Drops at Rest on a Tilted Plane

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A liquid drop on a tilted plate can remain at rest, provided that an hysteresis for the contact angle exists. We examine in this paper the case of small contact angle hysteresis, for which the drops are found to be nearly spherical caps, despite the slope. We derive in particular the condition (both in angle and hysteresis) under which the drop remains stuck on the surface: a simple model is proposed and compared with experimental data.

1. Presentation

A liquid drop can remain stuck on a tilted plane, despite gravity, if the contact angle is different at the front and at the rear of the drop (contact angle hysteresis).[1−3] The rear angle being smaller than the front one, a capillary force exists, which opposes the gravity force. The capillary force is bounded (it is related to the cosines of the angles), so that there is a threshold in weight for the drop above which the drop cannot remain at rest.

We first describe a method for measuring in situ the average contact angle of the drop. Then we discuss the critical volume above which the drop slips. A simple model is proposed and compared with the data, *in the limit of small hysteresis* ($\Delta\theta < 30°$). This limit concerns the case (interesting for practical applications) where the material tends to not retain the droplets.

2. Contact Angles

2.1. Spherical Caps. In the limit of small hysteresis, a drop deposited on a solid can have a nearly circular contact line, even if the solid is tilted.[3,4] Then, it forms a spherical cap, as drawn in Figure 1, where R is the radius of curvature of the drop, ϕ is its diameter if seen from above, and θ is the mean contact angle (Figure 1a, $\theta < 90°$; Figure 1b, $\theta > 90°$).

The volume of the drop can be expressed as a function of θ and R:

$$\Omega = \frac{\pi}{3}R^3(2 + \cos\theta)(1 - \cos\theta)^2 \qquad (1)$$

2.2. Method for Measuring Contact Angles. Equation 1 shows that, knowing the drop volume, the contact angle can be directly deduced from measuring the diameter ϕ of the drop observed from above. If the contact angle is smaller than 90° (Figure 1a), we have $\phi = 2R\sin\theta$, and thus

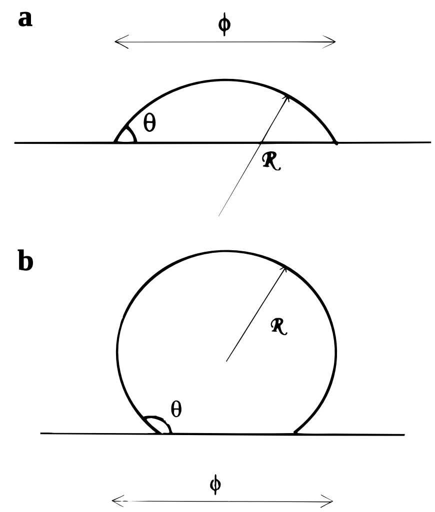

Figure 1. Side view of a drop deposited on a solid in a partial wetting situation: (a) $\theta < 90°$; (b) $\theta < 90°$. R is the radius of curvature of the spherical cap formed by the drop and ϕ is its diameter when it is observed from above.

$$\phi = 2\left(\frac{3}{\pi}\right)^{1/3}\frac{\sin\theta}{(2 + \cos\theta)^{1/3}(1 - \cos\theta)^{2/3}}\Omega^{1/3} \qquad (2a)$$

In the case of a contact angle larger than 90° (Figure 1b), the situation is less favorable: the diameter of the patch seen from above is the drop diameter ($\phi = 2R$), which gives

$$\phi = 2\left(\frac{3}{\pi}\right)^{1/3}\frac{1}{(2 + \cos\theta)^{1/3}(1 - \cos\theta)^{2/3}}\Omega^{1/3} \qquad (2b)$$

The conversion between the contact angle and the drop diameter ϕ is finally achieved by drawing eq 2, as in Figure 2, where it is done for a drop of volume 10 μL (which corresponds to a radius of 1.3 mm).

Hence, it appears to be an excellent method for measuring small contact angles (an error of order 0.1 mm in the measurement of the diameter leads to $\Delta\theta \sim 1°$ for θ of order 20°). Conversely, this method cannot be used for large angles: for $\theta > 120°$, the drop diameter (defined in Figure 1b) is nearly constant up to $\theta = 180°$.

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(2) Kawasaki, K. *J. Colloid Sci.* **1960**, *15*, 402.
(3) Wolfram, E.; Faust, R. In *Wetting, Spreading and Adhesion*; Padday, J., Ed.; Academic Press: New York, 1978; pp 213−222.
(4) Brown, R. A.; Orr, F. M.; Scriven, L. E. *J. Colloid Interface Sci.* **1980**, *73*, 76.

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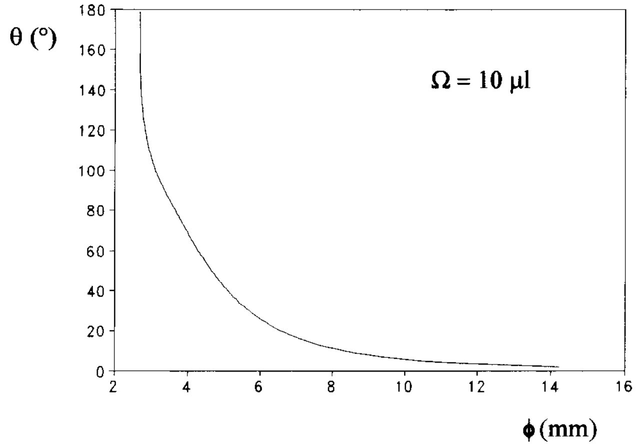

Figure 2. Contact angle of a drop of fixed volume ($\Omega = 10\ \mu$L) versus the drop diameter (defined by the observation of the drop seen from above, see Figure 1). The line represents eq 2.

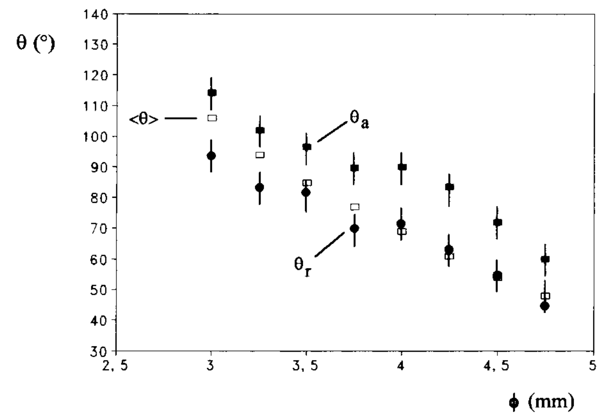

Figure 3. Contact angle of a drop of fixed volume ($\Omega = 10\ \mu$L) versus the drop diameter. Full squares are the contact angles (advancing and receding ones) measured on an horizontal plate with a goniometer. Empty squares are the data deduced from Figure 2 from a simple measurement of the drop diameter, when deposited on a vertical plate.

2.3. Measurements. Figure 3 shows contact angles deduced from diameter measurements, for droplets of pure water deposited on various float-glass substrates on which different hydrophobic treatments (based on fluorinated silanes) are done. For each substrate, receding and advancing angles are measured with a goniometer by connecting the drop with a syringe: the advancing angle is the largest angle measured before the contact line moves when filling the drop, while the receding angle is the smallest one when pumping. For each measured diameter, these angles are reported with black squares: each square is the average of the measurements, and the bars indicate the dispersion. The whole collection of data is displayed in Table 1.

Then, drops of constant volume ($\Omega = 10\ \mu$L) are placed on the same substrates inclined at an angle of 45°. The diameters parallel and perpendicular to the slope are measured with a linen tester (precision of ±0.25 mm). These two lengths are the same for 30 of the 44 different measurements (see Table 1); a difference of 10% is found in 10 measurements, a difference of 20% is found once, and a difference of 30% is found once. In all cases, the length parallel to the slope is logically found to be larger than the other one. Then, the corresponding contact angles are deduced from the average of these two lengths with the abacus of Figure 2 and displayed in Figure 3 (empty squares).

In each case and taking into account the error bars, the (mean) angle measured is found to be in the interval defined by the receding and advancing angles. Thus, this simple test appears to be a convenient way to determine a contact angle, particularly suitable if the measurement must be done in situ and on a tilted plane (for example, water droplets on car windshields). Furthermore, in the case of small hysteresis (it can be seen in Figure 3 to be of order 20°), the hypothesis of a nearly spherical drop appears to be fulfilled—at least for angles larger than 50°. Below that, the contact line is not circular any longer.

3. Sliding Volume

3.1. Condition for Remaining Stuck. A drop at rest on a tilted plate (angle α) is represented schematically in Figure 4, where we have supposed the drop just before sliding: the rear angle is close to the receding one, and the front angle is close to the advancing one.

As emphasized above, if the hysteresis is small, the droplet is close to a spherical cap. Along the contact line, the contact angle passes from the receding value to the advancing one. Since these angles are supposed to be close to each other, we simply write that the upper half of the droplet makes with the solid the angle θ_r, while the lower one joins the solid with the angle θ_a.

Then, the condition for the drop to be stuck on the solid is[2,5]

$$\pi r\gamma(\cos\theta_r - \cos\theta_a) \geq \rho\Omega g \sin\alpha \tag{3}$$

where r is the radius of the contact line (considered as circular), γ and ρ are the surface tension and density of the liquid, and g is the gravity acceleration. Since the actual continuous variation of the contact angle is ignored, eq 3 overevaluates the sticking power of the angle hysteresis.

Using eq 1 and the relation between R and r ($r = R\sin\theta$) provides another expression for this condition:

$$\cos\theta_r - \cos\theta_a \geq \frac{1}{3}R^2\kappa^2\frac{(2+\cos\theta)(1-\cos\theta)^2}{\sin\theta}\sin\alpha \tag{4}$$

where κ^{-1} is the capillary length ($\kappa^{-1} = (\gamma/\rho g)^{1/2}$), which is 2.7 mm for pure water.

We now introduce as natural parameters the radius R of the drop before it hits the solid (we have of course $\Omega = 4\pi/3R^3$) and the difference $\Delta\theta$ between the advancing and the receding contact angles. Introducing the average angle θ ($\theta_r = \theta - \Delta\theta/2$ and $\theta_a = \theta + \Delta\theta/2$), eq 4 becomes

$$\Delta\theta \geq \frac{4^{2/3}}{3}(R\kappa)^2\frac{(2+\cos\theta)^{1/3}(1-\cos\theta)^{2/3}}{\sin^2\theta}\sin\alpha \tag{5}$$

Relation 5 is the simplest analytical expression which can analytically be expressed as a function of the (measurable) parameters of the problem. It is the leading term of a more general equation derived by Dussan in the same limit of small hysteresis.[6] Note that as long as the drop size remains smaller than the capillary length, the hysteresis at the threshold given by eq 5 remains small, consistent with our main hypothesis.

Inequality 5 divides the diagram ($\Delta\theta$, θ) into two regions, as shown in Figure 5 where it is drawn for (supposedly) realistic values: a rain drop of radius $R = 0.5$ mm on a

(5) Dussan, V E. B.; Chow, R. T. P. *J. Fluid Mech.* **1983**, *137*, 1 (and references therein).

(6) Dussan, V E. B. *J. Fluid Mech.* **1985**, *151*, 1.

Table 1. Experimental Data Obtained by Depositing Drops of Pure Water on Glass Plates Treated in Different Ways[a]

advancing angle (deg)	receding angle (deg)	average angle (deg)	hysteresis (deg)	drop length (mm)	drop width (mm)	critical volume (μL)	
						($\alpha = 90°$)	($\alpha = 45°$)
120	100	110	20	3.0	3.0	10	16
120	94	107	26	3.0	3.0	12	20
117	98	107	19	3.0	3.0	12	19
117	94	106	23	3.0	3.0	11	17
116	95	106	21	3.0	3.0	14	
115	100	107	15	3.0	3.0	7	
115	100	107	15	3.0	3.0	11	
115	90	103	25	3.0	3.0	12	20
114	96	105	18	3.0	3.0	13	
112	91	101	21	3.0	3.0	15	25
111	89	100	22	3.0	3.0	12	19
107	84	95	23	3.0	3.0	13	21
106	90	98	16	3.0	3.0	14	
104	86	95	18	3.5	3.0	13	21
101	90	95	11	4.0	3.0	16	
101	85	93	16	4.0	4.0	16	
100	81	90	19	3.5	3.0	13	
100	83	91	17	4.0	4.0	14	22
100	86	93	14	3.5	3.5	12	19
98	85	91	13	3.5	3.5	14	22
97	80	88	17	3.5	3.5	13	21
97	73	85	24	4.0	4.0	14	
95	80	87	15	3.5	4.0	13	21
93	72	82	21	4.0	4.0	15	24
93	76	84	17	3.5	3.5	15	23
93	79	86	14	4.0	4.0	17	25
90	66	78	24	4.0	3.5	15	
90	73	81	17	3.5	3.5	15	25
89	66	77	23	4.0	4.0	16	25
88	73	80	15	4.5	4.0	18	
87	64	75	23	4.5	4.0	18	
87	73	85	24	4.0	4.0	17	27
84	68	76	16	4.0	4.0	18	27
84	64	74	20	4.0	3.5	16	
83	60	71	23	4.5	4.0	19	30
82	68	75	14	4.5	4.0	17	27
81	65	73	16	4.5	4.0	19	29
80	58	69	22	4.5	4.0	17	
78	56	67	22	4.0	4.0	17	
78	61	69	17	4.0	4.0	18	28
75	55	65	20	4.5	4.5	19	
72	58	65	14	5.0	4.0	14	
69	51	60	18	4.5	4.5	19	
60	44	52	16	5.0	4.5	12	18

[a] First, on each substrate displayed horizontally, the advancing and receding angles are measured (columns 1 and 2), from which the average contact angle and the hysteresis are deduced (columns 3 and 4). Then, the substrate is displayed vertically and a drop of fixed volume ($\Omega = 10\ \mu$L) is deposited and the wetted area characterized by two dimensions is taken: the length of the patch (parallel to the slope, column 5) and its width (perpendicular to the slope, column 6). Finally, the critical volume above which the drop slides is measured on the substrate displayed vertically (column 7) and inclined 45° (column 8). In the latter case, all the substrates were not tested, which explains the blanks in the table.

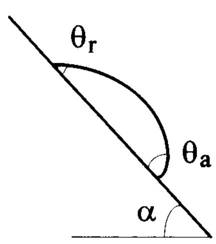

Figure 4. Drop at rest on a tilted plate: close to the threshold of sliding, the front angle is close to the advancing angle and the rear one is close to the receding one. α is the tilting angle of the plate.

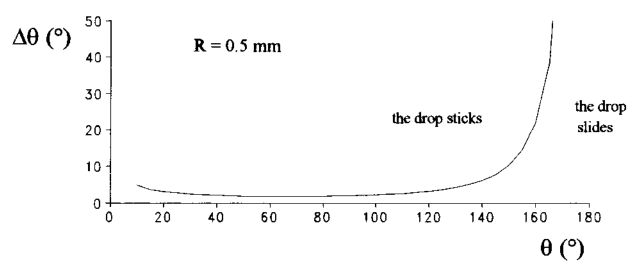

Figure 5. Dividing line between the region of sticking and the region of sliding for a rain drop of fixed volume (here, it is a drop of radius $R = 0.5$ mm) in the space ($\Delta\theta$, θ) where $\Delta\theta$ is the contact angle hysteresis and θ is the average contact angle. The line represents eq 5.

vertical substrate ($\alpha = \pi/2$). For a given angle, the hysteresis must be smaller than some critical value for making the drop slide (condition 5). For θ varying from 10° to 140°, this threshold is nearly constant versus the angle—and it is found in this example to be very low (less than 5°). Then, it sharply increases with θ (above $\theta = 160°$, the approximation of small $\Delta\theta$ is not valid any longer). Conversely, for a given hysteresis, the drop remains stuck if the angle is smaller than some critical value, which is large (of the order 150° in this example) in most practical situations (where $\Delta\theta > 10°$). It is logical to find such a threshold, since large angles (see Figure 1b) imply a small contact area between the solid and the liquid and thus favor the sliding.

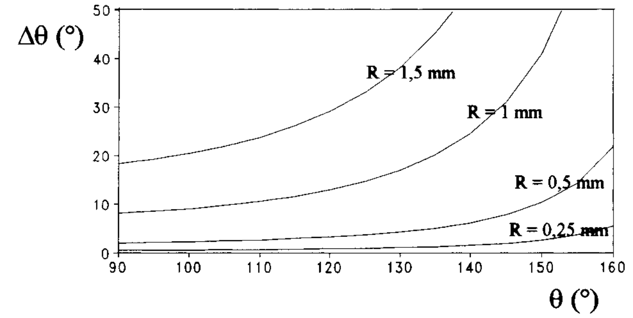

Figure 6. Same representation as in Figure 5 for different drop sizes (R is the radius of the spherical drop which is deposited on the solid).

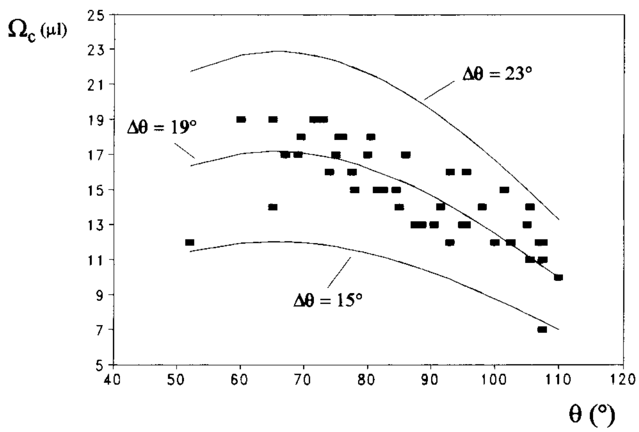

Figure 7. Critical volume (above which a drop slides on a vertical solid) as a function of the average contact angle. Squares are experimental data obtained on different substrates with pure water. The lines are eq 5 drawn for a constant hysteresis (a condition roughly satisfied in the experiments). The middle line corresponds to the average hysteresis ($\Delta\theta = 19°$), the lower to $\Delta\theta = 15°$, and the upper to $\Delta\theta = 23°$.

Finally, it must be stressed that the threshold in hysteresis highly depends on the drop size (as shown in eq 5, where $\Delta\theta$ increases as R^2). Figure 6 is a plot similar to Figure 5, but it is presented for several drop sizes (the largest size corresponds to a summer rain, while the smallest one corresponds to a drizzle).

3.2. Experimental Determination of the Critical Volume. A series of experiments was done, to determine the critical volume above which the drop slides. The substrates which were used are the ones on which contact angles were measured (see Figure 3 and Table 1). It must be emphasized that the common feature of these different substrates is the smallness of the hysteresis (its average is 19°), in agreement both with our hypothesis for the calculation and with the practical aim (it is often desirable that water droplets do not remain stuck on the solids). Furthermore, the hysteresis is nearly constant (it varies around its mean value of about 5°) while the angles lie in a large interval (between 52° and 110°).

The critical volume is measured by depositing drops of pure water of different sizes on a vertical substrate. The volume is increased (with a step of 1 μL), up to the value for which the sliding occurs. On a given substrate, the experiment is reproducible with respect to both time and drop location: the error in determination of the critical volume is $\pm 2\ \mu$L. All the results are reported in Table 1 and displayed in Figure 7, where the critical volume Ω_c (in μL) is plotted as a function of the mean contact angle.

In the same figure, the data are compared with eq 5 (where R must be replaced by $(3\Omega/4\pi)^{1/3}$, since it is the volume which is measured). Equation 5, drawn with a constant hysteresis of $\Delta\theta = 19°$ (the average value of the hysteresis in these experiments), is the central line in Figure 7. Two other lines are drawn, corresponding to the extreme values of the hysteresis ($\Delta\theta = 15°$, lower line; $\Delta\theta = 23°$, upper line). All the data lie inside these lines, and are gathered around the mean one: the agreement with eq 5 appears to be satisfactory. In particular, the obtained curves have a remarkable characteristic, which is the (nontrivial) existence of a maximum around $\theta \approx 65°$, in agreement with the prediction of Dussan.[6]

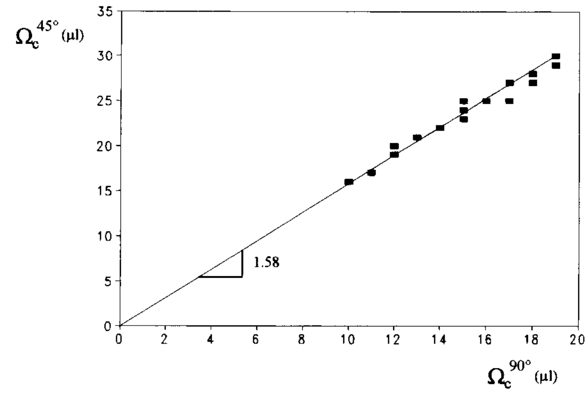

Figure 8. Critical volume measured on a plane inclined 45° versus the same quantity determined on the same plate inclined 90°. The liquid is pure water, and the line is the best fit: it is a straight line passing through the origin, of slope 1.58 ($\pm$0.05).

3.3. Influence of the Slope. A last test was done. On a given substrate, the critical volume Ω_c was measured for two different slopes: $\alpha = 90°$ (it is the slope in buildings) and $\alpha = 45°$, close to the slope of most car windshields. The data are displayed in Figure 8, where the critical volume for $\alpha = 45°$ is plotted as a function of the one determined with $\alpha = 90°$.

In each case, the critical volume is found to be larger on the smallest slope. The straight line passing through the origin drawn in Figure 8 confirms the proportionality between the two quantities: its slope is 1.58, in satisfactory agreement with the expected value (from eq 5, we have $\Omega_c \sim \sin^{3/2}\alpha$), which is 1.68.

4. Conclusion

We have characterized quantitatively the conditions under which a drop remains stuck on a solid surface. The critical volume above which a drop slides on a given substrate was measured and was found to be often large at the capillary scale (rain drops, of millimeter size, generally stick on windows). Conversely, the minimum hysteresis ensuring the sticking is low (commonly of order 10° or less, see Figure 6). The only way of increasing it (logically) consists of obtaining a surface of high hydrophobicity, like the so-called water-repellent surfaces of the Kao group, for example.[7] Then (see Figure 5), the constraint in hysteresis becomes weak, and "anti-rain surfaces", of practical importance, become conceivable.

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