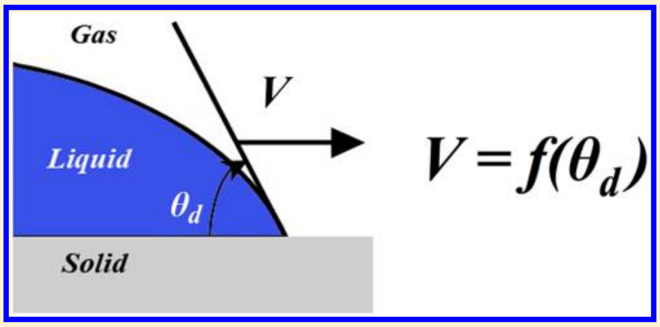
Langmuir
Article
pubs.acs.org/Langmuir

Toward a Predictive Theory of Wetting Dynamics

Damien Duvivier,* Terence D. Blake, and Joël De Coninck

Laboratory of Surface and Interfacial Physics (LPSI), University of Mons, 7000 Mons, Belgium



ABSTRACT: The molecular kinetic theory (MKT) of dynamic wetting, first proposed nearly 50 years ago, has since been refined to account explicitly for the effects of viscosity and solid–liquid interactions. The MKT asserts that the systematic deviation of the dynamic contact angle from its equilibrium value quantitatively reflects local energy dissipation (friction) at the moving contact line as it traverses sites of solid–liquid interaction. Specifically, it predicts that the coefficient of contact-line friction ζ will be proportional to the viscosity of the liquid η_L and exponentially dependent upon the strength of solid–liquid interactions as measured by the equilibrium work of adhesion Wa^0. Here, we analyze a very large set of dynamic wetting data drawn from more than 20 publications and representative of a very wide range of systems, from molecular-dynamics-simulated Lenard–Jones liquids and substrates, through conventional liquids and solids, to molten glasses and liquid metals on refractory solids. The combined set spans 9 decades of viscosity and 11 decades of contact-line friction. Our analysis confirms the predicted dependence of ζ upon η_L and Wa^0, although the data are scattered. In particular, a plot of $\ln(\zeta/\eta_L)$ versus Wa^0/n (i.e., the work of adhesion per solid–liquid interaction site) is broadly linear, with 85% of the data falling within a triangular envelope defined by Wa^0 and $0.25Wa^0$. Various reasons for this divergence are explored, and a semi-empirical approach is proposed to predict ζ. We suggest that the broad agreement between the MKT and such a wide range of data is strong evidence that the local microscopic contact angle is directly dependent upon the velocity of the contact line.

■ INTRODUCTION

The wetting of solids by liquids is a ubiquitous phenomenon, familiar in nature and everyday life and playing an important role in many technological processes. Although it has been a source of academic interest for more than 200 years, the systematic study of wetting dynamics is much more recent. By the early 1960s, no more than a handful of papers had been published on the topic, yet now, the number of publications runs into many thousands. With recent developments in such areas as nanotechnology and microfluidics, the field is still expanding.

Many people have been responsible for this burgeoning interest, but from among them, de Gennes in Europe and Scriven and Dussan V. in the U.S.A. may be singled out as highly influential. A March 2013 search of the Web of Science database using the keywords "dynamic wetting" returned 12 472 hits. This must be a lower limit to the total number of papers published, because the search did not include other associated keywords, such as "spreading". For seminal publications, such as Huh and Scriven's 1971 paper[1] and Dussan's 1979 review,[2] Google Scholar listed 777 and 822 citations, respectively. For the 1985 general review of wetting by de Gennes,[3] the figure was 4320. The field of dynamic wetting has gathered momentum partly because, if the first question to be asked is how well a liquid will wet a solid, the second is usually how fast can it be made to wet or dewet, because this is frequently a limiting factor in process design.

When it comes to quantifying wetting, the key experimental parameter used to characterize the degree of wetting is the equilibrium angle of contact θ^0, i.e., the angle (measured through the liquid) that the liquid/vapor interface makes with the solid surface at the three-phase contact line.[3] This angle determines the equilibrium configuration of the system. If θ^0 is zero, the liquid is said to completely wet the solid. If it is greater than zero, the system is said to be partially wetting. Liquids for which $\theta^0 < 90°$ are described as wetting liquids, whereas if $\theta^0 > 90°$, they are said to be non-wetting.

An arbitrary drop of liquid placed on a perfectly flat and homogeneous surface will tend to spread or contract to minimize its surface free energy until the contact angle achieves its equilibrium value. The angle exhibited during this process is called the dynamic contact angle θ_d. In general, advancing contact angles increase ($\theta_d > \theta^0$) with wetting velocity V, whereas receding angles decrease ($\theta_d < \theta^0$). Because most real surfaces are neither perfectly flat nor homogeneous, the process usually terminates at some intermediate free-energy configuration, a local minimum, at which the contact line pins. The associated contact angles are known, respectively, as the static advancing or receding contact angles, $\theta_A > \theta^0$ or $\theta_R < \theta^0$, according to whether the drop is spreading or contracting before pinning.[4]

Received: May 13, 2013
Revised: July 5, 2013
Published: July 11, 2013

dx.doi.org/10.1021/la4017917 | *Langmuir* 2013, 29, 10132−10140

It is now recognized that, as the contact line moves across the solid surface, several channels of dissipation may come into play to oppose its motion. At low Reynolds numbers, the two principal channels are viscous dissipation within the liquid and more localized losses at the contact line, the so-called "contact-line friction".[5] Although this latter channel has gained increasingly wide acceptance, its physical origin and significance are still a matter of debate. The main aim of this paper is to collate a substantial amount of the experimental evidence and to demonstrate the utility of the molecular kinetic theory (MKT)[6,7] in providing not only a quantitative explanation of contact-line friction but also a significant level of predictive ability.

The hydrodynamic influence of viscosity on the relationship between contact-line velocity V and the dynamic contact angle is usually modeled using the lubrication approximation, invoking either a microscopic cutoff length beyond which the solution is truncated or a region of local slip between the liquid and the solid in the immediate vicinity of the contact line.[8,9] One or the other of these devices is introduced because of the conflict between a contact line that moves and the standard no-slip condition at the solid boundary, which otherwise leads to divergent stress fields.[1] According to this classical model, the variation in the experimentally observed contact angle is due to changes in the slope of the interface at a mesoscale, below that of observation but larger than the microscopic scale at which, it is assumed, the equilibrium contact angle still persists. Contact-line friction is not invoked. It is not necessarily ruled out but is considered beyond the scope of hydrodynamics.[8] The classical model has inherent limitations, not least of which is that it predicts a non-physical stagnation point on the liquid/vapor interface at the contact line. Nevertheless, it does account for the velocity dependence of the contact angle seen with many experimental systems, most notably those in which the liquid completely wets the solid.[10]

An alternative hydrodynamic approach introduced by Shikhmurzaev[11] circumvents the contact-line problem by including the material properties of the interfaces in the various equations for flow near the contact line. His continuum treatment accommodates viscous dissipation using standard hydrodynamics but also includes losses because of the interfacial creation and destruction processes occurring as the contact line moves across the surface. Thus, contact-line dissipation is an integral part of the model. One consequence is that the microscopic contact angle is coupled directly to the flow and emerges as a solution to the equations. It is not an imposed quantity. It deviates from the equilibrium contact angle because the local surface tensions differ from their equilibrium values as a direct consequence of interface creation and destruction. Shikhmurzaev's approach is successful in modeling the velocity dependence of the contact angle for a wide range of systems. Significantly, it also accounts for non-local effects, whereby changes in the flow field, in addition to the contact-line velocity, appear to have a direct influence on the dynamic contact angle, the so-called "hydrodynamic assist" of dynamic wetting,[12] something the classical models do not do.[13] However, in common with all dynamic wetting models, it is not yet fully predictive and some degree of curve fitting is required to extract key parameters.

Because we are, as yet, unable to resolve the dynamic contact angle at a sufficiently refined scale, it has proven difficult to establish the validity of one model over another by direct experiment. Therefore, most commentators fall back on first-principle arguments, about which there is a distinct lack of consensus. Perhaps the most significant question is whether the local, microscopic contact angle is dependent upon the velocity of the contact line or able to adjust with sufficient rapidity to maintain its equilibrium value. While it has been argued that it is highly unlikely that the balance of forces at the contact line would be so totally indifferent to the motion of the line that the local, microscopic angle would remain constant,[7] others have dismissed this possibility as unnecessary to explain the experiment. Evidence for the physical reality of contact-line friction would be strong support for the former view, i.e., a velocity-dependent local angle, because the latter implies local dissipation.

In this paper, we show that the contact-line friction model as embodied in the MKT does indeed provide a cogent explanation of the velocity dependence of the contact angle for a very wide range of systems, from molecular-dynamics (MD)-simulated Lenard–Jones liquids and substrates, through conventional liquids and solids, to molten glasses and liquid metals on refractory solids. The combined data span 9 decades of viscosity and 11 decades of contact-line friction. Furthermore, the data confirm two of the main predictions of the MKT, namely, that the coefficient of the contact-line friction ζ is proportional to the viscosity of the liquid η_L and exponentially dependent upon the strength of solid–liquid interactions, as reflected by the equilibrium work of adhesion Wa^0.

The MKT has been explained in detail in previous papers, but a summary here is helpful to provide the background for the subsequent discussion. Before proceeding, we should mention that at least two "combined" models have been proposed[14,15] that exploit the MKT to account for local variations in the contact angle, together with versions of the classical hydrodynamic model to accommodate changes at the mesoscale. This combined approach can also fit experimental data with good accuracy. However, conceptually useful though it is, it does not add anything to the hydrodynamic model itself or directly address the question of whether or not the local angle changes. On the other hand, if we can not only model dynamic contact angle behavior for a diverse mass of data using the MKT without recourse to additional concepts but also make reasonably accurate predictions of the effects of both viscosity and solid–liquid interactions (independently verifiable quantities that have a demonstrable effect on wetting dynamics), then this would suggest that the concepts on which the MKT is based are valid, including the velocity dependence of the microscopic contact angle.

Readers in search of more complete surveys of the various models of dynamic wetting might like to consult the reviews by Kistler,[16] Shikhmurzaev,[11] Blake,[10] and Bonn et al.[17]

■ MOLECULAR KINETIC THEORY

According to this model, first introduced by Blake and Haynes in 1969[6] and later extended by Blake[7] and Blake and De Coninck,[18] the movement of the contact line is determined by the collective dynamics of the individual molecules within the three-phase zone (TPZ), where the solid, liquid, and gas phases meet. On the molecular scale, this zone is small but finite and has a thickness comparable to its component interfaces. The key parameters that characterize the dynamics of this region are the equilibrium frequency of molecular displacements κ^0 (Hz) and the average distance of each displacement λ (m). Because of interactions with the solid, κ^0 is significantly smaller than the frequency of thermal displacements within the bulk liquid.

By analogy with the Frenkel−Eyring theory of liquids,[19,20] we can write

$$\kappa^0 = \frac{k_B T}{h}\exp\left(\frac{-\Delta g_W^*}{n k_B T}\right) \tag{1}$$

where Δg_W^* and n are the specific activation free energy of wetting and the number of sites of solid−liquid interaction (adsorption sites) per unit area, respectively, and k_B, h, and T are the Boltzmann constant, Planck constant, and absolute temperature, respectively.

As originally conceived, the velocity dependence of the contact angle is principally due to the disturbance of interfacial adsorption and, hence, to local changes in one or more of the interfacial tensions as the contact line moves across the solid surface. In this respect, there are similarities with the Shikhmurzaev model. These changes generate a surface tension stress $\sigma = \gamma_L (\cos \theta^0 - \cos \theta_d)$ that drives the system in the direction required to restore equilibrium. Here, γ_L (N/m) is the surface tension of the liquid. At equilibrium, the net frequency of molecular displacements is the same in the backward and forward directions; therefore, the contact line is stationary. If equilibrium is disturbed, the resulting stress modifies the activation energies required for a displacement, lowering them in the direction of σ (the forward direction) and increasing them in the reverse direction. This increases κ^0 to κ^+ in the forward direction and reduces it to κ^- in the backward direction. The contact line therefore moves to relieve the stress at an average velocity $V = \lambda(\kappa^+ - \kappa^-)$, which leads to[6,7]

$$V = 2\kappa^0 \lambda \sinh\left(\frac{\gamma_L(\cos \theta^0 - \cos \theta_d)}{2 n k_B T}\right) \tag{2}$$

If the argument of the sinh is small (typically γ_L is small, n is large, or $\theta_d \sim \theta^0$)

$$V = \frac{\gamma_L}{\zeta}(\cos \theta^0 - \cos \theta_d) \tag{3}$$

where $\zeta = k_B T/\kappa^0 \lambda^3$ (Pa·s) is the coefficient of contact-line friction per unit length of the contact line. Note that it has the same units as shear viscosity. The parameters κ^0, λ, and ζ can be obtained by fitting dynamic contact angle data to these equations over a sufficient wide range of angles and speeds. It is usually found that λ is of the order of molecular dimensions or a little larger, whereas κ^0 can vary over many orders of magnitude but is always less than that expected for the bulk liquid.

Blake[7] argued that molecular displacements within the TPZ will be retarded not only by interactions with the solid but also by viscous interactions with neighboring liquid molecules. Thus, Δg_W^* will have contributions Δg_S^* and Δg_{vis}^* arising, respectively, from surface and viscous interactions; i.e., $\Delta g_W^* = \Delta g_S^* + \Delta g_{vis}^*$. From Eyring's theory of viscosity[19]

$$\eta_L = \frac{h}{\nu_L}\exp\left(\frac{\Delta g_{vis}^*}{n k_B T}\right) \tag{4}$$

where ν_L is the volume of the unit of flow, which for simple liquids can be taken as the molecular volume. Combining this with eq 1 gives

$$\kappa^0 = \frac{k_B T}{\eta_L \nu_L}\exp\left(\frac{-\Delta g_S^*}{n k_B T}\right) \tag{5}$$

Thus, the MKT can provide a non-hydrodynamic model of dynamic wetting that includes the effects of viscosity.

It was initially pointed out[7] that experimental values of Δg_S^* were similar to γ_L; however, Blake and De Coninck[18] later presented evidence for a stronger and intuitively more logical correlation with the reversible work of adhesion $Wa^0 = \gamma_L(1 + \cos \theta^0)$ (J/m^2), leading to

$$\kappa^0 = \frac{k_B T}{\eta_L \nu_L}\exp\left(\frac{-Wa^0}{n k_B T}\right) \tag{6}$$

This equation offers the possibility of predicting κ^0 by experimental determination of viscosity, surface tension, and equilibrium contact angle, leaving only λ in eqs 2 and 3 to be determined by curve fitting. Over the last 20 years or so, a considerable body of evidence has accumulated supporting eq 6 based on experiments.[21−23] The evidence has been summarized in a recent publication in which a formal link between the MKT and the more general Kramers theory of rate processes has also been established.[24] In particular, it was shown here that, for a simple system interacting through Lennard−Jones potentials, Wa^0 is likely to be a good approximation for Δg_S^*.

When all of these ideas are combined, the expression for contact-line friction becomes

$$\zeta = \frac{\eta_L \nu_L}{\lambda^3}\exp\left(\frac{Wa^0}{n k_B T}\right) \tag{7}$$

or equivalently

$$\ln(\zeta/\eta_L) = \ln(\nu_L/\lambda^3) + Wa^0/n k_B T \tag{8}$$

Thus, it is predicted that ζ is linearly dependent upon η_L and exponentially dependent upon Wa^0. It is these predictions that we have set out to test in the present paper by examining as many viable sets of dynamic wetting data, drawn from both experiments and simulations, as we could glean from the literature. In most cases, the papers also disclose other information necessary to test the equations, such as surface tensions, viscosities, and temperatures, but where these were not reported, we made estimates based on other published sources.

RESULTS AND DISCUSSION

Data have been extracted from a total of 20 publications. References to the papers and the ranges of values found for Wa^0, η_L, and ζ are listed in Table 1.

Two strategies were employed to obtain ζ if its value or, equivalently, that of κ^0 and λ were not reported in the original paper. Where there were sufficient data covering a wide enough range of θ_d and V, then values of κ^0 and λ were extracted by fitting eq 2 and used to calculate ζ. Alternatively, for more limited data and θ_d not too far from θ^0, ζ was obtained without recourse to a specific model simply from the slope of a plot of $(\cos \theta_0 - \cos \theta_d)$ versus V. For the fits to eq 2, we used *G-dyna* software.[42,43] This freeware was developed especially for dynamic wetting studies and exploits a Levenberg−Marquardt algorithm to fit the data and the bootstrap technique to assess fit robustness. In a few cases, published values of ζ were confirmed by refitting the original data.

Table 1. Ranges of the Values of Wa^0, η_L, and ζ Found for the 20 Publications Collated in This Study[a]

source	Wa^0 (mJ/m^2)	viscosity, η_L (Pa·s)	friction, ζ (Pa·s)
Blake and Shikhmurzaev[25]	89.4−93.4	0.00152−0.104	0.015−1.84
Duvivier et al.[26]	127−144	0.0010−0.159	0.85−42.9
Vega et al.[27]	38.9−125	0.001−0.035	0.26−18.3
Ray et al.[22]	57.0−131	0.06	4.02−31.9
Semal et al.[28]	20.15−59.9	0.035	0.146−0.460
Stalcup et al.[29]	87.12−94	0.098−2.80	9.21−46.10
Vega et al.[30]	39.4−43	0.005−0.5	0.38−9.19
Saiz et al.[31]	38.4−2185	0.00103−561	0.0107−738000
Brooks et al.[32]	58.5−72.14	0.081−4.3	14.7−321
de Ruijter et al.[33]	60.35−94.7	0.0196−0.209	3.18−33.1
Goossens et al.[34]	83.9−103.0	0.0003−0.033	1.07−5.87
Blake[10]	42.6−93.6	0.001−98.8	0.01−358
Inverarity[35]	130−142	0.008−0.41	10.6−139
Hoffman[36]	42.6−60.4	0.958−109	35.8−358
Li et al.[23]	36.8−40.1	0.033−0.33	0.773−5.57
Schwartz and Tejada[37]	36.9−78	0.00033−0.101	0.406−2.38
Ström et al.[38]	0.0369−0.0874	0.078−4.88	27.1−377
Seveno et al.[39]	**12.6−20.1**	**0.000035**	**0.00203−0.00691**
Bertrand et al.[40]	**0.53−4.6**	**0.000248**	**0.000089−0.0011**
Seveno et al.[41]	**10.3−18.7**	**0.000035**	**0.0037−0.0063**

[a] The MD simulations are in bold.

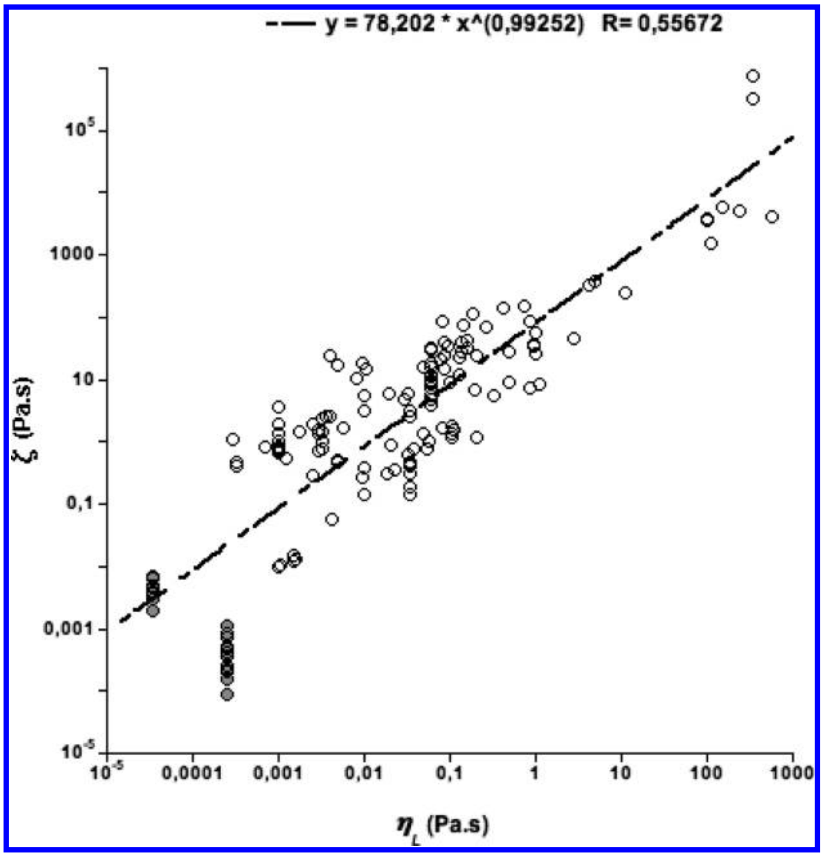


Figure 1. Plot of contact-line friction ζ versus viscosity η_L together with the associated trendline for the 20 publications collated in this study. Gray circles are data from MD simulations.

A log−log plot of ζ versus η_L is shown in Figure 1. Although there is considerable scatter, it is clear that the two parameters are closely linked, with the slope of the collected data equal to 0.992, in near perfect agreement with eq 7. This relationship has already been demonstrated experimentally,[7,23,26,34] but this is the first time it has been verified for such a wide range of systems and over such an extreme range of viscosities. With reference to eq 7, one can argue that the scatter arises because neither ν_L/λ^3 nor Wa^0/nk_BT will be constant across all systems. The effect can be seen most clearly with the simulations (gray circles on the lower left of the plot). Here, η_L, ν_L, λ, and n are all held constant, while Wa^0 is systematically varied by changing

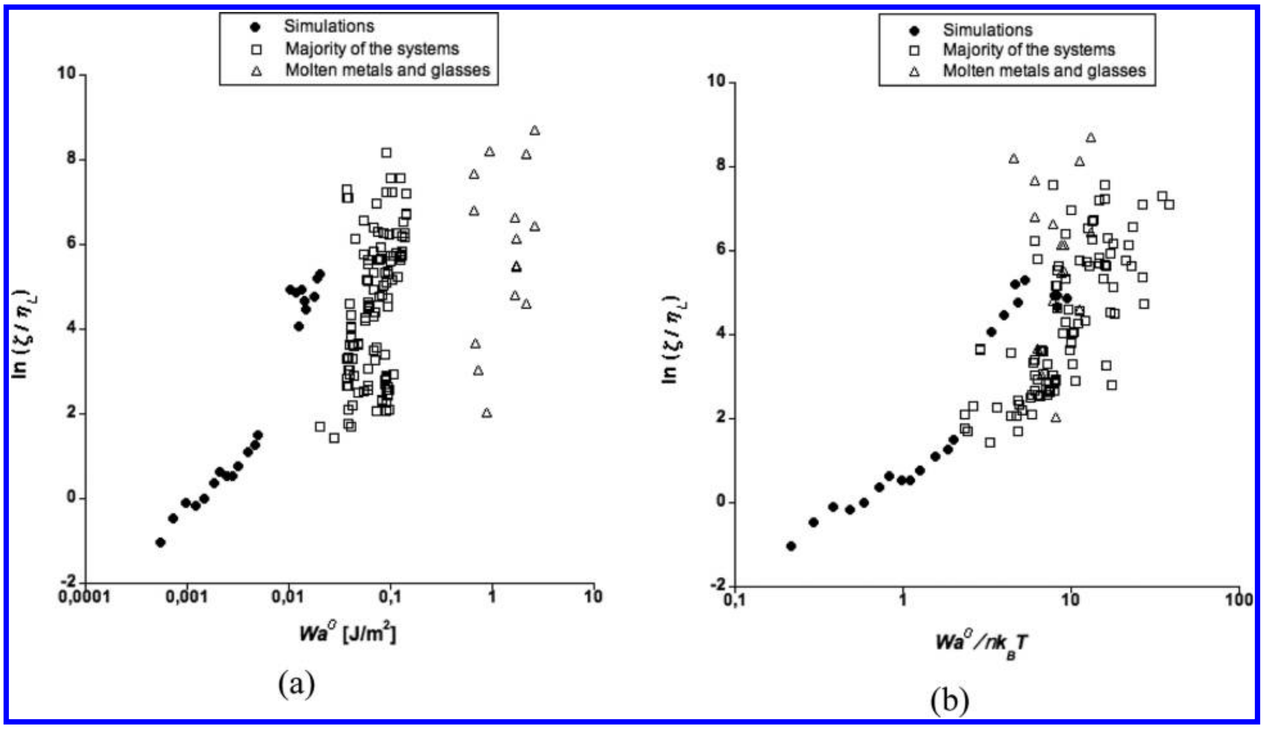


Figure 2. Plots of $\ln(\zeta/\eta_L)$ versus Wa^0 and Wa^0/nk_BT for all 20 publications.

the solid−liquid interaction potential. The net result is stacked data with ζ increasing progressively at constant η_L. The experimental work by Puah et al. cited above,[21] on the influence of surface charge on wetting kinetics for water on modified titania, also demonstrate the benefits of being able to hold η_L, ν_L, λ, and n constant while systematically varying Wa^0 as a means of cogently testing eqs 6−8.

The influence of Wa^0 on ζ in our collected data is revealed in Figure 2. The left-hand graph (Figure 2a) shows $\ln(\zeta/\eta_L)$ for the same 20 publications plotted directly against Wa^0. There is clearly a trend, but the data fall into three distinct groups: one at low Wa^0 for the simulations ($T = 33.3$ K), a second at intermediate Wa^0 for common solid/liquid systems at ambient temperatures, and a third at high Wa^0 for molten metals and glasses ($T \sim 1500$ K).

The second graph (Figure 2b) shows the same data plotted versus Wa^0/nk_BT, i.e., the reversible work of adhesion per interaction site expressed in units of k_BT. This is in direct accordance with eqs 7 and 8 and has the immediate effect of collapsing the data (by more than a factor of 10 in the x direction) and making the trend more evident, although it is notable that the spread increases progressively with Wa^0. Again, with reference to eq 7, one may argue that this scatter arises partly from the fact that ν_L/λ^3 will vary from system to system and can, therefore, be expected to increase with the diversity of systems considered.

However, there is an additional source of uncertainty. When fitting data from experiments, we usually assume that the interaction sites are uniformly distributed and that $\lambda = 1/(n^{1/2})$. In contrast, for the MD simulations,[40,44] n is known precisely from the lattice spacing of the solid δ (i.e., $n = 1/\delta^2$) but direct analysis of the distribution of molecular displacements shows that, on average, they tend to be slightly longer. Displacements can be along the lattice diagonal as well as directly between nearest neighbor sites, and some jumps will be longer still. The net result is that, on average, $\lambda > 1/(n^{1/2})$. This uncertainty will clearly affect ν_L/λ^3 and potentially Wa^0/nk_BT. Furthermore, for some of the data sets included in our analysis, neither λ nor n was disclosed and estimates were necessary. For the liquid metals and glasses, we based λ on the substrate lattice parameter. For Semal et al.[28] and Brooks et al.,[32] we assumed $\lambda = 0.75$ nm, the mean value for all of the other publications considered. In each case, we assumed $n = 1/\lambda^2$.

Figure 2b confirms a clear correlation between ζ and Wa^0/nk_BT (for the combined data, the Pearson correlation coefficient is 0.45; a coefficient of 1 would indicate perfect correlation). This is explored further in Figure 3. Figure 3a shows the collated data plotted against a linear Wa^0/nk_BT axis. Also shown are three dotted lines based on eq 8. Line A is a fit to the results from the simulations, with the slope set to Wa^0/nk_BT. The resulting intercept $\ln(\nu_L/\lambda^3) = -0.51$ (i.e., $\nu_L/\lambda^3 = 0.6$). This line is also a reasonable fit to a good proportion of the data for the molten metals and glasses and seems to provide an upper limit for all of the data. In other words, it would appear that, when all of the quantities in eqs 7 and 8 are known with some certainty, as in MD simulations, then $\Delta g^{\ddagger}_{S} \sim Wa^0$ and contact-line friction does indeed behave exactly as predicted by the model. All of the rest of the data lie to the right of line A, implying either a weaker dependence upon Wa^0 or that we are systematically underestimating n from the experiments. We explore these two possibilities below.

Line B shows the result of reducing the dependence upon Wa^0 by 50%, and line C shows the result of reducing the dependence upon Wa^0 by 75%. In both cases, ν_L/λ^3 is kept constant at 0.6. Some 85% of all of the data lie between lines A and C. Figure 3b shows the same data plotted with a logarithmic ordinate axis for comparison to Figure 2b.

One explanation for overestimating the influence of Wa^0 on ζ in experimental studies is that it could be due to the roughness and/or heterogeneity of real solid surfaces, as compared to the idealized surfaces in simulations. From the outset,[6,7] sources of contact-line dissipation other than an

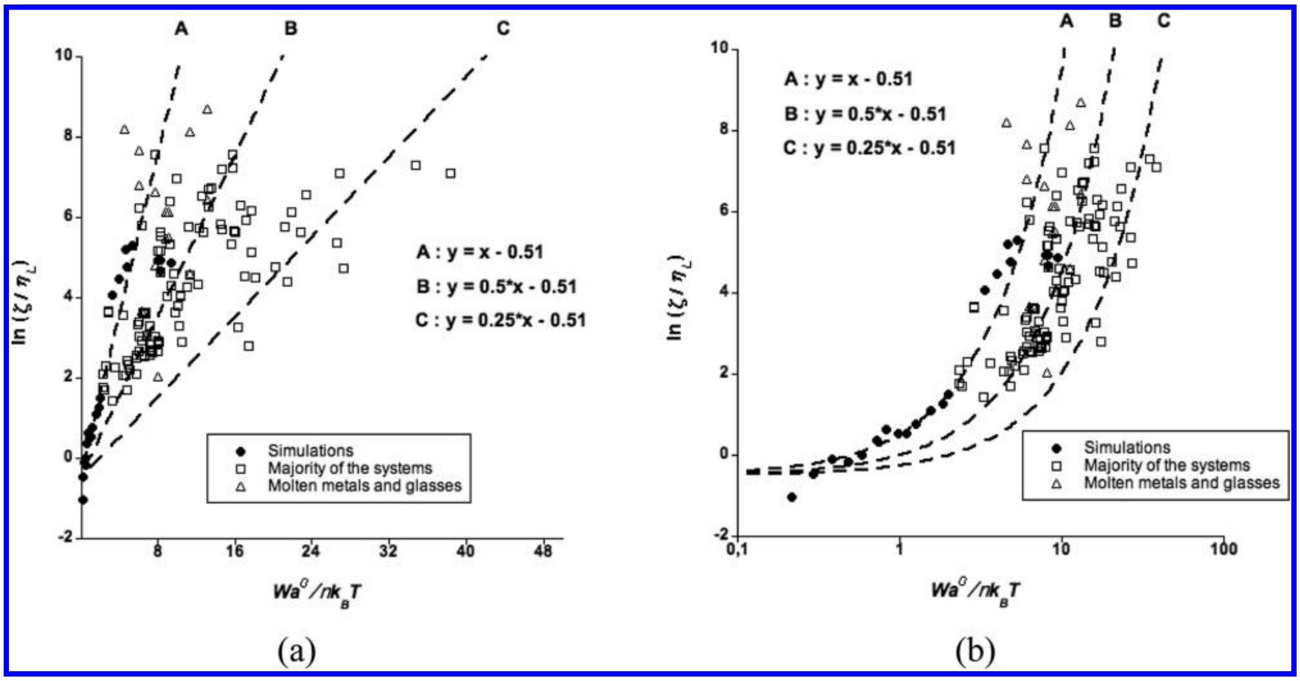


Figure 3. $\ln(\zeta/\eta_L)$ versus Wa^0/nk_BT for the 20 publications. Line A is a fit of eq 8 to the simulation data. Line B shows the effect of reducing the influence of Wa^0 by 50%, and line C shows the effect of reducing the influence of Wa^0 by 75%. More than 85% of the data lie between lines A and C.

adsorption/desorption process were envisioned, provided that they were susceptible to Maxwell–Boltzmann statistics. As cogently argued elsewhere,[45−47] roughness could provide such an alternative source, arising from the pinning/depinning events that occur as the contact line moves across the solid surface from one set of asperities to another. On an appropriate scale, these events may still be modeled as activated rate processes and could dominate or at least modify the observed dynamics, leading to a reduction in the influence of the solid–liquid interactions that give rise to adhesion. The same roughness would be expected to cause contact angle hysteresis, which would confound estimates of Wa^0. Similarly, if the surface were heterogeneous, one would expect the sites of the strongest solid–liquid interaction to dominate the kinetics in much the same way as pinning/depinning events, whereas all of the solid–liquid interactions, both weak and strong, would contribute to the equilibrium work of adhesion. Thus, $\Delta g_S^* < Wa^0$.

The other possibility, that we are systematically underestimating n in the fits to experimental data, is also worth exploring in relation to the potential heterogeneity of real surfaces. We have already pointed out that the molecular displacement distance λ obtained by fitting eq 2 is likely to be larger than δ, the lattice parameter of the solid surface, and that this effect has been seen in MD simulations.[40] The actual ratio found was $\lambda = 1.1\delta$. If the surface were heterogeneous, sites of strong interaction would require larger activation energies for molecular displacements than weaker sites. Displacements between the former would therefore tend to dominate the observed dynamics; i.e., they would become rate-limiting. Thus, the values of λ extracted by fitting eq 2 would tend to reflect the distance between the strongly interacting sites and would be larger that the average distance between all sites. In consequence, with n set equal to $1/\lambda^2$, its calculated value would be smaller than the total number of sites and, when used to calculate Wa^0 per site, would result in a significant overestimate of Δg_S^*. It may also be significant that we usually find good agreement with theory for the metals and glasses where we based n on the substrate lattice parameter rather than a fitted value of λ.

These potential effects of surface roughness and heterogeneity are also consistent with the fact that the values of λ found in experimental studies tend to be a little larger than molecular dimensions. For example, 1–2 nm is not uncommon, and larger values have been reported that have been attributed to roughness.[45] Furthermore, because the basic tenet of the MKT is that the average velocity of the contact line is the result of the collective action of its constituent molecules, it is probable that these large values are the result of some sort of averaging process involving a multiplicity of energy barriers and interbarrier distances from various sources, including pinning at asperities and heterogeneities as well as simple intermolecular solid–liquid interactions. Taken together, these arguments suggest that it is far more likely that $\Delta g_S^*/nk_BT$ will be overestimated than underestimated and ζ/η_L will be less than predicted.

One may ask why we do not include the specific values of ν_L in our calculations, because the relevant data are often available. We did investigate this and were able to improve the correlation between $\ln(\zeta/\eta_L)$ and Wa^0/nk_BT by a small margin; the Pearson correlation coefficient increased slightly from 0.45 to 0.52. The problem, however, lies not with ν_L but with λ^3, which appears in the key ratio with ν_L in the first term on the right-hand side of eqs 7 and 8. For the reasons discussed above, λ is subject to some uncertainty, which is significantly increased for λ^3. In fact, the calculated values ν_L/λ^3 for the systems studied all lie in the interval 0.1–2, with a mean value of 0.57, which is consistent with our best fit value of 0.6 in Figure 3a. Given that the effect of including ν_L is so marginal, we thought it more straightforward to explore the relationship between $\ln(\zeta/\eta_L)$ and Wa^0/nk_BT directly rather than introduce an additional term, which we felt might obscure our conclusions.

What then can we do about this if we wish to use the MKT and, more particularly, eq 7 to predict the contact-line friction

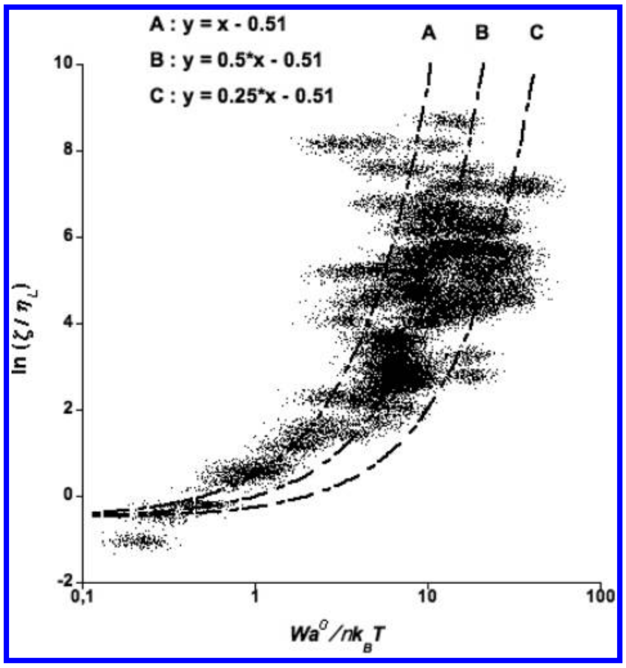


Figure 4. Clouds of 200 points generated around each experimental point in Figure 3 using random values of ζ, η_L, λ, and Wa^0 with Gaussian distributions.

in real systems? Furthermore, if we do use eq 7 in this way, how confident can we be in our predictions?

To illustrate the effect of potential errors on the expected value of $\ln(\zeta/\eta_L)$, we have taken the data of Figure 3 and generated clouds of 200 points around each experimental point using random values of ζ, η_L, λ, and Wa^0 with Gaussian distributions. To do this, we assumed that the standard deviations for each parameter were as follows: ζ, ±10%; η_L, ±1%; λ, ±10%; and Wa^0, ±1%. The result is plotted in Figure 4. The values of the standard deviations are, of course, quite arbitrary, although it is clear that the experimental parameters (η_L and Wa^0) will be known to greater precision than λ and ζ. However, our purpose here is simply to illustrate how well eqs 7 and 8 correlate the data and the difficulty of making exact predictions.

A logical approach might be to assume that $Wa^0 \geq \Delta g_S^*$ and treat the values of ζ predicted by eqs 7 and 8 as an upper bound, i.e., line A in Figure 3. In addition, we could probably improve on our estimates of n using information about the surface structure of the solid rather than simply setting $n = 1/\lambda^2$. However, if this is not possible and given that the majority of the experimental data lie to the right of line A, then a semi-empirical way to proceed would be to find the best fit to all of the data and use this to predict ζ. If we adopt the same intercept as before (−0.51), then a linear fit in accordance with eq 8 has a slope of 0.343. That is to say, to predict ζ, we would have to multiply Wa^0 by a factor $\alpha = 0.343$. However, the standard deviation on $\ln(\zeta/\eta_L)$ for this line is rather large (2.64). This is not altogether encouraging, although one should bear in mind that we are considering an extremely wide range of systems for which, in some cases, only limited data are available.

If one takes the results of individual studies that report extensive sets of dynamic contact angle data and all of the necessary additional parameters (T, λ, ν_L, γ_L, θ^0, and η_L), then we find a much greater degree of consensus. For example, the value of α required to give agreement with eq 8 for the data by Hoffman[36] (silicone oils on glass) is 0.45. Similarly, for Blake and Shikhmurzaev[25] (aqueous glycerol solutions on polyethylene terephthalate), $\alpha = 0.47$; for Duvivier et al.[26] (aqueous glycerol solutions on glass), $\alpha = 0.64$; for Vega et al.[30] (silicone oils on polyethylene terephthalate), $\alpha = 0.58$; for Li et al.[23] (ionic liquids on a fluoropolymer), $\alpha = 0.49$; and for Schwartz and Tejada[37] (organic liquids on a range of polymers and metals), $\alpha = 0.43$. The mean value of α for all of these studies is 0.51 ± 0.082, which implies that, if we set

$$\ln(\zeta/\eta_L) \sim \ln(\nu_L/\lambda^3) + Wa^0\lambda^2/2k_BT \tag{9}$$

i.e., we assume $\Delta g_S^* = 0.5Wa^0$ with $n = 1/\lambda^2$ (line B in Figure 3), we can predict $\ln(\zeta/\eta_L)$ with an accuracy of better than 60% over the full range of the data considered. It therefore seems reasonable to recommend this semi-empirical approach until such time as we have better data or a better model.

Equation 9 implies that $\lambda = 2^{1/2}\delta$. This would be the case if all displacements were along the diagonals of a square lattice. However, no evidence to support this seductive idea can be found from our MD simulations.

■ CONCLUSION

In this paper, we set out to test the predictions of the MKT of dynamic wetting, in particular, the prediction that the contact-line friction ζ is linearly dependent upon the viscosity η_L and exponentially dependent upon the work of adhesion Wa^0. To do this, we collated a very large set of dynamic wetting data drawn from more than 20 publications and representative of a very wide range of systems, from molecular-dynamics-simulated Lenard−Jones liquids and substrates, through conventional liquids and solids, to molten glasses and liquid metals on refractory solids. The combined set spans 9 decades of viscosity and 11 decades of contact-line friction.

Although the data are scattered, the predicted dependencies have been substantially confirmed. Thus, a log−log plot of ζ versus η_L (Figure 1) is clearly linear with a slope equal to 0.992, in near perfect agreement with the model. Furthermore, a plot of $\ln(\zeta/\eta_L)$ versus Wa^0/n (i.e., the work of adhesion per solid−liquid interaction site) has a linear trend, with 85% of the data falling within a triangular envelope defined by Wa^0 and $0.25Wa^0$ (Figure 3a). Very good agreement has been found for the simulations and for some of the liquid metals. Various reasons for the scatter observed for the other systems have been explored, including the effects of roughness and heterogeneity on the dynamic wetting of real solid surfaces, as compared to the ideal surfaces used in the simulations. One problem highlighted is the difficulty in estimating the total number of solid−liquid interaction sites responsible for adhesion when calculating the specific activation free energy of wetting Δg_S^* from Wa^0. This number may be significantly larger than the number of sites that influence the dynamics of wetting. In general, it seems that $Wa^0 \geq \Delta g_S^*$. In practice, this means that Wa^0 sets an upper limit on Δg_S^* when estimating the contact line friction for real solids and liquids. Analysis of experimental systems where we have comprehensive dynamic wetting data suggests that a reasonable estimate of ζ might be obtained by taking $\Delta g_S^* = Wa^0/2$.

Overall, we have shown that it is possible not only to model dynamic wetting for a very diverse range of systems using the MKT but also to make sensible predictions of the effects of both viscosity and solid−liquid interactions (independently verifiable quantities that have a demonstrable effect on wetting dynamics). We suggest that this is strong evidence that the concepts on which the MKT is based are valid, including the assertion that the local microscopic contact angle is directly dependent upon the velocity of the contact line and, therefore, should not be treated as a constant and equal to the equilibrium contact angle, as frequently the case in applications of classical hydrodynamic models.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: damien.duvivier@umons.ac.be.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research has been funded by the Interuniversity Attraction Poles Programme (IAP 7/38 MicroMAST) initiated by the Belgian Science Policy Office. We also thank the Ministère de la Région Wallonne and the Fonds National de la Recherche Scientifique (FNRS) of Belgium for the partial financial support.

■ REFERENCES

(1) Huh, C.; Scriven, L. E. Hydrodynamic model of steady movement of a solid/liquid/fluid contact line. *J. Colloid Interface Sci.* **1971**, *35*, 85−101.

(2) Dussan V., E. B. On the spreading of liquids on solid surfaces: Static and dynamic contact lines. *Annu. Rev. Fluid Mech.* **1979**, *11*, 371−400.

(3) de Gennes, P.-G. Wetting: Statics and dynamics. *Rev. Mod. Phys.* **1985**, *57*, 827−863.

(4) Blake, T. D.; Haynes, J. M. Contact-angle hysteresis. *Prog. Surf. Membr. Sci.* **1973**, *6*, 125−138.

(5) de Ruijter, M. J.; Blake, T. D.; De Coninck, J. Dynamic wetting studied by molecular modeling simulations of droplet spreading. *Langmuir* **1999**, *15*, 7836−7847.

(6) Blake, T. D.; Haynes, J. M. Kinetics of liquid/liquid displacement. *J. Colloid Interface Sci.* **1969**, *30*, 421−423.

(7) Blake, T. D. In *Wettability*; Berg, J. C., Ed.; Marcel Dekker: New York, 1993; pp 251−309.

(8) Voinov, O. V. Hydrodynamics of wetting. *Fluid Dyn.* **1976**, *11*, 714−721.

(9) Cox, R. G. J. The dynamics of the spreading of liquids on a solid surface. *Fluid Mech.* **1986**, *16*, 169−194.

(10) Blake, T. D. The physics of moving wetting lines. *J. Colloid Interface Sci.* **2006**, *299*, 1−13.

(11) Shikhmurzaev, Y. D. Moving contact lines in liquid/liquid/solid systems. *J. Fluid Mech.* **1997**, *334*, 211−249.

(12) Blake, T. D.; Bracke, M.; Shikhmurzaev, Y. D. Experimental evidence of nonlocal hydrodynamic influence on the dynamic contact angle. *Phys. Fluids* **1999**, *11*, 1995−2007.

(13) Wilson, M. C. T.; Summers, J. L.; Shikhmurzaev, Y. D.; Clarke, A.; Blake, T. D. Nonlocal hydrodynamic influence on the dynamic contact angle: Slip models vs experiment. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2006**, *73*, 041606-1−041606-10.

(14) Petrov, P. G.; Petrov, J. G. A combined molecular-hydrodynamic approach to wetting kinetics. *Langmuir* **1992**, *8*, 1762−1767.

(15) Brochard-Wyart, F.; de Gennes, P.-G. Dynamics of partial wetting. *Adv. Colloid Interface Sci.* **1992**, *39*, 1−11.

(16) Kistler; S. F. In *Wettability*; Berg, J. C., Ed.; Marcel Dekker: New York, 1993, pp 311−429.

(17) Bonn, D.; Eggers, J.; Indekeu, J.; Meunier, J.; Rolley, E. Wetting and spreading. *Rev. Mod. Phys.* **2009**, *81*, 739−805.

(18) Blake, T. D.; De Coninck, J. The influence of solid−liquid interactions on dynamic wetting. *Adv. Colloid Interface Sci.* **2002**, *96*, 21−36.

(19) Glasstone, S.; Laidler, K. J.; Eyring, H. J. *The Theory of Rate Processes*; McGraw-Hill: New York, 1941.

(20) Frenkel, J. I. *Kinetic Theory of Liquids*; Oxford University Press: Oxford, U.K., 1946.

(21) Puah, L. S.; Sedev, R.; Fornasiero, D.; Ralston, J. Influence of surface charge on wetting kinetics. *Langmuir* **2010**, *26*, 17218−17224.

(22) Ray, S.; Sedev, R.; Priest, C.; Ralston, J. Influence of the work of adhesion on the dynamic wetting of chemically heterogeneous surfaces. *Langmuir* **2008**, *24*, 13007−13012.

(23) Li, H.; Sedev, R.; Ralston, J. Dynamic wetting of a fluoropolymer surface by ionic liquids. *Phys. Chem. Chem. Phys.* **2011**, *13*, 3952−3959.

(24) Blake, T. D.; De Coninck, J. Dynamics of wetting and Kramers' theory. *Eur. Phys. J.: Spec. Top.* **2011**, *197*, 249−264.

(25) Blake, T. D.; Shikhmurzaev, Y. D. Dynamic wetting by liquids of different viscosity. *J. Colloid Interface Sci.* **2002**, *253*, 196−202.

(26) Duvivier, D.; Seveno, D.; Rioboo, R.; Blake, T. D.; De Coninck, J. Experimental evidence of the role of viscosity in the molecular-kinetic theory of dynamic wetting. *Langmuir* **2011**, *27*, 13015−13021.

(27) Vega, M. J.; Gouttière, C.; Seveno, D.; Blake, T. D.; Voué, M.; De Coninck, J. Experimental investigation of the link between static and dynamic wetting by forced wetting of nylon filament. *Langmuir* **2007**, *23*, 10628−10634.

(28) Semal, S.; Voué, M.; Vanden Eynde, J. J.; Bauthier, C.; Gouttebaron, R.; De Coninck, J. Spontaneous spreading of liquid droplets on mixed alkanethiols monolayers: Dynamics of wetting and wetting transition. *J. Phys. Chem. B* **2000**, *104*, 6225−6232.

(29) Stalcup, E. J.; Seemann, R.; Herminghaus, S.; Law, B. M. Dissipation mechanisms in ionic liquids. *J. Colloid Interface Sci.* **2009**, *338*, 523−528.

(30) Vega, M. J.; Seveno, D.; Lemaur, G.; Adão, M.-H.; De Coninck, J. Dynamics of the rise around a fibre: Experimental evidence of the existence of several time scales. *Langmuir* **2005**, *21*, 9584−9590.

(31) Saiz, E.; Tomsia, A. P.; Rauch, N.; Scheu, C.; Ruehle, M.; Benhassine, M.; Seveno, D.; de Coninck, J.; Lopez-Esteban, S. Nonreactive spreading at high temperature: Molten metals and oxides on molybdenum. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2007**, *76*, 041602-1−041602-15.

(32) Brooks, C. F.; Grillet, A. M.; Emerson, J. A. Experimental investigation of the spontaneous wetting of polymers and polymer blends. *Langmuir* **2006**, *22*, 9928−9941.

(33) de Ruijter, M. J.; De Coninck, J.; Blake, T. D.; Clarke, A.; Rankin, A. Contact angle relaxation during the spreading of partially wetting drops. *Langmuir* **1997**, *13*, 7293−7298.

(34) Goossens, S.; Seveno, D.; Rioboo, R.; Vaillant, A.; Conti, J.; De Coninck, J. Can we predict the spreading of a two-liquid system from the spreading of the corresponding liquid−air systems? *Langmuir* **2011**, *27*, 9866−9872.

(35) Inverarity, G. Dynamic wetting of glass fibre and polymer fibre. *Br. Polym. J.* **1969**, *1*, 245−251.

(36) Hoffman, R. A study of the advancing interface. I. Interface shape in liquid−gas systems. *J. Colloid Interface Sci.* **1975**, *50*, 228−241.

(37) Schwartz, A. M.; Tejada, S. B. Studies of dynamic contact angles on solids. *NASA Contract. Rep.* **1970**, CR-72728.

(38) Ström, G.; Fredriksson, M.; Stenius, P.; Radoev, B. Kinetics of steady-state wetting. *J. Colloid Interface Sci.* **1990**, *134*, 107−115.

(39) Seveno, D.; Ogonowski, G.; De Coninck, J. Liquid coating of moving fiber at the nanoscale. *Langmuir* **2004**, *20*, 8385−8390.

(40) Bertrand, E.; Blake, T. D.; De Coninck, J. Influence of solid−liquid interactions on dynamic wetting: A molecular dynamics study. *J. Phys.: Condens. Matter* **2009**, *21*, 464124-1−464124-14.

(41) Seveno, D.; Dinter, N.; De Coninck, J. Wetting dynamics of drop spreading. New evidence for the microscopic validity of the molecular kinetic theory. *Langmuir* **2010**, *26*, 14642−14647.

(42) Seveno, D.; Vaillant, A.; Rioboo, R.; Adao, H.; Conti, J.; De Coninck, J. Dynamics of wetting revisited. *Langmuir* **2009**, *25*, 13034−13044.

(43) Laboratory of Surface and Interfacial Physics (LPSI), University of Mons. *G-dyna Software*; LPSI, University of Mons: Mons, Belgium, https://hosting.umons.ac.be/php/lpsi/Home.

(44) De Coninck, J.; Blake, T. D. Wetting and molecular dynamics simulations of simple liquids. *Annu. Rev. Mater. Res.* **2008**, *38*, 1−22.

(45) Prevost, A.; Rolley, E.; Guthmann, E. C. Thermally activated motion of the contact line of a liquid ^{4}He meniscus on a cesium substrate. *Phys. Rev. Lett.* **1999**, *83*, 348−351.

(46) Semal, S.; Blake, T. D.; Gueskine, V.; de Ruijter, M. J.; Castelein, G.; De Coninck, J. Influence of surface roughness on wetting dynamics. *Langmuir* **1999**, *15*, 8765−8770.

(47) Ramiasa, M.; Ralston, J.; Fetzer, R.; Sedev, R. Nanoroughness impact on liquid−liquid displacement. *J. Phys. Chem. C* **2012**, *116*, 10934−10943.