Publication information

Title	Flow and slip transition in nanochannels
Author(s)	Li, Long; Mo, Jingwen; Li, Zhigang
Source	Physical Review E , v. 90, (3), September 2014, article number 033003
Version	Published version
DOI	https://doi.org/10.1103/PhysRevE.90.033003
Publisher	American Physical Society

Copyright information

© 2014 American Physical Society

Notice

This version is available at HKUST Institutional Repository via

<http://hdl.handle.net/1783.1/63883>

If it is the author's pre-published version, changes introduced as a result of publishing processes such as copy-editing and formatting may not be reflected in this document. For a definitive version of this work, please refer to the published version.

Flow and slip transition in nanochannels

Long Li, Jingwen Mo, and Zhigang Li*

Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

(Received 11 June 2014; published 5 September 2014)

We experimentally investigate the Poiseuille flows in nanochannels. It is found that the flow rate undergoes a transition between two linear regimes as the shear rate is varied. The transition indicates that the nonslip boundary condition is valid at low shear rate. When the shear rate is larger than a critical value, slip takes place and the slip length increases linearly with increasing shear rate before approaching a constant value. The results reported in this work can help advance the understanding of flow slip in nanochannels.

DOI: [10.1103/PhysRevE.90.033003](https://doi.org/10.1103/PhysRevE.90.033003)

PACS number(s): 47.61.-k, 83.50.Rp, 68.08.-p

I. INTRODUCTION

Motivated by the applications of nanofluidics in a variety of areas, many efforts have been made to understand nanoscale fluid transport in the past decades. In nanoscale flows, fluid adsorption and slip at the interface are probably the most popular phenomena, which may lead to different flow scenarios and have attracted great attention [1–9]. Flow slip has been observed in experiments and simulations at the nanoscale, and the slip length, which is the length beyond the interface where the extrapolated velocity vanishes, has been reported to range from a few nanometers to tens of nanometers [4,10–21]. Since flow slip can enhance fluid transport, which is essential in nanofluidic systems, slip at solid surfaces in nanochannels is sought in many applications, such as sea water desalination and molecular separation [22,23]. Although the phenomenon of slip has been well accepted, most of the results in the literature about flow slippage are inconsistent and the detailed mechanism of slip requires intensive exploration.

Previous findings about the slip length for simple fluids at the nanoscale appear to be controversial. Some experiments and simulations showed that the slip length is independent of the shear rate [10,12,20,21], which agrees with the prediction of classic slip theories [24]. However, there is increasing work showing that slip length is shear rate dependent, especially at the nanoscale [9,13–17,25–27]. It is more interesting that the dependence of slip length on the shear rate has been found in different ways. There are mainly three distinct fashions for the slip length as the shear rate is varied. One is the linear dependence on the shear rate, where the slip length increases linearly with the shear rate when the shear rate is larger than a critical value, which depends on the surface wettability [4,5,14,15,28,29]. Another one is nonlinear dependence, where the slip length may or may not be described by a simple expression [4,9,10,15,16,25]. In these two cases, the slip length appears to be unbounded as the shear rate goes to infinity. However, theoretical analyses and molecular dynamics (MD) simulations have shown that the slip length asymptotes to a constant at high shear rates [17,27]. These different slip behaviors seem to be supported by certain mechanisms. This might be due to the fact that slip is affected by many factors, including the fluid-wall

binding energy, surface roughness, and thermal motion of wall atoms [15,16,30]. These parameters are usually coupled and make the slip nontrivial. Another reason that might account for the discrepancy in the literature is that the shear rate in experiments is usually below 10^5 s^{-1} [10,13,14,26,28], while in simulations the shear rate is in the range from 10^8 to 10^{11} s^{-1} [4,10,15–18], which is unrealistic and cannot be reached through experiments. Nevertheless, extensive work is needed to gain a clear picture about slip.

In this work, we experimentally investigate Poiseuille's flow in 100-nm-deep silicon nanochannels with shear rate ranging from 8×10^3 to $1.38 \times 10^5 \text{ s}^{-1}$. It is found that slip occurs when the shear rate is higher than $1.0 \times 10^5 \text{ s}^{-1}$, after which the slip length increases linearly with increasing shear rate before it approaches a constant value when the shear rate is larger than $1.1 \times 10^5 \text{ s}^{-1}$. The general behavior of slip length observed herein agrees well with previous theoretical and MD analyses [17] but the shear rate range is much lower than that in Ref. [17].

II. FABRICATION OF NANOFLUIDIC DEVICE

The nanofluidic chips consist of an array of parallel nanochannels, which perpendicularly join two microchannels at the ends and the microchannels are in connection with four reservoirs. The schematic of the fluidic system is shown in the top panel of Fig. 1. The chips were fabricated by the traditional photolithography method described in the literature [31]. The nanochannel structure was defined by the photolithography technique on a clean silicon wafer coated with an $\sim 1\text{-}\mu\text{m}$ -thick photoresist layer. SF_6 plasma reactive ion etching (RIE) was employed to remove the oxide layer on the silicon surface and Cl_2 plasma was used to etch silicon. After the develop process, the nanochannels were fabricated on the silicon wafer through RIE with an etching rate of $2.5 \mu\text{m}/\text{min}$. This etching rate could guarantee a well control for the channel depth with small surface roughness. After etching, the photoresist layer was removed by a PS210 photoresist asher machine. The microchannels were etched following similar approaches using the dry reactive ion etching (DRIE) technique. Then, an oxide layer was grown on both sides of the silicon wafer to protect the microchannels and nanochannels during the following backside DRIE process for the fabrication of fluid reservoirs. Before bonding the channels, a 300-nm-thick wet thermal oxide layer was uniformly developed on the silicon wafer in

*mezli@ust.hk

FIG. 1. (Color online) Schematic (top panel) and fabricated chip (bottom panel) of the nanofluidic system.

a furnace at 1000 °C. This thermal oxide layer could prevent the nanochannels from collapsing during the final bonding. Finally, the channels were enclosed through anodic bonding with a clean glass wafer under 380 °C and 800 V. The bottom panel of Fig. 1 shows a fabricated chip. There was a total of 100 parallel, 50- μm -spaced nanochannels (10 channels in the center part were 500- μm -spaced for fluorescent flow observation). The dimensions of the nanochannels were defined as 100 nm, 100 μm , and 1.5 mm in depth, width, and length, respectively. To check the structure of the nanochannels, the silicon wafer was investigated by atomic force microscopy (AFM) before the final bonding, as shown in the top panel of Fig. 2. The channel height was 105.6 nm and the roughness of channel surface was less than 1.1 nm, which is negligible compared to the channel height. The length, width, and height of the microchannels were 10 mm, 500 μm , and 40 μm , respectively.

Before the experiments, fluorescent dye-laden deionized (DI) water was flushed through the fluidic system to check whether there was collapse in the nanochannels. A snapshot of the flow is depicted in the bottom panel of Fig. 2, which shows that the flow (green parts) was quite smooth. To avoid leakage at high pressures, Polytetrafluoroethylene (PTFE) tubings (Cole-Parmer Instrument, USA) were used to connect the reservoirs and the joints were sealed with 2-mm-diameter rubber O rings. The experimental setup is illustrated in Fig. 3.

DI water obtained from a NANOpure Diamond (Barnstead Int., Dubuque, IA) source with a specific resistivity of 18 M Ω cm was driven through the channels by a stainless steel syringe (Cole-Parmer Instrument, USA) mounted on an ultrahigh linear force syringe pump (Nexus 6000, Chemyx, Inc., USA), which was used to control the flow rate with an accuracy of 0.001 $\mu\text{l/h}$. Pressure transducers (25 MPa with an accuracy of 0.5% limit point calibration and 0.25% best-fit straight line, Swagelok, USA) were employed to measure the pressures of the reservoirs. Valves were used to make sure that air was removed from the system before experiments. Two nanofluidic devices were used and similar results were obtained. All the data reported in this work were from one of the devices and the experiments under the same conditions were repeated at least three times.

III. RESULTS AND DISCUSSION

Since the flow resistance in nanochannels is much higher than that in microchannels, the pressure difference between the inlet and outlet reservoirs, $P_1 - P_3$ (Fig. 3), can be approximately treated as the pressure drop over the nanochannels [8,32,33]. For each flow rate, P_1 and P_3 were recorded till they became stable. Figure 4 shows the time variation of P_1 at the flow rates (in each channel) of 0.03 and 0.11 $\mu\text{l/h}$, where P_1 converged to a constant value after 30 min. The reservoir, to which the pressure transducer for P_3 was connected, was open to the atmosphere and P_3 showed quite stable atmospheric pressure during the experiments. The plot of volumetric flow rate Q in each channel versus the pressure drop Δp is shown in Fig. 5. It is seen that the flow rate undergoes a clear transition between two linear regimes and the transition takes place for $2.8 < \Delta p < 3.2$ MPa. Such a relationship between Q and Δp is surprising and deviates from the prediction of the classic Poiseuille law for channel flows under a no-slip boundary condition, which reads

$$Q = \frac{h^3 w}{12\mu} \frac{\Delta p}{l_c}, \quad (1)$$

where h , w , and l_c are the channel height, width, and length, respectively, and μ is the dynamic viscosity of the fluid. The linear prediction of Eq. (1) is also shown in Fig. 5, where $\mu = 1.0 \times 10^{-3}$ Pa s is used for water at room temperature. At low pressure drops ($\Delta p < 2.8$ MPa), it is seen that the experimental results are quite close to the predictions of Eq. (1) though they are slightly lower than the theoretical results. This is consistent with previous work [33], where the flows were pressure driven. The relatively lower experimental results might be caused by the large flow resistance due to fluid adsorption in hydrophilic channels [6,32]. When the pressure drop is higher than 2.8 MPa, the experimental data start to deviate from Eq. (1) until reaching another linear regime, where the experimental results are about 20% larger than the predictions of Eq. (1).

Since the fluid velocity distribution in nanochannels remains parabolic even in channels of a few nanometers [6,32,34] and the viscosity variation in channels of ~ 100 nm is negligible [35], the discrepancy between the experiments and theory at relatively high pressure drops must be caused by the flow slip at the channel surfaces, where the fluid velocity

FIG. 2. (Color online) Nanochannel characterization. Top panel: AFM studies of nanochannels. Channel height is 105.6 nm with surface roughness less than 1.1 nm. Bottom panel: An image of a fluorescent flow in nanochannels.

is nonzero. With slip correction, Eq. (1) can be rewritten as

$$Q_{\text{slip}} = \frac{h^3 w}{12\mu} \frac{\Delta p}{l_c} \left(1 + \frac{6L_s}{h} \right), \quad (2)$$

where L_s is the slip length, which can be obtained by fitting the experimental data using Eq. (2). Following the previous work, the pressure drop Δp is converted to the shear rate $\dot{\gamma}$ through $\dot{\gamma} = h\Delta p/(2\mu l_c)$, and the slip length L_s as a function of $\dot{\gamma}$ is plotted in Fig. 6. It is found that the no-slip boundary condition appears to be valid for $\dot{\gamma} < 1.0 \times 10^5 \text{ s}^{-1}$ (the slip length herein actually is slightly negative, as is discussed later) When $\dot{\gamma} > 1.0 \times 10^5 \text{ s}^{-1}$, the slip length increases linearly with increasing shear rate before it roughly asymptotes to a constant

value at $\dot{\gamma} = 1.1 \times 10^5 \text{ s}^{-1}$. The average value for the constant slip length is 3.66 nm. Figure 6 is experimental evidence for the slip transition of simple fluids in nanochannels.

The slip transition in Fig. 6 can be explained by different slip mechanisms. In hydrophilic channels, usually a layer of fluid molecules is adsorbed by the surface due to the strong fluid-wall binding force. The motion of these ad molecules largely determines the boundary condition. When the fluid is driven by a pressure difference, an external force is acting on all the fluid molecules and the dynamics of the ad molecules depends on the competition between the external force and the fluid-wall binding force [6]. At low shear rate, the external force is weak compared with the fluid-wall binding force. In this case, the

FIG. 3. (Color online) Experimental setup of the fluidic system. DI water is driven by a syringe pump with a desired flow rate. Arrows indicate the flow directions. Pressures at the reservoirs are measured by pressure transducers.

admmolecules will stay in some low potential sites near the wall and remain being adsorbed, and the no-slip boundary condition is valid [3,6]. It should be noted that there could be several layers of admmolecules when the fluid-wall binding

FIG. 4. Time variation of P_1 in Fig. 3 for (a) flow rate $Q = 0.03 \mu\text{l/h}$ and (b) flow rate $Q = 0.11 \mu\text{l/h}$ in each channel.

FIG. 5. (Color online) Flow rate as a function of pressure drop. Error bars represent the standard deviation of three experiments. Dashed lines are a guide to the eye.

energy is very strong, where the slip length is considered as negative [32]. In our experiments, the slip length at low shear rate is slightly negative, which causes the flow rate to be lower than the theoretical results.

As the shear rate is increased, the external force becomes comparable to the fluid-wall binding force. In this case, some admmolecules may have enough energy to overcome the wall attraction (Peierls-Nabarro barrier [36]) and migrate in the external force direction, and then partial slip occurs. Such motion is also promoted by the thermal fluctuations of the admmolecules and wall atoms. Within a certain range of shear rates, the number of admmolecules joining the partial slip is roughly proportional to the shear rate [27]. This is why the slip length increases linearly for $1.0 \times 10^5 < \dot{\gamma} < 1.1 \times 10^5 \text{ s}^{-1}$ in Fig. 6.

When the shear rate is further increased, the external force can easily break the fluid-wall binding and lead to the collective motion of the admmolecules [27]. If all the admmolecules are

FIG. 6. (Color online) Slip length as a function of shear rate. Solid lines are a guide to the eye.

considered as an object, the forces acting on it are the external force due to the pressure difference, the shear force from the interior fluid, and the frictional force from the wall atoms. Since the shear force is the intermolecular force, which is much larger than the external force, the equation of motion for the admolecules can be expressed as [17]

$$m\ddot{x} = \alpha(V - \dot{x}) - \beta\dot{x}, \quad (3)$$

where m , x , $\dot{x}$, and $\ddot{x}$ are the mass, position, velocity, and acceleration of the admolecules, respectively. The terms $\alpha(V - \dot{x})$ and $\beta\dot{x}$ denote the shear and frictional forces. Here, α and β are the shear and friction coefficients, and V is the velocity of the interior fluid next to the admolecule layer given by $V = \dot{\gamma}(L_s + d)$, where d is a constant representing the liquid-liquid spacing normal to the wall surface and is about a few angstroms. In steady state, the two force terms in Eq. (3) are in balance and the slip velocity u_s is given by $u_s = \alpha V / (\alpha + \beta)$. Based on the definition of slip length, $L_s = u_s / \dot{\gamma}$, and using $\dot{\gamma} = (V - u_s) / d$, it is obtained that

$$L_s = \frac{\alpha}{\beta} d, \quad (4)$$

which is a constant. It is noted that α and β depend on the materials of the fluid and channel. At high shear rate, $u_s \approx V$ (the relative velocity $V - u_s$ could still generate a high $\dot{\gamma}$), which leads to $\alpha \gg \beta$. Therefore, L_s could range from a few nanometers to tens of nanometers. The experimental results in Fig. 6 indicate that $\alpha \sim 10\beta$. It is noted that Eq. (4) is valid under the assumption that the shear force and the friction in Eq. (3) are linearly related to velocity, which should be satisfied for the shear rate range considered in this work.

It is noted that the critical shear rate, where the slip transition occurs (Fig. 6), depends on the fluid-wall interaction, which can be altered by either changing the fluid or modifying the surface properties (e.g., coating the surface with other materials or changing the surface roughness). Strong fluid-wall

binding energy (hydrophilic channels) leads to high friction at the interface and requires a relatively high shear rate to generate flow slip. In hydrophobic channels (weak fluid-wall interaction), the slip transition in Fig. 6 is expected to shift to lower shear rates. It has been reported that nanobubbles or thin air films at the interface and surface roughness, which can greatly reduce the surface energy, could enhance the flow slip [19,21]. It is also worth mentioning that slip transition has been observed in complex and non-Newtonian fluids, such as polymer melts [37–39], where the slip length appears to increase with increasing shear rate. Moreover, the critical shear rate for the occurrence of slip could be very low for polymer melts [37,39]. However, the slip mechanisms for complex fluids could be different from those for simple fluids. Finally, we like to mention that the flow rate increase after 2.8 MPa in Fig. 5 should not be caused by the cross-sectional change of the channels because silicon nanochannels fabricated through anisotropic etching methods are estimated to stand a failure stress as high as 300 MPa [40].

IV. CONCLUSIONS

We have fabricated a nanofluidic system and investigated the Poiseuille flow in 100-nm silicon channels. The flow transition indicates that the slip length increases linearly with the shear rate when the shear rate is larger than a critical value. At high shear rate, the slip length converges to a constant value.

ACKNOWLEDGMENTS

This work was supported by the Research Grants Council of the Hong Kong Special Administrative Region under Grants No. 615710 and No. 615312. J. Mo was partially supported by a postgraduate scholarship through the Energy Program at HKUST. We thank the Nanoelectronics Fabrication Facility at the Hong Kong University of Science and Technology for the device fabrication.

-
- [1] U. Heinbuch and J. Fischer, *Phys. Rev. A* **40**, 1144 (1989).
 - [2] M. Cieplak, J. Koplik, and J. R. Banavar, *Phys. Rev. Lett.* **86**, 803 (2001).
 - [3] Z. Li and H. Wang, *Phys. Rev. Lett.* **95**, 014502 (2005).
 - [4] N. V. Priezjev, *Phys. Rev. E* **75**, 051605 (2007).
 - [5] Z. Li and L. Hong, *J. Chem. Phys.* **127**, 074706 (2007).
 - [6] C. Liu and Z. G. Li, *Phys. Rev. E* **80**, 036302 (2009).
 - [7] C. Liu and Z. G. Li, *Phys. Rev. Lett.* **105**, 174501 (2010).
 - [8] C. Liu and Z. G. Li, *J. Chem. Phys.* **132**, 024507 (2010).
 - [9] S. K. Kannam, B. D. Todd, J. S. Hansen, and P. J. Davis, *J. Chem. Phys.* **135**, 144701 (2011).
 - [10] P. A. Thompson and S. M. Troian, *Nature (London)* **389**, 360 (1997).
 - [11] R. Pit, H. Hervet, and L. Leger, *Phys. Rev. Lett.* **85**, 980 (2000).
 - [12] J. S. Hansen, B. D. Todd, and P. J. Davis, *Phys. Rev. E* **84**, 016313 (2011).
 - [13] V. S. J. Craig, C. Neto, and D. R. M. Williams, *Phys. Rev. Lett.* **87**, 054504 (2001).
 - [14] C. H. Choi, K. J. A. Westin, and K. S. Breuer, *Phys. Fluids* **15**, 2897 (2003).
 - [15] N. V. Priezjev, *J. Chem. Phys.* **127**, 144708 (2007).
 - [16] X. Yong and L. T. Zhang, *Microfluid. Nanofluid.* **14**, 299 (2013).
 - [17] A. Martini, H. Y. Hsu, N. A. Patankar, and S. Lichter, *Phys. Rev. Lett.* **100**, 206001 (2008).
 - [18] S. Lichter, A. Martini, R. Q. Snurr, and Q. Wang, *Phys. Rev. Lett.* **98**, 226001 (2007).
 - [19] C. Cottin-Bizonne, J. L. Barrat, L. Bocquet, and E. Charlaix, *Nat. Mater.* **2**, 237 (2003).
 - [20] C. Cottin-Bizonne, B. Cross, A. Steinberger, and E. Charlaix, *Phys. Rev. Lett.* **94**, 056102 (2005).
 - [21] C. Cottin-Bizonne, S. Jurine, J. Baudry, J. Crassous, F. Restagno, and E. Charlaix, *Eur. Phys. J. E* **9**, 47 (2002).
 - [22] B. Corry, *Energy Environ. Sci.* **4**, 751 (2011).
 - [23] R. Singhal, V. N. Mochalin, M. R. Lukatskaya, G. Friedman, and Y. Gogotsi, *Sci. Rep.* **2**, 510 (2012).

- [24] L. G. Leal, *Advanced Transport Phenomena* (Cambridge University Press, New York, 2007).
- [25] C. Sendner, D. Horinek, L. Bocquet, and R. R. Netz, *Langmuir* **25**, 10768 (2009).
- [26] Y. Zhu and S. Granick, *Phys. Rev. Lett.* **87**, 096105 (2001).
- [27] S. Lichter, A. Roxin, and S. Mandre, *Phys. Rev. Lett.* **93**, 086001 (2004).
- [28] E. Bonaccorso, M. Kappl, and H.-J. Butt, *Phys. Rev. Lett.* **88**, 076103 (2002).
- [29] P. Joseph and P. Tabeling, *Phys. Rev. E* **71**, 035303 (2005).
- [30] T. A. Ho, D. V. Papavassiliou, L. L. Lee, and A. Striolo, *Proc. Natl. Acad. Sci. USA* **108**, 16170 (2011).
- [31] C. Duan and A. Majumdar, *Nat. Nanotechnol.* **5**, 848 (2010).
- [32] C. Liu and Z. Li, *AIP Adv.* **1**, 032108 (2011).
- [33] Q. Wu, J. T. Ok, Y. Sun, S. T. Retterer, K. B. Neeves, X. Yin, B. Bai, and Y. Ma, *Lab Chip* **13**, 1165 (2013).
- [34] B. D. Todd, D. J. Evans, and P. J. Daivis, *Phys. Rev. E* **52**, 1627 (1995).
- [35] E. Akhmatkaya, B. D. Todd, P. J. Daivis, D. J. Evans, K. E. Gubbins, and L. A. Pozhar, *J. Chem. Phys.* **106**, 4684 (1997).
- [36] O. M. Braun and Y. S. Kivshar, *Phys. Rep.* **306**, 1 (1998).
- [37] K. B. Migler, H. Hervet, and L. Leger, *Phys. Rev. Lett.* **70**, 287 (1993).
- [38] C. Cheikh, and G. Koper, *Phys. Rev. Lett.* **91**, 156102 (2003).
- [39] L. Leger, H. Hervet, G. Massey, and E. Durliat, *J. Phys.: Condens. Matter* **9**, 7719 (1997).
- [40] K. Sooriakumar, W. Chan, T. S. Savage, and C. Fugate, *Proc. Electrochem. Soc. PV* **95-27**, 259 (1995).