

Direct measurement of slip length in electrolyte solutions

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Electrokinetic effects and electrostatic repulsion between tracer particles and glass surface have both been proposed as possible sources that would lead to false slip results obtained from velocimetry-based measurements. Using a three-dimensional total internal reflection velocimetry technique, we address such a concern by comparing the measured slip lengths between nonionic solutions and electrolyte solutions whose ionic concentrations have been predicted to reduce the electricity-induced slip effect to a submolecular level. It is observed that the presence of electrolytes has no effect on the measured slip lengths, suggesting that the observed slip velocities are most likely not due to electrostatic and electrokinetic effects, but are consequences of true boundary slip. © 2007 American Institute of Physics. [DOI: 10.1063/1.2539829]

The emergence of microfluidics over the past decade has brought about increased research interests in liquid boundary slip, which for many years has been regarded as negligible. Advancements in flow measurement techniques have resulted in many recent experiments reporting aqueous slip length with a wide range of values and various degrees of dependency on applied shear rate, surface hydrophobicity, and surface smoothness.¹⁻⁹ A total internal reflection velocimetry (TIRV) technique was recently reported to be an effective method in measuring liquid velocities in the region of less than 300 nm from solid surfaces.¹⁰ By conducting a three-dimensional TIRV (3D-TIRV) experiment, Huang *et al.* reported that slip length can be obtained within a 20-nm uncertainty.¹¹ They reported a small but non-negligible slip length for de-ionized aqueous solutions in shear flows over both hydrophilic and hydrophobic surfaces. However, some questions remained as to whether electrostatic and/or electrokinetic forces acting on the tracer particles could lead to false slip observation.^{12,13} In this Brief Communication, slip length measurement of ionic aqueous solutions using TIRV is presented and compared to the previous results of Huang *et al.*¹¹ as an attempt to answer these open questions.

The TIRV technique uses total internal reflection of an incident laser beam to generate a highly localized illumination of the near-boundary liquid phase and relies on tracking motions of individual tracer particles to determine fluid velocity vectors in the planes parallel to a solid surface (Fig. 1). The exponentially decaying evanescent field leads to determination of tracer particles' positions in the direction normal to the solid surface based on their fluorescent intensities. Subsequently, slip velocities and slip length can be inferred from the measured apparent velocity vectors by applying a statistical model for optical and hydrodynamic behaviors of small particles near a solid/liquid interface. A detailed description of the 3D-TIRV, including a discussion of various subtleties, was presented by Huang *et al.*¹¹ A brief summary

is presented here to facilitate the reader's understanding and resultant discussion.

When a fluorescent particle of radius a is illuminated by an evanescent field of incident wavelength λ_0 ($a < \lambda_0$), its emission intensity, I^e , exhibits the same exponentially decaying characteristic as the evanescent field energy does, namely,

$$I^e(z) = I_0^e e^{-h/p}, \quad (1)$$

where h is the distance between the particle center and the solid phase, I_0^e is the emission intensity of the particle when it is in contact with the solid phase ($h=a$), and p is the evanescent wave penetration depth. The penetration depth, which characterizes the length scale of the evanescent field, can be calculated from

$$p = \frac{\lambda_0}{4\pi} (n_1^2 \sin^2 \theta - n_2^2)^{-1/2}, \quad (2)$$

where n_1 and n_2 are the indices of refraction of the solid boundary and liquid, respectively. However, a variety of factors, including statistical variations in illumination intensity, quantum efficiency of the imaging system and, most importantly, nonuniformity of the tracer particle sizes, can lead to variations in the observed fluorescent intensities of an ensemble of nominally identical particles. Thus, a statistical analysis is carried out by characterizing these variations through a single parameter r , or effective emission radius, with which a joint probability density function (PDF), $P(h, I^e)$, of the particle distance to the solid surface and emitted fluorescent intensity can be obtained.

If near-wall velocities of a pure fluid are to be measured by tracking motions of tracer particles, it is important to recognize that shear and near-surface hydrodynamic effects can cause a tracer particle to rotate and translate at a velocity, U , lower than the velocity of the local fluid element in the same shear plane.¹⁴⁻¹⁶ Factors that determine the particle translation velocity include particle radius, a , particle distance to the solid surface, h , and the local fluid shear rate, $S(h)$. Therefore corrections need to be made when one converts observed particle velocities into corresponding fluid ve-

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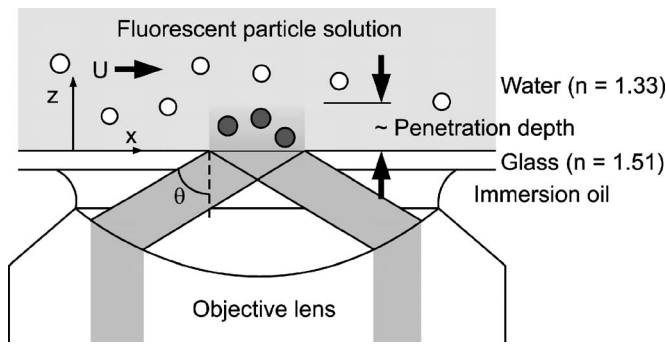


FIG. 1. Objective-based total internal reflection velocimetry (TIRV) system.

locities. It should be noted that in the presented analysis, the corrected particle translation velocity does not account for the possibility of slip between the fluid and the tracer particle, and thus any calculation based on U represents the no-slip case, although the correction is small.

Because tracer particles are used to probe near-surface shear flow, assurance is needed that the particle ensemble uniformly samples all shear layers. It has been suggested that shear-induced lift can be a source of particle migration away from the solid wall.¹⁷ However, based on the theory presented by Cherukat and McLaughlin,¹⁸ the shear-induced lift under the presented experimental conditions is insignificant.¹⁹

The ensemble-averaged velocity, \bar{U} , of a large number of uniformly distributed particles emitting in an intensity range of $\alpha < I^e < \beta$, and located in an imaging range of $h_1 < h < h_2$, can be calculated by

$$\bar{U} = \frac{1}{h_2 - h_1} \int_{h_1}^{h_2} U(h, a, S(h)) P(h, \alpha < I^e < \beta) dh. \quad (3)$$

Because Eq. (3) is based on a no-slip boundary condition, if there exists a slip velocity, U_{slip} , at the liquid/solid substrate interface, the same particle ensemble will exhibit an apparent velocity of

$$\bar{U}_{\text{app}} = U_{\text{slip}} + \bar{U} = \delta \dot{\gamma}_w + \bar{U}, \quad (4)$$

where U_{slip} is characterized as the product of the slip length, δ , and the wall shear rate, $\dot{\gamma}_w$. It should be noted that \bar{U}_{app} can be experimentally measured by finding an ensemble-averaged velocity of “trackable” tracer particles while $\dot{\gamma}_w$ is computed from flow rate and channel geometry. With \bar{U} calculated by using Eq. (3), one slip length can be obtained for each wall shear rate.

Monodispersed fluorescent polystyrene microspheres (Duke Scientific) with diameters of 100 ($\pm 10\%$) and 200 nm ($\pm 5\%$) suspended in de-ionized water (DI-water) or in sodium chloride (NaCl) aqueous solutions at 0.005–0.04% volume fraction were used as tracer particles in this experiment. These microspheres have a peak absorption wavelength of 542 nm and emit at 612 nm. Prior to each experiment, the fluid was degassed by placing the solution in vacuum for at least 30 min. This procedure has been reported to significantly eliminate nanobubble formation,²⁰ which could be an alternative source of apparent slip.^{12,21,22}

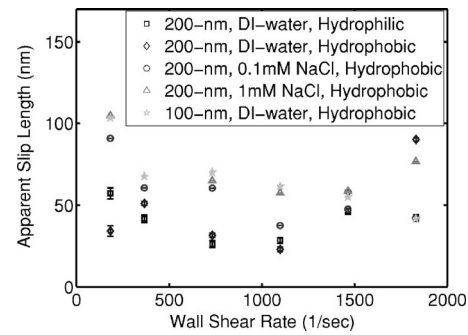


FIG. 2. Measured slip lengths of aqueous solutions. The error bar on each data point represents a 95% confidence interval of each ensemble calculation. The uncertainty of each slip length measurement (not drawn for plot clarity) is less than 20 nm, estimated based on penetration depth calibration and particle radius variation (Ref. 11). Data of “200-nm, DI-water, Hydrophilic” and “200-nm, DI-water, Hydrophobic” have been previously reported by Huang *et al.*

Test channels were fabricated using a polydimethylsiloxane (PDMS) (Dow Corning Sylgard 184) molding technique²³ and bonded onto polished glass wafers. The dimensions of the test channels were $50 \pm 1 \mu\text{m}$ deep, $250 \pm 1 \mu\text{m}$ wide, and 15 mm long. Hydrophilic and hydrophobic microchannels were created by oxygen plasma treatment of the PDMS mold and by bonding untreated PDMS channels onto octadecyltrichorosilane(OTS)-coated glass wafers, respectively. The hydrophilic and hydrophobic glass surfaces had an rms surface roughness of 0.47 and 0.35 nm, respectively.

A continuous-wave 514-nm argon-ion laser beam (Coherent) was directed through a Nikon PL Apo NA 1.45 100X TIRF oil immersion objective at an angle that created total internal reflection at a glass-water interface, thus illuminating the near-surface region of water with an evanescent field (Fig. 1). Fluorescent images of near-surface particles were captured by a Q-imaging intensified Retiga charge-coupled device camera (ICCD). Approximately 1000 images were captured at each flow rate. The flows were driven by a Harvard Apparatus 22 syringe pump, fitted with a gas accumulator, which eliminates pulsations, maintaining steady pumping. A detailed description and schematics of the experimental setup have been presented in Ref. 11.

The analysis of particle image pairs was performed using a custom particle-tracking algorithm. In summary, velocimetry analysis started with finding the positions and peak intensities of all particles via threshold identification and Gaussian fitting of the intensities of the pixels surrounding the peak. Subsequently each particle’s displacement was obtained with a limited-range nearest-neighbor matching. Finally, particles within a desired intensity range were selected for each flow rate and their mean streamwise velocity was defined as the apparent velocity of the ensemble and compared to theoretical no-slip values. Slip lengths were then obtained based on Eq. (4) (Ref. 11).

Figure 2 shows the measured slip lengths of aqueous solutions under various experimental parameters. The first observation to be made is that all measurements report slip lengths of approximately 100 nm or less. These results fur-

ther confirm previously reported measurements^{3,4,7,11} that there is minimal slip over smooth solid surfaces. Slip on a hydrophobic surface appears to be slightly higher than on a hydrophilic surface. A quantitative comparison of all measurements shows that the slip length attributed to surface hydrophobicity averages to 22 nm at the tested shear rates. The additional slip caused by surface hydrophobicity is in agreement with many experimental results,^{3-5,7} but is in sharp disagreement with some others.^{6,9}

Electrokinetic effects¹³ and electrostatic repulsion between tracer particles and glass surface¹² have both been proposed as sources that might cause an apparent slip and could affect the accuracy of slip velocity measurements. Their significance, however, is expected to decrease with increasing ionic strength of test fluids. Lauga¹³ suggested that for an aqueous solution with 1 mM NaCl concentration, the apparent slip length would become submolecular. As shown in Fig. 2, variations in aqueous ionic concentration do not change measured slip lengths significantly. This observation suggests that the measured slip lengths are most likely not due to ionic effects, but are consequences of true boundary slip.

Another important observation is that the slip lengths do not vary significantly over the tested range of shear rates. This observation agrees with experimental studies conducted under similar ranges of moderate shear rates.^{5,7,24} Still, this result does not suggest that slip length is independent of shear rates, as the conducted measurements span only one order of magnitude of shear rates. Zhu and Granick,⁴ Neto *et al.*,²⁵ and Choi *et al.*³ all tested over larger ranges of shear rates (>2 orders of magnitude) and reported shear-dependent slip lengths. It is physically plausible that the shear dependence of slip length is nonlinear and the shear effect is significant only at higher shear rates. To assess this, a TIRV system equipped with a very sensitive high-speed camera would be needed for measurements at high shear rates.

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