THEORETICAL CONSIDERATION OF CONTACT ANGLE HYSTERESIS

USING SURFACE-ENERGY-MINIMIZATION METHODS

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Abstract

In recent years, advances in coating manufacturing processes have allowed wetting characteristics of a surface to be tuned with micro/nano morphologies. Today, complex surface geometries can be created with various surface treatment methods. These advances can be implemented in phase-change heat-transfer applications, such as condensation, which relies on droplet behavior on a surface. Therefore, it is important to gain a fundamental understanding of wetting characteristics of textured surfaces having different geometrical configurations. This can be accomplished by studying the behavior of a single droplet on a given surface. Drop shapes and behaviors are affected by surface energies of different interfacial surfaces and surface morphologies. Contact angle hysteresis (CAH) – which is the difference between advancing and receding angles – can be estimated by utilizing concepts of surface-energy minimization. This is essential in heat transfer applications, as parameters such as drop size and distribution in condensation heat transfer are determined by CAH. In this study, a mathematical model has been developed to estimate CAH on different surface geometries and degrees of wetting. Modeling results suggest that CAH increases with increasing degree of wetting. Further, CAH remains low at both high and low droplet contact angles, whether the surface is hydrophilic or hydrophobic.

Keywords: wetting, energy-minimization, contact angle hysteresis, condensation

Nomenclature

A	Area of control surface, m^2
A_C	Drop cap area, m^2
A_{LG}	Liquid/gas interfacial area, m^2
A_{SG}	Solid/gas interfacial area, m^2
A_{SL}	Solid/liquid interfacial area, m^2
A_P	Drop projection area, m^2
b	Fin diameter, m
E	Surface energy, J
E_{drop}	Drop energy, J
E_{hys}	Hysteresis energy, J
F	Line force, N/m
f_w	Projected area fraction for fully wetting space
h	Fin height, m
L	Fin distance, m
R	Drop radius, m
r_f	Roughness ratio
V	Drop volume, m^3

Greek Letters

γ	Surface tension, N/m
γ_{LG}	Liquid/gas surface tension, N/m
γ_{SG}	Solid/gas surface tension, N/m
γ_{SL}	Solid/liquid surface tension, N/m
θ	Contact angle
θ_0	Young's contact angle
θ_{adv}	Advancing contact angle
θ_{rcd}	Receding contact angle
θ_E	Equilibrium contact angle
ϕ	Ratio of the solid/liquid area to projection area
θ_{CB}	Cassie-Baxter contact angle
θ_W	Wenzel contact angle
θ_1	Contact angle with Component 1 of non-homogenous surface
θ_2	Contact angle with Component 2 of non-homogenous surface
F	Force due to hysteresis
T_2	Contact area underneath the drop

1. Introduction

Wetting is an essential phenomenon in various natural and technological processes such as medicine, soil and climate science, botany, painting, filtration, printing, and textiles impregnation. In recent years, various theoretical and experimental approaches have enabled the investigation of droplet shapes and behavior on different surfaces. Advances in nanomaterials research have provided scientists and engineers with a handle to study super-hydrophobicity and other interesting wetting properties [1-13]. Non-homogeneous surfaces are often presented in studies of super-hydrophobic surfaces and other complex morphologies that produce complex wetting characteristics. In earlier studies of wetting properties, such as contact angles, researchers began incorporating the notion of roughness. Numerous research papers devoted to the study of wetting of rough surfaces have been published over the last two decades.

It is important to understand how a single drop behaves on a surface. Wetting properties of a single droplet strongly influences the drop-size distribution in condensation heat transfer [14, 15]. Thermodynamics of such a droplet on the surfaces need to be understood to better understand such behavior [16]. Gibbs free energy, E , provides a relationship between surface energies in terms of interfacial contact areas and their respective surface energies, as in Equation (1),

$$E = A_{LG}\gamma_{LG} + A_{SL}\gamma_{SL} + A_{SG}\gamma_{SG} \quad (1)$$

where A_{LG} , A_{SL} , and A_{SG} are liquid/gas, solid/liquid, and solid/gas interfacial areas, respectively; and γ_{LG} , γ_{SL} , and γ_{SG} are the corresponding surface energies per unit area.

According to Young [17], the shape of a liquid droplet is determined by surface tensions produced by interfacial forces. Liquid droplets tend to spread evenly on the wetting surface, and spreading stops when all interfacial forces are balanced, i.e., liquid/solid, solid/gas, or liquid/gas. A liquid droplet forms a unique angle with the solid surface, as shown in Figure 1.

Young's equation for contact angles is obtained by balancing the forces, as given by Equation (2):

$$\gamma_{LG} \cos \theta = \gamma_{SG} - \gamma_{SL} \quad (2)$$

Similarly, Equation (2) can be obtained by minimizing surface energies with respect to the interfacial area given in Equation (1) and obtained in Equation (3):

$$dE = 0 = dA_{LG}\gamma_{LG} + dA_{SL}\gamma_{SL} + dA_{SG}\gamma_{SG}. \quad (3)$$

Fig. 1. Surface tension and contact angle of a liquid droplet.

Young's equation provides an important insight on the behavior of a droplet on static homogeneous surfaces. However, it does not give information on how a droplet behaves under an external influence or information about the shape of the droplet on a non-homogeneous surface [18]. While Young's equation provides fundamental insights on wetting of flat surfaces, it has also been the basis of advanced wetting models on uneven surfaces [10, 12, 19-22]. Notably, Wenzel [21] was one of the first to examine wetting on rough surfaces. Wenzel established the relationship between the roughness ratio, which is the area of a rough surface to the area of the projected flat surface. Wenzel established the following equation for homogeneous wetting conditions:

$$\cos \theta_W = r_f \cos \theta_0 , \quad (4)$$

where r_f , θ_W , and θ_0 are the roughness ratio, the Wenzel contact angle, and Young's flat surface contact angle, respectively. Later, Cassie and Baxter [20] derived the equation for contact angles in non-homogeneous conditions to take into account the weighted average of various contact angles for different components:

$$\cos \theta_{CB} = \phi \cos \theta_1 + (1 - \phi) \cos \theta_2 , \quad (5)$$

where θ_1 and θ_2 are the contact angles for Component 1 and Component 2, respectively, and ϕ is the fraction of the solid/liquid contact area. Both the Wenzel and Cassie-Baxter models provide

some knowledge of wetting characteristics of rough surfaces. However, both models do not fully encompass the change occurring in wetting characteristics under the influence of external forces.

Contact angle hysteresis (CAH) is the most fundamental parameter which influences droplet behaviors. For example, several researchers have proposed models to explain how wetting changes with respect to CAH. The initiation of motion of drop on a surface has been explained by Gao and McCarthy et al. [23], where they note that the movement of a droplet is caused by the action of external forces from the environment. An external force deforms the shape of a droplet and causes an observable difference in contact-angle measurement. Contact angle hysteresis (CAH) can be defined as the difference between the maximum and minimum contact angles. CAH can be caused by an addition or subtraction of droplet masses, or by tilting the contact surface at an angle. It is very important to understand how the CAH process is initiated in order for it to be incorporated into an application such as condensation.

CAH can be measured experimentally in several ways [24]. One of the most common methods involves adding and drawing the liquid droplet mass in order to measure immediate advancing and receding angles. Another commonly used method involves measuring the advancing and receding angles of a droplet on a tilted surface. Notwithstanding, these methods may show large variations, and do not always represent accurate operating conditions on rough surfaces.

Additionally, CAH has been the subject of research for both experimental and theoretical models. Johnson [16] first explained the relationship between CAH and surface roughness. Over the past decade, experiments have advanced the understanding of the relationship between CAH and surface structure [11, 23, 25, 26]. For example, in experimental studies, micro-structured surfaces are often fabricated using known contact angles on flat surfaces [25]. Forsberg et al. [25] fabricated a micro-structured surface using various polymers with known flat-surface contact angles; they found that the cosine of CAH that resulted with these structured surfaces were linearly correlated with aspect ratios and fin densities. Forsberg [25] found that CAH increases with increasing fin heights of surfaces and roughness. Quere et al. [27] reviewed the relationship of roughness with surface energies and wetting characteristics. This group reviewed and adapted Young's equation and associated the equation for Gibbs energy to different roughnesses and geometries. Since wetting dynamics depend on surface tension and surface energy, Gibbs energy continues to be used in various wetting dynamic models, especially in CAH.

More recently, Hejazi et al. [28] proposed a multi-phase model to describe contact angle hysteresis for systems having multiple wetting components. Similar to the Wenzel and Cassie-Baxter models, this group described wetting under conditions of multi-phase surface energies. In their study, multiple rough surfaces were idealized as a single flat surface having various components with different wetting properties. The model took into consideration several geometrical factors, such as component spacing. The results of modeling for CAH were found to agree well with solid/water/air systems and solid/water/oil systems.

Since contact angle hysteresis is caused by additional energy supplied to the system, Adam and Jessop [29] proposed that the additional energy is proportional to the forces with CAH,

$$F = \gamma(\cos \theta_{rcd} - \cos \theta_{adv}) . \quad (6)$$

Similar models [30, 31] have explored contact angles and CAH in relation to the roughness contribution. Xu and Wang et al. [32] modified the Cassie-Baxter Equation and simulated contact line movements with different patterns of wetting components arrangements. It was found that the classic Cassie-Baxter Equation works relatively well when different components are homogeneously dispersed. However, contact line movement and CAH are highly depended upon the arrangement of wetting components. Moradi et al. [11] examined effect of geometry on spreading and CAH. They modeled the surface as parabolic cones, and modeled the spread of a drop on a surface, depending on geometries of the cones. It was found that CAH was highest with cones having high pillars. Other models [10, 28, 32-35] continued to modify the Wenzel and Cassie-Baxter drop models. McHale et al. [10] examined the limitations of these two models. In most cases, they were both good at describing trends of surface wetting. However, such factors as geometries potentially might be ignored in these models, and therefore could not be used above certain ranges, e.g., the Wenzel model on a super-hydrophobic surface.

Recent studies have found that geometrical factors, along with local wetting properties in surface morphologies, are very important. Wettability could be tuned by changing surface geometries of the same material [1, 11, 36-39]. In studies of nano-structured surface morphologies, relationships between wettability and geometrical factors continue to be of interest with regard to **drop behaviors**. The goal of this work is to provide a fundamental framework of the relationship between surface energy and geometry through mathematical modeling. CAH, which can be estimated, provides a design tool for tuning surface wettability.

2. Mathematic modeling

2.1. Single-drop modeling in relation to surface energy

For a liquid droplet to be stable on the surface, surface energies between solid, liquid, and gas interfaces are minimized with the respective interfacial areas, with surface energies equation as seen in Equation (1) and (3). Figure 2 illustrates the surface energies of a drop on a surface.

Fig. 2. (left)-Surface energies of a single drop. (right)-Typical water condensation on a sub-cooled copper surface

Assuming that a droplet resting on a surface is a spherical cap having drop radius R and contact angle θ , the drop volume, V (assuming a constant drop volume) and the cap surface area, A_C , are:

$$V = \frac{\pi}{3} R^3 [2 - 3 \cos \theta + \cos^3 \theta] \quad (7)$$

$$A_C = A_{LG} = 2\pi R^2 (1 - \cos \theta) . \quad (8)$$

Solid/gas surface energy, γ_{SG} , is responsible for spreading the drop, and solid/liquid energy, γ_{SL} , is responsible for holding the drop together. As the drop is spreading on the surface, there is a gain on solid/liquid interfacial area and the same amount of solid/gas interfacial area is lost. The changes in area for both interfaces should be the same, except with opposite signs, i.e., $\Delta A_{SL} = -\Delta A_{SG}$. The projected base area, A_P , is given by:

$$A_P = \Delta A_{SL} = -\Delta A_{SG} = \pi R^2 \sin^2 \theta . \quad (9)$$

Equations (1) and (3) could be rewritten as:

$$E = A_{LG}\gamma_{LG} + A_{SL}(\gamma_{SL} - \gamma_{SG}) \quad (10)$$

$$dE = 0 = \frac{dA_{LG}}{dA_{SL}}\gamma_{LG} + (\gamma_{SL} - \gamma_{SG}) \quad (11)$$

Applying conditions from Equations (7) to (11), Young's equation is obtained by minimizing the surface energy with respect to contact areas for a flat surface with Young's contact angle, θ_0 :

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos \theta_0 . \quad (12)$$

As a result, Young's equation states that the forces act in equilibrium on the contact line of the triple interfaces of solid, liquid, and gas as shown previously in Equation (2).

Assuming a constant volume, the drop radius R could be written in terms of V and θ so that the surface energy depends only on the contact angle. If so, the surface energy for a flat surface becomes:

$$E = \gamma[A_C - \cos \theta_0 A_P] \quad (13)$$

For convenience, the surface tension of a liquid, γ_{LG} , is replaced simply with γ . The liquid/gas interfacial area, A_{LG} , is replaced with A_C . The A_{SL} of a flat surface is projected by a flat surface area of the cap, A_P , for any contact angle θ .

In case of textured surfaces, additional parameters are needed to describe the surface geometries during wetting. The roughness parameters, r_f and r_s , are introduced for rough surfaces, where r_f is the ratio of the actual area to the projection area and r_s is the ratio of liquid/solid area as described in Cassie-Baxter equation. An idealized situation, where rough topographies are pillars extending from the surface, is shown in Figure 3.

Fig. 3. Idealized representation of surface roughness, where b is the diameter, h is the height, and L is the center-to-center separation distance.

L , b , and h represent pillar-to-pillar distance, diameter of the cylinder top, and the height of the pillars, respectively. In this representation, r_f and ϕ can be presented as follows:

$$r_f = 1 + \frac{\pi b h}{L^2} \quad (14)$$

$$\phi = \frac{\pi b^2}{4L^2} \quad (15)$$

For evaluating an equilibrium contact angle in textured surface, the surface energy of a droplet can be found, as shown in Figure 4. A fraction of the liquid could penetrate the spaces between the pillars when liquid droplet rests on the rough surface and starts to spread.

Fig. 4. Wetting on a textured surface.

A way to represent this phenomenon is needed in order to represent all wetting conditions on a rough surface. Therefore, f_w is introduced as the projected area fraction for a wetting space, where the fraction is between 0 and 1. The Cassie-Baxter state is achieved if f_w is 0, and the Wenzel state is achieved if f_w is 1, as shown in Figure 5.

Figure 5. Droplet with different wetting conditions for (a) the Cassie-Baxter state and (b) the Wenzel state.

Interfacial areas for liquid/gas, solid/liquid, and solid/gas should be found in order to determine the surface energy for a partially wetted textured surface. The liquid/gas area, A_{LG} , the solid/liquid area, A_{SL} , and the solid/gas area, A_{SG} , with given geometrical parameters, are expressed in Equations (16) and (17):

$$A_{LG} = 2\pi R^2(1 - \cos \theta) + (1 - f_w)(1 - \phi)\pi R^2 \sin^2 \theta \quad (16)$$

$$A_{SG} = -A_{SL} = [r_f f_w + \phi(1 - f_w)](\pi R^2 \sin^2 \theta) . \quad (17)$$

Substituting Equations (8) and (9) for the droplet cap and projection area, A_C and A_P , respectively, into Equations (18) and (19), the equations become:

$$A_{LG} = A_C + (1 - f_w)(1 - \phi)A_P \quad (18)$$

$$A_{SG} = -A_{SL} = [r_f f_w + \phi(1 - f_w)]A_P \quad (19)$$

On substituting Equations (18) and (19) into Equation (10), the surface energy becomes:

$$E = [A_C + (1 - f_w)(1 - \phi)A_P]\gamma_{LG} + \{[r_f f_w + \phi(1 - f_w)]A_P\}(\gamma_{SL} - \gamma_{SG}) \quad (20)$$

Using results for Young's contact angle from Equation (13) and substituting into Equation (20), the equation becomes:

$$E = \gamma \left[A_C - A_P \left([r_f f_w + \phi(1 - f_w)] \cos \theta_0 - (1 - f_w)(1 - \phi) \right) \right] \quad (21)$$

where $A_C = 2\pi R^2(1 - \cos \theta)$ and $A_P = \pi R^2 \sin^2 \theta$.

An equilibrium contact angle can be achieved when the surface energy is minimized and the differential of energy with respect to the contact angle is zero:

$$\frac{dE}{d\theta} = 0 = \gamma \left[\frac{dA_C}{d\theta} - \frac{dA_P}{d\theta} \left([r_f f_w + \phi(1 - f_w)] \cos \theta_0 - (1 - f_w)(1 - \phi) \right) \right] \quad (22)$$

As seen in the equation above, f_w and ϕ are taken as constants since the parameters represent the contact areas ratios for liquid, solid and gas. The area ratio should be the same with changing projection area as the drop spreads. When both sides are divided by γ and $dA_P/d\theta$, Equation (22) becomes:

$$\left(\frac{dA_C}{d\theta} \right) / \left(\frac{dA_P}{d\theta} \right) = [r_f f_w + \phi(1 - f_w)] \cos \theta_0 - (1 - f_w)(1 - \phi) \quad (23)$$

By simplifying left-hand side of Equation (23), equilibrium angle, θ_E , for a partially wetted textured surface is given as:

$$\cos \theta_E = [r_f f_w + \phi(1 - f_w)] \cos \theta_0 - (1 - f_w)(1 - \phi). \quad (24)$$

If no liquid penetrates into the spaces between the structures, then $f_w = 0$, where components 2 contact angle is assumed to be 180° with liquid/gas interface and the Cassie-Baxter equation is extracted from Equation (24) as:

$$\cos \theta_E = \phi \cos \theta_0 - (1 - \phi) \quad (25)$$

If spaces between structures are fully wetted, then $f_w = 1$ and Wenzel's equation can be extracted from Equation (24) as:

$$\cos \theta_E = r_f \cos \theta_0. \quad (26)$$

The equilibrium angle on a textured surface can be found with the given geometries, the contact angle on a flat surface, and the degree of wetting on a rough surface from Equation (24).

Contact angle hysteresis occurs when an external force acts on a droplet. This could be viewed as extra energy supplied to the system. This extra energy is included as an additional term in the surface energy equation:

$$E = E_{drop} + E_{hys} \quad (27)$$

A force, F , acting along the triple-phase contact line between solid, liquid, and gas, as shown in Figure 6, is responsible for the hysteresis energy, E_{hys} .

Fig. 6. Force, F , acting along the triple-phase contact line.

It is assumed that the force F acts in parallel to the wetting surface, and should be a minimum force that is required in order for the triple-phase contact line to move. The force F is directly proportional to the difference between the equilibrium angle and the advancing or receding angle. In case of an advancing angle, the resultant surface tension (because of F), γ_{res} can be written as:

$$\gamma_{res} = \gamma(\cos\theta_E - \cos\theta) \quad (28)$$

Force F acts on solid/gas and solid/liquid interfacial areas in order for the contact line to move parallel to the wetting surface. The hysteresis energy, then, can be written as:

$$E_{hys} = \gamma(\cos\theta_E - \cos\theta)[r_f f_w + \phi(1 - f_w)]A_P = F * T_2 \quad (29)$$

where:

$$T_2 = [r_f f_w + \phi(1 - f_w)]A_P .$$

T_2 represents the contact area underneath the drop. Substituting Equations (21) and (29) into Equation (27), the equation becomes:

$$E = \gamma\{A_C - A_P K\} \quad (30)$$

where:

$$K = [r_f f_w + \phi(1 - f_w)](\cos \theta_0 + (\cos \theta_E - \cos \theta)) - (1 - f_w)(1 - \phi).$$

Taking $dE/d\theta = 0$ in Equation (30) to find max/min angles, the equation becomes:

$$\frac{dE}{d\theta} = 0 = \gamma \left\{ \frac{dA_C}{d\theta} - \left(\frac{dA_P}{d\theta} \right) K - A_P \left(\frac{dK}{d\theta} \right) \right\} \quad (31)$$

where:

$$K = [r_f f_w + \phi(1 - f_w)](\cos \theta_0 + (\cos \theta_E - \cos \theta)) - (1 - f_w)(1 - \phi)$$

Dividing Equation (31) by $dA_P/d\theta$ and γ , the equation becomes:

$$0 = \frac{dA_C/d\theta}{dA_P/d\theta} - K - \frac{A_P}{dA_P/d\theta} \left(\frac{dK}{d\theta} \right) \quad (32)$$

$$\frac{dA_C/d\theta}{dA_P/d\theta} = \cos \theta$$

$$K = [r_f f_w + \phi(1 - f_w)](\cos \theta_0 + (\cos \theta_E - \cos \theta)) - (1 - f_w)(1 - \phi)$$

$$\begin{aligned} A_P &= \pi R^2 \sin^2 \theta, \frac{dA_P}{d\theta} = 2\pi R \left(\frac{dR}{d\theta} \right) \sin^2 \theta + 2\pi R^2 \sin \theta \cos \theta \\ &= 2\pi R \sin \theta \left(\frac{dR}{d\theta} \sin \theta + R \cos \theta \right) \end{aligned}$$

$$R = \left(\frac{3V}{\pi} \right)^{\frac{1}{3}} [2 - 3 \cos \theta + \cos^3 \theta]^{-\frac{1}{3}}, \frac{dR}{d\theta} = - \left(\frac{3V}{\pi} \right)^{\frac{1}{3}} \sin^3 \theta (2 - 3 \cos \theta + \cos^3 \theta)^{-\frac{4}{3}}$$

$$\frac{dK}{d\theta} = 2[r_f f_w + \phi(1 - f_w)] \sin \theta.$$

Simplifying Equation (32), one obtains:

$$\cos \theta = (f_w(r_f - \phi) + \phi)C_1 - (1 - f_w)(1 - \phi) \quad (33)$$

where:

$$C_1 = \cos \theta_0 + \cos \theta_E - \cos \theta + \frac{1}{2} \sin^2 \theta (\cos \theta + 2).$$

Thus, max/min angles can be solved with Equation (33) for known surface geometries and Young's contact angle.

3. Results and discussion

For studying a model, from Equations (14) and (15), the roughness factor, r_f , and the top-area projection factor, ϕ , are idealized as cylinders on a flat surface. The surface energy profile given in Equation (21) can change with varying pillar geometries and spacing. Changes in surface energy profiles in relation to varying contact angles are shown in Figure 7 for Young's contact angle, $\theta_0 = 60^\circ$, $\theta_0 = 90^\circ$, and $\theta_0 = 120^\circ$ for different f_w values; surface geometries are set at $b = 1\mu\text{m}$, $h = 2\mu\text{m}$, and $L = 3\mu\text{m}$. CAH can be affected by surface geometry factors as well as the ratio of a fully wetted area. Figure 8 demonstrates how CAH can be changed by varying the ratio of the fully wetted projected area with different pillar heights ($h = 0.5\mu\text{m}$, $1\mu\text{m}$, and $2\mu\text{m}$), while b and L are fixed at $1\mu\text{m}$ and $3\mu\text{m}$, respectively. The dependence of CAH on changes in the local flat-surface contact angle under varying wetting conditions can be seen from Figure 9. Surface geometries are fixed at $b = 1\mu\text{m}$, $h = 2\mu\text{m}$, and $L = 3\mu\text{m}$.

An increase in pillar height increases surface roughness and Figure 9 shows that CAH increases as roughness increases at $\theta_0 = 90^\circ$ across all values of wetting area ratio, f_w . CAH increases with $\theta_0 = 60^\circ$ for $f_w \leq 0.7$ but decreases for $f_w \geq 0.7$ as surface roughness increases. In the case of $\theta_0 = 120^\circ$, CAH decreases as roughness increases for all f_w values. At $\theta_0 = 90^\circ$, an increase in CAH with increasing roughness ratio could be explained as the presence of larger liquid/solid contact area for the same value of f_w . Therefore, a higher value of roughness ratio increases CAH. With a hydrophilic surface for $\theta_0 \leq 90^\circ$, the contact angle decreases as roughness increases; therefore, CAH increases with roughness. However, the contact angle decreases at a faster rate as f_w increases. As shown in Figure 7, the droplet spreads like a film at a faster rate as the wetting area increases, and CAH decreases at a higher value of f_w . The equilibrium contact angle increases on a hydrophobic surface when the value of the roughness ratio is large, as shown in Equation 26. The equilibrium contact angle increases at a faster rate at an increasing roughness ratio than the contact angle during the hysteresis state. Therefore, CAH decreases with an increased roughness ratio.

With a different roughness profile, CAH trends remain similar with respect to the projected wetting ratio, f_w , for each corresponding local Young's contact angle, θ_0 . Peak values are shown in Figure 7 in CAH for $\theta_0 = 60^\circ$. As has been explained earlier, as wetting area increases, CAH increases accordingly; at a high wetting ratio, f_w , as the contact angle approaches zero, CAH also decreases. At $\theta_0 = 90^\circ$, CAH increases as f_w increases; however, the rate of increase slows at

higher values of f_w . For intermediate Young's contact angles, an increasing solid/liquid contact area increases the surface energy; as a result, CAH increases. However, values for the equilibrium contact angle remain similar at higher values of f_w ; therefore, CAH remains flat at high wetting-area ratios. In cases of $\theta_0 = 120^\circ$, CAH increases with increasing f_w . This is due to a higher contact area of solid/liquid. When the drop spreads into spaces between the pillars, more and more energy is required to move the contact line of the drop. When the liquid is trapped inside the spaces between the gaps in a textured hydrophobic surface, it does not tend to spread to adjoining areas very easily. The liquid stagnates inside the gaps; thus more energy is required to induce movement on the contact line of a drop. CAH would increase with increasing values of f_w , as a result.

With fixed surface geometries, CAH increases with increasing wetted areas of a hydrophobic surface for $\theta_0 \geq 90^\circ$, as shown in Figure 9. In a hydrophilic surface with $\theta_0 \leq 90^\circ$, aside from a non-wetted surface where $f_w = 0$, CAH values are lower at $f_w > 0.75$; this phenomenon is more apparent when values for θ_0 decrease. Figure 9 shows that CAH values are at a peak with $f_w = 0.5$ if the surface is hydrophilic. These phenomena have been explained earlier for individual cases with regard to hydrophobic and hydrophilic textured surfaces. At $f_w = 0$, CAH remains flat and small with varying Young's contact angles. A minimum solid/liquid contact area is maintained; thus, little energy is required to move the droplet contact line. At $f_w = 0.25$, CAH decreases with increasing θ_0 . The droplet starts to spread out and the solid/liquid contact area increases. Since the contact line requires more energy to move in hydrophilic surfaces compared to hydrophobic surfaces, CAH tends to be higher with lower values of θ_0 . At $f_w = 0.5$, a similar trend is observed in the case of CAH vs. θ_0 . Since the contact area for solid/liquid is increased, more energy is needed to move the contact line in hydrophilic surfaces. At lower values of θ_0 , the drop starts to spread out and approaches film-like form and CAH starts decreasing. In cases of $f_w = 0.75$ and $f_w = 1$, there are clear maximum values of CAH with respect to Young's contact angle. The droplet spreads out and takes a film-like resemblance at a higher value of f_w as θ_0 decreases; thus, CAH is lowered as a result. As θ_0 increases, the equilibrium angle also increases; however, the maximum angle increases at a slower rate at the same time, as indicated in Equations (27) and (33).

Figure 7 Surface energy profiles vs. contact angles for (a) $\theta_0 = 60^\circ$, (b) $\theta_0 = 90^\circ$, and (c) $\theta_0 = 120^\circ$, where $b = 1 \mu\text{m}$, $h = 2 \mu\text{m}$, and $L = 3 \mu\text{m}$.

Figure 8 Contact angle hysteresis vs. fully wetted projection-area ratio, $b = 1 \mu\text{m}$ and $L = 3 \mu\text{m}$.

Figure 9 Contact angle hysteresis vs. Young's contact angles, $b = 1 \mu\text{m}$, $h = 2 \mu\text{m}$, and $L = 3 \mu\text{m}$.

4. Concluding remarks

In a **single-drop** model, contact angle hysteresis can be estimated using theories of surface energy. Roughness and the projected top-area ratios affect the surface energy profile with fixed Young's contact angles. Differences between surface energies in equilibrium states and the hysteresis state generally increases as the wetted solid/liquid area increases. However, differences in surface energies decrease in hydrophilic surfaces with increased wetted areas and roughness ratios. This indicates that the CAH can be lower when the droplet is in Wenzel's state than in partially wetted states. Differences in surface energies at low and high contact angles remain small in all wetting conditions. Results indicate that CAH remains low when Young's angle is either super-hydrophilic or super-hydrophobic ($\theta_0 \approx 0$ or $\theta_0 \geq 150^\circ$). It was found that CAH remains low with any Young's contact angle when the ratio for the totally wetted surface area is small. Further, CAH increases with increased roughness, in general. However, CAH was shown to have an optimum value with varying the wetted area ratio when the surface is hydrophilic. Moreover, CAH was shown to be lower with a higher roughness ratio when the wetting ratio is high ($f_w > 0.7$).

Generally, CAH values increased when comparing CAH against various Young's contact angles. In addition, peak values of CAH started to form with Young's contact angles with increased wetting. CAH decreased with increasing Young's contact angles at $f_w < 0.5$. Low values of CAH were observed to be either super-hydrophilic or super-hydrophobic ($\theta_0 \approx 0$ or $\theta_0 \geq 150^\circ$), as previously indicated. Droplet sizes in condensation often are determined when the contact line starts to move.

Future experiments should be designed to determine the degree of wetting based on the relationship between pressure and the contact angle. In condensation, contact angles are measured in atmospheric condition where there is air in the pores or gaps of the surface. However, non-condensable gases are removed in majority of the condensation studies. Partial pressure from non-condensable gases is eliminated. The wetting condition of condensate became different with different pressure condition as fundamentals of wettings and pressures are needed for further studies. New studies are being actively pursued for condensation with different morphologies and pressure conditions[40, 41].

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