] + O(\epsilon) \quad (38a)$$

$$\rho = \pm 2c_o\text{csch}(\sqrt{c_o}(y + K))\coth(\sqrt{c_o}(y + K)) + O(\epsilon) \quad (38b)$$

The constant of integration K , or equivalently the Stern layer voltage $\Delta\phi_S$, is determined by solving a transcendental equation provided by the Butler-Volmer kinetic boundary condition at $y = 0$ (see below)

$$j = -k_O(c + \rho)\exp(-\alpha_O\Delta\phi_S) + k_R(\gamma - 2j)\exp(\alpha_R\Delta\phi_S) \quad (39)$$

where $c(0) + \rho(0) = c_C(0)$ is a (generalized) Frumkin correction [31].

The expression for the electric field (35) can be integrated analytically to obtain the diffuse layer potential profile at leading order

$$\phi_e - \phi = \Delta\phi_i + 4 \tanh^{-1}\left(e^{-\sqrt{c_o}(y+K)}\right) \quad (40)$$

which is essentially the Gouy-Chapman solution to the Poisson-Boltzmann equation, although our boundary conditions (specifying K) are substantially different from the classical theory, which corresponds to the limit $\delta \rightarrow 0$. To clarify this connection, we let $\psi = \Delta\phi_i + \phi$, and observe (following some algebra) that the solution (40) satisfies

$$\partial_y\psi = 2\sqrt{c_o}\sinh(\psi/2) \quad (41)$$

and

$$\partial_y^2\psi = c_o\sinh(\psi) \quad (42)$$

which is the Poisson-Boltzmann equation. (Changing the current simply changes the bulk concentration $c_o = 1 + j$.) The Smyrl-Newman equation (27) is more general than the Poisson-Boltzmann equation, but the former is equivalent to the latter below the diffusion-limited current [20]. Combining (36) and (41), we obtain a relation between the Stern and diffuse layer voltages

$$\Delta\phi_S = 2\delta\sqrt{c_o}\sinh(\Delta\phi_D/2) \quad (43)$$

and from (40) the constant K can be related to the diffuse layer voltage

$$\tanh(\Delta\phi_D/4) = e^{-\sqrt{c_o}K}. \quad (44)$$

To determine K we must solve the transcendental system (36) and (39) numerically.

D. Application of the Electrochemical Boundary Conditions

The behavior of K as a function of the ratio of the kinetics constants $R_k = k_R/k_O$ and the current density j is reported in Fig. 2 (with $k_R = 1$ held constant). From (36) it is clear that large values of K correspond to small values of $\Delta\phi_S$ when $j = 0$, i.e. the symmetric case $c_o = 1$. The introduction of a nonzero value of j breaks the symmetry of the K versus $\log(R_k)$ curve. The plot of K versus j in Fig. 2(b) illustrates the dissymmetry of the redox couple, since when the current is positive the oxidation of neutral species produces positively charged cations which accumulate in the diffuse layer, thus hindering the negative charging of the diffuse-layer. In Fig. 2 we also display the Stern and total interfacial voltages, $\Delta\phi_S$ and $\Delta\phi_i = \Delta\phi_S + \Delta\phi_D$. We observe that when j increases beyond 0.3, $\Delta\phi_S$ and $\Delta\phi_i$ reach arbitrarily large values to compensate this excess of cations (see below). For $j = 0$, the plots of $\Delta\phi_S$ (Fig. 2(c)) and $\Delta\phi_i$ (Fig. 2(e)) are symmetric with respect to $R_k = 1$. This behavior is confirmed by the plot of the different spatial profiles c , ρ , $\partial_y\phi$ and ϕ , for two different values of j , in Figs. 3 and 4.

In Fig. 3 we focus on the case of zero current. When the kinetic constants are equal $R_k = 1$, this correspond to the p.z.c., but when $R_k \neq 1$, the system builds a charged diffuse layer to equilibrate the oxidation and reduction currents on each electrode. For comparison, we have also added in (dashed lines) the stationary Poisson-Boltzmann solution for $j = 0$, which corresponds to choosing K such that $\delta = 0$ in (40).

In Fig. 4, a positive current $j = 0.3$ has been chosen, with symmetric kinetic constants ($R_k = 1$). In this case, the system builds a charged diffuse layer to favor either reduction (negative Faradaic current) or oxidation (positive Faradaic current). In each figure, two values of λ_D have been chosen, one corresponding to a weak electrolyte concentration $\lambda_D = 100\lambda_S$, where the diffuse layer has a strong effect on the charge distribution and potential profiles, and another corresponding to a strong electrolyte concentration with $\lambda_D = \lambda_S$, where there is a much more significant potential drop in the Stern layer (and hence less influence from the diffuse layer). We note that for $j = 0.3$ the charge and electric field profiles shown in Fig. 4 start to diverge at $y = 0$, particularly so at the small value of $\delta = 1/100$.

To better understand this unexpected behavior observed for $j > 0.3$, we plot the influence of the ratio $\lambda_D/\lambda_S = \delta^{-1}$ on the potential drops of the diffuse layer $\Delta\phi_D$, Stern's layer $\Delta\phi_S$ and the whole double layer $\Delta\phi_i = \Delta\phi_D + \Delta\phi_S$ in Fig. 5. We notice that an exchange of potential drop between Stern's layer and the diffuse layer occurs when the size of the diffuse layer becomes larger than λ_S . The potential drops in Stern's layer and diffuse layer compensate exactly when $j = 0$, whereas the potential drop in the diffuse layer diverges when λ_D increases at a nonzero current larger than 0.3.

E. Theoretical Polarograms

For the electrochemist, polarograms bear a great significance. In the present study of stationary regimes in finite size cells such a representation of current j versus the total voltage between the reference and working electrodes $\Delta\phi_{tot} = \phi_e - \phi_{ref}$ is shown in Fig. 6. This includes leading order voltage drops calculated for both double layers and the bulk electroneutral region. It confirms again than for j positive large than 0.3, a limitation of the current occurs which is very different from diffusion limited current which are usually encountered in electrochemical cells. The standard current-potential curve ("PB", plotted as a dotted line in Fig. 6) shows a limiting current equal to $\gamma/2$ which occurs when $c_N \rightarrow 0$ at the working electrode surface. When $j > 0$ the production of cations increases due to oxidation of neutral species, to maintain the imposed current, the system usually increases $\Delta\phi_S$ to compensate this excess. When $\delta = \lambda_S/\lambda_D$ becomes much smaller than 1, the potential drop in the diffuse layer increases much more rapidly than the potential drop in the Stern layer, there is an enhancement of the electric field in the diffuse layer which tends to strip the cations from the anode. For a given current density ($j > 0.3$ in this case) the interfacial cation concentration tends to zero. This limitation of the current, however, is not due to transport but rather the reaction kinetics coupled to the diffuse layer charging.

The significance of $j = 0.3$ in our numerical results is most easily understood in the limit of a very weak electrolyte with $\lambda_D \gg \lambda_S$ ($\delta \rightarrow 0$) where it corresponds to a "reaction-limited current", generally given by

$$j_{RL} = \frac{k_R\gamma}{1 + 2k_R} \quad (45)$$

whenever this value is smaller than the Nernst diffusion-limited current $\gamma/2$, when $c_N(0) = 0$. (Recall that we have chosen $k_R = \gamma = 1$, so that $j_{RL} = 1/3$ and $\gamma/2 = 1/2$.) Instead of being caused simply by transport limitations, the reaction-limited current j_{RL} is determined by the electrochemical boundary conditions. Note that when $\delta = 0$ (no Stern layer), and the Butler-Volmer equation (39) takes the simpler form

$$j = -k_O(c + \rho) + k_R(\gamma - 2j), \quad (46)$$

and in this case, a limitation of positive current occurs because the first term representing the cathodic current is negative (but small) while the positive second term representing the anodic current decreases with applied current as the concentration of neutral species is reduced (but not necessarily depleted) at the electrode. When $\delta > 0$ (however small), the situation is quite different because the system can avoid the reaction limitation in (39) by producing a large positive Stern-layer voltage $\Delta\phi_S$

$$\Delta\phi_S \sim \frac{1}{\alpha_R} \log\left(\frac{j}{k_R(\gamma - 2j)}\right) \quad (47)$$

which suppresses the negative cathodic current and exponentially enhances the positive anodic current enough to maintain the applied total current. This also produces a large diffuse layer voltage for $j > j_{RL}$ according to (43), although this effect is reduced as δ is increased.

The actual limiting current in the system is controlled by the smaller of the reaction-limited current (45) and the diffusion limited current $|j| = \gamma/2$. Note that for negative currents one observes a diffusion limiting current at $j = -\gamma/2$ which corresponds to the annulation of the neutral species concentration at the counter electrode. Therefore, the system never reaches the classical limiting value $j = -1$ which would be obtained with a strongly supporting electrolyte (purely diffusing system).

IV. ANALYSIS OF THE LINEAR RESPONSE TO AN AC CURRENT MODULATION

In this section we derive the leading-order response of our simple electrochemical system to small amplitude AC current perturbations (around a steady nonzero DC current) using the same mathematical methods as in previous section, now applied to the Laplace transforms of the linearized equations. There have been very few attempts in the existing literature [34–36] to compute the impedance spectra for electrochemical systems with weak electrolytes (and large Debye lengths) in the absence of a supporting electrolyte. The modeling of voltammetric curves has received more attention [37–41], although most of these studies either neglect the diffuse layer entirely or assume its ionic concentration profiles are those of equilibrium. In this section we show that the diffuse-layer cannot always be approximated by an additional fixed capacitance in parallel with the Stern-layer capacitance because its dynamics can strongly influence the net interfacial impedance at intermediate frequencies.

To compute the response of the electrochemical cell to small applied AC current modulation δj of a DC current \bar{j}

$$j = \bar{j} + \delta j \quad (48)$$

we add a corresponding small modulation to each of the variables

$$c = \bar{c} + \delta c \quad (49a)$$

$$c_N = \bar{c}_N + \delta c_N \quad (49b)$$

$$\rho = \bar{\rho} + \delta \rho \quad (49c)$$

$$\phi = \bar{\phi} + \delta \phi \quad (49d)$$

$$(49e)$$

about the leading-order approximation of the steady-state solution described above (denoted by an overline), and linearize the time-dependent model of equations (14) around the stationary state to obtain the following system:

$$\partial_\tau \delta c = \partial_x^2 \delta c + \partial_x (\bar{\rho} \partial_x \delta \phi + \delta \rho \partial_x \bar{\phi}) \quad (50a)$$

$$\partial_\tau \delta \rho = \partial_x^2 \delta \rho + \partial_x (\delta c \partial_x \bar{\phi} + \bar{c} \partial_x \delta \phi) \quad (50b)$$

$$\partial_\tau \delta c_N = \partial_x^2 \delta c_N \quad (50c)$$

$$\delta \rho = -\epsilon^2 \partial_x^2 \delta \phi \quad (50d)$$

The electrochemical boundary conditions at both electrodes ($x = 0, 1$) are also linearized about the steady-state

$$-2\delta j_F = \partial_x \delta c + \bar{\rho} \partial_x \delta \phi + \delta \rho \partial_x \bar{\phi} \quad (51a)$$

$$-2\delta j_F = \partial_x \delta \rho + \delta c \partial_x \bar{\phi} + \bar{c} \partial_x \delta \phi \quad (51b)$$

$$4\delta j_F = \partial_x \delta c_N \quad (51c)$$

$$\delta j_F = [k_O \alpha_O (\bar{c} + \bar{\rho}) \exp(-\alpha_O \overline{\Delta \phi_S}) + k_R \alpha_R c_N \exp(\alpha_R \overline{\Delta \phi_S})] \delta \Delta \phi_S \quad (51d)$$

$$-k_O (\delta c + \delta \rho) \exp(-\alpha_O \overline{\Delta \phi_S}) + k_R \delta c_N \exp(\alpha_R \overline{\Delta \phi_S}) \quad (51e)$$

$$\delta \Delta \phi_S = \begin{cases} -(\delta \cdot \epsilon) \partial_x \delta \phi & \text{at } x = 0 \\ (\delta \cdot \epsilon) \partial_x \delta \phi & \text{at } x = 1 \end{cases} \quad (51f)$$

where the Stern-layer voltage is decomposed as the other variables $\Delta \phi_S = \overline{\Delta \phi_S} + \delta \Delta \phi_S$. In the time-dependent setting, the current modulation is broken into separate contributions from the Faradaic conduction and displacement current densities

$$\delta j = \delta j_F + \delta j_d \quad (52)$$

where

$$\delta j_F = -\frac{1}{2} (\partial_x \delta \rho + \delta c \partial_x \bar{\phi} + \bar{c} \partial_x \delta \phi) \quad (53a)$$

$$\delta j_d = -\frac{1}{2} \epsilon^2 \partial_\tau \partial_x \delta \phi \quad (53b)$$

The unperturbed DC current is entirely Faradaic ($\bar{j} = \bar{j}_F$, $\bar{j}_d = 0$), but the displacement current becomes important in the AC modulation, especially at large frequencies and small length scales.

To compute the impedance of the electrochemical cell, we consider a small amplitude AC perturbations of the form

$$\delta j = j_o \sin(\omega t) \quad (54)$$

and take the Laplace transform in time of the system of transport equations (50)

$$s \tilde{c} = \partial_x^2 \tilde{c} + \partial_x (\bar{\rho} \partial_x \tilde{\phi} + \tilde{\rho} \partial_x \bar{\phi}) \quad (55a)$$

$$s \tilde{\rho} = \partial_x^2 \tilde{\rho} + \partial_x (\tilde{c} \partial_x \bar{\phi} + \bar{c} \partial_x \tilde{\phi}) \quad (55b)$$

$$s \tilde{c}_n = \partial_x^2 \tilde{c}_n \quad (55c)$$

$$\tilde{\rho} = -\epsilon^2 \partial_x^2 \tilde{\phi} \quad (55d)$$

$$(55e)$$

where $s = i\omega L^2/D$ is the Laplace variable conjugate to time (the dimensionless forcing frequency, or imaginary decay rate) and tilde accents are used denote the transformed variables $\tilde{f} = \mathcal{L}f$. Since they do not depend explicitly on time, the interfacial boundary conditions (51) are the same for the transformed variables as for the original ones. Note that the displacement current modulation takes the form

$$\delta \tilde{j}_d = -\frac{1}{2} \epsilon^2 s \partial_x \tilde{\phi} \quad (56)$$

in Laplace space. Once we solve these equations for the perturbed variables, the (complex) impedance of the cell is calculated as the ratio of the voltage response versus the current modulation in Laplace space

$$Z(\omega) = \frac{\delta \Delta \tilde{\phi}_{tot}}{\tilde{\delta j}} \quad (57)$$

where $\delta \Delta \tilde{\phi}_{tot}$ is the total voltage modulation (in Laplace space) between the working electrode and the reference electrode.

The analysis begins by combining the transport equations (55) following the same steps as in the derivation of the Smyrl-Newman equation above, which leads to a system of two linear equations for $\tilde{\delta \phi}$ and $\tilde{\delta c}$:

$$-s \epsilon^2 \partial_x^2 \tilde{\delta \phi} = -\epsilon^2 \partial_x^4 \tilde{\delta \phi} + \partial_x (\tilde{\delta c} \partial_x \bar{\phi} + \bar{c} \partial_x \tilde{\delta \phi}) \quad (58a)$$

$$s \tilde{\delta c} = \partial_x^2 \tilde{\delta c} - \epsilon^2 \partial_x^2 (\partial_x \bar{\phi} \partial_x \tilde{\delta \phi}) \quad (58b)$$

Although these equations are linear, they cannot be solved analytically in terms of elementary functions, and they also possess singular perturbations which hinder numerical progress. As in the steady-state case, asymptotic analysis

in the limit $\epsilon \rightarrow 0$ once again allows us to solve the leading-order problem by decomposing the cell into a bulk electroneutral region which must be asymptotically matched with charged diffuse boundary layers. The resulting leading order equations for the inner and outer problems are difficult to solve analytically in this case, but they present no trouble for a numerical solution because the singular perturbations have been removed analytically. The details of these calculations will be presented elsewhere, but here we present a simple example of the rich time-dependent electrochemical behavior that can be predicted by the mathematical model.

In the framework of the asymptotic analysis, the total impedance of the cell is conveniently broken into separate leading-order contributions from the various regions

$$Z(\omega) = \frac{\delta\tilde{\Delta}\phi_S + \delta\tilde{\Delta}\phi_D + \delta\tilde{\Delta}\phi_b}{\delta\tilde{j}_F + \delta\tilde{j}_d} \quad (59)$$

where $\delta\tilde{\Delta}\phi_S$, $\delta\tilde{\Delta}\phi_D$ and $\delta\tilde{\Delta}\phi_b$ are the voltage modulations in the Stern layer, the diffuse layer and the bulk electroneutral zone, respectively. The asymptotic analysis for the limit $\epsilon \rightarrow 0$ assumes that the diffuse layers are stationary (quasi-steady) at leading order, which is valid when the forcing frequency is below the Debye frequency

$$\omega \ll \frac{D}{\lambda_D^2} \quad (60)$$

or in terms of the dimensionless frequency

$$|s| = \frac{\omega L^2}{D} \ll \frac{1}{\epsilon^2}. \quad (61)$$

This does not limit the applicability of our analysis because impedance spectroscopy experiments are conducted well below the Debye frequency.

It is interesting to consider the displacement current density over this range of time scales. From (56) we see that when $|s| \ll 1/\epsilon^2$ or $\epsilon^2 s \ll 1$ the displacement current $\delta\tilde{j}_d$ is always negligible in the outer electroneutral region. However, the situation is very different in the diffuse layers, where the natural length scale λ_D is much smaller. In the diffuse layer, we write the displacement current in terms of the inner coordinate $y = x/\epsilon$,

$$\delta\tilde{j}_d = -\frac{1}{2}s\epsilon\partial_y\delta\tilde{\phi} \quad (62)$$

and observe that it becomes comparable to the Faradaic current when $|s|\lambda_D\delta\tilde{\Delta}\phi_S/\lambda_S = O(\epsilon^{-1})$. Since the kinetic constants (k_O , k_R) are included in the value of $\delta\tilde{\Delta}\phi_S$, they will have strong influence on the current displacement and on the ‘‘crossover’’ frequency where the displacement and Faradaic currents become comparable.

Note that for the case of non-reacting system (zero kinetic constants, and zero Faradaic current) the characteristic frequency of Debye layer charging has recently been derived in the completely different context of electrohydrodynamic response to a spatially periodic applied AC voltage [42]:

$$\omega_c = \frac{D}{\lambda_D L} \quad (63)$$

This prediction is recovered by our model in the limit where $\lambda_D \gg \lambda_S$.

In Fig 7, a plot of the two current modulations versus the AC frequency ω gives a clear insight into the interchange of the reaction and diffuse layer charging processes with frequency. (The amplitude of the stationary current in this example is $j = 0.3$, near the steady-state reaction-limited current j_{RL}). The crossover frequency where the displacement and Faradaic current amplitudes are comparable is strongly affected by the parameter $\delta = \lambda_S/\lambda_D$. The larger is δ , the smaller is the diffuse layer size and the higher the frequency at which the displacement currents dominate, given (very roughly) by ϵ^{-1} .

The arguments of the current modulations are such that when λ_D increases the phases become shifted by π , showing an out of phase AC voltage response. This phenomena is often termed ‘‘negative impedance’’ [27–30] and has already been reported in the electrochemical literature as the source of instabilities (stationary or oscillatory). The impedance spectra corresponding to the current modulations reported in Fig. 7 are shown in Fig. 8. The two examples $\delta = 1$, $\epsilon = 10^{-8}$ and $\delta = 0.01$, $\epsilon = 10^{-6}$ are consistent with the phase shift that we have described in the current modulation curves. The amplitude of the impedance also increases very dramatically when the current density goes beyond 0.33. As already discussed in the stationary case, when the system reaches this ‘‘reaction-limited current’’ situation, a strong potential drop is established in the diffuse layer, which can explain the amplification of the electrochemical cell impedance. We hope to elaborate on this aspect of the theoretical predictions in comparison with real experiments in a future communication.

V. CONCLUSION

We have performed a leading-order asymptotic analysis of a realistic set of transport equations and boundary conditions for a three-species electrochemical cell in which cations are reduced into a neutral molecules in the presence of anions, in both stationary and time-dependent nonequilibrium situations. By solving the full nonlinear problem at leading order (numerically where necessary), we have made the first systematic exploration of the influence of the parameter $\delta = \lambda_S/\lambda_D$ (introduced in Ref. [20] to describe the coupling of the Stern and diffuse layers) on stationary and time-dependent interfacial kinetics. The mathematical model is able to predict very subtle effects related to the coupling between diffuse charge and interfacial reactions, such as the existence of both reaction-limited and diffusion-limited currents and negative impedances with nonnegligible displacement currents at large frequencies. The strength and novelty of these theoretical predictions is their firm analytical basis starting from realistic transport equations and boundary conditions.

An interesting extension of this study would be to electrochemical reactions involving the reduction of anions (or the oxidation of cations). Such systems have already been the subject of many investigations, both theoretical and experimental, but most these studies have not considered simultaneously the dynamics of the diffusion and diffuse layers and their possible interplay during the interfacial reactions, as we have in this work. Such situations would complicate the present analysis significantly because there would be more than two charged species, and it appears that any analytical solution of the inner problem at leading order would not be possible in such cases. However, as long as ϵ is small ($\lambda_D \ll L$), the mathematical machinery of asymptotic analysis can be used to derive simplified, well-behaved equations at leading order, which would be straightforward to at least integrate numerically.

Even restricting ourselves to the simple electrochemical system studied here, there are number of interesting directions for future work. Higher order corrections in ϵ could be derived (with some numerical computation required). It would also be interesting to solve the full system of equations with $\epsilon = O(1)$, where the asymptotic analysis breaks down. This limit, which corresponds to very small cells on the order of the Debye length, has increasing importance as microelectrochemical systems reach smaller and smaller length scales. It would also be interesting to solve the AC current problem more globally in the nonlinear regime, where our local linear stability analysis is no longer valid. In order to study nonlinear responses, such as those encountered in voltammetry or chronoamperometric methods, the full nonlinear system of equations would have to be solved numerically. Nevertheless, if ϵ is small (as is usually the case) asymptotic analysis provides the appropriate starting point for the mathematical modeling of diffuse-charge effects in electrochemical systems.

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- [1] A. Frumkin, *Z. Electrochem* **59**, 807 (1955).
 - [2] P. Delahay, *Chem. Rev.* **41**, 441 (1947).
 - [3] R. Parsons, in *Modern Aspects of electrochemistry*, edited by J.-O. Bockris and B. Conway (Butterworths, London, 1954), Vol. 1, pp. 103–179.
 - [4] P. Delahay, *Double layer and electrode kinetics* (Wiley-Interscience, New York, 1965).
 - [5] P. Delahay, *J. Phys. Chem.* **70**, 2373 (1966).
 - [6] J. Newman, *Trans. Faraday Soc.* **61**, 2229 (1965).
 - [7] W.-H. Smyrl and J. Newman, *Trans. Faraday Soc.* **62**, 207 (1966).
 - [8] R. D. Levie, *Adv. Electrochem. Electrochem. Eng.* **6**, 380 (1967).
 - [9] J. R. MacDonald, *Trans. Farad. Soc.* **66**, 943 (1970).
 - [10] J.-D. Norton, H.-S. White, and S.-W. Feldberg, *J. Phys. Chem.* **94**, 6772 (1990).
 - [11] S. Levine, *J. Colloid Int. Sciences* **3**, 619 (1971).
 - [12] W. Fawcett, *Electroanal. Chem. and Int. Electrochem.* **39**, 474 (1972).
 - [13] B. Damaskin, V. Safonov, and N. Federovich, *J. Electroanal. Chem.* **349**, 1 (1993).
 - [14] B. Damaskin, V. Safonov, and N. Federovich, *Elektrokhimiya* (translation) **29**, 1124 (1993).

- [15] W. Fawcett, in *Double layer effects in the electrode kinetics of electron and ion transfer reactions*, edited by J. Lipkowski and P. Ross (Wiley-VCH, N.Y., 1998), Chap. 8, pp. 323–371.
- [16] W. Fawcett, *Electroanal. Chem. and Int. Electrochem.* **43**, 175 (1973).
- [17] B. Levich, *Doklady Akad. Nauk SSSR* **67**, 309 (1949).
- [18] L. Gierst, in *Transactions of the Symposium on Electrode Processes, Electrochemical Society Series*, edited by Yeager (Wiley, N.Y., 1961), p. 109.
- [19] I. Borukhov, D. Andelman, and H. Orland, *Phys. Rev. Lett.* **79**, 435 (1997).
- [20] M. Bazant, asymptotic analysis of diffuse charge and limiting current in binary electrochemical cells (unpublished).
- [21] T. Brumeleve and R. Buck, *J. Electroanal. Chem* **90**, 1 (1978).
- [22] W.-D. Murphy, J.-A. Manzanares, S. Mafé, and H. Reiss, *J. Phys. Chem.* **96**, 9983 (1992).
- [23] B. M. Grafov and A. A. Chernenko, *Doklady Akad. Nauk S.S.S.R.* **146**, 135 (1962).
- [24] A. A. Chernenko, *Doklady Akad. Nauk S.S.S.R.* **153**, 1963 (1963).
- [25] I. Rubinstein and L. Shtilman, *J. Chem. Soc. Faraday Trans. II* **75**, 231 (1979).
- [26] J. Henry and B. Luoro, *Nonlinear Analysis* **13**, 787 (1989).
- [27] M. Koper and J. Sluyters, *J. Electroanal. Chem* **352**, 51 (1993).
- [28] M. Koper, in *Advances in Chemical Physics*, edited by I. Prigogine and S. Rice (John Wiley and Sons, New York, 1996), Vol. XCII, pp. 161–298.
- [29] P. Strasser, M. Eiswirth, and M. T.-M. Koper, *J. Electroanal. Chem* **478**, 50 (1999).
- [30] K. Krischer, in *Modern aspects of electrochemistry*, edited by J. B. B.E. Conway and R. White (Academic/Plenum Publishers, New York, 1999), Vol. 32, pp. 1–142.
- [31] J. Newman, *Electrochemical Systems* (Prentice Hall, Englewood Cliff, New Jersey, 1991).
- [32] *Electrified interfaces in physics, chemistry and biology*, Vol. 355 of *NATO ASI Series C: Mathematical and Physical Sciences*, edited by R. Guidelli (Kluwer Academic Publishers, Netherlands, 1992).
- [33] C. M. Bender and S. A. Orszag, *Mathematical Methods for Scientists and Engineers* (McGraw-Hill, New York, 1978).
- [34] J. R. MacDonald, *Electroanalytical Chemistry and Interf. Electrochem.* **53**, 1 (1974).
- [35] J. R. MacDonald, *J. Electroanal. Chem.* **99**, 283 (1979).
- [36] J. R. MacDonald, *J. Electroanal. Chem.* **223**, 1 (1987).
- [37] *Chemical kinetics*, edited by C. Bamford and R. Compton (Elsevier, Amsterdam, 1986), Vol. 26.
- [38] K. Oldham, *J. Electroanal. Chem* **337**, 91 (1992).
- [39] M. Bento, L. Thouin, and C. Amatore, *J. Electroanal. Chem* **446**, 91 (1998).
- [40] M. Bento, L. Thouin, C. Amatore, and M. Montenegro, *J. Electroanal. Chem* **443**, 137 (1998).
- [41] C. Amatore, L. Thouin, and M.-F. Bento, *J. Electroanal. Chem* **463**, 45 (1999).
- [42] A. Ajdari, *Phys. Rev. E* **61**, R45 (2000).

VI. APPENDIX A. LIST OF SYMBOLS

D	diffusion coefficient
μ	mobility
z_C, z_A, z	charge numbers $z_C = -z_A = z$
F	Faraday's constant
R	universal gas constant
T	absolute temperature
t	time
K_O, K_R	kinetic constants
k_O, k_R	dimensionless kinetic constants
C_S	capacitance of the Stern layer
ϵ_b	permittivity of the bulk solvent
ϵ_S	effective permittivity of the Stern layer
λ_S	effective width of the Stern layer
λ_D	Debye screening length
L	distance between the electrodes (working and counter)
δ	$= \lambda_S/\lambda_D$
ϵ	$= \lambda_D/L$
J	current density
J_F	Faradaic current
J_{DL}	diffusion-limited current
J_{RL}	reaction-limited current
C_C, C_A, C_N	concentrations of the species C, A and N
Φ	electric scalar potential
C^*	mean anion concentration
c_C, c_A, c_N	dimensionless concentrations
c	dimensionless average concentration of charged species
ρ	dimensionless charge density
ϕ	dimensionless electrical potential
j	dimensionless current density
j_F	dimensionless Faradaic current
j_d	dimensionless displacement current
$\Delta\phi_i$	dimensionless double layer voltage
$\Delta\phi_D$	dimensionless diffuse layer voltage
$\Delta\phi_S$	dimensionless Stern layer voltage

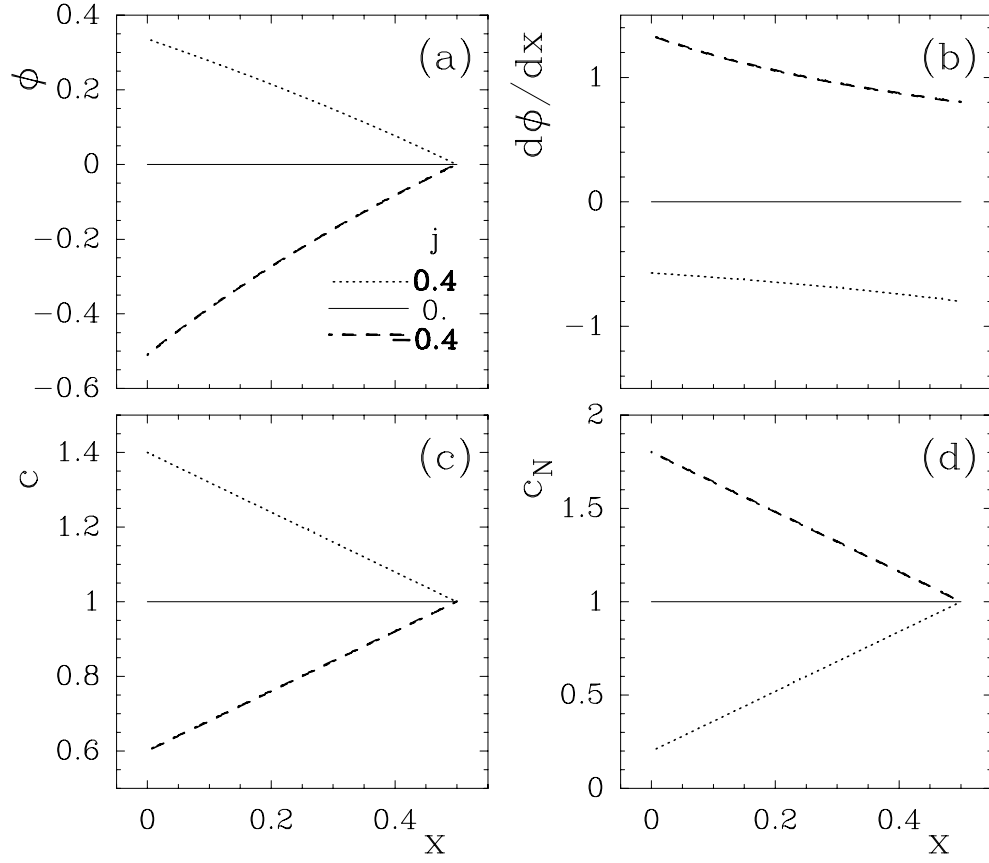


FIG. 1. Steady-state profiles of ϕ (a), $d\phi/dy$ (b), c (c), and c_N (d) at leading order in the “outer” (bulk electroneutral) region for $j = 0.4, 0$ and -0.4 and $\gamma = 1$. $\alpha_O = \alpha_R = 1/2$

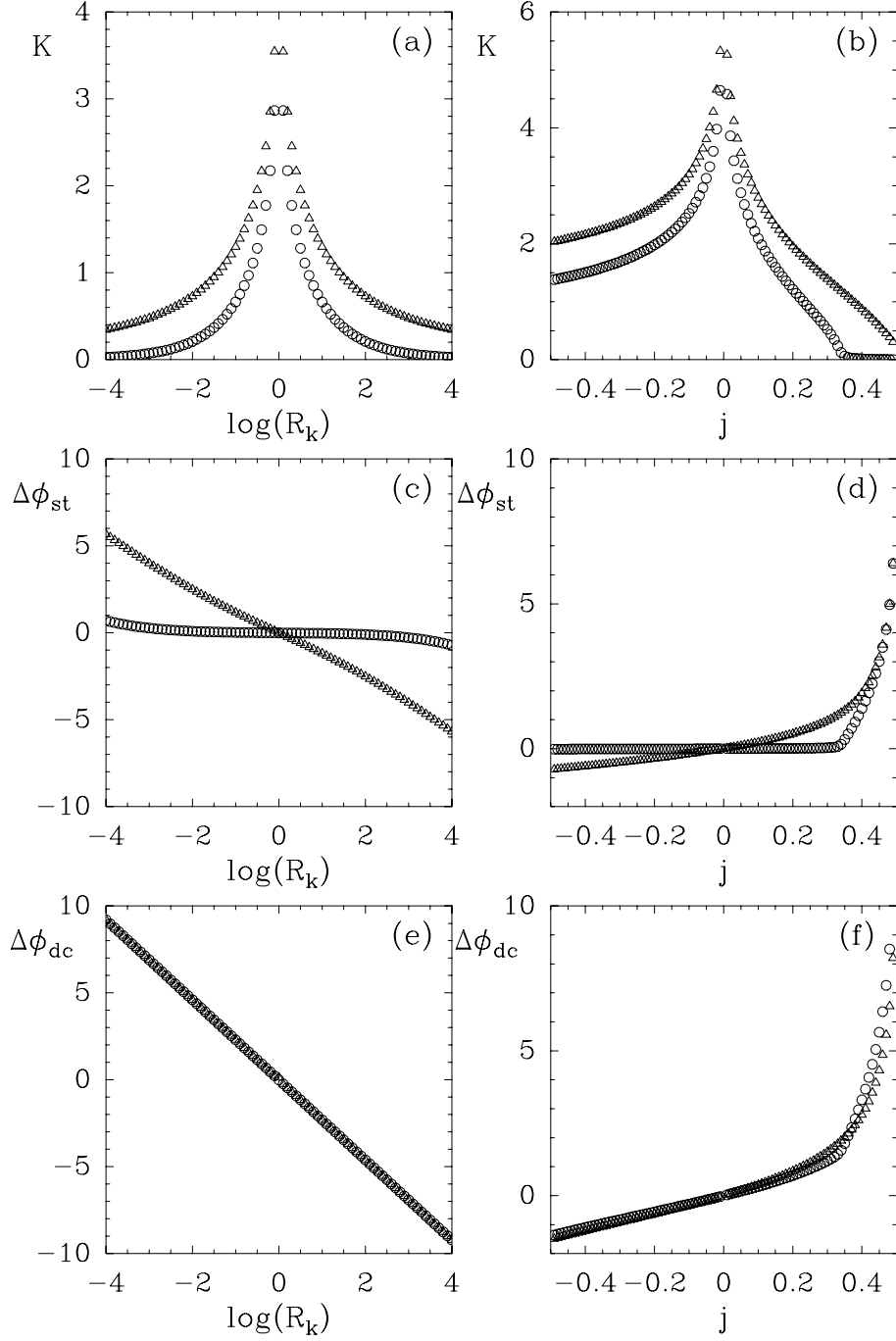


FIG. 2. (a) K versus $R_k = k_r/k_o$ in lin-log representation, ($j = 0$). (b) K versus j for $R_k = 1$. (c) $\Delta\phi_s$ versus R_k in lin-log representation, ($j = 0$). (d) $\Delta\phi_s$ versus j for $R_k = 1$. (e) $\Delta\phi_i$ versus R_k in lin-log representation, ($j = 0$), $\gamma = 1$. (f) $\Delta\phi_i$ versus j for $R_k = 1$. Two different ratios δ are illustrated in the six panels: circles $\delta = 0.01$, triangles $\delta = 1$. $\alpha_O = \alpha_R = 1/2$

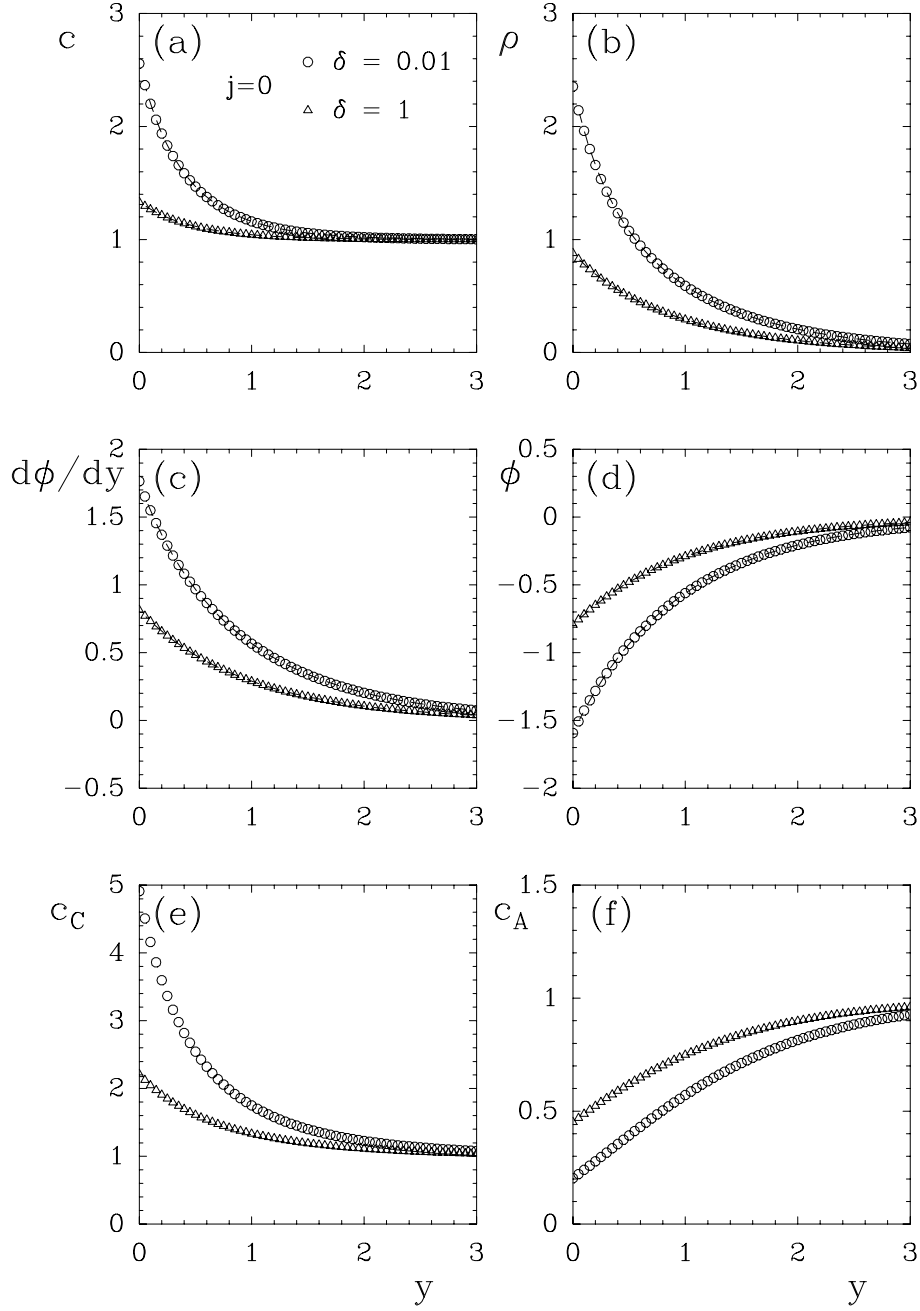


FIG. 3. Steady-state profiles of c (a), ρ (b), $\partial_y \phi$ (c), ϕ (d), c_C (e) and c_A (f) at leading order in the “inner” (diffuse) layer at $y = 0$ for $j = 0$, $R_k = 5$, ($k_r = 5$ and $k_o = 1$), $K = 0.972$ for $\delta = 0.01$ (circles) and $K = 1.629$ for $\delta = 1$ (triangles), For comparison the Poisson-Boltzmann’s profiles are reported as dashed lines which correspond to the limit $\delta = 0$.

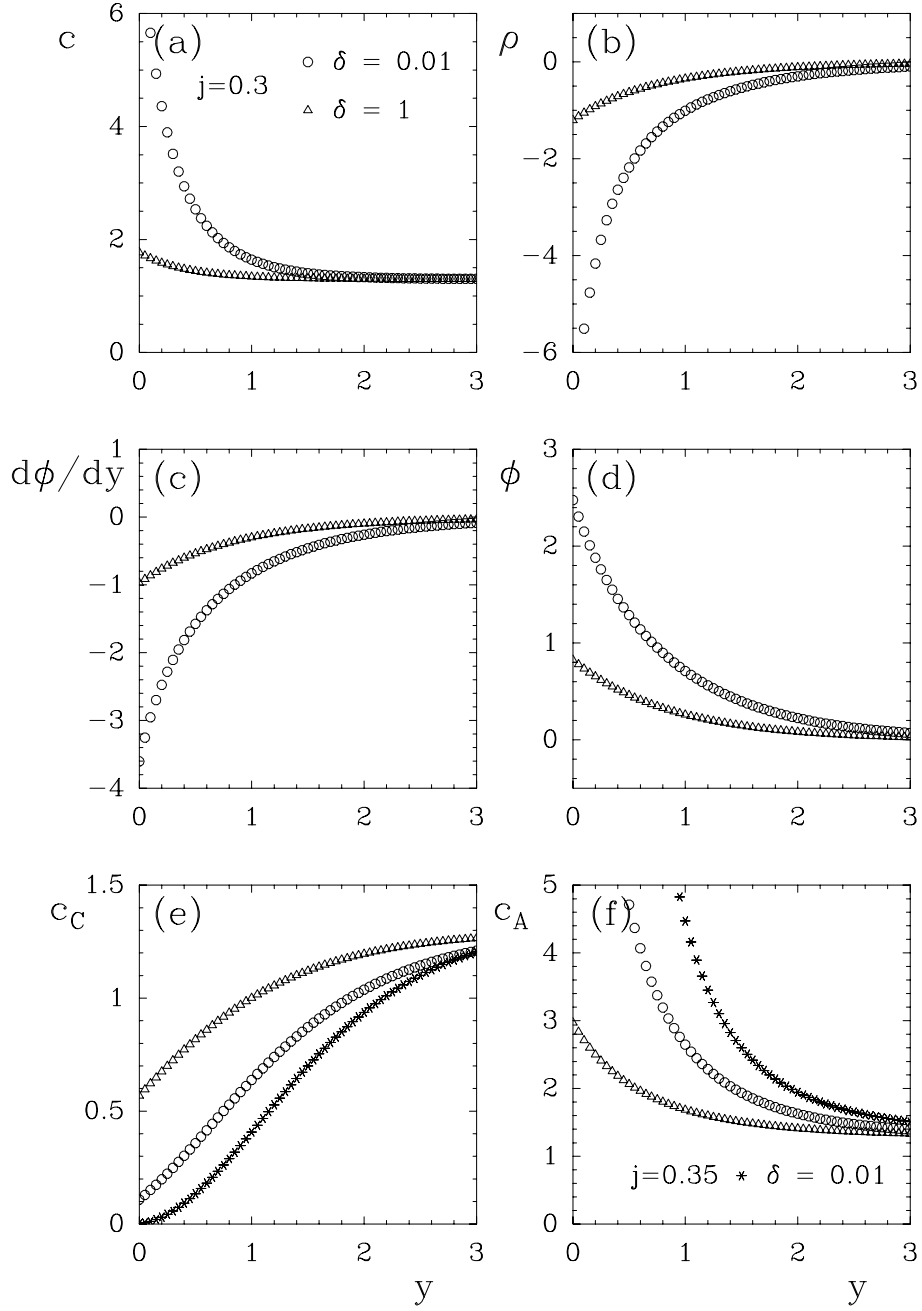


FIG. 4. Steady-state profiles of c (a), ρ (b), $\partial_y \phi$ (c), ϕ (d), c_C (e) and c_A (f) in the diffuse layer at leading order for $j = 0.3$, $R_k = 1$, $K = 0.523$ for $\delta = 0.01$ (circles) and $K = 1.394$ for $\delta = 1$ (triangles).

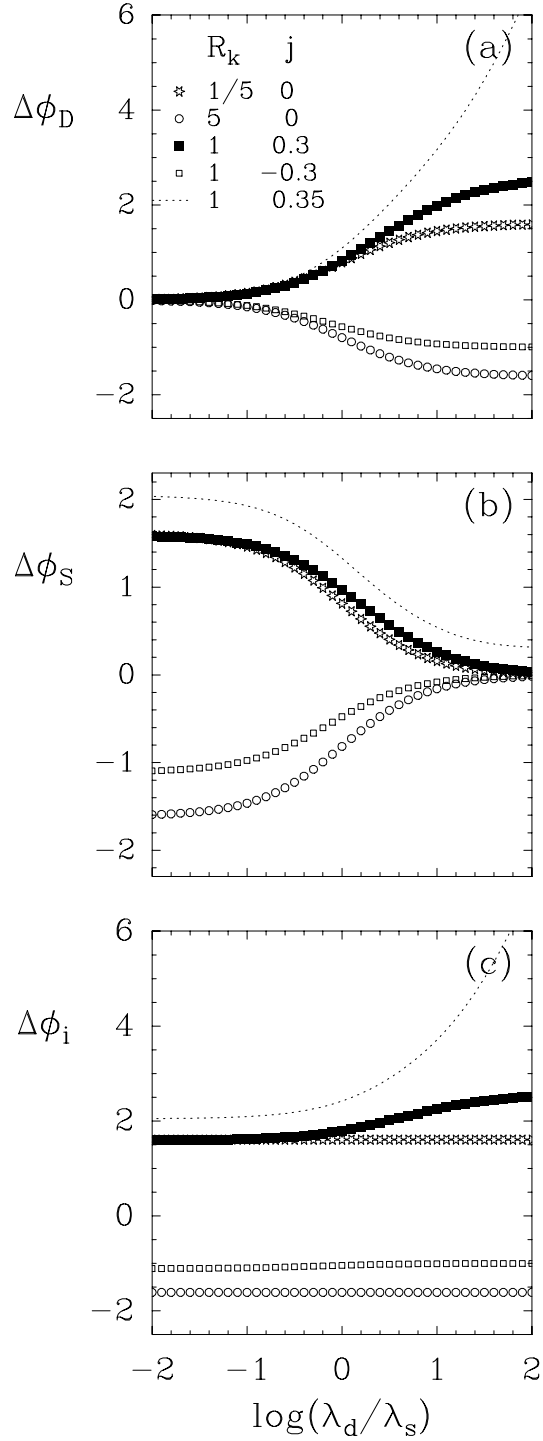


FIG. 5. Dependence of the potential differences $\Delta\phi_D$ (diffuse layer), $\Delta\phi_S$ (Stern's layer), $\Delta\phi_i = \Delta\phi_D + \Delta\phi_S$ (double layer) with $-\log\delta$. The different parameters R_k and j corresponding to each plot are inserted in panel (a).

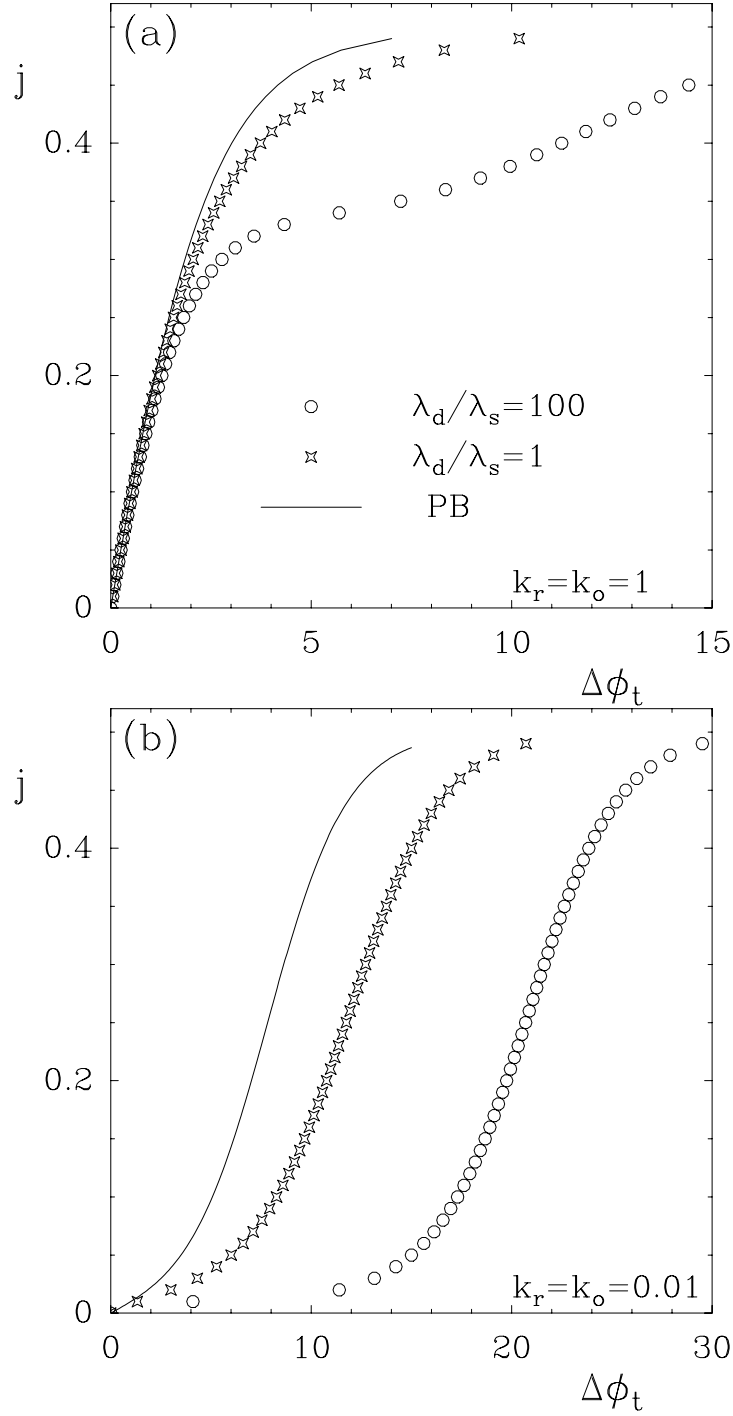


FIG. 6. Polarograms obtained from the asymptotic analysis for (a) $k_R = k_O = 1$ and (b) $k_R = k_O = 0.01$.

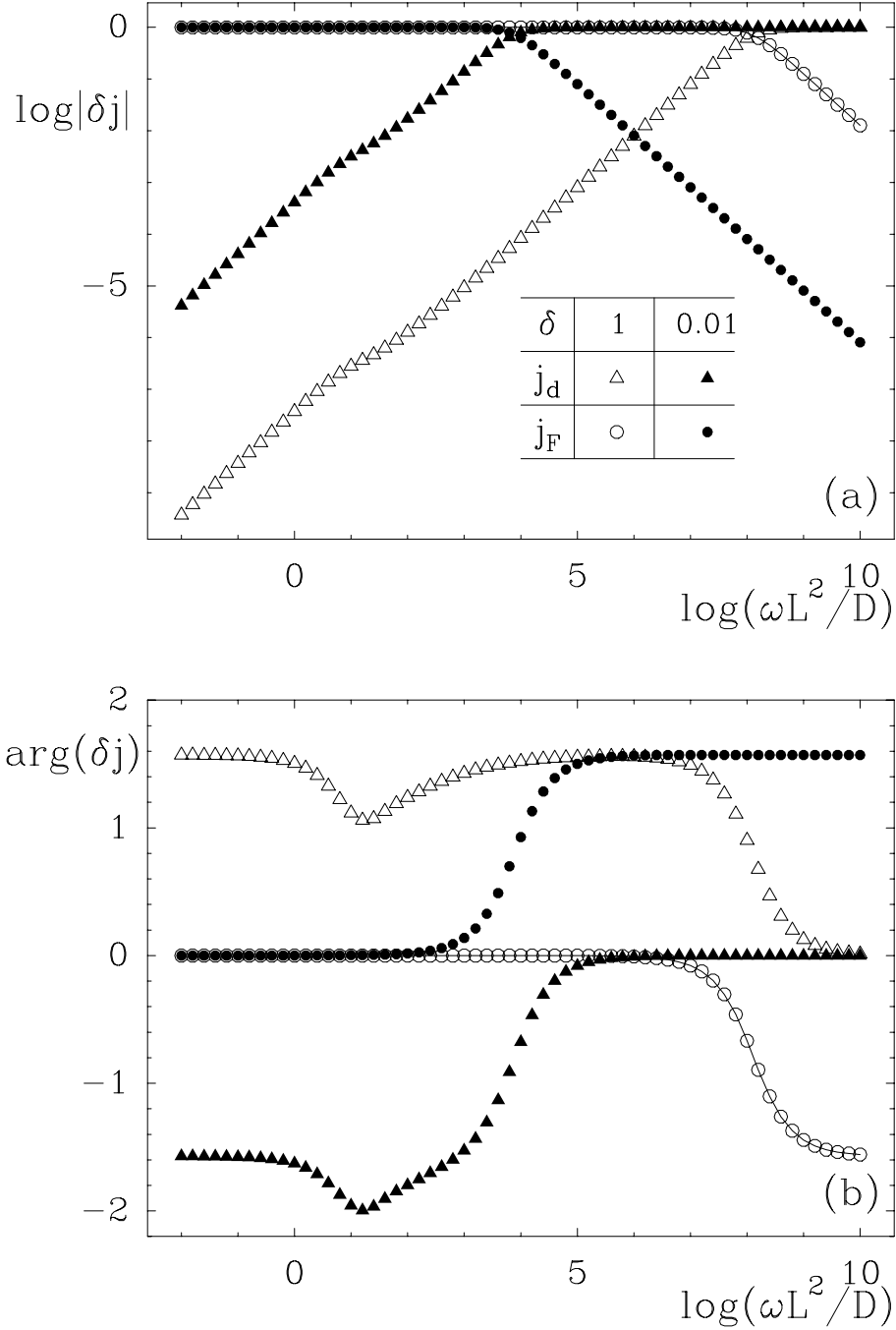


FIG. 7. The displacement and Faradaic current modulations versus the dimensionless frequency $\omega L^2/D$. Results for two different ratios $\delta = \lambda_S/\lambda_D$ are shown. (a) log of the modulus of current modulation δj . (b) argument of the current modulation δj . $\lambda_S = 1\text{\AA}$ and $L = 1\text{ cm}$, so $\lambda_D = 10\text{nm}$ corresponds to $\delta = 0.01$ and $\epsilon = 10^{-6}$, while $\lambda_D = 1\text{\AA}$ corresponds to $\delta = 1$ and $\epsilon = 10^{-8}$. Other parameters are $D = 10^{-5}\text{cm}^2\text{s}^{-1}$, $j = 0.3$, $k_R = k_O = 1$, $\gamma = 1$, $\alpha_O = \alpha_R = 1/2$.

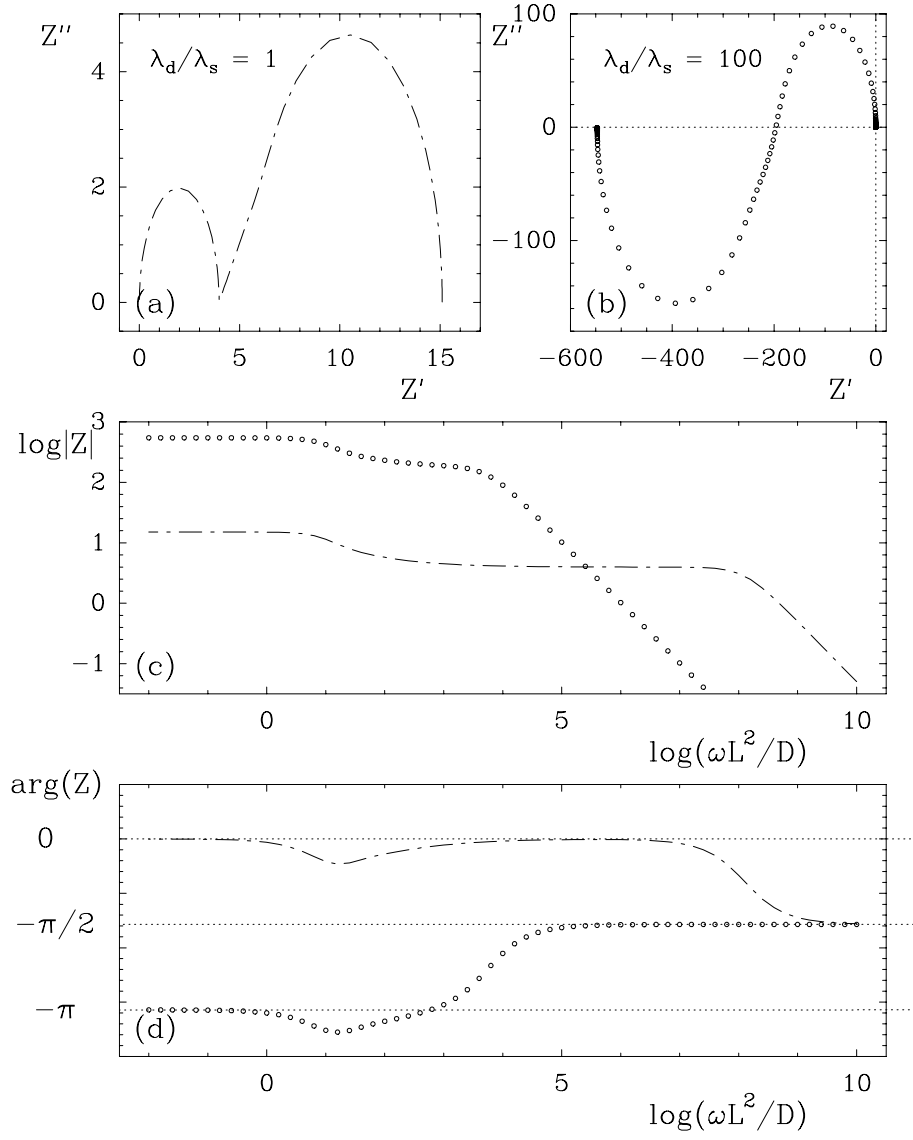


FIG. 8. Impedance spectra obtained from a linear stability analysis around the steady state $j = 0.3$. (a) Nyquist plot, (b) and (c) Bode plots for the modulus and argument of the total impedance $Z(s = i\omega) = \Delta\phi_{tot}(s)/\delta\tilde{j}(s)$. Same parameters as in Fig. 7