Impact and Spreading of Microdrops on Homo- and Heterogeneous Solids: Modelling and Benchmark Simulations

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Abstract The finite element framework developed for the high accuracy computation of dynamic wetting phenomena in Sprittles & Shikhmurzaev, Int. J. Num. Meth. Fluids 2011 is used to develop a code for the simulation of unsteady flows such as microdrop impact and spreading. The accuracy of the code for describing free-surface flows is tested by comparing its results to those obtained in previous numerical studies for the large amplitude oscillations of free liquid drops in zero gravity. The capability of our code to produce high resolution benchmark calculations for dynamic wetting flows, using either conventional modelling or the more sophisticated interface formation model, is demonstrated by simulating microdrop impact and spreading on surfaces of greatly differing wettability. The simulations allow one to see features of the drop shape which are beyond the resolution of experiments. Directions of our research programme that follows the presented study are outlined.

Keywords: Dynamic Wetting, Microdrops, Interface Formation, Patterned Surfaces, Finite Elements

1. Introduction

The impact and spreading of liquid droplets on solid surfaces is the key element of a range of industrial processes. Thus far, research activity has been overwhelmingly devoted to the behaviour of millimeter-sized drops where the spatio-temporal scales of interest allow experiments to be performed routinely (Rioboo et al., 2002). However, recently, a need to understand the dynamics of microdrops has emerged as inkjet printing technology is extended from its traditional applications in the graphic arts industry to the manufacture of fully functional microfluidic devices (Calvert, 2001). In such processes, the precise deposition of microdrops onto a solid substrate is directly related to the quality of the product.

The behaviour of micro/nanodrops as they impact on the solid substrate is very difficult to observe experimentally, especially with a sufficiently high temporal resolution, so that it becomes necessary to rely on a theory which, once validated against the data from experiments on millimeter-sized drops and other relevant free-surface flows, would allow one to obtain reliable information about this process. So far, the main emphasis in research on microdrop spreading has been on the effects of heat and mass transfer (e.g. Attinger et al., 2008). The focus of our research programme is on accurately capturing the process of dynamic wetting, which is the key physical effect in the drop impact phenomenon, and developing a benchmark numerical platform capable of incorporating complex mathematical models that describe the essential features of this process. Once this aspect is resolved, additional physical factors such as heat transfer, interaction with external fields, etc can be considered.

By pre-patterning the solid substrate with areas of high and low wettability, it has been shown experimentally that inevitable inaccuracies in the deposition of the drop can be self-corrected (Mock et al., 2005). Therefore, it is important that any developed model should be able to naturally account for this class of phenomena.

The issues surrounding the modelling of dynamic wetting flows are well known and have been reviewed in detail (Shikhmurzaev, 2007), with a general discussion of the merits of microscopic, mesoscopic and macroscopic modelling approaches given in Velarde, 2011. Here, we focus on the self-consistent framework of continuum mechanics where, in particular, it has been established that the classical model of fluid mechanics must be modified to allow for a solution to exist (Huh & Scriven, 1971; Shikhmurzaev, 2006). A common way to achieve this is to use a 'slip model' where the no-slip condition on the solid surface is modified to allow for slip between the liquid and the solid near the moving contact line, whilst the contact angle is prescribed as a function of the contact line speed and material constants (Shikhmurzaev, 2007). When incorporated into numerical software, such models have been shown to produce reasonable results for the spreading of millimeter-sized drops at relatively low impact speed where experiments can be easily analyzed to allow for the development of a semi-empirical analysis of the phenomenon (Yokoi et al., 2009).

An open question is whether the models that have been specifically developed for millimeter-sized drop dynamics can predict the behaviour of drops across a range of scales, i.e. towards micro/nanodrops, at a range of impact speeds.

A step in the direction of answering this question was taken in the study of Bayer & Megaridis, 2006. They found that, even with millimeter-sized drops, the contact angle is not simply a function of the contact-line speed, but is actually determined by the entire flow field. As they have shown, the dependence of the contact angle on the contact-line speed for given materials of the system is not unique; it varies with the speed of impact, i.e. it depends on the particular flow. This effect of the flow field on the contact angle has been well known in the process of curtain coating for a long time where it has been termed the 'hydrodynamic assist to dynamic wetting' (Blake et al., 1994). Significantly, this effect cannot be described using any interpretation of the conventional 'slip' models (Wilson et al., 2006).

Currently, the only model which predicts the influence of the flow field on the contact angle is the interface formation model, described in detail in Shikhmurzaev, 2007. Incidentally, the model had been developed before the effect of 'hydrodynamic assist' became available to the research community (Shikhmurzaev, 1993), and it has been shown to give excellent agreement with the experimental results published in the literature. By incorporating the interface formation model, alongside all conventional models of dynamic wetting, into a numerical code one should be able to find experimentally observable differences between the predictions of the two competing approaches.

Computation of dynamic wetting flows is complex: besides the effects of capillarity, viscosity and inertia, one must also capture the physics of wetting which typically occurs on a length scale much smaller than that of the bulk flow. As explained in detail in Sprittles & Shikhmurzaev, 2011, the majority of publications in the field fail to accurately account for the wetting dynamics on the smaller length scale and, consequently, it is impossible to distinguish physical effects from numerical errors. Such codes may provide realistically-looking results for millimeter-sized drops, where the accurate computation of the bulk dynamics may be sufficient, but on the micro/nano scale, where an increasing surface-to-volume ratio means that surface effects become more important, such codes become useless.

The first steps in the development of a benchmark code for such flows was described in great detail in Sprittles & Shikhmurzaev, 2011, where one can also find a user-friendly step-by-step guide to allow the reader to reproduce all results. Here, we shall present the first results from the extension of our code to unsteady problems. To verify the code's accuracy we compare our calculations to a known test-case from the literature on oscillating liquid drops, where reliable results exist for a problem in which inertia, capillarity and viscosity are all prominent. Having verified the code's accuracy, we demonstrate its capabilities for drop impact and spreading phenomena. Details of the numerical implementation of the interface formation model into our code, and a full investigation of the dynamics of impacting drops on both homo- and heterogeneous solid surfaces will be given in forthcoming publications.

2. Modelling

Throughout, we consider the flow of a Newtonian liquid, of constant density ρ and viscosity μ, surrounded by a dynamically passive gas of a constant pressure in a gravitational field with acceleration due to gravity g. For the simulations of oscillating liquid drops, where testing of our results against known numerical solutions allows us to verify how the code handles capillary, inertial and viscous effects in unsteady high-deformation free-surface flows, we use the standard kinematic and dynamic boundary conditions for the Navier-Stokes equations on the free-surface. In this case, the flow is fully characterized by the Reynolds, Stokes and capillary numbers, i.e., respectively

$$Re = \frac{\rho U L}{\mu}, \quad St = \frac{\rho g L^2}{\mu U}, \; Ca = \frac{\mu U}{\sigma}, \tag{1}$$

where L and U are the scales for length and velocity, and σ is the surface tension.

To describe microdrop impact and spreading phenomena, the specific physics of wetting must also be included into the model. For those simulations, our numerical platform allows us to test both the relatively easy to implement conventional models for dynamic wetting and the mathematically more intricate interface formation model. In each case, besides (1), one will have additional similarity parameters associated with the constants involved in the model which describes the specific physics of wetting.

2.1 The Interface Formation Model

Dynamic wetting is the phenomenon in which an initially dry solid is wetted by an advancing liquid. In other words, it is the process of creating a fresh liquid-solid interface, i.e. the process of interface formation. The interface formation model accounts for this additional physics of fresh interface being formed and, away from the contact line, relaxing towards its equilibrium state. Near the contact line the surface tension will be out of equilibrium and hence the Young equation (Young, 1805), which is a balance of surface tension forces acting on the contact line, predicts that the contact angle must deviate from its equilibrium value, i.e. it is *dynamic*. As the flow interacts with the surface relaxation process, and it is this relaxation process that determines the values of the surface tension at the contact line, there is a natural coupling between the flow and the dynamic contact angle, which produces the effect of 'hydrodynamic assist' seen experimentally.

Only when the contact line speed is relatively low and the bulk length scale is relatively large, is analytic progress possible and in this case the model predicts a unique relationship between the contact-line speed and contact angle. This explains qualitatively why for low impact speeds of millimeter-sized drops an empirical formula between the contact-line speed and dynamic contact angle produces reasonable outcomes whilst for higher impact speeds or smaller drops such models become useless and more complex models must be used. The aforementioned analytical results also provide a test-case to verify the accuracy of the numerical code.

The interface formation model is able to reproduce anything conventional models can achieve but, in contrast to these models' reliance on the *functions* empirically determined on a macroscopic length scale and known to be invalid on microscales, the interface formation model allows one to determine values for the model's material *constants* on scales where experiments can be easily analyzed, i.e. the millimeter scale, and then probe scales unobtainable to experiments. Furthermore, the material constants may be taken from unrelated experiments on dynamic wetting, or even other processes in which interface formation is present, and this is what we shall do here – taking values from plunging tape experiments (Blake & Shikhmurzaev, 2002).

3. Numerical Method

In the developed code, an arbitrary Lagrangian-Eulerian method is used for the mesh design so that, if required, areas where high resolution is essential, such as near the moving contact-line, evolve with the drop in time. Consequently, nodes in the bulk of the drop move at a speed fixed by the free surface motion, and care must be taken when taking temporal derivatives of the variables at such nodes (Jimack & Wathen, 1991).

The result of the spatial discretization is a system of non-linear first-order ODEs that we evolve using the second-order accurate Backward Differentiation Formula (BDF2). The BDF2 has been used for similar problems (Heil, 2004) and is described in detail in Gresho & Sani, 1999, p. 805. If required, this can be combined with an explicit method to provide a predictor-corrector scheme which automatically sets the time-step based on the tolerable error.

4. Oscillating Drops: Validation of the Unsteady Code

A benchmark calculation, which requires the effects of capillarity, inertia and viscosity to all be accurately accounted for whilst the free surface deformation is large, is to simulate oscillations of liquid drops. For small oscillations analytic results exist (Rayleigh, 1879), but for arbitrary viscosity and deformation numerical methods are required.

Parameters are chosen to allow a comparison of our results with the numerical studies, in Basaran, 1992 and Meradji et al., 2001. To do so, two simulations of the axisymmetric oscillation of a drop in zero gravity, i.e. $St = 0$, with $Re = 10, 100$ and $Ca = 0.1, 0.01$, respectively, are run. The deviation of the drop's initial shape from spherical is proportional to the second spherical harmonic. This setup is described in Basaran, 1992, p. 173. Our interest is in the largest deformation case, where the amplitude of the initial deviation equal to 0.9, see Figure 1 at $t = 0$.

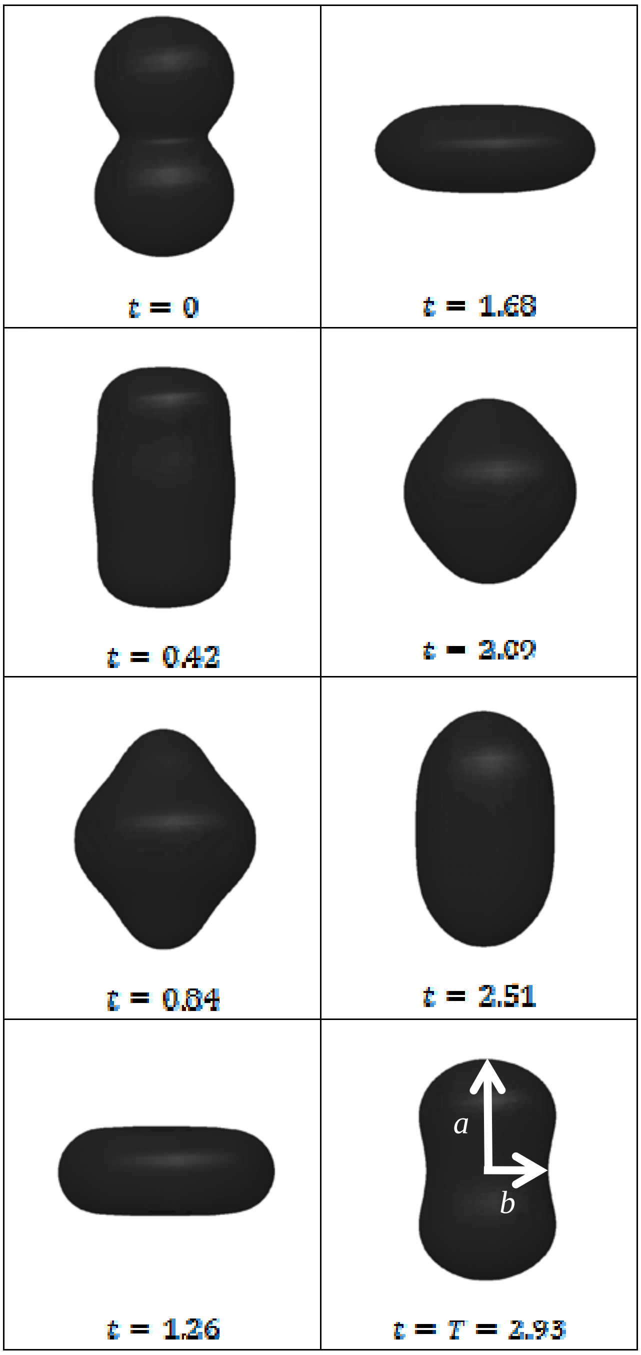
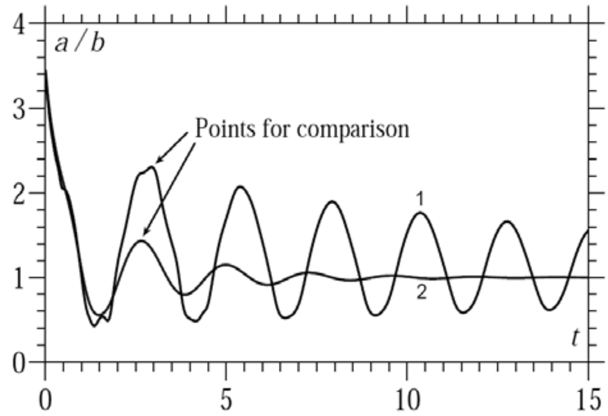


Figure 1: Simulation of a freely oscillating



drop in zero gravity with $Re = 100$ and $Ca = 0.01$ over one period.

Figure 2: Aspect ratio a/b of the oscillating drops as a function of time for 1: $Re = 100,\ Ca = 0.01$; 2: $Re = 10,\ Ca = 0.1$.

The calculations were performed with a mesh of 630 elements and a fixed time step of 0.001. Doubling the number of elements or reducing the time step by a factor of ten resulted in a change of less than 0.1% in the results.

Figure 1 shows the evolution of the drop over one period, which is what is required for our comparison with the other numerical studies. The high deformation of the free surface is clear and one can observe that at the end of the first period the drop's amplitude of oscillations has been damped by viscosity. As time evolves the drop will gradually tend towards its equilibrium shape of a sphere.

Figure 2 shows the time-dependence of the aspect ratio (a/b), i.e. the ratio of the polar diameter to the equatorial diameter (see Figure 1 at $t = 2.93$). The aspect ratio and time after one period ($t = T$) are then recorded and used to compare with the previous calculations.

Re=10 *Ca*=0.1	Basaran	Meradji et al.	Present Work
T (*a*/*b*)	2.660 1.434	2.640 1.432	2.656 1.432

Re=100 *Ca*=0.01	Basaran	Meradji et al.	Present Work
T (*a*/*b*)	2.905 2.331	2.930 2.304	2.936 2.305

Our results in the table are seen to be in good agreement with both studies. The values align most closely with those of Meradji et al., 2001 which is reassuring given the greater degree of resolution used in that study.

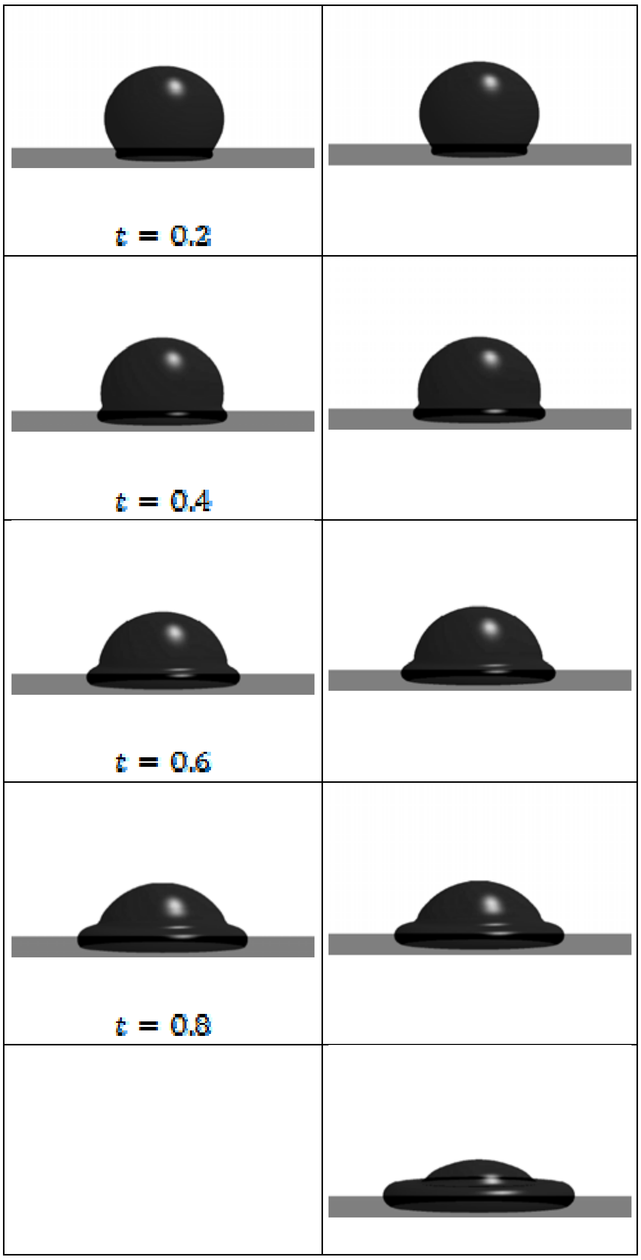
It has been demonstrated that our numerical framework is able to provide accurate results for complex unsteady flows. The oscillation of liquid drops is a problem of interest in its own right, and at this point we could look at comparing our results to experiments in the literature (Wang et al., 1996), to probe newly proposed analytic models for decay rates (Smith, 2010) or to consider the influence interface formation may have when oscillations are of high frequency and interface is forming or disappearing at a significant rate. All of these avenues of investigation are being pursued but lie beyond the scope of the present paper, and we now turn our attention to the code's capabilities at describing drop impact and spreading phenomena.

5. Microdrop Impact and Spreading Simulation

A new, robust and fully tested framework for handling dynamic wetting flows was outlined in Sprittles & Shikhmurzaev, 2011 and in a forthcoming publication we will explain in detail how the interface formation model was included into this code to allow the computations shown in this section. Here, microdrop impact on hydrophilic and hydrophobic substrates is simulated for typical parameter values to demonstrate the capabilities of our code. In particular, we see that our code is able to account for the two extreme outcomes of the drop impact and spreading process, i.e. deposition and rebound, and to recover information about the drop's dynamics which is experimentally unobtainable.

Consider a microdrop of water of radius $25\ \mu m$ which impacts a solid substrate at $5\ m/s$. Then, the non-dimensional parameters based on this impact speed are $Re = 130,\ Ca = 0.07,\ St = 0.001$ and estimates for the interface formation model's parameters are taken from Blake & Shikhmurzaev, 2002. All that remains to be specified is the wettability of the solid substrate, which is characterized by the equilibrium contact angle θ a free surface forms with the solid.

Two simulations are shown in Figure 3, where on the left $\theta = 30^{\circ}$ whilst on the right $\theta = 130^{\circ}$. It can be seen that in the early stages of spreading when inertia is dominant, roughly until $t = 1$ (which in dimensional terms for the microdrop considered above corresponds to $5\ \mu s$), the shapes of the two drops are indistinguishable. The contact line is forced outwards as fluid is pushed out radially from the centre of the drop. Eventually, the drop starts to feel the wettability of the solid on which it is spreading and since in both cases inertia has carried the drop past its equilibrium position, the contact line starts to recede. For the drop on the hydrophilic substrate this leads to small oscillations of the drop around its equilibrium shape which are gradually damped by viscosity; however, for the drop on the



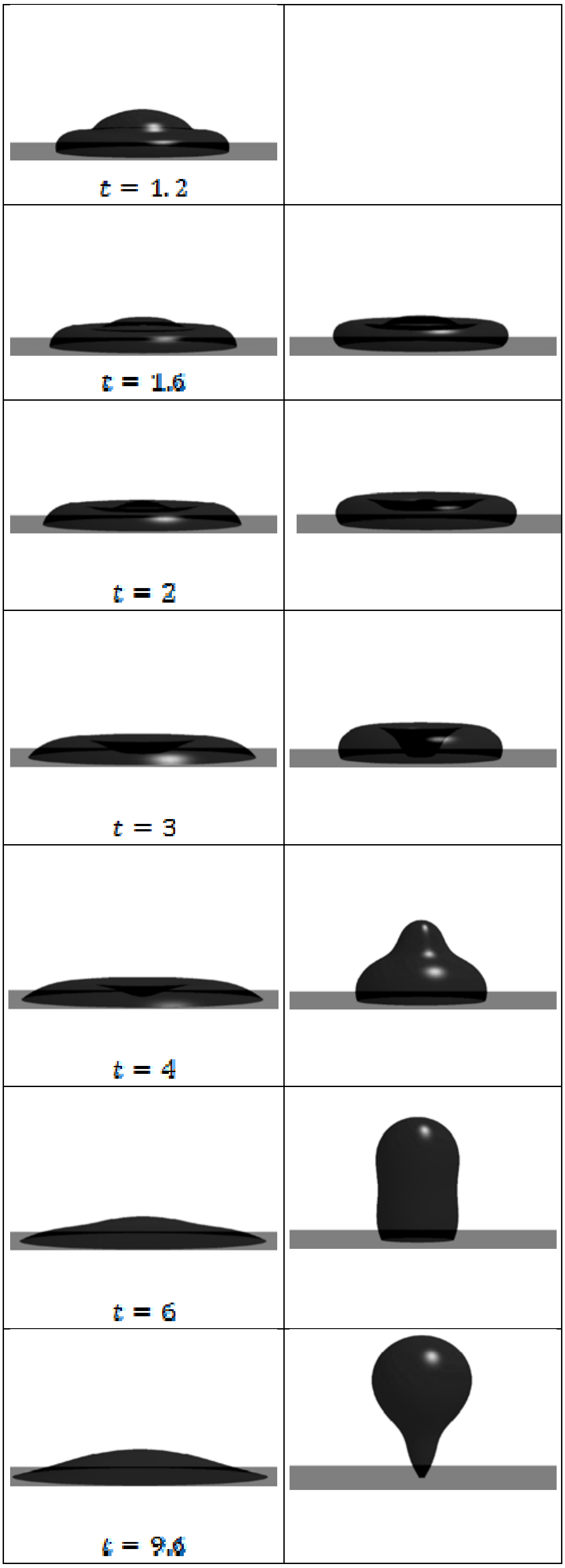
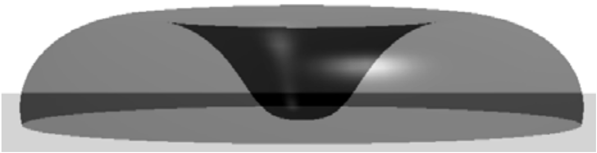


Figure 3: Microdrop impact and spreading simulations at $Re = 130, Ca = 0.07, St = 0.001$. The



solid in the left panels is hydrophilic ($\theta = 30°$) whilst the one on the right hand side is hydrophobic ($\theta = 130°$).

hydrophobic substrate, this dewetting of the substrate occurs so quickly that the drop detaches back off the substrate. This second stage of spreading is seen to be on a much larger time scale than the initial stages after impact.

Once the code is validated and the accuracy verified, its advantages over experiments are threefold: first, it can recover information which is inaccessible to experiments; second, one can map the influence of the system's

Figure 4: Close up image at $t = 3$ of impact on the hydrophobic substrate showing how close the apex gets to touching the solid.

parameters on the drop's dynamics and third, it is easy to attempt new things without the cost of full scale laboratory experiments.

As an illustration of the first of these advantages, in our simulations we are able to see the entire drop shape for the whole simulation. However, experimental images are unable to show the dynamics of the apex as it disappears below the rim of fluid which surrounds it, as shown in Figure 4. It can be seen that the apex gets extremely close to touching the solid substrate, i.e. to dewetting the centre of the drop, but that it manages to recover just in time: as the contact line is receding, the apex re-emerges out of the centre of the drop in a jet-like protrusion (see $t = 4$ on the right hand side of Figure 3).

With regard to the second advantage of reliable numerical simulations over experiment, determining for what parameter values a drop will rebound is an important piece of information, particularly when the substrate to be used in a given process is hydrophobic, and it is difficult to find this out from experiments where one cannot vary parameters of the system independently. With our numerical tool, parameter space can be mapped quickly, so that one can ensure the drop deposits on the substrate by, say, artificially changing the viscosity of the liquid or reducing the impact speed of the drop.

A good example of the code's cost-effectiveness with regard to the process is the impact of drops on a chemically patterned surface. Here, one can look at topologically different patterns to ascertain which will allow a required level of flow control on the drop to be obtained. These ideas are pursued in a forthcoming publication.

6. Future Directions

The ability of the developed computational framework to provide high-accuracy benchmark simulations for free surface flows and, specifically, for dynamic wetting phenomena has been demonstrated. In a forthcoming paper we describe in detail how to implement the interface formation model into this framework and validate the calculations against analytic results for limiting cases. This is followed by a work where we compare drop impact and spreading simulations to experiments, explore parameter space and provide experimentally verifiable differences between competing dynamic wetting models proposed in the literature.

It has already been shown that, in the absence of a free-surface, the interface formation model is able to naturally account for changes in the wettability at a liquid-solid interface and that its predictions, unobtainable with conventional continuum approaches, are in qualitative agreement with those from molecular dynamics simulations (Sprittles & Shikhmurzaev, 2007). The next step in this direction, which is part of a future work, is to look at how substrate patterning can alter the flow of a spreading drop, i.e. where the patterning interacts with both the bulk flow and the contact line. For example, it will be shown that on a patterned surface the final shape of an impacting drop can be significantly changed by only slightly altering the impact speed.

The finite element framework developed has already been shown to possess reasonable flexibility: it was used to consider flow over patterned surfaces (Sprittles & Shikhmurzaev, 2007), to simulate flow in a capillary (Sprittles & Shikhmurzaev, 2011) and here it was used for oscillating drop simulations and drop impact phenomena. This flexibility allows our research programme to branch out and simulate a whole array of different dynamic wetting flows, e.g. in the coating of fibres, where the high speeds of coating in confined areas suggest 'hydrodynamic assist' may be present, or it can be applied to entirely different flows where interface formation has also been shown to be critical, such as the coalescence of liquid bodies, breakup of liquid jets, disintegration of thin films, and other phenomena (Shikhmurzaev, 2007).

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