Shear-dependent apparent slip on hydrophobic surfaces: The Mattress Model

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Recent experiments (Zhu & Granick (2001) Phys. Rev. Lett. 87 096105) have measured a large shear-dependent fluid slip at partially wetting fluid-solid surfaces. We present a simple model for such slip, motivated by the recent observations of nanobubbles on hydrophobic surfaces. The model considers the dynamic response of bubbles to change in hydrodynamic pressure due to the oscillation of a solid surface. Both the compression and diffusion of gas in the bubbles decrease the force on the oscillating surface by a “leaking mattress” effect, thereby creating an apparent shear-dependent slip. With bubbles similar to those observed by atomic force microscopy to date, the model is found to lead to force decreases consistent with the experimental measurements of Zhu & Granick.

I. INTRODUCTION

The validity of the no-slip boundary condition is at the center of our current understanding of fluid mechanics. It remains however an assumption whose microscopic validity has been widely debated [1]. The widespread acceptance of the no-slip condition is based on a historical record of outstanding agreement between theories and experiments. It is commonly agreed that the no-slip condition results from inevitable microscopic roughness, which causes enough viscous dissipation to effectively bring the fluid to rest near the surface [2, 3, 4]. Remarkably, this explanation is independent of the nature of the solid and the liquid, contrary to ideas first proposed by Girard (see [5]).

The development of small devices has recently prompted a reexamination of fluid slip on length scales of nanometers and microns, both experimentally [5, 6, 7, 8, 9, 10, 11, 12] and theoretically [13, 14, 15, 16, 17, 18, 19]. The degree of slip is usually quantified by a slip length \( \lambda \), which is the distance below the solid surface where the velocity extrapolates linearly to zero [20]. In experiments, slip is usually found when the liquid partially wets the solid surface; measured slip lengths span four orders of magnitude, from molecular sizes to microns, and are usually shear-dependent in squeeze flow experiments, with \( \lambda \) an increasing function of \( \dot{\gamma} \). In particular, Zhu & Granick [8] reported squeeze flow experiments, in which two crossed cylinders oscillate about a fixed average distance. By measuring the viscous resistance, Zhu & Granick extracted the slip length over a wide range of oscillation amplitudes. These experiments lead to the largest shear-dependent slip lengths yet (up to \( \sim 2 \mu m \)).

The origin of this large shear dependent slip is heretofore mysterious. Nanobubbles have recently been observed on hydrophobic surfaces, using atomic force microscopy, with typical thickness \( h \sim 10 \text{ nm} \), typical radius \( R \sim 50 - 100 \text{ nm} \) and high surface coverage [21, 22, 23, 24]. Although the origin of these bubbles is unclear and skepticism remains in the community about their existence, they have been often invoked as a possible origin of the so-called hydrophobic attraction [25, 26, 27, 28, 29] and their existence points to a possible picture for such large slip [13, 22].

It is well known that there is in general a non-zero velocity at a liquid-gas interface, and therefore it is natural to wonder whether the existence of such a gas layer at the solid surface is sufficient to explain the experiments. When a fluid of viscosity \( \eta_1 \) adjoins a layer of fluid of thickness \( h \) with smaller viscosity \( \eta_2 \), the discontinuous strain rate at the fluid-fluid interface results in an apparent slip with slip length

\[
\lambda = h \left( \frac{\eta_1}{\eta_2} - 1 \right) .
\]  

Choosing \( \eta_1/\eta_2 = 50 \) appropriate for a gas-water interface leads to slip lengths as large as 500 nm. This estimate is however independent of the interfacial shear and therefore unable to explain the squeeze flow experiments; it also overestimates the slip length in the case of bubbles, as is discussed in section III. Note however that similar arguments are consistent with data from pressure-driven flow experiments where reported slip lengths to date are essentially shear-independent [10, 11, 18, 37, 31, 32].

In this article, we will assume bubbles exist on hydrophobic surfaces and will calculate their dynamic response to an imposed oscillatory shear. In an oscillatory squeeze flow experiment [8], we argue that the pressure fluctuations in the fluid cause the bubbles to act as a “leaking mattress”, with both compression and dilation of the gas in the bubble, as well as diffusion of gas into (and out of) the bubble. As the solid sphere oscillates, this periodic in-phase response of the bubbles sizes reduces the amount of liquid necessary to be squeezed out of the gap and thereby the force on the moving sphere, creating an apparent slip. Our calculations indicate that the magnitude of this apparent slip is consistent with the observations of Zhu & Granick. We present the details of our model in the next section and discuss the comparison with the experiment in section III.

\[
\frac{1}{\mu} \frac{d}{dt} \begin{bmatrix} u_1 \end{bmatrix} = \begin{bmatrix} a \end{bmatrix} \begin{bmatrix} u_1 \end{bmatrix} ,
\]

\[
R \sim \frac{1}{u_1} \begin{bmatrix} u_1 \end{bmatrix} = a \begin{bmatrix} u_1 \end{bmatrix} .
\]

\[
\frac{1}{\eta_1} \frac{d}{dt} \begin{bmatrix} \eta_1 \nu \end{bmatrix} = \begin{bmatrix} \nu \end{bmatrix} \begin{bmatrix} \eta_1 \nu \end{bmatrix} ,
\]

\[
R \sim \frac{1}{\nu} \begin{bmatrix} \nu \end{bmatrix} = a \begin{bmatrix} \nu \end{bmatrix} .
\]
II. INFLUENCE OF BUBBLES ON FORCE MEASUREMENTS

A typical oscillatory squeeze flow experiment is shown in Figure 1. A sphere of radius \(a\) oscillates with velocity \(V_{S}\) in a viscous liquid of viscosity \(\eta\) at a distance \(D\) of a planar surface (equivalently, the surfaces can be two crossed cylinders). The two surfaces are assumed to have the same physico-chemical properties. If no bubbles are present and the no slip boundary condition is satisfied on both surfaces, the lubrication force opposing the motion of the sphere is given by the Reynolds equation

\[
F(t) = e_z \cdot F(t) = -\frac{6\pi \eta a^2}{D} V_{S} \equiv F_{\text{lub}}. \tag{2}
\]

If however flow occurs on the surfaces with a slip length \(\lambda\), the viscous force is decreased by an amount \(f_{\text{slip}}\) given by

\[
f_{\text{slip}} = \frac{D}{3\lambda} \left[ \left( 1 + \frac{D}{6\lambda} \right) \ln \left( 1 + \frac{6\lambda}{D} \right) - 1 \right]. \tag{3}
\]

Equation 3 is used experimentally to infer effective slip lengths: the experimental viscous force \(F_{\text{exp}}\) is compared to the theoretical no-slip result \(F_{\text{lub}}\) and any difference is interpreted as fluid slip, with a slip length \(\lambda\) corresponding to \(f_{\text{slip}} = F_{\text{exp}}/F_{\text{lub}}\).

Let us now assume that the solid surface is covered with a percentage \(\phi\) of identical gas bubbles (Figure 1), and determine how the bubbles modify the dynamic response. Although this assumption has been made by previous authors \cite{18, 22, 24, 27, 28, 29}, the physical mechanism responsible for such bubbles is unknown. Simple estimates indicate that small bubbles are short lived in solution \cite{34}. However, stable bubbles could arise from any number of possibilities that are known to prolong bubble lifetimes, including surfactants, surface heterogeneities, or local supersaturation of dissolved gas \cite{35}. In this paper, we are interested in understanding whether the dynamic response of hypothesized bubbles is sufficient to rationalize slip experiments.

A. Total force

The total force \(F(t)\) resisting the oscillatory motion of the area \(S\) of the sphere has two components: (1) a viscous lubrication force \(F_h\), due to hydrodynamic pressure fluctuations and acting on an area \((1 - \phi)S\) and (2) an elastic bubble force \(F_b\), due to pressure fluctuations inside the bubbles and acting on an area \(\phi S\). The total force is therefore given by

\[
F(t) = (1 - \phi)F_h + \phi F_b, \tag{4}
\]

where

\[
F_h = (p - p_0)S, \quad F_b = (p_b - p_{eq})S. \tag{5}
\]

Here \(p\) and \(p_b\) (\(p_0\) and \(p_{eq}\)) denote the (equilibrium) pressures in the liquid and the bubbles respectively. Moreover, since \(D \ll a\), the surface \(S\) is given by \(S \approx \pi aD\).

B. Lubrication force

Let us first calculate the hydrodynamic force \(F_h\). The presence of bubbles modifies equation 2 in two ways. First, flow occurs over a distribution of bubbles located on an otherwise no-slip surface, so the viscous force is reduced by an amount \(f_{\text{slip}}\) given by equation 3, where \(\lambda\) is the appropriate effective slip length for flow over a distribution of bubbles \cite{18, 34}.

Second, the size of the bubbles changes in time in response to pressure fluctuations in the liquid. This volume effect will modify the amount of liquid necessary to be squeezed out of the gap at each cycle of the oscillations, hence the viscous force. Consequently, bubble dynamics has to be subtracted from the forcing \(V_{S}\) and the hydrodynamic lubrication \(F_h\) force is now given by a modified Reynolds equation

\[
F_h = -f_{\text{slip}} \frac{6\pi \eta a^2}{D} \left( V_{S} - \frac{dh}{dt} \right). \tag{6}
\]

where \(h\) is an average bubble thickness on each surface and the factor 2 accounts for the fact that each surface is covered with bubbles.

C. Rate of change of bubble height

In order to calculate \(dh/dt\) in equation 6, let us now consider the dynamics of the bubbles. We assume the bubbles are undeformed by viscous stresses and remain spherical, with radius of curvature \(R(t)\) and interior angle

\[
\begin{align*}
H &= D + \frac{r^2}{2a} \\
\theta &= \sin^{-1}(\frac{r}{2a}) \\
h(t) &= \frac{1}{2} \left( D^2 - r^2 \right)^{1/2} \cdot \sin(\omega t)
\end{align*}
\]
We neglect interactions between bubbles. We expect \( h(t) \) to depend explicitly on the forcing on the bubbles, i.e. \( F_b \).

At the small frequencies typical of squeeze flow experiments (1-100 Hz), the gas is isothermal, so the pressure in the bubble changes via the ideal gas law

\[
p_b(t) V(t) = \frac{p_{eq} V_0}{m_0},
\]

where \( V \) and \( m \) denote the volume and the mass of a single bubble. The average thickness of the gas layer is defined as \( h(t) = n V(t) \), where \( n \) is the number density of bubbles on the solid surface, so that equation (7) can be rewritten as

\[
\frac{p_b(t) h(t)}{m(t)} = \frac{p_{eq} h_0}{m_0}.
\]

Combining the time-derivative of (8) with \( F_b = (p_b - p_{eq}) S \) and linearizing around \( \{p_b, h, m\} \sim \{p_{eq}, h_0, m_0\} \), we obtain the equation for the rate of change of the mean bubble height

\[
\frac{dh}{dt} = \frac{h_0}{m_0} \frac{dm}{dt} - \frac{h_0}{p_{eq} S} \frac{dF_b}{dt}.
\]

We thus have that the rate of change of \( h \) is the sum of a rate of change governed by gas diffusion plus a second contribution due to the gas compressibility.

We now consider the rate of gas diffusion from the bubble. In our model for the oscillatory squeeze flow experiments, bubbles lose mass by both vertical diffusion across the liquid layer and radial diffusion along the apparatus; because of the scale separation \( D \ll a \), these two processes require separate treatment.

Let us first consider the case of vertical diffusion. Since for most common gases, \( \kappa \approx 10^{-9} \text{ m}^2/\text{s} \), the vertical Péclet number \( Pe_v = D^2 \omega / \kappa \) is much smaller than unity: on the experimental time scale \( \omega^{-1} \), the bubbles are approximately in instantaneous vertical diffusive equilibrium. The dissolved gas concentration above the bubble changes via the ideal gas law

\[
p_{eq} = \frac{p_\infty}{1 + \frac{p_\infty}{p_{eq}} - 1} h(t).
\]

Linearizing around \( h \approx h_0 \) and combining with \( p_\infty / \kappa = p_0 c_\infty / p_{eq} \), we get that \( \tilde{m} \) is proportional to the bubble force \( F_b \)

\[
\tilde{m} = \frac{c_0 (D - 2h_0)}{np_0 S} F_b.
\]

Consequently, the total rate of change of \( m \) is given by

\[
\frac{dm}{dt} = \frac{dm_r}{dt} - \frac{c_0 (D - 2h_0)}{np_0 S} \frac{dF_b}{dt}
\]

where \( \frac{dm_r}{dt} \) is the rate of change in the bubble mass governed by gas diffusion in the (slowly varying) radial direction of the apparatus; let us now evaluate this contribution.

In contrast to the vertical case, the radial oscillatory Péclet number, \( Pe_r = L^2 \omega / \kappa = a D \omega / \kappa \), is of order unity or larger, so that radial diffusion has to be accounted for explicitly. Assuming the dissolved gas is in vertical diffusive equilibrium, the time rate of change of the mass of a gas bubble \( \frac{dm_r}{dt} \) is given by a flux integral on the bubble surface \( S_b \)

\[
\frac{dm_r}{dt} = \kappa \int_{S_b} n \cdot \nabla c \, dS = \kappa R^2 I(\theta) \frac{dc}{\partial r}.
\]

where the assumption of spherical cap bubble implies that \( I(\theta) = \pi (2 (\pi - \theta) + \sin 2\theta) / 2 \).

In general, the radial concentration of dissolved gas \( c(r, t) \) verifies an advection-diffusion equation with shear dependent diffusivity \( D_r \). However, for the small amplitude oscillation in \( S \), both advection and Taylor dispersion are negligible, and \( c(r, t) \) satisfies a pure diffusion equation. We finally approximate radial concentration gradient by a simple linear law \( \partial c / \partial r \approx (c_\infty - c) / L_r \) where \( L_r \approx (\kappa / \omega)^{1/2} \approx L / Pe_r^{1/2} \) is the typical (shear dependent) radial gradient length scale. Equation (12) together with Henry’s law leads therefore to a linear relation between the rate of change \( \dot{m}_r \), and the bubble force

\[
\frac{d\dot{m}_r}{dt} = - \frac{\kappa R^2 I(\theta) c_0}{p_0 S L_r} F_b.
\]

Combining \( m_0 = p_0 h_0 / n \) with (13), (14) and (15), we finally obtain that the mean bubble height \( h \) satisfies the differential equation

\[
\frac{dh}{dt} = -k_1 F_b - k_2 \frac{dF_b}{dt}.
\]

where \( (k_1, k_2) \) are given by

\[
k_1 = \frac{n \kappa R_0^2 I(\theta) c_0}{p_0 p_0 S L_r},
\]

\[
k_2 = \frac{c_0 h_0}{c_\infty p_0 S} \left( 1 + \frac{c_\infty (D - 2h_0)}{p_0 h_0} \right).
\]

### D. Bubble force

We finally need to calculate the bubble force \( F_b \) in order to close the system of equations (6) and (14). This in general requires understanding the (equilibrium or nonequilibrium) mechanism responsible for the presence of these long-lived bubbles. However, we can bypass this unknown physics by assuming without loss of generality that the pressure fluctuations in the bubbles and that in the liquid are proportional

\[
\Delta p_b = \alpha \Delta p.
\]
where $\alpha$ is an unknown constant. Hence, bubble and hydrodynamic forces are proportional $F_b = \alpha F_h$, and the total force on the sphere can be expressed as

$$F = (1 - \phi + \alpha \phi) F_b = \left(\frac{1 - \phi + \alpha \phi}{\alpha}\right) F_b. \quad (18)$$

### E. Total force on the sphere

We can now combine (14), (15) and (18) to express the total force opposing the motion of the sphere $F$. We obtain

$$F(t) = -\frac{\delta}{2} (1 - \phi + \alpha \phi) \left( V_S + 2k_1 F_b + 2k_2 \frac{dF_b}{dt} \right), \quad (19)$$

where $\delta = 12\pi \eta a^3 f_{\text{slip}} / D$. Since $F$ and $F_b$ are related by equation (18), (19) can be transformed into an ordinary differential equation for $F$,

$$F(t) = -\frac{\delta}{2} \left( V_S + 2ak_1 F + 2ak_2 \frac{dF}{dt} \right), \quad (20)$$

where $V_S = (1 - \phi + \alpha \phi)V_S$. For an oscillating sphere velocity $V_S = d(d\sin \omega t)/dt$, the periodic solution to (20) is given by (14)

$$F(t) = f_{\text{slip}} \left( \frac{1 - \phi + \alpha \phi}{1 + \alpha k_1} \right) \left( 1 + \delta \omega k_1 \right)^2 \left( \frac{\delta \omega k_2}{1 + \delta \omega k_1} \sin \omega t \right). \quad (21)$$

### F. What is the value of $\alpha$?

By comparing our model (21) to the results of squeeze flow experiments, we find that the only choice consistent with available data at large separation distances is $\alpha \approx 1$.

To see this, consider equation (21) in the limit of large separations between the sphere and the planar surface $D$. Since equation (13) shows that $f_{\text{slip}} \sim 1$ when $D$ is large, we get $\delta \sim D^{-1}$. Moreover, $S \sim D$ so that, from (15) and (16), we obtain $\delta k_1 \sim D^{-2}$ and $\delta k_2 \sim D^{-1}$. Consequently, in the limit of large separations, we obtain that the ratio of the measured force, out-of-phase with the sphere displacement, to the expected no-slip force is given by

$$\lim_{D \to \infty} \left( \frac{F}{F_{\text{hub}}} \right) = 1 - \phi + \alpha \phi. \quad (22)$$

Within experimental errors, this ratio is always measured to be unity 2, 7, 8, 12, i.e., the expected lubrication no-slip force is recovered for large separation distances. We therefore need $1 - \phi + \alpha \phi \approx 1$ or $\alpha \approx 1$.

We emphasize that this conclusion is reached because we assume that the model presented in (11) is the major physical mechanism responsible for the force decrease observed in experiments such as 8.

### G. Final formula for the force ratio

We obtain from (21) that the ratio $f^*$ of the peak force out-of-phase with the sphere displacement to that expected with no-slip and no bubbles (4) is given by

$$\frac{f^*(\omega)}{f_{\text{slip}}} = \frac{1}{1 + \frac{\delta k_1 + (\omega \delta k_2)^2}{1 + \delta k_1}}. \quad (23)$$

The “leaking mattress” model therefore leads to an apparent slip effect, of dynamic origin. The effect is shear-dependent through the frequency dependence in (23): higher frequency and therefore higher shear rates lead to a larger apparent slip, in agreement with 2, 7, 8. The model was derived under the assumption of small amplitude oscillations $d$, which consequently does not appear in the final formula for $f^*$.

Note that in the limit of high frequencies the force ratio (23) becomes $f^*(\omega \to \infty) \sim \omega^{-2}$, whereas at low frequencies $f^*(\omega \to 0) \approx \frac{1}{1 + \delta k_1}$. In the low frequency limit $f^*$ is independent of frequency and depends only on separation distance. Furthermore, equation (23) implies that the apparent slip effect increases with the fluid viscosity, in agreement with experiments 7, 10. It also increases with the size of the sphere $a$, which might account for the large slip lengths reported in 8 (cm-size spheres) as opposed to other squeeze flow experiments (usually μm-size spheres). The model predicts that the measured overall apparent slip length is therefore not only a solid/liquid property but depends on the system size 13.

We finally note from (21) that the total pressure force on the sphere $F(t)$ also contains a non-zero component in-phase with the displacement of the sphere, and therefore out-of-phase with its velocity. If we denote by $g^*$ the ratio of this in-phase response to the expected no-slip no-bubbles out-of-phase response, we obtain

$$g^* = \frac{\delta \omega k_2}{(1 + \delta k_1)^2 + (\delta \omega k_2)^2} f_{\text{slip}} = \frac{\delta \omega k_2}{1 + \delta k_1} f^*. \quad (24)$$

Equation (24) is a prediction of the effective elasticity provided by the bubbles to the surface, which would occur in addition to other in-phase contribution such as intermolecular forces, and is experimentally testable. The values of the in-phase responses of the forces were unfortunately not reported by Zhu & Granick 8.

### III. COMPARISON WITH EXPERIMENTS

We present in this section a quantitative comparison of our model with the experimental results of Zhu & Granick in the case of deionized water, namely the four sets of data presented in Figure 2 of ref 8. The macroscopic water/solid contact angle in this case was 110° the sphere radius was $a = 2$ cm and we assumed that the liquid was saturated with O$_2$ at 25°C and 1 atm ($c_\infty = c_0$), for which $\rho_0 = 1.28$ kg/m$^3$, $c_0 = 8.3 \times 10^{-3}$ kg/m$^3$ and...
\[ \kappa = 2 \times 10^{-9} \text{ m}^2/\text{s}. \]

As a matter of comparison, we have also summarized in Table I the experimental results of [21, 22, 23, 24] on the typical size, distribution and morphology of bubbles observed by atomic force microscopy.

The “leaking mattress” model we have presented in the previous sections has three free parameters which we fit to the experimental data: (a) the area fraction of the bubbles on the surface, \( 0 \leq \phi \leq 1 \), (b) the size of the spherical bubbles, described by their radius of curvature \( R_0 \) and (c) the microscopic contact angle \( \theta \) at the bubble level, which significantly differs from the macroscopic contact angle because of both intermolecular forces at the nanometer scale. Note that \( \phi \) is related to the area fraction \( n \) by the formula \( \phi = n \pi R_0^2 \sin^2 \theta \).

Furthermore, in order to present a meaningful fit to available data, we require that in each experiment the two layers of bubbles fit in the gap between the sphere and the plane for all separation distance. This is a geometrical constraint written as \( 2h_0 = 2R_0(1+\cos \theta) \leq \min(D) \).

The model can be well fit to the experiments [8] with appropriate parameter choices. The best fits are obtained when we choose \( R_0 \approx 10 \text{ nm} \). This is illustrated in Figure 2 where the fits are compared to the small (a) and large (b) amplitude force ratio from the model to the small (a) and large (b) amplitude data from Zhu & Granick [8]; the values of the angles \( \theta \) were chosen for each curve to be the best in a least-square sense and \( \phi = 99\% \). As expected from the linearity of our model, the fit to the low amplitude data of [8] is better than that obtained for oscillations of larger amplitude.

We explore the influence of the three parameters of

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**FIG. 2:** Comparison between the experimental data of Zhu & Granick (2001) and the dynamic model (23) with \( R_0 = 10 \text{ nm} \) and \( \phi = 99\% \). (a): Small amplitude experimental data; (♦): measurements for \( d = 0.5 \text{ nm}, \omega = 1 \text{ Hz} \); dashed-dotted line: model for \( \theta = 177\degree \); (♦): measurements for \( d = 1.6 \text{ nm}, \omega = 10 \text{ Hz} \); solid line: model for \( \theta = 132\degree \). (b): Large amplitude experimental data. (♦): measurements for \( d = 0.5 \text{ nm}, \omega = 1 \text{ Hz} \); dotted line: model for \( \theta = 168\degree \); (♦): measurements for \( d = 6 \text{ nm}, \omega = 10 \text{ Hz} \); dashed line: model for \( \theta = 90\degree \).

**FIG. 3:** Comparison between the experiment from [8] with \( d = 1.6 \text{ nm} \) and \( \omega = 10 \text{ Hz} \) (♦) and the model for different bubble sizes, contact angles and surface coverage. (a): Influence of bubble size; model with surface coverage \( \phi = 0.99 \), contact angle \( \theta = 150\degree \) and bubble sizes \( R_0 = 1 \text{ nm} \) (dotted line), 25 nm (solid line) and 50 nm (dashed line). (b): Influence of contact angle; model with surface coverage \( \phi = 0.99 \), bubble size \( R_0 = 10 \text{ nm} \) and contact angles \( \theta = 120\degree \) (dashed line), 140\degree (solid line), 160\degree (dotted line) and 170\degree (dashed-dotted line). (c): Influence of surface coverage; model with bubble size \( R_0 = 10 \text{ nm} \), contact angle \( \theta = 120\degree \) and surface coverage \( \phi = 0.1 \) (dashed-dotted line), \( \phi = 0.25 \) (dotted line), \( \phi = 0.5 \) (solid line) and \( \phi = 0.99 \) (dashed line).
our model ($\phi, R_0, \theta$) in Figure 3-c for the measurements from [8] with $d = 1.6$ nm and $\omega = 10$ Hz.

We first find that the results of our model depend weakly on the bubble sizes: the results on Figure 3 are consistent with the experimental data for a large range of bubble sizes, $R_0 \sim 1$ to 50 nm. These sizes are in agreement with the experimental evidence of bubbles in [21, 22, 23, 24] as summarized in Table I, although somewhat smaller. As a matter of comparison, the data in [23] show large standard deviation (up to 70%) for the bubble area.

As a difference, we find that the results of our model depend both on the assumed microscopic contact angle $\theta$ and coverage of the surface by the bubbles $\phi$. We observe variations in the contact angles leading to best fit to the four experiments (Figure 2) and also note that we obtain a departure from the best fit when the angle is chosen to be significantly different (Figure 3). In three experiments out of four, we find that the microscopic contact is larger than the macroscopic contact angle $110^\circ$ characterizing the wetting of deionized water on the surfaces used in [8]. This result is consistent with the data in Table I where, in all cases, bubbles were found experimentally to be flat with microscopic contact angles larger than the macroscopic wetting angles. The fourth set of data from [8] is found to be consistent with a microscopic angle of about $90^\circ$. Although this is different from the data in [21, 22, 23, 24], it is consistent with theoretical studies which show that intermolecular forces lead to microscopic contact angles which are always closer to $90^\circ$ than their macroscopic counterpart [38]. Furthermore, we note that electrical effects are known to have significant impact on contact angles of bubbles and drops [39, 40].

Finally, we find that our model is consistent with the experimental data when the surface coverage is assumed to be large and almost equal to 100% (see Figure 3). This result compare well with the available data on bubbles where, in three out of four studies [22, 23, 24], the bubbles were found to cover almost entirely the solid surface. As a difference, the pictures in [21] show bubbles with lower surface coverage. We also note that our previous study of slip in pressure-driven flow experiments lead to a similar conclusion: in order for surface-attached bubbles to be responsible for the measured effective slip, surface coverage of almost 100% was necessary [18].

We emphasize that this mechanism is of dynamic origin, and is not a consequence of the microscopic slip at the bubble surfaces; in particular, we argue that this is why shear-dependent slip length have not been reported by investigations of slip in pressure-driven flow experiments to date, where no oscillatory pressure is present to trigger an effect similar to the one proposed here. Also, the mechanism we propose should also apply to squeeze flow experiments performed on super-hydrophobic surfaces such those reported in [41] with small air bubbles trapped on fractal surfaces (see also [12]).

Assuming the presence of bubbles, the calculations on the model have been performed with several simplifying assumptions and, in particular, additional contributions to the sets of coefficients ($k_1, k_2$) could come from bridging bubbles, large amplitude oscillations of the solid sphere or bubble interactions, deformation or displacement on the solid surface.

We have then presented a comparison between the results of our model when applied to the experiments of Zhu & Granick. We found that our model gives results which are in agreement with the force decrease measured experimentally, for bubble features which are consistent with available experimental data on nanobubbles (bubble size $R_0 \sim 10$nm, large macroscopic contact angles, large surface coverage). Finally, a formula has been proposed for the (additional) effective elasticity provided by the bubbles to the solid surface.

We note that our study does not rule out the possibility of bubbles with dynamically selected sizes. It has been reported experimentally in [43] that the jump-in distance between two hydrophobic surfaces in water, believed to be due to the presence of bubbles, depended on the history of the sample; performing the experiment several times lead to changes in the jump-in distances over time which was found to remain constant only after a few periods. A similar scenario could be envisioned in experiments such as [8].

To conclude, we present a simple prediction based on the results of our model. If a squeeze flow experiment was performed with two different surfaces, say a hydrophobic plane and a hydrophilic sphere, force ratio measurements displaying shear-dependant results should be able to test whether the ideas put forward in this paper are valid. Indeed, if the force decreases was really due, not to bubbles, but to a change in the hydrodynamic boundary condition for flow past the hydrophobic surface, the maximum force decrease one could expect to obtain is 1/4 for the case of a perfectly slipping surface (see [32] for the calculation; this result can also be found by symmetry about the plane where slip occurs). If alternatively the measurements are due to a “leaking mattress” effect similar to the one we propose here, equation (10) should also apply (with different prefactors) and therefore so is equation (20); consequently, force ratio smaller than 1/4 should be obtained in this case. This proposition for an experiment, together with the prediction for the in-phase response of the force (21), would allow our model to be
tested experimentally.

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[44] The general solution to (20) is also an exponentially decaying transient occurring on a time scale τ ∼ δk_2/(1 + δk_1) with τ ∼ 1 ms or less in experiments such as [8].
[45] The model also requires specification of the effective slip length λ in equation (13). Since a set of gas bubbles on a surface resists fluid motion more strongly than a gas layer, equation (20) is not appropriate. We have experimented with several models (see e.g. [18, 36]), all of which give slip length in the range (λ ∼ 10 − 100 nm depending on the experiment). Owing to the weak dependence of f* on the slip length, the precise value of λ has virtually no impact on the quantitative results of our fits.
Ishida et al. [21]   Tyrrell & Attard [22]   Tyrrell & Attard [23]   Steitz et al. [24]

|                            | Ishida et al. [21] | Tyrrell & Attard [22] | Tyrrell & Attard [23] | Steitz et al. [24] |
|-----------------------------|---------------------|------------------------|------------------------|--------------------|
| Projected area (nm²)        | 3.3 × 10⁵           | 4 – 6 × 10³            | 4 – 7 × 10³            | 2 – 11 × 10³       |
| Height h₀ (nm)              | 40                  | 20 – 30                | 20 – 30                | < 18               |
| Radius of curvature R₀ (nm) | ~ 50                | 40 – 60                | 30 – 100               | ~ 100%             |
| Surface coverage φ          | ~ 20%               | ~ 100%                 | ~ 100%                 | 89%                |
| Macroscopic contact angle   | 110°                | 101°                   | 101°                   | > 90°              |
| Microscopic contact angle   | 166°                | ~ 120°                 | 117° – 130°            | 130° – 147°        |

TABLE I: Summary of experimental data on nanobubbles as found in [21, 22, 23, 24] by atomic force microscopy: projected area of each bubble on the solid surfaces, height above the surfaces h₀, radius of curvature R₀, surface coverage φ, macroscopic and microscopic contact angle. The radius of curvature and microscopic contact angles were inferred from the other data assuming spherical cap nanobubbles.