PREDICTING THE DYNAMICS OF DEWETTING

Terence D. Blake and Joel De Coninck
Laboratory of Surface and Interface Physics, University of Mons, 700 Mons, Belgium

Presented at the 16th International Coating Science and Technology Symposium,
September 9-12, 2012, Midtown Atlanta, GA[1]

The dewetting of a solid by a liquid is an everyday phenomenon and key to many industrial processes, from mineral flotation and lithography to lubrication and microfluidics. It plays a special role in wetting-directed patch coating [1] (Fig. 1), which is the main motivation for the work presented here. In this process, the substrate is first patterned with areas of significantly different wettability. The prepared substrate is then over-coated with the appropriate functional layer, which subsequently dewets areas of poor wettability and retreats to areas of good wettability. Dewetting may occur naturally, or require initiation. The coating is then set, dried or cured. Various strategies can be employed to create the wettability differential, such as printing a wettable surface with a poorly wettable mask, or modifying a poorly wettable substrate using a laser or an oxidising plasma to create wettable islands in the desired pattern. The whole process can be done sequentially, in-line, from roll-to-roll, with the speed dictated primarily by the dewetting rate. However, although dewetting has been the subject of research over several decades, there remain significant gaps in our ability to model dewetting in sufficient detail to predict the speed at which a given liquid can be made to dewet a given solid. Here, we re-examine the problem, making use of existing models, but stressing the potential importance of contact-line friction [2]. The models are highly simplified and have well-known limitations; nevertheless, they capture much of the underlying physics. The approach may also be relevant to predicting air entrainment in coating, as the limiting speeds of dewetting and coating are both the consequence of dynamic wetting transitions.

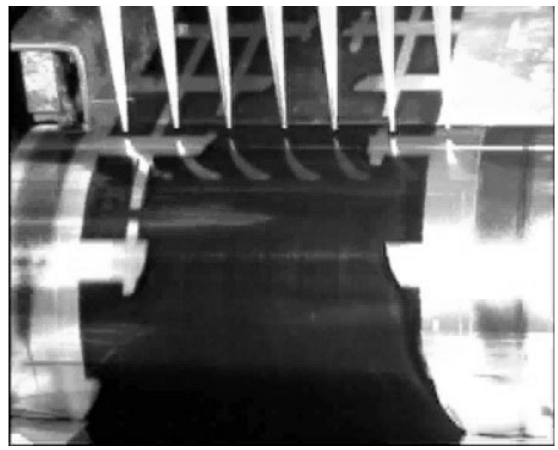

Fig. 1. Wetting-directed patch coating [1].

Many previous studies of dewetting have focussed on the point rupture and dewetting of thin, metastable liquid films previously applied to partially wetted surfaces. In such cases, experiment has shown that following rupture a nominally dry, circular hole develops and grows at a constant radial speed [3]. The entire process is driven by the surface free energy released by the creation of new solid-vapour (SV) interface and the simultaneous loss of equal areas of liquid-vapour (LV) and solid-liquid (SL) interface, i.e. $-\gamma_{SV} + \gamma_{LV} + \gamma_{SL} = \gamma_{LV}(1 - \cos\theta^0)$ where γ_{SV}, γ_{LV} and γ_{SL} are the respective interfacial tensions and θ^0 is the equilibrium contact angle. A characteristic feature of this type of dewetting is that the liquid from the film collects within a narrow rim or bead at the edge of the expanding hole. This bead exhibits a constant receding dynamic contact angle θ_D. Moreover, all the flow is within the bead and the capillary wave at its leading edge, while the remainder of the film is undisturbed. In order to model this, therefore, one need only consider dissipation within the bead, in particular that at the receding contact line and the advancing capillary wave.

[1] Unpublished. ISCST shall not be responsible for statements or opinions contained in papers or printed in its publications.

In the case we examine here, which is more relevant to web coating, the behaviour is rather different. Consider a dip coating process in which a partially wetted web is pulled vertically from a pool of liquid at velocity U_{web} [4]. As the rate of withdrawal is increased, θ_D falls steadily towards zero until, at some critical velocity U_{crit}, a dynamic wetting transition occurs and liquid begins to be entrained by the moving solid, i.e. the liquid coats the solid. For a useful coating to be made, the coating speed must be sufficiently fast to maintain the film until it is set, dried or cured. What interests us here, however, are the conditions that determine the onset of liquid entrainment, i.e. the point at which the withdrawal speed exceeds the rate of dewetting.

On a rectilinear web (Fig. 2), this dynamic wetting transition is characterised by the formation of a serrated contact line, each straight-line section of which is slanted at an angle ϕ to the direction of withdrawal, such that the velocity of the receding contact line normal to itself remains constant at $U_{crit} = U_{web} \cos\phi$ [4]. As the speed is changed, ϕ constantly adjusts to maintain this relationship. At sufficiently high speeds, rivulets are entrained from the trailing vertices. Something similar is also seen at the trailing edge of a liquid drop run-running down a partially wetted surface [5]. Crucially, the whole film drains under gravity and no significant bead is formed below the receding contact line. As a result, the rate of dewetting is controlled entirely by the dynamics of the contact line and we need consider energy dissipation in this region only. Since the same driving force is available, one might immediately anticipate a higher dewetting speed and a smaller dynamic contact angle than when a rim is present. Furthermore, experience shows that gravitational drainage is not a prerequisite for the occurrence of serrated contact lines. For example they also characterise the onset of air entrainment in liquid coating processes, irrespective of orientation [6], suggesting a common mechanism. More significantly for our purpose here, they are seen during wetting-directed patch coating, as shown in Fig. 1. Thus, it would seem that provided the geometry of the system is favourable, serrated contact lines are the norm once critical wetting or dewetting speeds are exceeded.

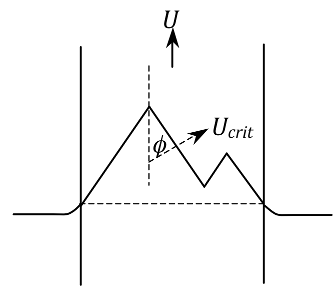

Fig. 2.

So, can we predict U_{crit} under these conditions? It was initially thought that the dynamic receding contact angle θ_{crit} at U_{crit} was close to zero, but this does not seem to be the general case. As U is increased and θ_D decreases, the viscous stress within the narrowing wedge of liquid of shear viscosity η_L must eventually exceed the opposing surface tension at some non-zero meniscus slope angle, leading to liquid entrainment at some critical capillary number $Ca_{crit} = \eta_L U_{crit} / \gamma_{LV}$. The question then is what precisely determines U_{crit} for any given system? In particular, is this limit affected by sources of dissipation other than simple viscous flow?

Another important characteristic of a dynamic wetting transition between steady dewetting and liquid entrainment is the appearance of a visible inflection on the liquid meniscus [7] (Fig. 3). This has lead some to conclude that even if the microscopic contact angle at U_{crit} is not zero, the apparent contact angle made by extrapolating the outer liquid meniscus is indeed zero, and to use this criterion to estimate U_{crit}. If this were always the case, one might expect the film, once entrained, to extend indefinitely and coat the solid surface completely. Such behaviour is seen in capillary flow. However, the formation of a serrated contact line does not seem

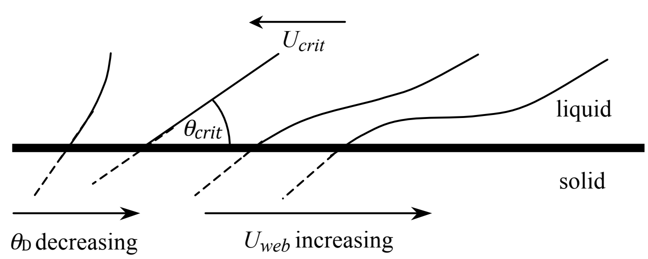

Fig. 3. Dynamic wetting transition.

consistent with a sudden divergence from steady wetting to complete entrainment. The way in which the inclination angle ϕ continuously adjusts to maintain a constant contact-line velocity implies a steady state, with a dynamic balance between surface tension and viscous forces.

Here, we propose that such a balance is achieved when the meniscus slope resulting from viscous bending of the interface equals the local dynamic contact angle due to contact-line friction. So long as the meniscus slope remains greater than or equal to the dynamic angle at the contact line, an inflection is avoided. Only if the meniscus slope and the local angle fall below some critical value will viscous dissipation become dominant, creating an inflection and triggering separation of the contact line from the bulk meniscus. This is illustrated schematically in Fig. 2. The energy incentive for the balance to be maintained arises from the cost of generating additional non-equilibrium LV and SL interface at the expense of SV interface. Provided the contact line can orient in such a direction as to avoid this penalty, it will do so. Along the slanted sections, the balance will therefore be self-regulating at $U = U_{crit}$ with $\theta_{\mathrm{D}} = \theta_{crit}$. At the trailing vertices, however, the mechanism must fail and liquid will be entrained.

Based on this idea of a balance between viscous and surface forces, it should be possible to estimate θ_{crit} and U_{crit} by writing expressions for θ_{D} as a function of wetting velocity U for both viscous bending and contact line friction and solving for θ_{crit}. For the former we can use an expression due to de Gennes [3]:

$$U = \gamma_{LV}(\cos\theta^0 - \cos\theta_{\mathrm{D}})\theta_{\mathrm{D}} / 3\eta_L \ln l \ , \tag{1}$$

were l is the ratio of appropriately chosen macroscopic and microscopic length scales. For the contact-line friction we can use the molecular-kinetic theory written in its simplified linear form [8,9]:

$$U = \gamma_{LV}(\cos\theta^0 - \cos\theta_{\mathrm{D}}) / \zeta \, , \tag{2}$$

where ζ is the coefficient of contact line friction. These equations have a solution at

$$\theta_{crit} = 3\eta_L \ln l_A / \zeta, \ \ U_{crit} = \gamma_{LV}[\cos\theta_{\mathrm{D}} - \cos\theta^0]/\zeta. \tag{3}$$

The solution exists only if the dissipation due to contact-line friction initially exceeds that for viscous bending as the dewetting velocity is increased from zero, i.e. $\zeta > 3\eta_L \ln l_A / \theta^0$. Under these conditions, the contact angle will be determined by contact-line friction until the capillary number is sufficiently high for viscous effects to reduce the meniscus slope angle to a lower value. The higher the friction relative to the viscosity, the smaller this angle will be. For solutions giving angles $\theta_{\mathrm{D}} > \theta^0/\sqrt{3}$, behaviour will subsequently be described by Eq. (1) with θ_{crit} at $\theta^0/\sqrt{3}$ (assuming Eq. (2) holds). However, for sufficiently high friction, $\theta_{\mathrm{D}} < \theta^0/\sqrt{3}$ and a dynamic balance will be necessary to avoid entrainment. Graphical solutions to Eqs. (1) and (2) are illustrated in Fig. 4 for increasing values of contact-line friction, taking $\ln l$ = 10 and using values of γ_L = 68 mN/m, θ^0 = 80° and η_L = 23 mPas, representative of the aqueous system studied by Blake and Ruschak [4]. Dewetting velocities are shown as negative. If these arguments are correct, Eq. (3) can be used to estimate θ_{crit} and U_{crit} directly. Figs. 5 and 6 illustrate the results obtained using the same values of γ_L, η_L, θ^0 and $\ln l$ as in Fig. 3 and increasing values of ζ expressed as multiples of η_L up

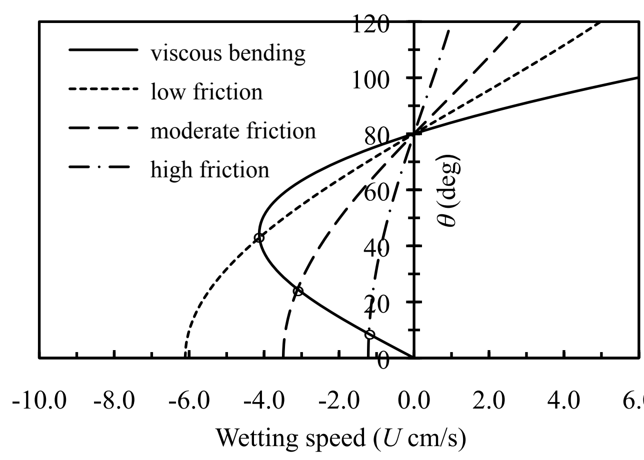

Fig. 4. Graphical solutions to Eqs. (1) & (2).

to 1000. For many aqueous systems θ_D is a very steep function of U and ζ/η_L can be as great as 10^2 – 10^3 [10]; θ_{crit} should therefore be small, as observed by Blake and Ruschak [4]. For the silicone oils on fluorinated surfaces frequently used in dewetting experiments [3,5], ζ/η_L is much smaller (~40) [10]; θ_{crit} is therefore larger.

One can readily extend the same arguments and calculations to the complimentary problem of predicting the onset of air entrainment, for which the same saw-tooth phenomena and inflection behaviour are observed experimentally [6]. Since the viscosity of air is very low (~18 µPa.s), then for reasonable choices of ζ and ln$l$, θ_{crit} (measured through the air) is only about 1˚. This is entirely consistent with the usual observation that the critical advancing contact angle for air entrainment is close to 180˚.

To conclude, the above analysis shows how contact-line friction may play an important role in determining the dynamics of dewetting. There is no doubt that the approach could be markedly improved, for example by using the fully integrated hydrodynamic model of Shikhmurzaev [11]. Opportunities also exist for computational fluid mechanics. Meanwhile, however, we suggest that since serrated contact lines are seen in wetting-directed patch coating, Eq. (3) is used to estimate dewetting speeds for this application.

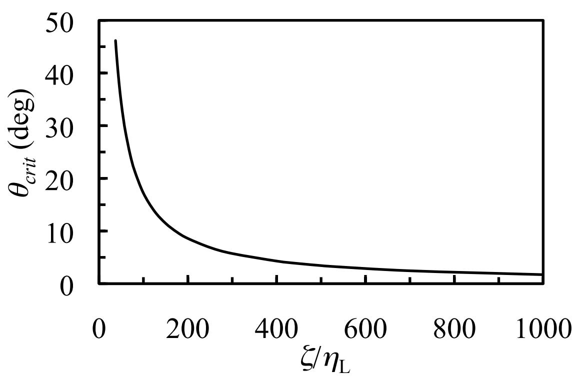

Fig. 5.

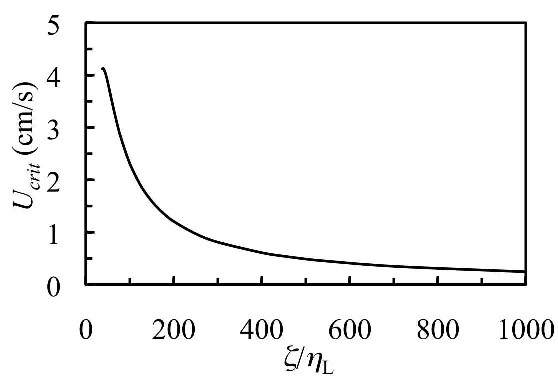

Fig. 6

References

1. C.L. Bower, E.A. Simister, E. Bonnist, K. Paul, N. Pightling, T.D. Blake, *AIChE J.* **53**, 1644–1657 (2007).
2. E. Bertrand, T.D. Blake and J. De Coninck, *Colloids Surfaces A* **369**, 141-147 (2010).
3. C. Redon, F. Brochard-Wyart, F. Rondelez, *Phys. Rev. Lett.* **66**, 715-718 (1991).
4. T.D. Blake, K.J. Ruschak, *Nature* **282**, 489-491 (1979).
5. T. Podgorski, J.M. Flesselles, L. Limat, *Phys. Rev. Lett.* **87**, 036102-1-4 (2001).
6. T.D. Blake, K.J. Ruschak, in P.M. Schweizer, S.F. Kistler (Eds.), *Liquid Film Coating* (Chapman & Hall, London, 1997), 63-97.
7. J.G. Petrov, R.V. Sedev, *Colloids Surfaces* **13**, 313-322 (1985).
8. T.D. Blake, J.M. Haynes, *J. Colloid Interface Sci.* **30**, 421-423 (1969).
9. T.D. Blake, in J.C. Berg (Ed.), *Wettability* (Marcel Dekker, New York, 1993), 251-309.
10. T.D. Blake, *J. Colloid Interface Sci.* **299**, 1-13 (2006).
11 Y.D. Shikhmurzaev, *Int. J. Multiphase Flow* **19**, 589-610 (1993).