Computational Simulation of Surfactant-Induced Interfacial Modification of Droplet Impact and Heat Transfer

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Abstract
Numerical investigation of heat transfer during drop impact, spreading, recoil, and rebound/break up has been carried out for water droplets with and without surfactant additives. The numerical model is based on a finite volume formulation on a structured grid. A volume-of-fluid (VOF) technique is used to track the deforming liquid-air interface. Comparisons between the numerical results and experimental data are presented, which show a remarkable agreement between the simulated impact-spreading-recoil behavior on a hydrophobic surface and high-speed visualization of the process. The simulations reveal that the water droplets spread and then recoil sharply so as to form a vertical column, which breaks up and ejects secondary droplets. The decrease in surface tension at the liquid-air interface and change in the wetting characteristics of the liquid-solid interface facilitates larger initial spreading and weaker recoil of surfactant solution droplets compared to water drops. As a result the transient heat transfer rate is significantly higher for aqueous surfactant solution droplets. The solution of lower molecular weight (higher mobility) surfactant (SDS) shows a higher maximum and final spread with weaker recoil compared to the higher molecular weight (lower mobility) Triton X-100 solution.

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Introduction

The phenomenon of droplet impact on solid substrates has been studied extensively for more than a century since the first reporting of such experiments by Worthington [1]. The surface “wettability” or its affinity for the liquid, liquid properties, droplet size and velocity are important factors that determine the outcome of liquid droplet impact on a surface, a process that is employed in many industrial applications including spray coating, deposition, inkjet printing, spray cooling, rain-ingestion in gas turbines [2, 3] crop spraying, aircraft icing. A recent article by Yarin [4] provides a detailed review of experimental and computational investigations of isothermal drop impact of pure liquid. The spreading, recoil, oscillations, and breakup or splatter are governed by the gravity, inertia, liquid-gas surface tension, liquid-solid adhesion, and viscous forces acting on the drop. For pure liquids, the drop-surface dynamics has been characterized by the scaling with the Weber number (We), the Reynolds number (Re), Ohnsorge number (Oh = We^{1/2}/Re), the Capillary number (Ca), and a parameter K = We×Oh^{2/5}.

At low Weber numbers (We < ~ 200), liquid droplet impacting on a substrate first spreads outward forming a thin liquid layer with a large surface area. The initial kinetic energy is converted to surface energy. The liquid then recoils to the center. The inertia and viscous forces govern the initial spreading process with a smaller effect of the surface wetting characteristics [3-8]. However, the substrate wettability has a significant effect on drop recoil. Typically, on a hydrophilic surface, there is slow recoil followed by several surface oscillations that dissipate energy through viscous effects. On the other hand, on a hydrophobic surface, strong recoil is followed by formation of a liquid column which may break to eject one or more smaller droplets[9]. The advancing contact angle is greater than the static contact angle, whereas the receding contact angle is typically lower than the static contact angle [10].

In recent years, the effect of additives like surfactants and polymers, in the phenomenon of droplet impact has received some attention. Surfactants or surface-active agents have a tendency to adsorb at surfaces and interfaces when added to water and other solvents [11]. They have a long-chain molecular structure consisting of a hydrophilic head and a hydrophobic tail. Based on the hydrophilic group, surfactants are classified as anionic (e.g., SDS), cationic (e.g., CTAB), Non-ionic (e.g., Triton X-100) and zwitterionic. Their adsorption at the liquid-gas interface alters the solution surface tension. This is a time-dependent phenomenon where the change in surface tension is governed by the mobility of the surfactant molecules that diffuse to a newly created liquid-air interface, their rate of adsorption, bulk concentration, and micellar dynamics[12]. The equilibrium surface tension (σ_{eq}) decreases with reagent concentration until a critical concentration is reach where micelles and agglomerates begin to form (Critical Micelle Concentration or CMC) and remains constant thereafter [12]. Furthermore, the physisorption of surfactant molecules at the liquid-solid interface changes the surface wetting characteristics. These phenomena at the liquid-air and liquid-solid interfaces significantly affect the dynamics of impact, spreading, and recoil of aqueous surfactant solution droplets [13-17].

Presence of surfactants adds further complexities to the drop impact dynamics. The initial spreading creates new liquid-air interface. The subsequent diffusion and adsorption of surfactants at the liquid-air interface lowers the surface tension and facilitates drop spreading. The time scale for this dynamic surface tension variation (~ milliseconds) is of the same order as the time scale of drop spreading and recoil. As a result the surface tension becomes time and flow dependent [4]. Experimental investigations of Mourougou-Candoni et al. [14, 15], Zhang and Basaran [13], Crooks et al. [16], and Gunjal et al. [17] have shown that the dynamic surface tension plays a significant role in surfactant solution drop impact-spreading-recoil phenomena. Zhang and Basaran [13] have suggested that convection of surfactant to the contact line can cause Marangoni stresses due to uneven concentration along the interface and resist drop spreading. However such effect has not been seen in other studies of surfactant solution drop impact.

The volume of fluid (VOF) method has been used to computationally model the drop impact spreading and recoil for pure liquids [6, 18, 19]. Gunjal et al. [17] simulated the impact of SDS solution drops on a hydrophilic surface with the VOF method using experimentally measured dynamic contact angles. The aim of the present study is to investigate the effect of surfactants on the droplet impact dynamics and heat transfer on a hydrophobic substrate and to develop a numerical model to predict the droplet dynamics. Two widely used surfactants were considered: SDS (anionic) and Triton X-100 (non-ionic). Table 1 and 2 provide properties of water and surfactants, respectively.
Numerical Solution

The finite volume method with a fixed non-uniform spatial grid was used to computationally model the process. From experimental images it is observed that the drop spreads symmetrically for the impact velocities considered in this study. Therefore a 2-D axi-symmetric computational domain was considered. The Volume of Fluid (VOF) method was used to track the interface between the liquid (water or surfactant solution) and gaseous (air) phases.

The VOF method

In the VOF method, a volume fraction variable is assigned for each phase (\( \alpha \)). In each control volume, the sum of the volume fractions of the two phases must be unity. The fields for all variables and properties are shared by the phases and represent volume-averaged values. When \( 0 < \alpha < 1 \), the cell contains the interface. The tracking of the interface between the phases is accomplished by the solution of a continuity equation for the volume fraction:

\[
\frac{\partial \alpha}{\partial t} + \vec{v} \cdot \nabla \alpha = 0
\] (1)

The properties appearing in the transport equations are determined by the presence of the component phases in each control volume and are calculated as volume-averaged values. For example, density is given by

\[
\rho = \alpha \rho_\text{water} + (1 - \alpha) \rho_\text{air}.
\] (2)

All other properties are computed in a similar manner. A single mass conservation and a single momentum conservation equation are solved throughout the domain, and the resulting velocity field is shared among the phases. The mass and momentum conservation equations are:

\[
\nabla \cdot \vec{v} = 0
\] (3)

\[
\frac{D\vec{v}}{Dt} = -\nabla p + \mu \nabla^2 \vec{v} + \rho g + \vec{F}_{sw}
\] (4)

Here \( \vec{v} \) is velocity, \( p \) is pressure, \( \vec{F}_{sw} \) is the continuum surface force, \( \mu \) denotes viscosity of the mixture, \( \rho \) density of the mixture, \( g \) is gravitational acceleration.

The governing equations were solved using the commercial CFD software Fluent v.6.2. The computational grid was created using Gambit v.2.2.30. The geometric reconstruction scheme was used for accurate calculation of the face fluxes in the VOF model [20]. The continuum surface force model proposed by Brackbill et al. [21] was used to determine the surface tension force at the liquid-air interface.

<table>
<thead>
<tr>
<th>Table 1 Properties of Water</th>
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<tbody>
<tr>
<td><strong>Liquid</strong></td>
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<tr>
<td>Viscosity, Pa.s</td>
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<tr>
<td>Surface Tension, dyne/cm</td>
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<tr>
<td>Density, kg/m³</td>
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<tr>
<td>Equilibrium Contact angle on glass, degrees</td>
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<td>Equilibrium Contact angle on Teflon, degrees</td>
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| Table 2 Physico-chemical Properties of Surfactants |
|-----------------|-----|-------|
| **Surfactant Name** | **SDS** | **Triton X-100** |
| Chemical formula | \( C_{12}H_{15}SO_4 \) | \( C_{14}H_{21}(OCH_2 \ CH_2)_{9-10}OH \) |
| Molecular wt. | 288.3 | 624(Avg.) |
| Ethylene oxide groups | 0 | 9-10 |
| Appearance | White Powder | Clear Liquid |
| CMC | 2500 wppm | 200 wppm |
| Manufacturer | Fisher | Union Carbide |
| Equilibrium Surface Tension dyne/cm [\( @2 \times \text{CMC} \)] | 38.0 | 33.1 |
| Equilibrium Surface Tension dyne/cm [\( @0.5 \times \text{CMC} \)] | 51.9 | 35.7 |

Figure 1. The computational domain with the two phases shown at the beginning of the computational run
Dynamic Surface Tension

Additives have surface-active properties that lower the surface tension of water considerably. The surfactant adsorption-desorption process, however, is time-dependent and it manifests in a dynamic surface tension behavior, which eventually reduces to an equilibrium value after a long time span. We have used experimental data from Zhang [22] for the dynamic surface tension coefficient (Fig. 2). The surface tension values at extremely small time scales are not available and the extrapolation method of Rosen and Hua [23]. A User-Defined-Function containing was developed to model this time-varying surface-tension-coefficient.

Figure 2. Dynamic surface tension behavior of surfactants

We have considered drops with diameters of about 2 to 3 mm and the maximum spread factor based was about 3. Hence the size of the axi-symmetric computational domain (Fig. 1) was chosen as 8 mm x 20 mm which ensured that there is no “overflow” from the sides and also was able to accommodate the rebound of the drop from the surface as expected from the Teflon surface. The grid was refined iteratively from 5 nodes per mm to 20 nodes per mm. Results from trial simulations [not shown here] indicated that 20 nodes per mm produced sufficiently fine cell sizes to track the interface accurately. Further refinement did not produce any significant changes in the results. Hence a grid size of 20 nodes per mm was adopted for all simulations.

The velocity components at the wall were set to zero. A symmetry boundary condition was set at the axis. A constant pressure boundary condition (pressure-inlet) was used at the top and sides of the computational domain.

Mass and momentum equations were solved using a second-order implicit method for space and a first-order implicit method for time discretization. Pressure interpolation was performed using a body force-weighted scheme. This scheme has been shown to work well for VOF simulations of cases with fluids having a substantial density difference [17]. Pressure implicit with splitting of operator (PISO) was used for pressure velocity coupling in the momentum equation. A time-step of 5 x 10^{-6} was used which was necessary to reduce the normalized residuals below 10^{-5} within 5-10 iterations per time-step. Simulated results were stored for every 1 ms of flow time to capture the dynamics of flow.

Results and Discussion

Model Validation

The photographic images of the droplet impact, recoil, and rebound available in Gatne et al. [24] were used to validate the numerical model. Gatne et al.[24] have used high-speed video camera to capture the droplet dynamics at 4000 frames per second. They have carried out image analysis to determine the droplet size. The droplet speed was calculated by comparing the distance traveled between two frames immediately prior to impact. They provide a sequence of images for Weber number of about ~ 20.

Impact of Water Drops

Fig. 3 shows the comparison of photographs of the impact-spreading-recoil-rebound dynamics of 3 mm diameter water drops at We ~ 20 on a Teflon substrate captured with a high-speed digital camera and the corresponding computational results. Water has a static contact angle of around 110° on Teflon and shows non-wetting behavior. Because of its initial kinetic energy, the drop spreads beyond its equilibrium diameter under inertia force creating a large surface area. The surface tension force acts to restore drop shape and the triple contact line experiences a restoring “backward” force which results in recoil [15]. The larger kinetic energy at higher Weber number facilitates increased spreading and subsequently sharper recoil. The liquid layer recoils into a vertical jet (with higher elongation for higher Weber numbers) and has a tendency to fracture into multiple droplets in a Rayleigh-type break up. At We ~ 20, one secondary droplet breaks up from the liquid column. From the comparison of computational results and experimental photographs shown in Fig. 3, it is evident that the numerical model using the VOF method is able to capture the dynamics of drop spreading, recoiling and bouncing quite well.

Dynamics of Surfactant-Solution Drops

Figure 4 shows images of the drop impact behavior for different surfactant solutions and water on a Teflon substrate. The velocity of impact in all cases is ~0.7 m/s and surfactant concentration is 2×CMC.
It is interesting to note that the drop rebound is not seen in the droplet impact of surfactant solutions. The reduction in surface tension at the liquid-air interface and altered wetting behavior at the solid-liquid interface due to the transport and adsorption of the surfactant molecules results in higher initial spread and a weak recoil. The difference in the behavior of the drops of different surfactant solutions can be attributed to the differences in the mobility of the surfactants, their dispersion and adsorption time scales. It is seen from Fig. 2 that the surfactants take different time to disperse and adsorb at the interface and equilibrium conditions are not reached during the time required for the drop to spread to its maximum spread diameter. The lower molecular weight surfactants have a shorter diffusion time when compared to their higher molecular weight counterparts which results in faster surface tension relaxation of SDS solution compared to Triton X-100 solution. Therefore the SDS solution showed higher spread and weaker recoil than Triton X-100 which takes longer to disperse and adsorb at the newly formed interface.

**Heat Transfer from a Hot Water Drop to a Cold Surface**

We have numerically simulated two cases to study heat transfer: drop cooling and drop heating. We first consider cooling of a hot water droplet (initial temperature of 353 K) impinging on a surface maintained at 300 K at a Weber number of 20. From

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**Figure 3** High-speed photographs and simulation results depicting impact of a water droplet on a hydrophobic (Teflon) surface at $\text{We} \sim 20$.

**Figure 4.** Comparison of droplet impact behavior of water, SDS, and Triton solution drops on a hydrophobic surface. Weber number for water $\sim 20$, SDS solution $\sim 28$, and Triton solution $\sim 28$. 

<table>
<thead>
<tr>
<th>Experimental Visualization</th>
<th>Computational simulation</th>
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<td>![Image]</td>
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<table>
<thead>
<tr>
<th>Water</th>
<th>SDS 2×CMC</th>
<th>Triton 2×CMC</th>
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<tr>
<td>![Image]</td>
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the temperature contours it is seen that the droplet cools to about 335-345K near the surface and about a couple of degrees hotter near the water-air interface. The droplet undergoes sharp recoil followed by a break-up of the liquid column into a secondary drop which eventually coalesces into the original drop. This gives rise to considerable mixing of the hotter and colder fluid in the droplet.

**Heat Transfer to a Cold Water Drop from a Hot Surface**

We now consider the impact of a cold droplet on a hot surface – a situation that is encountered in quenching and cooling applications where droplet sprays are used. We have investigated the heat transfer from a hydrophobic surface maintained at 353 K to a water droplet that is initially at 300 K as well as aqueous surfactant solution droplets. The total heat transfer to the droplet is directly related to the droplet bulk temperature change. Figure 6 shows the temporal variation of bulk fluid temperature for water, SDS and Triton X-100 solution at 2×CMC on a Teflon surface. The bulk temperature of SDS droplet shows the steepest rise where the drop heats up to approximately 323 K at the end of 50 ms. In the same duration, a Triton solution drop heats up to about 314K and the water drop to around 309K. It is clear that the greater wettability of SDS results in higher rate of heat transfer. The spike in the bulk fluid temperature between 30 and 40 ms can be attributed to the secondary water drop falling back into the original drop.

**Figure 6** Transient temperature variation for water, SDS, and Triton solution droplets on a heated surface. Initial drop temperature = 300 K, surface temperature 353 K, Weber number ~ 28.

**Conclusions**

Computational simulations of droplet impact dynamics were carried out for water and aqueous surfactant solution drops impinging on a hydrophobic surface (Teflon). The simulations show that the water droplet recoils sharply into a vertical column which undergoes a breakup to form secondary droplets. The decrease in surface tension at the liquid-air interface and change in the wetting characteristics of the liquid-solid interface facilitated larger initial spreading and weaker recoil with surfactant solution droplets. This is governed by the diffusion and

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**Figure 5** Temperature contours for cooling of a hot water drop impacting on a Teflon surface. Initial drop temperature = 353 K, surface temperature 300 K, Weber number ~ 20.
adsorption rate of the surfactants on the liquid-air and solid-liquid interfaces. The dynamic surface tension response underscores the differences in the relative performance of different surfactants. The lower molecular weight SDS solution showed a higher maximum and final spread and weaker recoil than the higher molecular weight Triton X-100 solution. As a result the transient heat transfer rate is significantly higher for aqueous surfactant solution droplets compared to water drops, and the bulk temperature of SDS solution drop changes faster than that of Triton solution droplet.

References