Dynamical trapping of colloids at the stagnation points of electro-osmotic vortices of the second kind

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By applying a stepwise overlimiting voltage to a nanoslot system in equilibrium, it is possible to follow the time evolution of the electroconvective instability vortex array via the depletion dynamics or, alternatively, by following dielectrophoretically trapped particles at the stagnation points of each of the hydrodynamic vortex pairs. Particles are advected to the stagnation point by the hydrodynamics, where they are trapped by a short-range dielectrophoretic force. It is experimentally confirmed that the wavelength selection process occurs at the diffusive time scale and that the wavelength selection mechanism, started by the Rubinstein and Zaltzman electroconvective instability is eventually determined by the system lateral geometry and dictated by Dukhin’s electro-osmosis of the second kind. The steady-state case was numerically studied by solving the fully coupled electroconvective problem, confirming that the vortex stagnation point is indeed of a converging type. The particle’s planar (two-dimensional) equations of motion are solved after adding a dielectrophoretic force that accounts for quasi-three-dimensional effects. It is shown that this force can account for trapping at the nanoslot interface.

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I. INTRODUCTION

Previous works have mostly used colloids as passive tracers to mirror the hydrodynamics developed in electrolytes interfacing ion-permselective nanochannel and/or membrane systems undergoing concentration polarization (CP) [1–4], where, upon the application of an electric potential, ionic concentration gradients in the form of depletion and enrichment regions are formed at opposite nanochannel and/or membrane-electrolyte interfaces [5–9]. More specifically, the current-voltage (I-V) curve is comprised of three distinct parts: ohmic, limiting, and overlimiting regions. The threshold current at which the limiting region occurs is often approximated by the classical diffusion limited current transport theory [10]. An electroneutral diffusion layer (DL) with an ion concentration gradient appears near the membrane-electrolyte interface of depleted ionic concentration where the counterion enters to enhance the flux via diffusion. This diffusive-flux enhanced current density saturates when both ion concentrations vanish at the surface [10]. Later theories [11] extended the above electroneutral approach to account for a space charge layer (SCL), much thicker than the electric Debye layer (EDL), that can appear between the EDL and the electroneutral DL to sustain an overlimiting current density. Recent work [12] has provided an explanation for the large but finite differential resistance in the limiting-resistance region of a microchannel-membrane system due to the effects of charged side walls, through either surface conductance or electro-osmotic flow, that enhance the overlimiting current. For sufficiently large applied voltages, beyond a critical value, the conductance increases dramatically to yield overlimiting currents well above the limiting value. This sudden increase was theoretically predicted to be a result of an electroconvective instability occurring at the membrane-electrolyte interface wherein a stable array of vortices is formed [13–15]. These electroconvection vortices suppress the diffusive propagation of the concentration polarization layer (CPL) towards the electrode [16] and select a much smaller depletion layer thickness on the size of the vortex [13] which, in turn, controls the overlimiting differential resistance. The correlation between the formation of the periodic vortex array and sharp rise in the current was confirmed experimentally for both a wide nanoslot [16], using a fluorescence electrolyte buffer, and a nanoporous membrane [3], using particles as fluid tracers.

While some indications of particle trapping and aggregation have been previously shown [1–4], no attempt was made to model these phenomena. Furthermore, the use of vortices induced by nonlinear electro-osmosis (EO) of the second kind (Dukhin mechanism [17]) or the electroconvective instability (Rubinstein and Zaltzman mechanism [13,14]) as an efficient trapping mechanism has been overlooked both in the case of nanoporous membranes and nanochannels. The goal of the current study is to shed some light on the unique behavior of colloids at a single and isolated nanoslot interface and define how it differs from that occurring at a nanoporous membrane which is comprised of many nonisolated pores.

Previous studies have shown that using geometric field focusing effects for single synthetic conical nanopore electrophoretic (EP) and dielectrophoretic (DEP) forces can facilitate colloid trapping at the entrance of the pore [18,19]. As will later be shown, it is the latter, DEP based trapping mechanism that dominates in our case. The former mechanism is nonexistent in our case since EP cannot trap the negatively charged particle colloids at the anodic side of the nanoslot entrance, but rather tends to drive them away from the entrance.

Efficient trapping via a combination of a short-range force (mostly DEP) and far-field hydrodynamics has been shown for a variety of flow generation mechanisms. These include induced charge electro-osmosis (ICEO) that exploits nonuniform surface zeta potential induced over a polarizable substrate or electrodes to produce hydrodynamic vortices [20–23]. Such vortices have been shown to trap particles at their stagnation points assisted by DEP [24]. In particular, AC electro-osmosis

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(ACEO), which uses electrodes embedded within the microchannel, has attracted a lot of attention as a means for vortex generation and particle trapping through hydrodynamic forces that focus the particles into the stagnation point of the vortices [25–30]. Recent evidence for the trapping of colloids at the stagnation point of a vortex pair generated via EO of the second kind interfacing a narrow nanoslot was observed [2]; however, no attempt was made to analyze this effect.

Here we will examine the specific case of particle trapping dynamics within electroconvective instability induced vortices during their complex wavelength selection process, while extracting additional information on the electroconvective instability. Additionally, as a proof of concept, it will be demonstrated that the electroconvective instability vortex array can be used to separate particles with different radii.

The paper is divided into the following sections. In Sec. II, we present the experimental setup and data collected for a wide nanoslot showing colloidal dynamics. In Sec. III, we construct a simple model to capture key results of the governing electrokinetics and hydrodynamics. Section IV models the colloidal dynamics and trapping, whereas concluding comments appear in Sec. V.

II. EXPERIMENTAL TECHNIQUES AND RESULTS

The microfabricated device consists of two microchambers that are connected by a single nanoslot with a length of 0.35 mm and a width of 2.2 mm (see Fig. 1 and Ref. [2] for additional fabrication information). Reservoirs made of flexible silicon (Grace Bio-Labs) were used on top of the openings wherein platinum electrodes were introduced. The nanoslot was filled by introducing an electrolyte into the large fluidic reservoirs and allowing capillary forces to draw the water across the nanoslot. The platinum wires in the reservoirs are connected to an electrical voltage source and I-V converter (Keithley 2636). The channels were cleaned of ionic contaminants by applying a voltage difference of 10 V between electrodes, with periodic flushing of the reservoirs with fresh solution until the current equilibrated to a minimum, which typically took an hour.

For visualization of CP, we chose, as in many previous studies ([6–8], and references therein), positively charged Rhodamine 6G dye molecules. These were added at a concentration of 10 μM either to an electrolyte with a KCl concentration of 100 μM or DI water. To visualize the inner flow structure of the CP as well as the dynamics of the stagnation points, negatively charged fluorescent polymer microbeads (Microgenics Corp.) of varying sizes (0.72, 1.2, and 5 micron) and a volumetric concentration of 0.02% were used.

When a voltage beyond the limiting to overlimiting current transition for the studied device (approximately 10 V [2]) is applied across the wide nanoslot, the electroconvective instability initiates, as clearly demonstrated in Fig. 2, displaying the time evolution of the instability for an applied voltage of 40 V. The instability manifests itself as an array of depleted regions, with the fluorescent buffer portraying CP within the microchamber interfacing the nanoslot anodic entrance. Each depleted region is comprised of a vortex pair [3,13,14,16]. In contrast, enrichment is visible at the opposite cathodic side of the nanoslot.

Initially the system is at equilibrium where it can be seen that the particle concentration is homogenous and clustering

![Diagram of the two Pyrex slides](image)

**FIG. 1.** (Color online) Schematic of the two Pyrex slides (top view) consisting of the chip: (a) Two square microchambers of 50 μm depth that were wet etched into a 1 mm Pyrex glass slide. The distance between the chambers forms the nanochannel of length $d = 0.35$ mm [marked by light blue in (d)]. Inlet and outlet access holes were mechanically drilled into each microchamber (green circles). (b) A rectangle of width $W = 2.2$ mm, length $l = 3.2$ mm (hatched lines), and depth $h = 190$ nm, etched into the deposited sacrificial polysilicon layer on top of a second 1 mm Pyrex glass slide. Note that the width of the nanochannels is smaller than that of the microchamber. (c) (Side view) Sealing of slides (a) and (b) form a nanoslot that connects two microchambers, as seen in the side view that corresponds to the cross section A-A of the chip. For convenience, in the schematic drawing, the nanoslot height has been magnified relative to the microchamber height. (d) Optical microscope image (top view) of the nanoslot with the direction of the applied voltage indicated. Arrow (orange) indicates the direction of the current-controlling counterion flux entering the nanoslot.
of particles at the nanoslot is not apparent. With the onset of the vortices upon voltage application, particles that were in the vicinity of the nanoslot are trapped within the stagnation points of the vortex pairs. During the complex process of vortex array wavelength selection, two small adjacent vortex pairs collide and annihilate to create yet a larger vortex pair, until the steady state is reached with a selected wavelength. Interestingly, the particles seem to mirror this complex process wherein neighboring stagnation points coalesce into a larger and brighter point at the stagnation point of the newer larger vortex. Hence, the particles are mimicking the dynamics of the vortex pair’s stagnation points, allowing further investigation of the wavelength selection process [3,13–16,31]. At much later times, edge effects dominate and instead of obtaining a stable array of vortices with a selected wavelength [15,16], we obtain a single vortex pair with its final size determined by the microchamber’s lateral dimensions (∼2.2 mm in the plane, Fig. 2). The increase in brightness and size of the stagnation points is a result of the continuous trapping.

A key point is that particles that are initially in the vicinity of the interface are trapped rapidly on a time scale that is short enough to enable mirroring of the vortex (depletion region) wavelength selection process. This is clearly seen from the increasing brightness of the stagnation points prior to the completion of the first visible annihilation-creation process of the array vortices. To calculate the wave number $k$ of the depletion regions, we count the number of depleted regions in the image and calculate their average length, which is simply the wavelength, $\lambda = 2\pi/k$, of a single vortex pair. Similarly, we do so for the stagnation points, where the wavelength is now defined as the length between two adjacent stagnation points. These experimentally measured wave numbers are marked $k_{\text{dep}}$ and $k_{\text{stag}}$, respectively. Theoretical predictions have shown that the ratio between the wavelength of a vortex pair to the DL, $\lambda/L$, is between 0.7 and 1.2 [15], while experimental observations have shown this ratio to be approximately 1.25 [16]. Using the latter observed value while taking the diffusive scaling for the DL growth, $L = \sqrt{2Dt}$ [32], allows the wave number to be modeled as

$$k_{\text{model}} = \frac{8}{5\pi \sqrt{2Dt}}.$$  \hspace{1cm} (1)

Curve fitting of the depletion data for 40 V yields $D = (4.98 \pm 0.6) \times 10^{-9}$ m$^2$/s, similar to the measured value in Ref. [16] (Fig. 3). Thus confirming that at early times the electroconvective instability wavelength selection process (Rubinstein and Zaltzman mechanism) evolves on the diffusive
time scale. At late times (~40 seconds), due to strong tangential fields existing at the nanoslot lateral edges (Dukhin mechanism), the selected wave number corresponds to a steady single vortex pair spanning the entire nanoslot width. Such a competition between these two mechanisms was recently demonstrated on a corrugated nanoslot [33].

Evidently, the net motion of particles outside the DL is towards the nanoslot due to electro-osmotic flow (EOF) dominating over EP. The former is directed from the anode to the cathode since the channel walls are negatively charged, while the latter acts in the opposite direction since the colloids are negatively charged. Hence, particles initially located further away from the channel require additional time until EOF transports them to the vortex array region where they are hydrodynamically convected towards the stagnation points. The fact that particles remain at the nanoslot entrances indicates that there is either a net EOF into the nanoslot or that a short-range attractive force exists, which are responsible for trapping. In actuality, trapping occurs due to both factors, but as will be further discussed below, it is the DEP short-range force that dominates at the nanoslot vicinity due to field focusing effects, associated with tremendous field gradients which result from the almost three order of magnitude abrupt change in geometry (from ~50 μm microchamber depth to ~190 nm nanoslot depth) at the microchannel-nanoslot junction. Such field focusing effects are unique to the isolated nanoslot geometry in contrast to the ion-permeselective membrane, wherein the multitude of pores and their close vicinity average out the field focusing effect resulting in a pseudo-one-dimensional treatment of the electrokinetic problem within the DL region [2,34].

Outside the region of the DL, particles are particularly influenced by the background hydrodynamics and are conveyed towards the nanoslot such that they arrive in between two separate vortex pairs, as shown schematically in Fig. 2(h). Since DEP scales with particle volume, small differences in particle radii can change the force’s magnitude significantly. In fact, two types of behaviors are observed for different sized particles at the in-between points of neighboring vortex pairs (or, equivalently, in between neighboring depletion regions). Small particles (0.72, 1, and 2 μm) aggregate at the hydrodynamic stagnation point of the converging vortex pairs while larger particles (5 μm) aggregate solely at the in-between points (Fig. 4), which are diverging stagnation points of two neighboring vortex pairs (see movies 1 and 2 in Supplemental Material [35]). These points are characterized by maximum lateral (in-plane) variations in the local electrolyte conductivity (due to CP regions) and extended space charge variations [31], which result in an additional contribution to the electric field gradients beyond that due to the geometric field focusing effect in the orthogonal plane. Hence, these points correlate to the location of maximal DEP force. It is most probable that the DEP force at these diverging stagnation points acting on the larger particles (5 μm) overwhelms the hydrodynamic forcing that tends to convect the particles along the nanoslot entrance towards the converging vortex pair stagnation point, resulting in their aggregation at the in-between vortex pair points. The converse is true for the smaller particles, which are advected to the vortex pair converging stagnation point. Yet, in both of the cases of small and large particle radii, the DEP force due to the field focusing in the orthogonal plane is sufficiently strong to trap them and initiate their aggregation at the nanoslot entrance. In addition, such a mechanism, which shows particle size dependent behavior, may be used to facilitate their separation through the vortex array (movie 3 in Supplemental Material [35]).

In order to strengthen the hypothesis that it is DEP rather than net EOF into the nanoslot that dominates the attraction of the particles to the anodic nanoslot entrance, we conducted additional tests in which we varied the ionic concentration of the bulk solution and observed the particle dynamics away from the nanoslot. For colloids of 1 μm radii and ionic concentrations above 10 μM, EOF dominates over EP and the negatively charged colloids within the microchamber interfacing the anodic side of the nanoslot are convected towards the nanoslot [1]. In contrast, for particles suspended in DI water, EP dominates over EOF and the particles are driven away from the nanoslot anodic entrance while accumulating on the cathodic entrance (Fig. 5). This repulsion is expected as the nanoslot electro-osmotic permeability decreases with decreasing ionic concentrations [1] (or, equivalently, increased...
The applied voltage, in this case 40 V, are rapidly trapped due to particles that are at the vicinity of the nanoslot prior to turning on dominated by EP and their net motion within the anodic side is away EDL overlap within the nanoslot [36]. In the latter case, particles that are sufficiently far from the nanoslot move towards the electrode, while particles that were initially at the nanoslot vicinity can be seen to be trapped there (Fig. 5). The fact that particles are attracted to the anodic entrance of the nanoslot instead of electrophoretically driven away is another indication that attractive DEP forces (i.e., $p$-DEP) dominate the nanoslot vicinity.

At the center of the final selected vortex pair, jetlike structures can be seen (Fig. 6 and movie 4 in Supplemental Material [35]). Here, particles oscillate back and forth from the nanoslot on this line of symmetry. This linear movement was previously explained as the projection of closed circular trajectories, due to back pressure, in a plane that is perpendicular to the plane of view [1]. However, this explanation was restricted to particle motion in the ohmic current regime. In this case, the jetting motion is a combination of two types of vortices occurring at orthogonal planes, with the vortex pair due to electro-osmosis of the second kind and the orthogonal vortex with its axis parallel to the nanoslot entrance. In addition to these jets, particles are observed to accumulate at the far corners of the nanoslot entrance [Fig. 5 and Fig. 4(f)]. This is most probably due to the stronger field focusing effect at the corners accompanied by stronger gradients than the polar field focusing occurring throughout the wide nanoslot. Once more, the fact that the particles are attracted to the corner where maximal field effects exist is yet another indication that particles are undergoing positive DEP.

III. NUMERICAL MODEL

The equations governing steady-state nonlinear ion transport are the Poisson-Nernst-Planck-Stokes equations. For a symmetric and binary electrolyte ($z_+ = -z_- = 1$) of equal diffusivities ($D_+ = D_- = D$), the nondimensional equations are

$$\nabla \cdot [\nabla c_+ + c_+ \nabla \phi - \text{Pe}(u c_+)] = -\nabla \cdot j_+ = 0, \quad (2)$$

$$\nabla \cdot [\nabla c_- - c_- \nabla \phi - \text{Pe}(u c_-)] = -\nabla \cdot j_- = 0, \quad (3)$$

$$\nabla^2 \phi = -(c_+ - c_-)/(2\delta^2), \quad (4)$$

$$\nabla \cdot u = 0, \quad (5)$$

$$-\nabla p + \nabla^2 \phi \nabla \phi + \nabla^2 u = 0, \quad (6)$$

where Eqs. (2) and (3) are the Nernst-Planck transport equation for cations $c_+$ and anions $c_-$, respectively, which are normalized by the bulk concentration $c_0$. The spatial coordinates are normalized by the diffusion length $L$, while the current fluxes $j_\pm$ have been normalized by $D c_0 / L$, wherein $D$ is the diffusion coefficient. Equation (4) is the Poisson equation for the electric potential, $\phi$, which is normalized by the thermal potential $RT / F$, where $R$ is the universal gas constant, $T$ is the absolute temperature, and $F$ is the Faraday constant. The symbol $\delta = \lambda_D / L$, where $\lambda_D = \sqrt{\epsilon_0 \epsilon_r RT / 2 F^2 c_0}$ is the Debye length. Herein, $\epsilon_0$ and $\epsilon_r$ are the permittivity of the vacuum and the relative permittivity, respectively. Equations (5) and (6) are the hydrodynamic equations for the conservation of mass and momentum for an incompressible fluid in the Stokes limit. The velocity $u$ and pressure $p$ are normalized by the following values, accordingly:

$$u_0 = \frac{\epsilon_0 \epsilon_r}{\mu L} \left( \frac{RT}{F} \right)^2, \quad p_0 = \frac{\mu u_0}{L}, \quad (7)$$

where $\mu$ is the fluid’s dynamic viscosity. Additionally, the Peclet number is

$$\text{Pe} = \frac{u_0 L}{D} = \frac{\epsilon_0 \epsilon_r}{\mu D} \left( \frac{RT}{F} \right)^2. \quad (8)$$

It is apparent from this equation that the Peclet number is a property of the ionic electrolyte and is not dependent on the geometry or the bulk concentration. Typical values for a water...
based electrolyte, \( \varepsilon_r = 80, \mu = 10^{-3} \text{ Pa} \cdot \text{s}, T = 298 \text{ K}, \) and \( D = 10^{-9} \text{ m}^2/\text{s}, \) give \( \text{Pe} \sim 0.5. \) In one-dimensional models, it is standard practice to decouple the hydrodynamics and electrokinetcs under the assumption that the contribution of the convective term is small. However, it is this nonlinear term in cooperation with the nonlinear slip velocity at the surface that is responsible for the electroconvective instability [13,14].

The domain is defined by a unit square (scaled by \( L \) \( \{-0.5 \leq x \leq 0.5, 0 \leq y \leq 1 \}, \) where \( x = \pm 0.5 \) are the side walls of the microchamber, whereas the ionic bulk is located at \( y = 1 \) and the nanoslot is located at \( y = 0 \) [see Fig. 7(a) and Fig. 8 for coordinate system]. Thus, for this two-dimensional domain, the velocity and current fluxes can be written in terms of the Cartesian components \( \mathbf{u} = u \mathbf{i} + v \mathbf{j} \) and \( \mathbf{j}_\perp = j_{\perp x} \mathbf{i} + j_{\perp y} \mathbf{j} \), respectively.

The following boundary conditions (BC) are imposed:

\[
\begin{align*}
y &= 1: \quad c_+ = c_- = 1, \quad \phi = 0, \quad v = 0, \quad \partial_x \mathbf{u} = 0, \quad (9) \\
y &= 0: \quad c_+ = N, \quad j_{-y} = 0, \quad \phi = -V - \log N, \quad \mathbf{u} = v = 0, \quad (10) \\
x = \pm 1/2: \quad j_{\perp y} = 0, \quad \partial_x \phi = 0, \quad u = 0, \quad v = -\zeta E_y. \quad (11)
\end{align*}
\]

At the DL-bulk solution boundary \( (y = 1) \), Eq. (9) prescribes a bulk solution that is experiencing no shear stress and zero inflow into the system. At the nanoslot-electrolyte boundary, Eq. (10) prescribes the standard BC for an ideal cation-perselective nanoslot, with a cationic concentration \( N \) that does not allow the transport of negatively charged anions through it. A total potential drop of \( V \) is applied between the bulk and nanoslot. The term \( -\log N \) accounts for the Donnan potential jump [37]. Additionally, the no-slip and no-penetration BCs for the velocities are required. At the microchamber walls, Eq. (11) prescribes zero ionic flux and electrical insulating condition as well as the classical Helmholtz-Smoluchowski (HS) slip velocity, \( \mathbf{u} \cdot \mathbf{t} = -\zeta E_x \), where \( t \) is the unit vector tangential to the walls and \( E_x \) is the tangential electric field component on the walls. A net EOF would enhance particle trapping at the nanoslot, thus nonpermeable velocity BC (no penetration) throughout the system allows us to isolate the effects of DEP on the particle dynamics, as will be seen shortly in Sec. IV.

Typical values of \( \delta \) range between \( 10^{-3} \) to \( 10^{-5} \) [13] depending on ionic concentrations and the observable diffusion length. As in previous works [2,11–13,34,38,39], we choose the value of \( \delta = 0.01 \) for numerical convenience. For cation ideal selective systems, another acceptable assumption is that the cationic concentration within the nanoslot is large \( (N \gg 1) \) [6]: a value of \( N = 10 \) is chosen. A typical value of the zeta potential in our system is approximately on the order of the thermal energy, \( \zeta = -1 \) [2,7,34,40]. Numerical simulations of the fully coupled nondimensional two-dimensional (2D) Eqs. (2)-(6) with BC (9)-(11) were solved using COMSOL [35].

Figure 7 demonstrates how the concentration and electric potential fields can no longer be considered one dimensional. Furthermore, the coupling term between the hydrodynamics and electrokinetcs also increases the current in the
overlimiting regime [Fig. 7(c)], in agreement with the EOF overlimiting current enhancement mechanism described by Dydek et al. [12]. In addition, the depletion region pattern, with maximal depletion length on the vortex center line, and the accompanying hydrodynamic vortex pair with a converging stagnation point due to the Dukhin mechanism, is similar to the vortex pairs constituting the periodic cell of the Rubinstein and Zaltzman electroconvective instability array [12,14,31].

Finally, it should be noted that the steady vortex pair has two additional stagnation points located at the vortices’ core (see Fig. 7). From a dynamics point of view, these points are center-type fixed points. Fluid particles circulating around this point in closed and isolated paths, as do unforced points are center-type fixed points. Fluid particles circulate around this point in closed and isolated paths, as do unforced fluid particles (ideal tracers). However, experiments show, through the observation of tracer particles, that isolated and closed paths do not exist, suggesting that the similarity between colloid and fluid dynamics breaks down at the vicinity of the nanoslot. In the following section, we shall model the force acting upon the particles and the resulting dynamics.

IV. PARTICLE DYNAMICS

Theoretical work by Liu and coworkers [41,42] studied the effects of various forces on the dynamics of particles within a predetermined background hydrodynamic flow. They showed that by adding short-range attractive forces, particle trapping is possible. The criteria for trapping (i.e., transforming a neutrally stable fixed point into a stable fixed point) was that the force be a nondivergence-free attractive force (NDF).

Limiting this work to the regime of low particle concentration and ignoring particle-particle interactions, the governing kinetic equations for immersed particles include only terms related to the hydrodynamics of the fluid and externally applied forces. For a spherical colloid located at \(x_p(t)\) and moving with velocity \(V_p(t)\), the dimensionless equation has the following form [42–44]:

\[
\frac{dV_p}{dt} = \text{St}(\rho_p \frac{Du}{D}) - \text{St}_f \frac{D}{2\rho_p} \left[ \frac{dV_p}{dt} - \frac{D}{Dt} \left( u + \frac{3F_a}{5} \nabla^2 u \right) \right] - (V_p - u - Fa \nabla^2 u) - \text{Ba} \int_0^1 \frac{1}{\sqrt{1 - \tau}} \frac{d}{d\tau} \left( \nabla \cdot (V_p - u - Fa \nabla^2 u) \right) + U_{\text{Force}},
\]

wherein St, Ba, and Fa are the Stokes, Basset, and Faxén numbers, accordingly. The derivatives \(d/dt\) and \(D/dt\) denote, accordingly, the regular Lagrangian time derivative for a moving particle and the convective derivative of a fluid element. The terms on the right-hand side represent, in the following order, the undisturbed flow, added mass, Stokes drag including the Faxén correction (Fa \(\nabla^2 u\)) and the Basset history force, as well as a general term for additional forces (\(U_{\text{Force}}\)). All forces in Eq. (12) are scaled relative to Stoke’s drag, while \(St = \frac{\rho_p \rho}{\rho_f} \frac{u_0}{L} \sim \frac{O(10^{-3})}{O(10^{-4})}\), \(St_f = \frac{\rho_p \rho}{\rho_f} \frac{u_0}{L} \sim \frac{O(10^{-3})}{O(10^{-4})}\), \(Fa = \frac{\rho_p \rho}{\rho_f} \frac{u_0}{L} \sim \frac{O(10^{-3})}{O(10^{-4})}\), and \(Ba = \frac{\rho_p \rho}{\rho_f} \frac{u_0}{L} \sim \frac{O(10^{-3})}{O(10^{-4})}\). Assuming that the fluid and particle densities are similar, the Stokes number is simply \(St = (2R_p^2 \rho_p u_0)/(9\mu L) \sim Re(R_p/L) \sim \text{Ba}^2\). Neglecting these terms reduces Eq. (12) to

\[
\frac{dx_p}{dt} = V_p = u + U_{\text{Force}}.
\]

For the case of \(U_{\text{Force}} = 0\), the particles are ideal tracers and follow the streamlines of the fluid. In contrast, particles under the influence of a nonzero force will not follow the streamlines of the fluid.

The electric field perpendicular to the plane of interest shown in the above figures (xy plane) follows a similar derivation given by Yossifon and Chang [1], who modeled the microchannel-nanochannel interface with a thin EDL as a converging sink flow into a 90° wedge,

\[
\varphi = m \log r,
\]

where \(m\) is the quasi-2D sink strength and \(r\) is the polar coordinate in the orthogonal plane (yz plane). The nanoslot is located at \(r = 0\). Requiring electric flux continuity between the nanochannel and microchannel gives \(m = 2E_0 h/\pi\), where \(E_0\) is the electric field within the nanochannels and \(h\) is the nanochannel height. However, \(E_0\) is usually unknown and is in itself a function of the nanochannel height. Fortunately, using scaling, this unknown can be bypassed. By transforming the \(r\) coordinate in Eq. (14) to the \(y\) coordinate, we account for polar field focusing effects in the orthogonal plane and effectively introduce 3D effects into our 2D model. Noting that the potential, in practicality, is not infinite at the interface, \(y = 0\), requires that the potential be modified in the following manner:

\[
\phi = m \log(y + \delta_{\text{cutoff}}),
\]

where the cutoff length will be given shortly. Requiring that the voltage drop across the microchannel be \(V\), then \(m = V/\log(\delta_{\text{cutoff}})\). Substituting this modified potential into the expression for the DEP force, \(F_{\text{DEP}} = 2\pi \varepsilon_0 \varepsilon_r K R_p^2 V |E|^2\), gives the following nondimensional DEP force:

\[
U_{\text{DEP}} = \frac{F_{\text{DEP}}}{6\pi \mu R_p u_0} = -\frac{2e_0 \varepsilon_r K R_p^2}{3\mu u_0 L^3} \frac{V^2}{\log^2(\delta_{\text{cutoff}})} \left( \frac{1}{(y + \delta_{\text{cutoff}})^3} \right),
\]

where \(K\) is the Clausius-Mossotti factor [in the steady-state case, \(K\) is real and of \(O(1)\)]. The \(y^{-3}\) indicates that this force is short range in nature as well as NDF. The normalized particle size \(R_p = R_p/L\) for the cutoff length, as this is the closest the particle can approach the nanoslot. Numerical integration of Eqs. (13) and (16) for four particles placed at different initial points illustrates that all particles are eventually trapped at the center stagnation point (Fig. 8). Furthermore, we demonstrate that the introduction of orthogonal field focusing effects into the particle’s dynamical equations of motion transforms the neutrally stable circle-type fixed points at the vortex cores into unstable fixed points and changes the saddle fixed point at the center of the vortex pair into a stable fixed point.

Our simple model for the NDF DEP force illustrates qualitatively the transformations of the system’s fixed point.
Yet, it should be noted that while the added DEP forces capture the behavior qualitatively, some features are missing. Most notably, the modeled DEP force of Eq. (16) does not account for the CPL at the microchannel-nanochannel interface, which would result in a further increase of the field gradients and in turn increase the DEP trapping force. Our model also does not account for the additional in-plane electric field gradients responsible for the accumulation of the larger colloids at the in-between depletion region points seen in Fig. 4. Both in the numerical simulations and the particle dynamics, we have not accounted for the corner effects, which would locally induce strong tangential fields and gradients at the nanoslot as well as trap particles at the corners [see Figs. 4(f) and 6]. As such, our simple quasi-2D DEP model would strongly underpredict field focusing at the corners. However, in reality, at the center of the wide nanoslot away from the corners, field focusing is 2D in nature and, as such, both simulations and particle dynamics imitate our observations qualitatively. Additionally, we neglect the net EOF through the nanoslot, which, if accounted for properly, would further enhance trapping.

V. CONCLUSIONS

We show here the time evolution of the stagnation points of the electroconvective vortex array, as visualized using tracer particles, concurrently with CP visualized using fluorescent dye molecules. The wavelength selection process is evident through the increasing size of the depletion regions (i.e., vortex pairs), but also through the number and increased brightness of the stagnation points which occurs due to the coalescence of stagnation points as well as additional trapping of particles arriving from the bulk. While particle trapping within the stagnation points appears to be just another method to follow the time evolution of the instability, in fact it provides an additional means of extracting quantitative data such as wavelengths as well the characteristic time scale for the wavelength selection process, which appears to be governed by the diffusive time.

The electroconvective instability occurring at a microchannel-nanochannel interface can be utilized not only to increase the conductance (i.e., overlimiting regime) and current within the system, but also to promote the efficient trapping of colloids at the interface via a combined short-range DEP force that traps the particle at the nanoslot entrance together with long-range electro-osmotic flow that drives colloids into the vortex. In fact, the existence of the DEP force can be ascribed to the unique geometry of the nanoslot, which does not cancel out field focusing effects—unlike the many pores membrane, where large scale homogeneity averages out field focusing effects and results in the annulment of DEP effects. Consequently, isolated nanoslot field focusing provides a trapping method that is incompatible with many pore membranes. It is important to note that a consequence of this strong DEP force is that particles in the vicinity of a nanoslot exhibit behavior which is distinctly different from the surrounding flow and, as such, cannot be used as ideal tracers. Furthermore, we have demonstrated that particles of different size behave differently in the vicinity of the nanoslot, thus allowing for a mechanism of particle separation.

Additionally, we study numerically the solution of fully coupled electrokinetic-hydrodynamic equations for the steady-state case—where the EO of the second kind single vortex pair size is selected according to the system lateral dimensions—and show similarities to the instability array. Far away from the nanoslot, the particles mimic the hydrodynamics, but near the nanoslot, strong field gradients apply a strong DEP force on the particles which induces trapping. The solution of the particle’s planar dynamical equations of motion while accounting for quasi-3D effects can qualitatively explain particle trapping at the nanoslot interface, as well as the accumulation of colloids at the center of a single vortex pair. An extension of the model is necessary to account for corner accumulation, as well as the additional impact of net EOF through the nanochannel, which would likely enhance trapping.

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