

Phase Field Modeling of Hysteresis in Sessile Drops

Srikanth Vedantam^{1,*} and Mahesh V. Panchagnula^{2,†}

¹*Department of Mechanical Engineering, National University of Singapore, Singapore 117576*

²*Department of Mechanical Engineering, Tennessee Technological University, Cookeville, Tennessee 38505, USA*

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We propose a novel approach to describe wetting of plane solid surfaces by liquid drops. A two-dimensional nonconserved phase field variable is employed to distinguish between wetted and nonwetted regions on the surface. The imbalance in the Young's force provides for the exchange of relative stability of the two phases. The three-phase contact line tension arises from the gradient energy and contact angle hysteresis from the kinetic coefficient. Using this theory, we discuss contact angle hysteresis on chemically heterogeneous surfaces. We show significant departure from the classical Cassie theory, which is attributed to defect pinning of the continuous triple line.

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The wetting of surfaces by liquid drops, as characterized by contact angles, has been studied for several decades due to the numerous practical applications [1]. Experimentally, the contact angle of a sessile drop has been observed to take a range of values. The highest (lowest) stable contact angle is termed the advancing (receding) angle θ_a (θ_r), above (below) which the radius of the wetted area will increase (decrease), thus bringing the drop to manifest this limiting value of contact angle. Intermediate drop contact angles, $\theta_r < \theta < \theta_a$ are all metastable states for the drop [1]. The contact angle *hysteresis* (CAH) $\Delta\theta = \theta_a - \theta_r$ proves to be an important quantity that determines the ease of drop movement and self-cleaning nature of the surface [2].

The origin of CAH is attributed to several factors such as surface roughness, chemical contaminants and solutes in the liquid [1], among others. Experimentally, CAH has been found to be either independent [3,4] or primarily caused by surface roughness and heterogeneity [5]. Theoretical models of CAH have focused on roughness [6] and heterogeneity [7] as providing energy barriers to the drop attaining the global free energy minimum. In this connection, it has been pointed out that the drop metastable state is a phenomenon associated with the one-dimensional three-phase contact line (CL) kinetics and not the two-dimensional surface energy [1,8]. Owing to the directional nature of the choice of the drop metastable state, a kinetic model of the triple line appears necessary for modeling CAH. In addition, it proves difficult to incorporate each of the potential sources of CAH explicitly. It is thus desirable to develop a coarse-grained model which demonstrates hysteresis without explicit consideration of the underlying causes.

In this Letter, we propose a simple phenomenological model of a sessile liquid drop on a solid surface. The model is developed in a Ginzburg-Landau framework (widely referred to as the phase field model) first used to describe superconducting phase transitions [9]. In the context of wetting by liquid drops, we note three distinctive features

of the model: (i) The three-dimensional system is described in a two-dimensional setting. Assuming the drop radius to be much smaller than the capillary length ($R \ll \sqrt{\gamma/\rho g}$) the drop shape is approximated by a spherical cap. The surface area of the liquid-vapor interface is then related to the wetted surface area on the solid surface and the contact angle. A two-dimensional description of the wetted and nonwetted regions on the solid surface is thus sufficient to describe the total energy of the solid-liquid-vapor system. (ii) A special form of the kinetic coefficient is chosen to describe rate independent CAH. (iii) The triple line tension arises naturally from the gradient energy term of the phase field model. For this model, the only constitutive information required is the advancing and receding angles and the surface energy of the liquid-vapor interface. The physical origin(s) of hysteresis is not explicitly considered.

We employ a two-dimensional field variable $\eta(\mathbf{x}, t)$, $\mathbf{x} \in A$ to describe the amount of wetting on the solid surface. The phase field variable $\eta(\mathbf{x}, t)$ takes a value 1 where the solid surface is in contact with liquid and 0 where the solid surface is in contact with vapor. The phase field variable suffers continuous but steep changes at the boundary between the wetted and nonwetted regions. Since our order parameter describes the amount of wetting of the solid surface, we are able to use a nonconserved phase field variable in contrast to [10] in which a three-dimensional conserved order parameter describes the volume of the liquid.

Consider a sessile drop on a smooth chemically homogeneous surface. Neglecting gravity, the drop takes the shape of a spherical cap and the wetted solid surface region is circular. For a drop volume V and wetted circle radius R , from geometrical considerations,

$$V = \frac{1}{3}\pi R^3(2 - 3\cos\theta + \cos^3\theta)/\sin^3\theta, \quad (1)$$

where θ is the contact angle of the drop.

We write the free energy of the system as

$$\mathcal{F} = \int_A \left(h(\eta) + \frac{1}{2} \lambda |\nabla \eta|^2 \right) dA, \quad (2)$$

where dA is the elemental area *on the solid surface*. The term $\frac{1}{2} \lambda |\nabla \eta|^2$ with $\lambda > 0$ represents a gradient energy which penalizes the presence of interfaces between regions of constant η . In the present context, the interface between the wetted and nonwetted regions of the solid surface represents the triple line between the solid, liquid, and vapor phases. The gradient term is thus associated with the triple line tension.

In Eq. (2), $h(\eta)$ is a double-well potential with minima at $\eta = 0$ and $\eta = 1$. Since $\eta = 0$ represents the nonwetted region, we account for the solid-vapor interfacial energy (γ_{SV}) by requiring $h(0) = \gamma_{SV}$. At $\eta = 1$, the energy contribution arises from both the solid-liquid (γ_{SL}) and the liquid-vapor (γ_{LV}) interfacial energies: $dE = \gamma_{SL} dA + \gamma_{LV} dA_{LV}$, where dA_{LV} is the elemental area on the spherical cap (the liquid-vapor interface of the drop). Using Eq. (1), we can show that $dA_{LV} = dA \cos\theta$. Thus, requiring $h(1) = \gamma_{SL} + \gamma_{LV} \cos\theta$ allows us to account for energy contributions of the solid-liquid and liquid-vapor interfaces. The Gibbs free energy of the three-dimensional system is thus reduced to a two-dimensional representation. For convenience, without loss of generality, we choose $h(1) = \gamma_{SL} + \gamma_{LV} \cos\theta - \gamma_{SV}$ and $h(0) = 0$ by shifting the reference energy of the system. The two wells have equal energy when $\gamma_{SL} + \gamma_{LV} \cos\theta_Y - \gamma_{SV} = 0$, which is the classical Young's equation for the thermodynamic equilibrium contact angle θ_Y .

We choose the form $h(\eta) = \gamma_{LV} \{ (1 - 3H)\eta^4 + 2(2H - 1)\eta^3 + \eta^2 \}$, where $H = \cos\theta - \cos\theta_Y$ is the Young's force imbalance which induces motion in the drop. This form is chosen such that $h(\eta)$ has minima at $\eta = 0, 1$ and $h(1) - h(0) = \gamma_{LV} H$. Figure 1 is a plot of the coarse-grained free energy of the system $h(\eta)/\gamma_{LV}$ for

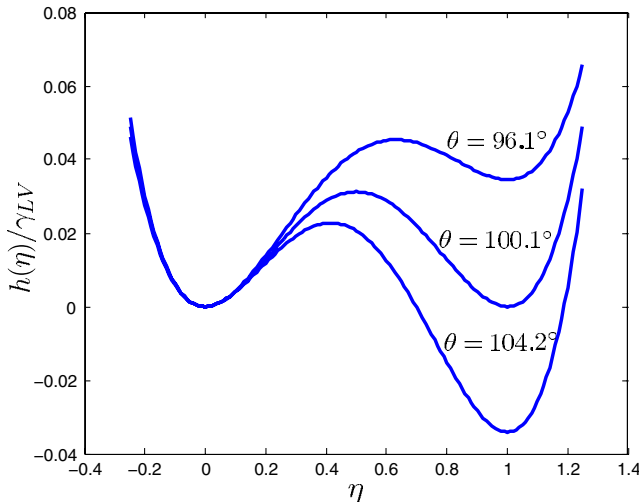


FIG. 1 (color online). Coarse grain energy $h(\eta)/\gamma_{LV}$ for three contact angles.

three different contact angles. The middle curve corresponds to the Young's equilibrium condition. The equilibrium Young's angle for the material is taken to be the average of the cosines of the advancing and receding angles $\theta_Y = \cos^{-1}[\frac{1}{2}(\cos\theta_a + \cos\theta_r)] = 100.1^\circ$; using typical values for a silanized surface $\theta_a = 104.2^\circ$ and $\theta_r = 96.1^\circ$, and $\gamma_{LV} = 72.8 \text{ mJ/m}^2$ [11].

The evolution equation in the Ginzburg-Landau framework is of the form

$$\beta \dot{\eta} = - \frac{\delta \mathcal{F}}{\delta \eta} = \lambda \nabla^2 \eta - \frac{\partial h(\eta)}{\partial \eta}, \quad (3)$$

where δ is the functional derivative and $\beta > 0$ is the kinetic coefficient. Equation (3) is solved in conjunction with the volume constraint Eq. (1) using the wetted circle radius of the drop $R(t) = \sqrt{(1/\pi) \int \eta(\mathbf{x}, t) dA}$. For a given drop volume $V(t)$ and wetted circle radius $R(t)$, the contact angle $\theta(t)$ is solved using Eq. (1). For $\theta < (>) \theta_Y$, $h(1) > (<) h(0)$ and the nonwetted (wetted) region is metastable. The resulting Young's force (H) causes the evolution of η which changes the wetted circle radius, thereby causing the contact angle to tend towards the equilibrium contact angle.

Next, we examine the role of the gradient term to make the connection with the triple line tension. For the case of a circular wetted footprint of radius R , of a sessile drop on the surface; the evolution Eq. (3) in polar coordinates is $\beta \dot{\eta} = \lambda [\partial^2 \eta / \partial r^2 + (1/r) \partial \eta / \partial r] - \partial h / \partial \eta$. Multiplying the equation by $\partial \eta / \partial r$ and integrating from $0 < r < \infty$, we obtain (assuming constant β)

$$\alpha \beta v = h(0) - h(1) - \alpha \lambda / R, \quad (4)$$

where we have used the boundary conditions $\eta = 1$, $\partial \eta / \partial r = 0$ at $r = 0$ and $\eta = 0$, $\partial \eta / \partial r = 0$ at $r = \infty$. Here, $v = (\partial \eta / \partial t)_r / (\partial \eta / \partial r)_r$ is the velocity of $\eta = \text{constant}$ surfaces [12] and $\alpha = \int_0^\infty (\partial \eta / \partial r)^2 dr$. Equation (4) is the sharp interface limit of the phase field theory [13]. For a stationary interface, Eq. (4) reduces to $\gamma_{SL} + \gamma_{LV} \cos\theta'_Y - \gamma_{SV} + \tau/R = 0$ which is the modified Young's equation accounting for triple line tension with $\tau = \alpha \lambda$ [14]. The contact angle for a spherical drop of finite radius θ'_Y is larger than the Young's contact angle θ_Y for positive line tension. We note that since the gradient coefficient plays the role of the line tension, negative values of τ reported in literature (e.g., [15]) cannot be treated using this theory. A full three-dimensional description may be required in such a case.

If the kinetic coefficient β is chosen to be constant, it can be seen from Eq. (4) that metastable contact angles are not allowed [16]. Furthermore, in this case CAH is dependent on the interfacial velocity and vanishes under quasi-static conditions (nearly zero interfacial velocity). However, it has empirically been observed that CAH is nonzero and nearly independent of the rate of interface motion at small expansion rates [3,17]. In general, the kinetic coefficient β is allowed to be a function of $(\mathbf{x}, t$,

η , $\dot{\eta}$, $\nabla\eta$) with the restriction that $\beta > 0$ for all admissible values of its arguments [13]. Thus we choose a modified kinetic coefficient of the form $\beta = (\delta\mathcal{H}(|\nabla\eta|) + \omega|\dot{\eta}|^m)/|\dot{\eta}|$, $\delta, \omega > 0$, where \mathcal{H} is the Heaviside function $\mathcal{H}(x) = 1$ for $x > 0$ and $\mathcal{H}(x) = 0$ for $x \leq 0$. δ is the rate independent contribution to the hysteresis width (and is related to θ_a, θ_r measured at quasistatic drop conditions) whereas $\omega|\dot{\eta}|^m$ provides a power law dependence of the hysteresis on the velocity of triple line. This form is similar to that used in [18] to model the hysteresis of isothermal stress-strain curves in shape memory alloys. Using this form for the kinetic coefficient, the evolution Eq. (3) can be rewritten as [18]

$$\omega^{1/m}\dot{\eta} = \left(\left| \lambda\nabla^2\eta - \frac{\partial h}{\partial \eta} \right| - \delta\mathcal{H}(|\nabla\eta|) \right)^{1/m} \times \text{sgn}\left(\lambda\nabla^2\eta - \frac{\partial h}{\partial \eta} \right), \quad (5)$$

where $\text{sgn}(S)$ gives the sign of S . In the above equation δ is the imbalance in the Young's force at which the drop remains stuck in the advancing and receding angles for $\dot{\eta} \rightarrow 0$; thus $\delta/\gamma_{LV} = \frac{1}{2}(\cos\theta_r - \cos\theta_a)$. Note that hysteresis in the current model arises from kinetics as hypothesized in [8].

We choose $\lambda = 2.25 \times 10^{-11}$ J, which yields a value for $\tau \sim 10^{-7}$ J/m, consistent with empirical observations [7]. The equations were spatially discretized using a grid of $dx = dy = 1.5 \mu\text{m}$ (typical wetted circle radius is $R = 1.2$ mm). For $\theta_a = 104.1^\circ$ and $\theta_r = 96.9^\circ$, the rate independent hysteresis parameter $\delta = 4.4$ mJ/m². The numerical simulations in this work are performed under quasistatic conditions. By this we mean that the drop contact angles and wetted radius are obtained as $\dot{\eta} \rightarrow 0$. The power law exponent is set to $m = 1$ (as is standard in the Ginzburg-Landau equation) and the rate coefficient $\omega = 20$ Js/m². In the current work only the rate independent term is obtained from the quasistatic hysteresis data. The rate dependent term does not contribute to hysteresis under quasistatic conditions [17]. The ω term facilitates the kinetic evolution of the drop from an arbitrary initial state to the final equilibrium condition.

We now employ our model to study chemically heterogeneous surfaces which are of great practical interest in automanipulation of sessile drops. Consider a smooth heterogeneous surface composed of two component materials A and B with equilibrium contact angles θ_Y^A and θ_Y^B , respectively. The equilibrium contact angle on the heterogeneous surface is given by the Cassie equation [19]

$$\cos\theta_Y^C = f\cos\theta_Y^A + (1-f)\cos\theta_Y^B, \quad (6)$$

where f is the area fraction of material A . Equation (6) can be derived from Gibbs free energy minimization [7]. It is worth emphasizing that the Cassie equation relates the *equilibrium* contact angles and area fractions of the component materials to the equilibrium contact angle on the

composite surface θ_Y^C . It has been widely hypothesized that Eq. (6) also holds for advancing and receding angles, which are determined by CL kinetics. Since the current model incorporates both surface free energy minimization as well as the CL kinetics, we are in a position to test this hypothesis. We accomplish this by modeling a sessile drop on a composite surface of two materials with identical equilibrium contact angles but with slightly different amounts of hysteresis: $\theta_a^A = 104.1^\circ$, $\theta_r^A = 96.9^\circ$ ($\delta^A = 4.4$ mJ/m²) and $\theta_a^B = 104.8^\circ$, $\theta_r^B = 96.2^\circ$ ($\delta^B = 5.3$ mJ/m²).

We perform numerical simulations of a drop spreading on a smooth surface composed of squares of material B of side a centered b apart embedded in material A . By varying a in the range of 0–75 μm and setting $b = 75 \mu\text{m}$ we obtain different area fractions of component B . Figure 2 shows the contact angle as a function of the area fraction of component B . The advancing and receding angles follow Cassie theory closely. It may therefore be inferred that for a case of a composite material of similar components, Cassie theory applied to advancing and receding angles is justified. For small differences in the component material properties such as the current case, the CL pinning strength at the sharp material property discontinuities is sufficiently low that the CL is relatively unwrinkled and remains circular [See Fig. 3(a)]. In addition, the inset in Fig. 2 shows that the model is capable of reproducing CAH. The effect of line tension becomes apparent from CAH observed when a water drop is cycled between volumes of 1 and 10 μL on a smooth homogeneous surface A (inset in Fig. 2). The slight decrease in the advancing angle θ_a with volume from points B to C is due to the decreasing effect of τ/R (see the modified Young's equation) [14].

We next examine the situation for composite materials with dissimilar component surfaces. When the hysteresis

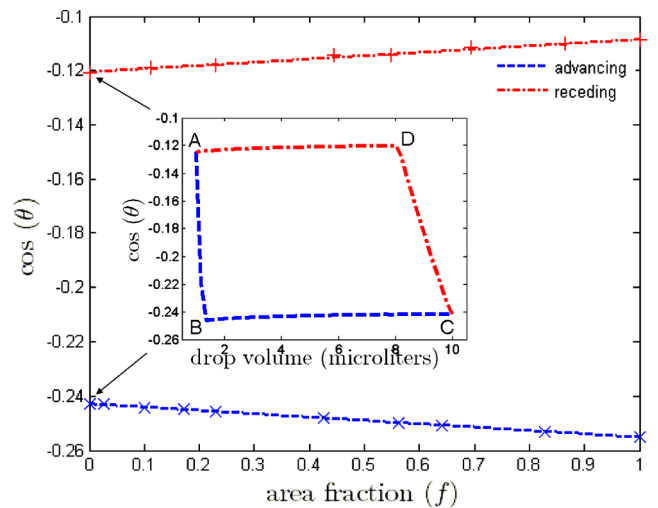


FIG. 2 (color online). $\cos\theta$ as a function of the area fraction of component B . The lines represent Cassie theory predictions and the symbols represent the numerical simulations. The inset shows the hysteresis for a homogeneous surface A .

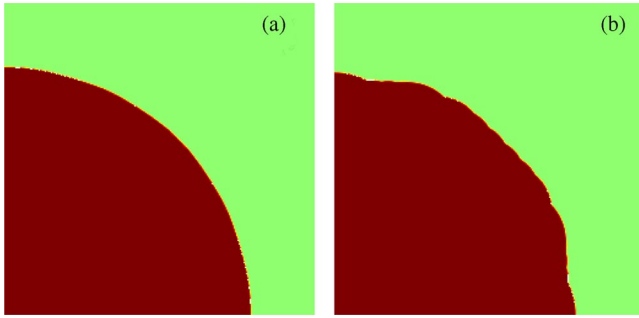


FIG. 3 (color online). (a) Three-phase contact line for $\theta_a^A = 104.1^\circ$, $\theta_r^A = 96.9^\circ$ and $\theta_a^B = 104.8^\circ$, $\theta_r^B = 96.2^\circ$. (b) Contorted three-phase contact line due to strong pinning when $\theta_a^A = 104.1^\circ$, $\theta_r^A = 96.9^\circ$ and $\theta_a^B = 119.9^\circ$, $\theta_r^B = 83.4^\circ$.

value of material B is increased to $\theta_a^B = 119.9^\circ$, $\theta_r^B = 83.4^\circ$ ($\delta^B = 22.1 \text{ mJ/m}^2$), Cassie theory is found to underpredict the advancing angle and overpredict the receding angle. When the difference between the wettability properties of the two component materials is sufficiently large, triple line is strongly pinned locally resulting in a wrinkled state [Fig. 3(b)]. The wrinkling of the CL and resulting deviation from Cassie equation has also been experimentally observed in [20]. Note that the contortion of the CL results in change in the local contact angle along the CL. We use the spherical cap approximation to determine the macroscopic contact angle. An asymptotic analysis shows that contortion of the CL provides an $\mathcal{O}(\varepsilon^2)$ correction to the equivalent spherical cap surface area, where ε is the ratio of the CL wrinkling amplitude to the drop average footprint radius. Thus this method is applicable to situations where $\varepsilon \ll 1$.

Finally, we test Cassie theory in the case of a composite surface consisting of a silanized surface (material A) and an “ideal superhydrophobic material” with $\theta_Y^B = 180^\circ$ and no hysteresis ($\delta^B = 0$) (material B). Figure 4 is a

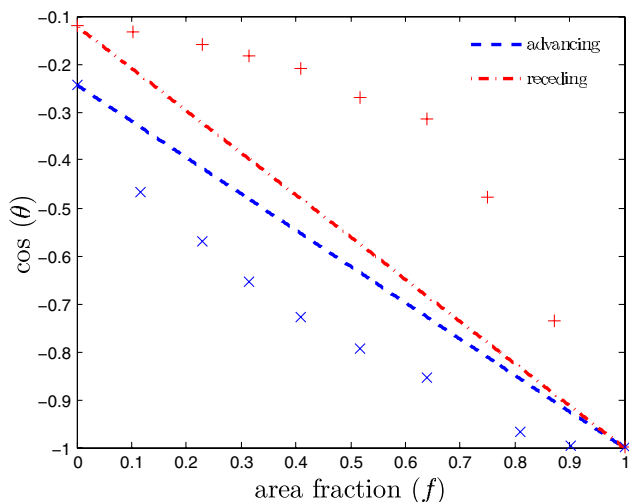


FIG. 4 (color online). $\cos\theta$ as a function of the area fraction of component B . The lines represent the Cassie theory predictions and the symbols represent the numerical simulations.

plot of $\cos\theta$ versus area fraction of material B . As can be observed, both advancing and receding angles are, respectively, greater and less than that predicted by Cassie theory due to the strong pinning forces that arise at the sharp discontinuities in surface properties, which cause the CL in the advancing (receding) situation to be constrained at a wetted circle radius less (greater) than the radius predicted based on Cassie theory.

In conclusion, we report a novel two-dimensional phase field method to describe wetting of surfaces by liquid drops. The exact three-dimensional description is reduced to a two-dimensional representation by assuming that the drop takes the shape of a spherical cap and is not distorted by local CL wrinkling. The gradient energy term describes the triple line tension and CAH is obtained through a modified kinetic coefficient. Numerical simulations of sessile drops on composite surfaces show deviation from the classical Cassie theory for large pinning effects originating at the discontinuities in the material properties. The pinning is apparent through wrinkling of the CL. The theory has potential for wide applicability in studying the behavior of sessile drops including the effect of defect pinning and in designing composite surfaces for sessile drop automanipulators.

*srikanth@nus.edu.sg

†mvp@ntech.edu

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