Nanoscopic Terraces, Mesas, and Ridges in Freely Standing Thin Films Sculpted by Supramolecular Oscillatory Surface Forces

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Supporting Information

ABSTRACT: Freely standing thin liquid films containing supramolecular structures including micelles, nanoparticles, polyelectrolyte—surfactant complexes, and smectic liquid crystals undergo drainage via stratification. The layer-by-layer removal of these supramolecular structures manifests as stepwise thinning over time and a coexistence of domains and nanostructures of discretely different thickness. The layering of supramolecular structures in confined thin films contributes additional non-DLVO, supramolecular oscillatory surface forces to disjoining pressure, thus influencing both drainage kinetics and stability of thin films. Understanding and characterizing the spontaneous creation and evolution of nanoscopic topography of stratifying, freely standing thin liquid films have been long-standing challenges due to the absence of experimental techniques with the requisite spatial (thickness <10 nm) and temporal resolution (<1 ms). Using Interferometry Digital Imaging Optical Microscopy (IDIOM) protocols developed herein, we visualize and characterize size, shape, and evolution kinetics of nanoscopic mesas, terraces, and ridges. The exquisite thickness maps created using IDIOM protocols provide much needed and unprecedented insights into the role of supramolecular oscillatory surface forces in driving growth of such nanostructures as well as in controlling properties and stability of freely standing thin films and, more generally, of colloidal dispersions like foams.

KEYWORDS: thin film, imaging, optical microscopy, micelles, surface forces, DLVO theory

Visualization, characterizing, and understanding the spontaneous creation and evolution of nanoscopic topography of freely standing thin liquid films have been long-standing challenges due to the absence of experimental techniques with the requisite spatial (thickness <10 nm) and temporal resolution (<1 ms). In contrast, significant progress in understanding of the structure and stability of supported thin films1−8 (with at least one solid/liquid interface) has occurred through the emergence and advances in several microscopy and force-based experimental techniques1−4 including surface force apparatus (SFA), fluorescence imaging, atomic force microscopy (AFM), total internal reflection microscopy (TIRM), ellipsometry, and electron microscopy. The stability and properties of supported thin films are of critical importance for coatings and thin-film technologies3−6 as well as stability, rheology, and applications of colloidal nanoparticle dispersions.1,9,10 Correspondingly, the forces and flows that drive drainage and rupture of individual freely standing films determine stability and physicochemical properties of soap bubbles, cell membranes, and colloidal dispersions like emulsions and foams with drops or gas pockets, respectively, as the dispersed phase.9,11,12 We show that using a combination of interferometry, digital imaging, and optical microscopy, referred hereafter as IDIOM protocols, provide the requisite spatial-temporal resolution for noninvasively imaging

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and characterizing the evolution of structure, dynamics, and topology of freely standing thin films. Using IDIOM protocols, we visualize distinct geometrical features like terraces, mesas, craters, and ridges, both flat and nonflat nanostructures, within freely standing thin films.

The study of freely standing films or soap films and "soap bubbles, their colors, and the forces that mold them," as well as the their stability and lifetime, has forever fascinated scientists and nonscientists alike.12–17 For films with thickness approaching molecular length scale, intermolecular and surface forces contribute a thickness-dependent excess pressure called disjoining pressure that can counterbalance capillary pressures12,14–17 and counteracting bulk and interfacial stresses, depends upon the physicochemical properties of the amphiphilic molecules that spontaneously adsorb at the liquid/air interface.18–24 Dispersion forces (van der Waals attraction) $\Pi_{vdW}(h)$ and repulsive electrostatic double-layer forces $\Pi_{el}(h)$ together provide a simple and useful estimate for disjoining pressure18–24 and form a basis of the DLVO theory for colloidal stability.18–20 Typically drainage in foam films is characterized by a monotonic decrease in thickness, culminating in formation of common black films (typically $10 < h < 30$ nm) as eventually disjoining pressure and capillary pressure balance each other.12,14–17 However, foam films containing supramolecular structures including micelles, bilayers, nanoparticles, smectic liquid crystals, and polyelectrolytes18–24 undergo stratification, i.e., exhibit stepwise thinning over time, and during drainage, thin films show coexistence of domains and nanostructures of discretely different thickness (see Figure 1). Stratification in these confined fluids is caused by layering of supramolecular structures,19,21,22 which results in additional non-DLVO, supramolecular oscillatory surface force contributions $\Pi_{os}(h)$ to disjoining pressure (see Supporting Information). We show that Interferometry Digital Imaging Optical Microscopy (IDIOM) protocols developed herein provide unprecedented spatial (thickness <10 nm) and temporal resolution (<1 ms) for visualization and analysis of the stratification process and the nanostructures sculpted by supramolecular, non-DLVO forces. The thickness maps provide critical insights into the role of supramolecular oscillatory surface forces in driving growth of such nanostructures as well as in controlling properties and stability of thin films and, more generally, of colloidal dispersions like foams.
thickness variations are produced and advected within these films.12–15 In contrast, the IDIOM protocols described here with use a white light source and rely on the high-quality CMOS or CCD sensors of digital cameras for capturing a pixel-wise, spatially resolved map of reflected light intensity, I(x,y,t) for each wavelength and for each snapshot. Freshly formed foam films illuminated by white light exhibit multicolored iridescent patterns that arise due to interference between light rays reflected from two liquid/gas interfaces and evolve as thickness variations are produced and advected within these films.12–15 Though interference colors are visible for thicker films (h > λ/2π), intensity modulated by interference provides a measure of film thickness even for black films that are only a few molecular-layers thick. Following Scheludko,28 a relatively accurate measure of thickness, h can be obtained by using the following equation based on a normalized measure of intensity, \( \Delta = (I - I_{\text{min}})/(I_{\text{max}} - I_{\text{min}}) \) that minimizes the influence of source intensity and background/detector errors:

\[
\lambda \\
\frac{2\pi n}{2\pi n} \arcsin \left[ \frac{\Delta}{1 + 4R(1 - \Delta)/(1 - R)^2} \right]
\]

(1)

Here \( I_{\text{max}} \) and \( I_{\text{min}} \) correspond to the maximum and minimum values of intensity, and \( R = (n - 1)^2/(n + 1)^2 \), the Fresnel coefficient is computed using the value of refractive index, n of the bulk solution (here \( n = 1.33 \)), which provides us a measure of “equivalent film thickness”. Eq 1 neglects absorption, includes multiple reflections within the film, assumes a near-normal incidence, and considers only zeroth order of interference; valid assumptions for films with thickness \( h < \lambda/2\pi \) (nominally \( h < 100 \, \text{nm} \)).
mesas are attached to the growing domain and are much thicker than the rest of the literature.\textsuperscript{20,21,29,30,35} Anachkov et al.\textsuperscript{29} posited that the change in step size with concentration of micellar solutions can be analyzed to determine micelle size, aggregation number, and charge, and we have verified that IDIOM protocols provide measures comparable to values obtained in spectroscopic and scattering studies.\textsuperscript{27} A simultaneous observation of nanoscopic structures that emerge during stratification shows that the thickness jumps are directly correlated with the lateral motion of thicker or thinner regions into the fixed spot of 20 \( \mu m \) used for intensity and thickness measurement.

Innumerable scientists, including Newton, Hooke, Brewster, Raman, Perrin, Mysels, and deGennes discussed patterns and colors in soap films, including black domains that can spontaneously emerge within soap films drained to nanoscopic thicknesses (\( h < 40 \text{ nm} \)).\textsuperscript{12–15} However, Johonnott (1906) was the first to discuss stratification and employ interferometry to study stratified soap films.\textsuperscript{32} Thereafter, Perrin examined stratified soap films\textsuperscript{30} and included stratification as an evidence for molecular reality, and discontinuous and periodic structure of matter, in his Nobel lecture in 1926. Decades later, stratification was observed and characterized in smectic liquid crystal mesophases\textsuperscript{23,24,37–39} (see Oswald and Pieranski\textsuperscript{23} for a comprehensive review). Interest in stratifying foam films (with no liquid crystalline mesophases present) reemerged due to a series of papers by Nikolov, Wasan, Kralchevsky, and collaborators in the late 1980s.\textsuperscript{22–24} The understanding that ordering induced by confining supramolecular structures like micelles, nanoparticles, and polyelectrolyte–surfactant complexes causes stratification in foam films is fairly recent\textsuperscript{18–22} and most of the studies so far have focused on characterizing thickness evolution and thickness jumps, emulated by data shown in Figure 1. However, the formation and evolution of nanoscopic structures that accompany stratification process have not received sufficient attention, as none of the existing techniques provide suitable spatiotemporal resolution for imaging topography of freely standing films. Using IDIOM protocols, we obtain the first time-resolved visualization of rich and complex topography present in stratifying foam films, and illustrative images and corresponding thickness maps are shown in Figures 2–3 (see video, included as Supporting Information).

Stratification occurs by the formation and expansion of one or more thinner domains that grow at the expense of thicker surrounding films (see Figure 2).\textsuperscript{17–23,31,40,41} As domains expand, they coalesce with each other or with the plateau border (see Figure 2b–e). In some instances, the growing domains appear to be flanked by a brighter halo, inferred to be due to the presence of a ridge or a rim, formed by the accumulation of fluid removed from the growth of thinner domain.\textsuperscript{13,40} Due to a topological instability, ridges sometimes evolve into one or more white spots or mesas (Figure 2d,e,h–j) that have been called lenses, pancakes, droplets, and globules in literature.\textsuperscript{12,17,41} Before the development of IDIOM protocols, no experimental technique possessed temporal and spatial resolution for analyzing such morphological evolution accompanying such topological instabilities and for understanding dynamical processes like nucleation or coalescence of domains or mesas. The IDIOM protocols not only allow access to the shape, size, and growth kinetics of ridges, thinner domains, and mesas but also enable us to probe and address several unanswered questions regarding hydrodynamics of thin freely standing films and the influence of intermolecular and surface forces.\textsuperscript{18–8,17–22,26,27,31}

For example, the asymmetrical shape of ridge formed at the periphery of growing domain in stratifying foam films can be henceforth visualized using IDIOM protocols (see Figure 3). The shape of this ridge is similar to that of rim formed near retracting contact line during dewetting of supported ultrathin polymer films.\textsuperscript{4,7,8,31} Both ridges and mesas are relatively low aspect ratio structures (height in nm, width in microns), and their shape and shape evolution involve interplay of contributions from oscillatory thickness-dependent disjoining pressure and curvature-dependent Laplace pressure. It is well

Figure 3. Nanoscopic structures include ridges, mesas, and terraces visualized and analyzed by the IDIOM protocols. Here the height coordinate is in nm range, while the in-plane coordinate is in 100 \( \mu m \) range, implying mesas and ridges are low-aspect ratio structures. (a) Cross-sectional profile of the foam film shows a ridge or a rim adjacent to the growing thinner domain that is several nanometers thicker than the surrounding film. Inset shows a three-dimensional thickness map wherein domain and flanking rim appear to resemble a crater. (b) Profile of the foam film with 80 mM SDS at \( t = 35.6s \) shows mesa formation, both flat top and nonflat top mesas as well as a terrace are shown. The mesas are attached to the growing domain and are much thicker than the rest of the film.

mM; \( c/\text{CMC} \approx 6 \) in a porous plate cell under a capillary pressure \( P_c \approx 130 \text{ Pa} \), is shown in Figure 1. The height evolution displays several discontinuous jumps or steps, and the height of each step is found to be constant with \( \Delta h = 13.5 \pm 0.3 \text{ nm} \). The step-size (\( \Delta \h \)) (see Figure 1c) decreases with an increase in concentration, and the values extracted from the IDIOM protocol are similar to those reported in the literature.\textsuperscript{20,21,29,30,35} Anachkov et al.\textsuperscript{29} posited that the change in step size with concentration of micellar solutions can be analyzed to determine micelle size, aggregation number, and charge, and we have verified that IDIOM protocols provide measures comparable to values obtained in spectroscopic and scattering studies.\textsuperscript{27} A simultaneous observation of nanoscopic structures that emerge during stratification shows that the thickness jumps are directly correlated with the lateral motion of thicker or thinner regions into the fixed spot of 20 \( \mu m \) used for intensity and thickness measurement.

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established that a disjoining pressure that includes attractive dispersion and an exponentially decaying repulsion contributions modulates flows and fluxes in supported thin films undergoing dewetting,1,4,8 and leads to formation of black spots in soap films.25 Correspondingly, for stratifying micellar foam films, since the disjoining pressure includes a longer-ranged supramolecular oscillatory structural force contribution, stratification occurs, and the intermicellar distance (which sets the step size) corresponds to the periodicity of oscillatory forces (see Figure 1 and Supporting Information). While terraced nanostructures occur also in confined simple fluids (characterized by ellipsometry)7 and smectic liquid crystals,23,24 appearance of mesas, including terraced mesas with flat tops, is a peculiar feature of these stratifying foam films containing micelles. A detailed analysis of shape evolution of rim as well as of mesas is underway, and our investigations suggest that including the supramolecular oscillatory force contributions in driving pressure term in the thin-film equation captures their characteristic growth dynamics.

CONCLUSIONS

In summary, we show that a combination of interferometry, digital imaging, and optical microscopy (or IDIOM protocols) can be used for visualizing and characterizing thickness variation and topological transitions in freely standing thin films with unprecedented spatial (thickness, z-direction <10 nm; in-plane, x−y < 1 μm) and temporal resolution (<1 ms). In this study, we focus on drainage and stratification in micellar foam films formed from aqueous solutions of sodium dodecyl sulfate, with the surfactant present at the fluid/fluid interfaces as well as in bulk as self-assembled supramolecular structures called micelles. Using IDIOM protocols, we visualize and analyze several characteristic features of stratification including discrete changes in thickness, coexistence of regions with different nanoscopic thickness, growth of thinner (darker) domains, and topological transitions that create nonflat structures like ridges and mesas. We believe that the noninvasive imaging and characterization of ridges, mesas, and terraces in freely standing thin films will revolutionize the study of nanoscale rheology and of surface and intermolecular forces, especially the understanding of non-DLVO, supramolecular oscillatory surface forces that underlie stratification. We hope that a widespread use of IDIOM protocols will lead to a better understanding of interactions, flows, and self-assembly in biology, in chemical physics, and in foams and other colloidal systems.

MATERIALS AND METHODS

Materials: Aqueous Solutions of Sodium Dodecyl Sulfate. An anionic surfactant sodium dodecyl sulfate or SDS (molecular weight of 288 Da, Sigma-Aldrich Co., St. Louis, MO, L6026, >99.0%) is used as-received without further purification to prepare aqueous solutions with deionized water (with resistivity of 18.2 MΩ). Horizontal foam films formed with aqueous SDS solution, with concentrations both below and above the critical micelle concentration (CMC) (literature values range between 7 and 10 mM at 25 °C).16 It is well-known that the presence of impurities or the presence of trace amounts of 1-dodecanol affect micellization, surface tension, and interfacial rheology.13,44 The concentration-dependent surface tension of aqueous SDS solutions measured using a maximum bubble pressure tensiometer shows a smooth transition near a CMC value of c = 8.2 mM, indicating that the as-made solutions are relatively free of impurities.55,44 No electrolytes are added to the solution, for it is well-known that high ionic content leads to suppression of the stratification phenomena.26

Thin-Film Apparatus and Imaging Systems. Drainage and stratification experiments in horizontal foam films were carried out in two types of geometries: (a) a porous plate cell (see Figure 1a) and (b) a Scheludko-like cell (see schematic in Zhang and Sharma).31 In both cases, a circular thin film with nearly plane-parallel interfaces is formed at the center of a closed cylindrical cell, and a syringe pump is used for controlling the fluid. In analogy with horizontal films within real foams, the thin film formed within the cell is always in contact with a thicker meniscus region (referred to as plateau border). To make a meaningful comparison between solutions with different surfactant and micellar concentration, we conducted experiments on films that are nearly plane-parallel and of similar initial size. The cell is placed within a closed container to minimize the effect of evaporation. The porous plate cell with hole diameter d_p = 1.0 mm was made from a porous glass frit with pore sizes in the range of 10−15 μm. The cell geometry and the mean pore size determine the attainable capillary pressure, which is in the range from 50−4000 Pa. In the Scheludko-like cell of internal diameter d_i = 1.6 mm, liquid is slowly withdrawn from the biconvex drop to create the desired film diameter (d_f ≈ 0.6 mm). The fluid volume is then maintained constant throughout the initial drainage process, and fluid withdrawal using the side arm induces latter transitions. Assuming perfect wetting of the inner wall of the cell holder and a small contact angle between the film and the border region, the capillary pressure in the Scheludko-type cell can be estimated by

\[ P = \frac{\gamma \cos \theta}{d_i - d_f} \]

Here γ is the surface tension of the solution (γ ≈ 36 mN/m for SDS solutions above CMC, measured using a maximum bubble pressure tensiometer designed within the laboratory), d_i and d_f are the inner diameter of the cell and the diameter of the thin film, respectively. The typical initial capillary pressure in experiments with Scheludko cells used in this study is P ≈ 50 Pa. Since the disjoining pressure becomes large at small thicknesses (as shown in Figure 1d and Figure S2a in the Supporting Information), the relatively small capillary pressure in Scheludko-like cell is not sufficient to induce further stepwise thinning, so fluid is withdrawal using the side arm to induce latter transitions. In an alternative protocol29,46 emulated for comparison, the cell container is opened briefly to allow evaporation, which results in an increase in the capillary pressure and consequently in a step transition. The high-resolution video and images of the stratification process are captured by an imaging system that consists of a high resolution, high-speed camera (Photron FASTCAM, Mini UX100) and a precision microscope lens system (Navitar Zoom 600, with added microscope objective). The IDIOM method can be realized with a variety of light sources and cameras including commercial grade digital-SLR cameras and light sources (see Supporting Information for detailed discussion). The images are postprocessed in MATLAB R2014a with specially written codes, and the “equivalent film thickness”26,3 is determined by using eq 1 and the reflected light intensity values for red, green, and blue (or R, G, B) channels, respectively.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.6b01012.

Experimental details and data (PDF)

Video of the stratification process (AVI)

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Notes

The authors declare no competing financial interest.
REFERENCES