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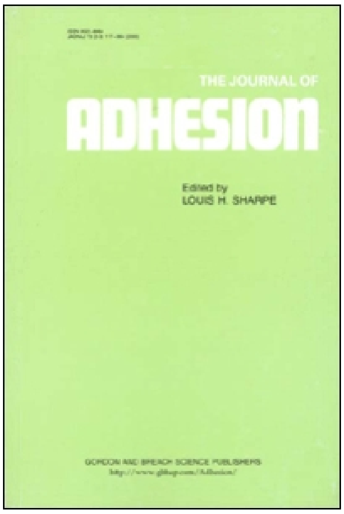

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The Effect of Drop (Bubble) Size on Contact Angle at Solid Surfaces

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The Effect of Drop (Bubble) Size on Contact Angle at Solid Surfaces*

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Examples of experimental contact angle data for varying drop and bubble volumes on different solids whose surfaces are smooth and homogeneous, rough and homogeneous, smooth and heterogeneous, and covered with unstable organic films are presented. The ideas and theoretical models as proposed in the literature for the interpretation of contact angle/drop (bubble) size relationships are critically reviewed. It is shown that major factors affecting the contact angle variation with drop (bubble) size such as surface heterogeneity, roughness, and stability, have been identified in the literature. However, there is still a need for experimental work with well-defined and well-characterized solid surfaces. Theoretical models that have been proposed in the literature are still inadequate. Advanced modeling of liquid behavior at heterogeneous and rough surfaces is required to understand further, and to predict, the contact angle/drop (bubble) size relationships at imperfect surfaces.

Keywords: Contact angle; contact angle hysteresis; advancing and receding contact angles; line tension; heterogeneous surface; rough surface; stable surface; monolayer instability; models; sessile drop technique; captive-bubble technique; theory; experiment

INTRODUCTION

The effect of drop and bubble size on contact angle was reported many years ago without any clear explanation [1, 2]. Only in recent years has this phenomenon received more experimental and fundamental treatment. Several contact angle/drop (bubble) size relationships are reported in the literature for a variety of three-phase systems [3–14].

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*One of a Collection of papers honoring Robert J. Good, the recipient in February 1996 of *The Adhesion Society Award for Excellence in Adhesion Science, sponsored by 3M.*

Both sessile-drop and captive-bubble techniques were used in those studies. We rediscovered the effect of drop size on contact angle at the Technical University of Gdansk (Poland) in 1988 during our laboratory experiments (unpublished data) with agglomeration of oil-in-water emulsions by hydrophobic solid particles (a reverse process to oil agglomeration [15]). It was found, during our microscopic observations of the oil droplet-solid particle aggregates in water, that oil droplets with a diameter of 5–20 μm attached to the polyethylene particles (0.1–1 mm diameter) as lenses with a contact angle varying from about 30° to 40°. These contact angles differed by 10–30° from the contact angles measured with a captive-drop technique and involving large oil drops (4–6 mm diameter) at a flat and smooth polyethylene plate (10–20° for advancing contact angle and 0–5° for receding contact angle). This discrepancy between contact angles (10–30°), as observed for "macroscopic" and "microscopic" systems, certainly surprised us. Inspired by this intriguing observation, we undertook a study at the University of Utah, a few years ago, to examine the effect of drop (bubble) size on contact angle in three-phase systems with solids of varying surface quality [5, 6, 11–14]. This short review summarizes the progress made in the understanding of the effect of drop volume on contact angles, with emphasis on important concepts developed as well as controversial ideas discussed in the literature with regard to this effect.

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THE CONTACT ANGLE/DROP (BUBBLE) SIZE RELATIONSHIPS AT SMOOTH AND HOMOGENEOUS SOLID SURFACES

Examples**

The advancing and receding contact angles for water drops of varying volume at the hydrophobic monolayer of 1-dodecanethiol, as meas-

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**The examples presented in this contribution include the experimental contact angle data as obtained with the static sessile-drop and dynamic captive-bubble (drop) contact-angle measurement techniques which have been published in our previous contributions. The static sessile-drop, static captive-bubble, and dynamic captive-bubble (drop) methods are well described in a previous contribution [6]. The contact angle measured for the liquid tending to advance is called the advancing contact angle and it is larger than or equal to the contact angle measured for the liquid tending to recede which is known as the receding contact angle. The difference between these two contact angles

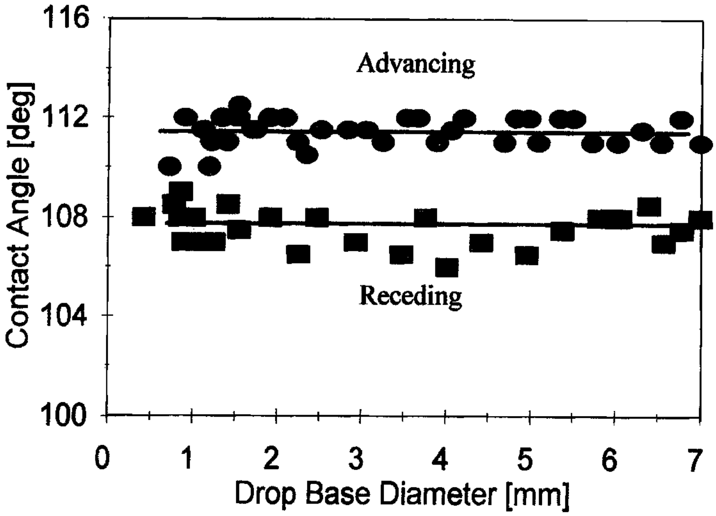

FIGURE 1 The effect of drop size on advancing and receding contact angles for the water/(dodecanethiol monolayer on gold) system as determined by the static sessile-drop technique[6]. Dodecanethiol forms self-assembled monolayer on the gold surface through gold-sulfur bond with the hydrocarbon chain oriented into the environment.

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ured by the sessile-drop technique, are shown in Figure 1. A uniform and homogeneous self-assembled monolayer of 1-dodecanethiol was formed on a smooth gold surface[6]. This monolayer represents a close-to-ideal surface, with regard to surface smoothness and homogeneity. For this particular system, the effect of drop size on contact angle was not seen for either the advancing or the receding contact angles (Fig. 1). If there is any effect at all it is equal to, or smaller than, the scatter observed in the contact angle data (~2 degrees).

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is called the contact angle hysteries. The static sessile-drop technique allows for measurements of the advancing and receding contact angles (we may say the recently advanced and recently receded contact angles). The contact angles obtained with the dynamic captive-bubble (drop) technique correspond to the receding contact angles for most of the systems studied. Particularly those with a smooth and homogeneous solid surface. For solid surfaces which have a significant heterogeneity and roughness features. both receding and intermediate contact angles (an intermediate values as between advancing and receding contact angles) are frequently reported [5, 6, 14].

Also, carefully cleaned quartz plates with smooth surfaces were used in our laboratory as close-to-ideal solids and contact angle/drop size relationships were examined using the dynamic captive-drop technique [11,14]. Figure 2 presents the contact angle/drop size relationships for the heptane/water/quartz and tetradecane/water/quartz systems. Again, only 2–3 degrees of change in the contact angle with drop volume was noticed in these systems. This change in contact angles is again close to the experimental error or scatter of contact angle data.

In summary, it appears from our experimental data that the contact angle variation with drop (bubble) size is difficult to detect for systems with smooth and homogeneous surfaces. On the other hand, much larger variation in contact angle was observed by other authors [7,9]. These data are discussed in the following section.

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Model

There is a general agreement between researchers that a change in contact angle with drop (bubble) size for liquid drops (gas bubbles) placed at smooth, homogeneous and rigid solid surfaces occurs ac-

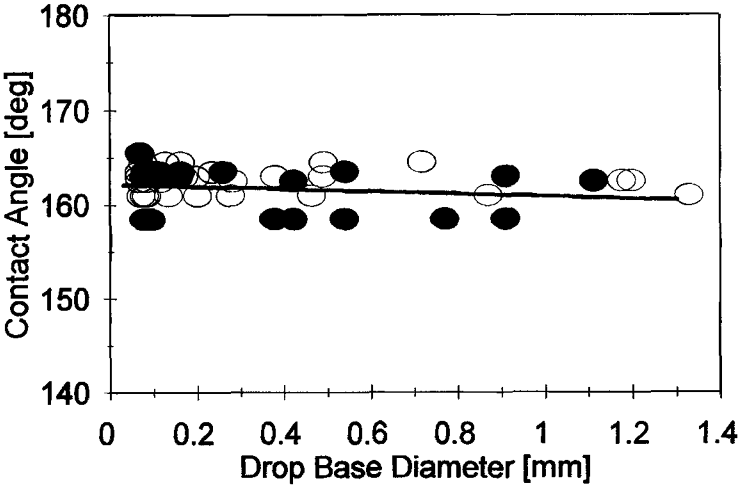

FIGURE 2 The effect of drop size on contact angle for the heptane/water/quartz (open circles) and tetradecane/water/quartz (filled circles) systems as determined by the dynamic captive- drop technique [11,14].

cording to the contribution of the line tension, which is defined as the excess free energy of the three-phase system (per unit length of the three-phase contact line) in the region of the triple junction [16–19]. The magnitude of the line tension in three-phase systems, particularly those involving solids, remains, however, controversial.

A linear relationship between the cosine of the contact angle and the reciprocal of the drop (bubble) base radius follows from a theoretical relationship known as the modified Young's equation [1, 19]:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV}\cos\theta + \frac{\gamma_{SLV}}{r} \tag{1}$$

which, for practical purposes, is expressed as:

$$\cos\theta = \cos\theta_{\infty} - \frac{\gamma_{SLV}}{r\gamma_{LV}} \tag{2}$$

where

$$\cos\theta_{\infty} = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}; \quad \theta = \theta_{\infty} \text{ for } r \to \infty$$

$\gamma_{SV}, \gamma_{SL}, \gamma_{LV}$ in the above equations are the interfacial tensions for solid-vapor, solid-liquid, and liquid-vapor interfaces, respectively; θ is the contact angle; r is the drop (bubble) base radius (radius of curvature of the contact line); γ_{SLV} is the line tension. The modified Young's equation (1) is applicable to smooth, homogeneous, isotropic, rigid, and horizontal support surfaces.

The modified Young's equation was adapted by several authors for the interpretation of contact angle/drop (bubble) size relationships and the line tension values were calculated from the $\cos\theta$ *vs.* $1/r$ relationships [1, 7, 9, 11, 14, 20, 21]. A wide variety of the line tension values was obtained, from 1×10^{-9}–1×10^{-8} J/m to 1×10^{-6}–1×10^{-5} J/m, depending on the three-phase system examined and the technique used.*** The "line tension" values measured are small (1×10^{-9}–1×10^{-8} J/m) [11, 13, 14, 20] when small drops (bubbles) with a diameter less

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***The line tension can be either negative or positive [22–24]. The sign of the line tension is, however, disregarded in this discussion as a minor issue of this review.

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than one millimeter (down to several micrometers) were used. On the other hand, the large "line tension" values ($1 \times 10^{-6} - 1 \times 10^{-5}$ J/m) [1,7,9,21] were reported (the only exception here follows from our experimental data [5,6] which do not support the large values of the line tension for systems with homogeneous and smooth solid surface; see also Figs. 1 and 2) when the contact angle/drop (bubble) size relationships were examined with a static sessile-drop (or captive-bubble) technique and the contact angles were measured for large drops (with drop base diameter larger than 2 mm). These values are 4–5 orders of magnitude larger than any theoretical estimate for the line tension [11,14]. Such large values seem to be unacceptable in view of the excess energy expected in the vicinity of, and associated with, the three-phase contact line [11,14]. The possible factors affecting the contact angle/drop (bubble) size relationship have been identified as solid surface imperfections, including surface heterogeneity, roughness, and deformability [3,5,6,11–14]. For example, it was observed for several systems that a linear relationship between the cosine of the advancing contact angle and the reciprocal of the drop base radius for large drops does not guarantee a high quality of solid surface examined, particularly with regard to surface homogeneity and smoothness. Such linearity has also been observed for several heterogeneous and rough surfaces (see also the next section) [5,6,25,26]. Of course, the value calculated from the $\cos\theta$ *vs.* $1/r$ relationship for nonideal systems cannot be attributed to the line tension. In view of this situation, additional research should be undertaken in this area in order to support or reject the existence of large "line tension" values in the three-phase systems with liquid drops (gas bubbles) of 2–10 mm diameter at smooth, homogeneous and rigid solid surfaces.

THE CONTACT ANGLE/DROP (BUBBLE) SIZE RELATIONSHIPS AT HETEROGENEOUS SOLID SURFACES

Examples

Good and Koo [3] measured the advancing and receding contact angles for polar and apolar liquid drops of varying size on several polymers. They observed a variation in contact angles with drop size

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and proposed that surface heterogeneity could be the reason for this effect. The concept of the effect of surface heterogenity on the contact angle/drop size relationship was mentioned previously by other researchers[1] but was not discussed to any great extent. The role of surface heterogeneity in the relationship between contact angle and drop (bubble) size has recently been verified experimentally for several different systems[5, 6, 11–14, 25, 26]. For example, Figure 3 presents the advancing and receding contact angles for water drops of varying volume placed on the hydrophobized surface of a fluorite crystal. Different degrees of surface hydrophobization of fluorite was achieved by the chemisorption of varying amount of oleic acid from aqueous solutions[26]. In this way, several surfaces with different degrees of heterogeneity, with regard to the area fraction of hydrophilic fluorite covered by hydrophobic oleate, were obtained. As another example, Figure 4 presents the contact angle data for an air bubble/water/methylated quartz system where different degrees of hydrophobization of quartz by trimethylchlorosilane were used to change the wetting characteristics of the surface. The air bubbles were deposited on the

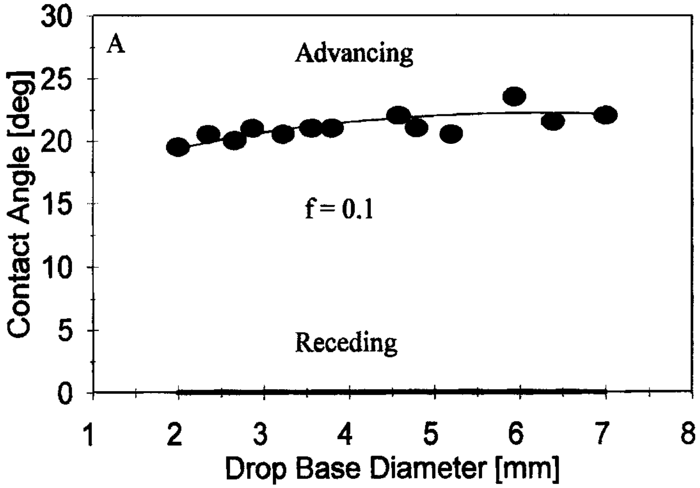

FIGURE 3 Advancing and receding contact angle data for water drops at a fluorite surface with different levels of oleate adsorption[26]. The experimental data were obtained with the static sessile-drop technique. f is the area fraction of the fluorite surface covered with adsorbed oleate groups. The area fraction equal to $f = 1.19$ indicates the amount of adsorbed species exceeding a monolayer.

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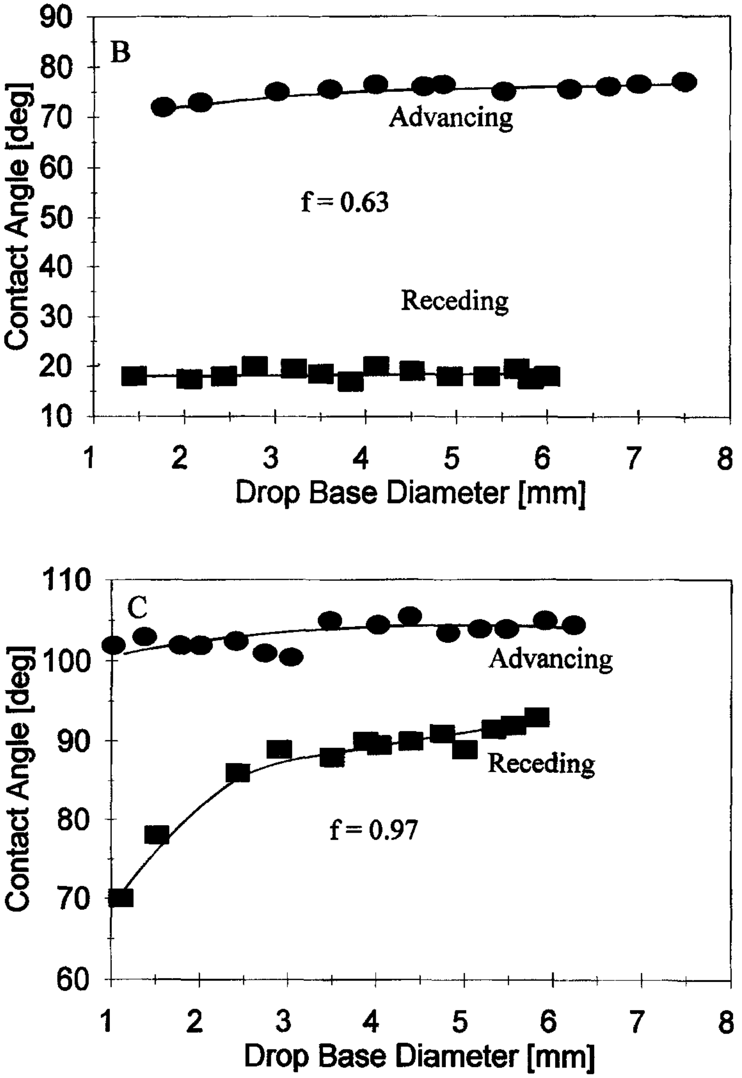

FIGURE 3 (Continued).

methylated quartz surface by the dynamic captive-bubble technique. Several other systems were also examined in our laboratory [5, 6, 11–14, 25–27] and the following conclusions have been drawn from contact angle data for all of these systems. The reader is referred to

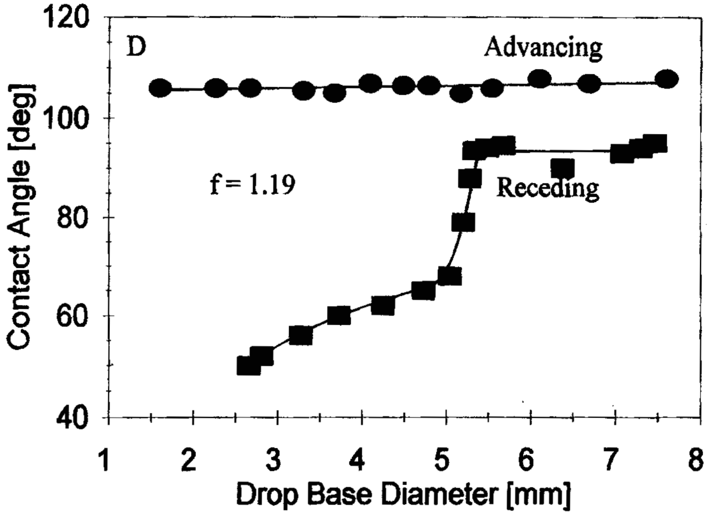

FIGURE 3 (Continued).

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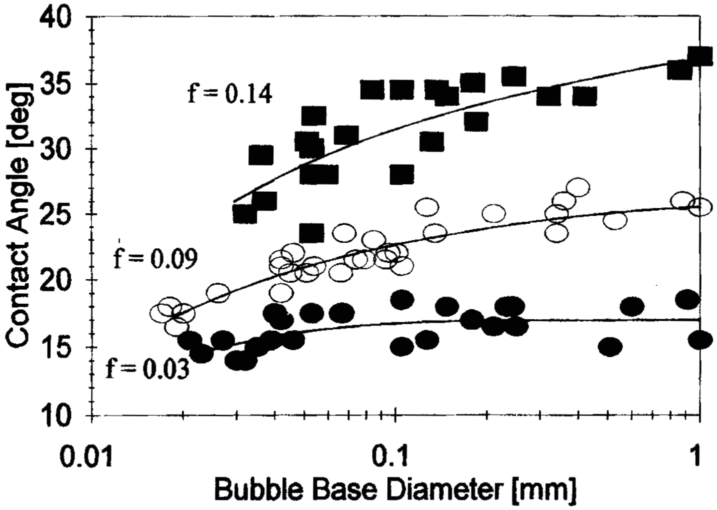

FIGURE 4 The effect of bubble size on contact angle for the air/water/methylated quartz system as determined by the dynamic captive-bubble technique [27]. Quartz surfaces were methylated with chlorotrimethylsilane. *f* is the area fraction of the quartz surface methylated with silane.

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the original literature for experimental details and a full spectrum of experimental data.

These experimental data clearly indicate that the effect of drop (bubble) size on contact angle is difficult to distinguish for surfaces composed of molecular-sized heterogeneity (molecular-size: ranging from a size of one molecular to a size of a cluster composed of a few molecules) [25–27]. Hydrophilic mineral surfaces with a small amount of adsorbed hydrophobic molecules were tested in our laboratory [25–27]. Figure 3a serves as an example. The effect of drop (bubble) size on advancing contact angle observed (Fig. 3a) for a narrow range of drop size (2–7 mm drop base diameter) was not significant. Also, a small effect of drop (bubble) size on contact angle was observed for surfaces with molecular-sized heterogeneity when the dynamic captive-bubble (drop) technique was used with bubbles (drops) smaller than 1 mm (Fig. 4) [12, 14, 27]. As the area fraction of adsorbed hydrophobic species at the hydrophilic surface increased, the effect of drop (bubble) size on contact angle became more evident, particularly for small drops (bubbles) with diameter < 1 mm [12, 14, 25–27], as shown from the contact angle data presented in Figure 4. However, the effect of drop size on contact angle still remains unclear when examined with the sessile-drop method for large drops of size greater than 1–2 mm (Fig. 3b). The variation of contact angle, particularly the receding contact angle, with varying drop (bubble) size becomes significant when the adsorbed molecules form a microscopic heterogeneous pattern at the mineral surface. For example, when a fatty acid adsorbs at a fluorite surface forming an incomplete monolayer, the contact angle variation was observed to be significant with varying drop size particularly for a submonolayer approaching a monolayer structure (Fig. 3c, d) [25, 26].

In summary, the effect of drop (bubble) size on contact angle depends on surface heterogeneity. All our experimental data [5, 6, 11–14, 25–27] suggest that a heterogeneous pattern of the surface (hydrophobic aggregates of adsorbed molecules on hydrophilic surface of mineral), with regard to the size of hydrophobic/hydrophilic area fractions, their distribution and wetting properties, affects the contact angle/drop (bubble) size relationships. Nevertheless, additional experiments with solids having a well-defined and uniform heterogeneous pattern at the surface need to be undertaken in order to clarify the details of the effect of size, shape, and distribution of "hydrophobic" and "hydrophilic" surface regions on the contact angle/drop (bubble) size relationship.

Model

There is no mathematical model which could well describe the experimentally observed correlations between drop size and contact angle on heterogeneous surfaces. A model proposed by Good and Koo [3], further discussed in the literature [6, 28], is, in our opinion, the best qualitative approach discussed in the literature for heterogeneous surfaces. The overall picture of this model is illustrated in Figure 5. The liquid drop (or gas bubble), when placed on a heterogeneous surface, has contorted both the three-phase contact line and the drop (bubble) surface in the vicinity of the contact line. This contortion is reinforced by the system, because the liquid tends to establish local equilibria in contact with surface areas of varying surface properties. The energy barriers between different positions of the three-phase contact line may have a strong impact on the entire contortion of the drop (bubble) which, in turn, influences the contact angle variation with varying drop volume. The total energy of the liquid drop (gas bubble) increases with increasing drop (bubble) volume and energy barriers become important system features for decreasing drop (bubble) volumes. The ratio between surface area for the liquid-gas (A_{LV}) interface and surface area for the solid-liquid (A_{SL}) interface may change with drop size when contortion of the drop surface takes place. This may also lead to an increase in the excess energy of the entire drop (bubble) per unit length of the three-phase contact line [3].

The macroscopic contact angle is a function of drop (bubble) size when the drop (bubble) base radius is comparable with the local contortion of the three-phase contact line (Fig. 5). Because the radius of the drop base for a large drop (r_1) is much larger than the radius of the local contortion of the three-phase contact line ($r_L; r_L \ll r_1$), the macroscopic contact angle (Θ_1) differs from any local contact angle ($\Theta_{L2} > \Theta_1 > \Theta_{L1}$). This situation changes with decreasing drop size and the macroscopic contact angle for a small drop (Θ_2) approaches the smallest local contact angle ($\Theta_2 \rightarrow \Theta_{L1}$).

The predicted variation of contact angle with varying drop (bubble) according to the above model, originally proposed by Good and

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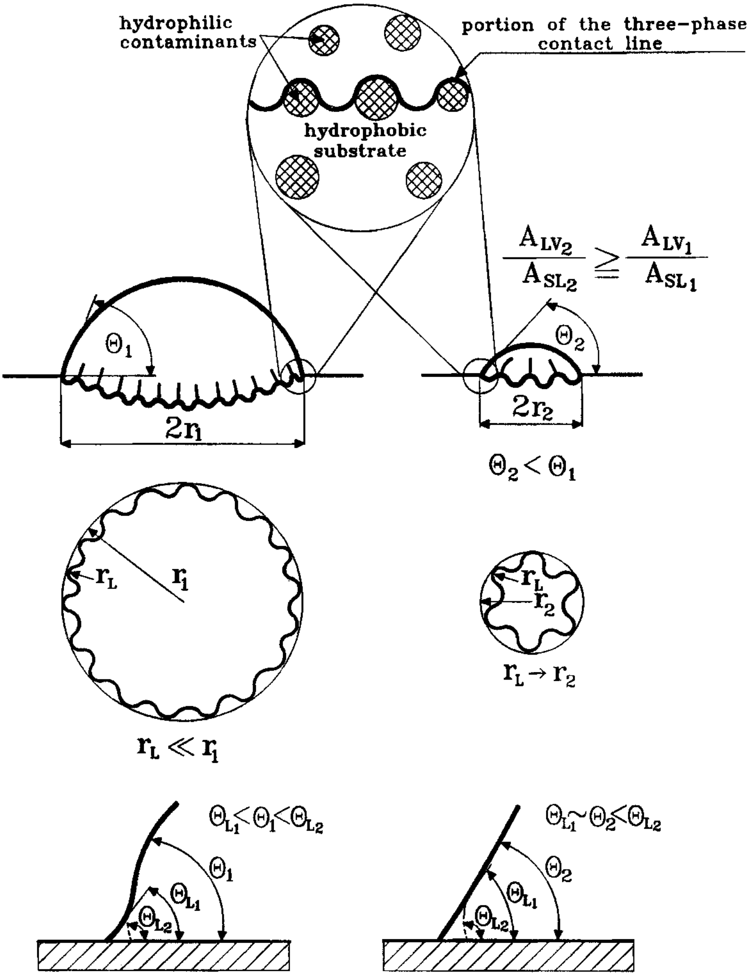

FIGURE 5 Schematic of a large drop and a small drop at a heterogeneous solid surface illustrating the effect of solid heterogeneity on contact angle variation with the size of sessile drop [6]. A_{LV}, A_{SL} are the interfacial areas; the L, S, and V subscripts correspond to liquid, solid, and vapor, respectively; θ is the contact angle; r is the drop base radius; the 1 and 2 subscripts correspond to a large and small drop, respectively.

Koo [3], is in good qualitative agreement with the experimental data for the contact angle/drop (bubble) size relationships reported in the literature for heterogeneous surfaces [5, 6, 25–27].

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Another concept for the variation of the contact angle with drop size was pre-sented by Li *et al.* [29]. This model assumes that the radii of a contorted three-phase contact line change with varying drop (bubble) volume. This concept, however, must be rejected for large drops (bubbles), 2–10 mm in diameter, which are currently used in the static sessile-drop and captive-bubble methods. The decrease in the radius of curvature for local segments of the three-phase contact line with decreasing drop (bubble) volume may certainly be expected for small drops (bubbles), probably with a diameter much less than 0.1 mm. This will happen for small liquid drops (gas bubbles) according to the Laplace pressure effect. The contorted shape of large drops (bubbles) will be smoothened for small drops (bubbles) in order to attain constant pressure across the surface (interface). When the drop (bubble) diameter is in the range of millimeters, this effect should not appear. Our recent contact angle data for model heterogeneous surfaces confirm this aspect [30].

Also recently, Lin and Li [31] analyzed theoretically the contact angle/drop size relationship for model heterogeneous surfaces composed of either concentric rings or a patchwise pattern (note that these models were introduced by Johnson and Dettre [32] for the discussion of contact angle hysteresis). They assumed that contact angle change with drop size can be attributed to the linear free energy and to the change of the curvature of the three-phase contact line due to varying size of the heterogeneous pattern at the solid surface (this concept, in general, was already presented in our previous contributions [27, 33]). There are, in our opinion, two unrea-sonable assumptions in the theoretical modeling presented by Lin and Li: 1) the line tension they selected (2–4 μJ/m) is at least 3–4 orders of magnitude too large (see previous section in this paper) [14]; 2) the authors completely ignored the metastable energetic states [32, 34, 35] in their model three-phase systems.

THE CONTACT ANGLE/DROP (BUBBLE) SIZE RELATIONSHIPS AT ROUGH SOLID SURFACES

Examples

It is now well documented that the surface roughness is responsible for the variation of contact angle with drop (bubble) volume. Experimental support for this concept has been provided only by our research group [5, 6, 14, 27]. All this work, however, was limited to the examination of rough surfaces with random and irreproducible topography. Figure 6 provides selected examples for the advancing and receding contact angles on roughened polymer surfaces. For most systems, the contact angle/drop (bubble) size relationships observed for several rough surfaces were similar quantitatively to those observed for systems with smooth but heterogeneous solid surfaces.

Model

Two models were proposed in the literature for the interpretation of contact angle/drop (bubble) size relationships at rough surfaces [6, 11, 14]. The first model was developed based on the modified Wenzel equation, including the line-tension term [11, 14]. Its application is limited only to specific rough surfaces and it has very limited applica-

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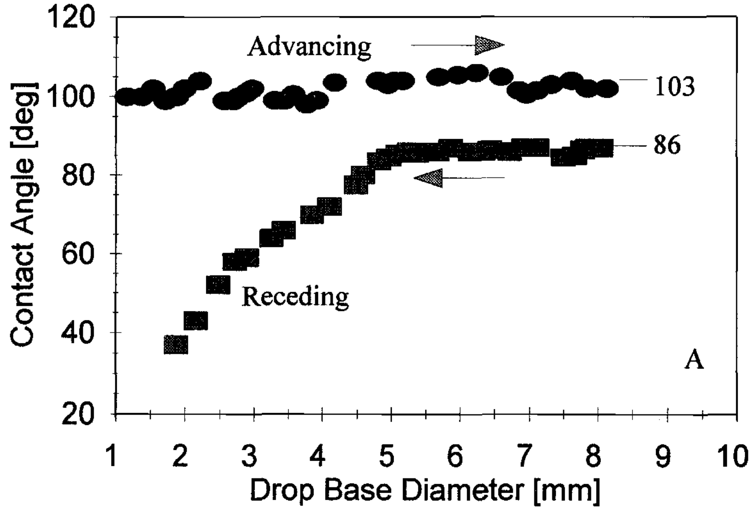

FIGURE 6 Advancing and receding angle data for water drops at a polyethylene film [6]. The polyethylene film was formed on (A) microscope glass slide, (B) roughened aluminium plate, from polyethylene-toluene solution after solvent evaporation. The contact angles were measured using the static sessile-drop method.

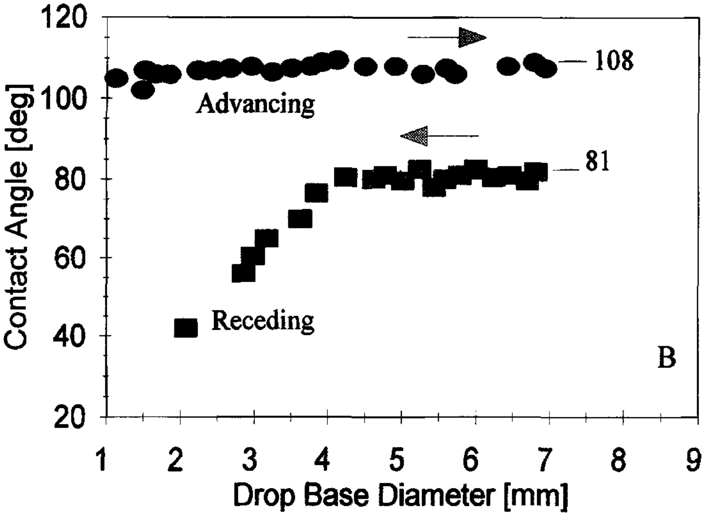

FIGURE 6 (Continued).

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tion. In this regard, this model will not be discussed in this paper. The second model was developed based on the concept of Good and Koo [3] for heterogeneous surfaces which was adapted for rough surfaces [6]. The illustration of this model is shown in Figure 7.

Figure 7 presents a large drop and a small drop at a rough solid surface. The three-phase contact line and the drop surface in the vicinity of the three-phase contact line are contorted for both drops. The roughness asperities with different shape reinforce this contortion. Mechanical barriers (asperities) for moving liquid have a strong effect on the contortion of the three-phase contact line and liquid surface in its vicinity, and on the energetic state of the liquid drop (gas bubble) [6]. The ratio between the surface area for the liquid-gas (A_{LV}) interface and the surface area for the solid-liquid (A_{SL}) interface may change with drop (bubble) size and may lead to an increase in the excess energy of the entire drop per unit length of the three-phase contact line.

The radius of the drop base for the large drop (r_1) is much larger than the radius of the local contortion of the three-phase contact line (r_L; $r_L \ll r_1$) (Fig. 7). Thus, the macroscopic contact angle (Θ_1), as

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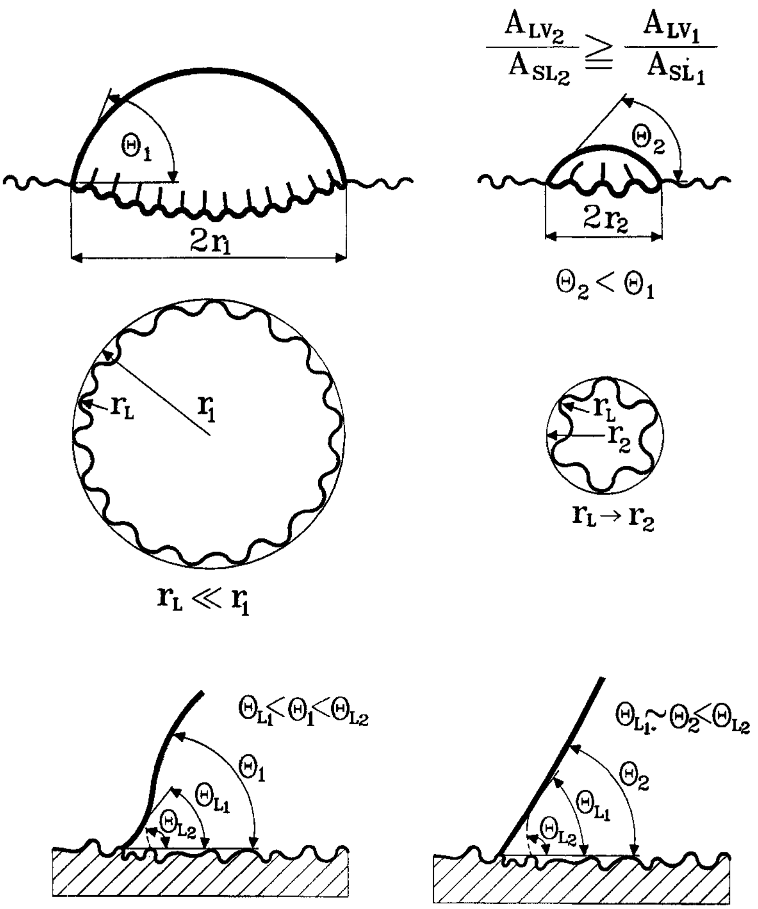

FIGURE 7 Schematic of a large drop and a small drop at rough solid surface illustrating the effect of solid roughness on contact angle variation with a size of sessile drop [6]. A_{LV}, A_{SL} are the interfacial areas; the L, S and V subscripts correspond to liquid, solid, and vapor, respectively; θ is the contact angle; r is the drop base radius; the 1 and 2 subscripts correspond to a large and small drop, respectively.

observed during contact angle measurements, corresponds to a value which is between two extreme contact angle values (Θ_{L1} and Θ_{L2}), characteristic for local controtions of the three-phase contact line ($\Theta_{L2} > \Theta_1 > \Theta_{L1}$). This situation changes with decreasing drop volume and the macroscopic contact angle for the small drop (Θ_2) approaches the smallest local contact angle ($\Theta_2 \rightarrow \Theta_{L1}$). In this regard, contortion of the liquid drop (gas bubble) base has such an effect that the contact angle decreases with drop (bubble) size. Nevertheless, mechanical barriers for a moving liquid at the rough solid surface may change the contact angle/drop (bubble) size relationship from a function which decreases with decreasing drop (bubble) volume to an increasing one. Here, the size and shape of asperities of the rough surface (together with wetting properties) are important properties of the system influencing the relationship between contact angle and drop (bubble) size.

THE CONTACT ANGLE/DROP SIZE RELATIONSHIPS AT UNSTABLE MONOLAYERS

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The contact angle measurements for varying drop volumes may also be used for examination of stability of solid surfaces. This approach was used in our systematic studies of Langmuir-Blodgett (LB) monolayers of fatty acids on calcite and fluorite crystals [36]. An example of contact angle/drop size relationships is presented in Figure 8. Although the advancing contact angle remains almost constant over the entire range of drop size examined, the receding contact angle decreases systematically to a zero value (Fig. 8). Such behavior of the system was only observed for unstable monolayers [36]. In the case of a stable monolayer, there was only a small effect of drop size on receding contact angle [36].

For the unstable system presented in Figure 8, liquid penetrates the structure of the transferred LB organic monolayer at a fluorite surface and reinforces a dissolution of organic molecules into the aqueous phase [36]. This reaction leads to changes in both the solid-liquid and liquid-vapor interfacial properties. The desorption of low-energy components from the surface leads to the increased exposure of the high-energy support. Also, released molecules as surface active components may absorb at the liquid-vapor interface and reduce the surface tension of the liquid drop.

Recently, we also reported a destructive effect of diiodomethane on the structure of a self-assembled monolayer composed of hexadecanothiol [30]. This case is presented in Figure 9. Again, there is a small effect of drop size on advancing contact angle and a large effect of drop size on receding contact angle.

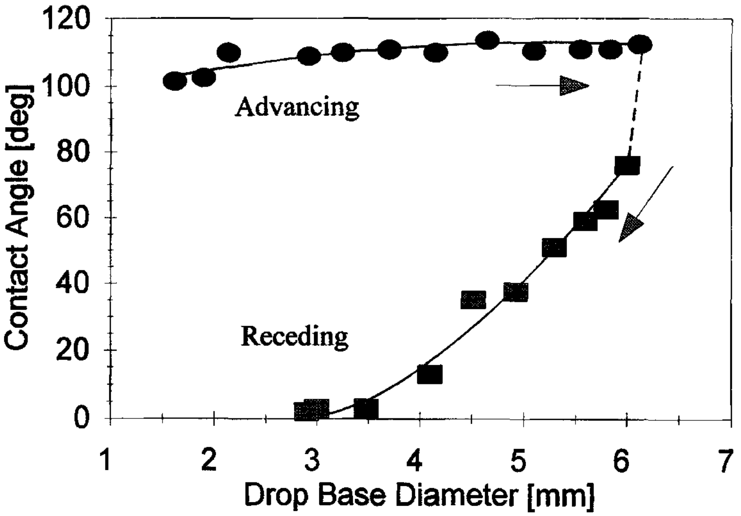

FIGURE 8 Advancing and receding contact angle data for water (pH = 11.0) drops on Langmuir-Blodgett monolayer of calcium distearate deposited at a fluorite surface [36].

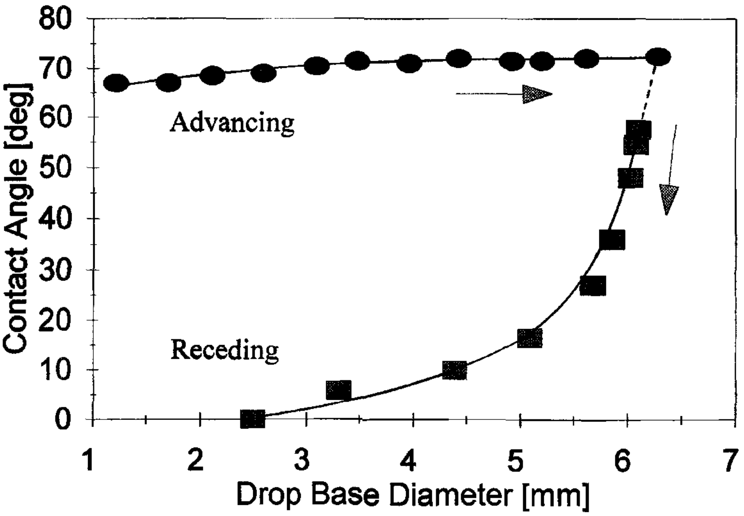

FIGURE 9 Advancing and receding contact angle data for diiodomethane drops on self-assembled monolyaer of hexadecanethiol as determined by the static sessile-drop technique [30]. Hexadecanethiol forms a monolayer on the gold surface through gold-sulfur bond with the hydrocarbon chain oriented into the environment.

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GENERAL REMARKS

The effect of drop (bubble) size on contact angle is an important property of the system, as already demonstrated in the literature for several systems. It also has several important practical consequences.

The experimental procedure for contact angle measurements using either the sessile-drop or the captive-bubble technique needs to be established, particularly with regard to the drop or the bubble size that should be used. Both contact-angle measurement techniques, sessile-drop and captive-bubble, should provide reproducible advancing and receding contact angles for all types of surfaces (*i.e.*, homogeneous, heterogeneous, smooth, and rough) and these data should also be comparable with the values determined by using other contact-angle measurement techniques. Our experimental data indicate that only a slight variation in the advancing contact angle value occurs over a few millimeters change in drop (bubble) base diameter. In this regard, the advancing contact angles obtained in different laboratories by using different techniques should be quite reproducible. Of course, the quality of the solid surface examined should be comparable in all these tests and the effect of kinetics during the three-phase system equilibration should be eliminated (or fixed at the same level) for reproducibility. A strong effect, however, of drop (bubble) volume on contact angle is observed for receding conditions. The effect of drop (bubble) size on receding contact angle is particularly significant for drops (bubbles) with a base diameter less than 5–7 mm. This critical size of drop (bubble) strongly depends on the quality of the solid surface examined and its characteristics. In this regard, it is recommended to use this critical size of drop as a minimum size in routine contact angle measurements involving the sessile-drop and captive-bubble (drop) techniques. Nevertheless, it is always a good practice to determine the contact angle/drop (bubble) size relationship for both advancing and receding contact angles for any new solid sample under investigation.

The relationship between the contact angle hysteresis and the drop (bubble) size provides much more information regarding the quality and stability of a particular solid surface than any contact angle data reported for fixed drop (bubble) volume. Although appropriate mathematical models do not exist at the present time to describe the correlation between the contact angle for varying drop (bubble) size and the quality of the solid surface, experimental data clearly indicate the advantages of such an approach in the characterization of imperfect solid surfaces.

Because of the drop (bubble) size effect on contact angle, the contact angles for dispersed systems, involving particles, droplets, or bubbles with size less than 0.05–0.1 mm, differ from those contact angles measured with the sessile-drop and captive-bubble contact-angle measurement methods and involving liquid drops or gas bubbles with a diameter of a few millimeters. In this regard, all processes involving dispersed phases such as flotation of solid particles, agglomeration of solid particles with dispersed liquid, stabilization of emulsions and foams by fine particles, separation of oil from oil sands or oil-contaminated soil, etc., may be influenced by this phenomenon. This should be taken into consideration in the future experimental and theoretical work in these areas.

The effect of drop (bubble) size on contact angles is well documented in the literature for solid surfaces of varying quality. It is now required to examine this phenomenon for well-defined solid surfaces with varying but reproducible heterogeneity and roughness features. Also, homogeneous and smooth surfaces need further consideration in order to clarify the magnitude of the line tension and its variation. Examination of well-defined surfaces will provide further insights into the effect of drop (bubble) size on contact angle. An interpretation of contact angle/drop (bubble) size relationships is almost limited to qualitative concepts. Mathematical and thermodynamic models describing the relationship between contact angle and drop (bubble) volume are required.

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