Effect of charged membrane on the particle motion through a nanopore

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A B S T R A C T
Electrophoretic motion of charged particles through a nanopore located in a membrane is numerically studied. The multi-ion model consisting of mass, charge, and momentum conservation equations is used to solve ionic concentration, velocity, pressure and electric fields. For membrane charged, electroosmotic flow (EOF) is resulted when an external potential is applied. The electric and flow fields suggest that the particle driven by the electrophoretic force may move in a stationary fluid, in a direction opposite to the EOF, or in the same direction as the EOF, depending on the type and magnitude of the membrane charge. Particle suspended in the electrolyte may or may not travel to the pore, depending on the coupled effects between intensified electric field and EOF in the region near the pore. Moreover, charged membrane can modify the current as particles travel through the pore, either decrease or increase as compared with uncharged membrane. Our numerical results show that relative current change is significant if the particle size is comparable to pore size. For smaller particles, relative current change is negligible indicating that it is difficult to detect the small particle from the current change.

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1. Introduction

The Coulter counter devices sort and characterize particles such as cells based on the conductivity change in the system [1]. In traditional Coulter counter, a membrane with certain pore size is placed in a channel, and a voltage bias or a pressure gradient is applied across the channel to move the particle through the pore (Fig. 1(a)). By measuring the electric resistance or the current change, the particle size, charge and concentration can be estimated [2]. The recent experimental studies have shown the feasibility of microscale Coulter counter for counting pollen and PMA particles in microfluidic device [3,4]. Due to the recent advances in nanotechnology, nanoscale fluidic systems can be successfully fabricated in the laboratory. Thus, Coulter counting principle can also be extended to nanoscale fluidic devices for the detection of chemical and biological agents. These devices are referred to as the molecular scale Coulter counter since the detection of molecules such as protein, DNA or RNA is of interest [5].

The fundamental operation principle of Coulter counter relies on the variation of ionic current as the charged particles pass through the pore. The ionic current is affected by many parameters such as externally applied voltage bias [6], size and charge density of particle [7], size and charge density of membrane pore [8], and the bulk electrolyte concentration [9]. Since there are many factors affecting the ionic distribution, better understanding is necessary in order to improve the design of the particle detection/counting device, especially for the molecular scale Coulter counter. Most of the previous Coulter counting studies considered electrically neutral membrane, and the flow field is basically induced by the electroosmotic motion of the particle. One can view this class of problem as the classical Stokes problem in which the particle moves in a stationary fluid [10]. The fluid flow is induced locally, but remains motionless at some distance far from the particle. For charged particles in the unbounded flow field, the particle velocity can be estimated by the force balance between electroosmotic force and Stokes drag. Electrophoretic motion of particle in bounded flow field also received much attention due to its importance in particle manipulation [11,12].

In micro/nanofluidic devices, many dielectric surfaces generally acquire surface charges when they are brought to contact with the electrolyte. Therefore, the membrane in the Coulter counting devices should also be charged. Upon the application of voltage bias across the channel, electroosmotic flow (EOF) will be generated. In contrast to the uncharged membrane, particle moves in a flowing fluid due to the induced EOF. Chang et al. [8] experimentally measured the ionic current during the translocation of DNA through a negatively charged silicon oxide nanopore. Recently, Qian et al. [13] studied the effect of a charged nanotube containing convergent–divergent section on the electrophoretic motion of spherical particles. Although molecular scale particle detection becomes an important area of contemporary research, none of the previous studies analyzed the particle translocation through
charged membrane. In this study, we specifically focus on the membrane charge effect on the particle motion in the nanoscale Coulter counting device. The influence of membrane charge on the flow field and the possibility of particle translocation through the nanopore in a charged membrane are examined using multi-ion model.

### 2. Physical and mathematical models

Following the concept of the Coulter counting, the flow field of interest can be simplified as a large chamber divided by a membrane (with a pore at the center) into two equal compartments (Fig. 1(a)) [3,4]. Upon the application of an electric field through the electrodes placed inside the chamber, particles will move due to the electrophoretic force acting on them. As the particle moves, the fluid motion is induced by the particle motion and a drag force with direction opposite to the electrophoretic force acting on them. While a particle passes through the pore the ionic distributions cause electric current change in the pore. Using this current change, one might detect the size and type of particle. Therefore should be solved simultaneously. After obtaining the fluid flow, ionic and potential distributions, the current density is assumed that both particle and membrane are electrically insulated.

Based on the continuum assumption, the equations governing the ionic distribution, electric potential and the fluid flow are described as follows. The net flux of charged species in the presence of electric field is given by the Nernst–Planck equation,

\[ \vec{j}_i = -D_i \nabla c_i - m_i z_i F \vec{E} \nabla \psi + c_i \vec{u} \]  

where \( \vec{j}_i, D_i, m_i, z_i \) and \( c_i \) are the molar flux, molecular diffusivity, mobility, valence and concentration of the \( i \)th ion in the flow field, respectively. \( \psi \) is the electric potential, \( \vec{u} \) is the velocity of bulk electrolyte and \( F \) is the Faraday constant. The right hand side of Eq. (1) represents the ion transport due to molecular diffusion, electromigration and flow convection. The mass conservation equation for no source (reaction) term can be written as,

\[ \frac{\partial c_i}{\partial t} = -\nabla \cdot \vec{j}_i \]  

Based on the operation of Coulter counting, the electric potential \( \psi \) in the flow field is contributed by the charged surfaces in the flow field and the externally applied voltage. For a charged surface such as the particle or membrane, the induced electric potential \( \psi \) is related to the ionic concentration by Gauss's electrostatic theorem,

\[ \nabla \cdot (\varepsilon \varepsilon_0 \nabla \psi) = -\rho_e = -F \sum_{i=1}^{N} z_i c_i \]  

where \( \varepsilon_0, \varepsilon, \rho_e \) and \( N \) are the permittivity of vacuum, dielectric constant of solvent, charge density and number of species, respectively. Eq. (3) is also known as the Poisson equation. The electric potential \( \phi \) in the flow field contributed by the externally applied voltage is described by the Laplace equation as,

\[ \nabla^2 \phi = 0 \]  

By assuming the electrical potentials in the flow field can be linearly superimposed, the total electric field can then be represented as

\[ \vec{E} = -\nabla \psi = -\nabla (\phi + \psi) \]  

The flow of incompressible electrolyte in the chamber is governed by continuity and Navier–Stokes equations,

\[ \nabla \cdot \vec{u} = 0 \]  

\[ \rho \left( \frac{\partial \vec{u}}{\partial t} + \vec{u} \cdot \nabla \vec{u} \right) = -\nabla p + \mu \nabla^2 \vec{u} + \vec{F}_e \]  

where \( \rho, p \) and \( \mu \) are the fluid density, pressure and viscosity, respectively, and \( \vec{F}_e \) is the electric body force per unit volume. By ignoring the electrostriction and gradient of permittivity in the electric field, the electric body force can be simplified as,

\[ \vec{F}_e = \rho_e \vec{E} \]  

The system of Eqs. (2)–(6) is known as the multi-ion model that describes the ionic distribution, electrical potential distribution and fluid flow. It is noted that these equations are coupled together and therefore should be solved simultaneously. After obtaining the fluid velocity and ionic concentration distributions, the current density in the flow field can be calculated as,

\[ \vec{i} = -A \nabla \psi - F \sum z_i D_i \nabla c_i + F \vec{u} \sum z_i c_i \]  

where \( A = F^2 \sum z_i^2 m_i c_i \) is the bulk conductivity of electrolyte. By integrating Eq. (8), current at any cross section can be obtained.

To complete the mathematical model, boundary conditions for the governing equation are needed to be specified. The boundary conditions for the fluid flow, ionic and potential distributions are given as follows by referring to Fig. 1(b):

![Fig. 1. (a) Principle of Coulter counting device. (b) Physical and computational domain.](image-url)
In above equations, \( \bar{r} \) and \( \hat{n} \) are the unit vector in the tangent and normal directions. It is assumed that the chamber is much larger than the membrane. Hence, the presence of membrane would not affect the conditions at inlet and outlet that are far away from the membrane. Based on the physical domain considered, all the governing equations and boundary conditions are written in a cylindrical coordinate system \((r, \theta, z)\). If the particle motion along the centerline is considered, the electric and flow fields become axisymmetric with respect to the centerline of the chamber.

3. Numerical approach

All the governing equations were solved using the commercial code Comsol 3.3 (Comsol Inc.). The finite element calculations were performed using quadratic triangular elements. Since the accuracy of the numerical solutions strongly depends on the mesh size, refined mesh is necessary in the region near the charged surface in order to capture the subtle changes in the potential, ionic concentration and velocity. Independence of the solutions on the mesh size was carefully studied before reporting the final results. The numerical results show that the solutions become mesh-independent when element number exceeds approximately 6000. Hence, the results presented in this study were for 8000–10,000 elements.

4. Results and discussion

4.1. Numerical parameters and validation

In this study, the chamber size is specified as \( L = 125 \text{ nm} \) and \( B = 40 \text{ nm} \). The membrane is located at \( z = 60 \text{ nm} \) and the pore radius is \( h = 5 \text{ nm} \). These dimensions are taken from the study of Liu et al. [5] in which translocation of a cylindrical particle through a nanopore was studied. The flow field was assumed to be axisymmetric with respect to the centerline of the chamber. To verify the numerical approach, we reproduced existing results [5] for the counter-ion and co-ion distributions around the charged cylindrical particle when it is located at the pore center. The KCl electrolyte with bulk concentration of \( c_0 = 0.01 \text{ M} \), the particle with surface charge density \( \sigma_p = 3.06 \times 10^{-2} \text{ C/m}^2 \), externally applied voltage \( \Delta \phi = \phi_{in} - \phi_{out} = 120 \text{ mV} \), and membrane surface density \( \sigma_m = 0 \), are used in computing the results (Fig. 2). The cylindrical particle has a length of 20 nm and radius of 1 nm with hemispherical ends and the computed velocity is 0.139 m/s. The particle velocity is computed based on the balance of electrophoretic and drag forces acting on the particle in the \( z \)-direction. The electrophoretic force \( (F_E) \) and the drag force \( (F_D) \) are given as,

\[
F_E = \int_S \sigma_p E dS
\]  
\[
F_D = \int_S \mu \left[ \left( \frac{\partial v}{\partial r} + \frac{\partial u}{\partial z} \right) n_r + 2\mu \left( \frac{\partial v}{\partial z} - p \right) n_z \right] dS
\]  

where \( S \) is the particle surface, \( n_r \) and \( n_z \) are the \( r \) - and \( z \) - components of the unit vector, respectively. A good agreement is obtained between the present study and those reported in the study of Liu et al. [5]. Slight difference between the ionic concentrations may be due to the sensitivity of the mesh.

Based on the numerical validation, we extend the computational approach to investigate the effect of membrane charge on the fluid
flow, ionic distribution and particle velocity. In the following results, the sizes of chamber, membrane and pore are kept same as before. The externally applied voltage is remained as $\Delta \phi = 120$ mV and the resulting electric field is in the positive $z$-direction. The particle charge density is fixed as $\sigma_p = 3.06 \times 10^{-2}$ C/m$^2$ and the membrane charge density $\sigma_{m}/\sigma_p$ is varied in the range of $-1.0$–$1.0$. The aqueous KCl solutions with bulk concentration of 0.01 M and 1 M are used as working electrolytes. The corresponding Debye lengths ($\kappa^{-1} = ((\varepsilon \varepsilon_0 RT)/(2c_0 \rho^2))^{1/2}$) for these two concentrations are 3.08 nm and 0.3 nm, respectively, which represent the thick and thin EDL cases.

**4.2. Effect of membrane charge on the electric and flow fields in the absence of particle**

We start our analysis by studying the characteristics of induced potential by the charged membrane. The induced potentials by the membrane charge for the cases with and without the externally applied voltage are shown in Figs. 3 and 4. For $c_0 = 0.01$ M (thick EDL case) and $\sigma_{m}/\sigma_p = -1$ case, as shown in Fig. 3(a), the induced potential is symmetric with respect to membrane if there is no externally applied voltage. The maximum potential which is also known as the zeta potential is found as $-87$ mV. An EDL is formed around the membrane due to the surface charge and ionic redistribution. On the other hand, when an external voltage with $\Delta \phi = 120$ mV is applied, the potential distribution becomes asymmetric with respect to the membrane (Fig. 3(b)). The maximum potential is also increased to $-113$ mV which is comparable with the externally applied voltage. The increase in potential and EDL deformation is obviously due to the ionic redistribution. Since the EDL is formed around the membrane, EOF will be generated due to the interaction between the EDL and externally applied voltage. Noting that the membrane acts like an obstruction and the pore can be viewed as a finite-length circular capillary, the flow field is complicated. The fluid flow alters the ionic distribution and consequently affects the potential distributions at the front and back sides of the membrane. A more detail discussion on the flow field will be given later.

When the bulk electrolyte concentration increases to $c_0 = 1$ M (thin EDL case) as shown in Fig. 4, the potential distributions are about the same for cases with and without externally applied voltage. This is due to the limited variation of ionic distribution in a thin layer around the membrane. It is also found that the maximum induced potential remains about the same value of approximately $-13$ mV for both cases of external electric field. The smaller induced potential for $c_0 = 1$ M case can be explained by the Graheme relation [14]. For monovalent electrolyte, relation between surface charge density, zeta potential and electrolyte concentration is given as:

$$\sigma = \sqrt{8\varepsilon_0 \kappa_b c_0 \sinh(\xi/2k_b T)}$$

where $k_b$, $\xi$ and $e$ are the Boltzmann constant, zeta potential and elementary charge, respectively. It is seen that zeta potential decreases with the increased bulk concentration for a given surface charge density.

From above discussion, it is clear that EOF will be generated when the membrane is charged. The flow field in the chamber is induced by the charged membrane. More detail examinations on
Fig. 5. Effect of membrane charge on the flow and electric fields in the absence of particle. \( c_0 = 0.01 \) M and \( \Delta \Phi = 120 \) mV. The normalized velocity and electric field vectors are used to indicate the flow and electric field directions. Line of zero electric field strength (solid line) in z-direction is used to indicate the size of negative electric field zone. (a) \( \sigma_m/\sigma_f = 1 \). (b) \( \sigma_m/\sigma_f = 0.1 \). (c) \( \sigma_m/\sigma_f = -0.1 \). (d) \( \sigma_m/\sigma_f = -1 \).

the electrical (bottom) and flow (top) fields are given in Figs. 5 and 6 for \( c_0 = 0.01 \) M and 1 M, respectively, for different values of membrane charge density. For the cases of positively charged membrane (Figs. 5(a) and (b), 6(a) and (b)), the fluid flow is in the negative z-direction due to the electric body force being in negative z-direction. For the electric field, there appears a zone with direction opposite to the externally applied electrical field in the region around the membrane in the lower chamber. This zone is termed as the negative electric field zone since its direction is opposite to the externally applied electric field. The size of the negative electric field region can be approximated by using a line having zero electric field strength in z-direction, and it depends on the membrane charge magnitude and the bulk electrolyte concentration. The size of this zone is reduced as the bulk electrolyte concentration is increased. For instance, when the bulk concentration increases from 0.01 M to 1 M, the size of this zone becomes very small and limited to a region close to the membrane. For positive charged membrane, the induced potential is positive and creates an electric field in the direction opposite to the externally applied electric field (negative z-direction) in the lower chamber. This induced potential also creates an electric field in the positive z-direction in the upper chamber. Therefore, the electric field strength is reduced in the lower chamber but is increased in the upper chamber. For the cases of negatively charged membrane (Figs. 5(c) and (d), 6(c) and (d)), the electric and flow results become mirror image of positive membrane case. The zone of negative electric field shifts to the upper chamber with the same sizes as those of positively charged membrane cases. Because of the presence of the zone of negative electric field, the fluid flow which is governed by the electric field becomes complicated. As shown in Fig. 5, recirculation zones can be found in both the lower and upper chambers because of the presence of membrane when \( c_0 \) is 0.01 M. For \( c_0 = 1 \) M case, the flow seems to be less affected by the presence of membrane and no recirculation zones can be found. More detailed character-
Fig. 6. Effect of membrane charge on the flow and electric fields in the absence of particle. $c_0 = 1 \text{ M}$ and $\Delta \phi = 120 \text{ mV}$. The normalized velocity and electric field vectors are used to indicate the flow and electric field directions. Line of zero electric field strength (solid line) in $z$-direction is used to indicate the size negative electric field zone. (a) $\sigma_m/\sigma_p = 1$, (b) $\sigma_m/\sigma_p = 0.1$, (c) $\sigma_m/\sigma_p = -0.1$, (d) $\sigma_m/\sigma_p = -1$.

Fig. 7. Flow field and electric field characteristics of such flow field are presented in Fig. 7 under the conditions of $\sigma_m/\sigma_p = -1$ and $\Delta \phi = 120 \text{ mV}$. In Fig. 7(a), the centerline velocity variations are shown for both $c_0 = 0.01 \text{ M}$ and $1 \text{ M}$ cases. As stated earlier, the flow is caused by the electroosmosis in the region around the membrane, the velocity in the regions far from the membrane would be small as shown in Fig. 7(a). For $c_0 = 0.01 \text{ M}$ case, velocity becomes slightly negative because of the appearance of recirculation zone in the lower chamber as discussed in Fig. 5(d). The flow starts to accelerate when it approaches to the entrance of the pore and reaches a maximum value of $0.095 \text{ m/s}$ at the pore center. After the pore center, the flow is decelerated and approaches to approximately zero velocity in the region far from the membrane. For $c_0 = 1 \text{ M}$ case, a different velocity variation is observed. As shown in Fig. 6(d), there is no recirculation zone present because of weaker electric body force. The flow velocity is approximately zero until it approaches to the region near the membrane. The flow is accelerated and reaches a maximum velocity of $0.044 \text{ m/s}$ at the pore entrance and decelerated to a velocity of $0.042 \text{ m/s}$ at the pore center. After the pore center, flow is accelerated again and reaches a maximum velocity of $0.044 \text{ m/s}$ at the pore exit and then decelerated to zero velocity in the region far from the pore.

The fluid flow characteristics can also be examined from the pressure variations along the centerline as shown in Fig. 7(b). For $c_0 = 0.01 \text{ M}$ case, a pressure rise is resulted due to the presence of the membrane. An adverse pressure gradient is created and therefore the flow is decelerated. The pressure keeps increasing and reaches a maximum value of $45 \text{ kPa}$ at the pore center. This effect is known as the electroosmotic pumping [15]. After the pore center, pressure decreases, and reaches zero pressure in the
Fig. 7. Velocity and pressure variations in the flow field. (a) Velocity along the centerline. (b) Pressure along the centerline. (c) Velocity profiles at the pore center.

region far from the membrane. For \( c_0 = 1 \) M case, a pressure drop is observed and reaches a minimum value of 6 kPa at the pore entrance. Inside the pore, pressure increases due to the electroosmotic pumping and reaches a maximum value of 8 kPa at the pore exit. The pressure variation agrees with the typical EOF involving a microchannel connected to two reservoirs studied by Zhang et al. [16].

The velocity distributions across the nanopore are shown in Fig. 7(c) for different bulk electrolyte concentrations. For thick EDL case \( (c_0 = 0.01 \) M), the velocity profile has parabolic shape. In this case, Debye length and pore size are comparable and EDL overlap effect becomes significant. When EDLs are overlapped, the parabolic velocity profile is resulted [17]. For thin EDL case \( (c_0 = 1 \) M), typical velocity profile in EOF with the adverse pressure gradient in a microscale channel is found.

The bulk electrolyte concentration also affects the potential and ionic distributions at the pore center. The potential and ionic distributions at the pore center for \( c_0 = 0.01 \) M and 1 M are shown in Fig. 8 under the same operating conditions of Fig. 7. As indicated in Fig. 8(a), larger potential can be obtained for lower bulk concentration for a given surface charge density as indicated by Eq. (11). It is noted that the value of potential far away from the charged wall is not zero for the \( c_0 = 0.01 \) M case because of the EDL overlap effect. For the ionic distributions (Fig. 8(b) and (c)), significant differences are also observed. For \( c_0 = 0.01 \) M case, the concentration of the counter-ions (K⁺) is much higher than the co-ions (Cl⁻). Because of the negatively charged surface, the pore attracts large amount of counter-ion in order to balance the charge while expels the co-ions from entering the pore. Therefore, the fluid inside the pore becomes almost uni-polar solution of K⁺ ions [17]. For \( c_0 = 1 \) M case, typical microchannel concentration profiles are obtained for both counter-ions and co-ions.

Besides the electric and flow fields, the current flow is also an important physical quantity. In Coulter counting devices, the current change from a base current as particle passing through the pore is measured and used to characterize the particle. The base current \( I_b \) can be regarded as the current in the flow field in the absence of particle. In Table 1, the base currents as functions of bulk electrolyte concentration and membrane charge magnitude are computed at various chamber locations. The base current at each section is obtained by integrating the current density expressed in Eq.(8) over the cross section area. As shown in Table 1, the currents at locations far away from the pore are approximately identical \((z/L=0.08 \) and \( z/L=0.72)\). This result also indicates the accuracy of the numerical code developed in this study. A slightly smaller base current is obtained at the pore center \((z/L=0.5)\) as compared with those at \( z/L=0.08 \) and 0.72 when membrane charge is high. For \( \sigma_p/\sigma_m = 1 \) and \(-1\), Table 1 shows that the current reduction percentages for

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Fig. 8. Electrical potential and concentration profiles at the pore center. (a) Electrical potential. (b) Concentration for \( c_0 = 1 \text{ M} \). (c) Concentration for \( c_0 = 0.01 \text{ M} \).

Fig. 9. Particle velocity at the pore center as function of \( \sigma_m/\sigma_p \) and particle size. \( \Delta \phi = 120 \text{ mV} \). (a) \( c_0 = 0.01 \text{ M} \). (b) \( c_0 = 1 \text{ M} \).

The \( c_0 = 0.01 \text{ M} \) case are more significant than the \( c_0 = 1 \text{ M} \) case. The current reduction is clearly due to effects of membrane charge and EDL overlap.

Note that the differences in the electric and flow fields are due to the bulk concentration. The effect of the bulk concentration can be represented by the dimensionless Debye length \( \kappa b \) which is the ratio of the pore size to the Debye length. For \( \kappa b \sim O(1) \) (\( c_0 = 0.01 \text{ M} \) case in this study), EDLs are considered to be overlapped. For \( \kappa b \ll 1 \) (\( c_0 = 1 \text{ M} \) case in this study), EDLs are considered to be separated. As discussed above, the EDL overlap has significant effect on the electric field, flow field, ionic distribution and the current flow.

4.3. Effect of membrane charge on the particle velocity and current flow

From the results discussed in Section 4.2, it is realized that the charged membrane induces the fluid flow due to the interaction between EDL around the membrane and the externally applied voltage. The dimensionless Debye length and the presence of membrane are the two main factors affecting the electric and flow fields and ionic distribution. As a charged particle suspended in the flow
Without loss of generality, we consider a positively charged particle suspended in the lower chamber and the externally applied electric field is in the positive $z$-direction. There will be two types of particle motion based on the charge of the membrane. For an uncharged membrane, particle will start moving in a stationary fluid under the electrophoretic force, which will create a fluid motion. On the other hand, for charged membrane, the particle will move in a moving fluid. For the positively charged membrane, particle moves in the direction opposite to the fluid flow. For negatively charged membrane, particle moves in the same direction as that of flow. For these two types of flow, drag force acting on particle is different and therefore the particle electrophoretic velocity would also be different. In addition to the membrane charge effect, an EDL with predominantly counter-ions ($\text{Cl}^-$) will form around the particle since particle is positively charged. For an externally applied electric field in the positive $z$-direction, there will be an EOF generated in the negative $z$-direction around the particle which produces the retardation effect and tends to reduce the particle electrophoretic velocity [18]. Thus, if the membrane is positively charged, particle can only possibly pass through the pore with large electrophoretic force to overcome the drag force and retardation effect. The electrophoretic force can be increased by either increasing the externally applied voltage or the particle charge density. For the negatively charged membrane case, particle can travel to the pore easier as compared with the positively charged membrane case. Whether the particle can pass through the pore to the upper chamber or not still depends on coupled effects on the electric and flow fields due to the presence of particle, membrane charge and narrowed flow passage.

In particle translocation through a pore, the change in current at the pore is the primary parameter of interest. Thus, we focus on the situation when particle travels to the pore center ($z/L = 0.5$). The particle velocity at this particular location can be obtained from the balance of forces acting on it [5]. To have the particle passing through the pore, particle velocity should be always in the positive $z$-direction. Once the particle velocity is determined, the ionic distribution and consequently the current can be obtained.

To demonstrate the current change behavior, we calculated the velocity and current when spherical particle is located at the pore center under the conditions of $\Delta \phi = 120 \text{ mV}$ and $\sigma_p = 3.06 \times 10^{-2} \text{ C/m}^2$. In addition to the effect of membrane charge and bulk concentration, particles with radius $a = 1 \text{ nm}$ and $4 \text{ nm}$ are used to examine the effect of particle size on the particle velocity and current. The calculated results are shown in Figs. 9–11. Fig. 9 indicates that particle velocity is higher when the membrane is negatively charged and lower particle velocity is obtained when membrane is positively charged. Because of larger electrophoretic force, larger particle has higher velocity as compared with that of
smaller particle for both electrolyte concentrations studied. This observation qualitatively agreed with the experimental measurement of Xuan et al. [19] and theoretical study of Qian et al. [13]. Particle velocity will decrease to zero when the membrane charge becomes positive. Physically one may attribute these phenomena to the attraction and repulsion between the charged surfaces. For both positively charged particle and membrane, the repulsion force causes the particle to slow down. However, the positively charge particle is accelerated when the membrane is negatively charged due to attraction. For the $c_0 = 0.01$ M case (Fig. 9(a)), particle velocity decreases to a large extent when membrane is negatively charged. This is because of the zone of negative electric field appeared in the upper chamber becomes stronger as the membrane charge increases. For the $c_0 = 1$ M case shown in Fig. 9(b), the velocity for particle with $a = 4$ nm depends on the membrane charge linearly. The linear dependence of particle velocity can be explained from the classical particle dynamics in a given flow field [20]. Motion of a large particle is dominated by its inertia force and the drag force produced by the fluid flow has little effect on its motion. Therefore, particle velocity is insensitive to the change of fluid flow. In contrast, the particle can respond to the change of local flow field spontaneously and tends to follow the fluid motion when its size is small. The particle velocity is then dependent on the local flow field.

The current densities corresponding to the cases studied in Fig. 9 are presented in Fig. 10. As indicated in Eq. (8), the current density is related to the local electric field, ionic concentration distribution and flow velocity. The local electric field is contributed by the external applied voltage, membrane charge and particle charge. Because of the presence of particle, the pore size is narrowed. Therefore, the electric field is intensified and EDL overlap effect is more significant. The current density is then expected to depend on the coupled effect of these factors. The current densities for $c_0 = 1$ M and $a = 1$ nm are shown in Fig. 10(a) for three membrane charges. In this case, dimensionless Debye length is still much smaller than unity. The current distributions for the three membrane charges studies are almost identical except at the pore surface when $\sigma_m/\sigma_p = -1$. Using the results of Fig. 10(a) as the comparison basis, current density distribution is found to be significantly dependent on the EDL overlap and membrane charge as indicated in cases with $c_0 = 0.01$ M and $a = 4$ nm shown in Fig. 10(b)–(d). As expected, the current density distribution for the weakly positively charged membrane cases is about the same as that of uncharged membrane.

By integrating the current density over the gap between the particle and pore, the current passing through the gap can be obtained. To quantify the effect of the presence of particle, membrane charge and Debye length on the current, the normalized electric current deviation is defined as [5].

$$\chi = \frac{(I - I_b)}{I_b}$$

where $I$ is the current passing through the pore when particle is located at the pore center and $I_b$ is the current passing through the pore without the presence of charged particle as listed in Table 1. The normalized current deviations as functions of particle size, membrane charge and bulk concentration are presented in Fig. 11. It is seen that the normalized current deviation strongly depends on the membrane charge, particle size and bulk electrolyte concentration. For relatively small particle size ($a = 1$ nm), the normalized current deviation is approximately equal to zero indicating that current is unchanged as compared to the base current. Thus, molecular Coulter counter would not be effective in sensing relatively small particle.

For relatively large particle size ($a = 4$ nm), nonzero $\chi$ values are resulted as shown in Fig. 11. This implies that it is more feasible to detect the particle using the current change when particle size is comparable to the pore. Due to the EDL overlap and membrane charge effects, normalized current deviation varies from negative values to positive values as shown in Fig. 11(a) for $c_0 = 0.01$ M case. That is, current is reduced or increased, depending on the membrane charge. For the $c_0 = 1$ M case shown in Fig. 11(b), the current is reduced due to the presence of particle ($a = 4$ nm) and the $\chi$ value is independent with the membrane charge. By examining the current density distributions in Fig. 10(d), it is seen that the area underneath the current density curves are almost identical and therefore result in constant current as particle located at the pore center.

### 4.4. Effect of the particle on the flow field

Finally, the flow field with the presence of charged particle at pore center are presented in Figs. 12 and 13 for $c_0 = 0.01$ M, and compared with those without the particle presented in Figs. 5 and 6. Only the flow fields with $c_0 = 0.01$ M are presented since the EDL overlap effect is more significant. In Figs. 12(a) and 13(a), the membrane is weakly positively charged and therefore the EOF is in negative $z$-direction when there is no charged particle. When positive charged particle is present, it moves in the positive $z$-direction...
brane. A small recirculation zone can also be observed in the pore particle, recirculation zones are formed in the region near the membrane. Because of the presence of Qian et al. [13].

The gap between particle and pore was also observed in the study is small (\(a = 1\) nm). Normalized velocity vectors are used to indicate the flow direction.

which is in the opposite direction of the EOF. For the cases shown in Figs. 12(a) and 13(a), the electrophoretic force is large enough so that particle can move in the positive \(z\)-direction and change the flow direction to be the same as the particle. Due to the interaction between the EOF moving in negative \(z\)-direction and particle motion in positive \(z\)-direction, large recirculation zones are found in the upper and lower chambers and a small recirculation zone is found in the gap between particle and pore when the particle is small (\(a = 1\) nm). The appearance of a small recirculation zone in the gap between particle and pore was also observed in the study of Qian et al. [13].

Figs. 12(b) and 13(b) show the fluid flow induced by a charged particle in an uncharged membrane. Because of the presence of particle, recirculation zones are formed in the region near the membrane. A small recirculation zone can also be observed in the pore when the particle is small. In the case of \(\sigma_m/\sigma_p = -1\), the presence of particle does not affect the flow field very much when particle is small by comparing Figs. 5(d) and 12(c). However, as the particle size is large, as shown in Fig. 13(c), recirculation zones disappear due to the presence of particle.

5. Summary

Fluid flow and particle translocation through a nanopore located in a charged membrane is examined numerically. The electric and flow fields without particle were studied first to understand the effect of the charged membrane. The numerical results show that the electric, flow and ion concentration fields strongly depends on the bulk concentration which is represented by dimensionless Debye length (the ratio of pore radius to the Debye length) in addition to membrane charge and flow geometry. For the electric field, it is found that a zone with electric field opposite to the applied electric field appeared in the region around the charged membrane. The size of this opposite electric field zone depends on the dimensionless Debye length and membrane charge magnitude. Since the EOF is related the electric field, the flow field is complicated. The flow field with thick EDL is different from those with thin EDL because of the EDL overlap effect. By examining the variations of pressure and velocity along the centerline, it is found that the electropumping phenomenon is quite different for thick and thin EDL cases studied here.

For particle translocation through a nanopore, we specifically study the particle velocity and current change when particle is located at the pore center. It is found that particle can easily travel to the pore center when the membrane has opposite charge sign to the particle. The particle velocity increased with the increase in particle size. On the other hand, for same polarity of particle and membrane, a particle can only travel to the pore center when membrane is slightly charged.

The electric current through the pore is calculated to quantify the relative current change. The effects of membrane charge, bulk electrolyte concentration and particle size on the relative current change are studied. It is found that the charged membrane can enhance the current, either decrease or increase, when particle is located at the pore center. For a relatively small particle, it is found that the current deviation is approximately equal to zero indicating that it is difficult to detect a small particle using the relative current change. For a particle size comparable to the pore size, the current deviation is different from zero indicating that it is more feasible to detect the large particles using the current change.

References