Viscous Bursting of Suspended Films

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Soap films break up by an inertial process. We present here the first observations on freely suspended films of long-chain polymers, where viscous effects are dominant and no surfactant is present. A hole is nucleated at time 0 and grows up to a radius $R(t)$ at time t. A surprising feature is that the liquid from the hole is not collected into a rim (as it is in soap films): The liquid spreads out without any significant change of the film thickness. The radius $R(t)$ grows *exponentially* with time, $R \propto \exp(t/\tau)$ [while in soap films $R(t)$ is linear]. The rise time $\tau \propto \eta e/2\gamma$ where η is viscosity, e is thickness (in the micron range), and γ is surface tension. A simple model is developed to explain this growth law.

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The rupture of soap films has been studied for more than a century. When the film is punctured, a hole grows at constant velocity $V = dR/dt$, surrounded by a rim collecting the liquid [1–4], whereas the film outside the rim remains undisturbed. The kinetics is entirely driven by *inertia*. The basic formula for V can be obtained from

$$\frac{dP}{dt} = V\frac{dM}{dt} = 2\gamma, \tag{1}$$

where M is the liquid mass in the rim (per unit length) and $P(= MV)$ is the radial momentum along the rim. M increases linearly with time as $dM/dt = \rho eV$, where ρ is the density. The driving force (for a film with two sides) is 2γ. The velocity V predicted from Eq. (1) is

$$V = \sqrt{\frac{2\gamma}{\rho e}}. \tag{2}$$

V is generally of order 10 m/sec.

McEntee and Mysels [5] found that the velocity is well described by the Dupré-Culick law [Eq. (2)], but that a precursor wave spreads ahead of the advancing rim. They interpret this as a shock wave in the surfactant film [6].

In the present Letter, we report the first observation of the bursting of *very viscous* suspended liquid films in the absence of any surfactant. Viscous dissipation dominates inertia and gives rise to new features in the bursting of thin liquid films.

We form suspended films by lifting a stainless steel ring (diameter 3 cm) from solutions of highly viscous polydimethylsiloxane (PDMS) in a good solvent (isopentane, boiling point = 27.9 °C). Molecular weights are high ($M \geq 260\,000$), corresponding to viscosities higher than 600 000 cP. Polymer volume fractions ϕ are adjusted to obtain the proper viscosity to form a film: $0.25 < \phi < 0.5$. This in turn controls the initial film thickness in the dipping process. When the film is suspended in air, the solvent evaporates rapidly, resulting in a freely suspended film of pure PDMS. These films are unstable (no surface agent stabilizes them), and get thinner by capillary drainage towards the ring. However, the high viscosity of the polymer greatly slows down this process. Spontaneous rupture occurs only after several hours have elapsed.

When a film is formed, its thickness ($5 < e < 50$ μm) is obtained using an IR absorption method. The reduction in intensity of a 0.5 mm diameter IR beam through the film is measured for 2 characteristic bands of PDMS. Results are calibrated using a glass-bottomed cell where the depth of liquid is known (14.4 μm). This technique also allows us to check the absence of solvent in the film: we do not observe any peak at the characteristic frequencies of isopentane. Right after this measurement we puncture the film with a sharp needle at the impact point of the IR beam. The film rupture is initiated immediately after the thickness measurement, and we neglect the thinning of the film during this delay. We visualize an area of about 0.5 cm^2 (for a total film area of 10 cm^2) around the nucleation spot with a $\times 20$ magnification ratio using a video recording apparatus. Holes observed were small enough to neglect the influence of the edges on the opening kinetics. We consider that the film is infinite. We follow the hole opening and measure its diameter versus time using an image analysis software, IMAGE (Fig. 1).

We have access to the velocity field in the film by depositing silver-coated glass spheres of diameter 100 μm at the surface (Fig. 2). We subtract two successive images of the bursting film and monitor the distance between the positions of the spheres against their distance to the center of the hole (Fig. 3).

We also perform a dynamic measurement of the film thickening. We illuminate the film with a laser beam (wavelength $\lambda = 514$ nm). The film can be considered to be flat despite the fringes indicating slight variations in its thickness. During the bursting, we follow the thickening through the scrolling of the interference fringes with time at different locations on the film (Fig. 4). Each interfringe represents a variation of $\lambda/2n$ (n is the refractive index

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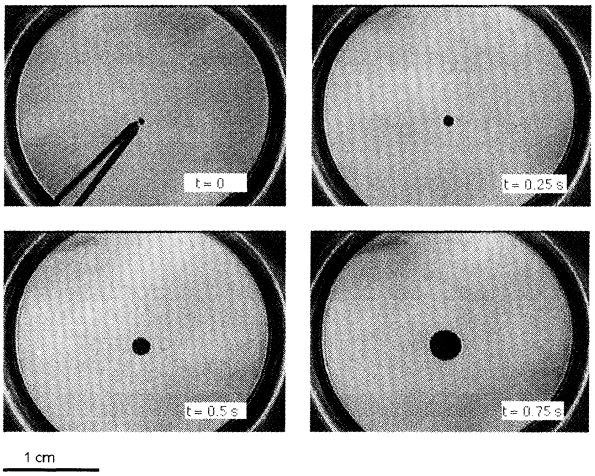

FIG. 1. Sequence of hole opening in a suspended polymer film ($\eta = 2\,500\,000$ cP, $e = 10$ μm).

of PDMS, $n = 1.41$) of the local film thickness. We compare this measurement to the evolution of the hole surface.

We were unable to prepare free standing films thicker than 50 μm using this procedure. We could nevertheless achieve thicker films ($50 < e < 500$ μm) from the same solution of PDMS in isopentane using an immiscible liquid substrate of *low viscosity* η_s [Polyfluoroalkylsiloxane (PFAS), $\eta_s = 1000$ cP] to support the films. The dewetting of PDMS films deposited on PFAS substrates has been studied before, and the experimental setup is precisely described elsewhere [7]. This work dealt with

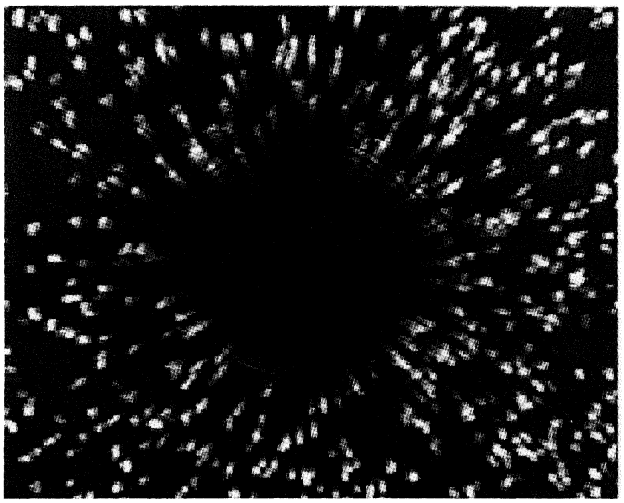

FIG. 2. Evidence of radial flows during the film rupture monitored by the motion of silver coated glass spheres (diameter = 100 μm). Superposition of five successive images from the film.

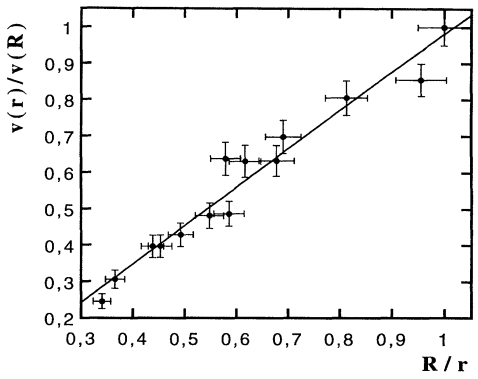

FIG. 3. Flow field in the film. r is the distance to the nucleation spot. R is the radius of the growing hole.

liquids of comparable viscosities ($1 < \eta_F/\eta_S < 10$). In this former study the opening kinetics was controlled by a viscous dissipation *in the substrate,* and the hole radius was found to open linearly with time [7]. Here, since the film is now much more viscous than the substrate ($600 < \eta_F/\eta_S < 2500$), the viscous dissipation is dominated *by the film.* Thus, the physics of these films appears to be exactly the same as for suspended films except that the driving force is here the spreading coefficient $|S|$ ($-S = 1.8 \pm 0.2$ mN m^{-1}) instead of 2γ.

We find that the radius of the hole grows *exponentially* with time, $R(t) = R_0 e^{t/\tau}$, as shown in Fig. 5. The exponential rise time τ is proportional to the thickness of the film (Fig. 6) and varies as the inverse of the film viscosity. The experimental data for τ can be written as

$$\tau = 1.4 \frac{\eta e}{2\gamma}. \tag{3}$$

For supported films, we find $\tau = 2.1\eta e/|S|$.

The velocity field $V(r)$ (r is the distance to the center of the hole) is found to be radial and to vary like

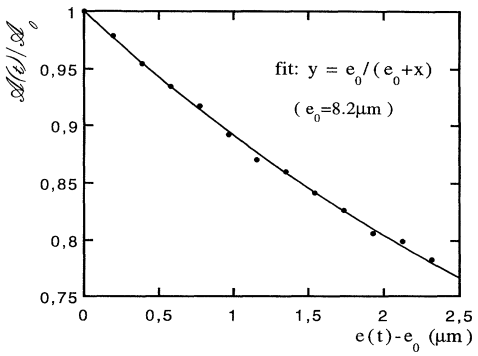

FIG. 4. Film thickening. $\mathcal{A}(t)$ is the film surface that remains at time t. $\mathcal{A}_0$ is the initial surface of the film (time $t = 0$). $e(t)$-e_0 measures the thickening of the film between time t and the nucleation time.

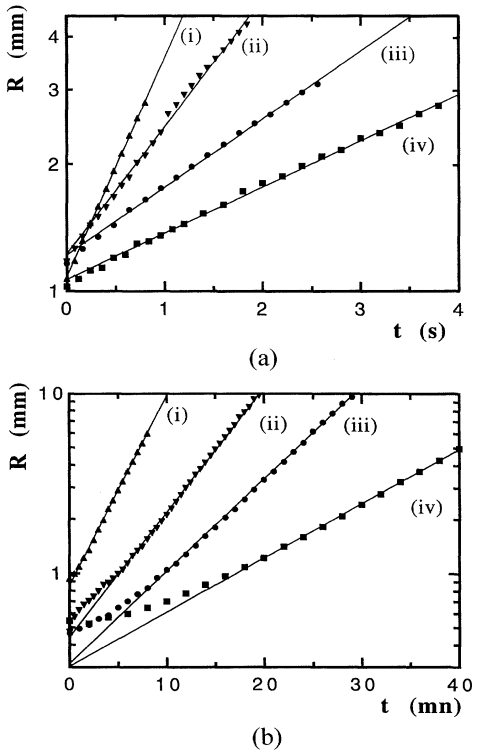

FIG. 5. Evolution of a hole of radius R versus time for different film thicknesses (a) in suspended films ($\eta = 2\,500\,000$ cP): (i) $e = 8.5$ μm, $\tau = 0.82$ s; (ii) $e = 17.0$ μm, $\tau = 1.44$ s; (iii) $e = 33.3$ μm, $\tau = 2.69$ s; (iv) $e = 45.2$ μm, $\tau = 3.95$ s. (b) in supported films ($\eta = 2\,500\,000$ cP, $\eta_B = 1000$ cP): (i) $e = 65$ μm, $\tau = 4.11$ mn; (ii) $e = 130$ μm, $\tau = 6.31$ mn; (iii) $e = 140$ μm, $\tau = 8.41$ mn; (iv) $e = 250$ μm, $\tau = 14.65$ mn.

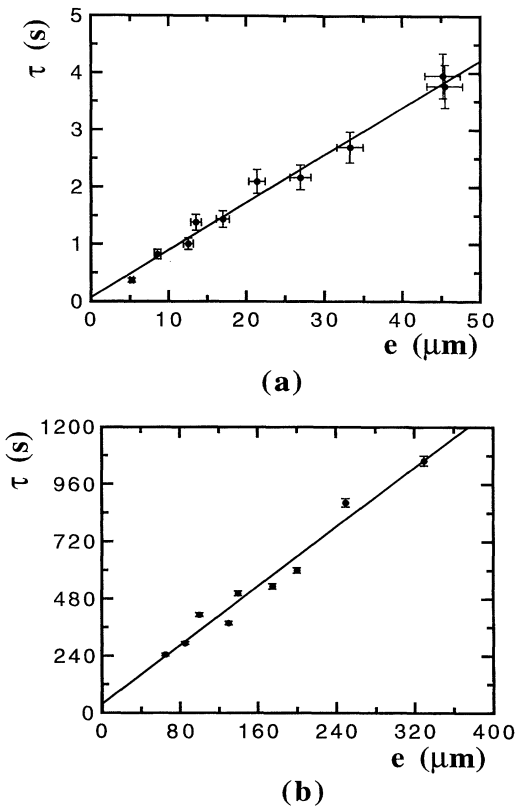

FIG. 6. Influence of the film thickness e (viscosity $\eta = 2\,500\,000$ cP) on the characteristic rising time τ of the hole opening for (a) suspended and (b) supported films. In this last case, an air bubble was injected in the substrate using a microsyringe to nucleate a hole. The deviation from the exponential curve at short times is due to the perturbation induced by the breaking of the bubble as it reaches the surface.

$V(r) \propto 1/r$ (Fig. 3). This is consistent with the measurement of the film thickening. We find that the thickening $\delta(t)$ is the same over the whole film and varies in time as $\delta(t) \propto R^2(t)/[L^2 - R^2(t)]$ (Fig. 4), where R is the hole radius and L is the ring radius. This indicates that all the liquid collected from the growing hole is homogeneously spread throughout the remaining film.

From the two previous results, we can deduce that we have a long range radial plug flow in the film:

$$V(r) = \dot{R}R/r\,. \tag{4}$$

The viscous dissipation can then be derived as

$$T\dot{S} = \int_R^\infty \left(2\pi r e\, dr\, \frac{\eta}{2}\left[\left(\frac{\partial V}{\partial r}\right)^2 + \left(\frac{V}{r}\right)^2\right]\right) \tag{5}$$

$$= 2\pi\eta e\dot{R}^2. \tag{6}$$

Equating this to the surface energy gained per unit time

$$\dot{F}_S = (2\gamma)2\pi R\dot{R}\,, \tag{7}$$

one arrives at

$$\frac{\dot{R}}{R} = \frac{1}{\tau}\,, \tag{8}$$

where τ is given by

$$\tau = \frac{\eta e}{2\gamma}\,. \tag{9}$$

The absence of a rim collecting the liquid associated with the long range flows in the film represents a new behavior in the field of thin liquid film rupture. An "instantaneous" thickening δ must be due to an elastic propagation: The film has a viscoelastic behavior. At short times it behaves like rubber, with an elastic modulus $\mu \approx kT/N_e a^3$ (typically 10^6 Pa) where N_e is the threshold for entanglement, and a is a molecular length. Above the reptation time τ_{rep} the film flows like a liquid. As a hole opens, the whole film is elastically

deformed by the surface tension (with a Laplace pressure $2\gamma/e$ at the edge of the hole): The stress is transmitted up to a distance $L_d = c\tau_{\text{rep}}$, where c is the transverse sound velocity in the rubber. Taking $c = 30\ \text{m s}^{-1}$ and $\tau_{\text{rep}} = 0.06$ s, we find $L_d \approx 2$ m, much larger than the size of our sample. The deformation field around a hole in an elastic membrane under tension is radial [8],

$$u(r) = \frac{\gamma}{\mu e}\frac{R^2}{r}, \tag{10}$$

and the corresponding stress that satisfies the boundary conditions $\sigma_{rr}(R) = -2\gamma/e$ and $\sigma_{rr}(\infty) = 0$ is

$$\sigma_{rr} = -\frac{2\gamma}{e}\left(\frac{R}{r}\right)^2. \tag{11}$$

After a time τ_{rep} the flow relaxes the stress but the hole has increased by $u(r = R)$ and the process iterates. The growth rate is then (omitting numerical coefficients)

$$\dot{R} \approx \frac{u(r = R)}{\tau_{\text{rep}}} \approx \frac{\gamma}{\mu e}\frac{R}{\tau_{\text{rep}}} \approx \frac{\gamma}{\eta e}R. \tag{12}$$

More quantitatively, as σ_{rr} varies with a characteristic frequency $\tau^{-1} \ll \tau_{\text{rep}}{}^{-1}$, the flow induced in the film corresponds to a zero frequency viscous response given by

$$\sigma_{rr} = \eta\frac{\partial V}{\partial r}, \tag{13}$$

i.e., using (11)

$$V = \frac{2\gamma}{\eta e}\frac{R^2}{r}. \tag{14}$$

Writing $V(r = R) = \dot{R}$ we get (8) and (9).

For suspended films, as the hole expands, the velocity increases ($\dot{R} = R/\tau$), up to a limiting value of $\dot{R} = \sqrt{2\gamma/\rho e}$. This defines a crossover radius R_c, beyond which we move into the inertial regime,

$$R_c = \eta\sqrt{\frac{2e}{\gamma\rho}}. \tag{15}$$

With $\eta = 2\,500\,000$ cP, $\gamma = 20\ \text{mN m}^{-1}$, $e = 1\ \mu$m, one finds $R_c \approx 0.5$ m. Above R_c the hole should open at constant velocity [Eq. (2)]. Experiments on thinner films and less viscous polymers, to approach the inertial regime, are under way.

For supported films, as the hole expands, the viscous dissipation in the substrate overcomes the dissipation in the film above a radius $R_c' = \frac{\eta_f}{\eta_s}e$. We then expect a crossover to the previously examined regime [7].

To conclude, two distinct features emerge: (a) the absence of a rim associated with 2D plug flows. All previous experiments, either on suspended [5,6] or on deposited films [7,9], have shown the existence of a rim collecting the liquid from the growing hole. The absence of a rim in the present process is due to the viscoelasticity of the films and their ability to transmit an elastic stress through the whole film. This stress is responsible for long range plug flows, related to a uniform thickening of the film. (b) An exponential rate of dewetting. During the inertial bursting of suspended soap films or the inertial dewetting of low viscous fluids [10], the hole grows at constant velocity. Viscous bursting of liquid films deposited on a solid substrate [9], or supported by a liquid substrate of comparable viscosity [7] (in that case the viscous dissipation takes place in the substrate), also gives rise to a constant velocity. This is the first observation of exponential kinetics in the rupture of thin films.

This work opens a new field of two-dimensional plug flows in wetting phenomena. Also interesting is the opposite case of a very viscous polymer that *spreads* on a nonviscous substrate. This case will be discussed in a forthcoming publication [11]. More generally the dynamics of wetting with highly viscous liquids will probably be very different from what we know with conventional liquids.

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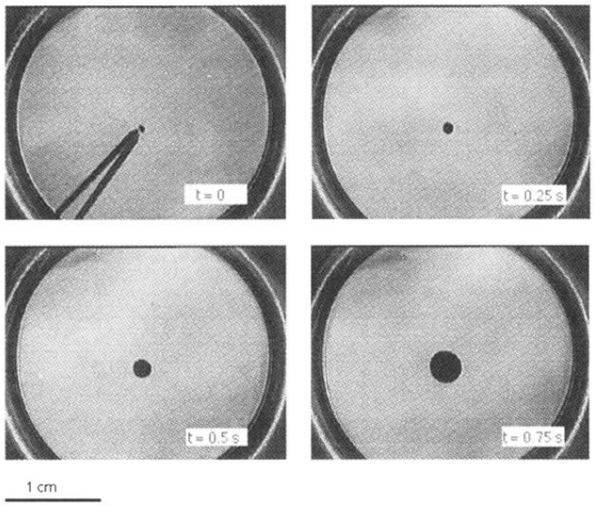

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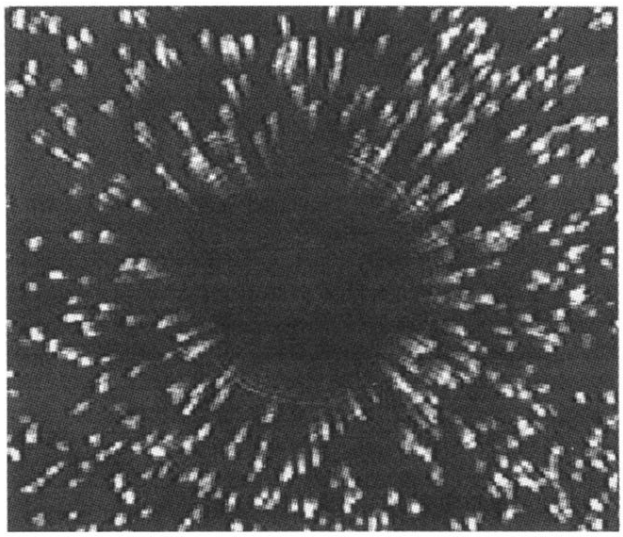

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