

# Generalized Onsager relations for electrokinetic effects in anisotropic and heterogeneous geometries

Edouard Brunet<sup>1</sup> and Armand Ajdari<sup>2,\*</sup><sup>1</sup>Laboratoire MMN, UMR CNRS-ESPCI 7083, 10 rue Vauquelin, F-75231 Paris Cedex 05, France<sup>2</sup>Laboratoire de Physico-Chimie Théorique, UMR CNRS-ESPCI 7083, 10 rue Vauquelin, F-75231 Paris Cedex 05, France

(Received 12 September 2003; published 26 January 2004)

We lay down a general formalism to describe the linear electrohydrodynamic response of systems of arbitrary topology, symmetry and heterogeneity, and through an explicit proof, we demonstrate a set of general Onsager relations between the corresponding electrokinetic coefficients. This generalizes a classical result of Mazur and Overbeek [P. Mazur and J.T.G. Overbeek, Recl. Trav. Chim. Pays-Bas. **70**, 83 (1951)] to situations that may become of practical relevance in particular in the field of microfluidic devices. Technically, our proof of the symmetry of the generalized conductance matrix relies on an adaptation of the reciprocal theorem of low-Reynolds-number hydrodynamics.

DOI: 10.1103/PhysRevE.69.016306

PACS number(s): 47.60.+i, 47.65.+a, 47.55.Mh, 85.85.+j

## I. INTRODUCTION

A few decades ago Mazur and Overbeek proved the existence of relations between electro-hydrodynamic couplings in a capillary containing an electrolyte solution [1]. In particular, the magnitude of the electro-osmotic effect (the solvent flow generated by the application of an electric field) is directly related to that of the streaming current effect (a pressure drop across the capillary can drive an electric current between its ends). This relation holds as a so-called Onsager relation, valid within linear response of fluxes to fields in the vicinity of thermodynamic equilibrium (see De Groot and Mazur [2]).

Formally their result is equivalent to the following statement: the matrix that relates, in the linear response regime, the flow of liquid  $Q$  and the electrical current  $I_{el}$  through the capillary (see Fig. 1, top), to the pressure drop  $\Delta p$  and electrostatic potential drop  $\Delta\phi$  across that channel,

$$\begin{bmatrix} Q \\ I_{el} \end{bmatrix} = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} \begin{bmatrix} -\Delta p \\ -\Delta\phi \end{bmatrix}, \quad (1)$$

is a symmetric matrix  $M_{12}=M_{21}$ . The sign convention is such that  $\mathbf{M}$  is a positive definite matrix.

Technically the proof of Mazur and Overbeek consisted of three pieces. First they showed explicitly, using coupled local equations for hydrodynamics and electrostatics, that the above-mentioned relation is true *for a capillary of arbitrary but constant cross section, and of constant surface (zeta) potential*. Second, using a general close-to-equilibrium thermodynamic formulation, they showed that one should expect such relations *for a channel connecting two points with identical ionic concentrations*. This second proof holds regardless of the specific description of electrohydrodynamics within the channel, and regardless of the channel wall properties. In a third step, they derived subsequent relations for a network of such 1D channels.

In the present paper, we complete the picture by providing a generalized explicit proof of Onsager relations between various electrokinetic coefficients, starting from the commonly used microscopic equations for hydrodynamics, electrostatics and ion transport in dilute electrolyte solutions. This proof holds for geometries of *arbitrary surface properties and shapes* [e.g., arbitrary strength and distribution of the surface (zeta) potential], of arbitrary topologies (e.g., devices with many inlets that cannot be described simply as networks of 1D channels), and for variations of the ionic concentrations.

A motivation for this study is the developing possibilities offered by microfabrication to tailor microfluidic or porous media of controlled heterogeneity and anisotropy for functional purposes such as (pumping, flow control, mixing, separation) [3–11]. In particular our proof is relevant for transverse effects in patterned microchannels, for nodes in circuits of microchannels, and for anisotropic (e.g., layered) porous materials.

To provide the reader with a flavor of our results, we provide two examples of consequences of our general approach (see the bottom of Fig. 1).

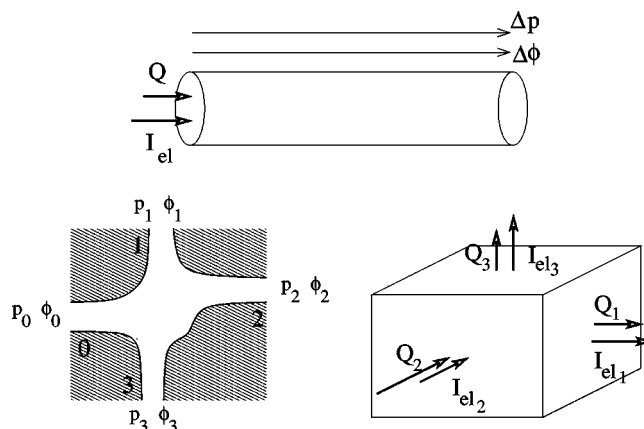


FIG. 1. Top: a simple capillary. Bottom: examples of geometries covered by our approach, a 4-branch node (left) and the unit cell of a periodic porous material (right).

\*Author to whom all correspondence should be addressed. Email address: armand@turner.pct.espci.fr

(a) The linear response of the 4-branch node in Fig. 1, is described (in the absence of applied ionic gradients) by a *symmetric* matrix relating the flow rate and electrical current exiting through each branch  $Q_\alpha$  and  $I_{el\alpha}$  ( $\alpha=0, \dots, 3$ ), to the pressures and potential (relative to that of the inlet 0)  $\Delta p_\alpha = p_\alpha - p_0$  and  $\Delta \phi_\alpha = \phi_\alpha - \phi_0$ :

$$\begin{bmatrix} Q_1 \\ Q_2 \\ Q_3 \\ I_{el1} \\ I_{el2} \\ I_{el3} \end{bmatrix} = \begin{bmatrix} M_{11} & M_{12} & \cdot & \cdot & \cdot & \cdot \\ M_{21} & M_{22} & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix} \begin{bmatrix} -\Delta p_1 \\ -\Delta p_2 \\ -\Delta p_3 \\ -\Delta \phi_1 \\ -\Delta \phi_2 \\ -\Delta \phi_3 \end{bmatrix} \quad (2)$$

with the conservation rules  $Q_0 = Q_1 + Q_2 + Q_3$  and  $I_{el0} = I_{el1} + I_{el2} + I_{el3}$ . Our main point is that this matrix is symmetric:  $M_{uv} = M_{vu}$ . So for example  $M_{26}$ , which describes how an electrostatic potential applied on branch 3 generates a flow in branch 2 (cross channel electro-osmosis), is equal to  $M_{62}$  which describes how a pressure applied on branch 2 generates an electric current in branch 3 (cross-channel streaming potential). In passing we also clarify when and in what sense one can use a *single* pressure  $p_\alpha$  and a *single* potential  $\phi_\alpha$  to characterize (the section of) an inlet, and therefore write compact expressions such as Eqs. (1) and (2).

(b) Currents through a 3D periodic porous medium, again in the absence of net ionic gradients can also be described by Eq. (2), with now the  $Q_\alpha$  and  $I_{el\alpha}$  being the flow and electrical current along one of the periodicity direction  $\alpha$ , and the  $\Delta p_\alpha$  and  $\Delta \phi_\alpha$  being the pressure and potential drop over a period in this direction (Fig. 1, bottom left). Again cross effects are related by the symmetry of the matrix.

We take a few steps to obtain these results, and proceed as follows.

In Sec. II we define notations and our starting equations. We then present their equilibrium solution, and the equations describing linear response for small deviations from the equilibrium.

In Sec. III, we perform a calculation analogous to the reciprocal theorem of low-Reynolds-number hydrodynamics which yields the essence of our generalized symmetry proof, at a formal level however.

To make things more explicit and practical, we specialize in Sec. IV to two cases: (Sec. IV A) a periodic system, and (Sec. IV B) a system with ports or inlets that are either smooth (so that integral quantities such as potential and pressure are well defined for each of them) or distant from one another (compared to the ports diameters of the ports). We then explore consequences of the symmetry proof for these two cases (Sec. IV C).

We close in Sec. V with a summary of our results, a few technical comments, and connections to related papers in the literature.

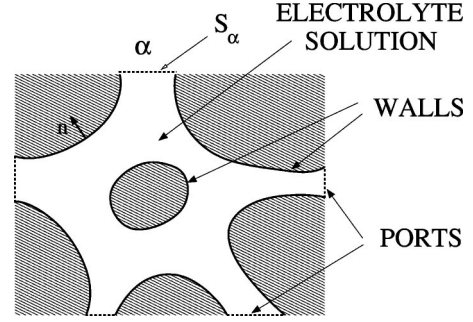


FIG. 2. Scheme of a volume of electrolyte (white) bounded by external and internal walls (hatched), and in contact with the outer world through  $N$  ports (here  $N=5$ ).

## II. STARTING POINT: LOCAL EQUATIONS AND NOTATIONS

As depicted in Fig. 2, we consider a dilute electrolyte solution in a region of space bounded by (1) walls (that can be internal or external) and (2)  $N$  surfaces  $S_\alpha$  (with  $\alpha = 0, \dots, N-1$ ) through which the electrolyte is connected to the outside, which we will call “ports” or “inlets” indifferently ( $N=2$  corresponds to the usual case of a simple channel).

*Bulk equations.* The solvent hosts  $K$  ionic species of respective ionic charge  $q_i$  and local concentration  $c_i(\mathbf{x})$ . The local charge density is thus  $\rho = \sum_{i=1,K} q_i c_i$ . The solution is taken incompressible and of viscosity  $\eta$ , and inertial effects are assumed negligible. Thus the flow field  $\mathbf{v}$  is given by

$$\nabla \cdot \boldsymbol{\sigma} + \rho \mathbf{E} = \mathbf{0}, \quad (3)$$

$$\nabla \cdot \mathbf{v} = 0, \quad (4)$$

where the hydrodynamic stress tensor is

$$\boldsymbol{\sigma} = -p \mathbf{I} + \eta (\nabla \mathbf{v} + \nabla \mathbf{v}^T), \quad (5)$$

with  $p$  the pressure.  $\mathbf{E} = -\nabla \phi$  is the local electric field, given by the Poisson equation

$$\epsilon \nabla^2 \phi + \rho = 0. \quad (6)$$

We focus on steady-state situations where the concentration fields  $c_i$  are governed by time independent conservation equations for the corresponding currents:

$$\mathbf{j}_i = -m_i c_i \nabla \mu_i + c_i \mathbf{v}, \quad (7)$$

$$\nabla \cdot \mathbf{j}_i = 0, \quad (8)$$

where  $\mu_i(\mathbf{x}) = q_i \phi + k_B T \ln(c_i)$  is the chemical potential of species  $i$ , and  $m_i$  its mobility.

Let us also introduce, for reasons that will become clear later,

$$\Pi = p - p_{osmotic} = p - k_B T \sum_{i=1,K} c_i, \quad (9)$$

$$\boldsymbol{\sigma}_0 = -\Pi\mathbf{I} + \eta({}^t\nabla\mathbf{v} + \nabla\mathbf{v}). \quad (10)$$

Equation (3) can be modified to read

$$\nabla \cdot \boldsymbol{\sigma}_0 - \sum_{i=1,K} c_i \nabla \mu_i = \mathbf{0}. \quad (11)$$

*Boundary conditions.* The above set of equation must be supplemented by boundary conditions on the walls and on the ports' surfaces.

On the walls, we require that there is no ion injection or absorption, and impose a no-slip boundary condition for the flow:

$$\mathbf{j}_i|_{wall} \cdot \mathbf{n} = 0, \quad (12)$$

$$\mathbf{v}|_{wall} = \mathbf{0}, \quad (13)$$

where  $\mathbf{n}$  is the local normal to the wall (oriented outwards from the solution). In principle, we then have to add a boundary condition for the electrostatic potential  $\phi$ , related to the local surface property of the wall. This local condition is typically that the surface potential is imposed or that a given surface charge density results in constraints for the normal gradient of the potential. However, it turns out that we need not specify this ‘‘electrical geometry’’ of the problem for the proof presented in this paper. Therefore, to limit the notations we proceed without formally expressing the electrostatic boundary condition on the walls.

The last elements to close the problem are the boundary conditions on the ports surfaces  $S_\alpha$ , which characterize the external forcing on the system. Depending on the problem at hand, these local boundary conditions can be expressed in terms of conditions on either the potentials ( $\phi, p, \mu_i$ ), or the fluxes ( $\mathbf{v}, \mathbf{j}_i$ ), or a combination of both.

The bulk equations together with the boundary conditions constitute a well-defined problem, whereby the system responds to the applied forcing described by the boundary conditions on the ports surface. Note that this response is in general nonlinear due to the nonlinear couplings in Eqs. (3) and (7).

*Thermodynamic equilibrium.* At thermodynamic equilibrium, the currents and flow are zero,  $\mathbf{v}_{eq} = \mathbf{0}$ ,  $\mathbf{j}_{ieq} = \mathbf{0}$ , and the related potentials are spatially homogeneous  $\nabla \Pi_{eq} = \mathbf{0}$  and  $\nabla \mu_{ieq} = \mathbf{0}$ , the latter corresponding to Boltzmann distributions for the ionic concentrations  $c_{ieq} = c_i^0 \exp(-(q_i \phi_{eq})/(k_B T))$ .

*Linear response.* To describe the linear response of the system, we denote with a hat the perturbations about the equilibrium values given above (e.g.,  $\mathbf{v} = \mathbf{v}_{eq} + \hat{\mathbf{v}}$ ,  $\mathbf{j}_i = \mathbf{j}_{ieq} + \hat{\mathbf{j}}_i$ , etc.). We then linearize the equations written above by retaining only terms that are first order terms in ‘‘hat’’ quantities. We therefore focus on the solutions to the following set of equations:

$$\nabla \cdot \hat{\boldsymbol{\sigma}} + \hat{\rho} \mathbf{E}_{eq} + \rho_{eq} \hat{\mathbf{E}} = \mathbf{0}, \quad (14)$$

$$\nabla \cdot \hat{\mathbf{v}} = 0, \quad (15)$$

with

$$\hat{\boldsymbol{\sigma}} = -\hat{p}\mathbf{I} + \eta({}^t\nabla\hat{\mathbf{v}} + \nabla\hat{\mathbf{v}}) \quad (16)$$

and  $\hat{\mathbf{E}} = -\nabla\hat{\phi}$ , where

$$\epsilon \nabla^2 \hat{\phi} + \hat{\rho} = 0. \quad (17)$$

$$\hat{\mathbf{j}}_i = -m_i c_i c_{ieq} \nabla \hat{\mu}_i + c_{ieq} \hat{\mathbf{v}}, \quad (18)$$

$$\nabla \cdot \hat{\mathbf{j}}_i = 0, \quad (19)$$

and also

$$\nabla \cdot \hat{\boldsymbol{\sigma}} - \sum_{i=1,K} c_{ieq} \nabla \hat{\mu}_i = \mathbf{0}. \quad (20)$$

The boundary conditions are a direct transposition of those for the full problem

$$\hat{\mathbf{j}}_i|_{wall} \cdot \mathbf{n} = 0, \quad (21)$$

$$\hat{\mathbf{v}}|_{wall} = \mathbf{0}. \quad (22)$$

For reasons stated above we will not explicit the linearized electrostatic boundary conditions. Note, however, that this boundary condition for the *perturbation* of the electrostatic potential  $\hat{\phi}$  is in general homogeneous, with no reference any more to the surface potential or charge density of the walls [this information is now fully contained in the  $c_{ieq}(\mathbf{x})$  fields].

This set of equations (14)–(22) and the unwritten electrostatic boundary condition is now a linear one, whereby the local flows and fields respond in proportion and additively to the effects applied on the ports surfaces  $S_\alpha$ . We will from now on limit ourselves to this linear response regime.

Let us however point out that the range of validity of this linearization procedure is difficult to express in a general way. Formally, we have neglected  $\hat{\rho}\hat{\mathbf{E}}$  in Eq. (14),  $-m_i \hat{c}_i \nabla \hat{\mu}_i + \hat{c}_i \hat{\mathbf{v}}$  in Eq. (18), and  $-\sum_{i=1,K} \hat{c}_i \nabla \hat{\mu}_i$  in Eq. (20). It is far from obvious to assert in a general way when those terms are, at steady state, negligible compared to those linear in the drivings. Physically, a clear requirement is that the structure of the charged double layers is only weakly distorted. This translates into the requirement that locally ‘‘applied’’ chemical potential gradients (created by potential drops or concentration differences between the ports) be weaker than  $e\phi_s/\lambda_D$  and  $k_B T/\lambda_D$  (where  $\phi_s$  represents a typical surface potential and  $\lambda_D$  the Debye length), and so should the typical local ‘‘applied’’ convective hydrodynamic drag  $\hat{v}/m_i$  in these charged layers. However these local ‘‘applied’’ quantities may depend in a complex fashion on the macroscopically applied driving. For example in a porous medium, the local field in a thin slot may be significantly larger than the macroscopically applied one. In general, the domain of validity of linear response thus depends on geometrical features of the specific system (tortuosity, surface charge patterns, etc.).

### III. RECIPROCAL THEOREM

We start by a variant of the reciprocal theorem for zero-Reynolds-number hydrodynamics [12], adapted to electrokinetic phenomena (in a way related but different than its adaptation in the nice derivation of electrophoretic mobilities of particles by Teubner [13]). We consider two independent solutions of the linearized problem (around the same equilibrium solution), that we design by superscripts (1) and (2). These two solutions correspond to different external forcings, i.e., different boundary conditions on the surfaces of the ports (for example one could be generated by applied pressure differences, and the other by potential differences, but we need not specify anything at this point). Then thanks to incompressibility for solution (2):

$$\begin{aligned} \nabla \cdot (\hat{\boldsymbol{\sigma}}_0^{(1)} \cdot \hat{\mathbf{v}}^{(2)}) &= (\nabla \cdot \hat{\boldsymbol{\sigma}}_0^{(1)}) \cdot \hat{\mathbf{v}}^{(2)} \\ &+ \frac{1}{2} \eta (\nabla \hat{\mathbf{v}}^{(1)} + \nabla \hat{\mathbf{v}}^{(2)}): (\nabla \hat{\mathbf{v}}^{(2)} + \nabla \hat{\mathbf{v}}^{(1)}). \end{aligned} \quad (23)$$

Then from Eq. (20), with  $\nabla \mu_{ieq} = 0$ :

$$(\nabla \cdot \hat{\boldsymbol{\sigma}}_0^{(1)}) \cdot \hat{\mathbf{v}}^{(2)} = \sum_{i=1,K} c_{ieq} \nabla \hat{\mu}_i^{(1)} \cdot \hat{\mathbf{v}}^{(2)} \quad (24)$$

which can be related to other quantities by

$$\begin{aligned} \nabla \cdot (\hat{\mu}_i^{(1)} \hat{\mathbf{j}}_i^{(2)}) &= \nabla \hat{\mu}_i^{(1)} \cdot \hat{\mathbf{j}}_i^{(2)} \\ &= -m_i c_{ieq} \nabla \hat{\mu}_i^{(1)} \cdot \nabla \hat{\mu}_i^{(2)} + \nabla \hat{\mu}_i^{(1)} \cdot (c_{ieq} \hat{\mathbf{v}}^{(2)}) \end{aligned} \quad (25)$$

where the first equality holds because the ionic currents are divergence free.

Using the three results above, the following quantity is symmetrical in the exchange between superscripts (1) and (2):

$$\begin{aligned} \nabla \cdot (\hat{\boldsymbol{\sigma}}_0^{(1)} \cdot \hat{\mathbf{v}}^{(2)}) - \nabla \cdot \left( \sum_{i=1,K} \hat{\mu}_i^{(1)} \hat{\mathbf{j}}_i^{(2)} \right) \\ = \nabla \cdot (\hat{\boldsymbol{\sigma}}_0^{(2)} \cdot \hat{\mathbf{v}}^{(1)}) - \nabla \cdot \left( \sum_{i=1,K} \hat{\mu}_i^{(2)} \hat{\mathbf{j}}_i^{(1)} \right). \end{aligned} \quad (26)$$

The next step consists in integrating these relations over the volume occupied by the electrolyte solution. We transform the integral of divergences into fluxes through the surface bounding the electrolyte. Given the boundary conditions (12) and (13), that apply similarly to the linearized perturbations  $\hat{\mathbf{v}}$  and  $\hat{\mathbf{j}}_i$ , the surface integrals over the walls vanish and we are left with the fluxes through the ports surfaces only. Therefore, the above symmetry, reads in integral form

$$\begin{aligned} \sum_{\alpha=0,N-1} \iint_{S_\alpha} dS \left( \mathbf{n} \cdot \hat{\boldsymbol{\sigma}}_0^{(1)} \cdot \hat{\mathbf{v}}^{(2)} - \sum_{i=1,K} (\hat{\mu}_i^{(1)} \mathbf{n} \cdot \hat{\mathbf{j}}_i^{(2)}) \right) \\ = \sum_{\alpha=0,N-1} \iint_{S_\alpha} dS \left( \mathbf{n} \cdot \hat{\boldsymbol{\sigma}}_0^{(2)} \cdot \hat{\mathbf{v}}^{(1)} - \sum_{i=1,K} (\hat{\mu}_i^{(2)} \mathbf{n} \cdot \hat{\mathbf{j}}_i^{(1)}) \right). \end{aligned} \quad (27)$$

*This symmetry is actually that of the linear operator relating the currents  $\hat{\mathbf{v}}$  and  $\hat{\mathbf{j}}_i$  through the boundaries of the system, to the generalized forces  $\hat{\boldsymbol{\sigma}}_0$  and  $-\hat{\mu}_i$  applied there. As such this expression is the core of this paper, in a rather formal presentation.*

To get closer to a more operational form such as that of Eq. (2) in the Introduction, a first step is to explicit for each port the average values of the driving potentials, and the fluxes emerging from this port. Let us define  $\hat{Q}_\alpha = \iint_{S_\alpha} dS \mathbf{n} \cdot \hat{\mathbf{v}}$  and  $\hat{J}_{i\alpha} = \iint_{S_\alpha} dS \mathbf{n} \cdot \hat{\mathbf{j}}_i$  the flow and ionic fluxes emerging from port  $\alpha$ , and  $\hat{\Pi}_\alpha$  and  $\hat{\mu}_{i\alpha}$  the average values of  $\hat{\Pi}$  and  $\hat{\mu}_i$  over the port section  $S_\alpha$ . Then the previous equation reads

$$\begin{aligned} - \sum_{\alpha=0,N-1} \hat{Q}_\alpha^{(2)} \hat{\Pi}_\alpha^{(1)} - \sum_{\alpha=0,N-1} \sum_{i=1,K} \hat{J}_{i\alpha}^{(2)} \hat{\mu}_{i\alpha}^{(1)} \\ + \sum_{\alpha=0,N-1} \iint_{S_\alpha} dS \mathbf{n} \cdot (\hat{\boldsymbol{\sigma}}_0(\mathbf{x}) + \hat{\Pi}_\alpha \mathbf{1})^{(1)} \cdot \hat{\mathbf{v}}^{(2)} \\ - \sum_{\alpha=0,N-1} \sum_{i=1,K} \iint_{S_\alpha} dS ([\hat{\mu}_i(\mathbf{x}) - \hat{\mu}_{i\alpha}]^{(1)} \mathbf{n} \cdot \hat{\mathbf{j}}_i^{(2)}) \\ = \text{same formula with } (1 \leftrightarrow 2). \end{aligned} \quad (28)$$

Although this formula appears more cumbersome than the previous one (27), we have actually made progress: indeed the first line is in a form that permits the compact matrix treatment alluded to in the Introduction, and in the two following ones appear quantities such as  $[-\hat{\Pi}(\mathbf{x})\mathbf{1} + \hat{\Pi}_\alpha \mathbf{1}]$  and  $[\hat{\mu}_i(\mathbf{x}) - \hat{\mu}_{i\alpha}]$  which are zero when averaged over the port area  $S_\alpha$ .

### IV. EXPLICIT ONSAGER SYMMETRY RELATIONS

In this section we focus on three situations where these terms [second and third line of Eq. (28)] either cancel out or are negligible compared to those of the first line. If the system is periodic the cancellation is exact, a case treated in Sec. IV A. These terms can be neglected in two other situations that we analyze in Sec. IV B: systems with ‘‘smooth inlets’’ and systems with ‘‘long inlets.’’ In both Secs. IV A and IV B we show that a general conductance matrix is symmetric, and bring the two cases to a common formalism, so as to be able to explore in Sec. IV C in a unified way the explicit consequences of this symmetry for the two cases.

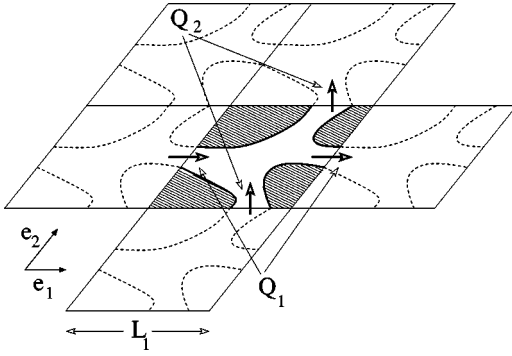


FIG. 3. *Top view* of a slab geometry with two nonorthogonal periodicity directions ( $D=2$ ) and with no obvious symmetry of the unit cell. The system is bounded by two parallel solid walls in the third perpendicular direction. The currents are periodic, so the quantities flowing through the periodic repeats of connecting ports are constant (here only the net flow  $Q$  is depicted but this holds also for the ionic currents). In contrast the local values of the potentials increase by a constant value from one unit cell to the next.

### A. Periodic systems

Suppose that the system we consider is actually periodic, so that we can focus on a unit cell, repeated at distances  $L_\gamma$  along the vectors  $\mathbf{e}_\gamma$  (that need not be orthogonal); see Fig. 3. The system need not have additional symmetries such as isotropy or centrosymmetry. Obviously the number of periodicity directions  $D$  is smaller than or equal to the spatial dimension (typically 3).  $D=1$  corresponds to a periodic channel,  $D=2$  to a periodic slab geometry (e.g., that of Fig. 3), and  $D=3$  is a three-dimensional periodic medium (see, e.g., Fig. 1, bottom left).

Due to the periodicity of the system, the solutions (1) and (2) described in Sec. III are then also periodic, which actually means that the velocities and currents are periodic, but that the potentials  $\hat{\Pi}$  and  $\hat{\mu}_i$  increase over a unit cell in the direction  $\mathbf{e}_\gamma$  by fixed values  $\Delta\hat{\Pi}_\gamma$  and  $\Delta\hat{\mu}_{i\gamma}$ . As a consequence, the quantities  $[\hat{\boldsymbol{\sigma}}_0(\mathbf{x}) + \hat{\Pi}_\alpha \mathbf{1}]$  and  $[\hat{\mu}_i(\mathbf{x}) - \hat{\mu}_{i\alpha}]$  in Eq. (28) are periodic, so that the terms where they appear cancel out when summing on the two opposite faces of the unit cell in a given direction.

So updating the notations in Eq. (28) so that  $\hat{Q}_\gamma$  and  $\hat{J}_{i\gamma}$  are the flow and ionic fluxes through the ports of the unit cell facing the direction  $\gamma$ , the symmetry relation (27) simplifies to

$$\begin{aligned} & \sum_{\gamma=1,D} \hat{Q}_\gamma^{(2)} \Delta\hat{\Pi}_\gamma^{(1)} + \sum_{\gamma=1,D} \sum_{i=1,K} \hat{J}_{i\gamma}^{(2)} \Delta\hat{\mu}_{i\gamma}^{(1)} \\ &= \sum_{\gamma=1,D} \hat{Q}_\gamma^{(1)} \Delta\hat{\Pi}_\gamma^{(2)} + \sum_{\gamma=1,D} \sum_{i=1,K} \hat{J}_{i\gamma}^{(1)} \Delta\hat{\mu}_{i\gamma}^{(2)}. \end{aligned} \quad (29)$$

This demonstrates the total symmetry of the  $D(K+1) \times D(K+1)$  “conductance” tensor  $\mathbf{M}$  that relates the generalized forces  $-\Delta\hat{\Pi}_\gamma, -\Delta\hat{\mu}_{i\gamma}$  to the generalized fluxes  $\hat{Q}_\gamma, \hat{J}_{i\gamma}$ . To make this point explicit let us use the convenient notation  $\hat{Q} = \hat{J}_0$  and  $\hat{\Pi} = \hat{\mu}_0$ . This is standard (see, e.g., Ref.

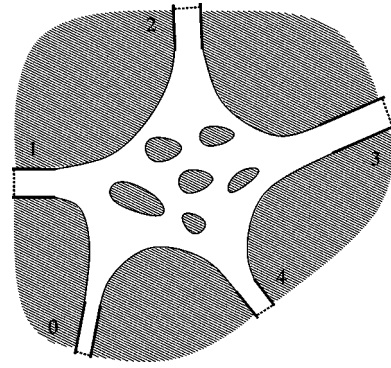


FIG. 4. Scheme of media connected to the outer world by “smooth sections” (thicker lines) of constant surface characteristics, so that the potentials  $\Pi_\alpha, \mu_{i\alpha}$  are well defined and constant on a section (dashed lines). In this specific case there are  $N=5$  ports.

[2], Chap. XV), with the index zero describing global quantities in the system and  $i=1,K$  the ionic species (alternatively one can describe the solvent explicitly as a species). The reason why  $\Pi$  is the proper “potential” related to  $Q$  is also described in [2]. Then the linear response of the system is defined by

$$\hat{J}_{i\gamma} = M_{i\gamma,j\delta} (-\Delta\hat{\mu}_{j\delta}) \quad (30)$$

with indices  $i$  and  $j$  running from 0 to  $K$ , and  $\gamma$  and  $\delta$  from 1 to  $D$ , and summation over repeated indices is implicit. The minus sign here is such that  $\mathbf{M}$  is a positive matrix [actually  $\sum_{i,\gamma} \hat{J}_{i\gamma} (-\Delta\hat{\mu}_{i\gamma})$  is the dissipation rate in the system, which is always positive]. Equation (29) now reads

$$\Delta\hat{\mu}_{i\gamma}^{(1)} (M_{i\gamma,j\delta} - M_{j\delta,i\gamma}) \Delta\hat{\mu}_{j\delta}^{(2)} = 0 \quad (31)$$

whatever the values of the potential drops, which leads us to the central result of this paper in compact form:

$$M_{i\gamma,j\delta} = M_{j\delta,i\gamma}. \quad (32)$$

### B. Smooth inlets or long inlets

We now focus on the case of a nonperiodic system, with  $N$  ports, that could be thought of as a complex node in a network, or maybe a complex subsection of the network (see Fig. 4). To be able to work practically with the integral relation (28), it is convenient to neglect the terms in the second and third line of Eq. (28).

Although this cannot be done blindly, there are two cases where it appears legitimate.

(a) If the ports consist of smooth homogeneous cylindrical sections, it is expected that the pressure and chemical potentials have almost constant value over the integration surfaces  $S_\alpha$ , so that  $[\hat{\boldsymbol{\sigma}}_0(\mathbf{x}) + \hat{\Pi}_\alpha \mathbf{1}]$  and  $[\hat{\mu}_i(\mathbf{x}) - \hat{\mu}_{i\alpha}]$  are very small.

(b) If the inlets are very long compared to the dimensions of the port, it is to be expected that the above mentioned quantities (that reflect differences within a section  $S_\alpha$ ) are small compared to the pressure and potential drop across the whole system, so that the terms in the first line of Eq. (28) will dominate.

We now make the assumption that one or both of these conditions is fulfilled and proceed. Then, using again for compactness the notations  $Q = J_0$  and  $\Pi = \mu_0$ , the relation between the potentials  $\hat{\mu}_{i\alpha}$  and the emerging fluxes  $\hat{J}_{i\alpha}$  at various ports for the two solutions (1) and (2) of the linearized response problem read

$$\sum_{\alpha=0, N-1} \sum_{i=0, K} \hat{J}_{i\alpha}^{(2)} \hat{\mu}_{i\alpha}^{(1)} = \sum_{\alpha=0, N-1} \sum_{i=0, K} \hat{J}_{i\alpha}^{(1)} \hat{\mu}_{i\alpha}^{(2)}. \quad (33)$$

Note the difference with the case of periodic systems: here local potentials (for each port) appear, rather than potential drops along a period. To restore the usual fact that linear response usually connects currents to potential differences, we remark that the local conservation laws for the flow and ionic species result at steady state in the obvious  $(K+1)$  global conservation rules:  $\sum_{\alpha=0, N-1} \hat{J}_{i\alpha} = 0$ . Then taking port 0 as the reference and defining here  $\Delta \hat{\mu}_i = \hat{\mu}_i - \hat{\mu}_0$ , Eq. (33) can be reformulated as

$$\sum_{\alpha=1, N-1} \sum_{i=0, K} \hat{J}_{i\alpha}^{(2)} \Delta \hat{\mu}_{i\alpha}^{(1)} = \sum_{\alpha=1, N-1} \sum_{i=0, K} \hat{J}_{i\alpha}^{(1)} \Delta \hat{\mu}_{i\alpha}^{(2)}. \quad (34)$$

From then on, all the results and formalism of the previous Sec. IVA for periodic systems can be applied, and the relations obtained there [Eqs. (30) and (32)] hold also in the present case, with the indices  $\alpha = 1, \dots, N-1$  replacing  $\gamma = 1, \dots, D$ , and the  $\Delta \hat{\mu}_i$  having different definitions.

This formal identity allows us to explore the consequences of the symmetry of the conductance tensor in a unified way below.

### C. Consequences of the symmetry of the conductance matrix

A more explicit and practically useful expression of the Onsager relations (30) and (32) is

$$\left( \frac{\hat{J}_{i\gamma}}{\Delta \hat{\mu}_{j\delta}} \right)_{\Delta \hat{\mu}_{j'\delta'} | (j', \delta') \neq (j, \delta) = 0} = \left( \frac{\hat{J}_{j\delta}}{\Delta \hat{\mu}_{i\gamma}} \right)_{\Delta \hat{\mu}_{i'\gamma'} | (i', \gamma') \neq (i, \gamma) = 0}. \quad (35)$$

Let us explore briefly ways to use this general result.

(i) *If concentrations are not varied (no osmotic stresses).* All the rather formal approach above simplifies a lot if the concentrations do not vary. Then  $\Delta \Pi = \Delta p$ ,  $\Delta \mu_i = q_i \Delta \phi$ , and the total electric current  $I_{el} = \sum_{i=1, K} q_i J_i$  naturally shows up. Then Eq. (29) is replaced by

$$\sum_{\gamma} (\hat{Q}_{\gamma}^{(2)} \Delta \hat{p}_{\gamma}^{(1)} + \hat{I}_{el, \gamma}^{(2)} \Delta \hat{\phi}_{\gamma}^{(1)}) = \sum_{\gamma} (\hat{Q}_{\gamma}^{(1)} \Delta \hat{p}_{\gamma}^{(2)} + \hat{I}_{el, \gamma}^{(1)} \Delta \hat{\phi}_{\gamma}^{(2)}). \quad (36)$$

We have therefore symmetry relations for the simplified conductance matrix. For periodic systems, this matrix is now  $(2D)^2$  and gives the flow  $Q_{\gamma}$  and total electric current  $I_{el, \gamma}$  through the unit cell in direction  $\gamma$ , as a function of pressure and electrostatic potential drops over a period  $\Delta \hat{p}_{\delta}$  and  $\Delta \hat{\phi}_{\delta}$

in direction  $\delta$ . For an  $N$ -port ‘‘node,’’ the matrix is  $(2(N-1))^2$ , and gives the flow  $Q_{\gamma}$  and total electric current  $I_{el, \gamma}$  exiting through the port  $\gamma$  ( $\gamma = 1, \dots, N-1$ ), as a function of the pressure and electrostatic potential of port  $\delta$  ( $\delta = 1, \dots, N-1$ ) relative to that of port 0,  $\Delta \hat{p}_{\delta}$  and  $\Delta \hat{\phi}_{\delta}$ .

Equation (35) is replaced by symmetry relations for the electric response,

$$\left( \frac{\hat{I}_{el, \gamma}}{\Delta \hat{\phi}_{\delta}} \right)_{\Delta \hat{\phi}_{\delta' \neq \delta} = 0, \Delta \hat{p}_{\beta} = 0} = \left( \frac{\hat{I}_{el, \delta}}{\Delta \hat{\phi}_{\gamma}} \right)_{\Delta \hat{\phi}_{\gamma' \neq \gamma} = 0, \Delta \hat{p}_{\beta} = 0} \quad (37)$$

for the hydrodynamic response,

$$\left( \frac{\hat{Q}_{\gamma}}{\Delta \hat{p}_{\delta}} \right)_{\Delta \hat{p}_{\delta' \neq \delta} = 0, \Delta \hat{\phi}_{\beta} = 0} = \left( \frac{\hat{Q}_{\delta}}{\Delta \hat{p}_{\gamma}} \right)_{\Delta \hat{p}_{\gamma' \neq \gamma} = 0, \Delta \hat{\phi}_{\beta} = 0} \quad (38)$$

and for the electrohydrodynamic couplings,

$$\left( \frac{\hat{I}_{el, \gamma}}{\Delta \hat{p}_{\delta}} \right)_{\Delta \hat{p}_{\delta' \neq \delta} = 0, \Delta \hat{\phi}_{\beta} = 0} = \left( \frac{\hat{Q}_{\delta}}{\Delta \hat{\phi}_{\gamma}} \right)_{\Delta \hat{\phi}_{\gamma' \neq \gamma} = 0, \Delta \hat{p}_{\beta} = 0}. \quad (39)$$

Equation (39) states precisely how in a periodic medium cross-direction streaming currents (a pressure drop along  $\mathbf{e}_{\delta}$  generates an electric current along  $\mathbf{e}_{\gamma}$ ) are related to cross-direction electro-osmotic effects (a potential difference along  $\mathbf{e}_{\gamma}$  results in a flow along  $\mathbf{e}_{\delta}$ ). A similar statement holds to relate consequences of action on various ports of a ‘‘node.’’ These equations are generalizations of relations in the paper by Mazur and Overbeek [1] which dealt with the case  $D = 1$  (and homogeneous geometries). An explicit application for the case  $D = 3$  has been given above in the introduction of the present paper.

As a note, we remark that although Eq. (38) was listed as describing the hydrodynamic response of the system, the coefficients appearing on its two sides potentially reflect (transverse) electroviscous effects, whereby a flow generates potential drops that in turn produce electro-osmotic flows that contribute to the global hydrodynamic response. Such effects are already present in straight channels (see, e.g., the discussion and references in [14]), although usually weak unless the channel is thin, the surface charge is strong and the ionic strength weak. The same limits should be relevant for the detectability of transverse electroviscous effects.

(ii) *Resistance matrix.* Of course the reverse matrix giving the potential drops as functions of the currents is symmetric too, so that in the general case:

$$\left( \frac{\Delta \hat{\mu}_{i\gamma}}{\hat{J}_{j\delta}} \right)_{\hat{J}_{j'\delta'} | (j', \delta') \neq (j, \delta) = 0} = \left( \frac{\Delta \hat{\mu}_{j\delta}}{\hat{J}_{i\gamma}} \right)_{\hat{J}_{i'\gamma'} | (i', \gamma') \neq (i, \gamma) = 0}. \quad (40)$$

In the absence of concentration biases, equations similar to Eqs. (37), (38), and (39) hold for the inverse (resistance) quantities. For example electrohydrodynamic couplings are related by

$$\begin{pmatrix} \Delta \hat{\phi}_\gamma \\ \hat{Q}_\delta \end{pmatrix}_{\hat{Q}_{\delta' \neq \delta} = 0, \hat{I}_{\text{el}\beta} = 0} = \begin{pmatrix} \Delta \hat{p}_\delta \\ \hat{I}_{\text{el}\gamma} \end{pmatrix}_{\hat{I}_{\text{el}\gamma' \neq \gamma} = 0, \hat{Q}_\beta = 0} \quad (41)$$

that relates a cross direction streaming potential to a cross-direction electro-osmotically induced pressure drop in a hydrodynamically closed system.

(iii) *Many more relations (but nothing new)*. Actually, as was done for the simpler cases considered in their seminal paper by Mazur and Overbeek [1], many relations can be obtained in addition to those displayed in Eqs. (35), (37), (38), (39), (40), and (41). Indeed up to now we have established equalities between coefficients describing the response of the system in situations where either all potential drops but one are fixed to zero (conductivity matrix) or all currents but one are fixed to zero (resistance matrix). Actually one can consider many other combinations where for each direction (or port)  $\gamma$  and each species  $i$  (including the global flow  $i=0$ ) either the corresponding current or the corresponding potential drop is zero, but for one of those quantities in the system which is the driving force.

For example, it is easy to demonstrate from the symmetry of the matrix in Eq. (2) in the Introduction that for the systems depicted in the bottom of Fig. 1,

$$\begin{pmatrix} \Delta \hat{\phi}_3 \\ \Delta \hat{p}_1 \end{pmatrix}_{\hat{I}_{\text{el}i=1,2,3} = 0} = - \begin{pmatrix} \hat{Q}_1 \\ \hat{I}_{\text{el}3} \end{pmatrix}_{\hat{I}_{\text{el}i=1,2} = 0} \quad (42)$$

$$\begin{matrix} \hat{Q}_2 = 0 & \hat{Q}_2 = 0 \\ \Delta \hat{p}_3 = 0 & \Delta \hat{p}_i = 0 \end{matrix}$$

Such equations are in some sense generalizations to more complex geometries of Saxén's law [15]; see [1] and Sec. 9.11.6 in [16]. Note that there is nothing new in these relations in the sense that they are all contained in the symmetry of the original conductance matrix  $\mathbf{M}$  (32). However it is worth pointing out that each of the response coefficients in these formulas corresponds to a particular experiment (with given boundary conditions), so one needs to be careful in laying down properly the formalism to assess to what extent the outcome of two different experiments are directly related to one another (see for example the discussion of the phenomenology of electrokinetics in different experiments by Lorenz [14]).

(iv) *A comment on matrix representation*. Let us make here a short practical statement: up to now the generalized conductance has been described by a tensor  $\mathbf{M}$  with components  $M_{i\gamma,j\delta}$ .

It is often simpler to describe the response in terms of a matrix, as was done for example in the Introduction, where all the flows and currents are treated as a multicomponent vector. The two forms are equivalent provided things are written properly. There are two convenient ways of writing such linear systems: either sort the components by species first, or by port or direction first. The first strategy leads to the following matrix:

$$\begin{bmatrix} \hat{Q}_1 \\ \hat{Q}_2 \\ \dots \\ \hat{J}_{i=1,\alpha=1} \\ \hat{J}_{i=1,\alpha=2} \\ \dots \\ \hat{J}_{2,1} \\ \hat{J}_{2,2} \\ \dots \end{bmatrix} = [C_{u,v}]_{v=1,\dots,\Gamma}^{u=1,\dots,\Gamma} \begin{bmatrix} -\Delta \hat{\pi}_1 \\ -\Delta \hat{\pi}_2 \\ \dots \\ -\Delta \hat{\mu}_{i=1,\alpha=1} \\ -\Delta \hat{\mu}_{i=1,\alpha=2} \\ \dots \\ -\Delta \hat{\mu}_{i=2,1} \\ -\Delta \hat{\mu}_{i=2,2} \\ \dots \end{bmatrix}, \quad (43)$$

where  $\Gamma = (K+1)D$  for a periodic system and  $\Gamma = (K+1) \times (N-1)$  for a  $N$ -port node.

The alternative sorting (by ports) yields

$$\begin{bmatrix} \hat{Q}_1 \\ \hat{J}_{i=1,\alpha=1} \\ \hat{J}_{i=2,\alpha=1} \\ \dots \\ \hat{Q}_2 \\ \hat{J}_{1,2} \\ \hat{J}_{2,2} \\ \dots \end{bmatrix} = [L_{u,v}]_{v=1,\dots,\Gamma}^{u=1,\dots,\Gamma} \begin{bmatrix} -\Delta \hat{\pi}_1 \\ -\Delta \hat{\mu}_{i=1,\alpha=1} \\ -\Delta \hat{\mu}_{i=2,\alpha=1} \\ \dots \\ -\Delta \hat{\pi}_2 \\ -\Delta \hat{\mu}_{1,2} \\ -\Delta \hat{\mu}_{2,2} \\ \dots \end{bmatrix}. \quad (44)$$

The matrices  $C$  and  $L$  defined above are both symmetric and the two formalisms can be used indifferently.

This picture is of course easily adapted to the simpler case where there are no applied ionic concentration gradients (see, e.g., the Introduction).

(v) *A last point*. Let us close this section by recalling that the most general form for the symmetry relation is the integral equations (27) and (28). To be able to replace the integral over each port surface  $S_\alpha$  by a local potential (osmotic pressure, chemical or electrostatic potential) times a flux, one needs additional hypothesis: we have exploited here two practically important ones: periodicity and smooth or long ports.

## V. DISCUSSION AND CONCLUDING REMARKS

To summarize, we have demonstrated that the electrohydrodynamic response of an electrolyte solution to applied pressures, electric fields, or chemical potential differences is described in the linear response regime by a symmetric matrix. This translates into general symmetry relations (35) and (40), and other combinations [see Sec. IV C (iii)]. When osmotic effects can be neglected (no ionic concentration drops) the description can be further simplified [e.g., Eqs. (37), (38), and (39)].

The proof presented here has a rather large range of validity, as it applies regardless of many features of the system (topology, shape, geometry, homogeneity or amplitude of the surface charge density or potential). The main restriction is

that the result is limited to the linear response regime. As discussed in Sec. II the extension of this regime in parameter space may be very system dependent, although an obvious constraint is that the average applied fields be weaker than the typical equilibrium ones in the charged double layers. Upon entering the nonlinear regime, which is clearly relevant for many high electric-field applications in microfluidics, there is no *a priori* reason for the “symmetry” between effects to remain valid, and a case by case study is required. A much weaker restriction on our results is that the formalism used (in particular for the expressions of the chemical potentials and osmotic pressure) is specific to dilute electrolyte solutions. It is of course possible to perform the same proof with a more general scheme, following Chap. XV in [2], but we chose to start with the equations of Sec. II as they are commonly used (see, e.g., the textbook [16]).

Beyond the formal symmetry relations per se, our systematic construction of the proof reveals a few noticeable features.

Quite remarkably, and as anticipated in the formulation of the problem (Sec. II), we never had to specify the value of the surface charge density on the surface of the walls. However, as discussed in Sec. II, they definitely affect the values of the linear response coefficients, as they determine the  $c_{ieq}$  for example. They likely also show up in an explicit computation of the range of applicability of the linear response formalism. In a related way, we never had to specify the explicit geometry of the system (shape, topology and size of the walls).

The formalism that we have developed is applicable to pure hydrodynamics in the case where there is no electrokinetic coupling. Then only flow rates and pressure drops appear, but the description of nodes or structured media by symmetric matrices remains true, the symmetry then relating cross channel hydrodynamic effects [see, e.g., Eq. (38)].

Our systematic approach also highlights that when addressing electrokinetic effects, one should keep in the description the ionic concentration differences and fluxes and the osmotic terms. This point is often forgotten for the simpler use of the sole global flow and electrical current variables, which yields an easier and more compact formalism (see, e.g., the Introduction of the present paper). To decide whether or not this simple approach is applicable or not to a specific experiment one should proceed with care.

A field of application of this work would be some extension of the work by Marino *et al.* [6]. In that elegant paper, equations similar to those of Sec. II are solved numerically for a few periodic porous geometries that are isotropic (at least statistically) and with constant surface charge. The au-

thors actually numerically demonstrated the symmetry of the matrix  $\mathbf{M}$  for these situations. More generally, for this kind of numerical work, Onsager symmetry relations can be either used as a control on the numerics by checking that they hold in the results, or taken for granted to bypass some computations and save computing time.

Another domain where these relations may find some use is the on purpose fabrication of anisotropic microfluidic devices. In [8] such devices were shown to allow for the realizations of various functionalities (flow detection, transverse pumping, mixing). The symmetry of the matrix was there taken for granted, and used to relate the various coefficients describing these effects. This symmetry could be of use for example to characterize microfabricated geometries independently of their use: for example one could validate the fabrication of an anisotropic structure for transverse electroosmotic pumping (see [11] for a working example) by measuring a transverse streaming current if this measurement is simpler to perform.

The relations presented in this paper for nonperiodic systems (Sec. IV B) could also be of use to describe nodes or crossings in a microfluidic system. Indeed if these crossing areas are not small, it is necessary to take them into account to describe the global response of the microfluidic network (i.e., they cannot be described by a set of simple scalar potentials and conservation laws as in Kirchhoff’s laws for electrical circuits). To apply the results of Sec. IV, it may be necessary to include in the “node” short sections of the channel emerging from it, so as to justify the approximations at the beginning of Sec. IV B which allow to characterize the state of an inlet by average scalar quantities (generalized potentials).

In conclusion, as is common with explicit demonstrations of Onsager symmetry relations, the outcome of this paper appears somewhat formal and not fundamentally surprising (as the symmetry is built in the local equations used at the beginning). However, the careful writing down of such a formalism, along the lines of the thermodynamics of irreversible processes, is a useful guide to connect with one another the outcome of various experiments, the more as the situation at hand can be rather complex (electrokinetic effects are complex even in simple geometries, and we are discussing geometries with heterogeneities and broken symmetries).

## ACKNOWLEDGMENTS

A.A. acknowledges support from The Ministère de la Recherche and helpful suggestions from Abe Stroock.

- 
- [1] P. Mazur and J.T.G. Overbeek, *Recl. Trav. Chim. Pays-Bas* **70**, 83 (1951).  
 [2] S.R. De Groot and P. Mazur, *Non-equilibrium Thermodynamics* (North-Holland, Amsterdam, 1969).  
 [3] A. Ajdari, *Phys. Rev. Lett.* **75**, 755 (1995); *Phys. Rev. E* **53**, 4996 (1996).

- [4] A.D. Stroock *et al.*, *Phys. Rev. Lett.* **84**, 3314 (2000).  
 [5] S.L.R. Barker *et al.*, *Anal. Chem.* **72**, 5925 (2000).  
 [6] S. Marino, M. Shapiro, and P.M. Adler, *J. Colloid Interface Sci.* **243**, 391 (2001).  
 [7] D. Erickson and D. Li, *Langmuir* **18**, 8948 (2002).  
 [8] A. Ajdari, *Phys. Rev. E* **65**, 016301 (2002).



- [9] A.D. Stroock, S.K. Dertinger, G.M. Whitesides, and A. Ajdari, *Anal. Chem.* **74**, 5306 (2002).
- [10] T.L. Johnson, D. Ross, and L.E. Locascio, *Anal. Chem.* **74**, 45 (2002).
- [11] I. Gitlin, A.D. Stroock, A. Ajdari, and G. Whitesides, *Appl. Phys. Lett.* **83**, 1486 (2003).
- [12] J. Happel and H. Brenner, *Low Reynolds Number Hydrodynamics* (Martinus Nijhoff Publishers, The Hague, 1983).
- [13] M. Teubner, *J. Chem. Phys.* **76**, 5564 (1982).
- [14] P.B. Lorenz, *J. Phys. Chem.* **56**, 775 (1952).
- [15] U. Saxén, *Wied Ann.* **47**, 46 (1892).
- [16] R.J. Hunter, *Foundations of Colloid Science* (Oxford University Press, New York, 1991).