Contact Angles and Hysteresis on Surfaces with Chemically Heterogeneous Islands

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Wetting behavior was studied on surfaces with a single, circular heterogeneous island. Lyophobic islands were created on lyophilic Si wafers using polystyrene. Alternately, lyophobic perfluoroalkoxy fluoropolymer film was etched to make lyophilic domains. Contact angles and hysteresis were measured with water and hexadecane. Small sessile drops were deposited on the center of an island and liquid was sequentially added, eventually forcing the contact line to advance beyond the island perimeter onto the surrounding area. Even though the underlying contact area contained a mixture of lyophilic and lyophobic domains, the contact angles, both advancing and receding, were equal to the angles exhibited by the homogeneous periphery. Or in other words, if the heterogeneity was completely contained with the contact area and did not intersect the contact line, then no area averaging of the contact angles occurred. These findings suggest that interactions at the contact line, not the contact area, control wetting of heterogeneous surfaces.

Introduction

Wetting is important in many industrial processes, such as cleaning, drying, painting, coatings, adhesion, heat transfer, and pesticide application. The most common method of evaluating wetting is contact angle measurements. Although these measurements are simple to perform, a variety of factors can complicate their interpretation. For example, surfaces usually show two stable values. Consider the case of a sessile drop, as depicted in Figure 1. If additional liquid is added, the contact line advances. Each time motion ceases, the drop exhibits an advancing contact angle, θ_a. Alternatively, if liquid is removed from the drop, the contact line remains pinned until the contact angle decreases to a receding value, θ_r, and then the contact line retreats. This difference between θ_a and θ_r is referred to as contact angle hysteresis, $\Delta\theta$,[1]

$$\Delta\theta = \theta_a - \theta_r \qquad (1)$$

Hysteresis can arise from molecular interactions between the liquid and solid or from surface anomalies, such as roughness or heterogeneities.[1] Numerous models have been proposed to describe the wetting of heterogeneous surfaces. The first model, put forth by Cassie,[2,3] predicts that the apparent advancing and receding angles, θ_i, of a heterogeneous surface vary as

$$\cos\theta_i = \alpha_1 \cos\theta_{i,1} + \alpha_2 \cos\theta_{i,2} \qquad (2)$$

where $\theta_{i,j}$ is the inherent advancing or receding contact angle of material j, $i = $ a for advancing angles, $i = $ r for receding angles, $j = 1$ for material 1, and $j = 2$ for material 2; α_j is the fractional area of material j, and

$$\alpha_1 + \alpha_2 = 1 \qquad (3)$$

More sophisticated models have been proposed.[4–13] They typically employ geometric features or patterns.

Figure 1. A small, sessile drop on a solid surface. (a) As liquid is added, the contact line advances. Each time motion ceases, the drop exhibits an advancing contact angle (θ_a). (b) Alternatively, if liquid is removed from the drop, the contact angle decreases to a receding value (θ_r), and then the contact line retreats.

Many of these models are reminiscent of those for rough surfaces, but here, surface energy rather than surface texture is varied. These models, including the original of Cassie, often fail to correctly predict contact angles,[14–20] perhaps because they assume that the interfacial contact area between the liquid and solid controls apparent contact angles. It has been suggested that contact angles are determined by interactions that occur at the contact line.[20–26]

Few systematic experimental studies have been performed on well-characterized heterogeneous sur-
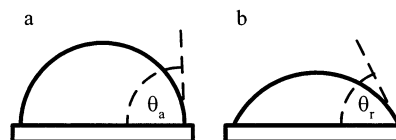
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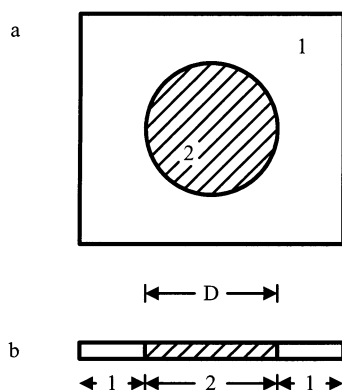(21) Pease, D. C. *J. Phys. Chem.* **1945,** *49,* 107.
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Figure 2. A small circular patch of material 2 on a substrate consisting of material 1: (a) plan view; (b) side view. D is the diameter of material 2.

faces.[15-17,19,20,23] Moreover, their interpretation often is complicated by domain sizes that were circuitous, poorly defined, or too small to be easily observed.[20] Therefore, in this study, circular heterogeneous islands were created on smooth surfaces as shown in Figure 2 and their influence on contact angles and hysteresis was examined in an attempt to answer the following questions. Which interactions determine contact angles on heterogeneous surfaces: those acting within the contact area or those present at the contact line? And, how do heterogeneities affect hysteresis?

Materials and Methods

Contact angle measurements were made with 18 MΩ deionized (DI) water and *n*-hexadecane (Alfa-Æsar, 99%). Perfluoroalkoxy (PFA) film (DuPont Teflon PFA 3000LP)[27] and 200 mm P ⟨100⟩ silicon wafers (Wafer-Net, part no. 402) were used as substrates. Heterogeneous islands with diameters of several millimeters were created with 1% polystyrene (PS, Novacor Chemicals) in toluene or a sodium naphthalene complex (Tetra-etch, TEC-1, Vishay Measurements Group). Prior to contact angle measurements or treatment, PFA film was rinsed with acetone (Fisher, GC Resolv grade) and DI water. To create lyophilic islands on the PFA film, the sodium naphthalene complex was applied with a polyethylene (PE) pipet, allowed to stand for 60 s, and rinsed with DI water, acetone, and finally DI water again. Si strips (30 mm wide) were taken from wafers and cleaned with oxygen plasma for 60 min. To create lyophobic islands on the Si surface, the PS solution was applied with a PE pipet. Diameter, D, of the heterogeneous islands was measured with a micrometer.

Roughness of the substrates was examined by an atomic force microscope (AFM, Nanscope III, Digital Instruments, Santa Barbara, CA). The AFM was operated in air with a standard silicon tip using the noncontact mode. Resident software within the AFM was used to calculate number-average roughness, R_a, root-mean-square roughness, R_q, and apparent area ratios, σ, from duplicate 100 μm × 100 μm images. The maximum slope, ϕ, of the asperities also was determined for each surface by placing a line across individual images and measuring ϕ along three of the steepest-rising asperities. This was repeated three times for each scan, and an average ϕ value from duplicate images was determined for each surface (total ϕ measurements per surface = 18).

Liquid surface tensions, γ_l, and contact angles were measured at room temperature in air with a relative humidity of approximately 30% using a Krüss DSA10 drop shape analyzer. Liquid surface tensions were determined from pendant drops having volumes of 5−10 μL and were found to be $\gamma_l = 73$ mN/m for water and $\gamma_l = 28$ mN/m for hexadecane, in agreement with literature values.[28] Advancing contact angles were measured

(27) PFA is perfluoroalkoxy copolymer comprised of >95% tetrafluoroethylene (TFE) monomer.

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Table 1. Roughness Parameters from Atomic Force Microscopy[a]

surface	j	R_a (nm)	R_q (nm)	$\sigma - 1$ (%)	ϕ (deg)
Si wafer	1	1.4 ± 0.1	3.3 ± 1.6	0.01 ± 0.01	<1
PS	2	12 ± 8	16 ± 11	0.01 ± 0.01	2 ± 2
PFA	1	32 ± 7	42 ± 10	0.8 ± 0.1	13 ± 5
etched PFA	2	28 ± 2	36 ± 2	0.6 ± 0.1	12 ± 4

[a] R_a is number average roughness, R_q is root-mean-square roughness, R_{max} is maximum roughness, σ is the apparent area ratio, and ϕ is maximum asperity slope.

Table 2. Contact Angles and Hysteresis on Homogeneous Portions of the Various Substrates[a]

		contact liquids					
		water			hexadecane		
surface	j	$\theta_{a,j}$ (deg)	$\theta_{r,j}$ (deg)	$\Delta\theta_j$ (deg)	$\theta_{a,j}$ (deg)	$\theta_{r,j}$ (deg)	$\Delta\theta_j$ (deg)
Si wafer	1	7 ± 3	<2	<7	<2	<2	<2
PS	2	95 ± 2	87 ± 2	8 ± 4	<2	<2	<2
PFA	1	107 ± 2	84 ± 2	23 ± 4	53 ± 2	43 ± 3	10 ± 5
etched PFA	2	67 ± 3	12 ± 3	55 ± 6	<2	<2	<2

[a] $\theta_{a,j}$ is the advancing contact angle, $\theta_{r,j}$ is the receding angle, and $\Delta\theta_j$ is contact angle hysteresis (=$\theta_{a,j} - \theta_{r,j}$) of homogeneous material *j*.

after sequential deposition with a small syringe and needle. A small drop was deposited on the surface, and then additional liquid was added to advance the contact line. In most cases, liquid was added with the needle positioned just above the apex of the sessile drop. For the PS islands on the Si surface, the needle was inserted into the drop during injection. This prevented drops from jumping off the lyophobic PS islands as the contact line advanced onto the lyophilic Si surface. For receding contact angles, liquid was withdrawn until the contact line retracted. Drop volumes for the contact angles ranged between 1 and 100 μL. Measurements were made on both sides of five or more drops and averaged.

Results and Discussion

Surface Roughness. Roughness values, area ratios, and maximum asperity slopes for the substrates are listed in Table 1. All surfaces were smooth and gently sloping. R_a values ranged from 1 nm for the Si wafer to 32 nm for the PFA film. The topographical area of the surfaces differed from the apparent area by less than 1%. Ignoring the occasional defect or particle, maximum asperity slopes, ϕ, of Si and PS on Si were effectively zero; ϕ values for PFA were larger, $\phi = 13°$. Etching did not affect the morphology of the PFA film.

Contact Angles on Homogeneous Regions of the Various Substrates. Table 2 shows advancing and receding contact angles measured on homogeneous regions of the various substrates. Contact angles were independent of drop volume and generally agreed with previously reported values.[23,29-34] The surface of the plasma-cleaned Si was effectively wet by both liquids and gave near-zero contact angles. Cast PS films had advancing water contact angles that were >90° with low hysteresis. The PFA film, the most lyophobic of the substrates due to its low surface energy, produced the highest contact angles. The advancing contact angles were 107° for water and 53° for

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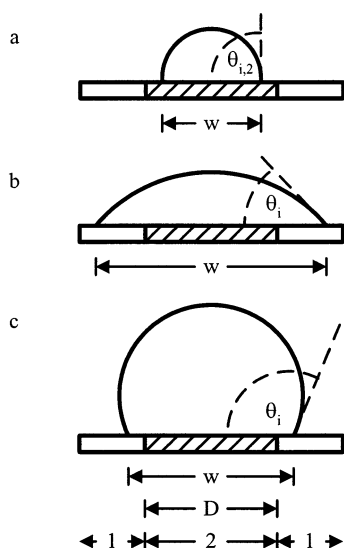
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Figure 3. Side views of a liquid drop on a heterogeneous surface. (a) A small liquid drop resides on a circular island of material 2; $w < D$ and $\alpha_2 = 1$. The drop exhibits an inherent contact angle of $\theta_{i,2}$. If additional liquid is added such that $w > D$, then the drop rests over a mixed surface, $\alpha_2 < 1$. (b) If material 1 is more lyophilic than material 2, the apparent contact angle decreases, $\theta_i < \theta_{i,2}$. (c) Otherwise, if material 1 is more lyophobic than material 2, the apparent contact angle increases, $\theta_i > \theta_{i,2}$.

hexadecane. Etching the PFA film caused a considerable reduction in contact angle of both liquids.

Contact Angles of Heterogeneous Domains. If a water drop was deposited on a PS island such that the width of the drop, w, was less than the diameter of the island, D, then it exhibited an advancing contact angle of $\theta_{a,2} = 95°$, as expected for water on a homogeneous PS surface, Table 2. (In Figures 2 and 3, Si is material 1 and PS is material 2.) As additional water was slowly added to the drop, $\theta_{a,2}$ remained constant as long as $w < D$ ($\alpha_2 = 1$). As soon as the contact line advanced onto the Si, the drop lurched forward, as shown in Figure 3 ($w > D$ and $\alpha_2 < 1$). The contact angle decreased abruptly, accompanied by a substantial increase in the drop width, w. For example, as water advanced across a 2.7 mm PS island and contacted the more lyophilic Si periphery, drop width increased to $w = 7.2$ mm. Here, the fractional PS contact area was $\alpha_2 = 0.14.$[35]

According to the Cassie equation, one would have expected an apparent advancing contact angle of $\theta_a = 33°$ on a heterogeneous PS/Si surface with $\alpha_2 = 0.14$, but this value was incorrect. The measured value, $\theta_a = 6°$, was the same as for the homogeneous Si surface, that is, $\theta_a = \theta_{a,1}$. Moreover, the θ_a value did not change with the further addition of water to the drop, even though α_2 decreased. Receding angles behaved in a similar fashion. If a small volume of water was withdrawn such that w was $>D$, angles decreased to the receding value of the Si, $\theta_{r,1}$.

One could argue that because the fractional area of PS was small and the interactions between the PS and water were relatively weak, the contribution of PS to θ_i may have been completely overshadowed by the interfacial interplay of the water and lyophilic Si. However, observations from the heterogeneous PFA surfaces reinforced the conclusions drawn from PS islands on Si. In the case of PFA, the relative phobicity was reversed: the etched island (material 2) was more lyophilic than the surrounding

(35) The fractional area of the island, α_2, was calculated as $\alpha_2 = (D/w)^2$.

Table 3. Apparent Contact Angles and Hysteresis for Water and Hexadecane on Heterogeneous Surfaces[a]

surface: material 2 on material 1	contact liquids					
	water			hexadecane		
	θ_a (deg)	θ_r (deg)	$\Delta\theta$ (deg)	θ_a (deg)	θ_r (deg)	$\Delta\theta$ (deg)
PS on Si	6 ± 2	<2	<6	<2	<2	<2
etched PFA on PFA	109 ± 3	84 ± 2	26 ± 5	<2	<2	<2

[a] θ_a is the apparent advancing contact angle, θ_r is the apparent receding angle, and $\Delta\theta$ is apparent contact angle hysteresis ($=\theta_a - \theta_r$) of heterogeneous surfaces where the contact width of the liquid drop, w, was greater than the diameter of the heterogeneous patch, D.

Figure 4. The side view of a small sessile drop of liquid with a sessile bubble trapped inside.

untreated area (material 1), Figure 3. As a result, it was much easier to advance the contact line from the lyophilic island to the lyophobic PFA fringe while still maintaining a relatively large α_2 value. For example, water on etched PFA gave $\theta_{a,2} = 67°$. Advancing the contact line just onto the untreated PFA periphery ($\alpha_2 = 0.73$) caused the advancing contact angle to increase to $\theta_a = 109°$ and $\theta_a = \theta_{a,1}$, even though most of the interfacial contact area was relatively lyophilic. Similarly, $\theta_r = \theta_{r,1}$.

Contact angles measured on the various heterogeneous surfaces are summarized in Table 3. Hexadecane also showed the same general behavior as water. If $w > D$, then the entire length of the contact line resided on material 1 and $\theta_i = \theta_{i,1}$. It has been suggested that contact liquids may interact preferentially with the heterogeneities,[5,6,21] where advancing angles may show greater affinity for lyophobic domains while receding angles may be biased by lyophilic domains. However, hysteresis on the surfaces with the heterogeneous islands was the same as on the homogeneous ones. The liquids did not sense the heterogeneous patch underlying their interfacial contact zone. Thus, *the apparent contact angles were determined by interactions at the contact line.*[36]

These findings are analogous to those presented by Bartell and Shepard for chemically homogeneous paraffin surfaces with rough islands.[22] They placed small drops of glycerol on a smooth paraffin surface and measured an advancing contact angle of 98°. A small area of the same paraffin surface was crosshatched to produce a rough surface. The glycerol contact angle on the roughened island was 148°. If enough glycerol was added to advance the contact line onto the smooth periphery, the contact angle was 98° again, even though most of the liquid/solid interface covered the rough portion of the surface.

As an addendum to this work, chemically heterogeneous interfaces were created by an alternative method. Air was injected inside water drops to create sessile bubbles, as depicted in Figure 4. The contact area of the solid was heterogeneous, consisting of interfaces that were both liquid/solid and gas/liquid. Here again, if the contact angle were determined by contact area, the air/liquid interface would have been expected to cause an increase in the apparent contact angles, but it did not. The advancing

(36) If the heterogeneous features have molecular dimensions, then the width of the contact line will be on par with the size of the heterogeneities. Here, partial contributions to the apparent contact angles should be computed on an area or molar basis.

contact angles of water drops with a trapped bubble on PS were the same as for homogeneous water drops, $\theta_a = 96°$.

On the basis of the examples presented here, it seems that the interactions that determine contact angles occur at the contact line, not the interfacial contact area. In this light, prevailing theories regarding the wetting of chemically heterogeneous surfaces should be reexamined.

Conclusions

Contact angles were measured on surfaces with a single, chemically heterogeneous island using sessile drops. If the width of the drop was greater than the diameter of the island, then the contact angles were equal to those exhibited by the homogeneous periphery. These findings suggest that contact angles are determined by interactions at the contact line, not by those within the interfacial contact area. Also, heterogeneous islands buried under liquid drops did not influence hysteresis.

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