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## Flow with slip at the wall: from simple to complex fluids

### Écoulements avec glissement à la paroi : des fluides simples aux fluides complexes

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#### Abstract

We present series of experiments based on a Near Field Laser Velocimetry technique, aimed to characterize friction mechanisms at fluid–solid interfaces. For simple fluids, we show that noticeable slip at the wall can occur in the case of a smooth surface even in total wetting conditions. For polymer fluids, entanglements between surface anchored chains and bulk polymer govern the friction. A dynamical decoupling associated to disentanglements between surface and bulk chains is observed at large enough shear rates, leading to high slip and low friction. More elastomer like polymers lead to stick–slip instabilities in a narrow range of shear rates. *To cite this article: H. Hervet, L. Léger, C. R. Physique 4 (2003).*

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#### Résumé

Plusieurs séries d'expériences basées sur une technique de vélocimétrie Laser en champ proche sont présentées, afin de caractériser, par mesure directe de la vitesse interfaciale, les mécanismes de la friction à différentes interfaces fluide–solide. Dans le cas de fluides simples, un glissement notable à la paroi est mis en évidence lorsque le solide est lisse, et ce même lorsque le liquide mouille totalement la surface. Pour des fluides polymères, on montre que la friction est pilotée par les enchevêtrements entre macromolécules ancrées à la paroi et chaînes du volume, avec apparition d'une transition entre forte et faible friction à taux de cisaillement suffisant, associée au désenchevêtrement surface–volume. *Pour citer cet article : H. Hervet, L. Léger, C. R. Physique 4 (2003).*

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#### 1. Introduction

When solving the hydrodynamic equations for a liquid flowing between solid walls, it is usually assumed that the relative fluid–solid velocity is equal to zero. This is the so called nonslip boundary condition (NSBC) [1]. This hypothesis, supported by experimental evidences at macroscopic scales [2,3], is not justified by strong physical arguments at microscopic scales and

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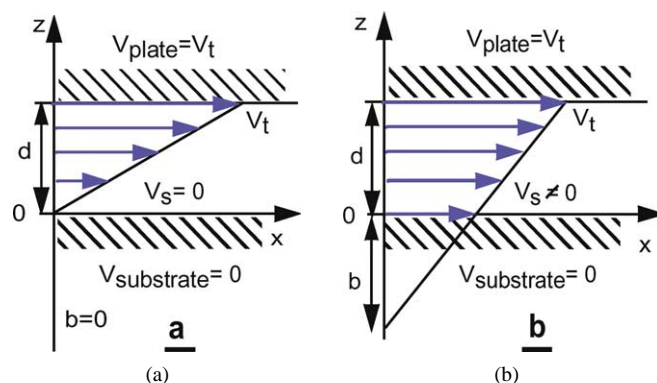


Fig. 1. Schematic representation of a no slip (a) or a slip (b) boundary condition for the fluid velocity at the solid wall. For the sake of simplicity, the top and bottom surfaces are assumed to be different and to lead to different boundary conditions for the flow velocity at the wall. Such a situation can be achieved experimentally by treating the two surfaces in a different manner, as it will be detailed in the presentation of the experimental results.

has been questioned as early as in the 18th century by Brillouin [4]. Since that time much research has been devoted to the investigation of the friction of liquid molecules at solid interfaces and to the possibility of flow with slip at the wall. The pioneering work of Coulomb [5] concluded that the NSBC was true even at microscopic scales. However, this conclusion was relying on experiments with a poor resolution [2] in distance from the solid wall. More recently several results, both from experiments [6,7] and from molecular dynamic simulations [8,9] suggest the possibility of slip at the wall in the case of a weakly bonding surface [6,8–16].

The situation for a simple shear flow is schematically presented in Fig. 1. The extrapolation length of the velocity profile to zero,  $b$ , can be either below the surface (positive  $b$ ) or above the surface (negative  $b$ ), depending on the fact that the fluid–solid interactions are weaker or stronger than the interactions within the liquid. In a simple fluid, it is usually admitted that the perturbation introduced by the presence of the interface cannot produce effects on a range much larger than that of the molecular interactions. The slip length,  $b$  is thus expected to be comparable to a molecular size (Fig. 1(a)). The situation could be quite different in complex fluids for which the range of the interactions can be much larger (Fig. 1(b)) as suggested by de Gennes [17] for entangled polymer melts without interactions with a solid surface.

In fact,  $b$  is directly related to the friction coefficient between the fluid and the surface. This can be easily seen by evaluating the friction force transmitted to the solid by the sheared fluid. The friction force can be estimated either as the product of the interfacial velocity  $V_s$  by the friction coefficient,  $k$ , or as the product of the fluid viscosity by the velocity gradient at the interface, i.e.,  $F_f = kV_s = \eta \partial V / \partial z|_{z=0} = \eta V_s / b$ , where  $\eta$  is the bulk viscosity. The friction coefficient is thus inversely proportional to the slip length. Any direct information on the local velocity profile close to the solid wall can be translated in terms of surface friction, provided the viscosity close to the wall is known. If one suspects that the viscosity close to the wall could differ from that of the bulk, the friction coefficient can be determined without any further assumption by simultaneous measurements of the friction force and of the local velocity  $V_s$ .

The above remark points out the interest of direct measurements of the fluid velocity at the fluid–solid interface. However, to decrease the spatial resolution from the wall from micrometers down to molecular sizes is a particularly difficult challenge. To reach this goal we have developed the Near Field Laser Velocimetry technique (NFLV) which allows us to increase significantly the spatial resolution, down to 50 nm, i.e., much lower than what is obtained with conventional velocimetry techniques [18] (even laser velocimetry). Furthermore the flow tracers are fluorescent molecules with a size comparable to that of the fluid molecules, avoiding any disturbance of the distribution of the flow velocity. This new technique has been used to measure the velocity of a polymer melt at the interface with a solid wall [19–24], and also to demonstrate that a simple fluid can exhibit significant slip on a smooth solid surface [25,26]. More recently techniques based on Surface Force Apparatus (SFA) [27,28] or drainage force measurements with a modified Atomic Force Microscope (AFM) [29,30] have been used and have confirmed that a simple fluid can slip on a solid wall. In those experiments the distance resolution from the wall is better than in NFLV, but the flow pattern is much more complicated than a simple shear flow, and the determination of friction laws appears more difficult.

In the present paper we review these results. In a first part, we briefly introduce the principle of the NFLV technique and discuss its main limitations. In a second part, the results obtained for a simple fluid (hexadecane) sheared on either oleophilic or oleophobic surfaces will be presented and compared with available data from SFA or AFM measurements on other simple fluids. In the last part, we review the results obtained for a polymer melt sheared along a solid wall covered by end grafted polymer

chains, a model situation representative of practical situations of polymer flows, for which, as in an extrusion die for example, polymer chains most often are adsorbed on the surface. These surface tethered chains deeply affect the fluid–wall friction, leading to a complex friction behaviour depending on the relative values of the longest relaxation time of the melt compared to the inverse of the shear rate experienced by the polymer. These behaviours have been modelled in terms of decoupling of the bulk fluid from the surface at high enough shear rates, decoupling between surface and bulk chains associated with the deformation of the surface chains under the effect of the friction forces.

## 2. Principle of the Near Field Velocimetry technique

Until recently, direct determinations of flow velocities close to a solid wall were scarce and generally obtained using small spheres as flow tracers, i.e., with a spatial resolution of the order of the diameter of the beads, not better than 150 nm [31–33]. To investigate the boundary condition of the fluid velocity at the solid interface without perturbing the flow, tracers of molecular dimensions are needed. It is also essential to reduce the dimension of the observation volume in the direction normal to the interface, ideally down to a molecular size. We have developed a technique aiming to fulfill these two requirements, first for polymer fluids [18,19] and second for simple fluids [25,26]. In both cases, the condition on the size of the tracers is matched using fluorescent molecules chosen so that they easily photobleach under intense illumination. Photobleached probes are produced by a local intense illumination of the sample (writing period of the experiment) and act as flow tracers. The way they are transported by the flow is monitored through the evolution with time of the fluorescence intensity, under attenuated illumination so that no further photobleaching occurs during the reading period of the experiment. The confinement of the investigated volume close to the solid–fluid interface is achieved by the use of optical evanescent waves for reading the fluorescence and eventually also to produce the photobleached probes. This technique, based on fluorescence recovery after photobleaching and evanescent wave induced fluorescence, has been named Near Field Laser Velocimetry (NFLV). Detailed descriptions of the experimental set up and of the data analysis of the fluorescence recovery after photobleaching in order to extract the interfacial velocity are reported in [34] both for polymers and simple fluids.

In the case of polymers, the fluorescent probe is chemically attached to the extremities of a few chains in the fluid (5% in weight of labeled chains). The diffusion of the photobleached probes is then very slow, and the evolution with time of the photobleached pattern printed in the sample is essentially due to convection by the flow. The re-entry of fluorescent probes in the illuminated volume can then be directly related to the average velocity in a slab of fluid close to the wall with a thickness comparable to the penetration depth of the evanescent wave,  $\Delta$ , used to read the fluorescence. A typical order of magnitude of that penetration depth is in the range 30–100 nm, i.e., comparable to the size of a polymer chain. NFLV thus gives a direct access to the fluid velocity at the interface, averaged over a thickness comparable to a molecular size.

This is no longer the case for simple fluids. The fluorescent probes are chosen very similar to the molecules of the fluid, in order to avoid preferential interactions at the solid surface, and their diffusion is then fast. The fluorescence recovery is then governed by both diffusion and convection. As a consequence, the experiment only gives access to a velocity close to the surface, averaged over distances from the surface comparable to the diffusion length during the characteristic time of the fluorescence recovery. For typical photobleaching beam diameters in the range of 50  $\mu\text{m}$ , this diffusion length (typically in the micron range) is much larger than the penetration depth of the evanescent wave. The kinetics of the fluorescence recovery remains however sensitive to the boundary condition of the flow velocity and appears more rapid in the case of flow with slip at the wall than without slip. The details of the experimental set up adapted to simple fluids along with the detailed description of the data processing which allows to deduce the slip length,  $b$ , can be found in [34].

## 3. Case of simple fluids

The NFLV technique has been used to investigate the boundary condition of the flow velocity of hexadecane on surfaces having different wetting properties [25,26,34]. We summarize here the main results of these investigations.

Hexadecane has been chosen as a model of non-polar lubricant, with a relatively high surface energy ( $\gamma_L = 27.4 \text{ mJ/m}^2$  at 20 °C). The fluorescent probe was NBD-dihexadecylamine at 5 ppm in weight. The solid surface was a disk of sapphire ( $\alpha\text{-Al}_2\text{O}_3$ , {001}), with a rms roughness of 0.4 nm, as measured by x-ray reflectivity. Sapphire has a high refractive index ( $n = 1.78$ ), leading to a small penetration depth of the evanescent wave (of the order of 35 nm) and the surface can be chemically modified. Four surface treatments have been investigated: (a) the sapphire surface was cleaned by a UV-ozone procedure [35], yielding a high energy surface, totally wetted by hexadecane; (b) the surface was modified by grafting a monolayer of octadecyltrichlorosilane (OTS), following an adjusted procedure similar to that used for silica [36,37], yielding an oleophobic surface ( $\gamma_S = 21 \text{ mJ/m}^2$  for an optimal treatment); (c) a surface covered with a grafted layer of perfluorodecanetrichlorosilane (FDS) ( $\gamma_S < 13 \text{ mJ/m}^2$ ); (d) surface covered by a layer of physically adsorbed stearic acid (octadecanoic acid) formed in situ

by incubating the sapphire surface with an hexadecane/stearic acid solution, inside the flow cell. X-ray reflectivity analysis of the FDS layer (surface (c)) suggested that the FDS molecules were not densely packed and that the monolayer was rather made of FDS islands. Typical rough data for the fluorescence recovery curves are reported in Fig. 2, for surfaces (a), (b), and (c), and for two different shear rates applied to the fluid. It is clear that the fluorescence recovery is faster on the OTS modified surface, and surprisingly enough, it appears faster on the totally wetting bare sapphire surface than on the most oleophobic FDS one. This is the signature of a more efficient convection of the photobleached probes out of the illuminated volume for surfaces (a) and (b) than for surface (c). A quantitative analysis of the curves, in terms of diffusion and convection of the probes can be conducted, as detailed in [34,38]. The results in terms of slip lengths are reported in Fig. 3, along with the corresponding results obtained for surface (d), after various incubation times. Fig. 3 clearly shows that the wetting properties of the surface (i.e., the strength of the interactions between the molecules of the fluid and the surface) are not the only parameter affecting the boundary condition of the flow at a solid wall: hexadecane slips on the totally wetting bare sapphire surface while the no slip surface is the FDS grafted layer, for which the interactions between the fluid molecules and the solid are the weakest. The roughness of that surface at molecular scales is, however, more important than that of the two other surfaces. The smooth OTS surface, with weak interactions and weak roughness, leads to high slip (slip length of the order of half a micrometer, much larger than a molecular size). For the progressively formed adsorbed stearic acid layer, the slip length evolves with time: slip first decreases, compared to the original bare smooth sapphire, and then progressively increases with time when the adsorbed layer becomes denser and smoother. These data clearly demonstrate that a simple fluid can develop noticeable wall slip, and that at least two

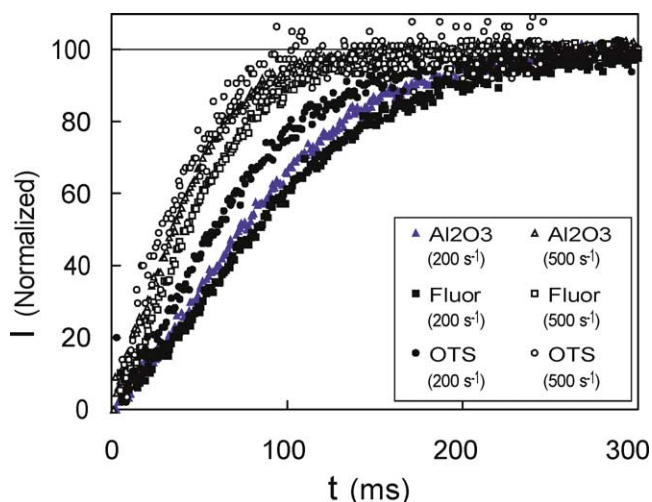


Fig. 2. Normalized fluorescence recovery curves as a function of time for hexadecane sheared along surfaces (a), (b), and (c), and two different applied shear rates: 200 and 500 s<sup>-1</sup>. The top surface is rendered rough, so that a no slip BC is achieved at the top surface.

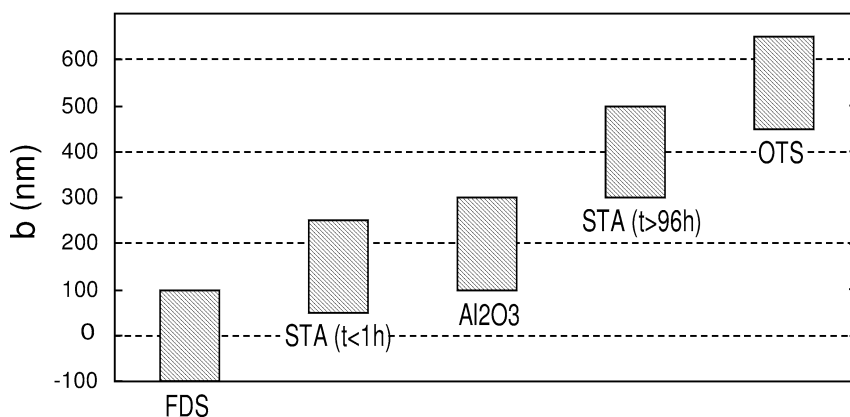


Fig. 3. Summary of the measured slip lengths for hexadecane sheared over the four surfaces (a), (b), (c), and (d) (the shear rates used for such determinations are in the range 200–5000 s<sup>-1</sup>).

factors deeply affect the amount of slip (i.e., the friction): (i) the strength of the interactions between the fluid molecules and (ii) the solid and the roughness of the surface, at molecular scales, both acting on the level of slip in an antagonist way. We are presently investigating other simple fluids, in order to test the generality of these behaviours. More recent experiments have been performed, based on measurements of the drainage force between two close surfaces, either in a surface force apparatus [27,28] or in a modified tip AFM [29,30], leading to conclusions quite similar to ours as far as the existence of wall slip is concerned, for water, water–ethylene glycol mixtures, and tetradecane. Slip at the wall thus seems to be a somewhat general feature for smooth surfaces. Our experiments do not give any evidences of a dependence of the slip length on the shear rate, contrary to what is found in [27], and the reason of that discrepancy is not yet fully understood. One has to notice that both in SFA and AFM experiments, the flow pattern is much more complicated than in our NFLV experiment. Here, deducing a slip velocity from the measurement of the drainage force necessitates a correct modelling of the flow pattern, which is a not so easy task. Moreover, in both SFA and AFM, the shear rate depends on the distance from the singular line which appears in the centre of the apparatus, and an analysis in terms of shear rates may be delicate. NFLV does not suffer such drawbacks, but the resolution in slip velocities (or more correctly in the resolution of the velocity measurement versus the distance from the solid wall) is limited by the mixing of the flow lines (Taylor dispersion) due to Brownian diffusion. Another important difference between AFM or SFA and the NFLV technique is the high degree of confinement of the fluid for both SFA and AFM, which may lead to different properties of the fluid.

#### 4. Friction and slip at polymer–solid interfaces

What happens when the fluid becomes complex, with longer relaxation times? In a first step high molecular weight polymers well in their Newtonian fluid regime have been investigated by NFLV. In order to gain information on the molecular mechanisms of friction at such interfaces, model systems for which the molecular parameters could be varied in a controlled manner have been used. They were made of low polydispersity polydimethylsiloxane (PDMS) melts in contact with smooth silica surfaces, covered with controlled densities of end grafted PDMS chains of various molecular weights. The choice of surfaces covered with end tethered chains was dictated by the fact that in practical situations where a polymer melt is sheared on a solid surface, the most probable situation is that corresponding to the spontaneous formation of a layer of surface anchored chains (even weak monomer – surface interactions result in strong polymer surface interactions, as a polymer chain has on the average  $\sqrt{N}$  monomers in contact with the surface, with  $N$  the polymerization index of the chain).

The important general result is that when the polymer melt is sheared against a surface on which polymer chains are strongly attached, with a surface density  $\Sigma$  (the number of surface anchored chains per unit area is  $\nu = \Sigma/a^2$ , with  $a$  the size of the monomer) three different friction regimes are observed when increasing the shear rate, provided the surface chains are able to entangle with the bulk polymer ones. This nontrivial friction behaviour is illustrated in Fig. 4, which presents velocity measurements at an interface between silica and a PDMS melt, the silica being covered with chemically end grafted PDMS chains, at low surface coverage (see caption for details). In order to prevent slip at the second wall, the top surface is covered with longer end grafted PDMS chains, with an adjusted surface coverage. Slip is always observed: the measured velocity, which is an average of the velocities within the optical penetration depth,  $\Delta$ , from the surface, is always larger than what would be obtained with a no slip BC, shown as the lower dashed line in Fig. 4(a). At low top plate velocities the corresponding slip length is small ( $b \sim 1 \mu\text{m}$ ) and constant (Fig. 4(b)), meaning that  $V_s$  is proportional to  $V_t$ . At intermediate  $V_t$  values,  $V_s$  increases more rapidly than linearly with  $V_t$  to finally reach a value close to  $V_t$  at high shear rates (quasi plug flow;  $V_s = V_t$  is the upper dashed line in Fig. 4(a)). In this intermediate regime,  $b$  appears proportional to  $V_s$  (see the log–log plot of Fig. 4(b)). As  $b$  is inversely proportional to the friction coefficient, this is a nonlinear friction regime, with a friction coefficient inversely proportional to the interfacial velocity. In the high shear rate regime  $V_s$  becomes again proportional to  $V_t$  and  $b$  is constant (linear friction regime), of the order of  $100 \mu\text{m}$ , implying a friction coefficient two orders of magnitude smaller than in the initial low shear rate regime. The striking feature is that, all through the intermediate regime, the shear rate experienced by the polymer,  $\dot{\gamma} = (V_t - V_s)/d$  ( $d$  is the cell thickness) remains constant, a fact which has been confirmed by direct measurements of the shear stress transmitted by the polymer fluid to the prism. If the solid surface is covered with short PDMS chains having a molecular weight smaller than the average molecular weight between entanglements, only the low friction regime is observed, confirming that entanglements between surface anchored and bulk chains are indeed the source of the nontrivial friction behavior in these systems [34,39].

A molecular model describing how a weak density of polymer molecules end grafted on a solid surface (surface chains independent of each other) and entangled with the bulk polymer affect the BC for the velocity at the polymer–solid interface have been developed by de Gennes and coworkers [40–42]. The theoretical predictions agree quantitatively with the NFLV results obtained for PDMS with low surface densities of surface chains. This model takes into account the fact that, due to entanglements, the surface chains act as obstacles to the flow of the bulk chains. These entanglements produce a large friction between the melt and the surface at low shear rates, and suppress the huge slip at the wall expected for ideal surfaces [17]. Surface chains are not however, rigid objects. Under the effect of the friction force, they can deform, and an elastic restoring

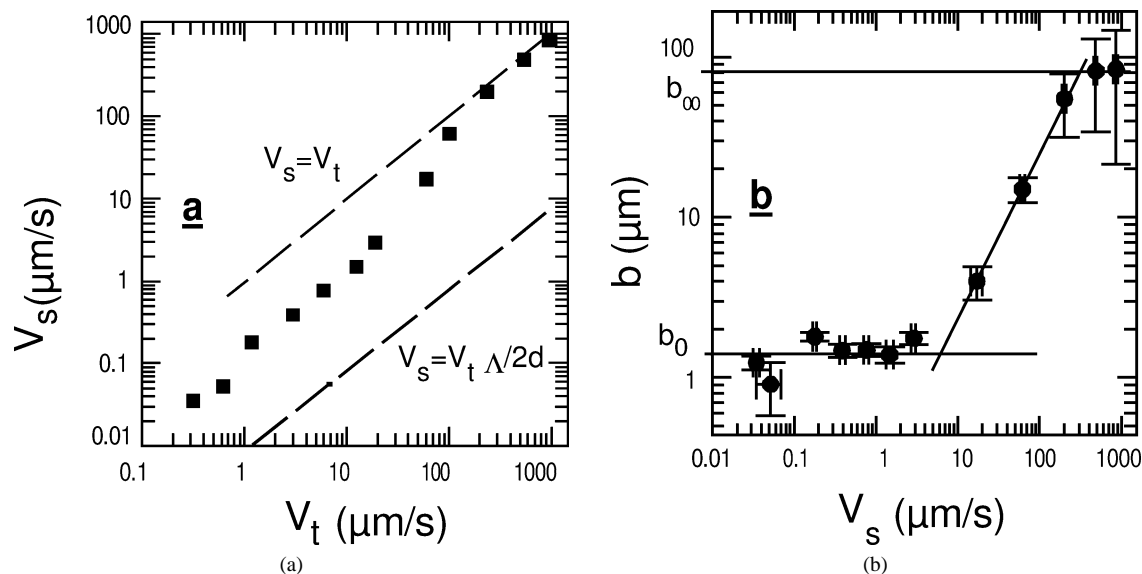


Fig. 4. Typical results for (a) the slip velocity and (b) the slip length, for a PDMS melt (molecular weight  $M_w = 970 \text{ kg/mol}$  ( $M_w/M_n = 1.14$ )), flowing against a silica surface covered with end grafted PDMS chains with  $M_w = 96 \text{ kg/mol}$  ( $M_w/M_n = 1.1$ ) and a surface density,  $\Sigma = 0.00025$  (the surface density  $\Sigma$  is related to the average number of grafted chains per unit surface,  $\nu$ , through  $\nu = \Sigma/a^2$ , with a size of a monomer,  $a = 0.5 \text{ nm}$  for PDMS). The top surface is treated by grafting the same PDMS chains with a larger grafting density, in order to prevent slip at the top surface.

force develops. In steady state, elastic and friction forces balance each other. Increasing the shear rate increases the friction force and the elongation of the surface chains. The initial high friction regime has to stop when the elongation of the surface chains becomes large enough so that the elongated chains are at the limit of disentangling from the melt. A distinct friction regime, called the marginal regime, is then encountered. The surface chains keep the limiting elongation corresponding to the limit of disentanglement for a large range of slip velocities (i.e., a range of imposed  $V_t$ ), because if elongated more, the surface chains would disentangle from the melt, the friction force would strongly decrease and would no longer balance the elastic restoring force. The surface chains would then re-entangle. In the marginal regime the shear force is thus fixed and independent of the slip velocity, implying a friction coefficient inversely proportional to  $V_s$ . This marginal regime is thus the intermediate shear rates regime of the experiments. The marginal regime ends when the frequency at which the surface chains can entangle and disentangle from the melt becomes larger than their relaxation frequency [41,42]. The surface chains then get fully disentangled, the melt dynamically de-couples from the surface, and the friction becomes constant and low, with a slip length  $b_\infty$  independent of  $V_s$  and comparable to what would be obtained on an ideal surface.

In all the three friction regimes the shear force per surface chain (which is directly measured in the experiment) is always much smaller than the force necessary to break a hydrogen or a covalent bond [39]. The observed transition from low to high slip at the wall is thus not due to tearing off of the surface chains. For PDMS melts with lower molecular weights mixed with glass beads [43] a slip transition has been observed and attributed to de-sorption of the PDMS chains from the glass surface. This may not be contradictory. The low to high slip transition is in fact the signature of a dynamic de-coupling between the surface and the bulk polymer. Depending on the physico-chemical conditions, this de-coupling may take place through different modes: tearing off of the surface chains under the shear stress, if the bonding force is weak, or elongation and disentanglement of surface and bulk chains when the bonding force is large. Only the disentanglement mechanism is associated with the existence of a marginal regime extending over several decades in slip velocities.

We have experimentally characterized situations with larger surface densities, as shown in Fig. 5, where the critical shear rate for the entrance in the marginal regime is reported as a function of the surface density of grafted chains. At low surface densities, the linear regime is characteristic of surface chains acting independently of each other for the friction. Above a given surface density, the critical shear rate decreases, indicating that the decoupling between the bulk polymer and the surface layer becomes easier than for lower surface densities. This can qualitatively be related to the fact that for high enough surface densities, one expects that the bulk chains can no longer fully penetrate into the surface layer [44]. The number of mutual entanglements should thus become a decreasing function of  $\Sigma$ , and the critical shear rate too. At present, we have, however, no detailed theoretical description, at molecular level, of this high density regime, in which the surface chains are no longer independent of each other. The experiments and models described above give however precise lines of thought to design surfaces with adjusted friction properties.

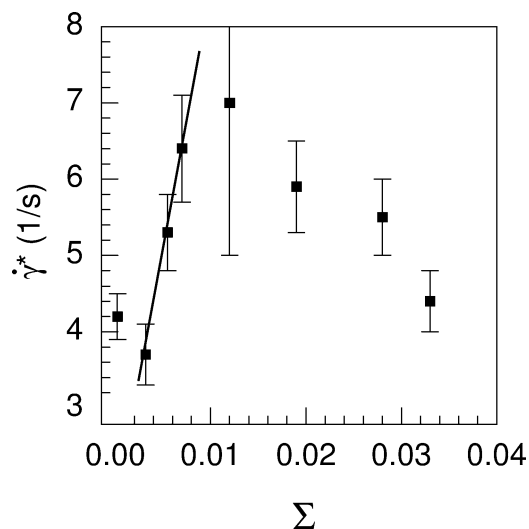


Fig. 5. Evolution of the critical shear rate  $\dot{\gamma}^*$  at the onset of the marginal regime as a function of the surface density of the grafted surface layer,  $\Sigma$ , for a PDMS melt with a molecular weight 970 kg/mol, and surface chains with a molecular weight 96 kg/mol. For small surface densities,  $\dot{\gamma}^*$  increases linearly with  $\Sigma$ , indicating that the surface chains contribute to the friction independently of each other. Above a surface density  $\Sigma = 0.01$  a collective behavior of the surface chains shows up.

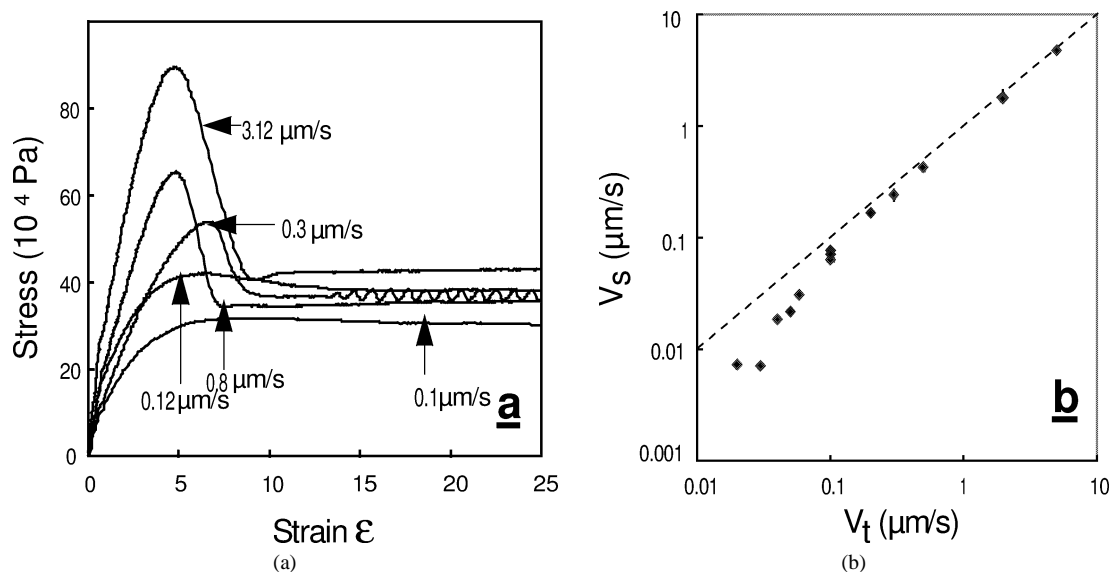


Fig. 6. Typical results for: (a) the shear stress as a function of the displacement of the top surface of the sample for different velocities of that top surface displacement. The polymer is a SBR melt with a weight average molecular weight 135 kg/mol. The surface under investigation bears an adsorbed layer of SBR molecules with a weight average molecular weight 50 kg/mol, and a surface density  $\Sigma = 0.005$ . A stick–slip oscillatory regime clearly appears at intermediate shear rates; (b) slip velocity as a function of top plate velocity for the same SBR melt as in (a), but in contact with a surface covered by a thin layer of PDMS, incompatible with SBR so that no entanglements between surface and bulk chains exist. High slip and a quasi plug flow is observed for the whole range of shear velocities investigated (the dashed line corresponds to  $V_s = V_t$  (plug flow)).

The case of non-Newtonian polymer fluids has also been investigated experimentally, using NFLV, and appears more complicated [45]. The experiments show the onset of a decoupling between the surface layer of anchored chains and the bulk polymer, but which can be accompanied by a nonstationary regime with stick–slip interfacial motion, as shown in Fig. 6: another polymer (Styrene-butadiene copolymer, SBR) has been investigated. The average distance between entanglements is smaller in SBR than in PDMS, so that for comparable molecular weights the reptation time,  $T_R$ , is much longer and the limit

$\dot{\gamma}T_R \geq 1$  can be easily reached in the shear rate range of the experiment. We have yet no full molecular explanation for the behaviour shown in Fig. 6, but it can be qualitatively understood assuming that for high enough shear rates, the bulk chains can no longer disentangle fast enough from the surface layer. In order to allow the slip motion, the surface chains need to be elongated and sufficiently deformed so that they are extracted from the bulk. Such a deformation corresponds to the initial transient in the constraint versus time curves. When the surface chains are extracted from the bulk, the interface can no longer sustain the constraint, and slip develops. At moderate top plate velocities, the deformation energy is relaxed during the initial slip motion, and the interfacial motion slows down, eventually enough to allow for a partial re-entry of the surface chains into the bulk, initiating this stick-slip behavior. In Fig. 6(b), we show that in the absence of entanglements between the surface layer and the bulk at the beginning of the experiment, only the high slip, low friction regime develops. These experiments appear as first steps towards trying to understand friction between crosslinked elastomers and solid surfaces.

## 5. Conclusions

We have briefly reviewed recent results on the friction and flow behaviour at fluid–solid interfaces, obtained through direct measurements of the interfacial velocity, using NFLV techniques. These experiments clearly demonstrate that a fluid can exhibit flow with slip at the wall, and that the no slip boundary condition postulated in most hydrodynamics investigations may be far to be fulfilled.

For simple fluids, we have demonstrated that the zero velocity assumption for the interfacial velocity at a solid wall was not always satisfied. We have established that in the case of a simple fluid, as hexadecane, the strength of the fluid–solid interactions and the roughness of the surface, at molecular scales were acting strongly on the level of wall slip, in an antagonist way. We have, at present, no real physical explanation for such a behavior, even if it is predicted by molecular simulations. Systematic additional work need to be done to demonstrate the generality of the phenomenon observed in the case of water and alkanes, and also to try to characterize what are the scales of roughness of the surface which are relevant to suppress wall slip. These results are not contradictory with macroscopic observations on macroscopic flows, for which the dimensions are much larger than the slip length, but they are certainly of first importance for the development of micro-fluidic devices with characteristic dimensions in the micrometer range or below.

In the case of polymer fluids, slip at the wall is not so surprising: entangled polymer have a mixed fluid and solid dynamic behaviour. The characterization of the interfacial velocity as a function of the molecular parameters of the system has allowed a full identification of the molecular mechanisms of friction at interfaces between a polymer melt and a surface bearing layers of strongly surface anchored polymer chains. The understanding of these mechanisms can lead to the design of surfaces with adjusted friction properties, a quite important objective in a large number of practical situations. Extending the investigation towards crosslinked elastomers should allow one to make steps towards understanding solid friction.

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