Dynamics of an impacting emulsion droplet

Maher Damak1,2, Joelt de Ruiter1,3, Sreedath Panat1, Kripa K. Varanasi1*

Emulsions are widely used in agriculture where oil-based pesticides are sprayed as an emulsion. However, emulsion droplets can bounce off hydrophobic plant surfaces, leading to major health and environmental issues as pesticides pollute water sources and soils. Here, we report an unexpected transition from bouncing to sticking to bouncing as the droplet impact speed increases. We show that the physics are governed by an in situ, self-generated lubrication of the surface leading to a suction force from the nascent oil layer around the droplet. We demonstrate that this phenomenon can be controlled by a careful balance of three time scales: the contact time of the droplet, the impregnation time scale of the oil, and the oil ridge formation time scale. We lastly build a design map to precisely control the bouncing of droplets and the oil coverage of the target surface. These insights have broad applicability in agriculture, cooling sprays, combustion, and additive manufacturing.

INTRODUCTION

The spraying of emulsions is a crucial process step in various industries. In agricultural sprays, one common approach is to use emulsifiable concentrates where the active pesticide ingredient is in an oil phase and is mixed with water to form oil-in-water emulsions (1, 2) with oil droplets that are typically in the micrometer range. These emulsions are atomized and sprayed onto plants. It is well known that the poor retention of agricultural sprays on hydrophobic plants is a major problem and causes a large amount of pollution (3, 4). A study found that pesticides could be detected 90% of the time in agricultural streams, 50% in shallow wells, and 33% in major deep aquifers across the United States (3), and another study found that up to 98% of sprayed chemicals do not end up on their intended target (5). Previous works have focused on enhancing the retention of sprays of pure water solutions (6–8), but none has studied the retention of emulsion droplets on hydrophobic leaves. The basic physical phenomenon of emulsion droplet impacts on hydrophobic surfaces remains elusive, and poorly designed emulsions for agricultural sprays continue to run off and pollute our environment (9).

Droplet impacts of pure liquids on superhydrophobic surfaces have been extensively studied in the literature (10–18). It is well known that at relatively low Weber numbers [\( \text{We} = \frac{\rho v^2 R}{\sigma} \)] (1), with \( \rho \) the density of the liquid, \( \sigma \) its surface tension, \( R\) the droplet radius, and \( v \) the impact speed, impacting droplets expand on the surface in a pancake shape, retract, and eventually bounce off (10, 11, 13). At higher Weber numbers, instabilities start forming at the rim of the droplet and splashing occurs (11, 15). One approach to reduce droplet bouncing is to use surfactants to reduce the surface tension (19). However, it has been shown that most surfactants are less effective in droplet impact scenarios because the droplet impact time scale can be lower than the time needed for surfactant molecules to diffuse to the liquid interface and be effective (20). Although some surfactants have been shown to work on shorter time scales (21), they are required to be compatible with various pesticide formulations used in agricultural sprays, which is a major challenge (22). In addition, surfactants lead to the formation of smaller droplets that are prone to drift (getting carried away by wind) (23), and surfactants themselves can be a toxic pollutant (24). Therefore, much recent research has focused on alternative solutions for pure water droplets (6, 7).

The knowledge on the impact of emulsion droplets is much scarcer. A few works focused on compound droplets, where an outer droplet contains one or a few inner droplets of another immiscible fluid, for applications including drug delivery and biomechanics (25–29). Most of these studies observed that the inner droplets were ejected out of the main drop and resulted in splashing, or modified the internal flow in the impacting drop. In a few cases, an inner oil droplet was observed to wet the underlying substrate and modify the surface properties. Another related area that received some interest is the impact of suspension droplets composed of solid particles in a water phase for applications in printing and coating processes (30–33). Most have observed a reduction in the maximal expansion and the retraction rate of the impacting droplets, as well as rebound suppression. These effects were mostly attributed to friction between the solid particles and the substrate, or, for high particle volume fractions, to higher apparent viscosities. However, the behavior of compound drops and suspensions cannot be generalized to emulsions as their physics depend heavily on the behavior of large internal drops or solid-solid interactions for suspensions, which are not present for emulsions.

Here, we study the impact of emulsion droplets on superhydrophobic surfaces (as a model for leaves). We show that the impact behavior varies in a nonintuitive manner as a function of the Weber number (calculated using the density and surface tension of water). Droplets bounce at low \( \text{We} \), stick at moderate \( \text{We} \), as the contact line starts destabilizing at the onset of splashing, and bounce again at high \( \text{We} \). We show that the surface can be impregnated in situ by the oil droplets in the emulsion during the spreading phase, and therefore, during the retraction phase, droplets effectively retract on a lubricant-impregnated surface (LIS) (34, 35). On that LIS, an oil ridge forms around the contact line and exerts a suction force on the droplet that is capable of arresting it when the vertical momentum of the droplet is low enough. We show that the vertical momentum is lowest for Weber numbers around the onset of splashing by measuring the restitution coefficient of equivalent water droplets. Therefore, we observe rebound suppression for a range of \( \text{We} \) around the onset of splashing. At higher \( \text{We} \), the droplet momentum becomes too large and the droplet bounces again. We lastly show that

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1Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA. 2Infinite Cooling Inc., 121 Madison st, Malden, MA 02148, USA. 3Thermo Fisher Scientific, Achtsweeg Noord 5, 5651 GG Eindhoven, The Netherlands. *Corresponding author. Email: varanasi@mit.edu
viscosity plays two conflicting roles: While it increases the suction force, it also increases the time scale of impregnation, making high viscosity oil emulsions noneffective at the time scale of droplet impact. Our results show that the usage of surfactants and other adjuvants in pesticide sprays may not be necessary and that metastable emulsions consisting of just the pesticide carrier (oil) and water can be more effective if used with the right emulsion and spraying parameters. Surfactants are often present in emulsifiable concentrate formulations (36) and are known to promote the formation of smaller droplets in sprays, which are prone to drift and cause major airborne pesticide run-off (23). Surfactant-free sprays would therefore prevent the spreading of large amounts of toxic chemicals in the environment and reduce costs.

**RESULTS**

**Emulsion drop impacts**

To study the behavior of emulsion droplet impacts, we mixed our model oil, hexadecane (oil viscosity \( \mu_o \approx 3 \) cSt), with water and used a probe sonicator to produce an oil-in-water emulsion of average oil droplet radius \( R \approx 700 \) nm, which is consistent with emulsified droplets in agricultural sprays (36). Hexadecane is only used as a model here and has properties (density, viscosity, and surface tension) that are on the same order as that of other oils that are used as solvents for oil-based pesticides (37, 38). We did not add surfactants to our formulations to clearly show that the observed effects do not come from surface tension changes and to prove that surfactant-free formulations with our approach can effectively ensure droplet retention. Indeed, these surfactant-free emulsions were observed to be metastable for durations of over 3 hours [visually through a change in transparency from opaque to transparent, and through dynamic light scattering (DLS) measurements in figs. S1 and S2 showing emulsion droplet radii remain essentially in the 500- to 1000-nm range], which is longer than the typical duration of spray applications (around 2 hours) (39). Therefore, emulsions could be made at the farm and sprayed while they are still stable. The added oil remains inside the droplet and does not noticeably change the surface tension of the main droplet as shown in the surface tension measurements in fig. S4. The experimental setup is shown in Fig. 1A. A needle dispensed droplets on a superhydrophobic surface (165° advancing contact angle, 5° hysteresis). The varied parameters were oil concentration in the emulsion (0 to 20 volume percent), diameter of the droplet (2.29 to 4.25 mm; by changing the needle), and impact speed (0.25 to 1.4 m/s; by changing the height). This allowed us to vary the Weber number of the impacting drops from 2 to 150, which is within the typical Weber number range (5 to 150) used for efficient agricultural sprays [droplet diameters are typically between 200 and 500 \( \mu \)m, and velocities between 1 and 8 m/s (40, 41)]. The goal is to arrest the carrier water droplet so that the pesticide molecules can reach the plant surface as the carrier water droplet evaporates once it is pinned to the surface, whether the pesticide is in the oil phase or the water phase.

The typical observed behavior is shown in Fig. 1B for both water and emulsion droplets of radius 2 mm and oil concentration 10%. At low and moderate Weber numbers (here \( We = 50 \)), emulsion droplets expand, retract, and bounce similarly to water droplets on the same surface. The only difference is that the bouncing is slightly delayed for the emulsion droplet. At higher Weber numbers (\( We = 87 \)), while water droplets still bounce, emulsion droplets stick to the surface. In all cases where this happens, the sticking coincides with the onset of splashing in the impacting droplet. When we increase the Weber number further (shown here \( We = 95 \)), water droplets splash and bounce, and emulsion droplets also start bouncing again. We have thus a bouncing-sticking-bouncing transition when we use emulsion droplets, and the sticking window coincides with the onset of splashing. This behavior was consistent across numerous experiments where droplet diameters and impact velocities were varied, and droplets were always arrested at Weber numbers around and after the onset of splashing.

To explain this phenomenon, we propose a three-phase mechanism: First (I), when emulsion droplets impact the surface, some of the oil droplets come to the surface and impregnate its texture. Second (II), the emulsion droplet retracts on a partially oil-impregnated surface (Fig. 1C), and an oil ridge forms around the droplet’s contact line, similar to what is classically observed on liquid-impregnated surfaces (34, 42). Third (III), toward the end of the retraction phase, the droplet acquires vertical momentum and starts to lift up, while
the formed oil ridge exerts a suction force on the droplet. The balance of these two effects dictates whether the emulsion droplet will bounce or stick.

I. Oil impregnation

We imaged the surface after the impact of an oil-in-water emulsion droplet under an optical microscope. To prevent multiple rebounds on the same spot, experiments were performed on a slightly inclined surface (≈10°). Figure 2A shows microscope images of the surface after impact of a single emulsion droplet, for different oil concentrations. We can see oil deposits that are uniformly distributed across the area under the droplet. The amount of oil increases with the concentration, which is expected. To verify that oil impregnation occurs during the spreading phase, we imaged an emulsion droplet impact on a transparent superhydrophobic surface from the bottom. The lens was focused at the surface. The images are shown in Fig. 2B, and we can see that oil droplets contact the surface during the spreading phase. The oil deposits remain on the surface as the droplet retracts, confirming the hypothesis that the droplet retracts on a partially oil-impregnated surface.

To quantify the impregnation of oil, we measured the diameter \( D_{\text{deposit}} \) of the deposit left on the surface from microscope images for various parameters and compared it to the maximum expansion diameter \( D_{\text{max}} \) (from high-speed movies). In the case of splashing, \( D_{\text{max}} \) was taken as the maximum diameter of the main droplet. The ratio \( D_{\text{deposit}} / D_{\text{max}} \) was close to 1 for all Weber numbers and oil concentrations, showing that oil gets deposited in all locations where the emulsion is in contact with the surface (Fig. 2C). We further measured the coverage \( \phi \) of the surface by oil, defined as the area covered by oil divided by the total area under the droplet. The coverage values showed some scatter, but no trend was observed as the Weber number was varied (Supplementary Materials). Average values of the coverage are shown in Fig. 2D as a function of oil concentration.

Given that the distribution of the oil residue is fairly uniform across Weber numbers, we assume that the impregnation of oil droplets on the surface is not driven by internal flow in the droplet. Deceleration-driven motion of oil droplets cannot explain the behavior either, because less dense oil droplets would tend to propel upward rather than to the surface. Therefore, we conclude that the dominant mechanism of oil impregnation is diffusion of oil droplets close to the surface and contact with the solid texture. The diffusion mechanism is also validated by the fact that gently depositing a droplet on the surface still covers it with oil. As shown in fig. S4, gently dropping a droplet from a height <1 cm (\( \text{We} \approx 5 \)) leads to the same amount of coverage as higher-speed impact at large Weber numbers for the same oil concentration.

The oil droplets wet the surface because the spreading coefficient of oil on the solid in the presence of water is positive: \( \sigma_{ab} - \sigma_{ao} - \sigma_{wo} > 0 \) [calculation in Supplementary Materials from measurements and references (34, 43)], where \( \sigma_{ab} \) is the interfacial tension between species \( a \) and \( b \), \( w \) is water, \( o \) is oil, and \( s \) is solid.

The diffusion coefficient of oil droplets in a water phase is given by

\[
D = \frac{k_B T}{6\pi \mu_w R}
\]

(2)

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, and \( \mu_w \) is the water viscosity.

The diffusion length \( l \) during the contact time \( \tau_c \) is given by

\[
1 \sim \sqrt{2D\tau_c}
\]

We assume a uniform distribution of the oil droplets in the water phase where the oil droplets form an array with a fixed distance between them. During impact, water droplet spreading may change the relative distance between oil drops, where the vertical spacing between oil droplets decreases and the horizontal spacing increases. However, since the oil concentration remains unchanged, the amount of oil in a certain layer of the water droplet is independent of the actual spatial distribution of the oil droplets. We assume the oil in the layer of thickness \( l \) will diffuse to the surface and impregnate it. The volume of oil in that layer per unit area is \( Cl \), where \( C \) is the volumetric oil concentration in the emulsion.
Looking at an individual oil droplet of radius $R$ in that layer, when it fully impregnates the texture of the surface, it spreads in a circular layer of radius $r$ (see inset of Fig. 2D) set by the height $\delta$ of the texture and its void fraction $f$ that can be filled with oil.

Conservation of volume gives (per unit area): $Cl = \varphi \delta f$, where $\varphi$ is the surface coverage with oil. Thus

$$\varphi = C \frac{1}{\delta f}$$

(4)

An atomic force microscopy (AFM) image (fig. S10) of the surface is in the Supplementary Materials and demonstrates that $f \sim 0.5$ and $\delta \sim 111$ nm.

Measurements for oil droplet radius show a distribution generally between 400 and 900 nm (fig. S1). Figure 2D shows the theoretical curve and experimental measurements of the coverage for various concentrations. We can see that the model can accurately predict the linear behavior of the coverage as a function of oil concentration and that the slope of the curve is accurately captured by the model with no fitting parameters. This model and Eq. 4 can therefore be used to estimate the fraction of the surface that is covered with oil at the end of the retraction phase of the impacting droplet.

II. Ridge formation

The second phase of the process is the formation of an oil ridge around the emulsion droplet. As the emulsion droplet retracts, it sees a surface that is partially filled with oil.

Some previous literature focused on the case where the surface is already covered with oil by studying the impacts of water droplets on lubricant impregnated surfaces (LIS) (34, 44–46). As oil that impregnates the surface spreads on the contact line of the retracting emulsion droplet, it starts forming the typical ridge observed at the contact line of droplets on LIS (34, 46). This ridge is concave, resulting in a Laplace pressure difference where the pressure in the oil layer is lower than the ambient pressure, resulting in a suction force as shown schematically in Fig. 3A. We assume no flow inside the texture of the surface and thus a uniform pressure in the oil layer. In reality, there is a slow flow of oil in the oil layer toward the center (compared to velocities in the water phase) (47), making the pressure in the center lower than the contact line. However, this additional suction due to flow does not change the order of magnitude of the suction pressure due to the ridge (see Supplementary Materials) and was neglected here. Figure 3B has photographs directly showing the oil ridge at different stages of the droplet impact. When the radius of curvature of the ridge is small enough, this Laplace pressure–driven force can be non-negligible (48–50). The suction pressure is approximately $P_{c} \approx \frac{2\sigma_{o}}{R}$ (see Supplementary Materials), where $\sigma_{o}$ is the surface tension of the oil and $h$ is the size of the transient oil ridge, since the ridge will not have reached its full size by the end of the retraction phase. Indeed, as can be observed in Fig. 3B, the ridge is still growing during impact. In the example of Fig. 3B, it takes 300 ms for the ridge to reach its steady-state size, while bouncing occurs after 40 ms.

Looking at Fig. 3A, the two surface forces that are exerted on the droplet are the suction force that is estimated as $F_s = \pi R_0^2 \varphi \sigma_{o}$ and the surface tension force on the contact line $F_{cl} = 2\pi R_0 \varphi \sigma_{o}$. Several assumptions are made here. The pressure under the droplet can be approximated as uniform and equal to the pressure in the oil ridge, as justified above and in the Supplementary Materials. The suction pressure is exerted over the area of a disk of radius $R_0$, the initial radius of the impacting droplet, as $R_0$ is the approximate radius at which the shape of droplet transitions from a retracting pancake to an upward jet at the end of the retraction phase. We also assume that the oil patches on the surface are connected and thus have the same pressure. For low surface coverages of oil, the connectivity assumption may not hold and our expression for the suction force will just be an upper bound.

In our case, $\frac{F_s}{F_{cl}} = \frac{\pi R_0}{2} \gg 1$, as the ridge size is orders of magnitude smaller than the droplet radius. Therefore, the suction force is the only surface tension–related force we will consider in our model.
To estimate the ridge size, we use the analysis from Lee et al. (44) where the transient height $h$ of the oil ridge around the droplet is estimated by balancing the driving capillary force with viscous dissipation in the growing oil layer $\sigma_o - \mu_w \frac{\delta}{2} h = \mu_w \frac{\delta}{2} \frac{\rho v^2}{\omega}$, where $V_o$ is the velocity of the oil spreading, $s$ is the thickness of the oil layer away from the droplet, and $\tau_c$ is the contact time (inset of Fig. 3C). Here we assume that $s = \delta$, which is the height of the texture. The size of the ridge just before bouncing is then

$$h = \left( \frac{\sigma_o \delta \tau_c}{\mu_o} \right)^{1/2}$$

(5)

We measured ridge size in the case of Fig. 3B (just before rebound) to be on the order of 100 $\mu$m, and the formula above predicts a size $h = 180 \mu$m, which has the same order of magnitude, thus verifying our scaling model for estimating the ridge size.

The suction force can be approximated as $F_s \sim 3\pi R_0^2 \phi$, where $\phi$ is the coverage of the surface by oil (Fig. 2D) and $\tau_c$ is the contact time ($\rho$ is the density of the emulsion) (51).

$$\tau_c \approx 2.6 \left( \frac{\rho R_0^3}{\sigma_o} \right)^{1/2}$$

(6)

For the contact time $\tau_c$, we use the previous formula that has been established in the literature for single-phase droplets and that was confirmed here to predict the contact time for bouncing emulsion droplets as well.

We then have

$$F_s \sim \left( \frac{\sigma_o \mu_w}{\delta \tau_c} \right)^{1/2} R_0^2 \phi$$

(7)

$F_s$ is independent of the impact speed.

III. Bouncing-sticking-bouncing transition

At the end of the retraction phase, there is an oil ridge around the contact line, and the oil layer under the droplet exerts a suction force on the droplet that can prevent it from bouncing (48). Meanwhile, as surface energy is converted back into kinetic energy, the emulsion droplet starts accelerating vertically with a typical “bouncing acceleration equivalent force” $F_b$. By performing a force balance on the droplet at the instant just before bouncing, we see that the droplet will stick if the suction force from the oil layer is high enough to balance the bouncing force $F_b$ of the droplet.

This proposed mechanism is in agreement with the observation that the retraction rates of emulsion droplets and the retraction rates of water droplets on liquid-impregnated surfaces (with viscosities up to 100 cSt) are not notably affected by the oil viscosity (fig. S5), showing that viscous dissipation can be neglected here, in agreement with what has been observed in the literature for homogeneous droplet impacts (52). The horizontal retraction rate does not depend on the vertical suction force and is set by the inertial-capillary balance (52). We conclude that the impregnated oil only minimally affects the horizontal retraction phase and that its main effect is the introduction of the suction force that arises when the droplet starts moving vertically at the end of the retraction phase.

The bouncing force is estimated as the force needed to accelerate the droplet to an upward velocity of $\epsilon_0 v$ (6, 45, 53–56) as detailed in Supplementary Materials.

$$F_b = \epsilon_0^2 \left( \frac{4}{3} \pi R_0^2 \rho v^2 \right)$$

(8)

Here, $\epsilon_0$ is a modified restitution coefficient of the impact of an equivalent pure water droplet. $\epsilon_0$ represents the ratio of vertical momentum after rebound to the momentum before impact. While restitution coefficients are commonly used for single connected droplets (no splashing) (53), we extend the definition here to splashing droplets by taking the ratio of the vertical momentum of the main part of the droplet that rebounds to the momentum of the whole droplet before impact. $\epsilon_0$ is measured experimentally for pure water droplets (fig. S6), where the vertical momentum of the droplet expels it upward and is not resisted by any suction force. Since the expansion and horizontal retraction phases are not significantly affected by the presence of oil in the droplet, we assume that the bouncing force experienced by pure water droplets is comparable to the bouncing force experienced by emulsion droplets of equal size and impact speed. The modified restitution coefficient is highly affected by the onset of splashing ($We \sim 45$ to 70), which causes it to sharply drop as part of the kinetic energy is expelled sideways into the smaller splashing droplets.

The ratio of these bouncing to the suction forces is given by

$$\frac{F_b}{F_s} \sim \frac{4 \pi \epsilon_0^2 \rho v^2}{3 \phi \left( \frac{\sigma_o \mu_w}{\delta \tau_c} \right)^{1/2}}$$

(9)

By plugging in Eq. 1 for the Weber number $We$ and Eq. 6 for the contact time $\tau_c$, we get

$$\frac{F_b}{F_s} \sim \frac{2.15 \pi \delta^{1/2} \sigma_o^{3/4} \rho^{1/4} \epsilon_0^2 (We)}{\phi}$$

(10)

$\phi$ is given by Eq. 4, and the equation for $\epsilon_0^2 (We)$ as a function of $We$ is given in fig. S6 and is based on the measured restitution coefficient for pure water droplets. Therefore, the term $\epsilon_0^2 (We)$ in the equation does not account for any oil effects and only captures the physics of the vertical momentum after bouncing in the case where oil is not added to the impacting droplet.

This ratio is plotted in Fig. 3C for three oil concentrations (5, 10, and 20%) where the quantity that is varied in the Weber number (5, 10, and 20%) where the quantity that is varied in the Weber number is the impact velocity.

The sharp drop between Weber numbers 45 and 65 corresponds to the drop in the restitution coefficient due to the onset of splashing. The origin of the bouncing-sticking-bouncing transition becomes clear: At relatively low Weber numbers, the bouncing force is higher than the suction forces and emulsion drops bounce. At Weber numbers just above the onset of splashing, the bouncing force drops and can be overcome by the suction force (in the case of 10 and 20% oil concentration in Fig. 3C), resulting in a ratio that is lower than 1, which leads to sticking drops. At high Weber numbers, the bouncing force grows again above the suction force, and the behavior transitions back to bouncing.

The experimental data indeed show that droplets stick in the predicted regime where the ratio $F_b/F_s$ is below 1. The two main experimental outliers occur in the 45 to 70 Weber number window (for the 20% concentration case) where the splashing behavior is most variable, resulting in a large variability in restitution coefficient as can be seen in Supplementary Materials (droplets sometimes exhibit a major splash at $We = 45$ and sometimes barely splash at $We = 70$).
lower oil concentrations (5% here), the surface coverage of oil is low, and thus, the suction force remains lower than the bouncing force for all Weber numbers and droplets never stick. Our model is further validated by the fact that similar behavior is observed for water droplet impacts on liquid-impregnated surfaces (LIS), which are dipcoated beforehand and have a complete layer of oil inside their texture. The LIS case represents a particular case of the previous model, where we know the coverage $\varphi = 1$, and our scaling model similarly correctly predicts the bouncing-sticking-bouncing transition (fig. S7).

While our model was developed for monodisperse emulsions with the average oil droplet radius of 700 nm, it should be noted that the oil radius only affects the bouncing to suction force ratio through the surface coverage $\varphi$, and the ratio is proportional to the square root of the oil droplet radius: $\frac{\mu_o}{\mu_o + \sigma} \propto \sqrt{R}$. For a polydisperse emulsion, the only change would be the coverage of the surface $\varphi$, with smaller oil droplets leading to a higher coverage. In our experiments, the oil droplet radius was essentially in the 500- to 1000-nm range, meaning that the force ratio $F_b/F_s(R) = (\sqrt{500 \text{ nm}}/700 \text{ nm} = 0.85 - \sqrt{1000 \text{ nm}/700 \text{ nm} = 1.2} ) F_b/F_s(R = 700 \text{ nm})$ is within 20% of what is shown in Fig. 3 for a 700-nm monodisperse emulsion. As long as the emulsion oil droplet sizes are in that range, the emulsion is metastable, and the retention effect is practically unchanged.

We also performed experiments using emulsion of soybean oil, one of the most commonly used plant-based oils in agricultural sprays (57–59), and demonstrated a similar bouncing-sticking-bouncing transition (fig. S8, see movies S11 to S13). This further demonstrates the generality of the described underlying physics of emulsion drop impact as long as the physical properties (see Materials and Methods) of different oils are similar.

### The effect of oil viscosity

In the case of hexadecane, a relatively low-viscosity oil, we assumed that the impregnation of the surface by the oil droplets was immediate. However, for more viscous oils, the kinetics of impregnation may become limiting. The time scale of impregnation is (see Supplementary Materials)

$$\tau_s = \frac{\mu_o}{\sigma} \left( \frac{4}{3} \pi \right)^2 \frac{R^6}{\delta^3}$$

This time is on the order of 4 ms for 3 cSt of oil, justifying the immediate impregnation assumption for the previous section where contact times are on the order of tens of milliseconds. However, for emulsion drops with higher viscosity oils, this time scale increases and can become larger than the contact time for a certain viscosity. Above that viscosity, the surface impregnation does not have enough time to occur and thereby the ridge formation phase does not occur either. Top-view snapshots of emulsion impacts with various viscosities are shown in Fig. 4 (A and B). For $\mu_o = 10$ cSt, as the droplet starts retracting, the oil has already spread into the texture. However, for $\mu_o = 1000$ cSt, individual spherical droplets can be seen after the droplet retracts and bounces, and they take a longer time to spread. In the intermediate regime of $\mu_o = 100$ cSt, only a few individual spherical oil drops can be observed as the droplet retracts (fig. S9).

We performed surface coverage measurements immediately after rebound of emulsion droplets of various viscosities at an oil concentration of 10% (inset of Fig. 4C). We found that the coverage was constant at 39% between 3 and 10 cSt and then started decreasing as the viscosity increased to reach only 0.6% for 1000 cSt, which is consistent with the explanation above. Similar to hexadecane, coverage values with silicone oil appeared independent of the impact Weber number.

Figure 4C shows experimental outcomes of emulsion impacts at different viscosities (with an oil concentration of 10%), as well as the impacts of water droplets on oil-impregnated surfaces (preinfused with oil before drop impact) with oils of the same viscosities.

As predicted, for low viscosities, the oil ridge is relatively large; thus, the suction force is low and cannot overcome the bouncing
force. In that regime, we expect all droplets to bounce off. Emulsion droplets are indeed all observed to bounce for \( \mu = 1.5 \text{ cSt} \), and water droplets impacting an LIS with the same oil were only able to stick in a narrow window of \( \text{We} \) around the onset of splashing (due to their higher coverage factor \( \varphi = 1 \)). As the viscosity increases, we observe the bouncing-sticking-bouncing transitions that we previously described both for emulsions and water on LIS impacts. For higher viscosities, when \( t_r > t_{\text{contact}} \), oil spreading becomes a limiting factor, the behavior diverges between emulsions and LIS. In the case of emulsions, the oil droplets do not have time to impregnate the surface, which means that there is no oil layer to generate a suction force after the retraction. We can see on the figure that for \( \mu_o = 1000 \text{ cSt} \), emulsion droplets bounce for all Weber numbers. For LIS surfaces where the impregnation phase is done beforehand using dipcoating, and at higher viscosities, the suction force overcomes the bouncing force at all Weber numbers, and we observe that all water droplets stick when impacted on surfaces impregnated with 100 cSt and higher-viscosity silicone oil. It should be noted that at high oil viscosities in LIS (higher than 100 cSt), viscous dissipation during the retraction may become non-negligible and also contribute to arresting droplets.

This plot gives a design map for effective emulsion sprays. There is an optimal range of viscosities where the generated suction force is strong enough to arrest droplets and where the impregnation of oil from emulsions is fast enough to occur during the contact time of the droplet impact. There is also an optimal range of Weber number, as discussed above and in Fig. 3, where oil ridge suction forces are able to overcome the inertia of the droplet and prevent it from bouncing. Hence, sprays should be designed such as the Weber number and viscosity regimes are met (9). It should also be noted that in spray applications, oil impregnation has a compounding effect. The infused oil layer not only arrests the droplet that creates it but also remains on the surface and can arrest further droplets that impact that area. As more droplets impinge, the surface coverage of oil increases and the surface turns into an LIS that is capable of arresting droplets in a broader range of Weber numbers as shown in Fig. 4C.

Last, we performed macroscopic experiments with sprays. Figure 5A shows snapshots of high-speed videos of water and emulsion (8% hexadecane) sprays impacting a superhydrophobic surface. As predicted, all water droplets bounce off, and the surface remains dry. However, many emulsion droplets stick to the surface, and we quickly observe an accumulation of liquid on the surface. Sparse sprays were used in these experiments for better visualization. To quantitatively capture the efficiency of emulsion sprays, we experimentally measured the retained volume of liquid on the surface for a fixed amount of sprayed liquid. The retention was determined by weighing the surface after each spray. The results are shown in Fig. 5B. The retained volume continuously increases for both water and emulsions, but the rate of retention is observed to be 10 times higher in the case of emulsions than for pure water.

**DISCUSSION**

In this study, we have unveiled a previously unknown mechanism with which emulsion droplets can stick to superhydrophobic surfaces. We have shown that for a certain range of oil viscosity, impinging oil-in-water emulsion droplets can create partly liquid-impregnated surfaces in situ, when emulsified oil droplets penetrate the surface texture. We have argued that the oil ridge around the contact line leads to a suction force during the impact and showed that, for a certain interval of Weber numbers, this suction force overcomes kinetic energy and prevents droplet rebound. We have observed that this happens only at the onset of splashing and explained it by the sharp drop in

![Fig. 5. Macroscopic spraying of emulsion on nonwetting surfaces.](image)

(A) Snapshots of high-speed video of water and emulsion (8% hexadecane in water) sprays on superhydrophobic surfaces. Spray droplets are on the order of 1 mm in diameter. Weber numbers were mostly in the 40-to-200 range. All water droplets bounce, while emulsion drops stick and accumulate on the surface (see movies S9 and S10). (B) Graphs of retained volume of sprayed liquid on superhydrophobic surface after repeatedly spraying fixed amounts of water and 20% hexadecane emulsions. Dashed lines are linear fits. The slope of the red dashed line corresponding to the emulsion case is 10 times larger than the slope of the water line. (C) Photograph of a hosta leaf after spraying the left side with water and the right side with a 20% hexadecane emulsion. The left side remains largely dry, while a film of liquid covers the right side.

| Table 1. Oil properties. SO, silicone oil. |
|------------------------------------------|
| Hexadecane | SO—1.5 cSt | SO—10 cSt | SO—100 cSt | SO—1000 cSt | Soybean oil |
| Viscosity \(10^{-3} \text{ Pa·s}\) | 3 | 1.5 | 10 | 100 | 1000 | 57 |
| Surface tension (mN m\(^{-1}\)) | 27 | 18 | 20 | 20.9 | 21.2 | 31.3 |
| Density (kg m\(^{-3}\)) | 773 | 851 | 935 | 965 | 970 | 915 |
restitution coefficient as splashing starts to occur. We have hastily shown that this technique is efficient in spray retention with our model surfactant-free system. Future work could help expand these results to cases where surfactants are added to the formulation. This method can be used in agriculture, where emulsified oil–based pesticides are routinely sprayed. By controlling the oil concentration, droplet size, and impact velocity according to the design maps we have provided here, retention of sprays could be largely improved while cutting the usage of unnecessary adjuvants like surfactants, to eliminate runoff and environmental pollution by pesticides and enhance efficiencies in various applications such as steel strip manufacturing (60), combustion (61), and additive manufacturing (9, 62).

MATERIALS AND METHODS

Emulsion preparation

The oils used here were hexadecane and silicone oils of various viscosities. Emulsions were prepared in 10-ml batches using a micropipette to add the appropriate volume of water and oil for a certain concentration in a vial. No surfactants were added. The solution was then mixed with a probe sonicator (Sonics Vibra Cell VCX 750) for 90 s at 60% power. Emulsions were used in the 30-min following preparation.

Surface preparation

Superhydrophobic nanograin surfaces were fabricated using reactive ion etching with O2 and SF6 on silicon substrates. The resulting surface has a random texture with features on the order of 200 nm and is superhydrophobic. The surface is then coated with octadecyltrichlorosilane (OTS), a hydrophobic modifier, to make it superhydrophobic. The advancing contact angle of deionized water on this surface is 165° ± 2°, and the receding angle is 160° ± 3°. Angles were measured with a Ramé-Hart model 500 goniometer at room temperature. An AFM image of the surface is shown in fig. S10. The same surface, without the OTS coating, was used to perform a control experiment on a superhydrophilic surface, with results in fig. S11 and movies S14 to S16.

Transparent superhydrophobic surfaces were made by dipcoating (at a speed of 10 mm/min) glass slides in a dispersion of OTS-coated silica nanoparticles of average size 12 nm (size range, 8–15 nm). The dispersion was prepared by mixing 1 weight % nanoparticles in ethanol for 2 min with probe sonication at 60% power.

LIS preparation

Liquid-impregnated surfaces were made by dipcoating OTS-coated surfaces in oil solutions. Both nanograin and surfaces with microtexture (square posts with 10-μm width, 10-μm pitch, and 21-μm height) were used. To have a film that exactly covers the texture of the surface is shown in fig. S10. The same surface, without the OTS coating, was used to perform a control experiment on a superhydrophilic surface, with results in fig. S11 and movies S14 to S16.

Emulsion size determination

The size of oil droplets in the emulsion was measured with DLS at room temperature. DLS measurements were performed using DynaPro NanoStar, capable of measuring droplets with radii in the 0.2 nm–to–2.5 μm range. DLS measurements were acquired 10 times for each sample.

Coverage determination

Emulsion impacts were performed on a slightly inclined surface (10°), so that the droplet does not rebound on the same spot. The original impact spot was then observed under an optical microscope (Zeiss Axio Zoom.V16). Areas impregnated with oil had appeared as colored because their thickness was in the hundreds of nanometers. There was no additional image processing. The surface texture height is roughly 100 to 150 nm, which is a quarter of the wavelength of light. Hence, when the texture is infused with oil, the resulting thin film would cause constructive interference. In other experiments where some liquid stuck to the surface after rebound and additional oil was deposited on the surface, we observed patches of yellow and orange, indicating thicker oil layers. Example microscope images are shown in figs. S12 and S13. Image processing using the software ImageJ was then used to calculate the fraction of the area that oil was occupying (9).

Physical properties of used oils

Various oils were used in experiments. Their properties are shown in Table 1.

SUPPLEMENTARY MATERIALS

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REFERENCES AND NOTES

1. G. Matthews, Pesticide Application Methods (John Wiley & Sons, 2008).
2. R. Wiwattanapatapee, A. Sae-Yun, J. Petcharit, C. Ovatlarnporn, A. Itharat, Development and evaluation of granule and emulsifiable concentrate formulations containing *Derris elliptica* extract for crop pest control. J. Agric. Food Chem. 57, 11234–11241 (2009).
3. R. J. Gilliom, J. E. Barbash, C. G. Crawford, P. A. Hamilton, J. D. Martin, N. Nakagaki, L. H. Nowell, J. C. Scott, P. E. Stackelberg, G. P. Thelin, D. M. Wolock, Pesticides in the Nation’s Streams and Ground Water, 1992–2001 (U.S. Geological Survey, 2006), pp. 184.
4. M. Massinon, F. Lebeau, International Advances in Pesticide Application: Aspects of Applied Biology 114, 2012, in Comparison of Spray Retention on Synthetic Superhydrophobic Surface with Retention on Outdoor Grown Wheat Leaves (Association of Applied Biologists, 2012), vol. 114, pp. 261–268.
5. D. Pimentel, Amounts of pesticides reaching target pests: Environmental impacts and ethics. J. Agric. Environ. Ethics 8, 17–29 (1995).
6. M. Damak, M. N. Hyder, K. K. Varanasi, Enhancing droplet deposition through in-situ precipitation. Nat. Commun. 7, 12560 (2016).
7. V. Bergeron, D. Bonn, J. Y. Martin, L. Vovelle, Controlling droplet deposition with polymer additives. Nature 405, 772–775 (2000).
8. D. B. Smith, S. D. Askew, W. H. Morris, D. R. Shaw, M. Boyette, Droplet size and leaf morphology effects on pesticide spray deposition. Trans. ASABE 43, 255–259 (2000).
9. M. Damak, PhD thesis, Massachusetts Institute of Technology (2018).
10. D. Richard, D. Quéré, Bouncing water droplets. EPL Europhys. Lett. 50, 769–775 (2000).
11. M. Rein, Phenomena of liquid drop impact on solid and liquid surfaces. Fluid Dyn. Res. 12, 61–93 (1993).
12. Y. Liu, L. Moevius, C. Xu, T. Qian, J. M. Yeomans, Z. Wang, Pancake bouncing on superhydrophobic surfaces. Nat. Phys. 10, 515–519 (2014).
13. J. C. Bird, R. Dhiman, H.-M. Kwon, K. K. Varanasi, Reducing the contact time of a bouncing drop. Nature 503, 385–388 (2013).
14. X. Deng, F. Schellenberger, P. Papadopoulos, D. Vollmer, H.-J. Butt, Liquid drops impacting superamphiphobic coatings. Langmuir 29, 7847–7856 (2013).
15. C. Daza, C. Ybert, C. Clanet, L. Bocquet, Making a splash with water repellency. Nat. Phys. 3, 190–193 (2007).
16. J. de Ruiter, J. M. Oh, D. van den Ende, F. Mugele, Dynamics of collapse of air films in drop impact. Phys. Rev. Lett. 108, 074505 (2012).
17. T. M. Schatzius, S. Jung, T. Maata, G. Graeber, M. Köhme, D. Poulikakos, Spontaneous droplet trampling on rigid superhydrophobic surfaces. Nature 527, 82–85 (2015).
18. C. Clanet, C. Béguin, D. Richard, D. Quéré, Maximal deformation of an impacting drop. J. Fluid Mech. 517, 199–208 (2004).
19. R. E. Gaskin, K. D. Steele, W. A. Forster, Characterising plant surfaces for spray adhesion and retention. J. Plant Prot. 58, 179–183 (2005).
20. X. Zhang, O. A. Basaran, Dynamic surface tension effects in impact of a drop with a solid surface. J. Colloid Interface Sci. 187, 166–178 (1997).

21. M. Song, J. Ju, S. Luo, Y. Han, Z. Dong, Y. Wang, Z. Gu, L. Zhang, R. Hao, L. Jiang, Controlling liquid splash on superhydrophobic surfaces by a vesicle surfactant. Sci. Adv. 3, e1602188 (2017).

22. F. Whitford, A. Patton, B. Johnson, B. Young, D. Linscott, J. Deveau, J. Reiss, K. Leigh, M. Olds, R. Cloyd, T. Overley, Avoid Tank Mixing Errors: A Guide to Applying the Principles of Compatibility and Mixing Sequence (2018), available at https://ppp.purdue.edu/wp-content/uploads/files/PPP-122.pdf.

23. M. C. B. Ellis, C. R. Tuck, P. C. H. Miller, How surface tension of surfactant solutions influences the characteristics of sprays produced by hydraulic nozzles used for pesticide application. Colloids Surf. A Physicochem. Eng. Asp. 180, 267–276 (2001).

24. R. M. Mann, J. R. Bidwell, The acute toxicity of agricultural surfactants to the tadpoles of four Australian and two exotic frogs. Environ. Pollut. 114, 195–205 (2001).

25. C. Josserand, S. T. Thronodduen, Drop impact on a solid surface. Annu. Rev. Fluid Mech. 48, 365–391 (2016).

26. S. L. Chiu, T.-H. Lin, Experiment on the dynamics of a compound drop impinging on a hot surface. Phys. Fluids 17, 121203 (2005).

27. P. Gao, J. J. Feng, Spreading and breakup of a compound drop on a partially wetting substrate. J. Fluid Mech. 682, 415–433 (2011).

28. S. Tasoglu, G. Kaynak, A. J. Szeri, U. Demirci, M. Muradoglu, Impact of a compound droplet on a flat surface: A model for single cell epithaxy. Phys. Fluids 22, 082103 (2010).

29. N. Blanken, M. S. Saleem, C. Antonini, M.-J. Thoraval, Rebound of self-lubricating compound drops. Sci. Adv. 6, eaay3499 (2020).

30. V. Grishaev, C. S. Iorio, F. Dubois, A. Amirfazli, Complex drop impact morphology. Langmuir 31, 9833–9844 (2015).

31. M. Nicolas, Spreading of a drop of neutrally buoyant suspension. J. Fluid Mech. 545, 271–280 (2005).

32. H. Ok, H. Park, W. W. Carr, J. F. Morris, J. Zhu, Particle-laden drop impacting on solid surfaces. J. Dispers. Sci. Technol. 25, 449–456 (2005).

33. Y. Ueda, S. Yokoyama, M. Nomura, R. Tsujiino, M. Iguchi, Bouncing behaviors of suspension liquid drops on a superhydrophobic surface. J. Vis. 13, 281–283 (2010).

34. J. D. Smith, R. Dhiman, S. Anand, E. Reza-Garduno, R. E. Cohen, G. H. McKinley, Lubrication mobility on lubricant-impregnated surfaces. Soft Matter 9, 1772–1780 (2013).

35. B. R. Solomon, S. B. Subramanyam, T. A. Farnham, K. S. Khalil, S. Anand, K. K. Varanasi, Lubricant-impregnated surfaces, in Non-Wettable Surfaces (2016), pp. 285–318.

36. G. W. J. Lee, T. F. Tadros, Formation and stability of emulsions produced by dilution of emulsifiable concentrates. Part I. An investigation of the dispersion on dilution of emulsifiable concentrates containing cationic and non-ionic surfactants. Colloids Surf. 5, 105–115 (1982).

37. J. Feng, X. Zhang, Q. Liu, Z. Zhu, D. J. Mc Clements, S. M. Jafari, Application of nanoemulsions in formulation of pesticides, in Nanoemulsions (Elsevier, 2018), pp. 379–413.

38. L. M. Diamante, T. Lan, Absolute viscosities of vegetable oils at different temperatures and shear rate range of 64.5 to 4835 s−1. J. Food Process. Eng. 2014, 234583 (2014).

39. P. Lebailly, V. Bouchart, I. Baldi, Y. Lecluse, N. Heutte, A. Gislard, J.-P. Malas, Exposure of four Australian and two exotic frogs. Environ. Pollut. 114, 195–205 (2001).

40. D. Nuyttens, M. De Schampheleire, P. Verboven, E. Brusselman, D. Dekeyser, Droplet size effect on spray deposition efficiency of citrus leaves. Langmuir 31, 9833–9844 (2015).

41. M. Salyani, Droplet size effect on spray deposition efficiency of agricultural sprays. J. Fluid Mech. 545, 271–280 (2005).

42. F. Schellenberger, J. Xie, N. Blanken, M. S. Saleem, C. Antonini, M.-J. Thoraval, Rebound of self-lubricating compound drops. Sci. Adv. 6, eaay3499 (2020).

43. H. Ok, H. Park, W. W. Carr, J. F. Morris, J. Zhu, Particle-laden drop impacting on solid surfaces. J. Dispers. Sci. Technol. 25, 449–456 (2005).

44. Y. Ueda, S. Yokoyama, M. Nomura, R. Tsujiino, M. Iguchi, Bouncing behaviors of suspension liquid drops on a superhydrophobic surface. J. Vis. 13, 281–283 (2010).

45. J. D. Smith, R. Dhiman, S. Anand, E. Reza-Garduno, R. E. Cohen, G. H. McKinley, Lubrication mobility on lubricant-impregnated surfaces. Soft Matter 9, 1772–1780 (2013).

46. B. R. Solomon, S. B. Subramanyam, T. A. Farnham, K. S. Khalil, S. Anand, K. K. Varanasi, Lubricant-impregnated surfaces, in Non-Wettable Surfaces (2016), pp. 285–318.

47. G. W. J. Lee, T. F. Tadros, Formation and stability of emulsions produced by dilution of emulsifiable concentrates. Part I. An investigation of the dispersion on dilution of emulsifiable concentrates containing cationic and non-ionic surfactants. Colloids Surf. 5, 105–115 (1982).

48. J. Feng, X. Zhang, Q. Liu, Z. Zhu, D. J. Mc Clements, S. M. Jafari, Application of nanoemulsions in formulation of pesticides, in Nanoemulsions (Elsevier, 2018), pp. 379–413.

49. L. M. Diamante, T. Lan, Absolute viscosities of vegetable oils at different temperatures and shear rate range of 64.5 to 4835 s−1. J. Food Process. Eng. 2014, 234583 (2014).

50. P. Lebailly, V. Bouchart, I. Baldi, Y. Lecluse, N. Heutte, A. Gislard, J.-P. Malas, Exposure to pesticides in open-field farming in France. Ann. Occup. Hyg. 53, 69–81 (2008).

51. D. Nuyttens, M. De Schampheleire, P. Verboven, D. Dekeyser, D. Dekeyser, Droplet size effect on spray deposition efficiency of citrus leaves. Langmuir 31, 9833–9844 (2015).

52. F. Schellenberger, J. Xie, N. Blanken, M. S. Saleem, C. Antonini, M.-J. Thoraval, Rebound of self-lubricating compound drops. Sci. Adv. 6, eaay3499 (2020).

53. H. Ok, H. Park, W. W. Carr, J. F. Morris, J. Zhu, Particle-laden drop impacting on solid surfaces. J. Dispers. Sci. Technol. 25, 449–456 (2005).

54. Y. Ueda, S. Yokoyama, M. Nomura, R. Tsujiino, M. Iguchi, Bouncing behaviors of suspension liquid drops on a superhydrophobic surface. J. Vis. 13, 281–283 (2010).

55. J. D. Smith, R. Dhiman, S. Anand, E. Reza-Garduno, R. E. Cohen, G. H. McKinley, Lubrication mobility on lubricant-impregnated surfaces. Soft Matter 9, 1772–1780 (2013).

56. B. R. Solomon, S. B. Subramanyam, T. A. Farnham, K. S. Khalil, S. Anand, K. K. Varanasi, Lubricant-impregnated surfaces, in Non-Wettable Surfaces (2016), pp. 285–318.

57. G. W. J. Lee, T. F. Tadros, Formation and stability of emulsions produced by dilution of emulsifiable concentrates. Part I. An investigation of the dispersion on dilution of emulsifiable concentrates containing cationic and non-ionic surfactants. Colloids Surf. 5, 105–115 (1982).

58. J. Feng, X. Zhang, Q. Liu, Z. Zhu, D. J. Mc Clements, S. M. Jafari, Application of nanoemulsions in formulation of pesticides, in Nanoemulsions (Elsevier, 2018), pp. 379–413.

59. L. M. Diamante, T. Lan, Absolute viscosities of vegetable oils at different temperatures and shear rate range of 64.5 to 4835 s−1. J. Food Process. Eng. 2014, 234583 (2014).

60. P. Lebailly, V. Bouchart, I. Baldi, Y. Lecluse, N. Heutte, A. Gislard, J.-P. Malas, Exposure to pesticides in open-field farming in France. Ann. Occup. Hyg. 53, 69–81 (2008).