Merging of Soap Bubbles and Why Surfactant Matters

Patricia Pfeiffer, Qingyun Zeng, Beng Hau Tan, and Claus-Dieter Ohl

1) Institute for Physics, Otto von Guericke University Magdeburg, Magdeburg 39106, Germany
2) Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371 Singapore, Singapore
3) Low Energy Electronic Systems, Singapore-MIT Alliance for Research and Technology, Singapore 138602, Singapore

(Dated: 23 January 2020)

The merging of two soap bubbles is a fundamental fluid mechanical process in foam formation. In the present experimental study the liquid films from two soap bubbles are brought together. Once the liquid layers initially separated by a gas sheet are bridged on a single spot the rapid merging of the two liquid films proceed. Thereby the connecting rim is rapidly accelerated into the separating gas layer. We show that due to the dimple formation the velocity is not uniform and the high acceleration causes initially a Rayleigh-Taylor instability of the liquid rim. At later times, the rim takes heals into a circular shape. However for sufficient high concentrations of the surfactant the unstable rim pinches off microbubbles resulting in a fractal dendritic structure after coalescence.

Soap bubbles, which merge with a flat film show a cascade of partial coalescence. This means a smaller bubble remains after the contact between bubble and film.

Here, we report about the merging of two soap bubbles at low approach velocity. Then a dimple forms, its shape just before coalescence is revealed through interferometry. Once the two films connect on a point-like liquid bridge, surface tension accelerates a rim connecting the two films radially outward. This process is studied with high-speed photography and an instability observed. While surfactants are important to stabilize the bubbles, we also demonstrate that they play a crucial part in the hydrodynamic merging process.

The soap bubbles are created by dipping tip of the syringes (Soft-Ject Insulin syringes with Luer connection, Henke-Sass, Wolf GmbH Germany) into a soap solution and inflating the flat film formed by pressing on the plunger. A bubble attached to the syringe tip is inflated to about 12 mm in diameter. Once two soap bubbles are created this way they are brought together. One of the bubbles is stationary and the second bubble is moved slowly towards the first with a translation stage (M1 micro manipulator, Helmut Saur Laborbedarf, Germany) at an approach velocity of ≈ 1 cm/s. During this approach the bubbles suddenly coalesce by forming a single soap film connecting the two bubbles (cf. supplementary material for a sketch of the experimental setup and Fig. 1). The dynamics of coalescence is observed with a high-speed camera (Photron AX200) at 22,500 or 67,500 frames/s (exposure time 1/900,000 s) and illuminated with either a white light source (Suger Cube Ulra, USHIO AMERICA, INC., USA) or a coherent light source (CW532-04 Series, Roithner Lasertechnik GmbH, Austria, CW laser, wavelength $\lambda = 532$ nm, intensity $\approx 2$ mW/cm²). To avoid electric charging of the two bubbles during the inflation at nozzle of the plastic syringes we connect both wetted tips of the syringes with a copper wire that is held on a fixed electric potential.

The bubbles are made of an aqueous solution of the anionic surfactant sodium dodecyl sulfate (Sigma-Aldrich, BioXtra $\geq 99.0\%$ (GC), critical micelle concentration (cmc) 7-10 mM at 20-25 °C). Two concentrations are used, namely 5 and 10 mM and their coefficient of surface tension has been measured with the capillary rise method to be $\sigma = 25 \pm 2$ mN/m.
and \( \sigma = 27 \pm 2 \text{ mN/m} \) for a 5 and 10 mM SDS solution, respectively. We measured their kinematic viscosity using an Ubbelohde viscometer, from which we calculated the dynamic viscosity, which is \( 1.01 \pm 0.02 \text{ mPa s} \) for both solutions.

Figure 1 is composed of selected snapshots from a high-speed imaging sequence showing the process of two bubbles merging. At the top of the first frame the syringe tips and the copper wire are visible. The bottom of this frame shows a darker area that is caused by liquid draining due to gravity. The first snapshot \((t = -44 \mu\text{s})\) is taken shortly before the bridging occurs. A weak fringe pattern is visible just before the two bubbles merge. The dashed circle at \( t = 44 \mu\text{s} \) indicates the point where the liquid bridge has connected the two films. Between \( t = 44 \mu\text{s} \) and \( t = 2489 \mu\text{s} \) the two bubbles merge. A compound bubble is formed through the sharing of a liquid film. The merged film will grow until the angle between the two soap films. Figure 2a just after coalescence demonstrates that the two films bridge between the crests of the dimple which is the shortest distance between the two films. Since the measurements are performed in transmission, the shortest distance has a bright fringe. That location is indicated in Fig. 2b with an arrow and is the zeroth order fringe \((k = 0)\). The distance between bright fringes of \( \lambda/2n \) \((n \) is the refractive index of the soap solution: \( n = 1.33) \) allows converting the line drawn in Figs. 2a and 2b into a height map of the air gap before and after coalescence, see Fig. 2d. The position of the fringes are determined by taking the mean gray values along several lines through the fringe pattern. The maximum thickness of the air film is \( 1.0 \pm 0.1 \mu\text{m} \). Repeating the experiment 50 times we find dimple heights between 0.4 \( \mu\text{m} \) and 1.0 \( \mu\text{m} \) at the moment of coalescence. The overall shape of the gap between the two films is sketched in Fig. 2d. Please note that the vertical axis is strongly magnified.

We now discuss the growth of the merged films starting from the location where the two films are bridged. Figure 3a shows a typical example of this merging dynamics. The dimpled region just before coalescence is indicated with a blue dotted circle and the arrow indicates the location of the liquid bridge. Bridging always happens on the crest of the dimpled region as shown in Fig. 3b. We see the rim expanding radially from the point of contact. Interestingly, that part of the rim which travels through the dimpled region has a dis-
torted and fuzzy front, while the part that travels outside is smooth and circular. Figure 3b shows a similar case with the only difference that the concentration of surfactant was doubled to [SDS]=10 mM. The liquid bridge forms on the lower left part of the dimpled region, again on a crest and the rim spreads circularly. In contrast the rim traveling through the dimpled region reveals an instability or modulation with a wavelength of \(44\) µm. Perturbations grow in the dimpled regime, i.e. \(44\) and \(89\) µm the smooth rim and the liquid bridge indicated with a blue circle and a red cross, respectively. The modulated rim that connects the two films propagates fastest through the dimpled region. (c) Sketch of the spreading rim from top and in side view. The rim propagates faster within the regime of the dimple (dashed blue circle) due to the higher curvature. In the side view the region which is already merged consists only of a single film, whereas still two separate films exist ahead of the rim.

We now address the mechanism destabilizing the rim’s circular shape. For this we estimate the acceleration \(G\) of rim due to surface tension \(\sigma\). Ignoring viscosity we balance inert-tia with the pressure gradient from surface tension, i.e.

\[
G = \frac{Du}{Dt} = -\frac{1}{\rho_H} \nabla p \approx -\frac{2\sigma}{\rho_H D^2},
\]

where \(u\) is the velocity of the fluid particle in the rim, \(\rho_H\) is the density of the liquid and \(\nabla p\) the pressure gradient. The latter we estimate with the Laplace pressure in the cylindrical rim of cross-section \(D\) and radius of curvature of \(\approx D/2\). Inserting suitable values for \(\sigma = 0.025\) N/m, \(\rho = 10^3\) kg/m\(^3\) and \(D = 1.6 \cdot 10^{-6}\) m we obtain a high values for the acceleration with \(G = 2 \cdot 10^6\) m/s\(^2\). While viscosity counteracts this acceleration we nevertheless expect this acceleration to act until viscosity has diffused. This picture has been confirmed with Volume of Fluid simulations in axisymmetry (cf. supplementary material for details to the simulations). Figure 4 depicts a simulation result for the parameters similar to the experimental material for details to the simulations). Figure 4 depicts a simulation result for the parameters similar to the experiment and accounting for viscous and compressible effects (solver Interfoam from the OpenFOAM framework). Within 0.5 µs the rim accelerates from 0 to a velocity of about 4.0 m/s.

Now we argue that this extreme acceleration of the rim from the liquid into the gas phase destabilizes the rim due to the Rayleigh-Taylor instability. The most amplified wavelength is \(\sqrt{\lambda_c}\) with \(\lambda_c = \sqrt{\sigma/(G\rho_H)}\), see Ref.\(^{18}\). Typical experimental values lie between 44 µm (as in Fig. 3b) at \(t = 89\) µs and 150 µm. Since the rim expands and hence the length-scale of the instability, the most unstable mode (i.e. how many lobes the rim has as a result of the instability) is taken as a quantitative measure. We obtain values for the unstable mode between 12 (as in Fig. 3b) and 44. Perturbations below a critical wavelength \(\lambda_c\) are stabilized by surface tension. The critical wavelength can be calculated as

\[
\lambda_c = \sqrt{\frac{\sigma}{G(\rho_H - \rho_L)}},
\]

where \(\rho_H\) and \(\rho_L\) are the densities of the heavier (water) and lighter (air) fluids, respectively. Since \(\rho_H \gg \rho_L\), we can neglect \(\rho_L\) in equation \((2)\).
The acceleration $G$ governs the dominant wavelength at the rim, which strongly depends on the dimple height. With an acceleration of $G = 2 \cdot 10^7 \text{m/s}^2$, $\lambda_c$ is $\approx 0.7 \mu\text{m}$.

The instability already occurs during bridging, and thus a diameter of the liquid bridge of 7 $\mu\text{m}$ with the initial wavelength of $\lambda_c/\sqrt{3} = 0.4 \mu\text{m}$ would lead to a wavelength of 44 $\mu\text{m}$ at a circumference of the rim of 2.4 mm. Thus, $\lambda_c \approx 0.7 \mu\text{m}$ seems an appropriate value.

The Rayleigh-Taylor instability leads to a pearling of tiny soap bubbles from the rim if the indentation is sufficiently large. The indentation leads locally to a higher curvature of the rim and thus a higher propagation velocity of the highly curved parts. The curvature decreases due to the reunion of the water columns and thus the velocity decreases. The rim becomes smooth after the propagation through the dimpled area and remains circular.

Upon the approach of two merging bubbles a dimple is formed between them. This is a general phenomenon when bubbles or droplets approach either each other or a substrate. The computed height of the dimple calculated using the Bragg equation agrees very well with the height in other experiments. The distance between the bubbles is shortest at the rim of the dimple and the film thickness at this point decreases, such that attractive van-der-Waals forces become important and lead to a rapid decrease of the film thickness. The point where the coalescence of the bubbles occurs is randomly distributed over the rim of the dimple.

The applied potential on the bubbles ensures reproducible results, however, a simple connection between the bubbles (i.e. a wire to exchange electric charges) yields the same results. In experiments without this potential, a deformation of the rim is only observed by chance. We speculate that the bubbles are charged by inflating them. A similar effect was investigated by Choi et al., who observed that droplets become charged during conventional pipetting.

The closure of the distorted rim depends strongly on the SDS concentration: with increasing amount of SDS more bubble pinch-off events are seen. However, when reaching the critical micelle concentration, a further increase of the bubble formation does not occur. The detachment of tiny soap bubbles from the rim is only possible, because more surface active molecules are available than necessary for the current surface. So the excess molecules can be used to create and stabilize a new surface in a much shorter time, which leads to the pearling of the droplets. The pearling is more pronounced directly after the formation of the liquid bridge than further away from the bridging point, since the distance of the films increases with distance from the bridging point and thus the closure dynamics slows down.

The measured wavelength of the indentation agrees with an impulsively acting Rayleigh-Taylor instability and growth by radial expansion. The high acceleration of the liquid within the first 50 ns after the coalescence, which is confirmed by simulations, induces the instability. Since the instability already occurs during bridging the instability timescale is consistent with the claim that the acceleration of the liquid is causing the instability.

Structures similar to those described in the current work were already found in similar systems at the receding rim of bursting fluid films or during the impact of a droplet on a fluid surface. Another work was provided by Thoraval et al., who investigated an impacting droplet on a liquid layer and found a formation of bubble rings in the impact region. Despite these structures look similar to those described in the current work, the mechanism of their formation differs.

In this work the coalescence of soap bubbles is studied. Prior to their coalescence the bubbles form a dimple and entrap a tiny volume of air. Upon merging, the rim of the spreading film is accelerated for a brief moment, simulations predict less than 1 $\mu$s. During that time a Rayleigh-Taylor instability sets in resulting in an instability of the rim front. The velocity of the rim is higher in the area of the dimple, due to a higher curvature in that regime and hence the velocity of the rim is faster. Depending on the surfactant concentration the entrapment of gas pockets is possible with increasing SDS concentration. However above the cmc no further effect of the SDS concentration on the instability of the rim is observed.

See supplementary material for a sketch of the experimental setup, details and snapshots of the simulations.

The Deutsche Forschungsgemeinschaft, DFG, is acknowledged for support within project DA 2108/1-1.

1B. B. Ferguson, C. Hinkle, and D. J. Wilson, “Foam Separation of Lead(II) and Cadmium(II) from Waste Water,” Separation Science 9, 125–145 (1974)

FIG. 4. Numerical simulations of the development of the rim radius over time (top row) and reaches a velocity of 4.0 m/s (center row). The rim accelerates within 0.5 $\mu$s to a velocity of 4.0 m/s, i.e. that results in an acceleration of $5 \cdot 10^7 \text{m/s}^2$ (bottom row). Dimple height: 1.6 $\mu$m, film thickness: 5.5 $\mu$m.
Merging of Soap Bubbles

2 A. K. Brown, A. Kaul, and J. Varley, “Continuous foaming for protein recovery: Part II. Selective recovery of proteins from binary mixtures,” Biotechnol. Bioeng. 62, 291–300 (1999)

3 R. G. Horn, L. A. D. Castillio, and S. Ohnishi, “Coalescence map for bubbles in surfactant-free aqueous electrolyte solutions,” Adv. Colloid Interface Sci. 168, 85 – 92 (2011)

4 R. R. Dagastine, R. Manica, S. L. Carnie, D. Y. C. Chan, G. W. Stevens, and F. Grieser, “Dynamic forces between two deformable oil droplets in water,” Science 313, 210–213 (2006)

5 R. Manica, J. N. Connor, S. L. Carnie, R. G. Horn, and D. Y. C. Chan, “Dynamics of interactions involving deformable drops: Hydrodynamic dimpling under attractive and repulsive electrical double layer interactions,” Langmuir 23, 626–637 (2007)

6 R. Manica, J. N. Connor, R. R. Dagastine, S. L. Carnie, R. G. Horn, and D. Y. C. Chan, “Hydrodynamic forces involving deformable interfaces at nanometer separations,” Phys. Fluids 20, 032101 (2008)

7 S. I. Karakashev and A. V. Nguyen, “Effect of sodium dodecyl sulphate and dodecanol mixtures on foam film drainage: Examining influence of surface rheology and intermolecular forces,” Colloids Surf. A 293, 229 – 240 (2007)

8 C. L. Henry and V. Craig, “Ion-specific influence of electrolytes on bubble coalescence in nonaqueous solvents,” Langmuir 24, 7979–85 (2008)

9 V. V. Yaminisky, S. Ohnishi, E. A. Vogler, and R. G. Horn, “Stability of Aqueous Films between Bubbles. Part 1. The Effect of Speed on Bubble Coalescence in Purified Water and Simple Electrolyte Solutions,” Langmuir 26, 8061–8074 (2010)

10 D. Y. C. Chan, E. Klaseboer, and R. Manica, “Film drainage and coalescence between deformable drops and bubbles,” Soft Matter 7, 2235–2264 (2011)

11 S. C. Ozan and H. A. Jakobsen, “On the effect of the approach velocity on the coalescence of fluid particles,” Int. J. Multiph. Flow 119, 223 – 236 (2019)

12 D. Valtkowska, K. Danov, and I. Ivanov, “Surfactants role on the deformation of colliding small bubbles,” Colloids Surf. A 156, 547 – 566 (1999)

13 L. Y. Clasohm, J. N. Connor, O. I. Vinogradova, and R. G. Horn, “The “wimple”: Ripple deformation of a fluid drop caused by hydrodynamic and surface forces during thin film drainage,” Langmuir 21, 8243–8249 (2005)

14 G. Pucci, D. M. Harris, and J. W. M. Bush, “Partial coalescence of soap bubbles,” Phys. Fluids 27, 061704 (2015)

15 D. Choi, H. Lee, J. S. Kang, G. Lim, D. S. Kim, K. H. Kang, et al., “Spontaneous electrical charging of droplets by conventional pipetting,” Scientific reports 3, 2037 (2013).

16 Y. Zhou, “Rayleigh–Taylor and Richtmyer–Meshkov instability induced flow, turbulence, and mixing. I,” Physics Reports 720-722, 1 – 136 (2017)

17 Y. Zhou, “Rayleigh–taylor and richtmyer–meshkov instability induced flow, turbulence, and mixing. ii,” Physics Reports 723-725, 1 – 160 (2017)

18 D. Sharp, “An overview of Rayleigh-Taylor instability,” Physica D 12, 3 – 18 (1984)

19 E. Klaseboer, J. Chevaillier, C. Gourdon, and O. Masbernat, “Film drainage between colliding drops at constant approach velocity: Experiments and modeling,” J. Colloid Interface Sci. 229, 274 – 285 (2000)

20 R. Manica, E. Klaseboer, and D. Y. C. Chan, “Dynamic interactions between drops – a critical assessment,” Soft Matter 4, 1613–1616 (2008)

21 B. Liu, R. Manica, X. Zhang, A. Buusomiëre, Z. Xu, G. Xie, and Q. Liu, “Dynamic interaction between a millimeter-sized bubble and surface microparticles in water,” Langmuir 34, 11667–11675 (2018)

22 L. R. Fisher, E. E. Mitchell, D. Hewitt, J. Ralston, and J. Wolfe, “The drainage of a thin aqueous film between a solid surface and an approaching gas bubble,” Colloids and Surfaces 52, 163 – 174 (1991)

23 R. C. A. van der Veen, T. Tran, D. Lohse, and C. Sun, “Direct measurements of air layer profiles under impacting droplets using high-speed color interferometry,” Phys. Rev. E 85, 026315 (2012)

24 M. H. W. Hendrix, R. Manica, E. Klaseboer, D. Y. C. Chan, and C.-D. Ohl, “Spatiotemporal evolution of thin liquid films during impact of water bubbles on glass on a micrometer to nanometer scale,” Phys. Rev. Lett. 108, 247803 (2012)

25 R. D. Richtmyer, “Taylor instability in shock acceleration of compressible fluids,” Commun. Pure Appl. Mathematik 13, 297–319 (1960)

26 J. Ding, J. Li, R. Sun, Z. Zhai, and X. Luo, “Convergent Richtmyer–Meshkov instability of a heavy gas layer with perturbed outer interface,” J. Fluid Mech. 878, 277–291 (2019)

27 Y. Zhou, T. T. Clark, D. S. Clark, S. Gail Glendinning, M. Aaron Skinner, C. M. Huntington, O. A. Hurricane, A. M. Dinitz, and B. A. Rennington, “Turbulent mixing and transition criteria of flows induced by hydrodynamic instabilities,” Physics of Plasmas 26, 080901 (2019)

28 K. Reysset and D. Quéré, “Bursting of a fluid film in a viscous environment,” Europhys. Lett. 76, 236–242 (2006)

29 H. Lhuissier and E. Villermaux, “Soap films burst like flagging flags,” Phys. Rev. Lett. 103, 054501 (2009)

30 S. T. Thoroddsen, M.-I. Thoraval, K. Takehara, and T. G. Etoh, “Micro-bubble morphologies following drop impacts onto a pool surface,” J. Fluid Mech. 708, 469–479 (2012)

31 M.-I. Thoraval, K. Takehara, T. G. Etoh, and S. T. Thoroddsen, “Drop impact entrapment of bubble rings,” J. Fluid Mech. 724, 234–258 (2013)