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Dewetting of a water film between a solid and a rubber

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Abstract. A water film (thickness e) between two hydrophobic solids is metastable. If contact is established (over an initial disc of radius $R(0) > R^*$, where R^* is a certain nucleation size), the dry path expands (up to a size $R(t)$ at time t), and the rejected water forms a rim (of width $l(t)$) around the patch. We predict $R(t) \sim t^{3/4}$ and $l(t) \sim t^{1/2}$. Typically, over 5×10^{-3} s we expect $R(t) \sim 1.6$ mm.

1. Aims

A water film, placed on a hydrophobic surface, nucleates dry patches, which grow with a constant velocity (Brochard-Wyart and de Gennes 1992, Redon *et al* 1991, Reiter 1992)

$$V = \text{constant} \times \gamma/\eta\theta_e^3 \qquad (\theta_e < 1) \tag{1}$$

where γ is the surface tension, η the viscosity, and θ_e the equilibrium contact angle of a water droplet on the solid. (Hysteresis is assumed to be negligible.) Ahead of the dry patch, the water builds up a rim; both the width and the height of the rim increase with time.

Our aim here is to extend this picture to the case shown in figure 1, where the water film is not at a solid/air interface, but rather at a solid/rubber interface. This is (remotely) related to the problems of driving on wet roads: here a given piece of the outer surface of the tyre is exposed to water during a contact time of order 5×10^{-3} s. The crucial question is whether, during this time, the water film has been expelled, thus restoring an acceptable level of adhesion.

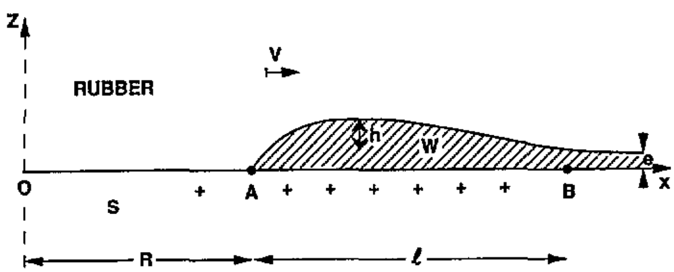

Figure 1. Proposed structure for a growing dry patch in a water film W between a solid S and a rubber. The dry patch was initiated near point O, and has a growing radius $R(t)$. The water rejected from the dry region builds up a rim of width $l(t)$.

In the present paper, we discuss this only for an idealized case, where both the solid and the rubber are completely flat. The solid is assumed to be perfectly rigid. The water and the rubber are taken as incompressible, but can of course be deformed. We also assume that the thickness e of the original film is relatively large ($\geqslant 1\ \mu$m), so that the long-range effects of Van de Waals forces can be neglected.

A precise discussion of the rim shape requires the use of singular integral equations, relating the vertical stress at one point x on the rubber surface to the deformations of this surface at all other points. In the present paper, we try to avoid this complicated approach, using simple (but tentative) scaling arguments.

2. Two-parameter descriptions of the rim

(1) As shown in figure 1, we idealize the rim as a region of width l, and thickness $e+h \sim h$ ($h \gg e$). Our requirement of incompressibility then imposes

$$2\pi R l h = \pi R^2 e \qquad (l \ll R). \tag{2}$$

(2) The driving force F for the drying process is a combination of interfacial energies γ_{ij}.

$$F = \gamma_{\mathrm{WR}} + \gamma_{\mathrm{WS}} - \gamma_{\mathrm{RS}} \tag{3}$$

where W denotes water, R, rubber, and S, solid. We translate this into a pressure head p around point A:

$$p = F/h. \tag{4}$$

(3) This pressure head induces a Poiseuille flow in the rim, with an average velocity

$$V = -(\partial p/\partial x)(e+h)^2/12\eta \cong (\partial p/\partial x)h^2/12\eta. \tag{5}$$

Here, we estimate roughly

$$-\partial p/\partial x \cong p/l = F/hl. \tag{6}$$

(4) We also write that the deformation of the rubber around the rim is induced by the pressure p:

$$p \cong \mu h/l \tag{7}$$

where μ is the shear modulus of the rubber (4)

$$\mu = kT/Na^3 \tag{8}$$

N being an average number of monomer units between crosslinks, and a a monomer size.

3. Growth laws

Comparing (4) and (7), we obtain

$$h = (F/\mu)l/h = h_0 l/h \tag{9}$$

where $h_0 \equiv F/\mu$ is typically in the range 100–1000 Å.

The Poiseuille equations (5) and (6) can be rewritten as

$$V/V^* = h/l = h_0/h \tag{10}$$

where $V^* = F/\eta$.

Thus, using the two form of (10) plus (2)

$$(V/V^*)^2 = h_0/l \qquad (V/V^*)^3 \cong h_0^2/eR. \tag{11}$$

Writing $V \sim R/t$, this gives the scaling form of the growth law

$$R(t) \cong (V^* t)^{3/4} h_0^{1/2} e^{-1/4}. \tag{12}$$

We can then obtain the width $l(t)$ of the rim, using (10)

$$l = (Re)^{2/3} h_0^{-1/3}. \tag{13}$$

Thus whenever $R \gg e^2/h_0$, we expect $l \ll R$: the rim represents a small annulus around the dry patch. Finally, from (9), the increase in width of the rim should scale as

$$h = (lh_0)^{1/2} = (Reh_0)^{1/3}. \tag{14}$$

Again when $R \gg e^2/h_0$, we can check that $h > e$.

The related deformations

$$h/l = h_0/h = (h_0^2/Re)^{2/3} \tag{15}$$

are correspondingly small.

4. Discussion

(1) Consider for instance a hydrophobic solid with surface properties comparable to those of rubbers ($\gamma_{RS} \cong 0$), and assume $\gamma_{RW} = \gamma_{SW} = 35$ mJ m^{-2}. This leads to $V^* = 70$ m s^{-1}. Taking $e = 1$ μm, $h_0 = 100$ Å, and $t = 5 \times 10^{-3}$ s, we obtain from (12) a dry patch radius $R \sim 1.6$ mm. Of course, the coefficient in (12) is very uncertain, but we do see that spontaneous dewetting is not fully effective to restore ahesion between a tyre and a *flat* solid surface: we would require $R \sim 1$ cm, rather than 1 mm.

(2) Of course, in pratice, the tyre is facing a rough solid surface, with granularities ranging from millimetres down to micrometres. An interesting challenge for the future is to extend our primitive model towards random surfaces.

(3) Model experiments on ideal surfaces may still be useful, to check whether our simple picture has a real meaning.

(4) Clearly, near the tip of the wet region, we expect elastic stresses much larger than suggested by (7), but they should be localized in an area $\sim e^2$ (of the xz phase) near point A. They lead to a line energy T for the edge of the dry patch $T \sim \mu e^2$. Then the total energy becomes

$$E = 2\pi RT - \pi R^2 F \tag{16}$$

and the patch will grow only when R is larger than a certain *nucleation radius*

$$R^* = T/F \cong e^2/h_0. \tag{17}$$

It is worth noting that the condition $R \gg R^*$ automatically imposes $l \ll R$ and $h > e$, as discussed after (13).

(5) All our analysis was based on the low-frequency response of the rubber, described by a single modulus μ. Actually, the rim motion drives elastic perturbations at frequencies

$$\omega \sim V/l \sim R/lt. \tag{18}$$

$\omega/2\pi$ is expected to be in the 100 cycle range. If the rubber has a strong viscoelastic behaviour at these frequencies, the simple growth law (12) may be strongly modified.

(6) It may be worth noting that, at our level of description (incompressible materials), and overall pressure p_0 acting on the structure should have no effect.

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