

# Wetting Dynamics with Variable Interfacial Tension

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**Résumé — Dynamique du mouillage : influence d'une tension interfaciale variable** — La théorie hydrodynamique classique du mouillage prédit une relation (approximativement) linéaire entre la force capillaire et la vitesse d'étalement. Lorsque la tension interfaciale substrat/liquide,  $\gamma_{SL}$ , varie pendant l'étalement (réactivité, relaxation moléculaire, diffusion de contaminants), le comportement se modifie de façon importante. Si  $\gamma_{SL}$  augmente avec le temps, un rétrécissement et/ou un mouvement spontané de la goutte peuvent être attendus.

Mots-clés : contamination, diffusion, étalement, goutte posée, orientation, réactivité, relaxation.

**Abstract — Wetting Dynamics with Variable Interfacial Tension** — Classic hydrodynamic wetting theory leads to an (approximately) linear relationship between capillary force and spreading speed. When substrate/liquid interfacial tension,  $\gamma_{SL}$ , varies during spreading, due to reactivity, molecular relaxation or the diffusion of contaminants, behaviour can be considerably modified. If  $\gamma_{SL}$  increases with time, drop shrinking (and/or spontaneous motion) may be expected.

Keywords: contamination, diffusion, orientation, reactivity, relaxation, sessile drop, spreading.

## INTRODUCTION

Wetting and spreading phenomena are of considerable importance in many biological and industrial situations. Young's equation describes equilibrium at the triple line solid/liquid/fluid (vapour or second, immiscible liquid) by matching surface/interfacial tension components in the direction parallel to the solid surface and normal to the triple line. However, dynamic aspects of wetting (or dewetting) invoke the viscosity of the liquid in addition (de Gennes, 1985). If the solid is sufficiently soft, mechanical properties of the solid may even override viscosity effects (Carré and Shanahan, 1997)! Notwithstanding, in most wetting problems, surface/interfacial tensions are treated as constants of the system under investigation. The purpose of this article is to review briefly various cases in which the substrate/liquid interfacial tension, in particular, may *not* be regarded as a

constant during the wetting process. We shall commence with a brief recall of the classic hydrodynamic theory of wetting and follow this up by a review of modifications which must be taken into account when the solid/liquid interfacial tension becomes a function of time of contact. The three causes of variable interfacial tension considered are reactivity, molecular relaxation and contamination, although others may exist.

## 1 HYDRODYNAMIC WETTING EQUATIONS

In the classic theory of de Gennes (1985), we consider a dynamic force balance near the triple line of a spreading, sessile drop. Physically, it simplifies to consideration of an unequilibrated Young force leading to triple line motion, the speed being moderated by essentially Poiseuille, shear flow,

causing frictional resistance in the liquid. This theory seems to work most successfully when:

- spreading speeds are low (natural wetting, for example);
- when the contact angle is low.

Other theories based on modified Eyring theory as applied to adsorption near the solid/liquid boundary (Hansen and Miotto, 1957) or molecular “hopping” mechanisms (Blake and Haynes, 1969) may be more appropriate under certain circumstances.

In the hydrodynamic theory, we have an unbalanced Young force at the triple line,  $F_S$ , causing spreading:

$$F_S = \gamma_S - \gamma_{SL} - \gamma \cos \theta(t) = \gamma (\cos \theta_0 - \cos \theta(t)) \quad (1)$$

where  $\gamma_S$  and  $\gamma$  are the solid and liquid surface tensions,  $\gamma_{SL}$  their common interfacial tension,  $\theta_0$  the Young equilibrium contact angle and  $\theta(t)$  the dynamic angle, function of time,  $t$ .

Assuming a low contact angle, the frictional resistance due to the liquid wedge (parabolic flow with shear parallel to the solid surface),  $F_F$ , is given by:

$$F_F \approx \frac{3\eta\ell U}{\theta(t)} \quad (2)$$

where  $\eta$  is liquid viscosity,  $\ell$  is the logarithm of the ratio of a macroscopic distance (ca. drop radius) to a microscopic cut-off (treated as constant) and  $U$  is spreading speed. Equating (1) and (2), we obtain the dynamic wetting relation:

$$\theta(t) [\cos \theta_0 - \cos \theta(t)] \approx \frac{3\eta\ell U}{\gamma} \equiv 3\ell \left( \frac{U}{U^*} \right) \quad (3)$$

where  $U^*$  is a characteristic speed given by  $\gamma/\eta$ . In Equation (3), all surface/interfacial tensions are considered constant and we obtain an (approximately) linear relation between spreading force and spreading speed. But what happens if one (or more) of the surface terms changes with time? We shall hereafter briefly consider three possible scenarios.

## 2 REACTIVE WETTING

Some very elegant experiments were performed both in Oxford (Bain *et al.*, 1994) and in Paris (Domingues dos Santos and Ondarçuhu, 1995). In the former case, a drop of decane containing a fluorinated fatty acid (PFOA) was placed on a glass substrate. In the latter case, either octane or dodecane containing a chlorosilane was used as the liquid. Both systems are reactive: the liquid contains a reagent which, after reaction with the solid, makes it less wettable. The drop tries to avoid its own track and steady state motion can be attained, as described in Brochard-Wyart and de Gennes (1995). The physical explanation is as follows. If the drop is in steady state motion, its leading edge has only just contacted the solid and thus the local, *equilibrium* contact angle is  $\theta_0$  ( $t = 0$ ) where  $t$  here is contact time.

At the trailing edge, contact has been established for time ( $d/U$ ) where  $d$  is drop length and thus the *equilibrium* contact angle is  $\theta_0(d/U)$ , such that  $\theta_0(d/U) > \theta_0(0)$  as a consequence of the autophobic surface reaction. However, the Laplace pressure rapidly equilibrates the actual contact angles such that both at the leading and trailing edges, the same angle,  $\theta$ , is manifest and  $\theta_0(d/U) > \theta > \theta_0(0)$ . Thus we have a leading edge force (per unit length of triple line),  $F_L$ , *pulling* the drop, and a trailing edge force,  $F_T$ , *pushing* the drop. The net force,  $F = F_L + F_T$ , leads to spontaneous motion of the drop! The reader is referred to the original article for further details (Brochard-Wyart and de Gennes, 1995).

Under axisymmetric conditions, before the drop has any “preference” to start its spontaneous motion in a given direction (caused by some slight asymmetry in the system: surface heterogeneity, solid surface not quite horizontal, etc.), we may expect a phenomenon of drop “shrinking” (Shanahan and de Gennes, 1997). The term giving  $\gamma \cos \theta_0$  in Equation (1) is  $(\gamma_S - \gamma_{SL})$  which was assumed constant. Due to contact time and reactivity,  $\gamma_{SL}$  (and to a lesser extent  $\gamma_S$ ) will change (and therefore the hypothetical, equilibrium contact angle, now a function of time  $t$ :  $\theta_0(t)$ ). We take it that the value of  $(\gamma_S - \gamma_{SL})$  at time  $t$  is given by:

$$(\gamma_S - \gamma_{SL})_t = (\gamma_S - \gamma_{SL})_0 - \gamma_1 u(t) \quad (4)$$

where  $u(t) = 1 - \exp(-t/\tau)$  would represent a first order chemical reaction of time constant,  $\tau$ , and  $\gamma_1$  is a constant of the dimensions of surface tension. After substitution of Equation (4) into Equations (1) and (3), use of a constant volume condition and some simplification, we obtain an equation for the spreading rate  $U$ :

$$U \approx \frac{\theta_0}{\eta\ell} \left[ \gamma \theta_0^2 \frac{(r_0 - r)}{r_0} - \gamma_1 \frac{u(t)}{3} \right] \quad (5)$$

where  $\theta_0$  and  $r_0$  represent equilibrium values of contact angle and contact radius *without* any chemical reaction. By assuming reaction times,  $t$ , to be long compared with the initial relaxation time of spreading towards equilibrium contact radius  $r_0$ , we see that spreading will attain (approximately)  $r_0$  and then shrinking will occur as the autophobic reaction sets in (*Figs. 1a and 1b*). Finally, contact radius will equilibrate at a value of  $\tilde{r}_0$  given approximately by:

$$\tilde{r}_0 \approx r_0 \left( 1 - \frac{\gamma_1}{3\gamma\theta_0^2} \right) \quad (6)$$

Further details may be found in the original paper (Shanahan and de Gennes, 1997); the essential point being demonstrated here is that, following reaction between solid and liquid, the *hypothetical*, equilibrium contact angle may change with time due to variation of  $\gamma_{SL}$  (and possibly  $\gamma_S$ ) and thus the equilibrium “target” becomes a function of time! Wetting direction can even reverse spontaneously, as discussed above.

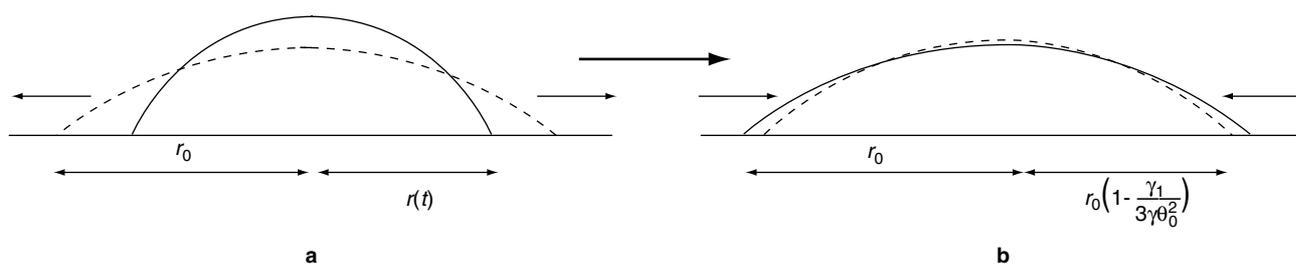


Figure 1

Behaviour of a reactive drop. (a) Spreading to unreacted equilibrium. (b) Shrinking following autophobic reaction.

### 3 MOLECULAR RELAXATION

A second case of “changing” target during dynamic wetting may correspond to the unusual behaviour of tricresyl phosphate (TCP) observed on various solids (Shanahan *et al.*, 1998). A schematic representation of the results showing the salient points is given in Figure 2. A regression line corresponding to  $\log \{ \theta(t) [\cos \theta_0 - \cos \theta(t)] \}$ , essentially the normalised spreading force, as a function of  $\log (U/U^*)$ , or normalised spreading speed, has a gradient very close to unity when the results of spreading of a silicone oil (poly(dimethylsiloxane)—PDMS) on various solids (glass, polypropylene and a halogenated polymer) are analysed. This is indeed what may be expected from Equation (3). However, equivalent data for TCP spreading on the same solids show rather different behaviour. The relation is still linear yet:

- its gradient is notably lower (ca. 0.8);
- for a given (normalised) spreading rate, a considerably higher (normalised) force is required.

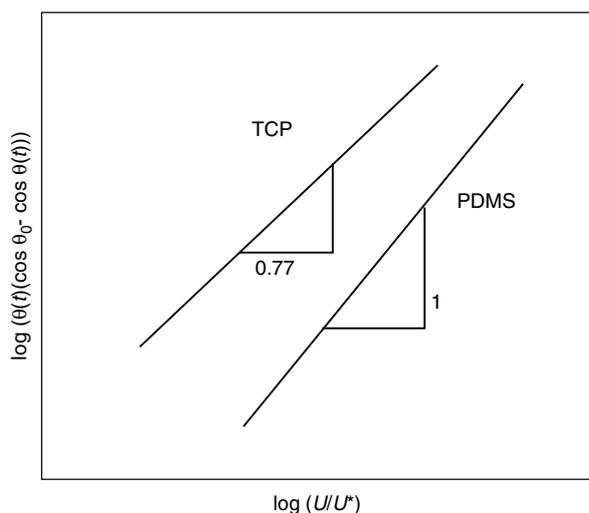


Figure 2

Schematic representation of (normalised) spreading force vs. (normalised) spreading rate ( $U/U^*$ ), both on logarithmic scales. Liquids: PDMS and TCP.

Several explanations have been considered, including the adoption of an additional molecular “hopping” mechanism (Blake and Haynes, 1969), but to present, at least, the favoured explanation is that of molecular relaxation or orientation. A TCP molecule is asymmetric with an oxygen appendage, yet is considered to be an apolar liquid (Fowkes, 1964). This is probably due to its orientation, under equilibrium conditions, with the organic groups uppermost at a free surface. We conjecture that during the spreading process, TCP molecules are laid down on the solid surface in a random manner and thus the *local* value of  $\gamma_{SL}$  will contain a contribution corresponding to the interaction between the oxygen of the liquid and the solid. In other words, the initial value of  $\gamma_{SL}$ , immediately after solid/liquid contact, will be higher than the equilibrium value.

However, even a short distance away from the triple line, within the liquid, molecular relaxation and therefore orientation will have taken place. The “active” value of  $\gamma_{SL}$  at the triple line will be some sort of average from the triple line itself over a very short distance within the liquid, at the interface. Clearly, the faster the liquid front is advancing, the smaller the number of molecules in this region which have “had the time” to orientate to the equilibrium configuration. Thus the local value of  $\gamma_{SL}$  at the triple line becomes a function of spreading speed! The mathematical development of the analysis is to be found in Shanahan *et al.* (1998), but the final, modified version of Equation (3) becomes:

$$\cos \theta_0(0) - \cos \theta(U) - \frac{\phi U}{v} \left[ 1 - \exp \left( \frac{-v}{U} \right) \right] \approx \frac{3\ell}{\theta(U)} \left( \frac{U}{U^*} \right) \quad (7)$$

where  $\theta_0(0)$  refers to the equilibrium contact angle at zero spreading rate,  $\theta(U)$  is the actual angle at speed  $U$ ,  $\phi$  is related to the variation of effective interfacial tension following orientation and  $v$  is a characteristic molecular speed. The overall effect of the variability of  $\gamma_{SL}$ , and therefore the hypothetical equilibrium contact angle as a function of spreading speed  $U$  is to add an extra term to Equation (3), *i.e.* the 3rd term of the left hand member of

Equation (7). This renders the relationship between spreading force and spreading speed non-linear, as exemplified by the gradient of ca. 0.8 given in Figure 2.

#### 4 CONTAMINATION

As a third example of wetting behaviour modified by variable  $\gamma_{SL}$ , we consider the effects of contaminants, or maybe in some cases, wetting aids! Consider the use of steel sheet, galvanised or otherwise in, for example, the motor industry. This is often covered with a thin layer of mineral oil by the manufacturer both to protect against corrosion and to help in the shape-stamping process. Adhesive bonding is commonly employed in car body assembly and in many cases, structural adhesives are used without prior degreasing. The study of such oil-accommodating adhesives is a subject in its own right (Greiveldinger, 2000)! A similar situation arises in the application of sizing to fibres to be embedded as reinforcements in composite materials. In both cases, and other examples may no doubt be found, we have the wetting of a liquid on a solid surface presenting a thin film of another substance at its surface.

We now present a simplified model of wetting behaviour accompanied by the diffusion of the thin film of “pollutant” into the spreading drop (Shanahan, 2000). Consider a small drop (negligible gravitational distortion) of a liquid 1 deposited on a solid surface,  $S$ , covered by a thin film (ca.  $1 \mu\text{m}$ ) of a liquid, 2, capable of diffusing into liquid 1 (Fig. 3). Due to its being extremely thin, any motion of the layer of liquid 2 parallel to the solid surface is neglected. Assuming Fickian diffusion of liquid 2 into liquid 1 and a (plausible) linear dependence of effective substrate ( $S$ )/drop ( $D$ ) interfacial tension,  $\gamma_{SD}(t)$ , on the concentration of liquid 2 remaining at the interface at time  $t$ , we obtain:

$$\gamma_{SD}(t) = \gamma_{SD}^F - \frac{kM}{(\pi D t)^{1/2}} (\gamma_{SD}^F - \gamma_{SD}^I) \quad (8)$$

where  $\gamma_{SD}^I$  and  $\gamma_{SD}^F$  represent initial and final (equilibrium) values of interfacial tension,  $k$  is a constant related to initial conditions,  $M$  is initial surface coverage of  $S$  by 2 and  $D$  is a (constant) diffusion coefficient. Equation (8) is valid from some small finite time, say  $\delta t$ , onwards. Considering Equation (1) in the light of Equation (8), with variable  $\gamma_{SD}$  ( $\equiv \gamma_{SL}$ ), we note that we may express the spreading force as:

$$F_S = \gamma [\cos \theta_0 - \cos \theta(t)] + \beta t^{-1/2} \quad (9)$$

with  $\beta = kM (\gamma_{SD}^F - \gamma_{SD}^I) / (\pi D)^{1/2}$ , and  $\theta_0$  corresponding to the final, equilibrium value of contact angle, assuming infinite dilution of 2 in 1 (reasonable with a very thin layer of 2 compared to the drop thickness). We may now equate Expression (9) to Expression (2), to obtain a modified version of Equation (3). Making use of the small angle approximations,  $\cos \theta \approx 1 - \theta^2/2$ , and  $V \approx (\pi/4) r^3 \theta$ , where  $V$

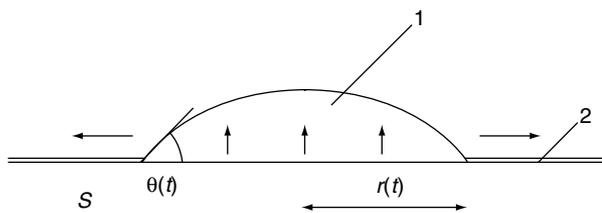


Figure 3

Schematic figure of a drop of liquid 1 spreading on solid  $S$  covered with a thin film of liquid 2. Diffusion of 2 into 1 is concomitant with spreading.

is drop volume, and defining  $y = r/r_0$ , where  $r$  and  $r_0$  are respectively drop contact radius and its value at equilibrium (corresponding to  $\theta_0$ ), we obtain:

$$\frac{U}{r_0} = \frac{dy}{dt} = A \left( \frac{1}{y^9} - \frac{1}{y^3} \right) + \frac{B}{y^3 t^{1/2}} \quad (10)$$

$U$  representing, as before, the spreading speed.  $A$  is equal to  $\gamma \theta_0^3 / (6\eta \ell r_0)$  and  $B$  corresponds to  $\beta \theta_0 / (3\eta \ell r_0)$ . Equation (10) has no analytical solution, as far as the author is aware, but its qualitative features are depicted in Figure 4. Initially, after deposition, the drop spreads somewhat faster in the presence of a layer of liquid 2 than in its absence. In fact,  $y$  scales with  $t^{1/8}$ , as opposed to  $t^{1/10}$  on a dry solid (de Gennes, 1985). Of more interest is the behaviour towards  $y = 1$ . When the triple line attains  $y = 1$  for the *first* time, it is still spreading and “overshoots” the equilibrium position. It then slows down, stops and reverses direction! The drop starts to shrink: its behaviour may be compared to that described in the above section on reactive wetting. Finally, the triple line approaches  $y = 1$  asymptotically.

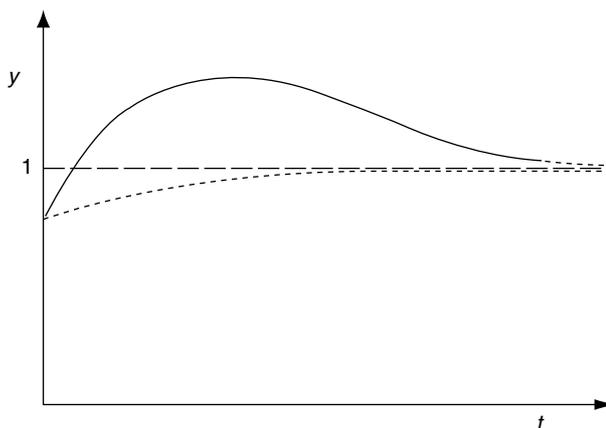


Figure 4

Qualitative behaviour of (normalised) drop radius,  $y$ , vs. time,  $t$ , for a drop on a dry solid (broken line) and for a drop on a solid covered with a film of contaminant (full line).

We earlier mentioned spontaneous motion in the context of reactive drops. Similar behaviour may be possible following diffusion of a contaminant. Since  $\gamma_{SD}$  increases with contact time, by hypothesis, the leading edge of a (two-dimensional) drop will correspond to an interfacial tension  $\gamma_{SD}(t = \delta t)$  and the trailing edge to  $\gamma_{SD}(t = d/U)$  where  $U$  is speed and  $d$  is drop length:  $\gamma_{SD}(\delta t) < \gamma_{SD}(d/U)$ . With the Laplace pressure equilibrating  $\theta$  at the leading and trailing edges, we find a total “propulsion” force of:

$$F(\text{total}) = (\gamma_S - \gamma \cos \theta - \gamma_{SD}^I) + (\gamma_{SD}(d/U) + \gamma \cos \theta - \gamma_S) \quad (11)$$

This force may be written more explicitly using Relation (8), and, by realising that viscous dissipation of the sort given in Equation (2) occurs at both leading and trailing edges, we obtain an (implicit) expression for drop “crawling” speed,  $U$ :

$$\frac{6\eta\ell U}{\theta} \approx \Delta\gamma_{SD} \left[ 1 - \frac{MU^{1/2}k}{(\pi dD)^{1/2}} \right] \quad (12)$$

where  $\Delta\gamma_{SD} = (\gamma_{SD}^F - \gamma_{SD}^I)$ . Clearly, if  $D$  is large, Equation (12) reduces to a simple expression giving  $U$  directly. If  $D$  is small, the right hand member tends to zero, and drop crawling is slow, or inexistent.

## 5 DISCUSSION

We have briefly considered three cases of wetting with variable  $\gamma_{SL}$  (or  $\gamma_{SD}$ ). In all cases, the essentially linear relationship between spreading force and spreading speed becomes modified. Reactive wetting and wetting in the presence of a contaminant (as modelled here, at least) have in common the fact that the interfacial tension between the drop and the substrate *increases* with contact time: they both represent what may be termed *autophobic behaviour*, leading to a higher, hypothetical equilibrium contact angle, function of time. In both cases, initial spreading in the axisymmetric configuration may be followed by shrinkage and a receding triple line as final equilibrium is approached asymptotically. It has been shown elsewhere, both experimentally (Bain *et al.*, 1994; Domingues dos Santos and Ondarçuhu, 1995) and theoretically (Brochard-Wyart and de Gennes, 1995), that reactive drops with *increasing* equilibrium contact angle may show spontaneous motion. The same type of behaviour may potentially be expected with the contamination scenario.

In the case of molecular relaxation during spreading, *decreasing*  $\gamma_{SL}$  will not permit this spontaneous “crawling” and a log (force) vs. log (speed) graph should have a gradient less than unity. Whether  $\gamma_{SL}$  will increase or decrease in any given situation will depend on considerations outside the scope of this article, in particular entropy effects would have to be allowed for.

It is conjectured that the overshoot behaviour may be exploited in certain industrial situations to increase surface coverage. For example, an adhesive applied to oiled steel will spread during its curing cycle. If the onset of the hardening process occurs at maximum overshoot, the receding phase may be avoided.

In all cases considered, we have a variable, hypothetical equilibrium contact angle, due to changing  $\gamma_{SL}$ . It is as though the “target”, equilibrium position is moving. Zeno of Elea (ca. 490-430 B.C.) considered that Achilles could never catch up with a tortoise by running, since in the time necessary to reach the slowly-moving reptile, the latter will have gone further. Similarly, it is “impossible” to shoot a bird with an arrow! The problem, not appreciated in the days of Zeno, was of course that mathematical series may be convergent or divergent. By analogy with Zeno’s problems, we may term the behaviour described here as “Achillean” wetting!

## CONCLUSION

Classic wetting behaviour in the hydrodynamic regime may be described by an unequibrated Young force being compensated by viscous friction, leading to an (approximately) linear relationship between force and spreading speed. By allowing the interfacial (drop/substrate) tension to change during spreading for one of several reasons (reactivity, molecular relaxation, contamination and diffusion), this linearity no longer holds. In cases where the interfacial tension effectively increases with time, we may obtain drop shrinking and, even “self-propelled” drops, subsequent to initial spreading. These unusual phenomena may be of use in biological or industrial applications.

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