Modeling the coalescence of sessile droplets

M. Sellier^{1,a)} and E. Treluyer^{2,b)}

¹*Department of Mechanical Engineering, University of Canterbury, Private Bag 4800, Christchurch 8140, New Zealand*

²*Université Pierre et Marie Curie, Batiment Esclangon, Case courrier 164, 4 place Jussieu, 75252 Paris Cedex 05, France*

(Received 29 January 2009; accepted 7 May 2009; published online 19 June 2009)

This paper proposes a simple scenario to describe the coalescence of sessile droplets. This scenario predicts a power-law growth of the bridge between the droplets. The exponent of this power law depends on the driving mechanism for the spreading of each droplet. To validate this simple idea, the coalescence is simulated numerically and a basic experiment is performed. The fluid dynamics problem is formulated in the lubrication approximation framework and the governing equations are solved in the commercial finite element software COMSOL. Although a direct comparison of the numerical results with experiment is difficult because of the sensitivity of the coalescence to the initial and operating conditions, the key features of the event are qualitatively captured by the simulation and the characteristic time scale of the dynamics recovered. The experiment consists of inducing coalescence by pumping a droplet through a substrate which grows and ultimately coalesces with another droplet resting on the substrate. The coalescence was recorded using high-speed imaging and also confirmed the power-law growth of the neck. © 2009 American Institute of Physics. [DOI: 10.1063/1.3154552]

I. INTRODUCTION

The coalescence of sessile droplet has recently been identified as a potential mechanism to mix reagents in microfluidic systems.¹ The advancing technologies to displace and control discrete droplets open up new opportunities in digital microfluidics.^{2–4} An example of the recent breakthroughs allowed by a deeper understanding and control of the coalescence of droplets is the development of improved coatings for dew collection.⁵ In addition to the potential technological interest, the coalescence of sessile droplets is a fascinating fluid dynamical event which encompasses challenging modeling features such as a free surface and a dynamic contact line. The ability to accurately capture these features is paramount to the development of open microfluidic technologies. The modeling of the contact line motion is still a very active area of research and the coalescence constitutes an excellent benchmark problem to assess the ability of the models to capture the contact line dynamics. The phenomenon has recently been studied experimentally, see Refs. 3 and 6–10, for example, but very few modeling attempts have been reported and the case of partially wetting droplets has not previously been explored. Diez and Kondic¹¹ considered the coalescence of fully wetting droplets as a benchmark problem for the computational method they developed for quasi-three-dimensional unsteady flows of thin liquid films on a solid substrate. The work of Menchaca-Rocha *et al.*¹² is also noteworthy. They studied the coalescence of two mercury drops experimentally and numerically. They found a good agreement between the two but the fluid/substrate system was chosen to minimize the wetting effects. The experimental results reveal

^{a)}Electronic mail: mathieu.sellier@canterbury.ac.nz. URL: <http://www.mech.canterbury.ac.nz/people/sellier.shtml>.

^{b)}Electronic mail: emmanuel.treluyer@wanadoo.fr.

FIG. 1. Top view of an imaginary droplet system. The red line indicates the footprint of the droplet system.

a lack of apparent universal behavior. For example, the growth rate of the neck joining the two coalescing droplets varies considerably depending on how the droplet coalescence is induced, the size of the droplets, and the wetting behavior of the system.⁷

Beysens and co-workers^{6-8,10} studied extensively the coalescence of sessile droplets experimentally and theoretically. They distinguished three stages of the droplet coalescence as follows:¹⁰

- (1) An initial stage where the contact line does not move appreciably. A liquid bridge (or neck) nucleates between the parent drops and grows linearly with time T perpendicular to the substrate and with $T^{1/2}$ parallel to the substrate. Note that this growth rate was observed experimentally by Kapur and Gaskell⁹ and also by Ristenpart *et al.*⁵ for fully wetting droplet systems. The latter group of authors invoked a mass conservation argument to justify this growth rate.
- (2) An intermediate stage where the contact line starts to move and where the bridge relaxes exponentially, eventually creating an ellipsis like drop.
- (3) A final stage where, limited by the contact line motion, the drop slowly relaxes to a circular shape. The dynamics of this process is six or seven orders of magnitude slower than that predicted by the bulk hydrodynamics.

In this paper, we propose a very intuitive scenario to explain the coalescence dynamics. This scenario relies on simple geometrical considerations. It assumes that the neck dynamics can be described by considering the intersection of the droplet footprint contours. This scenario provides a natural explanation for the variety of behaviors observed experimentally. This simple argument is developed in Sec. II and Sec. III to VI provide numerical and experimental evidences which support the proposed view.

II. A SIMPLE VIEW ON THE COALESCENCE DYNAMICS

We propose a description of the neck growth inspired by the work of Diez and Kondic.¹¹ A schematic of the system of droplets considered is given in Fig. 1. Droplets 1 and 2 have radii R_1 and R_2 , respectively. Both radii grow with time as the droplets spread. The neck bridging both droplets is perpendicular to the line joining the centers of droplets 1 and 2 (O_1 and O_2 , respectively)

and is located at a distance d_1 from the center of droplet 1 and d_2 from the center of droplet 2. During the neck growth, in virtue of Pythagoras' theorem the neck semiwidth R_x must satisfy

$$R_x^2 = R_1^2 - d_1^2, \quad (1)$$

$$R_x^2 = R_2^2 - d_2^2. \quad (2)$$

The observed fact that during the neck growth the extent of the droplet system remains approximately constant suggests the assumption whereby $d = d_1 + d_2$ remains constant. Using this assumption, the previous two equations can be combined to obtain an expression for the semiwidth of the neck as follows:

$$R_1^2 + R_2^2 - 2R_x^2 - d^2 + 2\sqrt{(R_1^2 - R_x^2)(R_2^2 - R_x^2)} = 0. \quad (3)$$

This nonlinear equation can be solved for R_x and d_1 and d_2 can be recovered from Eqs. (1) and (2).

A particular case of interest is that of the coalescence of a symmetric pair of droplets spreading under the action of surface tension only. The capillary induced spreading of a droplet has been studied by Tanner.¹³ He showed theoretically and confirmed experimentally that the radius of the footprint of a single droplet spreading grows according to the power law $R_{1,2} \approx AT^\alpha$, where T is the time, A is a constant related to the volume of the droplet, and the exponent α is typically 0.1.¹³ His analysis holds for small contact angles and in the creeping flow regime. This result was later confirmed by others.^{14,15} In the symmetric case for which $R_1 = R_2$, Eq. (3) reduces to

$$R_x = \sqrt{A^2 T^{2\alpha} - \left(\frac{d}{2}\right)^2}, \quad (4)$$

a result previously proposed by Diez and Kondic.¹¹

The next sections provide numerical and experimental evidence to support this simple view on the coalescence dynamics.

III. DESCRIPTION OF THE DROPLET COALESCENCE MODEL

A. Governing equations

Droplet coalescence is a fluid mechanics problem and as such is governed by the Navier–Stokes equations with appropriate boundary and initial conditions. The computational expense of modeling three-dimensional free surface problems and the ill-defined nature of the boundary condition at the dynamic contact line calls for the problem to be simplified. Indeed, there is an incompatibility in the contact line region where the liquid, gas, and solid meet between the normally accepted assumption that the liquid adheres to the solid surface and the fact that the liquid must displace the gas from the surface for the droplet to be in motion. This incompatibility is known as the contact line paradox. We adopt here the lubrication approximation which reduces the three-dimensional problem to a two-dimensional one by neglecting inertia terms and averaging quantities across the thickness of the fluid layer. Moreover, the contact line singularity is relieved using the disjoining pressure model proposed by Schwartz and Eley.¹⁴ This model assumes a thin precursor film of thickness H^* ahead of wetting lines and relates the observed contact angle for partially wetting systems to intermolecular forces that become important for liquids of submicroscopic dimensions. It is somehow artificial since it introduces a fictitious precursor film not observed for partially wetting systems but it has been shown to reproduce the dynamics of single droplets spreading on partially wetting substrates under certain conditions.^{14,16} The resulting governing equations read

$$\frac{\partial H}{\partial T} = \nabla \cdot \left(\frac{H^3}{3\mu} \nabla P \right), \quad (5)$$

$$P = -\sigma \nabla^2 H - \Pi(H, H^*), \quad (6)$$

where the droplet thickness normal to the substrate $H(X, Y, T)$ and the pressure $P(X, Y, T)$ are the dependent variables, σ is the surface tension, and μ is the dynamic viscosity. The disjoining pressure term is given by

$$\Pi(H, H^*) = \frac{(n-1)(m-1)}{H^*(n-m)} \sigma (1 - \cos \Theta_s) \left[\left(\frac{H^*}{H} \right)^n - \left(\frac{H^*}{H} \right)^m \right], \quad (7)$$

where n and m are the exponents of the interaction potential and Θ_s is the equilibrium contact angle. Note that the disjoining pressure term is zero for a fully wetting system since $\Theta_s = 0$ for such systems. Equation (5) expresses the conservation of mass and Eq. (6) expresses the balance of normal stresses at the interface. Notwithstanding the corrections in the contact line region, a steady solution of Eqs. (5) and (6) is a paraboloid of revolution. Based on the equilibrium configuration of a droplet of volume V_0 lying on a substrate with equilibrium contact angle Θ_s , a characteristic droplet radius R_0 and maximum thickness H_0 can be defined. Indeed, if we assume the equilibrium droplet to be a paraboloid of revolution, its volume will be $V_0 = (\pi/2)H_0R_0^2$ and its contact angle $\Theta_s = \arctan(2H_0/R_0)$ or $\Theta_s \approx 2H_0/R_0$ in the limit of small $\epsilon = H_0/R_0$ relevant to the lubrication approximation. The latter can be rearranged to express the droplet radius and thickness as

$$R_0 = \sqrt[3]{\frac{4V_0}{\pi\Theta_s}}, \quad (8)$$

$$H_0 = \frac{\Theta_s}{2} \sqrt[3]{\frac{4V_0}{\pi\Theta_s}}. \quad (9)$$

Introducing these scales along with $T_0 = 3\mu R_0^4 / \sigma H_0^3$ in the governing equations, Schwartz and Eley¹⁴ showed that the governing equations could be recast into

$$\frac{\partial h}{\partial t} = \nabla \cdot (h^3 \nabla p), \quad (10)$$

$$p = -\nabla^2 h - B \left[\left(\frac{h^*}{h} \right)^n - \left(\frac{h^*}{h} \right)^m \right], \quad (11)$$

where h^* is the dimensionless precursor film thickness and $B = 2(n-1)(m-1)/h^*(n-m)$. The constants (n, m) are set to (9, 3) which corresponds to a Lennard-Jones interaction potential. The pressure P is scaled with $P_0 = \sigma \epsilon / R_0$. The solution is known to depend on the precursor film thickness^{14,16} as thicker films tend to overpredict the spreading rate. This model is somewhat related to the one proposed (but not implemented) by Andrieu *et al.*,⁶ although they suggest a different approach to alleviate the singularity at the contact line.

B. Solution procedure

The governing equations are solved in the commercial finite element package COMSOL. This package has been proven particularly convenient and accurate to model thin layer flows.¹⁷ Details on the implementation can be found in Refs. 17 and 18. Given our model and scales, a paraboloid of radius and height equal to unity is the equilibrium configuration for a droplet of volume $(\pi/2)H_0R_0^2$ (dimensional) or $\pi/2$ (dimensionless). As an initial condition to the coalescence problem, we choose two droplets out of equilibrium with an initial height $2H_0$ (or 2 in dimensionless units) and volume $(\pi/2)H_0R_0^2$, the centroids of which are placed at $1.8R_0$ apart such that the coalescence occurs when the droplets have almost reached their maximum spread radius. The computational domain Ω , shown in Fig. 2, is a $(4R_0 \times 2R_0)$ rectangle, which is discretized uniformly with $\sim 10\,000$ elements. The problem has two symmetry lines: one that joins the centers of

FIG. 2. Computational domain and corresponding mesh.

each droplet ($y=0$) and one perpendicular to it which intersects halfway through the centers ($x=2$, dimensionless units). The initial profile for each of the droplets (1 and 2) is $h_{1,2}(r) = \max[h^*, h^* + 2(1 - 2r^2)]$, where r is the distance from the centroid of each droplet located at (1.1,0) and (2.9,0) in dimensionless units. Only half of the droplet system is modeled for obvious symmetry reasons. Quadratic Lagrange elements are used to increase the accuracy of the solution and natural boundary conditions are applied at the edge of the computational domain such that $\nabla h \cdot \vec{n} = \nabla p \cdot \vec{n} = 0$, where $\vec{n}$ is the normal to the boundary pointing outward. Since the droplets remain at all times in the computational domain, the solution is insensitive to the latter.

C. Validation of the solution procedure

To validate the implementation of the solution procedure, a set of equations similar to Eqs. (10) and (11) but with an analytical solution is first solved. The solution emulates the “spreading” of a “drop” of constant volume V_{val} governed by the equations

$$\frac{\partial h}{\partial t} = \nabla \cdot (h \nabla p), \quad (12)$$

$$p = -\nabla^2 h. \quad (13)$$

This case is nonphysical but bears the same features as the original system and admits a self-similar analytical solution,¹⁹ which can be used to assess the validity of the numerical solution. Diez and Kondic¹¹ showed that for an initial profile which approximates the delta function and Neumann boundary conditions, the evolution of the maximum film thickness h_{val} satisfies

$$h_{\text{val}}(t) = \left(192 t_{\text{val}} \left(1 + \frac{t}{t_{\text{val}}} \right) \right)^{1/3} \quad (14)$$

with

$$t_{\text{val}} = \frac{\pi}{3 V_{\text{val}}} \frac{1}{192}.$$

Figure 3 shows the analytical and numerical solutions with $V_{\text{val}} = \frac{\pi}{3}$ and a 0.01 thick precursor film. The maximum difference between the numerical solution and the analytical solution is around 5% and it occurs for early times when the effect of the choice of initial profile is most significant. The good agreement between the two confirms the correct implementation in COMSOL of the system of equations and boundary conditions and provides the necessary confidence in the reliability of the results.

FIG. 3. Comparison of the COMSOL and analytical solutions for the maximum “film thickness” h_{val} . The black circles indicate the COMSOL numerical solution and the red line indicates the analytical one.

IV. COALESCENCE DYNAMICS: NUMERICAL RESULTS

Figure 4(a) shows the evolution of the footprint of a system of droplets initially separated by $d=1.8R_0$ and with a precursor film of thickness 0.04. Note that the presence of a precursor film makes the definition of the contact line ambiguous. In the present work, it is arbitrarily defined as the points where the film thickness is 0.05, a value slightly larger than the precursor film thickness to filter out small film thickness fluctuations occurring in the contact line region. It is expected that this minor shift will have minor consequences on the description of the coalescence. Adopting the notation of Narhe *et al.*,⁷ R_x and R_y denote the lengths of the minor axis (semiwidth of the neck) and major axis, respectively [see Fig. 4(a)]. An animated sequence of the droplet coalescence can be seen in Fig. 4(b). The sequence clearly shows the major stages of the droplet coalescence reported in Refs. 6–8 and 10: the independent initial spreading of each droplet, the initial contact and appearance of a neck between the two droplets, the growth of the neck at almost constant lateral extent, and the contraction of the droplet to recover a spherical cap configuration. A more quantitative picture is achieved by considering the free surface profiles along the symmetry axis ($y=0$ and $x=2$ in Figs. 5(a) and 5(b), respectively). Note that the droplet profiles are artificially distorted because of the disparity between the in-plane length scale R_0 and the length scale normal to the plane H_0 . Figure 5(a) shows that the coalescence starts approximately at $t=10^{-2}$. During the neck growth, the major axis length does not vary appreciably. It starts decreasing and therefore the contact line starts receding when the two droplets have fully merged. The neck profile along $x=2$ can be seen in Fig. 5(b). The symbols represent the numerical results while the full lines represent parabolas of the form

$$h_{\text{neck}}(y,t) = h_{\text{neck}}^{\text{max}}(t) \left(1 - \left(\frac{y}{R_x(t)} \right)^2 \right) \quad (15)$$

fitted through them. The fit at all times is excellent indicating a form of self-similarity of the neck profile. The functions $h_{\text{neck}}^{\text{max}}(t)$ and $R_x(t)$, which represent the maximum height of the neck and its semiwidth, are plotted in Fig. 6. Clearly, both functions increase with time to reflect the fact that the neck grows with time. According to Eq. (4) in Sec. II, we expect the square of the semineck width to vary according to $A^2 T^{2\alpha} - (d/2)^2$. Figure 6 shows a curve of this form fitted through the numerical results. The agreement between the numerical results and the fitted curve is optimum

FIG. 4. Numerical solution: (a) Plot of the footprint of the droplet system at different times. (b) Animated sequence of the droplet coalescence (enhanced online).

for A^2 and 2α equal to 2.18 and 0.23, respectively (the correlation coefficient is around 0.97). Note that the value of the exponent α is close to 0.1, the expected value from Tanner's analysis.¹³ For fully wetting systems, Diez and Kondic¹¹ reported a value for α of 0.12. Figure 6 also reports the computed ratio of the semiwidth of the neck to its height ($R_x(t)/h_{\text{neck}}^{\text{max}}(t)$). Remarkably, after a short initial transient, this ratio settles to an almost constant value of ≈ 0.9 . This feature has been observed experimentally by Narhe *et al.*¹⁰ and the authors reported a constant value of order unity.

FIG. 5. Numerical solution: (a) Plot of the variation in the free surface profile along $y=0$. Full lines are drawn as a guide to the eye. (b) Plot of the variation in the free surface profile along $x=2$, i.e., the neck profile, with the corresponding fitted curves of the form of Eq. (15).

This can be easily explained by the fact that R_x and $h_{\text{neck}}^{\text{max}}(t)$ do not vary independently. Indeed, while the width of the neck is set by Eq. (3), the height of the neck is imposed by the fact that the neck is a minimal surface subject to the contact angle constraint which requires that $\theta_s = \arctan(2h_{\text{neck}}^{\text{max}}(t)/R_x(t))$ or $h_{\text{neck}}^{\text{max}}(t) \approx \theta_s R_x(t)/2$. Since Θ_s is equal to $2H_0/R_0$, its dimensionless analog θ_s must be equal to 2 which explains why the semiwidth to height ratio of the neck ($R_x(t)/h_{\text{neck}}^{\text{max}}(t)$) is approximately equal to 1.

Another result of interest is the position of the center of gravity (COG) of the system computed according to

$$x_{\text{COG}} = \frac{\int_{\Omega^*} (h - h^*) x d\omega}{\int_{\Omega^*} (h - h^*) d\omega} \quad (16)$$

for the x -coordinate. By symmetry the COG lies on the symmetry line ($y=0$). Figure 7 shows the variation in the x -coordinate of the COG as follows:

FIG. 6. Log-log plot of the neck height ($h_{\text{neck}}^{\text{max}}$) and neck semiwidth (R_x) variation obtained numerically. A curve of the form of Eq. (4) is fitted through the numerical results for R_x^2 .

FIG. 7. Plot of the computed variation in the x -coordinate of the COG of the system of droplets (black line with circle) and the left-hand droplet (blue line with diamond). Full lines are drawn as a guide to the eye.

- The whole droplet system. In that case $\Omega^* = \Omega = [0, 4][0, 2]$ in Eq. (16) (dimensionless units).
- The left-hand side of the computational domain which corresponds to the left-hand droplet precoalescence. In that case $\Omega^* = [0, 2][0, 2]$.

As previously observed experimentally by Andrieu *et al.*,⁶ the computed location of the COG of the whole droplet system does not change during coalescence. Although this result is obvious for symmetry reasons in the present case, it also holds for nonsymmetric systems. In contrast, the COG of the left-hand droplet remains fairly constant in the early stage of the coalescence (during the neck growth) but then converges rapidly toward the COG of the whole system during the later stage of the coalescence. The right-hand droplet obviously behaves symmetrically. This rapid motion corresponds to a mass transport on a very short time scale. If controlled in a suitable fashion, this form of capillary actuation could have interesting microfluidic applications.

However two features are not captured by the simulation because they are not inherently accounted for in the model. First, for substrates with large contact angle hysteresis, the equilibrium shape of the final coalesced droplet is not a spherical cap. It is normally more elongated in one direction having a peanut shape.⁹ This can be explained by the fact that in the neck region, the contact line advances and therefore adopts the advancing contact angle while it recedes in the perpendicular direction, thereby taking the receding contact angle value. Hysteresis is not included in the model and therefore such phenomena cannot be possibly captured. The other unresolved features are the oscillations usually accompanying the coalescence. Although it has not been established that these have an effect on the equilibrium configuration, they result from inertia effects and therefore are not encompassed in the present model.

V. COMPARISON WITH PREVIOUS STUDIES

The coalescence dynamics appears to be at least qualitatively reproduced but how well do the results fit in with the existing literature? The work of Beysens and co-workers^{6-8,10} provides an invaluable source of experimental data. In their analysis, the authors distinguish the three stages of the coalescence reported in Sec. I. The early stage corresponds to the nucleation of a liquid bridge between the two parent drops. During that stage the capillary number $Ca = \mu U_{cl} / \sigma$ is large because the characteristic contact line velocity U_{cl} is large. The present model based on the lubrication approximation is unlikely to capture that stage adequately since this approximation only holds for

FIG. 8. Plot of the computed variation in the minor axis R_x with time for two different initial droplet separations ($d=1.8$ and $d=1.5$). The plot also shows the fitted curves according to Eq. (18).

small Ca . During the intermediate stage, the neck grows until the droplet system adopts an ellipsis like shape. The growth is limited by the contact line motion and the corresponding capillary number is much lower such that the lubrication approximation is more likely to be valid. The authors attribute the final stage to condensation or evaporation causing a very slow variation in the residual droplet.

An exact comparison with the experimental data of Narhe *et al.*¹⁰ is impossible because as highlighted by these authors, the coalescence dynamics is very sensitive to the initial conditions, the droplet deposition procedure, and the material properties. We will therefore restrict ourselves to order of magnitude estimates. At the intermediate stage, Narhe *et al.*¹⁰ argue that the neck has an exponential growth of the following form:

$$L^* = 2R_x = a(1 - e^{-t^*/\tau}), \quad (17)$$

where a is a constant, t^* a dimensionless time, and τ is a time constant. For diethylene glycol on a silicon substrate making an equilibrium contact angle of $\approx 26.3^\circ$ the authors found $\tau \approx 12T_{\text{coal}}$, where $T_{\text{coal}} = R_0(\mu/\sigma)$ is a characteristic coalescence time. Remembering that $\Theta_s \approx 2H_0/R_0$, T_{coal} is related to the present time scale T_0 through $T_0 = 3(2/\Theta_s)^3 T_{\text{coal}}$ or $T_0 = 246.6T_{\text{coal}}$. For later times, the authors observed a linear growth of the neck.⁷ This suggests fitting the numerical results with curves of the following form:

$$R_x(t) = A_1 e^{-t/t_c} + A_2 + A_3 t. \quad (18)$$

Figure 8 shows the variation in the semiwidth of the neck when the initial distance between the droplets is $d=1.8$ and $d=1.5$. The figure illustrates the strong effect of the initial conditions. Clearly, if the droplets are closer at the time of the coalescence, they have more energy in the form of surface tension energy which speeds up the dynamics of the process. The figure also confirms that the numerical results are remarkably well fitted with curves of the form of Eq. (18). The optimal values for the time constant t_c are 0.046 for $d=1.8$ and 0.015 for $d=1.5$. This corresponds to $T_c = 11.3T_{\text{coal}}$ for $d=1.8$ and $T_c = 3.7T_{\text{coal}}$ for $d=1.5$. The time constant is in close agreement with the experimental results of Narhe *et al.*,¹⁰ ($\tau \approx 12T_{\text{coal}}$) for $d=1.8$ but out by a factor 3 for $d=1.5$. However, given the fact that the numerical simulation does not perfectly replicate the experimental setup of Narhe *et al.*,¹⁰ we cannot hope for better than an order of magnitude agreement between the simulation and the experiment. The numerical results suggest that the

FIG. 9. Sketch of the experimental setup (side view).

linear growth of the semiwidth of the neck could be attributed to the contact line dynamics instead of a condensation process as stated by Narhe *et al.*⁷

VI. COALESCENCE DYNAMICS: SOME EXPERIMENTAL RESULTS

To test further the simple model proposed in Sec. II, the simple experiment sketched in Fig. 9 was setup. The concept of the experiment is similar to the one proposed by Kapur and Gaskell⁹ and is not meant to be exhaustive but to test the hypothesis of Sec. II. One of the droplets is marked with food dye and deposited on the substrate using a standard micropipette. The other is pumped with a syringe through a small hole drilled in the substrate. The droplet grows until it meets and coalesces with the other static droplet lying on the substrate. The static droplet is placed at a distance from the hole such that the radius of each droplet is approximately equal at the time of coalescence. Note that a precise control of the coalescence event is hard to achieve.

The substrate is a 3 mm thick acrylic sheet (Plexiglas(R) GS clear F00). It was cut to $\sim 20 \times 20$ mm² and two 1 mm drill holes were made. The first hole in the edge of the acrylic piece is 7 mm deep; the second is through the top surface and intersects at right angles with the first drill hole. A small hollow of 1 mm in diameter steel tube was coated with rapid curing epoxy and inserted in the edge of the acrylic. After curing this forms a water tight friction fit seal. Plastic tubing was expanded over the protruding steel tube and connected to a syringe. The substrate was cleaned with ethanol between experiments. Demineralized water was used for the experiment. The static contact angle was measured with a KSV CAM 200 goniometer by depositing a droplet on the substrate, recording the equilibrium droplet shape, and fitting this to the Young–Laplace equation. It was found to be $68^\circ \pm 2^\circ$. The coalescence was recorded using a Redlake MotionPro X3 high-speed camera at a rate of 1380 fps. The event was monitored from above to be able to measure the neck width.

A sequence of pictures capturing the droplet coalescence can be seen in Fig. 10. The pictures illustrate the rapid growth of the neck up to ~ 0.024 s. Subsequent pictures show that the contact

FIG. 10. Picture sequence of the coalescence. The sequence reads from left to right and top to bottom.

line dynamics is then much slower. This coincides with the later stage of the coalescence described by Narhe *et al.*¹⁰ At all times, the contact line motion appears to be smooth at the observed length and time scales. Another interesting feature is the lack of mixing between the two droplets. Up to $t=0.051$ the boundary between the two droplets is clearly distinct. At later stages, the dye starts to penetrate the clear droplet through the sides and diffusion starts to contribute to the mixing. This lack of mixing suggests that the coalescence may not improve mixing efficiency as much as anticipated. This picture sequence supports the simple model described previously, whereby the neck grows as a result of the spreading of each individual droplet.

The width of the neck was evaluated directly from the pictures using the program ImageJ, a public domain, Java-based image processing program developed at the National Institutes of Health.²⁰ The millimeter paper in the background was used as a reference dimension. The resolution of the picture (512×1024 pixels) allowed a measurement of the neck width to within 0.05 mm (conservative estimate). Figure 11 shows a plot of the logarithm of R_x^2 versus the logarithm of t for the three sets of experiment recorded. In virtue of Eq. (4), one would expect a straight line with a slope equal to 2α . The very good fit between the experimental results and straight lines observed in Fig. 11 corroborates again the coalescence scenario described in Sec. II (the r -squared values range between 0.9725 and 0.996). The exponent α (equal to half of the coefficient in front

FIG. 11. Plot of the logarithm of the measured value of R_x^2 vs the logarithm of t .

of x in the legend) ranges between 0.3 and 0.39. This value is larger than the one expected for spontaneous spreading driven by capillary. However, this discrepancy may be attributed to three reasons as follows:

- In the experiments, the droplet diameter is more than twice the capillary length of water. The effect of gravity is therefore expected to be non-negligible. Lopez *et al.*²¹ showed that the radius grows with $t^{1/8}$ for a constant volume droplet forced to spread under the action of gravity.
- The droplet is not spreading with a constant volume since fluid is injected through the substrate. The spreading law of droplets with increasing volume is quite different from the one of spontaneously spreading droplets.^{22,23} For example, the radius of a droplet with a linearly increasing volume grows with $t^{1/2}$ and the exponent is strongly dependent on the injection rate.
- The contact angle is quite large and lies beyond the range for which lubrication approximation applies. For a static contact angle of 68° and assuming that $\tan \Theta_s = (2H_0/R_0)$, a value of 1.23 is obtained for $\epsilon = H_0/R_0$.

The variety of spreading laws for individual droplets could explain the wide range of coalescence dynamics observed experimentally. The present results establish a trend but a more carefully controlled experimental investigation is required to exactly relate the coalescence dynamics to the pumping rate and contact angle hysteresis. In particular, one of the shortcomings of the current experiment is the unquantified pumping rate.

VII. CONCLUSIONS

This paper proposes a possible scenario for the coalescence of sessile droplets. This scenario relies on simple geometrical considerations: it assumes that each droplet keeps on spreading as if the other one did not exist and the neck formation results from the intersection of the droplet footprint contours. As a result of this simple assumption, the neck width is shown to grow according to a power law, the exponent of which depends on the driving mechanism for the spreading. This idea is tested against numerical and experimental results. The numerical model is based on the lubrication approximation. In spite of the simplifying assumption, the main features of the coalescence dynamics are well captured: the independent spreading of each droplet, the nucleation of a liquid bridge, the growth of the neck until the system adopts an ellipse shape, and

the relaxation to a spherical cap. The numerical results have been convincingly compared to those of the existing literature for the intermediate stage. Indeed, the computed time constant representative of the contact line dynamics is found to be in the same range as the one found experimentally and reported by Narhe *et al.*¹⁰ High-speed imaging was also used to analyze the coalescence. The growth of the neck observed experimentally was also found to follow a power law but the exponent was two to three times larger than the one obtained in the numerical simulation. This difference is attributed to the difference in the spreading mechanisms: the spreading is capillary induced in the numerical simulation whereas it is induced by volume growth in the experiment. Beyond the numerical and experimental results presented here, this paper provided a missing unifying framework to explain the differences in coalescence dynamics observed experimentally.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to A. Clow for manufacturing the experimental device and to D. Sellier and J. MacPhee for carefully proofreading the manuscript.

- ¹H. A. Stone, A. D. Stroock, and A. Ajdari, *Annu. Rev. Fluid Mech.* **36**, 381 (2004).
- ²J. Atencia and D. J. Beebe, *Nature (London)* **437**, 648 (2005).
- ³W. D. Ristenpart, P. M. McCalla, R. V. Roy, and H. A. Stone, *Phys. Rev. Lett.* **97**, 064501 (2006).
- ⁴L. Y. Yeo, R. V. Craster, and O. K. Matar, *J. Colloid Interface Sci.* **306**, 368 (2007).
- ⁵M. Muselli and D. Beysens, *Science & Vie* **1091**, 90 (2008).
- ⁶C. Andrieu, D. A. Beysens, V. S. Nikolayev, and Y. Pomeau, *J. Fluid Mech.* **453**, 453 (2002).
- ⁷R. Narhe, D. Beysens, and V. S. Nikolayev, *Langmuir* **20**, 1213 (2004).
- ⁸R. Narhe, D. Beysens, and V. S. Nikolayev, *Int. J. Thermophys.* **26**, 1743 (2005).
- ⁹N. Kapur and P. H. Gaskell, *Phys. Rev. E* **75**, 056315 (2007).
- ¹⁰R. D. Narhe, D. A. Beysens, and Y. Pomeau, *EPL* **81**, 46002 (2008).
- ¹¹J. A. Diez and L. Kondic, *J. Comput. Phys.* **183**, 274 (2002).
- ¹²A. Menchaca-Rocha, A. Martínez-Dávalos, R. Núñez, S. Popinet, and S. Zaleski, *Phys. Rev. E* **63**, 046309 (2001).
- ¹³L. H. Tanner, *J. Phys. D* **12**, 1473 (1979).
- ¹⁴L. W. Schwartz and R. R. Eley, *J. Colloid Interface Sci.* **202**, 173 (1998).
- ¹⁵J. Diez, L. Kondic, and A. L. Bertozzi, *Phys. Rev. E* **63**, 011208 (2000).
- ¹⁶P. H. Gaskell, P. K. Jimack, M. Sellier, and H. M. Thompson, *Int. J. Numer. Methods Fluids* **45**, 1161 (2004).
- ¹⁷M. Sellier, Y.-C. Lee, H. M. Thompson, and P. H. Gaskell, *Comput. Fluids* **38**, 171 (2009).
- ¹⁸M. Sellier and S. Panda, *Int. J. Numer. Methods Fluids* (unpublished); (<http://www3.interscience.wiley.com/journal/108061200/issue>).
- ¹⁹R. Ferreira and F. Bernis, *Eur. J. Appl. Math.* **8**, 507 (1997).
- ²⁰T. J. Collins, *BioTechniques* **43**, S25 (2007).
- ²¹J. Lopez, C. A. Miller, and E. Ruckenstein, *J. Colloid Interface Sci.* **56**, 460 (1976).
- ²²H. E. Huppert, *J. Fluid Mech.* **121**, 43 (1982).
- ²³R. Chebbi, *J. Colloid Interface Sci.* **300**, 688 (2006).