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Wetting characteristics of liquid drops at heterogeneous surfaces

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Abstract

Well-defined heterogeneous surfaces consisting of hydrophobic and hydrophilic regions were prepared on gold (a 2000 Å gold film supported on an Si/SiO₂/Ti substrate) by patterning self-assembled monolayers (SAMs), using an elastomer stamp. One surface was composed of alternating and parallel hydrophobic (2.5 μ m) and hydrophilic (3 μ m) strips, and the second surface consisted of alternating hydrophilic squares (3 μ m × 3 μ m) separated by hydrophobic strips (2.5 μ m). The wetting characteristics of these well-defined heterogeneous solid surfaces were examined by contact angle measurements. The contact angles for water drops, which varied in pH from 5.8 to 10.0, were measured with the strips both tangential to and normal to the three-phase contact line. The experimental contact angles are in good agreement with theory as calculated from the Cassie equation when the three-phase contact line is non-contorted (i.e. the three-phase contact line is situated along the hydrophobic strip). On the other hand, when the strips are normal to the drop edge, corrugation of the three-phase contact line affects the contact angle significantly. Contact angles, measured with the strips normal to the drop edge, were lower by 7–16 than those calculated from the Cassie equation. Analysis of these measurements, together with contact angle drop size measurements for fully hydrophobic and hydrophilic surfaces, demonstrate the validity of a modified Cassie equation that includes a term describing the line tension contribution.

Keywords: Contact angle; Gold; Line tension; Thiol; Wettability

1. Introduction

Measurements of contact angles are among the most rapid and convenient methods of characterizing surfaces, and are among the most popular methods used in scientific and industrial laboratories for this purpose. These solid surfaces, whether polymers, minerals or metals, are not always homogeneous and clean. Some are composed of two or more components that differ in surface/interfacial properties, and thus exhibit heterogeneous characteristics. Such surface heterogeneity may also result from material anisotropy, or non-uniform dissociation of functional groups located at the surface. Many intrinsically homogeneous surfaces are actually heterogeneous because of the adsorption of contaminants and/or the deposition of dust particles.

Composite smooth solid surfaces with varying degrees of heterogeneity were analyzed by Cassie and Baxter [1,2] and Cassie [3]. Cassie derived an equation describing contact-angle changes for two-component surfaces as follows [3]:

$$\cos\theta^{\rm C} = f_1 \cos\theta_1 + f_2 \cos\theta_2 \tag{1}$$

where f_1 is the fractional area of the surface with

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contact angle θ_1 , and f_2 is the fractional area of the surface with contact angle θ_2 (the superscript C indicates Cassie contact angle). Eq. (1), known as the Cassie equation, reduces to the Cassie– Baxter equation (Eq. (2)) for a porous surface, such as a mesh or screen surface [1,2]:

$$\cos\theta^{\rm C} = f_1 \cos\theta_1 - f_2 \tag{2}$$

In this case, f_2 is the fraction of air spaces (open area).

Cassie and Baxter [1] experimentally verified Eq. (2) for water drops on copper screens coated with paraffin. Agreement of theory with experiment was less satisfactory when the water drops were placed on wool yarn [2]. Crawford et al. [4] found that the advancing and receding contact angles for water drops on methylated quartz plates varied with area fraction of trimethylsilyl groups in a manner similar to that predicted by the Cassie equation (Eq. (1)). Bain et al. [5] studied selfassembled monolayers (SAMs) of alkanethiols $(HS(CH_2)_nX)$ with different functional groups (X: -OH, -Br, CN, -COOH) adsorbed onto gold. They found that the Cassie equation holds strictly only for systems where intermolecular forces between surface functionality and probe liquid are dispersive. When water was used as a probe liquid. on surfaces where specific hydrogen bonding effects were strong, the contact angle varied non-linearly with surface composition. This non-linearity suggests a limitation of the Cassie equation for some surfaces with molecular-scale heterogeneities. Thermodynamic analysis of the Cassie equation for three-phase systems shows that this equation should be applicable for surfaces composed of macroscopically heterogeneous regions [6] although the situation is less clear for molecularscale heterogeneities. In this regard, Israelachvilli and Gee proposed another theoretical equation for the description of surfaces with heterogeneities of molecular or atomic size [7]. Further, it was recently postulated that the Cassie equation requires modification to account for the contribution of the free energy associated with the threephase contact line [8]. This modification (presented later on) seems to be important, especially for heterogeneities of small dimensions (several micrometers and less) [8].

The Cassie equation can be derived from thermodynamic considerations of the free energy change at the three interfaces, solid/vapor, solid/ liquid and liquid/vapor (or liquid/liquid). Gibbs postulated [9] that an additional free energy component for such a three-phase system should be included to provide a more complete description of the system. This additional free energy component, the line tension, results from an excess free energy for molecules located at or close to the three-phase contact line. The excess energy associated with the triple junction was not considered in the derivation of the Cassie equation. Young [10] also did not consider this excess energy in his examination of the three-phase system. Boruvka and Neumann [11] took into account the line tension and re-examined the equilibrium contact angle for liquid drops at homogeneous, rigid, isotropic and smooth solid surfaces; they modified Young's equation as follows [11]:

$$\gamma_{\rm SV} - \gamma_{\rm SL} = \gamma_{\rm LV} \cos \theta + \gamma_{\rm SLV} \kappa_{\rm gs} \tag{3}$$

where γ_{SV} , γ_{SL} and γ_{LV} are the interfacial tensions for solid vapor, solid liquid and liquid/vapor interfaces respectively; θ is the contact angle; γ_{SLV} is the line tension (note that the tension term is used in the literature to describe the force γ_{SLV}) defined thermodynamically as the free energy change for the three-phase system (δF) caused by the change in the three-phase contact line length δL at constant temperature T, volume V and interfacial area A. Thus $\gamma_{SLV} = (\delta F \ \delta L)_{T,V,A}$. It should be noted that $\kappa_{gs} = \cos \alpha \rho$ is the geodesic curvature of the three-phase contact line which is equal to the reciprocal of the drop base radius ($\kappa_{gs} = 1/r$) for a spherical drop sitting on a flat, horizontal and homogeneous surface, α is the angle between the solid surface and the plane containing the wetting perimeter, and ρ is the radius of curvature of the three-phase contact line.

The force balance, in terms of the interfacial free energies, at a solid surface involving a three-phase system, in which the equilibrium contact angle is established, is shown in Fig. 1.

Although some controversy exists about the magnitude of the line tension, there is a general consensus that it is of small magnitude











 $X_{1} = X_{1} = Y_{1} \cos \Theta = \frac{X_{SD}}{\Gamma}$

Fig. 1. Thermodynamic equilibrium for a spherical liquid drop on a rigid and homogeneous solid surface.

 $(10^{-9}-10^{-12} \text{ Jm}^{-1})$ [12-17]. Poor accuracy and precision of experimental techniques and difficulties in preparation of atomically smooth and molecularly homogeneous samples make the determination of the line tension difficult. Also, the theoretical bases for the calculation of line tension are very uncertain owing to our limited knowledge on the contribution of short-range forces to the line free energy (theoretical models for the calculation of the excess energy at the triple junction have been recently proposed; see for example Refs. [18–20]).

Small values of the line tension $(10^{-9} \cdot 10^{-12} \text{ Jm}^{-1})$ indicate that the line-tension term contributes significantly to the modified Young's equation (Eq. (3)) only for small drops or bubbles (radii of the drop (bubble) base smaller than several micrometers). When the liquid is in contact with a heterogeneous surface composed of chemically distinct patches, the three-phase contact line is corrugated, as illustrated in Fig. 2 [8,21–25]. Local deformations of the three-phase contact line may have diameters smaller than several microns. In such systems the excess energy at the triple junction may contribute significantly to the equilibrium contact angle, even for large drops or bubbles. Consideration of the corrugation of the threephase contact line led to another modification of the Cassie equation [8,26,27]:

$$\cos \theta^{\rm MC} = \sum f_i \cos \theta_i - \frac{1}{\gamma_{\rm LV}} \sum f_i \gamma_{\rm SLVi} \kappa_{\rm gsi}$$
(4)

For a smooth and horizontal surface composed of two components uniformly distributed with circular curvatures of the three-phase contact line (Fig. 2), Eq. (4) is simplified as follows:

$$\cos \theta^{\text{MC}} = f_1 \cos \theta_1 + f_2 \cos \theta_2 - \left(\frac{1}{\gamma_{\text{LV}}}\right)$$
(5)
$$\times \left(\frac{f_1 \gamma_{\text{SLV1}}}{r_1} - \frac{f_2 \gamma_{\text{SLV2}}}{r_2}\right)$$

On the basis of a theoretical analysis of Eq. (5) it is expected that a corrugation of the three-phase contact line with radii of local deformation on the order of hundreds of micrometers should not contribute significantly to the equilibrium contact angle, and for such systems the contact angle calculated from the Cassie equation (Eq. (1)) is a good approximation to the observed contact angle [8,27]. The line-tension term should be of importance, however, for systems where the radii of deformation of the three-phase contact line are less than several micrometers [8.27]. An upper limit for the size of heterogeneous patches that affects contact angles through the line-tension term was discussed in our previous contributions [8,27]. The lower size limit for the heterogeneity dimension is more difficult to predict. Neumann [28] estimated that there is no contact angle difference between the contorted and the smooth three-phase contact line for surfaces with heterogeneous strip dimensions of approximately 0.1 µm or less. In this model, Neumann did not consider the contribution of the excess energy associated with the triple junction. In another contribution, Boruvka and Neumann [21] predicted that a corrugation of the three-phase contact line can be expected for heterogeneous patches as small as 10 Å. Again, they did not consider a contribution of the line tension to the free energy of the three-phase system, and they suggested that this patch size limit would be larger if the line tension was included.

Parallel Strips







Fig. 2. Nature of the three-phase contact line for heterogeneous surfaces.

From theoretical considerations, it appears that the lower limit for the heterogeneous patch size that affects a corrugation of the three-phase contact line may be somewhere between 10 and 1000 Å. No experimental effort has, however, examined the effect of heterogeneity, both size and distribution, on the contact angle. Theoretical considerations may also be flawed when the radius of curvature approaches molecular size, since the macroscopic and microscopic thermodynamic properties of the system may be different. For example, the line tension may change as a result of the curvature of the three-phase contact line (note that the effect of curvature on surface tension has already been discussed [29,30]).

To determine the validity of the modified Cassie equations (Eqs. (4) and (5)), examination of solid surfaces with well-defined heterogeneity is required. Preparation of well-defined heterogeneous surfaces, especially with heterogeneities of several micrometers or less in size, has been technically difficult. Recent work has shown that adsorption of thiols from solution onto a gold surface leads to the preparation of SAMs that are model organic surfaces [31-35]. Patterning of the SAM on gold by contact printing using an elastomer stamp [35] is an especially convenient technique for the preparation of well-defined heterogeneous surfaces. Mosaic patterns with micron dimensions can be prepared using this technique and the organic functionality exposed at the surface can be controlled easily.

Model organic surfaces with well-defined heterogeneity were prepared by patterning SAMs on a gold surface to examine the validity of the Cassie and modified Cassie equations, as part of a cooperative research program between University of Utah and Harvard University. Two heterogeneous surfaces were prepared. Alternating and parallel hydrophobic and hydrophilic strips, and hydrophilic squares separated by hydrophobic strips. were examined by contact angle measurements. Experimental contact angle data for water drops placed on these surfaces support the contention that a corrugation of the three-phase contact line is of particular significance in contact angle measurements at heterogeneous surfaces. The experimental results also provide evidence for the validity of the Cassie equation (systems with a noncontorted three-phase contact line) and for the validity of the modified Cassie equation (systems with a corrugated three-phase contact line).

2. Experimental procedure

2.1. Preparation of surfaces

Stamps were fabricated from polydimethylsiloxane (PDMS); Fig. 3 describes the process. A template consisting of the desired features was made using conventional photolithography. The template was placed in a plastic petri dish. A 10:1(v:v) mixture of PDMS–Sylgard Silicone



Fig. 3. Schematic for the fabrication of model heterogeneous surfaces.

Elastomer 184 and Sylgard Curing Agent 184 (Dow Corning Corp., Midland, MI) was poured into the petri dish. It was not necessary to put the mixture of PDMS-elastomer and curing agent under vacuum to remove dissolved oxygen. The PDMS cured at room temperature in the laboratory ambient for 30-60 min. This cure was followed by additional curing at 65° C for approximately 1 h or until the polymer was rigid. After cooling to room temperature, the PDMS stamp was carefully peeled from the template.

A piece of lint-free paper was moistened with a solution of hexadecanethiol $(HS(CH_2)_{16}CH_3, 1-10 \text{ mM} \text{ in ethanol})$. Inking was accomplished by simply touching the active surface of the stamp to the moistened paper. Alternatively, the ink was

poured directly onto the stamp, and the stamp was allowed to dry. The stamp was then placed on the substrate with the inked side in contact with the bare gold surface (gold film was prepared by electron beam evaporation of high purity gold onto a silicon wafer that had been precoated with titanium to improve adhesion). After removal of the stamp, the gold surface was washed for 1-5 s with a 1 mM solution of diundecane disulfide carboxylic acid (S[(CH₂)₁₁COOH]₂) in ethanol. The surface was first washed in a stream of ethanol for a few seconds and then dried in a stream of nitrogen. Fig. 4 presents scanning electron micrographs of the model heterogeneous surfaces examined.

Slides with freshly deposited gold film were



Fig. 4. Scanning electron micrographs of model surfaces. Upper photograph: 3 μ m hydrophilic strips (Au-S[(CH₂)₁₁COOH]₂) and 2.5 μ m hydrophobic strips (Au–S(CH₂)₁₆CH₃). Lower photograph: 3 μ m × 3 μ m hydrophilic squares in hydrophobic field.

immersed for about 5 s into the 1 mM ethanol solution of hexadecanethiol or the 1 mM ethanol solution of diundecane disulfide carboxylic acid in order to prepare homogeneous surfaces of hydrophobic and hydrophilic nature respectively. After removal from the adsorbate solution, slides were washed with ethanol and then dried in a stream of nitrogen.

2.2. Contact angle measurements

The sessile-drop technique for contact angle measurements was used as described in the literature [36] using an NRL goniometer (Ramé-Hart, Inc., USA). The surfaces were washed with ethanol and distilled/deionized water before each experiment and placed in a controlled-atmosphere Ramé-Hart chamber. A water drop was introduced onto the solid surface through a microsyringe and the needle remained in contact with the drop. The three-phase contact line of the water drop was made to advance or retreat by adding or withdrawing a small volume of water and the advancing and receding contact angles, respectively, were measured after 30-45 s at both sides of the drop. The drop base diameter was controlled to be 4-5 mm for all systems examined. The contact angles were measured for 8-12 drops on both sides, for each system, and the average contact angle values are reported. All measurements were made in water-saturated air. Distilled and deionized water (pH 5.8 ± 0.1) and commercial buffers of pH 7.0 and 10.0 were used in all experiments. A stereoscopic microscope coupled with a camera (Carl Zeiss, Jena, Germany) was used to record the three-phase contact line for the water drop.

The dynamic captive-bubble technique was used for the examination of the bubble size effect on the contact angle (discussion of this technique is presented in Refs. [37,38]). The air bubbles of varying size were generated in water with a syringe under the solid surface. Released bubbles were captured at the solid surface as a result of bouyant transport and attachment. A Zeiss stereo microscope coupled with a camera was used to examine the shape of the bubbles at the solid surface. The contact angle was measured from photographs with an accuracy of $\pm 2^{\circ}$ for large bubbles and $\pm 3^{\circ}$ for small bubbles.

A ring technique was applied for surface tension measurements of water using a Digital-Tensiometer K10T (Kruss, GmbH, Germany) with an accuracy of 0.2 mN m⁻¹. The results obtained with the instrument were corrected in relation to the liquid density and the height of the lamella in maximum tension using factors of Harkins and Jordan as specified in the instrument manual.

All experiments were performed at a temperature of $22 \pm 1^{\circ}$ C.

3. Results and discussion

3.1. Advancing and receding contact angle data

The advancing and receding contact angles for water drops were measured for hydrophilic, hydrophobic and heterogeneous surfaces. The experimental data are presented in Table 1. The advancing contact angle values $(107-108^{\circ})$ measured for the hydrophobic surface were in close agreement with those $(110-112^{\circ})$ reported in a previous contribution [39]. The contact angle hysteresis (i.e. the difference between the advancing and receding contact angle) of 14-16° was close to the hysteresis of 10° reported in the literature

Table 1 Contact angle values (deg) for

Contact angle values (deg) for water drops (4-5 mm drop base diameter)

[39]. Poorer agreement between experimental and literature contact angle values was observed for the hydrophilic surface. For example, the advancing contact angle for the distilled water drop was found to be 61° whereas that reported in a previous contribution was about 50° [39]. Also, the contact angle hysteresis for the hydrophilic surface was found to be $20-25^{\circ}$ compared to $40-50^{\circ}$ reported by Troughton et al. [39].

The advancing contact angles measured for heterogeneous surfaces differed significantly, depending on the position of the water drop edge at which the contact angle was measured (see Table 1). For the heterogeneous surface composed of alternating and parallel strips, the advancing contact angles measured with the drop edge normal to the strips were found to be much lower $(8-16^{\circ})$ than those measured with the drop edge tangential to the strips (Fig. 5 illustrates the drop sides at which contact angles were measured). When the water drop was placed onto a heterogeneous surface composed of hydrophilic squares surrounded by hydrophobic strips, two distinct advancing contact angles were also observed. When the threephase contact line crossed the hydrophilic squares advancing contact angles were found to be 7-12 lower than those measured at the drop edge attached to the hydrophobic strip (Fig. 5 illustrates the edge positions of the water drop at which

pН	Hydrophilic		Hydrophobic	Heterogeneou	neous surfaces		
		surface Au–S[(CH ₂) ₁₁ COOH] ₂ θ_1	surface Au-S(CH ₂) ₁₆ CH ₃ θ_2	3 μm hydrophilic 2.5 μm hydrophobic parallel strips		$3 \ \mu m \times 3 \ \mu m$ hydrophilic squares in hydrophobic field	
				Measured tangentially to the strips. θ^{c}	Measured normally to the strips, θ^{MC}	Measured at the boundary of the pattern, θ^{c}	Measured across the pattern, θ^{MC}
5.8	Adv	61.1 ± 1.8	108.4 + 2.8	85.8 + 3.5	69.4 ± 3.4	93.0 ± 2.0	81.1 ± 1.7
	Rec	38.4 ± 3.7	92.6 ± 3.3		54.2 ± 4.4		
7.0	Adv	50.1 ± 1.0	107.8 ± 2.4	76.5 ± 3.0	68.3 ± 1.5	88.3 ± 2.3	81.2 ± 2.1
	Rec	30.6 ± 3.4	91.6 ± 2.7		50.9 ± 4.6	- 2011	_
10.0	Adv	31.7 ± 1.8	106.9 ± 3.1	70.5 ± 2.1	58.5 ± 3.7	83.8 ± 3.2	74.2 ± 2.0
	Rec	10.3 ± 2.6	92.7 ± 2.9	_	39.3 ± 5.1		

Adv, advancing contact angle; Rec, receding contact angle.

Parallel Hydrophilic/Hydrophobic Strips



Hydrophilic Squares in Hydrophobic Field



CASSIE EQUATION:

 $\cos\Theta^{c} = \mathbf{f}_{1}\cos\Theta_{1} + \mathbf{f}_{2}\cos\Theta_{2}$

MODIFIED CASSIE EQUATION:

$$\cos\Theta^{\rm MC} = f_1 \cos\Theta_2 + f_2 \cos\Theta_2 - \frac{1}{\gamma_{\rm IV}} \left(\frac{f_1 \gamma_{\rm SLV1}}{r_1} + \frac{f_2 \gamma_{\rm SLV2}}{r_2} \right)$$

Fig. 5. Contact angle measurements for a water drop on two well-defined heterogeneous surfaces. The contact angle θ^{MC} is observed for a corrugated three-phase contact line and θ^{C} for a non-corrugated three-phase contact line.

contact angles were measured). The data presented in Table 1 support the statement that corrugation of the three-phase contact line has a significant impact on contact angle.

Some of the receding contact angle measurements for model heterogeneous surfaces were also performed. At this time, the only acceptable experimental data for the receding contact angle are presented in Table 1 and they were obtained at the heterogeneous surface composed of parallel strips and measured with the drop edge normal to the strips. For a heterogeneous surface composed of squares it was difficult to specify the position of the retreating three-phase contact line with respect to the hydrophilic squares or hydrophobic strips. Mostly, there was non-uniform movement of the retreating drop edge across the strips and also the three-phase contact line was observed to jump from one surface site to another. In view of the above, the only reproducible receding contact angles for heterogeneous surfaces were obtained when measured with the drop edge normal to the strips. Measurements of the receding contact angles for model heterogeneous surfaces will receive more attention in our future experiments.

3.2. Line/pseudo-line tension data for "homogeneous" surfaces

The effect of bubble size on contact angle was examined for hydrophilic and hydrophobic surfaces in order to determine the line tension values (note that receding contact angle or intermediate contact angle, contact angle between receding and advancing, are measured with the dynamic captivebubble technique [38]). The experimental data are shown in Figs. 6 and 7 for hydrophilic and hydrophobic surfaces respectively. Non-linear correlations between $\cos \theta$ and 1/r were obtained for both hydrophilic and hydrophobic surfaces (Figs. 6 and 7). Such non-linearity has also been observed



Fig. 6. The effect of bubble size on contact angle for the hydrophilic surface $(Au-S[(CH_2)_{11}COOH]_2)$.



Fig. 7. The effect of bubble size on contact angle for the hydrophobic surface (Au $S(CH_2)_{16}CH_3$).

for other systems in our previous studies [25–27,37,38]. Several factors were examined to account for the non-linearity in previous systems and these included surface heterogeneity, surface roughness, the effect of gravity, and solid strain in the vicinity of the three-phase contact line. It has been found that surface heterogeneity is responsible for the non-linearity [25-27,37,38], but the nature of the heterogeneity for such "homogeneous" surfaces has not been identified. In this study, contact angle hysteresis of $20-25^{\circ}$ and $14-16^{\circ}$ was observed for hydrophilic and hydrophobic surfaces respectively. Oxidation of thiols and/or contamination of the surface during transportation of the samples from Harvard University to the University of Utah could have occurred. Also owing to the extremely short time of contact of the gold film with the ethanol-thiol solution (1-5 s) during organic monolayer preparation microdefects in self-assembled monolayers could occur and contribute to the surface heterogeneity. Further, it should be noted that the hydrophilic surface is composed of thiols adsorbed onto gold with carboxylic groups exposed to the environment. These carboxylic groups dissociate on contact with water as follows:

$$-S(CH_2)_{11}COOH = -S(CH_2)_{11}COO^- + H^+$$

The extent of dissociation of the carboxylic groups depends on the pH of the aqueous phase, and from previous results [39] it can be expected that significant dissociation of carboxylic groups occurs under alkaline conditions. The contact angle measurements were made with water drops in which the pH was changed from 5.8 to 10. For such systems, the hydrophilic surface is naturally heterogeneous at the molecular scale owing to the presence of dissociated, $-COO^-$, and undissociated, -COOH, carboxylic groups (note the scatter in the contact angle data and deviation from the linear $\cos \theta$ vs. 1/r relationship decrease with increasing pH for the experimental data presented in Fig. 6).

Owing to the non-linearity between $\cos \theta$ and 1/r, the modified Young equation (Eq. (3)) could not be used to calculate a true line tension value. but a pseudo-line tension value could be determined [26.27.37]. The concept of the pseudo-line tension was suggested by Good and Koo [22] for interpretation of the observed changes in contact angle with drop (bubble) size for systems with surface heterogeneity. The pseudo-line tension γ_{SLV}^* can be calculated from the linear range of a plot of $\cos \theta$ vs. 1/r for hydrophilic and hydrophobic surfaces, $\gamma_{SLV}^* = [\Delta(\cos \theta)/\Delta(1/r)] \gamma_{LV}$, but of course this is an approximation: it changes for the entire range of bubble sizes (Figs. 6 and 7). Two ranges of bubble size were selected from Figs. 6 and 7; those with $r > 100 \,\mu\text{m}$ and those with $r < 55 \,\mu\text{m}$ for the hydrophilic surface, and those with $r > 125 \,\mu\text{m}$ and $r < 110 \,\mu\text{m}$ for the hydrophobic surface. These ranges were selected because in each range the $\cos \theta$ vs. 1/r relationship can be approximated as a linear relationship and the results for systems with varying pH can be compared.

On the basis of contact angle data for different bubble sizes, the pseudo-line tension values (γ_{SLV}^*) were calculated and are presented in Table 2. As recognized by Gershfeld and Good [40] there exists the two-dimensional analog of the Laplace pressure, γ_{SLV}^*/r , across such a curved three-phase contact line. The pseudo-line tensions were found to be negative for all systems when the contact angle was measured through the aqueous phase. The negative value indicates that the vector of the two-dimensional Laplace pressure is directed away from the aqueous phase. The pseudo-line tension, as calculated for the hydrophilic surface, was found to be in the range, -5.0×10^{-7} to

Table 2		
Pseudo-line	tension	values

рН	Surface tension, 7 _{LV} (mN m ⁻¹)	Hydrophilic surface			Hydrophobic surface		
		Pseudo-line tension, 7 [*] _{SLV1} (J m ⁻¹)		r_1^{C}	Pseudo-line tension. $\sum_{SLV2}^{*} (J m^{-1})$		r_2^C
		$r > 100 \ \mu m$ (1/ $r < 10$)	$r < 55 \ \mu m$ (1/ $r > 18$)	(µm)	$r > 125 \ \mu m$ (1/ $r < 8$)	$r < 110 \ \mu m$ (1 $r > 9$)	(µm)
5.8	72.4	$-(8.5\pm2.4)\times10^{-7}$	$-(4.1 \pm 3.3) \times 10^{-8}$	68	$-(2.4\pm0.9)\times10^{-7}$	$-(0.5\pm6.0)\times10^{-8}$	114
7.0	72.0	$-(9.3 \pm 1.3) \times 10^{-7}$	$-(2.4 \pm 2.1) \times 10^{-8}$	83	$-(1.7\pm0.7)\times10^{-7}$	$-(0.4 \pm 4.6) \times 10^{-8}$	84
10.0	72.0	$-(5.0\pm0.8)\times10^{-7}$	$-(5.0\pm2.2)\times10^{-8}$	84	$-(2.1\pm0.6)\times10^{-7}$	$-(0.1 \pm 3.5) \times 10^{-8}$	116

 -9.3×10^{-7} J m⁻¹ for large bubbles (bubble base radius $r > 100 \,\mu$ m), and -2.4×10^{-8} to -5.0×10^{-8} J m⁻¹ for small bubbles (bubble base radius $r < 55 \,\mu$ m). In the case of the hydrophobic surface, the corresponding pseudo-line tensions were found to be about one order of magnitude smaller.

3.3. Experimental verification of Cassie equation for well-defined heterogeneous surfaces

The experimental contact angle data were compared with those calculated from the Cassie equation and the modified Cassie equation for heterogeneous surfaces. When the contact angle was measured for a model heterogeneous surface composed of parallel strips and with the threephase contact line tangential to the strips (see Fig. 5) or composed of squares and with a drop base edge located at the hydrophobic strip (see Fig. 5) (no corrugation of the three-phase contact line), the Cassie equation (Eq. (1)) was found to be applicable:

$$\cos\theta^{\mathbf{c}} = f_1 \cos\theta_1 + f_2 \cos\theta_2 \tag{6}$$

where subscripts 1 and 2 describe the hydrophilic and hydrophobic regions respectively. The hydrophilic and hydrophobic area fractions of the model surfaces were calculated from the dimensions of strips and squares, and found to be $f_1 = 0.5455$ and $f_2 = 0.4545$ for the model surface with parallel strips, and $f_1 = 0.2975$ and $f_2 = 0.7025$ for the surface with squares. The advancing contact angles for water drops on fully hydrophilic or hydrophobic surfaces were determined experimentally and are presented in Table 1. On the basis of these data, the contact angles for the model heterogeneous surfaces were calculated from the Cassie equation and results are presented in Table 3 for conditions where the three-phase contact line is not contorted. i.e. the drop edge does not cross the pattern. Good agreement between contact angle values measured at a position where the three-phase contact line was not affected by heterogeneous strips or squares (no contortion of the triple junction by hydrophilic or hydrophobic regions of the model pattern), and those calculated from the Cassie equation was obtained. The difference between experimental contact angle values and those calculated from the Cassie equation did not exceed 3[°] as is evident from the data presented in Table 3.

3.4. Experimental verification of modified Cassie equation for well-defined heterogeneous surfaces

When the drop edge crossed the pattern, for both heterogeneous surfaces, corrugation of the three-phase contact line was observed and did significantly affect the contact angle (Table 1). Contact angles, measured at such positions, were found to be significantly lower than those calculated from the Cassie equation (compare experimental data from Table 1 with those calculated from the Cassie equation and presented in Table 3). Only the modified Cassie equation for a binary system (Eq. (5)), incorporating the pseudo-line tension term, can reasonably describe such contact angles (Eq. (7); note that the complexity of this equation follows from the non-linear $\cos \theta$ vs. 1/rrelationships for the "homogeneous" hydrophilic and hydrophobic surfaces, Figs. 6 and 7):

$$\cos \theta^{MC} = f_{1} \cos \theta_{1} + f_{2} \cos \theta_{2}$$

$$- \frac{f_{1}}{\gamma_{1,V}} \left[\frac{\gamma_{SLV1}^{*}(r > r_{1}^{C})}{r_{1}^{C}} + \frac{\gamma_{SLV1}^{*}(r < r_{1}^{C})}{r_{1}} \right]$$

$$- \frac{f_{2}}{\gamma_{LV}} \left[\frac{\gamma_{SLV2}^{*}(r > r_{2}^{C})}{r_{2}^{C}} + \frac{\gamma_{SLV2}^{*}(r < r_{2}^{C})}{r_{2}} \right]$$
(7)

where γ_{SLV}^* is the pseudo-line tension, γ_{LV} is the surface tension of aqueous phase, r_1 and r_2 are the half-widths of hydrophilic and hydrophobic strips or squares respectively, r^c is the characteristic value of the bubble base radius as determined from the data presented in Figs. 6 and 7 (see Table 2).

For simplification it has been assumed that the corrugations of the three-phase contact line in the hydrophilic and hydrophobic regions are symmetrical and the local deformations affected by these regions are circular with a diameter equal to the width of the strips or squares. This assumption allows for the calculation of the contact angle for the water drop with a corrugated three-phase contact line but should be considered as a rough approximation. Although the shape of the drop edge might have been more complex [27], microscopic observation indicated that the shape of the

Table 3

Contact angle values (θ^{C}) as calculated from the Cassie equation (Eq. (6)) using contact angle data for hydrophilic and hydrophobic surfaces, and as determined experimentally for model heterogeneous surfaces (the three-phase contact line is not contorted)

pН	Advancing contact angle, θ^{C} (deg)					
	Parallel stri	ps	Squares			
	Calculated	Experimental	Calculated	Experimental		
5.8	83 ± 2	86 <u>+</u> 4	95 <u>+</u> 2	93 <u>+</u> 2		
7.0	78 ± 2	77 <u>+</u> 3	91 <u>+</u> 2	89 ± 2		
10.0	71 ± 2	71 ± 2	87 <u>+</u> 2	84 ± 3		

three-phase contact line was close to the assumed shape (see Fig. 8). Limited magnification and resolution capabilities of the optical equipment did not permit a more detailed analysis of the corrugation.

The contact angle values for heterogeneous surfaces when the drop edge crossed the pattern were calculated using the modified Cassie equation (Eq. (7)) together with both contact angle data (Table 1) and pseudo-line tension values (Table 2), as determined for fully hydrophilic and hydrophobic surfaces, and they are presented in Table 4. The calculated contact angle values differ by $1-9^{-1}$ from those determined experimentally (Table 4). The difference may be attributed to the uncertainty in the determination of the pseudo-line tensions and the uncertainty in the local deformation of the three-phase contact line.

An additional comment is required to explain why the line tension effect was not observed in previous investigations of the effect of surface heterogeneity on contact angle. In experiments of Cassie and Baxter [1,2], heterogeneous surfaces were composed of hydrophobic wires (70 and 130 μ m in diameter) or fabrics (18 μ m in diameter) with contact angles larger than 100. The heterogeneous surfaces were composed of much larger patches than examined in our systems, and of



Fig. 8. Corrugation of the three-phase contact line as observed by optical microscopy for a water drop located at the model heterogeneous surface composed of $3 \mu m$ hydrophilic (Au-S[(CH₂)₁₁COOH]₂) and 2.5 μm hydrophobic (Au-S(CH₂)₁₆CH₃) parallel strips. The liquid drop edge is observed from the top.

Table 4

Contact angle values (θ^{MC}) as calculated from the modified Cassie equation (Eq. (7)) using contact angle data and the pseudo-line tensions calculated from the contact angle/drop size relationships for fully hydrophilic and hydrophobic surfaces, and as determined experimentally for model heterogeneous surfaces (the three-phase contact line is contorted)

pH		Contact angle, θ^{MC} (deg)				
		Parallel strips		Squares		
		Calculated	Experimental	Calculated	Experimental	
5.8	Adv	63 ± 4	69 ± 3	86 ± 4	81 ± 2	
	Rec	51 ± 4	54 ± 5			
7.0	Adv	64 ± 4	68 <u>+</u> 2	85 ± 4	81 ± 2	
	Rec	50 ± 4	51 <u>+</u> 5			
10.0	Adv	50 ± 4	59 ± 4	80 ± 4	74 ± 2	
	Rec	46 ± 4	39 ± 5			

Adv, advancing contact angle; Rec. receding contact angle.

course, the corrugation of the three-phase contact angle becomes less significant for such heterogeneities as examined by Cassie and Baxter. Also, as presented in this contribution, there is only a small effect of the line tension on contact angle for hydrophobic surfaces. Even smaller changes in contact angle with bubble size were observed for a carefully prepared polyethylene film [27]. In this regard, the effect of three-phase contact line corrugation on contact angle may have been too small to have been observed by Cassie and Baxter.

Additional experimental support for the Cassie equation was provided by Crawford et al. [4] for methylated quartz plates. However, a careful analysis of the experimental data presented by Crawford et al. [4] indicates that in most cases the contact angles are not predicted by the Cassie equation. The scatter in contact angles may be attributed to the experimental uncertainty of the measurements but also may be the effect of corrugation of the three-phase contact line. There are also additional effects that make the interpretation of contact angle data on methylated quartz surfaces difficult, such as non-uniform methylation and formation of multilayer films or molecular clusters [25,41,42].

4. Conclusions

By patterning a self-assembled monolayer using an elastomer stamp, well-defined heterogeneous

surfaces consisting of alternating and parallel hydrophobic and hydrophilic strips (sample 1 called "parallel strips") and hydrophilic squares separated by hydrophobic strips (sample 2 called "squares") were prepared on an evaporated gold film supported on a silicon wafer. The wetting characteristics of these model heterogeneous solid surfaces consisting of mosaics of self-assembled monolaver films were examined by contact angle measurements. The contact angles for water drops in the pH range 5.8-10.0 were measured. The experimental contact angles were in agreement with those calculated from the Cassie equation, when the three-phase contact line was noncontorted (the strips were tangential to the drop edge for the "parallel strips" sample or the water drop edge was in the hydrophobic field for the "square" sample).

When the drop crossed the "square" pattern surface or when the strips were normal to the drop edge for the "parallel strips" surface, corrugation of the three-phase contact line influenced the contact angle significantly. Contact angles, measured in these cases, were much lower than those calculated from the Cassie equation. Analysis of these measurements, together with those for fully hydrophobic and hydrophilic surfaces, demonstrates the necessity for a modified Cassie equation that includes a term describing the line tension contribution to the three-phase system.

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