I, Arun Sanjeev, hereby submit this work as part of the requirements for the degree of: Master of Science in: Mechanical Engineering

It is entitled: Computational Study of Surfactant-Induced Modification of Droplet Impact Dynamics and Heat Transfer on Hydrophobic and Hydrophilic Surfaces

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Computational Study of Surfactant-Induced Modification of Droplet Impact Dynamics and Heat Transfer on Hydrophobic and Hydrophilic Surfaces

A Thesis Submitted to the University of Cincinnati in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in the Department of Mechanical Engineering of the College of Engineering of the University of Cincinnati, 2008

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Abstract

Computational simulations of the spreading, recoil, and rebound/break up of liquid droplet on a horizontal surface were carried out with a finite volume method on a structured grid. A volume-of-fluid (VOF) technique was used to track the deforming liquid-air interface. Simulations were carried out for water and aqueous surfactant solution drops impacting on hydrophilic (glass) and hydrophobic (Teflon) surfaces in the range of Weber numbers between 20 ~ 80. The computational predictions were compared with high-speed visualization of isothermal droplet impact reported by Gatne (2006) to validate the numerical model. The computational scheme based on the VOF method was able to capture the dynamics of this droplet-surface interaction phenomenon observed in the experiments. The numerical treatment included the dynamic surface tension variation for surfactant solutions and different values for the advancing and receding contact angles, which resulted in accurate prediction of the drop impact-spreading-recoil behavior. The computational simulations show that the water droplets spread and then recoil sharply so as to form a vertical column, which breaks up and ejects secondary droplets on a teflon surface but on a glass surface they spread, recoil to a lesser extent and oscillate to rest without rebound. 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. The solution of lower molecular weight (higher mobility) surfactant (SDS) showed a higher maximum and final spread with weaker recoil compared to the higher molecular weight (lower mobility) Triton X-100 surfactant. The heat transfer phenomena in droplet impact were studied for both cooling and heating of water and aqueous surfactant solution drops. The results indicated that the wettability of the substrate has the biggest impact on heat transfer. SDS solution droplets resulted in higher heat transfer compared to water droplets due to better wettability and less recoil exhibited by these
droplets. Surfactant solutions containing higher concentrations showed higher heat transfer rates as they have lesser recoil which results in more contact surface area with the surface.

This study shows that addition of surfactants to water profoundly changes the droplet impact dynamics and concomitant heat transfer and this provides a method to passively modify and control the droplet impact-spreading-recoil processes.
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# Table of Contents

Introduction ......................................................................................................................................... 1

1.1 Background ................................................................................................................................... 1

1.2 Objectives and scope of the present work .................................................................................... 7

Numerical Solution of Droplet Dynamics .......................................................................................... 9

2.1 The VOF method .......................................................................................................................... 9

2.2 Surface Tension and Wall Adhesion ............................................................................................. 11

2.3 Dynamic Contact Angle ............................................................................................................. 13

2.4 Dynamic Surface Tension ........................................................................................................... 17

2.5 Evaluating Heat Transfer ............................................................................................................ 21

2.6 Validation of Heat Transfer CFD Model ....................................................................................... 23

Results and Discussion ....................................................................................................................... 29

3.1 Drop impact under isothermal conditions ................................................................................... 29

3.1(a) Impact of Water Drops ........................................................................................................... 29

3.1(b) Effect of Weber number on Hydrophobic surface .................................................................... 32

3.1(c) Effect of Weber number on Hydrophilic surface ..................................................................... 33

3.2 Impact of Surfactant-Solution Drops ......................................................................................... 35

3.2(a) Effect of Surfactant Concentration ......................................................................................... 36

3.2(b) Effect of Molecular Weight of Surfactants ............................................................................ 38

3.3 Heat Transfer ............................................................................................................................... 42

Conclusions and Scope for Future Work ......................................................................................... 63
List of Figures

Fig 1. The Computational Domain ........................................................................................................ 10
Fig 2  Dynamic Contact Angle Validation for Water on Glass at We~20 ........................................ 15
Fig 3  Dynamic Contact Angle Validation for Water on Glass at We~77 ........................................ 16
Fig 4 Dynamic surface tension behavior of surfactants @ 2CMC ......................................................... 18
Fig 5 Effect of Surface Wettability on Droplet Impact [Water on Glass and Teflon @ We~20]. .... 30
Fig 6 Effect of Weber number on Droplet Impact [Water on Teflon @ We~20 & We~80] .......... 33
Fig 7 Effect of Weber number on Droplet Impact [Water on Glass @ We~20 & We~80] .......... 34
Fig 8 Dynamics of Surfactant drops [Water, SDS & Triton X-100 on Teflon @ We~28] ........... 36
Fig 9 Effect of Surfactant Concentration [SDS on Teflon @ We~28 at 2CMC and half CMC] ... 38
Fig 10 Effect of Molecular Weight of Surfactants [SDS and Triton X-100 on Teflon @ We~28 at an equilibrium surface tension value of 42.5 mN/m] ................................................................................. 40
Fig 11 Surface Tension variation with time of SDS and Triton X-100 on Teflon @ We~28 at an equilibrium surface tension value of 42.5 mN/m ............................................................................................................ 41
Fig 12 Water on Glass @ We~20 .......................................................................................................... 43
Fig 13 Water on Glass @ We~77 .......................................................................................................... 44
Fig 14 Water on Teflon @ We~20 ........................................................................................................ 46
Fig 15 Water on Teflon @ We~28 ........................................................................................................ 48
Fig 16 SDS 2CMC on Teflon @ We~28 ............................................................................................. 49
Fig 17 Triton X-100 2CMC on Teflon @ We~28 ............................................................................. 50
Fig 18 SDS HalfCMC on Teflon @ We~28 ...................................................................................... 51
Fig 19 SDS at equib. Surf. Tension value of 42.5 mN/m on Teflon @ We~28 ......................... 52
Fig 20 Triton X-100 at equib. Surf. Tension value of 42.5 mN/m on Teflon @ We~28 .......... 53
Fig 21 Tbunt variation with time (Effect of surfactants) [Water on Teflon, SDS & Triton @ 2CMC on Teflon @ We~28] ................................................................................................................. 56
Fig 22 Variation of “U” with time (Effect of surfactants) [Water on Teflon, SDS & Triton @ 2 CMC on Teflon @ We ~28] ................................................................. 57

Fig 23 Tbulk variation with time (Effect of surfactant concentration) [SDS on Teflon @ We ~28 at 2CMC and half CMC] .............................................................................................................. 59

Fig 24 Variation of “U” with time (Effect of surfactant concentration) [SDS on Teflon @ We ~28 at 2CMC and half CMC] .............................................................................................................. 60

Fig 25 Tbulk variation with time (Effect of Mol. Wt of Surfactants) SDS and Triton X-100 on Teflon @ We ~28 at an equilibrium surface tension value of 42.5 mN/m ........................................ 61

Fig 26 Variation of “U” with time (Effect of Mol. Wt of Surfactants) SDS and Triton X-100 on Teflon @ We ~28 at an equilibrium surface tension value of 42.5 mN/m ........................................ 62
List of Tables

Table 1 Physical Properties of Water............................................................................................................. 6
Table 2 Physico-Chemical Properties of Surfactants .................................................................................. 7
Table 3 Heat transfer rate from the wall for different grids........................................................................ 25
Chapter 1

Introduction

1.1 Background

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 in 1876-[Roisman et al. (2002)]. 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 - [Eckmann et al. (2001)] including spray coating, deposition, inkjet printing, spray cooling, rain-ingestion in gas turbines - [Chandra et al. (1991)] crop spraying, aircraft icing. A recent article by Yarin (2006) 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} via different experimental analysis and computational modeling.

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 – [Bennet et al. (1993), Chandra et al. (1991), Mao et al. (1997), Pasandideh-Fard et al. (1996), Sikalo et al. (2006) and Yarin (2006)]. 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 drops - [Gatne et al. (2007)]. The advancing contact angle is greater than the static contact angle, whereas the receding contact angle is typically lower than the static contact angle - [Gatne et al. (2006)]. The heat transfer during droplet impact has been primarily studied for two applications that involve phase change process, first is the spray coating processes that involve solidification on the surface and the second is fuel droplet impact of a heated surface that results in boiling of the liquid. Chandra et al. (1991) studied the effect of surface temperature on the impact dynamics. They conducted experiments by varying the surface from room temperature to beyond the Leidenfrost point of the liquid. Gao et.al. (2000) studied the wetting process of a molten solder drop. Based upon non-equilibrium thermodynamics, they proposed a theoretical model by introducing the kinetic laws that characterize the motions of the solder surface and the triple point line. Benintendi et al. (1999) studied the effect of the slip coefficient and the mobility capillary number on the spreading of a thin axisymmetric liquid droplet with uniform heating/cooling of the solid surface is examined. Their results show that increasing the slip coefficient reduces the spreading/shrinking behavior of the droplet and that the final equilibrium states are slip dependent.

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 – [Holmberg et al. (2003)]. 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 – [Zhang et al. (2005)]. The equilibrium surface
tension (t_σ→∞) 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 - [Zhang et al. (2005)]. 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 - [Zhang et al. (1997), Mourougou-Candoni et al. (1997), Mourougou-Candoni et al. (1999), Crooks et al. (2001), and Gunjal et al. (2005)].

The addition of these surfactants in small amounts can change the solution properties dramatically and may give strikingly different results which can be used to control and improve processes such as spray coating, deposition and inkjet printing. Apart from these, spray-fired incinerators, automotive engines, liquid atomizers, and spray cooling.

However, presence of surfactants adds 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 – [Yarin (2006)]. Experimental investigations of [Mourougou-Candoni et al. (1997), Mourougou-Candoni et al. (1999), Zhang and Basaran et al. (1997), Crooks et al. (2001), and Gunjal et al. (2005)] have shown that the dynamic surface tension plays a significant role in surfactant solution drop impact-spreading-recoil phenomena. Zhang and Basaran et al. (1997) 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 effects have not been seen in other studies of surfactant solution drop impact. Clay et al. (2004) studied the effects of surfactant and temperature on the spreading of a viscous droplet. Lubrication theory is used to develop a model for the evolution of the droplet.
They assumed the surfactant to be insoluble and transport onto and off of the droplet interface at the contact line was allowed. They allowed a linear temperature gradient plus a gradient in the surface energy along the substrate. They found that these effects together can increase the speed of the translation of the droplet. Though these studies have investigated the effect of temperature on droplet impact and particularly the spreading phenomenon they do not give much insight into the heat transfer mechanisms that occur during droplet impact without phase change. Bharadwaj et al. (2007) have investigated the impingement of a liquid micro droplet on a glass substrate at different temperatures. They have performed a combined numerical and experimental study and assessed the imperfect thermal contact between the liquid and solid substrate for a range of interfacial Biot numbers. Tarozzi et al. (2007) also have investigated the cooling of water droplets on hot substrates. They have used non-intrusive infra-red measurements to obtain the interface contact temperatures.

The process of droplet impact and spreading is very fast, of the order of milliseconds, and the drop sizes may range from millimeter to a few microns, as such the process can not be captured by the naked eye - [Gatne et al. (2006)]. Therefore numerical simulations of the process (termed as CFD-Computational Fluid Dynamics) have been performed to helps provide tremendous insight into this process. These numerical simulations have generally used Volume-of-Fluid (VOF) method to track the interface between two-liquids. This method was developed by Hirt and Nichols (1981). Pasandideh-Fard et al. (1996), Fukai et al. (1995) and Sikalo et al. (2005) have used it to model the drop impact spreading and recoil for pure liquids. Gunjal et al. (2005) simulated the impact of SDS solution drops on a hydrophilic surface with the VOF method using experimentally measured dynamic contact angles. While there have been many numerical studies to model surface deformations of pure liquids, there have been few that incorporate the effects of surfactants. Renardy et al. (2002) have simulated 3-D drop deformation under shear with surfactants using the VOF method. James et al. (2004) have
reported a surfactant-conserving VOF method for interfacial flows but this has not been applied to normal impact with a solid substrate.

In this thesis, the droplet impact dynamics, spreading, recoil, and column breakup phenomena for a droplet impinging on a flat surface has been investigated via computational methods. The heat transfer between the surface and the impacting drop is studied for water and aqueous surfactant solutions. To validate the computational model, the results must be compared with experimental data. To this end, the experimental data from Gatne (2006) is used. Gatne (2006) carried out a detailed experimental investigation of normal, isothermal droplet impact for pure liquids (Ethanol, propylene glycol, glycerol, and water) as well as aqueous surfactant solutions using high speed video and image analysis. As reported in Gatne (2006), the droplets were generated manually using a syringe in his experiments. The syringe had provision for interchangeable needles for varying the orifice diameter. The syringe was mounted on a stand that could be lowered or raised to release the droplet from different predetermined heights to obtain different values of impact velocity. Teflon or PTFE was used as the hydrophobic substrate material and glass as the hydrophilic substrate. The drop impact-spreading-recoil phenomena were captured using a digital high-speed camera system. The camera was aligned at zero degrees to obtain a frontal view of the impact. Image processing software was used for enhancement and measurement of the captured photographs. The droplet diameter was measured as the average of several angular diameters from the image just before impact. The calibration was achieved by measuring the needle diameter which was known. The droplet velocity and hence the Weber number was varied by changing the height from which the drop was released. The static contact angles were measured by the sessile drop method using a Kernco GI contact angle meter. The physical properties of water are given in Table 1. Two different surfactants were used: SDS (anionic) and Triton X-100(non-ionic). Table 2 provides properties of the surfactants used. Gatne (2006) carried out an uncertainty analysis for his experimental data and found that the maximum uncertainty in the measurement of the
drop diameter and velocity was 1.4% and 1.31% respectively. This resulted in an uncertainty of 2.37% in the Weber number and 1.92% in the Reynolds number. For surfactants, the maximum uncertainty in the surfactant concentration was found to be 1.6% for SDS and 2.81% for Triton X-100. The details of the uncertainty analysis are available in Gatne (2006).

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity $\times 10^3$, Pa.s</td>
<td>1</td>
</tr>
<tr>
<td>Surface Tension $\times 10^3$, N/m</td>
<td>73</td>
</tr>
<tr>
<td>Density, kg/m$^3$</td>
<td>1000</td>
</tr>
<tr>
<td>Equilibrium Contact angle on glass, degrees</td>
<td>38</td>
</tr>
<tr>
<td>Equilibrium Contact angle on Teflon, degrees</td>
<td>110</td>
</tr>
</tbody>
</table>

*Table 1 Physical Properties of Water*
### Table 2 Physico-Chemical Properties of Surfactants

<table>
<thead>
<tr>
<th>Surfactant Name</th>
<th>SDS</th>
<th>Triton X-100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>$\text{C}<em>{12}\text{H}</em>{15}\text{SO}_4$</td>
<td>$\text{C}<em>{14}\text{H}</em>{21}(\text{OCH}_2\text{CH}<em>2)</em>{9-10}\text{OH}$</td>
</tr>
<tr>
<td>Ionic Nature</td>
<td>Anionic</td>
<td>Nonionic</td>
</tr>
<tr>
<td>Molecular wt.</td>
<td>288.3</td>
<td>624 (Avg.)</td>
</tr>
<tr>
<td>Ethylene oxide groups</td>
<td>0</td>
<td>9-10</td>
</tr>
<tr>
<td>Appearance</td>
<td>White Powder</td>
<td>Clear Liquid</td>
</tr>
<tr>
<td>CMC</td>
<td>2500 wppm</td>
<td>200 wppm</td>
</tr>
<tr>
<td>Manufacturer</td>
<td>Fisher</td>
<td>Union Carbide</td>
</tr>
<tr>
<td>Purity</td>
<td>$\geq$99%</td>
<td>-</td>
</tr>
<tr>
<td>Equilibrium Surface Tension dyne/cm @ 2 CMC</td>
<td>37.5</td>
<td>33.1</td>
</tr>
<tr>
<td>Equilibrium Surface Tension dyne/cm @ 0.5 CMC</td>
<td>51.9</td>
<td>35.7</td>
</tr>
</tbody>
</table>

Table 2 Physico-Chemical Properties of Surfactants

1.2 Objectives and scope of the present work

The aim of the present study is to investigate the droplet impact dynamics, spreading, recoil, and column breakup phenomena for a droplet impinging on a flat surface using computational methods. The heat transfer between the surface and the
improving droplet impact is studied to understand how the dynamics of the droplet deformation affects the heat transport processes.

The effect of wettability of the substrate on droplet impact is investigated by considering two surfaces Teflon and glass. Teflon acts as a hydrophobic or “de-wetting” and glass as hydrophilic “wetting” surface. For both these substrates, droplet impact simulations were performed at two Weber numbers by varying the speed of impact, one at We~20 and the other at We~80. Next the effect of surfactants in improving the wettability of a substrate is studied by considering two surfactants SDS (low molecular weight) and Triton X-100 (high molecular weight) to obtain the effects of molecular weight of the surfactant molecules on the droplet impact process. This was performed on a Teflon substrate. The simulations were performed to emulate two concentrations 2 CMC (Critical Micellar Concentration) and Half CMC. The effect of molecular wt. of the surfactants was investigated by considering concentrations of SDS and Triton such that they produced the same equilibrium value of 42.5 mN/m.

The heat transfer mechanisms in the droplet impact process is investigated by considering two scenarios, the cooling of water droplets (353K) impacting cold surfaces (300K) in ambient air and the heating up of water and surfactant droplets (300K) impacting a hot substrate (353K). The cooling process is simulated for both glass and Teflon substrates. The effect of velocity is analyzed on a glass substrate at two Weber numbers 20 and 80 approx. The heating of the drops are simulated for both pure liquids and surfactants on the Teflon substrate. The effect of surfactant concentration on heat transfer is investigated for SDS at two concentrations 2CMC and Half CMC. The effect of molecular wt. of surfactants on heat transfer is also studied.

The heat transfer process is analyzed by applying a global heat balance on the drop and extracting two parameters, the bulk fluid temperature and the overall heat transfer coefficient. The variation of these two parameters with time is plotted for analysis.
Chapter 2
Numerical Solution of Droplet Dynamics

Computational model of the process of droplet impact requires simulation of two phases (liquid and air) and tracking of the phase interface which undergoes large, unsteady deformations. The Volume of Fluid (VOF) method (Hirt et al. 1981) was used to track the liquid/gas interface. The governing continuum conservation equations for two phase flow were solved using the commercial software package Fluent v.6.2 and v6.3 [Fluent Inc.]. The computational grid was created using commercial software called Gambit v.2.2.30 [Fluent Inc.]. The finite volume method with a fixed non uniform spatial grid was used to computationally model the process. From experimental images available in Gatne (2006) 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.

2.1 The VOF method
This method is applicable to immiscible fluids. In the VOF method, a volume fraction variable is assigned for each phase (α). 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:

\[
\frac{\partial \alpha}{\partial t} + \mathbf{v} \cdot \nabla \alpha = 0
\]  

(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

\[
\rho = \alpha \rho_\alpha + (1 - \alpha) \rho_\beta
\]  

(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:

\[
\nabla \cdot \mathbf{v} = 0
\]  

(3)

\[
\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} = -\frac{\nabla p}{\rho} + \nabla \cdot \left[ \mu (\nabla \mathbf{v} + \nabla \mathbf{v}^T) \right] + g + \frac{F_{sf}}{\rho}
\]  

(4)
Here \( \vec{v} \) is velocity, \( p \) is pressure, \( F_{SF} \) is the continuum surface force, \( \mu \) denotes viscosity of the mixture, \( \rho \) density of the mixture, \( g \) is gravitational acceleration.

The geometric reconstruction scheme was used for accurate calculation of the face fluxes in the VOF model used by Ibrahim et al. (2007). The continuum surface force model proposed by Brackbill et al. (1992) was used to determine the surface tension force at the liquid-air interface. Fluent's control-volume formulation requires that convection and diffusion fluxes through the control volume faces be computed and balanced with source terms within the control volume itself.

The geometric reconstruction scheme in Fluent is the most accurate for the calculation of the face fluxes in the VOF model. This scheme represents the interface between fluids using a piecewise-linear approach. It assumes that the interface between two fluids has a linear slope within each cell, and uses this linear shape for calculation of the advection of fluid through the cell faces. The first step in this reconstruction scheme is calculating the position of the linear interface relative to the center of each partially-filled cell, based on information about the volume fraction and its derivatives in the cell. The second step is calculating the advecting amount of fluid through each face using the computed linear interface representation and information about the normal and tangential velocity distribution on the face. The third step is calculating the volume fraction in each cell using the balance of fluxes calculated during the previous step.

2.2 Surface Tension and Wall Adhesion

The surface tension model in FLUENT is the continuum surface force (CSF) model proposed by Brackbill et al. (1992).

The surface curvature is computed from local gradients in the surface normal at the interface. Let \( n \) be the surface normal, defined as the gradient of \( \alpha_q \),

\[ n(x, y, z) = \nabla \alpha_q(x, y, z) \]
\[ n = \nabla \alpha_i \] (5)

The curvature, \( \kappa \), is defined in terms of the divergence of the unit normal, \( \hat{n} \)

\[ \kappa = \nabla \cdot \hat{n} \] (6)

Where,

\[ \hat{n} = \frac{n}{|n|} \] (7)

The surface tension force can be written in terms of the pressure jump across the surface. The force at the surface can be expressed as a volume force using the divergence theorem. It is this volume force that is the source term which is added to the momentum equation. If only two phases are present in a cell, the surface tension force reduces to the form,

\[ F_{sv} = \sigma_{ij} \frac{\rho \kappa \nabla \alpha_i}{2} \frac{1}{(\rho_s + \rho_v)} \] (8)

The effects of wall adhesion at fluid interfaces in contact with rigid boundaries in equilibrium can be estimated in terms of the contact angle between the fluid and wall. Rather than impose this boundary condition at the wall itself, the contact angle that the fluid is assumed to make with the wall is used to adjust the surface normal in cells near the wall. This boundary condition adjusts the curvature of the surface near the wall. If \( \theta_v \) is the contact angle at the wall, then the surface normal at the live cell next to the wall is

\[ \hat{n} = \hat{n}_w \cos \theta_v + \hat{t}_w \sin \theta_v \] (9)

where \( \hat{n}_w \) and \( \hat{t}_w \) are the unit vectors normal and tangential to the wall, respectively. The combination of this contact angle with the normally calculated surface normal one cell
away from the wall determine the local curvature of the surface, and this curvature is used to adjust the body force term in the surface tension calculation.

2.3 Dynamic Contact Angle

Wall adhesion boundary conditions are quite complex when the contact line is in motion, i.e., when the fluid in contact with the wall is moving relative to the wall - [Dussan (1979)]. The advancing and receding contact angles are different from the equilibrium contact angle and depend on the local flow and wall conditions. It is well-known that for large capillary numbers (Ca = νμ /σ), the dynamic contact angle is not a material property – [Dussan (1979)]. Recent studies indicate that the macroscopic hydrodynamics affects the dynamic contact angle for all capillary numbers – [Hirt et al. (1981)]. Several empirical relationships involving the Capillary number and the dynamic contact angle are available.

Cox (1986) in his theoretical analysis of the creeping velocity field in the corner has come up with a relation which is valid for both spreading and receding contact lines:

\[
Ca = \left( \ln(\varepsilon^{-1}) - \frac{Q_1}{f(\theta_d)} + \frac{Q_2}{f(\theta_r)} \right)^{-1} [g(\theta_d) - g(\theta_r)] + O\left( \frac{1}{\ln(\varepsilon^{-1})} \right)^3
\]

(10)

Q₁ and Q₂ are constants associated with the outer flow and with the wall slip, ε is a small dimensionless parameter associated with the micro region of the contact line, f (•) and g (•) are empirical functions.

All existing empirical models of the dynamic contact angle are simplifications of the general expression by Cox (1986). The most widespread working relation describing the contact angle is given by the so-called Hoffman–Voinov–Tanner law - [Sikalo et al. (2005) for small Ca,

\[
\theta^i - \theta_i^i \cong \varepsilon \gamma Ca \quad (11)
\]
Where \( c_T \) is a constant given to be about 72, with some dependence on the flow system size.

Jiang et al. (1979) also give an empirical correlation for dynamic contact angle

\[
\frac{\cos(\theta_s) - \cos(\theta_d)}{\cos(\theta_d) + 1} = \tanh(4.96 C^a 0.702)
\]  

(12)

A more recent empirical correlation for the dynamic contact angle is given in the form, \( \theta_d = f_{HOFF}[Ca + f_{HOFF}^{-1}(\theta_d)] \) where \( f_{HOFF}^{-1}(.) \) is the inverse function of the “Hoffman’s” function, \( f_{HOFF}(.) \) defined as

\[
f_{HOFF}(x) = \arccos\{1 - 2 \tanh[5.16(x \frac{x}{1 + 1.31 x^{0.99}})^{0.706}]\}
\]

(13)

Blake et al. (1993) has also developed a model which is based on molecular kinetics,

\[
V_d = A \sinh[B \cos(\theta_d) - \cos(\theta_d)]
\]  

(14)

where,

\[
A = 2 \kappa^* \lambda h / (\mu \nu)
\]

(15)

\[
B = \gamma / (2nkT)
\]

(16)

with \( \kappa^* \) the frequency of molecular displacements at equilibrium, \( \lambda \), the average length of an individual molecular displacement in the three-phase zone, \( h \) Planck’s constant, \( \nu \) the molecular flow volume, \( n \) the number of adsorption sites per unit area, \( k \),Boltzmann’s constant and \( T \) the temperature. The values of some of these parameters are unique for every solid-liquid-gas system under investigation. Sikalo et al. (2005) have evaluated these empirical correlations for pure liquid drops. They showed that the use of static contact angle model predicts the spreading of the drop reasonably well, but not the receding phase. A dynamic contact angle input is necessary to obtain
more realistic results. Secondly, dynamic contact angle is not only a function of the contact line speed but also a function of the flow field in the vicinity of the moving contact line - [Blake et al. (1999)]. As such a unique functional dependence of the dynamic contact angle for the full range of contact-line speeds is difficult to obtain. The dynamic contact angle models are based on quite scattered experimental data and one model does not satisfactorily predict the dynamic contact angle for all Capillary numbers or on all gas-liquid-solid systems. Blake’s model appears to provide predictions closer to experimental data, however some of the physical parameters are not known for many systems. Furthermore, for surfactant solutions, dynamic the contact angle is not a unique value as it depends on the history of the interface. Unfortunately none of the models account for the contact angle hysteresis.

![Dynamic Contact Angle (DCA) v/s time](image)

**Fig 2**  Dynamic Contact Angle Validation for Water on Glass at We~20
Figures 2 and 3 above show the comparison of some of the empirical relations for dynamic contact angle with 2 cases, water on glass at Weber numbers 20 and 77. From the graphs it is very clear that the three empirical relations behave very similar to each other with the relation proposed by Jiang et al. (1979) predicting angles slightly higher than the other two. However comparing these values with the experimental measurements we find that they under-predict the angle in the advancing phase and over-predict during the receding phase. Even though the predictions come close to experimental values for We~20, the error percentage at the higher Weber number is more than 100%. Since the simulations are quite sensitive to the contact angle in both the advancing and receding phase and considering the limitations of the available empirical correlations, we have used contact angles measured from experimental visualization in computational simulations.
2.4 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 (2004) for the dynamic surface tension coefficient (Fig. 4). The surface tension values at extremely small time scales are not available and the extrapolation method of Hua and Rosen (1988). At constant surfactant concentration in the bulk and at constant temperature, they described that

\[
\gamma(t) = \gamma_m + \frac{\gamma_0 - \gamma_m}{1 + \left(\frac{t}{t^*}\right)^n}
\]  \hspace{1cm} (17)

Where \( \gamma(t) \) is the dynamic surface tension co-efficient, \( \gamma_m \) is the meso-equilibrium surface tension and \( \gamma_0 \) is the surface-tension of the pure solvent, \( t^* \) and \( n \) are constants that are evaluated for each surfactant solution and for each concentration.

A User-Defined-Function (an example of this is shown in Appendix) containing this time-varying surface-tension coefficient was developed to model the surfactant solution drop dynamics. It can be seen from the figure that the surfactants take a much larger time to disperse and adsorb at the interface and equilibrium conditions are not reached when the drop has reached its maximum spread value. It is reported in Zhang et al. (2005) that lower molecular weight surfactants have a shorter diffusion time when compared to their higher molecular weight counterparts which is seen as the faster surface tension relaxation of SDS solution when compared to Triton x 100 solutions.
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. It was found 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 boundary conditions chosen were based on the model adopted by Gunjal et al. (2005). The velocity components at the wall were set to zero. A symmetric boundary condition was set at the axis. Because velocity profiles at the other two planes (other
than symmetry and wall planes) of the solution domain are not known, a constant pressure boundary condition (pressure-inlet) was used at these planes.

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 is useful when the body force is comparable to pressure force. This scheme computes the face pressure by assuming that the normal gradient of the difference between pressure and body forces is constant. This ensures that any density-weighted body force (such as gravity force) is balanced by pressure. This scheme performs better for VOF simulations of cases with fluids having a substantial density difference. Pressure implicit with splitting of operator (PISO) was used for pressure velocity coupling in the momentum equation. One of the limitations of the SIMPLE and SIMPLEC algorithms available in Fluent is that new velocities and corresponding fluxes do not satisfy the momentum balance after the pressure-correction equation is solved. As a result, the calculation must be repeated until the balance is satisfied. To improve the efficiency of this calculation, the PISO algorithm performs two additional corrections: neighbor correction (set to 1 in Fluent) and skewness correction (set to 0).

The default setting in Fluent to solve the volume fraction equation(s) once for each time step was used. This means that the convective flux coefficients appearing in the other transport equations will not be completely updated after each iteration since the volume fraction fields will not change from iteration to iteration.

Two time scales are used in the transient VOF problems using Interface Reconstruction

- Physical time step (user specified) $\Delta t$
- VOF sub-time step (internally computed by FLUENT) $\Delta \tau$
Momentum, turbulence, energy, and other scalar equations are solved with the $\Delta t$. Volume fraction $\alpha$ equation is solved explicitly with $\Delta \tau$.

Fluent will refine the time step for VOF automatically, based on the maximum Courant Number allowed near the free surface. The Courant number is a dimensionless number that compares the time step in a calculation to the characteristic time of transit of a fluid element across a control volume:

$$\frac{\Delta t}{\Delta x_{\text{cell}}/\sqrt[3]{V_{\text{fluid}}}}$$  \hspace{1cm} (18)

In the region near the fluid interface, Fluent divides the volume of each cell by the sum of the outgoing fluxes. The resulting time represents the time it would take for the fluid to empty out of the cell. The smallest such time is used as the characteristic time of transit for a fluid element across a control volume, as described above. Based upon this time and the Courant Number in a time step is computed for use in the VOF calculation. For example, if the maximum allowed Courant number is 0.25 (the default), the time step will be chosen to be at most one-fourth the minimum transit time for any cell near the interface. To calculate a stable and efficient time-step, the following procedure was used: Simulation was started with a small time step $\Delta t_1$, allowing good convergence within 20 iterations per time step. The simulation was continued for a few more time-steps to get the flow going. A very large time step $\Delta T$ (at least 6 orders of magnitude larger than originally) was specified and the simulation was run for 1 iteration. Fluent indicates an error message detailing the number ($N$) of VOF sub-time steps needed to cover the specified $\Delta T$. Now the VOF sub-time step can be computed simply as
$$\Delta \tau = \frac{\Delta T}{N} \quad (19)$$

The simulation was carried on with a physical time step $\Delta t_2$ of about 10-20 times $\Delta \tau$.

Based on this procedure a time-step of $1 \times 10^{-5}$ was used. For surfactant solutions a time-step of $5 \times 10^{-6}$ was necessary to reduce the normalized residuals to $10^{-6}$ within 5-10 iterations per time-step. Simulated results were stored for every 1ms of flow to capture the dynamics of flow. The initial condition for the simulation is based on the initial impact velocity. A circular region with diameter equal to the droplet diameter is patched with a water volume fraction of 1. This region is assigned the impact velocity which is computed from the Weber number.

2.5 Evaluating Heat Transfer

The VOF model in Fluent has been used to compute the heat transfer characteristics of the droplet impact process (without phase change). It has also been extended to surfactant solutions. Two scenarios are considered here:

1) A hot drop impacting a wall (at a colder constant temperature) and cooling off.

2) A cold drop impacting a hotter wall (at constant temperature )

In both cases, the heat transfer process has been evaluated mainly by studying the temperature contours in around the droplet and also the heat fluxes generated at the wall.

Since there is very little or no data available in literature and since experimental techniques are very complex and expensive, computational droplet cooling studies provide a useful insight into the problem.
The Energy Equation:

The energy equation, also shared among the phases, is shown below

\[
\frac{\partial}{\partial t} (\rho E) + \nabla \cdot (\rho \mathbf{u} E) = \nabla \cdot (k_{\text{eff}} \nabla T) + S_h \tag{20}
\]

The VOF model treats energy, \( E \), and temperature, \( T \), as mass-averaged variables.

\[
E = \frac{\sum_{q=1}^{\alpha} \alpha_q \rho_q E_q}{\sum_{q=1}^{\alpha} \alpha_q \rho_q} \tag{21}
\]

Where \( E_q \) for each phase is based on the specific heat of that phase and the shared temperature. The properties \( \rho \) and \( k_{\text{eff}} \) (effective thermal conductivity) are shared by the phases. The source term, \( S_h \), contains contributions from radiation, as well as any other volumetric heat sources. As with the velocity field, the accuracy of the temperature near the interface is limited in cases where large temperature differences exist between the phases. Such problems also arise in cases where the properties vary by several orders of magnitude. For example, if a model includes liquid metal in combination with air, the conductivities of the materials can differ by as much as four orders of magnitude. Such large discrepancies in properties lead to equation sets with anisotropic coefficients, which in turn can lead to convergence and precision limitations.

The heat transfer properties are taken into account in Fluent by switching on the energy equation in the pre-processor menu. The solution domain marked for water is patched with the drop temperature along with velocity and volume fraction and the thermal boundary conditions at the wall is specified (either constant temperature or fixed heat flux). The boundary conditions at the other domain boundaries are set to symmetry boundary condition in Fluent. The density of air is calculated using the Boussinesq model. This is to account for any buoyancy effect that might occur in the process with air
getting heated up by the plate and also some air losing heat near the water/air interface with the deforming water droplet. The rest of the computational model is exactly the same as the model developed only for fluid flow analysis.

The Boussinesq model can be used for natural convection problems involving small changes in temperature. This model treats density as a constant value in all solved equations, except for the buoyancy term in the momentum equation:

\[
(\rho - \rho_0)g \approx -\rho_0 \beta (T - T_0)g
\]  

(22)

Where \( \rho_0 \), the (constant) density of the flow, \( T_0 \) is the operating temperature, and \( \beta \) is the thermal expansion coefficient. The above equation is obtained by using the Boussinesq approximation

\[
\rho = \rho_0 (1 - \beta \Delta T)
\]  

(23)

to eliminate \( \rho \) from the buoyancy term. This approximation is accurate as long as changes in actual density are small; specifically, the Boussinesq approximation is valid when \( \beta (T - T_0) \) is much smaller than 1 which is the case in this study.

Sections 2.1, 2.2 & 2.5 are from Fluent`s user manual termed "Fluent 6.1 User`s Guide"

2.6 Validation of Heat Transfer CFD Model

Since no experimental results are available to validate the numerical results for heat transfer cases, grid dependence studies along with the verification of heat flux values served as validation tests for the CFD model.

Flux Convergence:

The heat flux value given out by Fluent was validated by manually computing the heat flux values at different locations along the wall using second and third order accurate schemes for the temperature gradient.
\[ q''(x) = -k \frac{dT}{dy_{wall}} \] (24)

\[ q''(x) = \text{Heat flux variation along the wall per unit area (W/m}^2) \]

\[ k = \text{Thermal conductivity (W/m-K)} \]

\[ \frac{dT}{dy_{wall}} = \text{Temperature gradient at the wall}. \]

This was calculated using a 2\textsuperscript{nd} and 3\textsuperscript{rd} order scheme:

\[ \frac{dT}{dy_{wall}} = \frac{-11T_1 + 18T_2 - 9T_3 + 2T_4}{18\Delta y} \] (3\textsuperscript{rd} order accurate scheme) (25)

\[ \frac{dT}{dy_{wall}} = \frac{-3T_1 + 4T_2 - T_3}{2\Delta y} \] (2\textsuperscript{nd} order accurate scheme) (26)

\( T_1, T_2, T_3 \) and \( T_4 \) are nodal temperatures adjacent to the wall at a specific location along the wall.

\( \Delta y \) = distance between adjacent nodes or grid density

\( q''(x) \) computed thus was compared to the heat flux calculated by FLUENT for two thermal boundary conditions: Constant temperature (353K) and Constant Heat flux (100 W/m\(^2\)). The comparison was made after giving sufficient time for heat transfer to take place, 42ms for the constant temperature case and 20ms for the constant heat flux case.

1) Constant temperature : Fluent over-predicted the flux values by about 8% for both the second and third order schemes.
II) Constant heat flux: The difference in Fluent and computed values was about 4% for both the schemes.

Grid dependence:

The dependence of heat flux values and total heat transfer rate from the substrate on grid density was next investigated to ensure reasonable results from Fluent.

The heat transfer rate from the wall was computed for 3 different grid densities

a) 8mm (wall) X 20(axis) mm grid divided into 240 points along the wall and 600 points along the axis.

b) Grid which is 1.5 times denser, i.e., 360 X 900 grid points

c) Grid which is 2 times denser, i.e., 480 X 1200 grid points

<table>
<thead>
<tr>
<th>Q (W/m²)</th>
<th>1ms</th>
<th>3ms</th>
<th>5ms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1X Grid</td>
<td>13.70</td>
<td>26.52</td>
<td>28.97</td>
</tr>
<tr>
<td>1.5 X Grid</td>
<td>18.06</td>
<td>34.03</td>
<td>35.49</td>
</tr>
<tr>
<td>2X Grid</td>
<td>21.69</td>
<td>36.54</td>
<td>36.80</td>
</tr>
</tbody>
</table>

Table 3 Heat transfer rate from the wall for different grid densities

From the table above it can be seen that the heat transfer rate Q, changes significantly for the original grid and the denser grids indicating the need for a denser grid. The difference diminishes for the two denser grids. Typically a simulation with the original grid for a flow-time of 100ms takes about 22-24 hrs but with the 1.5 X grids, computation time increased 4 or 5 times and a 2X grid took more than double the time of that of a 1.5
X grid. Since the difference in heat transfer rate between the 2 denser grids is only about 3.5%, the 1.5 X grid is chosen for subsequent runs.

With the flux value validation and grid dependence established for the heat-transfer model, the results obtained through CFD simulations can be viewed, with some confidence, as giving insight into the heat-transfer mechanism in droplet impact scenarios.

Global Heat Balance of the drop:
The results from the heat transfer simulation are analyzed to compute the bulk fluid temperature \( T_{\text{bulk}} \) at different time-steps and also the overall heat transfer coefficient \( U \) at each time step. \( T_{\text{bulk}} \) and \( U \) give us an indication of the rate of heat transfer to the water droplet or a feel of “how much the water drop is getting heated up by the hot plate”. Since there is no experimental data available for comparison owing to the fact that measuring the bulk fluid temperature at different times for the deforming fluid drop is virtually impossible, the results obtained from this computational model provide significant insight into the heat-transfer mechanisms in the droplet impact phenomenon for which extensive data is not available in the literature.

To find \( T_{\text{bulk}} \)

\[
m c_p \frac{dT_{\text{bulk}}}{dt} = q_{\text{total}} \tag{27}
\]

\( m \) = mass of water drop (kg)

\( c_p \) = Specific heat of water (kJ/kg.k)

\[
\frac{dT_{\text{bulk}}}{dt} = \text{Variation of } T_{\text{bulk}} \text{ with time (K/s)}
\]

\( q_{\text{total}} \) = Total heat transfer rate to the drop = \( \sum_i q_i A_i \)

\( q_i \) = Surface Heat flux at node i along the wall (W/m²)
\[ A_i = \text{Surface area corresponding to that node (m}^2) = \pi \left( r_i^2 - r_{i-1}^2 \right) \]

\[ r = \text{radial co-ordinate (along the wall) (m) } \]

This implies that

\[ \frac{dT_{\text{bulk}}}{dt} = \frac{q_{\text{total}}}{mc_p} \quad (27) \]

or,

\[ T_{\text{bulk}_{(i+2,3)}} - T_{\text{bulk}_{(i)}} = \frac{\Delta t}{mc_p} \sum_i q_i A_i \quad (28 \ a) \]

or,

\[ T_{\text{bulk}_{(i+2,3)}} = T_{\text{bulk}_{(i)}} + \frac{\Delta t}{mc_p} \sum_i q_i A_i \quad (28 \ b) \]

To find U:

\[ UA(T_{\text{wall}} - T_{\text{bulk}}) = q = \sum_i q_i A_i \quad (29) \]

This implies,

\[ U = \frac{\sum_i q_i A_i}{A(T_{\text{wall}} - T_{\text{bulk}})} \quad (30) \]

U= Overall heat transfer coefficient (W/m².k)

A = surface area covered by the water drop (m²) = \( \sum_i A_i \)

\[ T_{\text{wall}} = \text{Wall temperature} = 353K \]

The water drop was identified from the computational domain by identifying those cells which have water VOF between 0.5 and 1
Studying the temperature contours, we can see that the air and water get heated up roughly to the same temperatures and therefore the temperature gradient across the air-water interface can be neglected. Hence while applying the global heat balance to the water drop; heat loss to the surrounding air was neglected.
3.1 Drop impact under isothermal conditions

To validate the computational model, simulations of isothermal drop impact-spreading-recoil were carried out for drops of water and aqueous surfactant solutions for the same conditions used by Gatne (2006) in his experiments. Both hydrophobic (Teflon) and hydrophilic (glass) surfaces were considered. Simulations with water drops were performed at two Weber numbers (We = 20 and 80). Impinging droplet behavior was studied for aqueous surfactant solutions of SDS and Triton X-100 at two different surfactant concentrations (2×CMC and 0.5×CMC)

3.1(a) Impact of Water Drops

Simulations with water drops were performed at two Weber numbers (We = 20 and 80). Impinging droplet behavior was studied for aqueous surfactant solutions of SDS and Triton X-100 at two different surfactant concentrations (2×CMC and 0.5×CMC)
Water on Teflon @ We ~ 20
Water on Glass @ We ~ 20

Fig 5 Effect of Surface Wettability on Droplet Impact

[Water on Glass and Teflon @ We~20]
Fig. 5 shows the comparison of photographs of the impact-spreading-recoil-rebound dynamics of 3 mm diameter water drops at $\text{We} \sim 20$ on a Teflon and a Glass substrate captured with a high-speed digital camera and the corresponding computational results. The contours of $\text{VOF} = 0.5$ are shown as the liquid air interface in the computational results. Water has a static contact angle of around $110^\circ$ on Teflon and shows non-wetting (hydrophobic) behaviour. 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 – [Brackbill et al (1992)]. The larger kinetic energy at higher Weber numbers facilitate increased spreading and subsequently sharper recoils. 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 $\text{We} \sim 20$, one secondary droplet breaks up from the liquid column. The secondary drop eventually falls back and coalesces with the liquid on the surface. Subsequent oscillations of the drop shape dissipate energy through viscous forces until the drop finally achieves an equilibrium state. On the other hand water has a static contact angle of around $38^\circ$ on Glass and shows wetting (hydrophilic) behaviour. From the figure we see that the water drop recoils slowly and undergoes a few weak oscillations until it reaches equilibrium. It can be seen from the photos as well as the iso-$\text{VOF} = 0.5$ that the spreading behavior for the two surfaces is very similar until the drops reach a maximum spread and minimum thickness, though the spread on glass is slightly higher than on Teflon. It is also noticed that the drop takes slightly longer time in all cases to come to rest and the oscillations are more pronounced than those observed in the experiments. This can be attributed to the contact angle stipulation and how the contact angle affects advancing and receding motion of the liquid layer, and the corresponding variations in kinetic and surface energy and viscous dissipation. Gunjal et
al. (2005) have shown that the scale of variation of surface energy is higher than the potential and kinetic energy variations and it is very sensitive to the contact angle. Therefore small changes in the values of contact angle can explain the differences observed in the oscillation time and magnitude. Since only one value for advancing and one value for receding contact angle was specified as opposed to a continually varying contact angle observed in experiments, slight differences in the computational predictions are experimental observations are not surprising

3.1(b) Effect of Weber number on Hydrophobic surface

Fig 6 below shows the comparison of water droplet impact on a teflon surface at two Weber numbers 20 and 80. It can be seen from the results that the larger kinetic energy at higher Weber number facilitates increased spreading and subsequently sharper recoil. At We = 20, one secondary droplet breaks up from the liquid column. At We = 80, there is a neck formation after the release of the first drop but it does not result in another break-up. The secondary drop eventually falls back and coalesces with the liquid on the surface and the drop eventually comes to rest. We can also see from the images that the droplet spreads more at higher speeds due to higher initial kinetic energy and also that the thickness of the droplet at maximum spread is much thinner. Also due to the sharper recoil at We~80, the droplet recoils into a longer column than the slower drop. All these features are captured satisfactorily by the CFD model.
Water on Teflon @ We ~ 20

Fig 6 Effect of Weber number on Droplet Impact

[Water on Teflon @ We~20 & We~80]

3.1(c) Effect of Weber number on Hydrophilic surface

Fig 7 below shows the comparison of water droplet impact on a glass surface at two Weber numbers 20 and 80. As in the Teflon case we see a larger maximum spread at
higher impact speeds. The magnitude of oscillations decrease for We~80 due to increased viscous dissipation as a result of lower thickness at maximum spread. These features again are captured by the numerical model quite well.

Water on Glass @ We ~ 20

Water on Glass@ We ~ 80

Fig 7 Effect of Weber number on Droplet Impact

[Water on Glass @ We~20 & We~80]
3.2 Impact of Surfactant-Solution Drops

Figure 8 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 \( \sim 0.7 \text{ m/s} \) and surfactant concentration is \( 2\times\text{CMC} \). Since water has a higher surface tension, drop size produced by the orifice was larger than that for the surfactant solution. 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. 3 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 shows higher spread and weaker recoil than Triton X-100 which takes longer to disperse and adsorb at the newly formed interface.
3.2(a) Effect of Surfactant Concentration

Figure 9 shows the comparison of droplet impact evolution of two SDS solutions at different concentrations (2×CMC and 0.5×CMC). It is seen from the figure that the higher concentration drop has a higher spread and its surface oscillations die out faster. No rebound is seen in either case. As the surfactant concentration is increased, the
equilibrium surface tension goes on decreasing until it reaches CMC after which it remains constant. As a new interface is formed, surfactant from the bulk is transported to it which reduces the surface tension and the bulk is depleted of it. This diffusion depends on the concentration gradient. With a higher surfactant concentration, the gradient due to the formation of the new interface is higher which results in faster diffusion of the surfactant to the new interface reducing the surface tension more rapidly than at a lower concentration. For concentrations above the CMC, the micelles start dissolving and replenish. As such the effect of surfactant adsorption is quicker and stronger at 2 CMC compared to that at 0.5 CMC.
### 3.2(b) Effect of Molecular Weight of Surfactants

Figure 10 below shows the comparison of droplet impact evolution of two surfactant solutions, SDS and Triton X-100 on a Teflon surface at about 0.68 m/s and at such different concentrations so as to give the same equilibrium surface tension value of 42.5
mN/m. This was done to highlight the effect of surfactant molecule diffusion rates and how it affects the droplet impact dynamics. SDS molecules are lighter than Triton. This leads to a much faster diffusion rate as can be seen from the surface tension variation curve (Fig 11). The SDS solution reaches its equilibrium surface tension at roughly 45 ms whereas Triton takes around 60ms to reach its equilibrium value. Even though both the solutions reduce the surface tension to the same value, the lighter SDS molecules are able to diffuse to the interface much faster than the heavy Triton molecule and thereby give rise to a faster rate of reduction in surface tension which can be clearly seen from the experimental as well as the CFD results. The SDS drop spreads more on the substrate, has a considerably lesser amount of recoil and also experiences weaker oscillations. These features have also been successfully captured by the CFD model. The results clearly indicate that molecular weight has a significant influence on the dynamics of droplet impact. It also tells us that not only the final equilibrium surface tension value but also the rate of reduction to that final value plays an important role in determining the outcome of droplet impact.
Fig 10 Effect of Molecular Weight of Surfactants

[SDS and Triton X-100 on Teflon @ We~28]

[At an equilibrium surface tension value of 42.5 mN/m]
Fig 11 Surface Tension variation with time of SDS and Triton X-100 on Teflon @

We ~28 at an equilibrium surface tension value of 42.5 mN/m
3.3 Heat Transfer

The heat transfer mechanisms in the droplet impact was investigated through CFD simulations. Heat flux values computed by Fluent were validated and the dependence of these values on the grid density was also conducted. Apart from instantaneous temperature distribution, bulk temperature of the fluid and the overall heat transfer coefficient were computed from the numerical results. The results of these simulations are presented in the following section.

Cooling of Water Droplets Impinging on Hydrophobic and Hydrophilic Surfaces:
The present study investigates the heat transfer characteristics of a hot water droplet (at 353K) impinging a cold surface (300K) in ambient air. Studies were conducted on two surfaces, glass (hydrophilic) and Teflon (hydrophobic). The droplets impacted the substrates at two velocities or Weber numbers (20 and 80). Experimental results available for isothermal droplet impact. As such, CFD simulations provide a way to predict and understand the heat transfer process. The transient variations of temperature distribution help in evaluating the different processes by which the hot droplet cools as it impacts and deforms on the cold substrate and gives a very good insight into the heat transfer phenomenon.

Fig 12 shows a hot water drop at 353K impinging on a cold glass substrate (300K) in ambient air at a Weber number of 20. From the temperature contours it is seen that the droplet cools to about 335-340K near the glass surface but it is much hotter near the water-air interface (around 345K). Since glass is a hydrophilic surface, the drop does not recoil as sharply as on teflon and as a result there is very little internal mixing of the fluid. This results in the “hot spots” seen near the water-air interface. We also see that only the air around the immediate vicinity of the water drop gets heated up and the air further away or near the edges of the computational domain is not affected at all.
**Fig 12 Water on Glass @ We~20**
Fig 13 Water on Glass @ We~77
Fig 13 shows a hot water drop at 353K impinging on a cold glass substrate (300K) in ambient air at a Weber number of 77. From the temperature contours it is seen that the droplet cools to about 325-335K which is considerably lesser than the drop impacting at We~20. This can be attributed to the fact that the drop spreads more on the glass substrate it is in contact with the cold surface for a longer time than at We~20. As the predominant mode of heat transfer is through the solid glass surface, the drop gets cooled to a greater extent in this case.

Fig 14 below shows a hot water drop at 353K impinging on a cold teflon substrate (300K) in ambient air at a Weber number of 20. From 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. From the dynamics of the droplet impact it is seen that there is sharp recoil and even the break-up of the drop into a secondary drop which eventually coalesces into the original drop. This gives rise to considerable mixing of the fluid in the droplet. From the temperature contours it is also clear that due to the mixing the temperature throughout the droplet is more uniform than the glass case at the same Weber number. But the drop in this case has not cooled as much as that on glass even after thrice the time duration due to the time and area of contact with the colder substrate. The water drop spends more time in contact with the glass surface than the case with teflon which is a hydrophobic surface. The sharp recoiling behaviour of the droplet on teflon also leads to a much less contact area with the colder substrate. It can be inferred that the droplet cools by 3 processes-

- Heating the air around it
- By convective currents inside the droplet due to fluid mixing brought about by the spreading and recoil
- Due to its contact with the cold surface
Expt | CFD
--- | ---
(Temperature Contours)

0ms | 0ms
2ms | 2ms
5.5ms | 5ms
10ms | 13ms
17ms | 20ms
23ms | 26ms
28ms | 31ms
Equib. | 148ms

Fig 14 Water on Teflon @ We~20
From this study it is clear that the wetting characteristics of the substrate play a predominant role in the heat transfer characteristics of the droplet impacting it.

Heat Transfer of Surfactant-Solution Drops:

The aim of this study was to get a comparative picture on pure-liquid and surfactant solutions in terms of heat-transfer characteristics. To achieve this, simulations were conducted on a Teflon substrate for the following cases:

- A water droplet impinging the surface at \( \text{We} \sim 28 \).
- Surfactant drops of SDS at 2CMC and half CMC impinging at \( \text{We} \sim 28 \). This gives a comparison of the effect of surfactant concentration on heat transfer.
- Surfactant drop of Triton X-100 at 2CMC impinging the substrate at \( \text{We} \sim 28 \). This gives a comparison of the effect of different surfactants with contrasting molecular weights and how it affects the heat transfer characteristics.

The comparisons were made based not only on the inspection of temperature contours, but also on relevant parameters like the time-variation of average bulk fluid temperature and transient heat transfer coefficient of the droplets.
Temperature Contours

Fig 15  Water on Teflon @ We~28
Temperature Contours

Fig 16 SDS 2CMC on Teflon @ We~28
Temperature Contours

Fig 17 Triton X-100 2CMC on Teflon @ We~28
Temperature Contours

Fig 18 SDS HalfCMC on Teflon @ We~28
Fig 19 SDS at equib. Surf. Tension value of 42.5 mN/m on Teflon @ We~28
Temperature Contours

Fig 20 Triton X-100 at equib. Surf. Tension value of 42.5 mN/m on Teflon @ We~28
Figs 15-20 show the temperature contours of various droplets at 300K impinging a hot Teflon substrate at 353K. The droplets have roughly the same impact velocity. The figures clearly indicate that the domain far away from the plate and the drop towards the edge of the computational domain is not affected by the presence of the hot surface as sufficient time has not elapsed for the heat from the plate to reach these areas. One more point to be noted is that during the advancing phase i.e 0-5 ms for water and approximately 0-3ms for surfactant solutions there is very little heat transfer taking place. Also the average temperature gradient across the water-air interface can be neglected when compared to the heat-transfer taking place through the solid substrate as shown in the previous section on droplet cooling. It is also seen from comparing figs 15 and 16 that the surfactant drop heats up to a significantly higher temperature than the water drop. This can be attributed to the reduction in surface tension brought about by SDS molecules which has greatly increased the wettability of the Teflon surface. The droplet in this case spreads more on the surface thereby increasing the contact area with Teflon and thereby the enhanced heat transfer. Comparing figs 16 and 17 it is evident that the SDS molecules, on account of being lighter than the triton x-100 molecules and therefore having the ability to decrease the surface tension of the interface at a faster rate, are responsible for greater heat transfer to the drop on account of greater wettability. The triton molecules even though increase the wettability of the surface when compared to pure-water; the rate of reduction in surface tension is not as high as SDS. This results in a greater degree of recoil in the triton laden water drop which reduces the contact area of the drop with the hot substrate. Even though there is more mixing of the fluid inside the drop leading to a more uniform temperature, the SDS molecules indirectly enhance the heat transfer in the drop by affecting the wettability to a greater extent. Comparing figs 16 and 18, we can see that the rate of heat transfer in the drop with SDS at 2CMC concentration is higher. This is again directly attributed to the degree of
wettability that these 2 concentrations affect. As discussed earlier in the section on
droplet dynamics the drop with lower concentration leads to greater recoil and lesser
contact area and thereby a lesser degree of heat transfer. Comparing figs 19 and 20 it is
clear that even though the equilibrium surface tension value is the same in both the
cases, the lighter SDS molecules on account of their faster diffusion rates lead to a
greater surface tension reduction rate and they not only affects the dynamics of the
droplet impact but also the heat transfer rates. From the temperature contours of figs 19
and 20 it is clear that the SDS drop heats up more than the triton drop due to more
spread on the substrate and also lesser oscillations observed in that case.

Even though the temperature contours provide useful information on the process,
better and more comprehensive inferences can be drawn by a quantitative analysis of
the heat transfer mechanism by computing the bulk fluid temperature of the drop at
various times and also the overall heat transfer coefficient. The method to compute
these variables have been discussed earlier. Comparative plots of these variables are
shown below.
Fig 21 T(bulk) v/s time (Effect of surfactants)

[Water on Teflon, SDS & Triton @ 2 CMC on Teflon @ We ~28]
Figs 21 and 22 show plots of bulk fluid temperatures and overall heat transfer coefficient (U) varying with time for 3 cases: water, SDS and Triton X-100 at 2CMC on Teflon. The value of U is very high initially as the cold drop comes in contact with the hot substrate. The value of U for all the cases hover around 10000 W/m². The somewhat cyclic variation of U in the case of surfactant drops can be explained by the change in the surface area of the substrate caused by oscillations of the drop as it spreads and recoils cyclically on the surface. We therefore see higher amplitudes of variation in Triton, which experiences higher recoil and stronger oscillations than SDS. In case of pure water on Teflon, the value of U keeps decreasing owing to the fact that the surface area of the
drop on the surface keeps decreasing and stays constant to a certain extent as the drop recoils into an elongated column before a secondary droplet breaks off. There is a significant spike in the pure water curve between 30 and 40ms. This can be attributed to the instant where the secondary drop coalesces with the original drop giving rise to the peak. Studying the variation of T<sub>bulk</sub> we see that the SDS case gives rise to the steepest curve. The drop in this case heats up to approximately 320-323K at the end of 50ms as seen from the curve. The triton drop heats up to 314K and the water drop to around 309K at the same instant. It is clear that the greater wettability caused by SDS results in much better heat transfer, around 12-13K. The difference between SDS and Triton drop is around 5-7K and between water and triton is again about 5-6K. This proves that surfactants not only increase wettability by reducing surface tension but also enhance the heat transfer characteristics of the drop. As mentioned earlier SDS not only increases wettability but also heat transfer in the drop better than triton. The spike in the bulk fluid temperature between 30 and 40ms is again attributed to the secondary drop joining back into the original drop.

Figs 23 and 24 below show plots of bulk fluid temperatures and overall heat transfer coefficient (U) varying with time for 2 cases: SDS @ 2CMC and half CMC on Teflon to highlight the effect of surfactant concentration on heat transfer. In fig 25 we can see that the drop with half CMC has higher amplitudes of variation than 2 CMC owing to greater reduction of surface tension by SDS present at higher concentrations which leads to greater wettability and weaker oscillations of the liquid drop. It can also be seen from the T<sub>bulk</sub> plot that the SDS half CMC drop heats up to around 317-318K which is just a couple of degrees cooler than SDS @ 2 CMC. This shows that even though surfactant concentration has noticeable effect on wettability, the effect on heat transfer is not that pronounced. This proves that the molecular weight or the ability of the surfactant
molecules to diffuse to the interface has a bigger influence on heat transfer than the concentration of the surfactant molecules in the liquid.

*Fig 23 T_{bulk} variation with time (Effect of surfactant concentration)*

*[SDS on Teflon @ We ~28 at 2CMC and half CMC]*
Fig 24 Variation of “U” with time (Effect of surfactant concentration)

[SDS on Teflon @ We ~28 at 2CMC and half CMC]

Figs 25 and 26 show plots of bulk fluid temperatures and overall heat transfer coefficient (U) varying with time for 2 cases: SDS and Triton each solution varying in concentration but producing the same equilibrium surface tension value of 42.5 mN/m. From the bulk variation we see that the SDS drop heats up to around 317K where as Triton heats up to 313K. This is attributed to better spread and weaker oscillations of SDS drop due to faster diffusion rate which leads to more contact area with the hot substrate. From the heat transfer coefficient curve it is evident that the Triton drop experience stronger oscillations than the SDS drop. From these results it is clear that the molecular
weight of the surfactants not only affects the dynamics of droplet impact but they have a considerable effect on the heat transfer process as well and that faster diffusion rates lead to better heat transfer rate.

*Fig 25 T\text{bulk} variation with time (Effect of Mol. Wt of Surfactants)*

*SDS and Triton X-100 on Teflon @ We ~28 at an equilibrium surface tension value of 42.5 mN/m*
Fig 26 Variation of “U” with time (Effect of Mol. Wt of Surfactants)

SDS and Triton X-100 on Teflon @ We ~28 at an equilibrium surface tension value of 42.5 mN/m
Chapter 4
Conclusions and Scope for Future Work

4.1 Conclusions

Computational investigation of droplet impact dynamics was carried out for water and aqueous surfactant solution drops impinging on a hydrophobic (Teflon) and hydrophilic surface (glass). The numerical model employed the volume of fluid (VOF) method to track the transient deformations of the liquid air interface. The dynamic surface tension variation and different values for the advancing and receding contact angles were used in the simulations. The computational solutions were compared to experimental results from Gatne (2006). The computational model was able to predict the impact, spreading, recoil, and column breakup behavior that was in very good agreement with high speed visualization reported in Gatne (2006). Heat transfer characteristics associated with the droplet impact phenomenon were investigated computationally for both droplet cooling and droplet heating scenarios and the results provide useful insight into the phenomenon in the absence of extensive experimental results for heat transfer in the literature.

The computational simulations showed that the hydrophilic or hydrophobic nature of the surface has significant influence on the drop spread and recoil behavior. Water drop impact on a hydrophilic surface (glass) resulted in weak oscillations and large spread. Increase in impact velocity results in higher spread. 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 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. Reduction in surfactant concentration results in lesser spreading of the impacting drop and gives rise to stronger oscillations. The faster diffusion rates of SDS solutions to the interface lead to a greater surface tension reduction rate and therefore result in higher spread and weaker oscillations than Triton solutions even though the concentrations were chosen such that they produced the same equilibrium surface tension. It was also shown that not only the final equilibrium surface tension value but also the rate of reduction to that final value plays an important role in determining the outcome of droplet impact.

Heat transfer in the droplet impact phenomenon was investigated by the computational model. From the results it can be concluded that heat transfer through the solid substrate is the predominant mode of heat transfer. Therefore the wettability of the surface or in other words the contact area of the drop with the surface dictates the amount of heat transfer to or from the droplet. Therefore surfactants which increase the wettability also enhance the heat transfer or in other words SDS showed better heat transfer characteristics than triton or pure liquid. Also higher concentrations of surfactants which are able to reduce the surface tension and increase spread also result in higher heat transfer rates. Therefore SDS at half CMC did not result in as much heat transfer as SDS at 2CMC concentration. It is also observed that the lighter molecules of SDS give rise to better heat transfer rate than the heavier Triton molecules on account of faster diffusion rates. This study shows that addition of surfactants to water provide an effective method to modify and control the droplet impact dynamics and droplet-surface heat transport.
4.2 Scope for future work

The present study shows that the computational model developed here can predict droplet impact phenomena and concomitant heat transfer well. The model can be extended to simulation of aqueous solutions with a variety of additives (surfactants and polymers), further investigate the effect of surface wettability, and incorporate phase change heat transfer in the computational model.

The present study is limited to two surfactants. The study can be extended to other surfactants and polymers additives used in many industrial applications to get their dynamic and heat transfer behaviour. With many polymeric additives, the solution may exhibit non-Newtonian viscous behavior. This is expected to significantly alter the drop impact phenomena predicted with water drops.

The computational model can also be used on different substrates; the study of cooling of droplets on silicon surfaces has significant practical applications in the electronic cooling field.

The present model includes a dynamic surface tension value which is derived from experiments and interpolated to the time-scales used here. A more realistic variation can be incorporated if the diffusion of surfactant molecules can be modeled and a surface tension coefficient which depends on the dynamic concentration of the surfactant along the interface is used. Also only 2 contact angle values are used in this study. A dynamic contact angle which is computed by the code as part of the solution as a factor of the triple-contact-line velocity will improve the results significantly.

The present heat transfer model does not include phase change process. Future investigations including phase change in their model will serve to be a very useful improvement especially for spray quenching applications.

Furthermore, extending the model to include 3-D effects would prove to be very useful to investigate drop impact at high Weber numbers. A computational model of this
problem that includes the modifications listed above will prove to be a comprehensive tool in understanding the dynamics and heat transfer characteristics of the droplet impact phenomenon.
Bibliography


67


Appendix

Example of a User Defined Function used in Fluent to simulate the dynamic surface tension variation in surfactants

#include "udf.h"

DEFINE_PROPERTY (dyn_surf_tension, cell, thread)
{
real dst;
real t=CURRENT_TIME;
dst=141121*pow(t,5) - 38978*pow(t,4) + 3817.5*pow(t,3) - 148.84*pow(t,2) + 1.3033*pow(t,1) + 0.071;
return dst;
}

Where

dst = Dynamic Surface tension Coefficient mN/m

t = Flow time in sec