

Dewetting at Soft Interfaces

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We observe by optical interferometry the removal of a thin liquid film (thickness in the range of 100 nm) intercalated between a soft rubber and a hydrophobic glass plate. The film dewets by nucleation and growth of a single solid/rubber contact. The dry patch is surrounded by a very flat rim that collects the liquid. We find that (i) the shape of the rim squeezed by the rubber is quasistatic, and (ii) the radius $R(t)$ of the contact increases with time t according to an unusual power law $R(t) \propto t^{3/4}$. These results can be interpreted in terms of a hydrodynamic model, assuming viscous dissipation in the moving rim while the rubber is purely elastic. [S0031-9007(98)05819-0]

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Dewetting of liquid films exposed to air has been studied intensively for the past ten years [1–3]. A liquid film deposited on a nonwetttable substrate [$S = \gamma_{s0} - (\gamma_{SL} + \gamma) < 0$, where γ_{ij} are, respectively, solid/air, solid/liquid, and liquid/air interfacial tensions] dewets by nucleation and growth of a dry patch. As the dewetting proceeds, the dry patch [radius $R(t)$] is surrounded by a rim, collecting the liquid. The profile of the rim is a portion of a circle (i.e., quasistatic) because pressure equilibrates fast in the thick part. The dry patch grows at velocity $V = dR/dt$ constant in time. Using silicone oils (PolyDiMethylSiloxane, PDMS) to vary the viscosity (η) and alkanes to vary the surface tension (γ), Redon [1] has established the fundamental law that governs the drying process:

$$V \propto V^* \theta_e^3, \quad (1)$$

where $V^* = \gamma/\eta$ is a characteristic velocity of the liquid and θ_e is the static contact angle for a droplet deposited on the same substrate. This result was interpreted [4] by a balance between the driving capillary force acting on the rim, $|S| \cong (1/2)\gamma\theta_e^2$ (θ_e small), and the friction force dominated by the liquid wedge [$\propto \eta(V/\theta_e)$], both constant in time.

Here, our aim is to extend this picture to the case of a liquid film intercalated between a soft deformable material—a type of rubber (Young's elastic modulus $E \sim 1$ MPa)—and a hydrophobic solid. To escape, the liquid must deform the rubber. Elastomers have been used in lubricated contact with a variety of surfaces for decades [5], and asking for the stability of intercalated liquid films is of crucial interest for many practical applications. One indicative example is the irreversible rupture of the lachrymal film, which has been observed with silicone contact lenses [6]: The elastomer adheres strongly to the cornea and can cause severe damages when it is removed. On the contrary, when driving on a wet road, we require the water film to be squeezed away—in order to maximize grip—during the time when the tyre is exposed to water (typically 5 ms). Very few attempts to monitor the withdrawal of liquid films sandwiched between solids

and rubbers have been reported. Roberts was the first to prepare optically smooth rubber surfaces (by molding polyisoprene) and to look at lubricated contacts against glass by optical interferometry [7].

In this Letter, we provide the first quantitative measurements of the kinetics of growth of single solid/elastomer contacts nucleated through intercalated liquid films. The stability of these films is controlled by the spreading coefficient $S = \gamma_{SR} - (\gamma_{SL} + \gamma_{LR})$ which compares interfacial energies between “dry” contacts γ_{SR} and lubricated contacts $\gamma_{SL} + \gamma_{LR}$. When S is negative, the system gains energy by excluding the intercalated liquid.

We have shown previously [8] that S can be determined directly from the equilibrium profile of sessile droplets standing at the solid/rubber interface. These droplets are flat semiellipsoids with thicknesses H (in the micrometer range) related to their radii R (of the order of 100 μm) by

$$H^2 = \frac{6}{\pi} h_0 R, \quad (2)$$

where $h_0 = |S|/E$ defines a characteristic length scale, where capillary and elastic energies become comparable. By monitoring H and R , one can deduce h_0 and then S . With water between a PDMS rubber (Young's modulus $E = 0.74$ MPa) and a silanized glass plate, $h_0 = 640 \pm 50$ Å and $-S = 50 \pm 5$ mN/m. Using a fluorinated silicone oil instead of water, we find $h_0 = 100 \pm 10$ Å and $-S = 7 \pm 1$ mN/m.

Let us now consider an intercalated film (thickness e) and bring the elastomer in contact with the solid to make a bridge of radius R . The free energy of the system has varied by an amount ΔF given by (omitting numerical coefficients)

$$\Delta F \cong SR^2 + E \left(\frac{e}{R} \right)^2 R^3. \quad (3)$$

The first term is the surface energy we gain to create a dry contact of radius R ($S < 0$) which competes with the elastic energy of deformation (evaluated for a typical deformation e/R which spreads over a volume R^3 inside

the rubber volume). The maximum of ΔF defines a critical radius R_c over which the solid/rubber patch will expand and the liquid film is excluded:

$$R_c \propto \frac{e^2}{h_0}. \quad (4)$$

An intercalated film is less fragile than a film of equal thickness deposited on a nonwetable solid (in the later case, R_c would be of the order of the film thickness e). Here, we have to go down to microscopic film thicknesses to get reasonable critical radii: Taking typical values $e = 0.1 \mu\text{m}$ and $h_0 \sim 100 \text{ \AA}$, one gets $R_c \sim 1 \mu\text{m}$.

The experimental geometry is shown in Fig. 1. Intercalated films are formed by elastic indentation of a rubber cap pressed against a glass plate through a separating liquid drop. We have chosen to work with “ideal” materials. Our elastomer—PolyDiMethylSiloxane—is homogeneous, optically smooth, and behaves like a pure elastic medium (Young’s modulus $E = 0.74 \text{ MPa}$). It is prepared from a commercial reaction mixture (two equal parts, Sylgard 170A&B, Dow Corning Corp.) from which undesirable reinforcing fillers have been removed by centrifugation. Liquid droplets of the mixture are deposited on a nonwetable surface (a fluorinated glass slide). They form spherical caps. Cured at 65°C during 48 h, we get rubber lenses (radius of curvature $\mathcal{R} = 1\text{--}2 \text{ mm}$) and the cross-linking process is complete. The solid substrate displays low contact angle hysteresis (about 8°) and is obtained by silanization of microscope glass slides following

a standard procedure [9] (using octatrichlorosilane). The liquid—a fluorinated silicone oil (Hüls-Petrarch Corp., used as received)—is pure and immiscible with our PDMS [3]. We use viscous liquids (viscosities η range between 1 Pa s and 20 Pa s) in order to slow down the dynamics of dewetting. Characterizations and sample preparations are described in more detail elsewhere [8]. The elastomer cap is attached to the arm of a micromanipulator (Narishige) which enables us to control its position very accurately (a fraction of micron). We follow the normal approach of the lens along the axis of an objective ($\times 20$) of an inverted microscope (Zeiss, Axiovert 135) using, in its simplest form, a technique known as reflection contrast interferential microscopy [10]. The absolute thickness is obtained after complete extrusion of the liquid, when the rubber is in intimate contact with the glass plate.

When the elastomer is not in contact with the plate, we observe Newton rings corresponding to a spherical rubber lens. As we approach the lens toward the plate (speed of the order of $1 \mu\text{m s}^{-1}$) below the micron, the lens is deformed and a flat film of radius $a \sim 100 \mu\text{m}$ is formed. At this stage, we hold the position of the rubber. The deformation of the elastic medium is $\epsilon \cong a/\mathcal{R} \cong 10\%$. The total stress P at the lubricated contact can be evaluated using Hooke’s law $P \cong E\epsilon \approx 1 \text{ atm}$ and is responsible for the drainage of the intercalated liquid film. Notice that the ploughing length of the rubber sphere, $\delta \cong a\epsilon = 10 \mu\text{m}$, is much larger than the film thickness ($< 1 \mu\text{m}$). The imposed stress remains almost constant during the film thinning. For a given radius, we have followed the evolution of the film thickness e at its center with time t and found that it is well described by a classical Reynolds law with $e(t) = \frac{b_{\text{th}}}{\sqrt{t}}$ at long times. Here, $b_{\text{th}} = \sqrt{(27\pi/64)(\eta\mathcal{R}a/E)}$ is expressed as a function of the flat area a directly related to the applied external force by Hertz theory [11]. With $E = 0.74 \text{ MPa}$, $\eta = 15 \text{ Pa s}$, $\mathcal{R} = 1.8 \text{ mm}$, and $a = 400 \mu\text{m}$, we measure $b_{\text{exp}} = 4 \mu\text{m s}^{1/2}$ (result not shown) in good agreement with Reynolds prediction $b_{\text{th}} = 4.4 \mu\text{m s}^{1/2}$. Typically, it takes a few 100 s to reach a film thickness of $0.15 \mu\text{m}$. When we let the film drain, we eventually observe a spontaneous dewetting—the “collapse.” Some liquid droplets are trapped and their profiles, given by a few fringes, enable us to measure the spreading parameter S of our system.

Nucleation of a single contact at the center of the film is the tricky part of the experiment. This was achieved first by taking advantage of the presence of “defects” at the surface of the rubber lens (atomic force microscopy has shown the presence of a few blisters at the surface of the elastomer). Another better method is based on hitting the surface of the lens with a needle. This allows us to initiate a dewetting well before the spontaneous collapse of the film.

Figure 2 shows the opening sequence of a single rubber/solid contact. The liquid is collected into a rim that

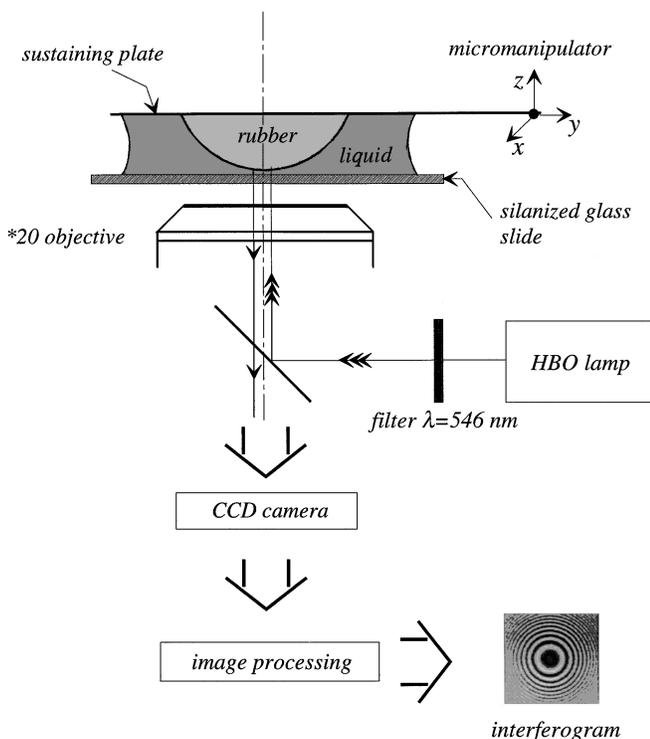


FIG. 1. Experimental setup to form and observe thin liquid films sandwiched between a rigid solid (a silanized glass plate) and a PDMS rubber.

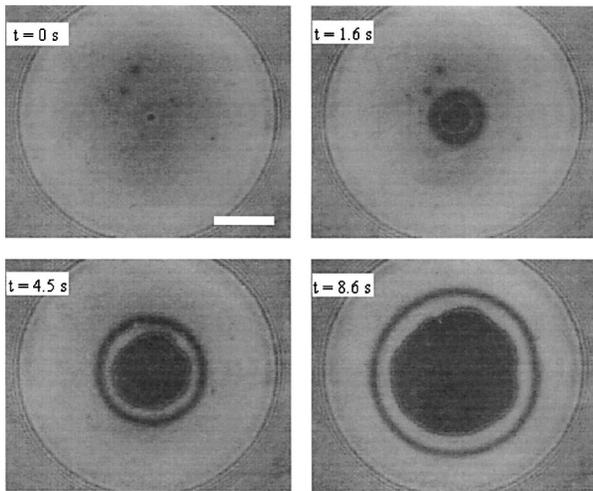


FIG. 2. Opening sequence of a single dry solid/rubber contact nucleated through an intercalated liquid film (viscosity $\eta = 2.65$ Pa s, thickness $e = 130$ nm). On the first image, we can notice the presence of a “defect” at the center of the film. The white bar corresponds to a $50 \mu\text{m}$ length. Here, the edge of the film is maintained within the screen. A flat rim surrounding the dry patch is clearly visible.

surrounds the hole. The dewetting is slow (velocities in the $1-10 \mu\text{m s}^{-1}$ range), and the profile of the rim, at least the part going to the solid plate, is very similar to the shape of a sessile droplet: It is very flat, goes abruptly to the solid surface, and we measure a ratio $(h + e)^2/\ell$ of the order of h_0 (Fig. 3).

We have measured the evolution of the radius R of the dry patch versus time t for different liquid viscosities η . One can notice that in our experiments the film thickness e is imposed by the size of the defect and the nucleation requirement [Eq. (4)] $e = 120 \pm 30$ nm. In this thickness range, the dewetting is much faster than the film drainage, and the film thickness remains constant [$(\Delta e)/e \leq 3\%$ during the dewetting process]. We find that $R(t)$ is described perfectly by a power law dependence [Fig. 4(a)]

$$R(t) = k(\eta)t^{0.75 \pm 0.05}. \quad (5)$$

The factor k decreases with the liquid viscosity and the dependence $k(\eta)$ is also well described by a power law

$$k \propto \eta^{-0.6 \pm 0.1}. \quad (6)$$

The size of the rim which collects the liquid from the dry patch increases as the rubber/solid contact expands. We have measured the evolution of its width ℓ with time t [Fig. 4(b)]. We find

$$\ell(t) \propto t^{0.4 \pm 0.1}. \quad (7)$$

The interpretation of our experimental laws [Eqs. (5)–(7)] is based on a recent, crude, hydrodynamic model [12] restricted to the level of scaling laws.

(i) A dry patch of radius R has been nucleated at point O

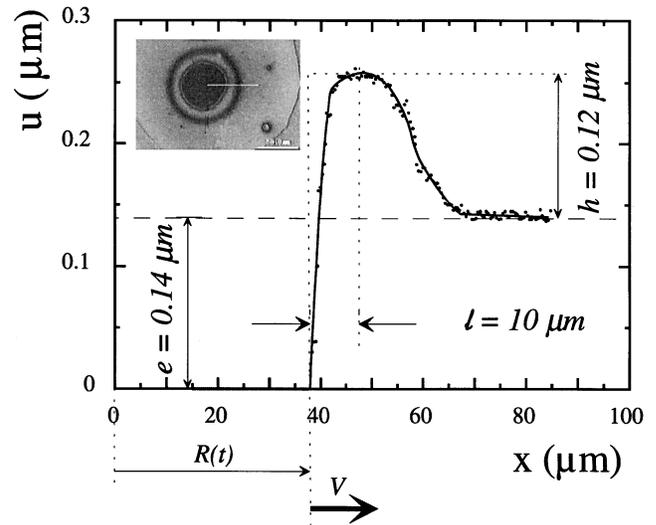


FIG. 3. Profile $u(x)$ of a rim (shown in the inset) given by the dewetting of a film of thickness $e = 140$ nm and viscosity $\eta = 7$ Pa s, 17 s after nucleation. We find $(h + e)^2/\ell = 70 \text{ \AA}$.

and the liquid is collected in a rim (height $h + e$, width 2ℓ) moving at velocity V (Fig. 3). Assuming $R \gg \ell$ and $h \gg e$, volume conservation gives

$$Re = 4\ell h. \quad (8)$$

(ii) The profile of the rim is assumed to be quasistatic (i.e., similar to the profile of a sessile droplet at a solid/rubber interface [8]):

$$h^2 \approx h_0 \ell. \quad (9)$$

(iii) The gain of surface energy is entirely dissipated in the moving liquid rim, while the rubber is purely elastic. Using a lubrication approximation ($\ell \gg h$) to estimate the viscous dissipation and assuming $R \gg R_c$ to neglect elastic deformation energies [13], we write the energy balance (per unit time) as

$$-SRV \approx \eta \left(\frac{V}{h}\right)^2 \Omega \approx \eta \frac{\ell}{h} V^2 R, \quad (10)$$

where $\Omega \propto h\ell R$ is the rim volume. Equation (10) leads to

$$|S| \approx \eta \frac{\ell}{h} V. \quad (11)$$

Using Eqs. (8) and (9), one finds

$$\frac{\ell}{h} \approx \frac{(Re)^{1/3}}{h_0^{2/3}}. \quad (12)$$

The growth law is then obtained from Eqs. (11) and (12):

$$R(t) = K \left(\frac{|S|}{\eta} t\right)^{3/4} \frac{h_0^{1/2}}{e^{1/4}}, \quad (13)$$

where K is an unknown numerical prefactor. Combining Eqs. (9), (12), and (13), we also get

$$\ell(t) \approx (eV^*t)^{1/2}, \quad (14)$$

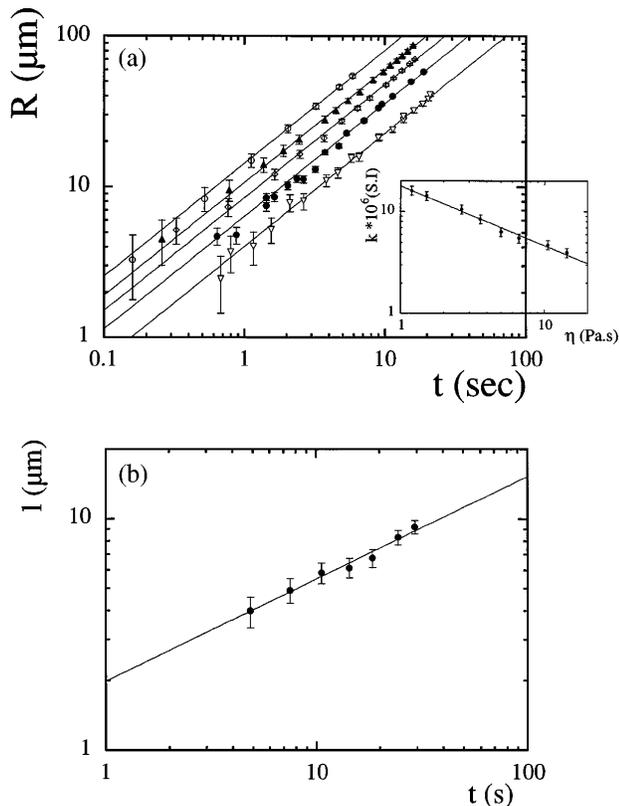


FIG. 4. (a) Evolution of the radius $R(t)$ of a solid/rubber contact versus time t in a log-log plot (open triangle: $\eta = 14.3$ Pa s; solid circle: $\eta = 4.9$ Pa s; open diamond: $\eta = 3.595$ Pa s; solid triangle: $\eta = 2.65$ Pa s; open circle: $\eta = 1.52$ Pa s). Our results are fitted by the power law $R(t) = kt^{3/4}$. The inset shows the evolution of k versus the liquid viscosity η . The best power-law fit gives $k = 18\eta^{-0.6}$. (b) Evolution of rim length $\ell(t)$ versus time t in a log-log plot. The best power-law fit gives $\ell = 2t^{0.44}$.

where $V^* = |S|/\eta$ defines a characteristic dewetting velocity. One can notice that $\ell/R = e/h = h/\ell = (R_c/R)^{1/3}$ and all of our geometrical requirements will be met as soon as $R \gg R_c$.

Our kinetics results $R(t)$ and $\ell(t)$ follow power laws on two decades with exponents 0.75 ± 0.05 and 0.4 ± 0.1 , respectively, in good agreement with the theoretical prediction. Concerning the viscosity dependence, the experimental exponent is systematically a little too weak. The numerical prefactor K in Eq. (13) can be estimated from our experiments: $K = 0.20 \pm 0.02$.

Thus, we can understand relatively simply the dewetting of liquid films against rubbers—provided that the dissipation in the rubber is weak—as is the case for usual rubbers. This should provide a useful starting point for the analysis of more practical cases where (i) the substrate is rough and chemically heterogeneous, and (ii) the rubber is strongly dissipative (e.g., race car tires). The ultimate hope is to reach simple concepts covering very different situations of adhesion on *wet* substrates, from biomedical research to road construction.

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 - [13] The calculation of $R(t)$ is done for $R \gg R_c$, where the elastic energy of deformation of the rubber is negligible compared to surface energies. If $R \geq R_c$, we must keep both contributions, and one finds an exponential growth for $R(t)$: $[R(t) - R_c]/R_c = \{[R(t=0) - R_c]/R_c\}e^{t/\tau}$, with $V^*\tau \sim R_c^2/e$. This characteristic time τ is such that $R(\tau)$ in the scaling growth equation is just R_c .