Comments

Comment on "Effects of the Surface Roughness on Sliding Angles of Water Droplets on Superhydrophobic Surfaces"

Introduction

In ref 1, Miwa et al. (for the rest of the text Miwa) propose a new theory that would explain the equilibrium of liquid drops on inclined rough surfaces such that their contact angle is very high. Apparently, the air trapped at the interface would play a crucial role because it reduces the effective contact area between solid and liquid. This is very reasonable. In fact, quantitative theories exist relating the contact angle to the trapped air. However, as stated in Miwa's Introduction, no clear relationship has been established between the equilibrium of drops and the contact angle. They present one possible explanation, which could be credible in view of their comparison to experimental results (their Figure 9). However, we think that their theory should be rendered clearer from the conceptual point of view. Once clarified, we will be able to discuss its validity.

The departure point of this comment is constituted by the following considerations:

(a) Fifty years ago, several theories[2−5] were proposed to explain the empirical relationship between sliding (or critical) angle, α_c, and drop size

$$\sin \alpha_c = k\frac{2r\pi}{mg} \tag{1}$$

where mg is the drop weight and r is the radius of the wetted area (see also ref 6). Those theories tried to relate the constant k to the surface tensions and the contact angle. Although they did not establish any explicit relationship between k and surface roughness, we think that it would be suitable to formulate this relationship on the basis of those previous theories. At least, the theory by Miwa should be compared to that of Furmidge,[2] because the authors cite it explicitly (their eq 1) and use it to discuss some of their experimental results (first paragraph of their Discussion).

(b) Without hysteresis of the contact angle, θ, the equilibrium of tilted drops would not be possible. In Figure 1a, the external forces acting on a drop and contributing to its sliding behavior are sketched. The downward component of weight ($mg \sin \alpha$) can be equilibrated only if the back contact angle (θ_b) is smaller than the front one (θ_f). This condition is expressed by Furmidge's eq 2,

$$mg \sin \alpha \approx \gamma_{LV}(\cos \theta_b - \cos \theta_f)w$$

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(1) Miwa, M.; Nakajima, A.; Fujishima, A.; Hashimoto, K.; Watanabe, T. *Langmuir* **2000**, *16*, 5754.
(2) Furmidge, C. G. L. *J. Colloid Sci.* **1962**, *17*, 309.
(3) McDougall, G.; Ockrent, C. *Proc. R. Soc. London* **1942**, *180A*, 151.
(4) Rosano, H. L. *Mem. Serv. Chim. Est.* **1951**, *36*, 437.
(5) Bikerman, J. J. *J. Colloid Sci.* **1950**, *5*, 349.
(6) Roura, P.; Fort, J. Equilibrium of drops on inclined hydrophilic surfaces. *Phys. Rev. E* **2001**, *64*, 011601.

Figure 1. (a) Profile of a tilted drop; (b) when viewed from above, some such drops slip down leaving a wetted area (shaded surface) behind them.

where $w = 2r$, and γ_{LV} is the liquid−vapor surface tension. When a drop is tilted, α in Figure 1 increases until the drop begins to slide down ($\alpha = \alpha_c$). When this happens, one may assume that the back and front contact angles are close to their minimum and maximum possible values (θ_- and θ_+, respectively).[7] Then,

$$mg \sin \alpha_c \approx \gamma_{LV}(\cos \theta_- - \cos \theta_+)w \tag{2}$$

Both of the former two equations are approximations, because in reality the contact angle varies continuously along the contact line. However, there is reasonable agreement between Furmidge's equation and experiment (see Table 2 in ref 2). Thus, we conclude from eqs 1 and 2 that the "sliding constant" k is related to hysteresis (i.e., to the fact that $\theta_- \neq \theta_+$) for sure. Despite this evidence, following Murase[8] Miwa[1] assume that k is "related to the interaction energy between solid and liquid" (last sentence in their Background) and that k is proportional to the product of roughness, r, and the fraction of wetted area, f (assumption 2 in their model). These hypotheses should be deduced, if possible, from the value of the contact angle hysteresis. Below, we present a model with this aim.

At the time when the paper by Miwa[1] was published, we were working on a paper in which we showed that for small contact angles the equilibrium of drops can be understood on the basis of a liquid film left behind when drops slide down smooth hydrophilic surfaces.[6] In this comment, we will modify our theory in ref 6 slightly, so as to adapt it to the case of rough surfaces. Although Miwa's smooth surface is slightly hydrophobic ($\theta = 105.4$), we will show that the experimental results of Miwa can be interpreted in terms of the formation of a water film that partially wets the solid surface left behind. In fact, this physical model leads naturally to the same results as Miwa's theory,[1] and it states more clearly the physical

(7) Burdon, R. S. *Surface tension and the spreading of liquids*; Cambridge University Press: Cambridge, U.K., 1949.
(8) Murase, H., et al. *J. Appl. Polym. Sci.* **1994**, *54*, 2051.

Figure 2. Drop over a partially wetted rough surface.

grounds on which the hypotheses in ref 1 are sustained. The conclusion of our analysis will be that the validity of Miwa's theory[1] is doubtful.

Equilibrium Condition in Terms of Work and Energy

Furmidge's equation (eq 2) can be expressed in terms of work and energy if we consider that the drop slides down a virtual displacement δx. When we multiply both sides of eq 2 by δx, the result can be interpreted as follows. The gravitational energy lost (left-hand side) is invested in the work done by surface tension at the front and back water lines. The question is now which has been the physical result of this work. It will depend on the nature of the process of water line displacement. If it is irreversible, then energy will be lost as heat. If it is reversible, there must be some way to store the energy. In this second case, a wetted surface will be left behind the sliding drop (Figure 1b). This has been observed and explained in ref 6. Here, we need only note that in this second case, Furmidge's equation is in fact an equation of energy balance. When the solid surface is progressively inclined, the drop will slide down just at the angle $\alpha = \alpha_c$ such that gravity can furnish the energy necessary to develop the back wetted surface. As far as eq 2 remains approximately valid, the energy used to create a unit area of this surface will be

$$\gamma_{LV}(\cos \theta_- - \cos \theta_+) \qquad (3)$$

so the interpretation of constant k as related to the solid−liquid energy of interaction seems possible.

Hysteresis of Contact Angle and Roughness

A reversible process is, in fact, an evolution through equilibrium states. This means that both the advancing and receding contact angles must be equilibrium contact angles and obey Young's equation:

$$\frac{\gamma_{SV\pm}^{R} - \gamma_{SL}^{R}}{\gamma_{LV}} = \cos \theta_{\pm} \qquad (4)$$

where γ_{LV} is the liquid−gas surface tension, and the superindex R is used to denote rough surfaces. As explained in detail below, $\gamma_{SV\pm}^{R}$ (γ_{SL}^{R}) corresponds to the surface energy per unit *apparent* area of the solid−gas (solid−liquid) interface in front of the advancing (+) water line and at the back of the receding line (−). So, within the hypothesis of a reversible process, an explanation should be found for the fact that $\gamma_{SV+}^{R} \neq \gamma_{SV-}^{R}$. The most natural explanation is to consider that when the drop slides down, it leaves behind a partially wetted solid surface. The calculation of θ_- and θ_+ is very simple if we assume that the structure of the solid surface is that sketched in Figure 2:

(a) We define the roughness r such that the real (microscopic) surface area of the solid surface is r times its apparent (macroscopic) area, $A_r = rA_a$ (with $r \geq 1$ and $A_r = A_w + A_d$ in Figure 2; the subindexes w and d stand for wetted and dry, respectively).

(b) Roughness does not modify the surface energies per unit of microscopic area (γ_{SV}, γ_{SL}); that is, their values are identical to those of a flat surface.

(c) We define the wetted fraction as $f \equiv A_w/A_r$. Thus, $A_w = frA_a$ and $0 \leq f \leq 1$.

(d) The liquid−vapor interface, resulting from the trapped air, occupies a fraction $(1 - f)$ of the apparent surface area below the drop; that is, $A_t/A_a = (1 - f) = (A_r - A_w)/A_r = A_d/A_r$. Note that this yields $A_t = 0$ if $A_d = 0$ (no trapped air), as it should, and $A_t = A_a$ if $A_d = A_r$, also as expected from Figure 2.

(e) Once the drop has slid down, the solid surface will remain wetted at the same regions that were in contact with water when the drop was above them. That is, a fraction fr of the apparent surface will remain wetted behind the drop.

With this model, we can easily calculate the surface tensions of the rough surfaces (γ_{ij}^{R}) as a function of the corresponding values for an ideal flat surface (γ_{ij}) by simply adding the contributions to the surface energy at the microscopic level. The surface energy of the interface below the drop will be

$$A_a\gamma_{SL}^{R} = A_w\gamma_{SL} + A_d\gamma_{SV} + A_t\gamma_{LV} = frA_a\gamma_{SL} + (1 - f)rA_a\gamma_{SV} + (1 - f)A_a\gamma_{LV}$$

that of the dry solid surface at the front of the drop is

$$A_a\gamma_{SV+}^{R} = A_r\gamma_{SV} = rA_a\gamma_{SV}$$

and at the back of the drop we have, according to assumption e above,

$$A_a\gamma_{SV-}^{R} = A_w(\gamma_{SL} + \gamma_{LV}) + A_d\gamma_{SV} = frA_a(\gamma_{SL} + \gamma_{LV}) + (1 - f)rA_a\gamma_{SV}$$

From these values, the advancing and receding contact angles can be easily obtained by using eq 4. This yields

$$\cos \theta_+ = fr \cos \theta_s + f - 1 \qquad (5)$$

where θ_s is the horizontal contact angle for a smooth (i.e., flat) surface,

$$\frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} = \cos \theta_s$$

Equation 5 agrees with eq 12 in Miwa's paper,[1] and it reduces to Wenzel's law for $f = 1$ and to Cassie's law for $r = 1$, as it should (see eqs 3 and 5 in ref 1). We also find that

$$\cos \theta_- = fr + f - 1 \qquad (6)$$

At this point, we must note that formulas 5 and 6 are exact under the hypotheses of our model, which include the special shape of the surface depicted in Figure 2. The agreement of eq 5 with Miwa's result is due to the fact that for such a surface shape Miwa's definition of f (see p 5757 in ref 1) is the same as ours. In fact, f has been defined differently by other authors.[9] For a surface of

(9) Fuji, H.; Nakae, H. *Philos. Mag. A* **1994**, 72.
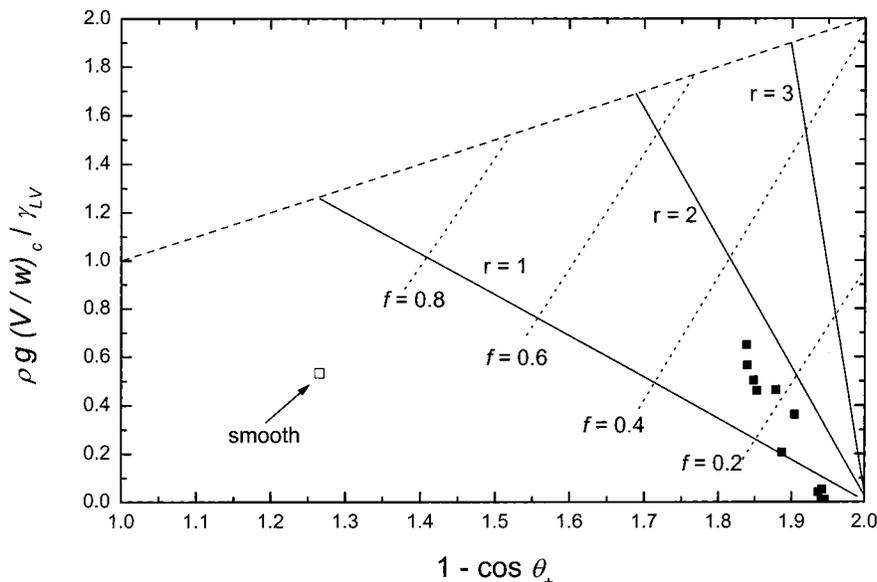
Figure 3. Predicted maximum dimensionless size of nonslipping drops. Dashed line: prediction for smooth surfaces, assuming also that the liquid−solid−vapor combination is such that slipping drops leave a continuous liquid film behind them (this line has been derived theoretically and checked experimentally in ref 6). Full and dotted lines: predictions for rough surfaces, from eqs 5−7. A contact angle over smooth horizontal surfaces of $\theta_s = 104.5$ has been used (this is the value measured in ref 1). Filled squares: experimental results for rough surfaces (Figure 4 in ref 1). Empty square: experimental result for Miwa's smooth surface (Figure 5 in ref 1).

arbitrary shape, it is not possible to derive eqs 5 and 6 as exact. However, in such a general case, f and r can be taken as phenomenological parameters.

Drop Critical Size and Comparison with Experiment

Once θ_- and θ_+ are known, the sliding constant k in eq 1 can be calculated by introducing them in Furmidge's formula (eq 2). This procedure can be done for different solid surfaces, characterized by their values of r and f. Instead of that, it will be more useful for our purposes here to calculate the critical drop size $(V/w)_c$ defined as the maximum drop size that can stand in equilibrium on a vertical surface ($\sin \alpha_c = 1$). According to this definition, eqs 1 and 2 yield

$$\left(\frac{V}{w}\right)_c = \frac{k\pi}{\rho g} = \frac{\gamma_{LV}(\cos \theta_- - \cos \theta_+)}{\rho g} \tag{7}$$

where V is the drop volume and ρ is its density. In Figure 3, this result is plotted for $\theta_s = 105.4$ (as measured in ref 1) and compared to the "experimental" values by Miwa.[1] These points have been calculated from the experimental sliding slopes of their Figures 4 and 5 by obtaining V from w and their values of the contact angle through the spherical-shape assumption, which is well-known to be valid for sufficiently small drops. Also, the contact angles in ref 1 have been approximated to θ_+ in the horizontal axis in Figure 1. This is a reasonable approximation because when a drop is deposited slowly over an horizontal surface, the contact angle will increase up to θ_+ before its radius increases (similarly, when a drop is observed to evaporate through a microscope, its radius decreases at sudden moments but not continuously. Indeed, the contact angle decreases down to θ_- before the radius begins to decrease).

Although slight quantitative differences are observed between our Figure 3 and Figure 9 of Miwa,[1] the conclusions concerning the dependence of drop stability on the surface features are essentially the same. The

observed decrease in critical size when contact angle (θ_+) increases is easily interpreted if we substitute eqs 5 and 6 into eq 7,

$$\left(\frac{V}{w}\right)_c = fr\frac{\gamma_{LV}}{\rho g}(1 - \cos \theta_s) \tag{8}$$

For the whole set of rough surfaces in ref 1, the factor $(\gamma_{LV}/\rho g)(1 - \cos \theta_s)$ is constant. So, the large variation of $(V/w)_c$ is interpreted as due to the product fr. In fact, in view of Figure 3, r would be essentially constant ($r \approx 1.8$) for the set of surfaces with $\theta_+ < 155°$ ($1 - \cos \theta_+ < 1.9$). Within this set, drop stability would be controlled by f. On the other hand, for surfaces with $\theta_+ > 158°$ drop stability would yield unrealistic values of $r < 1$.

In Figure 3, we have included an additional experimental point (open square) corresponding to the flat surface in ref 1. As mentioned above, its contact angle ($\theta_s = 105.4°$) has been used in eqs 5 and 6 for the calculation of the theoretical curves. So, in contrast to its position in Figure 3, one would expect $r = 1$ and $f = 1$ for this point.

Discussion

In a previous paper, we have shown that the sliding angle of drops on hydrophilic surfaces (low contact angles) is explained by the formation of a liquid film that completely wets the solid surface left behind the drop.[6] Formally, this theory leads to the same formula as Furmidge's (eq 2) with $\theta_- = 0$. In this particular case, the critical drop size depends only on the contact angle (dashed line in Figure 3). After a thorough review of the published experimental data, we observed as well that at high contact angles drops became much less stable than predicted, even on flat surfaces (see Figure 3 in ref 6). This means that in such cases the liquid film behind the drop does not form (at least as a continuous film). The current explanation is then that hysteresis of the contact angle controls the mechanical equilibrium of forces.[10]

(10) Joanny, J. F.; De Gennes, P. G. *J. Chem. Phys.* **1984**, *81*, 552.

Miwa et al. have obtained solid surfaces on which contact angles are extremely high due to roughness. Although they implicitly accept that equilibrium depends on the contact angle hysteresis, they propose a theory to explain it in terms of roughness and fraction of wetted surface. In fact, they implicitly propose to predict hysteresis of the contact angle from the surface structure. In this comment, we have clarified conceptually their hypotheses and funded them on more solid grounds. In particular, (i) we have given a physical model of contact angle hysteresis that derives the proportionality of critical drop size (or, equivalently, their sliding constant k) to the product rf and (ii) we have shown in which instances (i.e., reversible displacement of water lines) contact angle hysteresis can be related to the solid−liquid interaction energy. Essentially, our model leads to the same results as those by Miwa et al.[1] The quantitative discrepancies between our theoretical curves and theirs (compare Figure 3 here to Figure 9 in ref 1) arise because $r < 1$ and $f < 1$ for their smooth surface (the hollow square in Figure 3 here), whereas Miwa et al. assume that $r = 1$ and $f = 1$ for that surface (the value of k in their eqs 13 and 14 is taken as that for their smooth surface). However, the discrepancies between our theoretical curves and those in ref 1 are not relevant from a conceptual perspective. So, we think that the theory proposed by Miwa is now ready for discussion concerning its validity.

The existence of contact angle hysteresis has been historically a troubling problem for people working in the subject of surface tension. Pioneering theories that tried to explain why the receding contact angle always was smaller were based on the modification of the solid surface left behind (orientation of molecules[11] or formation of a wetted surface[3,7]). Essentially, the receding contact angle was considered as the equilibrium one of this wetted solid

surface and, consequently, the water line movement was a reversible process. Despite the simplicity of this explanation, careful experiments were done with the aim of detecting the wetted surface but the result was negative.[3] Later on, Johnson et al.[12] demonstrated both experimentally and theoretically that contact angle hysteresis can result from surface roughness. Their theory has been recently completed and extended to the case of surface chemical inhomogeneities.[9] The relationship between surface structure and contact angle hysteresis does not follow any simple trend, and contrary to Miwa's theory, it cannot be deduced from the interaction energy of the wetted solid surface below the drop. In this widely accepted theory, the displacement of water line is an irreversible process. Therefore, eq 4 does not hold.

At this point, we conclude that the lack of experimental support on the formation of a wetted surface behind slipping drops that would explain contact angle hysteresis [eqs 5 and 6] leaves Miwa's theory, as developed in more detail in the present comment, with the burden of a missing direct check. In our modest opinion, experimental tests designed to this aim will deliver, as in ref 3, a negative result: it is difficult to understand why water should wet a hydrophobic solid surface ($\theta_s = 105.4$). This work has been partially funded by the CICYT, Grant Nos. REN 2000-1621 CLI and BFM 2000-0351.

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