Droplet Coalescence in 2D Thermal Convection of a Thin Film

M. Winkler\textsuperscript{1} and M. Abel\textsuperscript{1}

E-mail: Michael.Winkler@uni-potsdam.de
E-mail: Markus.Abel@physik.uni-potsdam.de
\textsuperscript{1} Institute for Physics and Astronomy, University of Potsdam

Abstract. We show first results on the dynamics of ultrathin regions, black film (BF) – bubbles, in a two-dimensional thermal convection experiment with already very thin aqueous films. The formation of such stable regions in thin films is a new feature which makes it possible to study the collision dynamics of BF-bubbles in detail. This is of high interest due to the analogy to bubbles in a fluid in 3D situations. For our experiment, we use a Rayleigh-Bénard setup and an extremely well-controlled chemistry: n-dodecyl-β-maltoside is used as the surfactant stabilizing the sheet of water making it possible to reach stable black films. We demonstrate how the formation and coalescence of bubbles can be tracked and give an overview about shape and size variation during this process.

1. Introduction

Liquid thin films are found often in nature, e.g. in cellular membranes, condensation layers on surfaces, and as interfaces between material domains. This contribution reports on experiments on a soap film captured in a frame, that combines three scientific areas: free-standing, thin, liquid films, thermal convection, and droplet coalescence. Thin films are not only beautiful as soap film, but highly important for process engineering and life sciences. Further, the limits of physical theories are tested when films become exceedingly thin, i.e., on the nanometer scale. Convection is often considered in the context of Rayleigh–Bénard (RB) convection as a model for large systems like the earth–mantle convection and atmospheric, thermally driven turbulence. Droplet coalescence, finally, is very important in the study of rain and cloud formation. In the presented study two approaches are combined: thin liquid films in their equilibrium regime and Rayleigh-Bénard convection. Due to perturbations in the film, stable bubbles are formed and their creation, convection and coalescence can be analyzed. Here, only the case of bubble coalescence will be presented.

When a fluid is subject to a temperature difference where the gradient is directed inverse to the gravitational force, above a critical value, the onset of turbulent convection is observed. This "cooling from above, heating from below" scenario leads to Rayleigh-Bénard convection which is well-studied \textsuperscript{[1, 2]}. Yet some fundamental questions are still unsolved, regarding the scaling behavior of Nusselt vs. Prandtl for high Rayleigh numbers or the dependence on aspect ratio and the question of universality.

Thin liquid films are typically composed of a layer of amphiphilic molecules on each surface and a liquid core separating these layers \textsuperscript{[3]}. Depending on the chemical details of the solution...
there exist two stable equilibrium thicknesses [4]. In contrast to previous convection experiments with thin liquid films in the transient state the presented setup makes it possible to study convection in films at their equilibrium thickness.

For the experimental investigation, a thin-film forming system was investigated in a special experimental setup. The scenario is very similar, but not identical to classic RB convection. In contrast to usual RB convection the system is necessarily open on both surfaces, and an exchange of matter through the surface happens. This means that heat exchange with the surrounding atmosphere must be considered, in addition to the heat flux through the container, which is in our case just a metal frame.

2. Thin Film Convection

The thinning of a liquid film can terminate in two distinct equilibrium states. One being the Common Black Film (CBF) and the other one being the Newton Black Film (NBF) [5]. The latter is a bilayer formation of the surface stabilizing surfactant molecules without an aqueous core. This state can only be reached with an electrolyte concentration high enough to shield the long range molecular repulsion forces of the two surfaces. Thus, the final thickness is only determined by the balance between surface pressure and molecular short-range repulsion forces.

Common Black Films on the other hand are achieved when there are only very few free ions present and the film is stabilized due to electrical double layer repulsion. Because of the dissimilar stabilizing mechanism it is expected that there is a distinct difference in the convection behavior. Typically a Newton Black Film reaches a thickness of roughly 5 nanometers whereas Common Black Films develop at a thickness of approximately 15 nanometers [6]. Since we are forcing the film it is necessary to keep in mind that these results are equilibrium values. Therefore the actual thickness in our experiment may vary and we refer to black film (BF), not distinguishing further the two possible states.

When the thin film is heated, convective motion sets in, which can be observed visually and in real time, hence video recording is used and the images subsequently characterized by statistical analysis and tracking of the fluid.

The temperature difference achievable by the experiment ranges from $\Delta T = 20K$ to $\Delta T = 50K$. The used frame has a height of 20 mm; this results in temperature gradients from $\frac{\partial T}{\partial y} = 10K/mm$ to $\frac{\partial T}{\partial y} = 25K/mm$ generating convection which is observable by the naked eye. The accessible Rayleigh numbers are $Ra \simeq 1 \cdot 10^6 - 1.5 \cdot 10^7$. The maximum temperature difference is limited by decreased film stability at high temperatures and increased condensation at the top border of the frame at temperatures close to the freezing point. A sketch of the experiment is given in Fig. 1. The temperature difference used in the analysis below was $\Delta T = 30K$ with a Rayleigh number of $Ra = 6 \cdot 10^6$.

The system is described by the Navier-Stokes equations, here, we use the 2D approximation with temperature in the Oberbeck Boussinesq approximation, the thickness is described in the lubrication approximation coupled to the fluid through the boundary conditions. The lubrication approximation assumes that scales in $x$ and $y$ are large compared to the typical film thickness ($z$-axis). An equation for the film thickness $h(x, y) = h_f(x, y) - h_b(x, y)$ is derived by multiscale expansion [7], assuming independence of the back and front surfaces $h_b, h_f$.

$$\mu \frac{\partial}{\partial t} h + \vec{\nabla}_1 \left[ \left( \vec{\tau} + \vec{\nabla}_1 \sigma \right) \left( \frac{1}{2} h^2 + \eta h \right) \right]$$
$$- \vec{\nabla}_1 \left[ \left( \frac{1}{3} h^3 + \eta h^2 \right) \vec{\nabla}_1 \left( \Delta \Phi - \sigma \vec{\nabla}^2_{\perp} h - \Pi \right) \right] = 0 ,$$

with $\mu$ the (dynamic) fluid viscosity, $\vec{\nabla}_1 = (\partial_x, \partial_y)^T$, $\sigma$ the surface tension, $\eta$ the slip coefficient between surface and air, $\Delta \Phi = \Phi|_{z=h_i} - \Phi|_{z=h_c}$, $\Phi$ describes a body force, here this is gravity, and
at small scales, disjoining pressure, $\tau$ and $\Pi$ are tangential and normal forcings at the surface.

In the bulk of the film we assume the Oberbeck-Boussinesq approximation \[1\]

\begin{align}
\rho(\partial_t \vec{u} + \vec{u} \cdot \nabla \vec{u}) &= -\nabla_1 p + \mu \Delta_1 \vec{u} + \beta \vec{y} \theta, \\
\rho \gamma(\partial_t \theta + \vec{u} \cdot \nabla_1 \theta) &= \kappa_{th} \Delta_1 \theta,
\end{align}

with $\rho$: density, $\beta$: thermal expansion coefficient, $c$: specific heat, $\kappa_{th}$: thermal conductivity. At the boundaries, $h_b$, and $h_f$, respectively, we have

$$
\kappa_{th} \vec{n} \cdot \vec{v} + \alpha_{th}(\theta - \theta_{\infty}) = 0,
$$

with $\alpha_{th}$: heat transfer to ambient, $\theta_{\infty}$: outer temperature, $\vec{n}$: vector normal to the surface. For a two–dimensional thin film one can assume to 0th order that the thickness is advected passively. But the surface tension depends parametrically on the temperature, and thus certainly becomes important in the next higher order. Of course, in contrast to usual thermal convection, chemical potentials and surfactant forces matter.

3. Experimental Details
For the experimental investigation, a thin-film forming system was placed in a closed container to prevent evaporation and to ensure thermodynamic control. The setup is based on a measuring cell that was designed at the Chinese University of Hong Kong in the fluid physics group, similar to [8]. Very thin translucent films and thicker opaque films can both be prepared with a lifetime

\begin{figure}
\centering
\includegraphics[width=0.6\textwidth]{setup.png}
\caption{Experimental Setup: a) light source, b) diffuser, c) top, cool aluminum cylinder, temperature controlled, d) bottom, hot aluminum cylinder, temperature controlled, e) video camera, f) reservoir of thin film solution, located within the bottom aluminum cylinder (heated), g) sliding frame which is delved into the solution at the bottom, when lifted the thin film is produced, h) thin film inside the measurement cell. The measurement chamber is sealed and placed between the two slotted aluminum cylinders c) and d) with a stainless steel frame clamped in between them. The chamber is transparent with a black backside, the thin film area has a size of 20 x 20 mm$^2$.}
\end{figure}
of several hours. The frame holding the thin liquid film was heated from below and cooled from above by two large aluminum cylinders, thus creating a thermal gradient.

A film consisting of pure water ruptures almost immediately due to the capillary forces generated by the surface tension. Adding a surfactant that covers the surface of the film reduces the surface tension and increases the surface elasticity, therefore stabilizing the sheet of water. Several further components help to maintain film stability over hours, as described below.

Macroscopic, quasi–two–dimensional liquid films are obtained by spanning a stainless steel or PVC frame with surfactant solution. The base solvent is deionized water, as it reduces contaminations with non-conducting carbon chain remnants or residual ion concentrations [6].

Glycerin is also required to achieve macroscopically large films with an area of several square centimeters or meters [9, 10], serving to adjust bulk and surface viscosity. Due to its high viscosity ($\eta = 945 \text{ mPa s}^{-1}$, compared to $\approx 1 \text{ mPa s}^{-1}$ for water) it reduces the thinning speed of vertical films and allows the film to remain stable for a longer period of time [11]. Typically, a concentration of 25 % vol is used, yielding a net viscosity of $\approx 2 \text{ mPa s}^{-1}$ (cf. [12]). Our experimental setup thus differs from the experiments on turbulence in soap films [13], and is quite similar to previous ones on convection [14].

The electrolyte concentration has a major effect on film stability and thickness [15]. The addition of ions shields the electrostatic double-layer repulsion as described by the DLVO (Derjaguin-Landau-Verwey-Overbeek) theory [3] hence permitting the appearance of a black film. Here, sodium chloride was chosen, since it has negligible influence on surface tension and critical micelle concentration (CMC). To eliminate any surface active contaminations, the laboratory grade NaCl (Merck, Darmstadt, Germany) was roasted at 600$^\circ$C.

The chosen surfactant, n-dodecyl-$\beta$-maltoside (here after $\beta-$C$_{12}$G$_2$), belongs to a new generation of sugar-based surfactants which are non-toxic, biodegradable and of low cost. $\beta-$C$_{12}$G$_2$ is a non-ionic surfactant which consists of hydrophilic head group, made up of two glucose rings (C$_6$H$_{12}$O$_6$) connected by an ether bond, and a hydrophobic alkyl chain (C$_{12}$H$_{25}$). The surfactant is soluble in water so that the hydrophilic head group is submerged in the core liquid. The hydrophobic tail is oriented normal to the liquid-air-interface and is not in contact with film surface. All experiments were performed with a concentration above the CMC, to guarantee that the equilibrium surface tension remains constant. Above CMC, deviations in surface surfactant density are compensated by diffusion of surfactants from or to the bulk liquid.

4. Bubble Movement and Tracking

To capture the movement of the soap film turbulence we use a generic HD video camera which is able to record 1920 times 1080 pixel at 25 frames per second. The average angular velocity of the convection roll is approximately $\pi/s$ and the maximum speed is 18 mm/s so that the frame rate limited minimal resolution is roughly 0.5 mm. We use a demountable measuring cell that encloses a stainless steel or PVC frame holding the film and a reservoir of the solution. The film is quadratic with a side length of 20 mm, i.e. an area of $A = 400 \text{ mm}^2$.

It is vitally important for the long term stability of the film to keep the atmosphere saturated with vapor to prevent evaporation of solution from the film. This is achieved by a closed container with a glass front. The film is illuminated through this viewing window by an array of high power white LEDs which are placed behind a diffuser. To minimize reflections the rear panel of the measuring cell is covered by a sheet of black cellular rubber. Additionally, to avoid direct reflections of the light source from the viewing window the measuring cell is tilted with respect to the liquid film plane.

The diffused light is reflected by the front and back side of the film whereas the front reflection is shifted by $\pi/2$ due to reflecting of an optically thicker medium. If the film thickness is much smaller than $\lambda/4$ of the smallest emitted wavelength the light waves interfere $\pi/2$ out-of-phase and no light is reflected. Hence the name black film although more precisely it is transparent.
The reason why there is no smooth transition in the intensity of the reflected light is the abrupt change in thickness when the black film is formed. At $\lambda/4$ of the smallest wavelength, which is blue ($\sim 450 \text{ nm}$) in the case of the used white LEDs, the reflected waves interfere constructively. In addition, every other wavelength is reflected as well which sums up to a white color with a blue tint. Before that thickness is reached the film exhibits an orange tint as the film is approximately 200 nm thick which corresponds to the cancellation of blue light. To get an absolute value of the thickness corresponding to a certain color displayed one needs to take into account that the refractive index of the solution is slightly higher than that of pure water.

We study domains of black film which are enclosed in thicker colored film, for convenience we call these spots BF-bubbles, cf. Fig. 2. One might consider calling them “holes” as they are stable spots of reduced thickness within the thicker, homogeneous liquid film. Due to the higher pressure in the black film and the vast thickness difference between the two phases, the system can be considered as a composition of two immiscible fluids - thicker film and the BF-bubbles. Since the BF-bubbles are stable, they grow due to the pressure gradient at their interface towards the colored film. This growth can be considered as a front motion, as known from evaporating films on substrates with interesting secondary instabilities [16]. However, this is not relevant here.

During motion the BF-bubbles experience a gravitational force, so while being convected they are lifted upwards. On the other hand, light media is drawn towards the center of rotational motion due to centrifugal forces. Obviously, these two forces are concurrent and which one wins basically depends on the size of the BF-bubble; in this experiment the BF-bubbles remain below the critical size which would drive them to escape towards the top of the experimental frame. Due to the disjoining pressure gradient across the interface line between black and colored film the shape of the BF-bubbles approaches a minimal circular shape when not disturbed by shear or adhesion of other bubbles.

It is worth noting that the BF-bubbles are not rigid and can deform due to shear stress or upon impact on one another. They have a line tension, analogous to surface tension of free droplets or bubbles in 3D. The exact value of it depends on the chemistry used. This makes them an ideal playground to study the collision of deformable bubbles in 2D in a controlled manner.

To track the paths of the domains of black film we employ a selective color tracking algorithm. A narrow range of colors matching the desired feature is selected and marked as black and the rest of the image is masked with white. These identified "clusters" are then tracked through

![Sample frame of the convection in real color with manual thickness overlay information.](image)
Figure 3. Left: Real color sequence of frames. The experiment has been run approximately 10 minutes at the upper left frame. Times shown are relative to the previous frame, numbering is left-right, and top-down.
Right: Same sequence as left, shown as a binary image identified by the tracking algorithm. Bubbles are black, the remainder is coded in white.

Each frame. Here, we calculate for each instant of time the center of mass, the principle axes, the corresponding eigenvalues, giving the stretching/contraction rate, and the volume evolution. From these data we calculate the velocity by finite differences.

Due to the relatively low frame rate available during the experiment the data was interpolated from 25 frames per second to 200 frames per second, thus realizing a good connectivity of the cluster instances over time. A frame sequence, as recorded, is shown in Fig. 3. Although the calculated Rayleigh-number is in a relatively narrow range for the given bulk viscosity and temperature gradient the thin liquid film exhibits different turbulent motion depending on the atmospheric conditions (humidity and temperature of the surrounding gas). In this example one of the most common scenarios is presented with formation of a long term stable convection with one primary convection roll and several secondary eddies at the edge. The artifacts on the upper right side are condensation droplets on the front window. In the upper left corner a convection cell consisting of black film is present, this is not the topic of this publication and will be discussed elsewhere. The gravitationally driven thinning of the liquid layer leads to the formation of a stripe of black film where convection is present, too. However, due to the nature of the capturing technique this motion remains hidden.

In Fig. 3 the BF-bubble identification is illustrated. Real colors are transformed to black and white pictures which are then processed: To analyze the behavior of domains of the same thickness the video data is converted into a binary image where white corresponds to a single color or thickness, respectively. As the spectrum repeats continually this technique is only valid if the overall thickness deviation is smaller than a full period of the smallest wavelength. In
Figure 4. Example of the identification of clusters for one frame (time slice). The colors correspond to the unique indices of the domains of equal thickness, they have no physical meaning and serve for better visualization. The crossed lines correspond to the principle axes, their length to the unscaled weight, the crosspoint is the center of mass.

particular for the BF-bubble tracking, all black areas were extracted. Subsequently in each frame all spots are numbered and consecutively linked through the following frames (cf. Fig. 4). This enables us to track a BF-bubble uniquely with its volume, velocity, and deformation rate. Even the rotation rate can approximately be determined for non-circular bubbles by the rotation of the principle axes. For each bubble the velocity is calculated using the shift of its center of mass per frame. The deformation rate is calculated by determining the change of the scale of the principal components per frame. The algorithm is operating with a linear backwards memory of variable depth. The memory must be limited, because merging or separating clusters would be considered connected and a unique tracking is not possible. We set a memory of one frame in order to maintain connectivity of an individual cluster during its time evolution.

5. Bubble Coalescence

Let us have a closer look at the BF-bubbles in Fig. 3. The black film bubbles form due to local fluctuations, mainly at the boundary of the film which drive the thin liquid film to collapse to its equilibrium state. A preceding state is the formation of domains of very thin film (≈ 100 nm) which appear as white spots in the convection. As shown in Fig. 3 the bubbles move along similar streamlines and change their relative position due to small perturbations in the flow. Once two bubbles reach a critical distance they stick together and move in the flow field as a conglomerate. The Young-Laplace-Equation $\Delta p = -\gamma \Delta \cdot \vec{n}$ gives an additional pressure term to the disjoining pressure balance and effectively reduces the pressure at the curved interface between black film and colored film. There remains an interstitial barrier of thicker film between the bubbles which will eventually break due to shear and lead to the coalescence of the bubbles as shown in frame 5 of Fig. 3. In this example a conglomerate of 3 bubbles is formed until the first coalescence occurs.

Initially, we observe (in Fig. 3 top left, i.e. after about 10 min.) 4 bubbles which rotate about the center. As explained above two bubbles approach inevitably due to small velocity differences (Fig. 3 top right), and the individual bubbles rotate about their mutual center of mass due to the
Figure 5. Sequence of 7 frames of the coalescence of two bubbles beginning just before the merge and ending with the complete withdrawal of the interstitial fluid. Time steps are given relative to the previous frame.

different velocities on their paths. This is like the common tumbling mechanism of non-circular particles in a shear flow. At their interface, they exert an attractive force onto each other. We suggest a fluid motion to cause this force, since the region between the bubbles is thicker as the surrounding, thus liquid is pushed outwards yielding an attraction. In addition, the black film wants to grow as the stable phase. All in all both bubbles stick together. A theory will have to involve a generic model for the line tension of the BF-bubbles and the repulsive and attractive forces of the BF-bubbles. With a third bubble, this game is repeated, cf. Fig. 3, middle.

The details of the coalescence of three bubbles are shown in Fig. 5. We see that first two bubbles merge to form a banana–shaped structure, which then unites with the third bubble. It is not clear in how far two bubbles can survive separately, rotating about a common center of mass. The rotation counteracts partially the attraction such that even a stable period orbit of the system might exist. Eventually, the third BF-bubble is swallowed by the now bigger and thus slower (relative to the surrounding fluid) “banana” and the resulting big bubble rotates about the center. One can nicely observe the vortex generated by the different rotation velocity of the bubbles with respect to the surrounding fluid: below the (global) center it is slower, above it is faster, resulting in a leading and trailing vortex respectively. It is seen in white since it is thicker fluid and originates on the rim which surrounds the bubbles.

Now, this spot is big enough to escape the rotation, because gravity is strong enough and the big BF-bubble escapes to the top of the experiment whereas the fourth stays trapped for quite a while. The volume evolution of the bubbles during the coalescence process is readily available from the cluster tracking algorithm. In Fig. 6 the volume of the bubbles involved in the coalescence is shown.

6. Conclusion

We have presented a prototype for an experiment on 2D BF-bubbles, where collision properties in rotating flows can be studied in detail. We suggest using the setup on a larger scale with dedicated bubble generation, e.g. by electrical forces. One drawback of the setup is that one can hardly generate bubbles with different mass, except one accepts changing the size.

However, under the given restrictions we can already state that the collision and sticking of the BF-bubbles is a very interesting phenomenon with parallels in other situations. Of course, the three dimensional world is different in that the contact forces are 2D instead of 1D, the motion has more degrees of freedom, and so on. Nevertheless, we think that principles can be tested on the playground of 2D to end up in dedicated experiments in 3D.

With respect to foam, our experiment has further implications: The coalescence of two or more bubbles is the intrinsic mechanism of foam collapse which can be studied in detail with this experiment as the time scales of the actual merging process are much larger than in the typical air and soap solution ensemble. The bubbles are very robust and can deform to a great extent until a permanent deformation, rupture or coalescence with surrounding bubbles occurs.
Due to the pressure balance at the interface line of these black spots their area increases over time which is a unique feature and opposite to the usual volume decrease of bubbles in foam due to the higher inner pressure and gas permeability of the soap film.

The area tracking algorithm provides detailed information about the flow field and is adaptable to work on any data of deformable clusters with high enough contrast with respect to their surrounding.

Generally, we think that with our extremely simple experiment we can touch deep physical questions on the microscopic nature of thin film flows and treat at the same time very practice-oriented topics.

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