How geometry determines the coalescence of water drops

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The coalescence of water drops on a substrate is studied experimentally. We focus on the rapid growth of the bridge between the two drops, which just after contact ensues from a balance of surface tension and liquid inertia. For drops with contact angles well below 90°, we find that the bridge grows with a self-similar dynamics that is characterized by a size $h \sim t^{2/3}$. By contrast, the geometry of coalescence changes dramatically for contact angles close to 90°, in which case the global drop size becomes important. We present scaling arguments that quantitatively capture the departure from the 2/3 law and show how a new asymptotic regime $h \sim t^{4/3}$ emerges at 90°. The model unifies the coalescence of sessile drops and freely suspended drops.

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The splitting and merging of liquid drops are key processes during cloud formation, condensation and splashing [1–3]. The rate at which these processes take place is very important for technologies involving sprays and printing [4, 5]. Breakup and coalescence are singular events during which the liquid topology changes from a single drop to multiple drops, or vice versa [6]. Near the singularity, i.e. right before the moment of pinch-off or just after coalescence has been initiated, a tiny bridge of liquid connects two macroscopic drops. The size of this bridge vanishes at the singularity and gives rise to power-law divergence of stress and speed.

The dynamics near pinch-off is universal in the sense that it is completely independent of initial conditions and drop size. For low-viscosity liquids such as water the bridge size vanishes as $\tau^{2/3}$, where $\tau$ is the time remaining before pinch-off [7, 8]. Interestingly, the situation is markedly different for the coalescence of spherical water drops: the bridge grows with time as $t^{1/2}$ and the prefactor depends explicitly on the drop size [9–12]. The outer scale enters the coalescence problem through the peculiar initial condition, which consists of two spheres touching at a single point. This geometry even modifies the scaling law with respect to pinch-off, as it strongly enhances the capillary forces that drive the coalescence.

In this Letter we reveal the coalescence dynamics of water drops on a substrate. This is of comparable practical interest to that of freely suspended drops, but now the influence of geometry becomes even more apparent (Fig. 1): the drop shape looks very different when viewed from the side or from the top. This situation was recently investigated for high-viscosity drops [13–15], with evidence for self-similar dynamics during the initial growth [16]. For water drops, by contrast, the initial coalescence dynamics has remained unknown. Two-dimensional inviscid theory for “coalescing wedges” suggest a 2/3 exponent [17–19], as for pinch-off, but experiments for water drops on a substrate were interpreted using the classical 1/2 law [20]. In addition, it is not known whether and how the substrate wettability influences the coalescence.

Here we access the coalescence of water drops on a substrate with previously unexplored length and time scales. By comparing “conical drops” to “spherical drops”, we explicitly demonstrate how the dynamics can be manipulated by changing the liquid geometry. We present scaling arguments that quantitatively account for all observations, and in particular capture the dependence on contact angle $\theta$. The key result is that for $\theta < 90^\circ$ the initial coalescence is self-similar and displays a 2/3 exponent. However, the range over which this asymptotics can be observed is continuously reduced upon approaching $\theta = 90^\circ$. In this limit, our theory recovers the 1/2 exponent and thus unifies the coalescence of sessile drops and freely suspended drops.

Experimental setup. — Two drops of pure water (milli-Q, surface tension $\gamma = 72$ mN.m$^{-1}$) are grown at the tip of flat dispense needles and get in contact with transparent glass substrates that are covered with two different fluorinated coatings, leading respectively to equilibrium contact angles $\theta_{eq} = 65^\circ$ and $\theta_{eq} = 75^\circ$. Coalescence is achieved by very slowly advancing the contact lines, and hence the static advancing angles $\theta = 73^\circ$ and $\theta = 83^\circ$ actually determine the interface angle at the moment of contact. In order to avoid dynamical effects, the approach speed of the two contact lines is always smaller than 20 $\mu$m.s$^{-1}$ (the initial speed of coalescence measured experimentally is about 2.5 m.s$^{-1}$). The shape of each drop can be adjusted by moving the needle up and down. There is a position of the needle where the drop takes a nearly perfectly conical shape [Fig. 1(a)]. Such conical shapes appear as wedges in side-view [Fig. 1(b)], and are very advantageous for revealing coalescence dynamics — as will be demonstrated, the straight interface enhances the range over which scaling can be observed.

The spatial and temporal resolution required for capturing the initial stages of coalescence is achieved by combining high-speed recording and long-range microscopy. We use two synchronized high-speed cameras to image the coalescence simultaneously from the side and from below [Fig. 1(b-c)]. A Photron SA1.1 is coupled to a long-
FIG. 1: (a) Coalescence geometry for “conical” drops. The inset shows a cross-section of the liquid bridge, which here is sketched as a circle of contact angle \( \theta \). (b) Side-view snapshot of the two drops on the last frame before contact. The two needles holding the drops can be seen at the top of the image. (c) Bottom-view image of the liquid bridge of width \( d \) 500 \( \mu \)m after contact. (d) Sideview of the bridge of height \( h_0 \) that joins the two drops 278 \( \mu \)s after contact. The advancing contact angle \( \theta \) determines the geometry at contact.

distance microscope (Navitar 12X Zoom coupled with a 2X adapter tube) and records images from the side with a resoving power of 4.8 \( \mu \)m/pixel. Combined with backlight diffusive illumination, it can record up to 200,000 frames/s. For the bottom viewing imaging, we use an APX-RS combined with a Navitar 6000 lens with a resolving power of 2.7 \( \mu \)m/pixel. Reflective illumination allows for a frame rate of 90,000 frames/s. Once the drops are in contact and coalesce we measure the shape and evolution of the liquid bridge using a custom-made edge-detection algorithm in Matlab. It is based on a convolution procedure that finds the maximum image intensity slope in every frame. Contact time is chosen half-way in between the last frame where no bridge is observed and the first frame where we can measure the bridge height.

Conical drops. — A snapshot of the bridge profile during coalescence of two conical drops is presented in Fig. 1(d). In this side-view, the drops appear as nearly perfect wedges of contact angle \( \theta = 73^\circ \), connected by a thin bridge of height \( h_0 \). The bridge height grows rapidly in time and emits a capillary wave on the surface of the drops, as can be seen from the still image. Note that the bridge shape is markedly different from highly viscous coalescing drops, for which no such waves were observed [16]. This suggests that for water drops, which have a low viscosity, the dynamics is limited by liquid inertia rather than by viscous effects.

To reveal the growth dynamics of the bridge, we measure the evolution of the minimum height \( h_0 \) as a function of time after contact \( t \) [Fig. 2(a)]. Experiments are extremely reproducible and data correspond to an average over 6 different coalescence events. The diamonds in Fig. 2(a) clearly suggests a power-law growth of the minimum height, \( h_0 \sim t^{2/3} \). This regime over which this scaling is observed covers more than 3 decades in time and more than 2 in space, until \( h_0 \) is of the order of the initial size of the conical drops (around 1 mm) at time \( t > 5 \) ms. Inspired by results from pinch-off [6], we now attempt to collapse the experimental bridge profiles using a similarity Ansatz. The wedge-like shape of a conical drop does not provide any length scale, apart from the size of the needle. However, this large scale feature is not expected to influence the very early stages of coalescence, leaving the local bridge height \( h_0 \) as the only characteristic length scale of the problem. We therefore suggest that the bridge dynamics is governed by a similarity solution of the form

\[
h(x, t) = h_0(t) \mathcal{H}(\xi), \quad \text{with} \quad \xi = x/h_0.
\]  

This scaling is verified in Fig. 2(b), comparing side-view profiles for a single experiments at 5 different times after contact. The collapse of the experimental data confirms that the bridge shape is preserved during the initial stages of coalescence; the coalescence dynamics is indeed self-similar.

The appearance of a 2/3 exponent suggests that the coalescence dynamics is governed by a balance between surface tension, \( \gamma \), and inertia characterized by the liquid density, \( \rho \). Namely, this same scaling was obtained for inviscid liquids, for pinch-off of drops [7] and for merging of two-dimensional wedges [17–19]. In the present context, however, the force balance has singular behavior when the contact angle approaches \( \theta = 90^\circ \). This can be seen from the capillary pressure in the bridge, which scales as

\[
P_{\text{cap}} \sim \frac{\gamma}{w}, \quad \text{with} \quad w = \left(\frac{\pi}{2} - \theta\right) h_0.
\]  

The width \( w \) is defined in Fig. 1(d) and provides the characteristic curvature \( \kappa_{xz} \sim 1/w \) of the interface in the \((x, z)\)-plane. The curvature diverges at the moment
FIG. 2: Coalescence of conical drops. (a) Height of the bridge \( h_0 \) (diamonds) and its width \( d \) (triangles) as a function of time. Data are averaged over 6 experiments, statistical error bars indicate reproducibility. The contact angle is \( \theta = 73^\circ \) at the moment the drops come into contact. The solid line is the prediction (4) with a prefactor \( D_0 = 0.89 \). The dashed corresponds to (5).

(b) Rescaled profiles \( H = h(x,t)/h_0(t) \) versus \( \xi = x/h_0(t) \) for 5 different times \( t = 27.5, 72.5, 122.5, 197.5 \) and \( 397.5 \) \( \mu \)s after contact. The collapse reveals self-similar dynamics at the early stages of coalescence.

(c) Comparison of the experimental profile (background snapshot) and the numerical similarity solution from two-dimensional potential flow (solid line, from [18, 19]). The numerical curve actually corresponds to \( \theta = 75^\circ \), which was slightly rescaled here to match \( \theta = 73^\circ \).

of contact where the bridge size goes to zero, and this effect is dramatically enhanced for contact angles near \( 90^\circ \). The very strong capillary pressure (2) drives the rapid flow of liquid into the bridge, yielding a dynamical pressure

\[
P_{\text{iner}} \sim \rho v^2 \sim \rho \left( \frac{h_0}{T} \right)^2. \tag{3}
\]

Balancing these two pressures, one gets the scaling law for the bridge growth

\[
h_0 = D_0 \left[ \frac{\gamma}{\rho (\frac{\pi}{2} - \theta)} \right]^{1/3} t^{2/3}. \tag{4}
\]

Fitting this to the diamonds in Fig. 2(a) gives a numerical constant of order unity, \( D_0 = 0.89 \), suggesting that the balance is correct. Clearly, the scaling law and the underlying similarity hypothesis must break down when the contact angle \( \theta \to 90^\circ \), due to the vanishing denominator of (4).

Before pursuing this limit in more detail, it is interesting to compare our experiments to previously obtained similarity solutions for two-dimensional coalescing wedges [18, 19]. While the scaling law in this two-dimensional inviscid theory is consistent with (4), the numerically obtained profile \( H(\xi) \) does not capture the shape observed experimentally. This is revealed in Fig. 2(c), where we overlap the experimental profile and the two-dimensional potential flow solution (red solid line). Unlike the experiment, the theoretical profile is extremely flattened at the bottom of the bridge, and the capillary waves on the drop surface are much more pronounced. This discrepancy with two-dimensional theory suggests that the three-dimensional nature of coalescence cannot be ignored. Namely, the bridge exhibits a second curvature in the \((y,z)\)-plane, which scales as \( \kappa_{yz} \sim h_0/d^2 \) [Fig. 1(a), inset]. Since the bridge topology is a “saddle”, this curvature is of opposite sign compared to \( \kappa_{xz} \sim 1/w \).

The curvature \( \kappa_{yz} \) can influence the coalescence, provided that it is of comparable magnitude – the width of the bridge \( d \) should thus have the same \( 2/3 \) power-law evolution during the initial growth. Assuming the cross-section in Fig. 1(a) is a circular arc of (advancing) contact angle \( \theta \), one actually predicts

\[
d/ h_0 = \frac{2 \sin \theta}{1 - \cos \theta}. \tag{5}
\]

To test this hypothesis we measure \( d \) from the bottom-view [Fig. 2(a), triangles]. Indeed, the initial dynamics for \( d(t) \) is consistent with the \( 2/3 \) power law. The dashed line is the prediction by (5) with \( \theta = 73^\circ \). This indeed gives a good description of the data. We thus conclude that both principal curvatures \( \kappa_{xz} \sim \kappa_{yz} \) are comparable, making the problem inherently three-dimensional (Fig. 1).

Spherical drops. — A more natural geometry for drop coalescence is of course encountered for spherically shaped drops (Fig. 3). The role of the contact angle becomes very clear in this case: the drops will initially touch at the contact line when \( \theta < 90^\circ \), while contact is established above the substrate when \( \theta > 90^\circ \). In the latter case, the initial growth will not be affected
by the substrate and the bridge dynamics is identical to that of freely suspended drops [21]. Intriguingly, the growth exponent for spherical drops without a substrate is 1/2, with a prefactor depending on the drop size [9–12]. This strongly contrasts the 2/3 scaling proposed in Eq. (4), which is completely independent of drop size. Here we concentrate on the transition between these scaling regimes, by studying spherical drops on a substrate with \( \theta \) near 90\(^\circ\).

The results shown in Fig. 3 correspond to a coalescence experiment with \( \theta = 83^\circ \) and a macroscopic radius of curvature \( R = 1.45 \) mm. These spherical drops were obtained by lowering the distance in between the needles and the substrate. Once again, we characterize the growth of the liquid bridge from side view. Figure 3 shows that \( h_0 \) initially follows a 2/3 power law, as for the conical drops. However, the prefactor is larger by a factor of about 1.3. This agrees very well with the \( \theta \)-dependence suggested by our scaling analysis: the contact angle is now only 7\(^\circ\) from the divergence at 90\(^\circ\), while in Fig. 2 the difference was 17\(^\circ\). Indeed, the dashed line in Fig. 3 corresponds to (4) and describes our data using the same prefactor \( D_0 = 0.89 \).

However, at times \( t > 2 \cdot 10^{-4} \) s, we observe a departure from the 2/3 scaling that was not observed for conical drops. This effect can be associated to the presence of an outer scale \( R \) in the problem. The geometry sketched in the upper inset of Fig. 3 is that of two intersecting circles of radius \( R \), from which we find the meniscus size:

\[
\frac{w}{R} = \sin \theta - \left[ 1 - \left( \frac{h_0}{R} + \cos \theta \right) \right]^{1/2}.
\]

While for asymptotically small \( h_0 \) this expression is identical to the wedge-shape of (2), it captures the spherical geometry that is particularly important near 90\(^\circ\). With this refinement, the bridge dynamics can be predicted over the whole experimental range as

\[
\frac{D_0^2 \gamma t^2}{\rho} = h_0^2 R \left[ \sin \theta - \left[ 1 - \left( \frac{h_0}{R} + \cos \theta \right) \right]^{1/2} \right].
\]

The red solid line in Fig. 3 compares this prediction to the experimental data, without fitting parameter (again \( D_0 = 0.89 \)). The agreement is confirmed even when analyzing the logarithmic derivative, or apparent exponent, \( \alpha = d \ln h_0 / d \ln t \). The lower inset of Fig. 3 shows that the departure from the \( \alpha = 2/3 \) asymptotics is indeed very well captured by (7).

Discussion. — Our results reveal that coalescence dynamics is dictated by the geometry at the moment two drops come into contact. For contact angles well below 90\(^\circ\), the bridge dynamics is self-similar with a size growing as \( t^{2/3} \). The geometric interpretation of coalescence, in particular (6) and (7), reveals a transition at \( \theta = 90^\circ \). Namely, the 2/3 scaling is valid over a limited range \( h_0 \ll R/\left(\pi/2 - \theta\right) \), for which the unperturbed meniscus can be approximated by a wedge. This asymptotic regime completely disappears at \( \theta = 90^\circ \). In this limit \( w \sim h_0^2/R \), and a new scaling law \( h_0 \sim t^{1/2} \) emerges. This limit of our theory indeed recovers the coalescence law for freely suspended spherical drops [10, 11]. We thus conclude that the change in exponent from 2/3 to 1/2 is due to the change in geometry at contact, which evolves from “merging wedges” to “merging spheres”. Our results highlight the key importance of geometry on the coalescence, and provides a way to manipulate the dynamics of merging drops.

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