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Viscous drops rolling on a tilted non-wettable solid

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Abstract. – A viscous liquid drop sliding down an inclined solid that it partially wets runs all the faster since it is large. Here we examine what happens in the limit of very high contact angles, on a so-called super-hydrophobic surface. It is shown that a droplet rolls instead of sliding, which leads to a surprising law for the velocity as a function of the drop radius: the smaller the droplet, the larger the running velocity. A recent model of Mahadevan and Pomeau allows us to propose an explanation for this paradoxical behaviour.

It is often proposed that a drop moving down a tilted non-wettable solid has some rolling motion, instead of sliding [1-3]. Here we present new observations related to this old problem, both on the velocity of the drop and on the details of the flow. These observations could be done thanks to recent progresses with *super-hydrophobic solids*, by the Kao group [4-7] and others [8-10]. These materials are both *hydrophobic* (contact angle larger than 90° for flat surfaces) and *porous*. Air remains trapped below a drop deposited on these surfaces [11, 12], which leads to a contact angle θ close to 180° [10]. Furthermore, the associated contact angle hysteresis is generally small ($< 20°$) [11]. Some plant leaves have such properties [12, 13]: on lotus or water lily, water drops adopt *pearls*.

Our aim (to observe a droplet moving on an inclined plane) appears simple but there is a basic difficulty. On the one hand, the droplet must be small to keep a spherical shape: gravity would flatten a drop of radius R larger than the millimetric *capillary length* κ^{-1} ($\kappa^{-1} = (\gamma/\rho g)^{1/2}$, with γ the liquid surface tension, ρ the liquid density and g the gravitational acceleration). On the other hand, a small droplet generally remains stuck when deposited on a solid, because of the contact angle hysteresis $\Delta\theta$ ($\Delta\theta = \theta_a - \theta_r$, with θ_a and θ_r the static *advancing and receding angles*) [14]. Sticking occurs when the capillary force (of order $\pi r\gamma(\cos\theta_r - \cos\theta_a)$, with r the contact line radius) is larger than the weight ($4/3\pi R^3 \rho g \sin\alpha$, noting R the radius of the deposited drop and α the tilting angle of the solid). Thus, drops smaller than κ^{-1} generally satisfy this condition and remain stuck. Even in the limit of super-hydrophobic surfaces (for which the radius of contact $r \approx R\sin\theta$ becomes small), this sticking condition is easily satisfied: for $\theta = 160°$, $R = 0.5$ mm and $\alpha = 20°$, the sticking should occur for hysteresis $\Delta\theta$ smaller than 7° (a very low value, indeed).

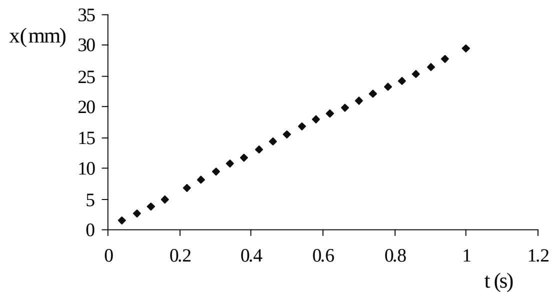

Fig. 1. – Glycerol drop ($R = 1$ mm) running down a super-hydrophobic ($\theta_\mathrm{a} = 165°$) surface of small contact angle hysteresis ($\Delta\theta = \theta_\mathrm{a} - \theta_\mathrm{r} < 10°$). The motion is filmed and the position of the centre of mass of the drop x can be reported as a function of time t (the drop is put at $t = 0$ in $x = 0$). It is observed that the descent velocity V is a constant in such an experiment. The tilt angle $\alpha = 13°$ is large enough to avoid that the drop remains stuck on the surface, because of the contact angle hysteresis. The surface tension γ, density ρ and viscosity η of glycerol are, respectively, 63 mN/m, 1200 kg/m^3 and 950 mPa s.

The first step therefore consists in finding a super-hydrophobic surface of contact angle hysteresis as low as possible. Among all the possible samples, we chose a fibrous surface (fiber radius of order 500 nm) created by V. Coustet (Saint-Gobain). The contact angle θ is $170 \pm 5°$ against water and $165 \pm 5°$ against glycerol, with respective hysteresis lower than 5° and 10°. Note that even in this case, we must keep in mind that working with small droplets can easily bring us back to the sticking threshold.

The experiment consists in depositing a drop (radius R) on the substrate tilted with an angle α and recording the motion. The drop is made of glycerol, of surface tension and density comparable with water ($\gamma = 63$ mN/m and $\rho = 1200$ kg/m^3; thus, we have: $\kappa^{-1} = 2.3$ mm), but of much larger viscosity η ($\eta = 950$ mPa s, measured before and after each experiment). This allowed us to reach stationary regimes on a sample of centimetre size. In fig. 1, the position x of a drop is plotted *versus* time t, for $R = 1$ mm and $\alpha = 13°$. It can be observed that *the speed of descent is constant*, with some slight fluctuations due to the presence of surface defects. Even this simple point must be stressed: on a surface of nearly zero wetting where the contact between the drop and the solid (and thus the viscous force) is minor, the motion could be close to a free fall. When doing the same experiment with water, a pure acceleration is indeed observed during the first centimetres.

The running velocity V was measured for different drop radii R and solid slopes. In fig. 2, V is displayed as a function of R, for two different tilting angles $\alpha = 13°$ (full circles) and $\alpha = 45°$ (empty circles). The drop radius is normalized by the capillary length and the velocity by a characteristic velocity of descent V_0, defined in eq. (1) below, which is related both to the liquid and to the tilting angle (V_0 scales as $\gamma/\eta \sin\alpha$). The velocities of descent are rather high (in spite of the large viscosity of glycerol): between 2.5 and 5 cm/s for the smallest slope, and between 6 and 12 cm/s for the largest one. Note finally that error bars related to the fluctuations of velocity (see fig. 1) are of order 10%.

Two regimes can be observed in fig. 2. For large drops ($R > \kappa^{-1}$), the velocity tends to a constant. For smaller ones, large fluctuations of the velocity can be observed (which could be related to the vicinity of the sticking threshold), but the most remarkable point is that the data have *a decreasing envelope*. The (maximal) velocity is thus larger for smaller drops, which is a surprising feature with a driving force (gravity) varying as R^3.

We first consider the case of large drops. As stressed above, a drop larger than the

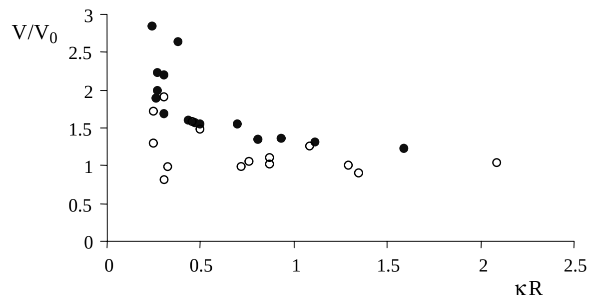

Fig. 2. – Running velocity V of glycerol drops as a function of the drop radius R, for two different tilting angles α of the super-hydrophobic solid: $\alpha = 13°$ (full circles) and $\alpha = 45°$ (open circles). The velocity V is scaled by a characteristic velocity of descent V_0 (of order $\gamma/\eta \sin\alpha$) derived in the text (eq. (1)). This velocity is 1.9 cm/s for $\alpha = 13°$ and 3.1 cm/s for $\alpha = 45°$. The drop radius R is scaled by the capillary length κ^{-1} (2.3 mm for glycerol). For large drops (puddles), V tends to V_0. For small droplets ($R < \kappa^{-1}$), the velocity increases as the drop size decreases. At the same time, large fluctuations of the measured velocity are observed, because we get closer to the threshold of sticking (we have $\Delta\theta > 0$) and to the lower limit of validity of the model due to a non-zero wetting ($\theta < 180°$).

capillary length κ^{-1} is flattened by gravity and forms a *puddle*. The thickness h of this puddle results from a balance between capillary forces and gravity. For large puddles, it writes: $h = \sqrt{2(1-\cos\theta)}\kappa^{-1}$ (where θ is the contact angle) [15]. The viscous force (per unit volume) associated with a liquid layer flowing along a plane is classically $3\eta V/h^2$ (Poiseuille law), where h is the thickness of the liquid layer. Balancing this force with the gravity force $\rho g \sin\alpha$ yields an expression for the velocity V_0 of a puddle falling down a tilted plate:

$$V_0 = \frac{2(1-\cos\theta)}{3}\frac{\gamma}{\eta}\sin\alpha\,. \tag{1}$$

This velocity is scaled by an interfacial velocity intrinsic to the liquid (γ/η, which is 6.6 cm/s for glycerol but 1000 times larger for water) but surprisingly does not depend on ρg: gravity fixes both the driving force and the puddle thickness, and thus the viscous dissipation. V_0 is the velocity chosen in fig. 2 for normalizing the data and it is indeed observed that V/V_0 tends towards unity, for κR larger than 1.

We now look into the case of small drops. Mahadevan and Pomeau have recently calculated the viscous dissipation in a drop moving on a solid that it does not wet [1]. In spite of a contact angle of 180°, a contact zone (of size ℓ) forms between the solid and the liquid because of gravity, which tends to lower slightly (of a quantity δ) the mass centre of the drop. At the same time, the droplet, of radius smaller than the capillary length ($R < \kappa^{-1}$), remains quasi-spherical. For weakly deformed droplets, ℓ and δ are thus related by: $\ell^2 \sim R\delta$. Gravitational and surface energies are of the same order at equilibrium, which is written: $\rho g R^3\delta \sim \gamma\ell^4/R^2$. The latter term expresses the increase of surface energy if compared with a liquid sphere tangent to the solid. It is calculated considering the solid/liquid surface tension of order the liquid/vapour one, which is a good approximation in a situation of nearly zero wetting where the frontier below the drop mainly consists in pieces of liquid/vapour interfaces [10]. The two lengths characterising the deformation of the droplet can be finally expressed: $\delta \sim R^3\kappa^2$ and $\ell \sim R^2\kappa$.

Mahadevan and Pomeau considered that a (slow) motion of the drop does not affect these scalings. In the steady state, the droplet velocity is determined by balancing the rate of decrease of the gravitational energy and the viscous dissipation. The latter is minimum for a Stokes flow (for given boundary conditions), which is achieved by maximising the volume in

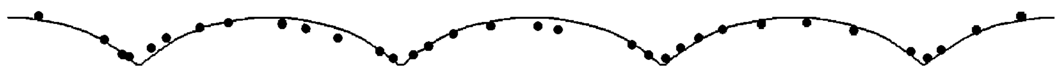

Fig. 3. – Trajectory of a track (a bubble of size 100 μm) placed just below the surface of a glycerol drop of radius $R = 1.6$ mm running down a super-hydrophobic plate. The points are the data deduced from a film (error bar of order the point size). The line is a cycloid of equation: $x = t + 0.75 \sin t$, $y = 0.75 \cdot 0.73 \cos t$, where the coefficients 0.75 and 0.73, respectively take into account the position of the track inside the drop and the eccentricity of the drop ($\varepsilon = 1.3$) due to gravity.

rigid rotation, which induces no dissipation. With such a flow, the only region where viscosity must be considered is the contact zone, of size ℓ. The fluid velocity V and velocity gradient in this region are of respective order $V\ell/R$ and V/R. Thus, the flow dissipation $T\overset{\circ}{S}$ scales as $\eta(V/R)^2\ell^3$, from which the droplet velocity can be calculated [1]:

$$V \sim V_0 \frac{\kappa^{-1}}{R}\,, \qquad (2)$$

where V_0 is given by eq. (1). Hence, the drop velocity is found to *increase as the droplet size decreases*, which is in good qualitative agreement with our observations. In fig. 2, the maximal descent velocity $V(R)$ increases by a factor of about 3 as κR passes from 0.75 to 0.25, which is consistent with an hyperbolic behaviour.

It was thus necessary to test the central hypothesis leading to eq. (2): does a non-wetting droplet falling down a tilted plate *roll*? This had been previously reported close to a contact line [2] and qualitatively observed on dust in a moving drop of mercury [16]. Our test consisted in incorporating a 100 μm mark (either a bubble of air or a piece of rubber) just below the liquid/vapour interface of a droplet of radius 1.6 mm. Because of the very high viscosity of glycerol, the mark does not move in the referential drop during the motion. Once again, the descent was filmed and the trajectory of the mark recorded. It is displayed in fig. 3, where a cycloid is superimposed on the data. This curve is drawn taking into account both the position of the bubble below the surface (which explains that the cusps have not a vertical tangent) and the slight eccentricity of the drop due to gravity ($\varepsilon = 1.3$). The cycloid fits the data quite well, proving a quasi-rigid rotation for the drop during its motion.

We finally examine the limits of eq. (2), in terms of drop size and velocity.

1) A first limit on the size was discussed above: for remaining spherical, a drop must be smaller than κ^{-1}, the capillary length. A second limit is related to the degree of hydrophobicity of the substrate. If the contact angle is appreciably smaller than 180°, the wetting condition imposes the development of a solid/liquid interface of radius $r \approx R \sin\theta$, as briefly mentioned above in discussing the sticking condition. For eq. (2) to be valid, the size r of the wetted area must be smaller than the size ℓ of the gravitational contact. This condition ($\ell > r$) leads to: $\kappa R > \sin\theta$. For $\theta \sim 165°$, $\sin\theta$ is of order 0.25, while in the experiments κR is larger than 0.22. Thus, the smallest droplets ($R = 0.5$ mm) define the limit of validity of the model. This point might partially explain the fluctuations of the velocity at small radii, together with the proximity of the sticking threshold. For $\ell < r$, the zone where viscous dissipation takes place is of size r *scaling as* R. There is only one length to consider in the calculation, namely R, which yields a descent velocity V scaling as R^2. Hence, the hyperbolic behaviour for $V(R)$ (eq. (2)) should be preceded for $R < \kappa^{-1} \sin\theta$ by a parabolic one tending to 0 for $R = 0$.

Thus, the behaviour predicted by Mahadevan-Pomeau (eq. (2)) should only concern drops of radius in the interval $[\kappa^{-1}\sin\theta, \kappa^{-1}]$ and the velocity presents a maximum for $R = \kappa^{-1}\sin\theta$. These results are in good agreement with the data in fig. 2 and stress again the necessity to be in a super-hydrophobic situation, so that $\kappa^{-1}\sin\theta$ can be significantly lower than κ^{-1}. Even in this case, this interval is generally narrow, which makes difficult a quantitative test of a scaling law such as eq. (2).

2) There are also some limits on the velocity. For allowing us to consider the flow as a Stokes flow, the Reynolds number ($Re = \rho VR/\eta$) must be smaller than unity. This condition was fulfilled using glycerol, making Re smaller than 0.1. Justifications that we can keep a quasi-spherical shape for the droplet are that both the Weber ($We = \rho V^2 R/\gamma$) and capillary ($Ca = \eta V/\gamma$) numbers are smaller than unity. Because of the small velocities (typically, $V < 10$ cm/s), the first condition is satisfied: we have $We < 0.1$. The second one is less obvious. Equation (2) shows that the capillary number can be written: $Ca = \kappa^{-1}/R\sin\alpha$. Taking a small slope ensures $Ca < 1$ for all the droplets studied. But it is not always the case for a larger slope, which could explain in fig. 2 that the data with $\alpha = 45°$ are less divergent at small R than the data with $\alpha = 13°$. There is also a limit at small velocity: because of the motion, the angle at the front of the drop is larger than the angle at the rear (even in the limit $\Delta\theta \to 0$), so that a dynamic capillary force opposes the motion. For drop sizes around κ^{-1}, this force should be larger than the viscous one only in the limit of very small capillary numbers, which is not reached in our experiments. Dussan [14] has shown that the velocity in this limit should scale as R^2, since it results from a balance between a capillary force and gravity, of respective scaling R and R^3.

We have shown that viscous droplets in a situation of nearly zero wetting have a remarkable motion, when deposited on a tilted plane. They roll (instead of sliding), which leads to an unusual law for the stationary velocity V, since V increases as R decreases. We have stressed the rather narrow interval in droplet radius for which this law can be observed. An interesting complement would be to understand if such a rolling motion has the ability to clean efficiently a dirty surface, as observed on hydrophobic plants (this self-cleaning effect seems to be responsible for the sacred nature of lotus in India). Another complementing study would consist in looking at the limit of smaller viscosities: in preliminary experiments with water, we observed that the drop constantly accelerates during the first centimeters. At the same time, the trajectory of a track put below the free interface but far from the contact line is a straight line. The study of the transition between this (nearly) pure sliding motion and the (nearly) pure rolling motion reported here is in progress.

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