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Asymmetric Wetting of Patterned Surfaces Composed of Intrinsically
Hysteretic Materials

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Wetting of chemically heterogeneous surfaces is modeled using a phase field theory. We focus on a chemically
heterogeneous surface composed of squares of one component material embedded in another. Unlike previous studies
where the component materials were characterized only by an equilibrium contact angle, in this paper each of the
component materials is constitutively allowed to exhibit hysteresis. Using this approach, we investigate the effect of
heterogeneity length scale on observed macroscopic behavior. Cassie theory is found to be applicable only in the limit of
vanishing length scale. For surfaces with a finite heterogeneity length scale, the advancing and receding contact angles
deviate from Cassie theory. We find that this deviation and its length scale dependence are asymmetric and depend on
the wetting properties of the embedded material relative to the contiguous substrate.

Introduction

Wetting of chemically heterogeneous surfaces is of importance in a wide range of practical applications ranging from inkjet
printing to biofluidic manipulation. In most of these applications, small quantities of liquid, usually in the form of sessile drops
are manipulated on composite surfaces. The composite surfaces are fabricated by regular arrangement of two or more com-
ponent materials with different wettability properties. The objective of such a design is to employ surface energy forces that
originate from the relative hydrophobic/hydrophilic interaction to manipulate and control the motion of the liquid. Because
of fabrication limitations, the component materials in turn are not entirely defect-free and could therefore exhibit contact
angle hysteresis. As we will show, the size of the component materials plays an important role in the macroscopically observed
behavior.

A fundamental quantity that describes this process is the contact angle, θ, which a sessile drop subtends at the triple line
where liquid, vapor, and solid phases meet. The equilibrium contact angle, θ_E, on a pure smooth surface can be obtained
theoretically from minimizing the system Gibbs free energy. However, for a real surface, where the drop could be subject to
pinning forces at various defect locations on the surface, this equilibrium condition is difficult to realize empirically owing to
a plethora of metastable states in the immediate energetic vicinity of the equilibrium (global energy minimum) state.1 The wettability
of real surfaces are therefore empirically characterized by the advancing and receding contact angles, which are measured
during a series of advancing and receding events respectively.2

The equilibrium apparent contact angle on a smooth chemically heterogeneous surface composed of pure component materials A
and B is given by the Cassie equation:3

\[
\cos\theta^C_j = f^A \cos\theta^A_j + (1-f^A) \cos\theta^B_j
\]

Here, we state the Cassie equation using the notation, θ^C_j (j = a, r, Y and j = A, B, C) refer to advancing, receding, and equilibrium
contact angles, respectively, for the pure materials A and B and the composite surface C, and f^A is the area fraction of material
A. First, eq 1 can only be derived for the equilibrium contact angle (j = Y) on a composite surface using the principle of Gibbs free
energy minimization. The extension of the same qualitative relationship to advancing and receding contact angles on com-
posite materials is mostly based on empirical observations.4,5 Some reports of theoretical justification6 and modifications7 have
also been published. This extension has typically been met with a mixed bag of results, with some researchers claiming success while
others claim a deviation from this relationship, especially for the receding angles.4,6,9 Second, Cassie eq 1 for the equilibrium
contact angles assumes that the pure materials A and B are intrinsically alloyed on the chemically heterogeneous surface. In
other words, any elemental area on the heterogeneous surface dA contains f^A dA of material A and (1 − f^A) dA of material B,
however small dA is allowed to become, which is the case only in the limit of vanishing length scale.10 Any real surface is, however,
bound to have a finite length scale associated with the heterogeneity, either from fabrication limitations or by design (for example,
in the case of droplet confinement for inkjet printing). The contact angle and therefore the wetting properties of such surfaces deviate from the Cassie theory, which assumes perfect homogeneity, as has been reported from experimental measurements by Woodward et al.11 and Cubaud and Fermigier.12 It
is therefore important to understand the implication of the

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finite of the length scale associated with the chemical heterogeneity on the advancing and receding angles on the composite surface in order to design such surfaces for targeted applications. We use a phase field theory to study these effects in this paper.

The phase field theory which has been recently reported is used to model the evolution of the sessile drop on a smooth heterogeneous surface such as seen in Figure 1. A few key details are reiterated herein for completeness. More details of this model can be found in the works of Vedantam and Panchagnula.\(^ {13,14}\) In this approach, a two-dimensional nonconserved phase field function, \(\eta(x,t)\), is used to distinguish between wetted and nonwetted regions on the surface. Similar diffuse interface approaches to modeling sessile drop dynamics, while not including the effects of contact angle hysteresis, have also been published recently.\(^ {15–18}\)

The system free energy functional can then be given by

\[
F = \int_A \left( f(\eta) + \frac{1}{2} \lambda |\nabla \eta|^2 \right) dA
\]

(2)

Here \(\lambda\) is the classical gradient coefficient and is shown to be related to the triple line tension associated with the solid—liquid—vapor triple line.\(^ {13,14}\) An evolution equation for \(\eta(x,t)\) is written in the Ginzburg—Landau framework to describe the evolution of the "wettedness" of the composite surface, which also describes the motion of the triple line separating the wetted and the dry regions on the solid substrate. The imbalance in the Young’s force, \(Y = \cos(\theta) - \cos(\theta_d)\) is incorporated into \(f(\eta)\) as a parameter that provides for the exchange of the relative stability of the two states. In this model, triple line tension arises naturally from the gradient coefficient, and contact angle hysteresis arises from the form of the kinetic coefficient. This kinetic coefficient and therefore the phase field model require only the advancing and receding contact angles of the component materials as constitutive inputs. The governing evolution equation for \(\eta(x,t)\) becomes

\[
\omega^{1/m} \dot{\eta} = (\lambda \nabla^2 \eta \frac{\partial f}{\partial \eta} - \delta \eta (|\nabla \eta|) \right)^{1/m} \times \text{sgn} \left( \lambda \nabla^2 \eta - \frac{\partial f}{\partial \eta} \right)
\]

(3)

Figure 1. Schematic of a chemically heterogeneous surface.

Here \(\omega\) is the rate dependent contribution to the contact angle hysteresis, and \(m\) is the power law coefficient in the rate dependent term. The values for \(\omega\) and \(m\) are chosen to match qualitative experimental observations that the measured contact angle hysteresis is relatively insensitive to the rate of volume injection and withdrawal. These values are therefore set to 1 in order to ensure that only the rate-independent term contributes to hysteresis during the kinetic evolution of the drop. \(H(x)\) in eq 3 denotes a function that takes on a value of 1 for \(x > 0\) and 0 for \(x \leq 0\), \(\text{sgn}(x)\) is a function that takes a value of 1 for \(x > 0\), −1 for \(x < 0\), and 0 for \(x = 0\), and \(\delta\) is the rate independent contribution to the hysteresis. This equation is solved by an explicit finite difference method on a fixed grid.

Results and Discussion

Initially, sessile drop kinetics simulations on a chemically homogeneous surface using the phase field theory are verified against the quasistatic experimental measurements from advancing and receding processes. The advancing and receding angles were measured on smooth hydrophilic and hydrophobic surfaces. Two specimens were considered: a silicon wafer with a thin oxide layer at the surface that is intrinsically hydrophilic, and a similar wafer rendered hydrophobic. The advancing and receding contact angles on the silicon wafers were measured to be 62° and 40° respectively. For this reason, the silicon sample was considered as a hydrophilic material.\(^ {19}\) The purpose of using this silicon sample is to use the wetting characteristics of "real" engineering silicon surfaces. The hydrophobic surface is attained by a vapor-phase reaction of the silicon wafer with organosilane reagent: heptadecafluoro-1,2,2,2-tetrahydro-decyldimethylchloro silane (FDDCS) that results in a self-assembled monolayer on its surface. The advancing (receding) contact angle of a water drop on the two specimens was measured using a dynamic contact angle analyzer\(^ 4\) employing the captive needle technique.\(^ 4\) Figure 2 represents the hysteresis loops of the contact angle versus the wetted circle radius (defined as the average radius of the circular triple line) on silicon (loop ABCD) and silane (loop PQRS) surfaces as the drop volume is cycled from 2.54 to 39.52 µL and 3.56 to 45.20 µL, respectively. The solid lines represent the contact angle predictions from the phase field theory. The circular and triangular symbols represent the instantaneous contact angles. From A to B (P to Q), the contact angle increases at a constant

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wetted circle radius until the advancing angle of silicon (silane) is reached. Further increase in the volume yields the asymptotic advancing angle with increase in wetted circle radius from B to C (Q to R). When the volume of the drop reaches 39.52 μL (45.20 μL), the volume withdrawal process is initiated. The drop contact angle is now observed to decrease at a constant radius from C to D (R to S) until the receding angle of silicon (silane) is reached. Further decrease in volume yields the asymptotic receding angle from D to A (S to P) at decreasing radius. From this figure, good agreement between the measured contact angle data and phase field theory can be noted, indicating the ability of the model to handle the quasistatic drop evolution process.

The phase field theory is now exercised to study sessile drop behavior on chemically heterogeneous surfaces of three cases of heterogeneities. The component materials employed are a hydrophobic material, HP ($\theta_a = 145^\circ$ and $\theta_r = 125^\circ$), and a relatively hydrophilic material, HL ($\theta_a = 95^\circ$ and $\theta_r = 83^\circ$). As mentioned before, the objective of this effort is to demonstrate the effect of the heterogeneity length scale on the macroscopic contact angle. In the first set of simulations (case I), we consider a situation where the two materials are intricately alloyed. We achieve this condition numerically by generating a random number between 0 and 1 to assign surface properties to each grid point. When the value of the random number is less than the desired area fraction of HP, the grid point is assigned the properties of HP; else, the properties of HL are assigned to that grid point. We use this set of simulations to demonstrate the effect of the lack of a heterogeneity length scale. In the second set of simulations (case II), we consider squares of HP of a side, $a$, separated by a distance, $b$, at centers and embedded in a surface of material HL on a square lattice of centers (see Figure 1). For this case, we consider the effect of changing the length scale, $b$, while maintaining the same HP area fraction, $f^A = 1 - a^2/b^2$. In the third case (case III), we consider a composite surface similar to case II, except that squares of HL are embedded in HP. The motivation for formulating cases II and III arises from the recent work of Priest et al., where they demonstrated an asymmetric deviation from Cassie theory for both advancing and receding angles.

Figures 3–6 show the variation of cosine of the advancing and receding contact angles on the composite surface plotted against the HP area fraction. The solid line in all the figures represents the values estimated by the Cassie eq 1. The data plotted in these figures was obtained as an average of a series of advancing and receding simulations. An initial condition is assumed for each simulation. For the advancing simulations, the drop was initially at an angle much larger than the advancing angles of the two component materials. For the receding simulations, the drop was initially at the just advanced state. From this initial state, eq 3

Figure 3. Effect of length scales on advancing contact angle measurements on the composite surface of material HP embedded in HL material (case II).

Figure 4. Effect of length scales on advancing contact angle measurements on the composite surface of material HL embedded in HP (case III).

Figure 5. Effect of length scales on receding contact angle measurements on the composite surface of material HP embedded in HL material (case II).

Figure 6. Effect of length scales on receding contact angle measurements on the composite surface of material HL embedded in HP material (case III).

was solved under constant volume conditions until the system reached an equilibrium state. At this point, a small volume is either added to or removed from the drop (for advancing or receding simulations respectively) without changing the phase field variable distribution and the process continued. At each drop volume, an instantaneous angle for the sessile drop is output. Figure 7 is a plot of the cosine of instantaneous angles and radius of the drop versus volume obtained from advancing simulations for case III for two different heterogeneity length scales ($b = 32 \mu m$ and $b = 128 \mu m$) at an HP area fraction of 0.5. As can be observed from the advancing simulations, the drop undergoes a series of pinning/depinning events where the contact angle increases as the volume increases, indicating pinning and relaxation of that angle to a smaller value indicating depinning.\textsuperscript{21-23} As can also be observed from this figure, the variation in the instantaneous angle increases with increasing length scale. This is due to the fact that when the drop comes depinned from a defect location, the triple line advances over the entire defect (which is larger in size for the larger length scale) before it equilibrates at a new location. The data presented in Figures 3-6 are obtained as an average of the instantaneous contact angles over at least two pinning/depinning events.

Figure 3 is a graph of the cosine of the macroscopic advancing contact angle versus HP area fraction for cases I and II. The circles in this figure represent the data for the case I where the materials are intricately alloyed. It may be noted that this case is consistent with the intent of Cassie’s derivation.\textsuperscript{10} The data for case I simulations follow the predictions from Cassie equation. Figure 3 also includes the advancing angle data from case II simulations. The data for different length scales, $b = 32, 64, \text{and } 128 \mu m$ are represented by the diamonds, squares, and triangles, respectively. These simulations predict the sessile drop behavior on surfaces with different length scale, $b$, for the same HP area fraction. As can be observed from this figure, the data show deviation from the Cassie theory. However, varying the length scale at a constant area fraction shows negligible variations in the macroscopic contact angle. Both of these observations are consistent with the experimental data from Woodward et al.\textsuperscript{11} and Cubaud and Fermigier,\textsuperscript{12} which were obtained under different heterogeneity length scale ranges

(10–100 nm in Woodward et al.\textsuperscript{11} and 100 to 400 \(\mu m\) in Cubaud and Fermigier\textsuperscript{12}) from the current study.

Figure 4 shows the variation of the cosine of the advancing contact angles with HP area fraction for a composite surface of squares of HL, embedded in HP (case III). The data for varying length scales, $b = 32, 64, \text{and } 128 \mu m$ are represented by open diamonds, squares, and triangles, respectively. The data shows an increasing deviation from the Cassie theory with increase in the length scale.

Figure 5 is a graph of the cosine of the receding contact angles versus HP area fraction for a composite surface of squares of HP embedded in HL (case II). The data for different length scales, $b = 32, 64, \text{and } 128 \mu m$ are represented by the solid diamonds, squares, and triangles, respectively. The deviation from Cassie theory increases with an increase in the length scale. It may be recalled that the advancing angles for the same surface showed a significant deviation from Cassie theory with the difference that varying the heterogeneity length scale had little effect on the advancing contact angle.

Figure 6 is a graph of the cosine of the receding contact angles versus HP area fraction for a composite surface of squares of HL, embedded in HP (case III). It can be observed from data in this figure that there is negligible effect of varying length scale.

In summary, in case II, the advancing angles show significant deviation from Cassie theory, which is independent of length scale, whereas the deviation of the receding angles from Cassie theory is strongly dependent on the length scale of the heterogeneities. On the contrary, the deviation of the advancing angles for case III from Cassie theory is strongly dependent on length scale, whereas the deviation for the receding angles is not. The non-dependence of the macroscopic contact angles on length scale, for advancing processes in case II and for receding processes in case III can be explained by studying the local structure of the triple line in the vicinity of a single heterogeneity. Figure 8 represents a series of triple lines obtained during advancing and receding processes for an area fraction of 0.5 for case II and case III.\textsuperscript{24} These figures are generated after zooming into a small region involving only three

(22) Johnson, R. E.; Dettre, R. H. Contact Angle, Wettability, and Adhesion; American Chemical Society: Washington, DC, 1964, p 43.
(23) Iwamatsu, M. J. Colloid Interface Sci. 2006, 297(2), 772–777.
(24) It may be observed that Figure 8 is qualitatively similar to the experimental photographs of contact line structure from Cubaud and Fermigier (see Figure 7a therein).
squares for clarity. It may be recalled that case II represents a surface where squares of a relatively hydrophobic material are embedded in a hydrophilic material. A fundamental difference between cases II and III is in the nature of the contiguous material. In case II, the contiguous material is hydrophilic, whereas in case III the contiguous material is hydrophobic. During the advancing event, the hydrophobic material attempts to pin the triple line since a relatively high local contact angle is required to manifest on the hydrophobic square, before the triple line can advance to wet additional material. In this case, the pinning centers are discrete, and the triple line remains pinned by the hydrophobic squares (defect line) independent of the length scale of the defect (Figure 8a). The contact angle for this case therefore deviates from the Cassie theory because of the contorted nature of the triple line, but that deviation is independent of the length scale of the defect. For a constant length scale, the number of squares per unit area, however, scales with area fraction, and hence the overall macroscopic contact angle is still a function of area fraction. This case is identical to the experimental observations of Woodward et al.11 and Cubaud and Fermigier.12 In addition, this qualitative observation is also consistent with our own advancing contact angle measurements on surfaces with square cavities, where the point defect density (corners of the squares) is independent of both length scale and area fraction.9

In case III, the triple line lies almost entirely on the contiguous hydrophobic material (Figure 8c). In the advancing event, the triple line advances over the contiguous hydrophobic material until it meets the row of hydrophilic squares and jumps over them almost instantaneously. The distance the triple line moves forward over the hydrophilic material is dependent on the length scale of the hydrophilic squares, and thus the effective contact angle strongly depends on the length scale of the squares.

During the receding process, the hydrophilic material is the “pinning” material since a smaller contact angle is required to be achieved before the triple line can recede over this material. Thus, in case II, the contiguous material attempts to pin the triple line, while, in case III, the discrete square areas provide the pinning locations. Again as in the advancing case, the discrete pinning centers in case III (Figure 8b) cause the triple line to become contorted, but the number density of the pinning locations does not depend on the length scale of the embedded squares. However, in case II (Figure 8d), the triple line once again lies almost entirely on the contiguous hydrophilic material during the receding process and recedes readily and rapidly over the hydrophobic material. The distance it jumps over the hydrophobic material depends on the length scale of the hydrophobic material, therefore affecting the macroscopic contact angle of the drop. Thus, in summary, the wetting properties of the contiguous material play a key role in determining the effect of the length scale of heterogeneities on the contact angle and its deviation from Cassie predictions.

Another phenomenon that we would like to report relates to the violation of symmetry during the advancing or receding processes. Figure 9 is a plot of triple lines observed during the advancing process on a case II surface of area fraction 0.5. The initial condition is a perfectly symmetric drop with a circular triple line, exhibiting an overall 4-fold symmetry. As the advancing process proceeds without explicitly imposing the condition of symmetry, the triple line naturally evolves into and through a series of states that violate the initial 4-fold symmetry. The drop chooses these intermediate states owing to the fact that these states offer lower energy alternatives to the state with 4-fold symmetry. We present this result as evidence of the need to perform sessile drop kinetics and dynamics simulations without explicit imposition of symmetry, which is typically invoked to save computational cost.16

From the above observations, it can be summarized that the phenomenon of “asymmetric” hysteresis can be observed on the chemically heterogeneous surface where either the advancing or the receding contact angle deviates from the Cassie curve for a surface of same area fraction and length scale. Similar behavior has also been experimentally reported on gold surfaces, although their conclusions were related to the effect of defect energy on the hysteresis asymmetry.20 According to the Cassie theory, the
chemical heterogeneity in the surface is such that a small elemental area, dA, of the surface contains \( f_A dA \) of material A and \( (1 - f_A) dA \) of material B. This can be achieved for the case where the two materials were considered to be intricately alloyed. The effect of the length scale would be absent in such consideration. Thus we see agreement of both the advancing and receding data with the Cassie theory, as can be seen from the solid and open circles in Figures 3–6. But many of the real surfaces have finite length scales associated with the chemical heterogeneity. Fabrication of the composite surface as squares of one material in another brings in this effect of the length scale, thus exhibiting a deviation from the Cassie curve. Further, it may be noted that all the data points presented were obtained on surfaces where the characteristic length scale associated with the heterogeneity was at least 10 times smaller than the drop wetted circle radius \( R \approx 1 \text{ mm} \). This implies that, on the length scale of the drop, the surface can be considered to be a nearly homogenized heterogeneous surface. However, a significant deviation from Cassie theory is still noticed even for the small characteristic length scale of the heterogeneity \( b/R \approx 0.032 \). The nature of the modification of a nearly circular triple line owing to the local variations in surface energy can be observed for the composite surface of these materials.\(^{17,25,26}\) This variation in the triple line structure is carried over into macroscopic contact angle observations. Thus, for a constant area fraction of HP, we observe that the nature of the contiguous material has an effect on the macroscopic contact angle.

Cassie eq 1 was derived from Gibbs free energy minimization principles. As the drop advances, the triple line, however, encounters several metastable wells in the energy landscape and could remain trapped in one of such wells. This mechanism has been proposed to explain the difference between the advancing angle and the thermodynamic equilibrium angle. However, the metastable well associated with chemical heterogeneity has to be based on the local change in surface energy at the triple line as a change in wetted area. This change in free energy is in turn related to the local area fraction in the neighborhood of the triple line as opposed to the global area fraction obtained from the geometric arrangement of the squares. Therefore, the local area fraction that the triple line experiences as it advances is apt for the calculation of the expected contact angle. Similarly, the area fraction that is pertinent to the receding angle calculation is that obtained near and just inside the triple line.

In conclusion, we studied wetting hysteresis on a smooth, chemically heterogeneous surface and investigated the effect of the length scale associated with this heterogeneity. The advancing and the receding measurements are observed to be significantly different based on the arrangement of the two materials on the heterogeneous surface. We propose that this asymmetric hysteresis depends on the distinct wetting behavior close to the triple line of the drop. We show that the size of the component materials plays a significant role in the realized macroscopic contact angles only when pinning is not significant. This work provides insight into the significance of the fabrication procedure, taking into account the length scale effect, for a chemically heterogeneous surface of desired applications.


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