

Supplemental materials

A. Notes on electric field calculation

Electric field inside nanonozzles is 2D axisymmetric and can be calculated by finite element methods (e.g., COMSOL software). Known electric potentials are imposed in the inlet and outlet, and non-penetration condition $\mathbf{E} \cdot \mathbf{n} = 0$ on walls, respectively. The symmetric conditions are held on other boundaries.

B. Notes on 2D and 3D analogue difference discussion

Different from 2D case, the large ratio of EDL/Characteristic Length in 3D nanonozzles may violate the assumption of Boltzmann distribution used in equations 2 and 3 for our FEM simulation. If Boltzmann's distribution isn't satisfied, a more generalized equation, Poisson-Nernst-Planck (P-N-P) equation, have to be used to calculate EOF:

$$\nabla^2 \Psi = -\frac{1}{\varepsilon} \rho_e = -\frac{1}{\varepsilon} \sum_i z_i e n_i \quad (\text{S1})$$

$$\frac{\partial n_i}{\partial t} = -\nabla \cdot \mathbf{J}_i \quad (\text{S2})$$

where Ψ is the total electric potential in the aquatic solution, ε is the permittivity of the media, ρ_e is the net charge density, which is the summation of all different ion species; z_i is the valence for species i , and e is the electronic charge. For ion species i , its concentration n_i obeys the convection-diffusion equation 2, where the ion flux for species i is given by

$$\mathbf{J}_i = -(D_i \nabla n_i + \frac{z_i e}{k_B T} D_i n_i \nabla \Psi) + n_i (\mathbf{u} + \mu_{DEP} \nabla (\mathbf{E} \cdot \mathbf{E})) \quad (\text{S3})$$

where $\mathbf{E} = -\nabla \Psi$ is the electric field and μ_{DEP} is the DEP mobility (E. B. Cummings and A.K. Singh, *Analytical Chemistry*, 2003, **75**, 4724-4731). This will make the case quite complicated

and further investigation is needed but not available yet.

C. Notes on other effects in asymmetric transport

The formation of the internal vortices near the channel surface depends strongly on the ζ -potential of the channel surface and assembly molecules. The interactions between electroosmosis (EO) and electrophoresis (EP) can be estimated by the ratio of EP mobility (μ_{EP}) and EO mobility (μ_{EO}), μ_{EP}/μ_{EO} . The increase of this dimensionless ratio will increase the extensional component of colloidal motion, which would lead to the reduction of recirculation motions or vortex size.

Dielectrophoresis (DEP) may also play important roles, especially in the locations close to the small opening end. Similarly, dielectrophoretic mobility (μ_{DEP}) can be applied to estimate the DEP effect and their relative interactions to EO and EP by their mobility

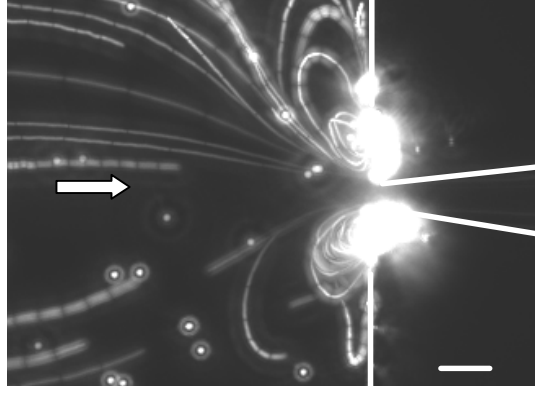
ratio, $\frac{\mu_{DEP}}{\mu_{EP} - \mu_{EO}} \frac{\nabla(\mathbf{E} \cdot \mathbf{E})}{(\mathbf{E} \cdot \mathbf{E})} \cdot \mathbf{E}$. A strong DEP is expected when this ratio is larger than 1.0. This threshold reaches in the region of high E (e.g., the small opening end) because μ_{DEP} is proportional to E^2 .

Since the speed of charged particles near the small end is so large that their movements will induce the surrounding fluid to flow and eventually the induced flow affects the motions of particles. This is the effect of hydrodynamic interaction and also needs to be considered near the small end. The completed mechanism is still under exploration.

D. Notes on flow patterns

In diverging direction, dual vortices were not observed until a very high electric field is applied. Figure S1 shows microscopic streak images of the trajectory of particle motions was shown in a 20 μm diverging channel with a electric bias of 180V added in a distance of 1.5 cm).

The channel edges are outlined for clarity and arrows indicate the particle motion directions. The scale bar presents 20 μm .



E. Notes on DNA dynamics

It has been thoroughly studied that DNA stretching in the pure extensional hydrodynamic flow is related to the value of Deborah number, which is defined as $De = \tau_{relax} \dot{\epsilon}$, where τ_{relax} is the longest relaxation time for DNA chains and $\dot{\epsilon}$ is the extensional rate of the flow. We also studied the behavior of DNA chains at different “electrophoretic” Deborah number since the pure electrophoretic motion is still extensional. Due to the non-uniform electric field, the “electrophoretic” Deborah number is not constant in the whole microfluidic device even at the same controlling parameter E_0 . Since DNA molecules experience stretching in the contraction area and compression in the expansion area, we have the dimensional localized extensional (or

compression) rate $\dot{\epsilon} = \frac{1}{d_1} \frac{k_B T}{b \xi} E_0 \|\nabla \mathbf{E}\|_2 \text{sgn}(\alpha)$, where d_1 is the size of the small end of the

contraction channel, $\|\cdot\|_2$ is the ℓ_2 -norm of a matrix, $\|\nabla \mathbf{E}\|_2 = \frac{1}{E_0} \sqrt{\alpha^2 + \beta^2}$ and $\text{sgn}(\cdot)$ is the

sign function. Thus we allow the negative sign of $\dot{\epsilon}$ to stand for compression.

F. Notes on pH value

The pH value was measured after preparation of diluted particle suspensions and the value tends to change during the electrokinetics-assisted transportation because of CO₂ absorption. The final pH value of particle suspensions varies between 5 and 6. The pH value of DNA TE buffer solution did not change after adding DNA and other additive materials in TE buffered solution.

Supplemental Movie I

Time-resolved fluorescence microscopic images showing the motion of weakly charged particles (e.g., $\mu_{EP} = -0.78 \times 10^{-8} \text{ m}^2/\text{sV}$ for 3 μm beads) in the converging direction. A DC bias of 100 V was added across a converging channel from the large end to the small end. PS beads with the solid content of 0.00265 wt% were continuously fed.

Supplemental Movie II

Time-resolved fluorescence microscopic images showing the motion of weakly charged particles (e.g., $\mu_{EP} = -0.78 \times 10^{-8} \text{ m}^2/\text{sV}$ for 3 μm beads) in the diverging direction. A DC bias of 100 V was added across a diverging channel from the large end to the small end. PS beads with the solid content of 0.00265 wt% were continuously fed.