Short and long time drop dynamics on lubricated substrates

A. Carlson1,2,4(a), P. Kim3,4, G. Amberg2 and H. A. Stone4(b)

1 School of Engineering and Applied Sciences, Harvard University - Cambridge, MA, USA
2 Department of Mechanics, Linné Flow Center, Royal Institute of Technology - Stockholm, Sweden
3 Department of Bio and Brain Engineering, Korea Advanced Institute of Science and Technology - Daejeon, South Korea
4 Department of Mechanical and Aerospace Engineering, Princeton University - Princeton, NJ, USA

received 21 September 2013; accepted in final form 7 November 2013
published online 5 December 2013

PACS 47.55.D- – Drops and bubbles
PACS 47.55.N- – Interfacial flows
PACS 68.15.+e – Liquid thin films

Abstract – Liquid infiltrated solids have been proposed as functional solvent-phobic surfaces for handling single and multiphase flows. Implementation of such surfaces alters the interfacial transport phenomenon as compared to a dry substrate. To better understand the interface characteristics in such systems we study experimentally the dynamics of a pendant water drop in air that contacts a substrate coated by thin oil films. At short times the water drop is deformed by the oil that spreads onto the water-air interface, and the dynamics are characterized by inertial and viscous regimes. At late times, the oil film under the drop relaxes either to a stable thin film or ruptures. In the thin film rupture regime, we measure the waiting time for the rupture as a function of the drop equilibrium contact angle on a dry substrate and the initial film height. The waiting time is rationalized by lubrication theory, which indicates that long-range intermolecular forces destabilize the oil-water interface and is the primary mechanism for the film drainage.

Copyright c⃝ EPLA, 2013

Introduction. – Humans [1], animals [2], insects [3] and plants [4] have all developed liquid-coated substrates for different functional purposes. With inspiration from these biological surfaces, “liquid-infused” substrates were developed recently [5–10]. These substrates have been demonstrated with their anti-stickiness to in many ways out-perform conventional super-hydrophobic substrates [6]. Such a surface property is particularly beneficial for multiphase flow applications e.g. oil-gas transport, fluid filtration, nuclear industry and refrigeration. It is well known that the small-scale, drop size physics determine the large-scale multiphase flow phenomena and the transition between flow regimes [11]. One consequence of substituting a conventional substrate with a “liquid-infused” substrate in a multiphase flow application is that the interfacial transport processes will be altered.

In this article we address the characteristic times and dynamics of a drop that contacts a lubricated substrate. We present a two-fold experimental approach that captures both short and long time dynamics of a pendant water drop in air that comes in contact with a solid pre-wetted by a thin silicone oil film that wets the water drop. Through high-speed imaging we probe short time dynamics where we demonstrate the qualitative and quantitative features of the encapsulation of the water drop by the oil film. At long times we characterize the stability region for the thin film that separates the drop and the substrate. By optical imaging we measure the time for film rupture and the dynamics related to water re-wetting the substrate. The short and long time dynamics are illustrated in fig. 1 where the short time dynamics is independent of the water drop’s equilibrium contact angle (θsw) on the dry substrate, which however determines the dynamics at long times.

Experimental system. – Our experimental configuration to study this class of problems is shown in fig. 2(a).

In our experiments a pendant water drop with density ρw = 998 kg/m³, viscosity μw = 10⁻³ Pa·s and radius R is formed at the tip of a micro-needle (fig. 2(a)). The solid substrate is a glass plate, which is coated with a thin film of silicone oil with density ρo = 960 kg/m³, where we vary the film viscosity 4.8 × 10⁻³ ≤ μo ≤ 4.8 Pa·s. The oil film is deposited on a glass plate by a spin coating technique, where the initial film height is hi ≈ 5 ± 3 μm.
Fig. 1: Characteristic drop dynamics at short and long times. Initially the substrate is coated with a $h_i = 8 \mu m$ thick silicone oil film, with a viscosity $\mu_o = 4.8 \times 10^{-3}$ Pa s. At short times the drop deforms as the oil film spreads onto the air-water interface and eventually engulfs the water drop. The equilibrium drop shape at long times is determined by water’s affinity to the solid substrate, which is measured through its equilibrium contact angle ($\theta_{sw}$) on a dry substrate. For $\theta_{sw} = 108^\circ$ the oil film under the drop is stable and for $\theta_{sw} = 45^\circ$ the film becomes unstable and water wets the substrate.

We control the equilibrium contact angle ($\theta_{sw}$) for the water drop on the dry glass plate by a standard silanization method [12]. There is no observable difference in the equilibrium contact angle ($\approx 2^\circ$) for the silicone oils on the different chemically treated substrates. The drop dynamics following contact with the oil phase are recorded with a high-speed Phantom V7 camera, where the images are taken from the side of the drop and we vary the frame rate according to the film viscosity ($5-50 \times 10^3$ frames per second).

In the experimental system three different phases appear, namely air, water, and oil respectively, labeled below with the subscripts ($a, w, o$). Since the largest relevant length scale in these experiments is on the order of a millimeter, capillarity is expected to dominate the drop dynamics after contact with the oil film and gravitational effects are neglected below. Thus, we identify the surface energies to be important material parameters. In such a gas-liquid-liquid system, the three surface energies [13] $\gamma_{wo} \approx 42$ mN/m, $\gamma_{oa} \approx 20$ mN/m and $\gamma_{wa} \approx 70$ mN/m determine the equilibrium shape of the interfaces. The equilibrium angle between the different phases can be derived through a Neumann construction [12] for the surface energies (see fig. 2(c)). If the surface energies generate three equilibrium angles, a drop deforms into a lens shape when it is brought in contact with a free surface [12]. In our experiments $\gamma_{oa} + \gamma_{wo} < \gamma_{wa}$, the triangle inequality shows that three equilibrium angles cannot exist, and consequently we expect the oil to spread onto the water-air interface as in a perfect wetting scenario. The simplified equilibrium scenario, with finite angles, illustrated in fig. 2(c) does not represent the dynamics as the oil engulfs the drop.

A sketch of the interface shapes at an instance in time when a pendant water drop contacts the film is shown in fig. 2(b). The silicone oil spreads over the drop forming a small radius of curvature towards the plane, which is expected to generate a capillary suction pressure that produces deformation of the drop. We denote by $r$ the apparent radius that is measured in the experiments during spreading and drop deformation.

**Drop engulfment.** – The typical dynamics we observe are illustrated in figs. 3(a), (b) with two sequences using very different film viscosities. We show drop shapes at four times after contact with the thin oil film, which generates the interface deformation. Additional experiments, not presented here, visualizing the drop dynamics from below, show that the oil film remains intact for the duration of the drop dynamics in fig. 3.

The early time evolution of the drop shape shown in fig. 3(a) ($t < 2$ ms) resembles coalescence [14] or spreading of liquids with low viscosity [15]. A capillary wave is
generated upon contact with the thin film, which travels across the drop (see SuppMaterial500cst.avi) [16]. The capillary forces cause drop deformation, which is limited by the acceleration of mass or viscous resistance. Subsequently, the drop detaches from the needle (fig. 3). The detachment time $\tau$ is defined as the time from first contact with the film until the drop detaches from the needle. Much later the drop has relaxed into its equilibrium shape, where it is engulfed by the oil.

Comparing the experimental images and the time scales in figs. 3(a), (b) it is clear that the drop dynamics is dictated by the material properties of the thin oil film. In fig. 3(b) the film is a thousand times more viscous than in fig. 3(a), which significantly changes the time scale for interface deformation and detachment (see SuppMaterial5000cst.avi). Nevertheless, the results in fig. 3 make clear that the shape of the drop as it detaches from the needle is approximately independent of the film viscosity. By assuming that gravitational effects are small, the final drop shape can be described by the balance of surface energies. As it is energetically favorable for the oil phase to engulf the water drop, an oil film forms on the air-water interface. Neglecting the shape of the oil meniscus, which is reasonable as long as $h_i \ll R$, then the equilibrium drop shape can be derived from a balance of surface energies: \( \cos^{-1}\left(\frac{2\gamma_{oa} - \gamma_{ow}}{\gamma_{oa}}\right) \approx 111^\circ \), which is in good agreement with the final drop shapes seen in figs. 3(a), (b).

The similarity in drop shape at the time of detachment for very different film viscosities identifies the detachment time to be a characteristic time scale for the experimental system. We conducted a set of experiments with different drop radii and film viscosities to measure the detachment time (fig. 4(a), [16]). For film viscosities $\mu_o \leq 0.01$ Pa s the detachment time $\tau$ appears to be independent of viscosity but depends on drop size. In contrast, $\tau$ varies significantly with viscosity when $\mu_o > 0.1$ Pa s.

Three contributions govern the flow: inertia, viscous and surface tension forces. A measure of the relative importance of these contributions is the Ohnesorge number

$$Oh = \frac{\mu_o}{\sqrt{\rho R^3 \gamma_{oa}}},$$

which gives the ratio between the viscous to the inertia-capillary force, here formulated with the material properties of the oil. The flow is driven by capillarity, whereas inertia and viscosity act as resistances. Dimensional analysis predicts two relevant time scales for the flow, an inertial time scale $\tau_\mu = \sqrt{\frac{\rho R^5}{\gamma_{oa}}}$ and a viscous time scale $\tau_\nu = \frac{\mu R}{\gamma_{oa}}$, where we have used the drop radius ($R$) as the characteristic length scale.

In an inertially dominated flow $\tau_\mu$ is expected to be the relevant time scale for the flow characteristics. In fig. 4(b) the measured detachment time is normalized by $\tau_\mu$ and approximately constant for $Oh < 1$, but for $Oh > 1$ they change and become nearly linear with respect to $Oh$. The results for the detachment times illustrate that for low viscosity films drop inertia is limiting drop deformation.

In contrast, if the film has a large viscosity, inertia can be neglected and the flow can be characterized by a viscous time scale $\tau_\nu$. By scaling the detachment times in fig. 4(a) with $\tau_\mu$ a different behavior is observed (fig. 4(c)). The detachment time in the viscous regime ($Oh > 1$) falls on a straight line, but is a function of $Oh$. The shaded areas in figs. 4(b), (c) mark the data for $0.2 < Oh < 2$, where we expect a transitional regime as the inertial and viscous contributions are comparable.

Next we focus on the characterization of the drop dynamics generated by the spreading of the oil film onto the air-water interface. A measure of the drop deformation in time is the apparent radius $r$ of the spreading film, which we extract along the horizontal direction of the substrate from first contact with the oil film (fig. 2(b)). In our experiments the thickness of the oil film is about a hundred times smaller than the initial radius $R$ of the water drop. This difference poses experimental challenges, as it is difficult to trace the microscopic dynamics of the spreading oil film and the macroscopic drop deformation. Since the oil film wets the water interface it is likely that an even thinner precursor film is formed as it spreads [12,17], which is difficult to identify on the drop. The extent of the spreading oil can, however, be significantly larger than $r$ (fig. 2(b)) and its leading edge may display a different dynamics.

Fig. 4: (a) Time ($\tau$) for the drop to detach from the needle as a function of film viscosity ($\mu_o$) and drop radius ($R$). The error bars in the square markers reflect the deviation from the mean value for several realizations (between 2 and 5) of the same experiment. (b), (c): detachment time scaled with $\tau_\mu$ and $\tau_\nu$ as a function of $Oh$ number. The gray shaded area (0.2 < $Oh$ < 2) illustrates the region where the inertial and viscous forces give similar contributions.
Measuring the apparent radius allows us to quantify the effect of film viscosity on the drop dynamics (fig. 5(a)). The influence of film viscosity is, however, a function of $Oh$ and only affects the rate of drop deformation where $Oh > 1$ (fig. 5(a)).

In the inertial regime $Oh < 1$, viscous resistance is less important and the apparent radius is approximately independent of the viscosity (fig. 5(a)) as observed for film viscosities $\mu_o = 4.8 \times 10^{-3}$ Pa s and $\mu_v = 9.6 \times 10^{-3}$ Pa s, where the apparent radius follows nearly the same curve until detachment time ($t \approx 2$ ms). When the drop detaches from the needle capillarity generates a force in the direction towards the substrate amplifying the radial flow inside the drop, which makes $r$ overshoot. Contrary to a drop spreading on a dry substrate, there is no contact line pinning and the drop oscillates on the thin film until the capillary wave is dissipated. The results for the lower viscosity films ($\mu_o = 4.8 \times 10^{-3}$ Pa s, $\mu_v = 9.6 \times 10^{-3}$ Pa s) show that both the amplitude and damping of the capillary wave are affected by the film viscosity.

Since the detachment time is rationalized by either an inertial or viscous time scale, it is intuitive to believe that the apparent radius should follow a similar scaling argument. By scaling the apparent radius with an inertial time scale, it is intuitive to believe that the flow are affected by the film viscosity.

A logarithmic representation of the data in the viscous regime (fig. 5(c)) demonstrates that $r/R$ has different slopes at short and long times. For $t/\tau_p < 1.0$ the apparent radius has a slope with an exponent $\approx 0.3$ (fig. 5(c), [16]), in contrast to a drop spreading on a dry substrate [12,18,19,21] and binary drop coalescence [14,22]. At later times $t/\tau_p > 1.0$ the curve has a much more gradual slope. This indicates that there are two viscous regimes where the viscous dissipation may take place at different length scales [14,22].

We suggest that the viscous resistance is mainly generated in two prominent film regions. A significant film flow is generated as the oil-air interface propagates along the radial direction. Since the film might be extended much further than $r$, viscous friction is also generated by the oily drop interface. Further theoretical development is needed to quantify the viscous resistance in these regions.

**Thin film rupture.** — After the drop has been deformed by the spreading oil film it reaches a quasi-steady state resting on the lubricated substrate. At long times the stability of the oil film determines the equilibrium interface shape. Although the oil completely wets the solid substrate, we observe that the oil film under the drop
becomes unstable for equilibrium contact angles $\theta_{sw} < 90^\circ$ (fig. 6(a)). Lubricant failure has been recently reported by [6,8,23] on liquid-infused structured substrates. One important aspect for the use of lubricated substrates in applications is to determine the longevity of the lubricant separating the drop and the solid. By combining imaging from the side and microscopic optical imaging from below we measure the late time drop dynamics on the lubricated substrate. In particular these steps allow us to quantify the characteristic waiting time ($\tau_w$) for thin film rupture, after which a small water hole is formed that expands radially [16]. The re-wetting of water onto the substrate is similar to a de-wetting process and the growth of the wetting hole follows a spreading dynamics as reported previously by [24], see [16].

The thin film ruptures at different places in each experiment, which is the hallmark of an instability. The perturbation generated by long-range forces destabilizes the oil film, which in our experiments may originate from chemical or structural substrate roughness. To determine the influence of the long-range forces on the thin film stability we perform experiments where we vary the initial film height and chemical treatment of the substrate, which changes the equilibrium contact angle ($\theta_{sw}$) of the drop on the dry substrate. The oil forms a film on all substrates, with a small contact angle ($\approx 2^\circ$). A microscopic nucleation site ($\ell$) that is much smaller than $R$ is observed [16], which grows radially in time. In our experiments $\ell$ is limited by the optical resolution ($\approx 10 \mu m$), which is likely to be larger than the size of the initial hole. Both $h_i$ and $\theta_{sw}$ are found to influence $\tau_w$ (fig. 6), which depends significantly on $\theta_{sw}$ indicating that the long-range force destabilizes the oil film under the drop.

In order to rationalize the behavior of $\tau_w$, both hydrodynamic and long-range intermolecular forces need to be modeled. Thin film dynamics and rupture have been well studied in the literature [25–29], but to the best of our knowledge the waiting time has not been quantified before. One modeling approach that encompasses the main physical contributions is the thin film lubrication theory including an attractive van der Waals potential [25] between the water-oil interface and the solid substrate,

$$\frac{\partial h}{\partial t} = \frac{\partial}{\partial x} \left( h^3 \frac{\partial}{\partial x} \left( -\gamma_{wo} \frac{\partial^2 h}{\partial x^2} + \frac{A}{h^3} \right) \right) = 0. \quad (2)$$

Here, $h = h(x,t)$ is the film height and $A$ is the Hamaker constant [25], which can be a function of the equilibrium contact angle $\theta_{sw}$ [30]. The film pressure $p = -\gamma_{wo} \frac{\partial^2 h}{\partial x^2} + \frac{A}{h^3}$ consists of two contributions from interface deformation ($-\gamma_{wo} \frac{\partial^2 h}{\partial x^2}$) and intermolecular interactions ($\frac{A}{h^3}$). By balancing these two terms gives a scaling estimate for the size of the nucleation hole $\ell \approx \left( \frac{2 \gamma_{wo} h}{A} \right)^{\frac{1}{2}} [12]$, though $h_i$ is expected to be much larger than the critical height and $\ell \ll R$.

We derive a scaling law $\tau_A$ for the waiting time from eq. (2), $\tau_A = \frac{\mu h_i L^2}{A} \sim \frac{\mu \gamma_{wo} h_i^2}{A}$ where $L^2$ is the lateral area under which the film drains that scales with the nucleation size $\ell^2$. The theoretical model is in qualitative agreement with the experiments (fig. 6(c)). The same time dependence for thinning was found by [31] for a film destabilized by the van der Waals force, which asymptotes towards a self-similar regime.

The initial film height in our experiments is much larger than what is expected to be within the range of intermolecular forces, which suggests that the engulfment of the drops rapidly thins the oil film under the drop. Inserting the measured waiting time (fig. 6(b)) for $\theta_{sw} = 3^\circ, h_i = 2.4 \mu m, \gamma_{wo} = 4.7 \times 10^{-3}$ s and assuming $A \approx 10^{-18}$ N m [29] gives a prediction for the critical film height $\approx \left( \frac{(\tau_A A)^{\frac{1}{2}}}{\mu \gamma_{wo}} \right)^{\frac{1}{5}} \approx 100 \mu m$, which is physically realistic [28,29] and indicates that intermolecular
forces dominates the film draining. Thus, the pre-factor $C$ in fig. 6(c) is significantly smaller than $\left(\frac{\mu_o \gamma_{sw} R^5}{A^2}\right)^{\frac{1}{2}}$.

Since the stability regime for the drop-lubricant system is now understood, we use this as a design principle to control drop motion on a lubricated substrate. We demonstrate in fig. 7 two examples where we control the two phase flow through the film stability. Figure 7(a), (b) shows the motion of a sliding drop on a lubricated substrate. By chemically treating a small part of the substrate area ($\theta_{sw} < 90^\circ$) generates a field that locally arrests the sliding drop motion on the thin film, while a nearby drop slides by.

Conclusions. – We have presented here the detailed dynamics of a pendant drop engulfed by thin viscous films. The reported time scales and dynamics may be particularly important with the increasing demand for implementation of “liquid-infused” substrates in industrial applications, where the interfacial transport processes may be determined by the small-scale drop physics at the wall. Our results describe drop dynamics on thin films at both short and long time scales and highlight that there are many more questions about the dynamics in these configurations that remain to be understood.

***

We thank M. Roche for stimulating discussions. This work was financially supported in part by the Swedish Research Council through the Linne Flow Center (AC and GA), the National Research Foundation of Korea (NRF 35B-2011-1-D00013) (PK) and the Office of Naval Research grant (ONR MURI grant N00014-12-1-087) (HAS).

REFERENCES

[1] Thody A. J. and Shuster S., Phys. Rev., 69 (1989) 383.
[2] Zouboulis C. C., Baron J. M., Böhm M., Kippenberger S., Kurzen H., Reichrath J. and Thielitz A., Exp. Dermatol., 17 (2008) 542.
[3] Federle W., Riehle M., Curtis A. S. G. and Full R. J., Integr. Comp. Biol., 42 (2002) 1100.
[4] Boin H. F. and Federle W., Proc. Natl. Acad. Sci. U.S.A., 101 (2004) 14138.
[5] Angelucci D., Moscatto T., Pauchet F. and Van Kelik R., US Patent No. 0283778 A1 (2011).
[6] Wong T.-S., Kang S. H., Tang S. K. Y., Smythe E. J., Hatton B. D., Grinthal A. and Aizenberg J., Nature, 477 (2011) 443.
[7] Epstein A. K., Wong T.-S., Belsle R. A., Boggs E. M. and Aizenberg J., Proc. Natl. Acad. Sci. U.S.A., 109 (2012) 13182.
[8] Anand S., Paxson A. T., Dhiman R., Smith J. D. and Varanasi K. K., ACS Nano, 6 (2012) 10122.
[9] Lafuma A. and Quéré D., EPL, 96 (2011) 56001.
[10] Smith J. D., Dhiman R., Anand S., Reza-Garduno E., Cohen R. E., McKinley G. H. and Varanasi K. K., Soft Matter, 9 (2013) 1772.
[11] Brennen C. E., Fundamentals of Multiphase Flow (Cambridge University Press) 2005.
[12] de Gennes P. G., Brochard-Wyart F. and Quéré D., Capillarity and Wetting Phenomena - Drops, Bubbles, Pearls, Waves (Springer) 2004.
[13] Kanellopoulos A. G. and Owen M. J., Trans. Faraday Soc., 67 (1971) 3127.
[14] Paulsen J. D., Burton J. C., Nagel S. R., App thu-raib S., Harris M. T. and Basaran O. A., Proc. Natl. Acad. Sci. U.S.A., 109 (2012) 6859.
[15] Bianc A. L., Clanet C. and Quéré D., Phys. Rev. E, 69 (2004) 016301.
[16] Supporting information, http://arxiv.org/abs/1309.6339.
[17] Hoang A. and Kavehpour H. P., Phys. Rev. Lett., 106 (2011) 254501.
[18] Carlson A., Quang M.-D. and Amber G., Phys. Rev. E, 85 (2012) 045302.
[19] Eddi A., Winkels K. G. and Snoeijer J. H., Phys. Fluids, 25 (2013) 013102.
[20] Eggers J., Lister J. R. and Stone H. A., J. Fluid Mech., 401 (1999) 293.
[21] Tanner L. H., J. Phys. D, 12 (1979) 1473.
[22] Yokota M. and Okumura K., Proc. Natl. Acad. Sci. U.S.A., 108 (2011) 6395.
[23] Vogel N., Belsle R. A., Hatton B., Wong T.-S. and Aizenberg J., Nat. Commun., 4 (2013) 2176.
[24] Redon C., Brochard-Wyart F. and Rondelez F., Phys. Rev. Lett., 11 (1991) 016301.
[25] Khesghi H. S. and Scriven L. E., Chem. Eng. Sci., 46 (1991) 519.
[26] Craster R. V. and Matar O. K., Rev. Mod. Phys., 81 (2009) 1313.
[27] Steinhuis B., Spicer P. T. and Shen A. Q., Langmuir, 22 (2006) 5308.
[28] Reiter G., Sharma A., Casoli A., David M.-O., Khannan R. and Auroy P., Europhys. Lett., 512 (1999) 46.
[29] Reiter G., Sharma A., Khanna R., Casoli A. and David M.-O., J. Colloid Interface Sci., 214 (1999) 126.
[30] Israelachvili J. N., Intermolecular and Surface Forces (Academic Press) 2011.
[31] Zhang W. and Lister J., Phys. Fluids, 11 (1999) 2454.