

Equilibrium of drops on inclined hydrophilic surfaces

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Why does not gravity make drops slip down the inclined surfaces, e.g., plant leaves? The current explanation is based on the existence of surface inhomogeneities, which cause a sustaining force that pins the contact line. Following this theory, the drop remains in equilibrium until a critical value of the sustaining force is reached. We propose an alternative analysis, from the point of view of energy balance, for the particular case in which the drop leaves a liquid film behind. The critical angle of the inclined surface at which the drop slips down is predicted. This result does not depend explicitly on surface inhomogeneities, but only on the drop size and surface tensions. There is good agreement with experiments for contact angles below 90° where the formation of the film is expected, whereas for greater contact angles great discrepancies arise.

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I. INTRODUCTION

The shape of liquid surfaces in mechanical equilibrium is governed by the well-established laws of Laplace and Young. According to Laplace's law, the liquid surface behaves like a membrane under biaxial tension. The stress per unit length is the liquid surface tension, γ_{LV} . On the other hand, Young's condition, namely [1,2],

$$\gamma_{SV} - \gamma_{LS} = \gamma_{LV} \cos \theta, \quad (1)$$

establishes that, when a liquid is in contact with a solid surface and a gas, the contact angle θ depends only on the surface tensions, γ_{ij} . In view of Fig. 1(a), this condition is usually interpreted as an equilibrium of forces. In this framework, the shape of drops on horizontal surfaces can be computed numerically and good agreement with experiment is obtained [3]. More complicated calculations are needed to derive the shape on inclined surfaces, mainly, because of the lack of axial symmetry. Anyway, a qualitative analysis of Laplace's law reveals that in this case the contact angles at the front and back lines of the drop must be different from the equilibrium contact angle θ [Fig. 1(b)]. This means that the drop will move down the inclined surface unless an extra force acts on the contact lines. This force is provided by surface inhomogeneities [1,4,5].

Even in apparently homogeneous surfaces, the existence of such inhomogeneities is revealed by the "advancing" and "receding" contact angles, θ_a and θ_r , respectively. They can be defined as follows [6]. When liquid is added to a drop on a horizontal surface, the contact line is pinned and the contact angle increases until it reaches θ_a [4]. Further addition of liquid leads to a displacement of the contact line. When a liquid drop vaporizes, the contact line is again pinned and the contact angle decreases down to θ_r . Further vaporization leads to a displacement of the contact line. So, inhomogeneities cause a pinning force with extreme values revealed by θ_a and θ_r [see Eq. (1)]. If this reasoning is applied to drops on inclined surfaces, it is concluded that they can stand in equilibrium as long as the contact angles at the front and back lines do not become greater than θ_a and smaller than θ_r , respectively. Half a century ago, several

authors [7,8] analyzed the equilibrium of drops from this point of view. The most accurate experiments were carried out by McDougall *et al.* [7], who established an equilibrium condition based on θ_a and θ_r that described correctly the case of water-repellent surfaces ($\theta > 90^\circ$). In the case of smaller contact angles ($\theta < 90^\circ$), these authors simply stated that a liquid film was observed behind the drops during slipping. However, no experimental results and theoretical predictions for slipping were reported. Our purpose here is to address this problem.

In the present work we will show that, when a liquid film develops during slipping, an equilibrium condition can be stated from energy balance arguments. The inclination of the

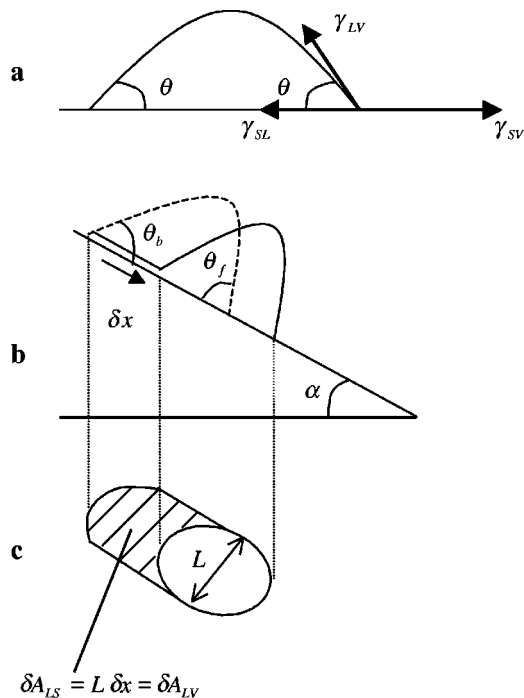


FIG. 1. (a) Definition of the contact angle of a drop on a horizontal surface. (b) Side view of a drop slipping down and leaving a thin film behind. (c) Upper view of the same drop. The shaded area represents the thin film left behind. Both the wetted and the free surface areas increase.

solid surface at which drops become unstable is related only to surface tensions γ_{SV} , γ_{LS} , and γ_{LV} , without any explicit reference to surface inhomogeneities. This is not at variance with the existence of contact line pinning, which indeed makes it possible for the film to form. We report good agreement between the predictions of our new model and experiments, without use of any free parameter, for a variety of hydrophilic surfaces ($\theta < 90^\circ$).

Besides the value of this new prediction from a fundamental point of view, it is of interest in those technological and biological applications where the stability or instability of drops is relevant. For example, drop stability reduces radiative transmission into greenhouses [9] and enhances the effectiveness of foliar pesticides [10]. Also, the instability of drops on water-repellent plant leaves has been shown to have a beneficial effect because it minimizes particulate contamination and hinders the germination of pathogens [11]. Much work and resources are being invested in modifying the chemical composition of surfaces [12] and to analyze their drop stability properties [13], which are also relevant in printing [14] and in the cleaning properties of portable satellite receivers and windscreens [12].

II. THEORY

When dealing with surface tension phenomena, forces can be deduced in a natural way from energy balance arguments [2]. In fact, energetic approaches are usually considered as more fundamental. So, the problem will be addressed from an energetic point of view. A drop is stable only if a differential displacement would increase its total energy. The energy has two contributions: one is due to gravity, U_g , and the other one is due to surface tension, U_γ ,

$$U_g = mgh, \quad U_\gamma = \gamma_{LV}A_{LV} + A_{LS}(\gamma_{LS} - \gamma_{SV}), \quad (2)$$

where m is the drop mass, h the height where its center of mass is located, and g the gravity acceleration. A_{LV} and A_{LS} are, respectively, the areas of the free surface of the drop and of its contact surface with the solid (see Fig. 1). γ_{LV} , γ_{LS} , and γ_{SV} are the corresponding surface tensions (i.e., energies per unit area). When the drop slips down slightly [Fig. 1(b)], a differential displacement δx will imply a decrease in U_g ,

$$\delta U_g = -mg \delta x \sin \alpha < 0. \quad (3)$$

The effect on the surface energy has to be analyzed in more detail, taking into account two points:

(i) Direct observation of water drops, slipping down hydrophilic surfaces ($\theta < 90^\circ$) of low contact angles reveals that usually a thin layer is left behind.

(ii) Surface energy changes can be accounted for by the increments of surface areas, each one multiplied by its corresponding energy per unit area (i.e., surface tension).

From points (i) and (ii) above, we find for the contribution of the layer left behind to the energy variation

$$\delta U_\gamma = L \delta x (\gamma_{LV} + \gamma_{LS} - \gamma_{SV}), \quad (4)$$

where L is the drop width (measured in the direction perpendicular to that with highest slope on the inclined plane), see Fig. 1(c).

In order to compare to experiment, we use Young's equation (1) into Eq. (4), yielding

$$\delta U_\gamma = L \delta x \gamma_{LV} (1 - \cos \theta). \quad (5)$$

For partial wetting ($\theta \neq 0$), $\delta U_\gamma > 0$. So, film formation requires energy and it will take place only when the surface is inclined enough so that the diminution of gravitational energy [Eq. (3)] overcomes the energy increase due to surface tension (5). By adding Eqs. (3) and (5) and equating the result to zero we obtain the critical angle α_c at which the drop becomes unstable due to film formation,

$$\sin \alpha_c = \frac{\gamma_{LV}(1 - \cos \theta)}{\rho g} \frac{L}{V}, \quad (6)$$

where α_c is the maximum value of the angle α (Fig. 1) that can sustain the drop in equilibrium, V is the volume of the drop, and ρ its density. For $\alpha > \alpha_c$, the drop will slip down. This very simple prediction has been tested experimentally, as reported in the next section.

A complementary view can be obtained if we analyze, which is the drop size below which equilibrium will be possible even on a vertical surface. For this particular drop, $\sin \alpha_c = 1$ and the critical value $(L/V)_c$ of L/V can be obtained from Eq. (6). In fact, it is well established that when drops become small enough their shape approaches that of a spherical cap. In this case the critical drop volume, V_c , and diameter, L_c , are no longer independent parameters and can be calculated from $(L/V)_c$. A simple calculation yields

$$L_c = \left(\frac{\gamma_{LV}}{\rho g} \right)^{\frac{1}{2}} \sqrt{\frac{24 \sin^3 \theta}{\pi(1 - \cos \theta)(2 + \cos \theta)}},$$

$$V_c = \left(\frac{\gamma_{LV}}{\rho g} \right) (1 - \cos \theta) L_c. \quad (7)$$

III. COMPARISON TO EXPERIMENT

An ensemble of smooth surfaces (glasses and plastic films) has been chosen in order to cover a broad range of contact angles θ . Drops of deionized water were placed onto each surface by means of a micropipette. The width orthogonal to the slope, L , was measured for each drop [see Fig. 1(c)]. The contact angle was determined by projection of the drop profile on a white wall or, alternatively, by considering the smaller drops as perfectly spherical caps and making use of their measured values of V and L . The solid surface sustaining the drop was then tilted progressively [see Fig. 1(b)] and the angle α_c , at which the water line at the front just started to move, was recorded.

In Fig. 2, we report the experimental dependence of α_c on L/V for water drops on different surfaces. It is seen that for a given surface, the maximum angle α_c increases with L/V . This ratio depends on the particular drop considered and may be regarded as the relative importance of surface tension

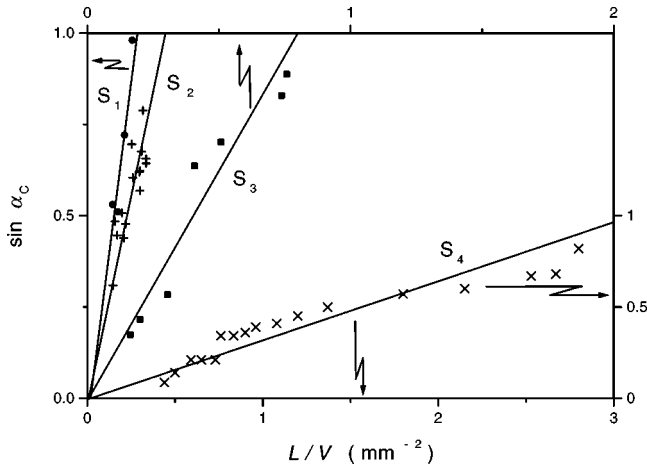


FIG. 2. Tilt angle of the solid surface at which water drops begin to slip down, as a function of their size. Symbols: experimental results for four different surfaces. Lines: linear fits. The dependence is linear, as predicted by Eq. (6).

(which tends to maintain equilibrium) and the effect of gravity (which tends to make the drop slip down). There is reasonable agreement with the functional dependence predicted by Eq. (6). The points measured for each surface have been fitted to a straight line that passes through the origin (Fig. 2), and their slopes have been determined.

In Fig. 3 the characteristic slope for every surface (obtained from measurements such as those in Fig. 2) has been plotted against the contact angle (filled up circles). In order to compare these experimental results to our theory, we have calculated the value predicted from Eq. (6), i.e., $\gamma_{LV}(1 - \cos \theta)/(\rho g)$ with $g = 9.8 \text{ m/s}^2$ and the tabulated parameters for water at room temperature and pressure, namely [15], $\gamma_{LV} = 72.75 \times 10^{-3} \text{ N/m}$ and $\rho = 1000 \text{ kg/m}^3$. This pre-

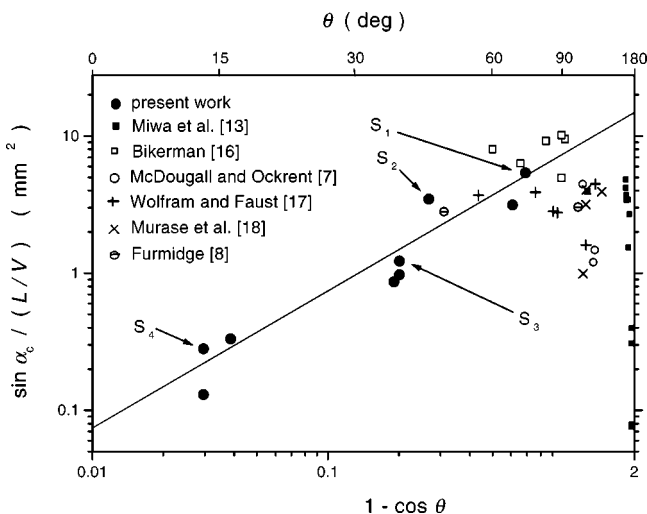


FIG. 3. Filled up circles: experimental proportionality constants between $\sin \alpha_c$ and L/V , obtained from the slope of linear fits such as those in Fig. 2, as a function of the contact angle θ . The line is the theoretical dependence predicted by Eq. (6), and no free parameters have been used. Experimental points from the measurements of other authors are also included.

dicted value corresponds to the solid line in Fig. 3. Although the dispersion of the experimental points is apparent, the agreement between theory and experiment is excellent. Not only are the functional dependences verified (Figs. 2 and 3), but also the value of the slope for each surface (filled up circles in Fig. 3) is predicted within experimental error. It is worth to emphasize that, in contrast to Fig. 2, the solid line in Fig. 3 is not a fit to the experimental points. The agreement between theory and experiment has been obtained without using any free parameter.

IV. DISCUSSION

At this point, it is worth to compare our theory with the experimental results reported by other authors [7,8,13,16–18]. The parameters L and θ are necessary for this purpose, but in some cases they were not explicitly reported. In such an instance, we have made a reasonable quantification of the values of L and θ , as follows. On the other hand, when L is not given explicitly it has been computed from the drop volume and the value of θ by assuming approximately spherical drops. In this way, we can compare to the experimental results by a variety of authors, as done in Fig. 3. Then, the range of validity of our theory becomes clear. If the contact angle approaches 90° , a systematic deviation from our theoretical prediction is implied by the results by Wolfram and Faust [17]. This deviation becomes absolutely clear for water-repellent surfaces ($\theta > 90^\circ$).

In spite of the simplicity of our theory, its usefulness in predicting the conditions for drop slipping is reasonably good for hydrophilic surfaces ($\theta < 90^\circ$), as seen from Fig. 3. The fact that the energy of these surfaces diminishes when wetted ($\gamma_{LS} < \gamma_{SV}$) and facilitates the formation of a water film during slipping, since this yields a lower energy increase [Eq. (4)] that has to be compensated by the energetic decrease due to gravity [Eq. (3)]. We have observed this film in the surfaces of lowest contact angles. It is a metastable film that breaks down shortly after it is formed, leading to very small droplets. However, for surfaces with higher values of θ , film formation becomes more difficult and the back contact line is released before the condition stated in Eq. (6) is fulfilled. This fact explains why the experimental points tend to be below the theoretical prediction if $\theta > 90^\circ$ (see Fig. 3). It must be mentioned that the slipping of drops without film formation has been already solved before (see specially Ref. [7]). Thus we shall not go into details for this case. In contrast, for their surface-liquid combinations with $\theta < 90^\circ$ the authors of Ref. [7] did observe film formation, but they did not explain the slipping of these drops. What the present paper adds to previous knowledge is precisely the solution to the problem of drop slipping when a film is formed behind the drop [Eq. (6) and the left half of Fig. 3].

In the past, several attempts have been made by other authors [16,19] to derive a slipping condition from energy balance arguments. They obtained equations similar to our Eq. (6). However, these authors did not take into account the

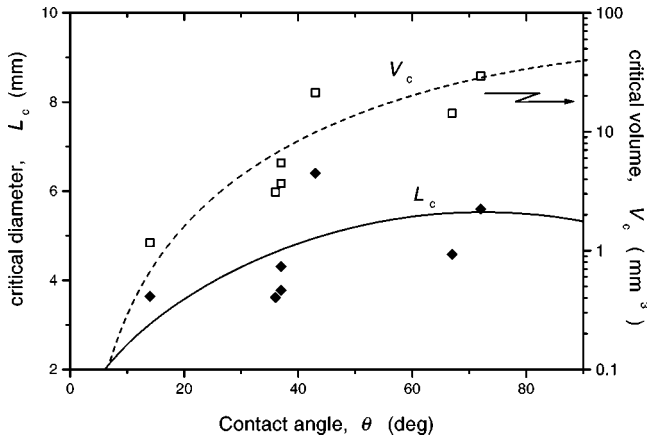


FIG. 4. Maximum water drop volume V_c and diameter L_c that can be sustained on a vertical surface, as a function of the contact angle θ . The lines correspond to the theoretical prediction. Note the small variation of the drop diameter L_c above 20° .

energy recovered due to the increase of wetted surface area [Eq. (4)]. This error passed unnoticed to these authors because of the lack of an experimental verification [19] or a too narrow range of values of θ [16] (see the experimental points corresponding to Ref. [16] in our Fig. 3).

Finally, our model will allow us to discuss the maximum size of drops that do not slip down even vertical surfaces. This has been discussed qualitatively (see, e.g., Ref. [20]), but to the best of our knowledge no quantitative prediction has been presented. In order to do so and compare to experiment, we have extrapolated our experimental values in Fig. 2 up to $\sin \alpha_c = 1$, in order to obtain the critical drop size for every surface. The “experimental” value thus obtained is then compared to the theoretical one obtained from Eqs. (7), as shown in Fig. 4. Concerning the critical volume, V_c , we observe reasonable agreement, whereas in the case of the critical diameter, L_c , the dispersion of the experimental points appears much greater. However, they do not differ from the theoretical value by more than 30%. It is worth to notice that the huge variation of V_c over one order of magnitude is not encompassed by a similar variation in L_c . In fact this critical diameter remains almost constant through the range of surfaces tested. This result is especially interesting when applied to the case of dew drops over plant leaves. The surface of leaves is usually water repellent with contact angles above 30° . Thus according to Fig. 4, drops on vertical leaves of whatever plant will wet a circular surface with a maximum diameter of 4 to 5 mm. This general conclusion, which had not been derived from theory in previous work, is easily tested by looking at dew drops in the garden (or, alternatively, on a glass window).

V. CONCLUDING REMARKS

The equilibrium of drops on inclined smooth surfaces has been analyzed from an energetic point of view. The formation of a thin film gives a limit inclination for the equilibrium of drops. This critical angle has been predicted without any specific assumption regarding which kind of inhomogeneities pin the contact line. We would like to stress that our approach is in accordance with the well-established view according to which surface inhomogeneities pin the contact line. Indeed, if the back line were not pinned, no drops could exist such that they leave a film behind when sliding.

To the best of our knowledge, the experimental results presented in Figs. 2–4 had not been explained before, in spite of their fundamental character and of the simplicity of our model. This may be due to the fact that no attention seems to have been given previously to the thin layer that drops leave behind them when slipping over sufficiently hydrophilic surfaces. In the theory presented, this thin film is of utmost importance since it is precisely a careful, albeit simple, analysis of its energetics that leads to quantitative predictions. Let us also stress that our model explains the experiments for hydrophilic surfaces ($\theta < 90^\circ$) without use of any free parameter (see Figs. 3 and 4). The hydrophobic case ($\theta > 90^\circ$) has not been considered here, since it had been explained previously [7].

Because of the agreement we have reported between theory and experiment in the case of hydrophilic surfaces, Eq. (6) is a proper starting point to predict slipping. It can also be used to avoid or enhance slipping by choosing materials with adequate parameters (γ_{LV} , θ , and ρ) for the typical drops used (L and V) in the biological [9–11] or engineering [12–14,21] application under consideration. For example, an important problem in the application of spray insecticides is how to ensure that spray drops do not slip down the leaves. Usually purely empirical procedures are applied [9]. However, our results allow for a physically-based approach to this problem. Indeed, Eq. (6) yields the analytical condition $\gamma_{LV} > \rho g(V/L)/(1 - \cos \theta)$, where the values of γ_{LV} and θ [see Eq. (4)] can be controlled by modifying the chemical composition of the insecticide [21]. Examples of this sort show that the long-standing basic physical problem of drop slipping over inclined hydrophilic surfaces, for which the new theory here presented yields good agreement with experiment, is also relevant from the perspective of applications.

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