

# Slip Boundary Conditions in Nanofluidics from the Molecular Theory of Solvation

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## ABSTRACT

Motivated by the fundamental questions raised by the most recent experimental achievements in nanofluidics, we propose the first-ever derivation and calculation of the hydrodynamic slip length from the first principles of statistical mechanics, based on a combination of linear response theory and equilibrium molecular theory of solvation. The slip length obtained is independent of the type of flow and is related to the fluid organization near the solid surface, as governed by the solid-liquid and liquid-liquid interaction. In the wide range of shear rates and surface-liquid interactions, the slip length is expressed in terms of the Green-Kubo-Nakano relations as a function of the anisotropic inhomogeneous time correlation function of density fluctuations of the liquid in contact with the surface. The presented treatment generalizes the phenomenological definition of the friction coefficient and the slip length to a tensor quantity, which reflects an anisotropic nature of an ordered crystalline surface. We derive generic analytical expressions for the liquid-surface friction coefficient and slip length for an arbitrary surface-liquid interaction potential. We further illustrate it by numerical calculations for the case of a laminar flow of several molecular liquids and water, at ambient conditions in contact with the (100) FCC surface of gold, copper and nickel modeled by using all-atom or united-atom models for liquids and the Steele potential for crystalline surfaces. The obtained values for slip length range from few to hundreds of nanometers and are consistent with experimental measurements. We complement calculations by obtaining pressure and temperature dependence of the slip length for water in wide range of these thermodynamic parameters. The information obtained is intended to be used, in particular, to control or manipulate the flow in electrokinetic processes.

**Keywords:** micro- and nano-scale flow phenomena, molecular liquids, statistical mechanics of classical fluids

## 1 INTRODUCTION AND THEORY

Microfluidics and nanofluidics have now crystallized into new independent branches of science targeting a variety of mechanical, physical, chemical, biological and

biomedical phenomena [1]. Potential applications of microfluidic and nanofluidic devices, in particular micro- and nano-electro-mechanical systems (MEMS/NEMS), have stimulated rapid development of these branches and led to their unprecedented advancement in terms of the speed of analysis, resolution, and automation of procedures [2–8]. Miniaturization of devices for analytical and bio-analytical measurements has reached in recent years a new qualitative level and have confidently entered into all depths up to nano. High demand in such type devices confirms the opinion that the fixed attention to this relatively young branch of investigation will stay for quite a long time.

From a theoretical point of view, there is generic understanding of processes occurring on these spatial and temporal scales [1, 9]. In particular, it is confirmed by the success in modeling of fluid flow over surfaces with exotic properties. However, phenomenological comprehension is not sufficient for rational design of devices and processes, as one needs fundamental understanding at the molecular level. It is seen especially well in the fields where no computer modeling approaches could help due to a number of essential limitations, including a large size of the system, number of particles, *etc.* Two giants of micro- and nanofluidics — mixing and separating devices — still have to rely, to large extent, on a model of fluid flow [10–12]. Even though some of their rheological properties can be accurately described within a continuum fluid mechanics approach in some cases, such a macroscopic treatment requires to specify hydrodynamic boundary conditions (slip length), which could not be easily obtained from the molecular properties of the solid-fluid interface [13].

In our recent study [14], we have proposed the first-ever derivation and calculation of the hydrodynamic slip length from the first principles of statistical mechanics, namely a combination of linear response theory and equilibrium molecular theory of solvation. Specifically, we considered a fluid of a shear viscosity  $\eta_S$  and equilibrium mass density  $\rho_0$ , filling the half-space  $z > 0$  and being bounded by a solid-liquid interface in  $z = 0$  plane. For definiteness, the solid was thought to be at rest, and the laminar fluid flow (low Reynolds number flow) was assumed to be parallel to the  $(x, y)$ -plane and be along the  $x$ -axis. The “partial slip” boundary condition for

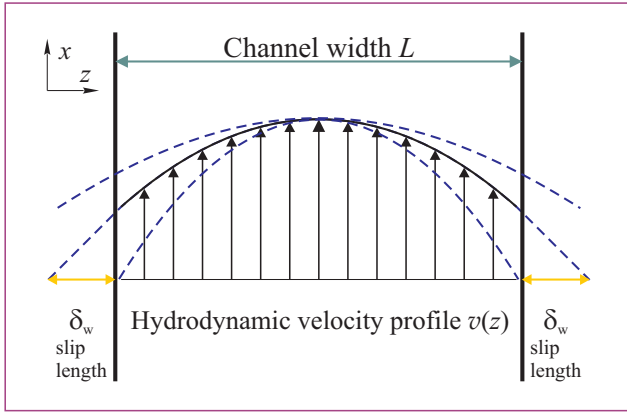


Figure 1: Hydrodynamic velocity profile of a laminar fluid flow in a channel between two infinite plates. By construction, the plates are oriented in parallel to the  $(x, y)$ -plane, so that the separation is along the  $z$ -axis. Vertical arrows represent the fluid velocity magnitude. Slip length  $\delta_w$  is marked at the left and right boundary for the case of a slip fluid flow. Inner and outer curves correspond, respectively, to the cases of a completely stick flow and a flow with somewhat larger slip length. In all cases, velocity profile decays to zero in the thin microscopic layer near the surface (not displayed here). Beyond this boundary layer, the fluid flow is of hydrodynamic character.

the tangential component  $v_{\perp}(\mathbf{r}; t)$  of the total velocity field  $\mathbf{v}(\mathbf{r}; t)$  at the solid-liquid boundary can be written as

$$\left. \frac{\partial v_{\perp}(\mathbf{r}; t)}{\partial z} \right|_{z=z_w} = - \frac{1}{\delta_w} v_{\perp}(\mathbf{r}; t) \Big|_{z=z_w}, \quad (1)$$

where  $\delta_w$  and  $z_w$  denote, respectively, the slip length and position of the wall (the boundary). A schematic draw of such system is shown in Fig. 1. If the wall separation  $L$  is much larger the size of a molecule of liquid  $l$ , i.e.  $L \gg l$ , and the system is far from the phase instability or transition, the microscopic picture near the boundary is equivalent to the one in the half-space without loss of generality. Typically,  $z_w$  is taken to correspond to the position of the first layer of atoms in the solid. The most commonly used boundary conditions, i.e. no slip or perfect slip, are obtained then as limiting cases of the expression above when  $\delta_w = 0$  or  $\delta_w = \infty$ , respectively.

In a phenomenological description, slip length  $\delta_w$  is obtained through the simple relation involving the liquid shear viscosity  $\eta_S$  and the friction coefficient  $\xi_w$ , the proportionality coefficient between the hydrodynamic velocity field near the boundary and the net friction force acting on the induced fluid flow by the surface. In our *microscopic* theory [14], we generalize this relation and take into account molecular specificity of both the liquid and the surface. We also calculate the friction coef-

ficient  $\xi_w$ . The final expression is of the form

$$\delta_{w,ab} = \eta_S / \xi_{w,ab}, \quad (2)$$

with  $a, b = \{x, y\}$ , which means that the slip length itself becomes a tensorial quantity. As for the friction coefficient, it can be compactly written as

$$\xi_{w,ab} = \frac{1}{S k_B T} \int d\mathbf{r}_1 d\mathbf{r}_2 \sum_{\alpha\gamma} Q_{ab}^{\gamma\alpha}(\mathbf{r}_2, \mathbf{r}_1) \times g^{\alpha}(\mathbf{r}_1) \chi^{\alpha\gamma}(r_{12}) \rho^{\gamma} g^{\gamma}(\mathbf{r}_2), \quad (3)$$

where  $S$  is the interface area,  $k_B$  is the Boltzmann constant,  $T$  is thermodynamic temperature,  $g^{\alpha}(\mathbf{r})$  is the three-dimensional distribution function of site  $\alpha$  of the liquid molecule near the surface,  $\chi(r_{12})$  is the site-site susceptibility of the bulk liquid,  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ , and  $Q_{ab}^{\gamma\alpha}(\mathbf{r}_2, \mathbf{r}_1)$  is potentials and geometry factor involving information about the transport properties of the bulk liquid. Indirectly, it also depends on the surface model. Its explicit form is rather lengthy and is omitted here for the sake of simplicity.

## 2 RESULTS AND SUMMARY

Fig. 2 contains the result of application of our theory to calculate the slip length for a set of molecular liquids taken at normal atmospheric pressure ( $P = 101.325$  kPa) and the room temperature ( $T = 298.15$  K). The obtained values for slip length range from few to hundreds of nanometers and microns, depending on the liquids. Our calculations demonstrate that basically there is a correlation between the viscosity of the liquid substance and its slip length, in accordance with the phenomenological picture: liquid with higher viscosity has longer slip length. At the same time, there is a notable deviation from this trend, in some cases. It is clearly seen that liquids with higher viscosity do not always have a larger value of the slip length. In particular, water and alcohols (methanol and ethanol) transgress the monotonic behavior that might be expected, based on the phenomenological approach and its generalization, Eq. (2). As an immediate interpretation to explain this deviation we used the fact that both water and alcohols have the ability to form hydrogen bonds between their molecules. The tetrahedral type hydrogen bonding network formed in water and zigzag type hydrogen bonding network formed in methanol and ethanol leave less degrees of freedom to molecules in solution, thus making it more difficult for them to move or rotate. As a result, friction between layers in these liquids is higher than in liquids without hydrogen bonding network, leading consequently to a larger value of the slip length. Moreover, the formation and rupture of hydrogen bonds between molecules in liquids is a continuing dynamical process dependent on many parameters, including temperature and external pressure. By changing them, one can affect this process, and as a result,

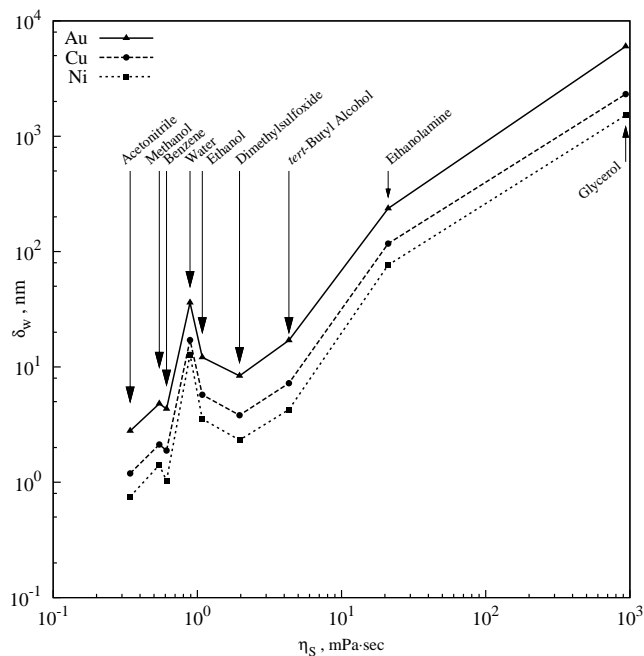


Figure 2: Slip length  $\delta_w$  versus shear viscosity  $\eta_S$  of liquids. Lines connecting individual points are used for the eye-guide, to visualize the trend.

change the slip length to an extent. Surely, variation of temperature and/or external pressure will change the value of the slip length for all substances. However, the cumulative effect for the hydrogen bond forming liquids is expected to be much more pronounced. We verify this expectation by performing explicit calculations for water [15]. Fig. 3 shows the result and demonstrates the change in the slip length with temperature for a set of different pressures. Remarkable for all calculations is the range of decrease for the slip length with temperature: from almost 140 nm to nearly 5 nm. Another type of anomalous behavior of water and aqueous solutions of acetonitrile and methanol we studied previously can be found in Refs. [16–20], where we describe the anomalous pressure and temperature dependence of their molecular mobility and orientational relaxation time. In Ref. [21] we comprehend anomalous ultrasonic absorption in liquids.

The most recent experimental investigation of molecular effects on boundary condition in micro/nanoliquid flows [22] shows excellent agreement with the qualitative predictions of our theory. We conclude our analysis and calculations by checking the accuracy of the theory. It should be mentioned that the slip length is an imaginary distance and its direct observation is not possible. At the same time, it is typical to estimate the slip length experimentally by measuring a related observable physical quantity: the drag force acting on the particle in the flow, its velocity, *etc.* Some broader insight into experi-

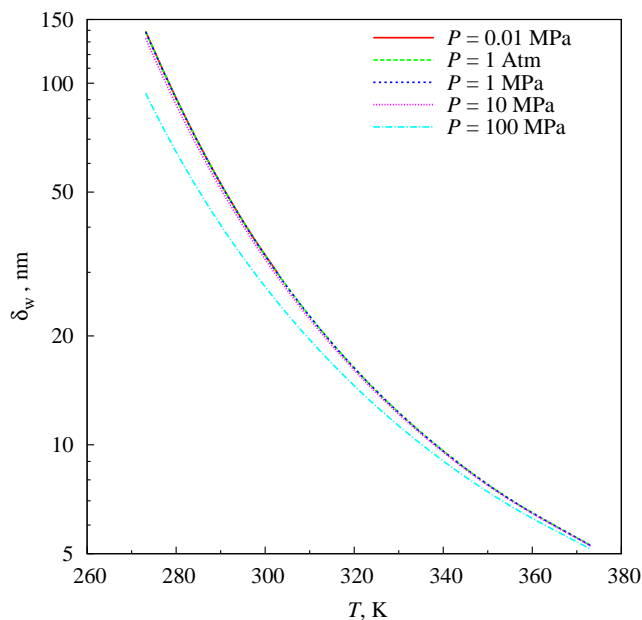


Figure 3: Slip length  $\delta_w$  versus temperature  $T$  of liquid water at various external pressures. Slip length is drawn in the log-scale. Lines connecting individual points are used as the eye guide.

mental methods can be found in Ref. [23] and references therein. As there is no agreement about the methods of measurements between experimentalists themselves, we compare our values with almost all (to our knowledge) available in recent years results in the literature. Fig. 4 collects experimental and theoretical data for the slip length of water and glycerol [24–30]. Although the surfaces in experiments are not the same as those considered by us, the slip length values obtained fall into the same range as in some experimental estimates. This is fairly true for water. For glycerol, however, situation is a bit ambiguous. Two sources of experimental estimation of the slip length report somewhat extreme values: very high [29], or very low [30], while our results come somewhere in between of them. Therefore, more experimental measurements may be needed to clarify the situation. In Ref. [23], the lack of measurements in this area is associated with the technical challenges to current methods.

To summarize, we have demonstrated the first-ever theoretical derivation *and* numerical computation of the hydrodynamic slip length, taking into account molecular specificity of both the liquid and the bounding solid surface. Our approach uses standard statistical mechanical tools and is a combination of the linear response theory and the equilibrium theory of solvation, both written within the formalism of interaction site model. A principal difference between our approach and ever-existing purely phenomenological estimation guides is that we determine the friction coefficients / slip length

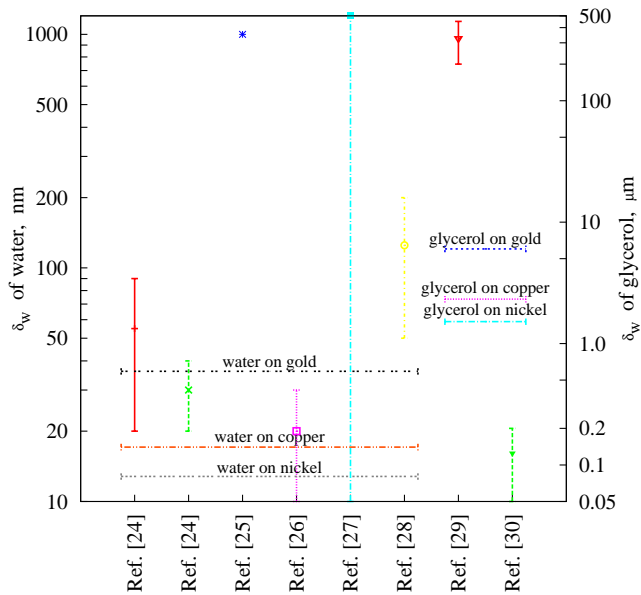


Figure 4: Experimental and theoretical data for the slip length of water [24–28] and glycerol [29,30]. To cover wider range, both left  $y$ -axis for numerical values of the slip length for water and right  $y$ -axis for numerical values of the slip length for glycerol are drawn in the log-scale. The units are: nm for water and  $\mu\text{m}$  for glycerol. Experimental values are displayed by symbols with  $y$ -errorbars. Calculated values are plotted by horizontal lines passing through all experimental data with errorbars. Lines overlap means match of the theory and experiment.

by using not only thermodynamic characteristics of liquid substances (viscosity, density, *etc.*) but also molecular geometries and types of intermolecular interactions between liquid molecules and solid walls. The level of detail is as deep as the interaction site representation, which makes our method unique and quite superior in the sense that it allows one to obtain the value of the slip length for each individual system at the molecular level. This also explains why we call it *molecular* theory of hydrodynamic boundary conditions. Explicit comparison of calculated by the microscopic theory [14,15] and estimated experimentally [24–30] values for the slip length presented here is made for the first time in scientific literature. The information obtained is relevant for rational design of new MEMS/NEMS devices.

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