



Research paper

# Electrokinetic energy conversion in a finite length superhydrophobic microchannel

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## ABSTRACT

We investigated the effect of superhydrophobic walls on electrokinetics phenomena in a finite-length microchannel with superhydrophobic walls (in both transient and steady-state). We implemented the effect of superhydrophobicity using Navier's slip-length. To include the importance of the electric double-layer, we scaled the slip-length with respect to Debye-length ( $\kappa^{-1}$ ). By increasing the slip-length from 0 to 144 nm ( $1.5\kappa^{-1}$ ), streaming-current, streaming-potential, flow-rate and electrokinetic energy conversion increased by 2.55, 2.44, 1.8, and 3.4 folds, accordingly. The electrokinetic energy conversion of each microchannel was in the order of picowatt. To produce more energy, an array of microchannels should be used.

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## 1. Introduction

Electrokinetics was first documented at the beginning of the 19th century, and the fundamental theories were derived from experiments of Wiedemann about half a century later [1]. Quincke discovered the phenomenon of streaming potential in 1859 [2]. Development of the electrokinetics theories was continued during decades by scientists such as Helmholtz [3] who first developed the electric double layer (EDL) theory, relating analytically the electrical and fluid flow parameters of electrokinetic transport, through modern times, i.e. Gouy [4], Chapman [5], Smoluchowski [6], Debye and Hückel [7]. When an electrolyte solution is pumped through a microchannel with charged walls, ions in the mobile part of the EDL are transported downstream. This creates an ionic current, referred to as the streaming or convection current. The streaming current and fluid flow are in the same direction [2]. The accumulation of ions downstream creates an electric field, which results in a conduction current. The direction of conduction current is opposite to the direction of streaming current. At steady state, when the conduction current becomes equal to the streaming current, the final electric potential difference between the two ends of the microchannel (called streaming potential) is attained [8].

A set of three equations are involved in analyzing the streaming potential phenomena: Navier-Stokes (N-S) for the hydrodynamic part, Poisson which relates the electric potential to charge density, and Nernst-Planck (N-P) for ion transport. These equations are presented here. The N-S equation for this electrokinetic problem is [9]:

$$\rho \left( \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \hat{\mathbf{A}} \cdot \nabla \mathbf{u} \right) = -\nabla p + \mu \nabla^2 \mathbf{u} - \rho_f \nabla \psi \quad (1)$$

where  $\rho$  ( $\text{kg}/\text{m}^3$ ) is the fluid density,  $\mathbf{u}$  ( $\text{m}/\text{s}$ ) is the 2D velocity field with two components in radial and axial directions (i.e.  $u$  and  $v$ , respectively),  $t$  ( $\text{s}$ ) is time,  $p$  ( $\text{Pa}$ ) is pressure,  $\mu$  ( $\text{kg}/\text{s}\cdot\text{m}$ ) is the viscosity,  $\rho_f$  ( $\text{C}/\text{m}^3$ ) is the free electrical charge density and  $\psi$  ( $\text{J}/\text{C}$ ) is the electrical potential. The  $\rho_f$  in Eq. (1) is defined as [9]:

$$\rho_f = \sum v_i e n_i \quad (2)$$

where  $v_i$  is the charge number or valence of the  $i$ th ionic species,  $e$  ( $\text{C}$ ) is the elementary charge, and  $n_i$  ( $1/\text{m}^3$ ) is the ionic number concentration of the  $i$ th species.

The Poisson equation is [9]:

$$\nabla^2 \psi = -\frac{\rho_f}{\epsilon} \quad (3)$$

where  $\epsilon$  ( $\text{F}/\text{m}$ ) is the dielectric permittivity of the liquid.

The N-P equation which captures convection, diffusion and migration ion transport in an electrolyte solution, and is subjected to the induced electrical field, becomes [9]:

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$$\frac{\partial n_i}{\partial t} = -\nabla \cdot \mathbf{J}_i = -\nabla \cdot \left( n_i \mathbf{u} - D_i \nabla n_i - \frac{v_i e n_i D_i}{k_B T} \nabla \psi \right) \quad (4)$$

where  $\mathbf{J}_i$  ( $\frac{1}{m^2 s}$ ) is the ionic flux vector,  $D_i$  ( $\frac{m^2}{s}$ ) is the diffusivity of the  $i$ th ionic species,  $k_B$  (J/K) is the Boltzmann constant and  $T$  (K) is the temperature.

Knowing the spatial distribution of  $\rho_f$  and the fluid velocity can help us finding the streaming current ( $I_{conv}$ ), as shown in [10]. It should be noted that our method does not embed any of the common approximations, e.g. the Debye-Hückel approximation used in [11].

The surface-to-volume ratio is high in microchannels, which results in surface-charge governed transport [8]. Most of the studies in recent years have solved, modeled, or experimented the electrokinetic problems assuming no-slip boundary condition at the walls e.g. [1,2,9,12–14]. When dealing with macro-scale problems on regular surfaces, no-slip boundary condition at the wall is a rational boundary condition. However, for micro and nano-scale channels, no-slip condition may become inaccurate [15]. Especially when dealing with superhydrophobic surfaces. Superhydrophobic surfaces allow the fluid to slip on them. The application of these surfaces is becoming widespread in microfluidics and electrokinetics. Therefore, development of solution with slip boundary condition is needed.

Regarding superhydrophobic surfaces, it should be noted that these surfaces are originally inspired by nature, e.g. lotus leaves. Due to the rough topography and low surface energy, water drops bead up and roll off easily on these surfaces [16]. Superhydrophobic surfaces are suggested for self-cleaning [17], anti-fogging [18], and drag-reduction [19] applications. Also, they have been suggested for increasing the efficiency of electrokinetic phenomena [17,20]. There are several methods of manufacturing these surfaces, including sol-gel based methods, chemical deposition, sublimation, controlled polymerization, self-assembly of nanorods/nanotubes on the surfaces, and electrochemical methods e.g. [17,21].

To quantify the slip velocity on superhydrophobic surfaces, researchers have used the Navier's slip-length [22]:

$$U_{slip} = \beta \left( \frac{\partial U_s}{\partial n} \right)_{wall} \quad (5)$$

where  $U_{slip}$  is slip velocity,  $\beta$  is slip-length,  $U_s$  is the liquid velocity parallel to the surface and  $n$  is the normal to the wall unit vector. A schematic of the definition of slip-length is shown in Fig. 1. Although, slip-length may be a function of flow parameters, but in

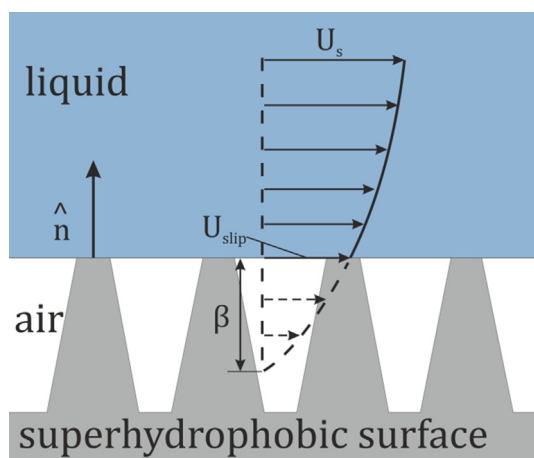


Fig. 1. Schematic of the fluid velocity profile, slip velocity and slip-length on superhydrophobic surfaces is shown.

general, on hydrophobic surfaces its value is in the order of tens of nanometer [22,23]. On superhydrophobic surfaces slip-length can be in the order of hundreds of micrometer [24] as long as wetting remains in the Cassie-Baxter state [17]. Although, both hydrophobic and superhydrophobic surfaces are made from materials with low surface energy [25]; the difference between them is in the existence of micro- and nano-scale roughness on superhydrophobic surfaces [26].

Studies analytically (e.g. [20,27–29]), semi-analytically (e.g. [11,30]) and numerically (e.g. [31]) showed that increasing the slip-length in the order of a few nanometers enhances the electrokinetic phenomena. Or in [32,33] using molecular dynamics method, it was shown that slip amplifies the electroosmotic effect and streaming current. The enhancement depends on the microchannel size and shape. For example, in [27] it was shown that for a 100 nm diameter microchannel a 6.5 nm slip-length increases the streaming potential by 30%.

Regarding utilization of superhydrophobic surfaces in electrokinetics, Yang and Kwok [34] analytically showed slip-length of 1  $\mu\text{m}$  in an infinite cylindrical microchannel with the radius of 20  $\mu\text{m}$  improves the electroosmotic flows. They reached similar results for other microchannel geometries as well [35,36]. Although most of the studies predict an increase in electrokinetic properties by increasing the slip-length, some indicate the opposite is true, e.g. [37,38]. In [37,38] it was stated that using superhydrophobic surfaces reduces the surface charge density. Based on that, they concluded that using superhydrophobic surfaces results in a reduction in streaming potential. However, reduction of surface charge density for superhydrophobic surfaces is the subject of debate. Squires [39] considered three different cases for distribution of charge on the air gaps: (i) charge is equal to that on solid-liquid interface, (ii) charge is different from that on the solid-liquid interface, and (iii) there is no charge on the gap. Bahga et al. [40] also considered two cases of charged and uncharged gas-liquid interface. In a recent study [41], via experiments, it was shown that the charge on the air gap is comparable to that on solid-liquid interface. The surface pattern in [41] was sharp tip cone (STC) nanotexture on silicon. The other interesting observation in [41] was that although the surface was superhydrophobic, the slip-length only reached  $44 \pm 4$  nm. This small slip-length on a charged superhydrophobic surface compared to the uncharged superhydrophobic surface is explained in [20]. It is stated that charge promotes wetting and hinders slip. So, on charged superhydrophobic surfaces, the slip-length is in the range of tens of nanometers [20,32,42].

Studying the effect of charged superhydrophobic walls on the efficiency of streaming potential with realistic slip-length values (in the order of hundred nanometers) is needed. Also, abovementioned studies (i.e. [11,20,27–36]), ignored the fully Nernst-Planck (N-P) equation, which accounts for ion transport. In other words, they have solved a 1D Poisson-Boltzmann equation and ignored any axial variation of ion concentrations within the channel, e.g. [43]. The axial ion concentration variation which is caused by ion rejections is only captured when N-P equation is included [9]. Furthermore, only [34–36] solved the problem in a time-dependent manner. We believe the transient solution can contribute to understanding electrokinetic slip flows and shed some light on the effect of superhydrophobic surfaces on the transport of mobile ions and net charge density.

In this paper, we study the electrokinetic behavior of a pressure driven flow in a finite length microchannel with charged superhydrophobic walls in both transient and steady-state. Numerical simulations are performed for two case studies with two channel radiuses of 0.1  $\mu\text{m}$  and 0.5  $\mu\text{m}$ . It is demonstrated that slip on walls of the microchannel affects the transport of ions, streaming potential, streaming current and efficiency of the electrokinetic energy

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