Experimental and computational studies of water drops falling through model oil with surfactant and subjected to an electric field

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Abstract—The behaviour of a single sub-millimetre-size water drop falling through a viscous oil while subjected to an electric field is of fundamental importance to industrial applications such as crude oil electrocoalescers. Detailed studies, both experimental and computational, have been performed previously, but an often challenging issue has been the characterization of the fluids. As numerous authors have noted, it is very difficult to have a perfectly clean water-oil system even for very pure model oils, and the presence of trace chemicals may significantly alter the interface behaviour. In this work, we consider a well-characterized water-oil system where controlled amounts of a surface active agent (Span 80) have been added to the oil. This addition dominates any trace contaminants in the oil, such that the interface behaviour can also be well-characterized. We present the results of experiments and corresponding two-phase-flow simulations of a falling water drop covered in surfactant and subjected to a monopolar square voltage pulse. The results are compared and good agreement is found for surfactant concentrations below the critical micelle concentration.

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I. INTRODUCTION

The study of a single fluid drop falling through some other fluid has a long tradition of study: the physics of raindrops has been debated ever since Aristotle’s ideas on the subject in ancient times. Pioneers in this field include Rayleigh, Kelvin, Stokes, Reynolds and Worthington, the latter of whom dedicated most of his career to the study of splashing drops and pioneered the use of flash photography for this purpose.

In spite of such prolonged study, some details elude our understanding still today. This basic phenomenon is also relevant for various industrial applications. In this paper our focus is on sub-millimetre-size water drops falling through a more viscous medium of slightly lower density, i.e. oil, with an eye towards understanding the processes that govern the operation of electrocoalescers used for crude oil processing [1].

In this context, a particular hurdle is the characterization of the two fluids and whether or not the drop surface is clean. To overcome this uncertainty we consider a system where a surface-active agent (Span 80) is added such that it dominates existing impurities. The whole system is then well-characterized in terms of viscosities, densities and interfacial tension as a function of surfactant concentration. We report the outcome of experiments with a falling drop in this fluid system, where in addition a monopolar square voltage pulse is applied to deform the drop. These experiments are compared with two-phase flow simulations where the electric field and the surface-active agent are taken into account.

II. THEORY

The equations that govern the two-phase flow system under consideration are the incompressible Navier-Stokes equations:

\[ \nabla \cdot \mathbf{u} = 0 \]  
\[ \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla)\mathbf{u} = -\frac{\nabla p}{\rho} + \frac{\eta}{\rho} \nabla^2 \mathbf{u} + \mathbf{f} \]

The above equations hold for a single fluid, or separately in each fluid for an immiscible two-phase system. Across the interface between the fluids there will be discontinuities in some quantities, e.g. the pressure. These discontinuities are enforced in a sharp manner using the ghost fluid method and the level-set method in the simulations. We will refer to the drop fluid as having properties with subscript 1 and the ambient (bulk) fluid as having properties with subscript 2.

For the fluids and drop sizes we consider, the Reynolds number will be \( Re \ll 1 \) such that the flow is laminar. The terminal velocity of a single falling clean drop can then be predicted by the Hadamard-Rybczynski formula [2, 3]

\[ v_{\text{T,HR}} = \frac{2(\rho_1 - \rho_2)gR^2(\eta_1 + \eta_2)}{3\eta_2(3\eta_1 + 2\eta_2)} \]  
while the terminal velocity of a contaminated drop will be closer to that of a falling rigid sphere, predicted by the Stokes formula [4]

\[ v_{\text{T,ST}} = \frac{2(\rho_1 - \rho_2)gR^2}{9\eta_2} \].

Note that \( g \) is a vector and the resulting velocity vector will have the correct sign for both a falling and rising drop. We note the curious fact that for a given \( R \) these velocities can never be equal, as long as the viscosities are both non-zero and finite. This allows an easy way of distinguishing a clean system from a contaminated one. In practice, it is easier to consider a log-log plot of the drag coefficient versus the drop Reynolds number, since both the Stokes theory and the Hadamard-Rybczynski theory predict these values should fall on a straight line, but they predict two different (parallel) lines.

In addition to the fluid flow, an electric field is imposed on the system. In the experiments this is done by applying a monopolar square voltage pulse to plane electrodes at the top and bottom of the fluid chamber. The electric potential \( \Psi \) can be calculated from boundary conditions corresponding to the...
Table I. IFT BETWEEN WATER AND OIL FOR DIFFERENT SURFACTANT CONCENTRATIONS

<table>
<thead>
<tr>
<th>Span 80 concentr. [wt%]</th>
<th>Interfacial tension [mN/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.030</td>
<td>10.0</td>
</tr>
<tr>
<td>0.020</td>
<td>10.1</td>
</tr>
<tr>
<td>0.015</td>
<td>13.9</td>
</tr>
<tr>
<td>0.010</td>
<td>18.8</td>
</tr>
<tr>
<td>0.001</td>
<td>29.4</td>
</tr>
</tbody>
</table>

The interfacial tension $\gamma$ between water and oil was measured using a SIGMA 703D tensiometer with a DuNuoy ring. The results for the different amounts of surfactant are given in Table I. The concentration is given in percent by weight, denoted by wt%. These results indicate that the critical micelle concentration for our system is 0.020 wt%. We will restrict ourselves to concentrations below this.

Figure 1. Side view of the experimental setup. The electric field is aligned with the gravitational field.

Figure 2. Example of image captured of elongated drop with major and minor axes $a$ and $b$ superimposed.

as shown in Fig. 2 where a slightly elongated water drop is seen with the axes superimposed.

The experimental procedure consisted of these steps:
1. Create a water drop of the desired size at the tip of the glass needle using the screw-in plunger. The field of view of the camera is at the needle tip.
2. Once a drop is created, move the test cell such that the field of view of the camera is at the center of the electrode gap.
3. Arm the camera to start recording on trigger.
4. Release the drop from the tip of the glass needle.
5. Once the drop comes into view of the camera, trigger the camera and voltage source.
6. The camera records a movie of the drop.
7. Extract the drop position and shape from the recorded movie.

B. Simulation and numerical methods

The Navier-Stokes equations (1) and (2) are solved numerically using an in-house code. All reported simulations are done using 2D axisymmetry. The equations are discretized with a finite-difference method, specifically WENO [7] for the convective terms and central differences for the viscous terms. The time integration is done with an explicit Runge-Kutta method (SSPRK (2,2) in the terminology of Gottlieb et
al. [8]). A standard projection method [9] is used to determine the pressure field such the velocity field is solenoidal, giving a Poisson equation for the pressure $p$. The solution of this Poisson equation demands the majority of the computing time; it is solved here using the Bi-Conjugate Gradient Stabilized method [10] with the BoomerAMG preconditioner [11]. The same methods are used to solve the Laplace equation for the electric field. We employ the PETSc and Hypre libraries for these methods [12, 13].

As stated, the Navier-Stokes equations are valid in each phase separately. The interface between the phases is tracked using the level-set method, see [14] and references therein for a thorough description of how we employ this method. To couple the two phases, the ghost-fluid method (GFM) [15]. [16] is used in the simulations to enforce the jumps in different quantities (like pressure) across the interface:

\[
\begin{align*}
[u] &= 0, \\
[p] &= \frac{\partial}{\partial t} \left( n \cdot \nabla u \cdot n + n \cdot \left[ M \right] \cdot n + \gamma K, \\
\left[ \nabla p \right] &= 0, \\
\left[ \Psi \right] &= 0, \\
\left[ n \cdot \nabla \Psi \right] &= 0.
\end{align*}
\]

To solve the Poisson equation for the pressure $p$, a Poisson equation for the pressure is solved here using the Bi-Conjugate Gradient Stabilized method. To an advection-diffusion equation which can be expressed in the same coordinates as all the other equations, by using the curvature of the interface $\kappa$ and the normal vector $n$,

\[
\frac{d\xi}{dt} + u \cdot \nabla \xi - n \cdot \nabla u \cdot n \xi = D_\xi \left( \nabla^2 \xi - n \cdot \nabla \nabla \cdot n \xi + \kappa (n \cdot \nabla \xi) \right),
\]

where the first two terms on the left-hand side and the first term on the right-hand side are the ordinary terms in an advection-diffusion equation, and the remaining terms constitute the restriction of this equation to the interface.

The surfactant transport equation, as well as the level-set equations for interface tracking, are discretized with finite-difference methods and integrated in time using explicit Runge-Kutta methods. We refer to Teigen et al. [16, 19, 20] for a thorough discussion and validation of these models.

IV. RESULTS

A. Terminal velocity

As a consistency check, experimental results for the terminal velocity of falling drops were compared with the theoretical values for drops with and without a surfactant covering. This was done for several drop diameters and surfactant concentrations, the results are shown in Fig. 3 (unfilled symbols). As this figure shows, the results fall on or close to the line for a solid sphere, which is as expected for a surfactant-covered drop. The dotted line shows the theoretical result for a drop with circulation according to the Hadamard-Rybczynski theory.

Some results from simulations of falling drops are also shown, using the same shapes but with filled symbols. The points plotted in green are simulations with surfactant-covered drops. These were done for a 1329 $\mu$m drop in 0.001 wt% Span 80 and for a 859 $\mu$m drop in 0.015 wt% Span 80. The points plotted in magenta are equivalent simulations according to the Hadamard-Rybczynski theory. It is seen that simulations without surfactant agree well with the Hadamard-Rybczynski theory, while simulations with surfactant agree well with the Stokes theory and with the experimental results.

These simulations were done with a $20R \times 40R$ computational domain and a grid resolution of 400×800. Grid refinement studies indicated that this was sufficient. A moving grid procedure was employed, such that the drop was always close to the center of the domain. The simulations were performed using the “laboratory” reference frame, where all velocities approach zero at the boundary conditions, which were identical on all sides of the domain. That is to say, full
slip (zero gradient) was used for the tangential velocity while the normal velocity (through the boundaries) was set to zero.

### B. Drop deformation

Several experiments were performed with different drop diameters, field strengths and surfactant concentrations. The parameters for each case are summarized in Table I. The drop shapes were extracted from the movies of the experiments using the SpotLight software. The ratio between the major axis \( a \) and the minor axis \( b \) could then be determined. Analysis of the various uncertainties that affected the measurements \( a \) and \( b \) was done according to the procedure described in [21], and the uncertainty in \( a/b \) was then computed assuming Gaussian error propagation. Herein, the fluid properties were assumed to be without error. This gave a relative error in \( a/b \) that was independent of \( a/b \) but dependent on the initial radius. The relative error was 2.0 % for the largest drops considered here and 3.4 % for the smallest.

Based on these experiments, equivalent simulations were set up and run. The values of \( a/b \) were also extracted from the simulation results, such that they could be plotted and compared directly to the experimental results. Such plots are shown in Figs. 4 to 8. As is seen in these plots, the agreement between simulations and experiments is good for a variety of parameters. Error bars are shown for the experimental values for every fifth point. The static deformation predicted by the Taylor theory [22] is shown with blue lines at the right-hand side. For Case 1 it is seen that this line agrees very well with the static deformation predicted by simulations without surfactant, thus it overpredicts the deformation in the presence of surfactant.

Note that for Case 3 (Fig. 6), the deformation is much larger so the scale is different. Since the Taylor theory is only valid for small deformations, it has not been applied here. For this case there is some disagreement between experiments and simulations regarding the maximum deformation and for the static deformation. This is likely due to the assumption of insoluble surfactant in the simulation: as the drop is stretched to such a large deformation, the interfacial area increases and there is room for more surfactant at the interface. Thus adsorption kinetics can become important in this case, making the simulations underpredict the deformation.

For Case 2 (Fig. 5) there is also a poor agreement. The cause of this is harder to identify, since the other similar cases gave good agreement. For this case, the difference between experiments and the Taylor theory is also much larger than for the other cases. Further investigations are needed to clarify this point.

For Case 1 (Fig. 4) a plot is also shown for a simulation without surfactant, but using the experimentally measured value for the interfacial tension at 0.015 wt% Span 80 (magenta curve). It is seen that this simulation overpredicts both the initial oscillation and the static deformation. This indicates that the Marangoni forces due to the surfactant are important both for the maximum and the static deformation.

In these simulations the grid resolution was \( 241 \times 482 \) in the radial and axial directions, respectively. Simulations using coarser grids indicated that this resolution was sufficient. All simulations were done in axisymmetric coordinates, corresponding to a plane intersecting half the drop. Initial simulations were performed with falling drops that had reached terminal velocity before the field was applied. These were compared with simulations done with a field applied to a drop in zero gravity in a quiescent ambient fluid, and it was found that the difference in deformation was small. Since the initial simulation with the falling drop reaching terminal velocity has a runtime of many days, subsequent drop deformation simulations were done for drops in zero gravity.

For these simulations without gravity, the full domain was \( 8R \times 16R \). The boundary conditions used were identical on all sides of the domain, namely full slip (zero gradient) for the tangential velocity while the normal velocity (through the boundaries) was set to zero. The pressure boundary condition is zero gradient in the normal direction, i.e. \( \partial p/\partial n = 0 \).

A detailed view of the simulation result from Case 1 is shown in Fig. 9. The axisymmetric solution is shown mirrored about the symmetry axis (y-axis). The drop is at its most extended. The terminal velocity has been subtracted from the velocity field, such that it appears in the drop reference frame. The orange colour indicates the pressure field and the green color shows the surfactant distribution. The vectors on the right-hand side show the velocity field, and the field lines on the left-hand side show the electric field. A reference vector for
The velocity field must be close to zero as it reverses direction. It is also seen that the surfactant distribution is slightly non-uniform, giving rise to Marangoni forces that counteract the velocity field tangential to the interface. The electric field lines shown on the left-hand side pass straight through the droplet, which has high conductivity, and otherwise appear as one would expect.

V. CONCLUSIONS

By experiments and computations we have investigated the behaviour of single water drops in Marcol model oil with added surfactant subjected to an electric field. This system is well-characterized in terms of bulk, drop and interface properties. In particular, the terminal velocity and the response to a sudden step in the electric field have been studied.

In our computations, the details of the two-phase flow are captured using the level-set method, and the interfacial jumps are accounted for using the ghost-fluid method (GFM). The surfactant is modelled as insoluble and the fluids are assumed to be perfect dielectrics. The calculated terminal velocities for a clean system agree well with the predictions of the Hadamard-Rybczynski formula. When the presence of surfactant is accounted for, the calculated terminal velocities agree well with the experimentally observed ones, which again
agree with those calculated using the Stokes formula for rigid bodies.

Our calculations of the dynamic drop stretching as a response to a step change in the electric field agree well with the laboratory observations (except for one case). Our results indicate that it is necessary to account for the presence and dynamics of surfactant in order to reproduce the dynamic behaviour of the drop.

Acknowledgments

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