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IMPACT OF DROPS ON VARIOUS NON-WETTING SURFACES

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ABSTRACT

We have carried out an experimental study of liquid drop impact on various superhydrophobic substrates. Our surfaces are of two kinds (1) a carpet of chemically coated nanowires and (2) a smooth warm substrate. In the latter case, the Leidenfrost effect (also called 'boiling crisis') ensures the existence of a thin layer of air coming from the evaporation of the drop, thus preventing the drop to touch the warm surface. Technically, in this latter situation the contact angle can then be considered as equal to 180 degrees, with no hysteresis. Due to its initial inertia, the drop experiences a flattening phase after it hits the surface, taking the shape of a pancake. Once it reaches its maximal lateral extension, the drop begins to retract and bounces back. We have extracted the lateral extension of the drop, and we propose a model that explains the trend. We find a limit initial velocity beyond which the drop (1) protrudes into the nanowire carpet (2) touches the hot plate, provoking a local violent boiling. We discuss the relevance of practical issues in terms of self-cleaning surfaces or spray-cooling.

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INTRODUCTION

The problem of liquid drops impacting on a solid surface has received much attention, owing to numerous related practical applications. Amongst them, the spray-coating, the application of pesticides or the cooling of hot surfaces offer situations that involve complex interactions of many droplets impacting on a solid. The understanding of the basic phenomena during impact necessitates to study the case of a single impacting drop. Even in this simpler case, complexity can arise [1, 2], for example from the wettability conditions. Although the influence of the contact-line can be neglected at the very first instants after impact, it generally plays a major role in the dissipation during the spreading and the retraction stages. Additionally, an instability can occur at the contact line, giving rise to a familiar fingering pattern [3].

Here, we study the simpler situation of a drop impacting on a very repelling surface. Under this condition, the difficulty related to the contact-line dynamics is removed, as the liquid is barely in contact with the solid. This is realized practically in at least two situations: (1) when an air cushion is sustained between the drop and the solid, for instance in a Leidenfrost situation [4, 5]. (2) when the surface is composed of micro-posts or nano-wire, together with an ad-hoc chemical coating, making it superhydrophobic. Previous studies have shown that a spherical drop impinging on such super-hydrophobic surface, bounces off the surface, sometimes with a quasi elastic behavior.

Numerous studies on impact on hot surfaces do not only present aesthetic interests. They have practical issues in metal cooling, combustion [6, 7] and heat transfer. In these applications, the boiling crisis is a limiting phenomenon for heat transfer and it is necessary to avoid it as much as possible.

Concerning super-hydrophobic surfaces made of micro- or nano-texturation, the main issue is to predict the criterion for protrusion through the surface, i.e. the transition from an 'fakir state' (Cassie-Baxter state) where the drop is supported by the top of the posts, to an 'impaled' state (Wenzel state) where some liquid protruded the texture (see [8] for a recent review). This is a crucial issue in the manipulation of micro-drops, because once the drop protruded the texture the sticking force is dramatically increased, making the drop's displacement much more difficult. On the contrary if the drop stays on top of micro-pilars or nano-wires, the liquid can slide on the surface with almost no friction.

We present here experimental results as well as a semi-analytical approach of the spreading and retraction phases of a drop impacting both a Leidenfrost surface and a nano-wire surface, at moderate Weber number. In this simpler situation, the drop bounces quasi-elastically, and the deformations keep sufficiently small in order to almost preserve the axisymmetry during the whole cycle. The results of this analysis are compared to pre-existing experiments as well as new ones, showing a pretty good agreement.

EXPERIMENTAL SET-UP

We used a dripping faucet that releases a drop of liquid from a sub-millimetric needle. The drop detaches from the needle as the action of gravity overcomes the capillary retention forces. Hence the diameter of the drop is determined by the capillary length, and is well reproducible at d = 2.7 $\pm$ 0.1 mm for water, and slightly smaller for the Glycerol mixtures. The physical parameters of the liquid are given on Table 1.

The height of fall h prescribes the velocity at impact: $V_0 = (2gh)^{1/2}$, which can be up to 1.5 m/s. Using backlighting together with a high-speed camera (at a maximal rate of 9500 frames/s, with a resolution of 300$\times$300 to 576$\times$576), the shape of the interface during the spreading and bouncing processes can be determined. The magnification allows for a maximal accuracy of about 15 μm per pixel. The dimensionless parameter that controls the experiment, is the Weber number We = $\frac{\rho V_0^2 d}{\gamma}$, and to a certain extend the Reynolds number Re=$\frac{V_0 d}{\nu}$.

The hot plate is a silicon wafer deposited on a heat generator. The smoothness of the surface (roughness is about a few hundreds of nanometers) ensures a better stability of the evaporation layer: indeed, most of the experiments done on Leidenfrost drops showed that the rougher the surface, the more unstable the vapour layer. For water, the Leidenfrost temperature - the temperature for which liquid is lifted up by its vapour flow - is about 160°C and the plate needs to be at much higher temperature in order for the vapour layer to be stable in a certain range of impact velocity V_0. We observed that this temperature has to be at least 50 degrees higher than the Leidenfrost temperature, for an impacting drop not to produce boiling. For the Glycerin/Water mixtures we used, the Leidenfrost temperature is slightly larger than that of water, so that we chose to operate at about 140 degrees higher than the water Leidenfrost temperature. Hence, the temperature is measured continuously and is kept 295 and 300 °C.

Liquid	Kin. viscos. ν (mm^2/s)	Surf. tension γ (N/m)	Density ρ (g/cm^3)
Water	1.00	0.72	1.00
W/Glyc. 50/50	5.32	0.67	1.1263
W/Glyc. 35/65	13.20	0.66	1.1675

Table 1. Physical properties of liquids

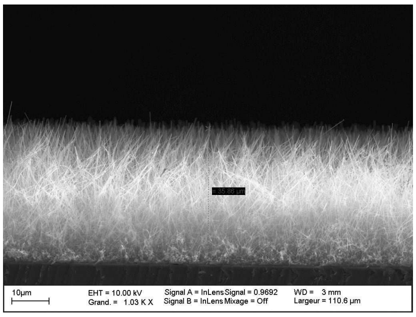

Figure 1. SEM images of the nano-wires carpet coated with C_4F_8.

THE SUPERHYDROPHOBIC NANOWIRES SURFACE

The process of nano-wires growth is detailed elsewhere [9]. In short, nano-wires grow on a SiO_2 substrate, using directed catalysis from nano-drops of gold. The nano-wires are coated by a hydrophobic coating. By changing the growth parameters (pressure, time), we obtained surfaces with different morphologies. Here, the obtained surface exhibits a two-layered structure: a dense layer of NWs with a height of 20 μm and a second upper layer with a low density and a height of 15 μm, the result is displayed on Fig. 1.

The sequence of Fig. 2 shows that a drop impacting on such a surface spreads radially, retracts, and finally bounces off the surface, being highly deformed. It is remarkable that the im-

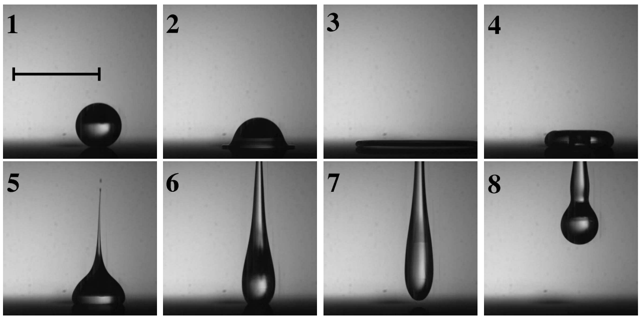

Figure 2. Successive shots showing the impact and the bouncing of a drop, without impalement (We = 600). The scale bar is 5 mm. The overall sequence lasts about 2.3 ms. The liquid is a Glycerol/Water mixture at 50/50, to prevent atomisation that would have occurred at this speed with pure water.

palement is avoided for impacts speed up to 5.5 m/s, which corresponds to a pressure of about 35 kPa. Hence, the impalement threshold is larger than 35 kPa. Previous experiments already addressed the impalement of drops on super-hydrophobic textured surfaces [10–12] but the impalement pressure threshold was limited to 10 kPa. This is very encouraging for the production of surfaces of high robustness to impalement, required for micro-drop handling using electrowetting [9] or other techniques. The presence of a double layer, one upper layer of straight wires and one lower layer of dense entangled wires, is involved in the robustness against impalement.

QUALITATIVE OVERVIEW

We first present the different behaviours of a drop impacting a hot plate. In this case, the liquid at the base of the drop starts to evaporate at a high rate, and hence this insulates the liquid from the hot plate, preventing it to boil. However, depending on how fast it impacts, the liquid can either never touch the solid, or either briefly enter in contact with it. In the latter case, the liquid boils violently: by observing it with a high-speed camera, we see that the drop locally pops and subsequently, capillary waves are launched along the drop, perturbing its shape and leading to additional contact between the liquid and the hot plate. On the contrary, for a purely evaporating state (no contact and hence no boiling), the drop stays nicely axisymmetric and the vapour layer remains. For each liquid used, the transition between the evaporating state and the boiling state occurs at a specific speed of impact. The different cases are summarised in sequences of Figs. 3, 4 and 5.

In Fig. 3, the vapour layer insulating the liquid from the plate is never pierced, and the drop never touches the solid. The drop first experience a step-wise shape, due to capillary waves, and later on the drop spreads. During its retraction stage, an air

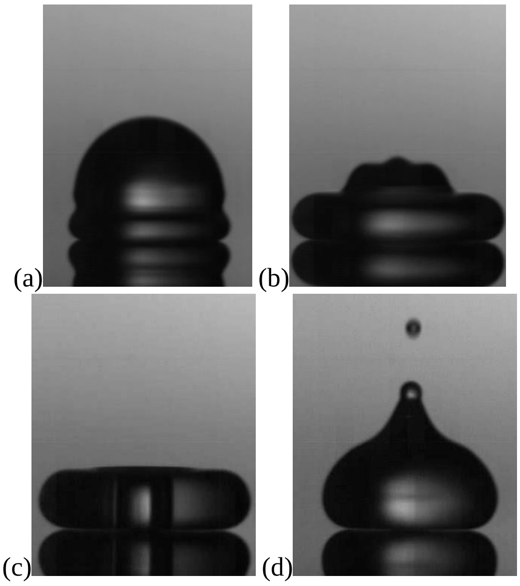

Figure 3. Successive shots showing the impact and the bouncing of a Glycerin/water (50/50) drop. V_0 = 0.52 m/s, Gly/W 50/50.

cavity develops at the centre of the drop, making it toroidal. Due to surface tension, the cavity retracts also and collapse, creating a jet directed upwards similar to that of Fig. 2, although much less sharp.

In Fig. 4 the drop first spreads gently and at some point, it starts to show moderate boiling. When it retracts and bounces, it has lost its symmetry and small bubbles lie inside.

In Fig. 5 the impact is much more violent and the vapour layer between the drop and the hot plate cannot be maintained. This leads to a strong boiling, as the drop touches the solid during a significant duration. Small droplets pop all around the drop and the drop is highly deformed. The height of bouncing is much smaller than for the two previous cases.

There three sets of snapshots show that the drop will spread more smoothly if the speed is small, and for comparable speeds, the drop will spread more smoothly if the liquid is more viscous. Comparing cases (1) and (2), it is striking that the viscosity of the liquid tends to stabilise the spreading: the vapour layer seems more stable for the Glycerol/Water mixture than for pure water.

To be more quantitative, the thresholds for entering the boiling state (determined at the minimal impact velocity for which the tiniest evidence of boiling was remarked) are: 0.43 $\pm$ 0.02 m/s for pure water, 0.55 $\pm$ 0.02 m/s for Glycerol/Water 50/50 and 0.70 $\pm$0.05 m/s for Glycerol/Water 65/35 (see Fig. 6).

QUANTITATIVE STUDY

From the high-speed movies, we extracted the radius of expansion versus time. At some point, the radius reaches a maxi-

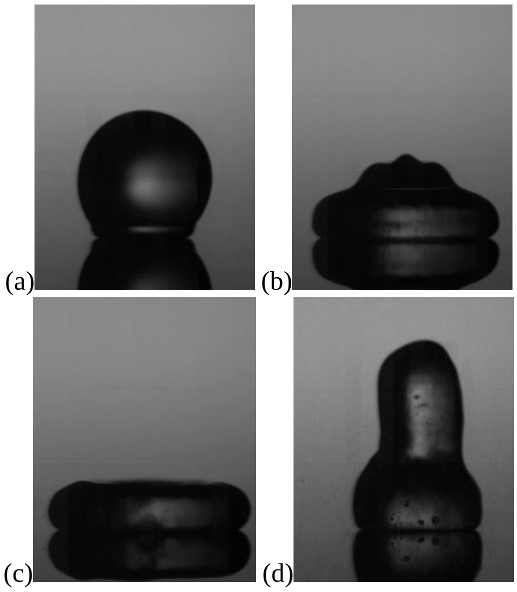

Figure 4. Successive shots showing the impact and the bouncing of a water drop. V_0 = 0.49 m/s, Pure water.

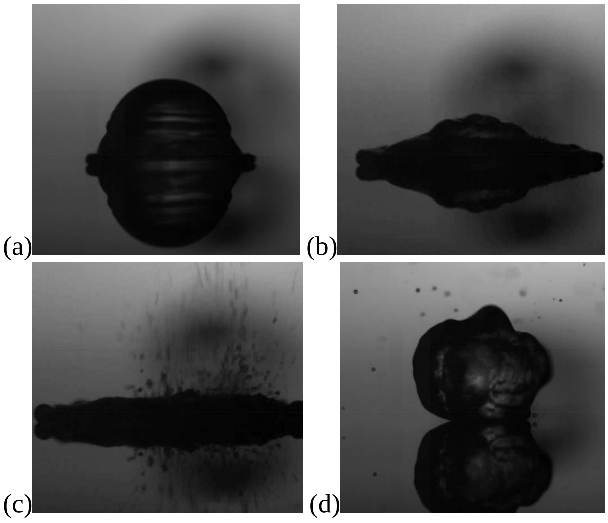

Figure 5. Successive shots showing the impact and the bouncing of a water drop. V_0 = 0.955 m/s, Pure water.

mum and then the drop retracts. This is shown in Fig. 7-a, for two different states: a pure evaporative state (no liquid/solid contact, similar to Fig. 3) and a intermittently boiling state where the evolution of the drop radius is much less smooth (similar to Figs. 4 and 5).

Similarly to what was measured previously [7, 13], the time t_M for maximal radius is almost independent of V_0, and scales as the inverse of the frequency of the Rayleigh (capillary-inertial)

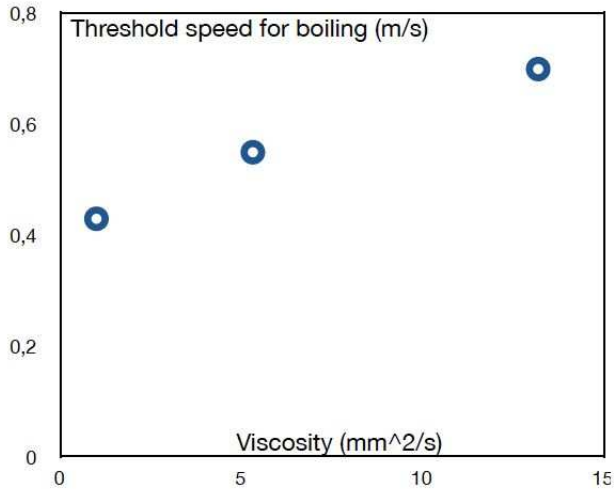

Figure 6. Threshold speed of impact for which some liquid touches the surface, leading to violent local boiling, versus liquid viscosity (T = 295°C).

mode of oscillation of the drop: $\tau \sim \sqrt{\frac{\rho d^3}{\gamma}}$. Anyway, we remarked a slight decrease of t_M with increasing viscosity: it is about 4.0×10^{-3} for water, 3.5×10^{-3} for the Gly/W 50/50 and about 3.0×10^{-3} for the Gly/W 65/35, something that cannot be explained only by the changes in ρ, d and γ. It is then remarkable that the viscosity decreases the spreading time, as it would have been expected that a larger viscosity would bring more internal dissipation and hence would have slowed down the spreading. We come back to this point later on.

We also extracted the maximal radius for various speeds of impacts and viscosity, as plotted on Fig. 7-b versus the Weber number. Like previous measurements [13, 14], we found that R_{max} scales like $\mathrm{We}^{1/4}$. The smaller values obtained for the glycerin/water mixtures can be partly explained by that we have to consider the dimensionless radius $\frac{R_{max}}{R_0} \sim \mathrm{We}^{1/4}$, and R_0 is slightly smaller for Glycerin/Water mixtures.

THEORETICAL APPROACH

The impact of a drop on a solid surface is a long standing problem, in which the difficulties lie in the multiple time and space scales involved in the problem. In particular, the treatment of the condition at the advancing (and deccelerating) triple line is still unsolved, and the tentative theoretical approaches need to be carried out at all scales, from macroscopic to microscopic (see [16] for a recent review). Here, an analytical approach is easier as the contact angle can be taken equal to 180° with no hysteresis.

One of the most important issue for both a practical and theoretical interests, is to predict the maximal radius that the

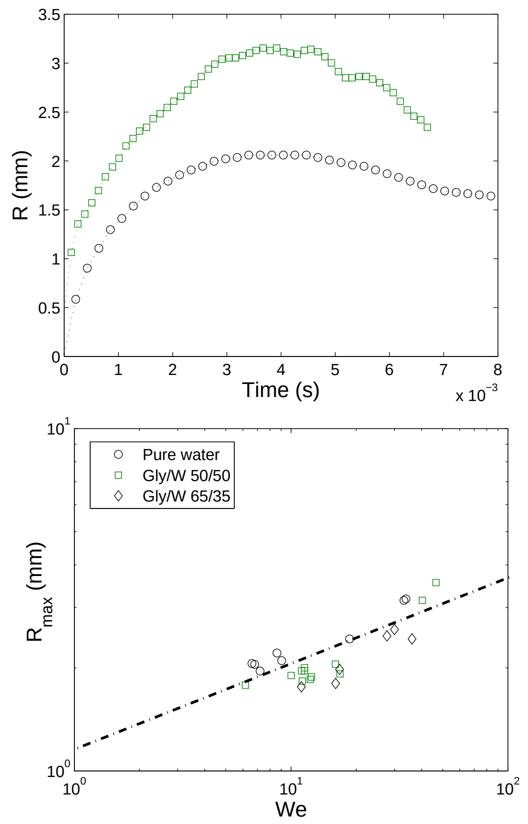

Figure 7. *Top* The drop's extension radius versus time, for a pure evaporation state (round symbols, V_0 = 0.422 m/s, pure water) and for an intermittent boiling state (square symbols, V_0 = 0.986 m/s, Gly/W 50/50). *Bottom* The maximal extension radius versus the Weber number, showing the trend $R_{max} \sim We^{1/4}$, for different speeds and for three different liquids.

drop reaches at the end of its extension stage. Experimentally, there is a consensus that R_M scales as the Weber number to the power $1/4$ [11, 13, 15]. It has been pointed out that the argument of a complete transfer between kinetic energy and surface energy does not hold, and it is attributed to that the whole spreading/bouncing process is dissipative (due for instance to vortical motion inside the drop). However, Biance et al. [15] studied the case of a quasi-elastic impact, where the drop almost bounces back to its initial height of fall, and the $1/4$ power law still holds. Several theoretical attempts have been proposed to predict this power-law. It has been invoked [13] that a dynamical capillary length, built by replacing the gravity g by the characteristic vertical deceleration at impact $a^* \sim \frac{V_0^2}{d}$, can predict the minimal thickness of the drop h_{min} (which roughly takes the shape of a puddle during its expansion phase). In clear, h_{min} is equal to 2 l_c^*, where l_c^* is the effective capillary length built on the effective acceleration a^*.

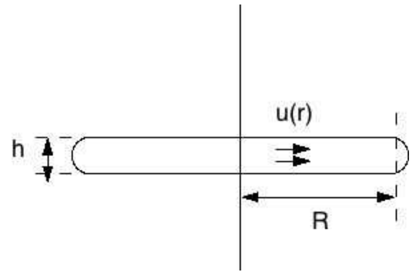

Figure 8. Sketch of the spreading drop (puddle).

Together with volume conservation $\frac{\pi}{3}d^3 = \pi R_{max}^2 h_{min}$, R_{max} is found to scale as We$^{1/4}$ [13]. However, this approach is sometimes questionable: first, the effective acceleration is generally 100 times the gravity constant (for speeds of about 0.5 m/s), which should lead to a thickness 10 times smaller than the drop diameter. This is clearly not the case: the thickness is much larger than the drop diameter divided by 10 (see Figs. 3 and 4). Second, the deceleration is impulsive and strongly decreases during the retraction phase.

Chen et al. considered an energy approach, taking into account the dissipated energy by viscous effects [7], with predictions that compare well with experiments. However, for the reasons emphasised above (the maximal radius is almost independent on viscosity), this assumption is also questionable.

Prediction for the maximal radius

Here, we revisit the problem by adopting an alternative approach, although still fully elastic. The drop is represented by a puddle of radius $R(t)$ and thickness h in its expanding phase, see Fig. 8. The contact angle is taken equal to 180°, assuming that the vapour layer still holds. We consider that the flow inside the drop is parallel ($\frac{\partial p}{\partial z} = 0$), except close to the periphery. This leads to a strong pressure gradient concentrated in a very small zone at the periphery. Let us denote p_R the pressure at the extremity of the drop. During the expansion phase, at given R, the infinitesimal work of the force due to this pressure is: $2\pi R h p_R dR$. During this phase, the surface energy varies like $d\left(2\pi\gamma R^2\right)$. Hence: $p_R = \frac{2\gamma}{h}$, and we recover the Laplace pressure.

The crucial point is to evaluate the characteristic width along which the pressure gradient is concentrated. Let us denote δ this width,which is necessarily smaller than h (as no rim is observed at the drop periphery). Dimensionally, we can write:

$$\frac{\partial p_R}{\partial r} = \frac{2\gamma}{h\delta}$$

for $r \sim R$. Hence, the equation of motion is $\frac{du}{dt} = -\frac{2\gamma}{\rho h \delta}$, in the absence of viscous dissipation. Otherwise, $\frac{du}{dt} = \frac{d^2R}{dt^2}$. As the work of the force associated to the pressure p_R contributes to the increase of the surface energy, the gradient $\frac{2\gamma}{h\delta}$ slows down fluid particles. Hence the surface $S_p = 4\pi R\delta$, which is the order of magnitude of the area where the pressure gradient is located, should not contribute to the increase of the surface energy. The surface S_p should keep constant during the whole spreading phase: it is initially equal to αR_0^2, with $R_0 = d/2$ the initial radius of the drop and α or the order of one. Hence, $\frac{d^2R}{dt^2} = -\frac{2\gamma R}{\rho h \alpha R_0^2}$. By volume conservation, we get: $h = \frac{4}{3}R_0^3 R^2$, and then:

$$\frac{d^2R}{dt^2} = -\frac{3\gamma R^3}{2\rho\alpha R_0^5}$$

A first integration, taking the impact speed V_0 as the initial radial speed, leads to:

$$\frac{1}{2}\left(\frac{dR}{dt}\right)^2 = V_0^2\left(1 + \frac{3\gamma}{4\alpha\rho V_0^2 R_0}\left(1 - \left(\frac{R}{R_0}\right)^4\right)\right)$$

For $R = R_{max}$, $\frac{dR}{dt} = 0$. Then, it yields:

$$\frac{R_{max}}{R_0} = \left(\frac{4\alpha}{3}We + 1\right)^{1/4} \quad (1)$$

which is consistent with most of the experiments [7, 13, 14]. To have an order of magnitude for α, let us take the results by Clanet et al. [13] who found that $\frac{R_{max}}{R_0} \simeq 2$ for We=10. This yields: $\alpha \simeq 1.125$, which is consistent with the hypothesis of a value close to one.

Then, our approach is to assume that the energy conservation is valid in this range, providing to take the contribution of the force due to Laplace pressure at the contour of the drop, and acting to push the drop inwards, slowing the fluid particles down close to the periphery. The energy conservation is then more complex than a simple transfer from the initial kinetic energy to surface energy, but no viscous dissipation is invoked.

The viscosity does not seem to be a major dissipative factor for the spreading on super-hydrophobic surfaces, at least at the range of viscosity we explored. Clanet et al. [13] measured a crossover to a $\mathrm{We}^{1/6}$ for the maximal radius at higher viscosity, which suggests that inner viscous dissipation could be significant once the power law $\mathrm{We}^{1/4}$ does not hold anymore. Otherwise, the viscous dissipation is only dominant when a contact-line exists, and in the presence of a significant contact-angle hysteresis. The compared measurements (for about the same impact velocity) of drop expansion versus time on a Leidenfrost surface and on a textured super-hydrophobic surface did not show any difference, see Fig. 9 (however, the retraction phase is slightly slower for the textured SH surface, evidencing a slight dissipation at the contact line during this later stage). On the contrary, for a drop in a Wenzel state (impaled liquid leading to a high hysteresis) on a super-hydrophobic surface, the expansion radius is smaller. This clearly shows the role of contact-angle hysteresis in the viscous dissipation process.

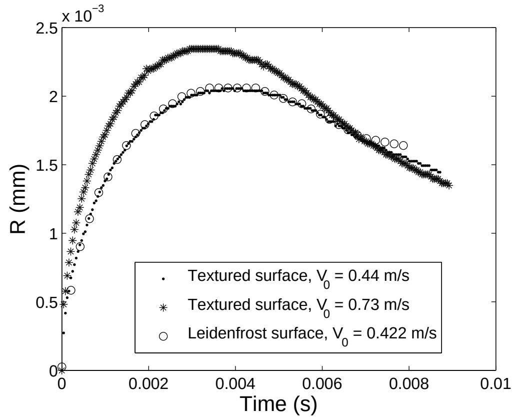

Figure 9. The drop's extension radius versus time, for a pure evaporation state (round symbols, V_0 = 0.422 m/s, pure water), and for a super-hydrophobic textured surface at room temperature (see Fig. 1) for V_0 = 0.44 m/s and 0.73 m/s. For similar speeds, the Leidenfrost and textured supehydrophobic surfaces show the same spreading dynamics.

CONCLUSION

In conclusion, we revisited the dynamics of a drop impact on a super-hydrophobic surface, using nano-textured surfaces and hot surfaces in Leidenfrost situations. Experiments with liquids of different viscosity, showed that providing the vapour layer is not pierced during impact, the spreading stage for Leidenfrost and textured surfaces are similar. The fact that a higher viscosity stabilises the vapour layer may suggest that capillary waves are involved in the local destruction of the layer. Viscosity is known to damp these capillary waves produced just after impact.

We recovered the trend $R_{max} \sim \mathrm{We}^{1/4}$ previously measured in several other situations, and we proposed a model based on energy conservation, with the contribution of an additional capillary force, to explain the trend.

The problem of drop dynamics in a boiling situation remains to be tackled. The vapour layer stability is a problem on its own: it is probably involved in the oscillating instability of a levitated drop [19, 20]. In a drop impact situation, the possibility of piercing the layer and of entering a boiling state is barely analysed, even in the most complete numerical simulations [18]. This is certainly one of the remaining challenges of Leidenfrost drops.

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