Electro-hydrodynamics of binary electrolytes driven by modulated surface potentials

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(Dated: March 8, 2005)

We study the electro-hydrodynamics of the Debye screening layer that arises in an aqueous binary solution near a planar insulating wall when applying a spatially modulated AC-voltage. Combining this with first order perturbation theory we establish the governing equations for the full non-equilibrium problem and obtain analytic solutions in the bulk for the pressure and velocity fields of the electrolyte and for the electric potential. We find good agreement between the numerics of the full problem and the analytics of the linear theory. Our work provides the theoretical foundations of circuit models discussed in the literature. The non-equilibrium approach also reveals unexpected high-frequency dynamics not predicted by circuit models.

PACS numbers: 47.65.+a, 47.32.-y, 47.70.-n, 85.90.+h

I. INTRODUCTION

Recently, there has been quite some interest in electro-hydrodynamics in microfluidic systems. AC-driven, modulated surface potentials have been used for pumping, fluid circulation, and mixing [1–13]. For an overview of AC electro-osmosis we refer to Refs. 14–19 and references therein.

Although AC electro-osmosis is typically analyzed with the help of homogeneous circuit elements open questions remain about the applicability of such approaches [19]. We revisit the problem studied by Ajdari [2] where an electrolyte is perturbed by an AC-driven spatially modulated surface potential, but include explicitly an insulating layer between the electrode providing the driving potential and the electrolyte. We primarily think of this insulator as an oxide grown intentionally for device purposes, but it could also represent the molecular Stern layer in case of non-oxidized electrodes. We develop a full non-equilibrium description of the electro-hydrodynamics of this system thus extending previous modeling of the surface and the Debye layer as simple capacitors. This allows us to study the full dynamics of ion concentrations, electrical potentials, velocity fields, pressure gradient-fields, and electrical currents as well as the justifications for a description based on homogeneous circuit elements.

In the following we consider a binary electrolyte, i.e., an aqueous solution of a salt containing a positive and a negative type of ions with charges +Ze and −Ze, respectively, where Z is the valence and e the elementary charge. In terms of Cartesian coordinates xyz the electrolyte is confined to the semi-infinite space x > 0 by an impenetrable, homogeneous and planar insulating layer with dielectric constant ɛ0 placed at −d < x < 0, see Fig. 1. The insulating layer is bounded by a conductor at x = −d which has been biased at the surface x = −d by a spatially modulated, external AC potential Vext(y, t) = V0 cos(qy)eiωt,

where V0 is the amplitude, q the wavenumber of the spatial modulation, and ω the driving angular frequency.

FIG. 1: A sketch of the system under study. The binary electrolyte is situated in the half space x > 0. Below it, for −d < x < 0, is a planar wall consisting of an insulating dielectric slab of thickness d and below that, for x < −d, is a semi-infinite conductor. The top surface, x = −d, of the conductor is biased by a periodically modulated potential Vext(y, t) of period 2π/q (dotted line), which gives rise to the formation of a Debye screening layer of thickness λD in the electrolyte (dashed line).

There is complete translation invariance along the z axis, so the x coordinate drops out of our analysis, and all positions r = xe_x + ye_y are therefore just referring to the xy plane.

The manuscript is organized as follows: in Sec. II we present the non-equilibrium description and in Secs. III and IV we analytically study linearized equations of the static and dynamic regimes, respectively. In Sec. V we study numerical solutions of the fully coupled non-linear electro-hydrodynamic problem. Finally, in Sec. VI we compare these solutions with the analytical solutions of the linearized equations, and furthermore contrast our results with the literature, before we in Sec. VII conclude.
II. NON-EQUILIBRIUM DESCRIPTION

The basic non-equilibrium formalism for continuum electro-hydrodynamics is well-known (see, e.g., Ref. 19), but as mentioned in the introduction we explicitly include an insulating layer in the description. We do not include an intrinsic zeta-potential, i.e., no un-passivated surface charges on the insulator-electrolyte interface. We note that experimentally any intrinsic homogeneous zeta-potential may be compensated by a corresponding DC-shift added to the applied AC potential. Due to heterogeneous surfaces, it may be anticipated that although the average zeta-potential is nulled out, there might be fluctuations left. These will be the topic for future work. For zero intrinsic zeta-potential we solve the full non-linear equations numerically, but to obtain analytical results we also study the linearized equation with special emphasis on the capacitance due to the insulating layer. In Sec. V we shall show that for experimental relevant parameters, the number densities of the ions couple to the potential \( \phi \) via Poisson's equation,

\[
\nabla^2 \phi(r,t) = 0, \quad \text{for} \quad -d < x < 0. \tag{2}
\]

B. The electrolyte, \( x > 0 \)

In the liquid electrolyte we consider the ionic densities \( n^\pm(r,t) \), the potential \( \phi(r,t) \), the ionic current densities (the ionic flux densities) \( i^\pm(r,t) \), the velocity field \( v(r,t) \) of the electrolyte, and the pressure \( p(r,t) \). In the following we suppress \( (r,t) \) unless needed for clarity.

The number densities of the ions couple to the potential via Poisson's equation,

\[
\nabla^2 \phi = \frac{Ze}{\epsilon}(n^+ - n^-). \tag{3a}
\]

The ionic current densities are coupled to the ionic densities by a continuity equation, which in the absence of any chemical reactions in the system is

\[
\partial_t n^\pm = -\nabla \cdot i^\pm. \tag{3b}
\]

The presence of convection or of gradients in the densities \( n^\pm \) and the electric potential \( \phi \) will generate ionic current densities \( i^\pm \). The Nernst–Planck equation gives these currents

\[
i^\pm = -D \nabla n^\pm + n^\pm v \mp \mu n^\pm \nabla \phi, \tag{3c}
\]

where, for simplicity, we have assumed that the two types of ions have the same diffusivity \( D \) and the same mobility \( \mu \). We remind the reader that both the diffusivity \( D \) and the electric conductivity \( \sigma \) are linked to the mobility \( \mu \) via the Einstein relation \( \sigma = D/\epsilon \).

Finally, the velocity field and pressure of the liquid are coupled to the potential and ionic densities by the Navier–Stokes equation

\[
\rho [\partial_t v + (v \cdot \nabla) v] = -\nabla p + \eta \nabla^2 v - Ze [n^+ - n^-] \nabla \phi, \tag{3d}
\]

where \( \rho \) is the mass density, \( \eta \) is the viscosity of the liquid, and \( p \) is the pressure. Furthermore, treating the electrolyte as an incompressible fluid we have

\[
\nabla \cdot v = 0. \tag{3e}
\]

The coupled field-equations, Eqs. (3a) to (3e), fully govern the physical fields \( n^\pm, \phi, i^\pm, v, \) and \( p \).

C. Boundary conditions

Assuming a vanishing zeta-potential the boundary condition for the electric potential is

\[
\phi(r,t)|_{x=-d} = V_{ext}(y,t), \quad \phi(r,t)|_{x=\infty} = 0. \tag{4a}
\]

At the interface between the electrolyte and the insulating region the normal component of the ionic current density vanishes,

\[
0 = \partial_x n^\pm(r,t)|_{x=0} \pm \frac{Ze}{k_B T} n^\pm(r,t) \partial_x \phi(r,t)|_{x=0}. \tag{5}
\]

Table I: Typical values of central parameters.

| Parameter               | Value          |
|-------------------------|----------------|
| Spatial modulation      | \( q^{-1} \)   |
| Insulator thickness     | \( d \)        |
| Debye length            | \( \lambda_D \) |
| Resonance frequency     | \( \omega^* \) |
| Debye frequency         | \( \omega_D = \sigma_\infty/\epsilon \) |
| Critical frequency      | \( \omega_c = (\eta/\rho)^{1/2} \) |
| Thermal voltage         | \( V_T = (1 + \delta)k_B T/Ze \) 250 mV |
| Convective voltage      | \( V_c = (1 + \delta)\eta D/\epsilon \) 100 mV |

| Property               | Value          |
|------------------------|----------------|
| Ionic density          | \( n_\infty \) 1 mol L\(^{-1}\) |
| Viscosity              | \( \eta \) 10\(^{-3}\) Pas |
| Mass density           | \( \rho \) 10\(^{3}\) kg m\(^{-3}\) |
| Ionic diffusivity      | \( D \) 10\(^{-9}\) m\(^2\) s\(^{-1}\) |
| Capacitance ratio      | \( \delta = C_D/C_s \) 10 |

Here, we have utilized Eq. (3c) and the absence of convection at the interface due to the no-slip boundary condition,

\[
v(r,t)|_{x=0} = 0. \tag{6}
\]
For the ionic densities we have

$$n^\pm(r,t) |_{x=\infty} = n_\infty,$$  \hspace{1cm} (7)

where $n_\infty$ is the homogeneous density of either of the two types of ions in the absence of an external perturbation, i.e., when $V_0 = 0$. For the pressure, we assume that we have no externally applied pressure gradients so that $p$ is the internal pressure caused by fluid flow and the electrical forces on the ions.

III. STATIC REGIME, $\omega = 0$

In the static regime we have equilibrium and neither current nor fluid flow, i.e., $i^\pm = 0$ and $\nu = 0$. The pressure gradient balances the electrical forces on the charges. The governing equations for $\phi$ and $n^\pm$ of course reduce to those of electro-statics.

In the insulating layer it follows from Eqs. (2) and (4a) that

$$\phi(r) = B_1 e^{-qx} + B_2 e^{qx} \cos(qy), \quad \text{for} \quad -d < x < 0, \hspace{1cm} (8)$$

where $B_1$ and $B_2$ are integration constants.

In the electrolyte $\phi(r)$ is governed by the nonlinear Poisson–Boltzmann equation [19]

$$\nabla^2 \phi(r) = \frac{k_B T}{Ze\lambda_D} \sinh \left( \frac{Ze}{k_B T} \phi(r) \right), \quad \text{for} \quad x > 0, \hspace{1cm} (9)$$

introducing the Debye screening length

$$\lambda_D \equiv \sqrt{\frac{ek_B T}{2Z^2e^2n_\infty}}. \hspace{1cm} (10)$$

For $q$ going to zero we have a constant surface potential

$$\lim_{q \to 0} \phi(r)|_{x=0} = \phi_0 \hspace{1cm} (11a)$$

and the solution to Eq. (9) is given by the well-known Gouy–Chapman solution [19]

$$\lim_{q \to 0} \phi(r) = \frac{4k_B T}{Ze} \text{arctanh} \left( \frac{Ze\phi_0}{4k_B T} e^{-x/\lambda_D} \right). \hspace{1cm} (11b)$$

For $q \neq 0$ we are not aware of any analytical solutions, but as we shall show, analytical results can be obtained in the Debye–Hückel approximation $Ze\phi \ll k_B T$, where Eq. (9) becomes linear,

$$\nabla^2 \phi(r) = \lambda_D^{-2} \phi(r), \quad \text{for} \quad x > 0. \hspace{1cm} (12)$$

Here, the corrections are to third order in $Ze\phi/k_B T$ because $\sinh(x) = x + O(x^3)$. The space charge follows from Poisson’s equation, Eq. (3a). From a straightforward solution for $\phi$ and $Ze(n^+ - n^-)$ we arrive at the following expression relating the total potential drop across the system and the accumulated charge in the electrolyte,

$$\phi(\infty, y) - \phi(-d, y) \equiv C_\text{eff}^{-1} \int_0^\infty dx Ze[n^+(r) - n^-(r)]. \hspace{1cm} (13a)$$

The coefficient,

$$C_\text{eff}^{-1} = \frac{[1 + (q\lambda_D)^2] \sinh(qd)}{qd} \frac{C_s^{-1}}{C_D^{-1}}$$

$$+ \frac{\sqrt{1 + (q\lambda_D)^2} \cosh(qd)}{C_D^{-1}}, \hspace{1cm} (13b)$$

is identified as the inverse of an effective series capacitance. The constant $C_s$ is the intrinsic surface capacitance and $C_D$ the capacitance of the Debye layer given by

$$C_s \equiv \frac{\epsilon_s}{d}, \hspace{1cm} (13c)$$

$$C_D \equiv \frac{\epsilon}{\lambda_D}. \hspace{1cm} (13d)$$

In Ref. 2 the potential in the bulk of the electrolyte $(x \gg \lambda_D)$ is governed by the Laplace equation, which is coupled to the external potential $V_\text{ext}$ by an effective capacitance $C_0$ given by

$$C_0 \equiv (C_s^{-1} + C_D^{-1})^{-1}. \hspace{1cm} (13e)$$

It follows from Eq. (13b) that this approach for $\omega = 0$ is valid up to second order in the parameters $q\lambda_D$ and $qd$.

IV. LINEARIZED DYNAMIC REGIME, $\omega > 0$

We now solve Eqs. (3) in the dynamic regime, $\omega > 0$. First the ionic current densities are eliminated by inserting Eq. (3c) into Eq. (3b). Using the incompressibility of the fluid, Eq. (3c), we get the continuity equation

$$\partial_t n^\pm = D \nabla^2 n^\pm - (\nabla n^\pm) \cdot \nu \pm \mu \nabla \cdot (n^\pm \nabla \phi). \hspace{1cm} (14)$$

A. Debye–Hückel approximation

To advance further by analytical methods, we now linearize the continuity equation, Eq. (14), in the density as follows. We assume $n^\pm(r,t)|_{x=\infty} = n_\infty$ and write

$$n^\pm(r,t) = n_\infty + \delta n^\pm(r,t), \quad \lim_{x \to \infty} \delta n^\pm(r,t) = 0. \hspace{1cm} (15)$$

Since we assume a zero intrinsic zeta-potential it is a non-zero $V_0$ that spawns $\delta n^\pm \neq 0$, and when the applied voltage $V_0$ is much smaller than the thermal voltage $V_T$, defined by $V_T \equiv (1 + C_D/C_s)k_B T/Ze$ (as we shall see in the next subsection), we have $|\delta n^\pm| \ll n_\infty$. In this limit the Debye–Hückel approximation is valid, and $n^\pm \nabla \phi$ is substituted by $n_\infty \nabla \phi$ in Eq. (14). We subsequently use Eq. (3a) to replace $\nabla^2 \phi$ with $-Ze\nu/\epsilon$ where

$$\nu \equiv n^+ - n^- = \delta n^+ - \delta n^- . \hspace{1cm} (16)$$
Finally, we form the difference of the "±"-versions of Eq. (14) and obtain the partial differential equation
\[
\partial_t \nu = \left[ D \nabla^2 - D \frac{1}{\lambda_D^2} - \nu \cdot \nabla \right] \nu. \tag{17}
\]

B. Diffusive regime

Our study of the static regime reconfirms the well-known result that the net charge density is non-zero only in the Debye layer, \( x \lesssim 3 \lambda_D \). In this region convection will be suppressed due to the no-slip boundary condition. Thus, convection can be neglected, diffusion will dominate (corresponding to a low Péclet number), and the electrodynamics can be solved independently of the hydrodynamics. On the other hand, the hydrodynamics of course still depends on the electrodynamics via the body-force. Since the density difference \( \nu \) changes over the length scales \( \lambda_D \) and \( q^{-1} \) for the \( x \) and \( y \) directions, respectively, the condition for the decoupling is \( |v_x|/\lambda_D + |v_y|q \ll Dq^2 \) for \( 0 < x \lesssim 3 \lambda_D \). In this limit Eq. (17) has a general \( \cos(qy)e^{i\omega t} \) modulated decaying solution of the form
\[
\nu = C_1 e^{-\kappa x} \cos(qy)e^{i\omega t}, \quad x > 0, \tag{18a}
\]
where the decay parameter \( \kappa \) depends on the ratio between the frequency \( \omega \) and the Debye frequency \( \omega_D \),
\[
\kappa \equiv \frac{1}{\lambda_D} \sqrt{1 + (q\lambda_D)^2} + i \frac{\omega}{\omega_D}, \tag{18b}
\]
\[
\omega_D \equiv \frac{D}{\lambda_D}. \tag{18c}
\]

For the potential we seek a solution of a form similar to Eq. (18a), \( \phi \propto \cos(qy)e^{i\omega t} \), and substituting this together with Eq. (18a) into Eq. (3a) yields
\[
(\partial_x^2 - q^2)\phi = -\frac{Ze}{\epsilon} C_1 e^{-\kappa x} \cos(qy)e^{i\omega t}. \tag{19}
\]
Demanding \( \phi(r,t)|_{x=\infty} = 0 \) the solution is
\[
\phi = \frac{Ze/\epsilon}{q^2 - \kappa^2} \left[ C_1 e^{-\kappa x} + C_2 e^{-q x} \right] \cos(qy)e^{i\omega t}, \quad x > 0. \tag{20}
\]
In the insulating layer we have the following \( \cos(qy)e^{i\omega t} \) modulated general solution to Eq. (2),
\[
\phi = \left[ C_3 e^{-q x} + C_4 e^{q x} \right] \cos(qy)e^{i\omega t}, \quad -d < x < 0. \tag{21}
\]
In order to determine \( C_1, C_2, C_3, \) and \( C_4 \) we first consider the boundary condition for the current. Applying the Debye–Hückel approximation to the second term in Eq. (5) and forming the difference of the "±" solutions we arrive at
\[
0 = \partial_x \left[ \nu(r,t) + \frac{C_D}{Ze\lambda_D} \phi(r,t) \right] |_{x=0}. \tag{22}
\]
Together with the boundary condition for \( \phi \) at \( x = -d \) as well as the continuity of \( \phi \) and \( \epsilon \partial_x \phi \) at \( x = 0 \) we may determine the constants straightforwardly keeping in mind that \( \kappa \) depends on \( q \) and \( \omega \). For the coefficients in the electrolyte we get
\[
C_1 = \frac{qV_0}{Ze} \frac{\kappa}{q} \epsilon \omega D \epsilon, \tag{23a}
\]
and
\[
C_2 = -i \frac{\omega}{\omega_D} C_1, \tag{23b}
\]
while for the insulator the coefficients have a similar, but less compact form. Above,
\[
C^{-1}_\text{eff}(\omega) = (\kappa \lambda_D)^{-2} \sinh(qd) C_s^{-1} \tag{23c}
\]
\[
+ \kappa \lambda_D \frac{q \lambda_D (q \lambda_D + \kappa \lambda_D) + i \omega}{q \lambda_D (q \lambda_D + \kappa \lambda_D)} \cos(qd) C^{-1}_D,
\]
which satisfies the definition in Eq. (13a) and reduces to Eq. (13b) in the DC limit. From the general solution for the potential in the electrolyte, Eq. (20), we may now in more detail examine the constraints on \( V_0 \) for the Debye–Hückel approximation to be valid. Straightforward calculations show that \( \max|\phi| \ll k_B T/Ze \) corresponds to \( V_0 \ll V_T \equiv (1 + C_D/C_s)k_B T/Ze \) for \( qd \ll 1, q\lambda_D \ll 1 \), and low frequencies.

C. Long-period and low-frequency modulation

Next, we consider the regime where the spatial period of the modulation is much longer than all other length scales, i.e., \( q\lambda_D \ll 1 \) and \( qd \ll 1 \). We also assume that \( \omega \ll \omega_D \) so that \( \kappa \simeq 1/\lambda_D \). In this limit we get
\[
\nu = -\frac{q\sigma V_0}{Ze\lambda_D} \frac{1}{\omega^2 - \kappa^2} e^{-q x/\lambda_D} \cos(qy)e^{i\omega t} + \mathcal{O}([q\lambda_D]^2), \tag{24}
\]
and
\[
\phi = V_0 \frac{i\omega}{\omega^2 + i\omega} e^{-q x/\lambda_D} \cos(qy)e^{i\omega t} + \mathcal{O}(q\lambda_D), \tag{25}
\]
where we have used the notation of Ajdari [2]
resonance frequency: \( \omega^* = q\lambda_D (1 + \delta) \omega_D \), \tag{26a}
conductivity: \( \sigma_\infty = [\sigma^+ + \sigma^-]|_\infty = \epsilon \omega_D \), \tag{26b}
capacitance ratio: \( \delta = C_D/C_s \). \tag{26c}

These results are equivalent to those in Ref. 2 if we similarly to Eq. (13a) introduce the Debye layer surface charge \( \sigma_D(y) = Ze \int_0^\infty dx \nu(x,y) \).
D. Body-force

Until this point we have used the exponential notation for the temporal dependence. However, since the body-force is essentially non-linear in the electrical potential/density [see last term in Eq. (3d)] we have to take the real part to get the body-force, i.e., $F = -Z e \nu \nabla \phi = -Z e \text{Re}\{\nu\} \text{Re}\{\nabla \phi\}$ so that we get

$$F = \frac{\eta v_1}{\lambda_D^2} \cos(2\omega t + \varphi) e^{-x/\lambda_D} \left[ 2 G \cos(2qy)e_x + \frac{G}{2} \sin(2qy)e_y \right] + \mathcal{O}([q \lambda_D]^2)$$

where following Ref. 2 we have introduced

$$v_1 = \frac{q e V_0^2}{4 \eta (1 + \delta)}$$

and the frequency dependent phase shift

$$\varphi = -\arctan \left( \frac{\omega}{2 \omega^*} - \frac{\omega^*}{2 \omega} \right).$$

In the derivation of Eq. (27a) we have used that

$${\text{Re}} \left\{ \frac{e^{i \omega t}}{i \omega + \omega^*} \right\} = \frac{1}{2} \left( \frac{\cos(2\omega t + \varphi)}{\omega} \right)$$

At low frequencies, $F \propto \omega$, it becomes maximal at the resonance frequency $\omega^*$, and then it falls off again at higher frequencies. We note that $\lim_{\omega \to 0} F = \mathcal{O}([q \lambda_D]^2)$, but this small force will just be balanced by a pressure gradient so that $\lim_{\omega \to 0} V = 0$ and $\lim_{\omega \to 0} 1^{3/2} = 0$.

E. Linearized flow in quasi-steady state

In order to solve the Navier–Stokes equation, Eq. (3d), we note that for a body-force of small magnitude and with slow temporal variation the fluid response is linear and the flow will approximately be at steady state at each moment in time. We begin by comparing the inertial terms on the left-hand side (LHS) with the viscous terms on the right-hand side (RHS). The body force has a characteristic frequency $\omega$ and two characteristic length scales $\lambda_D$ and $q^{-1}$ for the $x$ and $y$-directions, respectively. Since $\partial_t$ essentially gives a factor of $\omega$, and $\nabla$ essentially gives $\lambda_D^{-1} e_x + q e_y$, we can show that the viscous term dominates over the LHS when $\omega \ll \omega_c$ where

$$\omega_c = \frac{\eta}{\rho} \min\{q^2, \lambda_D^{-2}\}.$$ 

For $q \lambda_D \ll 1$ this means that $\omega_c = \frac{\eta}{\rho} q^2$. In this way, for small Reynolds numbers, we get

$$0 = -\nabla p + \eta \nabla^2 v + F, \quad \omega \ll \omega_c$$

which is the resulting quasi-steady flow problem which is linear in the velocity field. Slip-velocity approaches usually rely on this equation, see Ref. 2 and references therein. However, Eqs. (30) and (27a) can actually be solved exactly with a solution given by

$$v(r, t) = v_1 \frac{\cos(2\omega t + \varphi)}{\omega} e^{-2qx} \left[ 2 G \cos(2qy)e_x + \frac{G}{2} \sin(2qy)e_y \right]$$

$$p(r, t) = -4 q \eta v_1 \frac{\cos(2\omega t + \varphi)}{\omega} e^{-2qx} \left( \frac{1 + G(2q)}{1 + 2q \lambda_D^2} \cos(2qy) + G(0) \right).$$

as may be verified by direct insertion. Above,

$$G_1(k) = \frac{1 - 2q \lambda_D}{[1 - (2q \lambda_D)^2]^2} \times \left( 1 - e^{-k^2/\lambda_D^2} \right)$$

and

$$G_2(k) = \frac{1 + k \lambda_D}{4q \lambda_D} e^{-(\lambda_D^{-1} - 2q)x}$$

have been introduced. As seen the flow decays exponentially over a length scale of $1/q$ when $\omega \ll \omega_c$. When
the frequency becomes comparable to or larger than $\omega_c$ we have competing length scales since the $\partial_2 v$ term introduces an additional length scale, $(\eta/\rho \omega)^{1/2}$, which as mentioned becomes $(\omega_c/\omega)^{1/2} \times 1/q$ for $q \lambda_D \ll 1$. So in the above expressions for $v$ and $p$ we expect that the spatial cut-off length changes from $(2q)^{-1}$ to $\Lambda$ with

$$\Lambda(\omega) \sim \frac{1}{2q} \min \left\{ 1, \sqrt{\omega_c/\omega} \right\}.$$  

Even for $\omega \ll \omega^*$ the condition $\omega \ll \omega_c$ is not necessarily fulfilled. In fact, for the numbers in Table I we have $\omega_c < \omega^* < \omega_D$ so at resonance $2q \Lambda(\omega^*) = \sqrt{\omega_c/\omega^*} \ll 1$.

**F. Flow and separation of length scales**

As mentioned above the flow is typically analyzed by slip-velocity approaches and here we show how such an approach gives an asymptotic solution in full agreement with the exact solution. We study the flow over a $\lambda_D$-scale at the boundary first and then a $q^{-1}$-scale. For this boundary layer approach, we assume that for $x \lesssim 3 \lambda_D$, we have $v_s \approx 0$. Solving for the pressure and substituting into the $y$-component of Eq. (30) we get

$$v_y = v_s(y, t) \left( 1 - e^{-x/\lambda_D} \right) + \mathcal{O}(q \lambda_D), \quad x \lesssim 3 \lambda_D \quad (35)$$

with the prefactor

$$v_s(y, t) \equiv v_1 \frac{\cos(2 \omega t + \varphi)}{\omega^2 + \frac{\omega^*}{\omega}} \sin(2 q y). \quad (36)$$

In the limit $x \gtrsim 3 \lambda_D$ and $q \lambda_D \ll 1$ the velocity $v_s$ can be interpreted as a slip-velocity at the wall acting as a conveyor belt for the bulk fluid, see Fig. 2(d).

For $x \gtrsim 3 \lambda_D$ we have that $\mathbf{F}$ is exponentially suppressed and we solve Eq. (30) together with Eq. (3e) and the boundary condition

$$\mathbf{v}(\mathbf{r}, t) \big|_{x=0} = v_s(y, t) \mathbf{e}_y. \quad (37)$$

To lowest order in $q \lambda_D$ this gives

$$\mathbf{v} \approx v_1 \frac{\cos(2 \omega t + \varphi)}{\omega^2 + \frac{\omega^*}{\omega}} e^{-2qx}$$

$$\times \left( -2q x \cos(2qy) \mathbf{e}_x + (1 - 2qx) \sin(2qy) \mathbf{e}_y \right),$$

and

$$p \approx -4qv_1 \frac{\cos(2 \omega t + \varphi)}{\omega^2 + \frac{\omega^*}{\omega}} e^{-2qx} \cos(2qy). \quad (39)$$

If we now substitute into Eq. (3d) we get RHS $- \mathbf{LHS} \propto e^{-x/(\lambda_D)} + \mathcal{O}(\omega/\omega_D) + \mathcal{O}(q \lambda_D)^2$ which shows that Eqs. (38) and (39) are indeed excellent approximations to the full solution of the non-linear time-dependent Navier–Stokes equation, Eq. (3d), for $x \gtrsim 3 \lambda_D$. For the incompressibility constraint, Eq. (3e), our solution gives $\nabla \cdot \mathbf{v} = \mathcal{O}([q \lambda_D]^2)$. In Fig. 2(c) we show a plot of the velocity-field, Eq. (38), along with the contours for constant velocity.

We note that in the limit $x \gtrsim 3 \lambda_D$ the exact solutions, Eqs. (31b) and (32b) reduce to Eqs. (38) and (39) for the bulk.

**V. FULL NUMERICAL SOLUTION**

In this section we present results from numerical finite element simulations (Femlab) of the five coupled equa-
Figure 3 shows numerical results for the effective capacitance $C_{\text{eff}}$, see definition in Eq. (13a), as a function of the frequency for varying amplitudes $V_0$ of the external voltage. The dashed line shows the corresponding analytical result from Eq. (23c). As seen there is a good agreement between numerical results and our analytical predictions even for $V_0 > V_T$ where the Debye–Hückel approximation is typically expected to work poorly. We furthermore note that at low frequencies $\text{Re} \{C_{\text{eff}}\}$ approaches $C_0$ in full agreement with the analytics and the log-log plot also reveals two distinct regimes for $\omega < \omega^*$ and $\omega > \omega^*$. In fact, dissipation is maximal exactly at the resonance frequency $\omega^*$ predicted by the linear theory. The inset shows the relative error of the Debye–Hückel approximation which at large voltages saturates at a value of the order $(1 + \delta)^{-1}$, here equal to 0.09.

The linear theory predicts a harmonic velocity field with a vanishing time average and our numerical simulations confirm this low-frequency dynamics, see max$_r \{ \langle v(r,t) \rangle \}$ in Fig. 4(a). The corresponding solid line shows exact results within the Debye–Hückel approximation [20] and the dashed line shows $(\omega^* + \omega)^{-1}$ as suggested by Eq. (38). As expected the induced harmonic motions peaks at the resonance frequency $\omega^*$ with a characteristic speed $v_1$, Eq. (27b). However, in the high-frequency dynamics we observe the co-existence of a small, but non-vanishing time-averaged component, $0 < \text{max}_r \{ \langle v(r,t) \rangle \} < v_1$. Fig. 4(a) shows max$_r \{ \langle v(r,t) \rangle \}$ as a function of frequency for different external voltages. The corresponding corresponding solid line shows exact results within the Debye–Hückel approximation [20]. Panel (b) shows a particular example of the time-averaged velocity field $\langle v(r,t) \rangle$.

VI. DISCUSSION

We have analyzed the full non-equilibrium electrodynamics of the Debye screening layer that arise in an aqueous binary solution near a planar wall when applying a spatially modulated ac-voltage $V_0 \cos(\omega t)/c_{\text{ext}}$, Eq. (1). Using first order perturbation theory we have obtained analytic solutions for the pressure and velocity fields of the electrolyte and for the electric potential. Our analytical solution applies to the low-frequency Debye–Hückel regime where the amplitude $V_0$ of the external potential is lower than the thermal voltage $V_T$ and the driving frequency $\omega$ is lower than the inverse response-time of the electrolyte $\omega_D = \sigma_\infty/\varepsilon$ (see Secs. IV A and IV C). It should be noted that our analysis does not cover the special case of suddenly applied step voltages, where the system selects its own intrinsic time scale different from the external time scale $1/\omega$ [19].

Furthermore, we have limited ourselves to the diffusive regime where convection can be neglected corresponding to a sufficiently low driving amplitude, $V_0 \ll V_0$ where $V_0 \equiv \sqrt{(1 + \delta)\eta D/\varepsilon}$ is a convective voltage (see first paragraph of Sec. IV B, $\textbf{v} \sim v_1 \textbf{e}_y$ in the Debye layer). We
have also considered the low-frequency regime $\omega \ll \omega_c$ where viscosity dominates over inertia (see Sec. IV E).

Finally, we have considered the limit with the spatial modulation being much longer than all other length scales in the problem, i.e., $qD \ll 1$ and $q\lambda_D \ll 1$ (see Sec. IV C). In summary this means that the analytical studies of the effect of Eq. (1) are valid in the limits

$$q \ll \min \left\{d^{-1}, \lambda^{-1}_D \right\}, \quad \omega \ll \min \left\{\omega_D, \omega_c \right\}, \quad V_0 \ll \min \left\{V_T, V_c \right\}. \quad (40a, b, c)$$

As a main result we have supplied a proof for the validity of the capacitor model. The full dynamics seems however not to be captured by the capacitor model. Taking the time-average in Eqs. (27a) and (38) we get \(\langle F_\ell \rangle_t = 0\) and \(\langle v \rangle_t = 0\) (in full agreement with the discussion in Ref. 2). In contrast, we obtain \(\langle F_\ell \rangle_t \neq 0\) if we begin from Eqs. (18a) and (20) without expanding in $\omega/\omega_D$ and $q\lambda_D$, the result being finite even in the zero-frequency limit. Somewhat similar results were reported in another non-equilibrium study [5], though for a different geometry. Naïvely, this observation could suggest that \(\langle v \rangle_t \neq 0\) contrary to the statement in Ref. 2. However, by also averaging over the $y$-direction we get \(\langle F_y \rangle_t, y = 0\) suggesting that \(\langle v_y \rangle_t, y = 0\) in agreement with the symmetry arguments emphasized in Ref. 2. If the finite \(\langle F \rangle_t\) does not give the fluid a directional flow globally, we might speculate that, at high frequencies, it makes the fluid circulate in non-oscillating vortices, see Fig. 2(c), whereas the fluid is at rest at zero-frequency – despite \(\langle F \rangle_t\) being finite. The solution to this apparent contradiction lies in the pressure, which will compensate the body-force at low frequencies. We can explicitly show that the time-averaged body-force can be written as

$$\langle F_\ell \rangle_t = \nabla p_F (r) + \mathcal{O}\left(\omega/\omega_D^2\right) \quad (41)$$

where

$$p_F (r) = \frac{1}{4} e^2 V_0^2 \left[ \frac{q\lambda_D \cosh(qd)}{x_s} + \sqrt{1 + \frac{(q\lambda_D)^2 \sinh(qd))^2}{1 + (q\lambda_D)^2 \sinh(qd))^2} \right]$$

$$\times e^{-2\sqrt{1 + (q\lambda_D)^2 \sinh(qd)^2}} \cos^2(qy). \quad (42a)$$

$$\times e^{-2\sqrt{1 + (q\lambda_D)^2 \sinh(qd)^2}} \cos^2(qy). \quad (42b)$$

The form of Eq. (41) suggests that

$$\langle v_\ell \rangle_t = 0 + \mathcal{O}\left(\omega/\omega_D^2\right) \quad (43)$$

with $p_F$ being a pressure that compensates the low-frequency part of the body force, see Eq. (30). The time-averaged velocity field \(\langle v_\ell \rangle_t\) can be calculated rigorously and the complex expression (not shown) agrees fully with Eq. (43). At high frequencies we expect stationary vortices, Fig. 4(b), to co-exist with the harmonic fluid motion illustrated in Fig. 2(c), whereas at low frequencies the circulation vanishes and we are left with the pure harmonic motion. Our time-dependent finite-element simulations in Fig. 4 support this picture and similar time-averaged flow in a slightly different geometry has been observed both experimentally, theoretically, and numerically [4–6].

VII. CONCLUSION

Our results provide the theoretical underpinning of the capacitor model widely used in the literature [2–
4, 6, 7, 15, 19], and form a firm starting point for future studies of electro-kinetic pumps and mixers driven by spatially modulated surface potentials. In general for large values of $\delta$ we find that the Debye–Hückel approximation works well even at elevated voltages [agreement within less than $(1 + \delta)^{-1}$] where it is typically expected to work poorly. However, our non-equilibrium approach has also revealed interesting short-comings in the capacitor approach for high-frequency dynamics where static vortices appear along with the harmonic rolls also predicted by the capacitor model.

Acknowledgement

We thank A. Ajdari for stimulating discussions and T. S. Hansen for sharing initial numerical results with us. N. A. M. is supported by The Danish Technical Research Council (Grant No. 26-03-0073) and L. B. by a Socrates/Erasmus grant from the European Community.