The Physics of Moving Wetting Lines

T. D. Blake
Tring, U.K.

Scientists tend to think in terms of their most familiar models. It is not accidental that the earliest descriptions of the moving wetting line were in terms of displaced equilibria (chemists), friction (physicists) and viscous bending (engineers and mathematicians). Each of these approaches has progressed since its inception, but, while each reflects a different facet of the real underlying process, and each 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 paper 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.

1 Introduction

In all processes in which a liquid is coated onto a solid, the liquid must dynamically wet the solid surface. However, despite much research over many years, the precise mechanism by which a liquid front advances across a solid surface remains only partially understood. Our ability to predict wetting behaviour and model coating processes is therefore significantly restricted.[1]

This incomplete understanding stems from a number of factors. First, dynamic wetting operates on a scale that extends from the macroscopic to the molecular level, while our observations usually involve only macroscopic quantities such as wetting speed, viscosity, surface tension, and the contact angle formed between the liquid and the moving solid, measured at a resolution of no better than several micrometers.

Secondly, the materials involved in wetting processes are diverse and the relevant parameters span a wide range. The solids may vary from aqueous solutions to polymers or metals; the liquids may have viscosities η from <1 mPas (non-aqueous solvents) up to several kPas (polymers), and surface tensions γ from ~25 mNm^{-1} (hydrocarbons) to ~500 mNm^{-1} (liquid metals). The liquid may spread completely on the solid (static contact angle $\theta_S = 0$) or wet it only partially ($\theta_S > 0$). In industrial coating, the wetting velocity U can vary from less than 1 μms^{-1} (droplet spreading) to 10 ms^{-1} or more (curtain coating). Thus, the characteristic capillary number associated with coating, $Ca = U\eta/\gamma$, can easily span many orders of magnitude.

In contrast with this breadth, systematic experimental investigations of wetting have, with few exceptions, been restricted to relatively narrow velocity ranges, small selections of materials, and capillary numbers that are typically much less than one. Theoretical studies have shown similar limitations, being constrained both by the mathematical methods and the difficulty of identifying the physical mechanisms that may operate under the conditions of interest. Moreover, most studies have been restricted to the limiting case of small capillary and Reynolds numbers ($Re = \rho UL/\eta$, where ρ is the density of the liquid and L some length characterising the flow), which is far from the situation that pertains in typical coating processes. It is, perhaps, hardly surprising, therefore, that the problem has resisted solution and resulted in a diverse range of viewpoints with, as yet, no true consensus.

In what follows, the main theories of dynamic wetting are briefly reviewed and compared with experiment. Strengths and limitations of the theories are considered, as are some of the experimental difficulties. Mention is also made of a relatively new approach in which molecular dynamics (MD) simulations are being applied to wetting in order to elucidate the underlying physical mechanisms. The review is not exhaustive; the intention is simply to reflect the author's perspective on current progress. The paper concludes with some suggestions for future work.

2 The dynamic contact angle and its theoretical interpretation

The main parameters used to quantify the dynamics of wetting are the relative velocity at which the liquid moves across the solid, *i.e.* the contact-line velocity U, and the dynamic contact angle θ_D, *i.e.* the angle formed between the moving liquid interface and the solid surface. This angle is the key boundary condition for the wetting process. Significantly, the experimentally observed dynamic angle generally differs from the static contact angle θ_S and may refer to either an advancing (wetting) or a receding (dewetting) interface. Since solid surfaces are often rough or chemically heterogeneous, even equilibrium contact angles may not be single-valued, but will depend on whether the interface has been advanced or recessed, a phenomenon known as contact angle hysteresis. On such surfaces, wetting lines tend to pin, and when they do eventually move they do so in an unsteady way. Such factors complicate both the measurement and the interpretation of the contact angle. This is especially true on surfaces that react, swell or reorganise in some way on contact with the liquid.

In forced wetting, the contact line is made to move by application of an external force. In such cases, a relationship is expected between θ_D and U for a given system under a given set of conditions. On changing the system or the conditions (*e.g.* the flow rate in a coating experiment) the precise form of this relationship may change.[2,3] Nevertheless, it is generally observed that advancing angles increase while receding angles decrease with increasing rates of steady contact-line displacement. In other words, the contact angle depends on both the speed and direction of displacement, *i.e.* it is velocity dependent. This is shown schematically in Fig. 1 for a system that also exhibits contact angle hysteresis. While anomalies have been observed,[4] the relationship between θ_D and U is essentially monotonic. If hysteresis is present, very low, steady wetting-line velocities may be experimentally inaccessible.

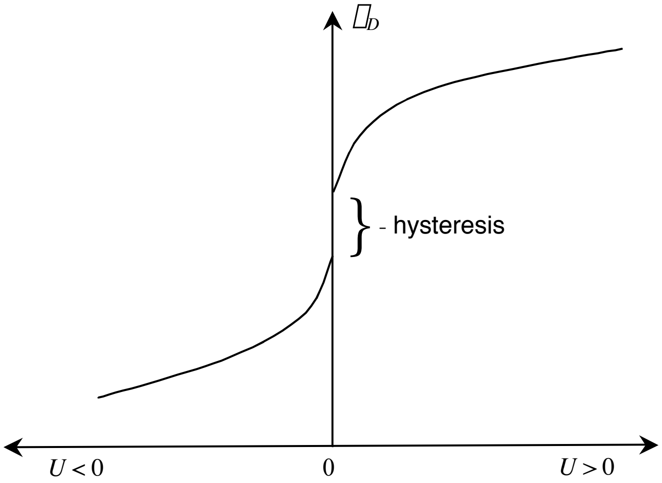

Figure 1. Schematic representation of the velocity dependence of the contact angle.[5]

On the other hand, if a drop of liquid is simply deposited onto a solid it will tend to spread spontaneously under capillary forces alone. Under these transient conditions, the instantaneous dynamic contact angle will relax, decreasing from 180°, at the moment of contact, towards its static value at equilibrium. At the same time, the wetting-line velocity will decrease, from its initial value at contact, to zero at equilibrium.[6]

Since both forced and spontaneous wetting are examples of moving contact lines, it should be possible to describe them in an equivalent way.[7] Since the wetting process occurs at a finite rate, possibly with associated changes in the shape of the liquid, but certainly with changes in the wetted area, the process must be dissipative. Indeed, the fact that the observed 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,[8] 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.

One of these two approaches, usually known as the *hydrodynamic theory*, emphasises dissipation due to viscous flow within the wedge of liquid near the moving contact line.[5,9-19] 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/vapour interface within a mesoscopic region at a scale below that of observation but greater than the molecular scale. The microscopic angle θ_m is usually assumed to be governed by short-range intermolecular forces and to retain its static value θ_S. There are thus three relevant length scales, as illustrated in Fig. 2.

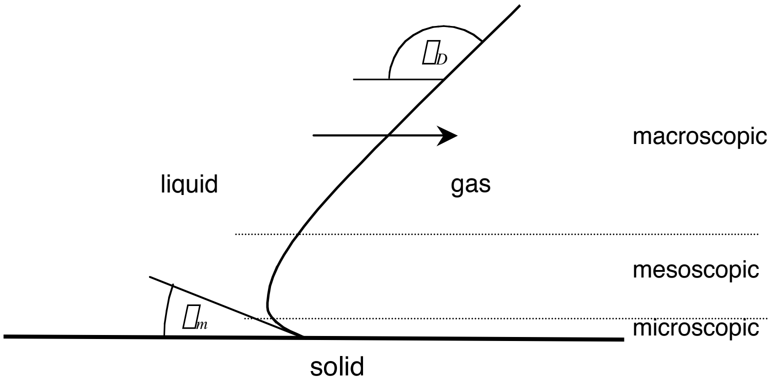

Figure 2. Schematic representation of viscous bending on the mesoscale for an advancing meniscus.

The second approach, which originates from the Frenkel/Eyring view of flow as a stress-modified molecular rate process,[20,21] discards dissipation due to viscous flow and focuses instead on that occurring in the immediate vicinity of the moving contact line due to the process of attachment or detachment of fluid particles to or from the solid surface.[4,22-24] According to this model, the channel of dissipation is effectively the dynamic friction associated with the moving contact line,[25] and the microscopic contact angle is velocity dependent and identical with the experimentally observed angle, *i.e.* $\theta_m = \theta_D$. Thus, there are just two length scales: the molecular scale, where the dissipation occurs, and the macroscopic where its effects are seen. This approach is usually termed the *molecular-kinetic theory* (MKT). A full discussion of these two theories or, more strictly, theoretical *models* is beyond the scope of this review, but it is helpful to outline the basic equations and give some examples of the magnitude of the relevant parameters. More complete overviews can be found in cited references.[1,5,8,26,27]

2.1 Hydrodynamic theory

As is now well known, the classical hydrodynamic approach to describing flow near a moving contact 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 near the wetting line, and the force exerted by the liquid on the solid becomes infinite.[10] One approach to dealing with this singularity has been to artificially truncate the solution at the molecular scale where the continuum description appears to break down.[11] Alternatively, the flow equations and boundary conditions have been modified by relaxing the no-slip boundary condition in the vicinity of the three-phase contact line.[5,10,13,14] In this case, the force exerted on the solid is then finite, though the stresses in the liquid remain unbounded. In both cases, the capillary number is presumed small, so that far from the wetting line the interface takes its static shape. The macroscopic dynamic contact angle is then determined by extrapolating the static interface to the solid surface. The equations are solved using the method of matched asymptotic expansions.

In its simplest form, the resulting equation describing the change in the dynamic contact angle due to viscous bending of the liquid/gas interface may be written in terms of the capillary number as

$$g(\theta_D) - g(\theta_m) = Ca \ln\left(\frac{L}{L_m}\right), \quad \theta_m = \theta_S \tag{1}$$

where the function $g(\theta) = \frac{1}{2}\int_0^{\theta}\left[\hat{\theta}/\sin\hat{\theta} - \cos\hat{\theta}\right]d\hat{\theta}$. For $\theta_D < 3\pi/4$, the integrand may be approximated by $2\hat{\theta}^2/3$; hence (1) becomes

$$\theta_D^3 - \theta_m^3 = 9Ca \ln\left(\frac{L}{L_m}\right), \quad \theta_m = \theta_S, \quad \theta_D < 3\pi/4, \tag{2}$$

where L and L_m are, respectively, appropriately chosen macroscopic and microscopic length scales. The assumption that local microscopic angle θ_m has its equilibrium value is usually taken, on the principle of Occam's razor, as the simplest initial hypothesis to be validated by the success of the model. However, several authors, including Voinov,[11] acknowledge that θ_m may itself be velocity dependent. Voinov's paper provides the first analysis leading to eq (1). Later treatments differ in their details, but still recover an equation of essentially the same form as (1). Those of Dussan V. and co-workers are perhaps the most revealing, and Cox's the most complete, giving the solution for the situation in which the receding fluid is another viscous liquid rather than an inviscid gas.[18] In such cases, the viscosity ratio of the two liquids is a key parameter, appearing in the function $g(\theta)$. Cox also considers higher order solutions in Ca and the possibility of other sources of dissipation resulting from flow in the inner and outer regions.

In Voinov's treatment, L_m is the distance from the solid at which the solution is truncated. In Cox's analysis, it defines the scale of the inner region where slip is important. Setting L = 10 μm, which is the approximate distance from the wetting line at which the contact angle can be measured, and L_m = 1 nm, *i.e.*, the order of molecular size, then $\ln(L/L_m)$ is estimated to be of the order of 10. Experimental values vary widely, though values of about 10 are often found, especially for liquids that completely wet the solid. Much larger values have sometimes been reported for non-wetting liquids,[27,28] especially at low Ca where one might have anticipated the model would be most effective. These are usually thought to be unphysical, since they would appear to involve sub-molecular microscopic length scales.

While there is no proven slip model, it turns out that the solution is insensitive to the details of the physics within the inner region;[12] so that the only information communicated outward to the intermediate region is the value of θ_m. However, these conclusions arise largely as a consequence of the physical assumptions inherent to the overall model. A related question is the way in which the intrinsic wettability of the solid influences the dynamic contact angle. Formally, this enters only through the value of θ_S, but, logically, one would also expect it to influence L_m through the degree of slip permitted by the solid/liquid interactions. That the experimentally determined values of $\ln(L/L_m)$ vary significantly would appear to support this conjecture.

For completely wetting liquids, a precursor film may spread ahead of the meniscus and the hydrodynamic problem is then greatly simplified, since the contact line is no longer directly involved. This has tempted some to invoke hypothetical precursor films as a way of avoiding the contact-line problem in computational modelling of coating flows. Precursor films have been observed experimentally, *e.g.* for spreading drops; but, in reality, they are unlikely to have much relevance at the wetting speeds encountered in industrial coating processes. It is also worth pointing out that, except in the case of wetting with a precursor film, there is little or no direct experimental evidence for viscous bending to the extent required to explain the behaviour of the dynamic contact angle. Indeed, a comparatively recent and very accurate study of the profile of a liquid meniscus rising between two parallel plates has found significant discrepancies with the predictions of the hydrodynamic model at distances $r < 10$ μm from the wetting line, leading to the conclusion that the microscopic contact angle also depends on contact-line speed.[29]

If the hydrodynamic model is applied to the spreading of small drops and small contact angles, eq (1) leads to simple scaling laws for the base radius R and the dynamic contact angle as a function of time t:

$$R(t) \sim t^{1/10} \tag{3}$$

$$\theta_D(t) \sim t^{3/10} \tag{4}$$

These relationships have been widely confirmed for small drops of completely wetting liquids.[15,30] This result is sometimes advanced as a more general demonstration of the validity of eq (1) and its underlying assumptions.

2.2 Molecular-kinetic theory

According to the contrasting viewpoint provided by the molecular-kinetic theory,[4,22-24] the motion of the contact line is determined by the statistical dynamics of the molecules within a three-phase *zone* where the solid, liquid and gas phases meet. On the molecular scale, this zone has a finite size, but is otherwise unspecified within the model. The key parameters are κ^0, the equilibrium frequency of the random molecular displacements occurring within the three-phase zone, and λ, the average distance of each displacement. In its essence, the model is based on the idea that the velocity-dependence of the dynamic contact angle is due to the disturbance of adsorption equilibria and, hence, the local surface tensions, as the three-phase zone moves across the solid surface.[31] Thus, 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: $\gamma(\cos\theta_S - \cos\theta_D)$. In this case, λ is supposed to be the distance between adsorption sites on the solid surface (although other possibilities have been considered[4]). The resulting equation for the wetting-line velocity is then

$$U = 2\kappa^0\lambda\sinh\left[\gamma(\cos\theta_S - \cos\theta_D)\lambda^2/2k_BT\right] \tag{5}$$

where k_B is the Boltzmann constant and T the absolute temperature. The characteristic frequency κ^0 may be written in terms of the activation free energy of wetting ΔG_w^*:

$$\kappa^0 = \left(\frac{k_B}{h}\right)\exp\left(\frac{-\Delta G_w^*}{Nk_BT}\right) \tag{6}$$

where h and N are the Planck constant and Avogadro number, respectively. While the experimentally determined values of λ are usually of molecular dimensions, those for κ^0 can vary widely, but generally decrease with increasing viscosity. Examples are listed in Table 1.

Table 1. Values of parameters obtained by applying the molecular-kinetic theory to experimental data for various systems.

Liquid/solid system	η (Pa s)	γ (mN m^{-1})	θ_S (deg)	λ (nm)	κ^0 (s^{-1})	ζ (Pa s)
Water on PET[a,4]	0.001	72.4	82	0.36	8.6×10^9	0.01
16% glycerol in water on PET[4]	0.0015	69.7	72.5	0.46	3.6×10^9	0.012
86% glycerol in water on PET[4]	0.104	65.8	65	0.46	3.5×10^7	1.2
Di-*n*-butyl phthalate on PET[6]	0.196	34.3	< 5	1.8	1.1×10^5	6.4
Silicone oil on glass[4,32]	0.958	21.3	0	0.80	2.3×10^5	35.9
Silicone oil on glass[4,32]	98.8	21.7	0	0.80	2.3×10^3	3580

[a] polyethelene teraphthalate tape

According to a later development of the model,[4] the relationship between κ^0 and viscosity is given by

$$\kappa^0 = \kappa_s^0 h / \eta \mathrm{v}_\mathrm{m} \tag{7}$$

where κ_s^0 is the frequency of molecular displacements when retarded only by solid/liquid interactions, and v_m is the molecular flow volume. Hence, κ^0 is inversely proportional to viscosity, as found experimentally (Table 1). More recently, it has been proposed that there is an approximate link between κ_s^0 and the work of adhesion between the liquid and the solid, *Wa*.[33] This leads to

$$\kappa^0 \sim \frac{k_B T}{\eta \mathrm{v}_\mathrm{m}} \exp\left(-Wa\right) \tag{8}$$

so that κ^0 decreases with increasing work of adhesion. Since both *Wa* and the driving force for wetting increase with wettability, eq (8) implies that there may be an optimum wettability to maximise the rate of wetting. Evidence for this, and an inverse relationship between κ^0 and *Wa*, can be found in the literature.[33]

If the argument of the sinh function is small, eq. (4) reduces to its linear form

$$\begin{aligned} U &= \kappa^0 \lambda^3 \gamma\left(\cos\theta_S - \cos\theta_D\right) / k_B T \\ &= \frac{1}{\zeta}\gamma\left(\cos\theta_S - \cos\theta_D\right) \end{aligned} \tag{9}$$

where $\zeta = k_B T / \kappa^0 \lambda^3$ may be thought of as the *coefficient of wetting-line friction*. This coefficient has the same units as dynamic viscosity. From eq (8),

$$\zeta \sim \eta\left(\frac{\mathrm{v}_\mathrm{m}}{\lambda^3}\right)\exp\left(Wa\right) \tag{10}$$

Consistent with this, experimental values of ζ are always larger than the viscosity of the liquid, and appear to increase both with viscosity and the strength of solid-liquid interactions (Table 1).

Notwithstanding these findings, there is no definitive way of predicting the values of λ, κ^0 and ζ for a given solid/liquid system, and so predicting wetting behaviour from independently measured quantities. In consequence, λ and κ^0 (or ζ) must usually be treated as adjustable parameters and obtained from experiment by curve fitting procedures. In doing this, great care must be taken that the data are sufficiently extensive and noise free and that the fitting procedures are robust. Statistical techniques such as the Bootstrap method[34] are sometimes applied to analyse the reproducibility of the fits and estimate errors.[6] In particular, a reliable value for λ is crucial, since it appears to the third power in eq (9). Another problem intrinsic to the molecular-kinetic model is that there is no obvious link to the wider hydrodynamics of the system. This stems from the fact that all the physics is located within the three-phase zone, which, in the limit of continuum mechanics is simply the contact line.

2.3 Combined models

Despite their fundamentally different physics and somewhat different predictions, both the hydrodynamic and molecular-kinetic models have been shown to be reasonably effective in describing the experimentally observed behaviour of the dynamic contact angle in a range of systems. With a free choice of the relevant adjustable parameters, good agreement is often obtained with either model.

Interestingly, while eq (1) predicts that for small angles $U \propto \theta^3$, eq (9) predicts $U \propto \theta^2$. This leads to scaling laws for spreading drops that differ from eqs. (3) and (4):

$$R(t) \sim t^{1/7} \tag{11}$$

$$\theta_D(t) \sim t^{3/7} \tag{12}$$

Comparison with experiment therefore appears to offer the opportunity of assessing which model is the more appropriate.

In the past, opinion regarding the two models has been somewhat polarized. Nevertheless, a point of view that is gaining increasing ground is the possibility that *both* wetting-line friction and viscous dissipation play a part in determining the dynamic contact angle.[11,35-37] Leaving aside the specific details of the two models, it seems self-evident, on simple thermodynamic grounds, that the microscopic contact angle will be disturbed by movement of the contact line, and equally self-evident that viscous flow in a small wedge of liquid near the contact line is likely to modify the meniscus profile in this region. The real question concerns the relative importance of the two effects and how they can best be described.

Petrov and Petrov[35] have formulated an integrated theory by the simple expedient of combining eqs. (2) and (5), using (5) to provide the value of θ_m in (2), yielding an equation with three adjustable parameters, λ, κ^0 and $\ln(L/L_m)$. Not surprisingly, curve fitting with this equation proved successful, usually giving better agreement with experimental data than either (2) or (5) alone, especially for receding wetting lines. In addition, the values of the parameters obtained from the analyses appeared reasonable. Similar results have been obtained by others.[1,27]

Brochard-Wyart and de Gennes[36] took a different, but more-or-less equivalent approach. Considering dynamic wetting as an irreversible process, the rate of energy dissipation per unit length of the wetting line is the product of the flux U and the out-of-balance surface tension force $\gamma\left(\cos\theta_S - \cos\theta_D\right)$. If you then suppose, as first suggested by Voinov,[11] that the total energy dissipation comprises the viscous dissipation in the (thin) wedge of liquid adjacent to the moving wetting line plus the dissipation due to wetting-line friction, then, using simplified arguments, one obtains

$$\gamma(\cos\theta_S - \cos\theta_D)U = \frac{6\eta U}{\theta_D}\ln\left(\frac{L}{L_m}\right)U + \zeta U^2 \tag{13}$$

i.e.

$$U = \frac{\gamma(\cos\theta_S - \cos\theta_D)}{\zeta + \frac{6\eta}{\theta_D}\ln\left(\frac{L}{L_m}\right)} \tag{14}$$

Here, the lengths L and L_m together with the angle θ_D define the wedge of liquid in which viscous dissipation occurs (estimated using the lubrication approximation). The length L characterises the size of the wedge, and L_m the molecular limit where continuum mechanics breaks down. Because the angle of the wedge θ_D occurs in the denominator of the viscous term, viscous dissipation dominates at small angles. Brochard-Wyart and de Gennes interpreted the friction coefficient ζ in terms of the molecular-kinetic theory, eq. (9).

Using a slightly different analysis, de Ruijter, *et al.* have derived an equation analogous to eq (14) for a spreading drop.[37] Their results suggest that the wetting-line friction regime precedes the viscous regime, which becomes dominant only as the contact angle becomes small. A later experimental study appeared to confirm this finding, showing the expected switch in the power law time-dependence, from eqs (11) and (12) to eqs (3) and (4), as spreading progressed.[38]

By combining the molecular-kinetic and conventional hydrodynamic models in this way, these authors have helped us to appreciate that the real physics of the moving wetting line is probably more complex than the individual models would suggest. Nevertheless, such a combination is essentially phenomenological. Furthermore, the resulting equations remain restricted to flow at very small capillary numbers, say, < 0.1. While they may be helpful in quantifying processes such as spray coating and ink-jet methods that involve droplet spreading, the equations can be of only marginal value in predicting the outcome of high-speed coating. The capillary number in continuous web coating routinely exceeds unity and is frequently much higher.[39]

2.4 The Shikhmurzaev model

A more radical and potentially far-reaching approach to modelling the moving contact line and the dynamic contact angle has been proposed by Shikhmurzaev.[8,40] His continuum hydrodynamics treatment accommodates dissipation through standard hydrodynamic channels, but also exploits non-equilibrium thermodynamics to include dissipation due to the interfacial transformation process occurring as the wetting line moves across the solid surface. One consequence of this approach 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, which successfully describe the experimental results found in the literature. Moreover, computational modelling based on this model offers the possibility of describing high-speed coating flows in an entirely self-consistent way. Despite this potential, Shikhmurzaev's approach has attracted dogged opposition from some, who appear reluctant to admit that there might be anything lacking in the conventional hydrodynamic treatment.[41]

Full descriptions of Shikhmurzaev's mathematical model, the associated analysis and comparisons with experiment can be found in his publications.[8,40] A more recent paper[42] provides an accessible summary of the analytical solution for the asymptotic case of steady motion at low *Ca* and *Re*, and applies the results to dynamic contact angle measurements with a plunging tape over a wide range of viscosities. Another experimental paper[3] provides an outline of the model in relation to curtain coating. Here, we simply summarise the essential features in a qualitative way.

A key element of the 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 through the contact line. This flux, which has been experimentally confirmed,[43] is missing from the conventional model, which has, instead, a stagnation point. Since the properties of the liquid/gas interface (surface tension, material density and distribution, *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. For example liquid/vapour interfaces are usually thought to have a sigmoidal density distribution on the scale of the liquid molecules, while the density of liquid adjacent to a solid surface is usually higher and often layered.

Reorganisation from one interfacial structure to the other will be diffusive in nature and require some small time to complete, as the liquid/gas interface disappears and the newly created solid/liquid interface attains equilibrium. As a result, at least the solid/liquid interfacial tension will be disturbed from its equilibrium value (the reverse will be true for a receding liquid). Hence, the balance of interfacial tensions at the contact line will also be disturbed, leading to a non-equilibrium value for the local contact angle θ_m. 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. Since the relaxation process is diffusive, it will depend on the viscosity of the liquid, becoming slower as the viscosity increases. If, on the microscopic length scale, the interface is a layer of characteristic thickness h_i, then

$$\tau \propto \mu h_i^2 \qquad (15)$$

In order to relate the interfacial tensions to the local material densities of the interfaces, Shikhmurzaev introduces a linear equation of state. In his notation,

$$\sigma = \gamma\left(\rho_0^s - \rho^s\right) \qquad (16)$$

where σ is the interfacial tension, and ρ_0^s and ρ^s are the equilibrium and instantaneous interfacial densities. The coefficient γ reflects the tendency of the interfacial layer to be rarefied or compressed due to the asymmetric influence of the intermolecular forces from the bulk phase. Hence, γ is an equilibrium property, independent of viscosity and inversely proportional the liquid compressibility. By introducing eq (16), the local variation in θ_m emerges as part of the solution through the mass and momentum balance conditions. While viscous bending of the interface remains possible, its significance is much reduced, leading to the conclusion that it is the variation in θ_m that is largely responsible for the observed variation in θ_D. More complex equations than (16) are possible, but this is the simplest that provides the required physics.

Another consequence of the model is that the stress singularity, which usually arises at the contact line as a result of the no-slip boundary condition, 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.

One of the difficulties with the model is that it introduces additional phenomenological coefficients α and β, linking the flow to, respectively, the surface tension gradients and the shear stress at the interface. It is not easy to see how these coefficients can be determined *a priori*. Fortunately, order of magnitude estimates are possible, and in the asymptotic solution for low *Ca* and *Re*, most of the coefficients can be lumped together in one scaling factor that is a function of the material properties of the system.

One potential advantage of the Shikhmurzaev model is that it may be used in combination with computational fluid mechanics to simulate complex coating flows at high capillary and Reynolds numbers, 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*. The high-speed limit to coating is usually the onset of dynamic wetting failure, which leads to air entrainment. The term hydrodynamic assist was 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[2] – a fact well known to coating engineers, but not anticipated by the earlier theories.

Visualisation of curtain-coating flows has shown that hydrodynamic assist causes a reduction in the dynamic contact angle for a given contact-line speed.[2,3] This means that θ_D is not just speed-dependent, but dependent on the *details* of the flow. Presumably, it is the reduction in θ_D that allows the postponement of air entrainment.[3,39] Scaling arguments[3] strongly suggest that the effect is due to a reduction in θ_m, rather than a reduction in the extent of any hydrodynamic bending on an intermediate scale below the optical resolution of the measurements (~20 μm). Because, in Shikhmurzaev's model, the dynamic contact angle is part of the solution, one would expect hydrodynamic assist to arise naturally from a properly formulated computational study based around that model.

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. Hydrodynamic assist appears to occur most strongly in coating flows at high *Ca* where the wetting line is confined within a small geometry. A feature of curtain coating is that the scale of the flow at the foot of the curtain is very small (typically < 1 mm) and so may approach the scale of the relaxation tail, maximising the potential for hydrodynamic assist. A recent computational study of curtain coating has shown that the standard hydrodynamic approach with various slip models is unable to explain the extent of contact-angle variation measured experimentally (some 20°).[44] It remains to be confirmed that Shikhmurzaev's model can succeed where the other fails. Either way, the existence of hydrodynamic assist clearly demonstrates that equations, such as (1) and (5), that predict a unique value of θ_D for a given value of *U* or *Ca* are not sufficient to describe the complex phenomenon that is dynamic wetting.[3]

3. Comparison with experiment

In this section, we examine the success of the models outlined above in describing the experimentally observed behaviour of the dynamic contact angle in a few cases chosen to illustrate the various models' strengths and limitations.

In dynamic contact angle experiments, it is clearly important to measure the angle as accurately as possible over the widest possible range of wetting-line speeds and angles. Unless this is done, it is difficult to assess whether or not any given theory is truly effective, or merely appears so when fitted to too noisy or too small a data set. One should also ensure that sufficient ancillary measurements are made to enable the results to be interpreted as fully and unambiguously as possible. For example, in specifying the liquid, sufficiently accurate measurements of viscosity (assuming this to be Newtonian, which is not always the case with coating liquids), surface tension and density will be necessary. Ideally, there will be a range of measurements in which the material properties of the system are varied in a systematic way, with minimum changes to the chemistry of either the liquid or the solid. Similarly, if comparisons are to be made between different flows, it is important to determine the parameters such as geometry and flow rate that properly characterize them. It may also be desirable to ascertain other factors such as the roughness of the solid surface.

Taken together, these requirements are very demanding and difficult to achieve. In consequence, we often have to make do with more limited data sets.

Hoffman's data[32] for silicone oils in a glass capillary are plotted in Fig. 3. Although the speed range of the measurements is moderate (about 1 to 400 μms^{-1}), the two oils have significantly different viscosities (0.96 and 99 Pas), but essentially the same chemical composition. Hence, the range and consistency of the data when plotted in terms of the capillary number is good. Both oils are completely wetting on glass, so a precursor film is probable.

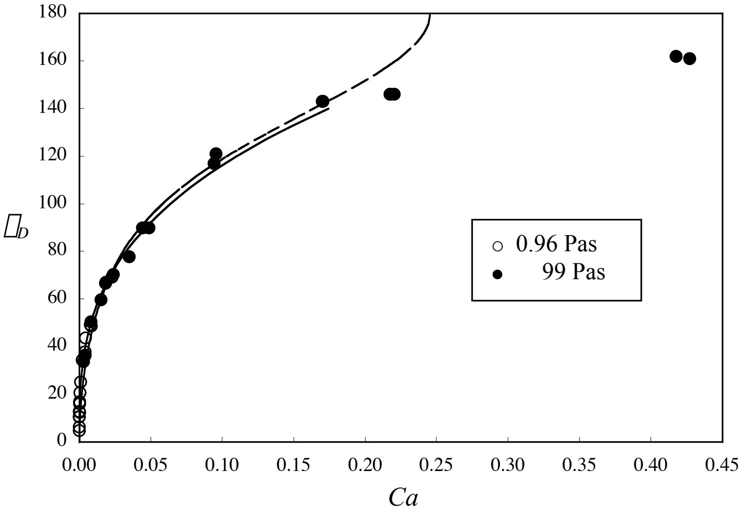

Figure 3. Dynamic contact angle of silicone oils on glass.[32] Solid curve: hydrodynamic theory, eq (2), with ln(L/L_m) = 9.3. Dashed curve: MKT, eq (5), with λ = 0.80 nm, and $\kappa^0 = 2.3 \times 10^5$ and 2.3×10^3 s^{-1} for the 0.96 and 99 Pas oils, respectively. $\theta_S = 0$ in both cases.

The curves shown in the figure were obtained by fitting the data to eqs (2) and (5). Both the conventional hydrodynamic theory and the molecular-kinetic theory are able to represent the data reasonably well, with sensible values of the fitting parameters. The fit to eq (2) is slightly better, with an R^2 of 0.994 compared with 0.982 for eq (5). The fit to eq (2) has been truncated at $\theta_D \sim 3\pi/4$ (135°), the accepted limit for the $g(\theta)$ approximation.[11] Cox[18] has shown that eq (1) in its full form is able to represent the data quite well at higher angles. Other researchers have found similar results with similar liquid/solid systems.[45] The good fit to these data is often advanced as evidence for accepting the hydrodynamic theory with $\theta_m = \theta_S$.[46] In comparison, Eq (5) does not fit the data well above 140°, predicting larger angles than found experimentally. A similar trend has been seen for other high-viscosity liquids and has been ascribed to a form of hydrodynamic assist.[4]

Fig. 4 shows the dynamic contact angle plotted as a function of contact-line speed for a polyethelene teraphthalate (PET) tape plunging into a pool of 16% aqueous glycerol solution (viscosity 1.5 mPas).[42] Here, the curves were obtained by fitting eqs (2) and (5) to the data for speeds of 7 cms^{-1} and above, with θ_S treated as an additional unknown. The reason neglecting the lower-speed data is given below. When this is done, both the hydrodynamic and molecular-kinetic theories represent the data quite well, with sensible values for the fitting parameters. However, the fit to eq. (5) is now better, with an R^2 of 0.987 compared with 0.979 for eq (2). Moreover, eq. (5) is effective up to angles approaching 180˚. Though not checked, it is likely that the hydrodynamic theory would provide a better fit at larger angles if the effect of the gas-to-liquid viscosity ratio were included using the formula given by Cox.[18] In this case, the ratio is small but significant (~0.01), whereas for the high-viscosity silicone oils of Fig. 3 it is effectively zero.

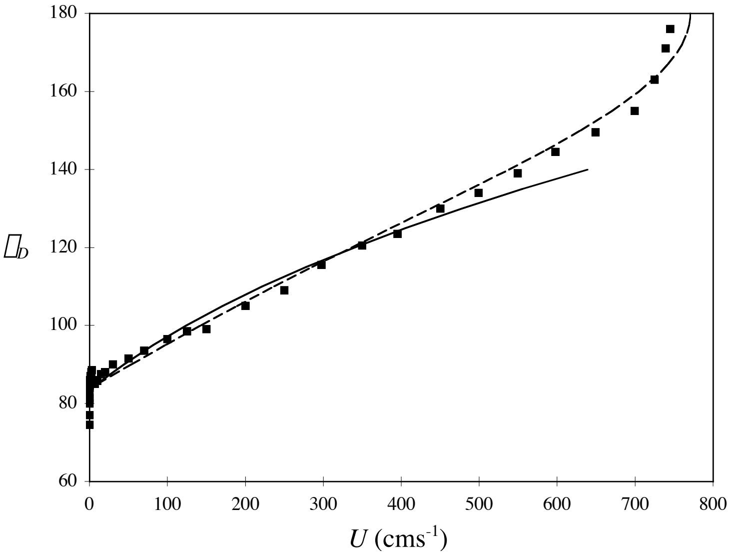

Figure 4. Dynamic contact angle of 1.5 mPas aqueous glycerol solution on PET at 22 °C.[42] Solid curve: hydrodynamic theory, eq (2), with $\ln(L/L_m) = 9.2$ and $\theta_S = 83°$. Dashed curve: MKT, eq (5), with $\lambda = 0.39$ nm, $\kappa^0 = 4.8 \times 10^9$ s^{-1}, and $\theta_S = 84°$.

The capillary number for the data shown in Fig. 4 never exceeds 0.2, but the much smaller viscosity of the aqueous glycerol solutions compared with the silicone oils used for Fig. 3, results in much higher wetting speeds. However, it is perhaps the lower-speed (and very low *Ca*) data that are most interesting. The dynamic contact angles in Fig. 4 were obtained over a speed range in excess of 5 orders of magnitude (30 μms^{-1} to 745 cms^{-1}), using specially designed apparatus. At speeds up to about 3 cms^{-1} ($Ca \sim 6 \times 10^{-4}$), the angle follows a very steep curve compared with that found at higher speeds. Immediately above this lower speed range, the angle actually falls by about 5°, and the shallower curve then appears to start at about 7 cms^{-1} (see Fig. 5.) The fall in the contact angle is associated with unsteady motion of the wetting line, which is absent at both higher and lower speeds. A similar effect has been reported for water and, to a lesser extent, for more viscous aqueous glycerol solutions on PET, and has been attributed to a change in the physical mechanism by which the wetting line advances across the solid surface.[4] This is the reason why the curves in Fig. 4 were obtained by fitting only the data for speeds of 7 cms^{-1} and above, and treating θ_S as an additional fitting parameter. Leaving to one side the question of what causes the transition, the lower-speed data still cover some 3 orders of magnitude in wetting-line speed and can, therefore, be treated independently.

The result of fitting just the low-speed data from Fig. 4 to eqs (2) and (5) is shown in Fig, 5. Evidently the fit to eq (2) is very poor, even if θ_S is adjusted. Moreover, the magnitude of $\ln(L/L_m)$ is physically quite unacceptable. Indeed, with $\theta_S = \theta_m$ and an acceptable value of $\ln(L/L_m)$, eq (2) is intrinsically unable to account for such steep changes in θ_D at such low *Ca* ($<10^{-3}$) unless θ_S is small – which is not the case here. In contrast, the molecular-kinetic theory provides a good fit based on the measured value of θ_S, and gives acceptable values of κ^0 and λ. The values are very different to those obtained from the high-speed data: κ^0 is some 7 orders of magnitude smaller and λ about 5 times larger. However, the values simply reflect the very steep dependence of θ_D on U or *Ca*, and, within the context of the model, simply imply a very strong interaction between the liquid and a relatively low density of adsorption sites on the solid that are resolved only when the wetting line is moving slowly. The literature suggests that small values of κ^0 and comparatively large values of λ are not unusual when the molecular-kinetic theory is applied to dynamic contact angles measured at low *Ca*.[27,28]

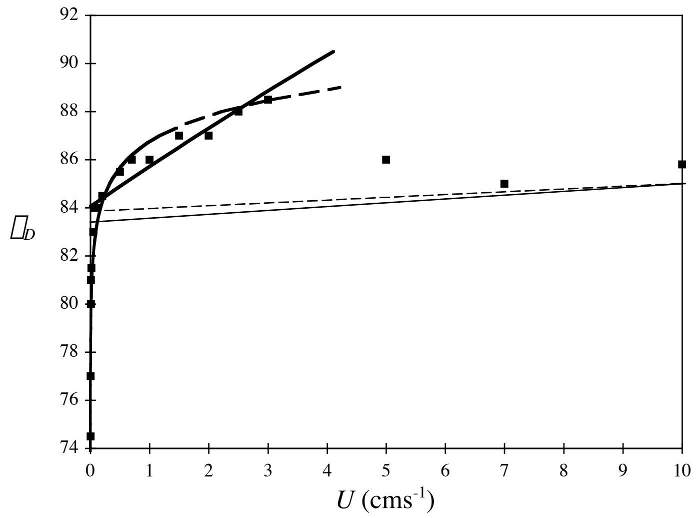

Figure 5. Low-speed data from Fig. 4 for 1.5 mPas aqueous glycerol solution on PET. Heavy solid line: hydrodynamic theory, eq (2), with $\ln(L/L_m) = 97$ and $\theta_S = 84°$. Heavy dashed curve: MKT, eq (5), with $\lambda = 2.1$ nm, $\kappa^0 = 6.2 \times 10^2$ s^{-1}, and $\theta_S = 72.5°$ (measured static advancing angle). The two lighter lines are the fits to the higher-speed data shown in Fig. 4.

Another comparison between the effectiveness of the hydrodynamic and molecular-kinetic interpretations is shown in Fig. 6. Here, the data are for di-*n*-butyl phthalate on PET at 55 ˚C. They were obtained by the author using the plunging tape method as part of a temperature series. As can be seen, both eq (2) and eq (5) provide very good fits if some latitude is given to θ_S. That for eq (5) is marginally better than that for eq (2), with $R^2 = 0.989$ compared with 0.986.

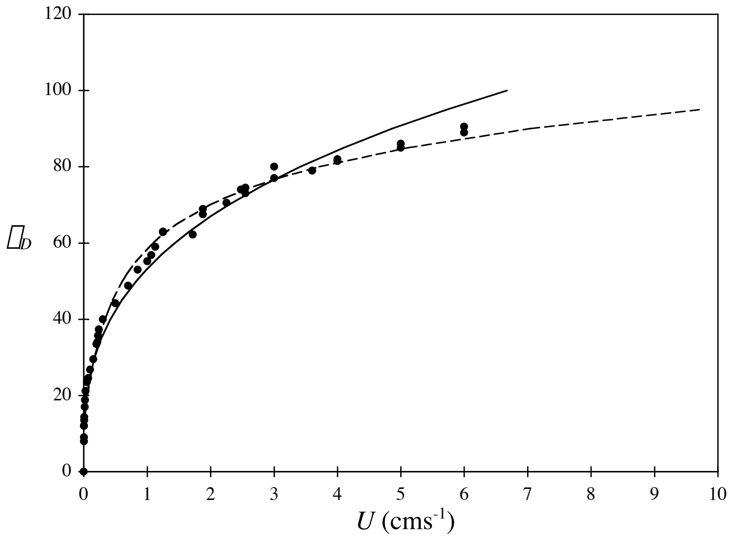

Figure 6. Dynamic contact angle of di-*n*-butyl phthalate on PET at 55 ˚C. Solid curve: hydrodynamic theory, eq (2), with $\ln(L/L_m) = 41.5$ and $\theta_S = 10°$. Dashed curve: MKT, eq (5), with $\lambda = 1.0$ nm, $\kappa^0 = 1.8 \times 10^5$ s^{-1}, and $\theta_S = 10°$. The measured value of θ_S was < 5°.

The fits are only slightly worse if θ_S is constrained to take a value of zero. The fitting parameters for eq (5) also have reasonable values, but the value of $\ln(L/L_m)$ for eq (2) is again physically unacceptable. It may be relevant that with this system, there is also an apparent change in the wetting mechanism, with a small drop in the dynamic contact angle in the transition region at a speed of about 6 cms^{-1} when θ_D = 90°. In Fig. 6, the data start at 30 μms^{-1} with θ_D = 8°, giving a speed range of at least 3 orders of magnitude.

The results presented above are fairly representative of other comparisons to be found in the literature where sufficiently extensive data are available. They show the molecular-kinetic approach to be, perhaps, a little more flexible and adaptable compared with the standard hydrodynamic theory. But they also illustrate how unsafe it may be to draw conclusions as to the general validity of either model simply on the basis of the quality of the fits to equations or the values of the resulting parameters. One exception to this is the case where one viscous liquid displaces another. Here, serious discrepancies have been found if the viscous bending model is used alone,[45,47] whereas adequate fits have been obtained with the molecular-kinetic equations.[23,48] Another exception is in the case of high-viscosity liquids, where the molecular-kinetic model appears to fail near 180°, and hydrodynamic effects are postulated to explain the results.[4] A similar problem exists at small angles when the wetting line is receding and viscous dissipation appears to be dominant.[35,38] Furthermore, in those cases, where the viscous-bending model predicts sub-molecular slip length-scales, we must suppose that either the model is invalid or that some additional mechanism is at work that makes θ_{m} dependent upon wetting-line speed. Overall, it seems that neither model is universally applicable, but that *both* hydrodynamic and molecular mechanisms are at work: that viscous bending may occur, but that θ_m is also speed dependent.

This brings us directly back to Shikhmurzaev's model. As things stand, his theoretical approach appears to be uniquely able to describe published experimental data in an entirely self-consistent way, without recourse to *ad hoc* concepts. Shikmurzaev's own publications[7,8,40,42] have shown many examples of how the asymptotic version of his model can account for the dynamic contact angle behaviour found in an exceptional range of systems, from Hoffman's oils on glass,[32] and data on two-liquid systems,[45] to molten glass on platinum.[16] Here, we give just a single example, based on dynamic contact angle measurements for three aqueous glycerol solutions on PET reported by Blake and Shikhmurzaev.[42] The data for one of these systems have already been presented in Fig. 4. The combined set, for 1.5, 4.2 and 10 mPas glycerol solutions, is shown in Fig. 7, together with the fits obtained by applying Shikhmurzaev's asymptotic equations using a constant set of three, *viscosity independent,* adjustable parameters (see Ref. 42 for details).

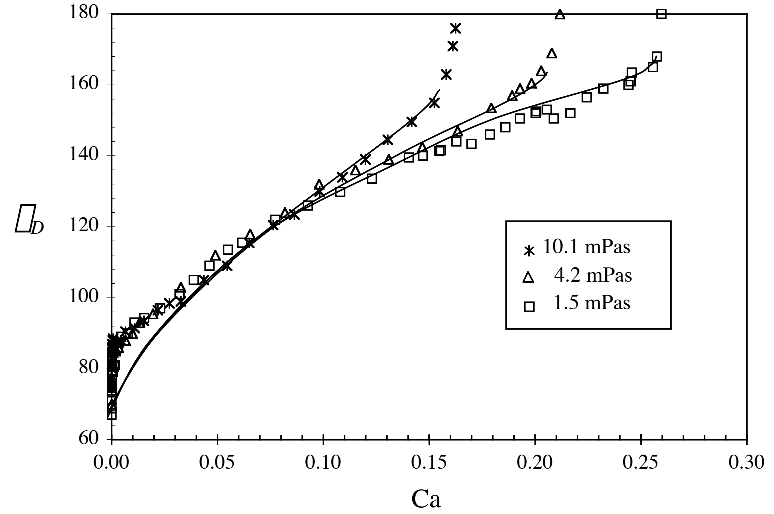

Figure 7. Dependence of the dynamic contact angle on the capillary number for 1.5, 4.2 and 10.1 mPas glycerol solutions on PET. Theoretical curves obtained using the Shikhmurzaev model with a constant set of fitting parameters.[42]

It is worth stressing that the fitted parameters contain only the material properties that one would expect to remain fixed if viscosity alone were changed. The differences in the curves enters through the viscosity ratio between the gas and the liquid, which varies from 0.01 to 0.0015 and comes into play as the dynamic contact angle approaches 180°. In fitting the data, no account has been taken of the possibility of a change in the mechanism of dynamic wetting at low speeds, so the fit is not good in this region. However, the data could just as well have been fitted selectively, as in Figs. 4 and 5 above; in which case much closer agreement would have been achieved. Moreover, as shown in the original publication, the same set of fitting parameters is able to describe, with good precision, not only these results, but also those obtained with solutions of progressively higher viscosity up to 672 mPas.

Analysis of the fitting parameters gives values of the interfacial relaxation time τ that range from 5.6×10^{-9} s – 1.9×10^{-8} s for the 1.5 mPas solution, to 2.5×10^{-6} s – 8.3×10^{-6} s for the 672 mPas solution. These values are not too different to the relaxation times $1/\kappa^0$ obtained by fitting eq (5) collectively to the same data, using eq (7) to account for the effect of viscosity: $3\times10^{-9} – 1.3\times10^{-6}$. As previously noted,[42] this agreement suggests a possible correlation between κ^0 and τ that requires further research, possibly using molecular dynamics, to which we now turn.

4. 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 in the study of dynamic wetting 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. Another advantage is that it can provide a level of control that would be very difficult or even impossible to achieve in physical experiments. For example the degree of wetting, as reflected by θ_s, can be adjusted, at will, by changing the solid/liquid coupling – something that could be done in a real experiment only by changing the chemical nature of the solid or the liquid. 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 simulations are therefore subject to significant thermal and statistical fluctuations. Details of the methods used can be found in the cited references. Here we review just the main conclusions that impact our understanding of dynamic wetting.

The first detailed MD study of the static contact angle known to the author is that of Saville.[49] However, it was not until the groundbreaking publications of Koplik, *et al.*[50,51] and Thompson, *et al.*[52,53] that convincing simulations of dynamic contact angles and moving wetting lines became available. These simulations, which involved Lennard-Jones liquids and several thousand "molecules" in Poiseuille and Couette flow, appeared to exhibit continuum behaviour at the system level. The simulations were for liquid/liquid displacement, rather than liquid/gas.

The Poiseuille studies[50,51] 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 wetting line, though the details could not be ascertained. The dynamic contact angle was seen to vary with wetting-line speed, with advancing angles increasing and receding angles decreasing, as observed experimentally. Furthermore, it was the *local* contact angle θ_m, as defined on a molecular scale, which was seen to vary. The Couette studies[52,53] also confirmed the no-slip condition at solid/liquid interface and was able to quantify the region of apparent hydrodynamic slip, suggesting that it was restricted to a zone of about 1.8σ around the moving wetting line, where σ is the molecular length scale of the liquid. However, it was concluded that θ_m was constant and equal to θ_S, although this is not entirely obvious from the published images (Figs. 8b and 8c in Ref. 53), and the method of assessing θ_D near the centre of the flow at a fixed distance of 6.38σ from the contact line seems arbitrary and unrelated to what one would do in physical experiments. With θ_D measured in this way, however, Thompson, *et al.* found good agreement between their results and the standard hydrodynamic model, but with unphysical values of $\ln(L/L_m)$ for the stronger of the two solid-liquid interactions modelled. This, it was suggested, was due to what amounts to energy dissipation in the slip region.

More recent, large-scale MD simulations of spreading liquid drops,[25,54] spreading cylinders,[55] capillary imbibition[56,57] and the dynamic wetting of fibres[58] seem to confirm what the Poiseuille study suggested: specifically that θ_m is not constant and equal to θ_S, but varies with wetting line speed. Because of entropic effects, its value very close to the solid appears to be slightly smaller than that θ_D when this is assessed by methods that mimic physical experiments, *e.g.* by fitting a circular profile to a spreading drop. However, for partially wetting liquids, none of these studies reveal any evidence of viscous bending of the liquid/gas interface, despite the fact that there is large variation in θ_D for a variation in *Ca* that is similar to that found experimentally.

As experience and computer power has increased, the simulations have become increasingly realistic. For example they now involve liquid molecules comprising chains up to 40 atoms, which reduces evaporation and also allows the effects of changing viscosity to be studied. In general, the simulations appear to behave globally as macroscopic physical systems. It is therefore all the more intriguing that the dynamic contact angle behaviour closely follows that predicted by the molecular-kinetic theory, eq. (5). Moreover, the molecular displacement frequencies at the solid-liquid interface, which can be ascertained directly from the simulations, agree closely with those obtained by fitting eq (5) to the dynamic contact angle data.[25,58] This suggests some underlying validity for the molecular-kinetic model.

What has not yet been determined is whether there is any direct evidence of a variation in the solid/liquid interfacial tension, γ_{SL}, near the moving contact line. By invoking the dynamic analogue of Young's equation, a local change in γ_{SL} can be inferred from the change in the contact angle from its equilibrium value, but the distance over which the change propagates along the solid/liquid interface cannot. At equilibrium, the three-phase zone in the simulations appears to be just a few σ in extent. Confirmation that it extends further along the solid/liquid interface during flow, would provide support for the "relaxation tail" in Shikhmurzaev model.

5. 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 more studies of this type are to be done to further our understanding, then they should be done on well-characterised solids that are smooth and homogeneous to avoid the ambiguities of contact angle hysteresis. They should also be carried out over the widest possible range of speeds and conditions, and preferably in varying geometries. The origins of hydrodynamic assist need to be confirmed by visualising more coating flows. The effects of replacing air with a vacuum need to be studied in detail. Already there is a strong indication that a reduction in air pressure leads to the postponement of air-entrainment,[59] but no results have been published on the dynamic contact angle under the same conditions. Such measurements should provide an indication of the mechanisms at work.

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 evaluated in CFD.

Molecular dynamics simulations have come a long way in answering our questions concerning the molecular details of dynamic wetting, at least for simple Lennard-Jones liquids on realistic Lennard-Jones solids. This work needs to be continued and developed as computational speed and refinements to the code accrue. Possible goals include a more detailed investigation of the three-phase zone and its comparison with the general solid/liquid and liquid/vapour interface, 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 hydrodynamic assist and effects due to viscous dissipation; 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.

Acknowledgements

All the mistakes in this review are mine. Nevertheless, in coming to my conclusions, I have benefited greatly from discussions with many people, from whom I would like to single out Mike Haynes, Jordan Petrov, Kenneth Ruschak, Andrew Clarke, Yulii Shikhmurzaev, John Ralston, and Joel De Coninck. The stimulation provided by others with differing viewpoints is also much appreciated.

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