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L Bruschi, E Carlin and G Mistura[1]

Istituto Nazionale per la Fisica della Materia and Dipartimento to di Fisica G Galilei,
Università di Padova, via Marzolo 8, 35131 Padova, Italy

E-mail: mistura@padova.infm.it

Abstract
We review recent experiments on the growth of cryogenic fluids adsorbed on
various substrates structured in different ways. On a very well defined array of
microscopic linear wedges sculpted on thin Si wafers, the film mass is found to
diverge as a power law in the chemical potential difference from saturation with
an exponent $x = -1.96 \pm 0.10$, in very good agreement with recent scaling
analysis results. For the other, more irregular patterns, the observed exponents
range from -0.95 to -2. In any case, they are always much smaller than those
found for flat or rough surfaces.

1. Introduction

Very recently, the wetting by liquids of patterned substrates, both geometrical [1] and
chemical [2], has become the object of increasing research effort in view of their potentially
relevant applications in fields as diverse as biophysics [3] and microfluidics [4].

This short review summarizes the main experimental results obtained in our laboratory
on the growth of a liquid film adsorbed on a linear wedge formed by joining two oblique
planes. In the case of complete wetting at coexistence—that is, when the liquid film covers the
wedge walls completely—this growth can be derived from simple stability conditions based
on the Laplace equation [5]. The main result of such an analysis is that the excess mass m_1 of
a liquid adsorbed in a linear 3D wedge is expected to grow as $m_1 \sim (-\delta\mu)^{-2}$ [5, 6], where
$-\delta\mu \equiv \mu_{\text{sat}} - \mu$ represents the difference of the chemical potential of a bulk vapour at a certain
pressure P and temperature T from the corresponding value at liquid–vapour coexistence. This
behaviour sharply contrasts with that observed for on a flat surface, where $m_1 \sim (-\delta\mu)^{-1/3}$,
if the liquid film is attracted to the surface by means of van der Waals forces. The exponent
$-1/3$ is that expected for non-retarded van der Waals interactions—that is, for film thicknesses
smaller than 10–15 nm [7], the situation encountered in our experiments.

The result for the linear wedge has been extended to power law wedges, whose height
profiles have the form $h = A|y|^\gamma$, where A is a constant, y is the lateral coordinate measured

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[1] Author to whom any correspondence should be addressed.

from the bottom of the channel and the exponent $\gamma > 0$ characterizes its curvature. According to recent scaling arguments [6], there exists a marginal value of the height exponent γ^* ($\gamma^* = 1/2$ for van der Waals forces) such that for $\gamma > \gamma^*$ a crossover is expected from planar-like to geometry-dependent behaviour, whose location depends on the size of the channels. In this latter regime, $m_1 \sim (-\delta\mu)^x$, where $x = \frac{\gamma+1}{\gamma-2}$ and $\gamma^* < \gamma \leqslant 1$. An interesting conclusion from this theory is that the exponent x depends only on γ. For a linear wedge, $\gamma = 1$, this implies that the resulting exponent x is equal to -2 no matter how wide the opening angle α of the wedge is.

2. Experimental set-up

To test the predictions for the linear channels we have used a torsional disc microbalance, in which the patterned substrate is attached to the extremity of a hardened steel rod and is driven to the resonant frequency of the system (see [8] for more details) by means of a piezoelectric crystal. As the sample is exposed to a vapour of pressure P, the resonance frequency changes because of a variation in the moment of inertia. The frequency decrease of the oscillator, $-\Delta\nu$, is caused by the mass of the adsorbed film and by the hydrodynamic contribution due to the mass of the viscously displaced vapour, whose effect can be easily accounted for by means of adsorption measurements at room temperature.

With this technique we have studied the growth of liquid Ar and liquid Kr films because these systems are very pure, characterized by simple van der Waals interactions and easy to thermocontrol by using a conventional liquid nitrogen cryostat, all conditions that guarantee a more stringent test of the theoretical predictions. The adsorption of these cryogenic fluids on four different samples patterned in various ways has been measured; the samples were: a very regular array of linear wedges sculpted on a thin Si wafer, two metal discs machined on the lathe with sharp cutting tools and a stainless steel (ss) disc patterned by laser ablation.

Their characteristic surface profiles are summarized in figure 1. These have been taken with an atomic force microscope except the scans for on the ss disc which have been measured with a profilometer. As expected, the silicon substrate displays the most regular structure. This is supported by micrographs taken at different enlargements with the electron microscope showing that the channels are parallel practically over the entire extent of the sample. The resulting pattern is a regular array of parallel linear wedges with an opening angle of 75°. The Al and ss discs, although produced with very diverse techniques, show qualitatively similar structure characterized by an almost periodic array of triangular channels. Their main difference is mostly quantitative: the Al grooves have a typical depth of $\sim$0.4 μm and a width of $\sim$30 μm, while the channels on the ss sample are much deeper ($\sim$20 μm) and wider ($\sim$60 μm).

Finally, the brass disc machined on the lathe has a very irregular structure, in contrast to the previous ones. We believe that the striking difference from the Al surface, which has been machined in the same way, is probably related to the different metallurgical properties of the two materials.

3. Experimental results

The film growth on these patterned samples was studied by measuring adsorption isotherms where the film mass is determined as a function of the bulk vapour pressure from $P = 0$ to P_{sat}. Figure 2 shows the logarithm of the vapour-corrected frequency shifts close to saturation as a function of $\log \ln(P_{\text{sat}}/P)$ for liquid Ar films adsorbed at 85 K on the patterned
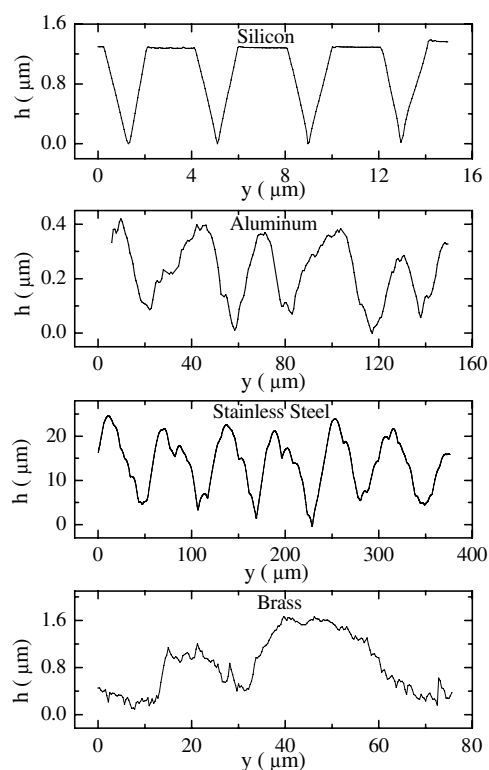
Figure 1. Surface profiles of the four samples used in this study. Note the different horizontal and vertical scales.

Si and ss samples. For comparison, in the same figure there appear the points of an Ar isotherm taken for a thin Si crystal, whose parallel faces are optically polished. The ratio $-\Delta \nu / \nu_0$, where ν_0 is the resonance frequency in vacuum, is proportional to the adsorbed mass, while the horizontal scale has been chosen because for the chemical potential difference from saturation we have used the ideal gas formula, that is $-\delta \mu = k_B T \ln(P_{sat}/P)$). We have also analysed these data taking into account the virial correction to $-\delta \mu$ without finding any appreciable difference in the calculated exponents. For a better comparison, we have employed different horizontal and vertical scales for the two data sets. The horizontal error bars are related to the finite resolution of ± 0.05 Torr in the measurement of the vapour pressure. The solid lines represent the results of linear fits to these extremities. The slopes of the lines corresponding to the flat silicon extend between $x = -0.31$ and -0.35 as expected.

In contrast, for the patterned Si, the adsorption isotherm clearly shows two distinct regimes: an initial growth characterized by an exponent $x = -0.35 \pm 0.01$ followed by a steeper increase near bulk liquid–vapour coexistence when the channels start to be filled with an exponent $x = -1.96 \pm 0.10$. In other words, there is a crossover from a planar to a geometrically dominated regime similar to that found numerically by Rascón and Parry [6] in their mean-field analysis of wedges of different shapes. The exponent measured near saturation is in good agreement with the predicted value of -2 [5, 6]. This behaviour is also quite different from the one that we have measured with the flat Si attached to the same torsional oscillator, indicating that the former is not an artefact of our technique.
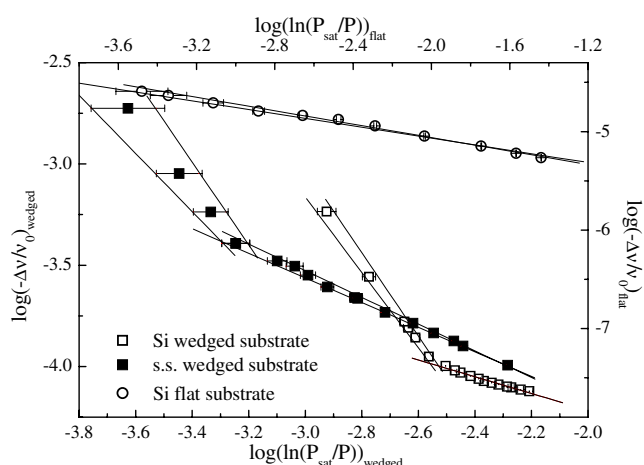
Figure 2. Determination of the growth exponents of the liquid film of Ar adsorbed on the patterned substrates and on a flat one. The left scale refers to the patterned samples, the right one to the flat substrate.

In the same graph, we have also plotted the final portion of an Ar adsorption isotherm measured at the same temperature but with the ss disc. Its behaviour closely resembles that observed for on the patterned Si. Again, there is an initial growth with an exponent $x = -0.6 \pm 0.05$ followed by a steeper increase very near saturation with an exponent $x = -1.8 \pm 0.25$. The discrepancy between the first exponent and the value of $-1/3$ expected for a flat surface is probably caused by the microscopic roughness (rms value $\sim$100 Å) of the ss sample produced by the laser ablation process. We have found similar variations of x with the substrate roughness in previous wetting studies on solid surfaces [9].

The exponent observed near P_{sat} is instead in agreement with the value expected for a linear wedge. In this case, the larger error bars are caused by the close vicinity to saturation. For instance, the final point of the ss isotherm in figure 2 refers to a pressure only 0.10 Torr less than $P_{sat} = 572.45$ Torr. The fact that even for this different pattern we get a growth exponent very close to -2 agrees with the theoretical prediction that x does not depend on the opening angle of a linear wedge.

Finally, another interesting feature of the data on the structured samples regards the location of the crossover from a flat-like to a wedge-like behaviour. As expected, the isotherms in figure 2 indicate that this crossover moves closer to P_{sat} as the characteristic wedge size increases. We have estimated the crossover position, P_{cros}, by equating the contribution expected for a flat substrate to the excess mass condensed in the wedge (see [10] for more details). The results are $\delta P \equiv P_{sat} - P_{cros} = 0.05$ Torr for the ss sample and $\delta P = 1.0$ Torr for the patterned Si. These theoretical values are to be compared with the experimental crossover positions deduced from the graph, which are, respectively, $\delta P = 0.32$ and 1.5 Torr. As expected, the agreement with our crossover criterion is much better for the Si pattern, whose geometry is very well defined.

In figure 3 we plot the final points taken on the Al and brass discs machined on the lathe. Again, for comparison, we also show the results taken with an optically polished quartz disc. The reason that the data points for the Al surface are fewer and further away from liquid–vapour coexistence is simply the use of a different sample cell, which caused very long equilibration times close to P_{sat}. The horizontal error bars are related to the finite resolution in
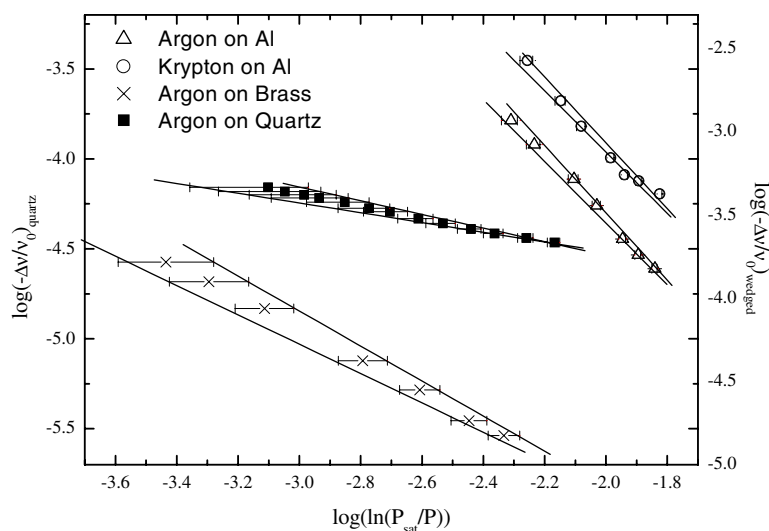
Figure 3. Determination of the growth exponents of the liquid films of Ar and Kr adsorbed on the geometrically structured aluminium and brass substrates and on the flat quartz disc. The left scale refers to the quartz disc, the right one to the patterned samples.

the measurement of the vapour pressure. We have used a capacitance pressure gauge attached to a room temperature gas system and got $P_{sat} = 591.0 \pm 0.2$ and 641.4 ± 0.2 Torr for Ar and Kr, respectively.

The solid lines represent the results of the linear fits to these extremities. The quartz data yield an exponent x between -0.27 and -0.37, somewhat compatible with the value of $-1/4$ expected for a retarded thick film adsorbed on a flat substrate [7]. Instead, the slopes of the linear fits on the Al surface are $x = -1.92 \pm 0.07$ for Ar and $x = -1.90 \pm 0.06$ for Kr. Again, these results are in good agreement with the value of -2 expected for a linear wedge [5, 6]. However, in contrast to the Si and ss samples, there is no evidence of a clear crossover from planar to geometry-dependent growth. This may well be caused by the wide distribution in the height and in the opening angle of the linear wedges present in the Al pattern which smears out the crossover position. Another possible reason may be related to the very wide and shallow wedges of the Al substrate that determine a location extremely close to the saturation value, beyond our pressure resolution.

Finally, for the brass disc we observe a growth exponent $x = -0.95 \pm 0.1$. This value is probably not the result of a geometry-dominated critical behaviour but rather the average response of different areas of the substrate that are characterized by quite distinct growth behaviours. However, it is interesting to note how the adsorption on these machined discs is markedly different from that observed on rough and self-affine surfaces produced by evaporation or sputtering, which exhibit growth exponents usually between $-1/3$ and -0.15 [11].

4. Conclusions

We have presented a brief review of recent experiments on various surfaces patterned with different techniques. On regular arrays of linear wedges, we have observed a crossover from a planar-like to geometry-dependent growth behaviour. If instead the geometric pattern shows

a wide distribution of V-shaped wedges with different heights and opening angles, there is no longer a clear crossover between those two regimes, although close to saturation a geometry-dependent exponent equal to -2 is observed. Finally, for a surface sculpted with an irregular array of microscopic channels with different shapes, we find an exponent $x = -0.96$ that is not related to any critical behaviour but is still well below the exponents observed for on rough and self-affine surfaces, which display growth exponents usually between $-1/3$ and -0.15. Since some of these patterns have been obtained by machining thin metal discs with a lathe, it is apparent that to assume a film growth dependence characterized by the flat-like exponent $-1/3$ is certainly wrong for films on surfaces prepared in this way.

Acknowledgments

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