

Is the knowledge of the surface topology and contact angles enough to define the drop impact outcome?

Ileana Malavasi,¹ Federico Veronesi,² Aurora Caldarelli,² Maurizio Zani,^{3,4} Mariarosa Raimondo,² Marco Marengo^{1,5*}

¹ Department of Engineering and Applied Sciences, University of Bergamo, Viale Marconi 5, 24044 Dalmine (BG), Italy.

² ISTECCNR - Institute of Science and Technology for Ceramics, Via Granarolo 64, 48018 Faenza (RA), Italy.

³ Department of Physics, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy.

⁴ Center for Nano Science and Technology @Polimi, Istituto Italiano di Tecnologia (IIT), Via G. Pascoli 70/3, 20133 Milano, Italy.

⁵ School of Computing, Engineering and Mathematics, University of Brighton, Lewes Road, BN2 4GJ, Brighton, UK.

ABSTRACT: It is well known that a superhydrophobic surface may not be able to repel impacting droplets due to the so-called Cassie-to-Wenzel transition. It has been proven that a critical value of the receding contact angle (θ_R) exists for the complete rebound of water, recently experimentally measured to be 100° for a large range of impact velocities. On the contrary, in the present work, no rebound was observed when low surface tension liquids such as hexadecane ($\sigma = 27.5$ mN/m at 25°C) are concerned, even for very low impact velocities and very high values of θ_R and low contact angle hysteresis. Therefore, the critical threshold of $\theta_R \approx 100^\circ$ does not sound acceptable for all liquids and for all the hydrophobic surfaces. For the same Weber numbers a Cassie-to-Wenzel state transition occurs after the impact due to the easier penetration of low surface tension fluids in the surface structure. Hence a criterion for drop rebound of low surface tension liquids must consider not only the contact angle values with surfaces, but also their surface tension and viscosity. This suggests that, even if it is possible to produce surfaces with an enhanced static repellence against oils and organics, generally the realization of synthetic materials with remaining self-cleaning and anti-sticking abilities in dynamic phenomena, such as spray impact for example, still remains an unsolved task. Moreover, it is demonstrated that also the chemistry of the surface and the physico-chemical interactions with the liquid drops and the possible wettability gradient of the surface asperity play an important role in determining the critical Weber number above which impalement occurs. Therefore the classical numerical simulations of drop impacts onto dry surfaces are definitively not able to capture the final outcomes of the impact for all the possible fluids, if the surface topology and chemistry and/or the wettability gradient in the surface structure are not properly reflected.

1 INTRODUCTION

2 The impact of drops onto dry solid surfaces is a phenom-
3 enon involved in many industrial applications, i.e. spray
4 cooling, ink-jet printing, spray painting, fuel injection,
5 raindrop erosion, etc. The investigation of the single drop
6 impact¹⁻³ is the first step toward the understanding and
7 the control of the liquid-solid interactions in complex
8 phenomena where the capillarity, the viscous forces and
9 the impact momentum play a key role. In the last decade,
10 notwithstanding the open issue of their durability⁴, su-
11 perhydrophobic surfaces (SHS) have attracted an increas-
12 ing interest in both the academic and industrial sectors,
13 due to their remarkable self-cleaning and anti-sticking
14 properties⁵⁻⁷, involving a wide range of potential applica-
15 tions: biomedical⁸⁻⁹, microfluidic¹⁰, corrosion resistance¹¹,
16 drag reduction¹², anti-icing¹³, contamination and oxidation
17 protection¹⁴, etc. SHS are highly hydrophobic surfaces on

18 which liquid water adhesion is very low, therefore result-
19 ing extremely difficult to be wetted. Superhydrophobicity
20 causes the water droplet to bead up on the surface instead
21 of spreading on it. In addition, capillary adhesion forces
22 are low and water drops typically preserve a high mobility
23 on the surface. The wetting behavior is evaluated by the
24 contact angle occurring when a liquid/vapor interface
25 meets the solid surface. In this work, advancing (θ_A or
26 ACA) and receding (θ_R or RCA) contact angles were
27 measured, respectively, by expanding and contracting wa-
28 ter and hexadecane sessile drops on a horizontal surface
29 (sessile drop method). In static conditions, θ_A and θ_R are,
30 respectively, the maximum and the minimum stable an-
31 gles. Both of them provide the range of contact angles at
32 equilibrium, while their difference $\Delta\theta = \theta_A - \theta_R$ - named as
33 contact angle hysteresis (CAH) - provides an indication of
34 the drop mobility (the lowest the $\Delta\theta$ value, the highest
35 the drop mobility). As reported in the literature, the

36 standard conditions are $\theta_R > 135^\circ$ and $\Delta\theta < 10^\circ$ for superhy- 90
37 drophobicity⁴, $\theta_A > 90^\circ$ for hydrophobicity and $\theta_A < 90^\circ$ for 91
38 hydrophilicity⁵. A surface able to repel liquids with a dif- 92
39 ferent polarity and physical properties (i.e. surface ten- 93
40 sion) is called amphiphobic or lyophobic¹⁶⁻²⁰, with both 94
41 terms being usually related to the liquids molecules and 95
42 not to the surfaces. Such particular non-wetting surfaces 96
43 can provide additional performances with respect to the 97
44 hydrophobic ones in many sectors. Similarly, superam- 98
45 phiphobic surfaces exhibit even larger values of static 99
46 contact angles and CAH lower than 5° . Different ap- 100
47 proaches can be used to achieve these surface properties. 101
48 For recent trends in the development, fabrication, and 102
49 characterization of superamphiphobic surfaces, the pa- 103
50 pers of Cavalli and Mugele⁶, Chua and Seeger²⁰ give use- 104
51 ful insights. Throughout the impact on such surfaces, the 105
52 drop mobility is related to a sort of “dynamic superam- 106
53 phiphobicity”, defined as the critical wetting value under 107
54 which an impacting drop with a given impact velocity 108
55 does not wet the surface, i.e. a complete drop rebound is 109
56 observed. In this case the impact velocity, the interfacial 110
57 tension, the viscosity of the liquid, the chemical and phys- 111
58 ical properties of the surface determine the drop outcome 112
59 as well as the spreading and the retraction dynamic. 113
60 Nonetheless, a few papers²¹⁻²³ have shown how superam- 114
61 phiphobic surfaces might not necessarily lead to a total 115
62 rebound of impinging water drops, especially above a giv- 116
63 en value of Weber number ($We = \rho v^2 D_o / \sigma$, where ρ is the 117
64 density of the fluid [kg/m^3], v is its impact velocity [m/s], 118
65 D_o is the droplet diameter [m] and σ is the surface tension 119
66 [N/m]). Eventually impalement can occur, leading to the 120
67 droplet deposition on the surface. In this sense a surface 121
68 only hydrophobic, but smoother or with a proper topolo- 122
69 gy can be more effective in repelling liquids even for a 123
70 large value of We . Recently Antonini et al.²¹ analyzed the 124
71 drop impact on horizontal surfaces and highlighted the 125
72 role of the θ_R on the drop rebound. Accordingly, the re- 126
73 bound can be observed only on surfaces presenting θ_R 127
74 greater than 100° with the rebound time decreasing as θ_R 128
75 increases. However, Antonini et al. only refer to water as 129
76 impacting liquid²¹.

77 To better understand the existence of a general criterion 130
78 to predict the drop impact outcome, and the key paramet- 131
79 ers governing the drop-surface interaction, the normal 132
80 impact of both water and hexadecane drops on solid dry 133
81 surfaces with different wettability was observed using a 134
82 high-speed camera. The wetting behavior of sandblasted 135
83 aluminum foils before (TQ sample) and after the deposi- 136
84 tion of: i) organic-inorganic hybrid coatings (S samples) 137
85 ii) infused hybrid coatings (SI samples), iii) grafting fatty 138
86 acid treatments (LAU) and iv) grafting FAS (FAS) has 139
87 been analyzed. The present study aims at establishing a 140
88 relationship between drop impact outcomes and the dif- 141
89 ferent parameters for both the liquid drop (impact veloci- 142
143

ty, surface tension, viscosity) and the solid surface (mor-
phology and roughness, chemistry, wettability).

EXPERIMENTAL SECTION

Surface fabrication – Four kinds of SHS have been prepared: S, SI, LAU and FAS. Moreover, the uncoated sandblasted aluminum surface taken as reference is named TQ. S samples were prepared by dip-coating aluminum foils in an aqueous alumina sol with average particle size of about 30 nm. After thermal treatments, also including boiling in deionized water, a nanostructured inorganic coating was obtained, which was then further functionalized by dipping in a commercial solution of fluoroalkylsilane in isopropanol (Dynasylan® SIVO CLEAR EC, Evonik), resulting into a hybrid organic-inorganic coating. More details on the fabrication of S samples were reported by Raimondo et al. in a previous work²⁴. SI samples were obtained by the same route, with an additional step of immersion into a fluorinated lubricant (Fluorinert™ FC-43, 3M™) allowing for the formation of a continuous liquid film on the material surface with the aim of changing the physical nature of the interface (from the solid-liquid-air of S samples to the liquid-liquid-air of SI ones, according to the so-called SLIPS approach²⁵⁻²⁶). Fatty acid surfaces (LAU) were fabricated on an aluminum substrate, previously etched in acid solution, to achieve the desired surface roughness, and subsequently grafted in an ethanol lauric acid solution⁴. FAS surfaces were fabricated by etching the surface in acid solution as for the LAU surface, and then functionalized in a water solution of perfluorooctyltriethoxysilane (FAS)²⁷.

Surface characterization - The average values of θ_A , θ_R and CAH with both water and hexadecane are reported in Figure 1. The contact angle θ was calculated automatically from drop images by measuring the tangent of a circle fitting the drop profile at the contact point (OCA 15, Data Physics Instr.). Typical drop volume was about 2 μl .

Surfaces have also been characterized in terms of topography and roughness. SEM images were obtained with a Tescan MIRA3 equipment, while roughness measurements were performed with a ContourGT-K (Bruker Nano GmbH) optical profilometer (vertical resolution < 0.01 nm, lateral resolution 0.38 μm). SEM images of S and SI surfaces (Figure 2) show a flower-like nanostructure made up of crossed, 200 nm long flakes and nanometric cavities. Previous results²⁴ proved that such structure is due to the γ -alumina coating obtained by deposition of Al_2O_3 nanoparticles and to the subsequent boiling in water. LAU and FAS samples display a terrace-like structure with sub-micrometric edges, as expected from the similar etching conditions held for both samples. On the sandblasted TQ surface taken as a reference, microabrasion by sand grains produced an irregular microstructure with asperities and cavities. Roughness data (S_a , S_q , S_v and S_z)²⁸ are

144 shown in Figure 3. S_a defines the average of the absolute
 145 values of the profile heights $Z(x,y)$ in the measured area
 146 while S_q is the root mean squared of $Z(x,y)$ in the meas-
 147 ured area. S_v expresses the maximum value of “valley”
 148 depth on the surface in the measured area and S_z express-
 149 es the sum of the maximum value of peak height and the
 150 maximum value of valley depth on the surface within the
 151 measured area. A $15 \times 15 \text{ mm}^2$ area was analyzed for every
 152 measure, and a minimum of three measurements were
 153 done on the same sample for repeatability reason. The

difference between coated (S, SI) and etched (LAU, FAS)
 samples can be remarked: the former have lower average
 roughness (S_a , S_q) but higher peaks (S_v , S_z). A comparison
 with the data obtained for a TQ surface led us to conclude
 that the hybrid nanostructured coating has a small influ-
 ence on the micrometric roughness of S and SI, while the
 main contribution belongs to the microstructure provided
 by sandblasting. On LAU and FAS surfaces, etching pro-
 vided a rougher structure, but with less pronounced as-
 perities and cavities.

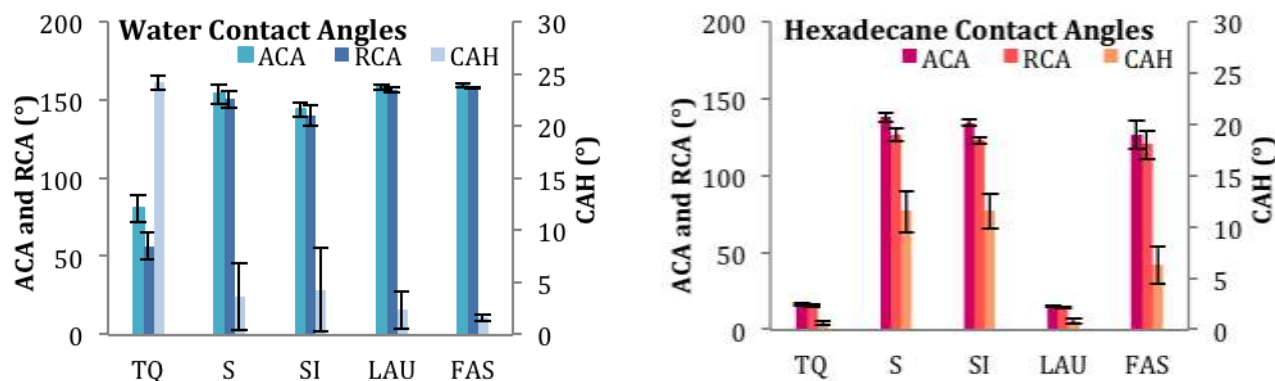


Figure 1. Average advancing (ACA) and receding contact angles (RCA) and contact angle hysteresis (CAH) with water (left) and hexadecane (right).

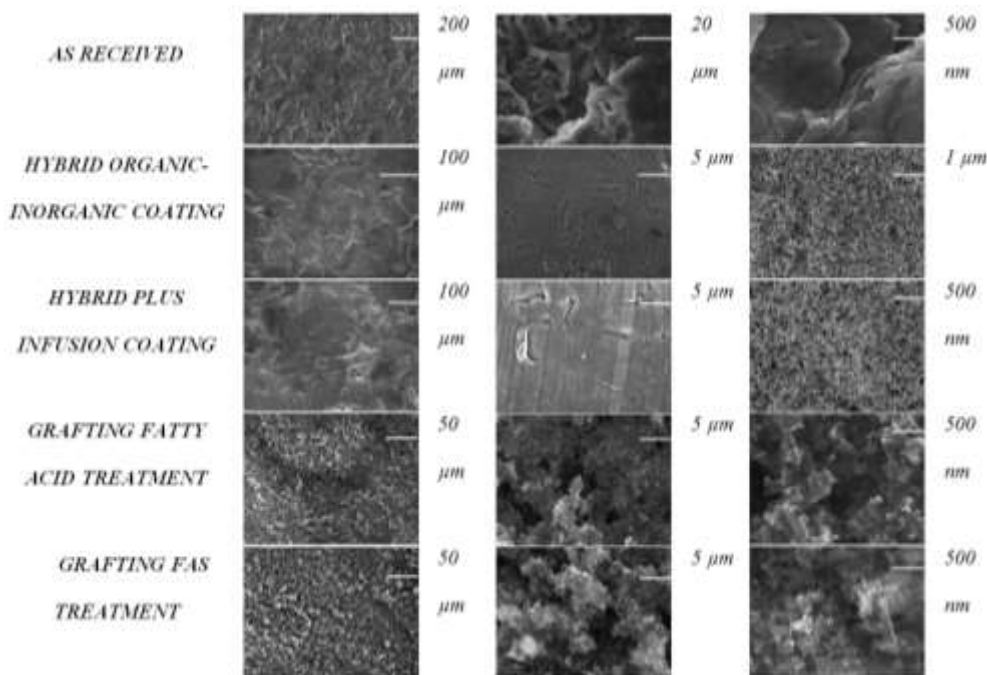


Figure 2. SEM images of the sample surfaces: as received sandblasted (TQ), hybrid organic-inorganic coating (S), hybrid plus infusion coating (SI), grafting fatty acid treatment (LAU) and grafting FAS treatment (FAS).

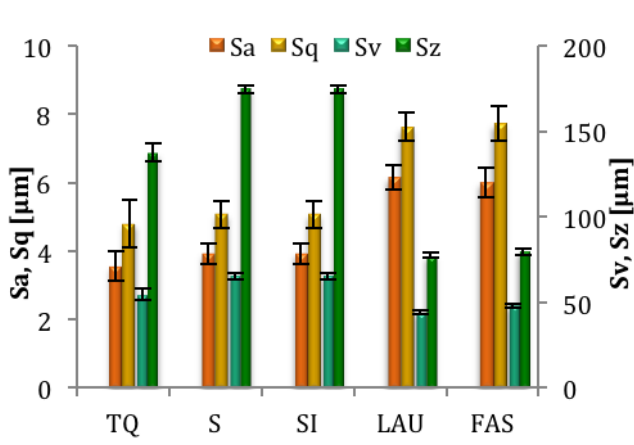


Figure 3. Surface roughness data obtained on TQ, S, SI, LAU and FAS samples. S_a and S_q values are referred to the left vertical axis, while S_v and S_z are referred to the right vertical axis.

RESULTS AND DISCUSSION

In Table 1 and in Figure 4 the summary of all the outcomes of the drop impact tests is reported. Five main regimes stand out: complete rebound, partial rebound, prompt splash, receding breakup and deposition. All the functionalized surfaces are able to generate a complete or partial rebound of water drops, while TQ surface promotes drop deposition for We up to about 200 and receding break-up for higher Weber numbers. Remarkably, surfaces S and SI are able to repel the water drops up to the maximum We value of 620. No splash is observed for the entire range of We , confirming the previous literature results²⁹. In the case of hexadecane, no rebound was observed for any of the surfaces, even if the contact angles and the hysteresis reached, respectively, very high and very low values (i.e. FAS surface, see Figure 1). The prompt splash appears to be an important outcome for $We > 200$. FAS sample shows a peculiar behavior, since it produces a partial rebound with water even for moderate values of We , while with hexadecane it is able to allow the generation of a singular jet³⁰ for very low We , and allows the receding breakup behavior for the higher analyzed We .

Image sequences of water and hexadecane liquid drops normally impacting on the tested surfaces are shown in Figures 5 and 6, respectively. Interestingly, when a water drop impacts on TQ at $We \approx 21$, deposition occurs with the generation of a singular jet³⁰, as shown in Figure 7. The same behavior can be observed in the case of hexadecane drop impacting on FAS surface at $We \approx 15$.

A schematic representation of the drop impact test outcome is reported in Figure 4.

Drop impact experiments - A typical experimental apparatus for drop impact studies was used: a drop was generated at the tip of a hydrophobic needle, and then was accelerated by gravity and impacted onto a dry, solid surface. Experimental conditions were the following: impact speed in the $0.05 < V < 4.2$ m/s range, drop diameter in the $1.5 < D_o < 2.6$ mm range, Weber numbers in the $0.1 < We < 635$ range, and Ohnesorge number ($Oh = \mu / (\rho \sigma D_o)^{1/2}$, where μ is the liquid viscosity [Pa s]) in the $0.0023 < Oh < 0.0186$ range. Images of drop impacts were recorded using a high-speed camera (PCO 1200-HS) with typical frame rates of 1568 and 2477 fps and a pixel resolution of 31 $\mu\text{m}/\text{pixel}$. Tests were repeated at least 10 times for each condition to assess experimental reproducibility. Images were manually analyzed to identify the drop impact outcome and eventually to measure the time of the drop rebound when occurring.

Table 1. Summary of the outcomes of the drop impact tests. R = rebound, PR = partial rebound, PS = prompt splash, RB = receding breakup, D = deposition. *Singular jet. ** Transition region.

Surface type	We (WATER)							We (HEXADECANE)						
	< 1.5	16 \div 35	40 \div 75	65 \div 100	150 \div 215	270 \div 360	500 \div 620	10 \div 20	30 \div 40	60 \div 75	85 \div 125	205 \div 275	325 \div 485	545 \div 635
TQ	D	D*	D	D	D	RB	RB	D	D	D	D	D	PS	PS
S	R	R	R	R	R	R	R	D	D	D	D	PS	PS	PS
SI	R	R	R	R	R	R	R	D	D	D	D	PS	PS	PS
LAU	R	R	R	R	R	R	PR	D	D	D	D	D	PS	PS
FAS	R	R	R	R	PR/R**	PR	PR	D*	D	D/RB**	D/RB**	D/RB**	RB	RB

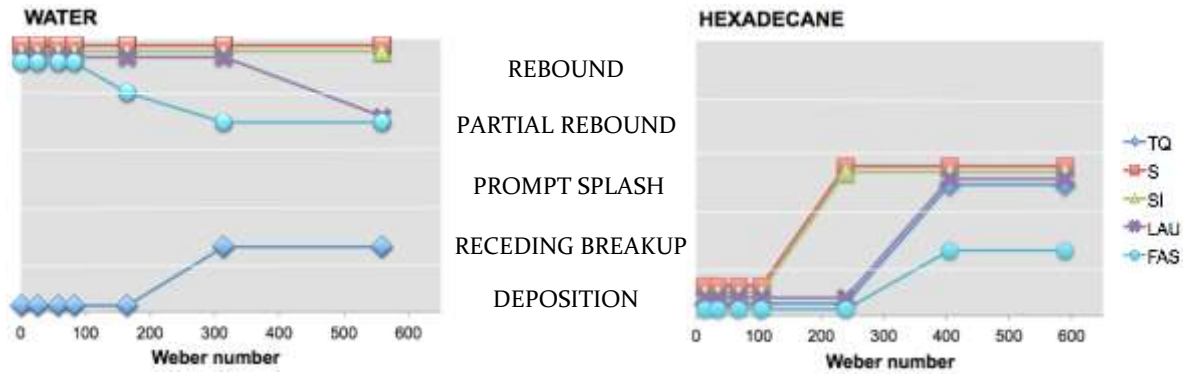


Figure 4. Schematic representation of the drop impact test outcome. In the graphs, the mean values of each We interval are reported.

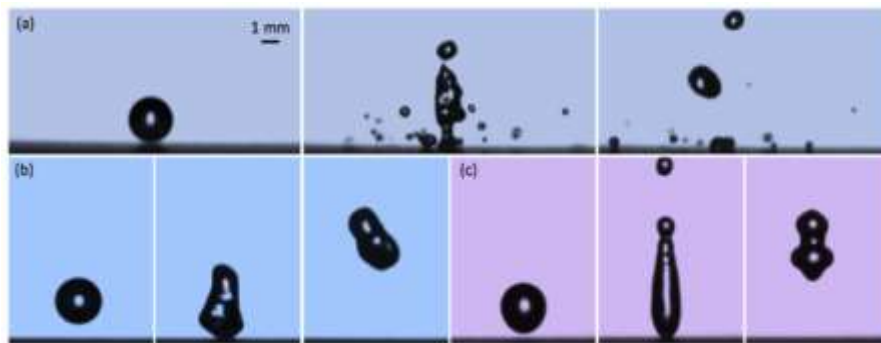


Figure 5. Image sequences of water drops (average diameter $D_0 = 2.45$ mm) impacting on three functionalized surfaces: (a) partial rebound with fragmentation on FAS sample at $We = 312$ at $t = 0$, 14.6 ms and 31.2 ms after impact; (b) rebound on SI sample at $We = 54$ at $t = 0$, 11.5 ms and 31.2 ms after impact; (c) rebound on S sample at $We = 21$ at $t = 0$, 14.0 ms and 21.6 ms after impact. The scale bar in (a) is valid for all images.

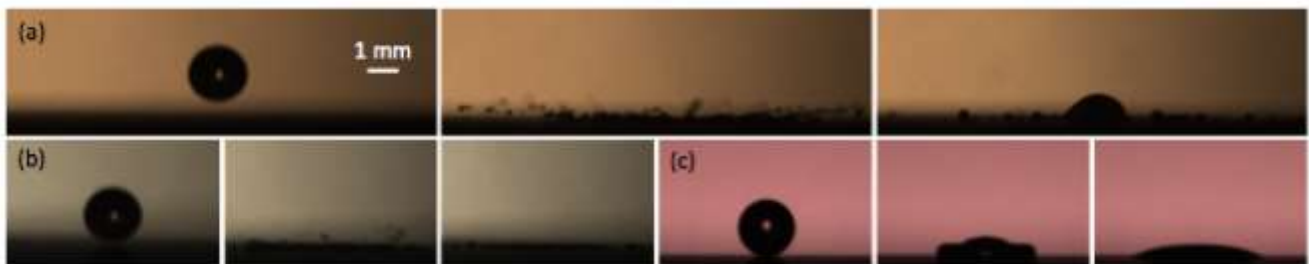


Figure 6. Image sequences of hexadecane drops (average diameter $D_0 = 1.66$ mm) impacting on three functionalized surfaces displaying different behavior: (a) receding breakup on FAS sample at $We = 560$; (b) splash on SI sample at $We = 580$; (c) deposition on LAU sample at $We = 17$. For every surface, images at $t = 0$, 2.0 ms and 17.6 ms after impact are reported. The scale bar in (a) is valid for all images.

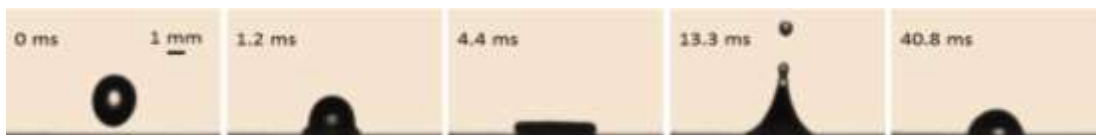


Figure 7. Image sequence of water drop (average diameter $D_0 = 2.35$ mm) impacting on TQ surface at $We = 21$. A deposition occurs with the generation of a secondary drop. The scale bar in the first frame is valid for all images.

1 The evolution of the spreading film diameter of water and 10
 2 hexadecane after the instant of impact is shown in Figures 11
 3 8a and 8b, respectively. The dimensionless diameter of 12
 4 the spreading film, called the spread factor, $\xi(t) = D(t)/D_0$ 13
 5 (i.e., the contact diameter at time t , made dimensionless 14
 6 by dividing it for the initial drop diameter) is shown as 15
 7 function of time. Different outcomes were observed from 16
 8 deposition to rebound (occurring for $t > 0$ when $\xi = 0$). In 17
 9 SHS cases, drops do not stick on the surface and the re- 18

bounds of the droplets can be observed. When the drop is
 detached from the surface, the contact diameter is zero,
 therefore the spread factor is zero. The time evolution of
 the spread factor suggests that the drop impact dynamics
 depends not only on the θ_R value, since, contrary to what
 reported by Antonini et al.²¹, even when θ_R reaches 120°
 indicating a very low wettability, complete drop rebound
 does not occur (see tests with hexadecane on FAS surfac-
 es, Figure 8b).

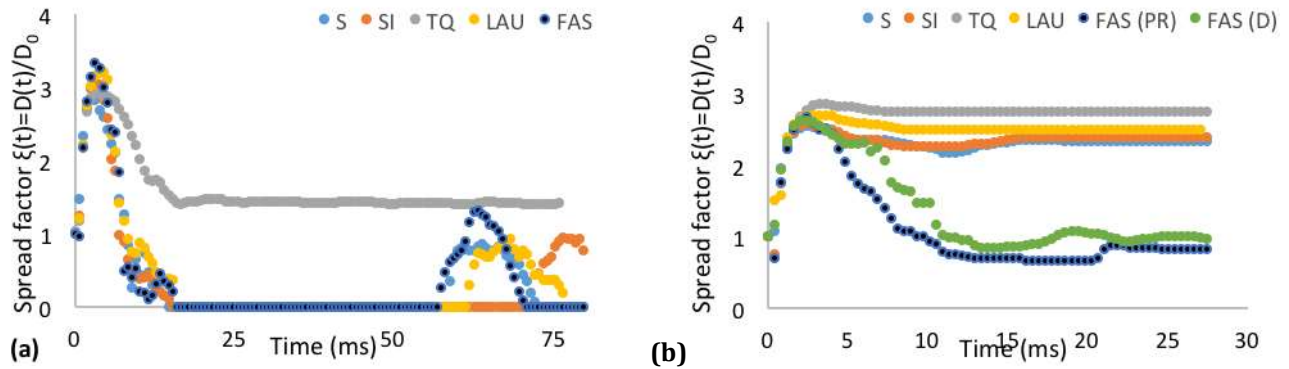


Figure 8. Spread factor time evolution, $\xi(t)=D(t)/D_0$, for the tested samples (single runs). (a) Water test conditions: $V = 1.6$ m/s, $D_0 = 2.5$ mm, and $We \approx 90$. (b) Hexadecane test conditions: $V = 1.5$ m/s, $D_0 = 1.7$ mm, and $We \approx 110$.

1 The fact that a surface is superhydrophobic, i.e. with an 30
 2 extremely high advancing contact angle and low hystere- 31
 3 sis, is not enough to assure the complete rebound, since 32
 4 impalement can occur.²¹ Therefore it is interesting to un- 33
 5 derstand when the impalement impedes the bouncing 34
 6 and which are the possible outcomes of drop impact for 35
 7 the different fluid and surface characteristics. The im- 36
 8 palement is usually described using alternatively four dif- 37
 9 ferent pressure mechanisms, the water hammer pressure 38
 10 P_{WH} , the dynamic spreading pressure P_{SD} ³¹, the capillary or 39
 11 anti-wetting pressure P_C ³² and the gas layer pressure P_{GL} ²². 40
 12 This last pressure term comes out considering the com- 41
 13 pression effects of the gas under the drop rather than the 42
 14 liquid compressibility. The initial impact of the droplet 43
 15 onto the surfaces generates a water hammer pressure P_{WH} 44
 16 due to the compression of the liquid³²⁻³⁴. The water ham- 45
 17 mer pressure P_{WH} is equal to $\rho_l C U$, where ρ_l is the droplet 46
 18 density, C is the velocity of sound in water, and U is the 47
 19 droplet impact velocity normal to the wall. Due to the 48
 20 complexity of the drop wall interaction, for example look- 49
 21 ing at the air entrainment, such water hammer pressure is 50
 22 usually reduced of a factor k , which has been experimen- 51
 23 tally evaluated lying in a very broad range, for example 0.2 52
 24 by Deng et al.³³ or 0.002 by Maitra et al.²² The real value of 53
 25 the impact pressure due to the liquid compressibility is 54
 26 here called effective water hammer pressure P_{EWH} . At the 55
 27 spreading stage, a liquid jump overtakes the outward 56
 28 moving contact line.³⁵ At this stage the spreading process 57
 29 implies a dynamic pressure $P_{SD} = 0.5\rho_l V^2$, where V is the 58

spreading velocity. For a normal impact P_{EWH} is supposed
 to be greater than P_{SD} . The capillary pressure can be de-
 fined as the liquid pressure level that it is necessary to
 overcome in order to squeeze a droplet through a pore
 cavity, such as a surface topology throat. For that reason
 it is also called “anti-wetting” pressure. The capillary pres-
 sure can be written as $P_C \approx \sigma(-\cos\theta_A)/r_p$, where σ is the
 surface tension, θ_A is the advancing contact angle of the
 corresponding smooth surface and r_p is a length scale of
 the surface cavities. The analysis of droplet impact on tex-
 tured surfaces showed that the compressibility of the air
 layer between droplet and the substrate is a key feature
 for the impalement. Maitra et al.²² showed that the men-
 iscus penetration is probably linked to the compressibil-
 ity of the draining air, rather than the water hammer
 pressure effect of the liquid. Therefore, instead of the wa-
 ter hammer pressure, using a dimensional analysis they
 defined a pressure term $P_{GL} = 0.88(R\mu_g^{-1}U^7\rho_l^4 Ca)^{1/3}/St^{4/9}$,
 where R is the droplet radius, μ_g the air viscosity, Ca the
 Capillary number, and St the Stokes number, as the criti-
 cal pressure above which Cassie-to-Wenzel Transition oc-
 curs.

The impalement can be total, i.e. the liquid is reaching
 the bottom of the surface when the same is textured with
 pillars or is completely wetting the surface structure for a
 random topology, or partial, when the liquid is not able to
 wet completely and some air is still present in the surface
 throats and cavities. One can distinguished three regimes,
 the Wenzel regime where impalement occurs and is pre-

59 sent until the final deposition, being the liquid imbedded
 60 into the surface structure, a fakir (or Cassie-Baxter) re-
 61 gime, when no impalement and no imbibition occur for
 62 all the duration of the drop impact, from the early stages
 63 until the possible rebound or deposition, and a third
 64 stage, called partially impaled state, when a partial im-
 65 palement is present. In the case $P_C > P_{EWH} > P_{SD}$, the surface
 66 textured structure resists wetting in the contact and in
 67 the spreading phase; in the case $P_{EWH} > P_C > P_{SD}$ the fluid
 68 penetrates during the contact stage. In the fakir state, for
 69 having a rebound as outcome of the drop impact is neces-
 70 sary that the liquid lamella is stretched enough to have
 71 sufficient energy at the end of the recoiling phase, thus
 72 promoting the drop detachment from the surface, i.e. it is
 73 necessary to have enough impact kinetic energy (the ki-
 74 netic energy of the impinging droplet has to be larger
 75 than the surface energy dissipated during the retraction
 76 stage^{31,36} (bouncing fakir droplet - B); otherwise the drop
 77 does not rebound (non-bouncing fakir state - NB). When
 78 the liquid meniscus penetrates the surface topology, the
 79 partially impaled state occurs: at low impact velocity a
 80 partially penetrated bouncing droplet state (PPB) occurs
 81 instead at higher drop impact velocity, i.e. for a given crit-
 82 ical velocity $U_{c,p}$, the so-called second non-bouncing
 83 droplet (2NB) state³² occurs. 138

84 The main problem is that there is still an open debate on
 85 the criteria for impalement, since, if it is clear that im-
 86 palement will appear when the anti-wetting pressure P_C is
 87 lower than a pressure linked to the impact dynamics, i.e.
 88 P_{EWH} , P_{GL} or P_{SD} , the actual threshold values are still un-
 89 known. Maitra et al.⁴⁷ suggested that $P_{GL} > 80 P_C$ should
 90 be used as an impalement criterion, which impedes the
 91 complete rebound. From this expression the critical We-
 92 ber number above which a complete rebound cannot oc-
 93 cur can be evaluated: $We_{cr,imp} = 18.2R^{1/2}\mu_g^{2/7}\rho_l^{-1/7}\sigma^{1/4}$
 94 $^{1/7}(\cos\theta_A)^{9/14}r_p^{-9/14}$. The smaller the cavity size, the higher
 95 must be the impact velocity above which also Cassie-to-
 96 Wenzel transition (CWT)^{22,37} will occur. This is in qualita-
 97 tive agreement with the different output we observed at
 98 high We on surfaces with different morphologies: S and SI
 99 samples have nanoscale cavities on their surfaces, hence a
 100 $U_{c,p}$ higher ($We(U_{c,p}) > 620$) than the maximum U investi-
 101 gated in these experiments. Instead, LAU and FAS surfac-
 102 es displayed only sub-micrometric voids which originated
 103 a smaller $U_{c,p}$ and therefore the CWT can be observed at
 104 $We \sim 550$ for LAU and $We \sim 200$ for FAS. However, it is very
 105 difficult to assess the critical Weber number for surfaces
 106 having a stochastic roughness, such as those used in the
 107 present work. $We_{cr,imp}$ and P_C are hard to determine due
 108 the length scale parameter for the surface cavities. More-
 109 over, Quan and Zhang³⁸ demonstrated how the initial and
 110 operating conditions, including the microstructured su-
 111 perhydrophobic surfaces geometrical shapes will signifi-
 112 cantly influence the bouncing ability of an impinging
 113 droplet on textured surfaces. 168

Because the drop mobility is related to a sort of “dynamic
 superamphiphobicity”, defined as the critical wetting val-
 ue under which a complete drop rebound is observed, the
 critical impact velocity for having a dynamical amphipho-
 bic surface is increasing with the surface tension, i.e., for
 the same advancing contact angles, a low surface tension
 fluid will have a lower threshold for impalement. Hence
 for a given impact velocity, a drop tends to deposit rather
 than to rebound when a lower surface tension fluid is in-
 volved. It is also important to stress that another im-
 portant dimensionless number, the Ohnesorge number,
 i.e. the viscous dissipation, may influence the drop re-
 bound. For water, the Ohnesorge number is about 0.0024,
 while for hexadecane is 7 times higher ($Oh_{Hex} \approx 0.0177$),
 therefore, the viscous dissipation prevents the liquid to
 rise back⁴¹ from the partial penetration to a Cassie-Baxter
 regime. Since for our experiments the drop rebound is not
 possible to be achieved using hexadecane, the single ef-
 fect of viscosity cannot be estimated. The rebound may
 therefore happen for a given impact velocity range $U_{r,min} <$
 $U < U_{r,max}$ ^{31,39,40}.

Finally in the present literature, the “chemistry” of the
 surface and of the liquid has never been considered a cru-
 cial factor for determining the CWT. However, it becomes
 clear that also the chemistry of the surface and the physi-
 co-chemical interactions with the liquid drops play an
 important role in determining $We_{cr,imp}$. For water drops
 with $We = 150 \div 360$, different outputs are observed for
 LAU and FAS surfaces notwithstanding their identical
 morphology (see Table 1 and Figures 2 and 8) and wetta-
 bility (see Figure 1). The difference between these surfaces
 must lie in their chemical composition, as LAU is func-
 tionalized with non-polar alkyl chains while FAS exposes
 polar fluorinated groups. Murase and Fujibayashi⁴²
 demonstrated that water forms hydrogen bonds with
 such fluorinated moieties on hydrophobic surfaces.
 Therefore, we may consider that these interactions cause
 kinetic energy dissipation in the drop. Nakajima et al.⁴³
 calculated that this dissipation depends on the contact
 area between the drop and the surface. At $We < 150$, drop
 spreading is limited, thus water-surface contact area is
 small and the interaction negligible. Increasing impact
 speed, drop spreading and contact area become larger,
 therefore hydrogen bonds start to play a role causing dis-
 sipation and hindering rebound. When $We > 500$, water
 drops penetrate the terrace-like morphology of both LAU
 and FAS samples (e.g. partial rebound), therefore the role
 of chemistry is no longer relevant. Instead, for hexade-
 cane drops, no influence of the surface chemistry can be
 recognized: the very low surface tension makes more
 probable to either splash at high We or deposit at low
 We , when the kinetic energy is insufficient to break the
 drop. Only a small influence of the surface structure is
 observed, causing the splash-deposition transition to shift
 to lower Weber values for the S and SI samples with a

169 flower-like surface morphology (Table 1). This is the first
170 time that this influence of chemistry on the drop impact
171 behavior on textured surfaces is reported. However, other
172 explanation can be evoked as well, e.g. a more inhomogeneous
173 grafting of FAS chains on unexposed parts of the
174 surface topology with respect to LAU molecules. Static or
175 quasi-static wetting measurements might not highlight
176 such differences in surface chemical composition, while
177 impinging drops could “touch” these areas and cause re-
178 tention of the drop. As if a wettability gradient along the
179 surface asperities is formed, that causes a different drop
180 surface interaction. Future work will extend the compre-
181 hension of such phenomena, possibly adding molecular
182 dynamics modeling of the interactions between the sur-
183 face and the drop.

185 CONCLUSIONS

186 The normal impact of water and hexadecane liquid drops
187 onto dry, rigid surfaces with different wettabilities has
188 been studied experimentally using a high-speed camera.
189 The results highlighted that it is not possible to easily cor-
190 relate contact angles (receding, advancing and hysteresis)
191 and drop impact dynamics of low and high surface ten-
192 sion liquids on different surfaces. The Cassie-to-Wenzel
193 transition can be observed even on statically repellent
194 surfaces. In order to explain the observed phenomena
195 physical and chemical characteristics of both the liquid
196 drops and the surface have to be taken into account. Sur-
197 face morphology is crucial in defining the critical velocity
198 over which impalement occurs: the smaller the surface
199 cavities, the higher $U_{cr,imp}$. Also, surface chemistry as hy-
200 drogen bonding between surface functional groups and
201 molecules in the liquid phase, can lower $U_{cr,imp}$ and favor
202 impalement, as the wettability gradient along the surface
203 asperities is relevant in determining the drop impact be-
204 havior. As far as the liquid properties are concerned, in
205 agreement with Butt³⁹, with increasing viscosity and lower
206 fluid surface tension the CWT shifts to smaller Weber
207 numbers. In the case of hexadecane drops, the CWT
208 threshold is so low that no rebound has been observed
209 even if the contact angles are well above the expected
210 critical values obtained from previous works focusing on
211 water drops. The effect of energy dissipation for high vis-
212 cous fluids is therefore important when the liquid retreats
213 from the texture^{44,45}. Finally, it is clear that, at the mo-
214 ment, there is still a lack of an agreed general and quanti-
215 tative evaluation of the impalement criteria after a drop
216 impact. For example, the proposed thresholds in litera-
217 ture are not yet able to properly describe the results ob-
218 tained using oils on amphiphobic surfaces.

219 A direct consequence of the study is linked to the numeri-
220 cal simulations of drop impacts onto rigid and dry sur-
221 faces. They consider the advancing and receding contact
222 angles and surface tension in order to represent the im-

223 pact outcomes⁴⁶. A direct and important consequence of
224 this study is that all the numerical simulations of drop
225 impact onto solid, dry surfaces will never be able to cap-
226 ture the final outcome of the impact for all the possible
227 fluids, if the surface topology and chemistry are not
228 properly considered. Static or quasi-static wetting meas-
229 urements might not highlight such differences in surface
230 chemical composition. Furthermore, the present results
231 emphasize how an accurate design of the surface proper-
232 ties must be pursued in the future research towards dy-
233 namically amphiphobic surfaces.

234 AUTHOR INFORMATION

235 Corresponding Author

*E-mail: m.marengo@brighton.ac.uk

237 Author Contributions

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1 TOC Graphic



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