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Dewetting of a water film between a solid and a viscoelastic liquid

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Résumé. — Un film d'eau écrasé entre un solide hydrophobe (S) et un polymère fondu (P) est métastable, et démouille par nucléation et croissance de zones sèches (rayon $R(t)$ au temps t) entourées d'un bourrelet (qui collecte l'eau rejetée). En tenant compte du comportement viscoélastique de P, on est conduit à prédire : a) un régime purement élastique si $R < R_c$, où le fondu a un comportement de caoutchouc, avec $R(t) \sim t^{3/4}$; b) un régime visqueux, aux temps longs, où le bourrelet est étiré par sa grande friction avec P, et se déplace à vitesse constante.

Abstract. — A water film squeezed between a hydrophobic solid (S) and a polymer melt (P) is metastable and dewets by nucleation and growth of a dry patch (radius $R(t)$ at time t) surrounded by a rim (collecting the rejected water). Taking into account the viscoelastic behaviour of P, we are led to predict : a) a pure elastic regime if $R < R_c$, where the melt behaves like a rubber, with $R(t) \sim t^{3/4}$; b) a viscous regime, at longer times, where the rim is extended by its friction against P, and moves at constant velocity.

1. Introduction : dewetting of water films exposed to air, rubber, or viscoelastic liquids.

The dewetting of liquid films has many practical applications. Current examples include :

- i) the fast drying of glasses in dish-washers induced by non-wettable chemical agents,
- ii) the stability of the lacrimal film controlled by the proteins of tears (mucyn) in the case of liquid films exposed to air,
- iii) the aquaplaning of cars on wet roads,
- iv) the adhesion of flexible contact lenses to the cornea-protected by a water film, and
- v) the stability of films intercalated between a solid and a polymer melt (or two polymer melts) in polymer extrusion and coextrusion respectively.

1) A water film deposited on a hydrophobic surface, in air, is metastable, and nucleates dry patches [1-3], which grow with a constant velocity :

$$V = \text{Cte} \frac{\gamma_w}{\eta_w} \theta_E^3 \quad (\theta_E \ll 1) \quad (1)$$

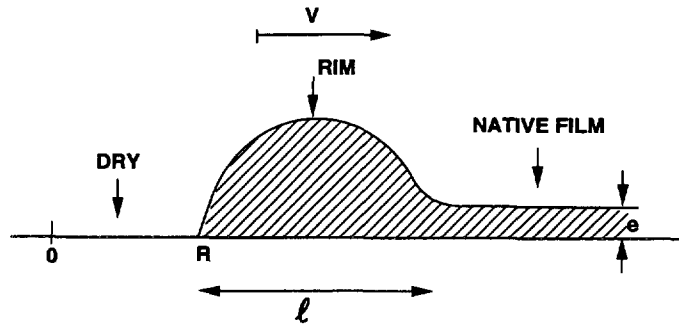


Fig. 1. — Dewetting of a water film exposed to air. The rim has a circular cross section.

where γ_w (η_w) are the surface tension (viscosity) of water. The ratio γ_w/η_w is a characteristic wetting velocity (~ 70 m/s).

The rejected water forms a rim, of width $\ell(t)$, at time t . The rim is shown in figure 1. The vertical profile of the rim (controlled by capillarity) is a portion of a circle, because the pressure equilibrates fast in most of the rim region.

Equation (1) results from a balance between: i) the interfacial driving force $F_d = \gamma_w + \gamma_{ws} - \gamma_{so} = |S| \cong \gamma_w \theta_E^2/2$, where the constants γ_{ij} are the water/air and water/solid surface tensions and ii) the viscous force, dominated by the dissipation inside the two wedges of the rim: $F_v \cong \eta_w/\theta_E V$.

2) Recently, we studied a more complex, but related problem: the dewetting of a water film of thickness e between a solid and a rubber [4]. Here again, if a dry contact is established, the dry patch expands, provided that the initial radius $R(0)$ is larger than a critical value:

$$R^* = e^2/h_0$$

where $h_0 = |S|/\mu$ is the ratio between the spreading coefficient and the elastic modulus μ of the rubber. h_0 has a physical significance, in conditions of partial wetting with a water droplet between rubber and air: a contact line creates a cusp of amplitude comparable to h_0 .

The rim shape results from a balance between capillary and elastic energies. The height h of the rim and its width ℓ are related by a quasistatic relation:

$$\ell = \frac{h^2}{h_0} \quad (2)$$

expressing that capillary pressures ($|S|/h$), and elastic pressures ($\mu h/\ell$) are comparable.

Here we rederive the laws of « elastic dewetting » from a different approach based on dissipation arguments. The velocity of the rim results from the transformation of interfacial energy into viscous dissipation in the (extended) water rim:

$$T\dot{S} = \eta_w \left(\frac{V}{h} \right)^2 h\ell = |S| V \quad (3)$$

where $|S| = \gamma_{RW} + \gamma_{SW} - \gamma_{SR}$ is the interfacial driving force acting on the rim; γ_{ij} are the rubber/water, water/solid and rubber/solid interfacial tensions. Equation (3) shows that for squeezed rims, the friction forces increase with ℓ . A relation between ℓ and R is provided by the conservation of water:

$$2 \pi R \ell h \cong \pi R^2 e. \quad (4)$$

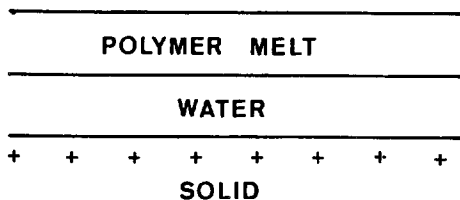


Fig. 2. — Water film intercalated between a hydrophobic solid and a polymer melt.

Equations (2), (3) and (4) then give :

$$V = V_w^* \left(\frac{\lambda}{V_w^* t} \right)^{1/4} \quad (5)$$

where we define $V_w^* = \gamma_w / \eta_w (\theta_E^2/2)$ and $\lambda = h_0^2/e$. Typically $h_0 \sim 10$ nm and $\lambda \sim 1$ Å for $e = 1$ μm. The velocity is now decreasing with time, because friction forces increase as the rim expands.

From the integral of $V = dR/dt \sim t^{-1/4}$ (Eq. (5)), we find that $R(t)$ increases as :

$$R \sim t^{3/4}$$

and

$$\ell(t)/h_0 = h_0 (Re/h_0^2)^{2/3} \sim t^{1/2}$$

3) Our aim, in the present note, is to extend these ideas to an intermediate case : the water film is now lying between a solid and a polymer melt (Fig. 2).

The spreading of a drop between a solid and a viscous polymer for $S = \gamma_{SP} - (\gamma_{SW} + \gamma_{WP}) > 0$, where γ_{ij} are the S/P , S/W and W/P interfacial tensions, has yet been studied [5, 6] : it is found that the drop spreads as in air if $\theta_E^3 < \eta_w/\eta_p$, where η_p is the polymer viscosity, but in the opposite limit, the spreading laws are modified. It has to be noticed that viscoelastic regimes are not expected in the spreading case.

Here we study the inverse mechanism of dewetting, which shows up under partial wetting conditions ($S < 0$). If the water wedge is not too thick ($\theta_E^3 < \eta_w/\eta_p$) the dissipation will also be dominated by water, and the velocity will be still given by equation (1). We focus here on the opposite case, of highly viscous polymers, characterized by a long relaxation time $T_{rep} = \eta/\mu$, where μ now is the plateau modulus. Contrary to the spreading case, we now expect viscoelastic effects : the viscoelastic liquid will behave like a rubber, if the transit time of the rim $t = \ell/V$ is smaller than T_{rep} , and like a liquid in the opposite limit. We describe the simplest rheological model available for an entangled melt in section 2. In section 3, we apply this model, and find a variety of possible regimes for dewetting.

Our study may have some practical applications such as the stability of a lubricant film in polymer extrusion, and may easily be transposed to the case of a water film squeezed between two viscoelastic polymer melts. This may be of some interest for polymer coextrusion.

Last but not least, melts are better controlled than networks, and may be used in model experiments on « elastic » dewetting which are under way [7].

2. Rheological model.

Our polymer melt is made of strongly entangled polymer chains. Let us call N_e (~ 100) the average chemical distance between entanglements points. We also call N the polymerisation

index, and assume $N \gg N_e$. For simplicity, we assume a single (long) relaxation time $T_{\text{rep}} \sim N^3/N_e^2$.

At frequencies ($\omega T_{\text{rep}} > 1$), the melt behaves like a rubber (plateau modulus μ). At low frequencies ($\omega T_{\text{rep}} < 1$), it flows like a liquid (viscosity η_p). With a single relaxation time, the complex elastic modulus $\mu(\omega)$ has the standard form [8]

$$\mu(\omega) = \frac{i\omega\eta_p}{1 + i\omega T_{\text{rep}}} = \mu' + i\mu'' \quad (6)$$

The real part describes the elastic deformation energy associated with displacement u

$$F_{\text{el}}|_m = \mu' (\nabla u)^2. \quad (7)$$

The imaginary part describes the viscous dissipation

$$T\dot{S}|_m = \mu'(\omega) \omega (\nabla u)^2 \quad (8)$$

For $\omega \rightarrow \infty$, $\mu(\omega) \sim \mu = \frac{\eta_p}{T_{\text{rep}}} \sim \frac{kT}{N_e a^3}$.

2.1 DISSIPATION IN THE MELT SURROUNDING THE RIM. — The deformation of the rubber-like liquid around the rim (extension ℓ , thickness h) shown in figure 3, leads to a viscous dissipation (per unit length):

$$T\dot{S}|_p = \frac{\eta_p \omega^2}{1 + \omega^2 T_{\text{rep}}^2} \frac{h^2}{\ell^2} \ell^2 \quad (9)$$

where $\omega = V/\ell$ is the characteristic frequency associated with the passage of the rim, h/ℓ the deformation, and ℓ^2 the area of the distorted polymer region. Equation (9) leads to :

$$T\dot{S}|_p = \eta_p V^2 \frac{h^2}{\ell^2} \quad (\omega T_{\text{rep}} < 1) \quad (9a)$$

$$T\dot{S}|_p = \eta_p \frac{h^2}{T_{\text{rep}}^2} \quad (\omega T_{\text{rep}} > 1). \quad (9b)$$

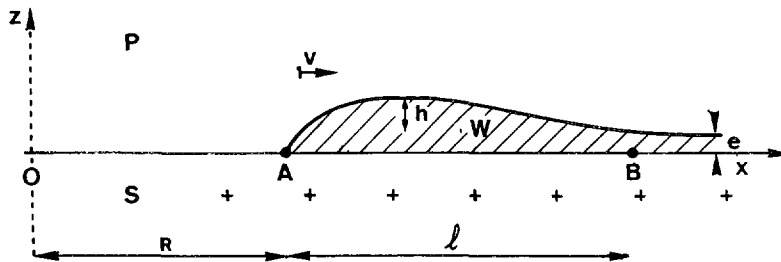


Fig. 3. — Structure of a growing dry patch in a water film W between a solid S and a viscoelastic polymer liquid P. Notice that the rim is more elongated than in air.

The dissipation in the viscous regime ($\omega T_{\text{rep}} < 1$) can be directly calculated in the hydrodynamic model of Huh and Scriven for the movement of a solid/liquid/liquid contact line [9]. The conclusion is the following : if the dynamic contact angle $\theta \sim h/\ell$ is larger than η_w/η_p , the velocity variations inside the polymer volume are of order $V\theta$, and the dissipation is given by

$$T\dot{S}_p \sim \int \eta_p \left(\frac{V\theta}{r} \right)^2 2\pi r dr \sim \eta_p V^2 \theta^2 \text{Ln} \left(\frac{r_{\text{max}}}{r_{\text{min}}} \right) \quad (10)$$

in agreement with equation (9a). If $\theta < \eta_w/\eta_p$, the dissipation in the polymer is no longer given by equation (9a), but the dissipation in the water becomes dominant as soon as $\theta < (\eta_w/\eta_p)^{1/3}$ and $T\dot{S}_p$ is negligible.

2.2 MOTION OF THE RIM. — The rim velocity can be deduced from the transformation of surface energy into viscous dissipation. The dissipation is the sum of a contribution from the melt, and a contribution from the water ; the latter is

$$T\dot{S}_w = \eta_w \frac{V^2}{h^2} h\ell. \quad (11)$$

The balance of viscous losses *versus* surface energy gain is written as

$$T\dot{S}_w + T\dot{S}_p = |S| V. \quad (12)$$

Using equations (9) and (11), this leads to

$$\eta_w V \frac{\ell}{h} + \eta_p \frac{V}{\ell^2 + V^2 T_{\text{rep}}^2} h^2 = |S|. \quad (13)$$

One must also add to equation (13) the conservation of the water collected in the rim. Ignoring numerical factors, this gives

$$\ell h \cong \text{Re}. \quad (14)$$

At this point, we have three unknowns : V , ℓ and h , and two relations (13) and (14). We need another relation between ℓ and h , to be discussed below :

a) In the *rubber regime*, the shape of the rim is imposed by a balance between elastic and surface forces described by equation (2) : this is the required relation. Note that, at the moment of nucleation, the rim size is

$$\ell^* = R^* = e^2/h_0.$$

Thus

$$\ell > e^2/h_0.$$

b) At later times, in the *viscous regime*, the shape of the rim results from an equilibrium between the viscous stress σ_p in the melt, and the pressure in the water. In the incompressible melt, near the rim, the vertical velocity is $V_z \sim Vh/\ell$. The flow is spread over a length ℓ , leading to a stress $\sigma_p \sim \eta_p Vh/\ell^2$. The pressure gradient p/ℓ in the water is given by Stokes' law $p/\ell \cong \eta_w V/h^2$. The balance $\sigma \cong p$ leads to

$$\frac{\ell}{h} = \left(\frac{\eta_p}{\eta_w} \right)^{1/3} \quad (15)$$

Two remarks.

i) Equation (15) corresponds to a minimum of the dissipation.

In the limit, $\omega T_{\text{rep}} < 1$, $T\dot{S}$ is given by

$$T\dot{S} = \left[\eta_w \frac{\ell}{h} + \eta_p \left(\frac{h}{\ell} \right)^2 \right] V^2 \quad (16)$$

Thus $T\dot{S}$ versus ℓ/h is minimum for $\ell/h = (\eta_p/\eta_w)^{1/3}$

ii) A relation similar to (Eq. (15)) was found a long time ago by Taylor for long droplets freely suspended in a viscous fluid in stretching motion, at the point of break up [10].

c) Interpolation form between viscous and elastic limits : we choose, for ℓ/h , the following simple expression

$$\frac{\ell}{h} = \frac{h}{h_0} \frac{VT_{\text{rep}}}{\ell + VT_{\text{rep}}} + \left(\frac{\eta_p}{\eta_w} \right)^{1/3} \frac{\ell}{\ell + VT_{\text{rep}}} \quad (17)$$

which does interpolate between the two limits $\omega T_{\text{rep}} < 1$ (Eq. (15)) and $\omega T_{\text{rep}} > 1$ (Eq. (2)). We are now equipped to solve our dewetting problem.

3. Discussion : rubber and viscous regimes.

The velocity of the rim ($V = dR/dr$) is deduced from equations (13), (14) and (17).

Let us introduce dimensionless variables :

$$u = \frac{VT_{\text{rep}}}{\ell} \quad H = \frac{h}{h_0} \quad H_c = \left(\frac{\eta_p}{\eta_w} \right)^{1/3}, \quad \lambda = \frac{h_0^2}{e}$$

where $h_0 = \mu/|S|$ ($h_0 \sim N_e a \sim 100$ nm, $\lambda \sim 10$ nm for $e = 1$ μm).

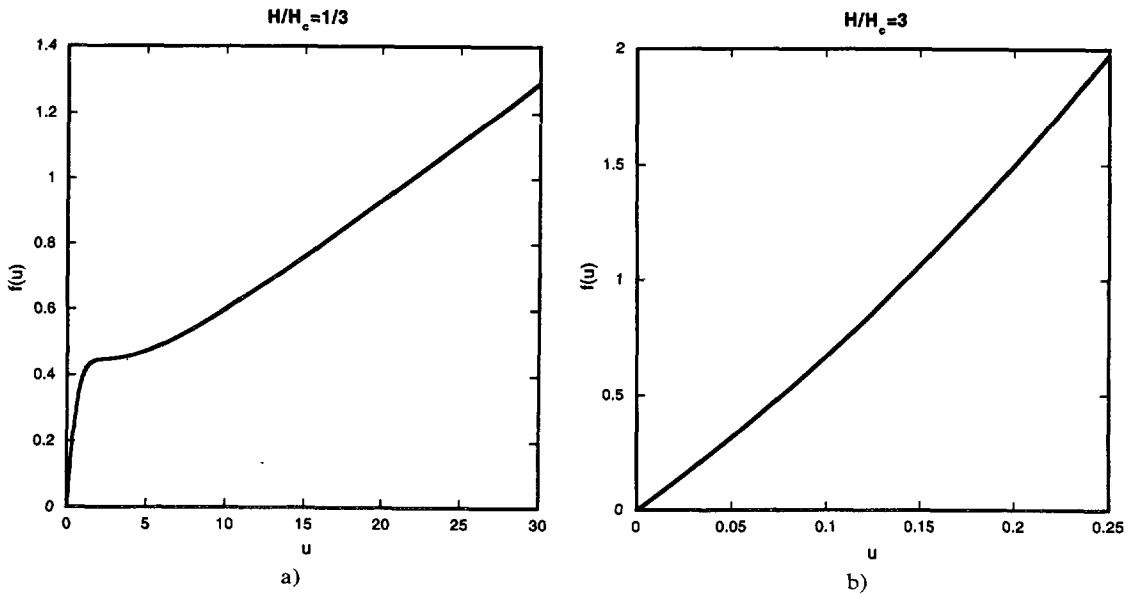


Fig. 4. — Plot of $f(u)$ for a) $\frac{H}{H_c} < 1$; b) $\frac{H}{H_c} > 1$.

From equations (13) and (17), we find

$$f(u) = 1 \quad (18)$$

with

$$f(u) = u \frac{H}{H_c} \left(\frac{H}{H_c} \frac{u}{1+u} + \frac{1}{1+u} \right)^2 + \frac{uH/H_c}{\left(\frac{H}{H_c} \frac{u}{1+u} + \frac{1}{1+u} \right) (1+u^2)}$$

In the viscous regime, $\ell/h = H_c$ (Eq. (15)). In the rubber regime, $\ell/h = H$ (Eq. (2)). Thus the crossover between the two regimes occurs for $H = H_c$. For $H < H_c$, we expect a rubber behaviour (a), and for $H > H_c$, a viscous regime (b). We have plotted $f(u)$ in figures 4a, b, covering the two situations.

3.1 RUBBER LIKE REGIME $H/H_c < 1$. — The solution of $f(u) = 1$ corresponds to $u \gg 1$, as shown in figure 4a, and $f(u) \cong u(H/H_c)^3$ in this limit.

This leads to

$$V = \frac{h_0}{h} \frac{S}{\eta_w} \quad (19)$$

which is exactly the force balance equation found for a rubber (Eq. (3)). h_0/h is derived from the conservation of water, equation (14) and from equation (2) (giving the shape of the rim) :

$$h\ell = \frac{h^3}{h_0} = Re, \quad \text{i.e.} \quad \frac{h}{h_0} = \left(\frac{R}{\lambda} \right)^{1/3} \quad (20)$$

Then, equation (19) becomes

$$V \left(\frac{R}{\lambda} \right)^{1/3} = \frac{S}{\eta_w} = V_w^* \quad (21)$$

and the radius $R(t)$ of the dry region increases as

$$R = (V_w^* t)^{3/4} \lambda^{1/4} \quad (22)$$

We recover the rubber behaviour described by equation (5). This regime holds for $H < H_c$, i.e.,

$$R < R_c = \lambda \frac{\eta_p}{\eta_w} \quad (23)$$

As seen before, $\lambda = h_0^2/e \sim 10$ nm for $e = 1$ μ and $R_c \sim 1$ cm for $\eta_p/\eta_w = 10^6$.

Let us now compare R_c to the radius for nucleation $R^* = e^2/h_0$. We find that $R_c > R^*$ when

$$\frac{\eta_p}{\eta_w} > \left(\frac{e}{h_0} \right)^3 \quad (24)$$

If, and only if, this condition is satisfied, and elastic regime can be seen.

3.2 VISCOUS REGIME $H/H_c > 1$. — For $H/H_c > 1$, $f(u) = 1$ has a root with $u < 1$, as shown in figure 4b, and the solution is simply

$$u \frac{H}{H_c} = 1, \quad (25)$$

$$\text{i.e.,} \quad V = V_w^* \left(\frac{\eta_w}{\eta_p} \right)^{1/3} \quad (26)$$

If we compare this velocity to the dewetting velocity for water in air, given by equation (1) ($V \equiv V_w^* \theta_E \sim \gamma_w / \eta_w \theta_E^3$), we see that for water embedded in polymer, the velocity of dewetting (26) is reduced if

$$\frac{\eta_w}{\eta_p} < \theta_E^3. \quad (27)$$

On the other hand, if $\eta_w / \eta_p > \theta_E^3$, the dissipation in the water wedge becomes dominant, as shown by Huh and Scriven [7], and we go back to the classical description : the rim has a circular shape ($h/\ell \equiv \theta_E$), and the velocity of dewetting is $V = V_w^* \theta_E$, independent of η_p .

4. Concluding remarks.

i) Highly viscous melts, $\eta_w / \eta_p < \theta_E^3$, act like a rubber for the dewetting of a water film, if the radius of the dry patch is less than a threshold value $R_c = \lambda \eta_p / \eta_w$, where $\lambda = h_0^2 / e$. The velocity of dewetting decreases with time as $V \sim t^{-1/4}$. This regime appears only if R_c is larger than the nucleation radius R^* , i.e., if $\eta_p / \eta_w > (e/h_0)^3$.

For larger holes, $R > R_c$, we expect to reach a viscous regime with a velocity constant in time

$$V = V_w^* \left(\frac{\eta_w}{\eta_p} \right)^{1/3}$$

where $V_w^* = |S| / \eta_w$ is the water typical wetting velocity. The steady long « slider » rim in this regime has a certain similarity with the Taylor droplets elongated by highly viscous shear flows.

ii) For less viscous melts, $\eta_w / \eta_p > \theta_E^3$, the velocity of dewetting is not modified by the presence of the polymer ! This θ_E^3 factor in equation (27) is our very surprising result. For a water film deposited on a viscous liquid polymer melt, and exposed to air, the criterion quoted in references [11] for dominance of the polymer dissipation was quite different, namely, $\eta_w / \eta_p < \theta_E$. However, it can be seen directly from the flow fields of wedges in motion calculated by Huh and Scriven [9] that the dissipation in the polymer is dominant only if $\eta_w / \eta_p < \theta_E^3$. We have analysed the consequences of this result for the spreading of a drop between a solid and a viscous polymer [6], and we have again found that for $\theta < (\eta_w / \eta_p)^{1/3}$ the drop spreads just like in air !

iii) It may be worth, meanwhile, to emphasize the difference between our viscoelastic problem (dewetting of water between a solid and a melt), and the problem of unstable polymer films (between a solid and air) studied in reference [12]. In the latter case, the limit of rubber-like behaviour corresponds to quenching of the instability. In our case, we never have quenching.

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