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2009 J. Phys.: Condens. Matter 21 144202

(http://iopscience.iop.org/0953-8984/21/14/144202)

IOP Publishing — Journal of Physics: Condensed Matter

J. Phys.: Condens. Matter **21** (2009) 144202 (4pp) doi:10.1088/0953-8984/21/14/144202

Effective slip lengths for flows over surfaces with nanobubbles: the effects of finite slip

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Received 11 July 2008
Published 18 March 2009
Online at stacks.iop.org/JPhysCM/21/144202

Abstract
We consider effective slip lengths for flows of simple liquids over surfaces contaminated by gaseous nanobubbles. In particular, we examine whether the effects of finite slip over the liquid–bubble interface are important in limiting effective slip lengths over such surfaces. Using an expression that interpolates between the perfect slip and finite slip regimes for flow over bubbles, we conclude that for the bubble dimensions and coverages typically reported in the literature the effects of finite slip are secondary, reducing effective slip lengths by only 10%. Further, we find that nanobubbles do not significantly increase slip lengths beyond those reported for bare hydrophobic surfaces.

1. Introduction

Over the last decade, the development of a number of new measurement techniques has led to the observation of nanoscale, and even microscale, violations of the no-slip boundary condition by simple fluids flowing over solid surfaces [1–4]. In fluid dynamics, slip has historically been described by Navier's slip boundary condition [5, 6], which states that at a solid boundary, $z = 0$ say, the slip velocity, u, is proportional to the shear rate, $\partial_z u$, i.e.

$$\delta\, \partial_z u|_{z=0} = u|_{z=0}\,, \qquad (1)$$

where the constant of proportionality, δ, is called the slip length. Unfortunately, inconsistencies in the experimental measurement of slip lengths have appeared frequently in the literature [7, 8]. Some of these inconsistencies may be due to poorly controlled microscopic factors that influence the measured macroscopic slip length, such as contamination by nanoscale air bubbles (or nanobubbles) [9].

On smooth, homogeneous surfaces, free from contaminants, the most recent experimental evidence suggests that slip lengths are typically of the order of a few molecular diameters, although on hydrophobic surfaces they may be as high as 20 nm [10]. However, for most surfaces, an experiment will measure an *effective* or *apparent slip*, which emerges from the interaction of microscopic chemical heterogeneity, roughness and contaminants. On a rough, heterogeneous surface, both $z = z(x, y)$ and $\delta = \delta(x, y)$ will vary spatially. If the slip length varies over a length scale ℓ and the characteristic scale of the roughness is r, then experiments which probe the boundary condition on some length scale L, where $L \gg \ell$ and $L \gg r$, will measure a homogeneous effective slip length, $\delta_{\rm eff}$. Thus, it is an important theoretical problem to determine the effective slip length given $z = z(x, y)$ and $\delta = \delta(x, y)$.

Experimentally, there is considerable evidence that the effective slip length can depend strongly on the scale of the heterogeneity. The largest slip lengths that have been measured occur for flows over superhydrophobic surfaces when the fluid does not wet the substrate [11, 12]. Such flows are essentially lubricated by a layer of air with drag only occurring at the few points of the surface where the flow makes contact with the substrate. In this case one can think of the substrate as consisting of two slip lengths, the first, δ_s, corresponding to flow over the points in contact with the substrate, and the second, δ_g, to flow over gas regions between the points of contact. Experiments where the lateral spacing ℓ between the points of contact with the substrate is varied find that the slip length is proportional to ℓ if the area of contact between the liquid and the solid substrate is held constant [12].

For similar reasons, it has been suggested that surfaces contaminated by nanobubbles may also exhibit large effective slip lengths [7, 8]. Nanobubbles are an interesting phenomenon in their own right, which have been characterized relatively recently using atomic force microscopy [9, 13–15]. In [15], for instance, AFM measurements revealed bubbles covering ~15% of the solid surface. They are typically very flat (tens of nanometres high but microns in diameter), so their Laplace pressure remains close to atmospheric. It has been suggested that they may occur quite frequently in polar liquids in contact with hydrophobic substrates if the liquid has not been carefully degassed [9]. However, slip lengths over very thin nanobubbles, whose height is comparable to the molecular mean free path in the bubble [15], are likely to be smaller than slip lengths over the vapour regions trapped in a superhydrophobic surface. Estimates for slip lengths over nanobubbles are of the order of microns [16, 17], rather than the hundreds of microns over the confined vapour regions on superhydrophobic surfaces [18]. In this case $\delta_g \sim \ell$, which suggests that the effective slip length might be substantially less than that for superhydrophobic surfaces.

From a theoretical point of view, effective slip lengths can be determined numerically from solutions of the Navier–Stokes equations with a heterogeneous slip boundary condition [19], by using mesoscale methods such as lattice Boltzmann simulations [20], or by atomistic molecular dynamics simulations [21]. Alternatively, in cases where exact or approximate analytic solutions can be found for flows with heterogeneous boundary conditions, one can obtain an effective slip boundary condition by taking the appropriate macroscopic limit. For instance, there are solutions known for flow over or along stripes of alternating shear-free ($\delta_g \rightarrow \infty$) and no-slip ($\delta_s \rightarrow 0$) regions [22, 23], which have been used to derive effective slip lengths [24]. In this case, it is found that the effective slip length scales as ℓ, the wavelength of the periodic patterning, if the stripe area fraction is held constant. More recently, effective slip lengths have been determined for random distributions of shear-free disks on a non-slip substrate [25], where again $\delta_{\text{eff}} \sim \ell$ if the disk area fraction is held constant. These results are consistent with the current experimental evidence for slip over superhydrophobic surfaces described above [12]. However, as discussed above, for surfaces contaminated by nanobubbles where $\delta_g \sim \ell$, the effects of finite slip may be important in determining effective slip lengths.

Our recent work has focused on predicting effective slip lengths for surfaces with patterned finite slip $0 < \delta(x, y) < \infty$ [26, 27]. As they concern finite slip lengths, our results may be useful for evaluating effective slip lengths over surfaces with nanobubbles, if the slip length over the bubble itself cannot be regarded as infinite. In this paper our goal is to use the recent AFM characterizations of nanobubbles, together with our previous results, to determine whether the finite slip length of the fluid over a nanobubble is an important factor to take into account in determining effective slip lengths. We begin by reviewing estimates for slip over nanobubbles, before considering the effective slip length for a surface covered in nanobubbles. We then give an expression for slip over nanobubbles that incorporates the effects of finite slip and discuss whether it is important for comparison with experimental data.

2. Slip length for flow over a nanobubble

The bubbles recently observed by Zhang and co-workers [14, 15] on OTS silicon in water have been found to be several tens of nanometres high and of the order of a micron in diameter. This gives the bubble a radius of curvature of the order of several microns, which is large enough to ensure that the pressure within the bubble remains close to one atmosphere. At these pressures the mean free path of the gas molecules in the bubble (20–30 nm) will be comparable to the height of the bubble. From the images available in [14, 15], the spacing between bubbles is typically several microns or more, and the total coverages seen were typically 10–20%. In contrast, the bubbles observed by Simonsen *et al* [13] in water on polystyrene were roughly 7 nm in height, 70 nm in radius, and covered approximately 60% of the surface.

For a gas layer in the Knudsen regime, where the mean free path of the gas is more than the layer height, De Gennes [17] has given an estimate of the slip length for a liquid flowing over the layer. In this case, the viscous shear in the liquid is balanced by a thermal friction in the gas, giving a slip length of

$$\delta_g \simeq \frac{\mu}{\rho v_{\text{th}}}, \tag{2}$$

where v_{th} is the thermal velocity of the gas molecules $\sim\sqrt{\frac{kT}{m}}$, ρ is the gas density and μ is the liquid viscosity. At 300 K, for molecules of air, $v_{\text{th}} \sim 300\ \text{ms}^{-1}$, so for water ($\mu = 10^{-3}$ Pa s) slipping over an air layer at one atmosphere this gives an estimate of $\delta_g \sim 3\ \mu$m.

At the opposite extreme, where the gas layer is much thicker than the mean free path in the gas, continuity of stress across the liquid–gas interface means that there will be a slip length of

$$\delta_g \simeq \left(\frac{\mu}{\mu_g} - 1\right) t \tag{3}$$

experienced at the interface, where μ_g is the viscosity of the gas, and t is the height of the gas layer. For water flowing over air $\mu/\mu_g \sim 50$, so for a layer thickness of 20 nm $\delta_g \sim 1\ \mu$m.

For gas bubbles of tens of nanometres in height, with mean free paths of a similar magnitude, the slip length will fall somewhere in between these two regimes. However, the two estimates give similar magnitudes for the slip length of around several microns. Thus for the results of Zhang *et al* the slip length at the nanobubble surface is comparable to the spacing between bubbles. For the bubbles observed by Simonsen *et al*, where the height of the bubbles was found to be less than the estimated mean free path, the slip length over the bubbles should still be several microns or more. However, in this case the slip length is much greater than the spacing between the bubbles ($\ell \sim 100$ nm).

3. Effective slip length for flows over nanobubble-covered surfaces

We now consider the problem of determining the effective slip length for a simple shear flow over a surface covered with nanobubbles. We will consider a periodic patterning of bubbles of radius a in a square lattice of cell length ℓ on the surface $z = 0$. Thus, the local slip is a periodic function of the xy coordinates on the plane $z = 0$:

$$\delta(x, y) = \begin{cases} \delta_g, & \sqrt{x^2 + y^2} \leqslant a \\ \delta_s, & a < \sqrt{x^2 + y^2}, \end{cases} \quad (4)$$

where $x, y \in (-\ell/2, \ell/2)$ and $\delta(x + \ell, y) = \delta(x, y + \ell) = \delta(x, y)$. As discussed in section 2 $\delta_g \sim 1\ \mu$m, whereas we expect the slip length over the bare solid surface δ_s to be 20 nm or less.

A simple shear flow over the surface induced (for instance) by a moving plate at some distance $W \gg \ell$ from the nanobubble-covered surface will be disrupted near the surface by the heterogeneity in (4). However, for Stokes flow, the perturbations in the flow induced by (4) will decay away from the boundary ($z = 0$) on a length scale ℓ [26]. Thus the moving plate will experience an effective slip. If we non-dimensionalize (1) by the length scale ℓ ($\hat{x} = x/\ell$, $\hat{y} = y/\ell$ and $\hat{z} = z/\ell$) and insert (4) we end up with boundary conditions on $\hat{z} = 0$ of the following form:

$$\begin{aligned} &(\delta_g/\ell)\ \partial_{\hat{z}} u|_{\hat{z}=0} = u|_{\hat{z}=0}, && \sqrt{\hat{x}^2 + \hat{y}^2} \leqslant \frac{a}{\ell} \\ &(\delta_s/\ell)\ \partial_{\hat{z}} u|_{\hat{z}=0} = u|_{\hat{z}=0}, && \frac{a}{\ell} < \sqrt{\hat{x}^2 + \hat{y}^2}. \end{aligned} \quad (5)$$

Clearly, to first order in δ_s/ℓ, the second condition on $a/\ell < \sqrt{\hat{x}^2 + \hat{y}^2}$ is no slip. In [25], the assumptions of no slip ($\delta_s \ll \ell$) and perfect slip ($\delta_g \gg \ell$) were used to derive an expression for the effective slip length over a surface with randomly dispersed nanobubbles. This gave the expression $\delta_{id} = (8/9\pi)\phi a/(1 - \phi)$ (subscript id for ideal) for the effective slip, where ϕ is the area fraction of the substrate covered by the bubbles. However, based on our estimates above, $\delta_g \simeq \ell$. So one might question whether the assumption of a perfect slip boundary condition (i.e. $\delta_g \gg \ell$) over the bubble region is valid in this situation. In our recent work [26, 27], one of the cases studied was the limit in which $\delta_s \ll \ell$ and $\delta_g \ll \ell$. In these limits, we were able to obtain perturbative solutions to the Stokes equations, which gave an effective slip length of $\delta_f = \phi\delta_g + (1 - \phi)\delta_s$ (subscript f for finite) to first order in δ_s/ℓ and δ_g/ℓ. This expression was also observed to hold in this limit in numerical simulations by Cottin-Bizonne *et al* [19].

It is not immediately clear how to interpolate between the two limiting expressions δ_f, which should hold when $\delta_g \ll \ell$, and δ_{id}, which should apply when $\delta_g \gg \ell$. However, based on numerical results, Ybert *et al* [18] have proposed a heuristic expression that has been observed to approximately bridge the two limits, $\delta_g \ll \ell$ and $\delta_g \gg \ell$, as follows:

$$\frac{1}{\delta_{eff}} = \frac{1}{\delta_f} + \frac{1}{\delta_{id}}. \quad (6)$$

Currently there is no rigorous derivation for this expression. Nonetheless, inserting the expressions for δ_f and δ_{id} above, we find that

$$\frac{1}{\delta_{eff}} = \frac{9\pi(1 - \phi)}{8\phi a} + \frac{1}{\phi\delta_g + (1 - \phi)\delta_s}. \quad (7)$$

From this expression one can see that the finite slip lengths become significant when $\delta_g \sim a/\pi(1 - \phi)$ or when $\delta_s \sim (1 - \phi)^2 a/\pi\phi$. One interesting feature of this expression is that it suggests that the criterion $\delta_g \ll a$ (rather than $\delta_g \ll \ell$) is a better estimate of the magnitude of δ_g for which the finite slip length is important.

We can use this result to estimate the value of δ_g when finite slip effects will become important: for the bubbles observed by Zhang *et al* we obtain a value of ∼300 nm, and for those of Simonsen *et al* ∼60 nm, compared to values of $\delta_g \sim 1\ \mu$m for slip over the bubbles themselves. Thus, in both cases, it appears that one can neglect the effects of finite slip over the nanobubbles, i.e. $\delta_{eff} \simeq \delta_{id}$ as $\delta_s \gg a/\pi\phi$. If we then use the result of [25] to compute the effective slip length for the bubbles of Zhang *et al* ($\phi \sim 15\%$ and $a \sim 500$ nm), then we arrive at an estimate for the effective slip length of $\delta_{id} \sim 25$ nm. Likewise, for the bubbles of Simonsen *et al* [13] we obtain $\delta_{id} \sim 30$ nm. In both cases, the effects of finite slip over the nanobubbles reduce the effective slip lengths by only 10%.

4. Discussion

Based on our analysis, for the nanobubbles described by Zhang *et al* in [14, 15] and by Simonsen *et al* in [13] the effects of finite slip over the bubble do not substantially influence the measured effective slip length. Instead, the order of magnitude of the effective slip length should be well described by the expression for the ideal slip length of a surface with no-slip and perfect slip regions. Using the expression from [25], one obtains estimates of the slip length of the order of several tens of nanometres for the sizes and densities of bubbles reported in most experiments. Surprisingly, these values are not significantly larger than those reported for bare hydrophobic surfaces [10]. This suggests that the presence of nanobubbles does not significantly enhance slip over hydrophobic surfaces.

Finally, we note that in the case where δ_s and δ_g are much larger than ℓ the expression

$$\frac{1}{\delta_{eff}} = \frac{(1 - \phi)}{\delta_s} + \frac{\phi}{\delta_g} \quad (8)$$

has been demonstrated to hold [19, 26]. Again, one can ask when this expression should be used rather than the ‘ideal’ slip length expression. In this case, numerical calculations indicated that this expression was well obeyed down to slip lengths $\delta_s \sim a$. Thus we would expect that finite size corrections due to this expression may become important for nanobubbles with radii of the order of $a \sim \delta_s$, which may be as large as 20 nm on hydrophobic substrates.

5. Conclusion

We have estimated the effective slip length for the nanobubble-covered surfaces characterized by Zhang *et al* [14, 15] and those characterized by Simonsen *et al* [13]. We have argued that, although the slip lengths over the bubbles themselves are comparable to the bubble spacing ($\delta_g \sim \ell$), the effects of finite slip over the bubbles may be neglected in this case. We conclude that such surfaces are likely to exhibit effective slip lengths of only several tens of nanometres, which is comparable to slip lengths measured on uncontaminated hydrophobic surfaces. In other words, nanobubbles do not significantly increase slip over hydrophobic surfaces.

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