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P. G. de Gennes

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# I

## Geography and explorations

The borders between great empires are often populated by the most interesting ethnic groups. Similarly, the interfaces between two forms of bulk matter are responsible for some of the most unexpected actions. Of course, the border is sometimes frozen (the great Chinese wall). But in many areas, the overlap region is *mobile*, *diffuse*, and *active* (the Middle East border of the Roman empire; disputed states between Austria and the Russians, or the Italians, ...).

At a certain naive level, these distinctions can be transposed to physical interfaces between two different forms of matter.

(1) The hard frozen surfaces of metals, of ionic solids, or of semiconductors can be studied under conditions of high vacuum: this allows us to probe them – using electron beams, or other radiations which extract electrons from the surfaces; or even beams of neutral atoms. The net result is, in our days, a highly sophisticated knowledge of these sharp robust fortifications.

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(2) The soft interfaces built from liquids, from polymers, from organic solids, or from detergents are much harder to probe. High vacuum is usually not acceptable. And even if it is, the probing beams can damage the interface. For many centuries, the main information on soft interfaces came from *mechanical* studies: adhesion, slippage, wear, ... During the last fifty years, *electrical* properties have also been helpful – in particular for the electric ‘double layers’ at the contact region between water and a solid.

More recently, a number of new tools became available:

(a) *Reflectance techniques*, using short-wavelength radiations such as X rays or neutrons.

(b) *Atomic force microscopes*, which can be used even in the presence of a liquid.

(c) ‘*Environmental*’ *scanning electron microscopes*, which can operate under finite water pressures, allowing us to retain the native structure of wet surfaces. (I have just discovered this instrument here at the Cavendish.)

From the point of view of soft interface physics, the present times are fortunate: centuries of empirical knowledge about ‘tribology’ (friction) or ‘colloids’ (ultradivided matter) can progressively be correlated to detailed structural data at the 10 Å level. It is especially pleasant for me to mention this in Cambridge, where *the* major advances on tribology have been

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achieved – by F. P. Bowden, D. Tabor, and their co-workers. Of course, I shall not try to redescribe this sector. But I will insist on some general features of soft interfaces which were mentioned at the start: borders which can be *mobile*, *diffuse*, and *active*.

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## II

### Mobile borders: the dynamics of wetting (or dewetting)

Since the days of Thomas Young, we know that a liquid ( $L$ ), when deposited on a flat, impermeable, solid surface ( $S$ ), may show two types of equilibrium behaviour: partial wetting (figure 1*a*) or total wetting (figure 1*b*). The choice is dictated by the interfacial energies  $\gamma_{SL}, \gamma_{SA}, \gamma_{LA}$  (where  $A$  stands for the air\*).

When the combination:

$$S = \gamma_{SA} - (\gamma_{SL} + \gamma_{LA}) \quad (1)$$

is positive, the energy of the solid/air interface is lowered by intercalation of a flat liquid film: this corresponds to complete wetting. But when  $S$  is negative, a liquid drop does not spread on the solid: it terminates in the form of a wedge, with a well-defined contact angle  $\theta_c$  (figure 1). We call this partial wetting.

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\* In the following text, we shall often use the shorthand  $\gamma_{LA} = \gamma$  for the liquid surface tension.

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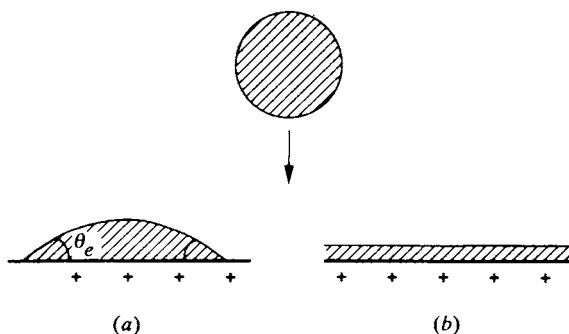


Figure 1. (a) Partial wetting. (b) Total wetting.

Balancing the tensions  $\gamma$  (projected along the solid surface, which defines the allowed direction of motion), Young found the admirable relation:

$$\gamma_{SA} - \gamma_{SL} = \gamma_{LA} \cos \theta_e \quad (2)$$

## 1 Dynamics of partial wetting

Equation (2) holds at equilibrium. What happens if we move out of equilibrium, for instance, by forcing a droplet on a surface, or by other experiments, displayed on figure 2? Let us discuss this for the case of partial wetting [1].

If the contact line of figure 3 moves at a velocity  $V$ , we expect a dissipation per unit length:

$$TS = FV \quad (3)$$

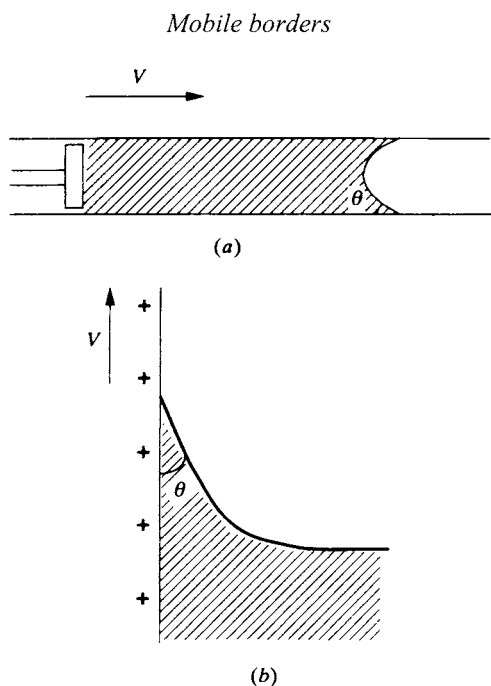


Figure 2. Schematics of two experiments to examine partial wetting.

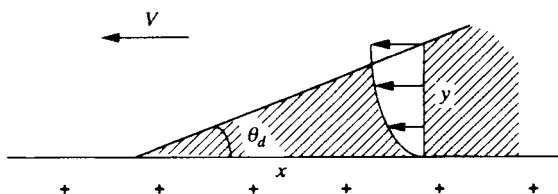


Figure 3. A wedge of liquid moving with velocity  $V$ .

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where  $F$  is the non-compensated Young force:

$$\begin{aligned} F &= \gamma_{SA} - \gamma_{SL} - \gamma_{LA} \cos \theta_d \\ &= \gamma_{LA} (\cos \theta_e - \cos \theta_d) \end{aligned} \quad (4)$$

$\theta_d$  being the dynamic contact angle. If we can find the dissipation mechanism, we end up with a relation between the driving force and the velocity.

The dissipation may have different origins: either molecular processes very near the contact line; or viscous processes in the whole moving fluid. The first may be sensitive to the chemical details of the molecules making the liquid and the solid. The second is more universal. There is one limit, when viscous flows must be dominant: namely when the dynamic contact angle is small ( $\theta_d \ll 1$ ). We can understand this by the following argument.

Inside the moving wedge of figure 3, the velocities  $v$  range from  $v \sim V$  at the free surface and  $v \sim 0$  at the lower surface. Therefore the viscous dissipation is of order:

$$T\dot{S} = \int dx \eta \left( \frac{V}{y} \right)^2 y \quad (5)$$

where  $y = \theta_d x$  is the local thickness. Equation (5) gives a logarithmic integral  $I = \ln(x_{\max} / x_{\min})$ . Putting in the correct coefficients:

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$$T\dot{S} = 3l \frac{\eta V^2}{\theta_d} \quad (6)$$

The logarithmic factor  $l$  is typically of order 12; it has worried the experts in fluid mechanics for many years. But it is not the dominant feature of equation (6): the really important feature is the presence of  $\theta_d$  in the denominator. At small wedge angles, the viscous dissipation becomes very large, and dominates over all molecular processes.

A careful reader may object to this simple discussion, since it contains a hidden assumption: the moving liquid profile near  $L$  is taken to be still a simple wedge ( $y = \theta_d x$ ). Could it, in fact, be more singular? We know the answer from singular perturbation calculations of Cox [2], or from simpler methods. There are indeed corrections to the simple wedge, of the form:

$$y = \theta_d x \left( 1 + k \frac{V\eta}{\gamma} \ln \frac{x}{x_{\min}} \right) \quad (7)$$

(where  $k$  is a numerical constant, and  $x_{\min}$  depends on molecular features or on the presence of long-range forces [3]). The crucial parameter here is the capillary number  $\text{Ca} = V\eta / \gamma = V / V^*$ . In practice, the velocities  $V$  of interest turn out to be always of order:

$$V \sim V^* \theta_d^3 \ll V^* \quad (8)$$

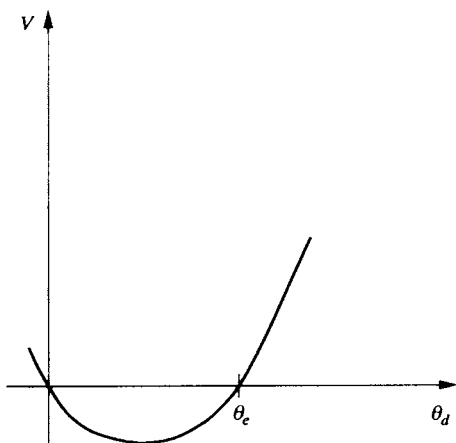


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[More information](#)*Mobile borders*Figure 4. Dynamic contact angle  $\theta$  versus velocity  $V$ .

and the corrections to the profile are thus not very important for the discussion of  $F(V)$ . But they have been seen in direct optical observations by E. Dussan and coworkers [4].

Returning now to equations (3) and (6), we end up with a basic dynamic formula (for partial wetting):

$$F \equiv \gamma(\cos \theta_e - \cos \theta_d) = 3l\eta V / \theta_d \quad (9)$$

valid for  $\theta_d \ll 1$ . A vast number of experiments (some of them depicted in figure 2) can be understood simply in these terms [1].

Figure 4 shows the relation between  $V$  and  $\theta_d$  in partial wetting. Of course,  $V$  vanishes at the equi-

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librium angle  $V(\theta_e) = 0$ . But  $V$  also vanishes at small  $\theta$ , where the dissipation is large.

**2 Complete wetting**

For complete wetting, the driving force is (always from the Young argument):

$$F = S + \gamma(1 - \cos \theta_d) \quad (10)$$

In the most interesting limit ( $\theta_d \ll 1$ ), this force is nearly constant:

$$F = S + \frac{1}{2} \gamma_{LA} \theta_d^2 \cong S \quad (11)$$

Experimentally, a number of experiments on spreading droplets, or on liquids pushed in wettable tubes, show that the resulting velocity  $V$  is in fact independent of  $S$ ! The observed spreading law is:

$$V = (\text{const}) V^* \theta_d^3 \quad (12)$$

The explanation for this anomalous behaviour [5] is based on the existence of a *precursor* film (figure 5) first observed in elegant experiments of Hardy (1919). The free energy described by  $S$  is ‘burned’ via high shear flow inside the precursor film: the macroscopic wedge is driven only by the residual force  $F - S = \frac{1}{2} \gamma \theta_d^2$ . Using this modified form, plus the dissipation formula (6), one easily reaches equation (12).