Physiochemical Hydrodynamics of Droplets and Bubbles Far from Equilibrium

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Droplets and bubbles are omnipresent in nature and industry. Often, they are subjected to gradients in concentration or temperature (or both). These gradients might change locally or evolve over time, placing the system far from its equilibrium. It gives rise to extraordinarily rich physics at the intersection of fluid dynamics, chemical engineering, and colloid and interface science, showcasing the importance of interdisciplinary research for the field of physiochemical hydrodynamics. Apart from its relevance in the context of climate change, solutions for energy storage and advancements in medical and industrial technologies, such out-of-equilibrium systems form the ideal scientific playground for young scientists to explore and encounter counterintuitive phenomena that stimulate their curiosity.

Objectives

During the Balzan research project Lohse's team aimed to explore well-defined examples of multi-component and multi-phase liquid systems involving droplets and bubbles, for which a successful quantitative description and one-to-one comparison between well-defined experiments, theory, and numerics could potentially be achieved and to identify the underlying physics. In particular, they are focusing on small-scale, idealized table-top experiments closely combined with theoretical and numerical modelling to study particles, drops, and bubbles under conditions that are far from equilibrium. For the latter, they consider droplets in density stratified mixtures (Part I) and droplets, particles, and bubbles at a water-ice interface during unidirectional solidification (Part II).

Part I: Immiscible droplets in a density stratified mixture

In this part the dynamics of an immiscible oil droplet in a stably and linearly stratified ethanol-water mixture was studied. In such a mixture, the ethanol fraction $w_e(y)$ increases linearly from the bottom to the top, as a consequence of which the mass density of the mixture $\rho(y)$ decreases linearly. When an immiscible oil drop is released into the stratified mixture it sinks towards the position where the density of the oil matches that of the surrounding liquid. During the descent, the ethanol concentration gradient applied over the drop leads to a gradient in surface tension along its surface, *i.e.*, the surface tension is larger at the bottom of the drop than at its top. To compensate this imbalance in surface tension, a downwards pointing Marangoni flow is generated, resulting in an upwards force that acts on the drop, against gravity. If the Marangoni flow is stable, the drop will stably levitate at a well-defined height above its density-matched position [1, 2]. However, an instability can be triggered, causing the Marangoni flow to become oscillatory, leading to the continuous bouncing of the oil droplet, see Fig. 1(*a*-*c*). The team looked in depth into the onset of the bouncing instability, what mechanism triggers it, and how it depends on the viscosity of the oil [1–3]. In short, they found that for oils with low viscosity ($\lesssim 10$ cSt) the instability is triggered once the Marangoni flow dominates over diffusion, resulting in a critical concentration gradient above which bouncing will occur. Alternatively, for high viscosity oils ($\gtrsim 50$ cSt), a critical drop size triggers the onset, as gravitational effects become too strong.

The dynamics and characteristics of a single bouncing cycle were studied in further detail, and scaling relations were obtained for the two heights in between which the drop bounces, as well as for the rising and sinking time [4]. The team then made use of numerical simulations that mimic the experiments in order to perform one-to-one comparisons, see Fig. 1(*d*), resulting in good qualitative and satisfactory quantitative agreement. The numerical simulations provided many more insights on physical quantities that are challenging to measure experimentally, such as the mass density of the mixture and the fluid velocity in close vicinity of the drop, see Fig. 1(*e*).

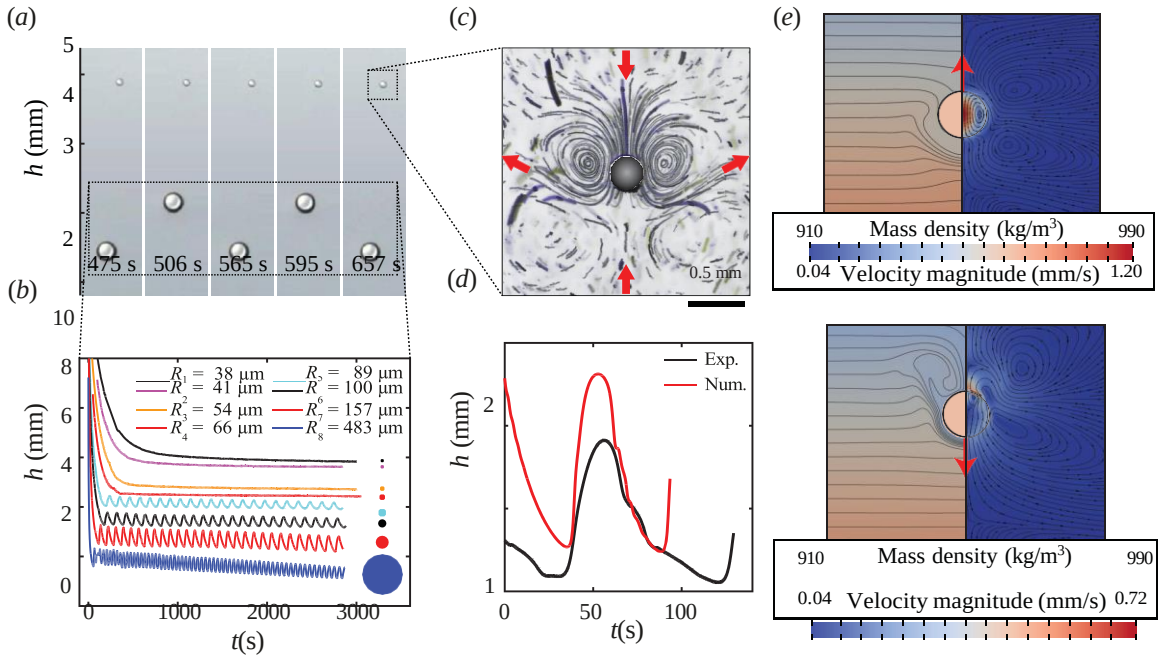

FIG. 1. (*a*) Successive snapshots of two 100 cSt silicone oil drops inside a linearly stratified ethanol-water mixture at times after they are released. The smaller drop ($R = 54 \pm 2$ µm) levitates at a constant height h, whereas the larger drop ($R = 143 \pm 2$ µm) bounces continuously above its density matched position, *i.e.*, above $h = 0$ [3]. (*b*) Trajectories of drops of different radii. Drops with radius R smaller than 66 µm levitate, while larger drops bounce [3]. (*c*) Streamlines around a levitating drop obtained by superimposing the trajectories of small tracer particles for an extended period of time (76.7 s). The red arrows indicate the flow directions [3]. (*d*) One-to-one comparison between the experimentally measured (black) and numerically determined (red) trajectory of a single bouncing cycle of a 100 cSt silicone oil drop with $R = 280 \pm 2$ µm inside a linearly stratified ethanol-water mixture [4]. (*e*) Snapshots of the numerical simulations showing the mass density of the surrounding liquid (left) and the velocity magnitude (right) around a rising and sinking drop, respectively [4].

Part II: Droplets, particles, and bubbles near a water-ice interface

The second part focuses on the unidirectional freezing of emulsions, suspensions, and sessile drops in order to study the behaviour of droplets, particles, and bubbles at a moving ice interface. A planar, slow-moving front is obtained by applying a thermal gradient over the sample and initiating freezing at the colder end. The front will then propagate with velocity V in the direction of the applied thermal gradient, *i.e.*, towards the warmer side.

When slowly freezing an emulsion, the dispersed silicone oil droplets interact with the advancing ice front. Experimental and numerical investigations have shown the importance of thermal Marangoni effects on the morphology of the ice front during this interaction [7]. Eventually, the drops are engulfed into the ice. As the front passes over a single droplet, it gets deformed and assumes a pointy tear-like shape once completely encapsulated, see Fig. 2(*a*). By increasing the advancing velocity V, *i.e.*, applying a larger thermal gradient, it turned out that the drops deform less, indicating that faster freezing is less intrusive for the shape of the frozen soft structures [5]. Thus, these deformations are mediated by interfacial flows in *nanometric* thin liquid films separating the non-solidifying dispersed droplets and the solidifying bulk. The flow profile is governed by the competition between repulsive, intermolecular interactions (disjoining pressure) and thermal Marangoni effects, see Fig. 2(*b*).
Aiming for a slightly more complex system, the team continued by looking into the unidirectional solidification of a double emulsion, *i.e.*, water-in-oil compound droplets submerged in water. Again, they observed that the compound droplets deform into pointy tear-like shapes as the solidification front passes over. Suddenly, however, a topological transition is triggered causing the compound droplet to burst and the interior water core to be expelled, see Fig. 2(*c*) [6]. High-speed imaging of the rapid bursting event (occurring within a millisecond) reveals the emergence of an expanding shock wave. We argue that the shock wave follows a heterogeneous cavitation event caused by the freezing of the encapsulating oil from the outside, which puts tension on the inner drop. While scanning the parameter space with respect to the size of the compound droplet we found that below a critical size the compound drops remain stable and do not burst, see Fig. 2(*d*) [6]. This critical behaviour is related to the existing theoretical models of nucleation and growth.

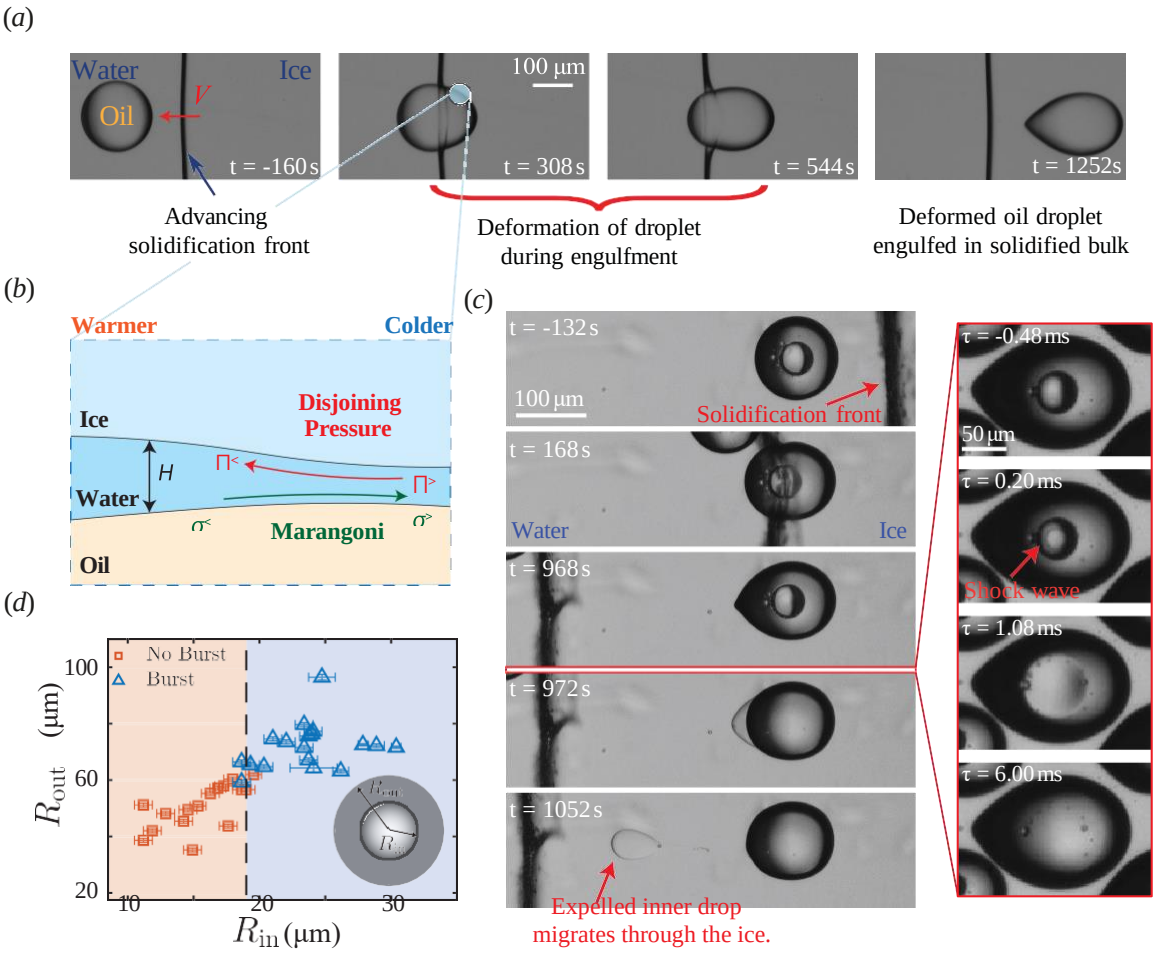

FIG. 2. (*a*) Top-view snapshots capturing the engulfment of a 5 cSt silicone oil droplet submerged in water by an advancing solidification front ($V = 0.4$ µm s^{-1}), *i.e.*, ice, first approaching and then passing over the droplet. At $t = 0$ the drop makes first contact with the front. The drop remains deformed in the solidified bulk after engulfment throughout the entire experiment (typically ~ 4 h) [5]. (*b*) Schematic visualizing of the thin intervening liquid film separating ice and oil. The flow within this thin film (and therefore its thickness H) is mediated by the competition between the disjoining pressure Π and thermal Marangoni effects. Depending on the profile of the thin film, the pressure within varies, which determines the local curvature of the oil-water interface and eventually the overall shape of the drop [5]. (*c*) Sequence of images capturing the engulfment of a water-in-oil compound droplet by a solidification front advancing at rate $V = 0.5\,\mu\text{m}\,\text{s}^{-1}$. The sudden topological transition (shown at $t \approx 968$ s) is captured through high-speed imaging, showing the emergence of a shock wave at the center of the inner drop that expands radially outward causing the compound droplet to burst. The expelled interior then migrates through the solidified bulk by a similar process to that of brine-pocket diffusion in sea ice [6]. (*d*) Phase space showing the dependence of the bursting phenomenon on the size of the compound droplet. Below a critical inner droplet size, $R_{crit} \approx 19$ µm, bursting does not occur [6].

Next, this line of research was extended to multiple particles in order to study their mutual interactions at a moving ice interface [8]. It was found that particles that are less thermally conductive than water repel each other, whereas more conductive particles attract and form clusters once frozen, see Fig. 3(*a-d*). We extend the existing models for single particle trapping in ice to multiple particles and find that the overall strength of the particle-particle interaction critically depends on the solidification front velocity and on the particle-front interaction. Moreover, it is the thermal conductivity mismatch between the particles and water that dictates the attractive/repulsive nature of the particle-particle interactions, highlighting the importance of thermal conduction during freezing.

Finally, and most recently, we started to investigate the freezing of a sessile drop sitting on a cold surface [9]. To overcome lensing effects of the sessile drop we only look at its cross-section by sandwiching the drop between two acrylic plates. As the water starts to solidify, air is rejected by the solidifying structure and accumulates at the moving front. Local supersaturation is achieved, causing heterogeneous nucleation of air bubbles near the ice interface, see Fig. 3(*e*). These bubbles initially grow diffusively but tend to a faster growth in a later stage. It is still an open research question on why this happens. If the front propagates, sufficiently fast the bubble growth is further restricted and the bubbles get trapped in the ice, assuming pear-like shapes. Remarkably, in a certain regime, the front does not advance quickly enough, and the bubbles grow continuously into elongated vertical tubes, see Fig. 3(*e*). The detailed dynamics of this phenomenon are yet to be revealed.

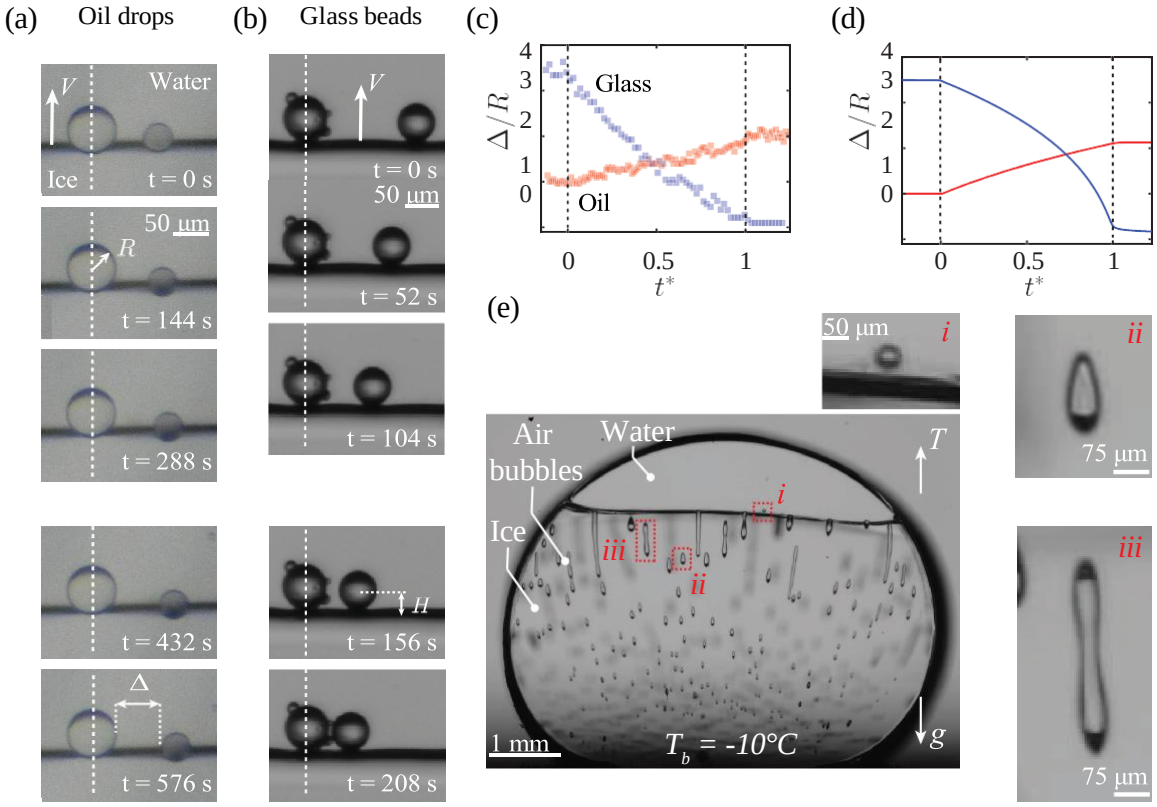

FIG. 3. Sequence of images capturing the particle dynamics of two (*a*) 50 cSt silicone oil droplets and (*b*) glass beads at an advancing solidification front in the reference frame of the larger particle. The velocity V at which the front propagates is only slightly larger than the critical velocity V_{crit}, that governs particle rejection or engulfment into the solidifying bulk [8]. (*c*) Experimentally determined and (*d*) theoretically predicted shortest lateral distance between the two particles $\Delta(t)$ as a function of normalised time t^*. The thermal conductivity mismatch between the particles and the surrounding water dictates whether they repel (oil drops, red) or attract (glass beads, blue) [8]. (*e*) Cross-section of a sessile drop, sandwiched between two acrylic plates, freezing from the bottom up. The temperature of the bottom plate is fixed at $T_b = -10\,^\circ$C. As the solidification front propagates air bubbles nucleate near the front (*i*) and grow. Dependent on the velocity of the front, the bubbles are engulfed either more quickly, resulting in pear-like shapes (*ii*), or are allowed to grow continuously for an extended period of time into long vertical tubes (*iii*) [9].

REFERENCES

[1] Y. Li, C. Diddens, A. Prosperetti, K. L. Chong, X. Zhang, and D. Lohse, Bouncing oil droplet in a stratified liquid and its sudden death, Physical review letters **122**, 154502 (2019).

[2] Y. Li, C. Diddens, A. Prosperetti, and D. Lohse, Marangoni instability of a drop in a stably stratified liquid, Physical review letters **126**, 124502 (2021).

[3] Y. Li, J. G. Meijer, and D. Lohse, Marangoni instabilities of drops of different viscosities in stratified liquids, Journal of fluid mechanics **932**, A11 (2022).

[4] J. G. Meijer, Y. Li, C. Diddens, and D. Lohse, On the rising and sinking motion of bouncing oil drops in strongly stratified liquids, Journal of Fluid Mechanics **966**, A14 (2023).

[5] J. G. Meijer, P. Kant, D. Van Buuren, and D. Lohse, Thin-film-mediated deformation of droplet during cryopreservation, Physical review letters **130**, 214002 (2023).

[6] J. G. Meijer, P. Kant, and D. Lohse, Freezing-induced topological transition of double-emulsion, *Manuscript in preparation*, (2023).
[7] D. Van Buuren, P. Kant, C. Diddens., J. G. Meijer, and D. Lohse, Interaction of drops with an advancing solidification front, *Manuscript in preparation*, (2023).
[8] J. G. Meijer, V. Bertin, and D. Lohse, Frozen cheerios effect: Particle-particle interaction induced by an advancing solidification front, *Manuscript in preparation*, (2023).
[9] A. M. Linnenbank, J. G. Meijer, and D. Lohse, Freezing sessile drops: from front tracking to bubble growth, *Bachelor thesis*, (2023).