Entry of a sphere into a water-surfactant mixture and the effect of a bubble layer

Department of Mechanical and Aerospace Engineering, Utah State University, Logan, UT, 84322-4130, USA

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A rigid sphere entering a liquid bath does not always produce an entrained air cavity. Previous experimental work shows that cavity formation, or the lack thereof, is governed by fluid properties, wetting properties of the sphere and impact velocity. In this study, wetting steel spheres are dropped into a water-surfactant mixture with and without passing through a bubble layer first. Surprisingly, in the case of a water-surfactant mixture without a bubble layer, the critical velocity for cavity formation becomes radius dependent. This occurs due to dynamic surface tension effects, with the local surface tension in the splash increasing during surface expansion and decreasing as surfactant molecules adsorb to the newly formed interface. The larger sphere radii take longer to submerge and hence allow more time for the surface tension to decrease back to the equilibrium value and decrease the critical velocity for cavity formation. When a soap bubble layer is present subsurface cavities form at all impact velocities. Our analysis shows that the bubble layer wets the sphere prior to impact with a patchy coating of droplets and bubbles. The droplets alter the splash and create an aperture for air entrainment which leads to cavity formation at wetted locations on the sphere surface. The water-surfactant entry behavior of these partially wetted spheres results in a progression of cavity formation regimes with increasing Weber number, similar to the cavity regimes of hydrophobic spheres entering water. Nonuniform droplet coatings create cavity asymmetries altering transitions between these regimes.

I. INTRODUCTION

When a rigid sphere impacts a liquid surface with sufficient velocity it creates a splash crown and an air-filled subsurface cavity. At low impact velocities, the splash crown adheres to the sphere, climbs up its surface and meets itself at the apex, suppressing cavity formation. Duez et al. showed that the behavior of the splash and consequently the presence or absence of a subsurface cavity for a smooth sphere depends on liquid surface tension ($\sigma$), viscosity ($\mu$), static wetting angle ($\theta$) and sphere impact velocity ($U$). For hydrophilic or wetting spheres ($\theta < 90^\circ$) cavities form when the impact occurs above a constant critical velocity, $U_{cr}$. For hydrophobic or non-wetting spheres ($\theta > 90^\circ$), the value of $U_{cr}$ decreases with increasing $\theta$. Zhao et al. expanded this work by showing that cavity formation also depends on sphere roughness $R_z$ with the critical velocity for cavity formation decreasing with increasing roughness.

Aristoff & Bush investigated cavities formed by small non-wetting spheres, identifying four distinct cavity types named quasi-static, shallow, deep and surface seal cavities. Spheres that are half wetting and half non-wetting produce asymmetric cavities and curved trajectories beneath the free-surface as shown by Truscott & Techet and Bodily et al. for slender torpedo-like bodies. Although the wettability of an object is important to water entry behavior, one might wonder what will happen if an object is partially wetted before entry. Cavity formation characteristics in surfactant mixtures, pools covered with a bubble layer or partially pre-wetted projectiles have not been addressed previously.

Herein, we first examine the effect of a surfactant on the critical velocity necessary for a sphere to form a cavity during free-surface entry. Second, bubbles commonly form in surfactant mixtures, and observations show that spheres that pass through a bubble layer before free-surface entry create cavities at lower impact velocities than anticipated. Hence, we examine the principle mechanism by which bubbles cause these unanticipated cavities (i.e., partial wetting). We then report on the cavity formation types.

II. EXPERIMENTAL SETUP

A schematic of the experimental setup is represented in Fig. 1. Experiments were performed with smooth ($R_z = 0.6 \pm 0.3 \, \mu m$) stainless steel spheres ($\rho_S = 7750 \, \text{kg/m}^3$) with radii $R_s = 1.59-12.70 \pm 0.0025 \, \text{mm}$. Spheres were dropped into a glass
Fig. 1. (a) Stainless steel spheres of radius $R_s$ and density $\rho_s$ were dropped from an electromagnet into a glass tank, impacting the liquid surface with velocity $U$. The tank was filled with a water-surfactant mixture having density $\rho$, viscosity $\mu$ and surface tension $\sigma$. For some experiments the water-surfactant mixture was covered with a bubble layer of height $h_B$ composed of average bubble diameters $d_b$.

The glass tank was filled with a water-surfactant mixture made with Ajax dish soap (189 parts water to 1 part soap, by volume). Ajax dish soap is composed of several different chemicals, four of which act as surfactants to decrease the surface tension: ammonium lauryl sulfate, ammonium laureth sulfate, lauramidopropylamine oxide and poloxamer 124. The water-surfactant mixture was characterized by the following physical properties: density $\rho_l = 999 \text{ kg/m}^3$, viscosity $\mu = 1.09 \pm 0.01 \times 10^{-3} \text{ Pa}\cdot\text{s}$, equilibrium surface tension $\sigma_e = 27.3 \pm 0.2 \text{ mN/m}$, and stainless steel advancing static contact angle $\theta = 30^\circ \pm 4^\circ$. Experimental work with the surfactant mixture was not performed for more than three days. Liquid properties ($\mu$, $\sigma_e$ & $\theta$) were measured with each new water-surfactant mixture, with 95% confidence of the mean values listed above. Surface bubble layers were created for heights $h_B$ ranging 5-100 mm which comprised of bubble diameters $d_B$ in the range of 1-20 mm.

III. RESULTS

Figure 2 displays images of smooth, wetting spheres impacting the water-surfactant mixture at various impact conditions. In (a) a sphere with radius $R_s = 4.76 \text{ mm}$ impacts the pool with a velocity of $U = 5.42 \text{ m/s}$ without forming a cavity. This impact velocity is much higher than the critical velocity for cavity formation for the equilibrium water-surfactant mixture as predicted by Duez et al.$^2$ ($U_{cr} = 0.1\sigma_e/\mu \approx 2.5 \text{ m/s}$). In (b) a larger sphere ($R_s = 11.11 \text{ mm}$) impacts at the same velocity forming a cavity. Hence, we see that the critical velocity for cavity formation is dependent on $R_s$ in a water-surfactant mixture. In (c) a sphere with radius $R_s = 4.76 \text{ mm}$ impacts the pool at $U = 2.43 \text{ m/s}$ without forming a cavity, but in (d) a sphere with the same radius and velocity forms a cavity after first passing through a bubble layer resting on the pool surface.

We first examine the effect of surfactant on the critical velocity for cavity formation $U_{cr}$ for a clean free-surface (no bubbles). As shown in Fig. 3(a), cavity formation in the water-surfactant mixture does not occur at a constant $U_{cr}$. Rather, as shown in (b), $U_{cr}$ varies with $R_s$, where $U_{cr}$ is approximately equal to the critical velocity in pure water for small $R_s$ and decreases towards the predicted critical velocity$^3$ of the equilibrium surfactant mixture as $R_s$ increases. Hence, $U_{cr}$ for a water surface mixture lies between the Duez prediction for water and a water-surfactant mixture.

To explain the dependence of $U_{cr}$ on $R_s$ we examine the influence of dynamic surface tension $\sigma_d(t)$. Upon sphere impact a splash crown forms, which locally increases the surface area of the pool. When the surface expands the surface density of the surfactant decreases, which increases the local surface tension above the equilibrium value $\sigma_e$. At this point, the surface tension of the newly formed surface begins to decrease back towards $\sigma_e$ as surfactant molecules adsorb to the newly formed surface.$^3$ The time required for the dynamic surface tension $\sigma_d(t)$ to decrease from the value of water $\sigma_w$ to $\sigma_e$ will
be denoted as \( t_o \) and is estimated using the pendant bubble technique\(^{12}\) described in Appendix A. Using this technique we found \( t_o \) to decrease as the initial expansion velocity of the bubble (local advection) increases, similar to the findings of He et al.\(^{11}\), Moorkanikkara and Blankschtein\(^{13}\), and Alvarez et al.\(^{14}\). The full surface tension drop time for the given water-surfactant mixture can be approximated by \( t_o = (\sigma_w - \sigma_e)/m \), where \( m \) is the rate at which the surface tension decreases, and is described by the fit \( m = aU^b \), where \( a = 1.42, b = 0.49 \) (see Appendix A for more details). Using these equations we estimate \( t_o \) using the two critical velocities shown in Fig. 4 (2.5 and 6.7 m/s) and find \( t_o \approx 13 - 20 \) ms.

We now compare \( R_s/U \) to the duration of the splash formation, calculated here as half the submergence time \( R_s/U \), to estimate the dynamic surface tension in the splash and approximate \( U_{cr} \) for the water-surfactant mixture. Using the transition data in Fig. 3(b) we see that \( R_s/U < t_o \) and \( \sigma_d(t) \) does not have sufficient time to reach equilibrium, but rather decreases to a value between \( \sigma_w \) and \( \sigma_e \). Therefore, at a certain impact velocity, \( U \), a larger sphere takes longer to submerge than a small one, and thus has more time for surfactant molecules to adsorb to the newly formed surface decreasing the surface tension and consequently \( U_{cr} \) as shown in the Fig. 3(b). Quantitatively, if we assume the drop in the surface tension from \( \sigma_w \) to \( \sigma_e \) is linear with time (Appendix A) we can write the following equation to estimate the dynamic surface tension at the time the sphere is half submerged, \( \sigma_d(R_s/U) \):

\[
\frac{\sigma_w - \sigma_d(R_s/U)}{R_s/U} = m. \tag{1}
\]

Solving for \( \sigma_d(R_s/U) \) we substitute this into the equation found by Duez et al.\(^4\) for the critical velocity \( (U_{cr} = 0.1\sigma/\mu) \) and obtain

\[
U_{cr} = \frac{0.1}{\mu} \left( \sigma_w - mR_s \right). \tag{2}
\]

Using the fit for \( m \) and noting that transition occurs when \( U_{cr} = U \) we rearrange to find an approximation for \( U_{cr} \) in the water-surfactant mixture described by

\[
R_s = \frac{1}{a} U_{cr}^{1-b}(\sigma_w - 10\mu U_{cr}). \tag{3}
\]

Eq. (3) is plotted in Fig. 3(b) and although it does not divide the cavity and no cavity regions very well, it does show the dependence of \( U_{cr} \) on \( R_s \) and divides the partial cavity and full cavity regimes. In order to improve the prediction of \( U_{cr} \) a better method of measuring the dynamic surface tension for large impact velocities (high advection rates) and similar geometry\(^1\) is required. To our knowledge such a method has not yet been developed, and hence we leave an improved prediction of the critical velocity in a water surfactant mixture for future research.

As the entry event transitions from non-cavity forming (Fig. 3(c)) to cavity forming cases (Fig. 3(f)), an intermediate stage is seen in which two types of partial cavities form, similar to the observations of Marston et al.\(^{12}\) in the water entry of Leidenfrost spheres. The first occurs when cavity formation initiates only at small localized sections of the sphere leading to a rapid pinch-off and a small asymmetric air pocket as seen in Fig. 3(d). The second generally occurs for larger sphere radii when the splash moves up the sphere sides in a nonuniform manner leading to an asymmetric closure at the sphere apex and a passage for a small amount of air to be entrained under the surface (Fig. 3(e)).
FIG. 3. (a) The critical velocity for cavity formation by spheres impacting onto a water-surfactant mixture for both a clean pool surface (no bubbles) and with a bubble layer resting on the surface is shown. Cavities form at all impact velocities when spheres first pass through a bubble layer. All the spheres are made of the same steel with static contact angle \( \theta = 30^\circ \pm 4^\circ \), but the data is spread between \( 26^\circ < \theta < 34^\circ \) for readability. (b) The critical velocity for cavity formation on a clean pool surface decreases as the sphere radius increases. At low impact velocities on a clean surface, spheres do not form cavities as shown in (c) although small bubbles may be pulled under the surface. A transitional region is seen in which small asymmetric air pockets (d) and small cavities (e) form, which we call partial cavities. At the highest velocities full cavities form (f). Theoretical estimates for \( U_{cr} \) for water (...) and the water-surfactant mixture (---) are based on Duez et al. The solid-black line represents (3) and only appears in (b). The uncertainty bands show the 95% confidence interval on the mean impact velocities.

When a bubble layer rests on the pool surface, cavities form at all impact velocities tested (Fig. 3(a)), regardless of varying \( h_B \) and \( d_B \). To investigate why the presence of a bubble layer leads to cavity formation we dropped a sphere through a bubble-filled tube and examined it while exiting into the air as shown in Fig. 4. As the sphere passes through the bubble layer, ruptured soap films adhere to the sphere forming small droplets and bubbles. The bubble layer thus partially wets the sphere prior to the free surface impact resulting in cavity formation.

To examine the mechanism by which small droplets on the sphere surface initiate cavity formation we place a single droplet of miscible red dye (food coloring, \( \mu = 2.50 \times 10^{-3} \) Pa.s, \( \sigma = 55.5 \) mN/m, and \( \theta = 80^\circ \pm 2^\circ \)) near the equator of a clean sphere before dropping it into tap water. Two separate impact events were recorded from top and side views (Fig. 5(a) & (b)) and aligned from the time of impact \( t = 0 \). When the sphere is approximately half submerged \( t = 1 \) ms, the dye droplet impacts the pool causing it to deform into a thin sheet, extending upward into the splash and initiating cavity formation (Fig. 5(c)). As the droplet deforms it pushes water away from the sphere near the equator in a manner reminiscent of non-wetting coatings. While water advances up the un-wetted portion of the sphere, the detachment created by the dye droplet results in a splash and a means for air entrainment, leading to cavity formation in the droplet vicinity. This localized cavity formation results in an asymmetric cavity that resembles those created by the water entry of half-wetting sphere and produces lateral motion. As the sphere descends further into the liquid, the droplet of dye continues to coat the cavity wall and deflect water away from the sphere \( t = 2 - 3 \) ms. The contact line, initially existing on only one sphere side, expands upward to un-wet the sphere as it moves towards the apex and down the other side; the cavity expands and effectively shifts contact from the upper-left side of the sphere (Fig. 5(b)) to the trailing side \( t = 2 - 5 \) ms. A similar sequence of events is observed when a sphere falls through a bubble-filled tube followed by an air gap before impacting a clean pool surface (as seen in Fig. 4).

The cavity formed by placing a droplet of dye on a clean sphere initially resembles that formed by a single droplet impact. When a single droplet impacts a pool it spreads out on the surface, pushing the fluid both downward and outward with the droplet liquid spreading over the surface of the newly formed cavity. The initial impact of a liquid jet on a pool behaves in the same way. The combination of
the two impact types (solid-liquid and liquid-liquid) causes wetting spheres to form cavities similar to those formed by non-wetting or rough spheres.

A similarity between non-wetting spheres and wetting spheres that pass through a bubble layer prior to impact is noted in the cavity types observed in Fig. 6. For the lowest We values, pinch-off occurs on or very near the sphere surface which is described as quasi-static seal (Fig. 6(a)). As the Weber number reaches We ≈ 800, 400 and 2,300, for Bo = 0.91, 8.2 and 58 respectively a larger cavity forms a shallow seal (Fig. 6(b)). When We ≈ 6,000 for Bo = 58, pinch-off occurs approximately midway between the sphere and free surface, resulting in a deep seal (Fig. 6(c)). At the highest values, We ≥ 1,300, 2,400 and 9,000 for Bo = 0.91, 8.2 and 58 respectively, the splash crown domes over leading to surface seal (Fig. 6(d)). These cavity regimes were identified by Aristoff & Bush, who obtained the same progression of regimes with increasing We for small non-wetting spheres with a similar comparison for $h_p$ and We as seen in Fig. 6(e). When looking specifically at the deep seal cases, $h_p$ scales better with Fr as shown in the inset, with $h_p$ slightly less than the predicted value similar to the data of Aristoff et al. for steel spheres in pure water.

Pre-wetting of wetting spheres in a water-surfactant mixture does not lead to a perfect overlap of pinch-off regimes found by Aristoff & Bush. For instance, the shallow seal events observed occurring at Bo = 58 (Fig. 6(e)), do not correspond with previously published results. The discrepancy is brought about in part by nonuniform wetting as the sphere passes through the bubble layer, resulting in asymmetric cavities. This non-uniformity can in turn lead to an asymmetric cavity collapse as seen in Fig. 6(b) (evidenced by the wide pinch-off point). The asymmetries are most prominent near the pool surface, before the cavity has migrated to the sphere wake. This effect can lead to much narrower cavity diameters near the surface affecting the quasi-static, shallow, and surface seal regimes more significantly. The phenomenon is more pronounced for the two smaller sphere radii where asymmetries near the pool surface cause shallow seal to occur rather than deep seal. Although the cavity asymmetries are caused by the asymmetric adhesion of droplets on the sphere surface, no trends were observed in the cavity types with changes in the bubble layer height ($h_B$) or bubble diameter ($d_B$). The discrepancy in the pinch-off regime transitions could also be explained by the change in $\sigma_d(t)$ over time, with the surface tension in the splash and on the cavity walls approaching $\sigma_w$ during the early moments after surface creation and subsequently decreasing toward $\sigma_e$ as surfactant molecules adsorb. This would initially result in lower values of Bo and We that would increase over a short time period.

IV. CONCLUSION

In conclusion, our experimental results show that the addition of a surfactant to a pool of water causes the surface tension to vary with time, thus altering the critical velocity for cavity formation and causing it to vary with sphere radius. The presence of a bubble layer resting on the surface of a water-surfactant mixture leads to the formation of subsurface cavities at all impact velocities tested. By observing a sphere falling through a bubble layer suspended above the free surface, we note that bursting bubbles lead to the formation of small droplets and bubbles on the sphere surface. Rather than enhancing the wettability of a sphere, these droplets disrupt the advancing fluid and alter the splash, which leads to air entrainment and cavity formation under conditions where this would not normally be expected. The pre-wetted spheres mimic the water-entry behavior of non-wetting spheres; forming the same four cavity regimes (i.e., quasi-static, shallow, deep and surface seal). But the non-uniform droplet coatings cause cavity asymmetries that disrupt transitions between
FIG. 5. Image sequences of two independent events recorded from (a) top and (b) side views where a stainless steel sphere \((R_s = 4.76 \text{ mm})\) enters tap water with a droplet of red dye placed at its equator prior to release. The spheres impact water with identical velocities \(U\), less than the critical velocity for air entrainment \(U_{cr}\). The droplet deforms upon impact \((t = 1 \text{ ms})\), spreading into the splash (a) and left edge of the cavity (b) to initiate cavity formation. The cavity and splash form only in the vicinity of the droplet with water climbing up the sphere surface in all other locations. The contact line moves towards the sphere apex \((t = 2 - 3 \text{ ms})\), the cavity expands and moves down the other side towards the equator at \(t = 4 - 5 \text{ ms}\). Supplemental Material videos 7 & 8 [URL will be inserted by publisher] correspond with (a) and (b) respectively. (c) The schematic shows droplet deformation pushing water away from the sphere near the equator in a manner reminiscent of non-wetting coatings\(^{16}\).

these regimes. It is also possible that the surfactant may disrupt the pinch-off transitions due to dynamic surface tension effects, which could be investigated further in future studies.

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Appendix A: Pendant bubble method

Previous research on dynamic surface tension generally focuses on low Peclet number experiments where diffusion is the dominant transport mechanism of the surfactant molecules to the interface and advection is minimal\(^{13}\). However, in our experiments the Peclet number \(Pe = O(10^4)\), indicating that advective mass transport dominates over diffusive mass transport. Moorkanikkara and Blankschtein showed that the commonly used pendant bubble technique for measuring dynamic surface tension inherently induces convective currents that increase the rate of surfactant transport and hence adsorption to the interface\(^{13}\). Alvarez et al. induced a flow in their newly developed microtensiometer\(^{14}\) to investigate the effects of advection and found that the surface tension decreases faster with increasing Peclet number. We exploit the inherent flow in the pendant bubble technique to find an estimate of the rate at which our surfactant decreases the surface tension of newly formed interface.

To find the time \(t_o\) for the surfactant to decrease the surface tension from water \(\sigma_w\) to the equilibrium value of the surfactant \(\sigma_e\), we use the pendant bubble technique, which has similar geometry to a sphere entering water\(^{15}\). To do this we blow a bubble out of a nozzle into the water-surfactant mixture and video the growth and shape of the bubble at 3,000 frames per second, as shown in Fig. 7(a). We expand the bubble quickly at first to induce a flow over its surface and then more slowly so that we can observe the shape change with time. We then track the radii of curvature at the tip and right hand side of the bubble as shown in Fig. 7(b) and use the Young-Laplace equation to calculate the pressure drop across the interface. Using the height between these two positions on the bubble we can calculate the surface tension for each frame.
The top has only one radius of curvature due to the axisymmetry of the bubble so the Young-Laplace equation is

\[ P_b - P_2 = 2\sigma_d \left( \frac{1}{R_1} + \frac{1}{R_2} \right). \]  

(A2)

Noting that \( P_1 = P_2 + \rho gh \), subtracting (A1) from (A2) and rearranging we obtain

\[ \sigma_d = \frac{\rho gh}{2 \left( \frac{1}{R_1} + \frac{1}{R_2} \right)} \]  

(A3)

for a specific instance in time.

Figure 6 shows two cases of the change in \( \sigma_d \) over time with the corresponding change in the surface area of the bubble. From these plots we estimate the rate at which the surface tension decreases by finding the slope \( n \) of a line drawn between the large blue/red dots shown in Fig. 6 for each case. The starting position (first large dot) is chosen as the location where \( \sigma_d \) drops below \( \sigma_w \) or as the peak if that is not available. The ending position (second large dot) is chosen as the point where \( \sigma_d \) begins to flatten out near \( \sigma_e \).

The surface tension decreases faster as the initial expansion velocity of the bubble \( U \) increases (Fig. 6), the initial expansion velocity is defined in the inset). Due to limitations of the setup, only expansion velocities in the range of \( U = 0.017 - 0.361 \) m/s could be achieved. Hence, for extrapolations purposes we fit the pendant bubble data in Fig. 9 to the equation \( m = aU^b \) and find \( a = 1.42 \) and \( b = 0.49 \) (Note that a must have units of kg s\(^{-3}\)m\(^{-b}\) if \( U \) has units of ms\(^{-1}\) and \( m \) has units of Nm\(^{-1}\)s\(^{-1}\)). The time required for the surface tension to drop from \( \sigma_w \) to \( \sigma_e \) can then be calculated as \( t_w = (\sigma_w - \sigma_e)/m \). Extrapolating the fit out to the range of the spheres' impact velocities we can estimate \( t_o \) for the sphere impacts.

\[ \frac{\rho gh}{2 \left( \frac{1}{R_1} + \frac{1}{R_2} \right)} \]


FIG. 7. (a) An air bubble is blown out of a nozzle (0.5 mm OD), expanding very quickly at first and then more slowly over time. The time between images is 10 ms. (b) The various radii and lengths measured from each image are labeled.

FIG. 8. Two example measurements of the surface tension over time using the pendant bubble method are shown. The small dots show the raw surface tension data calculated from \((A)\) and the thick solid and dashed lines show the moving mean over a window of 17 ms. The surface tension drop rate \(m\) is calculated by taking the slope between the large blue and red dots. The thin solid and dashed lines show the approximate surface area \(A_s\) of the bubble over time.

FIG. 9. The surface tension drop rate \(m\) is shown to depend on the liquid flow rate over the bubble \(U\). The solid line is the fit to the pendant bubble data, \(m = aU^b\), where \(a = 1.42\) and \(b = 0.49\), which we extrapolate out to the sphere impact velocities (...). The inset shows the method for calculating \(U\) for the same two cases in Fig. 8. The position of the bubble tip \(h_b\) is tracked over time, and the velocity \(U\) is taken as the slope of the line from \(h_b = 0\) to 75% of the maximum \(h_b\) (all indicated with open circles).


