

Wall slip at hexadecane – silica or sapphire interfaces: a comparison between Near Field Laser Velocimetry and Surface Force Apparatus experiments

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Hydrodynamics usually assumes that the boundary condition for a simple liquid flowing near a solid surface is a zero velocity at the wall. During the past few years, a number of experiments showing evidence that simple liquids could slip, exhibiting a non-zero velocity at the wall has appeared. This is correlated to recent improvements in detection tools for the fluid velocity and the use of new setups such as Atomic Force Microscopes (AFM) or Surface Force Apparatus (SFA) (for a review see^[1]). This question of possible slip at the wall for simple liquids is not only a fundamental one: with the recent advances in micro fluidic and the miniaturization of industrial processes, it becomes more and more important to know the exact behavior of the fluid near a solid interface.

To directly access this question, we have developed a Total Internal Reflexion – Fluorescence Recovery after Photobleaching technique (TIR-FRAP) which directly gives access to the slip length b (or the extrapolation length of the velocity profile to zero)^[2]. Due to intrinsic Taylor dispersion, the resolution of that technique in terms of flow velocity near the solid wall remains however limited: diffusion mixes the flow lines, and one only access to an average velocity close to the wall, with an averaged performed inside a slab from the wall with a thickness in the micrometer range for usual simple fluids^[2,3]. This average remains sensitive to slip as long as the slip length is not negligible compared to this average length due to diffusion. SFA or modified tip AFM experiments provide in principle a far better sensitivity in terms of slip length: they allow one to measure a drainage force for distances between the two walls limiting the flow as small as a few nanometers. At such distances, even a slip length in the nanometer range deeply affects the drainage. These techniques however do suffer from other limitations. For the AFM experiments, a glass sphere is usually glued close to the AFM tip, to increase the sensitivity in the drainage force. Then, the drainage force on the cantilever itself has to be taken into account which is not straightforward. Moreover, the control of the surface (both chemical nature and roughness, at nanometric level) of the glass bead is quite difficult, while it is now well documented that roughness or chemical heterogeneities at atomic level do strongly affect slip^[1,4]. To that respect, SFA appears as a more reliable technique. In most available machines however, the surfaces need be mica (to be able to accurately measure the distance between the two surfaces by FEEDCO fringes). A number of experiments have been performed with water and mica, which may be a tricky system, due to the complicated response of mica surface to water exposure (dissolution, hydration, ...)^[5]. It thus appears quite important to be able to use SFA with surfaces others than mica. This is indeed what has been achieved by the group of E. Charlaix in Lyon. Using their SFA machine, they have been able to produce reliable measurements of the slip length of water on silica: they showed that there were no slip on clean totally wetting silica and found $b = 20$ nm on OTS modified silica^[6]. It is however well documented now that both the nature of the interaction between the fluid and the surface and the shape of the fluid molecules themselves do play an important role on the level of slip^[3]. For example, TIR FRAP experiments on their side have revealed much larger slip length for hexadecane on smooth

132 sapphire surface. Quite surprisingly, hexadecane was observed to slip on a smooth bare totally wetting sapphire surface, with a slip length $b = 110$ nm. Much larger slip length ($b = 350$ nm) were measured on a optimized dense OTS layer deposited on the same smooth surface. It was also observed that very faint alterations of the OTS layer could lead to a drastic decrease of the slip length. In order to try to understand if this observed important slip is specific to hexadecane or if the data from TIR FRAP do suffer some systematic draw back, we have undertaken comparative experiments on the same surfaces through SFA and TIR FRAP. We shall present the results of these comparative experiments for both totally wetting and OTS modified surfaces, in the presence of hexadecane and of squalane.

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