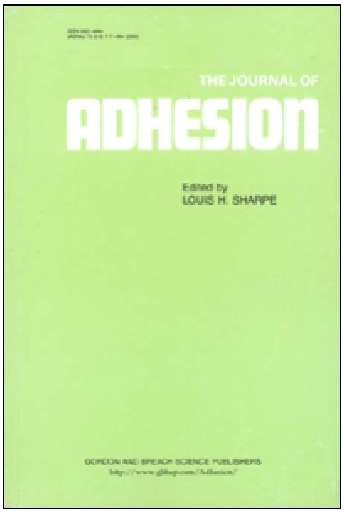

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Adhesion of a Soft Rubber on a Wet Solid*

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We study theoretically the dewetting of a liquid film intercalated between a flat solid and a weakly crosslinked rubber. The rubber is characterised by a static shear modulus, μ_0, a high frequency modulus, $\mu_\infty (\gg \mu_0)$ and a relaxation time, τ.

The film dewets by nucleation and growth of a dry contact zone (radius $R(t)$ at time t) surrounded by a liquid rim collecting the liquid. We expect three regimes:

a) at short times ($R < R_{c_1}$), the rubber behaves like a hard elastic solid ($\mu = \mu_\infty$) and the dissipation is dominated by the liquid rim. We call this *fast elastic dewetting*.
b) at intermediate times ($R_{c_1} < R < R_{c_2}$), the rubber behaves like an ultra-viscous liquid. We call this "*mixed viscous dewetting*" because both components dissipate.
c) at long times ($R > R_{c_2}$) the rubber behaves like a soft solid ($\mu = \mu_0$) and the liquid dissipation is again dominant. We call this *slow elastic dewetting*.

Keywords: Dewetting; viscoelasticity; intercalated thin liquid films; elastomers; adhesion; theory

I. INTRODUCTION

The stability of a liquid film (L) squeezed between a rubber (R) and a solid (S) is controlled by the spreading parameter S

$$S = \gamma_{RS} - (\gamma_{RL} + \gamma_{LS}) \qquad (1)$$

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where the γ_{ij}'s are the rubber/solid (*RS*), rubber/liquid (*RL*) and liquid/solid (*LS*) interfacial tensions. S measures the energy difference between dry and wet solid/rubber contacts. If S is positive, a liquid droplet intercalated between the rubber and the solid will spread (complete wetting) at the S/R interface. In that case, a liquid film is stable. If $S < 0$, the droplet intercalated between the rubber and the solid will not spread (partial wetting) and a flat liquid film is unstable [1]. It is expected to dewet by nucleation and growth of a dry patch (radius $R(t)$ at time t) surrounded by a liquid rim, collecting the rejected liquid.

S is the thermodynamic force which drives the dynamics of dewetting for $S < 0$. The value of S can be derived from the static shape of a liquid droplet intercalated at the R/S interface [2]. The free energy of a drop, F_d, is the sum of interfacial and elastic energies. It can be written (ignoring exact numerical coefficients) as

$$F_d = -S\,A + \mu_0 \left(\frac{H}{R}\right)^2 R^3 \tag{2}$$

where $A \sim R^2$ is the wetted area, μ_0 the shear elastic modulus of the rubber and H the thickness of the drop. The first term in Eq. (2) is the surface free energy of the droplet while the second term corresponds to the elastic energy, U_{el}, of deformation induced in the rubber by the formation of the droplet: a typical elastic deformation, H/R, extends in the rubber volume up to a typical distance R. For $S < 0$, the minimisation of F_d, with the constraint that the volume $\Omega \propto H R^2$ is constant, leads to

$$R = \alpha \frac{H^2}{h_0} \tag{3}$$

where $h_0 = (|S|/\mu_0)$ is a characteristic length (ranging from 100 Å for a hard rubber to 1,000 Å for a soft rubber). Sneddon [3] has calculated the distribution of deformations and stresses in the neighborhood of an axisymmetric crack formed in an infinite elastic medium by the application of an uniform internal pressure. As a droplet standing at a rubber/solid interface can be seen as a adhesive crack at equilibrium between the solid and the rubber, we can deduce the exact elastic energy term of Eq. (2) from his calculations: $U_{el} = (\pi^2/9) EH^2R$. As a consequence, we find that $\alpha = (\pi/6)$.

From the profile observed by optical interferometry we can, therefore, derive h and deduce S (the elastic modulus μ_0 is known) as described in [2].

We have previously calculated [4] the dynamics of removal in the case of a liquid film intercalated between a solid and a *hard* rubber, characterised by a single elastic modulus. Our aim here is to extend this calculation to the case of a viscoelastic rubber. For weakly-cured rubbers, many chains are free, or tied at one and only: the low frequency modulus, μ_0 (related to the network), is small. But the high frequency modulus, μ_∞ (which contains the effect of entangled free chains and of dangling ends), is high. Typically, one can achieve

$$\lambda = \frac{\mu_\infty}{\mu_0} \sim 10 \text{ to } 100$$

if the crosslink density is close to the sol-gel point.

The major assumption we impose, following [6], is that the mechanical relaxation inside the network is described by a single relaxation time, τ (τ can be very large, up to seconds, because the relaxation of tethered chains is exponentially long). The complex modulus, $\mu(\omega)$, as a function of the frequency, ω, is then the following

$$\mu(\omega) = \mu_0 + (\mu_\infty - \mu_0) \frac{i\,\omega\tau}{1 + i\omega\tau} \tag{4}$$

Naively, we would expect two regimes: a hard rubber regime for $\omega\tau > 1$ and a soft rubber regime for $\omega\tau < 1$. In fact, when $\lambda = (\mu_\infty/\mu_0) \gg 1$ we have *three* regimes as shown in [6]:

(i) at very low ω, $\omega\tau < (\mu_0/\mu_\infty)$, $\mu = \mu_0$. we deal with a soft rubber
(ii) when $1 > \omega\tau > (\mu_0/\mu_\infty)$, we can approximate $\mu(\omega) = i\omega\eta_P$. The modulus is purely imaginary: the rubber behaves like a liquid of viscosity η_P, with:

$$\eta_P = (\mu_\infty - \mu_0)\tau \cong \mu_\infty\tau \tag{5}$$

(iii) at high frequencies, $\omega\tau > 1$, we recover a hard rubber ($\mu = \mu_\infty$).

We want to discuss here the consequences of these viscoelastic properties on the dynamics of dewetting for intercalated films. When the dry patch (radius $R(t)$) expands with velocity $V = (dR/dt)$ the rejected liquid is collected into a moving rim (shown in Fig. 2). Near the $S/L/R$ contact line, at distances $x < V\tau$, we are concerned with small spatial scales, or short times, and we have a hard solid. At intermediate distances, $V\tau < x < V\tau\lambda$, we have a liquid, giving a large viscous dissipation. At even higher distances, $x > \lambda V\tau$, we have a soft solid.

In section II, we recall briefly the two extremes of a film intercalated between a solid and:

i) a **hard** rubber, where only the flows in the moving liquid rim participate in the viscous dissipation [4] (Fig. 1a)
ii) an ultra-viscous (not reticulated) **polymer melt** [7]. Here both liquids participate in the viscous dissipation (Fig. 1b).

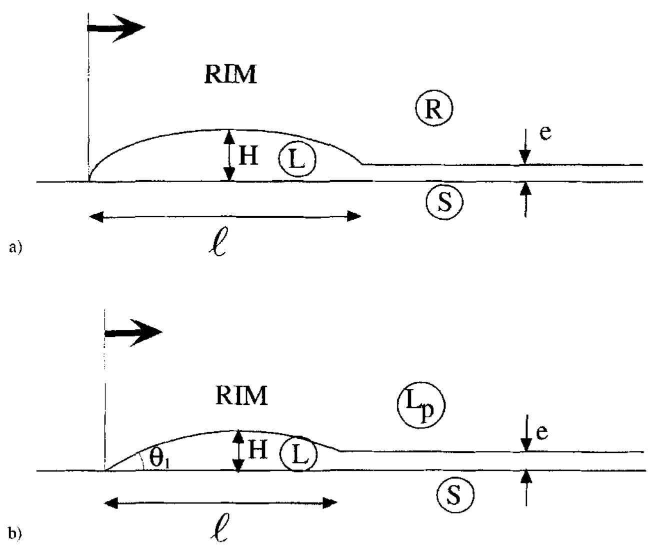

FIGURE 1 Shape of the rim surrounding a growing hole in an intercalated liquid film "L" (thickness e). The arrow shows the direction of motion.

a) between a solid substrate (S) and a semi-infinite **hard** (purely elastic) rubber (R). The rim is a very flat ellipsoid described by its thickness, H, and its length, ℓ.
b) between a solid substrate (S) and a **liquid paste** (L_P). The rim is here circular in shape with a dynamic contact angle θ_1.

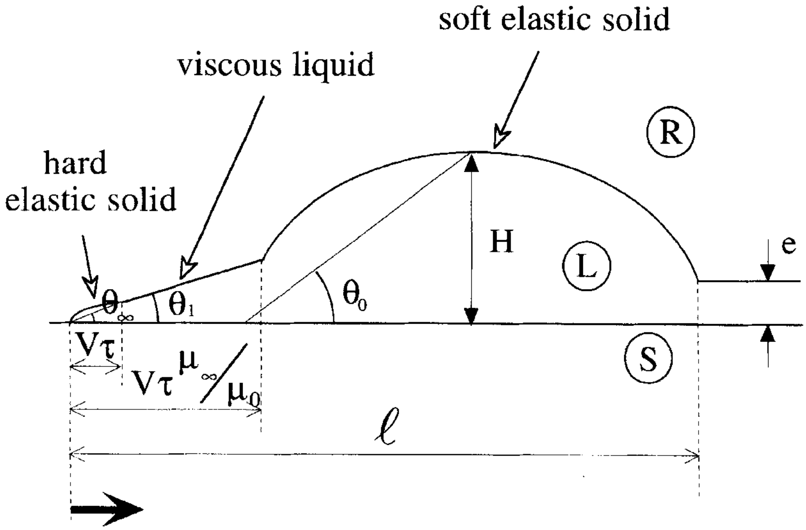

FIGURE 2 Shape of the rim (size ℓ) in the case of a liquid film (L) of thickness, e, intercalated between a solid substrate (S) and a **soft** rubber (R) described by a low frequency modulus, μ_0, a high frequency modulus μ_∞ and one relaxation time, τ. One can distinguish three regions:

(i) near the contact line $x < V\tau$, (R) behaves like a hard rubber and the shape is ellipsoidal;
(ii) for $V\tau < x < V\tau\ (\mu_\infty/\mu_0)$ (R) has a liquid response and the profile is circular;
(iii) $x > V\tau(\mu_\infty/\mu_0)$ (R) has a low frequency response and the profile is elliptical again.

The arrow shows the direction of motion.

In section III, we discuss all three regimes of dewetting for weakly crosslinked rubbers: they behave either like a solid (soft or hard), or like a ultra-viscous liquid (Fig. 2).

II. A REMINDER: FROM HARD RUBBERS TO LIQUID PASTES

As the rim moves (velocity V), and expands (width ℓ), the surrounding rubber is disturbed at a frequency $\omega \cong (V/\ell)$, which decreases as the rim expands. At high frequency, in the early stage of dewetting, the rubber will behave like a hard rubber ($\mu = \mu_\infty$). At intermediate frequencies, it will behave like a liquid. We review here these two limits.

A) Hard Rubber: Elastic Dewetting

Recently one of us studied the dewetting of a liquid film between a solid and a hard rubber characterised by one elastic modulus, μ [4].

As shown in Figure 1, we idealise the rim as a region of width, ℓ, and thickness, H. Our requirement of incompressibility then imposes:

$$R\ell H \propto R^2 e \tag{6}$$

We also assume that the rim has a quasi-equilibrium shape. ℓ is related to H by Eq. (3), which expresses the balance between the Laplace pressure and the elastic stress:

$$\frac{|S|}{H} \propto \mu \frac{H}{\ell} \text{ i.e. } H^2 \propto \ell h \tag{7}$$

where $h = (|S|/\mu)$.

The driving force on the rim is $-S = (\gamma_{RL} + \gamma_{LS}) - \gamma_{RS}$.

The friction restoring force, F_v, is derived following Ref. [5] from the viscous dissipation in the liquid (viscosity η), which is the volume integral of the velocity gradient: $F_v V \propto \eta(V/H)^2 H\ell$

i.e.:

$$F_v \propto \eta \left(\frac{V}{\theta}\right) \tag{8}$$

where $\theta \propto (H/\ell)$ is a dynamic angle. The balance between driving and restoring forces leads to:

$$\eta V \frac{\ell}{H} \propto |S| \tag{9}$$

From Eqs. (6), (7) and (9), one can derive V

$$V \propto V^* \left(\frac{h^2}{e R}\right)^{1/3} \tag{10}$$

where $V^* = (|S|/\eta)$.

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

$$R(t) \propto (V^* t)^{3/4} h^{1/2} e^{-1/4} \tag{11}$$

Finally, the height, H, and the length, ℓ, of the rim should scale as

$$H \propto (R\, e\, h)^{1/3}$$

$$\ell \propto (R\, e)^{2/3}\, h^{-1/3} \tag{12}$$

B) Viscous Paste

We studied in Ref. [7] the case of a liquid film (viscosity η) intercalated between an ultra-viscous polymer liquid (viscosity η_P) and a solid. In the limit $\eta_P/\eta \gg 1$, the viscous dissipation, following Huh and Scriven [8], can be written as

$$F_v V \cong \left[\eta_P \theta^2 + \frac{\eta}{\theta} \right] V^2 \tag{13}$$

where $\theta = (H/\ell)$.

The first term is the dissipation in the viscous polymer. The P/L wall behaves like a solid wall and the velocity field in the polymer is of order $V\theta$. This explains the θ^2 dependence.

The shape of the rim results from a balance between the viscous shear stress, σ_P, in the melt ($\sigma_P \propto \eta_P V(H/\ell^2)$) and the pressure inside the liquid rim, $p = |S|/H$. The pressure gradient, p/ℓ, is also given by the Navier-Stokes equation, $(p/\ell) \propto \eta\,(V/H^2)$. The balance, $\sigma_P = p$, yields

$$\frac{\ell}{H} \propto \left(\frac{\eta_P}{\eta} \right)^{1/3} \tag{14}$$

The rim is circular with a constant dynamic contact angle, $\theta_1 \propto (\eta/\eta_P)^{1/3}$, except at the wedge. One can notice that the elongated shape of the rim corresponds to a minimum of the viscous dissipation, arising for $\theta^3 = (\eta/\eta_p)$.

The balance between driving and friction forces gives:

$$V\left[\eta_P\theta_1^2 + \eta\frac{1}{\theta_1}\right] \cong |S| \tag{15}$$

i.e.

$$V \propto \frac{|S|}{\eta_P^{1/3}\eta^{2/3}} \tag{16}$$

The velocity of dewetting is now constant in time and depends on both viscosities.

III. SOFT RUBBER

We consider now the case of weakly-cured rubbers, with $\lambda = (\mu_\infty/\mu_0) \gg 1$. The rim, moving at velocity V, is represented in Figure 2, and is composed of three domains, if $\ell > V\tau(\mu_\infty/\mu_0)$:

1) Near the contact line, at distances $x < V\tau$,. *i.e.* at high frequency, the response of the rubber is fast and $\mu = \mu_\infty$. In this region the rubber behaves like a pure elastic medium. The tip of the rim near the contact line should have a quasistatic profile imposed by a balance between elastic forces and capillary forces (as for the droplet standing at a solid/rubber interface considered in the Introduction).

$$z = (h_\infty x)^{1/2} \tag{17}$$

with $h_\infty = (|S|/\mu_\infty)$. We set:

$$\theta_\infty = \frac{z}{x}\bigg|_{x=V\tau} = \sqrt{\frac{h_\infty}{V\tau}} \tag{18}$$

2) At distances $V\tau < x < V\tau\ (\mu_\infty/\mu_0)$, the rubber has a liquid response: by analogy with known cases [1,7], as we expect the profile to be dominated by capillary forces only, it should be approximately circular with a contact angle θ_1.
3) At distances $x > V\tau(\mu_\infty/\mu_0)$, the rubber is distorted at very low frequency and the response is elastic again but here with $\mu = \mu_0$:

$$z = (h_0 x)^{1/2} \tag{19}$$

with $h_0 = (|S|/\mu_0)$.

One can define the profile of the soft rubber region by

$$\theta_0 = \frac{H}{\ell} = \frac{h_0}{H} \tag{20}$$

The motion of the rim can then be described by the force balance

$$\eta\left(\frac{1}{\theta_\infty} + \frac{1}{\theta_1} + \frac{1}{\theta_0}\right)V \cong |S| \tag{21}$$

with $\theta_1 \propto (\eta/\eta_P)^{1/3}$.

IV. DISCUSSION

a) Long time limit: $\theta_0 \ll \theta_\infty, \theta_1$
θ_0 decreases as the rim expands, and will dominate the friction when $\theta_0 \ll \theta_\infty$, θ_1. The motion equation then reduces to:

$$V_0 \propto \frac{|S|}{\eta}\frac{h_0}{H} \tag{22}$$

The dynamics are given by Eqs. (10), (11), (12), with $h = h_0$. We call this regime the "soft elastic regime". The condition $\theta_0 < \theta_1$, with

Eq. (6) for the liquid conservation ($H = (Reh_0)^{1/3}$) leads to

$$\theta_0 = \frac{h_0^{2/3}}{(Re)^{1/3}} < \left(\frac{\eta}{\eta_P}\right)^{1/3}$$

i.e.

$$R > R_{c_2} = \frac{h_0^2}{e}\frac{\eta_P}{\eta} \tag{23}$$

b) Intermediate time limit: $\theta_0 > \theta_1$, $\ell > V\tau$
Assume first that $\theta_1 < \theta_\infty$. The motion equation (21) becomes

$$V = V_1 \propto \frac{|S|}{\eta}\left(\frac{\eta}{\eta_P}\right)^{1/3} \tag{24}$$

We call this regime the "mixed viscous regime", because the dissipation takes place both in the rubber and the liquid. One can calculate θ_∞ from Eqs. (18) and (24):

$$\theta_\infty \cong \sqrt{\frac{|S|/\mu_\infty}{(|S|/\eta)(\eta/\eta_P)^{1/3}\tau}} = \theta_1! \tag{25}$$

The viscoelastic tip is characterised by one single angle, θ_1, and Eq. (24) is always valid if $\theta_0 > \theta_1$, $\ell > V\tau$.

One can also calculate the extension of the rim at the crossover, $R = R_{c2}$:

$$\ell \cong \frac{(R_{c_2}e)^{2/3}}{h_0^{1/3}} = V_1\tau\left(\frac{\mu_\infty}{\mu_0}\right) \tag{26}$$

This means that, in the viscous regime, the soft part of the rim is not yet built up. The rim has a circular shape, $\theta = \theta_1$, terminated by a small elastic tongue. The volume conservation is then

$$\ell^2\theta_1 \cong Re \tag{27}$$

c) Short time regime: $\ell < V\tau$
For $\ell < V\tau$ the rim is purely elastic. This is the fast elastic dewetting, described by Eqs. (10), (11), (12) with $h = h_\infty = |S|/\mu_\infty$.

$$V_\infty \propto \frac{|S|}{\eta}\frac{h_\infty}{H} \tag{28}$$

The crossover between regime (b) and (c) is given by $V_\infty = V_1$,

i.e.

$$R = R_{c_1} = \frac{h_\infty^2}{e}\frac{\eta_P}{\eta} \quad \text{and} \quad \ell = \ell_{c_1} = V_1\tau.$$

V. CONCLUSION

The adhesion of a soft rubber on a wet solid should exhibit three regimes.

1) *A fast elastic regime* at short times ($R < R_{c_1}$). The rim has a quasi-elastic shape pictured in Figure 3a. The velocity $V = V_\infty$ is schematically shown in Figure 4.
2) *A mixed viscous regime* at intermediate times ($R_{c_1} < R < R_{c_2}$). Both rubber and liquid participate in the friction force. The shape of the rim is pictured in Figure 3b: it is a circular rim ($\theta = \theta_1$) terminated by a small elastic tongue ($\theta_0 = \theta_1$) of elliptical cross section.
   The velocity is constant ($V = V_1 \sim \eta^{-2/3}$).
3) *A slow elastic regime* at long times ($R > R_{c_2}$). The rim is very flat, elliptical (Fig. 3c) and terminated by a short viscoelastic tail. The velocity $V = V_0$ is pictured in Figure 4.
   Notice that, as the rubber elastic modulus decreases to zero, R_{c_2} becomes infinite and we recover our previous analyses for viscous pastes [7].

The experiments performed on the growth of a contact between a soft rubber (crosslinked poly(dimethylsiloxane)) and a silanated glass, by dewetting of various liquids (water, fluorinated silicone oils) will be published in a separate paper.

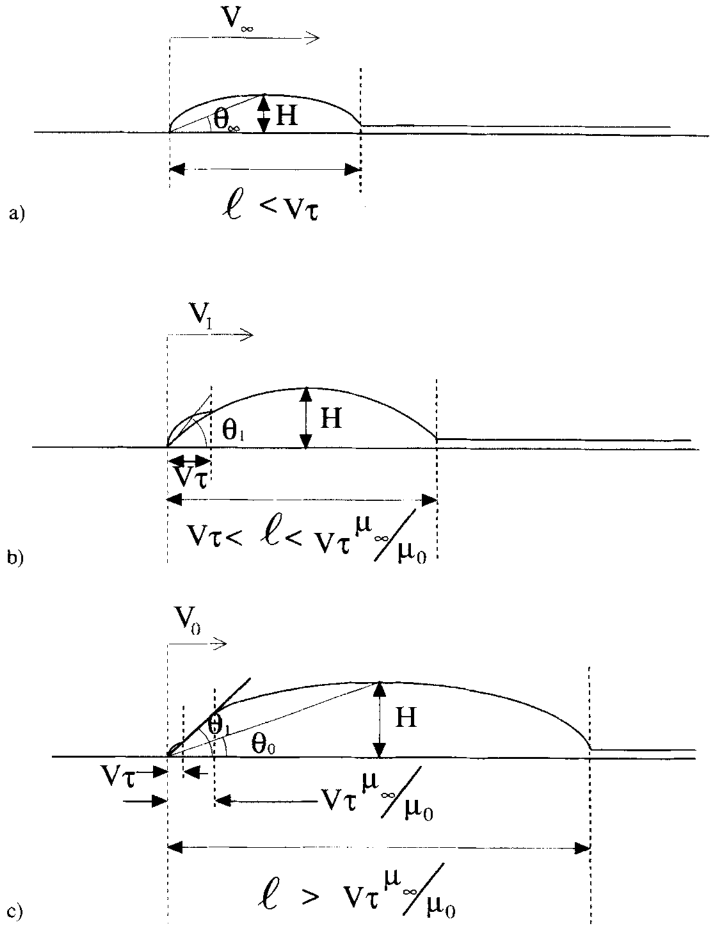

FIGURE 3 Expected evolution of the rim profile *versus* time:

a) at short times, for $R < R_{c_1}$, $\ell < V\tau$ and we have a "hard elastic rim" described by an elliptic profile with $H^2 \propto h_\infty \ell$ and $\theta_\infty = (H/\ell)$.
b) at intermediate times, for $R_{c_1} < R < R_{c_2}$, $V\tau < \ell < V\tau\,(\mu_\infty/\mu_0)$ and we have a circular rim with a small ellipsoidal tongue near the tip (with $\theta_\infty = \theta_1$).
c) at long times, for $R > R_{c_2}, \ell > V\tau\,(\mu_\infty/\mu_0)$ we get an elliptical profile with a small viscoelastic tongue near the tip and $H^2 \propto h_0 \ell$.

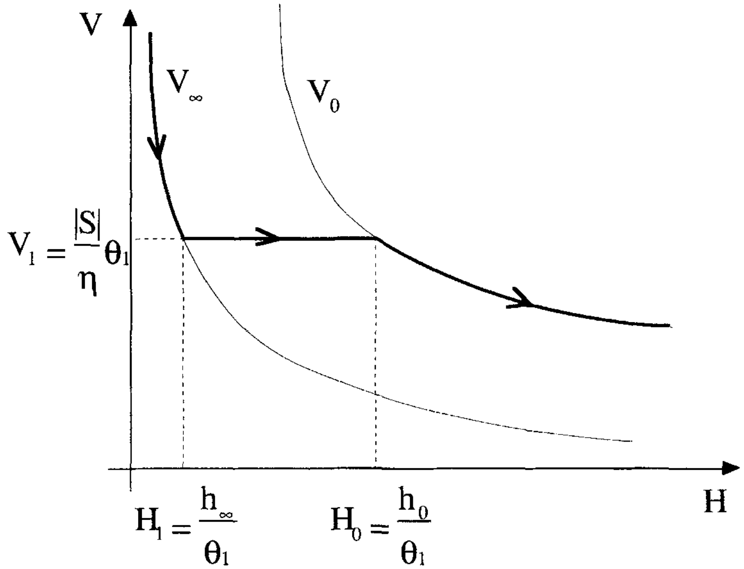

FIGURE 4 Velocity, V, of a growing dry patch as function of the rim thickness, H. We get three regimes:

(i) for $H < H_1$ (*i.e.*, $R < R_{c_1}$ or $\ell < V\tau$), $V = V_\infty$ and decreases as $1/H$. This is the fast elastic regime;

(ii) for $H_1 < H < H_0$ (*i.e.*, $R_{c_1} < R < R_{c_2}$, $V\tau < \ell < V\tau\,(\mu_\infty/\mu_0)$), $V = V_l$ and is constant. This is the mixed viscous regime;

(iii) for $H > H_0$ (*i.e.*, $R > R_{c_2}, \ell > V\tau\,(\mu_\infty/\mu_0)$), $V = V_0$ are decreases again as $1/H$. This is the slow elastic regime.

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