Failure mechanisms of air entrainment in drop impact on lubricated surfaces†

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Lubricated surfaces have recently been introduced and studied due to their potential benefit in various configurations and applications. Combining the techniques of total internal reflection microscopy and reflection interference microscopy, we examine the dynamics of an underlying air film upon drop impact on a lubricated substrate where the thin liquid film is immiscible to the drop. In contrast to drop impact on solid surfaces where even the smallest asperities cause random breakup of the entraining air film, we report two air film failure mechanisms on lubricated surfaces. In particular, using \( \approx 5 \mu \text{m} \) thick liquid films of high viscosity, which should make the substrate nearly atomically smooth, we show that air film rupture shifts from asperity-driven to a controlled event. At low Weber numbers \( \text{We} < 2 \), \( \text{We} = \rho U_o^2 R / \sigma \), \( U_o \) the impact velocity, \( R \) the drop radius, and \( \rho \) the density and \( \sigma \) the surface tension of the droplet), the droplet bounces. At intermediate We \( \text{We} > 2 < \text{We} < 10 \), the air film fails at the center as the top surface of the drop crashes downward owing to impact-induced capillary waves; the resulting liquid–liquid contact time is found to be independent of We. In contrast, at high We \( \text{We} > 10 \), the air film failure occurs much earlier in time at the first inflection point of the air film shape away from the drop center, where the liquid–liquid van der Waals interactions become important. The predictable failure modes of the air film upon drop impact sheds light on droplet deposition in applications such as lubricant-infused self-cleaning surfaces.

1. Introduction

Liquid drop impact, such as rainfall, is a ubiquitous natural phenomenon harnessed by nature in the capture of prey as well as aerosol release. It is also vital to many industrial applications such as liquid-infused self-cleaning surfaces, inkjet printing, spray coating, combustion and cooling. Recent studies have identified the existence and importance of a nanometer-scale air film that separates the liquid and the substrate before the drop makes direct contact with the substrate. For example, droplets bounce on smooth superhydrophilic mica surfaces without the drop ever touching the substrate, otherwise the air film would fail due to surface imperfections as observed by Kolinski et al. The resulting coefficient of restitution (the ratio of rebound velocity to impact velocity) is much smaller than when bouncing occurs on superhydrophobic surfaces, which suggests significant energy loss due to viscous dissipation in the air film during rebound. In addition, decreasing the ambient pressure suppresses splashing in drop impact and droplet–droplet collisions, which further highlights the importance of the surrounding air on impact outcomes.

Multiple imaging techniques have been used to probe the air film upon drop impact starting with direct high-speed imaging techniques as well as X-ray phase contrast imaging, total internal reflection microscopy (TIRM) and reflection interference microscopy (RIM). As a liquid drop of radius \( R \) impacts on a solid substrate, the air film is “squeezed” out and at a finite separation distance, the gas pressure \( P_g \) is balanced with the capillary \( (P_c) \) and inertial \( (P_i) \) pressures of the liquid according to \( P_g \approx P_c + P_i \). The dynamics are characterized by the dimensionless capillary number \( \text{Ca} = \mu_l U_o^2 / \sigma \) for the gas phase, Weber number \( \text{We} = \rho U_o^2 R / \sigma \) for the liquid phase, and Stokes number \( \text{St} = \rho U_o R / \mu_l \) accounting for both the liquid and gas phases, where \( \mu_l \) is the viscosity of the gas, \( U_o \) the impact velocity, \( \rho \) the density of the droplet, and \( \sigma \) the surface tension of the droplet. At low We, the capillary pressure \( P_c \) dominates and the entrained air film thickness scales with \( \text{Ca} \)

\[
H_g/R \sim \text{Ca}^{1/2}
\]

where \( H_g \) is the dimple height in the center of the air film. At higher We, \( P_l \) dominates, so that utilizing the stagnation pressure along the bottom of the drop, the air gap height scales with \( \text{Ca} \) and We following

\[
H_g/R \sim \text{Ca}^{1/2} \text{We}^{-1/2} \equiv \text{St}^{-1/2}
\]

However, if one assumes that the rapidly impacting droplet produces a potential flow in the liquid,
the scaling of the air gap height is predicted to be $H_d R \sim \alpha^{2/3}$, $\alpha^{-1/3}$, All of the above scaling laws were obtained from a combination of modeling and experiments using various types of droplets and surfaces. However, at high We, away from the central dimple, the curvature at the minimum air film thickness rapidly increases and eventually reaches a maximum at which the capillary pressure stops the approach of the droplet to the substrate. This gives rise to a kink height, $H_k$, following $H_k \sim R\alpha^{-14/9}\alpha^{2/3}$, based on theory predictions.\(^{20}\)

Most of the existing scaling relations only describe the pre-contact dynamics of drop impact and little is known about the contact dynamics. This is partially due to the stochastic nature of the air film breakup upon drop impact on solid surfaces, which is caused by random surface asperities that are comparable to the minimum air film thickness (i.e. $10^9$–$10^2$ nm).\(^8\) While asperities do not play a large role for the capillary pressure dominated regime\(^{25}\) where the air film thickness is sufficiently large (e.g., $O(1\, \mu m)$), at high We even the most minor asperities presumably cause air film rupture.\(^8,31,34\)

If the impacting surface can be made atomically smooth, for example using ultrathin liquid films of high viscosity, can the air film rupture shift from being asperity-driven to a controlled event? What happens to the dynamics when the air film thickness approaches the mean free path of the air molecules? Tran et al.\(^{16}\) observed that for drops impacting a liquid bath of the same material, the liquid–air interface of the bath deforms and the air film ruptures – presumably due to intermolecular forces – at a predictable distance from the lowest point of the pool deformation. For a drop impacting on a liquid film of the same material, Law and colleagues\(^{36,37}\) have observed that the impacting drop transitions back and forth between bouncing and merging onto the liquid film with varying film thickness. At lower impact velocities it has also been observed that the competition between the droplet and the deformed film retraction governs the coalescence dynamics, while at high impact velocities, intermolecular forces between the drop and film are postulated to be responsible for early merging, although no direct measurements of the air film morphology during coalescence were made.\(^{36-38}\) We seek to address the latter by investigating drop impact on lubricated surfaces with thin liquid films that are immiscible with the drop and have no detectable deformation upon drop impact.

Regardless of drop size, we identify two failure modes for the air film. At low We ($< 2$), the droplet rebounds, but at intermediate We ($2 < \text{d} < 10$), an inertial-capillary regime is observed where the liquid–liquid contact time scales as the inertial-capillary time regardless of We, which is very different from the dynamics for the same range of We in cases of drop impact on dry solid substrates.\(^{12}\) As We increases ($\text{d} > 10$), the inertial-capillary regime transitions to a regime where the disjoining pressure becomes important. In such cases, the minimum air film thickness is reduced to only a few nanometers and the intermolecular forces between the drop and the liquid film become important, which is a scenario that has not been reported for drop impact on dry solid surfaces. We successfully provide experimental evidence for the kink height predictions of Mandre et al.\(^{20}\) in the inertial-capillary regime and uncover the deviation from the theoretical prediction as the disjoining pressure becomes important. We also show that the critical We number for the transition between the two failure modes increases with the drop size.

2. Experimental methods

In this study, the air film morphologies under water drops of various radii ($R \approx 0.4, 0.6$ and $1.1 \, \text{mm}$) and impact velocities ($0.4–1.6$ m s$^{-1}$) were directly observed using a combination of total internal reflection microscopy and reflection interference microscopy (TIRM-RIM) at 50,000 fps on spin-coated glass slides with silicone oil films ($\mu_{\text{oil}} = 4.56, 96.0, 970$ mPa s yet similar densities $\rho_{\text{oil}} = 913, 960, 970$ kg m$^{-3}$, and film thickness $\delta_{\text{oil}} \approx 5$ nm). Fig. 1(a) shows the experimental setup using the combined TIRM-RIM technique; the working principle and calibration details can be found in the ESI.\(^\dagger\) The optical measurements in Fig. 1(a) demonstrate the temporal datum alignment of the TIRM-RIM technique where time $t = 0$ is set to be the frame when the initial dimple of the air film at the center is observed. Fig. 1(b) illustrates the air film at the maximal spreading of the droplets for We $\approx 8$ using both TIRM and RIM.

Fig. 2 depicts several important time-dependent length scales involved in the air film morphology, including the dimple height ($H_d$) at the center of the air film and the kink height ($H_k$) measured radially at the first inflection point from the center of the air film between the droplet and oil. The TIRM technique allows us to obtain the absolute air film thickness up to $\approx 100$ nm, the decay length of an evanescent wave, while the RI technique allows us to obtain the relative air film thickness of between $\approx 113$ nm and $\approx 3$ $\mu$m. Both methods have a temporal resolution of 20 $\mu$s. The combination of both the TIRM and the RIM techniques gives us the entire profile shape of the air film: the RIM technique is mainly used to study the dimple evolution, while the TIRM technique is used to study the evolution of the kink height.

3. Results

We observe that for low We ($< 2$), the droplets rebound on the lubricated surface, whereas at intermediate We ($2 < \text{d} < 10$), the air film fails at the center, and at high We ($\text{d} > 10$), the air film fails at the first inflection point of the air film morphology, i.e., there is a kink in the water–air interfacial profile. TIRM snapshots of the three cases are shown in Fig. 3(a–c) with the inertial-capillary time scale $\tau \equiv \sqrt{\rho R^2/\sigma}$ used to non-dimensionalize time. Typical values of $\tau$ are 0.94, 1.7 and 4.3 ms for $R \approx 0.4, 0.6$ and 1.1 mm, respectively. When the drop touches down on the lubricating film, the total internal reflection is suppressed and the light is refracted into the water droplet causing the liquid–liquid contact to appear black on the camera for the TIRM measurements (grayscale intensity = 0). In Fig. 3(a), the first frame is the starting time, but is only visible in the RIM technique; the second and third frames show the spreading and maximal spreading, respectively, where the droplet exits the TIRM view by
the fourth frame. In Fig. 3(b), the first frame is the initial dimple formation, the second frame the maximal spreading, the third frame the air film failure as indicated by grayscale intensity of zero (a black spot at the dimple), and the fourth frame is after failure of the air film. In Fig. 3(c), the first frame is the initial dimple formation, the second frame shows drop spreading, followed by the third frame depicting air film failure at the kink, and the fourth frame is a long time post-air film failure. A relevant time scale here is the liquid–liquid contact time, \( t_{\text{contact}} \), which is the elapsed time from the initial observation of the dimple with TIRM-RIM\(^{14,27}\) to the air film failure, \( t_{\text{contact}} \). The reflection interference microscopy (RIM) setup utilizes the same dove prism, which has a polished bottom surface, where another CLS illuminates the bottom of the droplet through a beam splitter (BS). (b) TIRM and RIM grayscale images at maximal spreading over the air film for \( \text{We} \approx 8 \) on a 970 mPa s, 5 \( \mu \)m thick silicone oil film. Scale bars represent 0.5 mm.

To further characterize the air film dynamics, Fig. 4 shows the dynamic collapse of the air film. In particular, the case of \( \text{We} \approx 3.2 \) is shown in Fig. 4(a), where the air profiles are taken in increments of \( \Delta t/\tau \approx 0.059 \). Beyond \( t/\tau \approx 0.68 \), the top of the dimple crashes downward where the air film finally fails at the center at \( t/\tau \approx 1.0 \). As the dimple fails, the resolution of the dimple shape is lost in the RIM data and thus only the TIRM data allows us to capture the inverted dimple at \( t/\tau \approx 1 \) (inset in Fig. 4(a)). The solid red curve in the inset shows the air profile prior to failure at \( t/\tau \approx 1 \) and the subsequent time increments marked by dotted and dashed curves represent \( \Delta t/\tau \approx 0.035 \). In Fig. 4(a), \( H_d \) continuously decreases with time, and the dimple collapse rate
Fig. 3  Air entrainment effects on impact regimes. (a) Total rebound for We ≈ 1. (b) Air film failure at the center for We ≈ 4 (black at the center). (c) Air film failure at the kink for We ≈ 20. (d–f) Instantaneous air film profiles either right before rebound (d) or before failure (e–f). Data represented have been conducted on 970 mPa s, 5 μm thick silicone oil films. The red arrows in (b and c) represent the air film failure locations and scale bars represent 0.5 mm.

Gravity, the air pressure can be scaled as $P_a \sim P_d + P_b + P_o$, where $P_d$ represents the disjoining pressure, $P_b$ the inertial pressure of the liquid and $P_o$ the capillary pressure. In particular, the disjoining pressure arises out of the attractive nature of two surfaces, $A$ where $P_d = A H_k^2$, $A$ is the Hamaker constant (e.g., $A \approx 4.6 \times 10^{-20}$ J calculated based on the Lifshitz theory for three planar surfaces made up of the oil, air and water layers resulting in a stronger liquid–liquid attraction as opposed to the liquid–gas attraction). The inertial pressure evaluated based on the unsteady Bernoulli equation gives $P_b \sim \rho U_{kink}^2 L H_d$, where $L$ is the lateral extension of the air film and scales as $L \sim \sqrt{RH_d}$ and the capillary pressure $P_o \sim \kappa l$ where $\kappa$ is the curvature of the air film.

The scaled oil–water contact time, $t_{contact}/t$, is plotted with respect to We in Fig. 6(a) with varying drop radii; two distinct behaviors are observed. For intermediate We ($2 < We < 10$), we obtain air entrainment failure on lubricated surfaces with the ratio $t_{contact}/t \approx 1$ (dimple failure ($H_d$) regime). For high We (We > 10), $t_{contact}/t < 1$ characterizes the kink failure ($H_k$) regime. Interestingly, although the kink height is orders of magnitude smaller than the dimple height, the air film fails at the dimple, which indicates that there is a large pressure opposing contact at the kink. The capillary pressure, although initially small, quickly takes over the dynamics where, $P_{o,kink} \sim \sigma H_k^2 / \ell^2$, where $\ell$ is the horizontal length scale of the kink and is given by $\ell \propto R U_k^{1/2} (H_d/R)^{1/2}$. Where $U_{kink}$ is the radial velocity of the kink, $U_{kink}$ normalized by the impact velocity following $U_{kink} = U_k / U_o$. In a representative experiment, $R = 1$ mm, $\rho_t =1000$ kg m$^{-3}$, $\sigma = 0.072$ N m$^{-1}$, $\mu_o = 1.82 \times 10^{-5}$ Pa s, $U_0 = 1$ m s$^{-1}$, $H_d = 2 \times 10^{-6}$ m, $H_k = 4 \times 10^{-9}$ m and $L = 1$ mm, the kink hardly moves before air film ruptures, which gives $U_{kink} \approx 3 \times 10^{-2}$. Note that, this kink velocity is limited by the time and pixel resolutions of each TIRM image, and is not a
function of the droplet size for the parameters considered in our study. For the above-mentioned representative experiment, we obtain the pressure ratio \( P_{w,kink}/P_0 = O(10^3) \), and hence the capillary pressure at the kink is much larger than the inertial pressure as the droplet approaches the substrate. The kink height can be determined by balancing the capillary pressure and the maximum gas pressure \( P_{g,max} \propto \mu_i U_0 U_h^{1/2} \text{St}(RH_k)^{1/2} \), which suggests \( H_k \sim R\text{St}^{-1/4}\text{Car}^{-2/3} \). Fig. 6(b) shows the experimentally measured kink height, \( H_k \), normalized by the drop radius, as a function of \( \text{St}^{-1/4}\text{Car}^{-2/3} \) for varying drop size. A slight deviation is observed between the scaling of \( H_k/R \sim \text{St}^{-1/4}\text{Car}^{-2/3} \) and the experimental data, and the deviation is possibly due to the rarefied gas effects, which were not considered in Mandre et al.\textquotesingle s work. The experimental data for different drop radii reasonably follows Mandre et al.\textquotesingle s prediction for \( \text{St}^{-1/4}\text{Car}^{-2/3} > 1.5 \times 10^{-5} \) (i.e., \( \text{We} < 10 \) in our experiments), however, significant deviations occur for \( \text{St}^{-1/4}\text{Car}^{-2/3} < 1.5 \times 10^{-5} \). The deviations occur when the disjoining pressure dominates the capillary pressure. We note that Mandre et al.\textquotesingle s kink height prediction has also been validated experimentally by De Ruiter et al.\textsuperscript{14} when \( H_k = O(100 \text{ nm}) \) and \( \text{We} \approx 4 \), which is well below the dimple to kink failure transition, as shown in Fig. 6(a). In contrast, in our experiments, we observe a new kink-failure regime, and within the new regime the disjoining pressure is of the same order of magnitude as the capillary pressure at the kink, i.e., \( P_{w,kink} \sim P_0 \), which provides \( \text{We}_c \sim R^{1/2}[\mu_i U_0^{-1/2} (U_h')^{-1}]^{1/16} \propto R^{1/2} \). This result is consistent with Fig. 6(a), where the critical \( \text{We} \) increases with drop size. Rescaling Fig. 6(a) with \( \text{CWe}^{1/2} \), Fig. 7 shows the collapse of the transition from dimple to kink failure at \( \log_{10}(\text{CWe}/R^{1/2}) \approx -1.2 \) as the drop size is varied, where \( C = [\mu_i U_0^{-1/2} (U_h')^{-1}]^{1/16} \). When the air film failure occurs at the kink, the scaled contact time decreases sharply with \( \text{We} \), until it finally converges to \( t_{\text{contact}}^{1/2} \approx O(10^{-3}) \), which is the temporal resolution of our experiments.

We next consider the viscous effects of the oil film. First, we suspect that on a less viscous oil film, surface waves may be generated by the impacting droplet prior to liquid–liquid contact, which may distort the oil–air interface and cause an
early onset of the air film rupture. Assuming that the surface excess energy of the oil $E_s$ is balanced with the viscous dissipation $E_m$ of the oil film, where $E_s = \sigma_{oil} \delta_{oil} R$ (where $\sigma_{oil}$ is the surface tension of oil) and $E_m = \mu_{oil} U_r^2 L^3 / (\delta_{oil} c_0)$ with $u_r(U_r \sim U_0 L^3 / \delta_{oil})$ representing the radial velocity of the oil, and $c_0 \sim \sqrt{\sigma_{oil} / \mu_{oil}} R$ representing the propagating velocity of a capillary wave. The resulting wave propagation length is $L^* \approx \left[ \sigma_{oil} \mu_{oil}^2 R^2 / (\mu_{oil} U_0^2 \rho_{oil}^{1/2}) \right]^{1/2}$. We find that, due to the small thickness of the oil film, the surface wave is overdamped within $O(10 \mu m)$ (for $\mu_{oil} \approx 5$ mPa s, $U_0 = 1$ m s$^{-1}$, and $R = 1$ mm), which is an order of magnitude smaller than the initial dimple radius of $r_d \approx 250 \mu m$ at $t \approx 0$. Thus, the oil-air interface can be treated as flat upon drop impact in our experiments. Consequently, we believe that the lack of deformation of the oil film surface that is greater than $10 \mu m$ away from the center makes this study different from the work of Tran et al. where the air film rupture is directly tied to the deformation arc length.$^{16}$

As shown in Fig. 8(a), for the least viscous film (i.e., $\mu_{oil} \approx 4.56$ mPa s), the contact time is smaller than for the higher viscosity cases of 96.0 and 970 mPa s with the same We. Furthermore, the critical $We_c$ that characterizes the dimple to kink failure transition for the 4.56 mPa s film is smaller than the cases of higher viscosities. Note that the $We_c$ scaling derived above is based on the assumption of a no-slip air film on a solid surface. However, for a low viscosity oil film, such no-slip condition may no longer hold and $We_c$ can vary with the film viscosity. We suspect that a slip boundary condition induces a greater escape velocity of the gas, $u_g$, where by continuity, $u_g \sim 1/H_k$, and thus a greater escape velocity should result in a smaller air film thickness. It is evident in Fig. 8(b) that the kink height for the 4.56 mPa s film is smaller than the cases of higher viscosities, leading to a stronger disjoining pressure and hence a smaller $St_{149}^{2}/Ca^{2/3}$.
4. Conclusions

In this study, we have examined air entrainment failure mechanisms of water drops of various sizes ($R \approx 0.4$–$1.1$ mm) impacting on silicone oil-lubricated substrates ($\mu_{\text{oil}} \approx 4.56$, 96.0, 970 mPa s). We find that the air entrainment failure time for intermediate $We (2 < We < 10)$ coincides with the inertial-capillary time scale where the air film fails at the center or the dimple due to impact-induced capillary waves. For high $We (We \gg 10)$, the disjoining pressure dominates the dynamics and causes the air film to fail away from the center and at the kink, where the transition $We_c$ increases with the drop size. The inertial-capillary time scaling as well as the influence of the disjoining pressure on air film rupture is different from the drop impact studies on dry solid surfaces where minor asperities cause random collapse of the air film. For the viscous effects of the oil film, a smaller viscosity can lead to an earlier onset of the air film breakup, when the no-slip condition at the air–oil interface no longer holds. Our study bridges the knowledge gap between drop impact on solid surfaces and liquid pools and adds to the extensive knowledge base on air entrainment dynamics relevant to applications such as lubricant-infused self-cleaning surfaces.

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