

The Physics of Moving Wetting Lines – a Personal View

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Introduction: Scientists tend to think in terms of their most familiar models. It is not accidental that the earliest descriptions of the moving wetting line and its associated dynamic contact angle were in terms of displaced equilibria (chemists), friction (physicists) and viscous bending of the liquid interface (engineers and mathematicians). These models have progressed since their inception, but, while each reflects a different facet of the underlying physical mechanism and offers at least a semi-empirical route to its description, none is complete. There is, as yet, no fully agreed treatment that is consistent with all three viewpoints and provides an effective basis for prediction – though at least one new hydrodynamic approach has emerged that goes some way in this direction.

This talk seeks to offer a status report: to briefly review each of the current approaches, to illustrate their successes and limitations as revealed by experiment and simulation, and to suggest ways in which the different aspects of wetting dynamics might be investigated in the future. The survey is not meant to be exhaustive; the intention is simply to illustrate the author's perspective on current progress and to provide a basis for discussion. A full paper with these objectives has been published recently [1].

The dynamic contact angle and its theoretical interpretation: The principal parameters used to quantify the dynamics of wetting are the relative velocity at which the liquid moves across the solid, *i.e.* the wetting velocity U , and the dynamic contact angle θ_d , *i.e.* the angle formed between the moving liquid-gas interface and the solid surface at the line of three-phase contact (the contact line). The dynamic contact angle is the key boundary condition. Significantly, the experimentally observed dynamic angle generally differs from its static value θ_s and may refer to either an advancing or receding liquid-gas interface.

Because dynamic wetting occurs at a finite rate, possibly with associated changes in the shape of the liquid, but certainly with changes in the wetted area, the processes involved must be thermodynamically irreversible and therefore dissipative. Indeed, the fact that the dynamic contact angle is velocity-dependent, and therefore differs from its equilibrium value, is clear evidence of this. Several attempts have been made in the literature to explain the observed behaviour. However, with one important exception [2], these boil down to essentially two approaches, which differ from each other both in terms of their conceptual framework and in their identification of the effective channel of energy dissipation.

The first of these approaches, usually known as the *hydrodynamic theory*, emphasises dissipation due to viscous flow within the wedge of liquid near the moving contact line. Although the various treatments differ in their details, the basic tenet remains the same: changes in the experimentally observed (and therefore macroscopic) dynamic contact angle are attributed to viscous bending of the liquid-gas interface within a mesoscopic region below the scale of observation. The microscopic angle θ_m is usually assumed to be governed by short-range intermolecular forces and to retain its static value θ_s , though empirical relationships between θ_m and U have also been proposed as a way of specifying θ_m . As is now well known, the classical hydrodynamic description of flow near a moving wetting line does not result in a physically acceptable solution. Because of the conflict between a contact line that moves and the conventional no-slip boundary condition between a liquid and a solid, stresses are unbounded at the wetting line, and the force exerted by the liquid on the solid becomes infinite. One way of dealing with this singularity has been to truncate the solution at the molecular scale where the continuum description breaks down [3]. Alternatively, the flow equations have been modified by relaxing the no-slip boundary condition in the vicinity of the contact line [*e.g.* 4-7]. This still leads to a logarithmic singularity, but the force exerted on the solid is then finite. In both cases, the capillary number is presumed small, so that far from the wetting line the liquid-gas interface takes its static shape. It is only on the mesoscale that viscous bending becomes important. The macroscopic dynamic contact

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angle is then determined by extrapolating the static interface to the solid surface. The flow equations are typically solved using the method of matched asymptotic expansions for low capillary (Ca) and low Reynolds numbers (Re).

The second approach to modelling dynamic wetting originates from the Frenkel/Eyring view of liquid transport as a stress-modified molecular rate process and is usually known as the *molecular-kinetic theory*. This approach discards dissipation due to viscous flow and focuses instead on that occurring in the immediate vicinity of the moving contact line due to the stochastic processes of attachment or detachment of fluid particles (molecules) to or from the solid surface [8-10]. In this case, the channel of dissipation is effectively the dynamic friction associated with the moving contact line. Moreover, it is now the microscopic contact angle that is velocity dependent and identical with the experimentally observed angle, *i.e.* $\theta_D = \theta_m$. The key parameters are ν^0 , the equilibrium frequency of the random molecular displacements occurring within the microscopic three-phase zone, and λ , the average distance of each displacement. The driving force for the contact line to move in a given direction is the out-of-balance surface tension force that arises when equilibrium is disturbed. An intrinsic disadvantage of this approach is that there is no link to the wider hydrodynamics of the system. All the physics is located within the three-phase zone, which, in the limit of continuum mechanics is simply the contact line.

Despite their fundamentally different physics and somewhat different predictions, both the hydrodynamic and molecular-kinetic theories have proved reasonably effective in describing the behaviour of the dynamic contact angle for many systems. Perhaps as a result, opinion regarding the two theories has tended to become somewhat polarized. However, there is now a growing consensus that *both* wetting-line friction and viscous dissipation play a role in determining the dynamic contact angle. This has led to the formulation of combined equations drawing on both theories [11-13]. These initiatives, though essentially phenomenological, have helped us appreciate that the real physics of the moving contact line is probably more complex than the individual models would suggest.

A more radical and potentially far-reaching approach to modelling the moving contact line has been proposed by Shikhmurzaev [2,14]. His continuum treatment accommodates dissipation through standard hydrodynamic channels, but also exploits non-equilibrium thermodynamics to describe dissipation due to the interfacial transformation processes occurring as the contact line moves across the solid surface. One consequence of this is that the microscopic dynamic contact angle is coupled directly to the flow and is not an independent quantity. Analytical expressions can be obtained for certain simplifying conditions, including low Ca and Re, which successfully describe the experimental results found in the literature.

A key element of the Shikhmurzaev model is the fact that as a liquid advances across a solid surface, liquid at the liquid-gas interface becomes transferred to the solid-liquid interface, *i.e.* there is a material flux from one interface to the other through the contact line. This flux, which has been experimentally confirmed, is missing from the conventional model, which has, instead, a stagnation point at the contact line that amplifies viscous bending. Since the properties of the liquid-gas interface (surface tension, material density, structure, *etc.*) will not in general be the same as those of the solid-liquid interface, some reorganisation of the molecules comprising the interfacial regions will be required as the material is transferred. Reorganisation from one structure to the other will be diffusive in nature and require some small time to complete. As a result, at least the solid-liquid interfacial tension will be disturbed from its equilibrium value. Hence, the interfacial tensions at the contact line will be modified, leading to a non-equilibrium value for the local contact angle θ_m , which will emerge as part of the solution to the problem through the mass and momentum balance conditions. In addition there will be an interfacial tension gradient, or “relaxation tail”, starting at the contact line and extending a distance of order $U\tau$ along the solid-liquid interface, where τ is the characteristic relaxation time of the interface.

Another consequence of this treatment is that the stress singularity at the contact line is eliminated, not in some arbitrary way, but by the thermodynamic behaviour of the interfaces. Away from the contact line the no-slip condition remains, while in the neighbourhood of the contact line there is apparent slip.

A potential advantage of the Shikhmurzaev model is that it may be used in combination with computational fluid dynamics to simulate complex coating flows at high Ca and Re, without introducing *ad hoc* concepts such as slip conditions or specifying, in advance, the behaviour of θ_m . That there has not been a flood of papers taking this approach suggests that the problems involved are not trivial. A benefit that might accrue, if these problems could be overcome, is to explain and model the effect known as *hydrodynamic assist* – a term first coined to emphasise the fact that coating flows may be manipulated to promote wetting and so beneficially postpone air entrainment to higher coating speeds [15]. Intuitively, one can see that the extension of the surface tension relaxation tail along the solid-liquid interface provides a mechanism by which changes in the flow field on a similar scale can influence the dynamic contact angle. A quantitative first-step in this direction has been published very recently [16].

Comparison with experiment: Examples of comparison with experiment for the three theories discussed above will be given in the talk and are set out in detail in [1]. The general conclusions are as follows.

Where sufficiently extensive data are available, the results to be found in the literature show that, within limits, both the standard hydrodynamic and molecular-kinetic theories are able to describe much of the observed behaviour of the dynamic contact angle. Indeed, it is sometimes quite hard to distinguish which is the more useful. Of the two, the molecular-kinetic theory is perhaps the more flexible and adaptable. The fitted values of $\bar{\theta}$ usually turn out to have dimensions consistent with a molecular interpretation, and the widely spread values of $\bar{\theta}^0$ decrease with increasing viscosity and increasing solid-liquid interaction as predicted [1,9,10]. On the other hand, good agreement with the hydrodynamic theory has been found for very viscous liquids that completely wet the substrate and for partially wetting liquids when the velocity dependence of the contact angle is weak [1,17,18].

However, the main conclusion to be drawn is that it is probably unsafe to speculate too far as to the general validity of either theory simply on the basis of the quality of the fits to equations or the values of the resulting parameters. This is especially true if the data are limited in range or restricted to a narrow class of liquids (common problems). Several instances have been found where one theory or the other fails. An example is where one viscous liquid displaces another. Here, serious discrepancies have been found if the hydrodynamic theory is used alone [18,19]. Another example is in the case of high-viscosity liquids at high contact angles, where the molecular-kinetic theory predicts larger angles than found experimentally and a hydrodynamic influence is postulated [9]. A comparable problem exists at small receding angles when viscous dissipation appears to become dominant [11,20]. Furthermore, in cases where the hydrodynamic theory predicts sub-molecular slip length-scales [1,21], we must suppose that either the model is invalid or that some additional mechanism is at work that makes $\bar{\theta}_m$ dependent upon wetting-line speed. Overall, therefore, it seems that neither theory is universally applicable, but that *both* hydrodynamic and molecular mechanisms are at work: that viscous bending may occur, but that $\bar{\theta}_m$ is also speed dependent.

This brings us directly back to Shikhmurzaev's theory. At present, his theoretical model appears to be uniquely able to describe experimental data in an entirely self-consistent way, without recourse to *ad hoc* concepts. Shikhmurzaev's publications [2,14,22,23] have shown many examples of how the asymptotic version of his model can account for the dynamic contact angle behaviour found in an exceptionally wide range of systems, from viscous oils on glass, and two-liquid systems, to molten glass on platinum.

Molecular dynamics: Molecular dynamics (MD) is one of the few tools available to explore the molecular details of wetting. However, it is only within the last 20 years that computer power has grown sufficiently to make it practical to compute the dynamics of quasi-macroscopic systems and so simulate a real experiment. The obvious strength of the technique is that it can delve into the process at the molecular level, while at the same time simulating the macroscopic behaviour of the system as a whole. On the negative side, most practical simulations are still restricted to small systems of the order of a few tens of nanometres and short times of the order of a few nanoseconds.

The first convincing MD simulations of dynamic contact angles and moving wetting lines were published by Koplik, *et al.* [24] and Thompson, *et al.* [25]. These simulations appeared to exhibit continuum behaviour at the system level. They involved Lennard-Jones liquids and several thousand "molecules" in Poiseuille and Couette flow. The studies confirmed the no-slip condition at the solid-liquid interface under normal conditions, but suggested that slip might be occurring in the vicinity of the moving contact line. However there remained a question as to whether the local contact angle $\bar{\theta}_m$ varied with speed, or whether it retained its equilibrium value.

More recent, large-scale MD simulations of spreading liquid drops [26,27a], spreading cylinders [27b], capillary imbibition [28,29], and the dynamic wetting of fibres [30] seem to confirm that $\bar{\theta}_m$ is not constant and equal to $\bar{\theta}_s$, but varies with wetting-line speed in a systematic way. Its value very close to the solid appears to be slightly smaller than that $\bar{\theta}_b$ when this is assessed by methods that mimic macroscopic experiments, *e.g.* by fitting a circular profile to a spreading drop. However, for partially wetting liquids, there is no real evidence of viscous bending of the liquid-gas interface, despite the fact that there is a large variation in $\bar{\theta}_b$ over a range of conditions ($0 < Ca < 0.3$) similar to those explored experimentally. Intriguingly, the dynamic contact angle behaviour has been found to follow the predictions of the molecular-kinetic theory. In particular, the values of $\bar{\theta}^0$, which can be ascertained directly from the simulations, agree closely with those obtained by fitting the theory to the dynamic contact angle data [26,30]. This suggests that the theory has some underlying validity, at least for simple liquids.

Conclusions and future directions: As we have seen, it is difficult to draw firm conclusions as to the origins of the dynamic contact angle from the results of simple dynamic contact angle measurements. They provide useful data,

but are not definitive. If further studies of this type are to be pursued, they should be on well-characterised solids that are smooth and homogeneous to avoid the ambiguities of contact angle hysteresis – unless, of course, it is the effect of controlled roughness and heterogeneity that is being explored. In addition, they should be carried out over the widest possible range of conditions, and in varying geometries.

The origins of hydrodynamic assist need to be confirmed by visualising more coating flows with simultaneous measurement of the dynamic contact angle. Computational fluid dynamics (CFD) applied to coating flows has tended to concentrate on global effects. The contact-line boundary conditions have often been chosen for computational convenience rather than on the basis of a valid physical model. Only part of the reason for this can be that the model is not yet fully established. In particular, it is highly desirable to see Shikhmurzaev's model properly incorporated in CFD code and compared with experiment.

Molecular dynamics has progressed a long way in answering our questions concerning the molecular details of dynamic wetting. This work needs to be continued and developed. Possible goals include: a more detailed investigation of the three-phase zone and its comparison with the general solid-liquid and liquid-vapour interfaces, with a view to testing the Shikhmurzaev model; extending simulations to higher Ca in forced wetting and dewetting situations, so that there is an increased probability of detecting effects due to viscous dissipation and hydrodynamic assist; and the introduction of more complex intermolecular forces in order to study structural effects. Two-liquid systems should also be examined in depth to investigate the effects of competitive wetting and viscosity ratio.

Evidently, dynamic wetting remains a fertile area of research, with much still left to investigate and opportunities for progress in both theory and experiment that are likely to have significant practical impact on the science and technology of coating.

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