Morphology and dynamics of droplet coalescence on a surface

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The coalescence of a pair of droplets on a surface is investigated experimentally with images from detailed flow visualisations revealing the morphology of the process. It is found that they merge and evolve to a final state with a footprint that is peanut like in shape, with bulges along the longer sides resulting from the effects of inertia during spreading. The associated dynamics involve a subtle interplay between (i) the motion of the wetting process due to relaxation of the contact angle and (ii) a rapid rise in free-surface height above the point where coalescence began due to negative pressure generated by curvature. During the early stages of the motion, a traveling wave propagates from the point of initial contact up the side of each droplet as liquid is drawn into the neck region, and only when it reaches the apex of each do their heights start to decrease. A further feature of the rapid rise in height of the neck region is that the free surface there overshoots significantly its final equilibrium position; it reaches a height greater than that of the starting droplets, producing a self-excited oscillation that persists long after the system reaches its final morphological state in relation to its footprint.

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INTRODUCTION

Droplet coalescence is an important feature of a multitude of processes such as raindrop formation, emulsion polymerisation, ink-jet printing, coating, and multiphase flows; it continues to be relevant in areas of recent scientific and technological developments, for example in lab-on-a-chip devices for chemical assay [1].

Considerable effort has been devoted to studying free-droplet coalescence occurring within a second continuous fluid phase—for example, aqueous droplets within air or oil. Depending on the initial conditions under which such droplets are brought together, the process can evolve to one of two states—they either bounce off each other or merge fully to form a larger droplet (which might subsequently divide). A key parameter that determines the eventual outcome for impacting droplets is their speed [2]. More recently, the physical properties of free droplets and the fluid surrounding them have been considered in order to determine nondimensional parameters that map out the boundaries between the possible outcomes [3–5]. Similar studies have been undertaken for the case of a droplet impacting with a liquid surface [6,7]; under conditions where a droplet is placed gently on the surface, a series of partial coalescence events take place, each ejecting a smaller droplet [8]. A particular difficulty in modeling the physics of free-droplet coalescence using conventional hydrodynamics is that of capturing the very beginnings of the process, and in general a cutoff length is used which provides an assumed boundary shape at the start of the event [9].

A second scenario, one which has received less attention but is just as important practically, concerns the coalescence of two droplets, residing on a solid, nonporous surface. In addition to the effects of surface tension seeking to draw droplets together and viscosity which acts to slow the process, there is now the added feature of the presence and motion of a three-phase contact line. An example of this is when liquid condenses onto a partially wetting cold surface to form so-called "breath figures" [10]. Early work examined the size distribution of such droplets as they grew and merged, but recently there has been a focus on the dynamics of the coalescence event itself, from both an experimental and a theoretical perspective [11,12]. In addition to studying spontaneous droplet coalescence in a condensation chamber, Narhe *et al.* [13,14] used a syringe to position one droplet next to another in an attempt to explore the coalescence event in more detail; oscillation of the coalescing bulk was observed and attributed to kinetic energy imparted to the system at the start of the process. Menchaca-Rocha *et al.* [15] investigated the coalescence of two nonwetting droplets on a surface with the initial contact taking place away from the three-phase line while Ristenpart *et al.* [16] explored the other extreme—that of droplets merging on a highly wettable substrate. The attendant problem of a single drop spreading on a surface has received considerably more attention with the rate of droplet spreading having been determined experimentally under a wide variety of conditions [17]. The modeling challenges are no less formidable than they are in the case of free droplets—predicting the motion of the contact line remains a fundamental problem with conventional hydrodynamic approaches requiring a mechanism to prevent the stress becoming singular at the wetting line [18–20].

This paper presents a series of experimental results which reveal the morphology and complexities of the dynamics associated with the coalescence of partially wetting droplet pairs on a surface. They show that self-excitation of the process occurs by the triggering of a capillary wave, as opposed to imparted kinetic energy as previously thought, before evolving to a final, peanutlike, equilibrium shape.

EXPERIMENTAL METHOD

A schematic of the apparatus is shown in Fig. 1. The test surface comprised of a standard glass microscope slide

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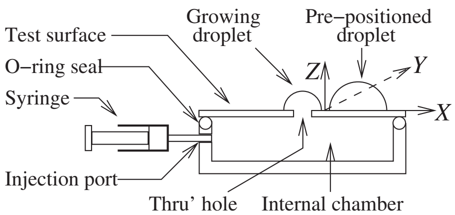

FIG. 1. Schematic of the droplet coalescence apparatus.

(roughness Ra 5.6 nm) with a 1-mm hole drilled through its center. Before experimentation, the surface was rinsed with excess distilled water and cleaned with acetone in an ultrasonic bath for 10 min. The slide was then rinsed with deionized water, dried with a microfiber cloth, and baked in an oven for 20 min at 85 °C. After cooling to room temperature, it was used within 30 min of preparation. A micropipette was used to preposition a droplet of known volume on the surface such that its footprint radius R_0 at the start of coalescence would be the same as the one to be grown adjacent to it using a micrometer-driven syringe to pump fluid very slowly through the chamber and out of the hole in the slide. R_0 was kept below 3 mm to ensure negligible flattening due to gravity. A high-speed camera (Kodak Ektapro Model 4540mx) mounted on a microscope captured the event at between 4500 and 13 500 frames per second, with illumination provided by a 150-W halogen source positioned to give good contrast. Recording of the dynamics lasted less than a second; a further comparison of the merged droplet shape was made after 1 min to verify no further movement had occurred.

Two liquids were used—distilled water (viscosity $\mu=1.07$ mPa s, surface tension $\sigma=74.0$ mN/m, density $\rho=1000$ kg/m^3, dynamic contact angle, 64° advancing and 58° receding) and a glycerine-water mixture ($\mu=5.7$ mPa s, $\sigma=70.5$ mN/m, $\rho=1045$ kg/m^3, dynamic contact angle, 56° advancing and 49° receding). The Ohnesorge number defining the ratio of the viscous time scale to the inertial time scale, $\mathrm{Oh}=\mu/\sqrt{\rho\sigma D}$, where $D=2R_0$ is the droplet diameter, is of the order of 0.001 and 0.01 for water and glycerine droplets, respectively, indicating that inertial effects are dominant in all cases.

RESULTS

Images of the evolution of the coalescence process, observed from directly above, are provided in Fig. 2. The black represents the liquid domain, with white "glare points" [21] in the region where the surface lies close to horizontal. The symmetry of the event confirms that the hole in the slide has no influence on the dynamics. At the instance of coalescence, the neck region spreads rapidly, driven by the negative curvature along the interface and the relaxation of the contact angle to its equilibrium value, in the Y direction—that is, perpendicular to the line of droplet centers. Simultaneously, there is a corresponding growth in the height H (Z direction) above the point of initial droplet contact. Figure 3 plots the lateral spread of the neck with time $T(s)$ for different-sized water and glycerine droplet pairs. Lelah and Marmur [22]

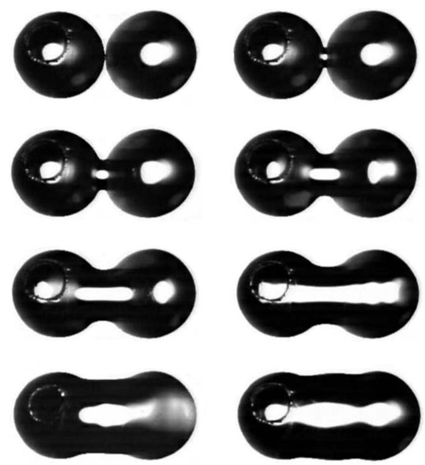

FIG. 2. Coalescence of a droplet pair (distilled water, initial radii $R_0=2.5$ mm) as viewed from directly above, at times 0, 0.777, 1.888, 4.111, 6.33, 8.55, 16.33, and 60 ms.

showed that the spreading rate of a single droplet could be correlated using $A=kT^n$, where A is the footprint area of the liquid-solid contact and k and n empirical coefficients. For the case of droplet coalescence, πR_c^2 is taken to be equivalent to A, where R_c is the semiwidth of the neck, giving $R_c=\sqrt{(kT^n/\pi)}$.

The data in Fig. 3 lead to values for n between 0.62 and 0.8 and values for k (cm^2 s^{-n}) between 0.82 and 2.9. Although these are towards the upper end of those found for the spreading of a single droplet [17], they show that spreading during coalescence occurs on a similar time scale. Furthermore, scaling the time with $\sigma/(\mu R_0)$ to give τ and the semiwidth of the neck with $2R_0$ to give d_m (as defined in [16]), and using the scaling relationship $d_m\propto\tau^\alpha$, gives α values between 0.42 and 0.57 during the initial phase ($0<T<0.01$). Interestingly, these values are remarkably close to those observed for the coalescence of two spreading droplets, which takes place on a completely wettable surface [16].

Figure 3 also shows that the motion of the wetting line is not completely smooth in the latter stages of spreading. This is due to a self-excited capillary wave, as discussed later,

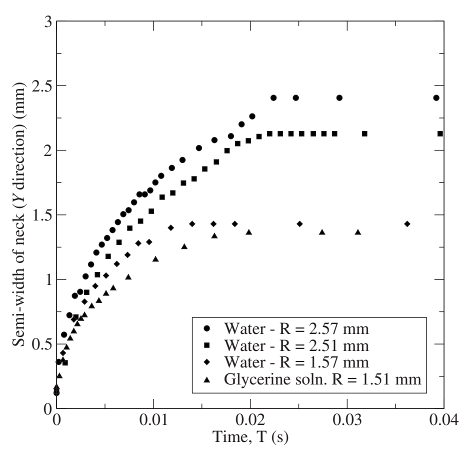

FIG. 3. Growth in the semiwidth of the neck (Y direction) as the wetting line moves perpendicular to the line of droplet centers.

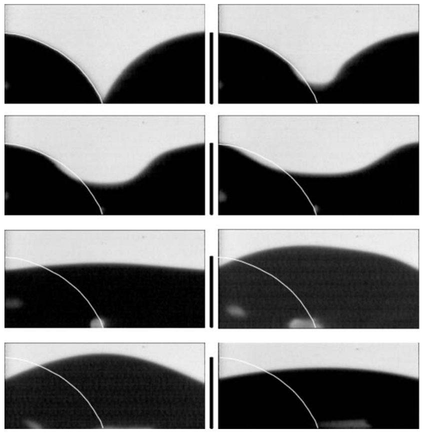

FIG. 4. Coalescence of a droplet pair (distilled water, initial radii $R_0=1.6$ mm) as viewed from the side, at times 0, 0.555, 1.222 2.0, 5.44, 13.2, 46.2, and 212.11 ms. The vertical scale bar between each pair of images is 1.6 mm long, and superimposed on each image is the initial shape of the left-hand droplet.

affecting the local pressure field at the wetting line and consequently the speed of the interface. The final resting droplet, when viewed from above, is peanut like in shape, the middle side bulges caused by the inertia of the fluid behind the advancing interface during spreading. Contact angle hysteresis plays a role in determining this final shape since the droplet does not evolve to form a spherical caplet at long times, unlike those in a condensation chamber [13,14]. This may be due in part to the lack of subsequent condensation in the current arrangement; additionally, it has been observed that humidity can affect the spreading behavior due to modification of the surface properties [22].

Figure 4 comprises a set of images showing coalescence viewed from the side. The initial profile (taken at 0 ms) of the left-hand droplet has been superimposed on each image to show how, as time progresses, fluid is pulled from beneath the free surfaces located on either side of the neck, resulting in a traveling wave that moves at constant angular speed up the interface. This wave reaches the apex of the original droplets (taking 2 ms in the case shown) before their initial height begins to reduce. This suggests it is the negative pressure within the neck that is responsible for its growth, rather than the hydrostatic pressures of fluid above this point, as the latter would result in a decrease in the height of the droplets right from the very start of coalescence. This can also be observed in the images of drop coalescence by [23], although this was not explicitly commented upon at the time. Direct comparison between the growth in the semineck width and height proved difficult, particularly at early times, since exact alignment of the data at the start of coalescence was not possible to within reasonable error bounds.

Fluid inertia drives the rapidly rising height of the neck region above the point of coalescence and results in it overshooting its final equilibrium position (Fig. 4). This triggers a capillary wave that travels the length of the droplet ($\pm X$ direction) before being reflected back from the wetting line at the extremes of the droplets. During the reflection the contact line remains pinned—Fig. 2 confirms that there is no horizontal motion in the X direction—and the contact angle must lie between its advancing and receding limits; if the contact angle were to fall outside these values, the wetting line would move [24] and provide an additional mechanism for dissipation of the energy contained within the wave. This wave traverses the bulk several times, causing large oscillations in its height to occur, before being damped out through viscous effects. For the conditions shown in Fig. 4, the final equilibrium shape of the merged droplets was reached after 20 ms (Fig. 3), although the capillary wave is not completely dissipated until ≈200 ms. The experiments also reveal that the rate of growth of the neck height is very similar for all droplet pairs investigated, while oscillations for the more viscous solution are less severe in amplitude and decay more quickly; see Fig. 5.

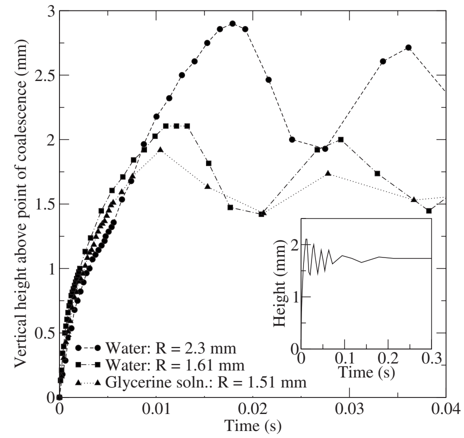

FIG. 5. Height of the merged bulk above the point of coalescence. The inset graphic shows the decay of oscillatory behavior for a water droplet pair of initial radius 1.6 mm.

Following [13], the period of oscillation, τ, for a freely suspended droplet, radius R, can be estimated from $\tau=\sqrt{(2\pi\rho R^3/3\sigma)}$. Basing R on the initial radius gives relaxation times of 18 ms, 11 ms, and 11 ms compared to values (taken from Fig. 5) of 20 ms, 15 ms, and 15 ms, for droplet pairs of radius (and composition) 2.3 mm (water), 1.61 mm (water), and 1.51 mm (glycerine solution), respectively. These results are in reasonable agreement given the significant difference in the geometry of the two systems and that the droplets considered here are in contact with a surface. In addition, by taking the vertical height of the interface above the contact point of the droplets, H, as equivalent to the radius of the neck in the case of free-droplet coalescence, it is possible to equate capillary and inertial forces through a scaling argument, [9,25]

$$\frac{H}{R_0}=c\left(\frac{T}{\sqrt{\rho R_0^3/\sigma)}}\right)^{1/2}. \quad (1)$$

Regression gives values for c between 0.98 and 1.29, which are in agreement with those found for the coalescence of free droplets [23,26,27]. We also note that the oscillations observed by Narhe *et al.* [13,14], in their experiments involving the mechanical positioning of one droplet next to another, were attributed entirely to the kinetic energy imparted to the system as a result of the deposition; conversely, for droplets formed in a condensation chamber they found no evidence of oscillations. Contrary to this the present work shows that self-excited oscillations arise as part of the coalescence process and are not necessarily the result of externally imposed disturbances.

SUMMARY

The intricate dynamics associated with droplet pairs coalescing on a nonporous surface and the accompanying changes in morphology are revealed. Features of the coalescence event have been observed previously: (i) the rate of spreading over the surface is similar to that observed in the coalescence of highly wetting drops [16] and (ii) the dynamics of the wave triggered at the start of the event is similar to that observed in the coalsescence of nonwetting drops [15]. However, the current work illustrates that, for the case of partially wetting drops, the dynamics results from a subtle interplay between the lateral movement of the wetting line at the point of contact due to the relaxation of the contact angle and the corresponding rise in height there due to the negative pressure generated by the curvature of the interface.

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