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Bouncing dynamics of impact droplets on the convex superhydrophobic surfaces

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Bouncing dynamics of impact droplets on solid surfaces intensively appeal to researchers due to the importance in many industrial fields. Here, we found that droplets impacting onto dome convex superhydrophobic surfaces could rapidly bounce off with a 28.5% reduction in the contact time, compared with that on flat superhydrophobic surfaces. This is mainly determined by the retracting process of impact droplets. Under the action of dome convexity, the impact droplet gradually evolves into an annulus shape with a special hydrodynamic distribution. As a consequence, both the inner and external rims of the annulus shape droplet possess a higher retracting velocity under the actions of the inertia force and the surface energy change, respectively. Also, the numerical simulation provides a quantitative evidence to further verify the interpretation on the regimes behind the rapidly detached phenomenon of impact droplets. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4984230]

As a research highlight, bouncing dynamics of impact droplets on solid surfaces have made a great progress under the inducement of some actual circumstances, such as rain droplets hitting umbrella, splashing droplets onto the container wall in chemical industries, and supercold droplets impacting the surface of aircrafts. 1-5 Also, it has been demonstrated that the bouncing dynamics are highly depended on surface texture and wettability, and the underlying physical mechanisms indicate that the moving processes (containing spreading and retracting) of an impact droplet on solid surfaces are mediated by the work done against wetting hysteresis resistance.⁶ Based on these physical mechanisms, many researchers utilized the synergistic actions of surface chemical compositions and microstructures to construct the hydrophobic or superhydrophobic surface for the purpose of compelling impact droplets to rapidly detach from solid surfaces. 7-12

Droplets impacting on superhydrophobic surfaces can bounce off quickly because of the lower wetting hysteresis at the solid-liquid interface, and the contact time can be shortened to a limit value of 12 ms with the circular symmetry mode. 13,14 The contact time of entire impact process is considered to be crucial to the applications of superhydrophobic surfaces, because it directly determines the extent of thermal and energy conversion between the water droplet and the surface. Thus, the emphases of current researches mainly focus on further reducing the contact time and inducing a rapider detachment of impact droplets from the solid surfaces. Bird and his co-workers reduced the contact time below

On this basis, we found that droplets impacting onto dome convex surfaces can also rapidly bounce off with the contact time decreasing to 8.0 ms. Although the reduction in contact time of impact droplets is not extremely remarkable compared with the above macroscopically flat surfaces, the convexity induces to produce a distinguishing bouncing regime. We hypothesize that the impact droplets on the superhydrophobic surface exhibit a certain extent of elasticity accompanying with their intrinsic hydrodynamics. It is demonstrated that the convexity can expedite the movement of impact droplets on solid surfaces, and the underlying physics revealed that the convexity can induce the impact

this theoretical minimum value of 12 ms, where the symmetry mode was broken by designing the macro ridge structures with the size of submillimeters on the superhydrophobic surfaces, and the contact time decreased to 7.8 ms. 15 Subsequently, Liu et al. showed that the superhydrophobic surfaces (patterned with lattices of submillimeter-scale posts decorated with nano-structures) could induce a counter-intuitive bouncing regime: impact droplets spread to the maximum deformation and then directly left the surface in a flattened, pancake shape without retracting. 16,17 This bouncing regime allows a fourfold reduction (only 3.4 ms) in contact time compared with the conventional circular symmetry mode. Furthermore, Hao and Cao both summarized some recent research progress in this field and expounded some recently reported approaches to enhance droplet mobility based on the effects of surface textures and chemical compositions.^{5,18} All of these studies imply that the surface morphologies, especially in the scale of sub-millimeters, play a vital role in reducing the contact time of impact droplets and might also induce some fresh regimes.

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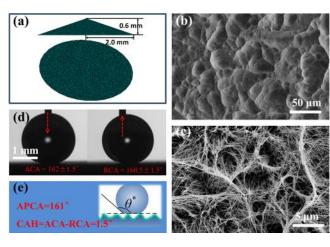


FIG. 1. Characterizations of the convex superhydrophobic surface and wettability. (a) The schematic diagram of the convex surface with a dome shape (height of 0.6 mm and radius of 2.0 mm). (b) and (c) Microscale structures formed by sand blasting and a layer of nanowires planting on the surface of the micro pits. (d) The optical images of droplets on the flat superhydrophobic surface with the advancing contact angle (ACA) $\approx 162^\circ$ and receding contact angle (RCA) $\approx 160.5^\circ$, (e) The interfacial contact regime between the droplet and the surface, and apparent contact angle (APCA) reaching 161° with the contact angle hysteresis (CAH) of 1.5° .

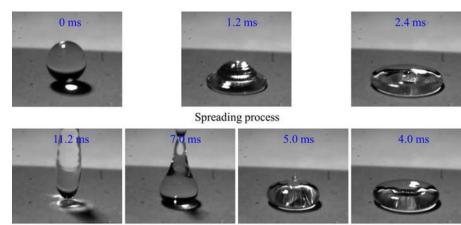
droplet to produce an upward inertia force perpendicular to the convex surface during the retracting process. All these mechanisms will be discussed in more details below.

First, a superhydrophobic Ti6Al4V [composition (wt. %): $\leq 0.3\%$ Fe, $\leq 0.1\%$ C, $\leq 0.05\%$ N, $\leq 0.015\%$ H, $\leq 0.2\%$ O, $5.5\sim6.8\%$ Al, $3.5\sim4.5\%$ V, and the rest is Ti] surface was considered as the research object, and designed to be dome shape with the size of radius $\approx 2.0 \, \text{mm}$ and height $\approx 0.6 \, \text{mm}$ [as shown in Fig. 1(a)]. Also, a layer of hierarchical micronanostructures from $\sim 50 \, \mu \text{m}$ to hundreds nm was preferentially selected and fabricated by means of a combined method of sand-blasting and thermal treatment. 19,20 The detailed experimental procedures of preparing samples and tests are shown in the supplementary material. Figures 1(b) and 1(c) illustrate the morphologies of hierarchical micronanostructures, and the as-prepared rough surface is selfassembled by a layer of low-energy groups from 1H, 1H, 2H, 2H-Perfluorodecyltriethoxysilane (FAS-17) under the assistance of a hydrogen bond-driven technique. As a consequence, the resultant surface exhibits a robust water repellency with a $4 \mu l$ droplet nearly suspending on the micro-nanostructure surface [see Fig. 1(d)] with the apparent contact angle (APCA) reaching 161° as well as the contact angle hysteresis (CAH) as low as 1.5° . This is mainly attributed to the fact that the hierarchical micro-nanostructures favor to trap a high amount of air pockets underneath the water droplet, resulting in the actual solid-liquid contact area being only $\sim 10\%$ of the apparent solid-liquid contact area, 21 as shown in Fig. 1(e).

In order to physically reveal and analyze the findings of convexity expediting the detachment of impact droplets from solid surfaces, it is still necessary to observe the impact process of a water droplet on the flat superhydrophobic surface, as illustrated in Fig. 2. The impact velocity V_0 is $1\,\mathrm{ms}^{-1}$, corresponding to the Weber number (We) ≈ 6.87 . Here, $We = \rho V_0^2 R_0/\sigma$, where ρ is the density of water droplets, and R_0 and σ are the radius ($R_0 = 1\,\mathrm{mm}$) and surface tension ($\sigma = 0.0728\,\mathrm{N/m}$), respectively. The impact droplet spends about 11.2 ms to complete the whole process containing the spreading out to maximal deformation (2.4 ms) and retracting process (8.8 ms). This result is consistent with the previous reported results from other research groups, $^{23-25}$ which also implies this value of 11.2 ms is limited by tuning the hydrophobicity or superhydrophobicity of solid surfaces.

However, when the water droplet impacts onto a convex superhydrophobic surface, the above limited value of contact time can decrease to 8.0 ms, with approximately 28.5% reduction. Figure 3 shows the moving process of the impact droplet at the same We as above on the convex superhydrophobic surface until leaving. It can be clearly found that the impact droplet first spreads to the maximum deformation and then starts retracting until bouncing off the surface. Also the spreading process needs approximately 2.4 ms, which is almost consistent with that on the flat superhydrophobic surface. Therefore, the 28.5% reduction in contact time is mainly determined by the retracting process. On the dome convex surface, the impact droplet gradually transfers into an annulus shape under the action of re-distribution of hydrodynamics, when the droplet reaches the maximum diameter. Subsequently, the spreading droplet starts to retract with the two concentric circles of triple-phases contact line, finally rounding up and bouncing off the solid surface for a shorter period.

Curiously, what are the underlying physics behind the phenomena, and why does the dome convexity promote the detachment of impact droplets from the solid surface? Regarding the droplet impacting dynamics, a typical way is



Retracting process

FIG. 2. The moving process of impact droplet (impact velocity $V_0 = 1\,\mathrm{ms}^{-1}$,) on the flat superhydrophobic surface, and the results indicate that the entire moving process spends approximately 11.2 ms containing the spreading time of 2.4 ms and retracting time of 8.8 ms. (Multimedia view) [URL: http://dx.doi.org/10.1063/1.4984230.1]

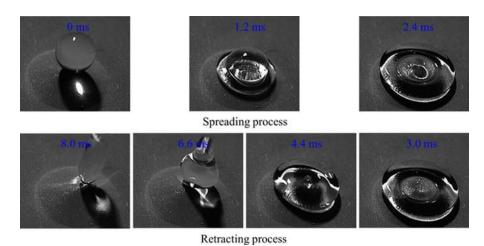


FIG. 3. The moving process of the impact droplet at $We \approx 6.87$ until bouncing off the convex superhydrophobic surface. (Multimedia view) [URL: http://dx.doi.org/10.1063/1.4984230.2]

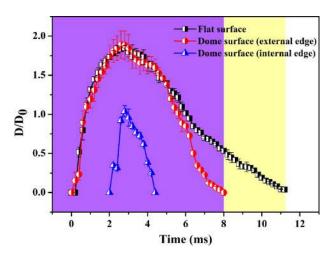
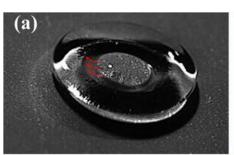


FIG. 4. Plot of the contact line position of the water droplet impacting on the flat and dome superhydrophobic surfaces, and the light-yellow square represents the reduction of contact time.

to record the time evolution of contact line position (D/D_0) , the ratio of wetting area diameter D and the initial droplet diameter D_0) of impact droplets on the flat and dome superhydrophobic surfaces, as plotted in Fig. 4. Obviously, the impact droplets on the both sample surfaces first spread to the maximal diameter (\sim 1.8 times as much length as an initial droplet diameter) at the almost same spreading velocity, and then, the retracting velocity shows some difference after the time reaching 4.8 ms $(D/D_0 \approx 1.5)$. The impact droplet on the dome surface can rapidly bounce off the surface at 8.0 ms, yet the time delays to 11.2 ms for that on the flat superhydrophobic surface. Also, because the dome convexity causes the change in hydrodynamic distribution, the impact droplet gradually changes into the annulus shape from

2.0 ms to 4.3 ms, resulting in generating a new contact line (the position evolution as a function of time is depicted by the blue symbol in Fig. 4). It can be clearly embodied that the inner contact line completes the spreading and retracting process at a very high speed (it can be perfectly explained by the formula $V_i = \sqrt{2\gamma/\rho h}$, where γ and ρ are surface tension and density of impact droplet, respectively, and h is the thickness of the inner rim of the impact droplet²⁶), which leads to the hydrodynamic distribution of the water droplet being not the same with that on the flat surface. We believe that this process of hydrodynamic re-distribution induces a high retracting velocity, finally expediting the detachment of impact droplets from the solid surface.

To confirm that the reduction in contact time is a result of high retracting velocity caused by the special hydrodynamic re-distribution, we particularly extract a representative image locating in the moment of starting retracting, as shown in Fig. 5. Careful inspection of Fig. 5(a) reveals that the mass of impact droplet greatly conveys to the external rim (the conveyed direction is marked by the red dotted arrows) under the assistance of hydrodynamics on the convex superhydrophobic surface. As a consequence, the external rim processes a high thickness, almost increasing 100% comparing with that on the flat superhydrophobic surface. Generally explaining, a high thickness of fluid rim will produce a low retracting velocity according to the energy conservation between the surface energy and kinetic energy. However, this approach is not appropriate when the thickness of fluid increases to a certain extent. Actually, the retracting velocity of the impact droplet on superhydrophobic surfaces mainly depends on two factors: change in the surface energy ΔE_s and the inertia force F^{L} . In this case, due to the mass of the impact droplet gradually conveying to the external rim, there



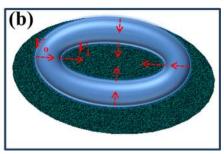


FIG. 5. (a) The image and (b) the schematic diagram of the impact droplet at the moment of starting to retract with an annulus shape.

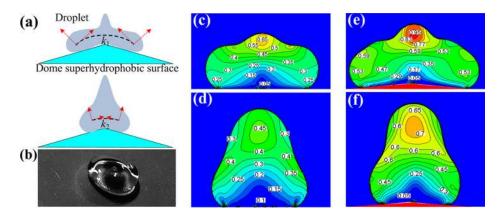


FIG. 6. The numerical calculation results of the retracting droplet at a particular moment. (a) The schematic diagram of forced direction variation from stage k_1 to stage k_2 during the retracting process. (b) The actual image of the impact droplet retracting at a particular moment. The numerical results of impact droplet retracting at the two particular moments on the flat (c) and (d) and dome convex (e) and (f) surfaces.

is a high inertia force at the external rim ($F^L \propto km$, where k is coefficient relative to motion state and m is the mass) and as a dominant element to affect the retracting velocity $V_{\rm o}$ of external rim. Therefore, the external rim of the impact droplet can also retract at a high velocity, meanwhile, the inner rim has a lower thickness under the action of surface energy change $\Delta E_{\rm s}$, also producing a high retracting velocity $V_{\rm i}$ ($V_{\rm i} = \sqrt{2\gamma/\rho h}$).

Furthermore, the forced analyses of the water droplet during retracting process might be utilized to rationalize the reduction in the contact time. We hypothesize that the impact droplet on the superhydrophobic surface exhibits a certain extent of elasticity. Thus, the retracting process of the impact droplet on the dome convex superhydrophobic surface might imply the gradual decrease in the bending curvature of the water droplet, such as the variation from stage k_1 to stage k_2 illustrated in Fig. 6(a). Comparing with retracting process of the impact droplet on the flat superhydrophobic surface, the gradual decrease in the bending curvature can produce a certain extent of bending stress, which also increases the retracting velocity. Of course, this is not the major contribution to the reduction in the contact time, because of the limited elasticity of the water droplet on superhydrophobic surfaces.

In order to conceivably verify these interpretations, we modeled the moving process of the impact droplets on the flat and dome convex superhydrophobic surfaces by a liquidair flow interface tracking method of VOF (Volume of Fluid) and coupling Level-set function.²⁷⁻²⁹ More details of equations and the numerical algorithm are provided in the supplementary material. The numerical calculation results of the retracting droplet at both the particular moments are shown in Figs. 6(c)-6(f), and the isovelocity lines are also clearly marked for the direct comparison of retracting velocity between the both cases. During the retracting process, the impact droplet on the dome convex superhydrophobic surface possesses a higher retracting velocity than that on the flat surface at any moment. The quantitative calculation results can powerfully prop up the above interpretations on the mechanisms behind the phenomenon of rapid detachment of impact droplets on convex superhydrophobic surfaces.

In summary, inspired by the sub-millimeters macrostructures inducing a valid reduction in the contact time of the impact droplet on solid surfaces, we found that droplets impacting onto dome convex superhydrophobic surfaces can also rapidly bounce off with a 28.5% reduction in the contact time compared with that on flat superhydrophobic surfaces. Also, the distinguishing bouncing regime behind this phenomenon clearly revealed that the reduction in the contact time was mainly determined by the retracting process. Under the action of dome convexity, the impact droplet produced a special hydrodynamic distribution with an annulus shape. This resulted in the high retracting velocities of the external and inner rims with assistances of the inertia force and the surface energy change respectively, which was also powerfully propped up by the quantitative numerical calculation results. The presented research is not restricted to the understanding on the regime behind some wetting phenomena but also exhibits a certain extent of application potential. ^{2,3,18,30}

See supplementary material for the detailed experimental procedures and the numerical algorithm on the retracting process of the impact droplet on the flat and dome convex superhydrophobic surfaces.

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