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Electroosmotic flow through nanopores in thin and ultrathin membranes

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We theoretically study how the electroosmotic fluid velocity in a charged cylindrical nanopore in a thin solid state membrane depends on the pore's geometry, membrane charge, and electrolyte concentration. We find that when the pore's length is comparable to its diameter, the velocity profile develops a concave shape with a minimum along the pore axis unlike the situation in very long nanopores with a maximum velocity along the central pore axis. This effect is attributed to the induced pressure along the nanopore axis due to the fluid flow expansion and contraction near the exit/entrance to the pore and to the reduction of electric field inside the nanopore. The induced pressure is maximal when the pore's length is about equal to its diameter while decreasing for both longer and shorter nanopores. A model for the fluid velocity incorporating these effects is developed and shown to be in a good agreement with numerically computed results.

I. INTRODUCTION

In recent years, nanopores in thin solid state membranes gained considerable attention due to their applications as low-cost, high-throughput biosensors and filters [1–7]. Short transit times in thin membranes for translocating biomolecules and nanoparticles as well as features in the ionic current result in high sensitivity and resolution of such devices. Signatures in the ionic current (the duration and the depth of the “current blockade” dips) are not only utilized to detect an object passing through the nanopore but they also convey information about its physical properties such as size, shape, and charge [5, 8–12]. As such, understanding of how various conductance mechanisms, such as those due to membrane surface and bulk charges, affect the motion of the nanosized objects through the nanopore is of crucial importance for correct interpretation and utilization of experimental data.

When an object translocates through a nanopore, two main forces typically affect its motion [13]. The first is the electric force originating from the applied electric field that results in the electrophoretic motion of the charged nanoparticle or biomolecule. The second force is due to the viscous drag exerted on an object by the fluid flowing through the charged nanopore in response to the applied electric field, or the, so called, electroosmotic flow (EOF). The EOF appears because the surface of the membrane is charged, so that the ionic solution within the nanopore attains a non-zero electric charge of opposite sign which is largely concentrated within the electric double layer formed at the walls of the nanopore. When the electric field along the axis of the pore is applied, the ions in the fluid filling the nanopore begin to move, and the fluid flow (EOF) appears. In the steady state regime, the bulk motion of the solution in the nanopore is generated (the fluid is viscous), so that the EOF is present through the total cross sectional area of the pore. Depending on the charges of the translocating object and membrane, the electric and drag forces may or may not be in one direction: For example, for a negatively charged nanoparticle attempting to permeate through a nanopore

with negative surface charge, these two forces point in opposite directions. Thus, their relative magnitudes will determine the direction in which the particle translocates as well as the time it spends in the nanopore attempting to move through it. As this time depends exponentially on the potential energy of the particle within the channel [14], even small variations in values of these forces will greatly affect the duration of the translocation event [15] and consequently, the membrane filtering and sensing characteristics.

To this end, in this work we conduct the theoretical analysis of the EOF through nanopores in solid state thin membranes [16–19]. For this purpose, we numerically compute the fluid flow velocity through a nanopore by solving on equal footing Poisson-Nernst-Planck equations to account for the charge and electric field distributions in and around the nanopore and Navier-Stokes equations to describe the EOF. Our results show that the flow in finite length nanopores with the diameter comparable to the length cannot be adequately described by the results for the long channel with the Debye approximation [20] as this approach overestimates the fluid velocity by as much as 100 %. The reason for this is the fluid flow outside the nanopore which affects the EOF through it. These “end effects” are manifested as a self-induced pressure gradient along the pore. When this effect is incorporated in the simple analytical model for the EOF velocity which we also develop on the basis of the classical model for the infinitely long nanopores [20], we find that the velocities given by this model agree very well with results of numerical calculations for a broad range of nanopore dimensions, electrolyte concentrations, and membrane surface charge densities.

The paper is structured as follows. In Section II, the nanopore geometry and the computational method employed are described with details on boundary conditions and parameters used in the setup of our model. In Section III, the results of computations are presented and discussed, the analytical model for the EOF fluid velocity is developed, and behavior of the EOF in our nanopore structure is elucidated. Finally, Section IV contains a brief summary of the work.

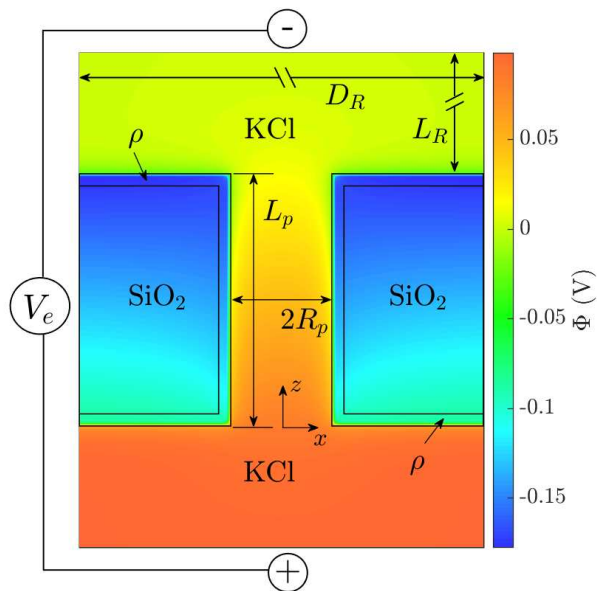


FIG. 1. (Color online) A schematic diagram of our modeled nanopore structure with the electric potential in the background. (For this plot, the membrane charge is $\rho = 0.4 \text{ e/nm}^3$ and the bulk electrolyte concentration is $C = 0.1 \text{ M}$).

II. MODEL AND METHODS

In Fig. 1, a schematic diagram of our modeled membrane-electrolyte structure with the electric potential overlaid is shown. The nanopore of radius R_p and length L_p is in the center of the structure: We consider pores with $R_p = 5$ and 10 nm while the length of the pore is varied between 15 and 100 nm . The reservoirs above and below the nanopore have dimensions which are much larger than the dimensions of the nanopore, $L_R = 120 \text{ nm}$ and $D_R = 280 \text{ nm}$, to ensure that far away from the nanopore the electric potential reaches constant values. The difference between these values is equal to the electrolyte bias $V_e = 100 \text{ mV}$ which is applied to generate the ionic flow through the nanopore. The 4 \AA -thick layer on the surface of the SiO_2 membrane is charged with the volume charge density ρ . In this work, we perform computations for two values of ρ : $\rho = 0.4 \text{ e/nm}^3$ and 1.2 e/nm^3 which correspond to the surface charge densities $\sigma = 0.16 \text{ e/nm}^2$ and 0.48 e/nm^2 , respectively.

To calculate the EOF fluid velocity and study its dependence on various system parameters, we first compute the electric potential $\Phi(\vec{r})$ and electrolyte charge distribution, i.e., concentrations of chlorine and potassium ions, $C_{Cl^-}(\vec{r})$ and $C_{K^+}(\vec{r})$, respectively, in our system. This is accomplished by solving Poisson-Nernst-Planck equations:

$$\nabla^2 \Phi = -\frac{e}{\epsilon_0 \epsilon_r} \rho(\vec{r}) \quad (1)$$

with

$$\rho(\vec{r}) = \begin{cases} \rho, & \text{in the } 4\text{-\AA} \text{ layer on the} \\ & \text{membrane surface,} \\ 0, & \text{everywhere else in the} \\ & \text{membrane,} \\ C_{K^+} - C_{Cl^-}, & \text{in the electrolyte,} \end{cases} \quad (2)$$

and

$$\nabla \cdot \left[z_i \frac{e D_i}{k_B T} C_i \nabla \Phi + D_i \nabla C_i - \vec{v} C_i \right] = 0, \quad (3)$$

$$i = K^+, Cl^-.$$

Here e is the elementary charge, ϵ_0 is the permittivity of free space, $\epsilon_r = 78$ is the relative permittivity of water, $z_i = \pm 1$ are the ionic charges of potassium and chlorine ions [15, 21], $T = 300 \text{ K}$ is the temperature of the system, \vec{v} is the EOF velocity, and D_i is the diffusion coefficient, $D_{K^+} = 1.95 \times 10^{-9} \text{ m}^2/\text{s}$ and $D_{Cl^-} = 2.03 \times 10^{-9} \text{ m}^2/\text{s}$. The first two terms in the ionic fluxes (3) represent the electromigrative flux due to the applied electric field (drift current density) and diffusive flux, respectively, while the last term which depends on the fluid velocity describes the convective flux of ions due to the EOF.

The EOF through the nanopore is described via the Navier-Stokes equation for an incompressible fluid without the inertial term [22] as the Reynolds number for our nanopore geometry is $\sim 10^{-3} - 10^{-4}$ depending on the pore's length:

$$\eta \nabla^2 \vec{v} = \nabla p - e(C_{K^+} - C_{Cl^-}) \nabla \Phi, \quad (4)$$

together with the continuity equation,

$$\nabla \cdot \vec{v} = 0, \quad (5)$$

where $\eta = 10^{-3} \text{ Pa}\cdot\text{s}$ is the dynamic viscosity, and p is the total pressure. The last term on the right in Eq. (4) is the electric force responsible for the appearance of the electroosmotic flow.

To get the velocity $\vec{v}(\vec{r})$ of the EOF through the nanopore, Eqs. (1) – (5) were solved self-consistently with COMSOL[®] Multiphysics 5.1 on the axisymmetric two-dimensional domain (Fig. 1). A triangular finite element mesh with sizes vaying from 0.35 \AA on the membrane surface to 1.4 \AA in the nanopore and 2.2 nm in the reservoirs and in the membrane was used in calculations. Small mesh sizes next to the membrane surface were required to capture very sharp variations in the electric potential for the larger membrane surface charge density. The simulations were terminated when the norm of the residual vector for the solution became smaller than 10^{-6} .

The boundary conditions imposed for solving Eqs. (1) – (5) were as follows: The normal components of the ionic fluxes were set to zero at the nanopore-membrane interface and side reservoir walls while at the top and bottom walls of reservoirs the ionic concentration was maintained at its bulk value. The normal component of the electric

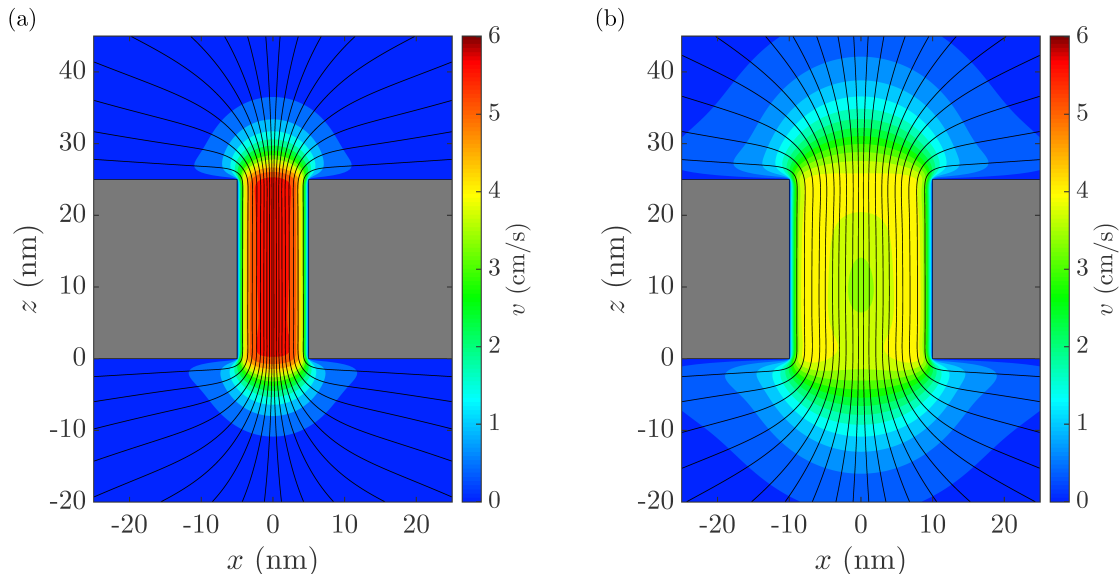


FIG. 2. (Color online) Contour plots of the computed EOF velocity with streamlines for a nanopore with (a) $R_p = 5$ nm and (b) 10 nm.

158 field was set to zero at the side reservoir and membrane
 159 walls, while $\Phi = V_e$ at the bottom and $\Phi = 0$ at the top
 160 boundaries of the reservoir. For the Navier-Stokes equation,
 161 no slip boundary condition ($\vec{v} = 0$) was imposed
 162 at the nanopore-membrane interface while a slip bound-
 163 ary condition (the normal component of the velocity and
 164 its gradient are both zero) was used on the side walls of
 165 the reservoirs. At the top and bottom boundaries of the
 166 reservoirs, the pressure was set to zero together with the
 167 assumption that the fluid flow is normal to those bound-
 168 aries.

169 For long cylindrical pores, the solution of the above
 170 system of equations for the fluid velocity is well
 171 known [20, 23]. Within the Debye approximation for the
 172 electric potential (which is valid for $\Phi \lesssim k_B T$) and as-
 173 suming separability of $\Phi(\vec{r})$ in z and x directions and no
 174 applied external pressure, the z -component of the EOF
 175 velocity is given by:

$$v_z(r) = -\frac{\epsilon_0 \epsilon_r E_z \Phi_0}{\eta} \left[1 - \frac{I_0(\kappa r)}{I_0(\kappa R_p)} \right], \quad (6)$$

176 where $\kappa = (\epsilon_0 \epsilon_r k_B T / 2 C e^2)^{-1/2}$ is the inverse Debye
 177 length, C is the bulk electrolyte concentration (except
 178 where it is noted, all calculations are performed for
 179 $C = 0.1$ M), E_z is the constant electric field along the
 180 central axis of the nanopore, $I_n(x)$ is the modified Bessel
 181 function of the first kind of the n -th order [24], and Φ_0 is
 182 the electric potential on the pore's surface which for zero
 183 applied electrolyte bias is equal to [25]:

$$\Phi_0 = \frac{\sigma}{\epsilon_0 \epsilon_r \kappa} \frac{I_0(\kappa R_p)}{I_1(\kappa R_p)}. \quad (7)$$

184 For the two membrane charge densities considered in the
 185 present work, $\Phi_0 = -40$ and -120 meV, respectively,

186 suggesting that the smaller charge density (barely) cor-
 187 responds to the Debye approximation while for the larger
 188 one ($0.48 e/\text{nm}^2$), this approximation, and consequently
 189 the above equation for v_z , cannot be used. However, as
 190 it is shown in the next Section, Eq. (6) works well in
 191 our analytical model if Φ_0 is replaced with the poten-
 192 tial difference $\Delta\Phi$ between the surface and the center of
 193 the nanopore, $\Delta\Phi = \Phi(R_p, L_p/2) - \Phi(0, L_p/2)$ (which is
 194 equal to -35 and -78 meV for our membrane charge val-
 195 ues) provided that the “end effects” are also accounted
 196 for.

197 Note that Eq. (6) predicts that the fluid velocity
 198 reaches a maximum at the center of the pore. In the
 199 limit of a thin double layer ($\kappa^{-1} \ll R_p$), Eq. (6) reduces
 200 to constant value of $v_z = \epsilon_0 \epsilon_r E_z \Phi_0 / \eta$ which is the clas-
 201 sical Helmholtz-Smoluchowski result for the EOF fluid
 202 velocity [26, 27].

III. RESULTS AND DISCUSSION

204 We first checked the validity of the above numerical
 205 approach against the results of Eq. (6) and found very
 206 good agreement between the two for long nanopores and
 207 smaller surface charge densities as expected (see Ap-
 208 pendix).

209 The computed EOF velocity contour plots with flow
 210 streamlines are shown in Fig. 2 for pore radii 5 and 10 nm
 211 and length of 25 nm. We see that within the nanopore,
 212 the direction of the fluid flow is along the pore's axis, as
 213 expected, since it is where the electric potential changes
 214 most rapidly in the z -direction (see Fig. 1), i. e., the elec-
 215 tric field is the largest in magnitude. The radial compo-
 216 nent of the fluid velocity is only noticeable near the pore's

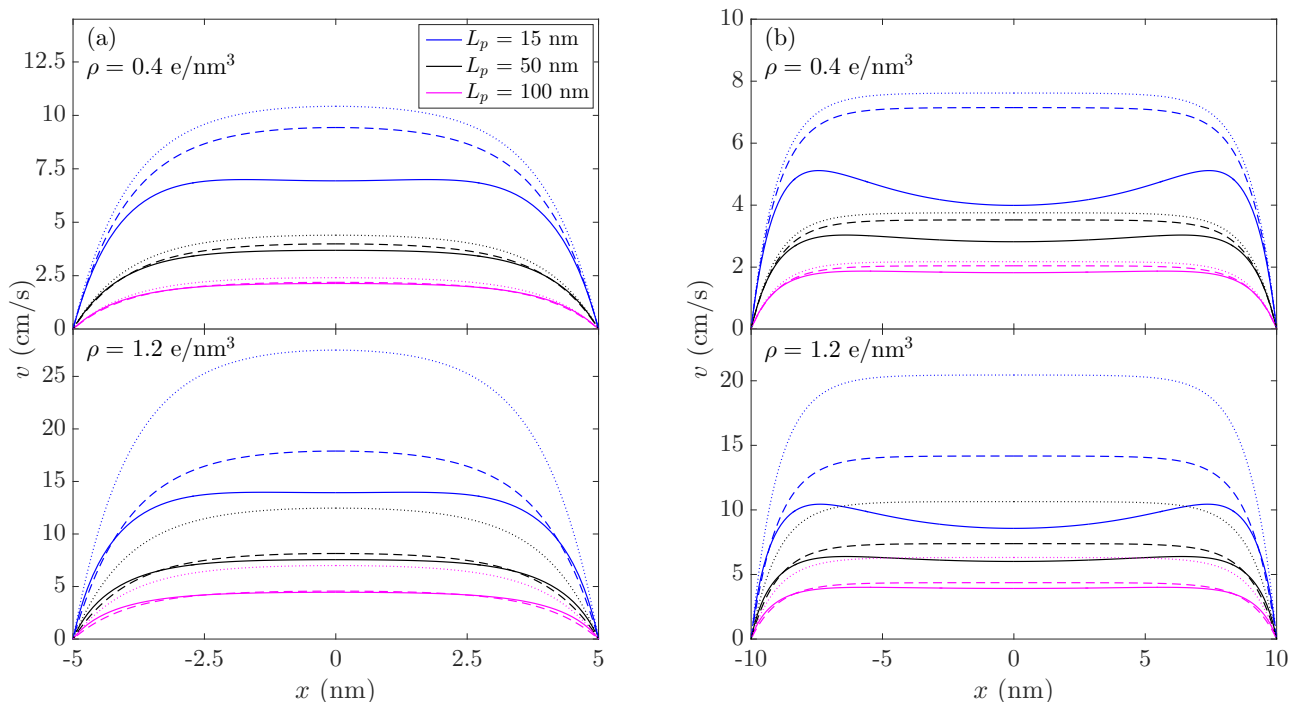


FIG. 3. (Color online) Fluid velocity profile in x -direction in the center of the pore for different nanopore lengths L_p and membrane charge densities: (a) $R_p = 5$ nm and (b) $R_p = 10$ nm. The solid curves are the results of the numerical simulations while the dashed (dotted) curves are the results of Eq. (6) with $\Delta\Phi$ (Φ_0). For both dashed and dotted curves, $E_z = V_e/(L_p + \alpha R_p)$ where values of parameter α are given in text (see Section III for details).

217 inlet and outlet, and in those regions, the fluid flow ex-
 218 tends over a distance of a few pore radii R_p away from
 219 the pore ends. We also observe the formation of a local
 220 *minimum* in the fluid velocity around the center of
 221 the pore with larger radius of 10 nm [Fig. 2(b)] while v
 222 remains maximal along the central axis of the nanopore
 223 when $R_p = 5$ nm [Fig. 2(a)].

224 Fig. 3 shows that the minimum appears and becomes
 225 deeper with decreasing length of the pore for a fixed R_p .
 226 The dashed and dotted curves in these plots correspond
 227 to the results given by Eq. (6), and one can immedi-
 228 ately draw several observations from the comparison be-
 229 tween the different types of curves: First, the velocities
 230 obtained from Eq. (6) with $\Delta\Phi$ (Φ_0) exceed the numeri-
 231 cally computed ones by as large as 40 % (100 %) partic-
 232 ularly for $\rho = 1.2$ e/nm³, and second, the fluid velocity
 233 v_z does not have a local minimum along the central axis.
 234 As the pore becomes longer, the concave shape of the nu-
 235 merically computed velocity profile gradually disappears
 236 and velocity reaches a maximum value along the central
 237 axis of the pore, qualitatively similar to the v_z profile
 238 predicted by Eq. (6). Note that the concave shape of the
 239 fluid velocity was previously observed in numerical cal-
 240 culations of the EOF through long nanopores (see, e. g.,
 241 Ref. [28]). However, in what follows we strive to provide
 242 a qualitative explanation for its appearance as well as to
 243 devise a way to rectify Eq. (6) so that values of v_z agree
 244 with the numerically computed EOF velocities.

245 One of the reasons for the apparent disagreement be-
 246 tween the numerically computed EOF velocity and the
 247 one determined by Eq. (6), is the magnitude of the elec-
 248 tric field E_z in the z -direction due to the applied bias
 249 V_e . A conventional argument that V_e changes linearly
 250 over the pore's length leads to $E_z = V_e/L_p$ since usu-
 251 ally $L_p \gg \kappa^{-1}$. However, as can be seen from the elec-
 252 tric potential distribution shown in Fig. 1, the potential
 253 changes over distances extending a few R_p 's away from
 254 the nanopore's ends. This is because inside the nanopore,
 255 the positive and negative ionic charges do not fully com-
 256 pensate each other (due to the presence of the membrane
 257 surface charge) and the nanopore as a whole has a non-
 258 zero electric charge. In this case, the electric field inside
 259 the pore can be approximated as [29, 30]

$$E_z = \frac{V_e}{L_p + \alpha R_p} \quad (8)$$

260 with α being a numerical parameter dependent on the
 261 nanopore radius, surface charge, and bulk electrolyte con-
 262 centration values.

263 The overall form of Eq. (8) can be justified by repre-
 264 senting the nanopore region in terms of the nanopore and
 265 two access sections. Using the nanopore and access res-
 266 sistances with the pore diameter modified by the surface
 267 charge [31] and substituting them into the equation for
 268 the potential drop along the nanopore length [25], one
 269 can find that parameter α in the above equation can be

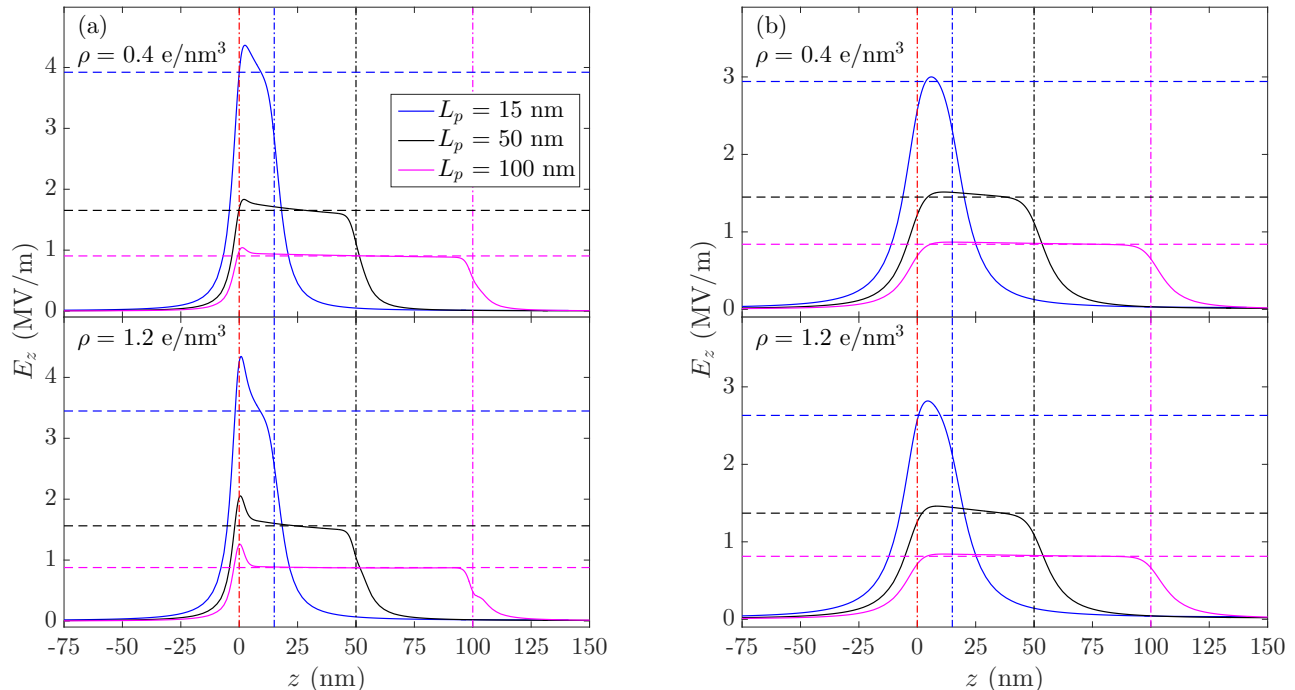


FIG. 4. (Color online) z -component of the electric field, E_z , along the central pore axis for a nanopore with (a) $R_p = 5$ nm and (b) $R_p = 10$ nm and different pore lengths. The horizontal dashed lines represent the values of the electric field as computed by $E_z = V_e / (L_p + \alpha R_p)$ with α given in the text, and the vertical dot-dashed lines show the location of the inlet ($z = 0$) and outlet ($z = 15$, $z = 50$, and $z = 100$ nm) for each nanopore.

270 expressed as

$$\alpha = \frac{\pi}{2} \frac{1 + Du}{1 + Du/4}, \quad (9)$$

271 where $Du \approx |\sigma|/CR_p$ is the Dukhin number [31]. For our
 272 nanopore radii $R_p = 5$ (10) nm, this gives $\alpha \approx 2.1$ (1.9)
 273 for $\rho = 0.4$ e/nm³ and 2.9 (2.3) for $\rho = 1.2$ e/nm³ which
 274 results is in excellent agreement between the numerically
 275 computed electric fields and the values given by Eq. (8),
 276 see Fig. 4, as well as with other calculations of the electric
 277 field in charged nanopores [29, 30].

278 However, the main reason for the concave shape of the
 279 velocity profile in the fluid flow through finite length
 280 nanopores is the presence of the self-induced pressure
 281 drop P along the pore shown in Fig. 5 for the larger mem-
 282 brane charge of 1.2 e/nm³ (results for the smaller charge
 283 are analogous and are not shown). The pressure changes
 284 approximately linearly along the pore's axis [32, 33]; The
 285 deviations from linearity are due to the concentration po-
 286 larization effects [34], i.e., the electric force in the Navier-
 287 Stokes equation (4) is not constant in the z -direction but
 288 rather exhibit a slight variation due to the changing ionic
 289 concentration along the pore's axis. This effect dimin-
 290 ishes as pore's radius increases which is manifested by a
 291 more linear pressure drop in Fig. 5(b) vs. Fig. 5(a).

292 This pressure drop appears due to the fluid flow expan-
 293 sion/contraction near the pore's outlet/inlet or in other
 294 words, it is the result of the finite length of the nanopore:

295 Outside of the nanopore's outlet, the fluid velocity de-
 296 creases with the distance away from the pore (streamlines
 297 diverge, see Fig. 2). Since the fluid is incompressible, one
 298 can write for its velocity outside the pore [35]:

$$v(R) \approx \frac{Q}{2\pi R^2}, \quad (10)$$

299 where R is the distance between the pore's exit and ob-
 300 servation point, and Q is the volumetric flow rate. This
 301 results in the appearance of the fluid friction force be-
 302 tween the layers of the fluid and as such, the pressure is
 303 induced to maintain the flow. We can estimate the indu-
 304 ced pressure δP by equating it to the fluid friction force
 305 per unit area [36] which leads to $\delta P = (1/2)\beta\eta Q/R_p^3$.
 306 Here we introduced a variational parameter β to relate
 307 R and R_p since the fluid velocity decays appreciably over
 308 a few R_p 's away from the pore. Note that because we
 309 consider the fluid flow outside the nanopore, β does not
 310 depend on L_p .

311 Near the pore's inlet, the situation is analogous but
 312 the pressure there drops below the fixed external value to
 313 compensate for the contraction of the fluid streamlines.
 314 Assuming that this decrease in pressure is the same in
 315 magnitude as its increase near the pore's outlet, for the
 316 total pressure change along the pore's length, one can
 317 thus write:

$$\Delta P = \beta \frac{\eta Q}{R_p^3}. \quad (11)$$

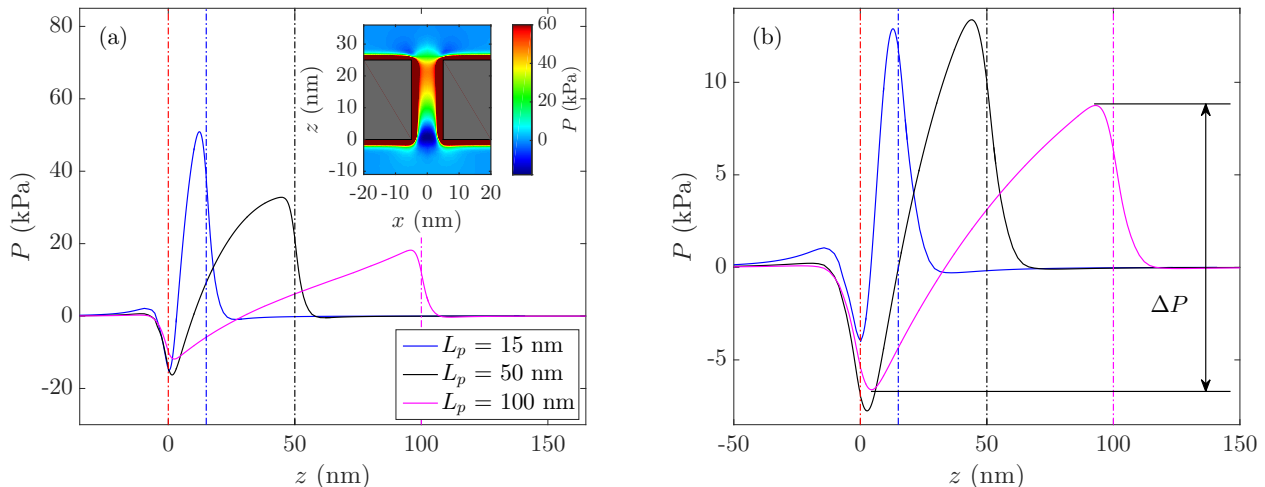


FIG. 5. (Color online) Induced pressure P along the central pore axis for nanopores of different lengths and (a) $R_p = 5$ nm, (b) $R_p = 10$ nm ($\rho = 1.2$ e/nm³). The total pressure drop ΔP is defined as difference between the maximum and minimum pressure values. The vertical dot-dashed lines show the location of the inlet ($z = 0$) and outlet ($z = 15$, $z = 50$, and $z = 100$ nm) for each nanopore. The inset in (a) shows distribution of the pressure in the fluid.

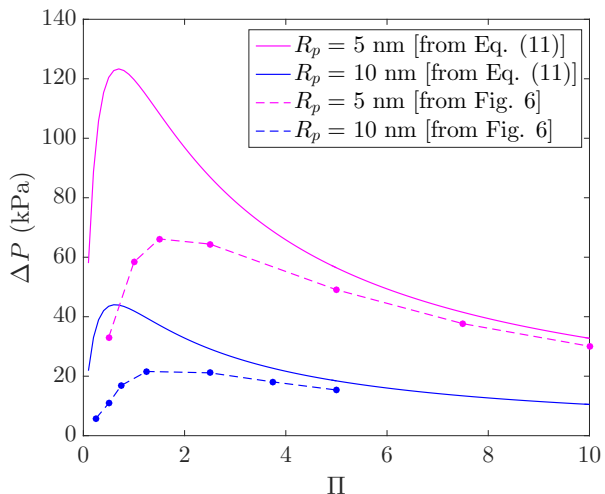


FIG. 6. (Color online) Induced pressure drop ΔP vs. aspect ratio of the pore $\Pi = L_p/(2R_p)$ for $\rho = 1.2$ e/nm³. Dots connected by dashed lines are the results of calculations, solid curves are the result of Eq. (13) with $\beta = 1.75$. Note that the same β is used for both $R_p = 5$ and 10 nm.

318 The fluid flow due to the induced pressure contributes
319 to the net EOF, so that Eq. (6) has to be modified to
320 account for its effect [32]:

$$v_z(r) = -\frac{R_p^2}{4\eta} \frac{\Delta P}{L_p} \left(1 - \frac{r^2}{R_p^2}\right) - \frac{\epsilon_0 \epsilon_r E_z \Delta \Phi}{\eta} \left[1 - \frac{I_0(\kappa r)}{I_0(\kappa R_p)}\right], \quad (12)$$

321 where for simplicity we assumed that the pressure-
322 induced flow is parabolic (Poiseuille flow) in the radial
323 direction and that the pressure changes linearly along

324 the pore (see Fig. 5).

325 To determine the value of β , we computed the pressure
326 drop along the pore from the data in Fig. 5 and compared
327 it with ΔP given by Eq. (11) in which Q was obtained by
328 integrating Eq. (12) over the pore's cross sectional area
329 which leads to

$$\Delta P = -\frac{8V_e}{R_p^2} \frac{\Pi}{\alpha/2 + \Pi} \frac{\epsilon_0 \epsilon_r \Delta \Phi}{1 + 16\Pi/\pi\beta} \left[1 - \frac{2I_1(\kappa R_p)}{\kappa R_p I_0(\kappa R_p)}\right], \quad (13)$$

330 where Π is the aspect ratio of the nanopore, $\Pi =$
331 $L_p/(2R_p)$, and we also used $E_z = V_e/(L_p + \alpha R_p)$. The
332 values of the pressure drop vs. the aspect ratio of the
333 nanopore are shown in Fig. 6 where one can see that the
334 agreement between the numerically computed and approx-
335 imate values of ΔP is quite good when $\beta = 1.75$, particu-
336 larly for pores with $\Pi \gtrsim 2$. The pressure reaches maxi-
337 mum at $\Pi \sim 1$ and decreases at smaller and larger values
338 of the aspect ratio. The deviations at smaller aspect ra-
339 tios are likely due to the fact that the EOF is not yet
340 established in short pores (for the pressure driven flow,
341 the flow becomes fully developed when $L_p \gtrsim R_p$ [32]),
342 i. e., the fluid velocity is smaller than the one given by
343 Eq. (6). In the opposite limit of the long pores $L_p \gg R_p$,
344 $\Delta P \propto L_p^{-1}$ due to the decreasing electric field magni-
345 tude.

346 With the value of β thus fixed, we can now find the
347 fluid velocity profile in the radial direction as given by
348 Eqs. (12) and (13). In Fig. 7, we replot the numeri-
349 cally computed EOF velocities (solid curves) but com-
350 pare them now with results of Eq. (12) (dashed curves):
351 The agreement between two sets of data is very good (un-
352 like Fig. 3) for all studied nanopores demonstrating the
353 importance of the induced pressure effects on the EOF
354 through the nanopores in thin and ultrathin membranes.
Note that an equation for the pressure drop similar

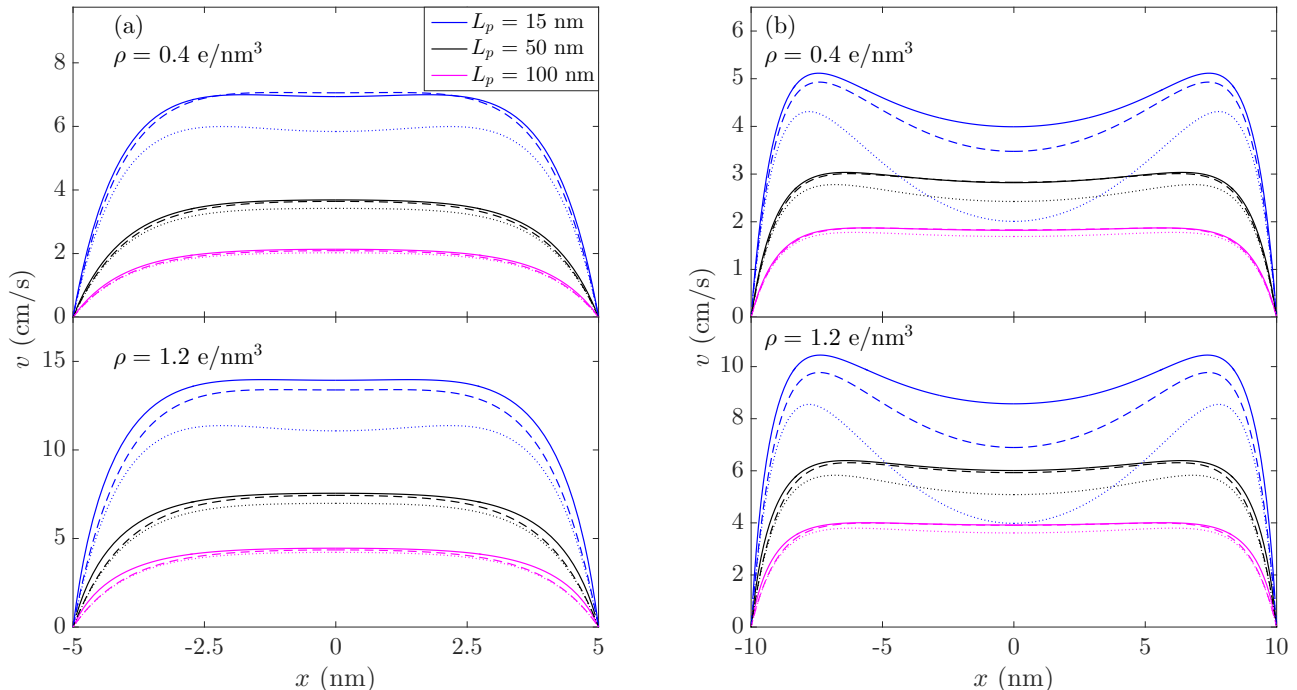


FIG. 7. (Color online) Same as in Fig. 3 but with dashed lines from Eqs. (12) and (13) with $\beta = 1.75$ and dotted lines with $\beta = 3$.

to Eq. (11) but with fixed $\beta = 3$ was derived for the pressure-driven flow through the circular orifice in the infinitely thin screen [37, 38]. It was later utilized for the description of the end effects in the pressure driven flow through the finite length channels [39], where a good agreement between the exact numerical and approximate results was found. However, as can be seen from the dotted curves in Fig. 7, the parameter $\beta = 3$ is much too large to provide a good agreement with the numerically computed EOF fluid velocities for our nanopores [25, 40].

Finally, in Fig. 8, we show how the electrolyte concentration, C , affects the fluid velocity. One can see from these plots that the dependence of v on C has a non-monotonic character for pores with $R_p = 5$ nm: Fluid velocity at the pore's center first increases with increasing electrolyte concentration and then decreases. This can be easily understood by analyzing concentration dependence of $v_z(r)$ in Eq. (12). The electric potential on the membrane surface Φ_0 [Eq. (7)] monotonically decreases with C [13]. However, for small electrolyte concentrations and $R_p = 5$ nm, the velocity at the center of the pore has not yet reached Helmholtz-Smoluchowski saturation limit, that is, the electric double layers from opposite sides of the pore overlap, and overall, v_z increases with C . When Helmholtz-Smoluchowski limit is reached, the only dependence on concentration in Eq. (12) is through Φ_0 , and thus, v_z decreases. For $R_p = 10$ nm, the velocity decreases with C [Fig. 8(b)] because in this case $\kappa R_p \gg 1$ in the studied range of concentrations.

In the same plots, we also compare the numerically

computed velocities with the ones given by Eq. (12). One can see that the agreement is very good for all concentrations except for the lowest one, $C = 10$ mM, when the approximate calculations significantly underestimate the numerical results. The main reason for this is a strong z -dependence of the electric field in and around the nanopore as compared to the ones shown in Fig. 4 and used in Eqs. (12) and (13). At low electrolyte concentrations, the electric field varies greatly along the nanopore length (there is a lot of the electric field “leakage” from the top and bottom membrane surfaces into the nanopore) and it is hard to ascribe just one value for it for the whole nanopore length. In other words, at low electrolyte calculations and/or nanopore aspect ratios, the full scale numerical calculations are better suited for the description of the EOF.

IV. CONCLUSION

In this paper, we theoretically studied the EOF through nanopores of variable radii in thin and ultrathin solid state membranes for different nanopore dimensions, electrolyte concentrations and membrane charges. Numerical analysis of the EOF fluid velocity is performed via self-consistent solution of the Poisson-Nernst-Planck and Navier-Stokes equation in two-dimensions accounting for large fluid reservoirs above and below nanopore. These large domains, while greatly increasing the computational cost, are necessary to properly account for the

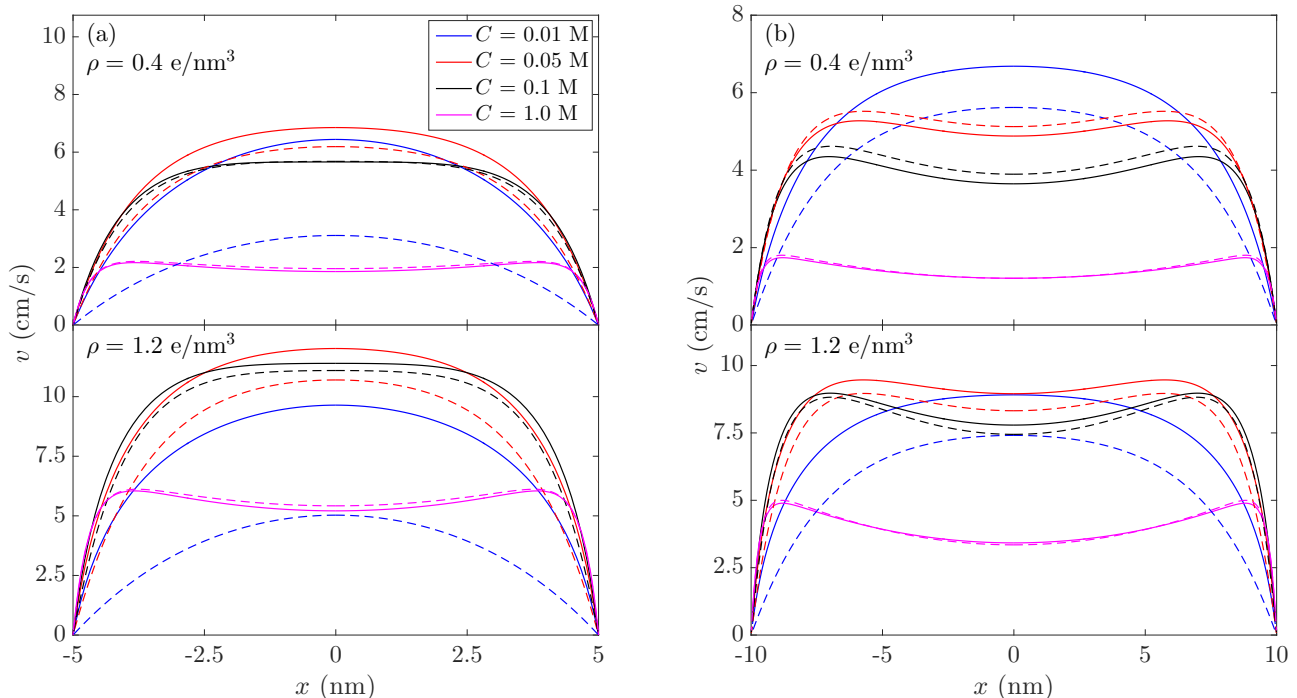


FIG. 8. (Color online) The fluid velocity profile in x -direction at the center of the nanopore of length $L_p = 25$ nm for different bulk electrolyte concentrations C : (a) $R_p = 5$ nm and (b) 10 nm. The dashed lines are the results of Eq. (12).

413 end effects around the inlet and outlet of the nanopore. 440
 414 We found that the computed fluid velocity profiles are 441
 415 not only different by as much as 100 % from the results 442
 416 predicted by classical equations derived for infinitely long 443
 417 capillaries, but that they also develop a concave shape 444
 418 for sufficiently wide and/or short nanopores. This behav-
 419 ior stems from the presence of the self-induced pres-
 420 sure gradient along the nanopore due to the flow expan-
 421 sion/contraction near ends of the pore as well as the re-
 422 duction of the electric field inside the nanopore due to
 423 the increase of the effective nanopore length caused by
 424 the access resistance and the membrane surface charge.
 425 Based on the classical model for the EOF in long pores,
 426 we also developed a simple analytical model incorporat-
 427 ing these effects, and found that its results are in a good
 428 agreement with those of the numerical calculations.

429 Although in this work we concentrate on thin and ul-
 430 trathin membranes, our results concerning the magnitude
 431 of the induced pressure and how it affects the EOF ve-
 432 locity are also applicable for other pore dimensions as
 433 Eq. (13) does not depend explicitly on the nanopore
 434 length. In this respect, they can be used to predict
 435 and quantitatively estimate the induced pressures near
 436 the nanopore inlet/outlet and their effect, for example,
 437 on translocation of “deformable” particles through the
 438 nanoporous membranes [33] and other nanofluidic de-
 439 vices.

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Appendix: Validation of the Approach

444 To check the validity of our numerical approach, we
 445 computed the EOF velocity in very long nanopores where
 446 numerical results are expected to approach the values
 447 given by Eq. (6) for smaller surface charge densities when
 448 the Debye approximation is valid. As results in Fig. 9
 449 show, this is indeed the case: For 200-nm-long pores,
 450 the relative difference between numerically computed and
 451 approximate values of the velocity is about 15(7) % for
 452 $\rho = 0.4(0.2)$ e/nm^3 while for a 500-nm long nanopore,
 453 the difference is $\sim 10(2)$ %.

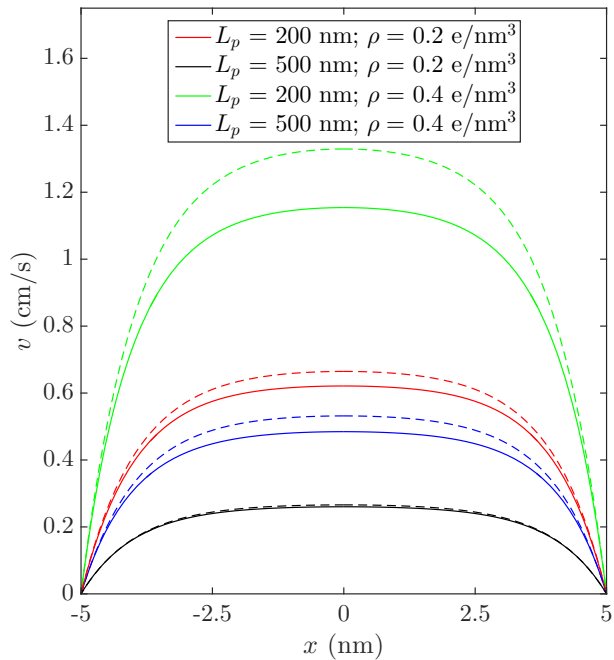


FIG. 9. (Color online) The fluid velocity profile in x -direction at the center of the nanopores with $R_p = 5$ nm and varying length L_p (solid curves). The dashed lines are the results of Eq. (6) with $E_z = V_e/L_p$.

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