REACTIVE FORCED WETTING

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In order to better understand the mechanism of dynamic wetting, we often strive to investigate ideal systems: typically, simple Newtonian liquids spreading spontaneously on rigid, smooth and homogenous solid surfaces. Similarly, most studies focus on liquids and solids that are relatively inert to one another. On the other hand, in many practical situations, such as those encountered in coating, the solid surfaces are neither smooth nor homogeneous. Moreover, in some cases, the liquids dissolve, react or otherwise modify the solid surface over which they are spreading. Examples of this latter behaviour occur when glasses or liquid metals spread on another metal or ceramic surface at high temperatures [1]. Here, reaction, dissolution and complex phase behaviour may markedly affect the spreading rate. In such cases, the dynamics and final outcome depend on the relative rates of the processes governing wetting and the various physicochemical changes that are occurring simultaneously. Only if the spreading rates are fast compared with these changes will the dynamics of wetting be largely unaffected.

Another example is a liquid spreading on a reactive polymer layer. For many years, the successful manufacture of photographic film has depended on the use of thin, gelatin subbing layers. These layers have relatively hydrophobic surfaces when dry. Hydrophobic surfaces reduce contact-line friction ζ (which quantifies dissipation at a moving contact line) and so promote high coating speeds [2]. However, after contact with water, the gelatin layers swell and undergo structural changes that render them highly wettable – thereby increasing the work of adhesion and providing a good bond between the photographic layers and the support when dry. Inevitably, these combined beneficial effects can accrue only if the rate of the surface physicochemical change is sufficiently slow compared with the rate of increase of solid-liquid interface, though not so slow as to allow subsequent dewetting.

In the experiments most often used to characterize the wettability of substrates, a drop of liquid, such as water, is contacted with the test surface and allowed to spread while the contact angle is continuously monitored. This approach can work well for a non-reactive surface [3]. However, if a drop of water is placed on a coated and dried gelatin layer, the rate of swelling and surface change quickly catches up with the rate of spreading and the contact line becomes more-or-less pinned at the very slowly evolving step between the swollen and, as yet, unswollen gelatin subphase. Ridge-controlled spreading is also seen in high-temperature metal/ceramic systems [1]. This makes it difficult to distinguish the dynamics of the various processes involved and

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may render the measurements relatively uninformative about the intrinsic wettability of the substrate.

In contrast, forced wetting, in which the test liquid is made to wet the substrate at a controlled speed, can go some way to solving this problem, provided it is carried out over a sufficient range of speeds. Specifically, it can reveal directly the way in which the contact angle θ evolves as the contact-line speed U is changed. The dynamic wetting apparatus [4], in use over many years at Kodak Limited and now being rebuilt in this laboratory, provides just such an opportunity for room-temperature systems, since it allows dynamic wetting to be studied over a very wide speed range: from 10^{-5} to 15 m/s.

Here we examine dynamic contact angle data obtained for a gelatin-subbed polyester support, in the form of a 35 mm wide tape, plunging vertically into a tank of water. The data are shown in Fig. 1, with contact-line speed U plotted on a logarithmic scale. The figure clearly shows three regimes. A low-speed regime, where the contact angle increases steeply with U, and a high-speed regime, where the speed-dependence is much reduced. The two are linked by a transition region in which θ actually falls as U is increased.
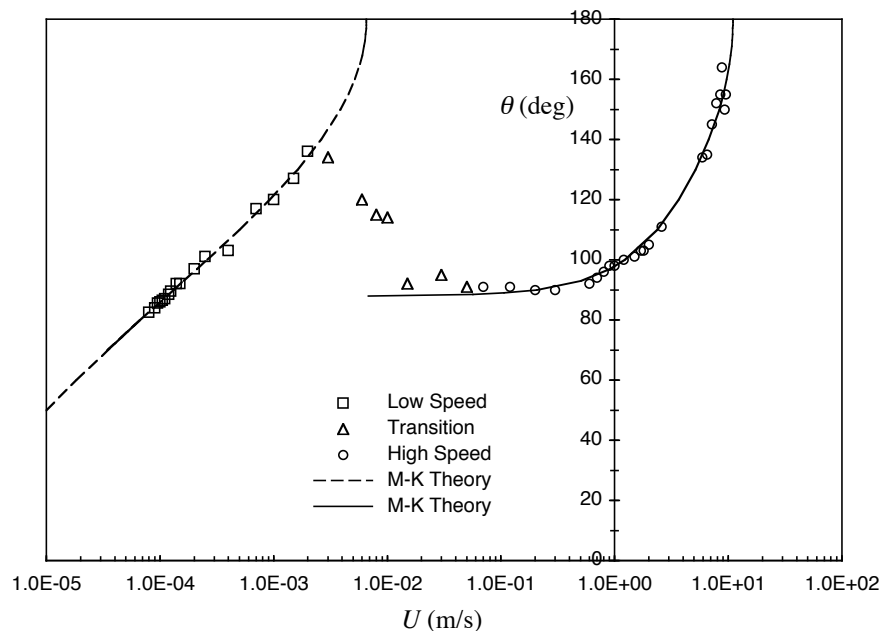

Fig. 1. Dynamic contact angle θ as a function of contact-line velocity U (logarithmic scale) for water on gelatin-subbed polyester tape [8].

The data may be analysed using the molecular-kinetic theory (MKT) of dynamic wetting [5]. This theoretical model has been found to explain a wide range of dynamic contact angle behaviour [5,6]. Furthermore, molecular-dynamics (MD) stimulations have shown it to be valid at the molecular scale [7]. One benefit of the model is that it allows us to relate the dynamics of wetting directly to the wettability of the substrate. In particular, ζ has been shown to depend linearly on the viscosity and exponentially on the work of adhesion.

When the MKT is applied systematically to the data of Fig. 1, it reveals how the wettability of the substrate changes with wetting rate. The curves through the data are the theoretical fits. The low-speed curve extrapolates to a static contact angle of zero, while the high-speed curve gives 88°. The equivalent works of adhesion are 145 and 75 mJ/m^2, respectively. Had the transition not occurred, the predicted maximum speed of wetting (low-speed curve extrapolated to θ =180°) would have been approximately 7 mm/s. After the transition, the maximum speed is approximately 11 m/s. The combined benefits of the surface reaction are clear.

An estimate of the rate of surface reaction can be obtained from the highest speed achieved in the low-speed regime $U_{L,max}$. Presumably, at this speed, most of the surface is still in the fully wetted state, so the rate of reaction k_R must be at least $U_{L,max}/\delta$, where δ is the length scale of the reacting surface groups. It is therefore tempting to try to describe the transition region in terms of competing kinetics by modelling the surface reaction using, say, first-order kinetics. However, there is a complicating factor. Forced wetting studies of water on a smooth, *non-reactive*, but chemically heterogeneous polymer surface also show three-stage dynamics similar to that illustrated in Fig. 1 [5]. The effect is less pronounced, but, significantly, the transition is characterized by bi-stability, where the dynamic contact angle alternates between values associated with the high- and low-speed regimes. The system exhibits static contact angle hysteresis, but there is no evidence of any permanent change in the wettability of the polymer surface, which readily dewets. In this non-reactive case, the behaviour has been attributed to the presence of both polar and non-polar groups at the polymer surface, with the polar groups dominating contact-line dynamics at low speeds, while the non-polar groups dominate at high speeds. The transition may be related to microscopic pinning–depinning events occurring as the contact line moves across the surface. This effect is currently being studied in this laboratory using MD simulations.

In the reactive case, it seems likely that as the contact-line speed is increased, surface heterogeneity will also increase, at least temporarily, as the surface changes from completely wetting to partially wetting. This will occur randomly but progressively, so that at intermediate speeds the surface will be composed of both polar and non-polar groups. Thus, here too, overlaying the overall change in wettability, we are likely to see pinning-depinning events moderating wetting behaviour in the intermediate region. Until we understand this better, it would be premature to attempt detailed modelling.

While the analysis given here is based on the supposed behaviour of a particular system, we may expect the same principles to apply to other reactive wetting systems. It is therefore recommended that forced wetting be exploited in other situations, such as wetting by molten metals, where the MKT has also proved very effective in describing spreading dynamics [1].

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