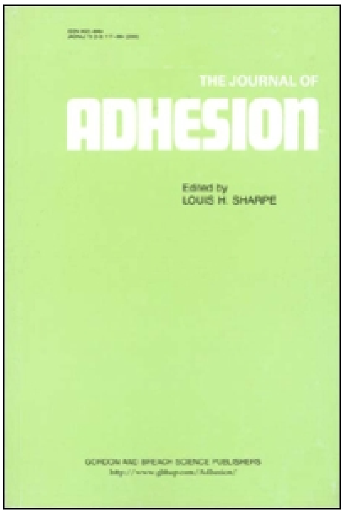


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# Drop Motion on an Inclined Plane and Evaluation of Hydrophobia Treatments to Glass

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# Drop Motion on an Inclined Plane and Evaluation of Hydrophobic Treatments to Glass*

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Hydrophobic and anti-rain surface treatments are increasingly used to treat various glass articles such as windscreens, windows, headlamps, wing mirrors, optical lenses, sunglasses, etc.

To evaluate the efficiency and durability of these treatments, we determine the smallest volume or critical sliding volume, $V_c$, of a water drop able to slide down spontaneously under gravity after having been deposited on a vertical treated, glass surface. The property of water repellency is considered to be better when $V_c$ is smaller. In this paper, a new simplified theory to describe the capillary force retaining the water drops on an inclined plane is proposed and verified practically.

The experimental method allows us to compare the efficiency and durability of a commercial anti-rain and of a Corning Inc. proprietary hydrophobic surface treatment for glass, both being based on silicone derivative chemistry. As defined in this paper, the critical sliding volume appears to be a practical parameter which may be used to characterize quantitatively the hydrophobicity of a solid surface.

KEY WORDS: contact angle; glass surfaces; hydrophobicity; liquid drop motion; water-repellency; wetting hysteresis.



## 1. INTRODUCTION

Numerous processes are known for making glass articles hydrophobic or water repellent by coating them with silicone or fluorinated resins. In this field, Corning Inc. has recently developed a coating composition and process to treat the surface of glass with a view to giving it excellent and durable properties of non-stickability, hydrophobicity and water repellency. The resulting coating is very thin ($< 1$ µm), transparent and invisible.

In order to evaluate quantitatively the hydrophobicity of the glass, we determine the smallest volume or the critical sliding volume, $V_c$, of a water drop able to move spontaneously under gravity along the glass surface. The method allows one to compare rapidly the efficiency and durability of the Corning Inc. surface treatment (CST) with another commercial anti-rain composition (CAC) for windscreens.

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In order to relate quantitatively the critical sliding volume, $V_c$, of a liquid to the contact angle hysteresis, a simplified theory to calculate explicitly the wetting force retaining a drop on a solid surface is proposed and experimentally verified.

## 2. THEORETICAL

The study is inspired by an article by Wolfram and Faust.[1] To obtain the critical sliding volume, $V_c$, a series of water droplets of different volumes, $V_i$, are deposited on a plate of the treated glass upon a tiltable plane which is initially in a horizontal position. The tilting angle with respect to the horizontal, $\alpha$, is increased continuously until each drop of volume $V_i$ moves down along the treated plate at a value $\alpha_i$ of the tilting angle.

When the critical tilting angle $\alpha_i$ is reached, the drop exhibits respectively at the front and at the rear of the triple line the well known advancing and receding contact angles, $\theta_a$ and $\theta_r$ (Figure 1a). At the center of the advancing edge Young's equation can be written as

$$\gamma_{sv} - \gamma_{lv}\cos\theta_a - \gamma_{sl} - f = 0 \tag{1}$$

$\gamma_{xy}$ being the interfacial free energy between phases $x$ and $y$ (solid-$s$, liquid-$l$, vapour-$v$) and $f$ the force resisting movement per unit length of contact boundary. At the center of the receding edge we have

$$\gamma_{sv} - \gamma_{lv}\cos\theta_r - \gamma_{sl} + f = 0 \tag{2}$$

and from equations (1) and (2) we obtain:

$$f = \frac{\gamma_{lv}}{2}(\cos\theta_r - \cos\theta_a). \tag{3}$$

To evaluate the total restraining force against the direction of drop movement, $F$, we will consider that the contact angle, $\theta$, of the drop is a function of the azimuthal angle $\phi$ (see Figure 1b) varying between the advancing value, $\theta_a$, at the leading edge ($\phi = 0$) and the receding value, $\theta_r$, at the trailing edge ($\phi = \pi$). In the calculation of the force, $F$, resisting drop movement down the inclined plane, we must allow for variations of $\theta$ along the triple line, as a function of $\phi$. The problem of assessing $\theta(\phi)$ is a complex one, related to the shape of a drop meniscus under the influence of a force field not acting along the axis of symmetry of the otherwise axisymmetric drop. It has been tackled by Brown *et al*[2]. using finite element techniques but, for our purposes, a less involved approach will be used, although leading to a similar dependence of $\theta$ on $\phi$.*

Considering Figure 1a, we may express the profile of a relatively flat drop (low contact angle) on an inclined plane, perturbed by gravity, in cylindrical polar coordinates, as

$$z(r, \phi) \simeq \frac{r_0^2 - r^2}{2R} + \varepsilon(r, \phi) \tag{4}$$

where $R$ is the radius of curvature of the unperturbed drop and $r_0$ the contact radius. (The contour of the drop is assumed, and observed, to remain circular). The first term

* It has since come to the authors' attention that a somewhat similar approach was used by Popova for evaluating the full profile of a drop on an inclined plane.[3]

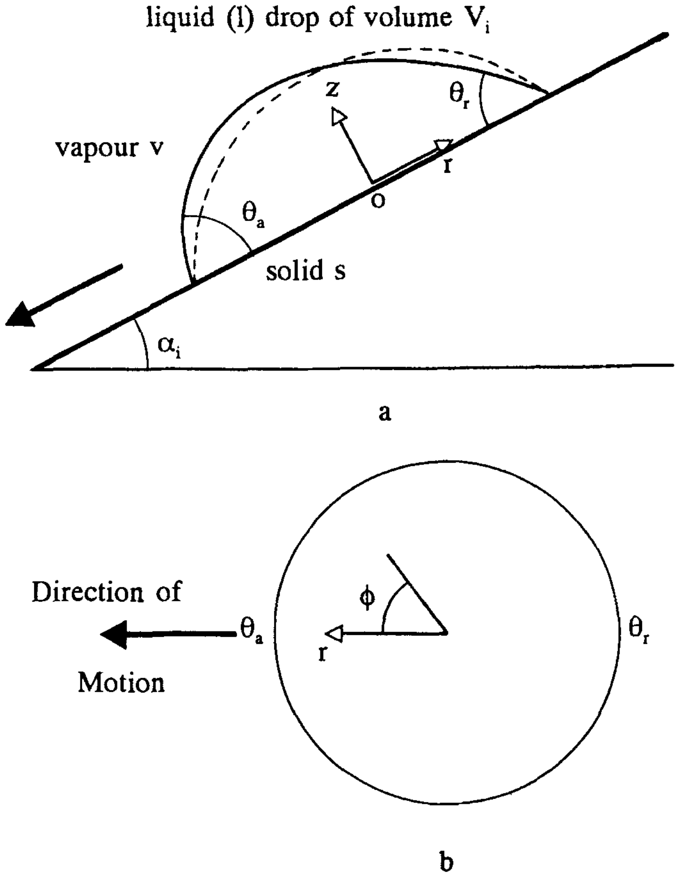


FIGURE 1 a–Profile of deformed drop (——) corresponding to spherical drop (---) perturbed by gravity. b–Plan view of drop on inclined plane retaining a circular boundary.



corresponds to the undisturbed form and $\varepsilon(r, \phi)$ is a perturbation caused by gravity. (A similar approach to the following has been employed for the evaluation of meniscus shape for a drop on a slightly heterogeneous surface.[4]) The free energy of the system, $E$, to be minimised as a necessary condition for equilibrium, corresponds to that due to the interfaces $\gamma_{sv}$, $\gamma_{sl}$ and $\gamma_{lv}$ and, in addition, the contribution pertaining to gravitational potential energy (taken arbitrarily with respect to the origin of the coordinate system). This total free energy must be minimised subject to the constraint of constant drop volume, $V$. Using a Lagrange multiplier, $\Delta p$, which in fact corresponds to the Laplace pressure of the unperturbed drop $(2\gamma_{lv}/R)$, we define the function, $J$, to be minimised

$$J = E - \Delta p.\, V = \int_{-\pi}^{+\pi} \int_{0}^{r_o} \left[ \gamma_{lv}(r^2 + r^2 z_r^2 + z_\phi^2)^{1/2} + (\gamma_{sl} - \gamma_{sv})r + \rho g z r \left( \frac{z}{2}\cos\alpha - r \sin\alpha \cos\phi \right) - \Delta p.r.z \right] dr\, d\phi \qquad (5)$$

where $z_r$ and $z_\phi$ have their usual meanings of derivatives, $\alpha$ is the slope of the inclined plane, $\rho$ is liquid density and $g$ gravitational acceleration. Defining $J'$ as the integrand of Eq. (5), a necessary condition for minimisation of $J$ is given by Ostrogradskii's equation:[5]

$$\frac{\partial J'}{\partial z}-\frac{\partial}{\partial r}\left(\frac{\partial J'}{\partial z_r}\right)-\frac{\partial}{\partial \phi}\left(\frac{\partial J'}{\partial z_\phi}\right)=0 \tag{6}$$

Using Eqs. (4–6), we obtain after some algebra, to $O(z_r^2)$ and $O(z_\phi^2)$

$$r^2\varepsilon_{rr}+r\varepsilon_r+\varepsilon_{\phi\phi}-\frac{\rho g r^2}{\gamma_{lv}}\cos\alpha.\varepsilon-\frac{\rho g r^2}{\gamma_{lv}}\left[\frac{(r_0^2-r^2)}{2R}\cos\alpha-r\cos\phi\sin\alpha\right]=0 \tag{7}$$

This equation will be very difficult to solve, but we may simplify it considerably, realising that its solution only near the triple line is of immediate significance

$$\frac{d}{dr}(r\varepsilon_r)\simeq\frac{-\rho g r^2\sin\alpha\cos\phi}{\gamma_{lv}};r\simeq r_0 \tag{8}$$

leading to:

$$\varepsilon_r(r_0)\simeq\frac{-\rho g r_0^2\sin\alpha\cos\phi}{3\gamma_{lv}} \tag{9}$$

Realising that $\theta=(-)\tan^{-1}[z_r(r_0)]$, we may now readily observe the dependence of $\theta(\phi)$ on $\cos\phi$ and from Eq. (9), write this in the form

$$\theta(\phi)\simeq\theta_y+\frac{\Delta\theta}{2}.\cos\phi \tag{10}$$

where $\Delta\theta=(\theta_a-\theta_r)$, for $\alpha=\alpha_i$, and $\theta_y$ is the Young's value of contact angle (at $\phi\simeq\pm\pi/2$).
From Figure 2, the restraining force for segment $\delta\phi$ is given by $\tilde{f}=f_1+f_2$, where:

$$f_1=\gamma_{sv}-\gamma_{lv}\cos\theta(\phi)-\gamma_{sl} \tag{11}$$

$$f_2=-(\gamma_{sv}-\gamma_{lv}\cos\theta(\phi+\pi)-\gamma_{sl}) \tag{12}$$

The total restraining force against the direction of drop motion is given by:

$$F=2r_0\int_0^{\pi/2}\tilde{f}\cos\phi\,d\phi \tag{13}$$

Using Eqs. (10) to (13), we obtain:

$$F=4r_0\gamma_{1v}\int_0^{\pi/2}\sin\theta_y\cdot\sin\left(\frac{\Delta\theta}{2}\cdot\cos\phi\right)\cdot\cos\phi\,d\phi\simeq\pi r_0 f \tag{14}$$

$$\text{with}\quad f=\frac{\gamma_{lv}}{2}(\cos\theta_r-\cos\theta_a).$$

Equation (14) gives a value of force only half that given in Reference 1. However, it is considered that this derivation is a more realistic assessment of the situation, particularly in as much as a continuously changing value of $\theta(\phi)$ is obtained. Physically

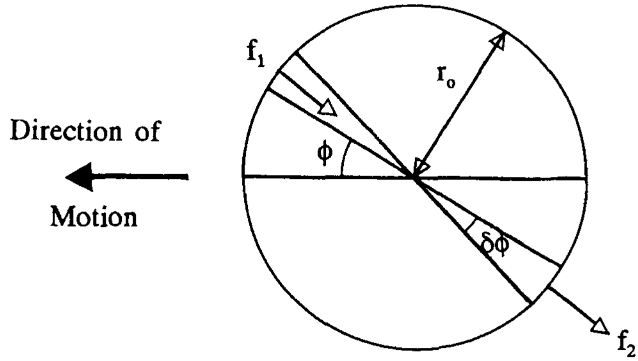


FIGURE 2 Schematic representation of forces restraining drop movement.

impossible, abrupt changes in $\theta$ are eliminated. It is true that some simplications have (necessarily) been introduced to make the problem tractable, but the dependence of $\theta(\phi)$ on $\cos\phi$ seems quite plausible and, indeed, inspection of Reference 2, Figure 5, shows a similar dependence, at least for relatively small differences between advancing and receding contact angles, as is the case in the experimental work reported here. Admittedly, the present treatment considers low values of contact angle whereas the experimental results concern, for the most part, high values, but the basic physics should be essentially the same, even though the mathematical treatment will be far more involved and, as stated above, Reference 2 lends credence to the dependence obtained.



Considering now that the contact angle on the horizontal plane ($\alpha = 0$) is $\theta_y$, we have[1]

$$\cos\theta_y = \frac{\cos\theta_a + \cos\theta_r}{2} \tag{15}$$

taking into account that contact angle hysteresis is not due to roughness of the glass surface (Wenzel[6] roughness factor = 1). Using $t = \tan(\theta_y/2)$ and a simple geometrical relationship to deduce $r_0$ from $V_i$, it may be shown that

$$V_i^{2/3}\sin\alpha_i = \frac{6^{1/3}\pi^{2/3}}{t^{1/3}(t^2+3)^{1/3}}\frac{\gamma_{1v}}{2\rho g}(\cos\theta_r - \cos\theta_a) \tag{16}$$

which may be simplified to

$$V_i^{2/3}\sin\alpha_i = A(\cos\theta_r - \cos\theta_a) = K \tag{17}$$

where $A$ is a constant for a given liquid/solid system. The product $V_i^{2/3}\sin\alpha_i$ should, therefore, be constant also for a given system. The smallest volume, $V_c$, corresponding to $\alpha_i = \pi/2$, is deduced from Eq. (17):

$$V_c = K^{3/2} \tag{18}$$

## 3. EXPERIMENTAL

Clean plates of soda lime silica glass were treated with a commercial anti-rain composition (CAC) for windscreens and with the Corning surface treatment (CST). The

CAC includes a polydimethylsiloxane and a mineral acid dissolved in an ethanol-isopropanol mixture. In contrast to the CAC, the CST is based on monomeric hydrophobic organosilicone compounds whose hydrolysable functions allow the formation of chemical bonding to glass. The resulting treated plates were submitted to the action of boiling and cold running water. Young's contact angle, $\theta_y$, and critical sliding volume, $V_c$, were measured on the different series of samples.

Use of equation (17) is illustrated in Figure 3. Several water drops ($V_i$ from 1 to 40 $\mu$l) were deposited on treated and untreated sodalime glass plates. Constancy of $V_i^{2/3} \sin \alpha_i$ as a function of $V_i$ is clearly observed for each glass substrate. Curve (1) gives the smallest volume able to slide, $V_c$, when $\alpha_i = \pi/2$ and the corresponding $K$ factor when drop retention is controlled uniquely by wetting hysteresis (Eqs. 17, 18). The values of $V_c$ for each substrate before and after ageing in boiling water are reported in Table I. It appears that the Corning surface treatment (CST) has a very high efficiency associated with good hydrolytic resistance, the smallest sliding volume for water droplets remaining close to 2 $\mu$l even after treatment in boiling water. This is not the case for the commercial anti-rain product (CAC).

It is interesting to note that the advancing and receding contact angles can be predicted from Eqs. (15) and (17) according to

$$\cos\theta_r - \cos\theta_a = \frac{K}{A} \tag{19}$$

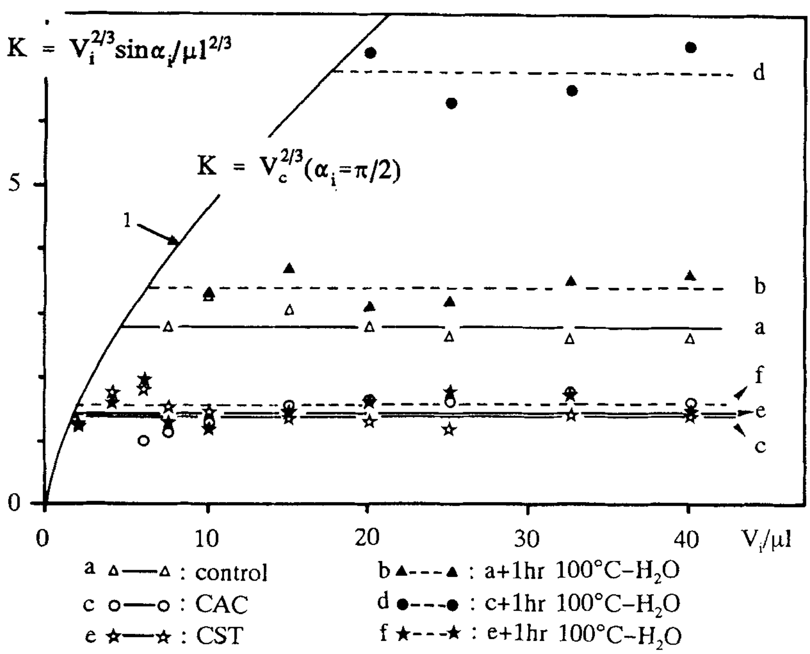


FIGURE 3 $V_i^{2/3} \sin \alpha_i$ as a function of $V_i$ for untreated and treated glass, before and after ageing in boiling water.

TABLE I
Critical sliding volume, $V_c(\mu l)$, and contact angle data $(\theta_y, \theta_a, \theta_r)$ for untreated glass plates (control) and those treated with a commercial anti-rain composition (CAC) and with the Corning surface treatment (CST) before and after ageing in boiling water

| Glass Treatment | No ageing | After 1 hr in 100°C—$H_2O$ |
|---|---|---|
| Control | $V_c = 4.9$ | 6.3 |
| | $\theta_y = 42.5$ | 51.5 |
| | $\theta_a = 51$ | 61 |
| | $\theta_r = 32.5$ | 41 |
| CAC | $V_c = 1.5$ | 17.7 |
| | $\theta_y = 108$ | 72 |
| | $\theta_a = 113$ | 91 |
| | $\theta_r = 103$ | 51 |
| CST | $V_c = 1.8$ | 2.0 |
| | $\theta_y = 105$ | 99.5 |
| | $\theta_a = 111$ | 105 |
| | $\theta_r = 99.5$ | 94 |

and

$$\cos\theta_r + \cos\theta_a = 2\cos\theta_y. \tag{20}$$

Thus, theoretical values of $\theta_a$ and $\theta_r$ have been calculated from $K$, $A$, and $\theta_y$ and are given in Table I. As an example, it has been verified with the CST treated glass that the experimental $\theta_a$ and $\theta_r$ values as measured from Figure 4 (110 and 100°) are very similar to the theoretical values (111 and 99.5°) calculated from Eqs. (19–20),

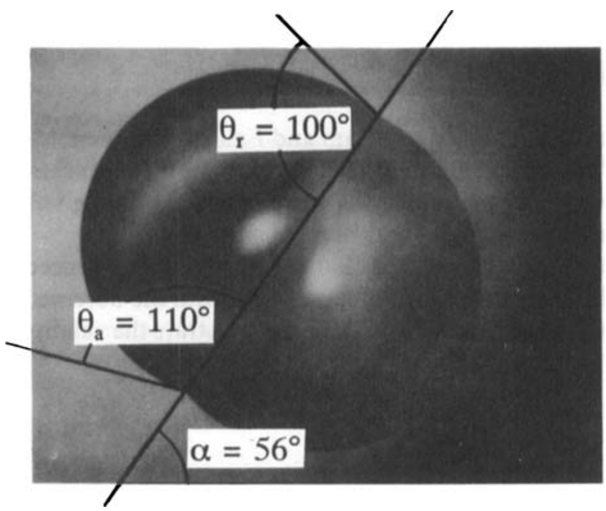


FIGURE 4 Advancing and receding contact angles of a 2 μl water drop sliding on a CST glass plate.

TABLE II
Critical sliding volume, $V_c(\mu l)$, and contact angle data ($\theta_y$, $\theta_a$, $\theta_r$) for untreated glass plates (control) and those treated with CAC and CST treatments before and after ageing in running water

| Glass Treatment | No ageing | After 30 hr in running water |
|---|---|---|
| Control | $V_c = 4.9$ | 6.5 |
| | $\theta_y = 42.5$ | 44 |
| | $\theta_a = 51$ | 54 |
| | $\theta_r = 32.5$ | 32 |
| CAC | $V_c = 1.5$ | 8.6 |
| | $\theta_y = 108$ | 96.3 |
| | $\theta_a = 113$ | 111 |
| | $\theta_r = 103$ | 82 |
| CST | $V_c = 1.8$ | 4.0 |
| | $\theta_y = 105$ | 103 |
| | $\theta_a = 111$ | 113 |
| | $\theta_r = 99.5$ | 94 |

the value of $\theta_y$ being 105°. This good agreement also justifies the analysis and the basic hypotheses.

Another series of examples is given in Table II. This time the glass surfaces have been submitted to the action of cold running water for 30 hrs. In all cases, ageing increases the critical sliding volume, $V_c$, of water droplets and the contact angle hysteresis. For the CAC and CST treated glass, ageing in cold or hot water seems to affect the receding rather than the advancing contact angle. This can be explained by an increase of the number of hydrophilic sites on the corresponding surfaces.

The better durability of the CST treatment can be attributed to covalent bonding between the hydrophobic species and glass surface.



## 5. CONCLUSION

From the improved analysis of Wolfram and Faust,[1] it is possible to characterize and compare the efficiency and durability of hydrophobic and anti-rain surface treatments for glass by determining the smallest volume or critical sliding volume, $V_c$, of a water drop able to slide under gravity on a vertical surface.

Furthermore, it has been verified that the advancing and receding contact angles deduced from the analysis are in good agreement with the observed values. This result and the constancy of the product $V_i^{2/3} \sin \alpha_i$ demonstrate the validity of the method and basic assumptions.

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