Water flow in micro- and nanochannels. Molecular dynamics simulations.

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Abstract. The flow in carbon nanotube is analysed using mathematical model that accounts for a depletion layer with reduced viscosity near the wall. The model by the author of the paper [Myers T G 2011 *Microfluid Nanofluid* 10 1141] is corrected. Moreover, the structure of the water flow inside 1 nm diameter and 1.5 nm length nanotubes is examined using molecular dynamics simulations. Molecular dynamics simulations of water flow velocity and flow rate though carbon nanotubes are reported too.

1. Introduction

Progress in micro- and nanotechnology in recent decades has led to the allocation and progress in new research areas in which combined existing science fields. The study of liquid behaviour at micro- and nanoscale (microfluidics and nanofluidics, respectively) is of great importance for various applications - biology, including cryobiology (transport of water, ions and macromolecules through pores, ice crystallization, etc), materials science (wettability surfaces, materials for artificial biological tissues, etc), microanalytical systems (micro Total Analysis Systems - TAS, MicroFluidicSystems - μ MFS, Lab-on-a-Chip – LOC, etc). The key issues here are effects of space restrictions, wettability and surface morphology on liquid properties and behaviour.

Methods used to study behaviour and properties of liquids in bulk (macro scale) are not applicable to micro- and nanoscales, but molecular dynamic method (simulations) is applicable, and is used for theoretical and numerical studies [1-11]. Density profile shows high oscillations in liquid layers adjacent to micro- and nanochannel walls, and as a consequence, there is an inhomogeneity of the liquid flow, which is not included in the classical hydrodynamic approach. In this case, predicted by Navier-Stokes velocity profiles and viscosities are violated at critical channel widths and diameters. In the case of water, these critical width or diameter of the channel corresponds to approximately 1.4 nm for the velocity profile and 5.1 nm for the viscosity [12].

Recent experiments [13-15] and molecular dynamics simulations [16-20] have shown that water is transported through carbon nanotubes (CNTs) at unexpectedly high flow rate. The flow rates of pressure-driven water through membranes of 1.6 and 7 nm diameter carbon nanotubes [21, 22] are two
to five orders-of-magnitude greater than those predicted by the continuum-based no-slip Hagen-
Poiseuille relation. These findings have a great effect on the molecular sieving, chemical detection,
and drug delivery fields, where such high flow rates would significantly increase device efficiency,
accuracy, and throughput [23]. The contained fluid structure has also been shown to depend upon the
CNT diameter: single-file molecule chains at the smallest diameters and high-density structures at
larger diameters. The flow of water inside CNTs of diameters below 1.66 nm is noncontinuum: the
problem cannot be accurately described using conventional continuum fluid mechanics with its
associated linear constitutive relations and no-slip boundary conditions [11, 20].

2. Models of flow in nanoscale channels
An important step towards understanding liquid flow in nanoscale systems is to predict the transition
from continuum to subcontinuum transport as the flow area decreases. In a continuum system, the
behaviour of a liquid can be described in terms of infinitesimal volume elements that are small
compared to the flow domain but have well defined thermophysical properties. Applying Newton’s
second law to a system of volumetric elements gives rise to the Cauchy and Navier-Stokes equations,
which can be used to derive the Poiseuille and other continuum-level flow relations [24]. In a system
where the size of a liquid molecule is comparable to the size of the flow domain, however, the notions
of a representative volumetric element and continuum-based relations are invalid. Within such
‘‘subcontinuum’’ systems, the movement of individual molecules must be considered when predicting
mass and momentum transport [25].

![Figure 1. The Hagen–Poiseuille equation, describes the classical model (a) and slip-length model (b) for flow in a circular cylindrical pipe.](image)

2.1. Boundary Conditions: No Slip-Length Model
The Hagen–Poiseuille equation, describes the classical model for flow in a circular cylindrical pipe
(see Figure 1a), is

\[ u_{HP} = \frac{-R^2}{4\mu} \frac{\Delta P}{\Delta z} \left( 1 - \frac{r^2}{R^2} \right), \]

where \( u_{HP} \) is the velocity in the \( z \) direction, \( \frac{\Delta P}{\Delta z} \) is the pressure gradient along the pipe, \( R \) is the radius
and \( \mu \) is the fluid viscosity. The corresponding flux is given by

\[ Q_{HP} = 2\pi \int_0^R u_{HP}(r) r dr = -\frac{\pi}{8\mu} \frac{\Delta P}{\Delta z} R^4, \]

and boundary conditions are
\[ \frac{\partial u}{\partial r} |_{r=0} = 0 \quad \text{and} \quad u(r) |_{r=R} = 0 \].

### 2.2. Boundary Conditions: Slip-Length and Depletion Layer Models

In carbon nanotubes, the flow is enhanced and the real value of the flux is significantly higher than this classical value. A popular approach to explain this enhancement is to introduce a slip-length (see Figure 1b) into the mathematical model, that is, the no-slip boundary conditions are replaced by

\[ \frac{\partial u}{\partial r} |_{r=0} = 0 \quad \text{and} \quad u(r) |_{r=R} = -L_s \frac{\partial u}{\partial r} |_{r=R} , \]

where \( L_s \) is the slip length.

The high values of slip-length in CNT studies have led some authors to question the validity of the slip modified Hagen–Poiseuille model [25, 26]. The authors of Ref. [27] state that the slip-length should have a single value independent of the tube radius and much less than those quoted in the literature. They attribute some of the high experimental values to contamination by hydrophobic particles. An alternative explanation to the slip-length is based on the fact that CNTs are hydrophobic [28-30] and that some experiments have shown the existence of depletion layers between water and hydrophobic surfaces [18, 27, 31, 32].

![Figure 2. Flow in a circular cylindrical pipe including a region of low viscosity (depletion layer) near the tube wall.](image)

A mathematical model for flow including a region of low viscosity (depletion layer) near the tube wall was investigated in the paper [33].

Consider a pipe of cross-section \( R \) occupied by two fluids (Figure 2). In the bulk flow region, defined by \( 0 \leq r \leq a \), the author of Ref. [33] imposes a viscosity \( \mu_1 \). In the annular region near the wall, defined by \( a \leq r \leq R \), we impose a viscosity \( \mu_2 \). The assumption of two regions with different viscosities leads to what is commonly termed a bi-viscosity model in the non-Newtonian flow literature. In this case, the boundary conditions are

\[ \frac{\partial u_1}{\partial r} |_{r=a} = 0 \quad \text{and} \quad u_1(r) |_{r=R} = 0 \]

\[ u_1(r) = u_2(r) |_{r=a} \quad \text{and} \quad \mu_1 \frac{\partial u_1}{\partial r} = \mu_2 \frac{\partial u_2}{\partial r} |_{r=a} \]

and pressure driven flow equations in cylindrical system are

\[ \frac{\partial u_1}{\partial z} - \frac{\mu_1}{r} \frac{\partial}{\partial r} (ru_1) \quad \text{and} \quad \frac{\partial u_2}{\partial z} = \frac{\mu_2}{r} \frac{\partial}{\partial r} (ru_2) \]

So, the velocities are

\[ u_1(r) = \frac{1}{4\mu_1} \frac{\Delta p}{\Delta z} \left( r^2 - a^2 \right) + \frac{1}{4\mu_2} \frac{\Delta p}{\Delta z} \left( a^2 - R^2 \right) \]

\[ u_2(r) = \frac{1}{4\mu_2} \frac{\Delta p}{\Delta z} \left( r^2 - R^2 \right) . \]
In the paper [33] there are mathematical errors in equations for fluxes $Q_1$, $Q_2$ and $Q = Q_1 + Q_2$ leading to the wrong expressions for the flow rate enhancement and ratio of viscosities. The correct expression for the total flux $Q$ is:

$$Q(r) = \frac{\pi \Delta p}{8 \Delta z} a^4 \left( \frac{1}{\mu_2} - \frac{1}{\mu_1} \right) - \frac{\pi \Delta p}{8 \Delta z} R^4 \frac{1}{\mu_2}$$

(8)

or taking into account the expression (2):

$$Q(r) = Q_{HP}(R, \mu_2) + Q_{HP}(a, \mu_1) - Q_{HP}(a, \mu_2),$$

where $Q_{HP}(a, \mu_1) = -\frac{\pi \Delta p}{8 \mu_1} a^4$, $Q_{HP}(R, \mu_2) = -\frac{\pi \Delta p}{8 \mu_2} R^4$

and $Q_{HP}(a, \mu_2) = -\frac{\pi \Delta p}{8 \mu_2} a^4$.

So, the flow rate enhancement and ratio of viscosities are

$$\epsilon = \frac{Q(r)}{Q_{HP}(R, \mu_2)} = 1 - \frac{a^4}{R^4} \left( \frac{\mu_2}{\mu_1} - 1 \right) \quad \text{and} \quad \frac{\mu_2}{\mu_1} = 1 + \frac{R^4}{a^4} (1 - \epsilon).$$

(10)

Since $\frac{\mu_2}{\mu_1} > 0$ and $\epsilon > 0$, then $0 < \epsilon < 1 + \frac{a^4}{R^4}$. In this case, since $R \geq a$ (see Figure 2), the range of flow rate enhancement to be $\epsilon \in (0,2)$. For the slip model (4), the corresponding enhancement is

$$\epsilon_{slip} = 1 + \frac{4 L_s}{R}.$$  

(11)

The wrong flow rate enhancement and ratio of viscosities in Ref. [33] are

$$\epsilon = \frac{a^4}{R^4} \left( 1 - \frac{\mu_1}{\mu_2} \right) + \frac{\mu_1}{\mu_2} \quad \text{and} \quad \frac{\mu_2}{\mu_1} = 1 - \frac{a^4}{R^4} (1 - \epsilon).$$

(12)

2.3. Depletion Layer Model Verification

To verify this model (10) the author of Ref.[33] considered an experiment described in Ref.[15]. Their flow enhancement indicates a slip length of 30–40 nm for pipes of radius $R=20$ nm. Setting $L_s = 35$ nm and $R = 20$ nm determines their enhancement factor (11) as $\epsilon_{slip} = 8$. To obtain $\frac{\mu_2}{\mu_1} = 0.018$, the author of [33] set $\epsilon = 8$ and also taken $a = 19.3$ nm in (12). Using the same data and the expression (10), we obtain $\frac{\mu_2}{\mu_1} = -4.8$ (using $\epsilon_{slip} = 8$, $R=20$ nm and $a=19.3$ nm) and $\epsilon = 1.85$ (using $\frac{\mu_2}{\mu_1} = 0.018$, $R=20$ nm and $a=19.3$ nm), but $\frac{\mu_2}{\mu_1}$ must be $>0$. At the same time, $\frac{\mu_2}{\mu_1} = 0.02$ from (10) at $\epsilon = 1.85$, $R=20$ nm and $a=19.3$ nm and this value supports the depletion layer model (the viscosity of oxygen in water is also approximately 0.02 [33]).

3. Enhancement. Molecular Dynamics Simulations

We use molecular dynamics (MD) simulation to investigate pressure-driven (28 pN per each water molecule) water flow through single wall CNTs with diameter 1 nm and length 1.5 nm. The configuration of used pressure-driven flow simulation domains are shown in Figure 3. The rigid TIP3P water model and Lennard-Jones CNT model without electrostatic are used. Water density is
1000kg/m³. Our MD simulations are performed using NAMD [34] and VMD [35], a parallelized non-equilibrium molecular dynamics solver, that is open-source and available to download from Theoretical and Computational Biophysics Group website (http://www.ks.uiuc.edu/).

![Image showing CNTs and water molecules](image)

**Figure 3.** Modelling CNTs: (a) single CNT and 101 water molecules (b) four CNTs and 248 water molecules.

Some simulation results are presented in Figure 4: (a) flow rate through the four CNTs as a function of simulation time; (b) enhancement factor of the water single chain as a function of simulation time too. One can see that the simulation time of about 30 ns is enough to obtain the convergence of flow rate and, consequently, enhancement factor. So, the flow rate is about 130 molecules per ns, the enhancement factor is 4.3 and the water molecule velocity is about 50 m/s.

![Graph showing flow rate and enhancement factor](image)

**Figure 4.** Simulation results for the flow through four CNTs: flow rate [molecules/ns] (a) and enhancement factor (b).

### 4. Conclusions

In conclusion, the depletion layer model is promising and should be further developed, e.g., by incorporating an approximation of the viscosity profile by second-degree polynomial. Molecular dynamics simulations, providing reliable information for concrete flow cases, also could produce benchmark solutions for the assessment of approximate theories.

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