UNIVERSITÀ DEGLI STUDI DI NAPOLI FEDERICO II



# Engineering of freestanding films

A thesis submitted for the degree of Doctor of Philosophy in Product and industrial process engineering coordinated by Professor Andrea D'Anna

Vincenzo Ferraro

Tutors

Professor Ernesto Di Maio and Professor Pier Luca Maffettone

July 2021

# Contents

Summary	
Chapter 1: Introdu	action and Background
1.1 Observat	ion techniques of freestanding films10
1.2 Main for	ces acting on freestanding films11
1.2.1	Capillarity13
1.2.2	Surface pressure isotherms
1.2.3	Disjoining pressure
1.2.4	Marangoni Effect24
1.3 Leveling	in freestanding films26
1.4 Buckling	and Wrinkling
Chapter 3: Full-Fi by Combining Digi	eld and Quantitative Analysis of a Thin Liquid Film at the Nanoscale tal Holography and White Light Interferometry
and real-time inves	imetric bare freestanding films of highly viscous fiquids: Preparation
and real-time myes	
Chapter 5: New ela	stic iris-like device to hold and form freestanding films111
Chapter 6: A nove	el spreading protocol shows new Graphene Sheet film transitions on
water-air interface	
6.1 Materials	s and Methods123
6.2 Results a	nd discussions126
Chapter 7: Contro	lled buckling wavelength for a film made of graphene sheets on water-

7.1 Materials and methods	
7.2: Results and discussion	135
Chapter 8: High stretchable conductive 2D materials made of	wrinkled PDMS film coated
by graphene sheets	
8.1 Materials and methods	143
8.2: Results and discussion	144
Chapter 9: Summary and key contributions	
9.1: Summary of the Thesis	
9.2: Future works and applications	
9.3: Conclusions	

wledgements153
----------------

## Summary

A film is a system in which two dimensions prevail over the third. In case of freestanding films both their surfaces are not in contact with a solid substrate; they can be supported by a solid frame of any geometry or floating on a liquid subphase, even bubbles are made of freestanding films.

The goal of the thesis has been focused on the investigation to develop new methods and devices and to understand their behavior during the formation and next dynamic evolutions. It is considered important to control the structure of a freestanding film in a simultaneous and controlled manner while attempting to greatly reduce production times for the films obtained by conventional techniques. At the aim to accomplish such objective my efforts have been addressed also toward the possibility to try the improvement behind the actual state of the art of interferometric techniques that usually are adopted to characterize freestanding films.

To achieve such a result, it was necessary to go through three fundamental steps:

- (1) study the state of the art about the phenomena and the forces that arise inside freestanding films to find out a way to use them to control their structure (*Chapters* 1,4,6-8)
- (2) develop an innovative technique to observe such systems that allows quantitative and live full field analysis of the thickness (*Chapters 2-4*)
- (3) design, fabrication and testing of a completely new device to handle and form wide freestanding films (*Chapters 4,5*).

The thesis is divided in 9 *Chapters*. In *Chapter 1*, named "*Introduction and background*", the reader will find the current state of the art concerning all the main forces, phenomena analyzed in *Chapters 2-9* and the current observation and thickness measurement techniques that are used, nowadays, to study freestanding films. In addition, the reader will find in *Chapter 1* all the possible applications of freestanding films, all the systems made up of freestanding films and which are the subject of study in many disciplines. *Chapter 2* and *3* are related to the Ph.D results about thickness measure of freestanding thickness measure of freestanding thickness.

maps by means of live self-reference measurements. The new techniques described in these two chapters are able to offer a more detailed spatial and temporal measurement of freestanding films that are flat or have a three-dimensional structure such as bubbles. This is a key step as until now it has not been possible to observe large freestanding liquid films.

In *Chapter 4*, titled "Axisymmetric bare freestanding films of highly viscous liquids: *Preparation and real-time investigation of capillary leveling*", there is an in-depth study of the axisymmetric leveling of a liquid freestanding film consisting of Newtonian fluid (Silicon Oil) and without surfactants or particles. This result is very important because in order to obtain a film with a controlled structure, it is of fundamental importance to be able to manage the thickness of a film. In fact, a number of physical properties are derived from the thickness of the film, including structural colors generated by the phenomenon of white light interference on thin films. Alternatively, thickness gradients within a freestanding liquid film can be used to control the motion of particles within it to arrange them in an orderly pattern and more.

*Chapter 5* describes a new device that I have designed and built that allows the formation and handling of freestanding films, both liquid and solid, starting with a drop of material, or an unformed solid sample, at the center of the device and then stretching it to form a freestanding film. This device is the first ever capable of imposing purely twodimensional axisymmetric and many other deformations.

In *Chapter* 6, named "A novel spreading protocol shows new Graphene Sheet film transitions on water-air interface", a new method for particle spreading at the liquid-air interface is introduced, which enables a very homogeneous distribution of graphene sheet particles. In the case of films consisting of particles, the arrangement of these objects in the plane is very important for the properties of the film. It can be seen, in fact, that a better spreading of particles gives a different compression behavior of the film on the surface pressure curve against the trough area.

In *Chapter 7*, named "*Controlled buckling wavelength for a film made of graphene sheets on water-air interface by distribution size control*", the reader is shown how a pattern can be imposed on a film of graphene sheets at the liquid-air interface by controlling the distribution of the diameters of these particles.

In *Chapter 8*, named "*High stretchable conductive 2D materials made of wrinkled PDMS film coated by graphene sheets*", a new kind of electrically conductive 2D stretchable material is developed. The material was obtained from freestanding films of different thicknesses obtained by spreading a drop of uncured PDMS at the water-air interface. The film was then coated with graphene sheets while being supported by hydrogel. Finally, the film was subjected to compression to induce wrinkling to generate a pattern whose wavelength is a function of the film thickness.

In *Chapter 9* the reader will find the future works, the applications and the conclusion of the PhD.

## **Chapter 1: Introduction and background**

In this chapter the reader will be introduced to the background and the most important concepts, that will be used in *Chapters 2-8*, to describe the current state of the art in freestanding film thickness measurements, freestanding film formation techniques and main driving forces that act on freestanding liquid films by focusing on Disjoining Pressure, Capillarity, Marangoni Effect and Surface pressure. The reader will be also introduced to the mechanical instability of buckling and wrinkling which are powerful tool to shape freestanding films. In particular, the aim of this *Chapter 1* is to answer to some basic questions like: how to observe these kinds of systems, which are the main driving forces acting on them and how it is possible to form and handle them in case of both solid and liquid films.

Freestanding film with a well-defined structure are useful for many applications such as: self-cleaning surfaces, flexible electronics, structural colors, micro fluidic devices, anti-reflective surfaces, liquid crystals, filter membranes, packaging films, tissue engineering, foams, food engineering. In addition, thin freestanding films are greatly studied as they have implications in multiple disciplines like medicine, biology, life science. On the other side, freestanding films are studied because they can be found in many natural systems like: emulsions, foams, magma bubbles, vesicles, cell membranes, sea foams and much more. Finally, if one considers that a freestanding film can be deposited on a liquid or solid interface, the possible applications increase even more in number.

Nowadays, the most used techniques to obtain single freestanding films include, spin coating, Langmuir–Blodgett film, film blowing, soft lithography, inkjet printing, electrospinning and interface spreading.

Each technique cited above have some issues, most of them require the film to be formed on a solid substrate (inkjet printing, soft lithography, electrospinning, spin coating) and then peeled away from the substrate to obtain a freestanding film. This kind of process severely limits the choice of materials, process parameters and achievable geometries. Furthermore, to date, it is impossible to construct freestanding nanometric films using those techniques. As said, among the techniques that can form a thin film on a liquid interface are Langmuir–Blodgett film and interface spreading. However, in such techniques it is necessary that the formed film has to be deposited on solid substrate as it is not possible to take out it from the interface without it breaks down or loses its properties.

Nowadays, the most widely used device to study freestanding films is the Sheludko cell [1]. This device consists of a ring capable of supporting the liquid film surrounded by air or liquids. The ring, porous or with microchannels, is connected to a system of capillaries to control the pressure inside the film or to a syringe pump system to control the amount of fluid and radial flows inside the film as shown in Figure 1.1.1.



Figure 1.1.1: first sketch of a Sheludko cell [1]

This device has been, and still is, of wide utility in the study of freestanding liquid thin films. In fact, it has been used to study drainage phenomena between drops, rigid spheres, between a drop and rigid sphere, between flat wall and rigid sphere and between a solid wall and drops [2]–[4]. In addition, this device has also been the subject of some studies to determine the contribution of disjoining pressure in free-standing films [4].

The Sheludko cell, however, has several limitations. Firstly, the diameter of the film cannot be modified during the experiments and is generally of the order of few millimeters. Another key limitation is the impossibility of carrying out extensional deformations since the diameter of the film is fixed. In fact, in this case the thickness of the film is controlled by the pressure imposed from outside through a system of capillaries and/or pumps [2], [4]. Another major limitation is represented by the

impossibility of imposing in a controlled way extensional deformation in the plane on the film.

## 1.1 Observation techniques of freestanding films

A film is an object in which one dimension is negligible compared to the other two. These kind of systems are very challenging due to their geometry which is characterized by hundreds of nanometers to tens microns in case of their thickness, the diameters space over hundreds of microns to millimeters and the curvatures radii that characterize them can be microns to meters. Moreover, these liquid films evolve over time and technique like SEM, AFM or Optical microscope are not able to get a thickness map of such systems.

Consequently, there is the need for an innovative observation technique capable of measuring the thickness and geometry of a liquid film as it evolves over time until it breaks, stabilizes, or solidifies.

The measure of the thickness of freestanding thin liquid film is a fundamental goal for this Ph.D. Nowadays, White Light Interferometry (WLI) [5], [6] is often used to estimate the thickness of freestanding liquid films but there are important limits such as low spatial resolution and thickness measuring range between  $\sim 100nm$  and  $\sim 2000nm$  [5], [6]. WLI measures the intensity of the color fringes generated by the interference of light reflected by the two interfaces of the film, see Fig. 1.1.3. The intensity is a function of thickness, film's refractive index, wavelength of the incident light and the relative angle between light source and film surface. In case of WLI, not only a single wavelength is used but a white light source, which is composed by a wavelength's distribution. The result is a colored fringe pattern in which each fringe corresponds to a thickness value. To do so, it is necessary to introduce the constructive interference formula, eq. (1.1.1a), and destructive interference one, eq. (1.1.1b), as a function of the wavelength of the incident light on the film.

$$h_{WLIc} = \left(m - \frac{1}{2}\right) \frac{\lambda}{2n_1 \cos\beta}$$
(1.1.1a)  
$$h_{WLId} = m \frac{\lambda}{2n_1 \cos\beta}$$
(1.1.1b)

Where  $m = 1,2,3,..., \lambda$  is the incident light wavelength,  $\beta$  is the incident angle of the light,  $n_1$  is the refractive index of the film.

The reader will find further details in Chapters 2-3-4.



Figure 1.1.2: thickness ranges in which the different measurement techniques can be used

To better analyze freestanding films Digital Holography (DH) was taken into account. This technique allows to capture holograms on a digital device such as CCD cameras. The hologram is a fringe pattern generated by the interference of two coherent light beam tilted and made of a single wavelength. The rendered image, or reconstruction of the object dataset, is made numerically from the digitized interferograms.

The measurement returns a phase shift map; the phase shift is generated by the different length path experienced by the light through the sample compared to the reference beam which pass through only air. The phase map values are proportional to the thickness of the film, see eq. (1.1.2). The elaboration process that leads to the thickness map start from the acquisition of the holograms by a CCD camera of the sample and the reference image. After that, the two-dimensional Fourier transform of the holograms acquired with the CCD are obtained (Figure 1.1.3). From the Fourier spectra only the first order is selected, excluding the rest which does not contain useful information. Then, from the Fourier spectrum, properly cleaned as described before, the wrapped map of the phase shift is generated. This map presents phase jumps from  $-\pi$  to  $+\pi$  which are then

unwrapped by an algorithm defined with the name PUMA on Matlab (Figure 1.1.3). The final result is a phase shift map in which all values are used to obtain the thickness map of the film by using eq. (1.1.2) (Figure 1.1.3).

The reader will find further details in Chapters 2-3-4.



**Figure 1.1.3**: (a) white light interference of a single light source beam and (b) sketch of the phase shift in transmission of a single wavelength coherent beam used for holography and the result of the elaboration process steps to retrieve the thickness map.

$$h_{DH} = \frac{\lambda_0 \varphi}{2\pi (n_1 - n_0)}$$
(1.1.2)

Where  $h_{DH}$  is the thickness value measured in one pixel,  $\lambda_0$  is the wavelength of the coherent light used,  $\varphi$  is the phase shift of the light measured in the single pixel,  $n_1$  is the refractive index of the film,  $n_0$  is the refractive index of the air (or the fluid that surrounds the film).

The spatial and time resolution of the thickness map obtained by holography depend mostly from the recording system (camera and lenses). The range of thickness that is possible to measure is wider then WLI but the minimum measurable thickness value is ~400nm which is higher than WLI (~100nm). But there still an issue, in fact, when DH is used by itself there is always the need of a reference image. This reference image must be subtracted from the acquired frames of the samples. However, it is not possible acquire a reference image for each frame because the sample evolves over time during the experiment. This means that this technique is not a self-reference measure.

To solve this problem, an innovative measurement system has been developed which is able to combine WLI and DH. The WLI is used to calibrate the holograms phase maps. To do so a video with the color fringes was recorded simultaneously with the holographic videos. The reader will find further details in *Chapters 2-3-4* about this new kind of technique.

## 1.2 Main forces acting on freestanding films

#### 1.2.1 Capillarity

When dealing with liquid films capillarity generally plays an important role in the structure evolution of these systems and even more in case of freestanding liquid films. Capillary forces arise from the surface tension which is a measure of the energy that bonds the molecules on the interface of a liquid. All molecules inside the liquids interact and these interactions in the bulk are balanced. On the other side, the molecules on the interface of forces that generates the surface tension of a liquid. Capillarity do not only affect the film morphology by pressure gradients inside the film which lead to liquid flows, but it can influence the film structure by moving particles depending on their shape, size, and physical properties. The surface tension of a liquid can be altered by surface-active molecules (e.g. surfactants) or surface-active particles.

Freestanding liquid films are most often found inside foams and emulsions. These films are the walls separating the dispersed phase represented by bubbles in foams as also droplets in emulsions.

The Laplace pressure  $P_c$  inside a liquid film is a depends from the geometry and surface tension of the liquid from which the film is made. The general expression is  $P_c = \gamma K_c$ where  $K_c = K_1 + K_2$  where  $K_i$  (i = 1,2) are the principal curvatures of the film surface and  $\gamma$  is the surface tension. Depending on the geometry of the film the capillary forces can lead to two different phenomena: drainage [4], [7]–[15], coarsening[16], [17] or leveling [18]–[20].

When the pressure difference between the periphery and the central region of the freestanding film is negative a drainage of fluid, that will induce a thinning of the film in the center arises [4], [7]–[15].

On the other hand, when the pressure difference between the periphery and the central region of the freestanding film is positive an inflow of liquid arises and the phenomena of coarsening or leveling show up [13]–[16]. In particular, leveling will be explained much more into detail in this *Chapter 1, Section 1.3*.

Both cases, thickening and thinning of a film, can be influenced by other forces such as gravity [9], [10], [21], [22], disjoining pressure [3], [4], [13], [23] or Marangoni effect [3], [24].

There are two main configurations of the film that generally are possible to find during the drainage:

- 1) When there is a non-spherical polyhedron bubble in case of low-density foams, then, the capillary pressure inside the Plateau border can be evaluated as  $P_c = 2\gamma/R_B$  where  $R_B$  is the curvature radius of the hypothetical bubbles/drops separated by the film.
- 2) In case of a plane parallel cylindrical film between two spherical bubbles, Sheludko provides the resulting formula  $P_c = 2\gamma \left(\frac{R_B}{R_B^2 R^2}\right)$  where  $R_B$  is the radius of the hypothetical bubbles/drops separated by the film and R is the radius that delimits the flat region of the film.

The pressure drop between the center of the film and Plateau border, as mentioned before, can induce a radial flow, in case of axial-symmetric films.

Drainage, coarsening and leveling can, however, be affected by surfactants which can impose a partial slip condition at the film interfaces. Many times drainage phenomenon is studied in case of bubbles and not only for freestanding flat films.

For example, in the case of a bubble consisting of a surfactant-free liquid, thinning follows the equation  $h^b = h_0^b \exp(-t/\tau)$  where  $\tau$  is a characteristic time proportional to the bubble radius,  $h^b$  is the thickness at the top of the bubble and  $h_0^b$  is the starting thickness at the top of the bubble.



**Figure 1.2.1**: (a) sketch of the Sheludko cell setup (b) cross-section view of a film inside the Sheludko cell with a flat region in the center.

Capillarity comes into play not only when there are flows within liquid films, e.g. it is important also for interfacial spreading phenomena or particle motion within liquid films.

#### Capillary spreading

When a drop of liquid is deposited on the interface of an immiscible liquid, the spreading will occur by capillarity. At first the forces opposing the spreading will be mainly inertial, but at a certain point viscous forces will start to prevail. When this happen the phenomenon is governed by the spreading coefficient:

$$S = \sigma_w - \left(\sigma_o + \sigma_{o/w}\right) \qquad (1.2.1)$$

Where  $\sigma_w$  and  $\sigma_o$  are the surface tensions of the "w" and "o" phases, whereas  $\sigma_{o/w}$  is the interfacial tension between the two previous phases, all of them are evaluated at the equilibrium. In case of immiscible fluids S is assumed constant during spreading. However, it is possible to have a gradient of S in space, in this case the Marangoni effect has to be taken into account, this last situation will be analyzed in more detail in this chapter, *Section 1.2.4*.

When a fluid drop of radius R is deposited on an immiscible liquid phase with a depth H. If the driven forces are the capillary ones and the viscous dissipation is related to the underlying liquid subphase, then the spreading will follow a power law  $R = k't^{n'}$ . Generally, the coefficient k' is a function of the physical properties of the fluids of both subphase and spread drop [25]–[27]. The exponent n' depends strongly from the depth of the liquid subphase [25], [28]. If the motion of the fluid of the subphase reach only a small fraction of the entire depth of the subphase then n' = 3/4 and  $k' \propto S^{\frac{1}{2}}/(\mu\rho)^{\frac{1}{4}}$ . If the entire subphase depth is affected by the spreading of the drop at the interface, then n = 1/2 and  $k' \propto (HS/\mu)^{\frac{1}{2}}$  where  $\mu$  is the cinematic viscosity and  $\rho$  is the density of the subphase [25], [26]. These n and k have different values and expression as the system have different spreading geometries [25], [26], [28], miscible liquids [25] or the presence of a liquid topphase [29].

#### Particle motion inside a freestanding liquid film

A further possibility to modify the structure of a freestanding film is the use of particles. When a particle floating on a liquid-air (or liquid-liquid) interface it will only stay on the interface without moving along a preferential direction on the plane of the interface. This happens because the capillary forces just let the particle float on the interface keeping the correct contact angle, as shown in Figure 1.2.2a.

The particles within a freestanding film do not follow random motion or matter flows. Their movement is also influenced by the thickness gradients in the film combined with the interfacial properties between the particles and the liquid of which the film is composed [30], [31]. There are 3 possible cases: the particles may be completely embedded within the film without interactions with the interfaces, it may be adsorbed on one interface of the film or it can interact with both the interfaces of a freestanding liquid film in case the thickness of the particles is higher than the film thickness.



**Figure 1.2.2**: Equilibrium position of spherical particles (a) with different contact angles on liquid-air interface (b) inside a liquid freestanding film. Where  $\theta_e$  is the contact angle between the particles and the liquid of the film.

As said before, when a particle interacts with only one interface, see Fig. 1.2.2, it will not be affected by any capillary forces capable of directing its motion on the interface. However, if a particle interacts with both interfaces of a freestanding film it will start to experience a driving force, which will depend on the thickness of the film, the size and the physical properties of the particles themselves [30], [31].

Let's assume that these particles have a spherical geometry, then we can have 3 possible cases: 1) the particles with high wettability will always be pushed towards the thicker

parts of the film (Figure 1.2.2), 2) the particles that are not wettable by the fluid will be pushed towards the thinner parts of the freestanding film (Figure 1.2.2), 3) the particles that have an intermediate wettability will find an equilibrium position that will correspond to a precise thickness region of the film itself (Figure 1.2.2).



**Figure 1.2.3**: side view of a sphere particle inside a freestanding liquid film with a linear gradient thickness; F is the resultant capillary force acting on a spherical wettable particle in position (a) within a freestanding film. The force F arise when the particle starts to interact with the two interfaces of the film has the diameter is similar to the thickness of the freestanding thin liquid film.

Yadav et al. found out a simple formula for the drag force *F* (represented in Figure 1.2.3) from an energy balance. In particular  $F = -2 \frac{dE(\zeta)}{dr} = -4\pi\gamma_{L-A}(\zeta - \zeta_e) \frac{d\zeta}{dr}$  in which  $E(\zeta)$  is the total surface energy for a particle absorbed on a liquid-air interface,  $\zeta$  and  $\zeta_e$  are the distances of the adsorbed particle's center from the interface out the equilibrium and at the equilibrium,  $\gamma_{L-A}$  is the interfacial tension between air and the liquid of the film, r is the radial coordinate (see Figure 1.2.3). By assuming that the slope of the surfaces of the film are negligible the drag capillary force can be written as:

$$F = f_d \pi \mu h V \quad (1.2.2)$$

In which  $\mu$  is the viscosity, *h* is the film thickness and *V* is the particle velocity and  $f_d$  is a fitting parameter.

By exploiting the interaction of the particles with the interfaces of a freestanding film, it is possible to obtain a controlled structure, controlled particle motion or use freestanding thin liquid films to sort particles and control the diameter distribution.

#### 1.2.2 Surface pressure isotherms

In Paragraph 1.2.1 the reader was already introduce to the concept of surface tension. In this Paragraph 1.2.2 the reader will be introduced to the concept of Surface Pressure. As it was already explained in Section 1.2.1, the air/liquid interface has an excess of free energy resulting from the absence of molecules balancing the interaction forces with the fluid, which is the case for molecules in bulk. This interfacial free energy can be assessed by a measurement of surface tension  $\sigma$ . For example, the surface free energy of water is very high, making it ideal for the deposition of molecules or particles at the air/water interface.

Depositing particles at the air/liquid interface generally requires the use of a volatile or miscible solvent capable of rapidly and uniformly covering the interface and distributing particles, surfactants, proteins, microgels, polymers and many others.

If the distance between the molecules is low, then their interactions on the interface plane will also be low. Therefore, when we talk about monolayers of molecules/particles at the interface we can assume that molecules/particles interact each other like the molecules of a gas. It is possible to decrease the area available for each particle by close the barriers and decrease the total area in which the molecules/particles. The decrease in the available space forces the particles to interact more, causing an increase in repulsive interactions between them. This two-dimensional analog of pressure is called surface pressure and it is given by the relationship  $\Pi = \sigma_0 - \sigma_1$ 



**Figure 1.2.4**: (a) sketch of the Wilhelmy plate immersed inside the liquid subphase with all the characteristic lengths and angles necessary in eq. (1.2.3); (b) sketch of a surface pressure curve as a function of the (trough area)/(number of particles or molecules), *G* represent the gas phase of the molecules layer adsorbed at the interface,  $L_1$  and  $L_2$  are the liquid phase transitions, *S* is the solid phase transition and *B* is the buckling transition

It is possible to distinguish different phase transitions as the pressure increases inside the layer on the interface, as shown in Figure 1.2.4. There can be also the coexistence of multiple phases during the passage through one phase to another, like the phases  $L_1$ and G in Figure 1.2.4, until the solid phase is reached. The solid phase transition, in principle, should have an infinite slope like the one shown in Figure 1.2.4 but in the reality it is not possible due to imperfections and the impossibility to compress the barrier at a speed slow enough to avoid kinetics phenomena.



**Figure1.2.5**: a typical Langmuir trough device made of a bath for the liquid subphase, 2 barriers to compress the interface and a Wilhelmy plate connected to a dynamometer to evaluate the surface pressure

#### Surface pressure measurement

To measure the surface pressure, it is necessary to place a Wilhelmy plate at the interface and connect it to a dynamometer to measure the Surface pressure, see Figure 1.2.5. The forces acting on the plate are: buoyancy due to the Archimedes' law upwards but gravity and surface tension downward and the resulting force is F. In case of a rectangular plate with dimensions  $l_p$ ,  $w_p$  and  $h_p$  with density  $\rho_p$  immersed to a depth of  $h_l$  inside a liquid of density  $\rho_l$  the net forces are giving from eq. (1.2.3), see Figure 1.2.4:

$$F = \rho_p g l_p w_p t_p + 2\gamma (t_p + w_p) (Cos\theta) - \rho_l g t_l w_l h_l \qquad (1.2.3)$$

Where  $\theta$  is the contact angle of the liquid on the plate but generally the measure is done with totally wetted plates which means that  $\theta \to 0$ , generally the plate is made of platinum, glass or filter papers to allow wetting. The resulting equation is:

$$\Pi = -\Delta\gamma = -\left[\frac{\Delta F}{2}\left(t_p + w_p\right)\right] = -\frac{\Delta F}{2}w_p, \text{ if } w_p > t_p \qquad (1.2.4)$$

As it is possible to notice in eq. (1.2.4) the sensitivity of the surface pressure is strictly connected to the Wilhelmy plate thickness.

The obtained surface pressure against mean molecular area isotherm, see Figure 1.2.4, returns important information about the material that we are studying such as phase transitions and mechanical properties of the film [32]–[38].

#### 1.2.3 Disjoining pressure

When it comes to liquid films, capillarity generally plays a significant role in governing the time evolution of these systems and this is even more true in freestanding liquid films. However, there are also other very important forces such as disjoining pressure. In fact, the thinner the film becomes, the more the contributions of the forces, which compose the disjoining pressure, increase.

Disjoining pressure " $\Pi_{dj}$ " consists, see eq. (1.2.5), of the sum of three components: electrostatic, Van der Waals and short range forces.

$$\Pi_{d\,i} = \Pi_{el} + \Pi_{vdw} + \Pi_{ar} \qquad (1.2.5)$$

Where:

$$\Pi_{\nu dW} = -\frac{A}{6\pi(2h)^3} \quad (1.2.6a)$$

$$\Pi_{ar} = C_1 \exp(-C_2 2h) \quad (1.2.6b)$$

$$\Pi_{el} = 64nkT\phi^2 \exp(-\kappa(2h-2\delta)) \quad (1.2.6c)$$

$$\phi = \tanh\left(\frac{ze\psi}{4kT}\right) \quad (1.2.7)$$

$$\kappa^{-1} = \left(\frac{2e^2z^2n}{\epsilon kT}\right)^{-\frac{1}{2}} \quad (1.2.8)$$

A is the Hamaker constant [4], [39], h is the thickness of the film,  $C_i$  (i = 1,2) are constants that depends on the liquid composition, n is the number of counterions per cubic centimeter in the solution,  $\delta$  the thickness of the adsorbed monolayer, z the valence, e the electronic charge,  $\epsilon$  the dielectric constant for the solvent,  $\psi$  the electrical potential at the interface, and 1/k the Debye-Huckel characteristic length.

 $\Pi_{el}$  represents the electrostatic forces, these forces arise from charges of equal sign which naturally accumulate on a liquid-air interface. Soap bubbles, for example, are also stabilized by this component because the surfactants on their surfaces generate an accumulation of electrostatic charges on them, stabilizing the thickness of the film.

 $\Pi_{vdW}$  is always generated by weak interactions between the two surfaces of the bubble. This component tends to destabilize the film as it is always of an attractive type between the two surfaces.

Finally, there is the  $\Pi_{ar}$  component generated by short-range repulsive forces. Usually, these forces originate from steric encumbrances of the macromolecules or from the coils of the polymer chains, which is why they are forces that only arise if the film reaches tens of nanometers.



**Figure 1.2.6**: A representation of how the components of disjoining pressure act on a freestanding liquid film.

#### 1.2.4 Marangoni effect

Marangoni effect occurs when there is a surface tension gradient. This surface tension gradient can arise from the presence of gradients in temperature, concentrations and more. Some examples of phenomena governed by the Marangoni effect are: tears of vine [40], Bénard-Marangoni instability [41], Marginal regeneration [9], [42] and some spreading mechanisms[25]–[29], [43]–[46].

In the case of soap films, the effect of Marangoni fluxes cannot be neglected as there are non-negligible phenomena (e. g. evaporation) that cause concentration gradients in these films.

The Marangoni effect can be used to obtain patterns, to control spreading of polymers, particles or surfactants distribution at the interface [47]–[49].

The way in which a droplet or a solution front is spread over a liquid-liquid or air-liquid interface is of great importance. This phenomenon can be used to obtain freestanding films [43], [45], [47], [50]–[52], there may be the need to avoid it or it can be studied in natural science. There are several mathematical models that describe the spreading at the interface of a solvent droplet loaded with particles, surfactants or polymers here the reader is going to be introduced to only some of them.

Spreading at the interface has already been introduced in Section 1.2.1 of this Chapter when it is driven only by capillary forces. When this occurs the spreading factor S of eq. (1.2.1) is assumed to be constant in time and space. However, what has just been said is correct only when all the fluids in contact are immiscible each other. If the drop deposited at the liquid-air (or liquid-liquid) interface consists of a liquid miscible with even just one between the subphase or topphase, then, the spreading factor S will no longer be constant in time or space. In this case the shear stresses generated by the Marangoni Effect are the main driving forces of the spreading.

$$S = \int_0^{R(t)} \frac{d\gamma}{dx} dx \qquad (1.2.9)$$

Where R(t) is the spreading length which is the distance of the edge of the fluid spread on the interface from the starting point of the spreading at the time t and  $\frac{d\gamma}{dx}$  is the surface tension gradient. Eq. (1.2.9) can be used instead of eq. (1.2.1) to predict spreading in case of miscible fluids. Berg, in his work [29], discovered that the assumption of a linear gradient of S in space is a good approximation to predict the spreading at a liquid-liquid interface of a fluid partially miscible with the subphase.

Spreading at the interface can be done with polymeric solutions, as also mentioned earlier in this section, to obtain thin and ultrathin polymeric membranes [43], [45], [47], [51], the process is sketched in Figure 1.2.7. There are not many studies concerning the formation of gel or polymer membranes at the liquid-air (or liquid-liquid) interface. So far, there have been no studies concerning the spreading of polymer solutions on freestanding thin liquid films.



**Figure 1.2.7**: A drop of polymer solution is spread on a liquid subphase at the liquid-air interface to form a polymeric membrane. (1) A drop of polymeric solution is dispensed on the liquid subphase; (2) the drop start to spread at the interface; (3) after the spreading a polymeric membrane is formed.

The Marangoni Effect is very important in freestanding thin liquid films also because it is the cause of "Marginal regeneration". Marginal regeneration was first observed in soap films, see Figure 1.2.8. These films always have moving "islands" within themselves. The islands move along the thickness gradient of the film to minimize surface free energy. These islands have a different local surfactant concentration at the interface respect to the surrounding film which is at the equilibrium [9], [42], Figure 1.2.8. This means that each island has a different surface tension and each of them tries to locate itself in a region of the film in which the surface energy can be minimized [9], [42]. The result is that thicker islands move to the thicker parts of the film and thinner islands move to the thinner regions.



**Figure 1.2.8**: A soap film formed by using the device described in *Chapter 5*, some of the marginal regeneration effects are highlighted in red circles

## 1.3 Leveling in freestanding films

Leveling in freestanding thin liquid film is a challenging phenomenon to quantitatively observe.

Today, few studies have been able to go into the details of this phenomenon. On the other hand, leveling in the case of thin films on solid substrates is much more studied in the state of the art [18]–[20], [53].

The phenomenon of leveling, as the word suggests, consists of the levelling of a liquid film which try to achieve a uniform value of thickness. The driving forces are the capillary ones opposed by the viscous dissipative forces of the liquid film. In case of the leveling of a liquid film on a solid substrate, the kinetics of leveling are slower than a freestanding liquid film due to the solid substrate that increases the viscous dissipation.

The leveling of a liquid film has multiple technological applications but it is also useful for studying several biological systems.

Depending on the gradient of curvature within a freestanding film, either leveling or drainage is possible. The phenomenon of drainage has already been widely studied in

the literature, whereas the leveling of a freestanding film has only recently been studied by Ilton et al. [18]–[20]

It was observed that thin stepped films placed on solid substrates increase the width w of the stepped profile according to a power law in time with an exponent of 1/4 [18], as explained in eq. (1.3.1):

$$w \propto (v_c h_2^3 t)^{\frac{1}{4}}$$
 (1.3.1)

Where  $h_2$  is the top step of the film,  $v_c = \eta \gamma$  is the capillary velocity, *t* is the time. Ilton et al. investigated also the leveling of freestanding stepped thin film [18]. The experiments consisted of making a polymeric freestanding stepped film, see Figure 1.3.1, from polystyrene and then cyclically heat it above the  $T_g$  of the polymer for a small amount of time and freeze it rapidly in order to measure its thickness profile by using an AFM after each cycle. The films used were only a few hundred nanometres thick and made from two freestanding stick together in order to obtain the step. They found out that the thin stepped freestanding films increased the width *w* of the stepped region according to a power law in time with an exponent of 1/2 [18], as explained in eq. (1.3.2):

$$w \propto (v_c h_2^3 t)^{\frac{1}{2}}$$
 (1.3.2)



**Figure 1.3.1**: (a) sketch of the evolution over time of stepped on a solid substrate (b) sketch of the evolution over time of a stepped freestanding film made by Ilton et al.

## 1.4 Buckling and Wrinkling

Buckling and wrinkling are mechanical instabilities that can affect objects such as beams and plates. Euler was the first to study the phenomenon of elastic instability of a beam under compression in the so called "Euler problem". However, these phenomena are observed not only in the case of macroscopic objects but also in the case of micrometric and nanometric objects. In particular, these instabilities also affect soft matter interfaces, which are the subject of increasingly innovative research to better understand the physics of their formation and their usefulness in modelling, measuring and organizing material properties at the micro and nanoscale. These instabilities are a very powerful tool to control the structure of freestanding films [32]–[38]. These instabilities are able to generate micrometric patterns on ultra-thin films that would otherwise be impossible to model on such a scale, in such a short time and with such precision.

Depending on the deformation field imposed on the film, it is possible to obtain a very specific wrinkling/buckling pattern. This pattern will also depend on the mechanical properties of the film, the morphology of the film and any surrounding substrates or

liquid phases. Deformations can be imposed with tools such as, for example, the Langmuir trough, the iris described in *Chapter 5* or by wetting, adhesion and swelling/shrinking.

In the case of a film adhered to a more yielding and elastic substrate, the classical equation is:

$$\overline{E_f}I\frac{d^4z}{dx^4} + F\frac{d^2z}{dx^2} + kz = 0 \quad (1.4.1)$$

Where  $\overline{E_f} = E_f/(1-\nu^2)$  is the plane-strain modulus of the film,  $E_f$  is the Young's modulus,  $\nu$  is the Poisson's ratio,  $I = wh^3/12$  is the moment of inertia (in which: w=width of the film, and h=thickness of the film), F is the uniaxial force or load applied to the sample and k is the Winkler's modulus of an elastic half-space ( $k = \overline{E_s} w \pi / \lambda$ , where  $\lambda$  is the wavelength of the buckling).



**Figure 1.4.1**: Scheme of how a thin film, attached to a softer material, generates wrinkling when the whole system is subjected to a compressive deformation.

From eq. (1.4.1) it is possible to retrieve the wavelength  $\lambda$  of the wrinkled film [32]:

$$\lambda = 2\pi h \left(\frac{\overline{E_f}}{2\overline{E_s}}\right)^{1/3} \quad (1.4.2)$$

Where *h* is the thickness of the film,  $\overline{E}_i$  (*i* = *s*, *f*) are the plane-strain modulus of the substrate and the film.

When there is not a solid substrate but a liquid subphase and molecules are spread on it forming a Langmuir monolayer the critical buckling wavelength of the monolayer under compression is:

$$\lambda = \left(\frac{\kappa}{g\Delta\rho}\right)^{1/4} \tag{1.4.3}$$

Where g is the gravitational acceleration,  $\Delta \rho$  is the density difference between the subphase and the topphase, K is the bending stiffness of the monolayer which is a function of molecular weight, temperature and coverage [54].

Several years later Vella et al.[55] studied the buckling behavior of a spherical latex particle monolayer on a water-oil interface under compression inside a Langmuir trough for many different diameters. What they find out is that the critical wavelength of the buckling is proportional to the square root of the film thickness ( $\lambda \propto h^{1/2}$ ). The model they retrieve is obtained from eq. (1.4.1) by substituting the last term kz with  $\rho gz$ . The resulting expression for the critical wavelength of the buckling of spherical particle layer on a liquid-air interface was:

$$\lambda = \pi \left(\frac{4}{3(1-\phi)(1+\nu)}\right)^4 \sqrt{L_c h} \tag{1.4.4}$$

Where  $\phi = A/A_s$  is the solid fraction of particles at the interface,  $\nu$  is the Poisson's ratio and  $L_c = \sqrt{\gamma/g\rho}$  is the capillary length.

As the geometry and physical properties of the particles change then the buckling phenomenon will change too [56], [57]. There could be a folding of the particle layer, ruptures or particle packing, aggregation and even flipping during compression [57], [58]. Also the presence of a meniscus of the interface can affect the buckling transition by generating a smooth cascade of the wavelength [59].

Imperiali et al. [58] studied much more into detail the buckling transition of XGO particles on a water-air interface which are similar to Graphene Sheet particle used in *Chapter 7*. The results of this work will be discussed in much more detail in *Chapter 7*.

## Reference

- [1] A. Sheludko, "Thin liquid films," *Adv. Colloid Interface Sci.*, vol. 1, no. 4, pp. 391–464, Dec. 1967.
- [2] A. Sheludko, "Thin liquid films," Adv. Colloid Interface Sci., vol. 1, no. 4, pp. 391–464, 1967.
- G. Singh, C. A. Miller, and G. J. Hirasaki, "On dimple formation in foam films," J. Colloid Interface Sci., vol. 187, no. 2, pp. 334–337, 1997.
- [4] J. E. Coons, P. J. Halley, S. A. McGlashan, and T. Tran-Cong, "A review of drainage and spontaneous rupture in free standing thin films with tangentially immobile interfaces," *Adv. Colloid Interface Sci.*, vol. 105, no. 1, pp. 3–62, 2003.
- [5] B. Mandracchia *et al.*, "Quantitative imaging of the complexity in liquid bubbles' evolution reveals the dynamics of film retraction," *Light Sci. Appl.*, vol. 8, no. 1, p. 20, 2019.
- [6] V. Ferraro, Z. Wang, L. Miccio, and P. L. Maffettone, "Full-Field and Quantitative Analysis of a Thin Liquid Film at the Nanoscale by Combining Digital Holography and White Light Interferometry," J. Phys. Chem. C, vol. 125, no. 1, pp. 1075–1086, 2021.
- [7] S. C. Ozan and H. A. Jakobsen, "On the effect of the approach velocity on the coalescence of fluid particles," *Int. J. Multiph. Flow*, vol. 119, pp. 223–236, 2019.
- [8] V. V. Yaminsky, 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*, vol. 26, no. 11, pp. 8061–8074, 2010.
- [9] L. Champougny, M. Roché, W. Drenckhan, and E. Rio, "Life and death of not so 'bare' bubbles," *Soft Matter*, vol. 12, no. 24, pp. 5276–5284, 2016.
- G. Debrégeas, P.-G. de Gennes, and F. Brochard-Wyart, "The Life and Death of 'Bare' Viscous Bubbles," *Science* (80-. )., vol. 279, no. 5357, pp. 1704–1707, 1998.
- [11] S. A. K. Jeelani and S. Hartland, "Effect of interfacial mobility on thin film drainage," *Journal of Colloid And Interface Science*, vol. 164, no. 2. pp. 296–308, 1994.

- [12] C. T. Nguyen, H. M. Gonnermann, and Y. Chen, "Film drainage and the lifetime of bubbles," vol. 14, no. 9, 2013.
- [13] S. S. Tabakova and K. D. Danov, "Effect of disjoining pressure on the drainage and relaxation dynamics of liquid films with mobile interfaces," *J. Colloid Interface Sci.*, vol. 336, no. 1, pp. 273–284, 2009.
- [14] J. Joye, C. A. Miller, G. J. Hirasaki, S. D. Company, and P. O. Box, "Dimple Formation and Behavior during Axisymmetrical Foam Film Drainage," vol. 10, no. 10, pp. 3083–3092, 1992.
- [15] J.-L. Joye, G. J. Hirasaki, and C. A. Miller, "Asymmetric Drainage in Foam Films," *Langmuir*, vol. 10, no. 9, pp. 3174–3179, Sep. 1994.
- [16] M. U. Vera and D. J. Durian, "Enhanced Drainage and Coarsening in Aqueous Foams," pp. 8– 11, 2002.
- [17] A. Saint-jalmes, "Physical chemistry in foam drainage and coarsening," no. July, 2006.
- [18] M. Ilton *et al.*, "Capillary leveling of freestanding liquid nanofilms," *Phys. Rev. Lett.*, vol. 117, no. 16, pp. 1–5, 2016.
- [19] J. D. McGraw, N. M. Jago, and K. Dalnoki-Veress, "Capillary levelling as a probe of thin film polymer rheology," *Soft Matter*, vol. 7, no. 17, pp. 7832–7838, 2011.
- [20] V. Ferraro *et al.*, "Axisymmetric bare freestanding films of highly viscous liquids: Preparation and real-time investigation of capillary leveling," *J. Colloid Interface Sci.*, vol. 596, pp. 493– 499, 2021.
- [21] W. Lv, H. C. Zhou, and J. R. Zhu, "Thickness measurement of full field soap bubble film in real time based on large lateral shearing displacement interferometry," *AIP Conf. Proc.*, vol. 1428, pp. 209–216, 2012.
- [22] H. Kočárková, F. Rouyer, and F. Pigeonneau, "Film drainage of viscous liquid on top of bare bubble: Influence of the Bond number," *Phys. Fluids*, vol. 25, no. 2, 2013.
- [23] V. Bergeron, "Disjoining pressures and film stability of alkyltrimethylammonium bromide foam films," *Langmuir*, vol. 13, no. 13, pp. 3474–3482, 1997.
- [24] L. Y. Yeo, O. K. Matar, E. S. Perez de Ortiz, and G. F. Hewitt, "Film drainage between two

surfactant-coated drops colliding at constant approach velocity," *J. Colloid Interface Sci.*, vol. 257, no. 1, pp. 93–107, 2003.

- [25] M. Santiago-Rosanne, M. Vignes-Adler, and M. G. Velarde, "On the spreading of partially miscible liquids," J. Colloid Interface Sci., vol. 234, no. 2, pp. 375–383, 2001.
- [26] V. M. Starov, "On the Spreading of an Insoluble Surfactant over a Thin Viscous Liquid Layer," vol. 113, no. 190, pp. 104–113, 1997.
- [27] P. Joos and E. Rillaers, "Spreading kinetics of Liquids on Liquids," *Physiochemical Hydrodyn*.
   *D.B. Spalding*, vol. 1, London, no. 3, pp. 133–139, 1977.
- [28] A. B. Afsar-Siddiqui, P. F. Luckham, and O. K. Matar, "The spreading of surfactant solutions on thin liquid films," *Adv. Colloid Interface Sci.*, vol. 106, no. 1–3, pp. 183–236, 2003.
- [29] S. Berg, "Marangoni-driven spreading along liquid-liquid interfaces," *Phys. Fluids*, vol. 21, no. 3, pp. 1–13, 2009.
- [30] C. Cheung, Y. H. Hwang, and X. Wu, "Diffusion of Particles in Free-Standing Liquid Films," pp. 2531–2534, 1996.
- [31] A. Yadav, E. J. Hinch, and M. S. Tirumkudulu, "Capillary-Induced Motion of Particles Bridging Interfaces of a Free-Standing Thin Liquid Film," *Phys. Rev. Lett.*, vol. 122, no. 9, p. 98001, 2019.
- [32] J. Y. Chung, A. J. Nolte, and C. M. Stafford, "Surface wrinkling: A versatile platform for measuring thin-film properties," *Adv. Mater.*, vol. 23, no. 3, pp. 349–368, 2011.
- [33] S. Cai, D. Breid, A. J. Crosby, Z. Suo, and J. W. Hutchinson, "Periodic patterns and energy states of buckled films on compliant substrates," *J. Mech. Phys. Solids*, vol. 59, no. 5, pp. 1094– 1114, 2011.
- [34] S. Bordács, A. Agod, and Z. Hórvölgyi, "Compression of langmuir films composed of fine particles: Collapse mechanism and wettability," *Langmuir*, vol. 22, no. 16, pp. 6944–6950, 2006.
- [35] H. Mei, R. Huang, J. Y. Chung, C. M. Stafford, and H. H. Yu, "Buckling modes of elastic thin films on elastic substrates," *Appl. Phys. Lett.*, vol. 90, no. 15, pp. 1–4, 2007.
- [36] Y. Mao, W. L. Wang, D. Wei, E. Kaxiras, and J. G. Sodroski, "Graphene structures at an

extreme degree of buckling," ACS Nano, vol. 5, no. 2, pp. 1395-1400, 2011.

- [37] E. Cerda, "Mechanics of scars," J. Biomech., vol. 38, no. 8, pp. 1598–1603, 2005.
- [38] J. Y. Chung, T. Q. Chastek, M. J. Fasolka, H. W. Ro, and C. M. Stafford, "Quantifying residual stress in nanoscale thin polymer films via surface wrinkling," ACS Nano, vol. 3, no. 4, pp. 844– 852, 2009.
- [39] J. Israelachvili, "Intermolecular and Surface Forces," Third Edit., Elsevier, Ed. San Diego: Academic Press, 2011, p. xix.
- [40] M. Gugliotti and T. Silverstein, "Tears of wine," J. Chem. Educ., vol. 81, no. 1, pp. 67-68, 2004.
- [41] M. Bestehorn, "Phase and amplitude instabilities for Bénard-Marangoni convection in fluid layers with large aspect ratio," *Phys. Rev. E*, vol. 48, no. 5, pp. 3622–3634, 1993.
- [42] V. Nierstrasz and G. Frens, "Marginal Regeneration and the Marangoni Effect.," J. Colloid Interface Sci., vol. 215, no. 1, pp. 28–35, 1999.
- [43] G. Choi *et al.*, "Understanding Marangoni flow-driven solidification of polymer semiconducting films on an aqueous substrate," *J. Mater. Chem. C*, vol. 8, no. 29, pp. 10010–10020, 2020.
- [44] J.-T. Zhang, L. Wang, D. N. Lamont, S. S. Velankar, and S. A. Asher, "Fabrication of Large-Area Two-Dimensional Colloidal Crystals," *Angew. Chemie*, vol. 124, no. 25, pp. 6221–6224, 2012.
- [45] Y. Tian *et al.*, "Kinetic Insights into Marangoni Effect-Assisted Preparation of Ultrathin Hydrogel Films," *Langmuir*, vol. 34, no. 41, pp. 12310–12317, 2018.
- [46] M. J. Large, S. P. Ogilvie, A. A. K. King, and A. B. Dalton, "Understanding solvent spreading for langmuir deposition of nanomaterial films: A hansen solubility parameter approach," *Langmuir*, vol. 33, no. 51, pp. 14766–14771, 2017.
- [47] D. Kim, S. H. Kim, and J. Y. Park, "Floating-on-water fabrication method for thin polydimethylsiloxane membranes," *Polymers (Basel).*, vol. 11, no. 8, 2019.
- [48] J. T. Zhang, L. Wang, D. N. Lamont, S. S. Velankar, and S. A. Asher, "Fabrication of large-area two-dimensional colloidal crystals," *Angew. Chemie - Int. Ed.*, vol. 51, no. 25, pp. 6117–6120, 2012.

- [49] N. E. Voicu, M. S. M. Saifullah, K. R. V. Subramanian, M. E. Welland, and U. Steiner, "TiO2 patterning using electro-hydrodynamic lithography," *Soft Matter*, vol. 3, no. 5, p. 554, 2007.
- [50] J. Kumaki, "Polystyrene Monomolecular Particles Obtained by Spreading Dilute Solutions on the Water Surface," *Macromolecules*, vol. 19, no. 8, pp. 2258–2263, 1986.
- [51] Y. Huang, K. Huang, N. Hussain, H. Matsumoto, and H. Wu, "Large-area, transferable sub-10 nm polymer membranes at the air-water interface," *Nano Res.*, vol. 11, no. 7, pp. 3833–3843, 2018.
- [52] Y. Tian *et al.*, "A facile approach to prepare tough and responsive ultrathin physical hydrogel films as artificial muscles," *ACS Appl. Mater. Interfaces*, vol. 9, no. 39, pp. 34349–34355, 2017.
- [53] B. Tsai, M. S. Carvalho, and S. Kumar, "Leveling of thin films of colloidal suspensions," J. Colloid Interface Sci., vol. 343, no. 1, pp. 306–313, 2010.
- [54] S. T. Milner, J. F. Joanny, and P. Pincus, "Buckling of langmuir monolayers," *Epl*, vol. 9, no. 5, pp. 495–500, 1989.
- [55] D. Vella, P. Aussillous, and L. Mahadevan, "Elasticity of an interfacial particle raft," *Europhys. Lett.*, vol. 68, no. 2, pp. 212–218, 2004.
- [56] T. D. Kassuga, "Buckling of Particle-Laden Interfaces," 2014.
- [57] Basavaraj, M.G., Fuller, Gerald G., Fransaer, J., and Vermant, Jan, "Packing, Flipping, and Buckling Transitions in Compressed Monolayers of Ellipsoidal Latex Particles," *Langmuir*, vol. 22, no. 19, pp. 6605–6612, 2006.
- [58] L. Imperiali, K. H. Liao, C. Clasen, J. Fransaer, C. W. MacOsko, and J. Vermant, "Interfacial rheology and structure of tiled graphene oxide sheets," *Langmuir*, vol. 28, no. 21, pp. 7990– 8000, 2012.
- [59] J. Huang, B. Davidovitch, C. D. Santangelo, T. P. Russell, and N. Menon, "Smooth cascade of wrinkles at the edge of a floating elastic film," *Phys. Rev. Lett.*, vol. 105, no. 3, pp. 2–5, 2010.
# Chapter 2: Quantitative imaging of the complexity in liquid bubbles' evolution reveals the dynamics of film retraction

In *Chapter 1* the reader was introduced to the observation techniques useful to characterize freestanding liquid/solid films. It was discussed how White Light Interferometry and Digital Holography can be used separately to obtain the thickness map over time of freestanding thin liquid films and which are the major issues that limit each technique.

This *Chapter 2* contains part of the result related to one of the main achievements of this work: the ability to measure freestanding films thickness, in this particular case semispherical bubbles, with high accuracy in space and time during their dynamic evolutions. This part of the PhD is related to step (2) previously described in the *Summary*. Indeed, before being able to manipulate complex and sensitive systems such as freestanding liquid films, it was necessary to be able to quantitatively observe them during their evolutions. It was therefore necessary to start investigating innovative measurement techniques to fill this experimental gap. For this purpose, an optical setup based on the Digital Holography was therefore designed and implemented. It succeeds in surpassing and improving the results obtained by the White Light Interferometry measurements made so far.

This first result was published in the journal "*Light: Science & Applications*" in 2019. The reader will find all the details in the attached article within this chapter together with supporting information. My contribution will be described below to highlight all aspects in which I was involved and I worked on personally. In particular, I contributed to the experiments regarding the acquisition and optimization of the setup to better observe the bubble during inflation and rupture but I also worked on the post processing, interpretation of the data and the theoretical part.

I choose the material used to form the bubbles, the experimental work has been conducted together with B. Mandracchia and Z. Wang using a Mach–Zehnder interferometer to observe the evolution of a bubble made of a polymeric solution. The bubble was formed on a commercial metal pipe connected to a syringe pump, see Figure S1 of the attached *Supplementary Information*. The thickness data acquired were

processed in order to obtain a thickness map of the bubbles. Then I learned how to retrieve the full-field thickness map from the wrapped phase map by using PUMA algorithm and eq. (1.1.2), the reader will find further details in the section "*Holographic thickness mapping for liquid films*" of the main text of the attached article. However, the thickness map of the bubble was not correct. In fact, this thickness map concerned the length of the light path through the walls of the bubble but in the direction orthogonal to the horizontal plane and not perpendicular to the bubble surface. It was necessary to correct the thickness measurement by using a trigonometric formula (section "*Estimation of the thickness normal to the bubble surface*" of the *Supplementary Information*).

Due to drainage, the wall of the bubble thins over time. In the case of a hemispherical bubble with a diameters of tens of millimeters and composed by an aqueous solution, I found in literature that the driving force behind the phenomenon is the gravity force. The analytical model used to evaluate the drainage is mentioned in *Chapter 1, Section 1.1*, it is also shown in *"Film thinning and bubble growth"* section of the attached article main text. However, during the inflation it was observed that the gravity drainage was negligible compared to the deformation undergone by the film as the thinning was linear over time during the bubble growth.

Immediately after inflation, a fingering pattern showed up on the bubble. This pattern is probably due to the occurrence of a liquid composition gradient between the top and bottom of the bubble generated by the coexistence of a gradient of Volume/Free-surface ratio and a evaporation flow independent from space. Therefore, it is possible that the pushing force is due to the Marangoni Effect and Marginal Regeneration. The characteristic wavelength of the pattern is of the same order of magnitude as that of a cylindrical flow with infinite length, further details about this effect can be found in section "*Fluid drainage and convection*" of the attached article main text.

# ARTICLE

#### Open Access

# Quantitative imaging of the complexity in liquid bubbles' evolution reveals the dynamics of film retraction

Biagio Mandracchia<sup>1</sup>, Zhe Wang<sup>1,2</sup>, Vincenzo Ferraro<sup>3</sup>, Massimiliano Maria Villone<sup>3</sup>, Ernesto Di Maio<sup>3</sup>, Pier Luca Maffettone<sup>3</sup> and Pietro Ferraro<sup>1</sup>

#### Abstract

The dynamics and stability of thin liquid films have fascinated scientists over many decades. Thin film flows are central to numerous areas of engineering, geophysics, and biophysics and occur over a wide range of lengths, velocities, and liquid property scales. In spite of many significant developments in this area, we still lack appropriate quantitative experimental tools with the spatial and temporal resolution necessary for a comprehensive study of film evolution. We propose tackling this problem with a holographic technique that combines quantitative phase imaging with a custom setup designed to form and manipulate bubbles. The results, gathered on a model aqueous polymeric solution, provide unparalleled insight into bubble dynamics through the combination of a full-field thickness estimation, three-dimensional imaging, and a fast acquisition time. The unprecedented level of detail offered by the proposed methodology will promote a deeper understanding of the underlying physics of thin film dynamics.

#### Introduction

Thin liquid films, such as soap bubbles, are ubiquitous in nature and technology. Biological vesicles, magma bubbles, insulating and food foams, detergents, and oil foams all share most of the physics, chemistry, and engineering of bubble formation and evolution<sup>1,2</sup>. Studying these films is also important since they mediate a wide range of transport processes, encompassing applications from nanotechnology to biology<sup>3–5</sup>. These films may display unusual dynamics featuring the formation of regular or chaotic structures, periodic waves, shocks, fronts, and "fingering" phenomena<sup>6</sup>. The entire research area is currently thriving with new discoveries and applications, particularly techniques for measuring both the long-range thickness mapping and its fast acquisition

Correspondence: Biagio Mandracchia (b.mandracchia@isasi.cnr.it)

© The Author(s) 2019

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

on evolving thin films. In fact, the measurement of the thin film thickness evolution as a consequence of manipulation, drainage, and rupture is key to understanding such behaviors<sup>7-9</sup>.

Currently, different techniques for quantitative phase imaging (QPI) are used to measure the thickness of transparent three-dimensional (3D) objects with one dimension thinner than the other two (films)<sup>10,11</sup>. In particular, interferometry is routinely used for the study of thin fluid films and surface topology, using both monochromatic and white light<sup>12,13</sup>. Interferometry measures the intensity of fringes produced by the interference of light reflected at the two interfaces of a thin film. Such intensity depends on the wavelength of light, the refractive index of the sample, and the thickness of the material. These techniques can be divided into two families, characterized by point-like or full-field inspection<sup>9</sup>. The first family of techniques measures the thickness in a very restricted area of the film's surface. Early studies used a photomultiplier to precisely measure the equilibrium thickness of soap films contained in a special cell,

<sup>&</sup>lt;sup>1</sup>CNR-ISASI, Istituto di Scienze Applicate e Sistemi Intelligenti "E. Caianiello" del CNR, Via Campi Flegrei 34, 80078 Pozzuoli, Napoli, Italy

<sup>&</sup>lt;sup>2</sup>College of Applied Sciences, Beijing University of Technology, 100124 Beijing, China

Full list of author information is available at the end of the article.

designed to isolate a thin film of liquid<sup>14</sup>. Modernized versions of this setup are currently used by several research groups<sup>15,16</sup>. Conversely, the full-field techniques measure the thickness across the entire surface of the film throughout the experiment<sup>17,18</sup>. Even though these systems can determine the film thickness with a resolution of a few nanometers, they lack the (lateral) spatial or temporal resolution necessary to follow the complex dynamics of an evolving thin liquid film.

In this study, we propose the adoption of a setup for the study of thin film dynamics based on off-axis digital holography (DH). Holographic microscopes are interferometers that allow for a pseudo-3D reconstruction of objects captured out of the best focal plane. This feature adds flexibility to the experimental procedure and in turn has kindled the spreading of DH beyond the field of metrology, from non-destructive testing for industry to label-free imaging of biological samples<sup>19-22</sup>. DH can accurately determine the phase and amplitude by means of dense carrier fringes down to fractions of the illumination wavelength. A benefit of digital holography with carrier fringes is that, unlike some other QPI techniques, e.g., phase shift interferometry<sup>23</sup>, the necessary information is completely gathered into a single frame, which is appropriate for high-speed data acquisition.

We report the measurement of the entire thickness distribution over an aqueous polymeric thin film solution during the formation of a bubble under non-ideal conditions, where several film thicknesses are simultaneously present in the film. Based on these data, the variation range and variation trend of the film thickness map are accurately measured, from the formation to the inflation and the bubble rupture. In particular, during the bubble growth, the location of the bubble surface changes continuously so that an imaging system in which the focusing of the image can be retrieved ex post from the experimental recordings is required. DH allows such a refocus of the sample by numerical processing of the recorded holograms<sup>24</sup>. In this way, it is possible to follow the position of the film surface a posteriori during bubble formation.

#### Results

#### Holographic thickness mapping for liquid films

The experimental setup was designed by embedding a custom setup to form and manipulate a thin liquid film within an off-axis Mach–Zehnder interferometer (see Figure S1a). The films are formed on top of a metal pipe with an internal diameter of 18 mm and a side inlet connected to a syringe pump (see Figure S1b-c). As a model system, we studied the temporal evolution of the thickness profile of bubbles formed from a film made of an aqueous solution of maple syrup and 0.05 wt% poly-acrylamide (PA). The bubbles were inflated by pumping

air from the side inlet of the pipe at a flow rate  $\phi = 0.015$ mL/s<sup>25</sup>. DH in off-axis geometry is based on the classic holography principle, with the difference being that the hologram recording is performed by a digital camera and transmitted to a computer, and the subsequent reconstruction of the holographic image is performed numerically (see Figure S1d-g). In DH, the interferometric acquisition system can only measure the phase modulo- $2\pi$ , commonly referred to as the wrapped phase. To recover the absolute phase, and then the thickness profile, we used the Phase Unwrapping Max-flow/min-cut (PUMA) method<sup>26</sup>. The PUMA method provides an exact energy minimization algorithm given the assumption that the difference between adjacent pixels is smaller than  $\pi$ rad. From the experimental point of view, this leads us to ensure that we have a good sampling of the observed area in order to assume that the thickness changes are sufficiently smooth in comparison to the fringe sampling, and no phase jumps are missed.

Once retrieved, the absolute phase gives a measurement of the optical path length experienced by the laser beam, which is equal to the thickness of the film multiplied by its refractive index. Thus, knowing the refractive index of the solution bunches used in the experiments (see Supplementary Information), we can easily map the evolution of the film thickness during the bubble growth and drainage (see Fig. 1a and Supplementary Videos 1 and 2).

Finally, DH acquisitions are pseudo-3D representations of the optical thickness of the sample. This means that the measured thickness profile, *s*, is a projection on the image plane of the three-dimensional structure of the sample (see Figure S3). However, the thickness normal to the bubble surface,  $\bar{s}$ , can be retrieved by geometric considerations (see Fig. 1b–d and Supplementary Video 3). It is worth noting that near the center, the two values are almost identical. For example, within 1.3 mm from the center, the estimated relative error is less than 1% (see Figure S4).

#### Film thinning and bubble growth

The shape of the bubble in our system is mainly controlled by the volumetric air flow,  $\phi$ , set by the pump, and, if  $\phi$  is constant, the volume of the bubble grows linearly in time:

$$V_{bubble} = \phi t \tag{1}$$

Considering the bubble as a spherical cap of height h and basal radius a, we can rewrite the previous equation as:

$$\frac{\pi}{6}h(3a^2+h^2) = \phi t \tag{2}$$

The geometric parameters of the bubble can then be fully controlled by the pump.



**Fig. 1 Holographic thickness mapping during inflation and drainage. a** Evolution of the film thickness during bubble inflation (left) and drainage (right). The thickness values were obtained by holographic measurements, where the refractive index of the sample was known to be 1.47. During the experiment, the film was inflated for 2 s and then allowed to drain naturally until rupture. **b** Corrected map of the film thickness. Assuming that the bubble surface can be approximated by a spherical cap, it is possible to retrieve the film thickness in the radial direction. Three-dimensional depictions of the radial thickness map are shown in (**c**) and (**d**). **e** Drainage and film thinning at the center of the bubble. Thickness maps of the center of a bubble obtained by digital holography. The bubble was allowed to grow for 14 s. Afterwards, the pump was turned off and the fluid was allowed to drain naturally until rupture. Scale bar 1 mm. **f** Plot of the thickness as a function of time during bubble blowing. **g** Plot of the thickness as a function of time during bubble blowing.

To study the film thinning due to the gravitational drainage of the fluid along the bubble surface, we adjusted the experimental parameters in order to maximize the bubble stability while approaching the hemispherical shape. We observed that reasonably stable bubbles could be formed by inflating air into the metal pipe with a relatively low flow of  $\phi$ =0.015 mL/s. Nonetheless, we found it difficult to reach a perfect hemispherical shape of the bubble (h~a). Furthermore, this configuration was impractical for the study of drainage towards the borders, as discussed in the previous section, so we decided to stop the pump at a height of approximately two-thirds of the basal radius (h~2/3a).

Bubbles were observed from the top and from the side. The top view was recorded by a CCD (charge-coupled device) camera at a maximum frame rate of 60 Hz. The side view was recorded by a CMOS (complementary metal-oxide semiconductor) camera (Apple Inc. iSight) at 30 Hz (see Supplementary Video 4). The experiments were conducted at 23 °C.

During inflation, h is a function of time and Eq. (2) can be rewritten as:

$$h(t)\left(h^2(t) + 3a^2\right) = \frac{6\phi}{\pi}t\tag{3}$$

From which we can derive the following formula:

$$h(t) = \frac{\sqrt[3]{\sqrt{4a^6 + b^2t} + bt}}{\sqrt[3]{2}} - \frac{\sqrt[3]{2a^2}}{\sqrt[3]{\sqrt{4a^6 + b^2t} + bt}}$$
(4)

with  $b = \frac{6\phi}{\pi}$ .

ł

A good fit of the experimental data is given by a firstorder approximation of Eq. (4) (see Figure S1h):

$$h(t) = \gamma \sqrt[3]{1+\beta t} - \frac{\gamma}{\sqrt[3]{1+\beta t}}$$
(5)

The thickness maps in Fig. 1e show an accumulation of the fluid in the central region, when the bubble is still flat (prior to pump starting, t = 0.1 s). During inflation, it is possible to observe a gradual thinning at the center that slowly continues when pumping is stopped. This process is the consequence of the gravitational drainage of fluid from the top towards the rim of the bubble.

Gravitational drainage causes the film thickness to decay exponentially with time<sup>27</sup>. Now, recalling that in the center,  $s = \overline{s}$ , we have that:

$$s = s_0 e^{-\frac{t}{\tau}} \tag{6}$$

where

$$\tau = \frac{\alpha}{h}; \alpha = \frac{\mu}{\rho g} \tag{7}$$

where  $\mu$  is the viscosity,  $\rho$  is the liquid density, g is the gravitational acceleration, and  $s_0$  is the initial thickness, see Fig. 1f.

During inflation, the film thickness of the bubble has a more complicated dependence with time. Indeed, the drainage is concurrent with the film stretching as a consequence of the increase in the bubble surface. However, the experimental data can also be satisfactorily approximated by a linear function (see Fig. 1g):

$$s = s_0(1 - \beta t) \tag{8}$$

#### Fluid drainage and convection

The continuous drainage towards the borders causes a decrease in the mass of the fluid with time. This is directly proportional to the volume of the film layer:  $V = M/\rho$ . Ideally, if the fluids were perfectly homogeneous, we would expect the drainage to be radial. This means that the thickness of the film does not depend on the polar angle but only on the latitude. This assumption fails for real films, where some level of inhomogeneity or asymmetry is present in the system and gives rise to various phenomena, such as convection of the fluid inside the film. As expected, the center of the bubble tends to become thinner the larger the bubble becomes (Fig. 2a, b and Supplementary Video 5). Nonetheless, this phenomenon is not homogenous. At the same time, it can be noted that this change in thickness does not happen uniformly, but it seems to be related to a momentary rearrangement of the fluid across the surface.

After an initial stasis period (Fig. 2c, gray area), the bubble volume drops with time and follows the expected exponential decay (red dashed line). Surprisingly, after reaching a plateau value, the volume begins to grow again a few seconds before the rupture (see Fig. 2c, yellow area). A more detailed analysis reveals that this increase is related to a change in the drainage dynamics of the fluid (see Fig. 2d, e). It is possible to devise two different contributions to this inversion of the trend, one at the center of the bubble and the other close to the edge of the pipe. The first contribution is due to a relatively small increase in the thickness of the film around the center (Fig. 2d-f, red arrows). The second contribution is given by a steady in-flow of part of the fluid from the edge of the pipe back towards the center of the bubble (Fig. 2d–f, black arrows). This in-flow takes the form of a regular pattern which can be devised after 4.5 s. The regular patterns observed at the latest stage of the film evolution dynamics, depicted in Fig. 2b, have been observed elsewhere for vertical and horizontal thin films and are usually addressed to as "fingers" due to the Marangoni effect, Plateau-Rayleigh instability, and/or marginal regeneration. In the context of Plateau-Rayleigh instability, in a cylindrical flow with infinite length, the characteristic wavelength of the pattern is:<sup>28</sup>

$$L = \frac{s}{4\pi}\sqrt{2 + 3\sqrt{2}Oh} \tag{9}$$

where  $Oh = \frac{\mu}{\sqrt{2\gamma\rho s}}$ . In our case, we found L=2.2 mm, which is of the same order of magnitude of the experimental value  $L_{exp} = 2\pi R/N=5.4$  mm, where N is the number of fingers on the image (N=9) and  $\mu$  is the viscosity. Furthermore, the motion of these patterns could be due to the marginal regeneration: along the edge of the film, where the film connects with the pipe, there is a "Plateau border" that has curved surfaces and a lower Laplace pressure than the central part of the film; thicker parts are bodily drawn into the border by the negative excess pressure, while the thinner film is pulled out of the border.

To give a plausible physical interpretation to the experimentally observed non-monotonic trend of bubble thickness shown in Fig. 2*c*, we performed a Finite Element numerical simulation of a system mimicking the experimental one. The mathematical model underlying the numerical simulation is created from the mass and momentum balance equations and the constitutive equation for the liquid film supplied with proper boundary and initial conditions (see the Supplementary Information for details). The constitutive parameters of the liquid have been derived from the rheological data of the fluid employed in the experiments (see the Supplementary Information).

The numerical temporal trend of the thickness at the center of the film h, normalized by its initial value  $h_0$ , is reported in Figure S2. By comparing Fig. S2c and Fig. 2c,



center with no particular ordering. It is possible to see very thin areas in the film randomly positioned. While the bubble is growing, however, most of the fluid is drained towards the edges and the thin films move to the center. **c** Plot of the volume as a function of time. After an initial stasis time, the mass drainage appears to follow the expected exponential behavior. However, just before the rupture time, the volume starts to increase once again. The derivatives along the time (**d**) and radius (**e**) show that this volume increase moves from the rim toward the center (see black arrows). **f** Thickness change vs time and azimuthal angle ( $\theta$ ) at three different distances from the bubble center, namely (I) 3 mm, (II) 6 mm, and (III) 9 mm. It is possible to observe some amounts of mass flowing back from the rim to the center

it is apparent that even if in the simulation a simplified system is considered, a good agreement holds between the experimental behavior of the volume of the bubble central portion and the simulated evolution of the film thickness, with an initial steep decrease while the bubble is inflated, an almost horizontal portion, and then an inversion of the trend, i.e., a thickening at the center of the bubble.

From the outcome of the numerical simulation, the latter can be ascribed to fluid drainage from the rim deposited on the pipe edge toward the center of the film due to the surface tension. Indeed, two opposite mechanisms act: during inflation, the film thins are at the center due to gravity and liquid adherence at the pipe wall, whereas surface tension makes the fluid move from the border to the center to minimize the film's external surface. Since inflation is fast, at the beginning, the effects connected to it dominate; then, when inflation ends, the "reservoir" constituted by the rim "pumps" the liquid back, thus making the film thicken at the center.

Figure 3a depicts a thin liquid film thickness evolution in a slightly different case in which the film is left for a long period of stasis before the inflation. In fact, thickening in the central part of the film is observed, due to sagging. Moreover, the topography of the film appears less



accumulates in the center. While the bubble is growing, however, the fluid is drained towards the edges. This process is chaotic and includes the presence of vortexes. **c** Plot of the volume as a function of time. The non-ideal nature of the drainage causes part of the fluid to come back towards the center of the bubble. This explains the presence of brief plateaus. Derivatives of the volume along time (**d**) and radius (**e**). **f** Thickness vs time and azimuthal angle ( $\theta$ ) at three different distances from the bubble center, namely (I) 3 mm, (II) 6 mm, and (III) 9 mm. The asymmetry of the process is especially clear in sections I and II

homogenous than in the case of Fig. 2, which is further evidence of the thickness measurement accuracy of the proposed technique, particularly when inhomogeneities are present. In these cases, the mass of the fluid tends to accumulate at the center of the film before inflation begins (see Fig. 3a, b). However, it quickly drains towards the rim once the bubble begins to grow. In this case, the dynamics of the drainage process are not only far from ideal but, at certain moments, the entire process seems to stop (see Fig. 3c, yellow areas). On the other hand, the rate of volume drainage does not go to zero, nor in time nor along the radius (see Fig. 2d–f). This supports the fact that the rapid movement of a large quantity of mass creates some complex movement of the fluid at the rim, which could temporarily counterbalance the draining process (see Supplementary Video 6).

#### Flow tracking

It is generally hard to describe a situation of complex motion such as the one depicted in Fig. 3. On the one hand, we have shown how it is possible to estimate the drift of the fluid and the dynamics of formation and dissolution of mass aggregates due to the presence of fluid vortexes. On the other hand, the assessment of the dynamics of liquid film rearrangement can be simplified following the displacement of particles dispersed in the fluid by holographic three-dimensional tracking.

We injected poly(methyl methacrylate) (PMMA) particles with a nominal diameter of 6  $\mu$ m into the PA solution and tracked them in three dimensions via automated numerical refocusing (see Fig. 4). After holographic amplitude reconstruction, three particles were selected from all visible points, which followed different paths along the bubble surface. To effectively identify and assess the movement of these particles, we used the correlation recognition tracking method<sup>29,30</sup>.

All three particles have different trajectories and show non-trivial flows within the film. Indeed, it is possible to observe how they can have both radial and swirling motion. The observed speed of the process and its span in the third dimension make tracking the particles difficult using standard imaging techniques. Holographic 3D tracking, conversely, has proven suitable for these situations. This piece of information can be useful for not only analyzing the mass flow on a bubble film surface but also for following the arrangement of colloids inside the film.

#### High-speed holographic imaging

The rupture of a bubble is a very fast process that requires the use of high-speed cameras to be observed. It can have very different dynamics, depending on the particular fluid or conditions of breakage<sup>31</sup>. One important parameter is the thickness of the opening rim and the possible presence of fluid droplets escaping from the film<sup>25,32</sup>.

To induce the rupture, we placed a needle on top of the metal pipe we used to grow the bubble. When the bubble reached an almost hemispherical shape, we gently lowered the needle until it was in contact with the film. To record the bubble rupture, we used a high-speed CMOS camera (Mikrotron, MC1310, 980 Hz).

Before the bubble rupture, it is possible to see a black film forming in correspondence with the tip of the needle (see Fig. 5a–c, white dashed line). The black film forms where the film thickness is half the illumination wavelength, when the local destructive interference cancels the light passing through. In holographic reconstructions, this local absence of light is associated with the generation of random values. This is why, in phase images, black spots correspond to areas of low signal-to-noise ratio. Finally, after approximately 453 ms, the boundary breaks and the bubble opens (see Supplementary Video 7).

High-speed holographic imaging can be useful for studying the mechanics of bubble rupture in deeper detail. Quantitative thickness mapping is essential for distinguishing the diverse profiles of the hole's rim, which characterize the retraction behavior of fluids<sup>33</sup>. Moreover, when asymmetric breakage profiles are observed<sup>34</sup>,

thickness mapping provides a link between the rupture path and the topography of the film.

For the first time, we observe the mass accumulation at the rupture edge during the film retraction, in accordance with the model proposed in ref. <sup>33</sup> (see Fig. 5d). During retraction, the film tends to accumulate at the rim, and then it becomes flatter during the last moments of the breakage. Also, the thinning process steadily continues and the black film rapidly expands around the needle. However, further analysis reveals that the boundary seems to move faster along the directions where the film is thinner ( $\theta = 180^{\circ}$  and 270°), probably following a least-resistance path (see Figure S3).

#### Discussion

The study of thin films and bubble rupture is of great interest to industrial processes and life science. Indeed, foams as well as plasma membranes or vesicles can be modeled in a manner similar to soap films and bubbles. The nature and properties of such structures have been the subject of extensive studies and continue to be attentively investigated<sup>35</sup>.

The characteristics of these systems, representing the hardest characterization challenges, can be summarized as follows. First, they have fast and ever-changing dynamics, and hence real-time imaging systems and possibly fast recording devices should be used. Second, the film thickness varies from tens of micrometers to a few hundred nanometers. This depends strongly on the nature of the solution and on the experimental conditions utilized for film formation. Last, but still important, the bubble film is not uniform. This means that the bubble surface is a complex system and has a unique structure each time a new sample is prepared. The distribution of the polymer across the film changes every time and, even under the same pumping conditions, the time to rupture is not constant. Using an air flow of 0.015 mL/s, we saw this time change from 3 s to 10 s. It is likely that such a difference is due to both the initial bubble thickness and the evolution dynamics. This is why evaluating the film thickness based on geometric considerations is not sufficient; instead, a continuous and quantitative inspection is necessary.

In this work, the design and implementation of a setup for imaging the dynamics of thin bubbles is presented. Our setup is based on DH to obtain quantitative images of the sample film dynamics. Throughout the past few years, many methods based on interferometry have been proposed to measure the actual film thickness and to monitor the interfacial rheological properties of these systems. Differential interferometry methods have also been described in investigations of contact angles<sup>36</sup> and bubble caps<sup>37</sup>. A method based on phase shift interferometry was developed for measurements on vertical films<sup>38</sup>. Other



approaches based on resonant differential interferometry, fringe patterns from a dual-wavelength reflection, and speckle interferometry have also been reported<sup>39,40</sup>.

Compared with the abovementioned interferometric techniques, DH combines several advantages. First, the spatial resolution is limited only by the optics used, which is not true for methods that use color matching, where the thickness is measured at a few points and then interpolated over the entire image<sup>9</sup>. Second, it gives the full-field three-dimensional information of the sample, unlike techniques that use photomultipliers to have very fast measurements but only at one point<sup>14</sup>. Third, DH does not require multiple exposures and can be matched with high-speed cameras to measure rapidly changing features<sup>23</sup>, such as the rim of the hole formed by the rupture of the liquid film.

Due to the spatial resolution and fast, full-field measurement of the liquid film thickness, we proved that this technique has several novel features. In Fig. 3, we showed the time dependence of the film thickness on an evolving geometry of the bubble (in the past, the only way to measure the bubble's thickness was without or after inflation). In Figs. 4 and 5, we showed the film volume's evolution and observed that, for example, in the last few seconds, the average film thickness increases, although drainage towards the bottom would have suggested a monotonic reduction of the average thickness. This thickening is caused by mass fluxes from the border of the film through the center, as is shown in Fig. 2 using gradient plots. As such, this technique can be used to investigate phenomena such as tear spreading or coffee ring formation<sup>3,9,41</sup>, where Marangoni effects, drainage, and wetting concur with the thin film evolution.

In conclusion, we proposed an experimental setup that for the first time gathers all the features required to study the liquid thin film evolution. Nevertheless, this comes at the price of a more complex data analysis. However, there are now diverse resources available for both hologram reconstruction and data analysis, so that a custom code is seldom needed. Furthermore, the local thickness is calculated assuming a certain degree of continuity, i.e., step heights of less than half a wavelength. Even if the results do not show any contrary evidence and seem to be in agreement with the expected values, it can still be viewed as a limitation. This limitation can be overcome by changing the system used for the bubble formation, e.g.,



growing bubbles on top of a glass surface. Then again, future work should focus on the implementation of a robust optical solution, such as dual-wavelength DH. This method can considerably extend the dynamic range of phase detection, removing most of the issues related to phase wrapping.

The application of DH is not limited to the proposed configuration but could be adapted to different ones without difficulty. The metal pipe, for example, can be replaced by a quartz cuvette, which would be useful to study the formation of gas bubbles in a fluid<sup>42</sup> (see Figure S4a). Alternatively, a configuration similar to the one proposed for phase shift interferometry can be used to study spherical bubbles pending from a nozzle<sup>23</sup> (see Figure S4b). If controlling the volume is not essential, the bubbles could be grown on a glass substrate or a Petri dish<sup>27</sup>, as in Figure S4c. In this case, the illuminating beam could be slightly tilted in order to avoid illuminating the needle. In this way, it is possible to image the very first moments of the bubble rupture close to the tip of the needle. Finally, virtually all the systems currently used for the study of flat bubbles could be easily integrated into a holographic microscope<sup>7,8,18</sup> (see Figure S4d).

#### Materials and methods Experimental setup

The DH setup consisted of an off-axis Mach-Zehnder interferometer with a sample stage adapted for the control of bubble growth. The experimental setup is schematically shown in Figure S1a. The illumination source was a HeNe laser ( $\lambda~=632.8\,nm$ ). In the Mach-Zehnder interferometer, the laser beam is divided into two parts by a polarizing beam-splitter cube. The resulting beams are referred to as the object and reference beam. The object beam illuminates the sample from the top and forms the image on the camera. On the contrary, the reference beam goes towards the camera without passing through the sample. The two beams are collected by a second beam-splitter cube, which is slightly tilted so that the two beams overlap with a small angle. This angle controls the period of the interference fringes and can be adjusted according to the sampling requirements. The image of the sample is de-magnified by a factor of 0.25 with two lenses put in front of the camera (f = 200 mm and 50 mm). With an estimated maximum diameter of the circle of confusion of 0.4 mm, the depth of focus of the system is 8 mm.

#### **Bubble formation**

The bubble growth was controlled using a custom metal pipe (see Figure S1b-c). The pipe had a diameter of 18 mm and a side inlet that was connected to a syringe pump (Harvard Apparatus). The rim of the top of the pipe was slightly grooved to maximize the contact surface with the bottom of the bubble. An aqueous solution of maple syrup (Maple Joe, Famille Michaud Apiculteur, Gan, France) and 0.05 wt% polyacrylamide (Saparan MG 500, The Dow Chemical Company, Midland, MI, USA) was used. Bubbles were created forming a film made of the solution on top of the pipe and placing the bottom on a glass Petri dish. The pipe was secured to the sample holder to prevent any possible movement during the measurements. Finally, a syringe pump (Harvard Apparatus, Model 22) was utilized to inflate the film and form a half bubble with a flow rate of 0.015 mL/s. A small amount of water was added onto the dish to avoid pumped-air leakage.

#### Wavefront reconstruction

Digital holography in off-axis geometry is based on the classic holography principle, with the difference being that the hologram recording is performed by a digital camera and transmitted to a computer, and the subsequent reconstruction of the holographic image is performed numerically.

The recorded intensity  $I_H(x_H y_H)$  at the hologram plane is the square module of the amplitude superposition of the object and reference waves. It is given by:

$$I_{H}(x_{H}, y_{H}) = |O_{0}(x_{H}, y_{H})|^{2} + |R_{0}|^{2} + O_{0}^{*}(x_{H}, y_{H})R_{0} + O_{0}(x_{H}, y_{H})R_{0}^{*}$$
(10)

The phase information of the hologram is provided only by the last two terms, which are filtered and centered in the Fourier space. We reconstructed the holograms by numerically propagating the optical field along the *z* direction using the angular spectrum method. If E(x,y;0) is the wavefront at plane z = 0, the angular spectrum  $A(\xi, \eta; 0)=F\{E(x,y;0)\}$  at this plane is obtained by taking the Fourier transform, where  $F\{\}$  denotes the Fourier transform;  $\xi$  and  $\eta$  are the corresponding spatial frequencies of *x* and *y* directions, respectively; and *z* is the propagation direction of the object wave. The new angular spectrum A at plane z = d is calculated from  $A(\xi, \eta; 0)$  as:

$$A(\xi,\eta;d) = A(\xi,\eta;0) \cdot exp\left\{j\frac{2\pi d}{\lambda} \left[1 - (\lambda\xi)^2 - (\lambda\eta)^2\right]^2\right\}$$
(11)

The reconstructed complex wavefront at plane z = d is found by taking the inverse Fourier transform as

$$E(x, y; d) = F^{-1}\{A(\xi, \eta; d)\}$$
(12)

where  $F^{-1}$  denotes the inverse Fourier transform. The

intensity image I(x,y;d) and phase image  $\phi(x,y;d)$  are simultaneously obtained from a single digital hologram by calculating the square module of the amplitude and the argument of the reconstructed complex wavefront:

$$I(x, y; d) = |E(x, y; d)|^{2}$$
(13)

$$\phi(x, y; d) = \arctan\left(\frac{Im[E(x, y; d)]}{Re[E(x, y; d)]}\right)$$
(14)

The workflow of the numerical reconstruction is shown in Figure S1d.

From the experimental data, we observed that for each frame's spectrum, the +1 order center changes with the bubble growth. We assumed that this phenomenon was due to the change in the bubble's surface. The bubble surface could be seen as a lens, twisting the object beam and slightly changing the off-axis angle during growth. Therefore, if we use the same filtering window for each frame of the holographic video, in the final phase result, we would obtain a random phase distortion, which would greatly affect the phase measurement accuracy. This issue was addressed using an automatic filtering algorithm during the holographic video reconstruction. This algorithm simply scans the Fourier spectrum for the maximum of the +1 diffraction order and centers the filter accordingly.

#### **Thickness estimation**

In DH, thickness estimation is directly related to the accuracy of the absolute phase recovery. Indeed, an interferometric acquisition system can only measure the phase modulo- $2\pi$ , commonly referred to as the wrapped phase. Formally, we have  $\phi(x, y; d) = \psi(x, y; d) + 2k\pi$ , where  $\phi$  is the absolute phase value,  $\psi$  is the wrapped phase, i.e., the measured value, and  $k \in \mathbb{Z}$  is an integer accounting for the number of  $2\pi$  multiples.

The main task of a phase unwrapping algorithm is the choice where the phase of the field should be shifted. In real experimental conditions, such a choice is often complicated by a phase noise, which can lead to erroneous phase unwrapping shifts. Since the phase noise often has a higher frequency than the desired signal, initial filtering of the wrapped phase field is the easiest and most intuitive way to simplify unwrapping<sup>43</sup>.

In this work, we used the PUMA method<sup>26</sup>. The PUMA method provides an exact energy minimization algorithm under the assumption that the difference between adjacent pixels is smaller than  $\pi$  rad. From an experimental point of view, this leads us to assume that the film thickness changes are smooth enough to be well sampled by the camera pixel. This assumption can be aided by changing the magnification of the system according to the homogeneity of the sample. A good sampling of the

Page 10 of 12

observed area is very important for an accurate thickness estimation. Indeed, when peaks or valleys are too steep in comparison to the fringe sampling, some phase jumps can be missed and a wrong absolute phase is recovered.

Furthermore, absolute phase estimation requires the assessment of a possible bias being unwrapped and real phase profile. This is usually done taking a reference point within the field of view. Here this reference point is given by the Newton black films that form during bubble inflation. The absolute thickness of these areas is half the illumination wavelength (in our case, 316 nm). In the frames where these are not present, we assumed that the process of film thinning is continuous and slow in comparison to the recording speed. At the end of the bubble's life, i.e., when close to rupturing, this assumption is not necessary because black films are usually present. However, more complicated situations in which the estimation of a reference thickness may be more difficult can be addressed by adopting one of the variant systems proposed in the Discussion section and sketched in Figure S3.

Once the absolute phase map is obtained, the local thickness estimation is given by the formula:  $s = \frac{\lambda}{2\pi} \frac{\phi}{n-1}$ , where  $\lambda$  is the illumination wavelength and *n* the refractive index of the solution. In this estimation *n* is considered a constant, which could induce some error when this is not true. In liquid films, of course, water evaporation alters the density of the solution and, in turn, the refractive index *n*. However, at the time scale of our experiments, we estimated that the error related to evaporation is negligible  $(\delta s < 5\%)$  (see Supplementary Information).

It is well known that holographic measurements yield pseudo-3D images. This means that the measured thickness profile, s, is a projection on the image plane of the threedimensional structure. However, the radial thickness,  $\overline{s}$ , i.e., the thickness along the normal to the bubble surface, can be retrieved by geometrical considerations (see Figure S6). Assuming that the upper and lower surface of the bubble are locally parallel, the relation between measured and radial thickness is  $\overline{s} = s_1 \sqrt{1 - \frac{r^2}{R^2}}$ , where r is the distance from the center in the image plane and R is the radius. It is worth noting that in terms of the center, the two values are almost identical. For example, we estimated a relative error  $\frac{\overline{s}-s}{s} = 1 - \sqrt{1 - \frac{r^2}{R^2}} < 1\%$ , for r < 1.3 mm (see Figure S7). On the other hand, in proximity of the pipe's border, the presence of meniscus deformation alters the estimation of  $\overline{s}$ (see Figure S8). For this reason, we used s instead of  $\overline{s}$  to calculate the volume or the draining rate at the borders because it conveys the same information with less geometrical assumptions (see Figure S9).

Herein, we used aqueous solutions that were sufficiently homogenous to not require any particular adjustment of the optical setup. However, when this is not the case and particularly inhomogeneous samples are to be studied, the use of two or more beams with different wavelengths is suggested<sup>44</sup>. Using different illuminating wavelengths with closer values gives us the possibility of creating a synthetic wavelength with a large value, and therefore we can enlarge continuous phase regions of the reconstructed wavefront. Often with this method, the unwrapping procedure is simplified or not required at all. Nonetheless, hologram registration with different light wavelengths results in a more complicated technique for both the hardware and software.

#### Acknowledgements

This work was supported by PNR 2015–2020 PON MIUR N. ARS01\_01183–SIRIMAP Project: "SIstemi di Rilevamento dell'Inquinamento MArino da Plastiche e successivo recupero-riciclo".

#### Author details

<sup>1</sup>CNR-ISASI, Istituto di Scienze Applicate e Sistemi Intelligenti "E. Caianiello" del CNR, Via Campi Flegrei 34, 80078 Pozzuoli, Napoli, Italy. <sup>2</sup>College of Applied Sciences, Beijing University of Technology, 100124 Beijing, China. <sup>3</sup>Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università di Napoli Federico II, Piazzale Tecchio 80, 80125 Napoli, Italy

#### Received: 2 October 2018 Revised: 13 December 2018 Accepted: 14 January 2019 Publiched enline: 20 January 2010

Published online: 30 January 2019

#### References

- Marmottant, P. & Hilgenfeldt, S. Controlled vesicle deformation and lysis by single oscillating bubbles. *Nature* 423, 153–156 (2003).
- Massol, H. & Koyaguchi, T. The effect of magma flow on nucleation of gas bubbles in a volcanic conduit. J. Volcanol. Geotherm. Res. 143, 69–88 (2005).
- Yu, G. H., Cao, A. Y. & Lieber, C. M. Large-area blown bubble films of aligned nanowires and carbon nanotubes. *Nat. Nanotechnol.* 2, 372–377 (2007).
- Salerno, A., Di Maio, E., Iannace, S. & Netti, P. A. Tailoring the pore structure of PCL scaffolds for tissue engineering prepared via gas foaming of multi-phase blends. J. Porous Mater. 19, 181–188 (2012).
- Ross, J. & Miles, G. D. An apparatus for comparison of foaming properties of soaps and detergents. *Oil Soap* 18, 99–102 (1941).
- Craster, R. V. & Matar, O. K. Dynamics and stability of thin liquid films. *Rev. Mod. Phys.* 81, 1131–1198 (2009).
- Champougny, L., Roché, M., Drenckhan, W. & Rio, E. Life and death of not so "bare" bubbles. Soft Matter 12, 5276–5284 (2016).
- Keal, L., Lapeyre, V., Ravaine, V., Schmitt, V. & Monteux, C. Drainage dynamics of thin liquid foam films containing soft PNiPAM microgels: influence of the cross-linking density and concentration. *Soft Matter* **13**, 170–180 (2017).
- Frostad, J. M., Tammaro, D., Santollani, L., Bochner de Araujo, S. & Fuller, G. G. Dynamic fluid-film interferometry as a predictor of bulk foam properties. *Soft Matter* **12**, 9266–9279 (2016).
- Gao, F., Muhamedsalih, H. & Jiang, X. Q. Surface and thickness measurement of a transparent film using wavelength scanning interferometry. *Opt. Express* 20, 21450–21456 (2012).
- Ta, V. D., Chen, R. & Sun, H. D. Tuning whispering gallery mode lasing from self-assembled polymer droplets. *Sci. Rep.* 3, 1362 (2013).
- Yoshino, H. et al. Measurement of thin film interfacial surface roughness by coherence scanning interferometry. J. Appl. Phys. 121, 105303 (2017).
- Maniscalco, B., Kaminski, P. M. & Walls, J. M. Thin film thickness measurements using scanning white light interferometry. *Thin. Solid Films* 550, 10–16 (2014).
- Radoev, B. P., Scheludko, A. D. & Manev, E. D. Critical thickness of thin liquid films: theory and experiment. J. Colloid Interface Sci. 95, 254–265 (1983).
- Nierstrasz, V. A. & Frens, G. Marginal regeneration and the marangoni effect. J. Colloid Interface Sci. 215, 28–35 (1999).

- Joye, J. L., Hirasaki, G. J. & Miller, C. A. Asymmetric drainage in foam films. Langmuir 10, 3174–3179 (1994).
- Lee, J., Nikolov, A. & Wasan, D. Surfactant micelles containing solubilized oil decrease foam film thickness stability. J. Colloid Interface Sci. 415, 18–25 (2014).
- Zhang, Y. R. & Sharma, V. Domain expansion dynamics in stratifying foam films: experiments. *Soft Matter* **11**, 4408–4417 (2015).
- Tian, L., Loomis, N., Domínguez-Caballero, J. A. & Barbastathis, G. Quantitative measurement of size and three-dimensional position of fast-moving bubbles in air-water mixture flows using digital holography. *Appl. Opt.* **49**, 1549–1554 (2010).
- Lebrun, D. et al. Size measurement of bubbles in a cavitation tunnel by digital in-line holography. *Appl. Opt.* **50**, H1–H9 (2011).
- 21. Cotte, Y. et al. Marker-free phase nanoscopy. Nat. Photonics 7, 113–117 (2013).
- Mandracchia, B., Gennari, O., Marchesano, V., Paturzo, M. & Ferraro, P. Label free imaging of cell-substrate contacts by holographic total internal reflection microscopy. J. Biophotonics 10, 1163–1170 (2017).
- Vannoni, M., Sordini, A., Gabrieli, R., Melozzi, M. & Molesini, G. Measuring the thickness of soap bubbles with phase-shift interferometry. *Opt. Express* 21, 19657–19667 (2013).
- 24. Memmolo, P. et al. Breakthroughs in photonics 2013: holographic imaging. *IEEE Photonics J.* **6**, 0701106 (2014).
- 25. Tammaro, D. et al. Elasticity in bubble rupture. Langmuir 34, 5646–5654 (2018).
- Bioucas-Dias, J. M. & Valadão, G. Phase unwrapping via graph cuts. *IEEE Trans. Image Process.* 16, 698–709 (2007).
- Debrégeas, G., De Gennes, P. G. & Brochard-Wyart, F. The life and death of "bare" viscous bubbles. *Science* 279, 1704–1707 (1998).
- Chandrasekhar, S. Hydrodynamic and Hydromagnetic Stability. (pp. p652. Dover Publications, New York, 1981).
- Su, T. W., Seo, S., Erlinger, A. & Ozcan, A. High-throughput lensfree imaging and characterization of a heterogeneous cell solution on a chip. *Biotechnol. Bioeng.* 102, 856–868 (2009).
- Mandracchia, B. et al. Holographic microscope slide in a spatio-temporal imaging modality for reliable 3D cell counting. *Lab. Chip.* 17, 2831–2838 (2017).

- Thoroddsen, S. T., Etoh, T. G. & Takehara, K. High-speed imaging of drops and bubbles. *Annu. Rev. Fluid. Mech.* 40, 257–285 (2008).
- 32. Savva, N. & Bush, J. W. M. Viscous sheet retraction. J. Fluid. Mech. 626, 211–240 (2009).
- Brenner, M. P. & Gueyffier, D. On the bursting of viscous films. *Phys. Fluids* 11, 737–739 (1999).
- Peco, C. et al. Influence of surface tension in the surfactant-driven fracture of closely-packed particulate monolayers. Soft Matter 13, 5832–5841 (2017).
- Saramago, B. Thin liquid wetting films. *Curr. Opin. Colloid Interface Sci.* 15, 330–340 (2010).
- Dimitrov, A. S., Kralchevsky, P. A., Nikolov, A. D. & Wasan, D. T. Contact angles of thin liquid films: interferometric determination. *Colloids Surf.* 47, 299–321 (1990).
- Nikolov, A. D., Kralchevsky, P. A. & Ivanov, I. B. Film and line tension effects on the attachment of particles to an interface: III. A differential interferometric method for determination of the shapes of fluid surfaces. J. Colloid Interface Sci. 112, 122–131 (1986).
- Greco, V., Molesini, G. & Quercioli, F. Accurate polarization interferometer. *Rev. Sci. Instrum.* 66, 3729–3734 (1995).
- 39. Kariyasaki, A. et al. Measurement of liquid film thickness by a fringe method. *Heat. Transf. Eng.* **30**, 28–36 (2009).
- Tebaldi, M., Ángel, L., Bolognini, N. & Trivi, M. Speckle interferometric technique to assess soap films. *Opt. Commun.* 229, 29–37 (2004).
- Paul, S. et al. Langmuir-Blodgett film deposition of metallic nanoparticles and their application to electronic memory structures. *Nano Lett.* 3, 533–536 (2003).
- Still, T., Yunker, P. J. & Yodh, A. G. Surfactant-induced Marangoni eddies alter the coffee-rings of evaporating colloidal drops. *Langmuir* 28, 4984–4988 (2012).
- Pritt, M. D. & Shipman, J. S. Least-squares two-dimensional phase unwrapping using FFT's. *IEEE Trans. Geosci. Remote. Sens.* 32, 706–708 (1994).
- Jeon, S., Cho, J., Jin, J. N., Park, N. C. & Park, Y. P. Dual-wavelength digital holography with a single low-coherence light source. *Opt. Express* 24, 18408–18416 (2016).

# Quantitative imaging of the complexity in liquid bubbles' evolution reveals the dynamics of film retraction

Biagio Mandracchia<sup>1,\*</sup>, Zhe Wang<sup>1,2</sup>, Vincenzo Ferraro<sup>3</sup>, Massimiliano Maria Villone<sup>3</sup>, Ernesto Di Maio<sup>3</sup>, Pier Luca Maffettone<sup>3</sup>, Pietro Ferraro<sup>1</sup>

<sup>1</sup>CNR-ISASI, Istituto di Scienze Applicate e Sistemi Intelligenti «E. Caianiello» del CNR, Via Campi Flegrei 34, 80078 Pozzuoli, Napoli, Italy. <sup>2</sup>College of Applied Sciences, Beijing University of Technology, 100124 Beijing, China. <sup>3</sup>Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università di Napoli Federico II, Piazzale Tecchio 80, 80125 Napoli, Italy.

The dynamics and stability of thin liquid films have fascinated scientists over many decades. Thin film flows are central to numerous areas of engineering, geophysics, and biophysics and occur over a wide range of lengths, velocities, and liquid properties scales. In spite of many significant developments in this area, we still lack appropriate quantitative experimental tools with the spatial and temporal resolution necessary for a comprehensive study of film evolution. We propose tackling this problem with a holographic technique that combines quantitative phase imaging with a custom setup designed to form and manipulate bubbles. The results, gathered on a model aqueous polymeric solution, provide unparalleled insight into bubble dynamics through the combination of a full-field thickness estimation, three-dimensional imaging, and a fast acquisition time. The unprecedented level of detail offered by the proposed methodology will promote a deeper understanding of the underlying physics of thin film dynamics.

Keywords: Metrology; Holography; Thin films, Thickness mapping.

### S1. Refractive index measurement

The phase signal obtained by DH is a measure of the optical path length experienced by the laser beam. This is related to the real space distance, *z*, covered by the light through the relation:

$$\phi = rac{2\pi n}{\lambda} z$$
 (1)

where n is the refractive index of the medium where the light is propagating.

To measure the actual thickness of the film, we have to evaluate the contribution to the optical path length due to the passage of light through the sample. This can be done using a hologram where no sample is present as a reference image. This image can be subtracted from the image of the sample and quantitative information about the thickness can be recovered:

$$z_s = \frac{1}{n_s - n_m} \frac{\lambda}{2\pi} \phi$$
 (2)

 $n_s$  is the refractive index of the sample and  $n_m$  the refractive index of the medium. In order to evaluate the actual thickness of the film, we need to know, then, its refractive index.

We measured the refractive index of PA 5% solution using a square microfluidic channel of 200  $\mu$ m thickness. We made two holographic maps of the channel: one with distilled water and the other with PA 5% solution. These were injected into the channel one after the other in order to look always at the same field of view, see Figure S2.

In the two phase images, the channel has the same profile but for a scaling factor due to the change in refractive index. Then, the refractive index of the solution could be obtained by the ratio:

$$\frac{\phi_s}{\phi_w} = \frac{n_s - 1}{n_w - 1}$$
 (3)

During the experiments two solutions bunches of PA 5% were used. The measured values of refractive index were  $1.47 \pm 0.09$  RIU and  $1.73 \pm 0.13$  RIU, respectively.

# S2. Numerical simulation of bubble growth

In order to give a plausible physical interpretation to the experimentally-observed non-monotonic trend of bubble thickness shown in Figure 2c of the main text, we have performed a Finite Element numerical simulation of a system mimicking the experimental one. An illustrative (not to scale) sketch of the computational domain is displayed in Figure S2a: we consider a cylindrical pipe with radius  $R_{\rm b}$  = 9 mm on the top of which, at time t = 0, a flat film of PA solution with initial thickness  $h_0 = 25 \,\mu\text{m}$  is laid. To simulate imperfect film deposition, a liquid rim with height  $h_{\rm r0} = 1 \,\text{mm}$  is deposited on the edge of the pipe. Air is pumped from the bottom of the film with pressure  $p_i$ , making it inflate until reaching an almost hemispherical shape, then air pumping is stopped and the film morphological evolution under the action of gravity and surface tension is followed. An illustrative image of the bubble at a generic time instant during its inflation is reported in Figure S2b. For simplicity, we have considered an axisymmetric geometry (assuming also the liquid rim around the film to be axisymmetric), thus the computational domain is the 2D "slice" bounded by curves  $\Gamma_1$ ,  $\Gamma_2$ ,  $\Gamma_3$ , and  $\Gamma_4$  in Figure S2a.

**Mathematical Model**. We have considered the system to be isothermal and the liquid incompressible. In addition, we have preliminarily evaluated the Ohnesorge number  $Oh = \mu/\sqrt{2\gamma\rho h_0}$ . By taking the liquid viscosity  $\mu \simeq 2.5$  Pa s, the density  $\rho = 1000$  kg m<sup>-3</sup>, the surface tension  $\gamma = 0.045$  N m<sup>-1</sup>, and the film initial thickness  $h_0 = 25 \mu$ m, we have got  $Oh \simeq 50 \gg 1$ , thus we have neglected the effects of inertia. Hence, the film dynamics is governed by the mass and momentum balance equations in the Stokes formulation, reading

$$\nabla \cdot \boldsymbol{u} = 0$$
 (S1)

 $-\boldsymbol{\nabla}p + \mu_1 \nabla^2 \boldsymbol{u} + \boldsymbol{\nabla} \cdot \boldsymbol{\tau} + \rho \boldsymbol{g} = \boldsymbol{0} \qquad (S2)$ 

where u, p, and  $\tau$  are the velocity, pressure, and viscoelastic stress tensor fields in the liquid (simulation outputs), g is the gravitational acceleration, and  $\mu_1$  is the "Newtonian" contribution to the liquid viscosity.

It is known from the literature (1) that polymeric solutions such as the one considered un our experiments can be modeled through the Giesekus constitutive equation

$$\lambda \boldsymbol{\tau}^{\nabla} + \boldsymbol{\tau} + \frac{\lambda \alpha}{\mu_2} \boldsymbol{\tau}^2 = 2\mu_2 \boldsymbol{D} \qquad (S3)$$

with  $\vec{\tau} = \frac{D\tau}{Dt} - (\nabla u)^{T} \cdot \tau - \tau \cdot \nabla u$  the upper-convected time derivative,  $\lambda$  the viscoelastic liquid relaxation time,  $\alpha$  the shear thinning parameter,  $\mu_2$  the non-Newtonian contribution to the viscosity of the liquid, and  $D = (\nabla u + \nabla u^{T})/2$  the symmetric part of the velocity gradient tensor. The values of the rheological parameters  $\mu_1$ ,  $\mu_2$ ,  $\alpha$ , and  $\lambda$  inputted in the simulations have been derived by fitting the experimental rheological for the PA solution used in the experiments and are  $\mu_1 = 0.5$  Pa s,  $\mu_2 = 2.0$  Pa s,  $\alpha = 0.3$ ,  $\lambda = 0.5$  s.

The balance equations that describe the system in Fig. S2a have been supplied with the following boundary conditions:

 $T \cdot n = \gamma n \nabla \cdot n + p_i n \text{ on } \Gamma_1 (S4)$   $u = 0 \text{ on } \Gamma_2 \quad (S5)$   $T \cdot n = \gamma n \nabla \cdot n \text{ on } \Gamma_3 (S6)$   $u \cdot n = 0 \text{ on } \Gamma_4 \quad (S7)$  $(I - nn) \cdot (T \cdot n) = 0 \text{ on } \Gamma_4 (S8)$ 

Equation S4, where  $\mathbf{T} = -p\mathbf{I} + 2\mu_1\mathbf{D} + \boldsymbol{\tau}$  is the total stress tensor in the fluid and  $\mathbf{n}$  is the outwardly directed unit vector normal to the boundary, is the Young-Laplace condition on the film bottom face with an extra-contribution given by the inflation pressure  $p_i$ . Equation S5 is the adherence condition between the liquid film and the solid edge of the cylindrical pipe. Equation S6 is the Young-Laplace boundary condition on the film top face. Finally, Equations S7 and S8 express the system axial symmetry.

Since the film has no inertia, no initial condition on the liquid velocity was needed, whereas, for what concerns the stress, we have assumed that, prior to the beginning of inflation, the sheet was stress-free, namely,  $\tau = 0$ .

**Numerical Technique**. The mass balance, the momentum balance, and the constitutive equations reported above have been solved through the Finite Element Method (FEM) with an Arbitrary Lagrangian Eulerian (ALE) formulation. The numerical code uses stabilization techniques widely described in the literature, such as SUPG and log-conformation (2-4). A detailed description of the algorithm employed to track the film surface is given in (5). As apparent in Figure S2a, the system has a symmetry axis coinciding with the *z* -axis, thus the physical domain could be reduced to a 2D axisymmetric computational domain. The latter has been discretized by an unstructured mesh made of triangular elements. During the simulation, the film deforms, making the mesh elements progressively deform. Every time the mesh quality went below a threshold, a re-meshing has been done and the computed velocity, pressure, and stress fields have been projected from the old mesh to the new one (6,7). Preliminary convergence tests have been performed in space and time, i.e., mesh resolution and time step for the numerical solution of the model equations have been selected such that invariance of the results upon further refinements has been ensured. Second order time integration has been used.

# S3. Estimation of the thickness normal to the bubble surface

It is well known that holographic measurements yield pseudo-3D images. This means that the measured thickness profile is a projection on the image plane of the three-dimensional one. However, the radial thickness, i.e. the thickness along normal to the bubble surface, can be retrieved by geometrical considerations, see Figure S3. Assuming that the upper and lower surface of the bubble are spherical and locally parallel, it is possible to calculate the radial thickness from the measured one using the relation  $\bar{s} = s \cos(\frac{\pi}{2} - \alpha) = s \sin \alpha$ . The relative error is  $\frac{\bar{s}-s}{s} = 1 - \sin \alpha$  where  $\sin \alpha$  can be replaced as a function of the radial position on the image plane using  $r = R \cos \alpha$  from witch  $\sin \alpha = \sqrt{1 - \frac{r^2}{R^2}}$ . Replacing  $\sin \alpha$  in the formula of the relative error found before  $\frac{\bar{s}-s}{s} = 1 - \sqrt{1 - \frac{r^2}{R^2}}$ , see Figure S4. For example, we estimated a relative error  $\frac{\bar{s}-s}{r} = 1 - \sqrt{1 - \frac{r^2}{R^2}} < 1\%$  for r < 1.3 mm

Figure S4. For example, we estimated a relative error  $\frac{\bar{s}-s}{s} = 1 - \sqrt{1 - \frac{r^2}{R^2}} < 1\%$ , for r < 1.3mm.

However, the bubble's shape deviates from the spherical geometry in proximity of the pipe's border. Here, the presence of meniscus deformation modifies the estimation of the radial thickness along the borders, see Figure S5.

## **S4.** Volume calculation

The estimation of the entire volume of the film was calculated as a sum of the parallelepipeds witch have got the pixels area as base and the measured thickness as height  $Vol = \sum \Delta x_i \Delta y_i \Delta s_i$ . The calculation of the volume is done using the measured thickness because the radial one in not well estimated along the pipe's border due to the meniscus, see Figure S6.

# **S5.** Water evaporation estimation

To evaluate all possibilities, we estimate also the effect of water evaporation on the refractive index during the experiments using  $\frac{n^2-1}{n^2+2} = \rho R(\lambda)$ , where *n* is the refractive index. The velocity of water evaporation is  $3 * 10^{-8} (g/mm^2)/s$ . After 3.6s, the density of the solution in a circle of  $1 mm^2$  area on top of the bubble increments by 0.5%, which leads to a 1% increment of the refractive index. Thus, the relative error on thickness estimation due to water evaporation is:

$$\frac{\delta s}{s} = \frac{\Delta n/n}{(n-1)/n + \Delta n/n} = 0.03$$

For n = 1.47 and  $\Delta n = 0.0147$ . Hence, we can argue that at the time scales of our experiments the effect of water evaporation, and the related change of the refractive index along the film, are negligible.

# References

- 1. Larson, R. G. Constitutive Equations for Polymer Solutions and Melts, Butterworths, Stoneham 1988.
- 2. Guénette, R.; Fortin, M. A new mixed finite element method for computing viscoelastic flows. J. Non-Newton. Fluid Mech. 1995, 60, 27–52.
- 3. Bogaerds, A. C.; Grillet, A. M.; Peters, G. W.; Baaijens, F. P. Stability analysis of polymer shear flows using the extended pom–pom constitutive equations. J. Non-Newton. Fluid Mech. 2002, 108, 187–208.
- 4. Brooks, A. N.; Hughes, T. J. Streamline upwind/Petrov–Galerkin formulations for convection dominated flows with particular emphasis on the incompressible Navier–Stokes equations. Comp. Meth. Appl. Mech. Eng. 1982, 32, 199–259.
- Villone, M. M.; Hulsen, M. A.; Anderson, P. D.; Maffettone, P. L. Simulations of deformable systems in fluids under shear flow using an arbitrary Lagrangian Eulerian technique. Comput. Fluids 2014, 90, 88– 100.
- 6. Hu, H.H.; Patankar, N. A.; Zhu, M. Y. Direct numerical simulations of fluid–solid systems using the arbitrary Lagrangian–Eulerian technique. J. Comput. Phys. 2001, 169, 427–462.
- 7. Jaensson, N. O.; Hulsen, M. A.; Anderson, P. D. Stokes–Cahn–Hilliard formulations and simulations of two-phase flows with suspended rigid particles. Comput. Fluids 2015, 111, 1–17.



**Figure S1: Holographic Setup for thin liquid film measurement.** a) Sketch of the experimental setup. BE: beam expander; M: mirror; HWP: half wavelength plate; PBS polarizing beam slitter; BS: beam splitter; L: lens. b) Side view of the metal pipe with a grown bubble on it. c) Top view of the pipe with the polymeric film on it before blowing. d-g) Depiction of the processing of digital holograms: recorded hologram (d), Fourier spectrum of the hologram (e), wrapped phase map of the object (f), final quantitative phase image of the object (g). h) The height, h, of the center of the bubble as function of the time with a constant in-flow of 0.015ml/s.



**Figure S2:** Numerical Simulation. (a) Sketch of the geometry of the computational domain at time t = 0. (b) Sketch of the geometry of the computational domain at a generic time instant during bubble inflation. (c) Numerical temporal trend of the thickness at the center of the film *h* normalized by its initial value  $h_0$ .



**Figure S3: Expansion of the black film during bubble rupture.** (a-d) Evolution of the black spot in four different directions:  $\theta = 0^{\circ}$ , 90°, 180°, and 270°, respectively. (e) The rim of the black film expands faster along the directions  $\theta = 180^{\circ}$  and 270°, in correspondence of thinner regions. The residual errors expected for PUMA unwrapping are smaller than the marker size.



**Figure S4:** Alternative implementations of DH for thin film evolution dynamic study. (a) the metal pipe can be replaced by a cuvette. (b) The object beam can image a bubble hanging from a nozzle. (c) The bubble can be grown on top of a glass surface. (d) A diaphragm can be used to grow and stretch a flat film.



**Figure S5: Refractive index measurement.** a) sketch of the microfluidic chip used for the assessment of the refractive index. b) Hologram of two microfluidic channels containing water and the PA %5 solution, respectively. c) Fourier transform of the hologram in b). d) Reconstructed phase map and e) average phase profile.



**Figure S6: Film thickness evaluation along the radial direction.** Scheme of the thickness measurement, as projected on the image plane, *s*, and the true thickness normal to the bubble surface,  $\bar{s}$ . By knowing the radius of the bubble, *R*, and  $\alpha$ , it is possible to retrieve  $\bar{s}$  from *s*.



Figure S7: Relative error as a function of the basal radius. Plot of the relative error as function of the basal radius of the bubble calculated for all the sample (left) and only the center (right).

# SUPPLEMENTARY INFORMATION



**Figure S8**: **Measured thicknesses of the bubble projected on the image plane.** In the red circles, the meniscus deformations close to the border of the pipe are evidenced. Below, the behavior of the thickness as a function of the coordinates  $(x_i, y_i)$ .

# SUPPLEMENTARY INFORMATION



Figure S9: Pseudo 3D holographic imaging. Depiction of the holographic thickness measurement as a projection of the three-dimensional profile.

# Chapter 3: Full-Field and Quantitative Analysis of a Thin Liquid Film at the Nanoscale by Combining Digital Holography and White Light Interferometry

In the previous *Chapter 2*, was given to the reader a detailed description about the holographic technique used to study, with an unprecedented accuracy and performances, freestanding liquid films, in particular bubbles. Furthermore, in *Chapter 1* the reader was introduced to another measurement technique used to characterize freestanding thin liquid films during this PhD: White Light Interferometry. In particular, the pros and the cons of both White Light Interferometry and Digital Holography were separately discussed, as well as in *Chapter 2*.

Here in *Chapter 3* the reader is going to find out how to overcome all the problems and limitations described above by merging together WLI and DH to achieve better results and the possibility to make in situ thickness measurements of a freestanding liquid film during its dynamic evolution. The work presented in this *Chapter 3* was published in *"The journal of physical chemistry"* in 2020 and the related article is attached below to let the reader find all the results and details. The technique described in this chapter is a new. The paper reports the results about this novel approach thus demonstrating its powerfulness and effectiveness to be used as metrological tool in the study of freestanding liquid films. I believe the reported results will open up new avenue in the field.

The experimental work has been conducted by using a Mach–Zehnder together with a White Light Interferometer at the aim to observe the thickness map evolution of aqueous freestanding thin liquid films stabilized by surfactants. The films were formed on a metallic ring and tilted respect to the horizontal to get a thickness gradient, induced by gravity forces, along a specific direction. The WLI data were used to calibrate the DH measure of the film thickness maps. In fact, the WLI measure is a self-reference method which has less resolution in space and time if compared to DH. Moreover, as shown in Figure 1.1.2, the measuring thickness ranges of the two techniques are different but still have an intersection. Thanks to this intersection the two methods can be used together to get, at the same time, the main advantage of each other, i.e. the self-reference feature

of WLI, and the high resolution of DH. The novel strategy to use jointly both methods allows for the first time a much wider measurable thickness range when compared to the two previous techniques separately.





pubs.acs.org/JPCC

Article

# Full-Field and Quantitative Analysis of a Thin Liquid Film at the Nanoscale by Combining Digital Holography and White Light Interferometry

Vincenzo Ferraro, Zhe Wang,\* Lisa Miccio, and Pier Luca Maffettone



**ABSTRACT:** Visualizing and measuring thin-film thickness at the nanoscale during dynamic evolution has been an open challenge for long term. Here, a joint-imaging method and the thereof innovative procedure are presented for merging digital holography (DH) and white light colorimetric interferometry (WLCI) measurement data in a single intelligent tool. This approach allows a complete quantitative study of the dynamic evolution of freestanding thin films under high spatial resolution and full-field modality over a large area. By merging interferometric and holographic fringes, it is possible to overcome the lack of DH in thickness measurements of ultrathin layers, providing a reliable reference for full-field quantitative mapping of the whole film with interferometric accuracy. Thanks to the proposed approach, the time-related and concentration-related evolution of surfactant film thickness can be studied. The thickness distribution curves reveal the small changes in the film thickness with time and concentration. The reported tool opens a route for comprehending deeply the physics behind the behavior of freestanding thin liquid films as it provides an in situ, continuous monitoring of film formation and dynamic evolution without limits of thickness range and in full-field mode. This can be of fundamental importance to many fields of applications, such as fluids, polymers, biotechnology, bottom-up fabrication, etc.

#### **1. INTRODUCTION**

Thin films are indispensable components of modern manufacturing; from electronic chips to household chemicals, they have accompanied mankind for centuries. Nowadays, even children can simply create a thin film with soap, but we are still looking for effective tools to measure their real-time thickness distribution. Quantitative thickness mapping for thin liquid films has been a widely studied issue over the past decades; visualizing and characterizing thin-film evolution are still longterm open challenges.<sup>1,2</sup> The analysis of thin films and bubbles has traditionally been performed by studying colored fringes resulting from the constructive and destructive interference of a specific wavelength beam; this technique is called thin-film interferometry or even white light interferometry (WLI).<sup>3,4</sup> WLI is a historic and reliable technique with multiple evolutionary branches. Many studies reveal that WLI has the capability to provide accurate local thickness for measurements

on smooth films. The reflection appears when the thickness of the film is proportional to a quarter of the recording wavelength so that its axial resolution could reach a quarter of the smallest illumination wavelength. In interferometry, when a transparent region is too thin, the thickness information cannot be probed by the light beam; this area is called black film.<sup>5</sup> Nevertheless, it is possible to determine the thickness of the entire film area by interference fringe recognition and calculating the theoretical value where black films appear during recording under visible light.<sup>6</sup> Note-

Received:October 22, 2020Revised:December 6, 2020Published:January 4, 2021





#### The Journal of Physical Chemistry C

worthily, films thinner than 100 nm can be observed with specialized detectors and light sources,<sup>7</sup> and measurement of local film thickness is possible under the assumption that the topographical structure of the film is simple (for example, flat with negligible defects). Nowadays, a major challenge with interferometry lies first in the inability to get accurate absolute thickness measurements when a black film is not presented in the imaging field of view (FOV). The second challenge lies in the difficulty of discerning structural information of the film surface. Typically, studies on thin films make use of very smooth areas with few defects rather than to study structurally complicated thin films.<sup>5</sup> The third challenge is related to the requisite spatial and temporal resolution of thin-film measurement under full FOV, for example, in the case of film instability and bubble rupture.<sup>8</sup> In these experimental cases, to get a complete data set, full FOV imaging is required; however, conventional interferometric technology is difficult to maintain high spatial and temporal resolution for full FOV.<sup>9</sup>

To overcome the above problems, a series of interferometric techniques, including colorimetric interferometry,<sup>6,10</sup> multiwavelength interferometry,<sup>11–16</sup> phase-shift interferome-try,<sup>5,17–19</sup> scanning interferometry,<sup>20,21</sup> and so on, have been proposed to address the thin-film challenges. Specifically, the colorimetric interferometry focuses on the challenge in the absolute thickness measurement; under the condition of the known relationship between film thickness and interferometric color scale, the film thickness distribution in a certain range can be extracted.<sup>22</sup> Multiwavelength interferometry mainly meets the needs for temporal resolution and imaging FOV; compared with the colorimetric one, it provides the measurement of complex surfaces with a relatively low spatial resolution. Phase-shift interferometry and scanning interferometry can guarantee high horizontal and vertical resolution at the same time; however, both of them have a abilities on revealing dynamicsweak temporal resolution. The interferometry, digital imaging, and optical microscopy (IDIOM) protocols proposed by Sharma et al. revealed the possibility of achieving dynamic thin-film measurements at high temporal and spatial resolution under certain limits.<sup>23</sup> For small-size freestanding thin films with a maximum thickness lower than a micron scale, IDIOM protocols show powerful capabilities in revealing dynamics of stratification and instability of freestanding films.<sup>24,25</sup> Overall, interferometry-based thin-film measurement tools have been fully studied in the past decade, but the existing approaches cannot meet easily all the needs of thin-film measurement requirements in various scenarios. We still lack measurement methods that have large FOV and high temporal and spatial resolution simultaneously.

In our previous study, as one of the interference imaging technologies, digital holography  $(DH)^{26-29}$  has been proven to be a reliable experimental method with the requisite spatial (thickness higher than half of the recording wavelength) and temporal resolution for full-field thin liquid film thickness measurements.<sup>30,31</sup> For the continuously growing film, the drainage process of the surface liquid flow can be accurately measured by the transmission DH approach, no matter how complicated the structure of the film is. Even though DH shows the ability to figure out two of the three challenges of interferometry, except for the first challenge mentioned above, it still has three aspects of limitations: (a) holographic recording of the entire life of one thin film is necessary for obtaining accurate thickness distribution, especially the last frame before film rupture when the common black film

pubs.acs.org/JPCC

(CBF)<sup>32</sup> appears in the hologram; (b) areas with local thicknesses less than half of the recording wavelength cannot be accurately recorded without a background reference; (c) due to the lens effect of the thin liquid film itself, it is necessary to build a three-dimensional evolution model of the film to remove phase distortion effectively. Therefore, for some liquid films that break quickly (e.g., low-concentration liquid film) or will not rupture (e.g., protein film), holography is difficult to apply on performing accurate thickness measurements.

As one of the state-of-the-art imaging technologies, DH has shown enough potential to compete for the optimal thin liquid film imaging tool. Here, we show that one possibility for improving thin-film measurements having a suitable tool in all conditions is a fusion approach between WLI and DH. Specifically, both WLI and DH share the same major challenge, i.e., the appearance of CBFs would be a necessary condition for most related thin-film thickness mapping technologies. Fortunately, for a thin liquid film, we notice that the colorimetric calculation of thin-film color fringes is an approach easy to implement and can overcome the black film dilemma in DH. It can provide the thickness of ultrathin areas that are missing in digital holographic measurements when measuring the thickness of the surfactant film.<sup>33,34</sup> Therefore, a wise solution could be to combine DH and colorimetric calculation to increase the thickness measurement range in thin liquid film imaging.

In this paper, we present a fusion method, which combines DH with white light colorimetric interferometry (WLCI), and achieved large FOV (radius > 5 mm), high sensitivity, a wide range of thicknesses (around 100 nm to 10  $\mu$ m), and highspatial-resolution thin-film measurement based on a pair of interference images. Thanks to this joint-imaging method, the above-mentioned challenges of holography and interferometry are solved at the same time. Meanwhile, the recording speed of the proposed method depends only on the recording equipment used, which means that high-temporal-resolution thin-film recording could be realized using a high-speed camera. Following our fusion approach strategy, we present a recording geometry that combines an off-axis Mach-Zehnder interferometer and an oblique illumination WLI system. This system uses two cameras and provides digital holograms and WLI interference fringe images simultaneously, thus allowing building the basis for the hybrid numerical reconstruction process that is able to furnish measurements in all of the FOVs without ambiguity. The essential advantage of the proposed hybrid method is that there is no need for CBF thickness selfreference or recording of complete film life cycles, which are indispensable in DH processing. The thickness calculation and calibration could be applied thanks to the fusion of holographic numerical reconstruction process<sup>26,27,30</sup> and the colorimetric fringe pattern process.<sup>35</sup> To prove the capabilities of the proposed approach, we carried out experimental investigations on nonionic surfactant films. A series of time-related and concentration-related tests were performed and revealed the relationship between the film thickness distribution and its dynamic variations. We believe that the technical requirements for dynamic thin-film thickness mapping will expand to more fields and emerging issues, e.g., thin-film dynamics,<sup>36</sup> branched flow of light,<sup>22</sup> controlled pyroelectric tweezers,<sup>37</sup> and so on.

#### 2. METHODS

DH in the off-axis geometry is also based on the holography principle, but different from conventional optical holography,
#### The Journal of Physical Chemistry C Article pubs.acs.org/JPCC BE Light source Camera Laser **Object Beam** HWP<sub>1</sub> PBS $HWP_2$ $n_0$ Thin Light source $n_1$ film Camera 1 $n_0$ Thin film (b) $L_2$ BS $M_2$ Metal ring Camera 2 (d) (a) (c)

**Figure 1.** Schematic diagram of the holographic and interferometric hybrid recording setup. (a) Geometry of the recording setup. Laser, a coherent light source of wavelength 532 nm; BE, beam expander;  $HWP_1/HWP_2$ , half-wave plates at wavelength 532 nm; PBS, polarizer beam splitter tube for wavelength 400–700 nm;  $M_1/M_2/M_3$ , mirrors; BS, beam splitter tube for wavelength 400–700 nm;  $L_1$ , a convex lens with a focal length of 50 mm; camera 1, a camera for colorimetric interferometric recording; and camera 2, a camera for holographic recording. (b) Principle diagram of thin-film colorimetric interferometry. (c) Metal ring for creating the thin liquid film. (d) Prepared nonionic surfactant film placed on the sample stage.

the recording of digital holograms is performed by a digital camera such as a charge-coupled device (CCD) or a complementary metal–oxide semiconductor (CMOS). The subsequent reconstruction imaging of the holograms is carried out numerically with the holographic reconstruction algorithm in a computer.<sup>28,29</sup> The optical setup for the proposed approach is designed based on an off-axis Mach–Zehnder interferometer with a WLI arrangement to the object arm of the holographic geometry. In this case, DH and WLI recordings can be implemented for the same thin liquid film simultaneously.

As shown in Figure 1a, the optical setup of off-axis transmission DH recording is configured with two coherent beams from a laser source of a wavelength of 532 nm (Thorlabs, CPS532). The laser is divided into two beams by a polarized beam splitter (PBS) prism after being enlarged by a beam expander (BE) structure, where the transmission beam is set as a reference beam and the reflected beam is set as an object beam. The first half-wave plate (HWP<sub>1</sub>) is placed in front of the PBS to adjust the splitting ratio of the two beams, and the second half-wave plate (HWP<sub>2</sub>) is located behind the PBS to adjust the polarization state of this beam. The thin liquid films are created and held by a metal ring with an inner diameter of 10.52 mm, as shown in Figure 1c. Once the film preparation is completed, the metal ring will hold the film until it ruptures. The sample is placed in the path of the object beam so that its amplitude and phase information can be loaded on the object beam. After passing through the beam splitter prism tube (BS), the object beam and reference beam with a certain

angle are combined into optical interference. In addition, a pair of lenses with different focal lengths is placed at a certain distance from the sample, which constituted a 4F system to resize the object beam. Herein,  $L_1$  is a convex lens with a focal length of 100 mm and  $L_2$  is a convex lens with a focal length of 50 mm. A digital single-lens reflex (DSLR) camera without a lens was employed for DH recording (camera 2 in Figure 1), which was a Canon EOS 5D Mark III with  $5760 \times 3840$  pixels of pixel size 6.22  $\mu$ m. For suppressing the scattering noise from a white light source, the camera's recording parameters were set intentionally as ISO-125, aperture f/0 (no lens), and exposure time 1/1000 s. This setting ensures that the peak intensity of the digital hologram is below 200 units when recorded in the proposed system. For extracting film thickness information using digital holography, thanks to the numerical reconstruction process, the relative phase information of the thin-film thickness can be obtained. The phase is based on the optical path length experienced by the object beam, which is equal to the thickness of the film multiplied by its refractive index (RI). Thus, once we reconstruct the phase  $\varphi$  from the digital hologram, the local thickness h of the film can be calculated by formula

$$h = \frac{\lambda \varphi}{2\pi (n_1 - n_0)} \tag{1}$$

where  $\lambda$  is the wavelength of the recording beam and  $n_0$  and  $n_1$  are the RIs of air and thin liquid film, respectively. Furthermore, to prove that the white light interferometric recording process will not affect the holographic recording and



**Figure 2.** Experimental results of the last frame before rupture recorded by DH and thin-film WLCI. (a) WLI imaging result. (b) WLCI thickness distribution based on the standard Newton color scale of the surfactant film. (c) WLCI thickness distribution based on self-reference colorimetric interferometry. (d) Digital hologram; the zoomed-in area reveals the interference fringes. (e) Holographic thickness distribution before calibration. (f) Holographic thickness distribution calibrated by the WLCI result in (c). (g) Average thickness curves in selected areas; the red curve, named as IntF, is extracted from (c), the blue curve, named as DH, is extracted from (e), and the green curve, named as DH-cal., is extracted from (f).

show the reliability of the proposed system, a transparent poly(methyl methacrylate) (PMMA) phase grating with the known refractive index and structure information was recorded by the DH method; please refer to Supporting Information B.

The optical geometry of thin-film WLI in the hybrid recording setup follows the conventional side-illumination structure.<sup>38</sup> The white light source, which is an incoherent light source, and the camera with an automatic zoom configuration are placed on the top side at a certain angle to constitute the entire structure, as shown in Figure 1b, where  $\alpha$  is the angle of incidence, which is  $37.3^{\circ}$  in our setup;  $\beta$  is the angle in the film, which could be calculated by Snell's law from  $\alpha$  and the known refractive index; and h is the local thickness of the film. In this case, the white light beam emitted by the light source is reflected by the upper and lower surfaces of the film and then creates multicolor interference fringes. A CMOS camera was employed as camera 1 for interferometry recording, which was a Sony Exmor RS IMX315 with  $4320 \times 3240$  pixels of pixel size 1.22  $\mu$ m. Once we illuminate the thin film with white light, the observation color at a specific angle is related to its thickness, and it also upon the angle of view. The visible light part will be converted into color information when a digital camera is used to record the reflected light waves. Thus, based on the hypothesis of known RIs, the thickness of the thin film can be obtained by formula

$$h = \left(m - \frac{1}{2}\right) \frac{\lambda_{\rm r}}{2n_1 \cos\beta} \tag{2}$$

where  $\lambda_r$  is the wavelength of the reflected beam and *m* is the order of wavelengths, related to the Newton color scale. For some special films, such as surfactant films, the relationship between the thickness and the recorded color under vertical white light illumination has been obtained through experiments and simulations.<sup>33</sup> Therefore, we can establish a clear one-to-one correspondence between the thickness and the

recorded color under certain illumination angle  $\alpha$ . Based on this correspondence, for the color fringes of the same surfactant films under a specific illumination angle, we can obtain the thickness information through color comparison; this method is known as WLCI.

In our setup, DH and WLI geometries record the same area of the film after fine adjustments; it is the foundation for the fusion and comparison of the two methods. The irradiation power of the white light source is 8  $\mu$ W and the laser power is 0.26 mW on the same plane, which is  $\approx$ 32 times that of white light. Under this condition, the influence of the signal-to-noise ratio (SNR) on hologram recording caused by white light scattering is less than 3%. In addition, a set of shutter sounds of the DSLR camera were used to synchronize the recording time between the two different methods. Even so, a slight difference in the recording time was still unavoidable, which was caused by the unstable shutter speed of the DSLR camera during continuous recording but can be adjusted by framerate matching (IMX315, 30 fps; EOS 5D Mark III, 5 fps).

Based on the hybrid recording system, as shown in Figure 1, a thin-film thickness extraction approach is proposed, which combines thin-film digital holographic thickness reconstruction with colorimetric processing in WLCI. To perform the fusion thin-film thickness calculation approach, DH and WLI are used to obtain the measurement results at the same FOV and recording time. Thus, the complementary characteristics of DH and WLI act as the core of fusion thickness calculations. The lateral resolution will depend on the DH setup, while the axial resolution depends on both DH and interferometry: once the film thickness is below half of the recording wavelength, the axial resolution depends on interferometry, otherwise relies on DH. Compared with two independent methods, the fusion approach can satisfy the following issues: (a) thickness calculation regardless of the presence of the black film; (b) phase calibration in DH no longer uses background

#### The Journal of Physical Chemistry C

subtraction; (c) the lower limit of the measurement range is determined by WLI, while the upper limit is ensured by DH, thus significantly extending the measurement range; and (d) the measurement of complex thin-film structures with high temporal and spatial resolution is achievable. In other words, this hybrid method can meet all of the challenges in the measurement needs of thin films.

Taking 60 mg/L Merpol solution to form a thin liquid film, a pair of digital holograms and color interference fringes was recorded when the thin film was close to rupture and then they were processed by different approaches; the results are shown in Figure 2. The reason to choose this time point is that it has a large black film area, where DH is unable to provide accurate thickness mapping once the thickness is lower than 266 nm.

In Figure 2, the results of DH and WLI were obtained at approximately the same time and then the thickness of the pair of data was calculated by independent digital holographic reconstruction, interference colorimetry, self-reference colorimetry, and the proposed approach. Figure 2a shows the original WLI result and the corresponding color-thickness scale in the ideal state (which does not consider the color differences introduced by the recording camera). A big black film is presented in the lower part of FOV. As seen from the colorimetric gradation, the thickness of the black film area in WLCI is less than 100 nm; Figure 2b,c shows the full-field thickness distribution calculated by colorimetry. In these cases, different colorimetric scales are used: (a) For Figure 2b, the thickness is calculated from the standard Newton color scale of the surfactant film. Herein, the mismatch between the standard color scale and the recorded colors causes a discontinuous distribution of the thickness; this is related to the insufficient color resolution of the CMOS chip. (b) For Figure 2c, the color scale is extracted from a continuously changing color band in Figure 2a and then compared and assigned to the existing color levels to optimize results; hence, the thickness distribution shown in Figure 2c smoothly changes. We named this approach as thin-film self-reference colorimetric interferometry (in Supporting Information A). However, the accuracy of thickness calculation for complex surfaces from the self-reference colorimetry method is poorer than that of the conventional one because complex surfaces usually require more accurate color resolution. This is the well-known drawback of the self-reference method. As seen from the region affected by Marangoni flow in the upper left corner of Figure 2c, the thickness distribution of the corresponding area could not be calculated due to the lack of color scales in selfreference color colorimetry.

Figure 2d,e shows the digital hologram of the recording area and the corresponding thickness distribution, respectively. The thickness map is reconstructed following the approach from a previous study.<sup>30</sup> Comparing the results in Figure 2e,c under the same color scale, there is a vast difference in the local thickness of the black film. As mentioned before, independent transmission holography cannot accurately reveal the local thickness, where less than half of the recording wavelength occurs (herein, around 266 nm) without the aid of reference points; it is providing an incorrect quantitative profile in Figure 2e. However, self-reference colorimetric interferometry provides more reliable thickness distribution results, as shown in Figure 2c. Thus, the WLCI results can be used to adjust the local thickness in holographic results.

To calibrate the thickness by holographic measurements, the effective thickness areas need to be extracted from WLCI results, thus fitting the thickness distribution of each area to get the trends. These trends will calibrate the holographic thickness distribution and can also be converted to an equivalent phase according to eq 1, so allowing for phase distortion calibration. Generally, off-axis DH geometry involves three types of phase distortions: (a) first-order phase distortion generated by the off-axis phase angle, (b) second-order phase distortion introduced by the optical system, and (c) secondorder phase distortion related to the lens effect of the thin film. These three distortions are treated as one higher-order phase distortion to be removed because they are difficult to process separately. For the measurement in Figure 2, the y-direction thickness calibration is taken as an example to show the calibration processing. The area within the dotted frame from Figure 2c is extracted and the thickness value is averaged along the *x*-direction. As a red line shown in Figure 2g. The range of the y-direction average thickness of the dotted frame area in Figure 2c is from 100 to 550 nm; it is a reliable thickness distribution measured by WLCI. The black film in DH will appear in the areas where thicknesses are less than 277 nm. For these areas, WLCL can reveal the thickness vector when they are smooth enough. Therefore, the holographic thickness vector taken from the same film area shows poor measurement results, as the blue line in Figure 2g. The y-directional holographic thickness vector shows a false trend; thanks to the WLI results in Figure 2a, we know that this lift is unreasonable, and it could be an error caused by holographic numerical phase dedistortion processing.

The core of thickness calibration is the conversion of two thickness vectors. First, sparse sampling is performed on the two thickness vectors; then, the thickness distribution of the corresponding coordinates is linearly fitted in related curves. As a result, the slope  $\tan \gamma$  of the holographic thickness fitting curve and the slope  $\tan \theta$  of the interferometric thickness fitting curve are obtained. The thickness calibration can be performed according to the following equation

$$h'_{\rm DH} = \frac{\tan\theta}{\tan\gamma} (h_{\rm DH} - h_{\rm DH\_min}) + h_{\rm WLCI\_min}$$
(3)

where  $h'_{\rm DH}$  represents the holographic thickness after calibration from  $h_{\rm DH}$ ,  $h_{\rm DH\_min}$  represents the minimum thickness of the selected area in the holographic results, and  $h_{\rm WLCI\_min}$  represents the minimum thickness of the selected area in interferometry results. Furthermore, due to the linear relationship between the phase and thickness in the holographic thickness calculation, the above thickness calibration process could be converted into a phase distortion calibration process

$$\varphi' = \frac{\tan \theta}{\tan \gamma'} [\varphi - \varphi_{\min}] + \frac{2\pi (n_1 - n_0) h_{\text{WLCI}\_\min}}{\lambda}$$
(4)

where  $\varphi'$  represents the holographic unwrap phase after calibration from  $\varphi$ ,  $\varphi_{\min}$  represents the minimum phase value of the selected area, and tan  $\gamma'$  represents the phase slope after fitting and it is equal to tan  $\gamma$ . Based on the above process, the holographic thickness vector after calibration is shown as a green line in Figure 2g. Herein, the holographic thickness vector in zone 400–500 nm after calibration shows a rugged curve, and these fluctuations also appear in the conventional holographic measurement result in a blue curve. The blue curve and the green curve maintain a high degree of consistency, as shown in the zoomed-in area in Figure 2g.



Figure 3. Time-related thickness mapping. Continuously record changes in film thickness using a hybrid method and the recording time points are 0.00, 1.74, 5.20, 9.47, and 12.70 s after film formation. (a) WL results within 12.70 s before the film ruptures. (b) WLCI thickness mapping calculated from (a) in the same time points. (c) Thickness mapping by conventional DH. (d) Thickness mapping by the hybrid DH and WLCI approach.

These ups and downs of the curves are caused by insufficient sampling; this is due to the high-frequency component of the object that is higher than the space-frequency resolution of the sampling CMOS, which can be solved by using a camera with a smaller pixel size (< 4.6  $\mu$ m) and bigger sensor size to record the holograms.

The thickness calibration for the entire FOV can be achieved by repeated applications of the above procedure, as shown in Figure 2f. By applying the same color-thickness scale, the overall thickness distributions in Figure 2c,f are found to be very close to each other. To verify the effectiveness of different methods, calculating the total volume of the full film area is a good solution for the results in Figure 2. After considering the difference in pixel size (in imaging plane) between different methods, the volumes are calculated: WLCI (standard color scale), 0.021 mm<sup>3</sup>; WLCI (self-reference color scale), 0.020 mm<sup>3</sup>; DH (conventional), 0.028 mm<sup>3</sup>; DH (after calibration), 0.022 mm<sup>3</sup>. It is clear that in addition to the conventional holographic method, the thicknesses by the other three methods have maintained a good consistency. This is fully supported evidence that the result after calibration is valid and credible.

Herein, the method not only has the ability to reveal the thickness below half of the recording wavelength, but it can also return the complex surface structure of the calibrated holographic thickness. As it can be seen from Figure 2f, the Marangoni flow structure at the edge of the film can be clearly identified, and the CBF area in DH is also revealed accurately. The application of the proposed procedure and the corresponding results can be implemented also in cases where there are multiple CBFs in the FOV or to cases where the thickness distribution is incomplete under WLCI. This is the case, for example, when the local thickness of some areas exceeds the limit of the colorimetric scale in WLCI, e.g., the edge of Marangoni flow in Figure 2c. The entire FOV needs to be divided into several parts according to the effective colorimetric thickness distribution then executing related approach separately, the discrete thickness points provided by the standard colorimetric method is used as a reference point to calibrate the thickness mapping of the holography, so a few available small thickness areas can complete the phase calibration of the holography. In this case, the overall thickness calibration can be carried out by general surface fitting for all the effective areas.

Regarding the experimental materials we used, nonionic surfactants are chosen in our experiments. Surfactants are usually divided into two categories, ionic and nonionic, based on whether they dissociate in an aqueous solution. The ionic surfactants place themselves at the interface in the case of freestanding films. This molecular-scale arrangement generates two charged layers at the interfaces that can repel each other. If a balance between repulsive and attractive forces is reached, then the film is stable and almost flat.<sup>39,40</sup> In contrast, thin liquid films made with nonionic surfactants are more unstable and, in the case of drainage, they are thinner because of the weak repulsive forces. This means that these films will have a more complex and sensitive structure. We used water as a solvent and Merpol as a surfactant to prepare thin liquid films, which have low foaming and low surface tension. For this type of thin surfactant film, the difference in RIs depending on the concentration is tiny, so we set a uniform value of 1.34 for the RI of the Merpol solution used for making the thin liquid film. Herein, Merpol is an alcohol phosphate and it is defined as a nonionic surfactant; it can be used as a detergent and lubricant agent for many materials and in metal processes; meanwhile, it receives growing importance in printing inks and coatings. The

pubs.acs.org/JPCC



Figure 4. Fusion DH and WLCI approach reveals the dynamic process of the thin liquid film over time. (a-e) 3D thickness mapping of five selected time points. (f) Time-related thickness distribution curves; different colored curves represent different time points after the recording started.

main reason for choosing Merpol as a surfactant is that the thin film will have a complex and changing structure, which is very suitable for judging the ability of the imaging approach. In our case, the major force that causes drainage inside the film is the gravitational one due to tilting of the film. Capillary forces and surface interactions shape the local structure of the surface, producing fingerings and spiral-like geometries, as displayed in Figures 2, 3, and 5.

#### 3. RESULTS AND DISCUSSION

Herein, we present two sets of data recording, reconstructions, and analyses by the fusion DH and WLCI approach, showing the advantages of the fusion method in thin liquid film thickness mapping. The proposed approach has high measurement sensitivity for film thickness changes, allowing a quantitative analysis of film thickness mapping in full FOV. Comparing with thin-film holographic thickness mapping, the proposed method has a larger axial measurement range, which means that the thickness distribution of the film, even though it will rupture soon or never rupture, can be accurately mapped. In addition, comparing with interferometric thickness mapping, the proposed method can provide more detailed information on the thickness distribution of the film, e.g., thickness of the Marangoni flow area. Meanwhile, for some factors that only cause a slight change in the thickness distribution, such as film concentration, the fusion method has the possibility of accurately revealing the tiny changes in thickness distribution.

In time-related thin-film evolution, thickness dynamic mapping of a thin liquid film was studied and analyzed by a hybrid approach. As said, a 60 mg/L Merpol solution was used

to form the film. In Figure 3, a set of continuously recorded experimental results is shown. Recording started when the thin liquid film was placed on the sample stage and ended after the film ruptured. Gravity was the only applied external force that caused film drainage and thinning. After 12.80 s, the film ruptured. During the entire recording cycle, five time points were selected (0.00, 1.77, 5.20, 9.47, and 12.70 s), and the thickness distribution from four different thickness mapping methods, WLI, WLCI, conventional DH, and hybrid approach, is shown in Figure 3a-d, respectively. In the areas where the average thickness of the film was larger than  $\sim 1 \ \mu m$  or where the surface of the film was complex, the WLI interference measurement would hardly provide an accurate and complete thickness distribution. There, however, the DH still worked well. This set of images highlights the main differences: the thinner the film (less than half of the recording wavelength), the more reliable the thickness mapping given by interferometry; the thicker the film (thicker than the recording wavelength), the more comprehensive and detailed the thickness mapping given by DH.

The frames in Figure 3a are WLI results after size correction; they reproduce the color-thickness scale based on the Newton color scale with a recording angle of  $37.5^{\circ}$ . For the surfactant films we used, the recognizable maximum thickness measured with WLI was always below ~1.5  $\mu$ m. However, the CMOS chip used was hard to record the right three-channel intensity values when the color fringes showed multiple green-pink interleaved bands so that the consequence was a thickness cutoff of around 1  $\mu$ m. As shown in Figure 3a, it is difficult to identify the local thickness at 0.00 and 1.77 s; however, for the 5.20, 9.47, and 12.70 s frames, the local thickness is easy to



**Figure 5.** Concentration-related thickness mapping. For thin films of different concentrations of the solute (60, 30, 6, and 3 mg/L), thickness mapping is measured at a certain time point, at  $7 \pm 1$  s before the film rupture. (a) WLI results at four different concentrations. (b) WLCI thickness mapping calculated from (a). (c) Thickness mapping by the hybrid DH and WLCI approach.

detect in the central region of the film because of its smooth distribution. It should be noticed that the periodic green—pink bands represent a smooth area with almost the same thickness, and it relates to the interference fringes of interferometric recording.<sup>41</sup>

Herein, we were not able to find in any frame an ideal thickness vector for a self-reference color scale, so that the film thickness colorimetric calculation processing was based on the standard Newton color scale. Unfortunately, due to the insufficient color resolution of CMOS chips we adopted, the thickness distribution in snapshots of all five time points are not continuous, as shown in Figure 3b. Herein, in the first frame of Figure 3b, we were not able to determine the local thickness of most areas in the FOV. This could be due either to regions with local thicknesses larger than 1  $\mu$ m or to the presence of regions with complex surfaces. Interestingly, what we can observe from the results in Figure 3b is that the areas where can be used to calculate the effective thickness are growing due to the general thickness decreases with the drainage process. In the thickness mapping at 12.70 s, we find out the thickness information in over 82% FOV, and this value is only 13% at 0.00 s.

The frames in Figure 3c are calculated by the conventional DH method of previous works.<sup>30,31</sup> For conventional holographic thickness processing, the black film has to be found in the last frame of the recorded hologram. In this case, we could only assume that the thickness of the edge of the black film was half of the recording wavelength. Comparing with the results of interferometry in Figure 3b,d, the result calculated by DH shows a distortion. Especially at 12.70 s, the local thickness of the upper part of the film is close to 1.5  $\mu$ m; however, from the results of WLI and WLCI, the thickness should be around 1  $\mu$ m. Nonetheless, conventional DH provides full-field thickness mapping for each frame, either when the film is too thick or when the film structure is complex so that once we compare the interferometric images with those obtained by DH for a flat film, we will find a good agreement between the film structures. However, when the film structure is more complex, DH becomes the best choice as a tool for the local film structure evaluation.

The frames in Figure 3d are thickness mapping from the present hybrid approach. The local thickness vectors, from WLCI results, were used to calculate the corresponding thickness from DH. The thickness vectors can also give distortion calibration in the related areas. So, through Figure 3d, we can get the continuous and correct thickness distribution in the five selected times. The general thickness continues to decrease, and the film structure becomes smoother. The thickness mapping at 5.20 s is the dividing point between interferometric and holographic methods in selected frames. There are more than 50% unresolved FOV in WLCI results before this time point, but DH still has the ability to provide the full-field thickness distribution. In addition, the thickness mapping of flows is restored by the hybrid approach: a liquid flow approaching the film center is observed, with a consequent thickening. Thanks to the fusion processing of the WLI and DH results in Figure 3a,c, not only thickness mapping but also the film structure are revealed. In Video S1, the time-related thickness evolution of the results of Figure 3a,d is shown.

To better analyze the time-related results, three-dimensional (3D) thickness mapping of five selected time points is revealed in Figure 4a-e. The concave bubbles, liquid flows, and drainage phenomena on the thin film can be clearly observed. In addition, the change trend of the overall thickness of the film can be judged by the color related to the thickness. From each curve of Figure 4e, the principal thickness  $T_{\rm p}$  of the corresponding FOV can be extracted, which is the thickness with the highest distribution rate. As time goes by, the principal thickness of the film continues to decrease from  $T_{p 0}$ =  $1230 \pm 20$  nm to  $T_{p_{-12}} = 940 \pm 20$  nm. We can estimate the complexity of the surface structure of the film for each frame. The smaller the standard deviation of the curves, the smoother the surface structure of the film. Interestingly, for the last frame before rupture, while the principal thickness of the film reaches the minimum, the film thickness distribution curve becomes lower; it means the complexity of the film structure tends to be smoother when compared with the snapshot in 9.47 s. We observed similar phenomena in related works.<sup>30</sup> In Video S2, the time-related thickness evolution in 3D is shown.

pubs.acs.org/JPCC



**Figure 6.** Concentration-related thickness distribution curves; different colored curves represent different concentrations. (a) Single-frame thickness distribution curves, using the corresponding frame in Figure 5c. (b) Thickness distribution curves from the average of multigroup experiments. We perform three sets of experiments for each concentration, and each set of experiments takes three consecutive frames at the same time zone for average calculation. We define the highest point of the curves as the principal thickness.

The above experimental results show that the hybrid method has a higher thickness measurement range during full-field thin-film imaging, and the thickness mapping of complex structures on the films is revealed in time-related experiments like the Marangoni flows.

In concentration-related thin-film evolution, the hybrid approach successfully revealed the change in film structure caused by a concentration difference. Figure 5 shows the results at different Merpol concentrations from 60 mg/L to 3 mg/L, which are 60, 30, 6, and 3 mg/L. We repeated the experiments three times for each concentration to draw the average thickness distribution curves. The frames were selected around  $7 \pm 1$  s before rupture in repeated experiments. Herein, the relationship between the thickness and film structure changes and different concentrations is revealed.

The frames in Figure 5a show thickness mapping at different concentrations from WLI measurements. It is apparent that at different concentrations dissimilar surface structures appear at similar times. By decreasing the solute content from 60 to 6 mg/L, the surface structure of the film turns smoother but film thickness fluctuations increase at 3 mg/L concentration. The same trend was observed in Figure 5b,c. The frames in Figure 5a show thickness mapping from WLCI and those in Figure 5c show thickness mapping from the hybrid approach, and they share the same color-thickness scale. Figure 5b reveals the change in film structure with concentration 60 mg/L; less than 50% area can be used to extract the thickness, and the effective calculated area is higher than 80% of FOV at concentration 6 mg/L. Under this experimental setup, the main forces that induce changes in the film are disjoining pressure, viscosity, surface tension, and gravity. Gravity force drains the liquid from the higher part of the film to the lower and generates the usual thickness gradient as shown in Figure 3c. Once the film becomes thinner, repulsive forces come into play.<sup>39,42</sup> They arise from the negative charges adsorbed at the air-water interface.<sup>43</sup> As a consequence, the thinner part is flatter and more stable. The complexity of the thicker parts stems from the combination of the Marangoni flows,<sup>44</sup> gravity,<sup>45,46</sup> drainage from the plateau border,<sup>39,47-51</sup> and disjoining pressure.<sup>39,42</sup> The result for the 3 mg/L concentration is

very peculiar and is due to the very low surfactant content of the film at this concentration.

Herein, it is possible to observe the thickness distributions for four different concentrations in Figure 6, where Figure 6a is calculated from the single snapshot and Figure 6b is calculated from the average of three frames. The frames are taken from repeated experiments for three groups but with the same recording time before rupture. In every analyzed frame, it could be observed that as the surfactant concentration decreases, the thickness uniformity increases except for the last case (3 mg/L). Such observation is also confirmed by the distribution in Figure 6b, which reveals the multigroup average result. For the cases at 60, 30, and 6 mg/L, film inhomogeneity is related to the amount and sharpness of "valleys" and "peaks", as shown in Figure 5c, and this kind of conformation is caused, probably, by a more pronounced marginal regeneration phenomenon as the tensioactive concentration increases.<sup>41,43,49</sup> In the case of 3 mg/L in Figure 5c, there are more valleys (blue regions) and yellow distribution; in Figure 6a, there is a higher amount of thinner regions. The thinner regions correspond to the regions where the attractive forces (Van der Waals interactions) are more pronounced between the two free surfaces. When the surfactant concentration is too low, the surface geometries can be easily disturbed. Herein, no matter how the concentration changes, the hybrid method provides a stable mapping of thin liquid film structure; this creates the possibility for further data analysis, as shown in Figure 6.

The average thickness curve shows high uniformity, where the principal thickness of different concentration films is concentrated at  $T_{p_ave} = 980 \pm 20$  nm. Meanwhile, the principal thickness percentage gradually increases as the concentration decreases from 60 to 6 mg/L in the frames we analyzed. This reveals that as the concentration decreases, the film tends to become smoother. Although 3 mg/L exhibits a different type of behavior, this is valuable information because it explains the possibility of further research on the properties of thin films using related methods. By comparing Figure 6a,b, a notable phenomenon is the difference between single-frame results and multiframe average results. Herein, this difference implies the necessity of a large number of experiments in the microfluidic study of thin liquid films; meanwhile, it also

#### The Journal of Physical Chemistry C

pubs.acs.org/JPCC

reveals that the measurement result error caused by the instability of nonionic thin films can be eliminated by multitime measurements.

Herein, one optical tool successfully reveals the full-field thickness mapping related to the liquid film concentration, and the thickness distribution characteristics of the film can be clearly identified. In particular, the curves in Figure 6 strongly evidence that the proposed method is an effective tool that can meet the needs of liquid film measurement experiments with high spatial and temporal resolution. It is important to note that the accuracy of thickness calibration mostly depends on color recognition of the camera. So, care should be adopted for choosing the camera. It is important to synchronize the acquisitions between the cameras, and a further step of improvement regards the implementation to guarantee dualcamera recording. In this case, interpolation could be a worthtrying solution. In the next step of this study, we will keep searching for the joint points of DH and other thin-film mapping approaches and further optimize the related methods. Also, for some solid films that can simulate the color scales,<sup>51</sup> we suppose that this method will also be applicable but still needs further experiments.

#### 4. CONCLUSIONS

In this paper, we present a fusion approach to map the thinfilm thickness; it combines DH and WLCI, both implemented on a thin liquid film simultaneously. We introduced the recording system, the joint reconstruction processing of this method, and a series of thin liquid film measurement experiments based on this approach were performed. As a result, this hybrid method demonstrates powerful measurement capabilities on dynamic liquid film measurements. It reveals the time evolution of the film and how the nonionic surfactant film structure is affected by the concentration.

Comparing with existing interferometric methods, the presented approach could achieve full-field, large-FOV dynamic measurements at the nanoscale, and it could accurately restore the thickness information of the film without relying on the CBF. As far as we know, this is the first time that the challenges of holographic and interferometric thin-film measurements are solved under real-time thickness mapping. Herein, based on the information obtained by WLCI, the calibration frame was made for the information obtained by DH; in contrast, DH provided complete thickness division information, which was not available in conventional interferometric methods. In comparison with our previous study on thin-film holographic measurements, the presented approach could tackle the shortcomings in thin-film digital holographic recording and reconstruction: (a) thickness information can be revealed without relying on full life cycle recording; (b) the thin-film area, where the thickness is less than half of the wavelength, can be measured; (c) film thickness calibration could be achieved without using background subtraction; meanwhile, the background hologram is not a necessary item in the holographic recording process.

In particular, we report that the general thickness of the film will become thinner as the duration of the film evolution increases, but its structural dynamics is indeed quite complex. Meanwhile, the concentration is another factor that affects the film thickness distribution; as the concentration decreases, the film thickness distribution, recorded at the same recording time point, will be smoother generally. We referred to the highest points of the curves in Figures 4 and 6 as principal thicknesses. All of the above experiments were based on the proposed hybrid method and prove its reliability and accuracy.

In the experiment on the time-thickness relationship, we showed the film thinning process. Meanwhile, we analyzed the thickness distribution of the film's full FOV, and we showed the thickness distribution curves for different time points. The results revealed two phenomena: (a) the principal thickness of the film gradually decreased with time; (b) in all cases shown here, the thickness distribution of the film becomes more homogeneous over time, but it gets more complicated just before rupture.

By comparing the thickness distribution of films with different concentrations at specific time points, the corresponding curves were drawn. In the results, the single-group experiment curve and the three-group experiment homogenization curve showed different shapes but the same trends. The principal thickness of the film remained at the same level for the relevant time, but the thickness distribution changed in a nonlinear way. Herein, the presented hybrid approach successfully revealed the tiny differences in morphology caused by the surfactant concentration and provided a reliable database for the development of related research. Furthermore, it can allow the evaluation of the surfactant concentration by measuring the film thickness distribution and so on.

In addition, these parallel experiments could also provide a reference when we have to make a choice between DH and interferometry. We had digital holographic and interferometric data side-by-side at different time points and surfactant concentrations. For thin films that are relatively flat and defect-free, both techniques can be used, and a comparison between the two shows good agreement. It could be even suggested that when films are very thin, interferometry is the better choice because it is possible to observe thicknesses a quarter of the wavelength of the recording beam. However, for more complicated surface structures and when films are thicker, interference patterns are difficult to make sense of or are absent. In these situations, DH is the better choice.

To sum up, the presented approach will provide an independent thin liquid film measurement process and does not require any additional recording conditions, e.g., full life cycle recording or limited measurement range. The relevant thickness extraction process combines DH and WLCI, and the real-time thickness mapping of a thin liquid film can be achieved. Thanks to the time—thickness and concentration thickness experiments on nonionic surfactant films, the proposed method's full-field sensitive measurement capability is verified. Meanwhile, based on these experimental data, the thickness ratio variation curves are drawn, and these curves reveal the variation of the films in statistics.

We believe that this method will open the way to wide uses of interferometric characterization in the fields of materials science, applied chemistry, and biomaterials at the nano- and microscale, making possible full and quantitative characterization of the dynamic evolution of liquid films and thus helping investigation and understanding of related phenomena.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c09555.

Generation of self-reference color scale (Figure S1), full field of view thickness mapping based on the selfreference color scale (Figure S2), and digital holographic thickness mapping for PMMA phase grating (Figure S3) (PDF)

Time-related thickness evolution of the results (Video S1) (AVI)  $\,$ 

Time-related thickness evolution in 3D (Video S2) (AVI)

#### AUTHOR INFORMATION

#### **Corresponding Author**

Zhe Wang – Department of Chemical Engineering, Materials and Industrial Production, University of Naples Federico II, 80125 Napoli, Italy; Institute of Applied Sciences and Intelligent Systems "E. Caianiello", Italian National Research Council (ISASI-CNR), 80078 Pozzuoli (Napoli), Italy;
orcid.org/0000-0002-0593-0413; Email: z.wang@ isasi.cnr.it

#### Authors

- Vincenzo Ferraro Department of Chemical Engineering, Materials and Industrial Production, University of Naples Federico II, 80125 Napoli, Italy
- Lisa Miccio Institute of Applied Sciences and Intelligent Systems "E. Caianiello", Italian National Research Council (ISASI-CNR), 80078 Pozzuoli (Napoli), Italy
- **Pier Luca Maffettone** Department of Chemical Engineering, Materials and Industrial Production, University of Naples Federico II, 80125 Napoli, Italy

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcc.0c09555

#### **Author Contributions**

The manuscript was written through the contribution of all authors. All authors have given approval to the final version of the manuscript. V.F. and Z.W. contributed equally to this work.

#### Funding

The research has been partly funded by Project PRIN 2017— Morphological Biomarkers for Early Diagnosis in Oncology (MORFEO) Prto. 2017N7R2CJ, and MIUR PON Project 2014–2020 PROSCAN.

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

This work was supported by the University of Naples Federico II and the Institute of Applied Sciences and Intelligent Systems "E. Caianiello", Italian National Research Council (ISASI-CNR).

#### REFERENCES

(1) Nikolov, A. D.; Kralchevsky, P. A.; Ivanov, I. B.; Wasan, D. T. Ordered micelle structuring in thin-films formed from anionic surfactant solutions: II. Model development. *J. Colloid Interface Sci.* **1989**, *133*, 13–22.

(2) Mysels, K. J. Soap Films and Some Problems in Surface and Colloid Chemistry. J. Phys. Chem. A. 1964, 68, 3441–3448.

(3) Israelachvili, J. N. Thin-film studies using multiple-beam interferometry. J. Colloid Interface Sci. 1973, 44, 259–272.

(4) Lin, C.; Sullivan, R. F. An application of white light interferometry in thin-film measurements. *IBM J. Res. Dev.* **1972**, *16*, 269–276.

(5) Greco, V.; Lemmi, C.; Ledesma, S.; Molesini, G.; Puccioni, G. P.; Quercioli, F. Measuring soap black films by phase shifting interferometry. *Meas. Sci. Technol.* **1994**, *5*, 900.

(6) Afanasyev, Y. D.; Andrews, G. T.; Deacon, C. G. Measuring soap bubble thickness with color matching. *Am. J. Phys.* **2011**, *79*, 1079–1082.

(7) Glovnea, R. P.; Forrest, A. K.; Olver, A. V.; Spikes, H. A. Measurement of sub-nanometer lubricant films using ultra-thin-film interferometry. *Tribol. Lett.* **2003**, *15*, 217–230.

(8) Tammaro, D.; Pasquino, R.; Villone, M. M.; D'Avino, G.; Ferraro, V.; Di Maio, E.; Langella, A.; Grizzuti, N.; Maffettone, P. L. Elasticity in bubble rupture. *Langmuir* **2018**, *34*, 5646–5654.

(9) Frostad, J. M.; Tammaro, D.; Santollani, L.; de Araujo, S. B.; Fuller, G. G. Dynamic fluid-film interferometry as a predictor of bulk foam properties. *Soft Matter* **2016**, *12*, 9266–9279.

(10) Hartl, M. J. I. P. M. R.; Krupka, I.; Poliscuk, R.; Liska, M.; Molimard, J.; Querry, M.; Vergne, P. Thin-film colorimetric interferometry. *Tribol. Trans.* **2001**, *44*, 270–276.

(11) Desse, J. M.; Albe, F.; Tribillon, J. L. Real-time color holographic interferometry. *Appl. Opt.* **2002**, *41*, 5326–5333.

(12) Desse, J. M. Real-time colour holographic interferometry (from holographic plate to digital hologram). *Academic* **2011**, 3–18.

(13) Desse, J. M.; Picart, P.; Tankam, P. Digital three-color holographic interferometry for flow analysis. *Opt. Express* **2008**, *16*, 5471–5480.

(14) Demoli, N.; Vukicevic, D.; Torzynski, M. Dynamic digital holographic interferometry with three wavelengths. *Opt. Express* **2003**, *11*, 767–774.

(15) Desse, J. M. Three-color differential interferometry. *Appl. Opt.* **1997**, *36*, 7150–7156.

(16) Kitagawa, K. Thin-film thickness profile measurement by threewavelength interference color analysis. *Appl. Opt.* **1997**, *52*, 1998– 2007.

(17) Abdelsalam, D. G. A comparison of digital holographic microscopy and on-axis phase-shifting interferometry for surface profiling. *Measurement* **2013**, *46*, 4121–4126.

(18) Vannoni, M.; Sordini, A.; Gabrieli, R.; Melozzi, M.; Molesini, G. Measuring the thickness of soap bubbles with phase-shift interferometry. *Opt. Express* **2013**, *21*, 19657–19667.

(19) Kim, J.; Kim, K.; Pahk, H. J. Thickness measurement of a transparent thin-film using phase change in white-light phase-shift interferometry. *Curr. Opt. Photonics* **2017**, *1*, 505–513.

(20) Gao, F.; Muhamedsalih, H.; Jiang, X. Surface and thickness measurement of a transparent film using wavelength scanning interferometry. *Opt. Express* **2012**, *20*, 21450–21456.

(21) Kim, S. W.; Kim, G. H. Thickness-profile measurement of transparent thin-film layers by white-light scanning interferometry. *Appl. Opt.* **1999**, *38*, 5968–5973.

(22) Patsyk, A.; Sivan, U.; Segev, M.; Bandres, M. A. Observation of branched flow of light. *Nature* **2020**, *583*, 60–65.

(23) Zhang, Y.; Sharma, V. Nanoridge Formation and Dynamics of Stratification in Micellar Freestanding Films. *Langmuir* **2018**, *34*, 1208–1217.

(24) Zhang, Y.; Sharma, V. Thickness-Dependent Phase Transition Drives Nanoridge-to-Mesa Instability in Micellar Freestanding Films. *Langmuir* **2018**, *34*, 7922–7931.

(25) Zhang, Y.; Yilixiati, S.; Pearsall, C.; Sharma, V. Nanoscopic terraces, mesas, and ridges in freely standing thin-films sculpted by supramolecular oscillatory surface forces. *ACS Nano* **2016**, *10*, 4678–4683.

(26) Goodman, J. W.; Lawrence, R. W. Digital image formation from electronically detected holograms. *Appl. Phys. Lett.* **1967**, *11*, 77–79. (27) Huang, T. S. Digital holography. *Proc. IEEE* **1971**, *59*, 1335– 1346.

(28) Leith, E. N.; Upatnieks, J. Reconstructed wavefronts and communication theory. J. Opt. Soc. Am. 1962, 52, 1123–1130.

(29) Schnars, U.; Jüptner, W. Direct recording of holograms by a CCD target and numerical reconstruction. *Appl. Opt.* **1994**, *33*, 179–181.

#### The Journal of Physical Chemistry C

Article

(30) Mandracchia, B.; Wang, Z.; Ferraro, V.; Villone, M. M.; Di Maio, E.; Maffettone, P. L.; Ferraro, P. Quantitative imaging of the complexity in liquid bubbles' evolution reveals the dynamics of film retraction. *Light: Sci. Appl.* **2019**, *8*, 1–12.

(31) Wang, Z.; Mandracchia, B.; Ferraro, P.; Ferraro, V.; Di Maio, E.; Maffettone, P. L.; Chen, W.; Fried, E. In *Fast and Accurate Thickness Mapping of Liquid Bubbles and Thin Protein Films*, 2018 International Conference on Manipulation, Automation and Robotics at Small Scales (MARSS); IEEE, 2018; pp 1–5.

(32) Joye, J. L.; Hirasaki, G. J.; Miller, C. A. Dimple formation and behavior during axisymmetrical foam film drainage. *Langmuir* **1992**, *8*, 3083–3092.

(33) Anachkov, S. E.; Danov, K. D.; Basheva, E. S.; Kralchevsky, P. A.; Ananthapadmanabhan, K. P. Determination of the aggregation number and charge of ionic surfactant micelles from the stepwise thinning of foam films. *Adv. Colloid Interface Sci.* **2012**, *183*, 55–67.

(34) Glassner, A. Andrew Glassner' s Notebook Soap Bubbles: Part 2. IEEE Comput. Graphics Appl. **2000**, *2*, 99–109.

(35) Molimard, J.; Querry, M.; Vergne, P.; Krupka, I.; Hartl, M. Calculation of pressure distribution in EHD point contacts from experimentally determinated film thickness. *Tribol. Int.* 2005, 38, 391–401.

(36) Shen, L.; Denner, F.; Morgan, N.; van Wachem, B.; Dini, D. Transient structures in rupturing thin films: Marangoni-induced symmetry-breaking pattern formation in viscous fluids. *Sci. Adv.* **2020**, *6*, No. eabb0597.

(37) Nasti, G.; Coppola, S.; Vespini, V.; Grilli, S.; Vettoliere, A.; Granata, C.; Ferraro, P. Pyroelectric tweezers for handling liquid unit volumes. *Adv. Intell. Syst.* **2020**, No. 2000044.

(38) González-Cano, A.; Bernabéu, E. Automatic interference method for measuring transparent film thickness. *Appl. Opt.* **1993**, 32, 2292–2294.

(39) Chan, D. Y.; Klaseboer, E.; Manica, R. Film drainage and coalescence between deformable drops and bubbles. *Soft Matter* **2011**, 7, 2235–2264.

(40) Coons, J. E.; Halley, P. J.; McGlashan, S. A.; Tran-Cong, T. A review of drainage and spontaneous rupture in free standing thin-films with tangentially immobile interfaces. *Adv. Colloid Interface Sci.* **2003**, *105*, 3–62.

(41) Abdelsalam, D. G.; Yao, B. Interferometry and its applications in surface metrology. *Opt. Interferom.* **2017**, 81.

(42) Anton, N.; Bouriat, P. Different surface corrugations occurring during drainage of axisymmetric thin liquid films. *Langmuir* **200**7, *23*, 9213–9220.

(43) Karraker, K. A.; Radke, C. J. Disjoining pressures, zeta potentials and surface tensions of aqueous non-ionic surfactant/ electrolyte solutions: theory and comparison to experiment. *Adv. Colloid Interface Sci.* 2002, 96, 231–264.

(44) Nierstrasz, V. A.; Frens, G. Marginal regeneration and the Marangoni effect. J. Colloid Interface Sci. 1999, 215, 28–35.

(45) Champougny, L.; Roché, M.; Drenckhan, W.; Rio, E. Life and death of not so "bare" bubbles. *Soft Matter* **2016**, *12*, 5276–5284.

(46) Debrégeas, G. D.; De Gennes, P. G.; Brochard-Wyart, F. The life and death of "bare" viscous bubbles. *Science* **1998**, *279*, 1704–1707.

(47) Ozan, S. C.; Jakobsen, H. A. On the effect of the approach velocity on the coalescence of fluid particles. *Int. J. Multiphase Flow* **2019**, *119*, 223–236.

(48) Singh, G.; Miller, C. A.; Hirasaki, G. J. On dimple formation in foam films. J. Colloid Interface Sci. **1997**, 187, 334–337.

(49) Sheludko, A. Thin liquid films. Adv. Colloid Interface Sci. 1967, 1, 391-464.

(50) Israelachvili, J. N. *Intermolecular and Surface Forces*; Elsevier: Santa Barbara, CA, 2011.

(51) Majaron, H.; Ravnik, M. Structural Coloration. In Seminar for the Department of Mathematics and Physics; University of Ljubljana: Ljubljana, 2013.

# Supporting Information A: Thin-film self-reference colorimetric interferometry

In general, the colorimetric thin-film thickness mapping is obtained by identifying the colors of recorded fringes. In white light colorimetric interferometry (WLCI), the white light is used to illuminate the film, then thickness distribution will be calculated based on Newton color scale and related color-thickness conversion formula. Nowadays, with the development of photoelectric conversion devices, different types of cameras are used in optical recording and experiments. This also create some new problems for thin-film colorimetry, such as the calculation errors and color gradation discontinuities caused by the chromatic aberrations of different cameras. Due to differences in the collection and conversion of optical signals, even though under the same experimental conditions, once the different cameras are used to record, usually we will receive different color distribution results. In conventional colorimetric calculations, the thickness difference caused by chromatic aberrations are usually treated as the recording error. One feasible method is to calibrate the color difference through specific repair software or algorithms. However, this kind of color operation often destroys the color continuity of the recorded image, resulting in a step-like or discontinuous thickness distribution when the standard Newton color scale is used to calculate the thickness. Herein, we proposed a selfreference colorimetric calculation method for thin-film thickness mapping, the thickness will be calculated by the color scale extracted from itself. The advantage of this approach is to generate color-thickness gradation under consideration of the color difference of camera, so that the

measured thickness distribution will be smoother than conventional method. But information will be lost for the colors in the non-customized self-reference color scale.

In the experiments we made for fusion-method, non-ionic surfactant Merpol solution was used to make the thin-liquid film. For processing the self-reference colorimetric calculation, one frame from interferometric video was selected, where the color gradient guarantees a wide range of color scale. There are two conditions on the selection frame: (a) Continuously changing colors need to be found in this frame. (b) A black film is required or any small blocks with a single color can be found. In a continuously recorded white light interferometry video, any frame that meets the above conditions can be used to generate self-reference color gradations. For the selected frame, the black film area is the optimal choice for color calibration. In a recording system with a certain wavelength source, the thickness of Common Black Film (CBF) area is known. Therefore, the pre-calibration of self-reference method is to adjust the color-thickness curves by referring the RGB levels from CBD area, where should be the standard black color. The calibrated results are shown in Figure S1(a). Then, several continuous color stripes are selected, and shown in Figure S1(a) I-IV, in order to generate enough sampling points. These color-sampling points will be used to create a RGB intensity three-dimensional space, as shown in Figure S1(b). The red, blue and green intensity are set as the axis x, y, z coordinates. This color curve shows the continuous change of the color scale in selected frame, and it will serve as the basic model of the self-reference color scale. Herein, more sampling points can improve the smoothness, but it is also limited by the pixel size and number of the imaging camera. For further study, this problem could be solved by applying a high-resolution color camera. Finally, we sample a series of points on the curve with equal frequency, and obtain the film thickness according to the color-thickness calculation formula of the surfactant film. In order to obtain the

thickness-color self-reference conversion relationship, we set the calculated thickness as the xaxis, and the RBG three-channel intensity corresponding to the thickness as y-axis, then the selfreference thickness gradation based on selected frame is shown in Figure S1(c). However, the RGB three-color curves of self-reference method are discontinuous and unsmooth, which is due to color distortion of image recording equipment.



**Figure S1.** Generation of self-reference color scale. (a) The frame used to extract the self-reference color scale, a black film can be found in the lower part. (b) The color scale curve in the three-dimensional space of RGB intensity, corresponding colors are shown in different positions of the curve. (c) Color-thickness gradation based on self-reference scale.

For the full field of view thickness mapping, a point cloud based on the RBG threedimensional space will be created, where each point represents the RGB value of a pixel in the field of view. Then, we associate to each pixel a point in the RGB space, and calculate the distance of all points from the self-reference curve in Figure S1(b), the minimum distance will identify one point of the curve which will be related to a thickness value. Here we divide all points into three categories: a) for points whose distance between the point and the curve is less than 10 intensity units, we will use the thickness value corresponding to the closest curve coordinate to assign it, as the deep blue points shown in Figure S2(a). b) For points whose distance between the point and the curve is less than 30 intensity units and more than 10 intensity units, the thickness will be set as the most approximate value through curve fitting from Figure S1(c), as the light blue points shown in Figure S2(a). c) For points whose distance between the point and the curve is more than 30 intensity units, they will be discarded, as the grey points shown in Figure S2(a). For this frame, the deep blue points take place as 61.9%, the light blue points take place as 29.0%, the sum of them is called the self-reference effective point ratio, which is 90.9%. So for this white light interferometric frame, 90.9% of the data points can be calculated by the self-reference colorimetric approach to get the thickness distribution, the thickness mapping result as shown in Figure S2(b). Obviously, comparing with the calculation results based on standard Newton color scale, the self-reference color scale produces a smoother thickness distribution result.

To summarize, in order to better compare the differences between optical thickness measurement methods and explore the boundary of interferometry, we have given a selfreference colorimetric interferometry for thin liquid film. Self-reference colorimetry is a compromise method to obtain non-step thickness mapping under the white light interferometry.

It must be used under certain conditions, including: 1) A smooth continuous thickness change in single direction should be found in the imaging field of view. 2) A CBF must appear in the field of view.



**Figure S2.** Full field of view thickness mapping based on self-reference color scale. (a) The distribution of all calculated points in the three-dimensional space of RGB intensity. The dark blue points will obey the self-reference color scale and directly give the thickness. The light blue points will find the most approximate thickness through curve fitting from Figure S1(c). The grey points will be abandoned. (b) Thickness mapping based on self-reference color scale, calculated from the result shown in Figure S1(a).

# Supporting Information B: Digital holographic thickness measurement for standard sample

Digital holography (DH) is a reliable tool on transmission sample measurement, its accuracy and reliability in thin film measurement has been proven by our previous study. <sup>[30]</sup> In related manuscript, we provide a versatile and reliable real-time thickness mapping method for thin liquid film by fusion DH and white light colorimetric interferometry. In order to further prove the accuracy of proposed system and method, one solution is to find a thin liquid film with stable CBF and known thickness as standard sample. About the possibility to have a well-known film for calibration purpose, it is difficult to obtain a stable thin liquid film with a common black film. We are far from the quantitative control of these kinds of film. There are a lot of challenging features regarding such film. Firstly, the great span of characteristic thickness is quite large, it goes from nanometers to microns. Secondly, the curvature radii of the surface will rapidly change during the same experiment. Thirdly, the complex geometries on film will be hard to 'freeze'. The capillary forces, Van der Waal forces, Disjoining pressure, gravity, viscosity and Marangoni flows work together to evolve the surface characteristics of the film in not predictable way. For this reason, in order to show the reliability of proposed system, we provided an alternate solution by using as sort of reference a solid micro-structure of known thickness, i.e. a target PMMA grating with known refractive index and thickness information. Herein, a laser etched PMMA phase grating was record by propose system, the refractive index of it is 1.49, the etching depth is set as 10 µm, the grating interval is 0.65 mm. The reconstruction results show in Figure S3.



**Figure S3.** Digital holographic thickness mapping for PMMA phase grating. (a) Recorded digital hologram when white light was switched on. Zone A shows the interference fringes of hologram. Zone B indicates the implementation area of numerical reconstruction. (b) Thickness mapping of grating. Negative thickness shows the depth of the laser etching. (c) Recorded digital hologram when white light was switched off. (d) Thickness mapping of same area with (b).

Figure S3 shows the holographic numerical reconstruction results when white light switched on and off. The yellow dotted area zone B in Figure S3(a) was processed by holographic film thickness extraction algorithm. From the results in Figure S3(b) and (e), the structural parameters of PMMA phase grating are accurately restored. The measured depth of etching groove is  $10.19\pm0.54$  µm, the measured grating interval is  $0.65\pm0.02$  mm. The measured information accurately reveals the structure of PMMA phase grating, and proves the reliability of the proposed system in microstructure measurement.

Meanwhile, the results in Figure S3 also provide the evidences to show the white light scattering will not affect the holographic recording. For the same phase grating, we show the holograms and reconstruction results when the white light source was switched on and off. As shown in Figure S3(e), the red curve represents the sectional thickness from dotted line in Figure S3(b), the blue curve shows the same from Figure S3(d). There is no significant difference between the two plots, the slight mismatches, which present on the bottom and the surface of the grooves, is within 2% of the wavelength instability error. Therefore, the signal-to-noise ratio (SNR) of an hologram recorded under the fusion imaging system will not be affected by the scattering from the white light source.

# Chapter 4: Axisymmetric bare freestanding films of highly viscous liquids: Preparation and real-time investigation of capillary leveling

Once a novel measuring technique was developed, as described in the previous *Chapters* 2 and 3, it is now possible to better study freestanding thin liquid films. Moreover, in *Chapter 1* the reader was introduced to the innumerable forces that can influence the morphology, and consequently the properties, of a freestanding (or not) liquid film. The most important between these forces is the capillary one. In case of freestanding liquid films, capillary forces may create thinning or thickening of the film depending on the film morphology, as already explained in *Chapter 1*. As far as film thinning is concerned, the phenomenon of drainage has already been extensively studied in the literature. However, the phenomenon of levelling of a freestanding liquid film remains under-explored.

Here in *Chapter 4* the reader will find a study concerning the levelling of a wide axisymmetric Newtonian freestanding liquid film not stabilized by surfactants and studied in real time at constant temperature, at best of my knowledge, for the first time. The film is sustained and formed by an optical iris diaphragm, a stepper motor opens the optical iris and the aperture radius and the opening velocity is controlled from a computer. The entire setup is shown in Figure 1 and 2 in the main text of the article attached below published in the "*Journal of colloid and interface science*" in 2021. Never before an optical iris was used to form freestanding liquid films.

Thanks to the new measurement techniques described in *Chapters 2*, 3 and this *Chapter 4*, it is now possible to observe and measure with extreme precision the live thickness map during the leveling phenomenon in case of a bare freestanding thin liquid film made of a Newtonian fluid. The obtained thickness maps of the film during leveling were also used to derive the radial velocity field of the fluid during leveling. The reader can find further details on the measuring protocol and setup used in the attached main text of the article, in the section "*Interferometric measurement of film thickness*", and *Supporting Information*, in the section "*Kinematics of Iris Opening*".

The thickness measures proved to be of fundamental importance in assessing the Reynolds number and verifying that the inertial forces were negligible compared to the viscous forces during leveling because  $Re = \rho \left(\frac{\gamma}{\mu}\right) \bar{h}/\mu < 10^{-6}$  where  $\frac{\gamma}{\mu}$  is the capillary velocity,  $\bar{h}$  is the mean thickness of the thickness map,  $\rho$  is the density used and  $\mu$  is the dynamic viscosity of the silicone oil. It was also possible to evaluate the Reynolds number during the opening and obtained that  $Re = \rho v \bar{h}/\mu < 10^{-3}$  where v is the radial opening velocity of the iris during the film formation. The contribution of gravity on leveling was also assessed using the Bond number defined as  $Bo = \Delta \rho g \bar{h}^2 / \gamma$  where  $\Delta \rho$  is the density difference between the liquid and air; in the studied cases  $Bo < 10^{-5}$ , it means that the gravity do not affect the leveling process.

The choice of material was also crucial as it was necessary to prevent the disjoining pressure from influencing the leveling so that the contribution of viscosity and surface tension had to be isolated. For this reason, silicone oil was chosen as it does not have any electrostatic charge adsorption at the liquid-air interface and it has very weak Van der Waals interactions, as well as being a purely Newtonian fluid. In Chapter 1 the Disjoining pressure equations were already explained and described. By using eq. (1.2.6a) and the Laplace pressure  $P_c$  it was possible evaluate the ratio  $\Pi_{dj}/P_c < 10^{-3}$  where  $\Pi_{dj} = \Pi_{vdw}$  and  $P_c = \gamma K_c$  where  $K_c$  is the average principal curvature of the film and was retrieved from the novel thickness measures.

The characteristic length of the leveling flow is the length of the step profile w, which is sketched in Figure 4.1. However, this measurement was not possible by our setup because the area of the film is too big compared to the field view of the measures and wcannot be entirely evaluated. Nevertheless, thanks to the high resolution of the adopted measuring technique, it was possible to retrieve the slope of the step profile which is a function of w and  $h_2$  because:

$$w = \frac{h_2}{2m} \tag{4.1}$$

Then, by substituting eq. (4.1) in eq. (1.3.2) we obtain:

$$m \propto \left(\frac{h_2}{2\nu_c}\right)^{\frac{1}{2}} * \left(\frac{1}{t}\right)^{\frac{1}{2}}$$
 (4.2)

But there is still a problem because this eq. (4.2) describe the evolution over time of the slope of the step during the leveling since the step was sharp as sketched in Figure 1.3.1. I therefore hypothesized that the initial profile of the experiments could be considered as a profile that had already evolved over time from the starting sharp configuration of Figure 1.3.1. In the light of the above, it is therefore necessary to add an additive constant to the time in eq. (4.2), which will be different for each performed experiment. Further details can be found in the main text of the attached article below in the sections "Interferometric measurement of film thickness" and "Leveling flow".



**Figure 4.1**: sketch of half of the step profile of a freestanding liquid film during the leveling.

After taking the thickness measurements and by using them in the analytical models, the achieved results were compared with simulations carried out by P. L. Maffettone and M. M. Villone. The comparison showed great agreement between the analytical formulas and the simulations. Furthermore, it was observed that below a critical thickness of 250nm at the center of the film there is the formation of a dimple during leveling. For

thicknesses above 450nm, no dimple was observed to form during leveling. Finally, by processing the experimental data obtained from the powerful measurement technique used, it was possible to observe that the average radius of curvature of the film increased over time during the iris opening. It is therefore possible to assert that the process of forming a freestanding liquid film by means of equibiaxial extensional deformation mimics the process of growing bubbles within a foam. This is an important result as it would allow for the first time, at best of my knowledge, the behavior of a film between two bubbles during the growing process. In fact, nowadays, the Sheludko cell has been used up to now, as it does not allow equibiaxial stretching to be imposed on the film under observation.



Contents lists available at ScienceDirect

### Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis



**Regular Article** 

### Axisymmetric bare freestanding films of highly viscous liquids: Preparation and real-time investigation of capillary leveling



Vincenzo Ferraro <sup>a,b,1</sup>, Massimiliano M. Villone <sup>a,b,1</sup>, Volodymyr Tkachenko <sup>c,b</sup>, Lisa Miccio <sup>b,c</sup>, Lorenzo Lombardi <sup>a,b</sup>, Daniele Tammaro <sup>a,b</sup>, Ernesto Di Maio <sup>a,b</sup>, Gaetano D'Avino <sup>a,b</sup>, Pier Luca Maffettone <sup>a,b,\*</sup>

<sup>a</sup> Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II, Piazzale Tecchio 80, 80125 Napoli, Italy <sup>b</sup> NEAPoLIS, Numerical and Experimental Advanced Program on Liquids and Interface Systems, Joint Research Center CNR - Università degli Studi di Napoli Federico II, Piazzale Tecchio 80, 80125 Napoli, Italy

<sup>c</sup> CNR-ISASI, Institute of Applied Sciences and Intelligent Systems E. Caianiello, Via Campi Flegrei 34, 80078 Pozzuoli, Napoli, Italy

#### G R A P H I C A L A B S T R A C T



#### ARTICLE INFO

Article history: Received 13 March 2021 Accepted 18 March 2021 Available online 27 March 2021

Keywords: Axisymmetric bare freestanding liquid films Capillary leveling flow Opto-mechanical device Direct numerical simulations Lubrication theory

#### ABSTRACT

*Hypothesis:* Thin liquid films are important in many scientific fields. In particular, films with both the surface layers exposed to a different fluid phase, known as freestanding films, are relevant in the ambit of foams and emulsions. Hence, there is a great interest in developing novel techniques allowing to form large and stable freestanding liquid films and to follow their dynamics.

*Experiments:* We develop a novel opto-mechanical tool allowing to perform and study the preparation and the capillary leveling flow of axisymmetric bare freestanding liquid films. The tool is composed by a customized motorized iris diaphragm and by an innovative joint imaging setup combining digital holography and white light color interferometry that enables real-time measurement of film thickness over a large field of view. The dynamics of films made of a model Newtonian fluid, i.e., high-viscosity silicone oil, is studied. Direct numerical simulations and a hydrodynamic model based on the lubrication theory are used to support the experimental results.

Findings: Iris opening induces the formation of large circular freestanding films with a stepped profile.

<sup>\*</sup> Corresponding author at: Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II, Piazzale Tecchio 80, 80125 Napoli, Italy.

E-mail address: p.maffettone@unina.it (P.L. Maffettone).

<sup>&</sup>lt;sup>1</sup> These two authors contributed equally.

Once iris opening is stopped, the films undergo a capillary leveling flow tending to flatten their profile. The leveling flow follows the theoretical scaling given by llton et al. [1]. We prove through numerical simulations that an equi-biaxial extensional flow occurs at the film center. Furthermore, we observe the formation and dynamics of dimples in bare freestanding films for the first time.

© 2021 Elsevier Inc. All rights reserved.

#### 1. Introduction

Thin liquid films are of interest in many scientific fields ranging from polymer physics to physiology, biophysics, micro-electronics, surface chemistry, thermodynamics, and hydrodynamics [2,3,4,5,6,7,8,9,10]. In particular, freestanding films, i.e., films with both the surface layers exposed to a different fluid phase (most commonly, a gas), are relevant in the field of foams and emulsions. These were first studied in the form of soap bubbles by Newton [11] and Gibbs [12], yet their formation, stability and break-up are still key issues in the scientific literature [13,1,14,15]. Capillary pressure gradients arise from the local curvature of the free surfaces, leading to liquid rearrangement. If the film is constrained between Plateau borders, the local curvature causes liquid drainage and drives film thinning [16,10]. When the film thickness goes below  $\mathcal{O}(10^2)$  nanometers, van der Waals or electrostatic forces generate the so-called disjoining pressure [17], which may drive the film either to break or to find a stable configuration. Destabilization can be triggered by thermal corrugations of the surface layers, which are relevant for very thin films [18,19]. The possible presence of surface-active materials adsorbed on the surface layers strongly affects film dynamics by imparting viscoelastic properties to the interfaces or even leading to surface immobilization [20,21]. On the other hand, surface tension can also smooth out small interfacial perturbations, eventually 'healing' the surface [22]. Recently, capillary leveling flows mediated by viscosity have been analyzed by Ilton et al. [1] on planar freestanding polystyrene films with an initially stepped profile. They prepared a polystyrene film in the glassy state below the glass transition temperature,  $T_{\rm G}$ , and then, upon heating at  $T > T_G$ , they observed the surfacetension-driven flow of the liquid. They measured the leveling dynamics, i.e., the evolution toward a film of uniform thickness, through atomic force microscopy (AFM) upon cooling the film below  $T_{G}$ . Several heating/cooling cycles for flow at  $T > T_{G}$  and AFM imaging at  $T < T_{G}$  were performed to reconstruct the film thickness dynamics. The most adopted device to form freestanding films and investigate their dynamics under different conditions is the so-called Sheludko cell [16], where a fluid is withdrawn through small tubes at the cell side to form a thin film connected with Plateau borders to a solid wall. Upon cessation of withdrawal, the film freely evolves, draining until break-up or, alternatively, reaching an equilibrium state. In such a device, films with a radius usually around 1 and thickness in the range 50-500 can be formed and studied [10.20].

In this paper, we present a novel opto-mechanical tool combining a customized motorized iris diaphragm and an innovative joint imaging setup complementing digital holography and white light color interferometry that allows to prepare large axisymmetric freestanding liquid films and study their leveling flow. In particular, we form bare (i.e., without surfactants) freestanding circular liquid films with an initial stepped profile made of silicone oil, then we report on liquid leveling flow measured real-time with the aforementioned imaging technique. The film leveling determines equi-biaxial extensional flow conditions at its center. We also show that, during the leveling flow, the formation of dimples can occur at the center of the film. Direct numerical simulations and a hydrodynamic model based on the lubrication theory support the experimental results

#### 2. Materials and methods

#### 2.1. Material

All the experiments are carried out on a pure model Newtonian liquid, namely, silicone oil (PDMS) [14], Dow Corning 200 Fluid, with density  $\rho = 976$  kg m<sup>-3</sup>, kinematic viscosity  $v = 6 \times 10^{-2}$  m<sup>2</sup> s<sup>-1</sup>, and surface tension  $\gamma = 21.5$  mN m<sup>-1</sup> at room temperature (25 °C). No surfactants, particles, salts, solvents or other polymers are present in the liquid, so the films can be considered completely bare. Since no concentration or surface tension gradients are expected in the freestanding films, we henceforth consider fully mobile interfaces. Moreover, the fluid is stable at room temperature and has a very low vapor tension, thus hindering evaporation. Heating up of the films can be also considered negligible because the light source used for the interferometric measurements is weak enough to avoid it [23].

#### 2.2. Freestanding film preparation

The formation of a freestanding liquid film with the proper shape to induce leveling flow is a key issue per se. We use a stainless steel motorized iris diaphragm (MID), Edmund Optics<sup>®</sup>, with 16 leaves with thickness 0.2, vertically oriented symmetry axis, external diameter 70 mm, and maximum aperture 50 mm, operated by a DC gear motor controlled by a programmable circuit board via a pc. The final radius of the iris hole and MID opening/closing velocity can be fixed at will between 0.5 and 17.5 mm and between 1 and 10 mm s<sup>-1</sup>, respectively. The film formation (see Fig. 1a) consists in the manual pipetting of a liquid droplet at the center of the closed MID, which has an initial hole radius around 1.1 mm, then, after a resting period of 1-2 min to allow drop shape smoothing, the iris is opened at a constant radial speed up to the desired final hole radius. All the experiments are run at room temperature with final radius  $R_0 = 8$  and opening radial velocity  $v = 1.5 \text{ mm s}^{-1}$ . It should be remarked that the film radii achievable with this device are one/two orders of magnitude larger than those of the circular films studied so far in the literature [10,20]. Typically, the film thickness at the end of MID opening ranges from 0.15 to 10 depending on the size of the deposited drop. It should be also remarked that the large films formed through the MID have shown to be stable for a sufficient time to observe the leveling phenomenon described below, which is in the order of 10<sup>2</sup>. Early film rupture has been never observed except in some rare cases due to the occurrence of external disturbances.

By exploiting the necking induced by the imposed extensional flow [24,25], the MID opening produces a film with a stepped configuration, as qualitatively sketched in Fig. 1b. Some relevant geometrical features are: the thickness  $h_T(t)$  of the thinner part at the center of the film, the thickness  $h_S(t)$  of the thicker outer region of the film, and the slope m(t) of the step, i.e., the intermediate region. In what follows, subscript 0 will denote values of quantities evalu-



**Fig. 1.** a: Schematic of material deposition on the iris, iris aperture, and liquid film leveling. b: Qualitative sketch of the side-view profile of the film at the beginning of the leveling flow.

ated at the end of MID opening. This film shape induces a capillary leveling flow driven by surface tension and slowed down by liquid viscous resistance. Such flow conditions hold true until the Plateau border effects come into play, i.e., the outer Plateau borders must be far enough, at least during the initial stages of the leveling phase, to avoid their influence on the dynamics, otherwise, instead of beginning to thicken, the film would carry on thinning even after the end of MID opening, until breaking-up. Furthermore,  $h_T(t)$ should be large enough to avoid film destabilization and breakage induced by disjoining pressure (see below) or thickness fluctuations.

We exclude gravitational effects by evaluating the Bond number Bo =  $\Delta \rho g h^2 / \gamma < 10^{-5}$ , with  $\Delta \rho$  the density difference between the two phases (in our case,  $\Delta \rho \approx \rho$ , i.e., the polymer density), g the gravity acceleration, and *h* the average film thickness at the end of MID opening. A further check on the irrelevance of gravity is been done by performing numerical simulations by taking gravity into account, whose results are exactly the same as those without gravity reported in Sec. 3. We also exclude inertial effects by evaluating the Reynolds number: during MID opening, this can be defined 'conservatively' as  $\text{Re} = \rho v R_0 / \mu \ 10^{-3}$ , with  $\mu$  the dynamic viscosity of the liquid, whereas, during the leveling phase, it is  $\mathrm{Re} = 
ho(\gamma/\mu)h/\mu < 10^{-6}$ , with  $\gamma/\mu$  the capillary velocity [1]. Disjoining pressure effects are also negligible since: *i*) electrostatic contributions are absent as silicone oil molecules are non-polar; *ii*) short-range interactions are relevant on the scale of tens of nanometers, but the films never attains such small thickness values in our experiments; iii) by comparing Van der Waals interactions  $P_{\sigma}$  and capillary pressure  $\Pi_{W}$ , one obtains  $P_{\sigma}/\Pi_{\rm W} = (\sigma/\kappa)/(A/(6\pi h^3)) \approx 10^3$ , with  $\kappa$  the characteristic curvature, i.e., a time-average of the values calculated through Eq. 5 in

the Supporting Information (SI), and  $A = 4.4 \times 10^{-20}$  J the Hamaker constant for PDMS [26].

#### 2.3. Interferometric measurement of film thickness

During both the film formation and the leveling flow, the film thickness is measured by an innovative joint imaging method merging digital off-axis holography, based on a Mach-Zehnder interferometer, with white-light color interferometry that allows for the real-time quantitative characterization of freestanding films with high spatial resolution over large areas. The digital holography optical setup is schematized in Fig. 2a and can be described as follows. A laser beam (HeNe emitting at 632.8 nm, exit power 5 mW) is filtered and expanded by the spatial filter SF combined with the lens L1, then it is divided into object and reference beams by the beam splitter BS1. The object beam passes through the film and normally illuminates it, then it is demagnified by the lenses L2 and L3 to fit the aperture of the digital camera CCD (UI-3000SE from IDS). The saturation of the CCD image sensor is avoided by controlling the power of the laser beam with the half-wavelength plate HWP1 together with the polarizing beam splitter PBS. A second beam splitter BS2 allows the interference between reference and object beams in front of the CCD camera. BS2 is slightly tilted so that the two beams overlap with a small angle, which can be controlled in order to adjust the period of the interference fringes. The contrast of the fringes is tuned by polarization and intensity of the interfering beams by using the second half-wavelength plate HWP2, placed into the reference arm of the interferometer, and the variable neutral density filter NDF, placed into the object arm. A color interferometry setup (schematically represented in Fig. 2b) is added. The light of a fluorescent lamp impinges on the film at a 67°-angle and it is reflected towards the second camera CIC (Logitech C920 HD Pro Webcam, 1280x1024px, 30fps). When the film thickness falls into the wavelength range of visible light, a colored region appears (see Fig. 2c). Each color recorded by the webcam corresponds to a thickness of the film through the mathematical relation given by Eq. (2) in Ref. [27]. CCD records digital holograms at 10fps during MID opening and film leveling flow to keep track of the whole process. The field of view (FOV) of the holographic tool is 80 mm<sup>2</sup> around the center of the MID hole. Simultaneously, CIC captures color images like those reported in Fig. 2c and Fig. 5a. Digital holography and white light interferometry 'acquire' the same area of the film and their complementary characteristics are the base of the fusion thickness calculations. More details on such technique are given in Sec. 2 in the SI and in the very recent paper by Ferraro et al. [27].

#### 3. Results

#### 3.1. Film formation dynamics

Fig. 3 shows the film thickness dynamics during MID opening for a sample with a volume of about 0.52  $\mu$ l: the extensional flow stretches the liquid and induces the formation of a film with a thinner central region, where the surface curvature is generally small. It should be remarked that the experimental thickness profiles refer to the central region of the film falling into the FOV of the optical setup and are obtained by averaging each datum over a 70- $\mu$ m-long radial range. At the end of MID opening, the film central portion has a similar shape to that sketched in Fig. 1b. The film thickness profile can be tuned by changing the initial amount of fluid or/and MID opening radius.

Since the experimental thickness profiles are limited to the film central region, direct numerical simulations are implemented to investigate the complete thickness profile induced by the MID

V. Ferraro, M.M. Villone, V. Tkachenko et al.



**Fig. 2.** a: Setup for thin liquid film thickness holographic measurement (SF: spatial filter; M1-M4: mirrors; HWP1-HWP2: half-wavelength plates; PBS: polarizing beam splitter; BS1-BS2: beam splitters; L1-L3: lenses; NDF: neutral density filter; MID: iris diaphragm with the polymer inside; CCD: digital camera). b: Schematic of the color interferometry setup. c: Typical image observed by CIC during the experimental campaign.



Fig. 3. Experimental radial profiles of the thickness of the film during MID opening for a sample with a volume of about 0.52  $\mu$ l.

opening. The motion equations for a Newtonian liquid with fully mobile gas-liquid interfaces and neglecting inertia (Stokes flow) are solved with a finite-element method (FEM). The mathematical model underlying FEM simulations and the details on the numerical technique are given in Sec. 3 in the SI. Fig. 4a1 depicts the geometry considered in the simulations before MID opening is started. When the MID is 'closed', its hole has radius  $R_c = 1$  mm, whereas the thickness of the liquid drop at the center of the hole is  $h_d = 2$ mm. The thickness of the lamellae is  $h_{\rm L} = 0.2$  mm. A cylindrical coordinate system is used and we impose both axial symmetry and top-down planar symmetry due to the irrelevance of gravity suggested by vanishing Bo and expected fast equilibration driven by pressure [28]. As a further verification of the irrelevance of gravity, some simulations are performed on a complete domain with no top-down symmetry by taking gravity into account, whose results overlap completely those without gravity. The lamellae move with constant velocity  $v = 1.5 \text{ mm s}^{-1}$  until the MID hole reaches its final radius  $R_0$ , as shown in panel a2 for a ratio between the final and the initial radius of the hole of the MID  $R_0/R_c = 8$ . The central part of the film 'necks' during MID opening, thus determining a sigmoidal stepped geometry where the film is thin and almost flat in a wide region around its center, with thickness  $h_0$ , then its thickness steeply increases in the radial direction approaching the iris lamel-



**Fig. 4.** a: Sketch of the computational domain for direct numerical simulations of film stretching and leveling with reference to MID opening start (b1) and stop (b2) for  $R_0/R_c = 8$ . b: Calculated radial thickness profiles of the film during MID opening for  $R_0/R_c = 8$ . c: Numerical and experimental time evolution of the thickness of the film at its center during MID opening.



**Fig. 5.** a: Concentric colored fringes generated by white light interferometry. b: Thickness map measured with holographic microscopy. c: Experimental thickness profile evolution during early stages of the leveling flow (see time-values in panel a) with  $h_0 = 60$  nm.

lae. Fig. 4b shows the numerically computed film stretching dynamics for the geometry shown in Fig. 4a. The qualitative agreement between the numerical and the experimental results in Fig. 3 is remarkable, yet quantitative differences arise that can be attributed to the fact that the experimental initial condition cannot be so 'clean' and regular as that considered in numerical simulations. In addition, the experimental curves only represent the 'left part' of the numerical ones due to the finiteness of the FOV of the optical tool, which is not an issue in the numerical case. The effect on film stretching of changing the MID aperture is reported in Fig. 4c, where we display the temporal history of the thickness at the cen

ter of the film, normalized by its initial value, for three values of  $R_0/R_c$  considered in the simulations and for the experimental case shown in Fig. 3. Of course, since an inertialess Newtonian liquid is considered, the numerical curves superimpose and stop at increasingly longer time at increasing  $R_0/R_c$ . Noteworthy, the agreement with the experimental data is very good, thus confirming that our direct numerical simulations can effectively describe the actual film formation dynamics.

#### 3.2. Leveling flow

. . .

The time evolution of the film thickness during the leveling flow is displayed in Fig. 5. Fig. 5a shows the color fringes: as the thickness of the central part of the film reaches the wavelength of the visible light, interference colors become visible in white light, then they change in time following the film thickness dynamics. At early time (t < 50 s), the colored region is almost circular and the fringes inside it move from the periphery to the center. At longer time, the effects of the regions close to the lamellae become relevant and the axial symmetry is lost (see the fourth snapshot in Fig. 5a). Fig. 5b reports the maps of film thickness at different times from holography, whereas the film thickness radial profiles are given in Fig. 5c, showing progressive film flattening. In addition, from both the last two snapshots in Fig. 5b and the last profiles in Fig. 5c the formation of a dimple at the center of the film is visible (see Sec. 3.3).

The FOV accessible with holography allows for the observation of the film intermediate region and the quantitative measurement of its slope *m* (see Fig. 1b). Fig. 6a reports m(t) in log scale at intermediate times for several experiments with different initial amounts of liquid. This is an example of the intermediate asymptotic behavior of capillary-driven flow in thin films [29]. As it is apparent, m(t) always follows a power-law decay with exponent -1/2, in agreement with the predictions by Ilton et al. [1]. Different positions of the data sets are due to different initial amounts of liquid from one experiment to another. Fig. 6b reports the slope values obtained from direct numerical simulations with different values of  $R_0/R_c$ , whose agreement with experiments is excellent. Like in Ilton et al. [1], the scaling can be validated with a model based on the lubrication long-wave theory, which makes use of the Young-Laplace equation in the small-slope approximation with negligible inertia, constant viscosity and surface tension, and noshear boundary conditions at each liquid-air interface. After derivation in axisymmetric geometry, given in Sec. 4 in the SI, the model reads

$$h_t + \frac{(rnu)_r}{r} = 0,$$

$$\left[ \frac{(rh_r + 3ru)_r}{r} \right]_r + \frac{2h_r}{h} \left[ \frac{(ru)_r}{r} + u_r \right] = 0.$$
(1)

Notice that all the quantities appearing in Eq. (1) are dimensionless, the usual superscript \* being omitted for brevity. The scales are  $h_{\rm T0}$  for lengths and  $h_{\rm T0}\mu/(\gamma\epsilon^2)$  for time, with  $\epsilon = h_{\rm T0}/R$ . The dimensionless film thickness h and radial velocity u only depend on time t and radial direction r. The subscripts  $_t$  and  $_r$  denote derivatives with respect to these variables. The derivation follows Munch et al. [30] for the free-slip limit, yet with an axisymmetric geometry. Once linearized at the lowest order in the small parameter  $h_{\rm T0}/R$ , the thickness dynamics obeys a diffusive-like equation and, at this order, the slope m(t) decreases at intermediate times with  $t^{-1/2}$ .

In view of the good agreement between experiments and finiteelement simulations, the numerical results can be safely used to characterize the flow conditions at the film center. Fig. 7a reports the time evolution of the dimensionless thickness at the center of the film during the leveling flow. From these data, we compute the strain rate  $\dot{\epsilon} = || - 1/(2h)dh/dt||$ . The stress difference  $||T_{zz} - T_{rr}||$  at r = 0 can be also extracted from the numerically com-



**Fig. 6.** Time evolution of the slope *m* of the film intermediate region. a: Experimental results for experiments with different initial amounts of liquid. b: Numerical results for three different values of MID hole opening radius (time scale  $2h_0\mu/\gamma$ ). Dashed lines are power laws  $\propto 1/\sqrt{t}$ .



**Fig. 7.** a: Calculated time evolution of the thickness at the center of the film during leveling flow (time scale  $2h_0\mu/\gamma$ ). b: Calculated dimensionless stress difference  $||T_{zz} - T_rr||^*$  (stress scale  $\gamma/h_0$ ) at the center of the film as a function of the dimensionless strain rate  $\delta^*$ . The dashed line reports the prediction for equi-biaxial extensional flow of a Newtonian liquid. In both panels, three values of the ratio  $R_0/R_c$  are considered, as reported in the legend.

puted stress fields. Fig. 7b shows the dimensionless stresses versus the dimensionless strain rate. It can be observed that, depending on the extent of MID hole aperture, different ranges of strain rate

are explored at the center of the film during leveling, the more the MID hole is opened the lower the strain rate during leveling. Furthermore, numerical simulations prove that at the film center the flow conditions are those of an equi-biaxial extensional flow, as the data obey the law  $||T_{zz} - T_{rr}|| = 6\mu\dot{e}$  characterizing the equibiaxial extensional flow of a Newtonian liquid.

#### 3.3. Dimple formation during leveling flow

The film thickness holographic maps and profiles in Fig. 5 show the formation of a dimple, also known as 'bump', namely, a local thickness maximum at the center of the film that induces a change of concavity in the film thickness radial profile. According to our experimental observations, this happens when  $h_0$  is below a critical value  $\approx 250$  nm at the end of MID opening. Fig. 8 displays an example of the two different scenarios appearing in the experiments, i.e., film capillary leveling without dimple formation for  $h_0 = 650$  nm (a) and with dimple formation for  $h_0 = 250$  nm (b). In planar freestanding films, bumps cannot form during leveling flows [1], whereas, in confined axisymmetric films, mass conservation might cause fluid accumulation near the center of the film resulting in bump appearance. Film thickness profile at the beginning of the leveling phase is also relevant for the formation of dimples. Indeed, by looking at the initial thickness profiles (the blue curves) in Fig. 8, it can be seen that, when the dimple does not form (a), the film thickness increases 'earlier' in the radial direction than when the dimple forms (b), where the almost flat region around the center of the film has a larger radial extent. As a further proof, we solve the lubrication model, Eq. (1), by choosing two different initial sigmoidal profiles and imposing symmetry boundary conditions at r = 0 and u = 0,  $h_r = 0$ , and  $h_{rr} = 0$  at r = R (so excluding the Plateau borders from the picture). Consistently with the experimental observations, the dimple is absent in the case where the initial film profile increases closer to the center (see Fig. 9a). whereas it readily appears where the flat central region is initially more extended (see Fig. 9b). The different scenarios might be attributed to the different 'graduality' of the curvature change from the central to the outer film region. The initial concavity of the profile in the central region is such that the liquid should move towards the outer region, whereas that in the outer region plays in the opposite direction: the relative importance of the two contributions determines the observed dynamics. It should be remarked that, in our lubrication model, the capillary flow does only depend on surface tension effects, no effect of disjoining pressure being taken into consideration.

#### 4. Final remarks

In this paper, we present a novel opto-mechanical tool to generate stable large circular bare freestanding liquid films with a motorized iris diaphragm (MID) and study their dynamics in real time with a joint imaging method combining digital holography and white-light color interferometry that gives detailed timeresolved data on film thickness over a large field of view. After iris opening, the films attain a stepped profile and undergo a leveling flow tending to flatten it. The model Newtonian liquid material used in our experiments, i.e., PDMS, is transparent, which makes it extremely suitable for digital holography. However, it should be said that the opacity of many other polymers in their bulk form would not be a significant experimental issue, because, when thin films are considered, these are always at least partially transparent to the visible light. In addition, if the transmitted light intensity is much weaker than the incident light intensity, the latter could be properly increased to adjust the signal and obtain a good measure.



**Fig. 8.** Experimental film thickness dynamics without dimple formation for  $h_0 = 450$  nm (a) and with dimple formation for  $h_0 = 250$  nm (b).



**Fig. 9.** Numerical solutions of the model based on the lubrication theory, Eq. (1). a: Dynamics without dimple formation. b: Dynamics with dimple formation. The initial profiles are the blue sigmoidal curves at earliest time. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The experimental findings are validated through direct numerical simulations and a model based on the lubrication theory in the same line of the results by Ilton et al [1]. At variance with them, we have an approximately circular film and, above all, in our experiments the polymer is always well above its glassy transition temperature and the film dynamics is measured real-time without the need of cooling and annealing. The equi-biaxial nature of the leveling flow field at the film center detected through numerical simulations might open the perspective of using the device to measure the equi-biaxial extensional viscosity of liquids, a usually quite elusive quantity whose measurement is very difficult to achieve. It is worth specifying that a direct measurement of stresses is not mandatory to this aim, since arguments analogous to the ones underlying the project equation of the Capillary Breakup Extensional Rheometer (CaBER) [31] for uniaxial extensional viscosity could be exploited to retrieve the value of the ratio between the surface tension and the liquid viscosity from the observation of the time evolution of the film thickness profile. (The details of such analysis go beyond the scope of this paper and will be given elsewhere.) There are, of course, practical limitations on the accessible strain rates, but the experimental window can be widened by

properly tuning MID opening. On the other hand, the manual operation of the MID and the inherent inhomogeneity of the wetting of its leaves represent a critical aspect of the proposed method and work has to be done to optimize the tool.

Finally, MID could be also used for analyzing decorated films and films with deposited particles, which could reveal very useful in understanding the role of particles in stabilizing foams and emulsions [15].

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgement

PLM thanks Howard A. Stone for fruitful discussions. The research has been partly funded by project PRIN 2017, Morphological Biomarkers for early diagnosis in Oncology (MORFEO) Prto. 2017N7R2CJ, and MIUR PON Project 2014-2020 PROSCAN.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcis.2021.03.102.

#### References

- M. Ilton, M.P. Couchman, C. Gerbelot, M. Benzaquen, P.D. Fowler, H.A. Stone, E. Raphaël, K. Dalnoki-Veress, T. Salez, Capillary leveling of freestanding liquid nanofilms, Phys. Rev. Lett. 117 (2016) 1–5.
- [2] A. Sharma, E. Ruckenstein, Stability, critical thickness, and the time of rupture of thinning foam and emulsion films, Langmuir 3 (5) (1987) 760–768.
- [3] R. Aveyard, J.H. Clint, Foam and thin film breakdown processes, Curr. Opin. Colloid Interface Sci. 1 (1996) 764–770.
- [4] E. Ruckenstein, C. Dunn, Stability of thin solid films, Thin Solid Films 51 (1978) 43–75.
- [5] A. Constantinescu, L. Golubovic', A. Levandovsky, Beyond the young-laplace model for cluster growth during dewetting of thin films: Effective coarsening exponents and the role of long range dewetting interactions, Physical Review E 88 (3) (2013) 032113.
- [6] J.D. McGraw, N.M. Jago, K. Dalnoki-Veress, Capillary levelling as a probe of thin film polymer rheology, Soft Matter 7 (2011) 7832–7838.
- [7] G. Singh, C. A. Miller, H. G. J., On dimple formation in foam films, J. Coll. Interface Sci. 187 (1997) 334-337.

- [8] G. Debrégeas, P.-G. de Gennes, F. Brochard-Wyart, The life and death of 'bare' viscous bubbles, Science 279 (1997) 1704–1707.
- [9] G. Debrégeas, P. Martin, F. Brochard-Wyart, Viscous bursting of suspended films, Phys. Rev. Lett. 75 (1995) 3886–3889.
- [10] D.Y.C. Chan, E. Klaseboer, R. Manica, Film drainage and coalescence between deformable drops and bubbles, Soft Matter 7 (2011) 2235–2264.
- [11] I. Newton, Optics, Vol. Part II Experiment IV, The Royal Society, London, 1704.
- [12] J. W. Gibbs, On the equilibrium of heterogeneous substances, Trans. Connecticut Acad. Arts Sci. 3 (May 1877 - July 1878) 343-524.
  [13] M. Rivetti, T. Salez, M. Benzaquen, E. Raphaël, O. Baümchen, Universal contact-
- line dynamics at the nanoscale, Soft Matter 11 (2015) 9247–9253.
- [14] L. Champougny, E. Rio, F. Restagno, B. Scheid, The break-up of free films pulled out of a pure liquid bath, J. Fluid Mech. 811 (2017) 499–524.
- [15] A. Yadav, E. J. Hinch, M. S. Tirumkudulu, Capillary-induced motion of particles bridging interfaces of a free-standing thin liquid film, Phys. Rev. Lett. 122 (098001).
- [16] A. Sheludko, Thin liquid films, Adv. Colloid Interface Sci. 1 (1967) 391–464.
- [17] B.V. Derjaguin, The definition and magnitude of disjoining pressure and its role in the statics and dynamics of thin fluid films, Kolloid Zh. 17 (1955) 205–214.
- [18] D. Langevin, C. Marquez-Beltran, J. Delacotte, Surface force measurements on freely suspended liquid films, Adv. Coll. Interface Sci. 168 (2011) 124–134.
- [19] S.I. Karakashev, E.D. Manev, Hydrodynamics of thin liquid films: Retrospective and perspectives, Adv. Coll. Interface Sci. 222 (2015) 398–412.
- [20] J.E. Coons, P.J. Halley, S. McGlashan, T. Tran-Cong, A review of drainage and spontaneous rupture in free standing thin films with tangentially immobile interfaces, Adv. Coll. Interface Sci. 105 (2003) 3–62.
- [21] A. Choudhury, V.K. Paidi, S.K. Kalpathy, H.N. Dixit, Enhanced stability of free viscous films due to surface viscosity, Physics of Fluids 32 (8) (2020) 082108.
- [22] M. Backholm, M. Benzaquen, T. Salez, E. Raphaël, K. Dalnoki-Veress, Capillary levelling of a cylindrical hole in a viscous film, Soft Matter 10 (2014) 2550– 2558.
- [23] B. Mandracchia, Z. Wang, V. Ferraro, M.M. Villone, E. Di Maio, P.L. Maffettone, P. Ferraro, Quantitative imaging of the complexity in liquid bubbles' evolution reveals the dynamics of film retraction, Light: Science & Applications 8 (1) (2019) 20.
- [24] D.M. Hoyle, S.M. Fielding, Necking after extensional filament stretching of complex fluids and soft solids, J. Non-Newt. Fluid Mech. 247 (2017) 132–145.
- [25] J. Seiwert, M. Monloubou, B. Dollet, I. Cantat, Extension of a suspended soap film: A homogeneous dilatation followed by new film extraction, Phys. Rev. Lett. 111 (094501).
- [26] J. Israelachvili, Intermolecular and Surface Forces, Academic Press, 2011.
- [27] V. Ferraro, Z. Wang, L. Miccio, P.L. Maffettone, Full-field and quantitative analysis of a thin liquid film at the nanoscale by combining digital holography and white light interferometry, The Journal of Physical Chemistry C 125 (2021) 1075–1086.
- [28] V. Bertin, J. Niven, H.A. Stone, T. Salez, E. Raphael, K. Dalnoki-Veress, Symmetrization of thin freestanding liquid films via a capillary-driven flow, Physical Review Letters 124 (18) (2020) 184502.
- [29] M. Benzaquen, T. Salez, E. Raphaël, Intermediate asymptotics of the capillarydriven thin-film equation, Eur. Phys. J. E 36 (82) (2013) 1–7.
- [30] A. Munch, B. Wagner, W. T.P., Lubrication models with small to large slip lengths, Journal of Engineering Mathematics 53 (2005) 359-383.
- [31] G.H. McKinley, A. Tripathi, How to extract the newtonian viscosity from capillary breakup measurements in a filament rheometer, Journal of Rheology 44 (3) (2000) 653–670.

## Supporting Information for "Axisymmetric bare freestanding films of highly viscous liquids: preparation and real-time investigation of capillary leveling"

Vincenzo Ferraro\*, Massimiliano M. Villone\*

Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II, Piazzale Tecchio 80, 80125 Napoli, Italy

NEAPoLIS, Numerical and Experimental Advanced Program on Liquids and Interface Systems, Joint Research Center CNR - Università degli Studi di Napoli Federico II, Piazzale Tecchio 80, 80125 Napoli, Italy

Volodymyr Tkachenko, Lisa Miccio

CNR-ISASI, Institute of Applied Sciences and Intelligent Systems E. Caianiello, Via Campi Flegrei 34, 80078 Pozzuoli, Napoli, Italy

NEAPoLIS, Numerical and Experimental Advanced Program on Liquids and Interface Systems, Joint Research Center CNR - Università degli Studi di Napoli Federico II, Piazzale Tecchio 80, 80125 Napoli, Italy

Lorenzo Lombardi, Daniele Tammaro, Ernesto Di Maio, Gaetano D'Avino, Pier Luca Maffettone\*\*

Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II, Piazzale Tecchio 80, 80125 Napoli, Italy

NEAPoLIS, Numerical and Experimental Advanced Program on Liquids and Interface Systems, Joint Research Center CNR - Università degli Studi di Napoli Federico II, Piazzale Tecchio 80, 80125 Napoli, Italy

Preprint submitted to Journal of Colloid and Interface Science

March 13, 2021

<sup>\*</sup>These two authors contributed equally.

<sup>\*\*</sup>Corresponding author.  $+39\ 081\ 7682282$ 

Email address: p.maffettone@unina.it (Pier Luca Maffettone)



Figure 1: Measured motion of a point on the edge of an iris lamella during aperture.

The kinematics of the film formation stage, i.e., motorized iris diaphragm (MID) aperture, is measured by following the motion of the contact line between the liquid and the lamellae of the MID. When the step motor drives the iris at constant speed, the liquid follows a composition of a rigid rotation and an extensional flow, as shown in Fig. 1, which illustrates the trajectory of a contact point between the liquid and a lamella. The measured radial and angular positions are plotted versus the video frames. It is apparent that the radius of the iris hole increases linearly in time.

#### 2. Optical Data Post-Processing



Figure 2: Wrapped phase signal (a) and unwrapped phase signal converted into thickness map (b) at the beginning of the leveling flow in a typical experiment.

Quantitative measurements of film thickness are obtained by processing the digital holograms recorded by the CCD [1, 2]. Digital holography (DH) allows the evaluation of the complex wave field of the light passing through a transparent liquid film and, consequently, of the maps of the phase difference induced by the transit through the The numerical propagation of the liquid. recorded holograms is based on the scalar theory of diffraction and it is implemented in MATLAB<sup>TM</sup> (R2018b). The phase-values are bounded between  $-\pi$  and  $\pi$  and the Puma algorithm [3] for phase unwrapping is implemented to retrieve continuous phase profiles in the sample plane. To show the steps of the CCD data post-processing procedure, images reporting the holograms referring to the first frame after MID opening is stopped are reported in Fig. 2 for a typical experiment. In particular, panel a reports the wrapped phase map, whereas panel b reports the unwrapped phase map converted into a thickness map.

From the phase map, the map of the thickness h is obtained as

$$h(x,y) = \frac{\lambda(\Delta\phi \pm 2\pi m)}{2\pi\Delta n},$$
 (1)

where  $\lambda$  is the wavelength of the laser beam employed for DH,  $\Delta n$  is the refractive index difference between air and the liquid,  $\Delta \phi$  is the phase difference between the hologram of the film and one where no film is present (the so-called reference image), and  $m = 0, 1, \ldots$ . Note that the term  $2\pi m$  appears due to the intrinsic uncertainty of phase measurements. Indeed, each frame measured with this technique is independent of the others and it is difficult to correctly correlate over time the phase values, thus DH leads to time evolutions of the phase signal at the center of the film like that in Fig. 3a.

To avoid this uncertainty, a color interfer-

ometry setup is added. Color interferometry, working in reflection, yields the values of the absolute thickness at the center of the film with an accuracy of about 50nm through Eq. (2) in Ref. [4]. These, in turn, are used to choose the proper value of m in Eq. (1), so adjusting all the thickness profiles obtained with holography, like that in Fig. 3a. This procedure is applied to all the images acquired by the CCD at 10 fps, yielding the evolution of the film thickness map. An example is shown in Fig. 3b for the MID opening and in Fig. 3c for the leveling stage. A check of the correspondence of holographic and interferometric results is given in Fig. 3d by comparing the film thickness profiles after MID aperture is stopped. In conclusion, we use the color interferometry data at the center of the film to properly shift the thickness maps obtained by holography. As it is apparent from Fig. 3d, there is a deep difference between the spatial resolutions of the two methods. The only color interferometry is not enough to retrieve the local slope and curvature of the film in its thicker parts due to the insufficient coherence length of the white light source. On the other hand, color interferometry measurements of the thickness at the center of the film are crucial as a reference for holographic measurements.

#### 2.1. Evaluation of the Radial Velocity Field

The radial velocity field in the film is determined from evaluation of volume variations in the different portions of the film. Data obtained from holographic measurements allow to measure the local film thickness for each pixel of the camera sensor. Under this as-



Figure 3: a: Temporal history of the phase shift signal obtained by holography at the center of the film during the leveling flow in a typical experiment. b,c: Time evolution of the thickness at the film center measured with color interferometry during MID aperture (b) and during the leveling flow (c). d: Film thickness profile obtained with holography and interferometry at the end of MID aperture, with  $h_0$  the thickness at the film center.



Figure 4: Sketch of film geometry at the beginning of leveling (blue solid line) and of how it can evolve during leveling (red dashed line).

sumption, the liquid volume inside a generic region of radius R (see Fig. 4) can be expressed as

$$V_{\rm R}(t) = p^2 \sum_{i}^{N} h_i(t), \qquad (2)$$

where p is the pixel length divided by the demagnification factor (1/3),  $h_i$  is the thickness value in the *i*-the pixel, and N is the total number of pixels inside the region with radius R. Then, the liquid radial velocity can be estimated as

$$u_{\rm R} = \frac{1}{\Delta t} \frac{\Delta V_{\rm R}(t)}{Np^2} = \frac{1}{\Delta t} \frac{\sum_i^N \Delta h_i(t)}{N} = \frac{\Delta h_{\rm R}(t)}{\Delta t},$$
(3)

with  $\Delta t$  the time lapse between each frame,  $\Delta V_{\rm R}(t) = V_{\rm R}(t + \Delta t) - V_{\rm R}(t)$ , and  $\Delta h_{\rm R}(t) = \sum_{i}^{N} \Delta h_i(t)/N$ .

#### 2.2. Measurement of Film Curvature

Quantitative measurements of the film thickness also provide a fine characterization of the film geometry. Indeed, such data can be used to obtain information on the evolution of the curvature radii during the MID aperture, as shown in Fig. 5. We find out that the following law fits very well the radial profiles of the film thickness measured



Figure 5: a: Film thickness radial profiles during MID opening fitted by Eq. (4) (red lines). b: Radial trends of the curvature radius of the film calculated with Eq. (4).

during the MID aperture:

$$h(r,t) = a(t)e^{b(t)r} + c(t)e^{d(t)r},$$
 (4)

where h(r, t) is the film thickness depending on the radial coordinate r and on time t, and a, b, c, d are time-dependent coefficients. From this function, we can calculate the radial profiles of the curvature radius of the film during MID aperture. It is clear from the data shown in Fig. 5b that the curvature radii of the film increase over time during the aperture.

#### 3. Direct Numerical Simulations

In order to perform direct numerical simulations aimed at elucidating the dynamics of steep sigmoidal film preparation and subsequent leveling, we initially consider the geometry shown in Fig. 4a1 in the Main Text, where the grey area represents the liquid domain and the red shaded rectangle represents the lamellae of the MID. On the basis of the experimental information, a cylindrical coordinate system is set with its center at the center of the deposited fluid and we consider both axial symmetry and top-down planar symmetry (due to the irrelevance of the gravity, as explained in the Main Text). Given the hypotheses that the system is isothermal and that inertia is negligible, the behavior of the liquid is modeled by the mass and momentum balance equations for a Newtonian fluid in the Stokes regime reading

$$\boldsymbol{\nabla} \cdot \boldsymbol{u} = 0, \tag{5}$$

$$-\boldsymbol{\nabla}p + \mu \boldsymbol{\nabla}^2 \boldsymbol{u} = \boldsymbol{0}, \qquad (6)$$

where  $\boldsymbol{u}$  is the fluid velocity field, p is the fluid pressure field, and  $\mu$  is the fluid viscosity.

The planar symmetry condition is imposed on  $\Gamma_1$  and axial symmetry is imposed on  $\Gamma_5$ . No-slip condition is imposed on the vertical edge of the lamellae  $\Gamma_2$ , i.e.,  $\boldsymbol{u} = \boldsymbol{u}_0$ , with  $\boldsymbol{u}_0 = (v, 0, 0)$  the MID imposed constant radial velocity. Slip conditions are imposed on the horizontal edges of the lamellae  $\Gamma_3$  reading

$$\begin{aligned} \boldsymbol{u} \cdot \boldsymbol{n} &= 0, \\ (\boldsymbol{I} - \boldsymbol{n}\boldsymbol{n}) \cdot \boldsymbol{T} \cdot \boldsymbol{n} &= 0, \end{aligned} \tag{7}$$

with I the identity tensor, n the unit vector normal to  $\Gamma_3$ , and T the fluid stress tensor. In addition, a contact angle of 45° between the liquid and the horizontal surface of the lamellae is imposed. Finally, the Young-Laplace boundary condition is imposed on the liquid free surface  $\Gamma_4$ , reading

$$\boldsymbol{T} \cdot \boldsymbol{n} = \gamma \boldsymbol{n} \boldsymbol{\nabla} \cdot \boldsymbol{n},$$
 (8)

with  $\gamma$  the surface tension between the liquid and the surrounding gas. As soon as the MID hole radius has reached its final value  $R_0$  (see Fig. 4a2 in the Main Text), the MID opening is stopped, and the leveling flow of the liquid starts. This means that, upon cessation of iris opening,  $u_0$  is set equal to **0**.

Mass and momentum balance equations on the liquid domains shown in Figs. 4a1-a2 in the Main Text are solved through the finiteelement method. A detailed description of the algorithm employed to track the free surface of the film is given in by Villone et al. [5]. The computational domain is discretized with an unstructured mesh made of triangular elements. During the simulations, the liq-
uid considerably stretches due to MID opening, thus the mesh elements deform progressively. Every time the quality of the mesh goes below a threshold, remeshing is performed. Preliminary convergence tests are performed, namely, mesh resolution and time step for the numerical solution of the model equations are selected such that invariance of the results upon further refinements is ensured. Second-order time integration is used.

#### 4. Lubrication Model

The derivation of the axisymmetric lubrication model, Eq. (1) in the Main Text, follows the approach reported in the literature for planar freestanding films, i.e., for the socalled strong slip condition [6, 7]. The starting point are the motion equations, Eqs. (5)-(6), for an incompressible liquid in the limit of negligible inertia. All the properties are assumed to be constant. The cylindrical domain is symmetric and is defined by

$$\Omega(t) = \begin{cases} 0 \le r \le R\\ (r, \theta, z) \in \mathbb{R}^3 & 0 \le \theta < 2\pi\\ 0 \le z \le h(r, t) \end{cases}$$
(9)

The boundaries of  $\Omega$  are

$$\Gamma_{\rm S} = \left\{ (r, \theta, z) \in \mathbb{R}^3 : z = 0; \ 0 \le \theta < 2\pi \right\}, \tag{10}$$

$$\Gamma_{\rm U} = \left\{ (r, \theta, z) \in \mathbb{R}^3 : z = h(r, t); \ 0 \le \theta < 2\pi \right\} \tag{11}$$

where  $\Gamma_{\rm S}$  is the symmetry plane and  $\Gamma_{\rm U}$  is the upper surface exposed to the air. The velocity field is assumed to be  $\boldsymbol{u} = (U, 0, W)$ . terisks) are expanded in terms of the small

The momentum balance equations read

$$-p_r + \mu \left[ \frac{(rU_r)_r}{r} + U_{zz} - \frac{U}{r^2} \right] = 0, \quad (12)$$

$$-p_{z} + \mu \left[ \frac{(rW_{r})_{r}}{r} + W_{zz} \right] = 0, \qquad (13)$$

with subscripts r and z denoting spatial derivatives along those directions. The kinematic boundary equation and the normal and tangential boundary conditions on  $\Gamma_{\rm U}$  are

$$h_t = W - Uh_r, \tag{14}$$

$$-p + \frac{2\mu}{1+h_r^2} [W_z + U_r h_r^2 - (W_r + U_z)h_r] =$$
(15)  
$$- \alpha^1 \left( \begin{array}{c} rh_r \\ \end{array} \right)$$

$$- {}^{r} \left( \sqrt{1 + h_{r}^{2}} \right)_{r},$$
  

$$2(W_{z} - U_{r})h_{r} + (W_{r} + U_{z})(1 - h_{r}^{2}) = 0.$$
(16)

Finally, the boundary conditions at the symmetry plane  $\Gamma_{\rm S}$  are  $U_z = 0$  and W = 0. The condition on  $U_z$  corresponds to a free slip condition.

The equations are made dimensionless by using the following scales:  $h = hh^*$ , z = $\hat{h}z^*, \ r = \epsilon^{-1}\hat{h}r^*, \ U = \hat{U}U^*, \ W = \epsilon\hat{U}W^*,$  $t = \hat{h}(\epsilon \hat{U})^{-1} t^*, \ p = \hat{p} p^*$ . In the scales, the small parameter  $\epsilon = \hat{h}/\hat{R}$  appears. In the free slip situation, one has to assume that the capillary number is of the order of  $\epsilon$ , i.e.,  $Ca = U\mu/\gamma = \epsilon.$ 

The dimensionless fields (avoiding the as-

parameter  $\epsilon$  as

$$U = U_0 + \epsilon^2 U_1 + O(\epsilon^4),$$
 (17)

$$W = W_0 + \epsilon^2 W_1 + O(\epsilon^4),$$
 (18)

$$h = h_0 + \epsilon^2 h_1 + O(\epsilon^4),$$
 (19)

$$p = p_0 + \epsilon^2 p_1 + O(\epsilon^4).$$
 (20)

(21)

At order 0, the model equations then become

$$U_{0zz} = 0, \qquad (22)$$

$$-p_{0z} + W_{0zz} = 0, (23)$$

$$\frac{(rU_0)_r}{r} + W_{0z} = 0. (24)$$

On  $\Gamma_U$ :

$$h_{0t} + U_0 h_{0r} - W_0 = 0, (25)$$

$$p_0 + 2(W_{0z} - U_{0z}h_{0r}) = \frac{(rh_{0r})_r}{r},$$
 (26)  
 $U_{0z} = 0.$  (27)

$$U_{0z} = 0.$$

On  $\Gamma_{\rm S}$ :

$$W_0 = 0,$$
 (28)

$$U_{0z} = 0.$$
 (29)

Thus, at this order, U and p depend just on r and t. By integrating on z Eqs. (23), (25), and (26), one gets

$$W_0 = -z \frac{(rU_0)_r}{r},$$
 (30)

$$-p = \frac{(rh_{0r})_r}{r} + 2\frac{(rU_0)_r}{r}, \qquad (31)$$

$$h_{0t} + \frac{(rU_0h_0)_r}{r} = 0.$$
 (32)

not achieved by using only the leading-order profile. For an initial step function with

terms, so one has to proceed to the next order of approximation. The term  $U_1$  suffices to close the problem. Then, by integrating the momentum balance r-component at order  $\epsilon^2$ along z between 0 and  $H_0$  one gets

$$-p_{0r} + U_{1zz} + \frac{(rU_{0r})_r}{r} - \frac{U_0}{r^2} = 0, \qquad (33)$$

and using the boundary condition on  $\Gamma_{\rm U}$  at the same order

$$2(W_{0z} - U_{0r})h_{0r} + W_{0r} + U_{1z} = 0, \quad (34)$$

one finally gets the free-slip equations (Eq. (1) in the Main Text)

$$h_{0t} + \frac{(rh_0 U_0)_r}{r} = 0, \qquad (35)$$

$$\left[\frac{(rh_{0r}+3rU_0)_r}{r}\right]_r + \frac{2h_{0r}}{h_0}\left[\frac{(rU_0)_r}{r} + U_{0r}\right] = 0.$$

#### 4.1. Linearization of the Lubrication Model

The power law that characterizes the dynamics of the slope of the intermediate zone can be captured with the linearized version of the lubrication model. Indeed, in the smallslope approximation, the model in axisymmetric geometry reads

$$\frac{\partial h}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial h}{\partial r},$$

$$h(r,0) = f(r),$$

$$\frac{\partial h}{\partial r}\Big|_{r=0} = \frac{\partial h}{\partial r}\Big|_{r=R} = 0.$$
(36)

Of course, at this order, the film thickness dynamics follows a diffusive-like equation. In As remarked by Oron et al. [6], closure is Eqs. (36), f(r) represents the initial film  $h = h_{\rm T0}$  for  $0 \le r < R_{\rm T0}$  and  $h = h_{\rm S0}$  for  $R_{\rm T0} \le r < R_{\rm S0}$ , the analytical solution is a series of Bessel functions

$$h(r,t) = h_{\text{ave}} + \sum_{i=1}^{\infty} C_i Exp^{\lambda_{mi}^2 t} J_0(\lambda_{mi} r), \quad (37)$$

where  $h_{\text{ave}}$  is the average film thickness,  $J_0(r)$  is the zero Bessel function,  $\lambda_{mi}$  are the zeros of the Bessel function  $J_1(r)$ , and the constants  $C_i$ , for the chosen boundary conditions, are given by

$$C_{i} = \frac{2(R_{\rm T0} - R)J_{1}(\lambda_{mi}R) + h_{\rm S0}RJ_{1}(\lambda_{mi}R)}{\lambda_{mi}R^{2}J_{0}(\lambda_{mi}R)^{2}}.$$
(38)

At this order, and as found by Ilton et al. for an infinite planar stepped film [8], the slope m(t) decreases as  $t^{-1/2}$  like in the experiments (see Sec. 3.2 in the Main Text).

#### References

- B. Mandracchia, Z. Wang, V. Ferraro, M. M. Villone, E. Di Maio, P. L. Maffettone, P. Ferraro, Quantitative imaging of the complexity in liquid bubbles' evolution reveals the dynamics of film retraction, Light Sci. Appl. 8 (1) (2019) 20.
- [2] Z. Wang, B. Mandracchia, V. Ferraro, D. Tammaro, E. Di Maio, P. L. Maffettone, P. Ferraro, Interferometric measurement of film thickness during bubble blowing., Proc. SPIE, Int. Soc. of Opt. Eng. 10333 (2017) 1–6.
- [3] J. Bioucas-Dias, G. Valadão, Phase unwrapping via graph cuts., IEEE Trans. Image Process. 16 (2007) 698–709.

- [4] V. Ferraro, Z. Wang, L. Miccio, P. L. Maffettone, Full-field and quantitative analysis of a thin liquid film at the nanoscale by combining digital holography and white light interferometry, The Journal of Physical Chemistry C 125 (2021) 1075–1086.
- [5] M. M. Villone, M. A. Hulsen, P. D. Anderson, P. L. Maffettone, Simulations of deformable systems in fluids under shear flow using an arbitrary lagrangian eulerian technique., Comput. Fluids 90 (2014) 88–100.
- [6] A. Oron, S. H. Davis, S. G. Bankoff, Long-scale evolution of thin liquid films, Reviews of Modern Physics 69 (3) (1997) 931–980.
- [7] A. Munch, B. Wagner, W. T.P., Lubrication models with small to large slip lengths, Journal of Engineering Mathematics 53 (2005) 359–383.
- [8] M. Ilton, M. P. Couchman, C. Gerbelot, M. Benzaquen, P. D. Fowler, H. A. Stone, E. Raphaël, K. Dalnoki-Veress, S. T., Capillary leveling of freestanding liquid nanofilms, Phys. Rev. Lett. 117 (2016) 1– 5.

# Chapter 5: New elastic iris-like device to hold and form freestanding films

In the previous *Chapter 4*, the phenomenon of leveling of a purely viscous freestanding liquid film was studied. The film was formed using an *optical iris* which, as it will be shown in this *Chapter 5*, presents certain limitations and problems that needs to be overcome.

Today, there is no setup capable of forming freestanding liquid films by means of fully customizable deformation, whether in 3D or 2D. In this *Chapter 5*, the reader will find an important result of the Ph.D., which is the invention of a completely new device capable of forming liquid freestanding films that can be exploited for many applications. Until now, as already explained in *Chapter 1*, the Sheludko cell was the most used device to study freestanding films. A first limitation of a Sheludko cell is that it does not allow the in-plane stretching and compressive deformations of the film. It only controls parameters such as pressure, fluid volume and fluid flows. The new device, that I have conceptually invented, designed and built, allows to control not only these three aspects but it allows controlled in-plane deformations of freestanding films. Moreover, in respect to a standard *optical iris*, the specific design of the system permits, as explained below: a better thickness holographic measure, better strain rate control, customable in-plane deformations and much more.

#### **Optical** iris

Prior to the construction of this device, an *optical iris* was used, Figure 5.1, which allowed important results described in *Chapter 4*. In fact, *Chapter 4* describes how an *optical iris* is used to form freestanding thin liquid films from a drop of liquid deposited in the center of the lamellae when the iris is closed. However, the *optical iris*, although it allows to impose equibiaxial extensional deformations in the plane, it has some severe drawbacks. The first limitation concerns the geometries that can be obtained. In fact, the *optical iris*, being made of rigid leaves, allows only axial symmetric freestanding liquid films. As further limitation, this device imposes shear stresses in the fluid on the leaves, thus generating non-uniform distribution of the fluid that coat the leaves. Such non-uniform distribution, in some cases, may influence the evolution of the film over time

during and after the opening, thus deviating its behavior from that of an axisymmetric film. Another problem regarding the *optical iris* was the presence of a small gap between the leaves to ensure that they can slide against each other. This gap between the blades represents a micro-channel that could suck small amounts of fluid out of the film.



**Figure 5.1**: *optical iris* holding a freestanding liquid film of Silicone Oil; the color fringes that are visible arise from the white light interference.

#### Iris valve

A new device has been designed and fabricated for the formation and investigation of free-standing film for the first time. Its design is inspired to the commercial *iris valve* but with some specific changes in order to avoid the main limitation of the *optical iris* such as the capillary withdrawal of fluid due to the gap between the blades. This new device was tested during my research work, after the *optical iris* (see Figure 5.2). Even if this device solved partially some of the problems related to the *optical iris*, in particular it significantly reduced the excess material on the leaves, some problems were not overcome. In fact, in the *iris valve*, the leaves were much thicker (2mm), which allowed the film to adhere even better to them, but due to the greater thickness the shear stresses at the edge of the film were still present and negligible only under certain conditions (e.g. low opening velocities). Moreover, a new problem arose as the device

sometimes blocked due to the friction among the various elements. In fact, to avoid any kind of contamination of the freestanding liquid film, it was not possible to use the lubricant to reduce the friction between the leaves. Any fluids or solid lubricant would have contaminated the freestanding liquid films dramatically and change its properties. Finally, it was not possible to obtain different geometries as it was fixed by the dodecagonal planar geometry imposed by 12 leaves from which the device was made.



**Figure 5.2**: (a) 3D model of the internal structure of the *iris valve* tested ;(b) the *iris valve* leaves holding a freestanding liquid film (20%vol Water + 80%vol Glycerol + 0.08%wt 10µm PMMA particles) (c) thickness map immediately after the aperture evaluated by using Digital Holography (d) unwrapped phase map of the data shown in (c)

To test the setup, films were formed based on a dispersion consisting of water, glycerol, surfactants and spherical PMMA micro particles with an average diameter of  $10\mu m$ . The result was that the PMMA particles tend to aggregate into large clusters of particles. These clusters form almost instantaneously during the opening of the *iris valve*. The diameter of these clusters depends on the radial position in which they are formed during opening, as shown in Figure 5.2(c-d). The formation of such clusters in a solution with so many particles may be a consequence of the model theorized by Yadav et al, see eq. (1.2.2), in which a particle totally embedded inside a freestanding thin liquid film is attracted by its neighbors due to the thickness gradient induced by them. In addition, all particles are pulled to the Plateau border during the experiments due to an additional thickness gradient induced by the leaves. This means that the milky part of the film attached to the *iris valve* leaves has an estimated minimum thickness. Therefore, this could use to induce a controlled thickness depending on the particles size.

#### New iris

The new device that has been developed after the *iris valve* solves all the abovementioned problems that concern both the *optical iris* and the *iris valve*. In fact, as will be described below, the film in the *new iris* is supported by an elastic band on which a controlled deformation is imposed and no shear stresses occur if desired. Some possible deformations, which are fully customizable, are shown in Figure 5.6.

There is very good control of the volumes deposited in the center of the *iris* as most of the liquid remains in the center of the elastic before and during the imposed deformations without being dispersed. To further control the volumes it is possible to place the device inside a controlled atmosphere box to prevent or slow down the evaporation of the solvents that make up the freestanding liquid film. The opening can be actionized by a step motor and can be controlled by Arduino and a computer.

This device performs very well when used to form freestanding thin liquid films i.e. it is possible to form very large liquid films even if they are made of pure deionized water. It is important to underline that in literature, freestanding water films generally do not exceed few millimeters diameters. On contrary, the challenging performance of this new device is that we are able to easily form aqueous thin freestanding films of deionized water up to 20 millimeters in diameter. These films are very sensitive to perturbations from outside, but despite this the device is able to form and sustain them for tens of seconds.

Another interesting feature of forming freestanding liquid films with this device is the possibility of simulating what happens to a film between two growing bubbles (or drops). In fact, the Sheludko cell has so far always been used by fixing the outer diameter of the film through a rigid porous ring connected to capillaries or syringe pumps. With this new device it is possible to study the classical case analyzed using the Sheludko cell, thus fixing the diameter of the elastic band supporting the film. Furthermore, as it has been seen (see Figure 5 in *Supplementary Information* of *Chapter 4*), that during the opening of the *iris*, in the case of Newtonian fluids without any surfactants, the average radius of curvature of the film is continuously increasing. The elastic bands opening therefore simulates what can happen to the film if it separates two bubbles within an expanding foam.

All the mechanical components of the new device were designed by me with Fusion360 software and made using an LCD resin 3D printer (Elegoo Mars 3D). Only the tie rods, the central elastic and the ball bearing balls, see Figure 5.4, were purchased.

An important advantage of this setup is that it will further improve the holographic measurements of the freestanding films as the object beam does not only pass through the sample, as shown in Figure 1.1.2. Since the object beam travel through the empty space between the elastic band supporting the film and the iris rings, it allows to always have a reference optical path in air. Thus, within each recorded frame of fringe pattern there is the acquisition of the hologram with one portion related to the sample and another portion of hologram in air. This made the holographic measurement a self-reference one for all the measurements thus greatly simplifying the measurement process and making it more accurate.

The elastic iris has several novel aspects and useful features that it was foreseen the possibility to patent it. A patent is pending as a patent has been filed in Italy (ref. 102021000016343, 22/06/2021).

The details about the device and related patent pending is described by using Figure 5.3 and Figure 5.4 where all the key elements are numbered. As explained above, the invented configuration can overcome some of the above problems such as the equibiaxial extensional flow, by ways of examples, by using enough strings (7) connect the element (9) to the element (5). The *iris* is preferably made of two rotating groups of rigid rings connected to the component (9), the relative rotation of these two rigid groups adjusts the deformation of the component (9). The component (9) is preferably connected to the component (1-5) by beams or strings (7). The strings (7) are preferably mounted at equal points around a circumference of the element (1-5), the strings are tied by the pins (6) on the element (2) during the relative rotation of the element (1-5) with respect to the element (2). In the space between the element (1) and (3) several spheres (8) are put inside to ensure relative rotation of the two groups of elements. A sketch of how the device transform a rigid rotation into a radial deformation is shown in Figure 5.6. Some possible deformations, which are fully customizable, are shown in Figure 5.5, Figure 5.7 and Figure 5.8.



**Figure 5.3**: (a) two cross section views of the *new iris* device (b) two cross section views of the *new iris* device after the rigid motion of the two rotating parts.



**Figure 5.4**: (a) photo overview of the new setup in which the device is connected to e stepper motor to control the opening dynamic (b) the same device opened with a freestanding liquid film made of water in the center.



**Figure 5.5**: all the film in the images are made of soap solutions (a) small triangular thin liquid film geometry (b) stretched triangular film geometry (c) small hexagonal film geometry (d) stretched hexagonal film geometry

A sketch of how the device transform a rigid rotation into a radial deformation is shown in Figure 5.6. A circular elastic band is anchored to 12 threads and each of them is anchored to the element 5. When the element 5 is rotated all the threads are tied by the fixed pins (elements 6).



**Figure 5.6**: (a,b) sketch of how the iris mechanism operation works during the rotation (c) only a single thread is sketched to show in detail how the rigid rotation of the elements 5 and 1 impose a radial motion of the anchor point thread on the central elastic.



**Figure 5.7**: Some possible geometries that can be imposed by the *new iris* to the elastic band.



**Figure 5.8**: A possible 3D film geometry obtained after a proper customization of the setup.

#### **Applications**

The central elastic can be chosen in such a way as to obtain not only multiple geometries by changing the number of threads or by fixing some anchor points of the elastic (see Figure 5.7). In fact, the rubber band can be replaced by a membrane with multiple holes in order to carry out more than one experiment at the same time. It is also possible to deform a membrane without holes and a deposition of fluids or cell cultures can be done in order to observe their behavior as the deformation state of the substrate on which they are deposited changes.

Using the concepts of *Chapter 1*, *Section 1.2*, it is then possible to exploit the motion of the particles within a freestanding liquid film to carry out a particle sorting. These particles then can be separated after or they can remain embedded in the film if it is allowed to solidify. In the latter case, it is possible to build ordered structures on very

large films in a short time by using this self-assembling process and any kind of solidification process.

Another possibility is to deposit thermosetting resins, photo-hardening resins, solutions capable of gelling, polymeric solutions capable of forming solid thin films as the solvent evaporates inside the central elastic. Then, it would also be possible to make 3D prints by means of the controlled deposition of polymer layers obtained from the above materials, achieving an accuracy of a few hundred nanometers in thickness.

Moreover, through suitable modifications, it would be possible to construct threedimensional films and not just planar ones like those illustrated in Figure 5.8.

Finally, a further application of the device can be foreseen also in a completely different field from thin films. In fact, the invented device can be useful in optics and imaging systems (cameras, microscopes, etc.). By replacing the central elastic with a perforated membrane it would be possible to produce an optical iris without leaves and capable of providing an almost perfect circular hole. In fact, the best optical irises are those with the largest number of leaves to obtain a hole as circular as possible.

## **Chapter 6: A novel spreading protocol shows new Graphene Sheet film transitions on water-air interface**

In *Chapter 1* the reader was already introduced to the concept of Surface Pressure (*Section 1.2.2*) and Marangoni Effect (*Section 1.2.4*). The concept of Surface Pressure is very important to characterize and control liquid films and monolayers of particles or molecules[1]–[4]. Marangoni Effect (*Section 1.2.4*) is fundamental to understand how to spread such objects on a liquid-liquid or liquid-air interface [5]. The work presented in this *Chapter 6* was carried during my study period abroad at the ETH University in Zurich. The work presented in this *Chapter 6* is of fundamental importance for the freestanding liquid film engineering because particles can be used to induce peculiar properties to the films or change some of the pre-existing ones.

In interfacial science the spreading process of particles and surfactants on an interface is critical. Graphene Sheets (GS) dispersions are challenging materials to spread because these particles "stick" to each other easily and, therefore, it is hard to have a starting uniform coverage of the interface. Moreover, due to their affinity and jagged shape high shear stresses arise during the compression of a GS monolayer [6], [7]. In this *Chapter* 6 a novel spreading protocol is presented to optimize the starting distribution of particles at the interface immediately after their spreading. The starting distribution of particles at the interface was characterized by a Reflex Camera and the surface pressure isotherms obtained after the two different spreading protocols are compared. The  $\Pi$ -A isotherms, measured after the new spreading method, allow the observation of new transitions of the GS film at air-water interface.

Graphene is a material which has got very interesting chemical and physical properties. It has lot of applications in many fields such as medicine, electronics, sensors, aerospace, and electronics. We can even say that Graphene is a material which still holds many surprises for the future.

The GS particles were synthetized by electrochemical exfoliation [8], [9]. These GS particles can be spread on a liquid-air interface to assemble wide GS films. Until now, the most common spreading protocol uses a syringe pump to control the flowrate of the spreading solution at the interface and a needle very close to the interface. The solution

is spread as gently as possible to avoid high Marangoni stresses at the interface that could lead to inhomogeneities of the particle distribution at the beginning [10], [11]. The main driven force are the Marangoni stresses generated by the concentration gradient between the solution injected from the needle and the liquid-air interface.

The problem is that in many cases, like for the GS dispersion in N-Methyl-2-Pyrrolidone (NMP), the concentration gradients are really high between the needle and the surface of the subphase. This leads to high Marangoni stresses that push hard the particles at the surface. Also gravity can affect the spreading and increase the velocity of the particle at the interface. Moreover, in case of water subphase and NMP the viscosity is really low and the slip conditions, at water-air interface, impose really low stresses which do not counter a lot the Marangoni flows and capillary forces. Another issue is the Reynolds-Plateau instability that sometimes induces a rupture of the meniscus that bridges the surface of the water-air interface and the needle used for the spreading; suddenly it may start dripping and ruin the spreading due to, for example, particles loss in the subphase or particle clusters formations at the interface.

As said above, the main force that drive the process are the Marangoni stresses arising from the concentrations gradients but these stresses could be a problem if too strong. To better control them sometime, as for the GS particles dispersion, is not possible to dilute the spreading solution with the liquid of the subphase. What it is possible to do is to control the gradient in space. In order to do that it is necessary to have a longer path experienced by the spreading solution before it arrive at the interface. However, if we raise the needle further from the face, the needle will drip and the droplets will fall off and ruin the spreading for the reasons explained above. To avoid all the above problems, I simply lay down a second needle on a solid Teflon surface and let its tip touch the liquid subphase surface while on the opposite end of it I spread the spreading solution.

## 6.1 Materials and Methods

The Graphene Sheets are obtained by Electrochemical Exfoliation. The protocol used is the same shown in [8], [9]. The electrochemical solution was made of 330mL water 0.2M of SNDS (Sigma Aldrich, >=98%). The Graphene (Alfa Aesar, 0.254mm thick, 99.8%)

and the copper foils (~50mm x 300mm) were immersed up to touch the bottom of the beaker. The distance between the foil was kept 50mm for the entire process. The Voltage was +10V in DC regime. The time of the synthesis was 1h. After that we filtered the resulting graphene dispersion under vacuum by using a membrane filter (Millipore, pore size  $0.45\mu$ m) and washed it 4 times with ~1ml of Milli-Q water to clean it from the salts.

After the synthesis the GS dispersion in NMP are centrifuged in a centrifuge for 1h at 6000rpm. The resulting dispersion has a concentration of  $\sim 3.3g/L$  of GS particles in NMP. The average diameter of the GS is  $\sim 1.3\mu$ m.

At this point, we are going to compare the spreading results of two different methods in terms of surface distribution of GS on water-air interface and surface pressure isotherms. The novel protocol is illustrated in Figure 6.1 and it requires a custom setup made of 2 needles, a syringe pump and a solid plane.



**Figure 6.1**: sketch of the old spreading method, the spreading dispersion of NMP and GS particles is injected at the interface with a needle connected to a syringe pump to control the flow rate.



**Figure 6.2**: (a) A photo of the setup used for spreading without the needle connected to the syringe pump (b) Sketch of the new spreading method (c) top and side view of a 3D reconstruction of both old and new spreading protocols.

The main forces that affect the spreading process, in general, can be: capillary forces, gravitational forces and Marangoni forces. The spreading and subphase solutions used in both spreading protocols are the same, this means that the only difference is given by the geometry of the system. This is why we can look at the characteristic lengths, which are proportional to the main forces, to compare the two protocols, see Figure 6.3. The capillary stresses are proportional to the curvature  $1/R_{c_i}$  (where i = 1,2 and are referred to Figure 6.3), the gravitational forces are proportional to the high differences  $H_{g_i}$  (where i = 1,2 and are referred to Figure 6.3) and the Marangoni stresses will be correlated to  $L_{m_i}$ . If we look at the curvature radii we have  $1/R_{c_1} \gg 1/R_{c_2}$  ( $R_{c_1} \sim 0.5mm; R_{c_2} \sim -$ 

0.5mm), this means that the capillary forces slow down the flow because they generate a negative pressure drop between the wetted needle and the water-air interface. For Marangoni stresses we have that  $1/L_{m_1} \gg 1/L_{m_2}$  this means that the surface tension gradient, due to the concentration gradient, is very small in the second case if compared to the first  $(L_{m_1} \sim 1mm; L_{m_2} \sim 50mm)$ . Finally, in the first case there is a height gap between the needle and the liquid-air interface  $(H_{g_1} \sim 1mm; H_{g_2} \sim 0mm)$  which is totally absent in the second case because the wetted needle is at the same level of the liquid-air interface meniscus of the trough.



**Figure 6.3**: (a) characteristic lengths that are proportional to the stresses generated by the major driving forces in case of the old spreading protocol; (b) characteristic lengths that are proportional to the stresses generated by the major driving forces in case of the new spreading protocol.

### 6.2 Results and discussion

Here we compare the spreading results of the two different methods in terms of surface distribution of GS on water-air interface from the beginning using the Langmuir tough experiments and related surface pressures isotherms.

The measure of the isotherm was obtained at a bar velocity of 2mm/min for every compression experiment. The spreading solutions were the same for each experiment.



**Figure 6.5**: two typical compression experiments in a Langmuir trough at 2mm/min compression rate by using the new spreading protocol (blue line) and the old spreading protocol (orange line). (A) the first part of the isotherm is related to the "gas phase"; (B) GS particles start to aggregate and some isles show up; (C) the isles rearrange themselves to create a more uniform film; (D) the last transition is related to the solid layer of GS particle formation.

In the Figure 6.5 it is possible to notice a big difference between the phase transitions of the two isotherms with the same spreading solution composition and compression rate. In particular, in the plot obtained with the new spreading protocol, two new phase transitions are visible. If we look at the pictures shown in Figure 6.5 it is possible to notice that the GS film structure has a short-range arrangement. This kind of arrangement was never observed before; this means that the starting particles distribution over an interface is important and it can affect the surface pressure isotherms.

Probably the old spreading imposes so high stresses at the interface that they forced the particles to merge together and generate clusters that influence the surface pressure isotherm shape. This is reasonable because during the expansion cracks, that are generated by a fragile rupture of the film, show up and a dramatic drop of surface pressure is measured. Furthermore, after few compressions and expansions the new phase transitions progressively disappear after each cycle, as shown in Figure 6.6.

Probably this means that GS particles rearrange themselves after each compression and sticks to each other to form isles and, at the limit of an infinite number of compressions, a single film of GS particles could form. The maximum value of  $\Pi$  reached in the second compression is a little bit lower than the first compression, this is a sign that some particles no longer contribute to the interface coverage. During the experiments I noticed that some black particle aggregates started to show up at high interface compression deformations, these aggregates might be the reason why we lose some particles.



**Figure 6.6**: Here two cycles of compression and expansion were imposed to the spread GS particles at the water-air interface inside the Langmuir trough by using the same NMP dispersion used also for the other experiments. The cycles were performed without any rest pause.

## References

- [1] S. T. Milner, J. F. Joanny, and P. Pincus, "Buckling of langmuir monolayers," *Epl*, vol. 9, no. 5, pp. 495–500, 1989.
- [2] V. Garbin, "Collapse mechanisms and extreme deformation of particle-laden interfaces," *Curr. Opin. Colloid Interface Sci.*, vol. 39, pp. 202–211, 2019.
- [3] D. Vella, P. Aussillous, and L. Mahadevan, "Elasticity of an interfacial particle raft," *Europhys. Lett.*, vol. 68, no. 2, pp. 212–218, 2004.
- [4] M. G. Basavaraj, G. G. Fuller, J. Fransaer, and J. Vermant, "Packing, flipping, and buckling transitions in compressed monolayers of ellipsoidal latex particles," *Langmuir*, vol. 22, no. 15, pp. 6605–6612, 2006.
- [5] J. T. Zhang, L. Wang, D. N. Lamont, S. S. Velankar, and S. A. Asher, "Fabrication of large-area two-dimensional colloidal crystals," *Angew. Chemie - Int. Ed.*, vol. 51, no. 25, pp. 6117–6120, 2012.
- [6] L. J. Cote, F. Kim, and J. Huang, "Langmuir-blodgett assembly of graphite oxide single layers," *J. Am. Chem. Soc.*, vol. 131, no. 3, pp. 1043–1049, 2009.
- [7] L. Imperiali, K. H. Liao, C. Clasen, J. Fransaer, C. W. MacOsko, and J. Vermant, "Interfacial rheology and structure of tiled graphene oxide sheets," *Langmuir*, vol. 28, no. 21, pp. 7990– 8000, 2012.
- [8] F. Liu *et al.*, "Synthesis of graphene materials by electrochemical exfoliation: Recent progress and future potential," *Carbon Energy*, vol. 1, no. 2, pp. 173–199, 2019.
- [9] J. M. Munuera, J. I. Paredes, S. Villar-Rodil, M. Ayán-Varela, A. Martínez-Alonso, and J. M. D. Tascón, "Electrolytic exfoliation of graphite in water with multifunctional electrolytes: en route towards high quality, oxide-free graphene flakes.," *Nanoscale*, vol. 8, no. 5, pp. 2982–2998, Feb. 2016.
- [10] J.-T. Zhang, L. Wang, D. N. Lamont, S. S. Velankar, and S. A. Asher, "Fabrication of Large-Area Two-Dimensional Colloidal Crystals," *Angew. Chemie*, vol. 124, no. 25, pp. 6221–6224, 2012.
- [11] N. Smith, A. Coukouma, S. Dubnik, and S. Asher, "Debye Ring Diffraction Elucidation of 2D Photonic Crystal Self-Assembly and Ordering at the Air-Water Interface," *Phys. Chem. Chem. Phys.*, vol. 19, Nov. 2017.

## Chapter 7: Controlled buckling wavelength for a film made of graphene sheets on water-air interface by distribution size control

In the previous *Chapter 6* the reader found how important is the spreading protocol to obtain the best result when it is necessary to manage with freestanding thin film made of particles. In this *Chapter 7* the reader will be introduced to a simple method to control the buckling wavelength of a film made of Graphene Sheets by tuning the distribution size of the Graphene Sheets (GS) deposited on the water-air interface.

In *Chapter 1*, *Section 1.3*, the reader was introduced to the Buckling instability concept. As explained before, buckling is a mechanical instability very important for beams and films. Moreover, graphene is a versatile material which is of great interest for many scientific fields nowadays due to its peculiar chemical and physical properties. It has got applications in many fields such as medicine, biosensors, electronic devices, antireflective surfaces, solar panels and much more. Graphene sheets are very easy and cheap to obtain using many different techniques: scotch tape, electrochemical exfoliation [1]–[4], exfoliation by microwaves [5], mechanical exfoliation (e.g. sonication and high shear mixing) [4], chemical vapor deposition [4] and much more. The work presented in this *Chapter 7* was carried during my study period abroad at the ETH University in Zurich.

It is possible to characterize some properties of this GS by spreading them on a waterair interface in a Langmuir trough by measuring the surface pressure isotherm during a compression. To control such systems the problem is that the characteristic buckling wavelength is defined by  $\lambda = \pi (B/\Delta \rho g)^{\frac{1}{4}}$  [6] where g is the gravitational acceleration,  $\Delta \rho$  is the density difference between the subphase and the topphase,  $B = Eh^2/12(1 - \nu^2)$ is the bending stiffness of the film generated by the merged GS particles, E is the Young modulus of the film, h is the thickness of the film and  $\nu$  is the Poisson's ratio. As the formula shows the only way to modify would be act on: E,  $\Delta \rho$  or h. The problem is that it is not possible to change freely the parameter  $\Delta \rho$  because the number of couples of fluids that it is possible to use is limited. On the other side, h it is very difficult to adjust because the single layer of GS has a defined thickness difficult to modify. The only reasonable way is to control E as it will be explained more deeply into detail in this *Chapter 7.* Never before someone has been able to control the characteristic wavelength of a Graphene Sheets film on a liquid-air (or liquid-liquid) interface, this is why this work is going to open new avenues in the study and application of GS particles.

### 7.1 Materials and methods

The Graphene Sheets are obtained by Electrochemical Exfoliation. The protocol used is the same shown in [2], [3]. The electrochemical solution was made of 330mL water 0.2M of SNDS (Sigma Aldrich, >=98%). The Graphene (Alfa Aesar, 0.254mm thick, 99.8%, ~50mm x 300mm) and the copper foils (~50mm x 300mm) were immersed up to touch the bottom of the beaker. The distance between the foil was kept 50mm for the entire process. The Voltage was +10V in DC regime. The time of the synthesis was 1h. After that we filtered the resulting graphene dispersion under vacuum by using a membrane filter (Millipore, pore size 0.45µm) and we washed it 4 times with 1ml of Milli-Q water each to clean it from the salts needed during the electrochemical exfoliation.

Different centrifuge protocols were used to control the diameter distribution of the GS dispersion batches, as shown in Table 1. This kind of particle sorting makes use of different sedimentation kinetics of different GS as a function of the centrifuge forces and particle properties.

Several different GS dispersions in NMP samples were obtained from a single first batch (GS01A-GS07A). All the different samples are obtained by centrifuge the first batch (GS01A). Each GSiA (for i = 2,3,4,5,6,7) sample is obtained by centrifuge the sample GS(i-1)A for 5minutes at (N + 250)rpm where N = 1000 for i = 2, as it is also listed in Table 7.1.

To measure the average diameter of the particles a spreading of a little amount of GS + NMP dispersion was done on a water-air interface for each batch immediately before the experiments in the Langmuir trough, the optic glass was deep coated by the GS particles previously spread on a water-air interface inside a petri dishes. The coated glass was observed under a transmission optical microscope to record the images of the particles (see Figure 7.4). The elaboration of the data was done by using Matlab and ImageJ.

I noticed that there were almost 7 different shades of grey for the GS when they were observed in transmission. I assumed that each shade corresponds to a well-defined number of graphene layers, the lighter one corresponds to the single layer GS and that there is an equal number of sheets for each shade of grey. This means that the average thickness of the GS particles, for all samples, can be estimated as  $\sum_{i=1}^{7} i * 0.8/7 = 3.2$ nm.

	rpm	Time [min]	Centrifuged sample	Graphene Sheets average size [µm]
GS01A	0	0	Graphene obtained after exfoliation	3,24
GS02A	1000	5	GS01A	2,73
GS03A	1250	5	GS02A	2,39
GS04A	1500	5	GS03A	2,11
GS05A	1750	5	GS04A	1,81
GS06A	2000	5	GS05A	1,50
GS07A	2250	5	GS06A	1,43

**Table 7.1**: list of all GSiA (where i = 1, 2, 3, 4, 5, 6, 7) dispersions in NMP.

The spreading protocol of the NMP dispersion with GS was the same described in [5], [6], and shown in Figure 7.1. The isotherm curves were obtained by compressing the

GS particles spread on the Langmuir trough (model) interface at a bar velocity of 2mm/min.

Under this velocity of 2mm/min the surface pressure isotherms are not affected by it, above this velocity a dependence of the isotherm form the bar velocity is appreciable.



**Figure 7.1**: sketch of the used spreading mechanism. A spreading solution is injected at air-water interface from a needle connected to a syringe pump to control the flow rate.

## 7.2: Results and discussion

The surface pressure isotherms of the spread particles were measured in a Langmuir trough and a different buckling wavelength showed up for each sample except for GS01A which did not show any buckling due to its chaotic corrugations during the compression.

In particular, as it is shown in Figure 7.2a, it seems that the critical wavelength of the buckling of the GS film is proportional to the GS average diameter of the sheets on the liquid-air interface.

The Young's modulus of the graphene films was estimated by  $\lambda = \pi (B/\Delta \rho g)^{\frac{1}{4}}$ [3] and  $B = Eh^2/12(1-\nu^2)$ , previously cited in the introduction. As thickness I used the average thickness of the GS particles (3.2nm) evaluated in the chapter "Graphene Sheets (GS)

synthesis and dispersion composition" and I assumed as Poisson ratio v = 0.5, the result is shown in Figure 7.2b.

In literature the reported Young's modulus of the GS and XGO is around  $10^{11}$ Pa [3], [6]–[8]. In the plot shown in Figure 7.2b the maximum value of *E* is 0.66*TPa* which probably overestimates the real Young's modulus of the film (in case we consider a thickness of 0.8nm then E = 570TPa). Maybe with a better characterization of the film thickness and *v* the resulting E would be adjusted.



**Figure 7.2**: (a) measured buckling wavelengths for each average GS diameter. It might be possible to have a linear dependence. (b) Young's modulus evaluated by using the analytical model in [6]

It might be possible that the connection between each GS could be considered as a "hinge" that might have a bending modulus lower than the single GS particles. By thinking in this way we can imagine that as we increase the number of "hinges" then the bending modulus should decrease and consequently the characteristic buckling wavelength should decrease, as sketched in Figure 7.3. Moreover, if it is true there will be a maximum buckling wavelength that will correspond to the maximum bending stiffness which should be reached in case there will be a single uniform and continuum Graphene layer inside the trough.



**Figure 7.3**: all the dashed lines represent a side view of films made of different size distribution of GS particles. Each segment of the dashed lines represents a Graphene Sheet.

In Figure 7.4 there is the same plot shown in Figure 7.2 but with one more point  $(0.2 \mu m; 7.6 \mu m)$ , these values correspond to the data in[6]. In that work the average diameter of the XGO particles was 200nm and the average wavelength of the buckling was  $7.6 \mu m$ . The main difference between my data and the added point is not only the huge average diameter gap in between but also the -OH groups which should be almost absent in my samples. It might be possible that the -OH groups do not affect the buckling critical wavelength. Moreover, there should also be a difference between the mechanical properties of XGO and GS.

In this work we present an easy, rapid and cheap way to make 2D high stretchable conductive materials by using wrinkled [3], [9], [10] free standing PDMS films [11] coated by Graphene Sheets (GS).



**Figure 7.4**: Images of the GS particles captured by a transmission optical microscope with the same magnification.

## References

- K. Parvez *et al.*, "Exfoliation of graphite into graphene in aqueous solutions of inorganic salts,"
   *J. Am. Chem. Soc.*, vol. 136, no. 16, pp. 6083–6091, 2014.
- [2] F. Liu *et al.*, "Synthesis of graphene materials by electrochemical exfoliation: Recent progress and future potential," *Carbon Energy*, vol. 1, no. 2, pp. 173–199, 2019.
- J. M. Munuera, J. I. Paredes, S. Villar-Rodil, M. Ayán-Varela, A. Martínez-Alonso, and J. M. D. Tascón, "Electrolytic exfoliation of graphite in water with multifunctional electrolytes: En route towards high quality, oxide-free graphene flakes," *Nanoscale*, vol. 8, no. 5, pp. 2982–2998, 2016.
- [4] S. S. Shams, R. Zhang, and J. Zhu, "Graphene synthesis: A Review," *Mater. Sci. Pol.*, vol. 33, no. 3, pp. 566–578, 2015.
- [5] J. Lin, Y. Huang, S. Wang, and G. Chen, "Microwave-Assisted Rapid Exfoliation of Graphite into Graphene by Using Ammonium Bicarbonate as the Intercalation Agent," *Ind. Eng. Chem. Res.*, vol. 56, no. 33, pp. 9341–9346, 2017.
- [6] L. Imperiali, K. Liao, C. Clasen, J. Fransaer, C. W. Macosko, and J. Vermant, "Interfacial Rheology and Structure of Tiled Graphene Oxide Sheets," *Langmuir*, 2012.
- [7] N. Smith, A. Coukouma, S. Dubnik, and S. Asher, "Debye Ring Diffraction Elucidation of 2D Photonic Crystal Self-Assembly and Ordering at the Air-Water Interface," *Phys. Chem. Chem. Phys.*, vol. 19, Nov. 2017.
- [8] J.-T. Zhang, L. Wang, D. N. Lamont, S. S. Velankar, and S. A. Asher, "Fabrication of Large-Area Two-Dimensional Colloidal Crystals," *Angew. Chemie*, vol. 124, no. 25, pp. 6221–6224, 2012.
- [9] L. Xue, J. Zhang, and Y. Han, "Progress in Polymer Science," *Prog. Polym. Sci.*, vol. 37, no. 4, pp. 564–594, 2012.
- [10] J. Y. Chung, A. J. Nolte, and C. M. Stafford, "Diffusion-controlled, self-organized growth of symmetric wrinkling patterns," *Adv. Mater.*, vol. 21, no. 13, pp. 1358–1362, 2009.
- [11] D. Kim, S. H. Kim, and J. Y. Park, "Floating-on-water fabrication method for thin

polydimethylsiloxane membranes," Polymers (Basel)., vol. 11, no. 8, 2019.

## Chapter 8: High stretchable conductive 2D materials made of wrinkled PDMS film coated by graphene sheets

Obtaining a high stretchable material that remains conductive under compression and expansion it is a very important goal nowadays. From electronics to medicine, deformable electronic devices have a wide range of applications. In this *Chapter 8* the reader will be introduced to a new method to obtain high stretchable electrical conductive materials by coating PDMS thin films with Graphene Sheets (GS) taking advantage from wrinkling. The material remains conductive under high compression and stretching deformations. The work presented in this *Chapter 8* was carried during my study period at the ETH in Zurich.

Graphene is a material of great interest in many branches like: medicine, electronic devices, sensors, biology, renewable energies and many others. What makes the Graphene so important are its unique chemical and physical properties and its high application versatility. One of the greatest challenges, nowadays, are the 2D high stretchable conductive materials. Until now, it was not possible to build this kind of material, especially an isotropic one. There were attempts in this way like [1]–[3].

The wrinkling mechanical problem is well-known in literature [4]–[12]. The critical wrinkling wavelength for a thin film on a compliance and elastic substrate is  $\lambda = 2\pi h \left(\frac{\overline{E_f}}{3\overline{E_s}}\right)^{\frac{1}{3}}$  where h is the film thickness,  $\overline{E_i}$  are  $E_i / (1 - \nu)$  (where i = f refers to the film and i = s to the substrate),  $E_i$  are the Young modulus [11]. It is possible to control the wrinkling pattern by tuning the mechanical properties of the film, substrate, film thickness or deformation tensor [11], [12]. After the pattern is obtained there is enough time to treat the wrinkled system in many ways to freeze it and obtain a new kind of material by using, for example, thermal gels or resins.

As it was said above, it is necessary to wrinkle a thin film of PDMS. The easiest way to make a freestanding thin film of PDMS is similar to the protocol described in [13]. Here a drop of uncured PDMS is spread on a water-air interface. After the spreading the PDMS was cured by waiting 48h. Spin coating was not used because it is very difficult handle such thin freestanding films made of PDMS, as also mentioned in *Chapter 1*.

## 8.1 Materials and methods

The Graphene Sheets are obtained by Electrochemical Exfoliation. The protocol used is the same shown in [14], [15]. The electrochemical solution was made of 330mL water 0.1M of (NH4)4SO4 (Sigma-Aldrich, >=99%). The Graphene (Alfa Aesar, 0.254mm thick, >=99.8%) and the copper foils (~50mm x 300mm) were immersed up to touch the bottom of the beaker. The distance between the foil was kept 50mm for the entire process. The Voltage was +10V in DC regime. The time of the synthesis was 1h. After that we filtered the resulting graphene dispersion under vacuum by using a membrane filter (Millipore, pore size 0.45µm) and washed it 4 times with ~1ml of milli-Q to clean the particles from the salts. The obtained dispersion was centrifuged 1h at 6000rpm (model centrifuge and rotor).

The PDMS free standing films (50mmx70mm) are obtained by spread a drop of uncured SYLGARD<sup>™</sup> 184 Silicone Elastomer Kit on a water-air interface, at room temperature, in a rectangular aluminum bowl (50mmx70mm) and leave it there 48h to polymerize at room temperature. The thickness of the film was controlled by the volume of silicone that we spread. The water subphase was gently replaced by the fish gelatin (60% wt fish gelatin 40% milli-Q), after the polymerization of the PDMS, and let it jellify for 2h, see Figure 8.1a.

After the gelification finished, the entire sample (the gel block covered by the PDMS film) was taken and dipped to coat it with a graphene sheet layer at 40 mN/m surface pressure surface concentration; the dipping angle was  $30^{\circ}$  during the entire execution. The PDMS coated film was dried from some residual water drops and, immediately after, a compression of ~50% was imposed to obtain the wrinkles, see Figure 8.1b-d.

The electrical properties of the films were evaluated by measuring the resistance at 20V at 1000mA using a multimeter (model) applying the four-point technique, the results are reported in Table 1.


**Figure 8.1**: (a) in the early stages there is the spreading of the uncured PDMS, the curing of the film for 48h at room temperature, the water replacement with the fish gel (60% wt fish gelatin 40% Milli-Q) and the jellification. (b) coating of the PDMS film by dipping it with an angle of  $30^{\circ}$  to the horizontal. The dipping was done at a surface pressure of ~40mN/m. (c) the electrical resistance of the sample was measured before the compression. (d) a compression deformation of 50% was imposed to the material to wrinkle it and then the electrical resistance was measured.

### 8.2: Results and discussion

First of all, the coated PDMS was electrically characterized by measuring with a multimeter (model) the resistance by using the 4-point technique (20V and 1000mA) on the relaxed and compressed samples. The results are shown in Table 8.1.

PDMS	film	Resistance	Resistance
thickness [µm]		(relaxed) [ <i>k</i> Ω]	(compressed)
			[ <i>k</i> Ω]
 Bare PDMS film	thick	~(50-70)*10^3	~(50-70)*10^3
5		~15-25	~(50-70)*10^3
10		~15-25	~15-25

15	~15-25	~15-25
20	~15-25	~15-25
30	~15-25	No wrinkling was observed

**Table 8.1:** the measured resistances  $[k\Omega]$  for each sample with the 4-point technique.

It is interesting to notice that the electrical resistance measured in case of the  $5\mu$ m PDMS film is the same as the pure PDMS. The reason could be a sort of delamination [9] of the coating film of GS that might cause the rupture of the film itself. It could be that the buckling characteristic wavelength of the GS film is too long compared to the shorter buckling wavelength of the PDMS.

The 50% compression imposed to the sample generates the possibility to obtain a 100% stretchable conductive material by just considering the relaxation of the wrinkling of the material.

## References

- T. Nishimura, N. Ito, K. Kinoshita, M. Matsukawa, Y. Imura, and T. Kawai, "Fabrication of Flexible and Transparent Conductive Nanosheets by the UV-Irradiation of Gold Nanoparticle Monolayers," *Small*, vol. 16, no. 12, pp. 1–8, 2020.
- G. Shi *et al.*, "A versatile PDMS submicrobead/graphene oxide nanocomposite ink for the direct ink writing of wearable micron-scale tactile sensors," *Applied Materials Today*, vol. 16. pp. 482–492, 2019.
- K. Parvez *et al.*, "Electrochemically exfoliated graphene as solution-processable, highly conductive electrodes for organic electronics," *ACS Nano*, vol. 7, no. 4, pp. 3598–3606, 2013.
- [4] S. Cai, D. Breid, A. J. Crosby, Z. Suo, and J. W. Hutchinson, "Periodic patterns and energy states of buckled films on compliant substrates," *J. Mech. Phys. Solids*, vol. 59, no. 5, pp. 1094– 1114, 2011.
- [5] H. Mei, R. Huang, J. Y. Chung, C. M. Stafford, and H. H. Yu, "Buckling modes of elastic thin films on elastic substrates," *Appl. Phys. Lett.*, vol. 90, no. 15, pp. 1–4, 2007.
- [6] E. Cerda, "Mechanics of scars," J. Biomech., vol. 38, no. 8, pp. 1598–1603, 2005.
- [7] R. Huang, C. M. Stafford, and B. D. Vogt, "Effect of surface properties on wrinkling of ultrathin films," *J. Aerosp. Eng.*, vol. 20, no. 1, pp. 38–44, 2007.
- [8] Y. Yan, B. Wang, J. Yin, T. Wang, and X. Chen, "Spontaneous wrinkling pattern of a constrained thin film membrane," *Appl. Phys. A Mater. Sci. Process.*, vol. 107, no. 4, pp. 761– 767, 2012.
- [9] H. Mei, C. M. Landis, and R. Huang, "Concomitant wrinkling and buckle-delamination of elastic thin films on compliant substrates," *Mech. Mater.*, vol. 43, no. 11, pp. 627–642, 2011.
- [10] J. Huang, B. Davidovitch, C. D. Santangelo, T. P. Russell, and N. Menon, "Smooth cascade of wrinkles at the edge of a floating elastic film," *Phys. Rev. Lett.*, vol. 105, no. 3, pp. 2–5, 2010.
- [11] J. Y. Chung, A. J. Nolte, and C. M. Stafford, "Surface wrinkling: A versatile platform for measuring thin-film properties," *Adv. Mater.*, vol. 23, no. 3, pp. 349–368, 2011.
- [12] J. Y. Chung, A. J. Nolte, and C. M. Stafford, "Diffusion-controlled, self-organized growth of

symmetric wrinkling patterns," Adv. Mater., vol. 21, no. 13, pp. 1358–1362, 2009.

- [13] D. Kim, S. H. Kim, and J. Y. Park, "Floating-on-water fabrication method for thin polydimethylsiloxane membranes," *Polymers (Basel).*, vol. 11, no. 8, 2019.
- [14] F. Liu *et al.*, "Synthesis of graphene materials by electrochemical exfoliation: Recent progress and future potential," *Carbon Energy*, vol. 1, no. 2, pp. 173–199, 2019.
- [15] J. M. Munuera, J. I. Paredes, S. Villar-Rodil, M. Ayán-Varela, A. Martínez-Alonso, and J. M. D. Tascón, "Electrolytic exfoliation of graphite in water with multifunctional electrolytes: En route towards high quality, oxide-free graphene flakes," *Nanoscale*, vol. 8, no. 5, pp. 2982–2998, 2016.

### **Chapter 9: Summary and key contributions**

In this *Chapter 9*, it is reported the summary of the entire thesis, the conclusions of this research work (i.e. a resume of the results to be published or already published) and the future applications and works.

### 9.1: Summary of the Thesis

In the first part of the thesis (*Chapters 2, 3* and 4), important innovations concerning the thickness measurement of freestanding liquid films were presented. These innovations have made it possible to observe, with unprecedented detail, phenomena as difficult to perceive as the leveling of freestanding thin liquid films. Another important innovation related to *Chapter 4* is the formation and the handling of the freestanding thin liquid film studied which was done using an optical iris that allowed the formation of wide freestanding liquid films.

To overcome the limits and the problems of the optical iris a totally new device was designed and realized, as explained in *Chapter 5*. This device will lead to numerous possible applications and studies related not only to freestanding thin liquid films but to many other fields if combined with the innovative thickness measurements.

The last three chapters (*Chapters 6*, 7 and 8) are interrelated in that all three deal with graphene particles deposited on a water-air interface. *Chapter 6* shows how the mode of initial particle deposition can greatly influence the properties of the interface. It follows that to optimize the results of the following chapters (*Chapters 7* and 8) it is better to use the new spreading protocol of *Chapter 6*. This protocol can be used for any other particle deposition at the liquid-liquid or liquid-air interface and can shed new light on the behavior of coated particle interfaces.

In *Chapter 7*, work is presented on how to control the buckling wavelength of a film made up of GS particles. Until now, no one has ever controlled the buckling wavelength of these systems in such a simple and inexpensive way by simply controlling the diameter distribution of the GS particles. Finally, in Chapter 8, a new method is presented for obtaining a 2D conductive and stretchable material by means of buckling.

In this case, however, the control of the characteristic wavelength is controlled by the thickness of the PDMS film on which the GS particles are deposited.

## 9.2: Future works and applications

The PhD work opens new avenues in many fields due to a new measurement method, a new device and new findings. As explained above in *Chapter 1* freestanding thin liquid films are very challenging systems. The first chronological result was a new thickness measuring method which will allow researchers to have better characterizations of such systems with simpler, faster and better results. The new measurement that combines Digital Holography and White Light Interferometry can be used not only for freestanding thin liquid films or not freestanding ones. Moreover, the measure can be used to investigate more in detail the opening process and rupture criteria of freestanding thin liquid films and bubbles.

The studies carried out in *Chapter 4*, combined with the new measurement and observation systems of these films shown in *Chapter 2,3,4*, will make it possible to study in more detail the leveling phenomenon even in the case of low viscosity fluids, thus being able to follow their sudden time evolution, at the best of my knowledge, for the first time. Moreover, thanks to the new measurement technique shown in *Chapter 2,3,4* combined with the study carried out in *Chapter 4*, it will be possible to study the role of the disjoining pressure, the viscoelastic effects or the behavior of particles inside freestanding thin liquid films during the leveling phenomenon after a prior and appropriate choice of the material to be used. It will then be possible, in the more distant future, to freeze the film structures by the use of hardening resins, gels, particles, polymer solutions and much more.

Further studies of leveling could lead to the measurement of the rheological properties of the materials of which the freestanding films are made. Such films could be formed using the new apparatus described in *Chapter 5*. In addition, theoretically, if one could measure the torque applied to the film in order to lay it down, one could derive the rheological properties of the film by means of extensional equibiaxial deformation. This

could be possible because the deformations and the deformation rates can be retrieved by the high resolution full-field thickness measures of such films.

The reader will find a schematic list of the possible future studies and applications already described in the thesis to which this Ph.D give rise; these are not divided into Chapters as each of them is, most of the time, a result of the combination of all achievements not related to a single Chapter:

#### Future works:

- Leveling as a tool to measure of the rheological properties
- Measure of the rheological properties of a fluid during the iris aperture and the film formation during different extensional deformations, in particular during an equibiaxial extensional deformation
- How disjoining pressure could affect leveling
- Freestanding film rupture criteria and dynamics
- Study of the particle motion inside freestanding films
- Drainage in case of not axisymmetric freestanding liquid films and/or wide films
- Dimple formation investigations during leveling and drainage
- Investigations about polymeric membrane formation by using spreading solutions on freestanding thin liquid films
- Investigation of multiple layer thin liquid films
- Investigations of the Buckling instabilities induced on a freestanding film coated by particles or not, liquid or not.

#### Some possible applications:

- Polymeric membrane formation by using spreading solutions on freestanding thin liquid films
- Polymeric membrane formation by freestanding thin liquid films made formed using my new device

- 3D printing by using the new iris setup to form each layer and by using the new measurement technique to measure and control the thickness evolution
- Particle sorting by using their motion inside freestanding thin liquid films
- Use the new device described in *Chapter 5* to make new optical iris
- Use the new device described in *Chapter 5* to make multiple thin liquid films by using a membrane with multiple holes unless only an elastic band
- Develop of a new holographic measure technique for freestanding thin liquid films by using my new device
- Conductive and stretchable 2D material taking advantage of the buckling instability of GS particle film

## 9.3: Conclusions

There are so many possibilities to control the structure and temporal evolution of freestanding films as there are so many factors that can contribute to the morphology of such systems, such as: capillary forces, disjoining pressure, surface pressure, Marangoni effect, film composition, particles. Each combination of the above factors will result in a unique evolution of the freestanding film. Furthermore, freestanding films are very delicate systems and difficult to observe, especially when they are in a liquid state. In this context, the research work during my PhD made possible to achieve the following main results:

- 1) Developed and a new optical measurement technique for a quantitative, in situ and self-reference measure of the freestanding film structure over time.
- 2) A deep study in the leveling flow which is necessary to control freestanding liquid film thickness evolution over time.
- 3) The study of the buckling mechanical instability at the aim to obtain a better particles distribution after their spreading at the liquid-air interface.
- 4) The successful development of a completely novel experimental apparatus, which is able to reach processing condition difficult to be achieved in typical film freestanding formation. This new device allows to handle and form freestanding film thus solve all the problems encountered in the devices previously used both in the thesis and in

the literature. Furthermore, this device is able to induce with great simplicity and precision not only purely equibiaxial extensional deformations but many more

Thanks to the experience abroad during the PhD it was possible to improve the spreading process (see *Chapter 6*). Moreover, a new way was found to control the buckling wavelength of a film of graphene sheets at the water-air interface in *Chapter 7*. Finally, a novel first material two-dimensional stretchable material by exploiting the buckling phenomenon from a layer of graphene sheets was obtained using the skills learned during the PhD and the period of training abroad at ETH Zurich. Such results obtained at ETH unfortunately are only preliminary due to the COVID-16 pandemic problems that limited my period spent there. However, those preliminary results appear to be quite promising for achieving further interesting results that I hope to complete in my next steps of future research.

# Acknowledgements

The research presented in this thesis has been carried out at the DICMaPI department of University of Naples – Federico II. The work has been performed between January 2018 and May 2021. Professors Ernesto Di Maio and Pier Luca Maffettone have been the main supervisor.

I would like to thank all of my supervisors for their ideas and support. I would also to thank Biagio Mandracchia, Zhe Wang, Lisa Miccio, Volodymyr Tkachenko for their valuable help with the optical setup. Also I would like to thank for the support Massimiliano Maria Villone.

I would like to express my gratitude to my family for their love and support.