Effect of nanochannel geometry on electrokinetic ion transport in a micro-nanofluidic system

Cite as: AIP Advances 9, 125213 (2019); https://doi.org/10.1063/1.5126284
Submitted: 03 September 2019 . Accepted: 19 November 2019 . Published Online: 10 December 2019

Jun-yao Wang, and Qi Hou
Effect of nanochannel geometry on electrokinetic ion transport in a micro-nanofluidic system

Cite as: AIP Advances 9, 125213 (2019); doi: 10.1063/1.5126284
Submitted: 3 September 2019 • Accepted: 19 November 2019 • Published Online: 10 December 2019

Jun-yao Wang and Qi Hou

AFFILIATIONS
School of Mechanical Engineering, Northeast Electric Power University, Jilin 132012, China

E-mail: junyao_0001@126.com

ABSTRACT
In this paper, the electrokinetic ion transportation in a micro-nanofluidic system is demonstrated through employing Poisson-Nernst-Planck equations coupled with Navier-Stokes equations. The effects of nanochannel geometry, volumic surface charge density, nanochannel length and nanochannel radius on the electric field, ion transport field, and fluid field are investigated. Theoretical research shows that the potential drop relies mainly on the nanochannel's volume instead of nanochannel geometry. Two acute-angle structures in a trapezoid nanochannel relative to a right-angle structure in a semicircular or rectangular nanochannel can intensify the electric double layer field. For a cross-sectional shape of the trapezoid, a higher ion concentration is obtained through enhancing the volumic surface electric charge, increasing the nanochannel length, and decreasing the radius. The results enabled the provision of a beneficial method for better understanding the design principle of the nanochannel structure.

© 2019 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

I. BACKGROUND
A microfluidic system with the advantage of rapid analysis, functional integration, and cost saving has been broadly utilized in biomolecule trapping, enzyme reaction, and immunoassay screening. Nevertheless, unsatisfactory efficiency is a significant shortcoming for the existing microfluidic system, which severely restricts its applications including detection, mixing, and concentration. To solve these issues, a nanofluidic biochemical analytical system with the characteristics of a little scale and a large specific surface area is used to enrich the molecules with millionfold factors. For years, some researchers have operated on the incomplete concept that negative ions are enriched near a nanochannel due to the nanochannel’s repulsive interaction, which assumed that the concentration level relied primarily on the overlapping extent of the electric double layer (EDL) in a nanochannel. At this period, some basic aspects of the theory were not fully understood, such as, the electrokinetic transport behavior of the positive ions (where the surface charge was set to be negative) was supposed to be same as that of the negative ions. To further develop the ion transport mechanism, positive ions should be concentrated in the nanochannel based on the attraction between the positive ions and the surface charge. Consequently, the electrokinetic transport behavior is attributed to the electric double layer (EDL) effect derived from the surface charge. Furthermore, some studies have indicated that reducing the ion concentration, increasing the nanochannel density, and decreasing the nanochannel size enhances the EDL effect. Although the nanochannel geometry effect has been researched, the influences of three nanochannel’s cross-section structures on electrokinetic ion transportation based on three-dimensional simulation has not been reported.

Various cross-sectional shapes for three types of materials, i.e., silicon, glass, and plastic, can be obtained using different methods. In particular, a semicircle channel for a glass chip and a trapezoid channel for a silicon chip are manufactured through wet etching with different solutions (hydrofluoric acid solution for glass and KOH solution for silicon). Meanwhile, a rectangle channel on a plastic chip (or a silicon chip) is fabricated via thermal pressing with a metal mold (or dry etching with the feature of more efficiency for fabricating a nanochannel). If the influence of disparate material performance on electrokinetic ion transportation is ignored, the cross-sectional shape of a nanochannel becomes a critical element. Several experiments have been developed to verify feasibility research on electrokinetic ion...
### TABLE I. Parameters for numerical simulation.

| Parameter | Value |
|-----------|-------|
| $D_1/D_2$ (m$^2$/s) | $1.97 \times 10^{-9}/2.01 \times 10^{-9}$ |
| $z_1/z_2$ | 1/1 |
| $\mu$ (Pa s) | $1.0 \times 10^{-3}$ |
| $\varepsilon_0$ (F/m) | $8.85 \times 10^{-12}$ |
| $\varepsilon_r$ | 80 |
| $\rho_0$ (kg/m$^3$) | $1.0 \times 10^{-3}$ |

FIG. 1. (a) The three-dimensional geometrical model with two microchannels and one nanochannel; [(b)–(d)] the local enlarged drawing of the nanochannel including a rectangle, trapezoid, and semicircle; [(e)–(g)] the cross-sectional structure of a rectangle, trapezoid, and semicircle nanochannel; “a” and “L” represent the nanopore radius and nanopore length, respectively.

FIG. 2. The potential along the center-line of the system: the effects of (a) the cross-sectional shape, (b) the surface charge, (c) the nanochannel length, and (d) the nanochannel radius on the electric potential are exhibited.
concentration and employed to improve concentration performance in a micro-nanofluidic chip. Nevertheless, the experimental differences resulting from various cross-sectional shapes have been given little attention. For instance, ion concentration is achieved in the plastic chip with a rectangle structure, whereas the concentration factor is inferior to that in the silicon chip with a trapezoid structure. Additionally, a high ion concentration factor is realized in the glass chip with a semicircle structure; nonetheless, the time dependent factor of the glass chip is worse than that of the silicon chip. The reasons behind this phenomenon are often overlooked. Simultaneously, for a given micro-nanosize, the concentration difference is difficult to be distinguished experimentally due to a minor variation of three cross-sectional shapes. Our research group attempts to search the effect of the structure differences on the ion concentration via theoretical simulation. Up to this point, no literature can be found that has analyzed the influence of nanochannel geometry on electrokinetic ion transportation in a micro-nanofluidic system.

In this paper, the Navier-Stokes equations coupled with the Poisson-Nernst-Plank equations are simultaneously employed to solve the effect of nanochannel geometry on electrokinetic ion transportation in a nanochannel. The influences of the cross sectional shape, the surface charge and the nanochannel dimensions on the electric potential, the ion concentration, and the liquid flow are discussed. Concluding remarks give an overview of how the cross sectional shape of the trapezoid increases ion concentration and affects electrokinetic ion transportation in a nanochannel.

II. METHODS

A. Ionic field

The Nernst-Planck equation (in the following equation) was utilized to investigate the distribution for the ion concentration. The ion concentration depends mainly on the influence of electrophoresis, electroosmosis, and diffusion on electrokinetic ion transportation in a micro-nanofluidic system,

$$\frac{\partial n_k}{\partial t} + \nabla \cdot (-\omega_k z_k n_k \nabla \phi - \nabla \cdot (D_k \nabla n_k)) = \nabla \cdot (n_k u), \quad (1)$$

where $n_k$, $z_k$, $\omega_k$, and $D_k$ are the concentration, the valence, the electrophoresis mobility and the diffusivity coefficient of the $k$th species, respectively, and $\phi$, $u$, and $t$ are the electrical potential, velocity, and time, respectively.

As seen in the following equation, the ion concentration is set to be a constant of 0.1 mol/m$^3$ for the terminal and the head end:

$$c = c_0. \quad (2)$$
The impermeability for the ions is shown when applied to the surfaces including the nanochannel and the microchannel, as shown in the following equation:

\[ n \cdot (-\omega_k n_k \nabla \phi - D_k \nabla n_k + n_k u) = 0. \]  

(3)

B. Electric field

The Poisson equation [Eq. (4)] was adopted to simulate the electrical potential relying mainly on the external voltage and the surface electric charge. The electric field strength is obtained through calculating the gradient of the electric potential, as shown in the second of the following two equations:

\[ \nabla \cdot (\varepsilon_0 \varepsilon_r \nabla \phi) = -\sum_{k=1}^{N} e z_k n_k, \]  

(4)

\[ E = -\nabla \phi, \]  

(5)

where \( \varepsilon_0 \), \( \varepsilon_r \), and \( e \) are the vacuum permittivity, relative permittivity, and elementary charge, respectively.

It can be seen from Eq. (6) that the surface charge for a boundary condition is utilized. The surface charge density including \(-4.0 \times 10^{-4} \text{ C/m}^2\), \(-6.0 \times 10^{-4} \text{ C/m}^2\), and \(-8.0 \times 10^{-4} \text{ C/m}^2\) are exploited.

\[ -n \cdot \varepsilon_0 \varepsilon_r E = \sigma_0. \]  

(6)

The electric potential for a boundary condition is shown in the following equation. The potentials at the head end and the terminal are set to be a constant of 5 V and 0 V, respectively,

\[ \phi = \phi_0. \]  

(7)

C. Flow field

The incompressible Navier-Stokes equations with the continuity equation, which refers to any change in the density of the liquid (which would be extremely small to the point of insignificance), are employed to solve the distribution of the fluid flow, which is shown in the following equations:

\[ \rho_0 (\partial_t u + u \cdot \nabla u) = -\nabla p + \mu \nabla^2 u - \rho_e \nabla \phi, \]  

(8)

\[ \nabla \cdot u = 0, \]  

(9)

where \( \rho_e \), which is expressed as \( \rho_e = \sum_{k=1}^{N} e z_k n_k \) (for \( k = 1, \ldots, N \)), is the net charge density sum of ion species. \( p \), \( \rho_0 \) and \( \mu \) are the pressure, density, and viscosity, respectively.

![FIG. 5](https://example.com/figure5.png)

FIG. 5. Ion concentration distribution at the center-line of the system: the influences of (a) the cross sectional shape, (b) the surface charge, (c) the nanochannel length, and (d) the nanochannel radius on the ion concentrations are demonstrated.
Pressure employed as one boundary condition is set to be a constant of 0 Pa at the head end and the terminal, as seen in the following equation:

\[ P = P_0. \] (10)

A boundary condition of no slip applies to the surfaces including the nanochannel and the microchannel, shown by the following equation:

\[ u = 0. \] (11)

The parameters for numerical simulation are demonstrated in Table I.

III. SETUP FOR NUMERICAL SIMULATION

As seen in Fig. 1(a), two microchannels with a length of 3 μm, a height of 1 μm, and a width of 1 μm, one nanochannel with a length of 0.1 μm–0.5 μm and a critical dimension of 50 nm–150 nm, and three cross sectional shapes including a trapezoid, semicircle, and rectangle are used to form a geometrical model. The position at which the voltage is applied is also shown. Figures 1(b)–1(d) display the local enlarged drawing of a nanochannel including a rectangle, trapezoid, and semicircle. In Figs. 1(c)–1(g) the cross-sectional structure of a rectangle, trapezoid, and semicircle nanochannel is demonstrated. “a” and “L” represent the nanopore radius and nanopore length, respectively. The grid sizes in the nanochannels and near the wall of the microchannels are 5 nm and 50 nm, respectively. The grids in the other regions are comparatively coarse. A different number of grids were employed to obtain results with no change. The software COMSOL 3.5a was utilized to calculate the ion transport process.

IV. RESULTS AND DISCUSSION

A. Electric field

Figure 2 demonstrates the variation in the electric potential along the centerline of the micro-nano interface. Figure 2(a) exhibits the influences of the nanochannel’s cross-section shape on electric potential distribution. For a uniform value of the nanochannel’s cross-section area (2.88 × 10⁻¹⁵ m²) and the surface charge (0.0008 C/m²), the average slope of the potential curve is nearly identical to the variation of the nanochannel’s cross-section shape. Apparently, once the nanochannel size and the surface charge are specified, the surface electric potential is a fixed value. Notably, the electric potential does not depend on the cross sectional shape. Furthermore, with the increase in the surface charge density, the local electric potential or Donnan potential induced by the overlapping of the double electrical layers enhances and brings about a local gradient of the electric potential in the opposite direction. Consequently, as revealed by Fig. 2(b), for a given trapezoidal nanochannel, increasing the value of the surface electric charge causes a slight decrease in the average slope of the potential curve along the micro-nano interface. The direction of the local potential gradient is from nanochannel to microchannel. Figure 2(c) exemplifies that for a given value of surface electric charge, the electric potential distribution in the microchannel’s cross-section is approximately a coincident line, but it tends to be gentler in the nanochannel’s cross-section with the increasing of L. For a longer total length of the micro-nanochannel while applying the electric potential of a constant value to the system, it is immediately evident that the potential curve is flatter due to the conservation law of Poisson’s equation. As shown in Fig. 2(d), one can conclude that for the same value of L, trapezoidal nanochannel, and surface electric charge, the average slope of the potential curve in the micro-nanochannel’s cross-section decreases with the increase in the nanochannel’s cross-sectional area. In Fig. 3, the voltage distribution along with the local enlarged drawing of different nanochannel structures including a rectangle, trapezoid, and semicircle is demonstrated. Furthermore, to verify the accuracy of our
numerical approach, comparisons between the results of this paper and those of the paper presented by Li were implemented. As an example, Fig. 4 demonstrates the influences of the nanochannel width on the average slope of the potential curve; these trends are in excellent agreement with the results of this paper.

B. Ion transport field

Among the main differences between electrokinetic flow through the micro- and nanochannels are concentrations of the positive and negative ions. As previously explained, due to the influence of the nanochannel’s assumed negative surface charge, more cations can pass through the nanochannel; conversely, more anions are enriched in another end of the nanochannel. For a given external voltage, the negative ion concentration largely relies on the EDL (electric double layer) effect. The stronger the EDL field is, the higher is the negative ion concentration in the nanochannel. Any parameter affecting the EDL in the nanochannel influences negative ion concentration. As shown in Fig. 5(a), one can conclude that a higher ion concentration is obtained for a cross sectional shape of the trapezoid. Two acute-angle structures forming in a trapezoid nanochannel intensify the EDL field, thereby promoting ion concentration. The increase of the Donnan potential induced by the EDL field brings about the decrease of the electric potential. This point can be confirmed from a potential distribution of 0–0.25 μm in the nanochannel shown in Fig. 2(a). Alternatively, increasing the value of surface electric charge, as shown in Fig. 5(b), intensifies the Donnan potential in the channel, and, as a consequence, increases the negative ion concentration. The change in the Donnan potential can be proved from the potential distribution wherein the electric potential decreases with the increase in the surface electric charge in a nanochannel of 0–0.25 μm, as shown in Fig. 2(b). It can be observed from Figs. 5(c) and 5(d) that increasing the nanochannel length or decreasing the radius results in a larger negative ion concentration. This is because of the Donnan potential. On the one hand, increasing the nanochannel length enhances the thickness of the Donnan potential. On the other hand, decreasing the radius of the nanochannel improves the ratio of the EDL thickness to the nanochannel’s cross-sectional area and, therefore, boosts the Donnan potential.

From Figs. 5(b) and 5(d), it is evident that increasing the surface electric charge or decreasing the radius brings about a larger concentration of negative ions at the nanochannel exit. This is due to ion polarization and excludes concentration of the co-ions. This phenomenon was achieved in a previous experimental study. Xu et al. demonstrated experimentally the ion polarization and large negative ion concentration phenomenon at the

![FIG. 7](https://example.com/fig7.png)

**FIG. 7.** The velocity field along the center-line of the system: the effects of (a) the cross sectional shape, (b) the surface charge, (c) the nanochannel length, and (d) the nanochannel radius on the velocity are displayed.
A qualitative verification exists between our simulation results and their experimental and simulation results. In Fig. 6, the concentration distribution along with the local enlarged drawing of different nanochannel structures including a rectangle, trapezoid, and semicircle is demonstrated. We recognize that simulation process is transient. The total time for the simulation is 100 s, and the minimum step size is 0.01 s. However, simulated results are steady quickly, which is consistent with the experimental results. The reason should be attributed to the strong electrophoresis effort that resulted from the applied voltage. A weak voltage should be enriched, given a long time.\textsuperscript{26}

C. Fluid field

Figures 7(a), 7(c), and 7(d) clearly show that by increasing the nanochannel length or decreasing the radius or adopting a trapezoid shape, the velocity is also decreased (while the surface charge density is fixed). For the narrow (or long or trapezoid shaped) channels, a local electric potential minimum resulted from the ionic polarization. Moreover, the positive ion concentration at the exit of the nanochannel gave rise to a local electroosmotic flow in the opposite direction and accordingly decreased the x-velocity. As the nanochannel radius increases (or the length decreases or the shape changes from a trapezoid to a rectangle), the local electric potential minimum becomes smaller. Consequently, the x-velocity is higher. The effects of surface electric charge on the x-velocity are exhibited in Fig. 7(b). For a fixed trapezoid shape, length, and radius, strengthening the surface electric charge increases the x-velocity in the nanochannel. In Fig. 8, the velocity distribution along with the local enlarged drawing of different nanochannel structures including a rectangle, trapezoid, and semicircle is demonstrated.

V. CONCLUSION

In this work, the electrokinetic ion transportation in a micro-nanofluidic system is exhibited. Through utilizing the Poisson-Nernst-Planck equations coupled with the Navier-Stokes equation, the influences of the nanochannel geometry, volumic surface charge density, nanochannel length, and nanochannel radius on the electric field, ion transport field, and fluid field are investigated. The theoretical research shows that the potential drop is attributed to the nanochannel’s volume instead of nanochannel geometry. Meanwhile, the EDL effect in a nanochannel depends mainly on an acute-angle structure. As such, two acute-angle structures in a trapezoid nanochannel relative to a right-angle structure in a semicircular or rectangular nanochannel can intensify the EDL field. The study also shows that the velocity in the nanochannel is suppressed by decreasing the volumic surface electric charge, increasing the length, narrowing the radius, and adopting the cross sectional shape of a trapezoid.

ACKNOWLEDGMENTS

This project is supported by the National Natural Science Foundation of China (Grant No. 51505077), the Project Agreement for Science and Technology Development of Jilin Province (Grant No. 20170520099JH), and the Science and Technology Innovation Development Project of Jilin City (Grant Nos. 201750230, 20166013, and 20166012).

REFERENCES

1. A. Barik, Y. Zhang, R. Grassi, B. P. Nadappuram, J. B. Edel, T. Low, S. J. Koester, and S. H. Oh, “Graphene-edge dielectrophoretic tweezers for trapping of biomolecules,” Nat. Commun. 8(1), 1867 (2017).
2. X. C. Yuan, L. Renaud, M. C. Audry, and P. Kleimann, “Electrokinetic biomolecule preconcentration using xurography-based micro-nano-micro fluidic devices,” Anal. Chem. 87(17), 8695–8701 (2015).
J. J. Jiang, X. Y. Lin, D. Ding, and G. W. Diao, "Enzyme-free homogeneous electrochemical biosensor for DNA assay using toehold-triggered strand displacement reaction coupled with host-guest recognition of Fe₃O₄@SiO₂@β-CD nanocomposites," Biosens. Bioelectron. 114, 37–43 (2018).

X. W. Guo, "Fe₃O₄@Au nanoparticles enhanced surface plasmon resonance for ultrasensitive immunoassay," Sens. Actuators, B 205, 276–280 (2014).

Z. Xu, J. Y. Wang, S. L. Hu, J. Q. Lu, C. Liu, and J. S. liu, "Electrokinetic concentrating with a nanofluidic device for magnetic beads-based antigen-antibody immunoassay," Microsyst. Technol. 22(2), 283–286 (2016).

J. P. Fu, P. Mao, and J. Han, "Continuous-flow bioseparation using microfabricated anisotropic nanofluidic sieving structures," Nat. Protoc. 4(11), 1681–1698 (2009).

C. Y. Li, Z. Q. Wu, C. G. Yuan, K. Wang, and X. H. Xia, "Propagation of concentration polarization affecting ions transport in branching nanochannel array," Anal. Chem. 87(16), 8194–8202 (2015).

Q. Pu, J. Yun, H. Temkin, and S. Liu, "Ion-enrichment and ion-depletion effect of nanochannel structures," Nano Lett. 4(6), 1099–1103 (2004).

A. Plecis, R. B. Schoch, and P. Renaud, "Ionic transport phenomena in nanofluidics: Experimental and theoretical study of the exclusion-enrichment effect on a chip," Nano Lett. 5(6), 1147–1155 (2005).

A. Plecis, A. Pallandre, and A. M. Haghiri-Gosnet, "Ionic and mass transport in micro-nanofluidic devices: A matter of volumic surface charge," Lab Chip 11(5), 795–804 (2011).

J. Y. Wang, Z. Xu, Y. K. Li, C. Liu, J. S. Liu, L. Chen, L. Q. Du, and L. D. Wang, "Nanopore density effect of polyacrylamide gel plug on electrokinetic ion enrichment in a micro-nanofluidic chip," Appl. Phys. Lett. 103(4), 043103-1–043103-5 (2013).

R. Schoch, J. Han, and P. Renaud, "Transport phenomena in nanofluidics," Rev. Mod. Phys. 80, 839–883 (2008).

Z. Xu, J. K. Wen, C. Liu, J. S. Liu, L. Q. Du, and L. D. Wang, "Research on forming and application of U-form glass micro-nanofluidic chip with long nanochannels," Microfluid. Nanofluid. 7(3), 423–429 (2009).

Y. Green, S. Shloush, and G. Yossifon, "Effect of geometry on concentration polarization in realistic heterogeneous permeisive systems," Phys. Rev. E 89, 043015-1–043015-9 (2014).

S. Pennathur and J. G. Santiago, "Electrokinetic transport in nanochannels. 1. Theory," Anal. Chem. 77, 6772–6781 (2005).

S. Pennathur and J. G. Santiago, "Electrokinetic transport in nanochannels. 2. Experiments," Anal. Chem. 77, 6782–6789 (2005).