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# LOW FRICTION FLOWS OF LIQUIDS AT NANOPATTERNED INTERFACES

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With the recent important development of microfluidic systems, miniaturization of flow devices has become a real challenge. Microchannels, however, are characterized by a large surface to volume ratio, so that surface properties strongly affect flow resistance in submicrometric devices. We present here results showing that the concerted effect of wetting properties and surface roughness may considerably reduce friction of the fluid past the boundaries. The slippage of the fluid at the channel boundaries is shown to be drastically increased by using surfaces that are patterned at the nanometer scale. This effect occurs in the regime where the surface pattern is partially dewetted, in the spirit of the 'superhydrophobic' effects that have been recently discovered at the macroscopic scales[1]. Our results show for the first time that, in contrast to the common belief, surface friction may be reduced by surface roughness. They also open the possibility of a controlled realization of the 'nanobubbles' [2] that have long been suspected to play a role in interfacial slippage [3, 4].

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The nature of the boundary condition for fluid flows past solid surfaces is a subject of ancient interest [5, 6], which has been revived recently by a large number of experiments and new theoretical approaches. The possibility of investigating flows at small scales in a quantitative manner, as opened by the development of nanoscale measurements (Surface force apparatus or Atomic Force Microscope) has allowed a number of experimental determinations of the 'slip length'  $\delta$  (see figure 1) that is used to characterize this boundary condition [7, 8, 9, 10, 11, 12]. Optical techniques, such as fluorescence correlation or recovery methods [13, 14] have also shown evidence for the existence of a nonzero slip length.

From a theoretical point of view, the parameters controlling the magnitude of the slip length are still largely unknown. At a macroscopic scale, the strength of the interaction between a solid and a liquid is most obviously characterized through the wetting behaviour. Weak interactions result in nonwetting behaviour, with large contact angles for a drop of liquid resting on the solid substrate. This characterization is purely thermodynamic, and has in principle no direct influence on nature of fluid flow past the interface. Molecular dynamics studies and mode coupling calculations [15, 16, 17], however, have shown that wettability of a perfect surface can be correlated to the magnitude of the hydrodynamic slippage. Qualitatively, a non wettable substrate is only weakly coupled to the liquid, with a depleted surface layer that can be seen as an atomic scale 'air cushion'. Therefore momentum transfer parallel to the interface is inefficient, and a large 'slip length' results.

Experimentally, it appears that although wettability is an important parameter, different results can be obtained for substrate/liquid combinations with similar wetting properties [11, 12, 13, 18]. Another parameter of obvious importance, which may explain such variability, and has not been taken into account previously in molecular simulations, is surface roughness. In fact, it was shown by Richardson [19] that roughness suppresses slippage on a macroscopic scale, for any type of microscopic conditions.

Zhu's experiments [11] have indeed shown that, in a situation where slippage is observed on smooth surfaces, it can be suppressed by increasing surface roughness. Other experiments carried out by Watanabe *et al.* [21] on highly water-repellent walls (i.e. walls bearing a pattern of narrow parallel grooves) resulted on the other hand on important slippage at the wall. In this work, we present a numerical study of slippage at interfaces bearing a model roughness, which takes the form of a nanoscale periodic pattern. The effect of such patterns on wetting properties has been studied extensively, both experimentally and theoretically, but their influence on dynamics has received much less attention.

The configuration considered in our study is a fluid slab confined between two parallel solid walls. The bottom wall is decorated with a periodic array of square shaped dots

of height  $h$  and width  $a$  (see figure ). The typical lateral size of the cell is  $L_x = L_y = t = 20\sigma$ . Periodic boundary conditions in the directions  $x$  and  $y$  parallel to the wall are used. In our simulations, all the interactions are of the Lennard-Jones type

$$v_{ij} = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - c_{ij} \left( \frac{\sigma}{r} \right)^6 \right] \quad (1)$$

The fluid and the solid atoms have the same molecular diameter  $\sigma$  and interaction energies  $\epsilon$ . The variation in the  $c_{ij}$  (the index  $i, j = F, S$  refers to the fluid or solid phase) is a convenient control parameters that can be varied to adjust the surface tensions. The solid substrate is described by atoms fixed on a the (100) plane of an FCC lattice. We have worked with two values of  $c_{FS}$ ,  $c_{FS} = 0.5$  or  $c_{FS} = 0.8$ , which correspond to contact angles (deduced from Young's law) of  $\theta = 137^\circ$  or  $\theta = 110^\circ$ , respectively[17]. The simulations are carried out at constant temperature  $k_B T / \epsilon = 1$ . In flow experiments, the velocity component in the directions orthogonal to the flow was thermostatted[17], in order to avoid viscous heating within the fluid slab. All results reported are obtained within a linear response regime. Most numerical results will be given in Lennard-Jones units (L.J.u.), taking the diameter  $\sigma$  as the unit of length and the energy  $\epsilon$  as the unit of energy.

We first briefly describe the static properties of the system, which were obtained using the following procedure. For a fixed number of liquid atoms  $N_L$  and distance between the planes, the normal pressure is obtained from the average force on the substrates along the  $z$  direction. This normal pressure can be varied either by changing the distance between the two walls at a fixed surface density, or by modifying the number of particles at fixed distance.

Figure shows the pressure-thickness curve obtained when using the first procedure. Two branches separated by a typical 'van der Waals loop' are clearly visible, indicating the existence of a phase transition between two possible situations. At higher normal pressures, the liquid occupies all the cell, including the grooves separating the square dots. At lower pressures, partial dewetting is observed and a composite interface is formed, the space between the dots being essentially free from liquid atoms (see figure 3). Note that the range of pressure in figure is rather small, so that the properties of the bulk fluid over this range are essentially constant (the relative density change being typically less than 0.2%)

In spite of the very small sizes involved, a qualitative interpretation of the observed behaviour can easily be given in terms of macroscopic capillarity. If we consider a system at fixed normal pressure  $P_N$ , the difference in Gibbs free energies between wetted configuration (case  $A$ ) and the formation of a composite interface (case  $B$ ) can be written

as:

$$G_B - G_A = (t^2 + 4ah - a^2) \cdot (\gamma_{LV} \cos \theta) + (t^2 - a^2) \cdot \gamma_{LV} + P_N(t^2 - a^2)h \quad (2)$$

The composite interface is therefore favoured when

$$P_N < P_{composite} = \frac{-\gamma_{LV} \cdot (\cos \theta + 1)}{h} - \frac{4a\gamma_{LV} \cos \theta}{t^2 - a^2} \quad (3)$$

Although a quantitative agreement can hardly be expected in view of the small sizes in our system, we have checked that equation 3 correctly predicts the general trends observed in our simulation, when the height or width or the square dots are varied. It can be used, e.g., to understand the influence of an increase in the corrugation wavelength ( $t$  and  $a$ ). At fixed amplitude  $h$ , such an increase results in a decrease of  $P_{composite}$ , down to unphysically negative pressures. However dewetting may persist up to large, say micrometric, scales for adequately chosen asperity sizes [1].

We now consider the essential objective of our study, namely the influence of roughness on dynamical properties of the confined fluid layers. Our study involved parallel Couette flow, with the upper wall is moved with velocity  $U$  and the lower wall is moved with a velocity  $-U$  (typically  $U = 0.3$  in reduced Lennard-Jones units). Thermostatting through velocity rescaling in the direction perpendicular to the flow is used to keep the temperature constant. For flat walls [16], the slip length  $\delta$  is defined as the distance between the wall position and the depth at which the extrapolated velocity profile reaches the nominal wall velocity,  $v = U$ . In the presence of square dots, the same definition is used. Obviously the presence of dots makes the choice of the wall position somewhat arbitrary. We choose to define the wall as the position of the bottom layer of substrate.

In the following, we will discuss the particular case of a fluid-solid interaction  $c_{FS} = 0.5$ , which corresponds to a contact angle  $\theta = 137^\circ$  on a flat substrate. For this particular value of the interaction, and in the range of pressures we have investigated, the fluid displays a moderate amount of slip at a flat interface, that can be characterized by a slip length  $\delta$  in the range  $20 - 25\sigma$  (the actual value being slightly pressure dependent). Taking a molecular size of  $0.5$  to  $1\text{nm}$ , this corresponds to a value of  $10 - 25\text{nm}$ .

In the presence of the square dot pattern, two very different situations have to be distinguished. The first case is that of a completely wetted substrate (figure 3). A typical velocity profile for this situation is shown in figure 4. First, it is seen from this profile that the introduction of the patterned substrate does not modify the flow in the vicinity of the upper, structureless wall. This boundary can still be characterized by a slip length  $\delta = 22\sigma$ , identical to what would be obtained with two flat substrates at the same pressure. In contrast, the slip is strongly suppressed at the lower wall, where it can be characterized by a value  $\delta \simeq 2\sigma$ . This value would be slightly higher ( $7\sigma$ ) if the

corrugation was taken at the crest of the pattern, but would still be much smaller than the value obtained for a perfectly flat surface.

A completely different result is obtained in the case where the pressure is low enough that a composite interface is formed. A typical velocity profile corresponding to this situation is shown in the right panel of figure 4. As in the wetted situation, the pattern on the lower wall does not modify the slip effect on the upper one. The slip effect on the lower wall is, on the other hand, strongly enhanced by the presence of the composite interface. Numerically, the slip length increases by a factor of about 2.5, reaching a value  $\delta \simeq 57\sigma$ .

Qualitatively, the increase in the slip length should be associated with the absence of friction at the vapour-liquid interface, which can be described by a zero stress boundary condition [18]. Hence, increasing the liquid vapour interfacial area by using a more 'spiky' pattern should result in larger slip length. Using a smaller value of  $a$  ( $a = 4.9\sigma$ ) we find indeed that the slip length can reach a value  $\delta = 130\sigma$ . It is also interesting to compare these simulations results with what could be inferred from approximate hydrodynamic calculations such as that of Hocking [20]. Hocking considered in particular flow past a composite interface, and showed that this results in a partial slip condition when the fluid filling the corrugation (in our case vapour) is of lower viscosity. Unfortunately, a direct comparison with our results is not possible, due to the use of rather different corrugation models and to the 'no-slip' condition used by Hocking at the molecular level. We nevertheless expect that our results should stimulate further work using continuum approaches.

Our results confirm that mesoscopic roughness at the solid liquid interface can drastically modify the interfacial flow properties, in the same manner as it affects static wetting properties. Experimentally, very few results involving surfaces of controlled roughness are available, and, as mentioned above, these experiments yield contrasting results. We believe this variability may find its roots in different wetting situations realized at the mesoscale. It has also been advocated that the existence of 'nanobubbles' at the liquid solid interface is an important factor in slippage phenomena. Our simulations, also they do not, strictly speaking, confirm the existence of such bubbles, show nevertheless that a composite interface can indeed enhance slippage considerably. In our simulations, this enhancement corresponds to an equilibrium situation, which is rapidly achieved at such small scales. Regarding this point, the situation in experiments, often done with surfaces bearing a micrometric pattern, is less clear cut since metastable trapping of bubbles (possibly made of dissolved gases) may occur into submicrometric channels. However, the essential ingredient of the effect studied here, i.e. dewetting, is known to be present on patterned surfaces, from the nanometer up to the micrometric scale. Therefore, although our simulations are performed at nanometer scales, a friction reduction is expected over

a large range of length scale, up to microscale patterns. The effect is however expected to be stronger for the more "spiky" nanometer pattern. In fact, very spectacular drops in the flow resistance of droplets have been reported [22] on surfaces that were decorated with a spiky nanoscale pattern, while the effect of a similar microscale pattern was less pronounced.

In summary, use of patterned surfaces, and treated to produce a 'water repellent' like effect, appears to be a promising way towards devices that would allow flow of liquids in small size channels with very small flow resistance.

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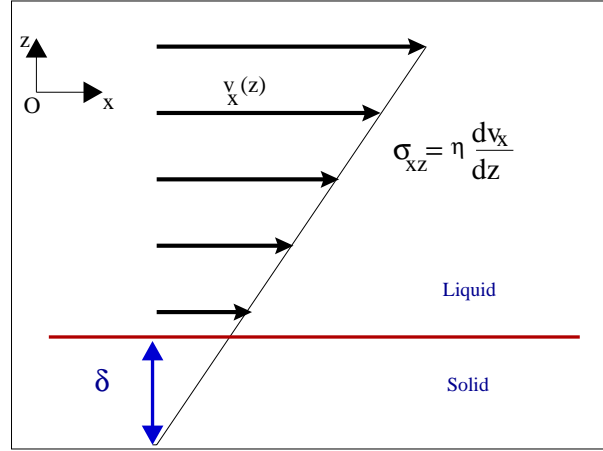


Figure 1: Schematic definition of the slip length. The linear velocity profile in the flowing, newtonian fluid (characterized by a Newtonian viscosity  $\eta$  and a constant shear stress  $\sigma_{xz}$ ) does not vanish at the solid boundary. Extrapolation into the solid at a depth  $\delta$  is necessary to obtain a vanishing velocity, as assumed by the macroscopic 'no-slip' boundary condition.

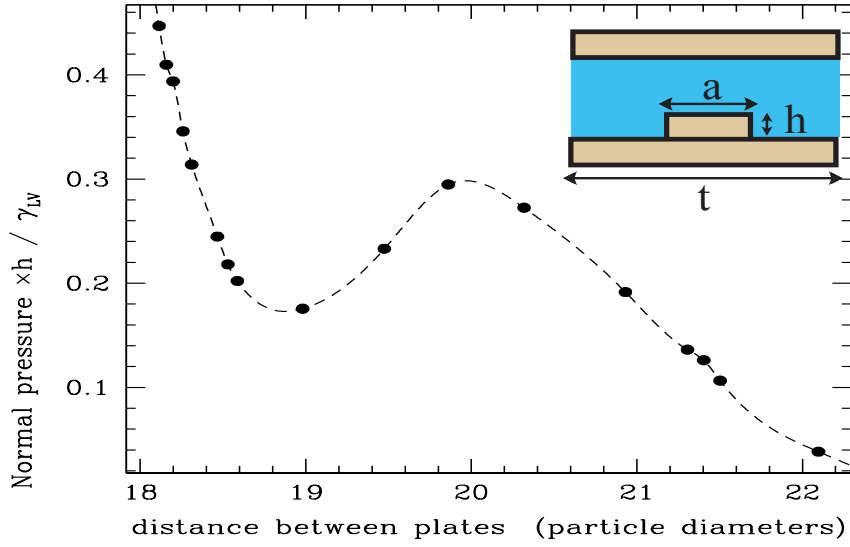


Figure 2: Normal pressure versus thickness. In order to facilitate comparison with experimental situations, the pressure has been rescaled by the typical pressure  $\gamma_{LV}/h$  (typically 100 bars for dots of 7nm in water). The dashed line is a guide to the eye. The inset is used to define the main geometrical variables that describe our setup. The curve shown in the figure corresponds to  $h = 5\sigma$ ,  $t = 20\sigma$ ,  $a = 6.6\sigma$ . With these parameters, a direct application of the macroscopic equation 3, with  $\cos \theta = -0.74$  [16], would yield a coexistence pressure  $P_{coex}h/\gamma_{LV} \simeq 0.014$ . Note that the range of distances for which the pressure increases with  $h$  is thermodynamically unstable, its observation being an artefact of small size simulations.

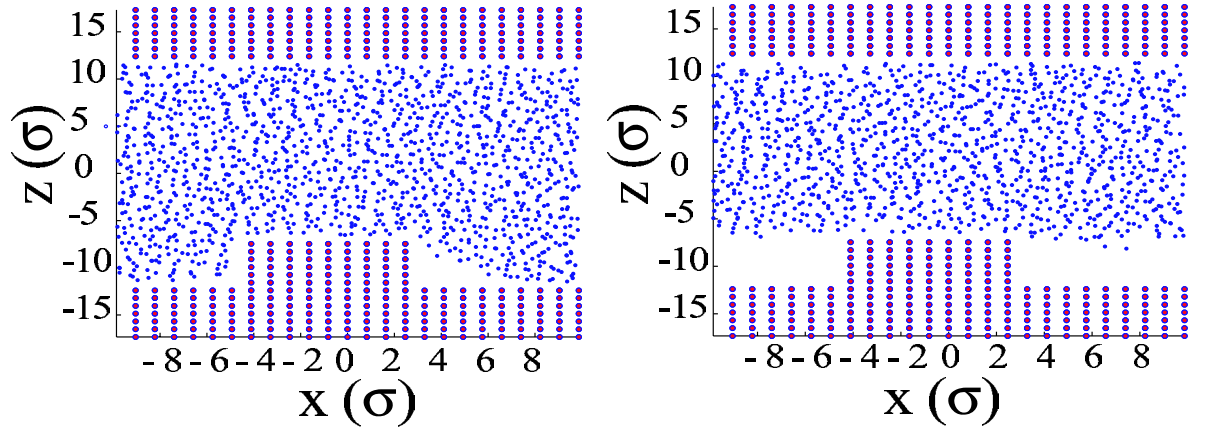


Figure 3: Left panel: transverse view of the atomic configuration in the 'wetted' situation. Atoms belonging to the liquid and solid are represented by points and round dots, respectively. The liquid occupies nearly all the available volume. Right panel: same as left panel, under conditions where a composite interface is formed.

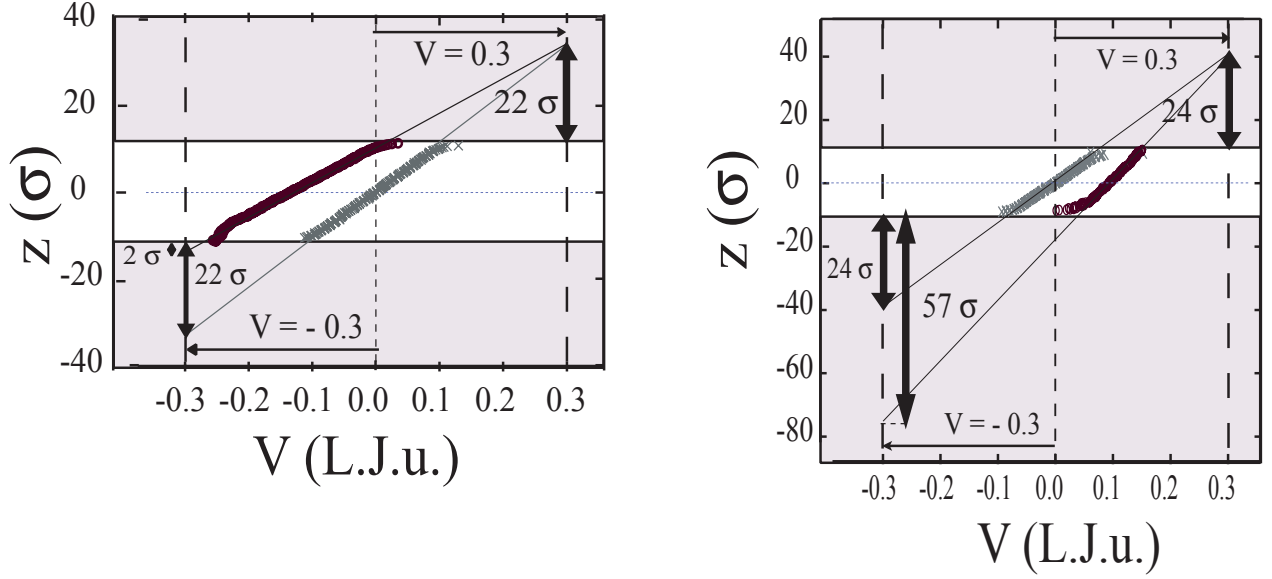


Figure 4: Left panel: Flow properties at a sheared solid-liquid interface, in a wetted situation. The normal pressure is  $P = 0.086 L.J.u.$ . Black dots: velocity profile in the presence of a square pattern on the bottom wall. The pattern is not represented in the figure. Grey points: velocity profile with two smooth walls (at the pressure  $P = 0.086 L.J.u.$ ). The walls are moved at fixed velocities  $U = \pm 0.3$  (in Lennard-Jones units). Slip length are deduced from the intersections of the velocity profiles with the axis  $V = \pm 0.3$ . Numerically,  $\delta = 22\sigma$  at the flat wall and  $\delta = 2\sigma$  at the patterned wall. Right panel: same as left panel, for a composite interface. The normal pressure is  $P = 0.024 L.J.u.$ . One now finds,  $\delta = 24\sigma$  at the flat wall and  $\delta = 57\sigma$  at the patterned wall.