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To cite this article: Yongqiang Ren and Derek Stein 2008 Nanotechnology 19 195707

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Slip-enhanced electrokinetic energy conversion in nanofluidic channels

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Received 10 January 2008, in final form 7 March 2008
Published 8 April 2008
Online at stacks.iop.org/Nano/19/195707

Abstract
We investigate theoretically the influence of hydrodynamic slip at the surface of a nanofluidic channel on the efficiency with which electrokinetic phenomena can be used to convert hydrostatic energy to electrical power. Slip is introduced by applying the Navier boundary condition to the pressure-driven and the electro- osmotic components of the fluid velocity. A strong enhancement in the efficiency is predicted for increasing slip length due to the resulting decrease in the fluidic impedance and increase in the streaming conductance. These effects are moderated by a decrease in the electrical impedance, which promotes dissipation. The maximum efficiency approaches 100% as the slip length diverges, and a potentially practical 40% efficiency is expected for a moderate 30 nm slip length in a 10 nm high channel. Recently reported slip lengths for carbon nanotube filters suggest that efficiencies above 70% and high power densities might be achieved in a graphitic system.

1. Introduction
The charged inner surface of a fluidic channel attracts a neutralizing layer of mobile counterions, called the double layer, whose motion is coupled to that of the fluid by viscosity. The electrokinetic phenomena known as streaming currents and streaming potentials arise when a pressure-driven fluid flow transports ions in the double layer by advection. It has long been recognized that these effects can be used to drive an external load, and therefore represent a mechanism for converting mechanical work into electrical power [1]. The idea has received renewed interest following advances in micro- and nanofluidic devices, whose surface to volume ratio is exceptionally high and whose dimensions can approach the Debye length, which characterizes the range of the double layer [2–6]. A practical energy conversion device must achieve a high efficiency and a reasonable power density, but two properties of ionic fluids present serious challenges to these goals: first, the conventional ‘no-slip’ boundary condition assumes the fluid to be stationary at a solid interface; second, the counterion density is highly concentrated near the channel walls. The coupling between fluidic and ionic transport is consequently weak. In silica nanochannels, the highest efficiency observed to date has not surpassed 3% [6], for which a theoretical maximum of only 7% was predicted [5].

While the no-slip condition is an excellent approximation for most purposes, it is not a fundamental principle, and recent work points to situations where hydrodynamic slip occurs along a solid surface [7–20]. Navier accounted for this possibility by proposing a more general boundary condition featuring a finite slip velocity that is proportional to the shear rate, i.e. \( u_{\text{slip}} = b(\partial u/\partial x)_{\text{boundary}} \), where \( u \) is fluid velocity, \( x \) is the coordinate normal to the surface and the slip length, \( b \), is the distance beyond the surface that \( u \) extrapolates to zero (figure 1) [21–24]. It is thought that slip occurs preferentially at extremely smooth and poorly wetting surfaces. Experiments on a variety of fluid–solid interfaces and under different experimental conditions provide evidence for slip lengths typically ranging from \( b = 0 \) nm (no-slip) to \( b = 100 \) nm [7, 8, 10–17]. Some studies have even reported slip lengths on the micrometer scale [9, 18, 19], while recent mass transport measurements on carbon nanotube filters report slip lengths as high as \( b = 33 \) mm [25, 26]. Although many experiments measured a model-dependent ‘apparent’ slip, results from the most direct measurement techniques and molecular dynamics simulations [20] are consistent with ‘molecular’ slip lengths of a few tens of nanometers. This is well within the range of actual nanofluidic device dimensions, which suggests that significant slip effects should be observable.
It has been predicted that giant amplifications of interfacially driven transport phenomena, including electro-, diffusio- and even thermal-osmotic flow, are among the consequences of moderate hydrodynamic slip \((b \approx 30 \text{ nm})\) [20, 27, 28]. It has also been recently pointed out that slip at a charged surface should improve the efficiency of an electrokinetic energy conversion device by increasing the advection of counterions [29–31]. The authors predict an efficiency of 35% in a 100 nm diameter tube with a 6.5 nm slip length and high surface potentials, but outline a calculation that employs approximations that are valid for low surface potentials and short Debye lengths. The notion of slip-enhanced energy conversion is intriguing, and deserves to be investigated in greater detail.

In this paper, we evaluate theoretically the influence of hydrodynamic slip on the electrokinetic energy conversion efficiency in slit-like nanochannels and establish the dependence on slip length, surface charge density and salt concentration down to the regime of strong double layer overlap. We first review recent molecular dynamics simulations and theoretical results to establish a valid theoretical framework in the presence of slip. Our calculations include slip effects on both the pressure-driven and the electro-osmotic components of the fluid flow using the full nonlinear Poisson–Boltzmann model of the double layer, and show striking enhancements in the efficiency at reasonable values of the slip length and surface charge density. We finally discuss how graphitic carbon nanochannels constitute a particularly promising system for exploring a practical energy conversion technology.

2. Theory

2.1. Electrokinetic effects in a linear fluidic device

A fluidic device capable of electrokinetic energy conversion consists of an inlet and an outlet that are connected by one or more arbitrarily shaped channels with charged walls (figure 2). Its electrokinetic properties in the linear regime are defined by the response of the ionic current, \(I\), and the volume flow rate, \(Q\), to the application of an electrochemical potential difference, \(\Delta V\), or a pressure difference, \(\Delta p\), between the inlet and the outlet, according to

\[
I = S_{\text{str}} \Delta p + \frac{\Delta V}{R_{\text{ch}}} \quad \text{(1)}
\]

\[
Q = \frac{\Delta p}{Z_{\text{ch}}} + S_{\text{str}} \Delta V \quad \text{(2)}
\]

where \(R_{\text{ch}}\) is the electrical impedance, \(Z_{\text{ch}}\) is the fluidic impedance and \(S_{\text{str}}\) is the streaming conductance of the channel. Only three electrokinetic response quantities are needed to fully describe the device because the voltage-driven fluid flow rate and the pressure-driven ionic current are related by the Onsager identity \(dQ/d\Delta V = dI/d\Delta p = S_{\text{str}}\) [32]. The values of \(R_{\text{ch}}, Z_{\text{ch}}\) and \(S_{\text{str}}\) for a particular device are determined by its geometry, and the distribution of ions and fluid flows within it.

The linear electrokinetic description of a device is expected to be valid under the following conditions [32–34]: the response of ions to an applied electric field must be linear, and the channel must have a cross section and a surface charge density that are constant over time. The distribution of ions must also be in thermodynamic equilibrium. This last requirement is met when the salt concentration is uniform along the channel, and when the double layer is only weakly distorted by applied potential gradients, which are kept smaller than \(k_B T/\kappa\), where \(1/\kappa\) is the Debye length and \(k_B T\) is the thermal energy. In practice, these conditions are satisfied in common nanofluidics experiments.

Van der Heyden et al derived an expression for the efficiency with which an external electrical load, \(R_L\), harvests electrokinetic power generated by a fixed applied pressure \(\Delta p\) across a fluidic device in terms of its linear response quantities [5]. The efficiency, defined as the electrical power consumed by the load divided by the input mechanical pumping power, has a maximum value of \(\epsilon_{\text{max}} = \alpha/(\alpha + 2(\sqrt{1 - \alpha} + 1 - \alpha))\), which occurs at the optimized load resistance \(R_L = R_{\text{ch}}/\sqrt{1 - \alpha}\), where \(\alpha \equiv S_{\text{str}} Z_{\text{ch}} R_{\text{ch}}\). The authors went on to calculate \(\epsilon_{\text{max}}\) for a slab geometry using the Poisson–Boltzmann and Navier–Stokes equations to describe the electrostatics and fluid flows, respectively. This approach
has been shown to be appropriate in experiments on slit-like silica nanochannels [35–37]. The fluid shear plane for those channels was taken to be the silica channel surface.

At surfaces where hydrodynamic slip occurs, recent molecular dynamics simulations of a solid–water interface indicate that the nonlinear Poisson–Boltzmann equation provides an excellent approximation to the charge distribution, as does the Navier–Stokes equation for the fluid dynamics [20]. This is somewhat fortuitous considering the layering of water and ions that occurred within the first few molecular diameters of the surface. The observation of slip at highly charged surfaces [the surface. The observation of slip at highly charged surfaces (σ ≈ 600 mC m⁻²) was particularly interesting, because charge would be expected to promote wetting and hinder slip. These results lend strong support to the theoretical framework we now apply to study the influence of slip on the energy conversion efficiency in a slab of length L and height h.

2.2. Modeling electrokinetic effects in a slit-like nanochannel with hydrodynamic slip

We begin with the Navier–Stokes equation for a fluid with a net ionic charge density:

\[
\frac{\eta}{\rho} \frac{d^2 u(x)}{dx^2} - \frac{\Delta V}{L} \int e^{-\psi(x)/2} \left( e^{-\psi(x)/2} \right) dx + \frac{\Delta p}{L} = 0 \tag{3}
\]

where \( \epsilon_0 \) is the permittivity of fluid, \( \eta \) is its viscosity, \( e \) is the electron charge and \( (k_B T/e) \psi(x) \) is the electrostatic potential. \( \psi(x) \) is related to the net ionic charge density, \( \rho(x) \), by Poisson’s equation, and to the densities of the different ionic species, \( n_i(x) \), by the Boltzmann equation. We take \( \psi(x) \) to be the analytic solution of the Poisson–Boltzmann equation [38]:

\[
\psi(x) = \psi(0) + 2 \ln \left( \text{JacCD} \left( \frac{\sqrt{L}}{2} \epsilon^{-\psi(0)/2} \right) \right) \tag{4}
\]

where \( \text{JacCD}(z|m) \) is the Jacobian elliptic function with argument \( z \) and parameter \( m \). This expression is exact through the regime of double layer overlap. Note that the dependence on the monovalent salt concentration, \( n \), is contained within the definition of the Debye length through \( \kappa^2 = 2e^2n/(\epsilon \epsilon_0 k_B T) \).

The effects of slip arise when the Navier boundary condition is applied to solutions of equation (3) at the channel surfaces (\( x = \pm h/2 \)). The surface should not differentiate between pressure-driven and electro-osmotically induced shear, so both flow profiles are modified. The pressure-driven velocity profile, \( u_p \), corresponds to flow in the absence of an applied potential (figure 1, red) and is given by [21–24]:

\[
u_p(x) = \frac{\Delta p h^2}{8 \eta L} \left( 1 - \frac{4x^2}{h^2} \right) + \frac{\Delta p h b}{2 \eta L}. \tag{5}
\]

The first terms in equation (5) give the velocity profile in the no-slip case, while the last term is the additional velocity due to slip. It is easy to show that the rate of viscous energy dissipation in a pressure-driven flow, which is proportional to \( \int_{-h/2}^{h/2} \Delta p \eta b^2 dx \), is independent of slip.

The electro-osmotic velocity profile, \( u_e \), corresponds to flow where \( \Delta p = 0 \). Additional, electrical boundary conditions are needed to fully define \( u_e \), so a constant surface charge density, \( \sigma \), is imposed using Gauss’s law, \( \sigma = \pm \epsilon e \frac{d \psi}{dx} \bigg|_{x = \pm h/2} \). This approach has the advantages of being exact for all \( \sigma \) and it provides a good description of experimental results for silica nanochannels [6, 35, 36]. The constant-\( \sigma \) condition also specifies the potential at the surface, \( \psi(\pm h/2) \), which we distinguish from the zeta potential because the latter is conventionally defined at the shear plane, and therefore lies inside the channel wall when there is slip. The solution to \( u_e \) is found to be

\[
u_e(x) = \frac{\epsilon e_0 \Delta V}{\eta L} \left( \frac{k_B T e}{4} \left( \psi(x) - (\psi(h/2)) \right) \right) - \frac{\Delta V}{\eta L} \sigma b. \tag{6}
\]

The first terms correspond to electro-osmosis in the no-slip case and the last term gives the increase due to slip. Equation (6) predicts that the slip velocity is independent of salt concentration. In contrast, the assumption of a constant surface potential leads to a salt-dependent slip velocity because increasing \( n \) implies a shorter Debye length and therefore greater shear at the surface [7, 9, 16].

It is straightforward to write down expressions for \( Z_{ch}, R_{ch} \) and \( S_{et} \) in terms of \( u_p \) and \( u_e \):

\[
\frac{1}{Z_{ch}} = \frac{\int_{-h/2}^{h/2} u_p(x) dx}{w(h^3 + 6h^2 b)} \tag{7}
\]

\[
\frac{1}{R_{ch}} = \frac{\int_{-h/2}^{h/2} \Delta V L \sum_{i} e \mu_i \rho_i(x) u_p(x) dx}{w} \tag{8}
\]

\[
S_{et} = \frac{\int_{-h/2}^{h/2} \rho(x) u_p(x) dx}{\Delta V L} \tag{9}
\]

In equations (7)–(9), \( \mu_i \) is the electrophoretic mobility of ion species \( i \).

3. Results and discussion

To study the behavior of a slab device, we calculated the quantities defined in equations (7)–(9) for an aqueous solution of potassium chloride [1]. Equations (4)–(9) were evaluated numerically using Mathematica to compute the values of \( R_{ch}, S_{et} \) and \( \epsilon_{max} \) presented in figures 3–5. First, the potential distribution (equation (4)) was calculated for a given \( h, n \) and \( \sigma \). This potential was then used to calculate the electrokinetic response quantities using equations (5)–(9), from which \( \alpha \) and \( \epsilon_{max} \) were finally obtained.

We note that this model makes several simplifying assumptions about figure 2 by focusing entirely on the properties of the slit-like channel. In particular, it ignores the entrance effects where the channel meets the reservoirs, takes the potential drop between the electrode and the electrolyte to be zero and only considers a simple solution of potassium chloride. In practice, the choice of channel geometry, electrode material and ionic species can influence the access impedances,
Figure 3. Salt-concentration dependence of $\varepsilon_{\text{max}}$ in nanochannels with hydrodynamic slip. The efficiency was calculated as a function of $n$ for $h = 100$ nm, $\sigma = 10$ mC m$^{-2}$, and slip lengths of $b = 0$ nm (no-slip, red), $b = 10$ nm (dark red) and $b = 50$ nm (black).

The falloff occurs around $n = 10^{-4}$ M, which roughly corresponds to the onset of double layer overlap. Remarkably, the peak efficiency of 7% that was calculated for the no-slip case was increased to 17% for $b = 25$ nm and to 37% for $b = 50$ nm. The $n$ dependence of $\varepsilon_{\text{max}}$ shows that the efficiency is highest in the low-salt regime, whatever the slip length. This occurs because, when the opposing double layers overlap, the counterion concentration extends maximally into the center of the channel, where the pressure-driven fluid velocity is highest.

Figure 4 plots the dependence of $S_{\text{str}}$, $R_{\text{ch}}$ and $\varepsilon_{\text{max}}$ on $b$ for three channel heights in the low-salt regime. $S_{\text{str}}$ increased modestly for short $b$, but then increased rapidly with $b$ beyond $b = 10$ nm for $h = 25$ nm. This shifted toward higher $b$ with increasing $h$. This strong influence of $b$ on $S_{\text{str}}$ is what accounts for slip-enhancement of $\varepsilon_{\text{max}}$. The streaming conductance is an indication of the coupling strength between the electrode polarization and the ionic mobility, respectively. These effects can be minimized in a real device, but they are not explicitly modeled here.

Figure 5. Surface-charge dependence of electrokinetic transport and energy conversion efficiency. (a) $S_{\text{str}}$, (b) $R_{\text{ch}}$ and (c) $\varepsilon_{\text{max}}$ are plotted against $\sigma$ for the slip lengths $b = 0$ nm (no-slip, red), $b = 10$ nm (dark red) and $b = 50$ nm (black). All plots correspond to $n = 10^{-6}$ M solution in channels where $h = 100$ nm, and $w/L = 1$.

Hydrodynamic slip results in large increases in efficiency. Figure 3 presents the salt-concentration dependence of $\varepsilon_{\text{max}}$ for 100 nm high channels with $\sigma = 10$ mC m$^{-2}$, and slip lengths of 0 (no-slip), 25 and 50 nm. In all cases the efficiency is maximal over a broad, low-salt plateau, followed by a decay to zero efficiency with increasing $n$. The falloff occurs around $n = 10^{-4}$ M, which roughly corresponds to the onset of double layer overlap. Remarkably, the peak efficiency of 7% that was calculated for the no-slip case was increased to 17% for $b = 25$ nm and to 37% for $b = 50$ nm. The $n$ dependence of $\varepsilon_{\text{max}}$ shows that the efficiency is highest in the low-salt regime, whatever the slip length. This occurs because, when the opposing double layers overlap, the counterion concentration extends maximally into the center of the channel, where the pressure-driven fluid velocity is highest.
I and $Q$. When the fluid near the wall acquires a finite velocity, the high concentration of counterions there can contribute to the streaming conductance.

$R_{ch}$ decreased modestly with $b$ before dropping sharply beyond the same onset as for $S_{crit}$. This reveals the facilitation of electrically driven ion transport by slip in the electro-osmotic flow profile. The value of $R_{ch}$ is essentially independent of $b$ because, in the low-salt regime, the transport of counterions in the double layer dominates [35]. Power is dissipated as $(\Delta V)^2/R_{ch}$ when an ionic current is electrically driven across the channel resistance, so the decrease in $R_{ch}$ with $b$ tends to a decrease $\epsilon_{max}$.

The net effects of slip on $\epsilon_{max}$ are shown in figure 4(c), where a sharp increase with $b$ can clearly be seen. The sharpest rise in efficiency begins at $b \approx 10$ nm in thin, 25 nm channels, and shifts to higher $b$ in larger channels. The efficiency of the electrokinetic energy conversion mechanism approaches 100% as $b$ diverges.

The influence of $\sigma$ on $S_{crit}$, $R_{ch}$ and $\epsilon_{max}$, is plotted in figure 5 for $h = 100$ nm and for slip lengths of $b = 0$, 10 and 50 nm, and reveals the important role that the counterion distribution plays. In the case of no-slip, $S_{crit}$ increases with $\sigma$ because this entrains more counterions into the channel, but this increase saturates somewhat at high $\sigma$ because of the nonlinearity of the Poisson–Boltzmann model. At high $\sigma$, additional counterions collect in a very thin and highly concentrated layer at the surface, where they are weakly advected. In the case of slip, that additional boundary layer charge is easily transported by a pressure-driven flow, which explains the strong increase in $S_{crit}$. There is also a sharper decrease in $R_{ch}$ than in the no-slip case because at high $\sigma$, the boundary layer of counterions imparts a tremendous shear on the surface, thereby increasing the slip velocity. Again, this decrease in $R_{ch}$ leads to increased energy dissipation and is more pronounced than is predicted using the linearized Poisson–Boltzmann model.

There is a peak in the plot of $\epsilon_{max}$ as a function of $\sigma$ (figure 5(c)) for all slip lengths. This reflects the competition between the efficiency gains from advecting more counterions in the double layer as $\sigma$ is increased, and the increased resistive dissipation caused by those additional counterions. As compared with the no-slip case, hydrodynamic slip ensures that there is a very gentle decrease in $\epsilon_{max}$ at high $\sigma$ because additional counterions in the boundary layer contribute significantly to the streaming current.

The most promising material for achieving large slip effects in electrokinetic experiments appears to be graphitic carbon. Its structural properties are perfectly suited to exhibit slip [39, 40], as the surface can be made atomically smooth and the nonpolar, covalent, inter-atomic bonds make it extremely hydrophobic. Recent mass transport experiments through carbon nanotube filters, like the one sketched in figure 6(a), have reported extraordinarily long slip lengths of several hundred nanometers [25] and even 68 mm [26]. Used as electrokinetic energy conversion devices, such nanotube filters would be expected to achieve $\epsilon_{max} = 74\%$ with $b = 300$ nm, and $\epsilon_{max} > 99\%$ with $b = 30$ nm (for $\sigma = 10$ mC m$^{-2}$ and 1 mM salt). Facilitated mass transport should also increase the output power density at a given pressure according to $Q\Delta p = (R_{ch} + R_i(1 - \alpha))/((R_{ch} + R_i)Z_\sigma)(\Delta p)^2$. The same nanopore filters would therefore be expected to generate 0.72 W m$^{-2}$ and 1.2 W m$^{-2}$, respectively, for $\Delta p = 1$ bar and $L = 2 \mu$m, and where the total area inside the tubes accounts for only $6.3 \times 10^{-7}$ and $1.9 \times 10^{-6}$ of the total filter area, respectively. Since the output power should scale with the number of tubes in a membrane, high power densities of several kW m$^{-2}$ (at $\Delta p = 1$ bar) could be expected from high density nanotube devices, where the fractional area of the tubes reaches 1%. We also note that for such high $\epsilon_{max}$, where $\alpha \approx 1$, the electrical impedance $R_i$ is expected to have a significant effect on the apparent fluidic impedance.

The impressive electrokinetic properties predicted for carbon nanotube channels have not yet been measured in careful experiments. A well-defined nanofluidic geometry made using highly oriented pyrolytic graphite (HOPG) surfaces (figure 6(b)) would be well suited for testing our predictions. The required surface charge density may be established through either chemical modification, embedding the nanotubes in a material that acts as a charge dopant or by applying a voltage to the surface to take advantage of the electrical conductivity of graphite. If hydrodynamic slip can be consistently realized in fluidic devices, it could have a tremendous impact on applications driven by electrokinetic effects, including energy conversion. In addition, such experiments would advance our understanding of the double layer. A layer of counterions that lies behind the shear plane, called the Stern layer, is often invoked to account for discrepancies in the surface charge or potential that are established by different techniques on the same system, e.g. streaming currents and electrical conductance in silica nanochannels [6]. Hydrodynamic slip establishes a shear plane behind the surface, which means that all counterions should be transported in a pressure-driven flow and the different measurements of the surface charge should converge.

4. Conclusions

In conclusion, our calculations have shown that hydrodynamic slip at the surface of a nanofluidic channel can greatly enhance the efficiency with which a pressure-driven fluid flow can be used to drive an external electric load. The electrokinetic
transport model is based on the nonlinear Poisson–Boltzmann description of the double layer, the Navier–Stokes description of fluid dynamics, and the application of the Navier slip condition to both pressure-driven and electro-osmotic flow. This approach remains valid in the regime of double layer overlap and high surface charge density, where the maximum energy conversion efficiency is predicted. For moderate slip lengths of tens of nanometers, the efficiency of a nanofluidic device should reach interesting values near 40% using practical, millimolar salt solutions. For the extraordinary slip lengths recently reported for carbon nanotubes, the predicted efficiency exceeds 70% and the predicted output power density may reach useful levels. Nanofluidic devices with graphitic surfaces appear, therefore, to offer an intriguing system in which to explore slip-enhanced fluidic technologies and the details of the solid–fluid interface.

Acknowledgments

The authors wish to thank Frank van der Heyden for useful discussions, Kenneth Breuer for useful discussions and advice on the manuscript and Brown University for funding.

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