ENERGY CONVERSION IN CARBON NANOTUBES

ABSTRACT

Liquid flow induced electric power generation in carbon nanotubes has attracted a great interest in the past few decades. Different flow regimes for oxide materials have been reported for varying setups which have shown poor reproducibility and simulations have not been verified experimentally [1],[2],[6],[7]. In this proposal we consider the role of the velocity slip condition and friction at the solid-liquid interface and how these affect the electric properties at the surface leading to the variations in the streaming potential and currents, for flow in a carbon-nanotube. We have proposed to develop a model to consider the entrance/exit effects, the pressure effects and the effect of the double layer on the volumetric flow through a carbon-nanotube. This volumetric flow rate could be used to evaluate the efficiency of a given system.

INTRODUCTION

Microfluidics has emerged to be an area of extensive research over the last few decades providing deep insights towards novel technological advancements in fluid dynamics [1]. A few of the technologies being studied include physical phenomena such as the capillary effects, species diffusion at the micro and nanoscales, electrokinetics, as well as hydrophobicity and hydrophilicity. Significant importance has been given to research in all of the above mentioned properties individually. In recent times, a considerable amount of research has been directed towards the interactions of electrokinetics and hydrodynamics in an attempt to gain efficient systems for electrical conversion in microsystems [2].

Improving the energy conversion efficiency has always been one of the primary goals in any system being studied and recent advancements in the various microfabrication techniques have led to the development of novel devices for conversion of energy at the microscale. How efficiently can mechanical energy be converted into electrical energy through a miniaturized microfluidic device?[4],[5] The main challenge has been the development of miniaturized flow channels that would give conversion efficiencies similar to those observed in the modelling simulations[2].

In general, most solid surfaces obtain a surface electrical charge when they are in contact with a polarizable electrolyte solution [2]. This interaction leads to a development of an electrical double layer (EDL) at the solid-liquid interface [2]. The charges developed on the walls are significant in the nano-regime due to the large surface area to volume ratio as the Debye length approaches the distance between the walls of the nanochannel[15]. When pressure-driven transport ensues in a microchannel, the fluid flow drives the net charge within the EDL downstream thereby resulting in an electric current, known as the streaming current [5]. Further, the accumulation of the charges downstream creates an electric potential between the ends of the channel, known as the streaming potential. The development of these currents and potentials provide the possibility of converting mechanical energy into electrical power [4],[5].

Flows in micro-channels are highly influenced by the surface properties due their large surface area to volume ratio. Understanding the fluid dynamics very close to the solid surface plays a significant role in the development of new devices and modelling techniques [15]. Studying the flow matter in fluids at small scales has become possible in recent years due to advancements in computational techniques, nanofabrication technologies, and measuring equipment[1],[2],[3],[4]. Specific examples include molecular dynamics, and optical velocimetry [4].

The principle differentiation between studies at the microscale and the macroscale is the assumption of a no slip boundary condition. Various studies have concluded that the no-slip boundary condition may be violated in many situations, which has been seen to be controlled by the wetting properties of the fluid on the solid surface [4],[7]. While the no-slip condition is satisfied on hydrophilic surfaces, a finite slip has been measured in several experiments on hydrophobic surfaces which originate due to the low liquid friction on the surface wall [1],[4],[7]. A major discrepancy arose between experimental and simulation results about estimates of the boundary conditions. While simulations predict higher magnitudes of both slip and surface potential, a question arises whether the two surface properties can be coupled and related to each other. One limitation is that that the experimental results have poor reproducibility [2],[6],[7].

LITERATURE REVIEW

The energy produced from nanofluidic channels is one of the most sought after technologies because of the simplicity of the device, the only requirements are a nanometre sized channel, a polarizable electrolyte and a pressure gradient [5]. The pressure gradient transports the electrolyte through the nanochannel, causing the generation of the streaming currents and potentials along the channel in the electric double layer (EDL) which can be used to drive external loads [5]. Simulations
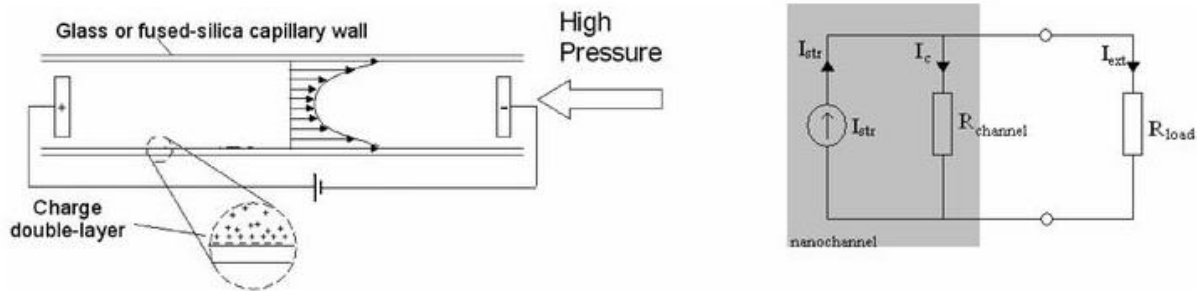

Figure 1: Illustration showing the electro-kinetic effects and the experimental nanochannel setup [5].

have shown that increasing the slip in nanochannels increases the streaming current effects. We can theoretically calculate the changes in the efficiency of the device due to liquid slip using simple models that account for the ionic conductance and the zeta potential due to overlapped double layers [5].

The efficiency of electrical conductance of the device can be calculated using the following relation [5]:

$$\epsilon = \frac{I_{str} V_{str}}{(\Delta P) Q} \tag{1}$$

Where, ΔP is the pressure drop across the channel, Q is the flow rate through the channel, I_{str} is the streaming current and V_{str} is the streaming potential.
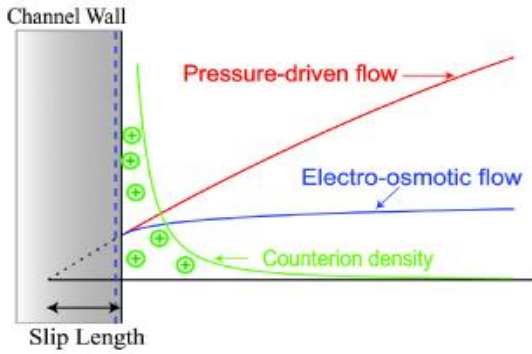

Figure 2: Hydrodynamic slip in a nanochannel [6].

The volumetric flow rate can be solved by integrating the velocity profile along the channel. This flow rate results from combination of pressure gradient and the electroosmotic flow (EOF) in a cylindrical channel according to Pennathur, Eijkel and van den Berg [5] is given by:

$$u(r) = \frac{(R + l_s)\Delta P}{4\mu L}\left(1 - \frac{r^2}{(R + l_s)^2}\right) - \frac{\epsilon_r \zeta V_{str}}{\mu L}\left(1 - \frac{\psi(r)}{\zeta}\right) \tag{2}$$

Where, R is the radius of the channel, l_s is the slip length, ε_r is the dielectric constant, L is the length of the channel, ζ is the zeta potential, $\Psi(r)$ is the transverse potential distribution, and V_{str} is the streaming potential. Thus the volumetric flow rate can be evaluated as [5]:

$$Q = 2\pi \int_0^R u(r)\,dr \tag{3}$$

The transverse potential distribution can be evaluated using the Poisson equation for cylindrical coordinates [5]:

$$\rho(r) = -\epsilon \frac{1}{r}\frac{d}{dr}\left(r\frac{d\psi(r)}{dr}\right) = -2ezn_\infty \sinh\left(\frac{ze\psi(r)}{kT}\right) \tag{4}$$

The streaming current in the channel can be evaluated similarly using the following equation [5]:

$$I_{str} = 2\pi \int_0^R u(r)\psi(r)\,dr \tag{5}$$

The streaming potential can be evaluated using the conduction current that arises from the electric field created due to the polarization of the charge along the positive x-axis. This current balances the streaming potential in power conversion studies, hence the two equations can be equated to find the streaming potential [5].

$$I_{cond} = 2\pi \int_0^R \left(\frac{\sigma(r)V_{str}}{L}\right) r\,dr \tag{6}$$

It is evident from macroscale fluid dynamics that the hydrophobicity of a surface is seen as the slipping of water over that surface [4]. The typical slip length is evaluated as a Navier-Stokes slip boundary condition given by [4]:

$$u(0) = l_s \frac{\partial u}{\partial n} \tag{7}$$

Where, u is the velocity along the direction of flow and n is the outward – normal coordinate to the solid-liquid interface. The value of slip length is generally determined experimentally [1],[7]. A theoretical study of the boundary condition over various surfaces showed that for an electroosmotic flow over slippery and non-slippery surfaces the zeta potential is proportional to $(1+l_s/\lambda_D)$, where

λ_D is the Debye length for the system under consideration[4],[5],[8]. The zeta potential can be written as:

$$\zeta = V_0 \left(1 + \frac{l_s}{\lambda_D}\right) \qquad (8)$$

Further, a perturbation analysis for slippery surface hydrodynamics over a surface with controlled wettability and surface charge shows a very important and interesting relation between the flow velocity and the double layer. It was observed that a decrease in the EDL resulted in a significant augmentation of the flow velocity, in contrast to what is expected for EOF where the velocity saturates with decreasing EDL[6].

In another study performed at Brown University showed positive results for the efficiency of the electric conversion for an aqueous solution of potassium chloride in a slit-like channel [13]. This model uses the nonlinear Poisson-Boltzmann equation for charge distribution and the Navier-Stokes equation for fluid dynamics. Hydrodynamic slip resulted in large increases in efficiency and concentration dependence proved that efficiency is the highest at lower concentrations. The study concluded that efficiencies of 40% could be achieved using practical systems with low concentrations for a moderate slip lengths of the order of 10nm [13]. For large slip lengths, as those reported for carbon nanotubes, the predicted efficiencies could exceed 70%. Hence, graphitic surfaces offer an opportunity to explore the slip-enhanced fluidic technologies [13].

While the oxide materials have sparked a remarkable amount of interest in the electrokinetic energy conversion process due to the relative ease of experimental access, results are poorly reproducible [2],[6],[7]. The surface properties depend on the experimental preparations and different experimental groups are unable to reproduce similar results [2]. Collaboration between simulations and experiment is therefore difficult [2]. The same surface properties that are under investigation

could also be studied more collaboratively in carbon nanotubes and biological pores. These materials could have more reproducible experimental characteristics thereby facilitating collaborations. These are difficult to assemble and so it is difficult to validate a specific model. Carbon nanotubes have been tested experimentally and high slip lengths have been confirmed [9],[12]. Carbon nanotube membranes can be fabricated by inserting the carbon nanotubes into a membrane into a synthetic membrane. The advantage is that these pores are atomically smooth and can create an almost unimpeded flow of water which is comparable to the transport of molecules through biological pores [10]. Similar processes have also been used to construct carbon nanotube membranes which have been shown to have high levels of slippage. The electric double layer effect is also observed with carbon nanotubes. The observed levels of slip are much higher likely due to their smooth surface [9].

PROPOSED RESEARCH

The overall approach to the research is to use the LAMMPS simulation package for the simulation of pressure driven pure water flow through carbon nanotubes of different heights [11]. The question is if a robust model of fitted data from multiple tube heights can be predicted by one model equation [11]. This research has practical implications for explaining special nanofluidic phenomena especially for the very small tube heights where water can transition between different flows including single file flow through the tube [12]. This is especially important because carbon nanotubes are difficult to use experimentally and could be a more reliable material than other oxide materials. There are electrical energy generating applications to this theory as well. The use of molecular simulations is the most suitable way to answer the research question because of the difficulty posed by experimentally working with nanochannels, and the relative ease with which

individual properties can be analyzed computationally. The criteria for validity and rigorousness will depend on the statistical significance and R^2 value as well as how well the model agrees with the experimental data.

A range of different carbon nanotubes should be simulated each with different heights. It would be particularly interesting to model carbon nanotubes with small heights of about 4 angstrom because water is expected only to flow in a single column through these channels. The simulation will be setup using an NVT ensemble consisting of a graphene nanochannel connected to two water reservoirs on both sides [11]. The water will be made to flow from one side of the reservoir to the other due to the force of a rigid piston made of an additional graphene sheet [11]. The Nose-Hoover thermostat can be used to maintain the temperature of the system at T=300 K [11]. The velocity-Verlet algorithm can be used to integrate the equations of motion and periodic boundary conditions can be imposed in all directions [11]. The intermolecular interactions between carbon atoms in the graphene sheet can be calculated with the Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential [11]. Water molecule interactions can be computed using the aid of the transferable intermolecular potential 4 points (TIP4P) [11]. The Lorentz-Berthelot mixing rule is taken to include cross interactions. Long-range electrostatic interactions were computed with the use of particle-particle-particle-mesh (PPPM) method [11]. The cutoff radius of 10 and 12 angstroms can be used to compute the van der Waals and Columbic interactions, respectively [11].

After the simulation data has been generated it can be fit to a cubic equation with respect to pressure and the channel radius respectively [11].

$$Q = a_1 P^3 + b_1 P^2 + c_1 P + d_1 \tag{9}$$

$$Q = a_2 r^3 + b_2 r^2 + c_2 r + d_2 \tag{10}$$

Equation (9) represents volumetric flow rate as a function of the pressure gradient for a constant radius whereas equation (10) represents the volumetric flow rate as a function of the radius of the channel for a constant pressure gradient.

Next consider the velocity profile defined by equation (2) which considers both the liquid slip length as well as the zeta potential. The zeta potential is defined in equation (7), which is also varies with slip length. Then the velocity profile can be integrated over the radial and angular dimensions to provide an analytical solution that depends on the slip length. Then the slip length can be solved numerically using the flow rate such that it satisfies the assumptions that were made in defining the flow profile as defined in equation (2) and (3). Once the actual value of the slip length has been defined, the zeta potential can also be evaluated using equation (7).

The equation defining the hydrodynamic resistance, R_0 is given by equation (11) [11]:

$$R_0 = \frac{\Delta P}{Q} \tag{11}$$

This equation can be seen as an analogy to the ohms law equation ($R = \Delta V/I$), where the pressure gradient is analogous to the potential drop and the volumetric flow rate is analogous to current [11]. Then the effective hydrodynamic resistance can be found by adding an additional term to the hydrodynamic resistance which accounts for the entrance and exit effects of the stream [11].

$$R_{eff} = R_0 + \frac{m\mu}{r^3} \tag{12}$$

The coefficient 'm' and the slip length can be fitted to simulation and experimental data [11]. The effective flow rate could then be given as:

$$Q_{eff} = \frac{\Delta P}{R_{eff}} = \left(R_0 + \frac{m\mu}{r^3}\right)^{-1} \Delta P \tag{13}$$

Furthermore, some theoretical and experimental studies have reported variations in viscosity inside nanochannels with the channel diameter [11],[12]. The change in viscosity of confined water could be presented as in equation (14) and can be considered to calculate a more precise value for the volumetric flow rate [11],[12].

$$\mu = \mu_0 \left(1 + b\, e^{\left(-\frac{R}{\alpha} \right)} \right) \tag{14}$$

The volumetric flow rate thus found could be used to evaluate the actual theoretical efficiency of the energy conversion system being considered.

CONCLUSION

Energy conversion enhancement is highly desired for practical applications in electroosmotic flow through nanochannels. We have summarized the advantages of exploring the use of carbon nanotubes in studies involving electrokinetic conversion and have suggested a model for flow through the channels that could induce electricity. The mechanism is extremely dependent on the interactions of the polar ions or molecules and the carbon surface of the nanotube, and this field has a great potential to be explored. The simulations and mathematical models for these systems can be further developed taking into consideration the interactions between molecules, transport mechanisms and dependence on the ionic concentration in the fluid flowing through the channels. Experimental verification is the key to the success of these simulation models.

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