

DRAINAGE OF A WETTING LIQUID: SLIP EFFECT OR MOLECULARLY ORGANISED LAYERS?

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ABSTRACT

A Surface Force Apparatus has been used to investigate the drainage of a blend of copolymer viscosity improver additive molecules in a base oil. A quasi-static squeeze of the interface is used to characterize the first repulsion layer and the confined adsorbed layer. Moreover, dynamical measurements enlighten a significant negative value of the immobile layer thickness (-50 nm). The occurrence of slip at the wall that may result in such effect, is discussed in terms of liquid-solid interface wettability, surface roughness and cleanliness, and friction experiments. As a consequence, a modeling of the interface consisting of two layers of different viscosity is proposed. This model of interfacial molecular organization allows us to explain the drainage behaviour of the wetting liquid.

INTRODUCTION

In nanoscopically confined geometries, the structure and the dynamic properties of the liquid located within the contact are modified [1]. Therefore, increasing attention has been dedicated to the study of dynamic properties of thin confined liquid films for the past decades, due to industrial developments in the fields of microfluidic and microelectromechanical devices [2]. The emergence of advanced techniques such as the atomic force microscope [2] and surface force apparatus [3-7] combined with molecular dynamic simulations [8-9] has recently revolutionized this field of investigation. In particular, the topic of the flow of confined Newtonian liquid and of the assumption that the liquid layer next to a solid surface moves with the same velocity as the surface, i.e. the no-slip boundary condition (BC), has been discussed and the slip length model has been developed [2, 10-12]. Many factors affect the occurrence and magnitude of slip: surface wettability, surface roughness, the presence of nanobubbles and gaseous films and the shear rate [2-4, 9, 13].

In this paper, a SFA is used to investigate the drainage behaviour of a confined liquid and the measurement of a

significant negative immobile layer thickness is discussed in terms of slip at the wall or flow molecularly organized layer.

NOMENCLATURE

$A_z(\omega)$ damping function of the interface,
D sphere/plane distance,
L thickness of the first repulsion layer,
 L_c thickness of the confined adsorbed layer,
 L_H thickness of the immobile layer,
h thickness of the surface layer,
 η bulk viscosity of the lubricant,
 η_1 viscosity of the surface layer,
 θ contact angle,
 ω pulsation

EXPERIMENTAL

The Surface Force Apparatus (SFA)

The SFA used in this study has been widely described in the literature [6-7]. A sphere can be moved toward and away from a plane in three directions (X, Y and Z) using the expansion and vibration of a piezoelectric crystal. The measurement of the surface relative displacements is performed with a resolution better than 0.01 nm in each direction using three capacitive transducers. The specificity of this device is its low compliance (2×10^{-6} m/N) and its high resolution force measurement (10^{-8} N). An oscillating normal and tangential motion can be superimposed on the linear (or tangential) displacement. From these dynamical displacement and force measurements, the elastic and viscous properties of the contact can be derived.

Materials

A couple of solid samples (sphere with a 2.30 mm radius and plane) consisting respectively of a fused silicate glass and of a silicon wafer, is prepared. Both surfaces are coated with a

50 nm thick metallic cobalt layer. Despite the presence of a very thin oxide layer, both surfaces are highly conductive and permit establishment of the displacement scale zero using sphere/plane capacitive measurement.

A blend containing a random copolymer added to a 150N base oil is studied. At room temperature, the bulk viscosity of the blend measured with a capillary viscometer 0.58 Pa.s.

Experimental procedure

The sphere/plane distance D reaches 10 μm when a droplet of the liquid is deposited between the two surfaces. Before the actual experiments, an adsorption time of 20h is allowed at this distance.

From an initial operating distance of 1 μm , quasi-static force is measured as a function of D by making inward and outward motions with a constant speed of 0.1 nm/s. In addition, frictional experiments are performed at constant normal load and for various sliding distances and velocities (from 0.1 to 5 nm/s).

All the experiments presented in this work are performed at room temperature (23°C).

RESULTS

From the force/displacement measurement, in the quasi-static squeeze of the lubricant within the contact, the thickness of the adsorbed layer on each surface, before and under confinement, respectively L and L_c , as defined in [6], can be evaluated. These thicknesses are reported in Table 1.

Table 1: Interface characteristic thicknesses and oil viscosity.

$2L$ (nm)	$2L_c$ (30MPa) (nm)	$2L_H$ (nm)	η (Pa.s)
22.5	3.6	-50	0.52

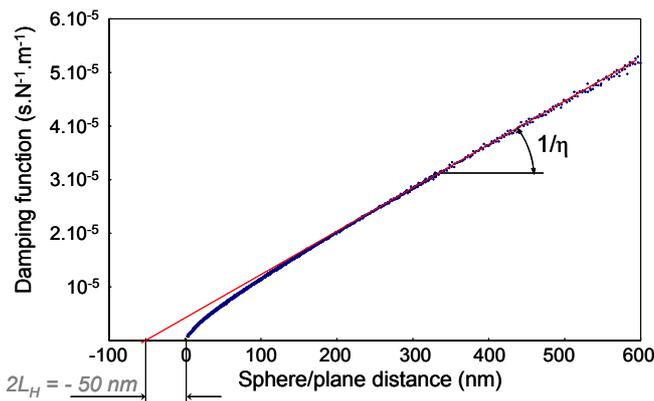


Figure 1: Variations of the $1/(A_z\omega)$ damping function. At large distance, the slope of the curve gives a viscosity of 0.52 Pa.s, which is consistent with the value of the bulk viscosity (0.58 Pa.s). The best fit of the curve for large distance intercepts the distance axis at -50 nm, which defines a negative hydrodynamic thickness.

In the dynamic mode, by superimposing an oscillatory motion of given amplitude and pulsation ω , the viscous damping $A_z(\omega)$ of the interface is measured. The plot of $1/A_z$ as a function of D , at a frequency of 38 Hz, is presented in figure 1. For large sphere/plane distances, according to Stokes' law, this allows us to determine the bulk viscosity of the lubricant (as reported in Table 1) which is in good agreement with the bulk viscosity value (0.58 Pa.s). Moreover, a large negative value of the immobile layer thickness (-50 nm) is observed which is usually interpreted in terms of slippage at the wall [3-4] (cf figure 2).

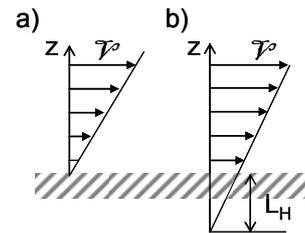


Figure 2: Schematic representation of (a) no-slip BC and (b) partial slip BC. \mathcal{V}^o represents the velocity of the liquid.

DISCUSSION

Lubricant Wettability

Since slip phenomena are usually correlated to the lubricant-surface non-wettability [2-4, 10], a 3 μL -droplet of lubricant has been deposited on a cobalt-coated-silicon-plane, as shown in figure 3. A contact angle inferior to 90° is measured thanks to a Pocket Goniometer X measuring head. This would tend to demonstrate a wetting liquid-solid interface.



Figure 3: Image of a lubricant droplet deposited on a cobalt plane using a Pocket Goniometer X measuring head.

Surface roughness and cleanliness

The surface cumulative peak to valley roughness does not exceed 0.5 nm. In comparison with the thicknesses of the adsorbed layers, the solid surfaces can be considered as very smooth. Before the droplet of lubricant is introduced in the contact, a preliminary approach of the sphere towards the plane (a few nanometers under nitrogen-controlled atmosphere) is performed to check the cleanliness of the substrate.

Friction coefficient

Friction experiments are performed on the molecular tribometer at a constant normal load of 3×10^{-2} and 1 mN, for a sliding length of 100 nm and sliding velocities varying from 0.2 to 5 nm/s. The stationary friction coefficient reaches a high value of 0.3 which seems contradictory with the hypothesis of existence of a slip effect.

Two-viscosity-layer modeling

As a consequence, in order to explain the evolution of the damping function with D , a simple modeling of the contact has been proposed [14], as shown in figure 4: it consists of two layers of different viscosity, respectively η and η_1 .

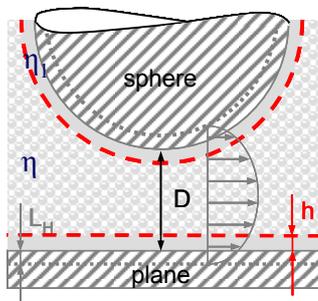


Figure 4: Modeling of the contact using two layers of viscosity η and $\eta_1 < \eta$. The surface layer has a thickness h of about 40 nm.

At large distances, far from the surfaces, as accurately described by Stokes' law, the viscosity η of the layer is equal to that of the bulk, i.e. $\eta = 0.52$ Pa.s. At the vicinity of the surfaces, a layer of lower viscosity, $\eta_1 = 0.28$ Pa.s $< \eta$, can be defined. The thickness, h , of this lower viscosity surface layer is approximately 40 nm. This peculiar organization of the copolymer macromolecules at the vicinity of the surfaces allows us to simulate accurately the variation of the damping function. Therefore, the drainage behaviour of this wetting lubricant can be attributed to a molecular organization of the interface and not to a slip effect at the wall.

CONCLUSIONS

From the quasi-static squeeze of the interface, the thickness of the first repulsion layer and that of the confined layer at 30 MPa can be estimated: they are respectively equal to 22.5 nm and 3.6 nm. Moreover, from the plot of the reciprocal of the damping function, in the dynamic mode, at large distance, a viscosity equivalent to that of the bulk is obtained. In addition, a significant negative hydrodynamic thickness is defined. This result is usually interpreted in terms of slip at the wall for non-wetting liquid-solid interface. In this study, contact angle measurements show that the considered liquid-solid interface is a wetting one. Friction coefficient as high as 0.3 is measured and tends to demonstrate the inconsistency of the "slip at the wall" hypothesis. As a consequence, a modeling of the interface is proposed. It consists of a two-viscosity-layer molecular organization. The surface layer exhibits a viscosity twice as low as the bulk layer, and its thickness is about 40 nm.

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