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Charged particle separation by an electrically tunable nanoporous membrane

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Abstract
We study the applicability of an electrically tunable nanoporous semiconductor membrane for the separation of nanoparticles by charge. We show that this type of membrane can overcome one of the major shortcomings of nanoporous membrane applications for particle separation: the compromise between membrane selectivity and permeability. The computational model that we have developed describes the electrostatic potential distribution within the system and tracks the movement of the filtered particle using Brownian dynamics while taking into consideration effects from dielectrophoresis, fluid flow, and electric potentials. We found that for our specific pore geometry, the dielectrophoresis plays a negligible role in the particle dynamics. By comparing the results for charged and uncharged particles, we show that for the optimal combination of applied electrolyte and membrane biases the same membrane can effectively separate same-sized particles based on charge with a difference of up to 3 times in membrane permeability.

Keywords: nanoparticle, semiconductor, Brownian dynamics, electro-osmotic, nanopore, separation, dielectrophoresis

(Some figures may appear in colour only in the online journal)

1. Introduction

In recent years the range of nanopore applications has increased due to the development of more sophisticated fabrication techniques [1–7]. Some of these applications have an extensive impact in medical research areas such as dialysis, protein filtration, pathogen isolation, cell harvesting, biosensing, and drug delivery [8, 9]. The nanoporous membranes can be made from different types of materials, such as semiconductors or dielectrics [1, 2]. Compared with biological membranes, synthetic membranes have superior stability in denaturing agents and customizable parameters such as membrane thickness, pore diameter, and pore geometry. Nevertheless, like any new field of science, the application of these membranes to filtering is confronted with challenges, and at times, unexpected observations.

Equipped with powerful computational resources today, theoretical studies through numerical simulations offer a comprehensive approach to studying such phenomena. Molecular dynamics can provide useful insights in particle–pore interactions at an atomistic level, such as the insights obtained from the pioneering work of Gracheval et al [10]. These data can be applied to coarse-grained models that use Brownian dynamics to obtain statistical results similar to those observed in actual experiments. In this way, computational models can provide practical recommendations for modifying the membrane structure or experimental conditions.

Recent experiments resulted in a better understanding of the biomolecules dynamics in nanoscale systems. In an earlier work [11] a metal nanoporous membrane with a pore radius as small as 0.8 nm demonstrated the selectivity of different charged particles, or selectivity of different sized particles [12]. In one [13] of the experimental studies the membranes made of nanoporous crystalline silicon showed excellent results in separating nanoparticles with sizes ranging from 4 to 160 nm. In another experimental study [14], it was shown that the major factors affecting the translocation process of proteins through silicon nitride nanopores are diffusion, electrophoresis, and
electro-osmosis. By altering the experimental setup, each of these factors can aid in the translocation process or hinder it.

The presented work is motivated by the possibility of separating differently charged proteins with a very specific type of membrane: the electrically tunable semiconductor membrane. Our simulated membrane is made of heavily n-doped silicon (n-Si) material. The n-Si membrane allows us to apply electric bias to the membrane which causes variations in the electric potential landscape within the nanopore that affects the motion of a charged nanoparticle through it.

This paper is organized as follows. Section 2 details our computational approach. The results of nanoparticles simulations for different biases applied to the n-Si membrane are presented and discussed in section 3. Finally, section 4 contains a brief summary of this work and concluding remarks.

2. Computational model and methods

A schematic of the simulated structure is shown in figure 1. It is a system comprised of n-doped silicon membrane of thickness $L = 260 \, \text{Å}$ with cylindrical nanopore in it. The membrane is immersed in KCl electrolyte solution. The bulk concentration of the solution is the same for all simulations, $c_{\text{KCl}} = 0.1 \, \text{M}$, which corresponds to the Debye screening length of $L_D = \sqrt{2e^2 c_{\text{KCl}} \varepsilon_0 \varepsilon_R / k_B T} \approx 9.6 \, \text{Å}$, where $\varepsilon_R = \varepsilon_0 \varepsilon_\infty$ and $\varepsilon_\infty = 8.85 \times 10^{-12} \, \text{F m}^{-1}$ and $\varepsilon_\infty = 78$ are the permittivity of free space and relative permittivity of KCl solution, respectively, $k_B$ is the Boltzmann constant, $T = 300 \, \text{K}$ is temperature, and $N_A$ is Avogadro’s number.

The dynamics of a particle translocation is controlled by applied electrolyte bias ($V_e$) and the applied membrane bias ($V_m$). For this study we have simulated different electrolyte and membrane biases $V_e = 0$, 25 mV and 100 mV, and $V_m = -1 \, \text{V}$, $-0.2$ and $1 \, \text{V}$. The studied nanoparticles have charge $q = -1e$ or $q = 0e$ (where $e$ is the positive elementary charge) with radius $R_{\text{np}}$ ranging from 4 to 10 Å. The model is set up to have two main steps of calculation: (i) the solving for the electrostatic potential distribution in the system through the Poisson–Nernst–Plank (PNP) approach, and (ii) the tracking of the position of the nanoparticle through Brownian dynamics (BD).

The continuum PNP approach is applied to obtain the electric potential distribution in the membrane and electrolyte [15, 16]. This is done by solving the Poisson equation:

$$\nabla \cdot \left[ \varepsilon(\vec{r}) \nabla \phi(\vec{r}) \right] = -\rho(\vec{r}), \quad \text{(1)}$$

together with the steady-state Nernst–Plank equations [15]:

$$\nabla \cdot \left[ \mu_i C_i \nabla \phi + z_i D_i \nabla C_i \right] = 0, \quad \text{(2)}$$

where $i = [\text{K}^+, \text{Cl}^-]$, to obtain the local concentrations of potassium, $C_{\text{K}^+}(\vec{r})$, and chloride ions, $C_{\text{Cl}^-}(\vec{r})$, $\mu_i$ is the mobility of the $i$th species, $D_i = \mu_i k_B T / e$, and $z_i = 1$ or $-1$ based on the charge of the ion.

The charge density $\rho(\vec{r})$ in the Poisson equation has contributions from the charge in the electrolyte, $\rho_e(\vec{r})$, and in the membrane, $\rho_m(\vec{r})$, given by:

$$\rho_m(\vec{r}) = e \left[ N_{\text{D}}(\vec{r}) - N(\vec{r}) - N_{\text{surf}}(\vec{r}) \right], \quad \text{(4)}$$

where $N(\vec{r})$ is the concentration of electrons and $N_{\text{D}}(\vec{r}) = 2 \times 10^{20} \, \text{cm}^{-3}$ the density of the donors in the semiconductor regions [17], $N_{\text{surf}}(\vec{r})$ represents negative surface charge on the membrane (in the SiO$_2$ layer) with a value of $4 \times 10^{20} \, \text{cm}^{-3}$. The electrons in the semiconductor region and the ions in the electrolyte regions obey Fermi–Dirac and Boltzmann statistics [18], respectively. Other details of the model are discussed elsewhere [19–21].

The nanoparticle is simulated as a rigid collection of beads, as shown in figure 1. The distance between centers of adjacent beads is 3 Å. To initiate translocation the particle is placed at a distance so that the center of mass is at least 20 Å away from the pore entrance ($z = 260 \, \text{Å}$, see figure 1). There is a confining cylinder of radius 40 Å and height 100 Å over the pore entrance which precludes the particle’s escape away from the pore during simulation. A particle in this volume corresponds to the bulk particle concentration of $\sim 3 \, \text{mM}$. The confinement ensures that the particle does not drift away from the nanopore. The movement of the nanoparticle through the system can be tracked solely by the movement of its center of mass (cm) due the rigid body composition.

Figure 1. (a) Schematics of the simulated structure (not to scale). The reference axes are as shown at the bottom center of the nanopore. The membrane has a thickness of $L = 260 \, \text{Å}$, the nanopore radius $R_{\text{pore}} = 20 \, \text{Å}$. There is a thin layer of SiO$_2$ of 8 Å that coats the surface of the solid state membrane. There is also the applied electrolyte bias $V_e$ and the applied membrane bias $V_m$ as shown. A cylindrical enclosure of radius 40 Å and height 100 Å above the pore center has a particle of radius of 10 Å that is about to enter the nanopore. (b) From left to right, particles simulated of radius 4 Å (7 beads), 6 Å (33 beads), 8 Å (81 beads) and 10 Å (171 beads).
Within the Brownian dynamics approach [22], the position of the nanoparticle center of mass, \( \mathbf{r}_{cm} \), at time \( t \), is given as

\[
\mathbf{r}_{cm}(t) = \mathbf{r}_{cm}(t - \delta t) + v_{\text{EOF}}(R_{xy}) \delta t - \nabla U[\mathbf{r}(t - \delta t)] \frac{\delta t}{\xi} + \sqrt{\frac{6 \delta t k_B T}{\xi}} \mathbf{\dot{u}},
\]

where the stochastic contribution due to the last term is responsible for the random movement of the nanoparticle. The three-dimensional unit vector \( \mathbf{\dot{u}} \) has components uniformly distributed in the interval \([-1, 1] \). The drag coefficient \( \xi \) is calculated using the Stokes formula: \( \xi = 6 \pi \eta R_{np} \) [23], where \( \eta = 10^{-3} \) Pa s is the viscosity for the solution. At each time step the position of each bead, \( \mathbf{r}_i \), is updated as \( \mathbf{r}_i = \mathbf{r}_{cm} + \mathbf{\lambda}_i \), where \( \mathbf{\lambda}_i \) is the position vector of the bead with respect to the center of mass, \( i = 1 \ldots N_b \), where \( N_b \) is the number of beads which varies according to the nanoparticle radius. Other parameters, such as temperature \( T \) and time step \( \delta t = 0.5 \) ps, are kept constant for all simulations.

The second term on the right hand side of equation (6) is the contribution from the electro-osmotic fluid flow. In the presence of an external electric field the mobile ions will move, and due to viscosity of the solution, this will result in the movement of the fluid. To fully describe the fluid velocity in the pore requires solving Navier–Stokes equations coupled with the electrical force that depends on the spatial distribution of charges within the pore [24, 25]. In the Debye approximation, which is valid for when \( L_D \ll R_{pore} \) [26], the fluid velocity \( v_{\text{EOF}} \) inside the pore is given by [27]

\[
v_{\text{EOF}}(R_{xy}) = \frac{\epsilon_s \Phi_{+(-)} V_c}{\eta L} \left[ 1 - \frac{I_0(R_{xy}/L_D)}{I_0(R_{pore}/L_D)} \right],
\]

where \( R_{xy} \) is the radial distance from the center of the pore to \( \mathbf{r}_{cm} \), \( \Phi_{+(-)} \) is the electric potential difference between the pore center and the membrane surface (see figure 3), \( I_0 \) is the zero order modified Bessel function of the first kind [28].

1. Due to the inhomogeneous charge distribution in the electrolyte inside the nanopore, there is also radial pressure \( P_r = \frac{\epsilon_s \Phi_{+(-)} k_B T}{2 \delta r} \) directed towards the pore’s center with the maximum value of \( \sim 5 \times 10^{-3} \) pN Å\(^{-2} \) on the surface. This pressure results in the effective narrowing of the pore cross-section which should affect the waiting times. However, since this process does not depend on the nanoparticle’s charge, its effect was neglected in the current model.

2. We also neglected the effect of the fluid flow outside the pore in our calculations. When the particle is in the vicinity of the pore, its motion is affected by the viscous drag force exerted by the fluid flow outside the pore which creates additional energy barrier/well repelling/attracting particle from/to the pore’s opening. Within the irrotational approximation [23], we can estimate the height of the energy barrier (or depth of the well) by the change in the velocity potential, \( \psi \), as \( \Delta U = \xi \psi \) where \( \psi \) is the velocity potential at the pore opening (\( z = L \)). To find \( \psi \), we will assume that fluid velocity is constant across the pore cross-section and equal to the average value over the pore’s cross-section, \( \bar{v} = 2 R_{pore}^2 \int_0^{R_{pore}} v_{\text{EOF}}(R_{xy}) R_{xy} dR_{xy} \). Then, the problem of finding the corresponding velocity potential becomes

\[
\psi = \int_0^z \bar{v} \eta d\bar{z},
\]

where the electrostatic potential profiles calculated as described in section 2 are shown in figures 2 and 3 along the z axis for \( V_c = 0.2 \) V and \( 1 \) V. They demonstrate the combined effects of the applied electrolyte bias, applied membrane bias, doping, membrane surface charge, and the electrolyte concentration. Analogous to calculating the electrostatic potential of the uniformly charged disc. Assuming that the dominant contribution comes from the motion along the central axis of the pore, we can write that \( \psi(z) = \frac{\xi L_D}{2 R_{pore}^2} (z - L)^2 + R_{pore}^2 (z - L) \), \( z > L \), so that \( \Delta U = \xi \psi \). (Note in passing that away from the pore’s entrance, \( z \to -\infty \), \( \psi \approx \frac{\xi L_D}{2 R_{pore}^2} (2z) \) so that \( v_{\text{EOF}} = -\nabla \psi \approx \frac{\xi L_D}{2 R_{pore}^2} (2z^2) \) as expected [27]). To see the effect of \( \Delta U \) on the particle’s dynamics, we compare it with the temperature, and for our structure parameters and considered nanoparticle size range, we find that the maximum \( \Delta U/(k_\text{B} T) \approx 0.24 \), so that \( \Delta U \) plays little role in particle’s motion and waiting times values.

The third term in equation (6) is the potential energy \( U(\mathbf{r}_i) \) which has three contributions:

\[
U(\mathbf{r}_i) = U_m(\mathbf{r}_i) + U_{\text{dep}}(\mathbf{r}_i) + q \phi(\mathbf{r}_i).
\]

The first contribution in equation (8) is the short-range Lennard-Jones (LJ) interaction energy between the particle and the membrane surface given by

\[
U_m(\mathbf{r}_i) = \epsilon_b \sum_{i} \left[ \left( \frac{\sigma_m}{d_i} \right)^{12} - 2 \left( \frac{\sigma_m}{d_i} \right)^6 \right],
\]

where \( d_i \) is the distance between the ith bead and the nearest point on the membrane surface [22, 29], \( \epsilon_b = 0.1 \) kcal mol\(^{-1} \) and \( \sigma_m = 2.5 \) Å are the interaction strength and LJ equilibrium radius, respectively.

The second contribution equation (8) originates from the dielectrophoretic force due to the electric field in the system [30]

\[
U_{\text{dep}} = -2\pi \epsilon_s R_{np}^3 K_{\text{CM}} \bar{E}^2,
\]

where \( \bar{E} = -\nabla \phi \) is the electric field, \( K_{\text{CM}} \) is the Clausius–Mossotti factor. Since the conductivity of the particle is usually much smaller than that of the solution [31–34], we set \( K_{\text{CM}} = -0.5 \).

The third contribution in equation (8) comes from the external electric energy \( \phi(\mathbf{r}_i) \) with the electric potential \( \phi \) calculated from the self-consistent solution of PNP (equations (1) and (2)).

For each set of parameters \( (V_c, V_m, q, R_{np}) \) studied, there were at least 10\(^3 \) simulations performed. For each simulation we recorded the particle waiting time, \( \tau_w \), and translocation time, \( \tau_t \). The waiting time is the time spent by the particle from the moment it is first placed above the pore entrance (at \( z = 260 \) Å) until the onset of the first successful translocation. Translocation time is the time taken for the particle to successfully move from the pore entrance to the pore exit (at \( z = 0 \) Å).

3. Results and Discussion

3.1. Electrostatic potential

The electrostatic potential profiles calculated as described in section 2 are shown in figures 2 and 3 along the z and x axis for \( V_c = 0.25 \) mV and 100 mV at membrane biases \( V_m = -1 \), \( -0.2 \), and 1 V. They demonstrate the combined effects of the applied electrolyte bias, applied membrane bias, doping, membrane surface charge, and the electrolyte concentration. Analogous to calculating the electrostatic potential of the uniformly charged disc. Assuming that the dominant contribution comes from the motion along the central axis of the pore, we can write that \( \psi(z) = \frac{\xi L_D}{2 R_{pore}^2} (z - L)^2 + R_{pore}^2 (z - L) \), \( z > L \), so that \( \Delta U = \xi \psi \). (Note in passing that away from the pore’s entrance, \( z \to -\infty \), \( \psi \approx \frac{\xi L_D}{2 R_{pore}^2} (2z) \) so that \( v_{\text{EOF}} = -\nabla \psi \approx \frac{\xi L_D}{2 R_{pore}^2} (2z^2) \) as expected [27]). To see the effect of \( \Delta U \) on the particle’s dynamics, we compare it with the temperature, and for our structure parameters and considered nanoparticle size range, we find that the maximum \( \Delta U/(k_\text{B} T) \approx 0.24 \), so that \( \Delta U \) plays little role in particle’s motion and waiting times values.
Figure 2. The electrostatic potential profile $\phi(\vec{r})$ through the center of the pore along the $z$-axis (at $x = y = 0$ Å) when $V_e = 0$ for (A) $V_m = 1$ V, (B) $V_m = -0.2$ V and (C) $V_m = -1$ V. The dotted vertical lines indicate the pore boundaries. $V_{+(-)}$ shows the height (depth) of the potential barrier (well). (b) Same as in (a) but for $V_e = 100$ mV (D, E, and F) and for $V_e = 25$ mV (G, H, and I).

When there is no applied electrolyte bias $V_e$, there is a distinct potential barrier (well) of height (depth) $V_{+(-)} = 21(-19)$ mV for membrane bias $V_m = 1(-1)$ V as shown in figure 2(a). The potential rises (falls) around the pore entrance and falls (rises) back to the bulk potential of the solution around the pore exit. For comparison, we have also computed the electrostatic potential for when $V_m = -0.2$ V (curve (B) in figure 2(a)) showing an almost flat profile within the pore. The magnitude of the slight potential variation for this $V_m$ at the pore entrance and exit is about $3$ mV $\ll k_B T = 25$ meV which is insignificant for particle dynamics. Thus, we regard the results for this case as results for a 'flat' pore potential.

With a non-zero applied bias $V_e$, the potential profiles show a steady increase from the pore entrance to the exit (figure 2(b)), however, the remnants of the characteristic well/barrier which was observed for $V_e = 0$ can still be seen. Depending on the magnitude of $V_e$, either the membrane bias or the electrolyte bias will have a dominating influence on the potential variation within the pore. When the applied bias $V_e = 25$ mV (dashed lines in figure 2(b)), there is very little potential difference between the pore entrance and the exit; also the height of the potential barrier is comparable to the height when $V_e = 0$. When $V_e = 100$ mV (solid lines in figure 2(b)), the potential variation along the pore is affected more by the electrolyte bias than by the membrane bias. This is observed from the larger potential variation along the $z$ direction as compared to the variation in the radial direction. When $V_m = 1(-1)$ V, the potential around the pore entrance rapidly increases (decreases). In the case of $V_m = -0.2$ V the potential profile exhibits an almost linear variation along the pore for both $V_e = 100$ mV (curve (E) in figure 2(b)) and $V_e = 25$ mV (curve (8) in figure 2(b)).

The potential profiles along the $x$ axis for $V_e = 0$ are shown in figure 3(a). The potential stays almost flat when $V_m = -0.2$ V, increases when $V_m = 1$ V or decreases when $V_m = -1$ V towards the membrane. This potential variation, $\phi_{+(-)} = 38(-34)$ mV, is one of the primary factors affecting fluid flow in the pore and can result in either steering a charged particle to or from the pore exit due to the direction of the arising electro-osmotic flow (see equation (7)). Figure 3(b) shows the potential profiles for when $V_e$ is applied. The presence of $V_e$ shifts these potential profiles in accordance

![Figure 3](image-url)
with the value of the applied electrolyte bias but preserves their general shape.

The complexity of the potential distribution in our system can be seen in greater detail in figure 4 for the case of $V_c = 100$ mV and (a) $V_m = -1$ V and (b) $V_m = 1$ V.

3.2. Nanoparticle dynamics

The efficiency of a membrane for particle separation is usually characterized by the membrane selectivity and permeability, or their inverse values—membrane sieving factor and membrane resistance [35], respectively. The sieving factor can be obtained by comparing the particle concentration in the cis region (see figure 1), and the particle concentration in the trans region, which was initially empty. This factor is specific to each particle species and essentially indicates how selective the membrane is to these species. The membrane resistance measures how easily the particles can enter the pore and how quickly they permeate through the membrane. A detailed formulation and analysis of these two factors can be found elsewhere [36]. Intuitively, one can argue that both of these factors depend on the waiting time of the particle $\tau_w$ [35, 36], and that the larger the difference in $\tau_w$ between charged and uncharged particles, the better the device at separating them while larger values of $\tau_w$ indicate lower permeability (higher resistivity). The correlation between $\tau_w$ and permeability of membrane is observed in this work for differently charged particles. For this purpose, in our work we focus on an analysis of membrane permeability, that is, we analyze the waiting time for the particles.

For all particles, we have performed simulations with and without the dielectrophoretic force term in the Langevin equation (equation (6)) and found that the changes in the waiting and translocation times are well within statistical variation, even for the particle of charge $q = 0 e$ when the motion is unaffected by the electric force $qE$ which always has a component along the z direction. This leads us to believe that the dielectrophoretic force does not play a significant role in particle dynamics for our particular pore geometry and considered particle parameters. This is understandable since the dielectrophoretic force calculated from $U_{\text{dep}}$ depends on the gradient of the electric field squared (see equations (6) and (10)) so that at every time step the resulting force would change its direction. For example, when the particle moves from $x = -5$ Å to $x = 5$ Å along the pore, the average dielectrophoretic force would be virtually canceled out resulting in very little contribution to the net particle displacement. Another factor is that this force is only significant near the entrance/exit of the pore where there is a strong variation in the electric field, but not in the pore nor in the cis region where the particle spends most of its time.

We have also performed simulations with and without the electro-osmotic flow term ($\nu_{\text{EOF}} = 0$ and $\nu_{\text{EOF}} \neq 0$) in the Langevin equation. We shall first look at the waiting and translocation times without this flow.

3.2.1. Zero electro-osmotic flow: $\nu_{\text{EOF}} = 0$. When the electrolyte bias is not present, $V_c = 0$, the electrostatic potential variation in our system is created only by the membrane under the applied membrane bias $V_m$ (see figures 2(a) and 3(a)). For a charged particle, this potential variation can either facilitate or hinder its entrance to the pore, hence affecting the waiting time. The waiting time versus particle radius for this $V_c$ is shown in figure 5(a) where negatively charged particles in the presence $V_c = 1$ V the rise in potential at the pore entrance makes it more feasible for the particle to enter, which in turn results in a shorter waiting time. On the other hand, for $V_m = -1$ V the decrease in potential is unfavorable for the negatively charged particle, so that it is more difficult for the particle to enter, and the waiting time is longer. For $V_m = -0.2$ V the results of charged particles are almost identical to those of uncharged particles, meaning that the potential has no effect on the waiting time of the charged particles since the potential is effectively flat in this case. The uncharged particles the potential variation is expected to have no effect on their waiting time. Our results concur with this expectation as the waiting times for all uncharged particles (dashed lines in figure 5(a)) are practically independent of $V_m$.

When the electrolyte bias is applied, $V_c = 25$ mV, the resulting electric field is directed in the positive z direction and pushes the negatively charged particle in the opposite direction, thus favoring particle translocation through the pore and a
Figure 5. Waiting time of different size charged particles (solid lines) and uncharged particles (dashed lines) in the presence of $V_m = 1$ V (circles), $V_m = -0.2$ V (triangles) and $V_m = -1$ V (squares) at different electrolyte biases: (a) $V_c = 0$, (b) $V_c = 25$ mV, (c) $V_c = 100$ mV. The insets are the probability distribution of translocation time of a particular case when $R_{np} = 10$ Å and $V_m = -1$ V for charged and uncharged particles.

shorter waiting time. This effect can be observed in the shifted solid lines (corresponding to $q = -1e$) of figure 5(b) towards the shorter times as compared to the case with $V_c = 0$ in figure 5(a). For the uncharged particles the electric field does not affect their dynamics, as such, the waiting time remains the same [the dashed lines in figure 5(b) are unshifted]. By increasing the electrolyte bias further to 100 mV, the stronger electric field pushes the particle with a greater force and in turn even shorter waiting times are observed (the solid lines in figure 5(c) are shifted to the smaller values).

Another clear trend in figure 5 is the increase in the waiting time due to increase in particle radius. This can be explained by considering pure geometrical considerations. For particle to enter the pore its center of mass must be positioned within a specific area just above the pore. This area is determined by $\pi (R_{pore} - R_{np})^2$. As the particle radius $R_{np}$ increases, this area decreases making entrance more difficult and resulting in longer waiting time.

The translocation times at different $V_c$ differ very slightly from the case of $V_c = 0$ and agree nicely with the calculated values of the unconditional mean first passage time [37]: $\tau_{nf} = L^2/6D$, where $D = k_B T/\xi$. In all simulated cases the translocation times for negatively charged particles at $V_m = 1$ V are slightly larger than for others as shown in figure 6 which is a result of the negatively charged particles being attracted towards the positive potential on the pore surface. This difference in translocation time due to attraction towards the pore wall has also been observed in previous work [29].

As for the translocation times in other cases, these values are so close to each other that it is difficult to consider any other phenomena besides statistical variation (note the wide spread of histograms in the inset in figure 6).

The results so far indicate that when no fluid flow is considered, the difference in the waiting times between charged and uncharged particles becomes larger as $V_c$ is increased. For $V_c = 0$, the ratio of $\tau_w$ for charged to uncharged particles is 2 to 1 for $V_m = -1$ V, and 1 to 2 for $V_m = 1$ V. The membrane with $V_m = 1$ V and $V_c = 100$ mV would seem to be the most ideal choice for separation as the waiting time ratio for charged to uncharged particles is $\sim 1\text{--}8$ for the same $R_{np}$.

3.2.2. Non-zero electro-osmotic flow: $v_{EOF} \neq 0$. The effect of the membrane bias $V_m$ becomes even more pronounced when the fluid flow is included in our simulations since the magnitude and the sign of $\Phi_{+(-)}$ depend on $V_m$ and as such, the particle can either be pushed towards or away from the pore by the fluid flow in addition to the electrostatic repulsion or attraction.

In figure 7, the effect of $V_m$ on particle dynamics can be seen as the particle makes multiple unsuccessful ‘attempts’
before a successful translocation for the $V_m = -1 \text{ V}$. In this case $\overline{V_{EOF}}$ is oriented oppositely to the particle translocation direction, thus pushing the particle away from the pore. The opposing drag force due to the electro-osmotic flow hinders particle translocation but is not strong enough to completely overcome the forward force from the electric field, so that translocation is still possible. For a particle in the presence of positive $V_m$ (see inset in figure 7) the translocation event occurs almost immediately, showing that the combined effect from $\overline{V_{EOF}}$ and $V_c$ may even overcome the effect from random movement (free diffusion).

There are four major changes in the behavior of the waiting times versus $R_{np}$ with the inclusion of the fluid flow (see figure 8). First, the waiting times $\tau_w$ of uncharged particles in different $V_m$ are no longer close in values as seen in the clearly separated dashed lines of figure 8 compared to figure 5. This is because $\overline{V_{EOF}}$ depends on $\Phi$ and not on the particle’s charge. In figures 8(a) and (b) for $V_m = -0.2 \text{ V}$, $\Phi \simeq 0$, and thus the results are unchanged. Second, the waiting times $\tau_w$ of both charged and uncharged particles are much shorter for $V_m = 1 \text{ V}$: in this case $\Phi = 38 \text{ mV}$, and along with the applied electrolyte bias this creates a fluid flow towards the pore exit which greatly favors the entering of the particle thus decreasing particle’s waiting times. Third, $\tau_w$ of both charged and uncharged particles are much longer for $V_m = -1 \text{ V}$: here, $\Phi = -34 \text{ mV}$ resulting in an opposing flow which makes particle entrance very unfavorable. Fourth, $\tau_w$ shows a much greater dependence on the magnitude of $V_c$: when $V_c = 25 \text{ mV}$, the waiting times show similar trends to that of when $\overline{V_{EOF}} = 0$, but when $V_c = 100 \text{ mV}$, there is a drastic increase in the waiting times as the particle size increases (by two orders of magnitude for $R_{np} = 10 \text{ Å}$). This is mainly due to the increased difficulty for the particle to reposition itself for entrance in the presence of an opposing fluid flow pushing it away from the pore.

From figure 8 one can see that the ratio of $\tau_w$ between charged to uncharged particles is not as large as in figure 5(c). Here, the ratio is $\sim 1-3$ for $V_m \pm 1 \text{ V}$. The largest ratio of $\sim 1-4$ occurs for the ‘flat’ case of $V_m = -0.2 \text{ V}$ when $\overline{V_{EOF}} \simeq 0$. Nevertheless, for $V_m = -1 \text{ V}$ there is a drastic increase in the waiting times, with time difference as large as $180 \text{ µs}$ is observed for when $V_c = 100 \text{ mV}$, which also means much lower permeability for these particle sizes during the separation process.

At $V_c = 25 \text{ mV}$, the translocation times (figure 9(a)) are very similar to those in figure 6(b) since the applied electrolyte bias is too small to have a significant impact on the magnitude of $\overline{V_{EOF}}$. When $V_c$ becomes larger, there is a decrease in translocation times for both $V_m = \pm 1 \text{ V}$ as the particle size increases. In the case of positive membrane bias ($V_m = 1 \text{ V}$), this is easily understood as the favorable direction of the fluid flow will increase the particle speed. For the case of negative membrane bias ($V_m = -1 \text{ V}$), this reasoning should have resulted in larger $\tau_t$, which is not what we have found. As shown before, in a membrane with large negative bias the particle suffers many failed attempts before a successful translocation (see figure 7). The only possible translocation must be so fast that the opposing fluid flow would not have time to push the particle back to outside the pore entrance [37]. As such, when there is a successful translocation, the translocation time should be small and in fact be comparable to that of particles in positive membrane bias, as shown by the results in figure 9(b). This imposition on $\tau_t$ indicates that $\tau_t \ll \tau_w$ regardless of the values of $V_c$ and

![Figure 7](image-url) The trace of the z coordinate of the particle shows the hindering effect due to the fluid flow in the presence of $V_m = -1 \text{ V}$. The facilitating effect is observed for positive $V_m$ (see inset). These traces of $z$ coordinates are simulated with $R_{np} = 6 \text{ Å}$ and $q = -1e$ at $V_c = 100 \text{ mV}$.

![Figure 8](image-url) Waiting time of different size charged particles (solid lines) and uncharged particles (dashed lines) in the presence of $V_m = 1 \text{ V}$ (circles), $V_m = -0.2 \text{ V}$ (triangles) and $V_m = -1 \text{ V}$ (squares) in the presence of fluid flow included for (a) $V_c = 25 \text{ mV}$ and (b) $V_c = 100 \text{ mV}$. In (b) the $\tau_w$ of $V_m = -1 \text{ V}$ (squares) are scaled down by 10 times for charged and uncharged particles.
uncharged particles (dashed lines) in the presence of
Figure 9. Translocation time of charged particles (solid lines) and
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These are simulated with fluid flow consideration. The solid black
In this work, we investigated the possibility of separating
diffusively tunable semiconductor membrane. The electro-
static potential distribution of the system is obtained via a
solution of the PNP equations and depends on the applied
electrolyte bias and applied membrane bias. The motion of the
nanoparticle is modeled through the BD approach which in-
corporates contributions from dielectrophoresis, fluid flow,
and electrostatic potential. The particle’s waiting and translocation
times are recorded and analyzed statistically to understand
localization of the electric field variation in our system is
around the pore entrance/exit.
We observed that in the absence of fluid flow at \( V_e = 0 \) V,
the charged and uncharged particles of the same radius have
waiting times that differ by two times the magnitude for
\( V_m = \pm 1 \) V because of the presence of the barrier/well before
the pore’s entrance and are approximately the same for the
‘flat’ potential at \( V_m = -0.2 \) V.
However, we also found that in the studied range of
parameters the largest ratio in the waiting times (the largest
selectivity) of \( \sim 1-4 \) (charged to uncharged) occurs for the ‘flat’
potential at \( V_m = -0.2 \) V when \( V_e = 0.1 \) V. In this case the
electro-osmotic flow is negligible, and the difference is solely
due to the effect of the applied electrolyte bias which speeds
up the capture and translocation of charged species only.
When \( V_m = -1 \) V, the waiting times are very large indicating
lower permeability (higher resistivity) of the membrane as
the electro-osmotic flow opposes the direction of the applied
electrolyte bias, and yet the ratio of waiting times is decreased
to \( \sim 1-3 \) because of the repulsive barrier hindering charged
particle translocation (this barrier is absent for \( V_m = -0.2 \) V).
On the other hand, for \( V_m = 1 \) V, the waiting times are very
small as the applied electrolyte bias and the electro-osmotic
flow are oriented in the same direction and tend to quickly
capture the particles. This ratio is also \( \sim 1-3 \) and decreases
with increasing particle size. We could surmise that for even
larger particles, the strong drag force created by the fluid flow
will eventually wash out the differences in times so that no
charge-specific selectivity will be observed as the waiting
times will approach the same limit of the mean first passage
time regardless of the charge. However, further work is needed
to corroborate this assumption for larger particles and pore
dimensions when the effects from the fluid flow are likely to
be the dominant.

To conclude, the unique characteristics of our electrically
tunable membrane—its ability to alter the direction of fluid
flow which can drastically increase or decrease the waiting
time of the particles when \( V_e \neq 0 \)—make it a viable candidate
for performing high-speed filtering of nanoparticles by charge
and/or size. With the same membrane, the selectivity
and permeability for the specific charge/size combination of
nanoparticles can be easily tuned by an appropriate selection
of applied electrolyte and membrane biases.

4. Conclusion

In this work, we investigated the possibility of separating
differently charged nanoparticles of various sizes with an
electrically tunable solid-state nanoporous membrane. The electro-
static potential distribution of the system is obtained via a
solution of the PNP equations and depends on the applied
electrolyte bias and applied membrane bias. The motion of the
nanoparticle is modeled through the BD approach which in-
corporates contributions from dielectrophoresis, fluid flow,
and electrostatic potential. The particle’s waiting and translocation
times are recorded and analyzed statistically to understand
particle dynamics above the pore and within the pore.

Our results indicate that dielectrophoresis has no major
influence on particle dynamics based on the comparison of
cases with and without the dielectrophoretic term in the
Langevin equation. We conclude that the insignificance of
dielectrophoresis is due to the small pore size, also that the

\[ V_m \text{ or the size of the filtered particles. For a larger ratio of } R_m/R_{pore}, \text{ the diffusion coefficient decreases } [38] \text{ (by a factor of 10 in our case) and thus } \tau_1 \text{ increases but we still observe } \tau_1 \ll \tau_w. \text{ This means that in the given range of particle sizes, the permeability of the membrane is defined by the waiting time only in agreement with our earlier intuitive analysis between } \tau_w \text{ and permeability } [36]. \]

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Figure 9. Translocation time of charged particles (solid lines) and
uncharged particles (dashed lines) in the presence of \( V_m = 1 \) V
(circles), \( V_m = -0.2 \) V (triangles) and \( V_m = -1 \) V (squares) at
different electrolyte biases: (a) \( V_e = 25 \) mV, (b) \( V_e = 100 \) mV.
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