

Comments

On the Range of Applicability of the Wenzel and Cassie Equations

Introduction

Gao and McCarthy¹ have recently studied the validity of the Wenzel and Cassie equations for wetting rough superhydrophobic surfaces. They pointed out that these equations are increasingly used in the literature because of recent advances in superhydrophobicity. However, it is still not clear under what circumstances these equations are valid. This question is related to the old discussion of whether the wetting of superhydrophobic surfaces is a 1D process, which is determined by thermodynamic equations for the free surface energies, or a 2D process, which is more adequately described by the kinetics of the triple line (the solid–liquid–vapor contact line) and surface tension. A large body of evidence has been presented for support of the validity of the Wenzel and Cassie equations based upon the energy approach^{2–3} as well as evidence that support the line tension approach.^{1,4–5} Gao and McCarthy¹ showed experimentally that the contact angle of a droplet is defined by the triple line and does not depend upon the roughness under the bulk of the droplet. A similar result for chemically heterogeneous surfaces was obtained by Extrand.⁵ Gao and McCarthy concluded that the Wenzel and Cassie equations “should be used with the knowledge of their fault”.¹ The question remains, however, under what circumstances the Wenzel and Cassie equations can be safely used and under what circumstances they become irrelevant.

The concept of the free surface energy was introduced in the 19th century, and it remains a well-founded basis for the physical chemistry of surfaces.⁶ At thermodynamic equilibrium, a system (such as a water droplet) remains at a local minimum of the net surface energy. It is easy to show⁷ that such a minimum is achieved when Young’s equation for the contact angle, θ_0 , is satisfied locally at the triple line

$$\gamma_{LV} \cos \theta_0 = \gamma_{SV} - \gamma_{SL} \quad (1)$$

where γ_{SL} , γ_{SV} , and γ_{LV} are the free surface energies of the solid–liquid, solid–vapor, and liquid–vapor interfaces, respectively.

Forces in physics are defined as derivatives of the energy by corresponding generalized coordinates,⁸ so the question of whether the forces or the energy governs a physical phenomenon is similar to the chicken and egg problem.⁹ For example, when

a liquid front spreads along a flat solid surface, the net free surface energy (per front length) is given by $W = (\gamma_{SL} - \gamma_{SV})x$, where x is the position (Figure 1a). The x component of the surface tension force, σ_x , is found as a derivative $\sigma_x = dW/dx = \gamma_{SL} - \gamma_{SV}$. It is observed that the concepts of the surface energy and the surface tension are, in a sense, equivalent. The work of the surface tension force σ_x needed to create a new interface dx is equal to the net free-energy change due to the creation of the solid–liquid and the destruction of the solid–vapor interfaces, $dx(\gamma_{SL} - \gamma_{SV})$. Because the configuration is 2D, all quantities are given per unit length of the triple line.

For a rough surface, the surface tension force, the work of which is equal to the free energy of the newly created interface, $dt(\gamma_{SL} - \gamma_{SV})$, is given by the derivative $\sigma_t = dW/dt = \gamma_{SL} - \gamma_{SV}$, where t is the length of the surface profile (Figure 1b). The quantity of practical interest is the component of the tension force that corresponds to the advancing of the liquid front in the horizontal direction for dx . This component is given by $dW/dx = (dW/dt)(dt/dx) = (\gamma_{SL} - \gamma_{SV})dt/dx$. Substituting this effective tension force, $(\gamma_{SL} - \gamma_{SV})dt/dx$, into eq 1 instead of $\gamma_{SL} - \gamma_{SV}$ defines the contact angle with a rough surface. It is noted that the derivative $r = dt/dx$ is equal to Wenzel’s roughness factor in the case when the roughness factor is constant throughout the surface.

$$\gamma_{LV} \cos \theta = r(\gamma_{SV} - \gamma_{SL}) \quad (2)$$

For a more complicated case of a nonuniform roughness, given by a certain profile $z(x)$, the local value of $r(x) = dt/dx = (1 + (dz/dx)^2)^{1/2}$ matters. In the case that was studied by Gao and McCarthy¹ and Extrand,⁵ the roughness was present ($r > 1$) under the bulk of the droplet, but there was no roughness ($r = 0$) at the triple line, and the contact angle is given by eq 1 (Figure 1c). In the general case of a 3D rough surface $z(x, y)$, the roughness factor can be defined as a function of the coordinates $r(x, y) = (1 + (dz/dx)^2 + (dz/dy)^2)^{1/2}$.

Our conclusion can now be formulated: the Wenzel equation is valid for uniformly rough surfaces, that is, surfaces with $r = \text{const}$, whereas for nonuniformly rough surfaces the generalized Wenzel equation should be used to determine the contact angle (a function of x and y) with a rough surfaces at the triple line

$$\cos \theta_{\text{rough}} = r(x, y) \cos \theta_{\text{smooth}} \quad (3)$$

Equation 3 explains the experimental results by Gao and McCarthy because it predicts that only roughness at the triple line matters. It is also consistent with the results of the researchers who confirmed the Wenzel equation (for the case of uniform roughness) and of those who reported that only the triple line matters (for the nonuniform roughness), as summarized in Table 1.

The Cassie equation for the composite surface can be generalized in a similar manner by introducing the local densities, f_1 and f_2 , of the two components that compose the heterogeneous surface. The contact angle, as a function of x and y , is given by

$$\cos \theta_{\text{composite}} = f_1(x, y) \cos \theta_1 + f_2(x, y) \cos \theta_2 \quad (4)$$

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(1) Gao, L.; McCarthy, T. J. *Langmuir* 2007, 23, 3762–3765.
 (2) Bhushan, B.; Nosonovsky M.; Jung, Y. C. *J. R. Soc. Interface*, in press, 2007, doi: 10.1098/rsif.2006.0211.
 (3) Barbieri, L.; Wagner, E.; Hoffmann, P. *Langmuir* 2007, 23, 1723–1734.
 (4) Bartell, F. E.; Shepard, J. W. *J. Phys. Chem.* 1953, 57, 455–458.
 (5) Extrand, C. W. *Langmuir* 2003, 19, 3793–3796.
 (6) Rowlinson, J. S.; Widom, B. *Molecular Theory of Capillarity*; Clarendon: Oxford, England, 1982.
 (7) Nosonovsky, M. *Langmuir* 2007, 23, 3157–3161.
 (8) Landau, L. D.; Lifshitz, E. M. *Mechanics*, 3rd ed.; Butterworth-Heinemann: Woburn, MA, 1996.

(9) To be more precise, there is a similarity with the classical Zeno’s paradox of the arrow (whether the moving material point is a 1D or 0D object). Arntzenius, F. *Monist* 2000, 83, 187–208.

Table 1. Summary of Experimental Results for Uniform^{2,3} and Nonuniform^{1,5} Rough and Chemically Heterogeneous Surfaces^a

experiment	roughness/ hydrophobicity at the triple line and at the rest of the surface	roughness at the bulk (under the droplet)	experimental contact angle (compared with that at the rest of the surface)	theoretical contact angle, Wenzel–Cassie equations	theoretical contact angle, generalized Wenzel–Cassie (eqs 3 and 4)
Gao and McCarthy ¹	hydrophobic	hydrophilic	not changed	decreased	not changed
rough	smooth	not changed	decreased	not changed	
smooth	rough	not changed	increased	not changed	
Extrand ⁵	hydrophilic	hydrophobic	not changed	increased	not changed
hydrophobic	hydrophilic	not changed	decreased	not changed	
Bhushan et al. ²	rough	rough	increased	increased	increased
Barbieri et al. ³	rough	rough	increased	increased	increased

^a For nonuniform surfaces, results are shown for droplets larger than the islands of nonuniformity. Detailed quantitative values of the contact angle in various sets of experiments can be found in refs 1–3 and 5.

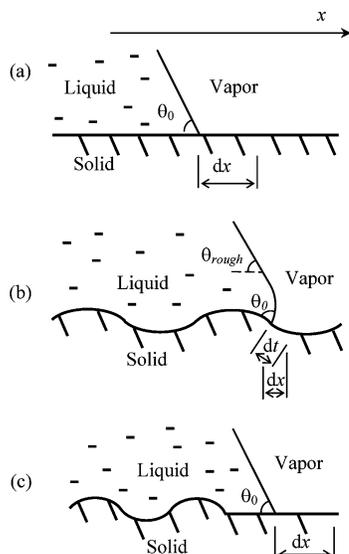


Figure 1. Liquid front in contact with (a) a smooth solid surface and (b) a rough solid surface. Propagation for a distance dr along the curved surface corresponds to the distance dx along the horizontal surface. (c) Surface roughness under the bulk of the droplet does not affect the contact angle.

where $f_1 + f_2 = 1$ and θ_1 and θ_2 are the contact angles of the two components.

The important question remains as to what should be the typical size of roughness/heterogeneity details in order for the generalized Wenzel and Cassie equations (eqs 3 and 4) to be valid. Some scholars have suggested that roughness/heterogeneity details should be comparable to the thickness of the liquid–vapor interface and thus “the roughness would have to be of molecular dimensions”,⁴ whereas others have claimed that roughness/heterogeneity details should be small comparing with the linear size of the droplet.^{2,3,7} The interface in our analysis is an idealized 2D object, which has no thickness. In reality, the triple-line zone has two characteristic dimensions: the thickness (on the order of molecular dimensions) and the length (on the order of the droplet size). The apparent contact angle, given by eqs 3 and 4, may be viewed as the result of averaging the local contact angle at the triple line by its length, and thus the size of the roughness/heterogeneity details should be small compared to the length

(and not the thickness) of the triple line. When the liquid–vapor interface is studied on the length scale of roughness/heterogeneity details, the local contact angle, θ_0 , is given by eq 1. The liquid–vapor interface on that scale has perturbations caused by the roughness/heterogeneity, and the scale of the perturbations is the same as the scale of the roughness/heterogeneity details. However, when the same interface is studied on a larger scale, the effect of the perturbation vanishes, and the apparent contact angle is given by eqs 3 and 4 (Figure 1c). This apparent contact angle is defined on the scale length for which the small perturbations of the liquid–vapor interface vanish, and the interface can be treated as a smooth surface. Therefore, the generalized Wenzel and Cassie equations can be used on the scale at which the perturbations of the interface vanish or, in other words, when the sizes of the solid surface roughness/heterogeneity details are small compared with the size of the liquid–vapor interface, which is on the same order as the size of the droplet.

Superhydrophobicity is a multiscale phenomenon that involves effects on the molecular, micrometer, and millimeter scales. When such a multiscale phenomenon is studied, it is tempting to describe it with a simple set of equations governing the macroscale parameters (such as the Wenzel and Cassie equations for the contact angle); however, there is always a risk involved in oversimplifying the physical processes. Therefore, it is crucial to determine the domain of validity of the macroscale equations. We used the surface energy approach to find the domain of validity of the Wenzel and Cassie equations and showed that they are valid for uniformly rough surfaces. We also generalized these equations for the more complicated case of nonuniformly rough surfaces. The generalized equations explain the wide range of experimental data, which could not be explained by the original Wenzel and Cassie equations. Thus, our short analysis complements the important work reported by Gao and McCarthy.

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