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Theoretical consideration of contact angle hysteresis using surface-energy-minimization methods

By Kuok Cheng [a], Blake Naccarato [b], Kwang J. Kim [b],*, Anupam Kumar [b]

[a] *Department of Mechanical Engineering, University of Nevada, Reno, NV, USA*
[b] *Active Materials and Smart Living Laboratory, Department of Mechanical Engineering, University of Nevada, Las Vegas, NV, USA*

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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.

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 Eq. (1),

$$E = A_{LG}\gamma_{LG} + A_{SL}\gamma_{SL} + A_{SG}\gamma_{SG} \tag{1}$$

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 Fig. 1.

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

$$\gamma_{LG}\cos\theta = \gamma_{SG} - \gamma_{SL} \tag{2}$$

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

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* Corresponding author.
E-mail address: kwang.kim@unlv.edu (K.J. Kim).

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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

$$dE = 0 = dA_{LG}\gamma_{LG} + dA_{SL}\gamma_{SL} + dA_{SG}\gamma_{SG}. \tag{3}$$

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:

$$\cos\theta_W = r_f \cos\theta_0, \tag{4}$$

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:

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

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.

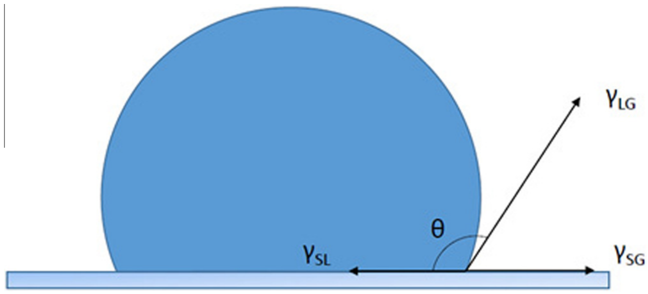

Fig. 1. Surface tension and contact angle of a liquid droplet.

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 varies 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