Dispersion control in nano-channel systems
by localized \( \zeta \)-potential variations

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Abstract

Turns and bends, such as an L-turn or a U-turn, in micro and nano-fluidic channels can induce significant dispersion leading to a low efficiency electrophoretic separation process. It has been shown that turn-induced dispersion can be lowered by optimizing the geometry of the turns. In this paper, we propose a new approach for controlling turn-induced dispersion in nano-fluidic channels. The approach is based on the idea of locally controlling the \( \zeta \)-potential at turns and bends. An optimization algorithm was developed to search for the optimal configuration of the \( \zeta \)-potential near turns. Results for an L-turn and a U-turn show that the dispersion can be lowered significantly by a localized \( \zeta \)-potential variation near the turn.

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1. Introduction

There has been a growing interest in developing miniaturized fluidic devices for transport, separation and detection of bio-samples. In many of these devices, capillary electrophoresis is used for sample separation, and electro-osmosis is used for sample transport. In several cases, both these processes occur together. Prior studies have shown that a longer channel can improve the separation efficiency. In applications like lab-on-a-chip where the device size is very small, turns must be introduced to integrate a long channel within the small area of a single chip. However, it has been found that such turns could induce serious dispersion which may negate the effect of using a long channel [1]. Experimental work by Culbertson et al. [1] indicated that the dispersion is influenced by: migration length differences, field strength differences and transverse diffusion in the turn. Many techniques have been proposed to control the excessive dispersion induced by the turn. Culbertson et al. [1] suggested the usage of narrow channels, control of analyte velocity as well as introducing complementary turns.

More recently, Griffiths and Nilson [2] and Molho et al. [3] suggested the development of optimized turns to minimize the dispersion. In both these works, numerical methods were used to find the optimal geometrical configuration of the turns. Experimental results show that such an approach is feasible [3]. However, fabrication of the optimized geometry may not always be possible because of manufacturing as well as other considerations. In this work, we propose to control the turn-induced dispersion by introducing a localized \( \zeta \)-potential variation. In this method, the \( \zeta \)-potential on channel walls near the turn is controlled and the turn geometries are not altered. This approach provides an alternative when an optimized turn geometry is difficult to implement in practice. Though flow control using localized \( \zeta \)-potential variations has been difficult in the past, recent results suggest that it is possible to use such an approach. For example, it was reported in [4] that a localized \( \zeta \)-potential control (through surface patterning) can be employed to produce non-axial flow in micro-channels.

The rest of the paper is outlined as follows: Section 2 describes the mathematical model used for modeling the electrokinetic flow in nano-fluidic systems, Section 3 introduces our proposed method for controlling the dispersion, Section 4 provides details on the two-step control approach used to minimize the particle dispersion, Section 5 shows results on the control of particle dispersion in a U-turn and conclusions are provided in Section 6.
2. Mathematical model

Fluid flow due to electrical potentials, also referred as electroosmotic transport, is described by the Laplace equation, the Poisson–Boltzmann equation and the incompressible Navier–Stokes equations. A detailed description of the electroosmotic transport model can be found in [5]. The model includes:

\[ \nabla^2 \phi = 0 \]  
\[ \nabla^2 \psi = \frac{1}{\kappa_D} \frac{RT}{F} \sinh \left( \frac{F \psi}{RT} \right) \]  
\[ \nabla \cdot \mathbf{u} = 0 \]  
\[ \mu \nabla^2 \mathbf{u} - \nabla p + \mathbf{F} = 0 \]  
\[ \mathbf{F} = \varepsilon \nabla \phi \nabla^2 \psi \]  

The Laplace equation (Eq. (1)) describes the potential in the electrokinetic geometry because of applied potentials and the Poisson–Boltzmann equation (Eq. (2)) describes the potential \((\psi)\) in the device because of the \(\zeta\)-potential at the solution–capillary interface. Eqs. (3) and (4) describe the fluid flow in the device because of the applied and \(\zeta\)-potential. Specifically, Eq. (3) is the incompressible continuity equation and Eq. (4) is the Stokes equation. In Eq. (4), \(\mathbf{F}\) is the body force, the definition of which is given in Eq. (5).

The mathematical model stated in Eqs. (1)–(5) along with the appropriate boundary conditions describes the electroosmotic problem. It is desirable to solve the above equations in three dimensions, however, this can be computationally expensive since the electric field and fluid flow characteristics need to be computed many times during the optimization process. A two-dimensional analysis, assuming that the channel depth is much longer compared to the channel width, can provide much of the fundamental information necessary to understand dispersion. Eqs. (1)–(5) are solved using the numerical algorithms developed in [5].

In some previous works (e.g. [2,3]), a potential flow is assumed and fluid velocity in electroosmotic flow is assumed to be proportional to the gradient of the applied electric field. This has been justified in [6] under several assumptions, of which the most important one may be that the \(\zeta\)-potential in the entire system must be uniform. Such an assumption can be quite stringent in certain practical situations as discussed in [7]. In addition, because we intentionally introduce non-uniform \(\zeta\)-potentials on the wall near turns, a full set of flow and electrokinetic Eqs. (1)–(5) need to be solved to obtain the flow field instead of using the simpler potential flow theory.

Dispersion can be caused by both advection and diffusion [2]. In a nano-diameter channel, diffusion can play an important role in dispersion control as the Peclet number \((Pe = Uw/D, \text{where } U \text{ is the characteristic velocity, } w \text{ the channel width and } D \text{ the diffusivity})\) is typically of the order of 10 (e.g. \(U = 2 \text{ mm/s, } w = 50 \text{ nm and } D = 1.0 \times 10^{-11} \text{ m}^2/\text{s}\)). In this paper, for simplicity, we consider only the dispersion caused by advection and neglect the influence of diffusion on dispersion. The approach can, however, be extended in a straightforward manner to account for diffusion. When diffusion is taken into account, the optimization approach introduced here need not be changed, though the optimal configuration of the \(\zeta\)-potential on the wall might change. The dispersion in the channel is calculated by tracking particles released at the upstream of the turn. The path of these particles is obtained by integrating:

\[ \frac{\partial \mathbf{x}}{\partial t} = \mathbf{u} \]  

where \(\mathbf{u}\) is the velocity computed by solving Eqs. (1)–(5).

Here, we assume that the velocity of the particles is the same as the local fluid velocity.

3. New control strategy: localized \(\zeta\)-potential variation

In nano-diameter channels, turns can induce serious dispersion. Shown in Fig. 1 is the distribution of particles after passing an L-shaped turn. For this case, the channel width is 50 nm and the Debye length used in the simulation is 2 nm. The \(\zeta\)-potential on the channel wall is taken as \(-15 \text{ mV}\). The particles were released at the upstream of the turn with the same position in the \(x\)-direction. It can be seen that a serious dispersion occurs as the particles go through the 90° turn. The dispersion stems from the fact that the particles near the inner channel wall travel a shorter distance compared to the particles near the outer channel wall. The differing velocity of the particles also contributes to the dispersion. An important observation in Fig. 1 is that the particles are no longer in the symmetrical position with respect to the center line of the

![Fig. 1. Distribution of particles after passing the 90° turn.](image)

Position of particles after passing the 90° turn.
channel after they have gone through the L-shaped turn. Note that we have used rectangular turn instead of a radial corner turn in all the examples of this paper. A rectangular turn presents a more difficult case compared to a radial turn for dispersion control because the difference of travel distance between particles near the inner and outer channel wall is larger for a rectangular turn.

One approach to minimize such dispersion is to make the particles travel approximately the same distance as they go through the turn. An alternative approach is to alter the velocity of the particles such that particles traveling longer distances move faster and particles moving shorter distances move slower. A combination of the two approaches can also be employed to minimize the particle dispersion. An example of the first approach is the work described in [2,3], where the geometry of the turn is optimized such that the particles travel approximately the same distance at roughly the same velocity.

We propose a new method in which by varying the $\zeta$-potential at the inner wall of the turn, we can change both the migration path of these particles as well as their velocities without changing the geometry of the turn. By varying the $\zeta$-potential, we change the electric field which in turn alters the migration path and the velocity of the particles. Thus, by controlling the $\zeta$-potential on the inner wall near the turn, the particle dispersion can be minimized.

In this research, we have developed a two-stage control strategy to minimize the particle dispersion. The control scheme is illustrated in Fig. 2 for an L-turn. In the first stage, the $\zeta$-potential near the turn is controlled such that the particles are at a symmetrical position with respect to the center line of the channel after they have passed the turn. In the second stage, the $\zeta$-potential is controlled such that the particle dispersion is minimized. For an L-shaped turn, the second control step implies that the vertical position ($y$-coordinate) of the particles is approximately the same.

Fig. 3 shows the position of the particles after passing the turn when only the first-stage control is employed. It can be seen that the particle profile is almost symmetric with respect to the center line of the channel. However, the particles near the channel wall lag behind the particles in the central portion of channel, indicating that the dispersion is still very high. Such a situation can be improved by employing the second-stage control. Fig. 4 shows the

![Fig. 2. Two-stage control strategy to minimize the particle dispersion.](image)

![Fig. 3. Distribution of particles after passing through the 90° turn. Only first-stage control is enforced. Observe that the particle positions are fairly symmetric about the center line of the channel.](image)

![Fig. 4. Distribution of particles after passing through the 90° turn. Both first- and second-stage controls are enforced. Observe that the particle dispersion is significantly lowered.](image)
position of the particles after passing the turn. Note that the dispersion is much less than that observed in Fig. 1. Even in Fig. 4, the particles very near the wall still lag behind the particles in the central portion of channel. This can be explained by the fact that if a particle is within or near the Debye layer, it has a smaller velocity compared to a particle that is in the central portion of the channel. Even in a straight channel, where there is no bend or a turn, such a dispersion, where the particles in the Debye layer lag behind the particles in the central portion of the channel, is observed. Fig. 5 shows the streamlines near the turn when the two-stage control is applied. It can be seen that though the geometry of the turn is not altered, the migration path of the particles is changed.

4. Approach

The approach used to minimize the particle dispersion is discussed in this section. In particular, the objective functions developed for each of the control steps are described. For the L-shaped channel example discussed in the previous section, for the first control step, where the objective is to make the particle profile symmetric with respect to the center line of the channel, the following objective function is employed:

$$F_1 = \sum_{i=1}^{n} |w_i(y_i - y_{2m+1-i})|$$  \hspace{1cm} (7)

In the development of Eq. (7), 2n particles are assumed to be released from the upstream of the channel. $y_i$ refers to the $y$-coordinate of the $i$th particle after the particle has gone through the turn (see Fig. 2). Note that in Eq. (7), the first particle is assumed to be the particle closest to the lower or the bottom channel wall and the $2n$th particle is the particle closest to the top or the upper channel wall. $w_i$ is the weight attached to each particle. As demonstrated in Fig. 3, minimization of Eq. (7) leads to a symmetric particle profile as the particles go through the turn. The minimization of Eq. (7) can be accomplished by employing standard optimization algorithms [8].

The objective of the second control step is to minimize the dispersion or scatter between the particles. The objective function for the second control step is taken to be:

$$F_2 = \sum_{i=1}^{2n} w_i \left| \frac{y_i - \bar{y}}{2n} \right|^2$$  \hspace{1cm} (8)

where $w_i$ is the weight assigned to each particle; $\bar{y}$ the mean vertical position of all the particles and $y_i$ the $y$-coordinate of the $i$th particle.

Eqs. (7) and (8) can be minimized by treating the $\zeta$-potential at each mesh point on the channel wall as a control parameter. While this may yield the best results, it may not be a very practical situation. Hence, we use the following parameters as control variables to minimize the dispersion in an L-shaped turn:

1. For the first control step, it is assumed that the $\zeta$-potential varies linearly within the control region, i.e. $\zeta$-potential varies linearly on OA and OB (see Fig. 2). The $\zeta$-potential at points A and B is assumed to be $\zeta_0$ ($\zeta_0$ is the known uniform $\zeta$-potential on the channel walls when no control strategy is applied) and the $\zeta$-potential at point O is the unknown. The length of the regions OA and OB is assumed to be the same and the $\zeta$-potential variation on OA and OB is as shown in Fig. 6. The two unknowns to be determined are the $\zeta$-potential at point O and the length of region OA or OB. These unknowns are determined by minimizing Eq. (7).

Fig. 6. Linear $\zeta$-potential distribution is assumed on OA and OB. Positions of points $O$, $A$, $B$ and $C$ are as shown in Fig. 2.
determined by the optimization algorithm are shown in Fig. 7.

2. For the second control step, we assume that the length of the region $BD$ or $B'D'$ is equal to the width of the channel and the $\zeta$-potential is constant on $BD$ or $B'D'$. The unknown in this case is the constant $\zeta$-potential on $BD$ or $B'D'$ and this can be computed by minimizing Eq. (8). We chose the length of $BD$ to be the width of the channel just to keep the approach simple. It is, of course, possible to treat the length of $BD$ also as an unknown. The optimal $\zeta$-potential on $BD$ (and $B'D'$) is determined to be $1.3\zeta_0$. Fig. 8 shows the $\zeta$-potential distribution near the L-turn when the optimal two-stage control strategy is applied.

The results for the L-turn suggest that the $\zeta$-potential need to be controlled only at positions very close to the turn, e.g. a few channel widths of the turn. Fig. 4 suggests that these control strategies are effective in significantly lowering the dispersion.

5. Results and discussion

The two-stage control approach can be applied to minimize dispersion in other electrokinetic geometries,
e.g. a U-turn. Shown in Fig. 9 is a sketch of the control strategy used for a U-turn. The channel width is 50 nm and the Debye length is 2 nm. The $\zeta$-potential on the channel wall is taken as $-15 \text{ mV}$. Similar to an L-turn channel, we have assumed that the $\zeta$-potential distribution on $o-a$ and $o'-b$ is linear and the $\zeta$-potential along $a-o'$ and $b-c$ is constant. In addition, the length of the second-stage control region (line $b-c$ and $b'-c'$ in Fig. 9) is set to be the channel width. Using the algorithm described above, the optimal configuration of the $\zeta$-potential can be found. Fig. 10 shows the dispersion of the particles before the control strategy was applied and Fig. 11 shows the dispersion of particles after the control strategy was enforced. It can be seen that the dispersion has been lowered significantly with the two-step control strategy. Fig. 12 shows the streamlines near a U-shaped turn after the optimal two-stage control is applied. It indicates that though the turn geometry is not altered, the distance traveled by the particles near the inner channel wall and near the outer channel wall is approximately the same.

In the above examples, the turn-induced particle dispersion in a nano-diameter channel can be lowered effectively by controlling the $\zeta$-potential near the turn. Such an approach is also applicable for micro-diameter channels—typically, the $\zeta$-potential variation would be similar to that in a nano-diameter channel. This is because, in the approach presented in this paper, the dispersion is minimized by controlling the velocity field (as demonstrated by the streamlines in Figs. 5 and 12) and for electroosmotic flow the velocity is dependent primarily on the external electric field and the $\zeta$-potential on the channel surface. For example, in a straight channel, the velocity is independent of the channel dimension provided that the Debye length is much smaller compared to the channel width. Recently, Johnson et al. [9] have demonstrated that the dispersion caused by a $90^\circ$ turn can be lowered significantly by laser modification of channel surface near the turn.

One important issue behind the control strategies described here is whether one can manipulate the $\zeta$-potential in the way that the optimization algorithm has suggested? Changing the $\zeta$-potential on the channel walls has been difficult in the past, but recently there has been a lot of work done that makes it possible to change the $\zeta$-potential at walls in a desired way. Various techniques such as altering buffer pH [10], adding buffer additives [11], surface modifications (e.g. coating of channel walls [12] and laser ablation of channel walls [9]) and applying external voltages across the channel wall [13] have been proposed. Of these approaches, surface modification (e.g. coating or laser ablation of the channel walls) and applying external voltages can be used to change the $\zeta$-potential on the walls locally. Flow control by coating the channel wall has been reported recently [4]. Important progress has also been made in controlling the
\( \zeta \)-potential by applying external voltages. For example, it has been demonstrated in [14] that the \( \zeta \)-potential on the channel surface can be controlled by applying only tens of volts across the channel wall.

6. Conclusion

In this paper, a novel technique is introduced to control the dispersion induced by turns and bends in nano-channel systems. In the proposed technique, \( \zeta \)-potential on the wall near the turn is controlled to minimize the dispersion, and the geometry of the turn is not altered. An optimization algorithm has been developed to search for the optimal \( \zeta \)-potential distribution. Our results on dispersion control in an L-turn and a U-turn suggest that:

1. The dispersion caused by the presence of a turn can be lowered significantly by locally altering the \( \zeta \)-potential distribution at the turn.
2. To minimize the dispersion, \( \zeta \)-potential need to be altered only within a few channel widths near the turn.

Though the discussion is focused on nano-channel systems, the technique can be applied to dispersion control in micro-channel systems. In addition, the motion of particles due to diffusion, which is neglected in this paper, can be accounted for in a straightforward manner. When diffusion is taken into account, typically, a different \( \zeta \)-potential distribution is necessary to minimize the particle dispersion.

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References