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# Capillary deformation of ultrathin glassy polymer films by air nanobubbles

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## Abstract

Confined glasses and their anomalous interfacial rheology raise important questions in fundamental research and numerous practical applications. In this work, we study the influence of interfacial air nanobubbles on the free surface of ultrathin high-molecular-weight glassy polystyrene films immersed in water, in ambient conditions. In particular, we reveal the counterintuitive fact that a soft nanobubble is able to deform the surface of a rigid glass, forming a nanocrater with a depth that increases with time. By combining *in situ* atomic-force-microscopy measurements and a modified lubrication model for the liquid-like layer at the free surface of the glass, we demonstrate that the capillary pressure in the nanobubble together with the liquid-like layer at the free surface of the glass determine the spatiotemporal growth of the nanocraters. Finally, from the excellent agreement between the experimental profiles and the numerical solutions of the governing glassy thin-film equation, we are able to precisely extract the surface mobility of the glass. In addition to revealing and quantifying how surface nanobubbles deform immersed glasses, until the latter eventually dewet from their substrates, our work provides a novel, precise, and simple measurement of the surface nanorheology of glasses.

## I. INTRODUCTION

The glass transition has been being a major enigma in solid-state physics [1] for almost a century, leading to an important literature for the bulk case [2]. Besides an hypothetical underlying phase transition, the tremendous dynamical slowing down of glass-forming supercooled liquids has been attributed to molecular caging, and the associated requirement for cooperative relaxation [3] in a region of a certain cooperative size [4].

The quest for the latter observable, and its possible divergence, led to an alternative strategy: the study of glasses in confinement [5–7]. In the particular case of thin polymer films, anomalies have been reported, such as reductions of the apparent glass-transition temperature  $T_g$  at small film thicknesses [8, 9], where the presence of free surfaces played an important role [10]. Furthermore, space-dependent  $T_g$  values were inferred from local measurements [11]. Besides, the free surface of a polymer glass was discovered to be much more mobile than the bulk, which was attributed to the existence of a nanometric liquid-like superficial layer capable to flow under external constraints [12–17], or equivalently for small enough molecules to undergo surface diffusion [18–20] as in crystals [21], which could even lead to striking engulfment phenomena [22]. The previous Stokes-Einstein-like equivalence between surface flow and surface diffusion in the mobile layer was shown to be eventually broken for long-enough surface polymer chains due to their anchoring into the bulk matrix [23], and ultimately the commensurability of their typical size with the sample thickness itself [24, 25]. Finally, among other interesting properties, spatial heterogeneities were associated with the dynamics of thin glassy polymer films [26]. To rationalize these observations, various numerical approaches [27, 28] and theoretical models [29–34] have been proposed, but a unifying picture is still at large.

In this work, we study the influence of air nanobubbles spontaneously-created at the free surface of ultrathin high-molecular-weight glassy polystyrene (PS) films when immersed in water, and in ambient conditions [35, 36]. In contrast to the bubble-inflation technique used for freestanding viscoelastic membranes [37], there is here no need for an externally-driven inflation, and the glassy films are supported onto rigid silicon wafers and thus much less compliant. The nanobubbles are gaseous air domains with nanometric height and width. As a consequence of these small sizes, and from the Young-Laplace equation, the pressure inside the bubble can reach up to  $\sim 10$  bar, which – despite being much smaller than the yield stress

of the bulk glass – can lead to an external driving force for the flow of the liquid-like layer at the free surface of the glass. Consequently, a nanoscopic crater is formed underneath the bubble, and grows in size with time, as observed using an atomic-force microscope (AFM). The latter observations are discussed in the context of a modified lubrication model for the capillary-driven flow of the liquid-like layer at the free surface of the glassy film, under an external driving force. The excellent agreement between the experimental AFM profiles and the numerical solutions of the axisymmetric glassy thin-film equation yields a novel, precise, and simple measurement of the surface mobility of glasses. The value found for the latter is compared to values in the literature, and discussed in terms of polymer entanglements and anchoring effects in confinement. Finally, the model predicts a dewetting scenario for ultrathin polymer films, which might have important practical consequences.

## II. EXPERIMENTAL

A schematic representation of the bubble-PS film interaction is shown in Fig. 1, where we define the bubble’s contact diameter  $L$ , the bubble’s radius of curvature  $r_b$ , the equilibrium contact angle  $\theta$ , and the initial PS film thickness  $h_0$ . Note that  $L$ ,  $r_b$ , and  $\theta$  are related through volume conservation. According to the Young-Laplace equation, the pressure inside the bubble reads  $p_b = p_{\text{am}} + 2\gamma_{\text{lv}}/r_b$ , where  $\gamma_{\text{lv}}$  is the water-air surface tension, and  $p_{\text{am}}$  is the ambient water pressure. In the following, we will quantify how the capillary pressure gradient can lead to the deformation of the glassy PS film, and to the spatiotemporal evolution of the PS nanocrater. The latter is characterized by its depth  $h_{\text{dep}}$  and rim height  $h_{\text{rim}}$ .

Ultrathin PS films with three different thicknesses  $h_0 \in \{2.8 \pm 0.6, 4.9 \pm 0.6, 7.1 \pm 0.8\}$  nm were prepared by spincoating a solution of PS (Sigma-Aldrich) in toluene onto a silicon wafer, at different toluene mass fractions  $\{0.07, 0.10, 0.08\}$  wt% and rotational speeds of  $\{1200, 1200, 1000\}$  rpm, respectively. The thicknesses of the PS films were measured by a scratching method [38]. The molecular weight of PS is about 350 kg/mol. After spincoating, the PS films were baked inside an oven at a temperature of 45°C for 4 h, in order to evaporate the remaining toluene. Here, we applied the temperature-exchange method to generate nanobubbles: cold deionized (DI) water at about 4°C was deposited on the PS films at about 30°C by a glass syringe. Upon immersion, nanobubbles were spontaneously nucleated.

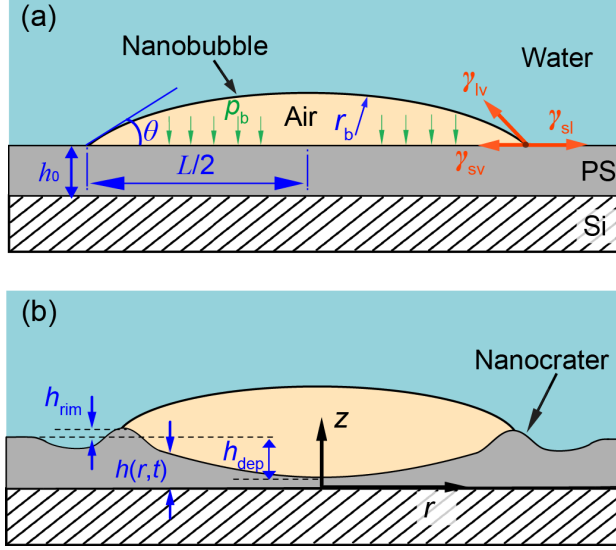


FIG. 1. Schematic of the bubble-PS film interaction. (a) An air nanobubble spontaneously forms at the PS-water interface right after immersion of the glassy PS sample in water. (b) Subsequently, a nanocrater appears beneath the nanobubble, and grows with time, as the liquid-like layers at both PS-fluid interfaces flow due to the capillary pressure gradient.

An AFM (Resolve, Bruker, USA) in tapping mode was used to image the samples both in air and water. A silicon NSC36/Al BS cantilever (MikroMasch) with a tip radius  $< 8$  nm and a quoted stiffness of 1.0 N/m was used. The measured resonance frequencies of the cantilever in air and water were about 76 kHz and 23 kHz, respectively. To minimize the force applied on the nanobubbles and sample surfaces, the setpoint for imaging was set to be only 95%-97% of the free amplitude. While imaging in air and water, the resonance frequency was selected as the driving frequency. The samples were scanned at a rate of 1.5 Hz with a scan angle of  $0^\circ$ .

### III. RESULTS AND DISCUSSION

Figure 2a shows a typical AFM image of the PS film in air with a thickness  $h_0 = 4.9 \pm 0.6$  nm. The root-mean-squared roughness is about 0.22 nm. After immersion in deionized (DI) water at room temperature, nanobubbles with diameters ranging from 30 to 100 nm spontaneously nucleated (Fig. 2b) at the PS-water interface [39]. The PS sample was kept in water for  $t_b \approx 240$  min, before the water was removed and the sample surface was dried

in air for  $t - t_b \approx 250$  min. The same area of the sample was then scanned again with the AFM, as shown in Fig. 2c. One observes the existence of nanocraters into the PS film. These nanocraters were generated at the exact same locations where the nanobubbles resided, when the sample was immersed in water (see also Fig. 4 in Appendix A for details).

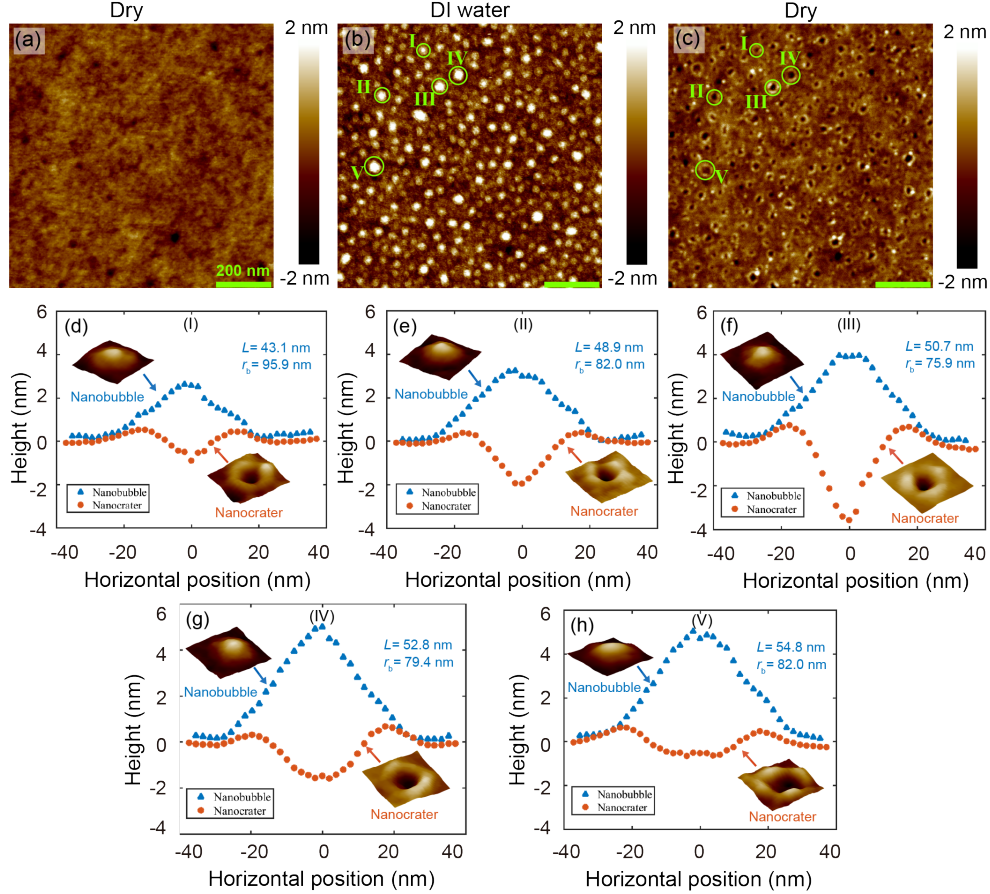


FIG. 2. Typical AFM images of an ultrathin glassy PS film with thickness  $h_0 = 4.9 \pm 0.6$  nm in various situations: (a) before immersion in water; (b) after immersion in water, where nanobubbles (white) with an average contact diameter of 50 nm appear on top of it; (c) after immersion in water for  $t_b \approx 240$  min, and subsequent removal of water followed by drying in air during  $t - t_b \approx 250$  min. (d-h) Five cross-sectional profiles of nanobubble-nanocrater couples (sorted by increasing  $L$  values):  $L = 43.1$  nm and  $r_b = 95.9$  nm (d, couple I);  $L = 48.9$  nm and  $r_b = 82.0$  nm (e, couple II);  $L = 50.7$  nm and  $r_b = 75.9$  nm (f, couple III);  $L = 52.8$  nm and  $r_b = 79.4$  nm (g, couple IV);  $L = 54.8$  nm and  $r_b = 82.0$  nm (h, couple V). The insets in each of those five panels are the 3D AFM images of the nanobubbles and the corresponding nanocraters.

The cross-sectional profiles for five different nanobubbles and their associated nanocraters

(sorted by increasing nanobubble size) are shown in Figs. 2d-h. Interestingly, these profiles qualitatively resemble the ones obtained on low-molecular-weight PS after embedding and subsequent removal of gold nanoparticles [12]. Moreover, it is clear that the lateral sizes of the nanocraters are approximately equal to the sizes of the nanobubbles – a commensurability valid for all samples in this study (see Fig. 5 in Appendix B). Nanobubbles with contact diameters  $L \leq 50$  nm typically generate steeper nanocraters, and  $h_{\text{dep}}$  increases with  $L$  for those. (Figs. 2d-f). When the contact diameter  $L$  is larger than 50 nm, the nanocraters are not as curved. Larger bubbles generate shallower craters with decreased  $h_{\text{dep}}$  and  $h_{\text{rim}}$  (Figs. 2g-h). With further increased  $L$ , nanocraters with nearly-flat bottoms are even created (see also Fig. 4 in Appendix A for details).

To rationalize these observations, we invoke a theoretical model that combines two ingredients: i) the existence of a liquid-like layer with viscosity  $\eta$  and thickness  $h_m$  of a few nanometers at the free surface (*i.e.* exposed to any fluid) of the glassy PS film [12, 14]; and ii) a lubrication flow in this liquid-like layer [15], driven by the pressure jump between  $p_b$  and  $p_{\text{am}}$  at the contact line where the three phases intersect, and opposed by the restoring capillary force due to the induced curvature at the PS-fluid interfaces. We note that the PS films employed in this work have thicknesses of a few nanometers only, which are: i) comparable to the typical thickness of the liquid-like layer [7]; and ii) much smaller than the radius of gyration of 350 kg/mol PS (tens of nanometers). Therefore, the PS chains are mostly located in the liquid-like layer, they are expected to exhibit a reduced entanglement density compared to the one in thicker films [40–43], and we expect no major anchoring effect [23]. Since the liquid-like layer thickness  $h_m$  is much smaller than the typical horizontal size  $L$ , the viscous flow in the layer can be described by lubrication theory [44], where the velocity is predominantly in the radial direction, the pressure is constant across the thickness of the liquid-like layer [45–47], and the viscous forces therein are balanced by the tangential pressure gradient discussed above. As the stresses remain relatively low compared to usual yield stresses and piezo-viscous thresholds for polymers glasses and melts, the viscosity  $\eta$  is assumed to be a constant.

In general, the stress and deformation fields associated to one bubble could be affected by the neighbouring bubbles. In a recent study involving two micro-sized droplets on a polymer film [48] (see also Fig. 6 in Appendix C), it is indeed found that the effective interaction between the two microdroplets is strongly influenced by their distance  $d$ , contact diameter



$L$ , and the film thickness  $h_0$ . When  $d > L/2$  or  $d \gg h_0$ , the two-body interaction mediated by the film vanishes. In the present work, the average value of  $d$  is around 50 nm,  $L$  is in between 20 nm and 45 nm, and  $h_0$  is less than 8 nm. It is thus clear that  $d$  is much bigger than  $L/2$  and  $h_0$ . Therefore, we neglect the influence of neighbouring bubbles in the model.

We define  $h(r, t)$  as the total thickness profile of the PS film (see Fig. 1), assumed to be axisymmetric given the symmetry of the nanobubble, where  $r$  is the horizontal radial spatial coordinate, and  $t$  is time. We further assume small slopes for the PS-fluid interfaces, as well as a no-slip boundary condition at the bottom of the mobile layer, located at  $z = h(r, t) - h_m$ , and a no-shear boundary condition at the PS-fluid interfaces, located at  $z = h(r, t)$ . All together, this leads to the axisymmetric version of the glassy thin-film equation [15], with a novel source term due to the presence of the nanobubble:

$$\frac{\partial h(r, t)}{\partial t} + \frac{h_m^3}{3\eta r} \frac{\partial}{\partial r} \left\{ r \frac{\partial}{\partial r} \left[ \frac{\gamma_i(r)}{r} \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} h(r, t) \right) - p_i(r) \right] \right\} = 0, \quad (1)$$

where the surface energy  $\gamma_i(r)$  indicates  $\gamma_{SL}$  (PS-water) for  $r \geq L/2$  and  $t < t_b$ , as well as  $\gamma_{SV}$  for either  $t > t_b$ , or  $t < t_b$  and  $r < L/2$ ; while the external pressure  $p_i(r)$  indicates  $p_b$  for  $r \leq L/2$  and  $t < t_b$ , as well as  $p_{am}$  for either  $t > t_b$ , or  $t < t_b$  and  $r > L/2$ . Due to the constant liquid-like layer thickness  $h_m$ , the equation is linear, and formally resembles the capillary-driven thin-film equation for bulk flow under perturbative profile variations [46, 49]. Just before the formation of the nanobubble (assumed to be instantaneous), the PS film has a uniform thickness  $h(r, t = 0) = h_0$ , which we use as an initial condition.

We now nondimensionalize Eq. (1) by rescaling the variables through  $h = H h_0$ ,  $r = R L/2$ ,  $t = T 3\eta L^4 / (16\gamma_{SV} h_m^3)$ , and  $t_b = T_b 3\eta L^4 / (16\gamma_{SV} h_m^3)$ , which leads to the dimensionless form of Eq. (1):

$$\frac{\partial H(R, T)}{\partial T} + \frac{1}{R} \frac{\partial}{\partial R} \left\{ R \frac{\partial}{\partial R} \left[ \frac{1 - \alpha(T)\Theta(R-1)}{R} \frac{\partial}{\partial R} \left( R \frac{\partial}{\partial R} H(R, T) \right) - \beta(T)\Theta(1-R) \right] \right\} = 0, \quad (2)$$

where  $\Theta$  is the Heaviside function,  $\alpha(T) = (\gamma_{SV} - \gamma_{SL})\Theta(T_b - T)/\gamma_{SV}$  and  $\beta(T) = L^2\gamma_{LV}\Theta(T_b - T)/(2h_0r_b\gamma_{SV})$ . We solve Eq. (2) numerically from the initial condition  $H(R, T = 0) = 1$ , by using a finite-element method where the equation is divided into two coupled second-order partial differential equations involving two fields [50]: the height  $H(R, T)$  and the total pressure  $P(R, T) = \frac{\alpha(T)\Theta(R-1)-1}{R} \frac{\partial}{\partial R} [R \frac{\partial}{\partial R} H(R, T)] + \beta(T)\Theta(1-R)$ . The fields are discretized with linear elements, and the coupled equations are solved with a Newton solver from the FEniCS library [51]. The numerical routine is performed with a

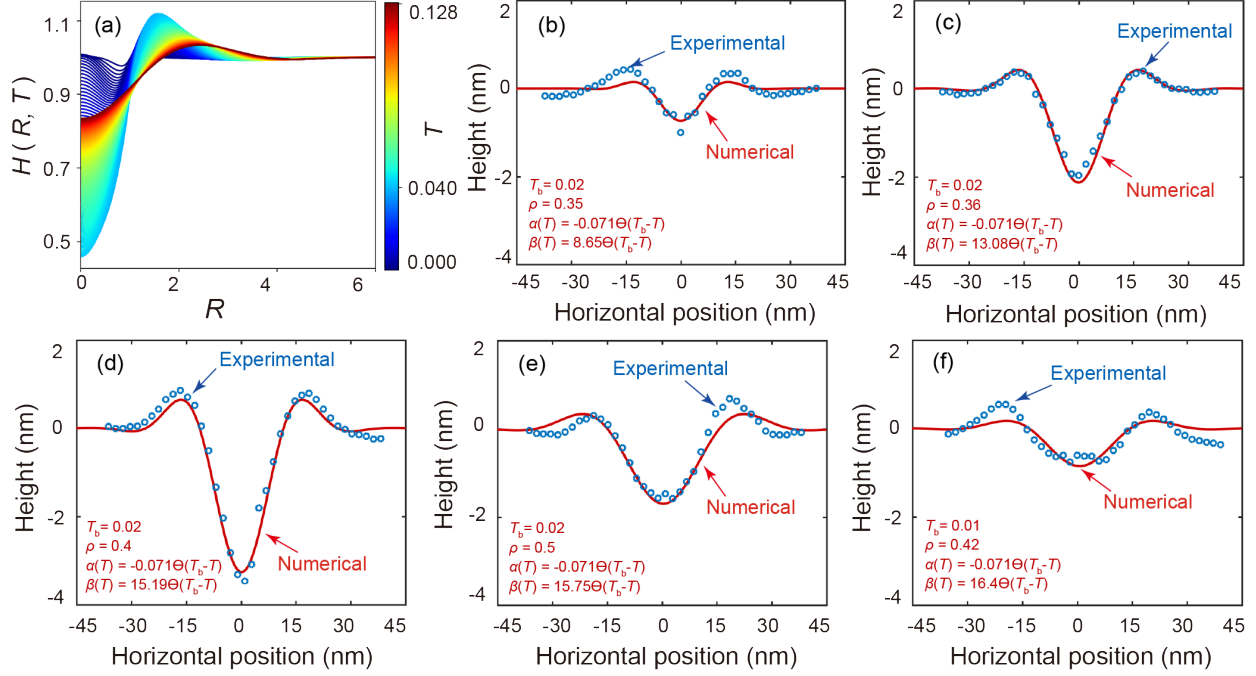


FIG. 3. Deformation of the PS film: (a) Numerical solution of Eq. (2) over a time interval  $T \in [0, 0.128]$ , for  $T_b = 0.01$ ,  $\alpha(T) = -0.071\Theta(T_b - T)$ , and  $\beta(T) = 5\Theta(T_b - T)$ . (b-f) Cross-sectional AFM profiles (blue circular markers) in air for the five selected nanocraters in Figs. 2d-h, and corresponding best fit (red solid curves) to the numerical solution with  $T_b = 0.02$ ,  $\rho = 0.35$ ,  $\alpha(T) = -0.071\Theta(T_b - T)$ , and  $\beta(T) = 8.65\Theta(T_b - T)$  (b);  $T_b = 0.02$ ,  $\rho = 0.36$ ,  $\alpha(T) = -0.071\Theta(T_b - T)$ , and  $\beta(T) = 13.08\Theta(T_b - T)$  (c);  $T_b = 0.02$ ,  $\rho = 0.4$ ,  $\alpha(T) = -0.071\Theta(T_b - T)$ , and  $\beta(T) = 15.19\Theta(T_b - T)$  (d);  $T_b = 0.02$ ,  $\rho = 0.5$ ,  $\alpha(T) = -0.071\Theta(T_b - T)$ , and  $\beta(T) = 15.75\Theta(T_b - T)$  (e);  $T_b = 0.01$ ,  $\rho = 0.42$ ,  $\alpha(T) = -0.071\Theta(T_b - T)$ , and  $\beta(T) = 16.4\Theta(T_b - T)$  (f). Note that the horizontal and vertical origins are arbitrarily shifted.

constant time step  $\Delta T = 5 \cdot 10^{-4}$  and a uniform spatial discretization step  $\Delta R = 5 \cdot 10^{-4}$ . Finally, as spatial boundary conditions at  $R = 0$ , we set the first-order derivatives of the two fields to be zero due to symmetry. Besides, we choose the size of the numerical domain such that no dynamics occurs at the large- $R$  boundary, and we thus impose the first-order derivatives to be equal to zero too at this boundary.

Figure 3a shows an example of a numerical solution of Eq. (2). It includes two subsequent steps. The first one (corresponding to the dimensionless  $T$  from 0 to 0.04) is the nanocrater growth process with a nanobubble on top of the nanocrater. During the process, both the dimensionless depth  $h_{\text{dep}}/h_0$  of the nanocrater and the dimensionless height  $h_{\text{rim}}/h_0$  of the

rim increase monotonically with dimensionless time. The second step (corresponding to the dimensionless  $T$  from 0.04 to 0.128) is the partial recovery of the nanocrater after the nanobubble is removed. The depth and height decrease monotonically with time. As the fluid in the liquid-like layer gets displaced, we also observe a continuous lateral shift in the dimensionless horizontal position of the rim.

In Figs. 3b-f, we fit the numerical solutions to the experimental profiles, for five nanocraters created by the five selected nanobubbles (shown in Figs. 2d-h) of increasing contact diameters  $L$  from b to f. To do so, we first put back dimensions in the numerical solutions, by using the experimental parameters:  $t - t_b = 250$  min,  $\gamma_{SV} = 40.7$  mN/m,  $\gamma_{LV} = 72.8$  mN/m, and  $h_0 = 4.9 \pm 0.6$  nm, as well as the values of  $t_b$ ,  $L$  and  $r_b$  for each nanobubble. As we determine the geometric parameters from a single snapshot of the nanobubble profile, which is not perfectly symmetric, there is some uncertainty in the obtained values. To account for this uncertainty, we multiply  $L$  and  $r_b$  by a dimensionless free parameter  $\rho$ . For all experiments in this study, the value of the latter is found to be in the 0.3 – 0.5 range, which is reasonably close to 1 and thus acceptable. We observe that the numerical solutions show a good agreement with experimental cross-sectional profiles for all five exemplary nanocraters. The depth  $h_{\text{dep}}$  of the nanocraters first increases and then decreases with increasing  $L$ . Interestingly, we find that it is actually  $r_b$  that determines  $h_{\text{dep}}$ . With increasing  $L$ ,  $r_b$  first decreases from 95.9 nm (bubble I) to 75.9 nm (bubble III). Then it increases from 75.9 nm (bubble III) to 82.0 nm (bubble V). The smaller  $r_b$  leads to the larger deformation in the PS film, *i.e.* the larger magnitudes of the rim height  $h_{\text{rim}}$  and crater depth  $h_{\text{dep}}$ . This is expected due to the Laplace pressure of the nanobubbles, that scales as  $\sim 1/r_b$ , and that drives the deformation of the PS layer.

From the fitting procedure detailed above, we extract a single relevant free parameter: the surface mobility  $h_m^3/(3\eta) = 2.31_{-1.92}^{+1.73} \times 10^{-10}$  nm<sup>3</sup>/(Pa.s) of 350 kg/mol PS at room temperature. Regardless of the total PS film thickness, and the nanobubble geometry, the different experiments self-consistently exhibit the same value of surface mobility. Previously, the surface mobility of glassy PS was investigated around  $T_g$  for a range of molecular weights [14, 15, 52]. Interestingly, the extrapolation to room temperature of the Arrhenius-like trends in these works would lead to a surface mobility over one order of magnitude lower than the one reported here. This brings two possible non-exclusive scenarios: i) a saturation of the surface mobility at low temperature; ii) a reduction of the entanglement density, and

thus viscosity, in strong confinement. Indeed, while it is known that in the near- $T_g$  region the surface mobility exhibits an Arrhenius-like dependence in the temperature, which is characteristic of a liquid-like behavior [15, 52], the mobility saturates at lower temperatures [12]. Regarding the entanglement density, it is found that polymer molecules at interfaces are less entangled than their bulk counterparts [41–43]. The entanglement density collapses rapidly when the film thickness becomes lower than the end-to-end distance of the polymer chains [40, 53]. This further implies a reduction in viscosity [54–56]. For these reasons, since the PS films used here are colder and thinner than in studies from the literature, one could expect a much higher mobility compared to Arrhenius-like extrapolations of the literature results.

Finally, we stress that the PS deformation profiles are transient, and that they in fact will continue to evolve with increasing time (see Fig. 3a), although very slowly. Moreover, a careful mathematical analysis of Eq. (1) reveals the absence of any relevant stationary state, which implies a dramatic consequence: due to the existence of a liquid-like surface layer, and provided the films are thin enough (*i.e.*  $h_0$  close to  $h_m$ ) to avoid anchoring effects at large molecular weights [23], the presence of surface nanobubbles should eventually lead to the dewetting of any ultrathin glassy PS film [57, 58]. The critical time for dewetting is solely controlled by the parameters  $\theta$ ,  $\gamma_{SV}$ ,  $\gamma_{LV}$ ,  $h_0$ , and  $L$  (or  $r_b$ , due to volume conservation) above, as well as the surface mobility  $h_m^3/(3\eta)$ .

#### IV. CONCLUSION

As a conclusion, we have shown that immersing ultrathin glassy polystyrene films in water, in ambient conditions, leads to the spontaneous nucleation of air nanobubbles, which then generate nanocraters into the free surface of the PS films. The mechanism of such a dynamical deformation process is found by combining experimental atomic-force microscopy with a mathematical model based on lubrication theory applied to the liquid-like layer present at the free surface of a glassy film. The liquid-like layer is driven to flow by the pressure jump at the contact line where the three phases intersect, between the nanobubble’s inner Laplace pressure and the outer ambient pressure, and opposed by the capillary force due to the induced curvature at the PS-fluid interfaces. Since the Laplace pressure scales as the inverse of the bubble’s radius of curvature, the size of the nanocraters can be

finely controlled. From the excellent agreement between the experimental profiles and the numerical solutions of the modified glassy thin-film equation, we extract the surface mobility of the glassy films. Comparison of the surface mobility with extrapolated results from the literature points towards the possible saturation of surface mobility at low temperature, and/or the reduction of polymeric entanglement density (and thus viscosity) in confinement. All together, our work provides a novel, precise, and simple measurement of the surface nanorheology of glasses. Furthermore, our results highlight the influence of surface nanobubbles on the stability of immersed ultrathin glassy polymer films: the nanobubbles can drive the film towards dewetting, which would have important consequences for nanoimprint lithography [59] and nanomechanical data storage [60], to name a few.

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## APPENDIX A: NANOBUBBLE-NANOCRATER CORRELATION

Figure 4a shows an atomic-force microscope (AFM) image of nanobubbles on the surface of an ultrathin polystyrene (PS) glassy film in deionized (DI) water. After water was removed, the AFM image of the exact same scanning area is shown in Fig. 4d. From the figure, one can see that the sample surface is covered with nanocraters. To demonstrate that those nanocraters were indeed produced at the exact same locations as the nanobubbles, the AFM images of nanobubbles and nanocraters were segmented, as shown in Figs. 4b and 4e, respectively. The obtained binary images of nanobubbles and nanocraters are shown in Figs. 4c and 4f. The overlapped image (Fig. 4g) from the two binary images indicates that the nanocraters were generated at the exact same locations as the nanobubbles.

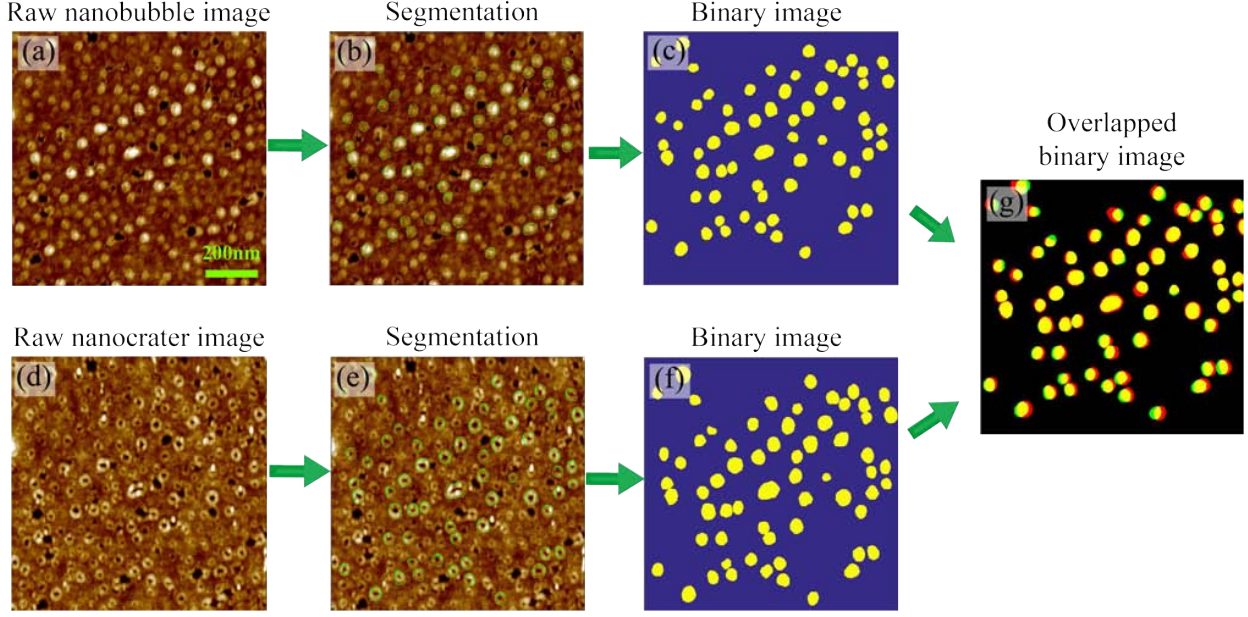


FIG. 4. (a) Raw AFM image of nanobubbles at the surface of an ultrathin glassy PS film in deionized (DI) water. (b) Segmentation of the nanobubble image. The green contours are extracted nanobubble boundaries. (c) The resulting binary image. The yellow masks are extracted nanobubble areas. (d) Raw AFM image of nanocraters at the exact same scanning area as in (a). (e) Segmented nanocrater image. (f) Resulting binary image of the segmented nanocrater image. The yellow masks are extracted nanocrater areas. (g) Superposition of the two binary images.

## APPENDIX B: NANOCRATER FORMATION ON SAMPLES WITH DIFFERENT THICKNESSES

Three PS films of different thicknesses were used. Figures 5a, d, and g are AFM images in air of the three PS films with thicknesses of  $2.8 \pm 0.6$  nm,  $4.9 \pm 0.6$  nm, and  $7.1 \pm 0.8$  nm, respectively. After immersion in DI water, the obtained AFM images are shown in Figs. 5b, e, and h. One can see that nanobubbles with different sizes were produced on the surface of the PS samples. After DI water was removed (Figs. 5c, f, and i), nanocraters were observed on the surface of the PS samples. The sizes of the nanocraters are highly correlated with those of the nanobubbles. Larger nanobubbles lead to nanocraters with larger lateral widths.

For the sample with a thickness of 2.8 nm, one could observe pre-existed holes. However, we believe that these holes are not due to the dewetting of the sample at room temperature



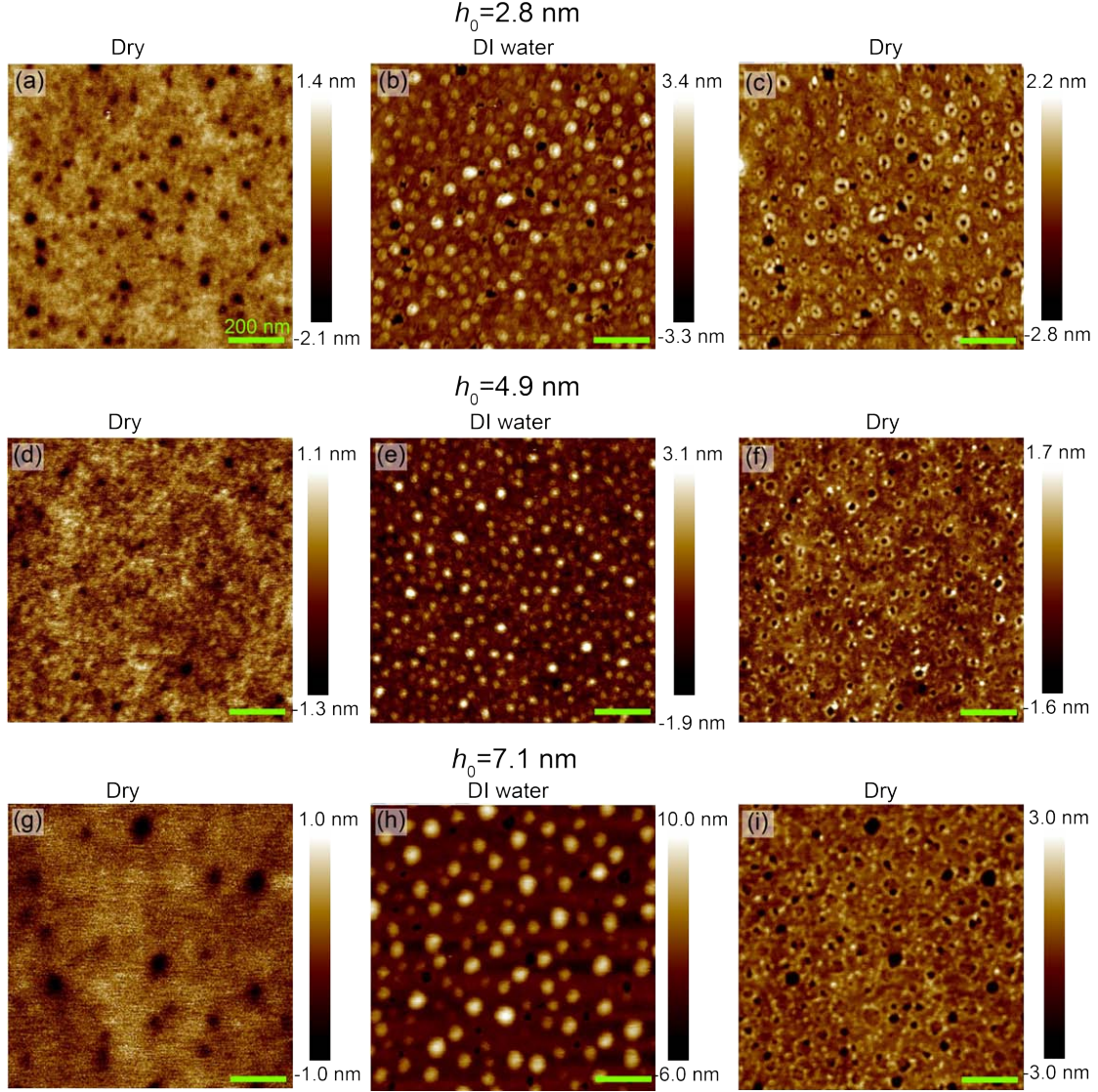


FIG. 5. (a) AFM image of the PS film with a thickness of 2.8 nm, obtained in air. (b) AFM image of the nanobubbles nucleated in the same scanning area as in (a), after immersion in DI water. (c) AFM image of the nanobubble-induced nanocraters, after DI water was removed. (d) AFM image of the PS film with a thickness of 4.9 nm, obtained in air. (e) AFM image of the nanobubbles nucleated in the same scanning area as in (d), after immersion in DI water. (f) AFM image of the nanobubble-induced nanocraters, after DI water was removed. (g) AFM image of the PS film with a thickness of 7.1 nm, obtained in air. (h) AFM image of the nanobubbles nucleated in the same scanning area as in (g), after immersion in DI water. (i) AFM image of the nanobubble-induced nanocraters, after DI water was removed.

(which would then impact the nanocrater dynamics), based on the following fact. If the film was close to dewetting, one would expect more holes to appear and grow with time. Figure 5 clearly shows that the number, locations, as well as sizes of the pre-existed holes do not change before and after water immersion. This clearly indicates that the surface of the solid-liquid interface is stable during the experiment, besides the nanocrater dynamics at stake. It is highly possible that the pre-existed holes were generated during the sample-preparation process, through the thermal-annealing step in particular.

### APPENDIX C: INFLUENCE OF NEIGHBOURING NANOBUBBLES

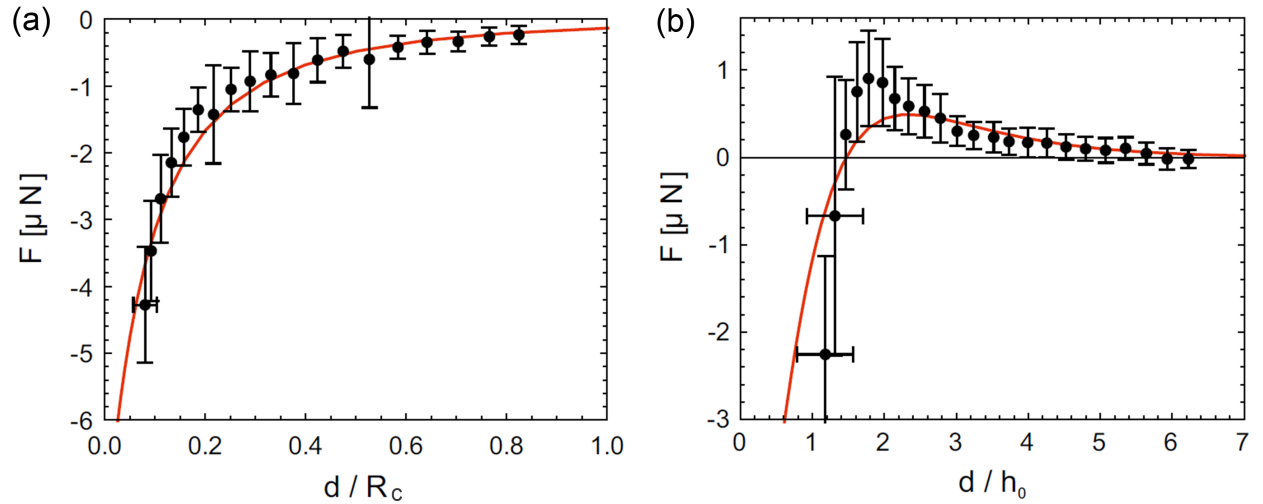


FIG. 6. Reproduction of Fig. 2 from Ref. [48]. (a) Interaction force (dots: measurements; line: model)  $F$  between two neighbouring droplets as a function of the ratio between their separation distance  $d$  and the contact radius  $R_c$ . (b) Interaction force (dots: measurements; line: model)  $F$  between two neighbouring droplets as a function of the ratio between their separation distance  $d$  and the substrate's thickness  $h_0$ .

For a given nanocrater, it is *a priori* possible that the stress and deformation fields are influenced by neighbouring nanobubbles. The influence from neighbouring nanobubbles depends on the following geometrical parameters: the distance  $d$  between the bubbles, the contact radius  $R_c = L/2$ , and the substrate's thickness  $h_0$ . When  $d \gg R_c$  or  $d \gg h_0$ , we expect the effects from neighbouring bubbles to vanish, which was verified in microdroplet experiments [48] (see also Fig. 6). According to the latter, when  $d/R_c$  becomes comparable



to or less than 1, and for large enough  $h_0$ , there is an attractive force  $F$  between the two droplets (see Fig. 6a). Besides, when  $d/h_0$  gets sufficiently larger than 1, the force becomes repulsive (see Fig. 6b).

In the present work, the distance  $d$  between two neighbouring nanobubbles is around 50 nm. The contact radii of the nanobubbles are in between 20 nm and 45 nm. The initial thicknesses of the three different ultrathin PS films are  $h_0 = 2.8 \pm 0.6$ ,  $4.9 \pm 0.6$ , and  $7.1 \pm 0.8$  nm. Therefore,  $d/R_c > 1$  and  $d/h_0 \gg 1$ , such that the influence of neighbouring nanobubbles can be safely neglected in our study (see Fig. 6).

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