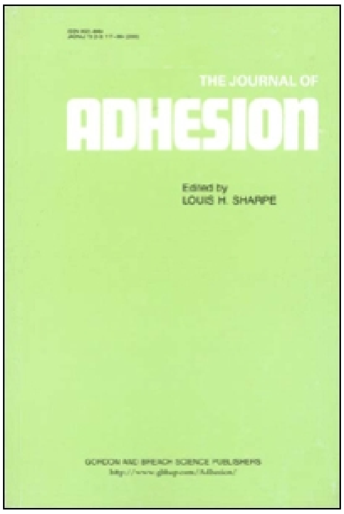
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Dynamics of Fast Dewetting on Model Solid Substrates

C. Andrieu[a]; C. Sykes[a]; F. Brochard[a]
[a] Laboratoire Physico-Chimie des Surfaces et Interfaces, Institut Curie, Paris cedex 05, France

To cite this Article Andrieu, C. , Sykes, C. and Brochard, F.(1996) 'Dynamics of Fast Dewetting on Model Solid Substrates', The Journal of Adhesion, 58: 1, 15 — 24
To link to this Article: DOI: 10.1080/00218469608014397
URL: http://dx.doi.org/10.1080/00218469608014397

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Adhesion, 1996, Vol. 58, pp. 15–24
Reprints available directly from the publisher
Photocopying permitted by license only

© 1996 OPA (Overseas Publishers Association)
Amsterdam B.V. Published in The Netherlands
under license by Gordon and Breach Science
Publishers SA
Printed in Malaysia

Dynamics of Fast Dewetting on Model Solid Substrates*

C. ANDRIEU, C. SYKES and F. BROCHARD**

Laboratoire Physico-Chimie des Surfaces et Interfaces, Institut Curie,
11, rue Pierre et Marie Curie, 75231 Paris cedex 05, France

(Received November 21, 1994; in final form July 11, 1995)

We describe inertial effects in the dewetting of a low viscosity liquid (like water) deposited on hydrophobic solid substrates. The liquid dewets by nucleation and growth of a dry patch. We expect three regimes depending on the liquid viscosity, the film thickness and the static contact angle: (i) purely inertial (similar to the bursting of soap films); (ii) semi inertial, where dissipation occurs in a hydrodynamic boundary layer; (iii) purely viscous, for small contact angles, or very viscous liquids.

KEY WORDS: Wetting; interface; dynamics; dewetting; liquid; solid substrate; hydrodynamics.

Downloaded At: 11:40 22 January 2011

INTRODUCTION

A small liquid drop deposited on a low energy surface forms a spherical cap, with an equilibrium contact angle, θ_e, related to the interfacial tensions by the Young equation:

$$\gamma_{so} = \gamma_{sl} + \gamma \cos \theta_e \qquad (1)$$

where γ, γ_{so} and γ_{sl} are, respectively, the liquid/air, solid/air, and solid/liquid interfacial free energies.

A liquid film deposited on this low energy surface is metastable if the thickness, e, is smaller than a critical thickness, e_c[1]:

$$e_c = 2\kappa^{-1} \sin \frac{\theta_e}{2}, \qquad (2)$$

where $\kappa = \sqrt{\gamma/\rho g}$ is the capillary length, ρ the liquid density, and g the acceleration due to gravity. Let us assume that at time $t = 0$, a hole is created at the centre of the film. A dry patch grows, with a radius $R(t)$. It is surrounded by a liquid rim, that collects the liquid.[1,2] The velocity $V = (dR/dt)$ of the rim may range from several cm per second (for water on hydrophobic solids) to microns per second for polymer melts. For viscous liquids, experiments[1] have shown that V is constant in time and inversely proportional to the viscosity, η, and to θ_e^3. Those results have been interpreted in terms of a simple hydrodynamic picture[2] displayed on Figure 1. Ahead of the dry patch, the liquid forms

---

* One of a Collection of papers honoring Jacques Schultz, the recipient in February 1995 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

** Corresponding author.

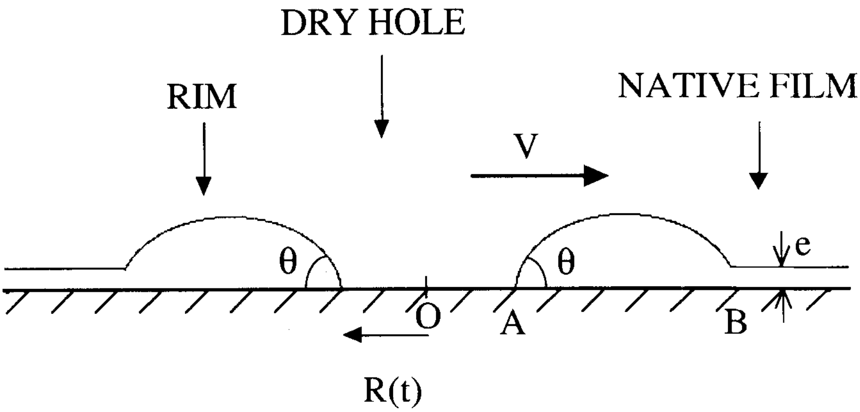


FIGURE 1 Dewetting of a liquid film by nucleation and growth of a dry hole (radius $R(t)$). The liquid is collected into a rim, moving with a velocity $V = (dR/dt)$.

Downloaded At: 11:40 22 January 2011

a rim extending from A to B. For small dynamic contact angles, θ, most of the dissipation is near the edges A and B and nearly all the rim is at constant pressure. The rim is thus (according to Laplace's law) a portion of a circle. This implies that the dynamic angles at point A and at point B are equal. Considering that the contact line in A recedes on the dry solid, and that the contact line in B advances on the liquid film, the motion of the two contact lines, A and B, at the same velocity, V, is ruled by a balance between

(i) non compensated Young force:

$$\begin{aligned} F_A &= \gamma \cos\theta + \gamma_{\text{sl}} - \gamma_{\text{so}} = \gamma(\cos\theta - \cos\theta_e), \\ F_B &= \gamma(1 - \cos\theta) \end{aligned} \tag{3}$$

since at point B the equilibrium contact angle between wedge and film is zero, and the wedge slips on a prewet solid;

(ii) friction force, F_v, from the liquid onto the solid. Let us denote $\zeta(z)$ the profile of the liquid interface; z is the vertical axis and x is the horizontal axis. In the lubrication approximation[3] the local flow velocities, $V_x(z)$, are simply parabolic (Fig. 2a):

$$V_x(z) = \frac{3V}{2\zeta^2}(2\zeta z - z^2), \tag{4}$$

where V is the average of $V_x(z)$ over the liquid thickness, $z = \theta x$:

$$\int_0^\zeta V_x(z)\,dz = V\zeta. \tag{5}$$

The friction force, F_v, from the liquid onto the solid is

$$F_v = \left[\int_{x_{\min}}^{x_{\max}} \eta \frac{\partial V_x}{\partial z}\right]_{z=0} = 3\eta \frac{V}{\theta} \ln \frac{x_{\max}}{x_{\min}}. \tag{6}$$

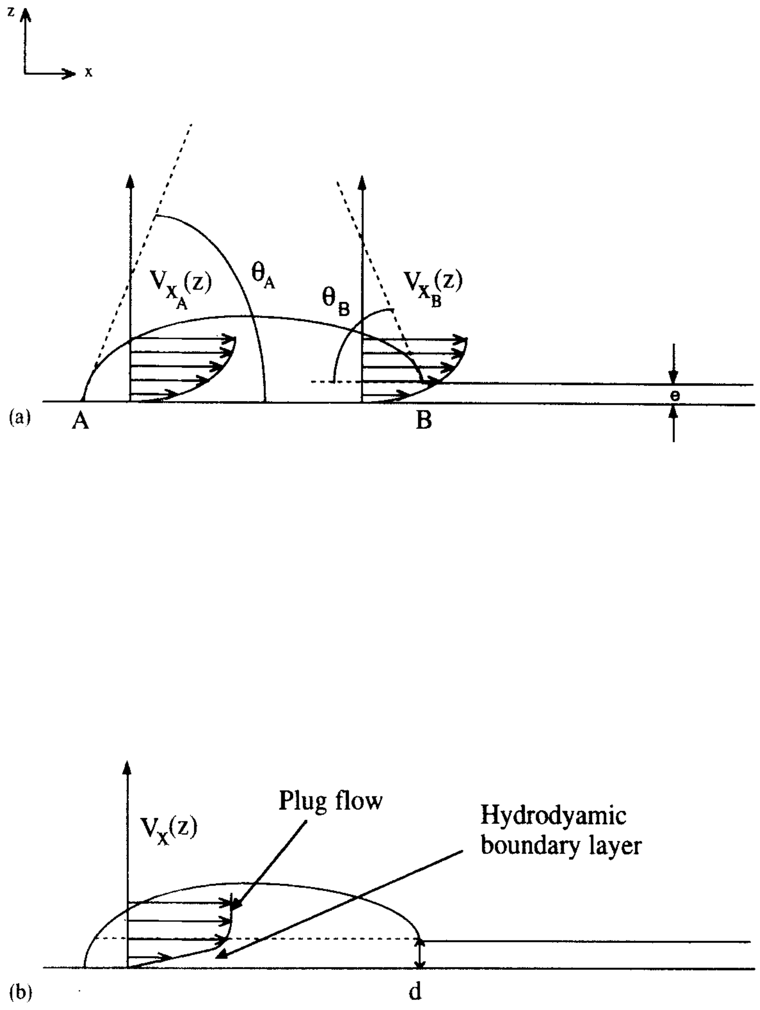


FIGURE 2 Profile $V_x(z)$ of the flow in a rim moving: (a) with small velocity (Poiseuille flow); notice the slippage effect at constant line B, (b) high velocity (plug flow), where the viscous dissipation is located in the hydrodynamic boundary layers.

Downloaded At: 11:40 22 January 2011

The cut off x_{max} in the logarithmic singularity is the width, ℓ, of the rim. x_{min} is comparable to a molecular size for a contact line advancing or receding on a bare solid surface.[3] On the other hand, on a wet substrate covered with a liquid film of thickness e, x_{min} can be large and given by $x_{\mathrm{min}} = (e/\theta)$.[4] x_{min} may also be large for entangled polymers, where slippage effects have been predicted[5] and observed[6] ($x_{\mathrm{min}} = (b/\theta$, where b is the hydrodynamic extrapolation length, of the order of fifty microns for very viscous polymers).[5]

Combining Eqs. (3) and (6) leads to:

$$V_A = \frac{V^*}{6\,\mathrm{ln}_A}\theta(\theta^2 - \theta_e^2),$$
$$V_B = \frac{V^*}{6\,\mathrm{ln}_B}\theta^3, \tag{7}$$

where $V^* = (\gamma/\eta)$ is a typical velocity, $\mathrm{ln}_A = \ln(\ell/a)\theta^2$ ($a =$ molecular length) for a simple Van der Waals liquid[4] and $\mathrm{ln}_B = \ln(\ell/e)\theta$.

If it is assumed that the size of the rim increases only slowly with time, $V_A = V_B = V$, this implies

$$\begin{cases} \theta = \dfrac{\theta_e}{\sqrt{k+1}} \\ V = \dfrac{V^* k}{6(k+1)^{3/2}\,\mathrm{ln}_A}\theta_e^3 \approx V^*\theta_e^3, \quad \text{for } \theta_e \ll 1 \end{cases} \tag{8}$$

where $k = (\mathrm{ln}_A/\mathrm{ln}_B)$. Previously, we assumed implicitly that $\mathrm{ln}_A = \mathrm{ln}_B$, leading to $\theta = (\theta_e/\sqrt{2})$. However, direct measurements of θ in dewetting experiments have shown that indeed $\theta < (\theta_e/\sqrt{2})$.[7] The only case where $\mathrm{ln}_A \approx \mathrm{ln}_B$ is the case of entangled polymers, where $\theta \approx (\theta_e/\sqrt{2})$ has been observed.[1] For simplicity'sake, we shall assume in the following that $\mathrm{ln}_A \approx \mathrm{ln}_B = \mathrm{ln}$.

Equation (8) agrees with the observation listed above on dewetting of viscous liquids and small contact angles. The main conclusion for the viscous regimes are then

i) V is constant in time
ii) $V \approx V^*\theta_e^3$ and
iii) V is the independent of the liquid thickness for $e \ll e_c$, give or take logarithmic corrections. As $e \leq e_c$, the driving force is reduced by gravitational pressures acting between the film and the rim.[8] The overall driving force on the rim is

$$F_d = -\tilde{S} = \gamma + \gamma_{\mathrm{sl}} - \gamma_{\mathrm{so}} - \frac{1}{2}\rho g e^2 = \frac{1}{2}\rho g(e_c^2 - e^2) \tag{9}$$

and the resulting equation of motion becomes

$$V \approx V^*\theta_e^3\left(1 - \left(\frac{e}{e_c}\right)^2\right). \tag{10}$$

Our aim here is to describe what happens for large contact angles and low viscosity liquids, corresponding to large V^*. Inertial effects become important when the Reynolds number, $\mathscr{R}$, becomes large

$$\mathscr{R} = \frac{\rho V \ell}{\eta} > 1. \tag{11}$$

For $V = 1$ cm/sec, $\eta/\rho = 10^{-3}\,\mathrm{cm}^2\mathrm{s}^{-1}$, and $\ell = 1$ mm, this leads to $\mathscr{R} = 100$.

Downloaded At: 11:40 22 January 2011

PURE INERTIAL REGIME

When viscous effects are negligible, the dewetting process becomes very similar to the rupture of soap films discussed by Dupré, Frankel and Mysels.[9] The motion of the rim is now ruled by a momentum balance:

$$\frac{dP}{dt}d\Omega = F_d ds, \tag{12}$$

where $d\Omega$ is the sector angle of the dry hole and ds the curved abscissa; P is the momentum of the moving rim (per unit angle) and $(ds/d\Omega) = R$. From the mass conservation equation, we find, $P = (MV/2\pi) = (1/2)R^2 Ve\rho$ (M is the total mass of the rim). Assuming motion at constant velocity, Eq. (12) leads to

$$V^2 = \frac{|\tilde{S}|}{\rho e}. \tag{13}$$

Equation (13) can also be derived from the transfer of surface energy $E_s = -\tilde{S}\mathscr{A}$, where $\mathscr{A}$ is the hole surface, into kinetic energy, E_c

$$E_c = \int \frac{dP}{dt} V dt = V^2 \int dm = MV^2. \tag{14}$$

The energy balance, with $M = \rho \mathscr{A} e$, also leads to $V^2 = (|\tilde{S}|/\rho e)$. It can be noted that E_c is not equal to $(1/2)MV^2$ because the mass of the rim increases with time. This factor of 2 has given rise to lengthy discussions regarding the rupture of soap films.

We have indeed observed the law $V \approx e^{-(1/2)}$ using pure water dewetting on a polymeric substrate. In order to attach the metastable film, we created a wettable ring by chemical treatment with sulfochromic acid (see photograph of Fig. 3a). The film of water was then scraped on the surface and kept attached by the ring. The hole was nucleated by blowing air in the middle of the liquid film. The velocity of dewetting was followed by a video camera and measured by image processing. The thickness of the film was monitored with an accuracy of $\Delta e \cong 10\,\mu\text{m}$ by a technique using two parallel rods, one of which was bent at one end: the liquid-air interface was detected when it came in contact with the rod, forming a meniscus; when this bent rod touched the solid-liquid interface, the two rods ceased to be parallel and this was detected by projecting on a screen. This method is described in more detail in Ref. 10. The experimental curve of the velocity *versus* thickness is shown in Figure 3(b) and demonstrates the $e^{1/2}$ divergence with thickness expected theoretically.

VISCOINERTIAL REGIME

Between the pure viscous and pure inertial regimes, one expects a mixed regime controlled by hydrodynamic boundary layers (Fig. 2b). If the rim of width ℓ moves at velocity V, the shear flow penetrates the liquid into a region of thickness d, given by the

Downloaded At: 11:40 22 January 2011

diffusion equation

$$d=\sqrt{\frac{\eta}{\rho}t} \tag{15}$$

where $t=(\ell/V)$ is time the rim takes to recede on a length ℓ.

The friction force of the liquid on the solid substrate (disregarding exact numerical coefficients) is

$$F_{vi}\cong\int\eta\frac{V}{d}\,dx\cong\eta\frac{V}{d}\ell. \tag{16}$$

The balance of driving and viscous force leads to

$$\eta^{1/2}\rho^{1/2}V^{2/3}\ell^{1/2}\cong|\tilde{S}|. \tag{17}$$

This equation must be supplemented by the mass conservation equation

$$\ell\cong\sqrt{R\frac{e}{\theta_e}}. \tag{18}$$

Downloaded At: 11:40 22 January 2011

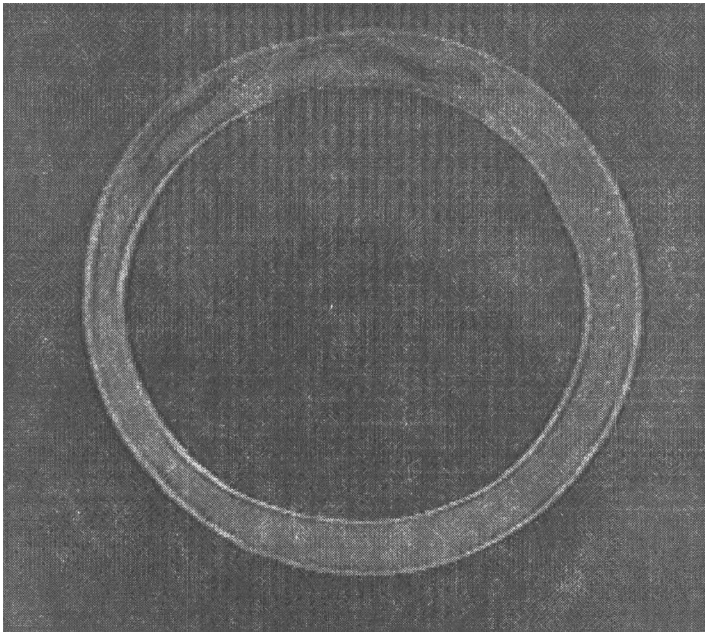

(a)

FIGURE 3 Dewetting of water on a PET (polyethyleneterephthalate) substrate. (a) wettable ring to maintain the metastable water film; (b) velocity of dewetting *versus* film thickness. The line represents the theoretical curve $V=\sqrt{\phi(\tilde{S}/\rho e)}$ where ϕ is a constant found to be equal to 0.1.

Downloaded At: 11:40 22 January 2011

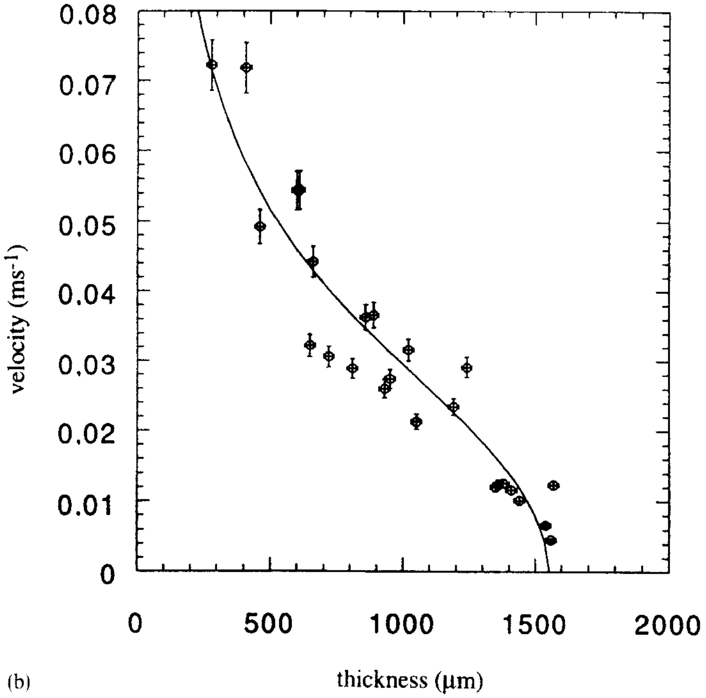


FIGURE 3 (*Continued*).

Equations (17) and (18) lead to the following growth law for the hole

$$R = \frac{|\tilde{S}|^{4/7}}{(\eta\rho)^{2/7}}\left(\frac{\theta_e}{e}\right)^{1/7} t^{6/7}. \tag{19}$$

The velocity of dewetting is now a slowly decreasing function of time.

Remark

In the fast-time regime, one should also include the molecular dissipation process near the contact line formulated by Blake.[11] The total viscous force can be written as

$$F_v = \left(6\eta\frac{\ln}{\theta} + C + \eta\frac{\ell}{d}\right)V, \tag{20}$$

where the fist term is the wedge contrbution, the second term is the molecular jump friction ($C = (W/k\lambda^3)\exp(W/kT)$, where W is the activation energy for hopping, λ the distance between hopping sites and k a jump freqüency) and the last term is the boundary layer friction, which becomes dominant when $(\ell/d) \gg 1$.

Downloaded At: 11:40 22 January 2011

DISCUSSION

Summary of Different Regimes

The motion of the rim can generally be written as

$$\frac{dP}{dt} = |\tilde{S}| - F_v \tag{21}$$

where $\tilde{S}$ (Eq. (9)) is the driving force, F_v (Eq. (20)) is the friction force, and $(dP/dt) = \rho e V^2$ is the rate of change of momentum. The crossover between inertial and viscous regimes $(\ell/d \ll 1)$ corresponds to $F_v(V = \sqrt{|\tilde{S}|/\rho e} = \tilde{S}$ or to a viscosity given by

$$\eta^2 = \rho e \tilde{S} \frac{\theta^2}{\ln^2}. \tag{22}$$

For $\rho = 1$, $e = 10^{-1}$, $\tilde{S} = 50$, $\theta \approx 1$, and $\ln \approx 10$, this leads $\eta \approx 10\,\text{cp}$.

The crossover between inertial and viscoinertial regimes $(\ell/d \gg 1)$ is given by $\tilde{S} = F_{vi}(\sqrt{|\tilde{S}|/\rho e})$, *i.e.*

$$\ell'_c = \tilde{S}^{1/2} \frac{e^{3/2}}{\eta} \rho^{1/2}. \tag{23}$$

The crossover between viscous and viscoinertial regimes occurs when $F_{VI} \cong F_V = S$ and is given by $(\ell/d) = (\ln/\theta)$, *i.e.*

$$\ell_c = \eta^2 \frac{\ln^3}{\rho \theta^3 |\tilde{S}|}. \tag{24}$$

Ultimately the different regimes are controlled by two parameters, for instance, the length of the rim, ℓ, and the viscosity, η. This is shown in Figure 4 using reduced co-ordinates $L = (\ell/e)$ (width of rim divided by native film thickness) *versus* $X = (\eta^2/\rho e S) = (V_i^2/V^{*2})$, where V_i is the inertial velocity and $V^* = (S/\eta)$ is a capillary typical velocity.

The inertial regime can only be observed with low viscosity liquids, such as water on hydrophobic surfaces, using relatively thick films or selecting large contact angles. The viscoinertial regime shows up more commonly with usual liquids. If we choose $e = 100\,\mu\text{m}$, $\eta = 5\,\text{cP}$, $\rho = 1$, $S = 50\,\text{mN/m}$, one finds $\ell_c \approx 5$. But it is difficult to prove its existence because

i) $V(t) \cong t^{-(1/7)}$ is almost constant
ii) $V(e) \cong e^{-(1/6)}$ is a slow decreasing function of thickness.

Molecular Friction

Molecular processes near the contact line may become important at large contact angles. However, we think that boundary layers are primary influences in fast dewetting.

Downloaded At: 11:40 22 January 2011

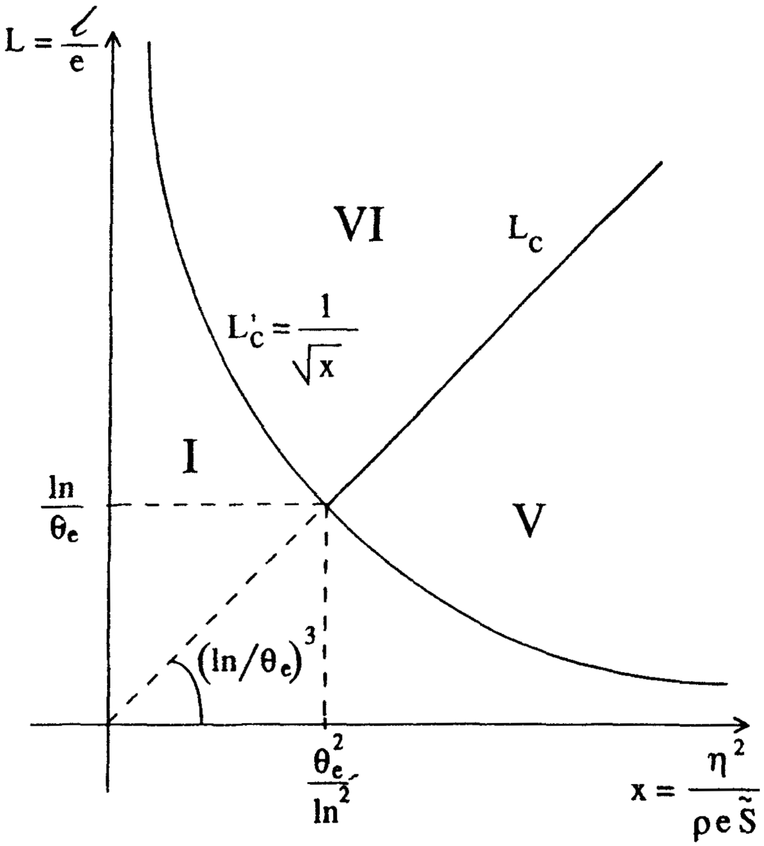


FIGURE 4 The three regimes of dewetting *I* (inertial), *V* (viscous), and *VI* (viscoinertial) (in reduced co-ordinates $L = (\ell/e)$ and $X = \eta^2/\rho e|\tilde{S}|$).

Comparison with Other Situations

Inertial effects are also important for the pulling out of a liquid film from a liquid bath. Inertial and boundary layer effects have also been predicted and observed[12] for this case.

Acknowledgements

We thank William Birch and Francis Sykes for reviewing the manuscript.

References

1. C. Redon, F. Brochard and F. Rondelez, *Phys. Rev. Lett.*, **66**, 175 (1991).
2. P. G. de Gennes, *C.R. Acad. Sci. (Paris)*, **303 II**, 1275 (1986). F. Brochard, J. M. Di Meglio and D Quéré. *C.R. Acad. Sci. (Paris)*, **304 II**, 553 (1987).
3. F. Brochard and P. G. de Gennes, *Adv. in Coll. and Interf. Sci.*, **39**, 1–11 (1992).
4. J. F. Joanny, Thesis, University of Paris, VI (1985).

5. P. G. de Gennes, *C. R. Acad. Sci.*, **308 II,** 1401 (1989).
6. C. Redon, J. B. Brzoska, F. Brochard, *Macromolecules*, **27**, 468 (1994). K. Migler, H. Hervet, L. Léger, *Phys. Rev. Lett.*, **70,** 287 (1993).
7. C. Andrieu, Thesis, University of Paris, VI (1995).
8. F. Brochard, C. Redon and F. Rondelez, *C.R. Acad. Sci.*, **306 II,** 1143 (1988).
9. A. Dupré, *Ann. Chem. Phys.*, **11,** 4 (1867).
   S. Frankel, K. J. Mysels, *J. Phys. Chem.*, **73,** 3028 (1969).
10. C. Sykes, C. Andrieu, V. Detappe and S. Deniau, *J. of Phys III France*, **4,** 775–781 (1994).
11. T. D. Blake and J. M. Haynes, *J. Coll. Interf. Sci.*, **30,** 421 (1969).
12. A. de Ryck and D. Quéré, *Euro. Phys. Lett.*, **25,** 187 (1994).

Downloaded At: 11:40 22 January 2011