Pumping liquids using asymmetric electrode arrays

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Following a general symmetry argument, I suggest using locally asymmetric electric geometries to pump liquid in channels or drive droplets on surfaces. This strategy, which requires no global gradient in the pumping direction, should be of interest for microfluidic devices and micro-electro-mechanical systems. A practical realization consists in using polar periodic arrays of electrodes addressed by an ac voltage difference. A simple electro-osmotic model provides an estimate of the pumping velocities achievable.

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I. INTRODUCTION

Microfluidics is a topic of great current interest due to the development of ''lab-on-a-chip'' devices and micro-electro-mechanical systems (MEMS). The ability to move small amounts of fluids containing various reagents along channels is an important requirement, which has prompted the exploration of various pumping strategies not involving mobile parts [1–7]. Pumping can be achieved by using separately or in combination electrochemical reactions [4], thermal gradients [1,2], piezoelectricity [7], and electric fields [5,3]. Electrohydrodynamic devices mostly rely on two schemes: either the application of a dc electric field along the channel to induce electro-osmosis [5], or that of an (ac) traveling wave on an electrode array to create pumping, thanks to coupling to thermal gradients (themselves also induced by the traveling wave) [1,2].

In the present work, I propose an alternative strategy based on a symmetry argument similar to those underlying recent ratchet models for separation techniques [8] and molecular motors [9,10]. Generically, if a fluid is placed in a *locally* asymmetric environment and if dissipation is induced by external means, then the fluid should be *globally* set into motion in the direction of broken symmetry, even in the absence of macroscopic gradients (of, e.g., pressure or potential). According to this argument, a fluid in the vicinity of an asymmetric periodic set of interdigitated electrodes (e.g., Fig. 1), should be pumped when the electrode array is addressed with a stationary ac voltage difference $V_0\cos(\omega t)$, provided the electrical activity induces *locally* flow of the fluid.

Recent studies have shown how fluid circulation can be created by AC potentials in the vicinity of electrodes [11,12,17]. I will focus here on the mechanism evoked in [11,12], whereby the fluid is set into motion by electro-osmosis, which occurs in situations of out of equilibrium ionic distributions where thin charged layers are exposed to tangential electric fields. A simple model will be used to demonstrate that if in *symmetric* geometries the resulting flow consists of a periodic pattern of rolls localized in the vicinity of the surface (Fig. 2), in a *locally asymmetric* geometry an additional component is present, that corresponds to a directional pumping of the whole fluid (i.e., not restricted to the surface) (Fig. 3) and at a velocity proportional to V_0^2. The model an estimate of amplitude and frequency dependence of the pumping effect. In a discussion section, modifications brought in by the occurrence of charge injection at the electrodes are briefly pointed out, and a few concluding remarks exposed.

II. SIMPLE MODEL

Consider the 2D geometry of Fig. 2: a flat surface ($x_s=0$) bearing a periodic array of electrodes faces a 1:1 electrolyte described by the Debye-Huckel theory. The ac potential applied to the array is modelled by a surface potential $V_{\rm ext}=V_0\cos(qy)e^{i\omega t}$, taken small enough for the electric response of the system to be linear. The thickness λ_D of the charged Debye layers in the vicinity of the surface is taken negligibly small compared to the other lengths of the problem ($q\lambda_D \ll 1$). Then the bulk of the electrolyte ($x > x_s+\lambda_D \simeq x_s$) is neutral and characterized by its conductivity σ and dielectric constant ϵ. The electric current is given by Ohm's law $\mathbf{J_e}=\sigma\mathbf{E}$, where $\mathbf{E}=-\boldsymbol{\nabla}\psi$ and the electric potential satisfies $\Delta\psi=0$.

The fluid can be set into motion by electro-osmosis [13]:

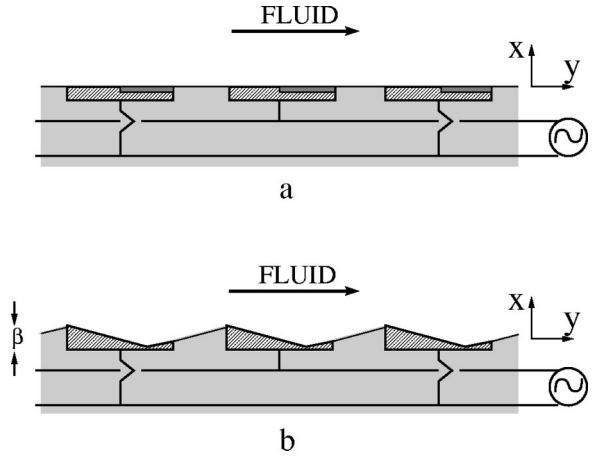

FIG. 1. Schematic examples of periodic asymmetric arrays of electrodes. The asymmetry or polarity is obtained by a modulation of (a) the surface electrochemical properties, or (b) the shape of the surface. When an oscillating potential is applied pumping in the y direction results.

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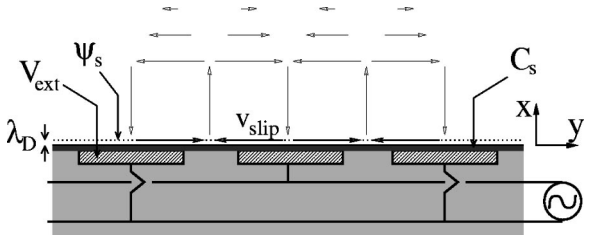

FIG. 2. Symmetric electrode array: schematic description of the instantaneous recirculation flow for fast vorticity diffusion. The flow alternates in time at a frequency ω/π.

the charged layers are dragged by the tangential field in the vicinity of the surfaces. As a result the velocity changes rapidly from **0** strictly on the surface (x_s) to a value $\mathbf{v}_{\rm slip}$ on the outside of the Debye layer ($x_s+\lambda_D$). The resulting flow in the (neutral) bulk electrolyte is then classically obtained by solving Stokes equation

$$\begin{cases} -\nabla p+\eta\Delta\mathbf{v}=\rho\partial_t\mathbf{v} \\ \nabla\cdot\mathbf{v}=0, \end{cases} \tag{1}$$

with an *effective boundary condition* $\mathbf{v}(x\to x_s)=\mathbf{v}_{\rm slip}$ (η and ρ are the fluid viscosity and density).

I limit myself here to situations *with no charge injection from the electrodes*. I also focus for simplicity on frequencies lower than the Debye frequency $\omega_D=D\lambda_D^{-2}$ (where $D=\sigma\lambda_D^2/\epsilon$ is a typical diffusion coefficient for the ions), so that the structure of the thin charged layers is equilibrated. These Debye layers are then fully characterized by their total (surface) charge density $\sigma_D(y,t)$ which verifies $\partial_t\sigma_D=-\mathbf{J_e}|_{x=0}\cdot\mathbf{x}$ [the surface divergence term is $O(q\lambda_D)$ smaller]. A classical calculation [13] gives the electro-osmotic slip velocity:

$$\mathbf{v}_{slip}=[\lambda_D\sigma_D(t)/\eta]\,E_y(x=0,t)\,\mathbf{y}. \tag{2}$$

Taking into account an intrinsic capacitance C_s of the surface, the potential $\psi_s=\psi(x\to x_s)$ on the outer side of the Debye layer is related to $V_{\rm ext}$ by C_s and the Debye layer ($C_D=\epsilon/\lambda_D$) in series, so $\psi_s-V_{\rm ext}=(C_s^{-1}+C_D^{-1})\sigma_D=(1+\delta)\lambda_D\sigma_D/\epsilon$, where $\delta=\epsilon/C_s\lambda_D$ is an adimensional measure of the electrode capacitance.

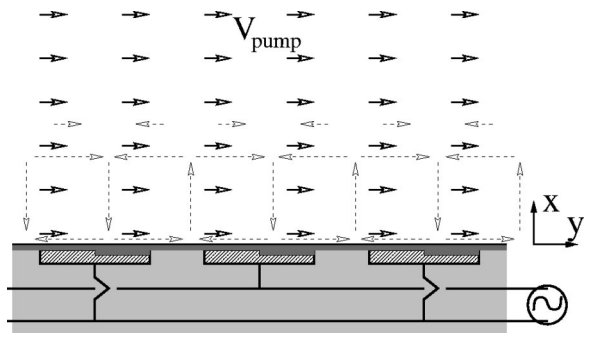

FIG. 3. Asymmetric electrode array: schematic representation of the the time-averaged flow as the sum of spatially periodic flows (dashed arrows) and of a homogeneous ''plug'' flow (solid arrows) due to a systematic bias in the slip velocity.

With this simple model let us examine the flows created by the applied potential in the absence of global gradients of pressure along y.

Symmetric array. If C_s is constant (Fig. 2), then $\psi=V_0(i\omega/\omega^*+i\omega)e^{i\omega t}e^{-qx}\cos qy$ and $\sigma_D=-q\sigma V_0(1/\omega^*+i\omega)e^{i\omega t}\cos qy$, where $\omega^*=Dq(1+\delta)/\lambda_D$ is roughly the inverse of the RC time of the equivalent circuit. The tangential field is $E_y(x=0)=-qV_0(i\omega/\omega^*+i\omega)e^{i\omega t}\sin qy$, so from Eq. (2) the slip velocity is periodic in time,

$$v_{\rm slip}=v_1\frac{1}{\omega/\omega^*+\omega^*/\omega}\sin(2qy)\cos(2\omega t+\theta), \tag{3}$$

where $v_1=[q\epsilon V_0^2/4\eta(1+\delta)]$, and θ is a frequency dependent phase. This slip velocity induces a pattern of recirculation rolls of spatial periodicity π/q and temporal period π/ω (the time average velocity is everywhere zero). For fast vorticity diffusion, the thickness of the rolls is $\simeq 1/q$ (see Fig. 2) [15]: $v_x\simeq -v_0(t)2q\cos(2qy)xe^{-2qx}$ and $v_y\simeq -v_0(t)\sin(2qy)(2qx-1)e^{-2qx}$. In all cases, the flow decays exponentially away from the surface {over a length $\max[q^{-1},(\eta/\rho\omega)^{1/2}]$}. The effect is maximal for $\omega\simeq\omega^*$ when both σ_D and E_y are not too small: at lower frequencies the field relaxes fast in the bulk, at higher frequencies charge does not have time to build up [14].

Taking $q^{-1}\simeq 10$ μm for a microelectrode array, $\lambda_D\simeq 1$nm for salty water, $\delta\simeq 10$, and values of η and ϵ characteristic of water, leads to $v_1\simeq 1V_0^2$ mm s^{-1} with V_0 expressed in volts. Taking further $D\simeq 10^{-9}$ m^{2}s^{-1} gives $\omega^*\simeq 10^6\,s^{-1}$, i.e., frequencies of order 100 kHz.

Asymmetric array. Let us now address situations with broken left-right $y\leftrightarrow -y$ symmetry. The introductory symmetry argument then predicts a net flow, which we are going to quantify and characterize in two cases.

First, I consider the case (Fig. 3) where a surface modification of the electrodes leads to a nonconstant C_s (and thus δ). To proceed analytically I choose the simple form $\delta=\delta_0[1+\beta\cos(2qy+\Psi)]$, and calculate the solution to first order in β, writing $\psi=\psi^{(0)}+\beta\psi^{(1)}+\cdots$, $\sigma_D=\sigma_D^{(0)}+\beta\sigma_D^{(1)}+\cdots$, etc. The zeroth order solution is the one obtained in the previous paragraph. From the electrostatic boundary condition, $\psi_s^{(1)}$ contains a term proportional to $\cos(2qy+\Psi)\cos(qy)$ so that the first order solution $\psi^{(1)},\sigma_D^{(1)}$ is the sum of a term proportional to $\cos(qy+\Psi)$ and of a term proportional to $\cos(3qy+\Psi)$.

The correction to the slip velocity to first order is $v_{slip}^{(1)}=(\lambda_D/\eta)(\sigma_D^{(1)}E_y^{(0)}+\sigma_D^{(1)}E_y^{(0)})$. Factors such as $\cos(qy+\Psi)\sin(qy)=1/2[\sin(2qy+\Psi)-\sin(\Psi)]$ lead to π/q periodic terms but also to spatially constant terms. Averaging over time the value of the slip velocity is now

$$\langle v_{\rm slip}\rangle_t(y)=v_{\rm pump}+\text{spatially periodic terms}, \tag{4}$$

with

$$v_{\rm pump}\simeq v_P\sin(\Psi)\left(\frac{\omega}{\omega^*}+\frac{\omega^*}{\omega}\right)^{-2} \tag{5}$$

and

$$v_P \simeq \beta \frac{\delta_0 q \epsilon V_0^2}{4\eta(1+\delta_0)^2}, \tag{6}$$

which corresponds to velocities of order βv_1. What is remarkable is that whereas the spatially periodic slip velocities lead to rolls of finite extension in the x direction, the constant term corresponds to a plug flow of unlimited extension (after a transient for vorticity to diffuse as in usual electro-osmosis over uniform surfaces).

In addition to surface rolls at velocities of order $\simeq v_1$ (spatial extension at most a few q^{-1}) there is thus a homogeneous ''plug'' flow of fluid along the y direction of order βv_1, which is the pumping effect announced in the Introduction. The effect is again maximal for $\omega \simeq \omega^*$. Using the previously quoted values for the parameters and $\beta \simeq 0.1$ the pumping velocity is of order $v_{\text{pump}} \simeq 100\,\mu\text{m s}^{-1}$ for $V_0 \simeq 1$ V, comparable to velocities achieved with other techniques [3,1].

It is possible to perform the same kind of calculation for the case where the $y \leftrightarrow -y$ symmetry is broken by a modification of the shape of the surface, i.e., C_s const but $x_s = \beta\cos(2qy+\Psi)$ [Fig. 1(b)]. This modifies the electrostatic boundary conditions, the expression of the electrohydrodynamic slip, and the computation of the overall flow pattern. At first order in β and for the simplest case $\delta = 0$, pumping can be shown to obey Eq. (5), with in this case $v_P \simeq \beta(q^2 \epsilon V_0^2/8\eta)$.

III. DISCUSSION

To summarize, a simple electro-osmotic model (i) validates the symmetry based pumping strategy presented in the introduction, and (ii) shows that the pumping velocities achievable should be comparable to those obtained with other methods and are frequency sensitive.

To elaborate on these results I have analyzed a more complete electro-hydrodynamic model where ionic currents are specifically described and charge injection can occur at the electrodes by activated processes. In the linearized version that I have studied the influx of ions of type i is proportional to the difference between their electrochemical potential in the solution $z_i e\psi + k_B T \log(c_i)$ and in the metal $z_i e V_{\text{ext}}$ (with $z_i e$ and c_i the ion's charge and concentration at the electrode surface). A proportionality constant K_i quantifies the efficiency of the charge transfer.

With this model I recover the results presented above for negligible charge injection and for frequencies lower than ω_D. When charge injection occurs, charges are permanently maintained out of equilibrium by the injected currents, so that hydrodynamic flows persist even in the $\omega \to 0$ limit (both roll patterns [12] and homogeneous pumping). This completely modifies the frequency dependence of the pumping achieved. As an illustration, Fig. 4 shows the rescaled pumping velocity as a function of the logarithm of the frequency, for different values of a parameter K controlling the rate at which one kind of charge can be transfered from the electrode to the solution. For $K = 0$ (no injection) the functional dependence (5) is recovered, but as K is increased the peak at ω^* drops and pumping occurs *in the opposite direction* at lower frequencies. This allows for the control of the pumping direction by monitoring the frequency. A more complete account of the results of this model will be given elsewhere.

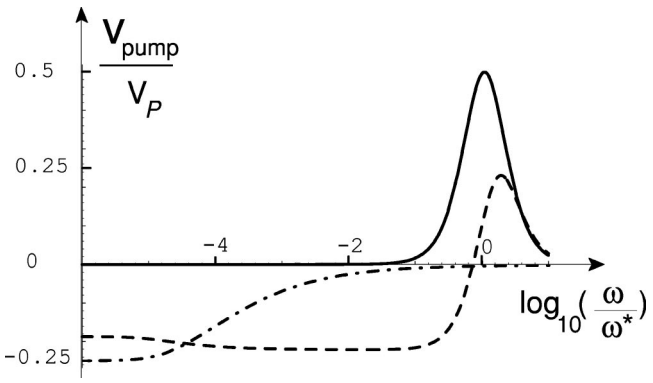

FIG. 4. Scaled pumping velocity v_{pump}/v_P as a function of $\log_{10}(\omega/\omega^*)$ for the geometry of Fig. 3, v_P given by Eq. (6), parameters as in the text: $q\lambda_D = 10^{-4}, \delta_0 = 10$. As charge injection is increased from $K=0$ (solid line) to $K=10^3$ (dot-dashed line) through $K=1$ (dashed-line), the peak at ω^* drops while pumping in the reverse direction appears at low frequencies.

IV. CONCLUDING REMARKS

(1) An even richer phenomenology is expected if one additionally considers modulations of the spontaneous potential of the electrodes (taken here to be zero) or of the charge injection parameters. Other geometries can be envisaged (e.g., a flat electrode facing a sawtooth-shaped one), the only requirement being an asymmetry of the pattern. A more complete exploration of the various cases and frequency behaviors is under way.

(2) Other electrohydrodynamic couplings may contribute as well. Joule heating induces temperature gradients and thus nonuniform permittivity and conductivity, which leads to space charges beyond the surface layers that also drive periodic recirculation patterns. This mechanism, at the basis of recent proposals using traveling waves [2,1], leads in the present geometries (Fig. 1) to pumping velocities proportional to V_0^4 at low voltages (the current-generated temperature gradient scales as V_0^2 [12]). The electro-osmotic pumping described here (proportional to V_0^2) should dominate for small V_0 [16]. Currents themselves also induce conductivity gradients neglected here, which coupled to modulations generate roll patterns [17], and thus presumably pumping in asymmetric geometries. Rectification should also be the rule for nonlinear phenomena and instabilities that may occur at large voltages [18].

(3) The effect being nonlinear, the actual shape of the spatial and temporal modulations matters. For example, pumping can be obtained in a symmetric modulated geometry $x_s = \alpha\cos(qy+\pi/2)$ with a voltage modulation $V_{ext} = V_0\cos(qy)f(t)$ if $f(t)$ is non-time-reversal symmetric: tuning the shape of the signal at the generator allows them to monitor the pumping direction.

(4) Undesirable flows in asymmetric structures designed for separation purposes have actually been reported [19–21], but not thoroughly studied.

(5) The strategy proposed here has many advantages:

(A) Compared to electro-osmosis it requires only small

voltages and no macroscopic voltage drop along the channel.

(B) Compared to traveling waves it requires a more complex electrode design (to get the asymmetry) but a simpler wiring as a single ac signal is required, which may be useful for the design of integrated systems.

(C) Its efficiency increases with miniaturization.

(D) The flow is surface generated: the complex pattern of rolls (thickness proportional to the pattern wavelength) is topped by a homogeneous and continuous flow of liquid. This permits pumping liquids in filled channels but also moving droplets on surfaces: a droplet larger than the pattern wavelength macroscopically ''slips'' on the surface at v_{pump}. This is of interest for applications where only minute amounts of fluid are handled [3,4], as an alternative to techniques based on the generation of differences of surface tension or contact line energy between the front and the back of the droplet [3,4,6].

(6) Eventually, I recall that the underlying symmetry-based argument extends beyond the specific mechanism studied here: a fluid in a *locally* asymmetric geometry *globally* drifts in the direction of broken symmetry under any external action that induces *local* flows.

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