ANNALS of the ORADEA UNIVERSITY.
Fascicle of Management and Technological Engineering

THE SLIP BOUNDARY CONDITIONS – A NEW CONCEPT IN NANOLUBRICATION

Alexandru RADULESCU
Universitatea "POLITEHNICA" din Bucuresti,
e-mail: sandu@meca.omtr.pub.ro

Keywords: Nanolubrication, Boundary conditions, Slip limits

Abstract: The no-slip boundary condition at a solid-liquid interface is at the centre of our understanding of fluid mechanics. However, this condition is an assumption that cannot be derived from first principles and could, in theory, be violated. In this paper, a review of recent experimental, numerical and theoretical investigations on the subject is presented. The physical picture that emerges is that of a complex behaviour at a liquid/solid interface, involving interplay of many physico-chemical parameters, including wetting, shear rate, pressure, surface charge, surface roughness, impurities and dissolved gas.

1. INTRODUCTION

The vast majority of problems in the dynamics of Newtonian fluids are concerned with solving, in particular settings, the Navier-Stokes equations for incompressible flow, [1]:

$$\begin{aligned}
\rho\left(\frac{\partial u}{\partial t}+u\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial y}+w\frac{\partial u}{\partial z}\right)&=\rho g_x-\frac{\partial p}{\partial x}+\mu\left(\frac{\partial^2 u}{\partial x^2}+\frac{\partial^2 u}{\partial y^2}+\frac{\partial^2 u}{\partial z^2}\right)\\
\rho\left(\frac{\partial v}{\partial t}+u\frac{\partial v}{\partial x}+v\frac{\partial v}{\partial y}+w\frac{\partial v}{\partial z}\right)&=\rho g_y-\frac{\partial p}{\partial y}+\mu\left(\frac{\partial^2 v}{\partial x^2}+\frac{\partial^2 v}{\partial y^2}+\frac{\partial^2 v}{\partial z^2}\right)\\
\rho\left(\frac{\partial w}{\partial t}+u\frac{\partial w}{\partial x}+v\frac{\partial w}{\partial y}+w\frac{\partial w}{\partial z}\right)&=\rho g_z-\frac{\partial p}{\partial z}+\mu\left(\frac{\partial^2 w}{\partial x^2}+\frac{\partial^2 w}{\partial y^2}+\frac{\partial^2 w}{\partial z^2}\right)
\end{aligned} \tag{1}$$

The list of problems for which this task has proven to be difficult is long. However, most of these studies assume the validity of the no-slip boundary condition, which means that all three components of the fluid velocity on a solid surface are equal to the respective velocity components of the surface. It is only recently that controlled experiments, generally with typical dimensions microns or smaller, have demonstrated an apparent violation of the no-slip boundary condition for the flow of Newtonian liquids near a solid surface.

In this paper, a tentative summary of what is known about the breakdown of the no-slip condition for Newtonian liquids is presented. Also, it discuss methods and results of experiments, simulations and theoretical models. This topic is of fundamental physical interest and has potential practical consequences in many areas of engineering and applied sciences where liquids interact with small-scale systems including flow in porous media, microfluidics, friction studies and biological fluids. Furthermore, since viscous flows are relevant to the study of other physical phenomenon, such as the hydrophobic attraction in water, a change in the boundary condition would have significant quantitative impact on the interpretation of experimental results [2], [3], [4].

The nature of boundary conditions in hydrodynamics was widely debated in the 19th century. Many of the great names in fluid dynamics have expressed an opinion on the subject at some point during their careers, including D. Bernoulli, Darcy, Navier, Poisson, Poiseuille, Stokes, Hagen and Couette. In his 1823 treatise on the movement of fluids, Navier introduced the linear boundary condition, which remains the standard characterization of slip used today: the component of the fluid velocity tangent to the surface is proportional to the shear rate at the surface, [5]:

$$u = \lambda \frac{\partial u}{\partial z} \tag{2}$$

In Eq. (2), λ has the unit of a length, and is referred to as the slip length. For a pure shear flow, λ can be interpreted as the fictitious distance below the surface where the no-slip boundary condition would be satisfied (see Fig. 1). A century of agreement between experimental results in liquids and theories derived assuming the no-slip boundary condition ($\lambda = 0$) had the consequence that today many textbooks of fluid dynamics fail to mention that the no-slip boundary condition remains an assumption, [5].

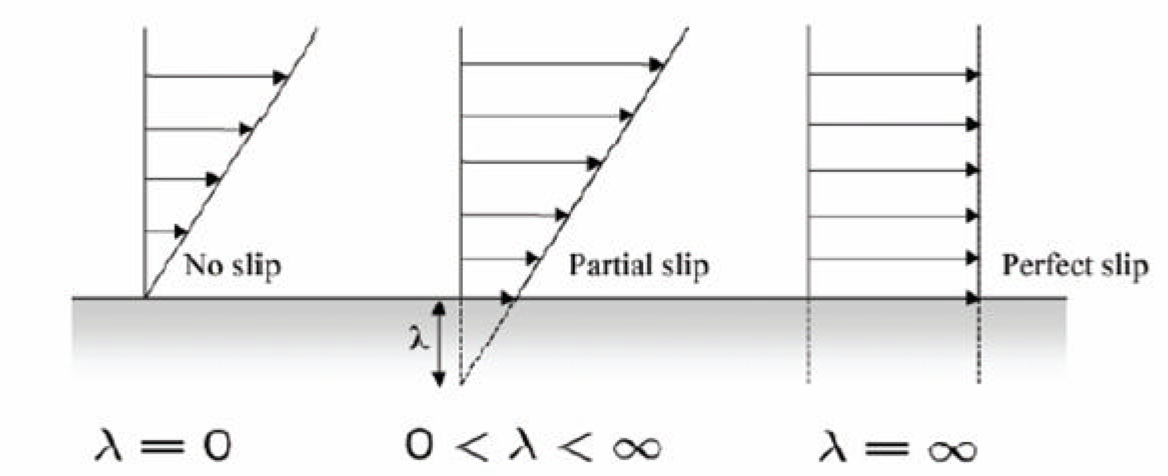


Fig. 1. *Interpretation of the Navier slip length l , [5]*

Table 1 shows a few values for the slip length λ, for different materials, surface roughness, surface treatment and different lubricants, [14].

Tab. 1 Summary of the parameters and results from the flow experiments, *[14]*

Liquids used	Water	Water Mercury	Water + glycerin	Water	Water Tetradecane Hexane Silicone oil
Type of surface	Glass	Quartz	Acrylic resin	Glass	Glass
Surface treatment	$(CH_3)_2SiCl_2$	$(CH_3)_3SiCl$	Hydrophobic silica	$CH_3(CH_2)_{17}SiCl_3$	–
Contact angle	–	70°–110°	150°	120°	–
Surface roughness	–	–	10–100 μm	2–3 Å	5 Å
System size R	250–800 μm	0.3–7 μm	6–12 mm	30 μm	40–200 nm
Shear rate $\dot{\gamma}$	100–3000 s^{-1*}	1–10 000 s^{-1*}	25–100 s^{-1*}	200 s^{-1*}	300–5000 s^{-1*}
Slip length λ_{eff}	2–8 μm*	20–90 nm	200–450 μm*	1 μm	10–30 nm
Slip velocity	0.3–25 mm s^{-1*}	0.02–500 μm s^{-1*}	1 cm s^{-1*}	200 μm s^{-1*}	3–150 μm s^{-1*}
Ratio λ_{eff}/R	0.01	0.005–0.1	0.03	0.03	0.08–0.2

2. PARTICULAR CASES WHERE THE SLIP OCCURS

The phenomenon of slip has already been encountered in three different contexts:

- Gas flow in devices with dimensions that are on the order of the mean free path of the gas molecules shows significant slip, [6];
- The flows of non-Newtonian fluids such as polymer solutions show significant apparent slip in a variety of situations, some of which can lead to slip-induced instabilities, [7];
- In the context of Newtonian liquids, molecular slip has been used as a way to remove singularities arising in the motion of contact lines, as reviewed in [8]. Solving the equations of motion with a no-slip boundary condition in the neighbourhood of a moving contact line leads to the conclusion that the viscous stresses and the rate of energy dissipation have non-integrable singularities.

The case of the Newtonian fluids is still controvertible. The development of the Surface Force Apparatus in the years 1970, [5] has allowed for more than thirty years of precise probing down to the nanometre scale of both structure and dynamics of many Newtonian liquids against mica [9]. Experimental methods have included squeeze and/or shear flow for a variety of polar and non-polar liquids displaying a wide range of wetting conditions and shear rates. These studies have confirmed the validity of the no-slip boundary condition and the bulk rheological behaviour down to a few nanometres. At smaller length scales, an increase in viscous resistance has been reported, with qualitative differences between the behaviour of water and other non-polar liquids.

Generally, the slip boundary conditions appears in the case of the Newtonian fluids if the surfaces involved are hydrophobic. From the technological point of view, the hydrophobic surfaces can be realized in a few distinctive ways:

- very smooth surfaces (R_a = 0,04 μm) obtained by polishing (see Fig. 2), [10];
- surfaces with micron-scale surface features, obtained by chemical erosion (see Fig. 3) [11];
- surfaces with micron-scale surface features, obtained by laser (see Fig. 4) [12];
- surfaces with micron-scale surface features, obtained by plasma (see Fig. 5) [13].

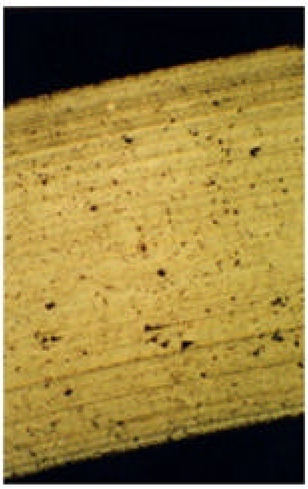


Fig. 2. *Very smooth surfaces (Ra = 0,04 mm) obtained by polishing, [10]*

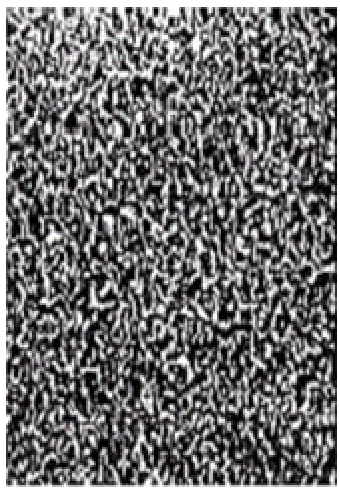


Fig. 3. *Surfaces with micron-scale surface features, obtained by chemical erosion, [11]*

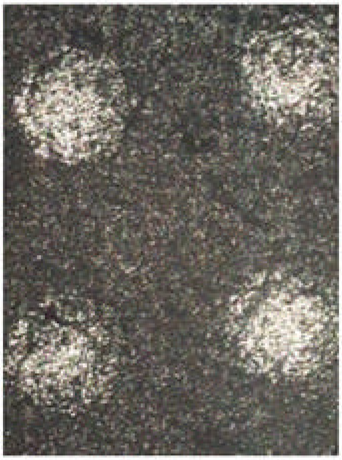


Fig. 4. *Surfaces with micron-scale surface features, obtained by laser, [12]*

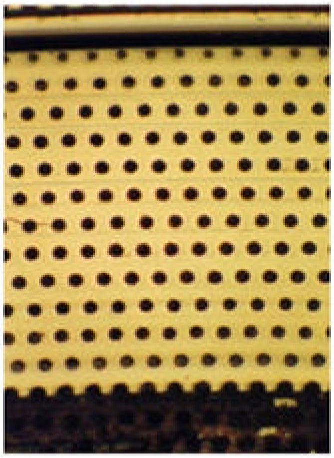


Fig. 5. *Surfaces with micron-scale surface features, obtained by plasma, [13]*

3. EXPERIMENTAL METHODS

As will be discussed below, a large variability exists in the results of slip experiments, so it is important to first consider the different experimental methods used to measure slip, directly or indirectly. In these setups, surface conditions may usually be modified by polymer or surfactant adsorption or by chemical modification. Two broad classes of experimental approaches have been used so far, indirect methods and local methods, [10], [12].

Indirect methods assume Eq. (2) to hold everywhere in a particular configuration and infer λ by measuring a macroscopic quantity. Such methods report therefore effective slip lengths, and they have been the most popular so far, [4]. If the effective slip length is λ, then a system size L at least comparable $L \sim \lambda$ is necessary in order for slip to have a measurable impact.

The local methods are more precisely, because the indirect methods have the disadvantage that the slip boundary condition is not verified directly, but instead is estimated via the assumed effect of slip on some other measured macroscopic parameters. Generally, the local methods are based on the visualisation of the flow process and they have been introduced that try to alleviate this indirect estimation of slip.

The main local techniques are:

- Particle image velocimetry (see Fig. 6 and Fig. 7). The method use small particles as passive tracers in the flow, to measure the velocities of the particles with an optical method and check whether the velocities extrapolate to zero at the solid surface, [15];
- Near-field laser velocimetry using fluorescence recovery (see Fig. 8). In this method, the velocity field of small fluorescent probes is measured close to a nearby surface. An intense laser illuminates the probes and renders them non fluorescent. Monitoring the fluorescence intensity in time using evanescent optical waves allows to obtain an estimate of the slip length, [16].
- Fluorescence cross-correlations (see Fig. 9). Fluorescent probes excited by two similar laser foci are monitored in two small sample volumes separated by a short distance. Cross-correlation of the fluorescence intensity fluctuations due to probes entering and leaving the observation windows allows to determine both the flow direction and intensity. The measured velocities are averaged over the focal size of microscope and the characteristics of the excitation laser, [17].

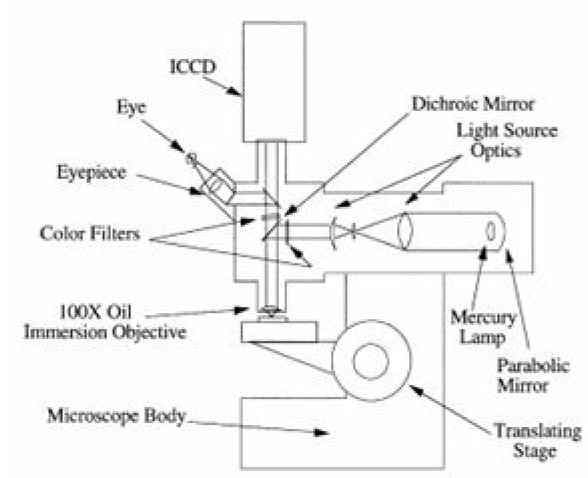
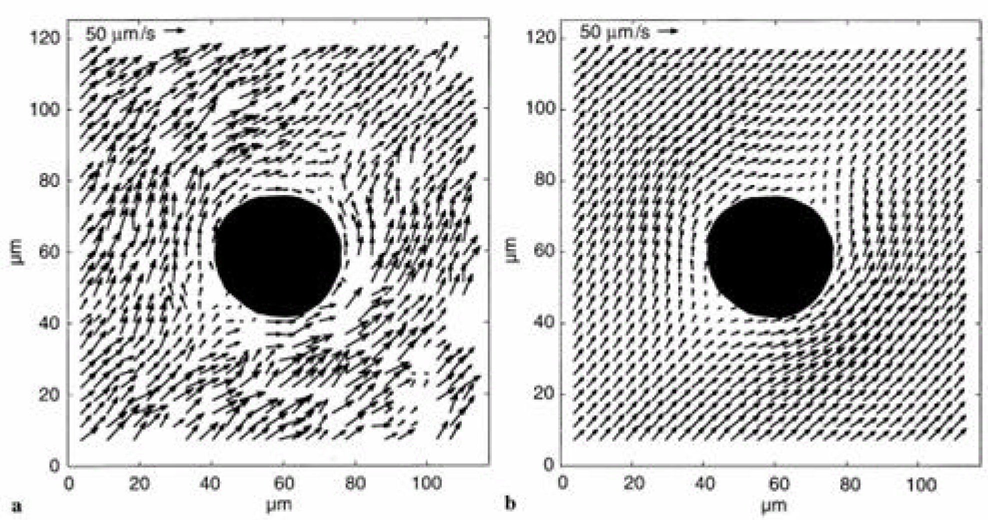


Fig. 6 *Schematic of the micro-particle image velocimetry recording system, [15]*



a) Instantaneous vector field measurement **b)** Image ensemble-averaged velocity vector field

Fig. 7 *Vector fields of a flow around a 30 mm wide obstacle. Each field contains approximately 900 velocity vectors covering a 120 mm x 120 mm field of view, [15]*

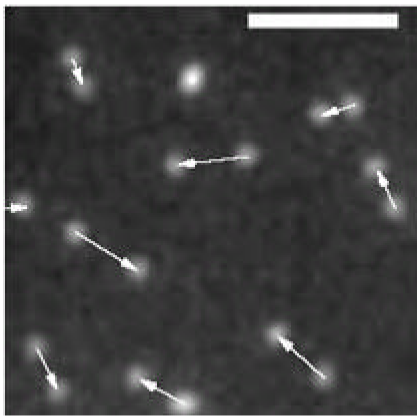


Fig. 8 *Flow visualization by the near-field laser velocimetry using fluorescence recovery, [16]*

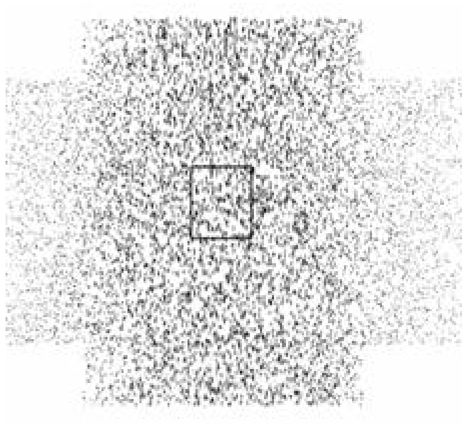


Fig. 9 *Velocity field obtained by using fluorescence cross-correlations method, [18]*

4. CONCLUSIONS

Because of the great advances in micro- and nano- fabrication technologies, the ability to engineer slip could have dramatic influences on flow since the viscous dominated motion can lead to large pressure drops and large axial dispersion. As was shown in this paper, the small-scale interactions between a liquid and a solid leads to extremely rich possibilities for slip behaviour, with dependence on factors such as wetting conditions, shear rate, pressure, surface charge, surface roughness and dissolved gas.

The slip lengths reported experimentally span many orders of magnitude, from molecular lengths up to hundreds of nanometres. The impact of slip on systems with typical dimensions larger than tens of microns will therefore likely be limited, unless the surfaces have been specifically designed to display super hydrophobic properties.

Other more complex behaviours remain to be understood, including dependence of the results on the molecular shape and size [5], probe size [8], or viscosity [10]. The development of alternative direct experimental methods would allow for a more precise quantification of slip phenomena. Similarly, it might be valuable to reproduce some of the experiments discussed above in degassed and clean environments to quantify the influence of dissolved gas on apparent slip. Answers to these questions will probably allow for a precise engineering of slip in small-scale systems.

5. REFERENCES

[1] Pinkus, O. et al. *Theory of hidrodinamic lubrication*, New York, Mc Graw Hill,1961
[2] Vinogradova, O.I. *Hydrodynamic interaction of curved bodies allowing slip on their surfaces*, Journal Langmuir, 12, 1996, pp.5963-5968
[3] Zhu, Y., Granick, S. *Rate-dependent slip of Newtonian liquid at smooth surfaces*, Physical Review Letters, 87, 2001, pp. 96-105
[4] Battal, T. *Determination of the Dynamic Surface Excess of a Homologous Series of Cationic Surfactants by Ellipsometry*, Journal Langmuir, 19, 2003, pp. 1244-1250
[5] Lauga, E. *Shear-dependent apparent slip on hydrophobic surfaces: The Mattress Model*, *Journal of Fluid Mechanics*, 471, 2001, pp. 145–152
[6] Muntz, E.P. *Rarefied-gas dynamics*, Annalytical Review Fluid Mechanics, 21, 1989, pp. 387-417
[7] Migler, B. et al. *Slip transition of a polymer melt under shear stress*, Phys. Rev. Lett., 70, 1993, pp. 287-290
[8] Dussan, E. B., Davis, S. H. *Motion of a fluid-fluid interface along a solid surface*, Journal of Fluid Mechanics, 65, 1974, pp. 71-95
[9] Craig, V.S.J. et al. *Shear-dependent boundary slip in an aqueous Newtonian liquid*, Phys. Rev. Lett., 87, 2001, pp. 54-59
[10] Jia O. *Laminar Drag Reduction in Microchannels Using Ultrahydrophobic Surfaces*, Phys. Rev. Letters, 85, 2000, pp. 980-988
[11] Alberdi, A. *Microstructured Surfaces for Tribological Applications*, 14th International Colloquium Tribology, Esslingen, Germany, Vol. I, 2004, pp. 269-278
[12] Etsion, I. *Laser Surface Texturing-Mesure to Reduce Friction*, 14th International Colloquium Tribology, Esslingen, Germany, Vol.1, 2004, pp. 329-334
[13] Zhu, Y. *Limits of the Hydrodynamic No-Slip Boundary Condition*, Physical Review Letters, 88, 10, 2002, pp. 325-336
[14] Lauga, E., Stone, H. *Effective slip in pressure-driven Stokes flow*, *Journal of Fluid Mechanics*, 489, 2003, pp. 55–77
[15] Santiago, J.G. et al. *A particle image velocimetry system for microfluidics*, Experiments in Fluids, 25, 1998, pp. 316-319
[16] Sickert, M., Rondelez, F. *Shear Viscosity of Langmuir Monolayers in the Low-Density Limit*, Phys. Rev. Letters, 90, 2, 2003, pp. 821-824
[17] Pit, R. et al. *Direct Experimental Evidence of Slip in Hexadecane: Solid Interfaces*, Phys. Rev. Letters, 85, 5, 2000, pp. 919-924
[18] Devasenathipathy, S. et al. *Particle imaging techniques for microfabricated fluidic systems*, Experiments in Fluids, 34, 2003, pp. 504–514