Absence of bulk electroconvective instability in concentration polarization

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The problem of bulk electroconvective stability of quiescent electric conduction from an electrolyte solution into a charge-selective solid (ion-exchange membrane) has been revised. It is shown through a numerical solution of the linear stability problem that previously reported bulk electroconvective instability does not exist. This numerical result is supported by the short wave asymptotic analysis. Our comprehensive study confirms the result of an earlier, less detailed, report by Buchanan and Saville.

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I. INTRODUCTION

The term electroconvection is being used in at least four different contexts. Thus, by this term one often refers to the electric-field-induced flow of nematic liquid crystals [1–3]. In addition, by the same term one relates to the flow of liquid dielectrics caused by the action of electric field on the space charge of ions of the appropriate sign injected in a low quantity into the fluid [4–6]. This term is also being applied to the effects of an electric fields acting on the surface charge accumulated at the interface between two weakly conducting fluids. Namely, this has been studied by Taylor, who in the mid-1960s introduced the leaky dielectric model to explain the behavior of droplets deformed by a steady field. This model, later extensively used by Melcher [7], formed an important step in the construction of a unified treatment of electrohydrodynamics of liquid dielectrics [8].

As opposed to the aforementioned systems, from here on we refer by the term electroconvection to the flow of strong electrolytes at moderate concentration, that is, to liquids abundant with charge carriers of both signs. This type of electroconvection has been invoked, in particular, as a mechanism crucial for "overlimiting" conductance through cation-exchange electrodialysis membranes [9,10] and important for ramified electrodeposition [11–13] and layering of colloid crystals on electrode surfaces [14,15].

The following two modes of electroconvection in strong electrolytes may be distinguished. The first is the relatively recently invoked "bulk" electroconvection, due to the volume electric forces acting on a macroscopic scale in a locally quasielectroneutral electrolyte. The second is the common electro-osmosis, either of the classical "first" kind or of the "second" kind, according to the terminology of Dukhin [16].

Electro-osmosis of the "first" kind relates to the electrolyte slip resulting from the action of the tangential electric field upon the space charge of a quasiequilibrium diffuse electric double layer. Electro-osmosis of the "second kind" invoked by Dukhin [16–18] pertains to the similar action of a tangential electric field upon the extended space charge of the nonequilibrium double layer [19]. Both types of electroconvection could arise either in a thresholdless manner, due to inhomogeneity of the solid/liquid interface (mechanical, such as roughness, or electric), or with a threshold, through instability of quiescent electric conduction through a solution layer near a uniform flat charge-selective (perm-selective) solid, such as an electrode or ion exchange membrane. Passage of a dc current through such a layer causes the formation of electrolyte concentration gradients—concentration polarization (CP) in electrochemical terminology.

Bulk electroconvective instability was first reported by Grigin [20]. In his paper, Grigin used the lowest-order Galerkin approximation to study the critical perturbation mode for unrealistic boundary conditions [20,21]. Grigin's papers were followed by an independent study by Bruinsma and Alexander in which they investigated the bulk electroconvective instability in a very thin polarization cell of finite width, for galvanostatic condition [23]. Below, we show that in terms of concentration polarization in a flat layer, this setup amounts to consideration of a short wave perturbation mode. The authors concluded that bulk electroconvective instability did exist, but, based on heuristic energy balance arguments, they argued that it could hardly develop into a major mixing mechanism on a macroscopic scale.

Following Ref. [20], a numerical study of linear bulk electroconvective instability in an electrolyte layer flanked by cation-selective surfaces has been carried out for galvanostatic and potentiostatic conditions in Refs. [24–26]. The conclusion of these studies was that instability did exist.

To gain physical understanding of this instability, a simple model of electroconvection in a loop was suggested [24]. The steady-state version of this one-dimensional fully nonlinear model admits an explicit analytic solution which predicts branching of electroconvective steady states from a quiescent conductive one above a certain current threshold. Thus, both the numerical and analytical studies, including the "thin cell" linear stability analysis by Bruinsma and Alexander [23] and the loop model, predicted the existence of bulk electroconvective instability.

On the other hand, in the numerical study by Buchanan and Saville [27], no evidence of this instability was found.

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Thus, so far, there was no ultimate clarity as to the existence of the bulk electroconvective instability. This lends a particular importance to the study of Bruinsma and Alexander, as containing the only analytical result suggesting the existence of bulk electroconvective instability (besides the less direct indication by the loop model [24]). Unfortunately, the linear stability analysis of Bruinsma and Alexander [23] employed fewer boundary conditions (four) than was the order of the basic equation of the model (sixth), which led the authors to fix arbitrarily certain integration constants in the solution of the relevant spectral problem. This rendered questionable the conclusion of these authors concerning the occurrence of instability. On the other hand, the unique position of this study as the only direct analytical evidence of bulk electroconvective instability motivates our current attempt to carry out a systematic short-wave linear stability analysis complementing that of Bruinsma and Alexander.

Our paper is organized as follows. In Sec. II, we formulate the basic model of bulk electroconvection in a solution layer flanked by two cation-selective ion exchange membranes. In Secs. III and IV, we derive the relevant spectral problem and carry out the short-wave asymptotic linear stability analysis. In Sec. V, the asymptotic boundary layer solution is compared with the exact one obtained numerically, and we present the numerical results of the linear stability analysis for the intermediate wave number range obtained by a numerical method differed from that used in Refs. [24,26]. The main conclusion attained is that of the nonexistence of bulk electroconvective instability.

II. EQUATIONS OF BULK ELECTROCONVECTION

Let us consider a domain in a univalent electrolyte characterized by a typical single length scale L, which is macroscopic but still sufficiently small for all inertia effects of fluid motion to be negligible. With a natural scaling, the dimensionless equations for convective electrodiffusion of ions, together with the Stokes equations and the incompressibility condition, read

$$c_t^+ + \mathrm{Pe}(\mathbf{v}\cdot\boldsymbol{\nabla})c^+ = \boldsymbol{\nabla}\cdot(\boldsymbol{\nabla}c^+ + c^+\boldsymbol{\nabla}\varphi), \tag{1}$$

$$c_t^- + \mathrm{Pe}(\mathbf{v}\cdot\boldsymbol{\nabla})c^- = D\,\boldsymbol{\nabla}\cdot(\boldsymbol{\nabla}c^- - c^-\boldsymbol{\nabla}\varphi), \tag{2}$$

$$\varepsilon^2\Delta\varphi = c^- - c^+, \tag{3}$$

$$-\boldsymbol{\nabla}p + \Delta\varphi\,\boldsymbol{\nabla}\varphi + \Delta\mathbf{v} = 0, \tag{4}$$

$$\boldsymbol{\nabla}\cdot\mathbf{v} = \mathbf{0}. \tag{5}$$

Here,

$$c^+ = \frac{\tilde{c}^+}{c_0}, \tag{6}$$

$$c^- = \frac{\tilde{c}^-}{c_0}, \tag{7}$$

$$\varphi = \frac{F\tilde{\varphi}}{RT} \tag{8}$$

are the dimensionless concentrations of cations and anions and the electric potential (dimensional variables being marked with tildes), and c_0 is the typical electrolyte concentration (e.g., the average concentration in the layer), F is the Faraday constant, R is the universal gas constant, and T is the absolute temperature. Furthermore,

$$\mathbf{v} = \frac{\tilde{\mathbf{v}}}{v_0} = v_x\mathbf{i} + v_y\mathbf{j} + v_z\mathbf{k}, \tag{9}$$

$$p = \frac{\tilde{p}}{p_0} \tag{10}$$

are the dimensionless velocity vector (bold notations hereon mark vectors) and the pressure, respectively, with the typical velocity v_0 and pressure p_0 determined from the force balance in the dimensional version of the momentum equation (4) as

$$v_0 = \frac{d(RT/F)^2}{4\pi\eta L}, \tag{11}$$

$$p_0 = \frac{\eta v_0}{L}, \tag{12}$$

where d is the dielectric constant and η the dynamic viscosity of the solution.

Finally,

$$t = \tilde{t}\frac{D_+}{L^2} \tag{13}$$

is the dimensionless time and D_+ is the cation diffusivity. The dimensionless spatial coordinates in Eqs. (1)–(5) are normalized by L.

Equations (1) and (2) are those of convective electrodiffusion of cations and anions, respectively. Equation (3) is the Poisson equation for the electric potential, with $c^- - c^+$ on the right-hand side (RHS) being the space charge due to the lack of local balance of ionic concentrations. The Stokes equation (4) is obtained from the full momentum equations by omitting the inertia terms. Finally, (5) is the continuity equation for an incompressible solution.

The dimensionless parameters in the system (1)–(5) are as follows.

(i) The dimensionless Debye length ε, defined as

$$\varepsilon = \left(\frac{r_d}{L}\right). \tag{14}$$

Here

$$r_d = \left(\frac{dRT}{4\pi C_0 F^2}\right)^{1/2} \tag{15}$$

is the dimensional Debye length.

For a realistic macroscopic electrolyte system $[10^{-4} < L\ (\mathrm{cm}) < 10^{-1}]$, $[10^{-5} < c_0(\mathrm{mol\ cm^{-3}}) < 10^{-3}]$, ε^2 is a very small number in the range

$$0.2 \times 10^{-12} < \varepsilon^2 < 2 \times 10^{-5}. \tag{16}$$

(ii) The Peclet number, defined as

$$\mathrm{Pe} = \frac{v_0 L}{D_+}, \tag{17}$$

or, using Eq. (11),

$$\mathrm{Pe} = \left(\frac{RT}{F}\right)^2 \frac{d}{4\pi\eta D_+}. \tag{18}$$

As mentioned in Ref. [1], Pe does not depend on c_0, L and for a typical aqueous low molecular electrolyte is of order unity, more precisely

$$\mathrm{Pe} \approx 0.5. \tag{19}$$

(iii) Finally, the relative anionic diffusivity is defined as

$$D = \frac{D_-}{D_+}, \tag{20}$$

where D_+ and D_- are the dimensional cationic and anionic diffusivities, respectively. For realistic aqueous electrolyte solutions, D may vary by two orders of magnitude in the range

$$0.1 < D < 10. \tag{21}$$

The extreme smallness of ε^2 motivates the commonly employed approximation of local "stoichiometric" electroneutrality, which amounts to setting $\varepsilon = 0$ in Eq. (3), yielding

$$c^+ = c^- \overset{\text{def}}{=} c \tag{22}$$

everywhere in the bulk of electrolyte, except for the boundary (electric double) layers of thickness ε. Note that although the space charge is very small (order ε^2) in the Poisson equation (3), it is sufficient to generate an electroconvective flow with Peclet number of order unity through the force term in the Stokes equation (4).

Summarizing, the dimensionless equations for steady-state convective electrodiffusion in the local electroneutrality approximation are

$$\mathrm{Pe}(\mathbf{v}\cdot\boldsymbol{\nabla})c = \boldsymbol{\nabla}\cdot(\boldsymbol{\nabla}c + c\,\boldsymbol{\nabla}\varphi), \tag{23}$$

$$\mathrm{Pe}(\mathbf{v}\cdot\boldsymbol{\nabla})c = D\,\boldsymbol{\nabla}\cdot(\boldsymbol{\nabla}c - c\,\boldsymbol{\nabla}\varphi). \tag{24}$$

By adding Eq. (23) to Eq. (24), divided by D, we arrive at the equation

$$\mathrm{Pe}(\mathbf{v}\cdot\boldsymbol{\nabla})c = D^\star \Delta c. \tag{25}$$

Here,

$$D^\star = \frac{2D}{1+D}. \tag{26}$$

Furthermore, by subtracting Eq. (24) from Eq. (23), we obtain

$$(1-D)\Delta c + (1+D)\,\boldsymbol{\nabla}\cdot(c\,\boldsymbol{\nabla}\varphi) = 0. \tag{27}$$

Equations (25) and (27) together with Stokes equation

$$-\boldsymbol{\nabla} p + \Delta\varphi\,\boldsymbol{\nabla}\varphi + \Delta\mathbf{v} = \mathbf{0} \tag{28}$$

and the continuity equation

$$\boldsymbol{\nabla}\cdot\mathbf{v} = \mathbf{0} \tag{29}$$

form the final set describing macroscopic bulk electroconvection in the local stoichiometric electroneutrality approximation.

III. LINEAR STABILITY OF QUIESCENT CONCENTRATION POLARIZATION

In this section, we address the issue of electroconvective instability for concentration polarization in a layer of a univalent electrolyte, flanked by two ideally cation-permselective surfaces (e.g., cation-selective electrodialysis membranes), under a specified electric current (a system equivalent to that considered by Bruinsma and Alexander [23]).

The relevant set of time-dependent versions of Eqs. (25)–(29) reads

$$-\boldsymbol{\nabla} p + \Delta\varphi\,\boldsymbol{\nabla}\varphi + \Delta\mathbf{v} = \frac{1}{\mathrm{Sc}}\mathbf{v}_t, \tag{30}$$

$$\frac{\partial c}{\partial t} + \mathrm{Pe}(\mathbf{v}\cdot\boldsymbol{\nabla})c = D^\star \Delta c, \tag{31}$$

$$(1-D)\Delta c + (1+D)\,\boldsymbol{\nabla}(c\,\boldsymbol{\nabla}\varphi) = 0, \tag{32}$$

$$\boldsymbol{\nabla}\cdot\mathbf{v} = \mathbf{0}. \tag{33}$$

Here $\mathrm{Sc} = \nu_k/D$ is the Schmidt number (ν_k is the kinematic viscosity).

In order to specify the boundary conditions, let us define a Cartesian coordinate system with the $\hat{x}$ axis directed from the left membrane to the right one. Thus, the electrolyte layer occupies the domain

$$\sum = \{0 < x < 1, -\infty < y < \infty, -\infty < z < \infty\}.$$

The simplest version of galvanostatic boundary conditions reads

$$v_x|_{x=0} = v_y|_{x=0} = v_z|_{x=0} = 0, \tag{34}$$

$$v_x|_{x=1} = v_y|_{x=1} = v_z|_{x=1} = 0, \tag{35}$$

$$(c_x + c\varphi_x)|_{x=1} = (c_x + c\varphi_x)|_{x=0} = -I = \mathrm{const}, \tag{36}$$

$$(c_x - c\varphi_x)|_{x=1} = (c_x - c\varphi_x)|_{x=0} = 0, \tag{37}$$

$$v, p_y, p_z, c_y, c_z, \varphi_y, \varphi_z \to 0 \text{ when } y^2 + z^2 \to \infty, \tag{38}$$

$$\int_\Sigma (c-1)\,dx\,dy\,dz = 0. \tag{39}$$

Equations (34) and (35) are standard nonslip conditions at the solid boundaries. The current condition (36) specifies a

constant electric current density I through the membrane (the expression in parentheses stands, with a minus sign, for the x component of the dimensionless cationic flux). Conditions (37) state the impermeability of these boundaries for anions (the expression in parentheses stands, with a minus sign, for the x component of the dimensionless anionic flux). Equation (38) is a standard boundedness condition at infinity.

Finally, the normalization condition (39) specified the total amount of anions in the layer (per unit area of membrane). This condition is necessary for uniqueness of concentration with flux conditions (36) and (37).

The steady-state version of the boundary value problem (30)–(39) possesses a trivial quiescent conduction (concentration polarization) solution,

$$c_0(x) = 1 + \frac{I}{2}\left(\frac{1}{2} - x\right), \tag{40}$$

$$\varphi_0(x) = \ln\left[1 + \frac{I}{2}\left(\frac{1}{2} - x\right)\right], \tag{41}$$

$$\mathbf{v}_0 \equiv \mathbf{0}, \tag{42}$$

$$p_0(x) = \frac{1}{2}\varphi_{0x}^2 + \text{const}. \tag{43}$$

Expression (41) yields the current-voltage relation

$$I = 4\frac{1 - e^{-V}}{1 + e^{-V}}, \tag{44}$$

where

$$V \overset{\text{def}}{=} \varphi_0(0) - \varphi_0(1) \tag{45}$$

is the voltage across the solution.

From Eqs. (44) and (45), when $V \to \infty$, $I \to I^{\lim} = 4$ and, simultaneously, by Eq. (40), $c_0(1) \to 0$. This is the key feature of the classical picture of the concentration polarization, namely saturation of the current density toward the limiting value with the increasing voltage, resulting from the vanishing interface electrolyte concentration at the cathode.

To formulate the linear stability problem for the solution (40)–(43), we assume an infinitesimal flow v' which creates small three-dimensional fluctuations c', p', φ' in the concentration, pressure and electrostatic potential. Let us consider a perturbation of the conduction solution (40)–(43) of the form

$$\underline{M} = \underline{M}_0 + \underline{M}_1. \tag{46}$$

Here,

$$\underline{M}_0 = \begin{pmatrix} c_0(x) \\ \varphi_0(x) \\ \mathbf{v}_0 \equiv \mathbf{0} \\ p_0(x) \end{pmatrix}, \quad \underline{M}_1 = \begin{pmatrix} c'(x,y,z) \\ \varphi'(x,y,z) \\ \mathbf{v}'(x,y,z) \\ p'(x,y,z) \end{pmatrix} e^{\lambda t}, \tag{47}$$

whence $\mathbf{v}' = v_x\mathbf{i} + v_y\mathbf{j} + v_z\mathbf{k}$ is the velocity perturbation vector.

Substitution of $\underline{M}$ into the boundary value problem (30)–(39), followed by linearization, yields a spectral problem for a $(c', \varphi', \underline{v}', p')$ and λ with the equations

$$\Delta\mathbf{v}' - \boldsymbol{\nabla} p' + \Delta\varphi_0 \boldsymbol{\nabla} \varphi' + \Delta\varphi \boldsymbol{\nabla} \varphi_0 = \frac{\lambda}{\mathrm{Sc}}\mathbf{v}', \tag{48}$$

$$\Delta c' = \mathrm{Pe} v_x \frac{dc_0}{dx}\frac{1}{D^\star} + \lambda c', \tag{49}$$

$$\boldsymbol{\nabla} \cdot \mathbf{v}' = \mathbf{0} \tag{50}$$

with $D^\star = 2D/(1+D)$. Assuming exchange of stability ($\lambda = 0$), Eqs. (48)–(50) yield the following set of equations for the marginally stable mode:

$$\Delta\mathbf{v}' - \boldsymbol{\nabla} p' + \Delta\varphi_0 \boldsymbol{\nabla} \varphi' + \Delta\varphi \boldsymbol{\nabla} \varphi_0 = \mathbf{0}, \tag{51}$$

$$\Delta c' = \mathrm{Pe} v_x \frac{dc_0}{dx}\frac{1}{D^\star}, \tag{52}$$

$$\boldsymbol{\nabla} \cdot \mathbf{v}' = \mathbf{0}. \tag{53}$$

Applying the operator ***rotrot*** to the linearized steady-state Navier-Stokes equation (48) yields

$$\Delta^2 v_x = -\frac{\partial\varphi_0}{\partial x}\left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Delta\varphi' + \frac{\partial^3\varphi_0}{\partial x^3}\left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\varphi'. \tag{54}$$

Substitution of the steady-state version of Eq. (31) into Eq. (32) yields for $D = 1$, assumed hereon (this is the case most favorable for short-wave instability),

$$\Delta\varphi = -\frac{1}{c}(\boldsymbol{\nabla}\varphi \cdot \boldsymbol{\nabla} c).$$

Linearization of this expression yield

$$-\boldsymbol{\nabla}\varphi_0 \cdot \boldsymbol{\nabla} c' - c'\Delta\varphi_0 = \boldsymbol{\nabla}\varphi' \cdot \boldsymbol{\nabla} c_0 + c_0\Delta\varphi'. \tag{55}$$

Thus, the final boundary value problem for marginally stable fluctuation reads

$$\Delta c' = \mathrm{Pe} v_x \frac{dc_0}{dx}, \tag{56}$$

$$\Delta^2 v_x = -\frac{\partial\varphi_0}{\partial x}\left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Delta\varphi' + \frac{\partial^3\varphi_0}{\partial x^3}\left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\varphi', \tag{57}$$

$$-\boldsymbol{\nabla}\varphi_0 \cdot \boldsymbol{\nabla} c' - c'\Delta\varphi_0 = \boldsymbol{\nabla}\varphi' \cdot \boldsymbol{\nabla} c_0 + c_0\Delta\varphi' \tag{58}$$

with the following boundary conditions resulting from Eqs. (34)–(39).

$x = 0$ (left membrane is the anode),

$$\left.\frac{\partial c'}{\partial x}\right|_{x=0} = 0, \tag{59}$$

$$\left.\left(\frac{-I/2}{1 + I/4}c' + (1 + I/4)\frac{\partial\varphi'}{\partial x}\right)\right|_{x=0} = 0, \tag{60}$$

$$v_x|_{x=0} = 0, \tag{61}$$

$$\frac{\partial v_x}{\partial x}_{x=0} = 0. \tag{62}$$

$x=1$ (right membrane is the cathode),

$$\left.\frac{\partial c'}{\partial x}\right|_{x=1} = 0, \tag{63}$$

$$\left.\left(\frac{-I/2}{1-I/4}c' + (1-I/4)\frac{\partial \varphi'}{\partial x}\right)\right|_{x=1} = 0, \tag{64}$$

$$v_x|_{x=1} = 0, \tag{65}$$

$$\left.\frac{\partial v_x}{\partial x}\right|_{x=1} = 0. \tag{66}$$

The basic question we address is whether the boundary value problem (56)–(66) possesses a nontrivial solution for some value of the control parameter I.

Let us look for the functions φ', c', v_x in the form

$$\varphi' = \Phi(x)\exp(i[k_y y + k_z z]), \tag{67}$$

$$c' = \xi(x)\exp(i[k_y y + k_z z]), \tag{68}$$

$$v_x = u(x)\exp(i[k_y y + k_z z]). \tag{69}$$

Substitution of these expressions into system (56)–(58) yields, taking into account Eqs. (40) and (41),

$$u = -\frac{2D^\star}{\mathrm{Pe}\, I}\left(\frac{d^2}{dx^2} - k^2\right)\xi, \tag{70}$$

$$\left(\frac{d^2}{dx^2} - k^2\right)^2 u = -k^2\frac{I}{2\left(1+\frac{I}{4}-\frac{I}{2}x\right)}\left(\frac{d^2}{dx^2} - k^2\right)\Phi + k^2\frac{I^3}{4\left(1+\frac{I}{4}-\frac{I}{2}x\right)^3}\Phi, \tag{71}$$

$$\left(1+\frac{I}{4}-\frac{I}{2}x\right)\left(\frac{d^2}{dx^2} - k^2\right)\Phi - \frac{I}{2}\frac{d\Phi}{dx} = \frac{I}{2\left(1+\frac{I}{4}-\frac{I}{2}x\right)}\frac{d\xi}{dx} + \frac{I^2}{4\left(1+\frac{I}{4}-\frac{I}{2}x\right)^2}\xi, \tag{72}$$

where

$$k = \sqrt{k_y^2 + k_z^2}, \tag{73}$$

with the following boundary conditions.

$x=0$ (anode),

$$\left.\frac{d\xi}{dx}\right|_{x=0} = 0, \tag{74}$$

$$\left.\left(\frac{-I/2}{1+I/4}\xi + (1+I/4)\frac{d\Phi}{dx}\right)\right|_{x=0} = 0, \tag{75}$$

$$u|_{x=0} = 0, \tag{76}$$

$$\left.\frac{du}{dx}\right|_{x=0} = 0. \tag{77}$$

$x=1$ (cathode),

$$\left.\frac{d\xi}{dx}\right|_{x=1} = 0, \tag{78}$$

$$\left.\left(\frac{-I/2}{1-I/4}\xi + (1-I/4)\frac{d\Phi}{dx}\right)\right|_{x=1} = 0, \tag{79}$$

$$u|_{x=1} = 0, \tag{80}$$

$$\frac{du}{dx}_{x=1} = 0. \tag{81}$$

IV. SHORT-WAVE ANALYSIS OF THE MARGINAL LINEAR STABILITY PROBLEM

In this section, we analyze the problem (70)–(72) for short-wave perturbation $k \gg 1$. Let us introduce the small parameter $\omega = k^{-1}$. For $\omega \ll 1$, Eq. (72) is singularly perturbed with two boundary layers at $x=0,1$.

In order to construct a boundary layer solution valid near $x=1$, we define the inner variable

$$s = \frac{1-x}{\omega} \tag{82}$$

while considering I in the vicinity of the limiting value $I=4$, such that

$$I \approx 4 - \omega^\beta \alpha \quad \alpha, \beta = O(1). \tag{83}$$

Substitution of expressions (82) and (83) into Eq. (72) yields

$$\frac{4s\omega^{1-\beta}+\alpha}{2\omega^{2-\beta}}\left(\frac{d^2}{ds^2} - 1\right)\Phi + \frac{2}{\omega}\frac{d\Phi}{ds} = -\frac{4}{\omega^{1+\beta}(4s\omega^{1-\beta}+\alpha)}\frac{d\xi}{ds} + \frac{16}{\omega^{2\beta}(4s\omega^{1-\beta}+\alpha)^2}\xi. \tag{84}$$

Equating powers of ω in the first terms on both sides of Eq. (84) yields $\beta = 1/2$. Thus Eq. (84) may be rewritten as

$$\frac{4s\sqrt{\omega}+\alpha}{2\omega^{3/2}}\left(\frac{d^2}{ds^2} - 1\right)\Phi + \frac{2}{\omega}\frac{d\Phi}{ds} = -\frac{4}{\omega^{3/2}(4s\sqrt{\omega}+\alpha)}\frac{d\xi}{ds} + \frac{16}{\omega(4s\sqrt{\omega}+\alpha)^2}\xi, \tag{85}$$

or, to the leading order in ω,

$$\left(\frac{d^2}{ds^2} - 1\right)\Phi = -\frac{8}{(4s\sqrt{\omega}+\alpha)^2}\frac{d\xi}{ds}. \tag{86}$$

By using expressions (82) and (83), Eq. (70) is rewritten to the leading order in ω as

$$u = -\frac{2D^{\star}}{\mathrm{Pe}\omega^2(4-\alpha\sqrt{\omega})}\left(\frac{d^2}{ds^2}-1\right)\xi, \tag{87}$$

and Eq. (71) as

$$\left(\frac{d^2}{ds^2}-1\right)^2 u = -\frac{4}{\sqrt{\omega}(4s\sqrt{\omega}+\alpha)}\left(\frac{d^2}{ds^2}-1\right)\Phi. \tag{88}$$

Substitution of Eqs. (86) and (87) into Eq. (88) yields the following "short-wave" equation:

$$\left(\frac{d^2}{ds^2}-1\right)^3 \xi = -\mu\frac{d\xi}{ds}. \tag{89}$$

Here

$$\mu = \frac{64\,\mathrm{Pe}\omega\sqrt{\omega}}{(4s\sqrt{\omega}+\alpha)^3}. \tag{90}$$

This equation is identical with the basic equation of the linear stability problem of Bruinsma and Alexander [23]. In line with their approach motivated by the smallness of μ, we employ the WKB method, that is, we look for a nearly exponential solution of Eq. (89). Thus, we seek $\xi(s)$ in the form

$$\xi(s) = \exp[W(s)], \tag{91}$$

where $W(s)$ is nearly linear in the sense that

$$\left|\frac{d^2W}{ds^2}\right| \ll \left|\frac{dW}{ds}\right|^2. \tag{92}$$

Substitution of Eq. (91) into Eq. (89) yields, using Eq. (92),

$$\left[\left(\frac{dW}{ds}\right)^2-1\right]^2 = -\mu\frac{dW}{ds}. \tag{93}$$

Let us look for W in the form

$$W = W_0 + W_1, \tag{94}$$

where

$$\frac{|W_1|}{|W_0|} \to 0,$$

when $\mu \to 0$. Substitution of Eq. (94) into Eq. (93) yields to the leading order in μ

$$W_0 = \pm s. \tag{95}$$

Furthermore, for the correction W_1, we have to the leading order

$$W_1 = \begin{pmatrix} -1 \\ \exp(\pm i2\pi/3) \end{pmatrix}\int_0^s \frac{\sqrt[3]{\mu}}{2}ds'. \tag{96}$$

Substitution of Eq. (96) into Eq. (91) yields for $\xi(s)$ the general solution

$$\xi(s) = A\exp[-s-w(s)] + B\exp\left[[-s+w(s)/2]\cos\left(\frac{\sqrt{3}}{2}w(s)\right)\right] + C\exp\left[[-s+w(s)/2]\sin\left(\frac{\sqrt{3}}{2}w(s)\right)\right] + F\exp[s-w(s)]$$
$$+ G\exp\left[[s-w(s)/2]\cos\left(\frac{\sqrt{3}}{2}w(s)\right)\right] + H\exp\left[[s+w(s)/2]\sin\left(\frac{\sqrt{3}}{2}w(s)\right)\right]. \tag{97}$$

Here

$$w(s) = \int_0^s \frac{\sqrt[3]{\mu}}{2}ds' = \frac{\sqrt[3]{\mathrm{Pe}}}{2}\ln\left(1+\frac{4s\sqrt{\omega}}{\alpha}\right)$$

and A, B, C, F, G, and H are constants to be determined from the boundary conditions (74)–(81). Boundedness of the solution at the outer edge of the boundary layer [$s\to\infty$ with $\omega\to 0$ for $1-x=O(1)$, however small] implies vanishing to the leading order in ω of constants F, G, and H,

$$F = G = H = 0.$$

Thus, a three-parameter boundary layer solution for $\xi(s)$ near $x=1$ is

$$\xi(s) = A\exp[-s-w(s)] + B\exp\left[[-s+w(s)/2]\cos\left(\frac{\sqrt{3}}{2}w(s)\right)\right] + C\exp\left[[-s+w(s)/2]\sin\left(\frac{\sqrt{3}}{2}w(s)\right)\right]. \tag{98}$$

Similarly, for the boundary layer near $x=0$ we introduce the inner variable

$$r = \frac{x}{\omega}. \tag{99}$$

In terms of r, Eqs. (70)–(72) yield to the leading order

$$\left(\frac{d^2}{dr^2}-1\right)^3 \xi = 0. \tag{100}$$

The three-parameter solution of Eq. (100) bounded at $r\to\infty$, analogous to the "right" boundary layer solution (98), is

$$\xi(r) = Me^{-r} + Nre^{-r} + Pr^2e^{-r}. \tag{101}$$

Boundary layer solutions (98) and (101) together with the "outer" solution $\xi=0$ yield a composite general leading-order solution of Eq. (89) in the form

$$\begin{aligned}\xi(s,r) = {} & A\exp[-s-w(s)] \\ & + B\exp\left[[-s+w(s)/2]\cos\left(\frac{\sqrt{3}}{2}w(s)\right)\right] \\ & + C\exp\left[[-s+w(s)/2]\sin\left(\frac{\sqrt{3}}{2}w(s)\right)\right] \\ & + Me^{-r} + Nre^{-r} + Pr^2e^{-r}.\end{aligned} \tag{102}$$

Boundary conditions to be satisfied by this solution are conditions (74)–(81) rewritten in terms of r and s as follows.

$x=1$ $[s=0,\ r=O(\omega^{-1})]$,

$$\frac{d\xi}{ds} = 0, \tag{103}$$

$$\left(\frac{d^2}{ds^2} - 1\right)\xi = 0, \tag{104}$$

$$\frac{d}{ds}\left(\frac{d^2}{ds^2} - 1\right)\xi = 0. \tag{105}$$

$x=0$ $[s=O(\omega^{-1}),\ r=0]$,

$$\frac{d\xi}{dr} = 0, \tag{106}$$

$$\left(\frac{d^2}{dr^2} - 1\right)\xi = 0, \tag{107}$$

$$\frac{d}{dr}\left(\frac{d^2}{dr^2} - 1\right)\xi = 0. \tag{108}$$

Substitution of Eq. (102) into Eqs. (103)–(108) yields a set of six homogeneous linear algebraic equations for constants A, B, C, M, N, and P with vanishing of the system's determinant as the nontrivial solvability condition. The determinant of this system is given by the following equality:

$$\begin{aligned}\mathrm{Det} = {} & \frac{384\ \mathrm{Pe}\sqrt{3}\omega^{3/2}}{\alpha^3}\left(1 + \frac{6}{\alpha}\sqrt{\omega} + \frac{2\ \mathrm{Pe}}{\alpha^3}\omega\sqrt{\omega} + \frac{4}{\alpha^2}\omega^2\right) \\ & + O(\exp(-1/\omega))\end{aligned} \tag{109}$$

and is positive for all ω. Thus, a nontrivial marginally stable short-wave solution does not exist.

V. NUMERICAL SOLUTION OF THE FULL LINEAR STABILITY PROBLEM

In this section, we seek a nontrivial marginally stable solution of the problem (70)–(81) as a linear combination,

$$\xi = \sum_{i=1}^{8} A_i\xi_i, \tag{110}$$

$$\Phi = \sum_{i=1}^{8} A_i\Phi_i, \tag{111}$$

$$u = \sum_{i=1}^{8} A_iu_i, \tag{112}$$

of eight independent (fundamental) solutions of the eighth-order system (70)–(72). Here A_i, $1\leqslant i\leqslant 8$, are arbitrary constants to be determined from the boundary conditions (74)–(81). The ith fundamental solution satisfies the initial conditions

$$\left.\frac{d\xi_i}{dx}\right|_{x=0} = \delta_{i1}, \tag{113}$$

$$\left.\left(\frac{-I/2}{1+I/4}\xi_i + (1+I/4)\frac{d\Phi_i}{dx}\right)\right|_{x=0} = \delta_{i2}, \tag{114}$$

$$u_i|_{x=0} = \delta_{i3}, \tag{115}$$

$$\left.\frac{du_i}{dx}\right|_{x=0} = \delta_{i4}, \tag{116}$$

$$\xi_i|_{x=0} = \delta_{i5}, \tag{117}$$

$$\Phi_i|_{x=0} = \delta_{i6}, \tag{118}$$

$$\left.\frac{d^2u_i}{dx^2}\right|_{x=0} = \delta_{i7}, \tag{119}$$

$$\left.\frac{d^3u_i}{dx^3}\right|_{x=0} = \delta_{i8}, \tag{120}$$

where

$$\delta_{ij} = \begin{cases} 0, i \neq j \\ 1, i = j,\ i, \quad j = 1, \ldots, 8. \end{cases}$$

Since the left-hand sides of the first four Eqs. (113)–(116) match those of the boundary conditions (74)–(77) at $x=0$, substitution of the solution (110)–(112) into boundary conditions (74)–(77) yields $A_i=0$, $i=1,\ldots,4$. Thus, it remains to satisfy the boundary conditions (74)–(77) at $x=1$, by a suitable (nontrivial) choice of the remaining constants $A_i=0$, $i=5,\ldots,8$. This requires vanishing of the 4×4 determinant

$$\det(A) = 0, \quad A = (a_{ij}), \quad i,j = 5, \ldots, 8, \tag{121}$$

where A is a matrix with elements

$$a_{i5} = \left.\frac{d\xi_i}{dx}\right|_{x=1}, \quad i = 5, \ldots, 8, \tag{122}$$

$$a_{i6} = \left.\left(\frac{-I/2}{1-I/4}\xi_i + \left(1 - \frac{I}{4}\right)\frac{d\Phi_i}{dx}\right)\right|_{x=1}, \quad i = 5, \ldots, 8, \tag{123}$$

$$a_{i7} = u_i|_{x=1}, \quad i = 5, \ldots, 8, \tag{124}$$

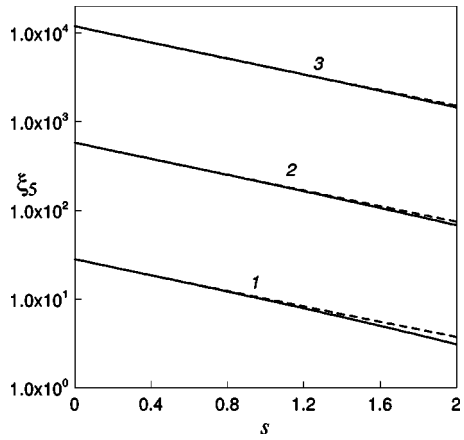

FIG. 1. Comparison between the numerical solution (continuous line) and the short-wave asymptotic one (dashed line) in the boundary layer for different wave number k: curve 1, $k=3$; curve 2, $k=5$; curve 3, $k=10$.

$$a_{i8} = \left.\frac{du_i}{dx}\right|_{x=1}, \quad i = 5, \ldots, 8. \tag{125}$$

Recall that the right-hand sides of Eqs. (122)–(125) coincide with the left-hand sides of boundary conditions (74)–(77), respectively.

The problems (70)–(72) and (113)–(120) have been solved numerically for various values of parameters $\mathrm{Pe}, D, \alpha, k$. In order to check the procedure, the numerically constructed fundamental solution ξ_5 was compared with the asymptotic boundary layer solution (98) near the singular end $x=1$, satisfying the initial conditions as provided by the numerical solution at this point. This comparison illustrated in Fig. 1.

Finally, in Fig. 2 we note that the determinant $\det(A)$ is strictly negative and monotonically decreasing with the increase of current I towards its limiting value 4. Thus, $\det(A)$ does not vanish for any finite value of k. This, together with the short-wave asymptotic analysis of Sec. IV valid for $k \gg 1$, implies the nonexistence of a nontrivial solution to problem (70)–(81) for any values of k, which in turn implies the nonexistence of bulk electroconvective instability.

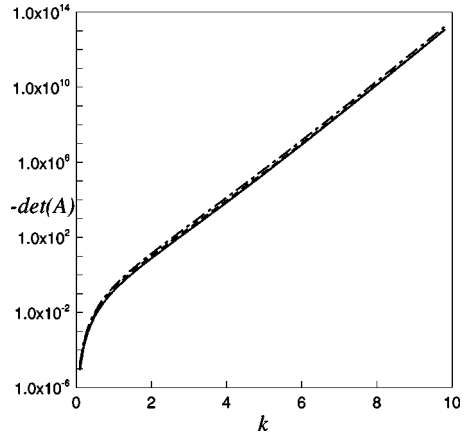

FIG. 2. Dependence of $\det(A)$ on k for three values of $I/I^{\mathrm{lim}}=0.9$ (continuous line), 0.99 (dashed line), and 0.999 (dashed-dot line).

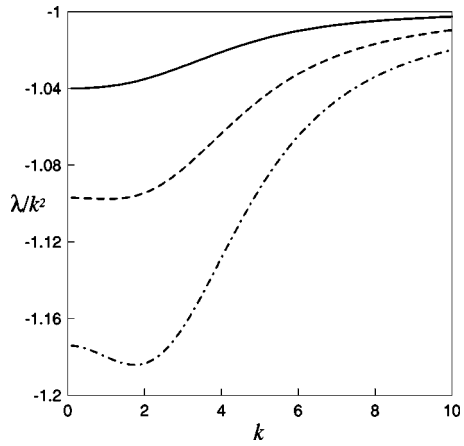

FIG. 3. Dependence of the largest eigenvalue λ on k for different currents I: continuous line, $I/I^{\mathrm{lim}}=0.8$; dashed line, $I/I^{\mathrm{lim}}=0.9$; dash-dot line, $I/I^{\mathrm{lim}}=0.95$.

This conclusion is confirmed by our calculated dependence of the largest eigenvalue λ [growth rate in Eqs. (47)] on k, illustrated in Fig. 3.

VI. CONCLUDING REMARKS

Bulk electroconvective instability of quiescent concentration polarization (steady-state conduction) through a permselective solid (metal electrode, ion exchange membrane) does not exist. (How this combines with the appearance of circulation in the loop model remains unclear and possibly worth study in spite of the only vague relation between the two systems.) Moreover, as will be shown in our forthcoming study [28], whenever instability does occur due to the nonequilibrium space charge near the interface (nonequilibrium electro-osmosis), taking into account the electric force term in the quasielectroneutral bulk has a stabilizing effect. In any case, all previous reports regarding the existence of instability resulted from either analytical inaccuracies or numerical artifacts. Thus, the corresponding conclusion of the only previous analytical study [23], in spite of its indisputable methodological value, was invalid due to lost boundary conditions. In fact, our current study, in its analytical part, is merely an orderly reproduction of the analysis by Bruinsma and Alexander in terms of systematic matched asymptotic expansions. Although it is difficult to assess the possible source of error in the previous numerical studies by other groups (we may only speculate that some numerical difficulties might have been related to the stiffness of the ordinary differential equations of the spectral problem [25], and slow convergence of the Galerkin expansions, besides the unphysical Dirichlet boundary conditions for the electric potential [20–22]), we may confidently identify the source of error in the previous numerical studies claiming instability by our own group [24,26]. This was rooted in too coarse finite difference grids we employed (uniform grids with 100 to 200 grid points, near the limit of our computer capabilities at that

time) undetected by insufficient tests. Our recent reproduction of these computations with twice as fine a grid showed the disappearance of the positive eigenvalue observed previously for currents sufficiently close to the limiting value. The particularity of our current report lies in the systematic testing of the numerical solution through its comparison with the asymptotic one. In conclusion, we wish to reiterate that Buchanan and Saville [27] are to be fully credited for their just claim of the nonexistence of bulk electroconvective instability.

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