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The effect of contact angle hysteresis on droplet coalescence and mixing

Michael A. Nilsson, Jonathan P. Rothstein*

Department of Mechanical Engineering, University of Massachusetts Amherst, 160 Governors Drive, Amherst, MA 01003-2210, United States

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ABSTRACT

In this work, droplet coalescence and the subsequent mixing in superhydrophobic surfaces is studied over a range of impact velocities and impact angles. Sanded Teflon surfaces are used as a novel twodimensional microfluidics platform. These superhydrophobic surfaces exhibit a constant advancing contact angle of $\theta_A = 150^\circ$ over a broad range of contact angle hysteresis. As a result, the effect of contact angle hysteresis on droplet coalescence and mixing can be studied. Based on the observed characteristics of coalescence, three different regimes of coalescence are identified as a function of both Weber number and impact angle. These regimes include oscillation dominated, rotation dominated, and mixed dynamics. It is shown that within Weber number ranges achievable in this experiment, hysteresis greatly reduces the deformation of the droplet coalescence process and the subsequent mixing. In head-on collisions, higher hysteresis is found to decrease the frequency at which the resulting dr oscillates. In the case of glancing collisions, where the resulting droplet is found to rotate, higher hysteresis increases the rate of rotation although the overall angular momentum is found to be independent of contact angle hysteresis.

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1. Overview

The study of droplet collisions and subsequent coalescence has generated significant interest and a wealth of research in the past few decades because of its importance in a number of commercial fields including combustion, spray coatings, and more recently microfluidics. The majority of the research has been performed on unconfined droplets collisions in air or other fluids [1–7]. In such experiments and simulations, droplets are not in contact with a solid substrate and the complexity introduced by the presence of a three-phase contact line does not need to be considered.

Four distinct classifications of droplet interactions are typically identified when droplets collide in air: coalescence, bouncing, disruption, and fragmentation [5]. The coalescence regime is defined by full combination of two droplets into one, and typically occurs at lower Weber numbers, $We = \rho V^2 D/\sigma < 20$ for unconfined droplets [2]. Here the Weber number is a ratio of the inertial forces to the surface tension force where ρ is the fluid density, *V* is the velocity of the drop, *D* is the diameter of the droplet, and σ is the surface tension of the fluid. Within the bouncing regime, droplets collide, but coalescence is prohibited by a thin gas lubrication layer. This is primarily seen in hydrocarbon droplet collisions at Weber numbers between 0.5 < *We* < 8.6 [6]. For water droplets, bouncing has only been observed for glancing collisions at high impact numbers

 $(I \ge 0.8)$ and Weber numbers larger than We > 5. The impact number, $I = 2\delta/(D_1 + D_2)$, is a measure of the directness of the collision. Here δ is defined as the normal distance from the trajectory of the center of mass of the colliding drop to the center of mass of the stationary drop, and D_1 and D_2 are the diameters of the two drops. Disruption and fragmentation are two regimes where the droplets separate after initially coalescencing. In disruption, the coalesced droplet separates back into two droplets, typically of similar size. In fragmentation, the coalesced droplet separates more violently, resulting in two or more main drops and many satellite droplets. Both disruption and fragmentation generally occur at Weber numbers greater than We > 20 [6].

Unlike unconfined droplet collisions, there has only been a limited amount of work done on the coalescence of sessile drops where the presence of the contact line plays an important role in the dynamics of droplet coalescence [8-16]. The main fields examined are the coalescence of sessile drops deposited on a substrate either by condensation or by the addition of volume to one drop with the primary focus of these studies being the dynamics of the meniscus bridge during the early timescales of coalescence. For sessile drops, droplet impacts are typically limited to the coalescence regime due to the relatively low Weber numbers that can be achieved. In these low Weber number collisions, surface tension dominates the flow and drop deformations are limited. It is interesting to note that, at these low Weber numbers, condensation-driven droplet coalescence has been observed to result in large-scale dynamics, including in some cases ejection from the surface [9-11]. Unlike the work presented here, the surfaces

^{*} Corresponding author. Fax: +1 413 577 0110.

E-mail addresses: mnilsson@student.umass.edu (M.A. Nilsson), rothstein@ecs. umass.edu (J.P. Rothstein).

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studied in the literature were all hydrophilic [8,12–15]. These drops were driven to coalesce by placing them directly next to each other and deforming the drop very slowly through the addition of water from a syringe [14,15], from a hole in the test surface [12,13], or through continuous condensation from a saturated environment [8-11,14,15]. For partially wetting drops, the dynamics of coalescence from the interaction between the contact line motion with the rise in bridge height caused by negative pressure in the meniscus bridge [3,12,17-21]. A number of recent studies have shown that the initial conditions, presence of capillary waves, and contact line dissipation can all have a significant effect on the dynamics of coalescence. However, it is important to note that none of these studies have investigated the role of contact angle hysteresis. For spherical drops, a weak logarithmic relationship between the rate of spreading of the meniscus bridge after coalescence and the drop diameter has been found [3], while in thin films the relationship has been found to more closely resemble a power-law dependence [17]. In this study, we will use a number of different superhydrophobic surfaces to study the impact of contact angle hysteresis, Weber number, and impact number on droplet coalescence and mixing.

Contact angle hysteresis is defined as the difference between the advancing contact angle, θ_A , and the receding contact angle, θ_R , for a given surface and liquid. Here we will focus on water as the liquid phase. Contact angle hysteresis inhibits the motion of drops along a surface [22], as it can be shown that the critical line force required to start a drop moving over a solid surface is directly proportional to the contact angle hysteresis [23]

$$F_D \propto \sigma D(\cos \theta_R - \cos \theta_A).$$
 (1.1)

Large contact angle hysteresis restricts the motion of droplets, and limits confined collisions to small Weber numbers [24]. With high hysteresis, before a drop can move it must deform and reach the receding contact angle at the rear of the drop and the advancing contact angle at the leading edge of the drop. Therefore, varying the contact angle hysteresis should play a large role in droplet collisions.

There has been some work investigating how contact angle hysteresis affects droplets impacting onto surfaces [25–30]. Many of these studies looked at the dependence of various factors, such as spread diameter, crown height, jet height, and droplet rebound on important dimensionless parameters. They have shown that a droplet hitting a surface with minimal hysteresis can bounce, often producing satellite droplets dependent on the Weber number upon impact. If droplets collide with a surface with a large degree of hysteresis, they can be pinned and the dynamics significantly dampened. This observation highlights how the surface–droplet interaction and specifically the contact angle hysteresis during spreading is of importance to drop motion [27,31].

A surface with little to no contact angle hysteresis and an advancing contact angle greater than 150° is classified as a superhydrophobic surface [32]. There has been much effort in developing these surfaces [33-36]. Superhydrophobic surfaces were originally inspired by the unique water repellency of many plants, most notably the leaves of the lotus [37,38]. In order to achieve superhydrophobicity with synthetic surfaces, two criteria must be met: chemical hydrophobicity and surface roughness. Chemical hydrophobicity alone can only achieve contact angles on the order of $\theta \simeq 120^{\circ}$ [34]. In order to achieve higher contact angles, the surface must have some degree of roughness to it, either precisely patterned or random. In the Cassie state [39], the hydrophobicity of the surface in conjunction with the surface roughness prevents the water from penetrating into the roughness and fully wetting the surface. The result is that a fraction of the water rests not on the surface, but forms an air-water interface. It has been shown that in this state the contact angle hysteresis is a function of the shape and size of the surface roughness [40] with contact angle increasing and hysteresis decreasing as the fraction of the solid in contact with the liquid decreases and the pitch of the surface roughness increases [23]. There is, however, a lower limit on the solid fraction beyond which static pressure can deflect the interface such that it advances into the roughness, fully wetting the surface [22]. This wetting state, which is referred to as the Wenzel state [41], can possess high advancing angles, but typically exhibits high contact angle hysteresis.

With the increasing interest in superhydrophobic surfaces, and the ability to move and direct drops easily on low hysteresis surface, knowledge of drop motion, collisions, and coalescence is critical if these surfaces are to be utilized to their full extent as a possible two-dimensional platform for digital (one drop at a time) microfluidics [42]. It is our hypothesis that for surfaces with very low contact angle hysteresis, the dynamics of droplet collisions will approach those of unbounded droplets, allowing for greatly enhanced dynamics, deformations and mixing.

The mixing of fluids at a micro-scale has been studied extensively in micro-fluidic devices. These devices are enclosed, and make use of many low Reynolds number effects, as well as many different driving mechanisms in order to effect mixing at microscales. An excellent review of this topic is provided in Stone et al. [43] and as such, the review in this paper will be limited to work towards mixing in droplets on digital microfluidic devices. The most recent work on droplet mixing focuses on the mixing of two droplets of water on a surface with varying contact angles and minimal contact angle hysteresis [44]. Because of the lensing effect of the drop, quantifying mixing in a drop is challenging, as at least two undistorted views (top, side) are required to make a quantitative assessment of the mixing [45]. Methods such as micro-PIV, using fluorescent dyes and particles have been used to study mixing in drops [44,46]. These experiments avoided some of the lensing issue by interrogating droplets with low contact angles on transparent cover slips from below using an optical microscope [44,47]. It was shown that based off of the rate of the mean velocity decay, diffusion effects became dominant at long times when the Peclet number became less than $Pe = LV/D_{12} \leq 1$. Here, *L* is a characteristic lengthscale and D_{12} is the diffusion coefficient. Therefore, important convection-based mixing, as would result from coalescence on low hysteresis surfaces, occurs at smaller timescales. They were also able to visualize internal flow fields, and show that the fluid in contact with the surface experiences a drag force, enhancing mixing of droplets in a microfluidic channel. Unlike the previous work in this area, our experiments will focus on the short-time dynamics of mixing on surfaces with varying hysteresis where the Peclet number is large and the flow is dominated by convection.

Our study utilizes a method of surface fabrication that allows for the creation of superhydrophobic surfaces with similar advancing contact angles, but with varying degrees of contact angle hysteresis [35]. This allows us to not only characterize droplet coalescence dynamics, but to also systematically observe the effects of contact angle hysteresis while holding all other parameters fixed.

2. Experimental design setup

The surface preparation for this work is described in detail in Nilsson et al. [35], however for completeness a brief overview of the fabrication process is presented here. Teflon surfaces with a backing treated to accept adhesive and epoxy were used. The Teflon was affixed to an aluminum base as seen in Fig. 1. Teflon was sanded with various grits of sandpaper, resulting in superhydrophobic surfaces (SHS) with high advancing contact angles and



Fig. 1. Sketch of experimental set up. The two water droplets rest on the sanded Teflon surface. The jet of air is provided through the tube to the right. The lights (not shown) would be located in front and behind the set up.

variable hysteresis which depends only on the grit size of the sandpaper chosen. The SHS were then placed on a precisely leveled surface attached to a vibration-reducing optical table. This was critical because droplets on low hysteresis surfaces can move with even the smallest perturbations. All of the surfaces had an advancing contact angle of 150°, but a variable hysteresis making it possible to explicitly investigate the effect of hysteresis on droplet coalescence. The surfaces used in this study had a hysteresis of 3° which corresponds to Teflon sanded with 240 grit-designation sandpaper; a hysteresis of 15° which corresponds to Teflon sanded with 120 grit-designation sandpaper, and a hysteresis of 30° which corresponds to Teflon sanded with 320 grit-designation sandpaper.

In order to facilitate drop movement, pressurized air was used to impart momentum onto a single moving drop while keeping the second drop stationary. The drops were initially separated by 18 mm allowing for the moving drop to develop a steady velocity and minimizing the impact of the pressurized air on the stationary drop. The pressure of the air used to propel the drop varied, but was varied between 13 and 34 kPa. A cowl with inner diameter of about 3 mm was attached to the end of the tube which aided in dissipating the direct jet of air formed in the tube and reduced the likelihood of atomization of the drops and minimized the amplitude of capillary waves the surface of the moving drop. A sketch of the set up is shown in Fig. 1.

In order to view the collision from multiple angles simultaneously, a pentaprism was mounted just above the drops to make both the side and top view visible. The collision and subsequent coalescence were captured using a Phantom v4.2 high-speed camera with a resolution of 384×512 at a frame rate of 2900 frames per second, outfitted with a Mitutoyo compact lens and illuminated by high power lamps. The high-speed video was broken out into a series of individual images so that important measurements could be made. ImageJ[™] was used to measure pre-collision quantities such as the initial droplet diameters, droplet velocities, and the impact factor from the offset in the droplet centers just before impact. A number of additional measurements were made after the collision. These include the deformation of the coalesced drop in both the collision direction the in-plane direction normal to the collision as well as the rotation rate of the coalesced drop for indirect impacts. In this work, we report a maximum deformation only after the two drops become indistinguishable in the final coalesced drop.

In order to quantify mixing, particles (11 μ m diameter hollow glass spheres from Spherical) were used to seed the moving drop and illuminated by a Northstar 250 W lamp. The diffusion time of the particles to travel through the drops is many orders of magnitude larger than our window of observation, so any particle motion observed (order μ s) is dominated by convection as the resulting Peclet number is very large. This is similar to prior work [44], with the exception that in this study the droplet collisions occur at much higher Weber numbers on opaque surface with much larger advancing and receding contact angles. As such, the camera cannot observe the internal flow from below, and the surface tension-driven dynamics resulting from coalescence cause a very uneven and quick-changing drop surface. Coupled with the lensing effect of the droplet surface, this leads to a difficulty in precisely knowing the location of the observed particles within the drops. As a result, the data in the following section that show enhanced mixing on low-hysteresis surfaces should be considered qualitative.

3. Results and discussion

The range of Weber numbers observed in this study were generally limited to between $0 \le We \le 6$. There were some higher Weber number collisions observed over the course of this study, however, in the case with surfaces of higher contact angles, these usually were characterized by the impacting drop being airborne before impact as a consequence of the large lift forces exerted by our air propulsion system. The other reason for the low Weber number range is that higher Weber numbers usually led to the coalesced droplets quickly leaving the field of view of the high speed camera which prevented the complete measurement of the impact dynamics. Both of these factors lead to an upper limit in Weber number. Furthermore, it is important to note the maximum achievable Weber number decreased strongly as hysteresis increases. This is primarily due to the fact that with higher contact angle hysteresis, a larger driving force is required to induce droplet motion, as seen in Eq. (1.1). Although these Weber numbers are rather small compared to unconfined collisions, it should be noted that the Weber number limit we observed is much higher than Weber numbers in other sessile drop studies previously discussed, which were typically much less than We < 1 [8–10,12–15,19].

Three general regimes of droplet coalescence were observed in this study. A phase diagram is presented in Fig. 3 which presents the general delineation of each regime as a function of Weber number and impact number for a surface with a contact angle hysteresis of 3° . The first regime is characterized by an oscillation-dominant drop motion following droplet coalescence. This typically occurs at low impact numbers, head-on collisions, and is characterized by the droplet oscillation alternating between elongations in the *x*- and *y*-directions. An example of an oscillation droplet collision is shown in Fig. 2a. Each image sequence in Fig. 2 represents a droplet coalescence progression with similar Weber

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(a) 3° t=17.9 t=0 t=1 4.5 t=6.9 15° -5 9 t=7.9 t=18.3 30° t=7.2 t=15.9 [] (b) 3° t=16.6 t=2.4 t=7.2 t=9. 15° t=17.9 t=25.2 t=2.1 t=8.6 30° t=20.0 t=15.5 =4.8 t=0 t = 10.7No. 12 =

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Fig. 2. A sequence of images following droplet collisions for surfaces with hysteresis increasing from top to bottom and (a) Weber numbers of approximately $We \simeq 4.3$ and low impact numbers of approximately $I \simeq 0.05$ and (b) Weber numbers of approximately $We \simeq 5$ and high impact numbers of approximately $I \simeq 0.8$. Time increases from left to right in milliseconds.



Fig. 3. Impact number as a function of Weber number highlighting the different regimes of sessile drop coalescence on a Teflon surface with (a) 3° contact angle hysteresis and (b) 30° contact angle hysteresis. Here, \blacksquare represents oscillation dominant collisions, \blacktriangle represents rotation dominant collisions, and \bullet represents collisions exhibiting both oscillation and rotation. The dashed lines serve to illustrate the boundaries of these regimes, and are intended only to guide the eye.

numbers and impact numbers, but with varying hysteresis. The time in milliseconds is also displayed, with t = 0.0 ms occurred just prior to the coalescence, and shown as the top image in each sequence. The images were chosen to reflect similar instances of each part of the oscillation process. In each image, the side view is on the bottom half of each image, and the top view is the upper half of each image. The top view is where the oscillation in the surface plane is most visible. Analysis of the frequency of oscillation as a function of contact angle hysteresis will be presented later.

The second main mode of collisions is characterized not by oscillations, but by rotation of the droplets after coalescence. This regime occurs at high impact numbers following an indirect or glancing collision of the drops. The rotation is a result of the large amount of angular momentum transferred from the impacting drop to the stationary drop. This mode has been seen for unconstrained droplet collisions in air [6]. Rotation is not observed for more direct collisions dominated by droplet oscillations. An example of rotation dominated dynamics is represented in Fig. 2b. The images show the progression of the drop coalescence dominated by rotation. From the images, it is apparent that droplets on the 15° hysteresis surface takes longer to achieve the same state of deformation than on the lowest 3° hysteresis surface. Interestingly, droplets on the highest 30° hysteresis surface proceed through their coalescence more quickly. As seen in Fig. 3, this mode is typically present only for impact numbers greater than I > 0.5 and Weber numbers greater than We > 1. This lower Weber number and lower impact number limit, which has been observed in freely coalescing drops, remains present as hysteresis increases, but shifts to lower Weber numbers and impact numbers. This demonstrates that the rotation of these droplets is strongly retarded as the hysteresis is increased. Another interesting observation is that even at high Weber numbers We > 7, our droplets were found to fully coalesce. This contrasts with the observations of droplet coalescence in air in the same Weber number range where droplets do not coalesce, but instead bounce off of each other [6].

The third type of collisions is a combination of both the rotation and oscillation regimes. As such, it possesses characteristics from both the oscillation dominant and rotation dominant regimes. In this regime the oscillations are observed to rotate about the new center of mass of the coalesced drop rather than maintaining oscillations in the x-y plane. This regime is encountered predominantly in the middle range of impact numbers, anywhere from $0.2 \leq I \leq 0.6$. This range, however, has a strong Weber number dependence. At low Weber numbers, We < 1, this regime stretches from about 0.5 to 1.0. There is a transition regime for Weber numbers between $1 \leq We \leq 3$, and at the largest Weber numbers tested, this regime settles into the impact number range of $0.2 \le I \le 0.6$. Finally, we observe that as the contact angle hysteresis increases, the width of the mixed-dynamic coalescence narrows, and the rotation regime at higher Weber numbers extends to a range between 0.35 < I < 1.0 as seen in Fig. 3b.

In Fig. 4, the maximum deformation of the drops after coalescence is plotted in the form of three-dimensional plots with Weber number on the *x*-axis, impact number on the *y*-axis, and the maximum deformation on the *z*-axis. In Fig. 4, the maximum deformation in the x-y plane is normalized by dividing it by the diameter of the impacting drop. In addition to the individual data points, a splined surface is superimposed over the data to help guide the eye and illustrate trends.

A number of qualitative observations about the role hysteresis on drop deformation following coalescence can be made in Fig. 4. An increase is observed in the maximum deformation with increasing Weber number. This is expected, as there is an increase in kinetic energy in the colliding drops. Additionally, this is a trend that has been observed many times in the past for airborne collisions [6]. Higher levels of deformation are observed at both low and high impact numbers than at middle impact numbers. At high and low impact numbers, the kinetic energy is transferred into a single mode of motion, either rotation or oscillation. In the middle regime of impact numbers, energy is transferred into both rotation and oscillation and the resulting deformation in each mode is not always additive resulting in reduced deformation induced by this more complex drop motion.

One general observation that can be made from the images in Fig. 2 and the data in Fig. 4 is that as the hysteresis increases, the overall magnitude of the droplet deformation decreases. In the case of the lowest hysteresis, a maximum deformation nearing three times the original drop diameter is achieved at large Weber and impact numbers. As the hysteresis increases, the droplet deformation following collisions consistently decreases. In the case of the highest hysteresis tested, the maximum deformations are slightly under two times the original droplet diameter. Note that for two drops of equal volume coalescing on a surface with a contact angle of $\theta_A = 150^\circ$, the final steady-state diameter of the coalesced drop should be approximately 1.4 times larger than the original diameter. Thus for high hysteresis, little real deformation is observed during the droplet coalescence. Additionally, these higher hysteresis cases have less overall variation in the deformation with varying Weber and impact numbers than in the lower hysteresis cases. The deformation surface shown in Fig. 4 for the 30° hysteresis case is essentially flat with only variation in the data provided by fluctuations in the data. When compared to the 3° hysteresis surface, the effect of increasing hysteresis is most obvious at high impact numbers where hysteresis is found to limit drop rotation and the resulting deformation.

For a more quantitative analysis, a statistical analysis was performed on the data by averaging the data over narrow windows in both impact numbers and Weber numbers. The results of this analysis are presented for a number of cases in Figs. 5 and 6. This averaging serves to more clearly illustrate the effect that contact angle hysteresis has on the droplet dynamics following coalescence. Each point in Fig. 5 represent a minimum of two data points to a maximum four data points, sorted by either impact number or Weber number as is appropriate. Fig. 5 is the collected data sorted into two impact number regimes dominated by oscillation and rotation to illustrate the effect of changing Weber number.

At higher Weber numbers the effects of hysteresis become most noticeable. For the lower (0.0 < I < 0.3) range of impact numbers shown in Fig. 5, there is less variation in deformation and similar trends across all Weber numbers and contact angle hysteresis. In all cases, little deformation is observed until a Weber number of We > 2.0 is exceeded. At the high impact numbers (0.6 < I < 1.0), the deformation of the lower hysteresis surfaces continues to increase with increasing Weber number; however, the deformation of the highest hysteresis studied remains unchanged and perhaps even decrease slightly at the highest Weber numbers investigated. These observations further illustrate that the contact angle hysteresis has the largest impact on the dynamics of the rotation dominated coalescence.

In Fig. 6, the data for Weber numbers greater than We > 4 is presented as a function of impact number. As seen in the three-dimensional plots at both low and high impact numbers, there is significantly higher deformation than at the middle impact numbers. Furthermore, as the hysteresis is increased at the higher and lower impact numbers, the impact of hysteresis on drop deformation becomes clear. Unlike the low hysteresis cases, the 30° hysteresis case results in lower deformation at all impact numbers. For the two low-hysteresis cases, a minimum is observed around an impact number of $I \sim 0.5$ and a large increase is observed as the impact number approaches $I \cong 1.0$. For the high hysteresis surface, the rotational motion is greatly suppressed and the maximum



Fig. 4. (a-c) Three dimensional plots showing the maximum deformation as a function of both Weber number and impact number. The amount of contact angle hysteresis in each case is (a) 3°, (b) 15°, and (c) 30°.



Fig. 5. Plots of maximum droplet deformation as a function Weber Number for impact number ranges from (a) 0.0 < *I* < 0.3 and (b) 0.6 < *I* < 1.0. In each graph, the 3° hysteresis results are represented by ■ connected by a solid line, the 15° hysteresis case is represented by ● connected by a dashed line, and the 30° hysteresis case is represented by the ▼ connected by a dotted line.



Fig. 6. Plots of maximum droplet deformation as a function of impact number at a large Weber number greater than $We \ge 4$. The results from the 3° hysteresis surface are represented by \blacksquare connected by a solid line, the 15° hysteresis surface is represented by \blacklozenge connected by a dashed line, and the 30° hysteresis surface is represented by \lor connected by a dotted line.

deformation is found to decrease monotonically with increasing impact number.

Hysteresis can have an effect on both droplet deformation and the dynamics of coalescence. One area in which the effects of hysteresis are prominent is on the oscillation frequency of coalesced drops following low impact number collisions and the angular velocity of the coalesced drops following high impact number collisions. Here we examine collisions from higher Weber numbers because the greatest affect of the hysteresis can be seen in this range. In Fig. 7a, the frequency of oscillation of the low impact number collisions $I = 0.06 \pm 0.02$ is plotted as a function of contact angle hysteresis. As hysteresis increases, the frequency of the drop oscillations decreases for head-on collisions. It is possible to compare the rates of oscillation to work of Rayleigh [48], who showed that the natural frequency of a free droplet is $f_R = \frac{1}{2\pi} \sqrt{\frac{8\sigma}{\rho R^3}} = 94$ Hz where *R* is the droplet radius *z* is the configuration of the second se where *R* is the droplet radius, σ is the surface tension, and ρ is the density of the liquid. This natural frequency neglects the effect of the surrounding gases, droplet viscosity, and any second-order effects, all of which are known to reduce the natural frequency. If the

presence of a surface is added, the frequency is greatly affected. Smithwick and Boulet [49] showed that the natural frequency for a drop on a surface with a pinned contact line goes as $f_N = \frac{1}{2\pi} \sqrt{\frac{\sigma}{\rho R^3 \lambda_n}}$ where λ_n are the eigenvalues of each mode and are dependent on the contact angle [49]. For a contact angle of $\theta = 150^\circ$, the natural frequency of the second mode of vibration is $f_2 = 44$ Hz [50]. This value is significantly smaller (40%) than the predictions for a free drop. As seen in Fig. 7a, the effect of the surface for the 30° contact angle hysteresis case results in an oscillation frequency that compares well with the predictions of theory [49,50]. As hysteresis decreases, the natural frequency is found to increase, moving away from the result for a pinned contact line and towards the predictions of McHale et al. [50] for a sessile drop with a fully mobile contact line $f_{MCL} = 138$ Hz.

In Fig. 7b, the rotation rate of a series of coalesced drops at varying impact number and a Weber number of $We \approx 4$ are presented. The rate of rotation is found to decrease from 3° to 15°, but then increase at 30° to a rate higher than the lowest hysteresis case. This observation can be explained if one considers not the angular velocity, but the angular momentum of the rotating drops. Assuming the final shape of the coalesced drops is ellipsoidal; the angular momentum of the rotating drops and minor axis. For the case of the highest hysteresis, although the angular velocity is large the droplets deformation is significantly smaller than the drops on lower hysteresis surfaces. This limits the moment of inertia of the drop, and as a result the drop rotates faster while maintaining approximately the same angular momentum in all three cases.

Finally, a preliminary investigation into the mixing occurring within the drop was performed. Shown in Fig. 8 is a comparison of images two droplet coalescence sequences, with the top sequence representing a surface with contact angle hysteresis of 3°, and the bottom sequence of a surface with 50° contact angle hysteresis. Both collisions were of low Weber number, $We \leq 0.15$, and low impact numbers $I \leq 0.04$. As one can see, the particles move about the low hysteresis coalesced drop more violently following paths that efficiently stretch and fold fluid elements from the two droplets together, reducing the distance fluid needs to diffuse and fully mix. With the higher hysteresis, the footprint of the drop changes only slightly on coalescence and as a result the mixing is confined to the area where the meniscus bridge is formed, reducing the overall magnitude of the internal flow of the drop. With lower hysteresis, there is larger undulations of the drop, as it behaves



Fig. 7. Oscillation frequency and angular velocity of coalescing drops as a function of contact angle hysteresis. All cases take place at Weber numbers of approximately We = 4. In (a) the oscillation frequency of low impact number ($We = 4.3 \pm 0.1$, $I = 0.06 \pm 0.02$) cases are represented by \blacksquare . The dashed line represents the theoretical predictions for the natural frequency of a sessile drop with a pinned contact line. In (b) the angular velocity and angular momentum of the middle impact number cases ($We = 5.1 \pm 0.3$, $I = 0.33 \pm 0.02$) are represented by \blacksquare . The open symbols represent the angular momentum corresponding to each case.



Fig. 8. Images demonstrating enhanced mixing for two drops on surfaces with different contact angle hysteresis. The top surface possesses 3° contact angle hysteresis with water, and the bottom surface possesses 50° contact angle hysteresis with water. In both cases, a particle-laden drop is collided with an unseeded drop and shown just prior

more akin to a freely suspended droplet collision, instead of one bounded by a surface. Additionally, the surface serves to reflect much of the capillary waves that occur, adding to the greater amount of mixing. It is clear from the images in Fig. 8 that after mixing for only t = 50 ms the drop on the low contact angle hysteresis surface is nearing complete mixing while the drop on the high hysteresis surface remains essentially unmixed. This acceleration in mixing far outpaces diffusive effects which for these drops results in a fully mixed droplet is many orders of magnitudes larger than the observation timescale. These observations were consistent for a number of other Weber numbers and impact number cases studied.

to impact and 50 ms following impact.

This qualitative result is further supported by Fig. 9, which plots the degree of mixing as a function of time for the two drops shown in Fig. 8. The degree of mixing is calculated as $\Phi = (\sigma_0 - \sigma)/\sigma_0$. Here, σ_0 is the initial standard deviation of the image at t = 0, and σ is the standard deviation. For a perfectly unmixed sample of binary particles/fluorescent fluid, it would result that $\sigma_0 = 0.5$, and $\Phi = 0$, where a value of $\Phi = 1$ would represent fully mixed. In this case, the images contain both white particles and non-white regions, and regions of intensity anywhere between which result from uneven lighting, shadows, and lensing effects. The mixing is calculated by a Matlab code that first thresholds the image so that only the drops are considered, and the background surface as well as bright reflections from the uneven lighting are ignored. The standard deviation $\sigma = \sqrt{\langle (D - \langle D \rangle)^2 \rangle}$, measures the intensity of the image using the density of distribution, D, as calculated by the method of Stone and Stone [51].

The results presented in Fig. 9 show that on low hysteresis surfaces. The mixing rate following coalescence is significantly larger



Fig. 9. Degree of mixing as a function of time for surfaces with varying contact angle hysteresis. The mixing on a surface possessing 3° contact angle hysteresis is represented by \blacksquare while the surface possessing 50° contact angle hysteresis is represented by \blacktriangle .

than that observed for surfaces with higher hysteresis. The degree of mixing for both high and low hysteresis cases increases very quickly after coalescence. However, the droplet dynamics and motion on the high hysteresis surface ceases very soon after coalescence with the majority of motion occurring in a small band located along the meniscus bridge, as has been observed in the past. As a result, the mixing in drops on the high hysteresis surface saturates very quickly and remains roughly constant at Φ = 0.35 at the end of the experiment as convection decays away and the drop continues to mix, but by diffusion of the seed particles alone. For the case of the low hysteresis surface, the dynamics persist for much longer and are of significantly larger amplitude (as seen in the previous section) resulting in faster and more significant mixing that continues to increase beyond $\Phi = 0.7$ as the experiment progresses past t = 50 ms. The trends observed in the qualitative results are consistent for a broad range of Weber numbers and impact numbers studied.

4. Conclusions

In this paper, the effect of contact angle hysteresis on the dynamics of the coalescence of sessile drops was studied. Three superhydrophobic surfaces were examined having the same advancing contact angle of $\theta_A \simeq 150^\circ$ and varied contact angle hysteresis values of 3°, 15°, 30°, and 50°. A range of Weber numbers from $0 \le We \le 12$ and impact numbers between $0.0 \le I \le 1.0$ were studied. Within the coalescence regime, we characterize three distinct modes: oscillation, rotation, and a blend between the two. The impact and eventual coalescence of each drop was observed to fall within one of these regimes based on the Weber number, the impact number, and the contact angle hysteresis of the superhydrophobic surface. At low contact angle hysteresis, the drop deformation and dynamics are especially violent with large oscillations observed in head-on collisions and large deformations and high rotation rates observed at large impact numbers. The low contact angle hysteresis surfaces result in droplet collisions similar to those observed in air and thus the influence of the surface is small. Its presence does, however, limit the Weber numbers that can be achieved for a sessile drop and regimes of bouncing, disruption, and fragmentation were not observed even on the low contact angle hysteresis surface because of this limitation. The frequency of oscillation for all surfaces tested were all found to be slightly above the predictions for a sessile drop with a fully-pinned contact line, with the largest deviation from theory being observed for the low contact angle hysteresis surfaces. These drops approached the predictions for sessile drops with fully mobile contact line.

With increasing contact angle hysteresis, the droplet deformation following coalescence decreases, to the point that for the highest hysteresis studied, the maximum deformations are only marginally above the expected analytical radius of two drops coalesced. In these cases, the dynamics of impact observed to remain localized primarily to the meniscus bridge formed between the two drops upon contact. Interestingly, for glancing collision with very high impact numbers, the angular velocity increased with increasing contact angle hysteresis. This was found to result in the reduced deformation in the drop, as in all cases angular momentum was conserved. Each of these observations become more intensified with increasing Weber number. Finally, while numerical studies are likely needed to accurately quantify the mixing benefits of coalescence on low contact angle hysteresis surfaces, experimental collisions on a low contact angle hysteresis surface were found to significantly increase the rate and degree of mixing over collisions of similar Weber and impact number on surfaces with high contact angle hysteresis.

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