Modelling flow enhancement in nanochannels: viscosity and slippage

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Abstract

With a large number of experimental and modelling papers reporting higher than expected liquid flow rates in both hydrophobic and hydrophilic nanochannels published in the last few years, there is a need to develop a coherent theoretical framework to explain these phenomena. In this work we will introduce a complete modelling and present a comparison between experimental data and predicted flows showing good agreement.

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1. Introduction

Over the last ten years numerous experimental and molecular dynamic (MD) simulations of liquid flow through carbon nanotubes (CNTs) and other hydrophobic nanochannels have shown unexpected high flow rates, with several orders of magnitude of flow enhancement compared to what predicted using classical fluid dynamics, see [1] and references therein. Moreover, water flow enhancements (albeit small) have been observed also in hydrophilic nanochannels [2, 3]. These results suggest that the observed flow enhancement is due to a combination of size confinement and solid-liquid intermolecular effects.

In a recent publication [4] the present authors have proposed a theoretical model capable of explaining both size confinement and solid-liquid interaction effects on flow in CNTs. The starting point to develop the model is the realization that when a polar liquid is flowing on a hydrophobic surface, the liquid molecules nearest to it have a higher mobility and, hence, a

lower viscosity due to an unfavourable energetic interaction [5, 6]. At the nanoscale, the effect of solid-liquid interactions is made more significant due to the higher proportion of surface liquid molecules being in contact with the channel wall compared to the bulk liquid ones: this -roughly speaking- causes the experimental flux enhancement.

The model for the viscosity used before is the so-called 2-phase model, introduced in [7]. The drawback of this model is that a discontinuity on the viscosity is introduced. In this paper a more realistic viscosity change along the tube radius has been added, and the relations between the two are considered. Finally the values for fluxes predicted by the two models are compared with the available experimental data finding good agreement.

2. The Model

2.1. Liquid flow in nanochannels

Our aim is to study a well developed laminar flow of an incompressible fluid inside a cylindrical nanochannel under an externally applied pressure gradient with variable viscosity along the channel radius. The velocity profile is invariant through the tube radius and has cylindrical symmetry. At fixed length, the Navier-Stokes equations reduce to a sole parabolic equation with a nonlinearity due to the viscosity; the velocity profile as function of the tube radius $u(r)$ solves the following:

$$\frac{1}{r}\frac{\partial}{\partial r}\left[r\mu(r)\frac{\partial u(r)}{\partial r}\right] = \frac{\Delta P}{L} \ \ \forall r \in [0, R] \, , \tag{1}$$

where μ is the viscosity of the liquid inside a nanochannel of radius R and length L, and ΔP is the externally applied pressure. Coherently with the symmetry hypothesis and conservation of mass, the following boundary conditions are considered:

$$\partial_r u(r) = 0 \, , \ r = 0 \ ; \ \ \lambda\partial_r u(r) + u(r) = 0 \, , \ r = R \, . \tag{2}$$

In Eq. (2), usually referred as linear Navier boundary condition, λ is the so-called slip length. When $\lambda = 0$ and $\mu(r) = \mu_B \ \forall r$, where μ_B is the bulk value of the liquid viscosity, integration of Eq. (1) using the boundary conditions in Eq. (2), results in the well-known no-slip model: the first monolayer of liquid molecules sticks at the wall, see [7] Eq. (1). Enhancement one can be introduced by having slip ($\lambda > 0$) or reduced viscosity ($\mu(r) \leq \mu_B$) in the model.

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2.2. Reduced Viscosity

Theoretical considerations on reduced mobility [5] and MD simulations [8] have demonstrated that the fluid viscosity is subject to 'confinement' effect near the solid boundary where the liquid is flowing with a reduced value compared to the bulk. As such, we will consider that the viscosity is such that $\mu(R) = \mu_W$, and that this is a fraction of the bulk value $\mu_B = \mu(0)$. The model considered in [7] interpolates the bulk and wall values for viscosity taking a 2-phase model:

$$\text{2-PHASE MODEL:}\quad \mu_{2-ph}(r) = \begin{cases} \mu_B & for\ r \in [0, R - \delta[\\ \mu_W & for\ r \in [R - \delta, R] \end{cases} ; \qquad (3)$$

where δ is the thickness of the annular region where the effect of the lower viscosity is felt. Notice that the the discontinuity of the viscosity introduces a new boundary layer for $r = R - \delta$ where some continuity of the trace and of the flux has to be imposed, see [7] Eq. (7). Adopting this model one can explicitly calculate the velocity profiles in the two regions, see [4] Eq. (10). Following [5] we consider the following model for the viscosity:

$$\text{EXPONENTIAL MODEL:}\quad \mu_{exp}(r) = \mu_B - (\mu_B - \mu_W)exp\left(\frac{r - R}{\delta}\right) . \qquad (4)$$

This interpolates only asymptotically the bulk value, but is very rapidly varying.
If we consider the mean viscosity, we obtain, respectively:

$$\langle \mu_{2-ph}(r) \rangle = \mu_B - (\delta/R)(\mu_B - \mu_W) ;$$
$$\langle \mu_{exp}(r) \rangle = \mu_B - (\delta/R)(\mu_B - \mu_W)\left[1 - exp\left(-R/\delta\right)\right] . \qquad (5)$$

The two-phase model, therefore, can be seen as an approximation of the exponential one: the difference decreases exponentially with increasing channel radius.

2.3. Slippage

The dimensional balance in Eq. 2, requires that λ has the units of a length. Significant effort has been made to relate λ to physical parameters of the chosen solid and liquid couple but no explicit dependence on the solid-liquid molecular interactions or channel geometry has been achieved [9]. On the other hand, there is experimental evidence of the need of a slip Navier

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condition to fit experimental data [10, 1].

In [4] the modelling of slippage on the wall boundary is enforced via the explicit expression of the velocity at the wall, see [4] Eq. (6). When the viscosity near the wall is considered constant to the value μ_W this leads, using Eq. (2) to an explicit expression for the slip length:

$$\lambda = 2\mu_W \frac{L}{R} \frac{D_S}{W_A} \, , \qquad (6)$$

where D_S is the surface diffusion of the liquid molecules on the channel wall due to the applied pressure gradient and W_A is the work of adhesion between the solid and the liquid. The latter represents the work required to separate the two surfaces and create a new interface.

3. Effects on flow enhancement

When the no-slip model with constant viscosity is considered, the liquid flow rate can be calculated via the so-called Haagen-Poiseuille equation:

$$Q_{HP} = \frac{\pi \Delta P R^4}{4\mu_B L}.$$

Deviations from this ideal behaviour are usually quantified via the flow enhancement parameter $\epsilon = \frac{Q}{Q_{HP}}$, where Q is the calculated or experimentally measured flow rate.

The results available in literature show enhancements up to $\approx 10^5$ [11]. In the case of constant viscosity near the boundary, the dependence between the flow enhancement and the slip length is linear and an explicit formula is available, see [4] Eq. (3). In the case of the use of the exponential model no explicit formula is available, but the value can be easily computed by numerical integration of Eq. (1).

3.1. Comparison between model predictions and literature data

In order to test the effectiveness of the proposed modelling for slippage, we compare the predictions made by the Eq.s (1-2) with available experimental data. These are linked to water -a polar liquid- flowing in channels with very different types of interactions: hydrophobic (graphitic CNT) and hydrophilic (water-alumina) tubes' walls, for different length and radius sizes. Following the procedure used in [4], enhancement values obtained numerically have

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Material	W_A $(10^{-3}Jm^{-2})$	D_S $(10^{-9}m^2s^{-1})$	δ $(10^{-9}m)$	$\frac{\mu_W}{\mu_B}$
Graphitic CNTs	97	2-4	0.7	0.7
Carbon Nanopipes	150	2	0.7	0.7
Alumina	800	1-2	0.7	0.7

Table 1: Values of relevant parameters used in Figure 1 for water flowing inside channels of different materials. The first two columns are derived respectively from references [12, 4, 13]. The values of δ and of the ratio between the wall and bulk viscosity have been taken as calculated respectively in [14, 11]. Notice that these last two do not affect considerably the results on enhancement, being the slip length the main term in the calculation, compare with [4] Eq. (3).

been re-scaled in a 'universal' enhancement curve, independent of the solid-liquid couple and of the channel length, see Figure 1. Experimental and MD data for water flowing in carbon nanotubes, carbon nanopipes and alumina also are normalized, and the coefficients used in order to normalize the data are reported in Table 1.

4. Conclusions

A universal model for liquid flow enhancement in nanochannels has been presented. Two different models for viscosity are compared, but no significant differences are noticed in all cases of interest. From a physical point of view the exponential model is to be preferred due to the fact that the effect of the interaction between molecules cannot be confined to a fixed region. On the other hand, considering the 2-phase model one obtains nice explicit formulae for slip and enhancement neglecting only a small part of the global effect (see Eq.s (3-4)).
Comparison with experimental data shows that the model can capture liquid flow in different types of nanochannels with different wetting properties. This model, therefore, can be used to predict liquid flow enhancement in nanochannels for any solid-liquid couple, provided that values for the surface diffusion, work of adhesion, bulk and wall viscosity are known. This predictive ability can be particularly useful in designing novel nanotube-based membranes for water treatment and desalination.
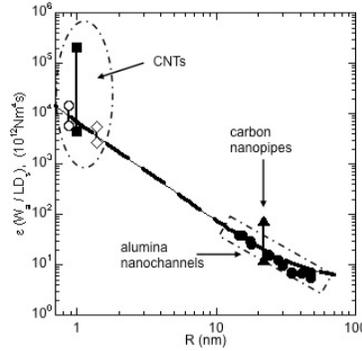
Figure 1: Normalized enhancement curves and experimental data. In symbols experimental and MD data: for CNTs ($\circ$, $\blacksquare$, $\diamondsuit$ refer, respectively, to [15, 11, 16]); carbon nanopipes ($\blacktriangle$ from [17]) and alumina ($\bullet$ from [2]). All data are normalized according to Table 1. The two lines represents the re-scaled enhancement relative to the model proposed in the present work, thus calculated using Eq.s (1-2-4). The dashed line represents the enhancement computed with the two-phase model for viscosity, namely [4] Eq. (8); the solid line represents the computed values using the exponential model. As it can be seen, the differences between the two predicting models are negligible in the case of interest.

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