

Dynamics of two immiscible and miscible fluids in two-component flows

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by

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CERTIFICATE

It is certified that the work contained in the thesis entitled **“Dynamics of two immiscible and miscible fluids in two-component flows”**, by Manash Pratim Borthakur (ID no. 146103023) has been carried out under our supervision and that this work has not been submitted elsewhere for a degree.

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Dedicated to my parents



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Abstract

Flows with two fluid components represent an important class of problems in fluid dynamics. The fluids may be mutually immiscible or miscible. The current investigations are aimed at the analyses of fluid flow configurations consisting of two immiscible and miscible fluids by performing extensive numerical simulations. The studies pertaining to the immiscible fluids configuration are considered in the first part of the thesis. In the second part of the thesis, the two-component miscible fluid flow configuration is considered.

The dynamics of formation, growth and breakup of liquid drops and jets emanating from orifices are investigated by performing direct numerical simulations. In the dripping regime, the viscosity of the drop liquid is fundamentally related to the phenomenon of interface overturning. A critical value of Ohnesorge number is identified beyond which overturning ceases. Two different modes of transition from dripping to jetting regime are observed, which can be clearly explained in terms of the relative importance of inertia and viscous effects on the dynamics of the processes. The ambient medium is entrained as the jet moves downstream with the creation of a vortical structure outside the jet signifying increased participation of the ambient medium in the dynamics of jet break-up at higher inflow rates.

The formation and breakup of a liquid jet in air with gravity acting normal to the direction of the liquid injection has been studied employing three-dimensional numerical simulations. It is observed that asymmetric perturbations develop on the liquid surface when liquid is injected perpendicular to gravity, thereby deviating from the assumption of varicose deformation in the Rayleigh mode. At higher values of Weber number, the liquid jet traverses a longer horizontal distance when released from the same vertical height. The liquid jet follows a parabolic path due to the influence of gravity, which curves the jet trajectory. The detached drops undergo rolling motion as well as shape oscillations while they migrate along their trajectories.

The influence of an external electric field on the dynamics of drop formation from submerged orifices is analyzed by solving axisymmetric electro-hydrodynamic numerical simulations. The simulations reveal that under the influence of an electric field, prolate shaped drops are formed at the orifice in the case of perfect dielectric fluids. In contrast, for leaky dielectric fluids, both prolate and oblate shaped drops can be formed depending on the combination of the fluid conductivity and permittivity ratios. The breakup time and detached drop volume can be suitably tuned by varying the strength of the applied electric field. The flow pattern inside the drop

is decided by the combination of the electrical conductivity and permittivity ratios under the influence of the applied electric field.

In addition to the aforementioned studies on drop and jet formation, the spatio-temporal deformation and pinch-off of compound droplets migrating inside a capillary tube have been investigated in detail. The simulations reveal that the deformation of the inner and outer interfaces of the compound droplet are opposite in nature; the outer drop deforms to a prolate shape whereas the inner drop attains an oblate shape at steady state. The inner drop migrates away from the initial concentric configuration and finally settles at a constant eccentricity. Furthermore, following the asymmetric deformation of the interfaces, the migrating compound droplet can undergo an uncommon breakup stimulated by the thinning of the outer shell leading to pinch-off. Interestingly, the kinetics of the thinning of outer shell is found to follow two distinct power-law regimes - a swiftly thinning stage at the onset followed by a rate-limiting stage before pinch-off.

In the second part of the thesis, the two-component miscible fluids configuration has been considered. The influence of an applied electric field on the separation of water-ethanol solution inside a carbon nanotube (CNT) is explored using a series of molecular dynamics simulations. The electric field is applied at an angle θ with respect to the axis of the CNT. The study depicts that the direction of the electric field exerts a contrasting influence on the behavior of the water and ethanol molecules. The water dipoles are favourably aligned at small values of θ creating an ordered water structure inside the CNT. Increasing θ disrupts the water dipole orientation and leads to preferential occupancy of the CNT by ethanol molecules. This can be attributed to the promotion (reduction) of intermolecular hydrogen bonding capacity of the ethanol (water) molecules at larger values of θ . The separation efficiency is found to improve with the increase in intensity of the externally applied electric field.

The findings from the present thesis shed light on the complex dynamics of formation, evolution and breakup of liquid drops and jets under a variety of practically relevant flow configurations. The critical conditions for interface overturning are obtained in the drop formation process. The crucial influence of gravity on the jet dynamics is revealed for liquid injected perpendicular to the direction of gravity. It is also demonstrated that electric fields can be effectively used to control the characteristics of drops forming at an orifice. The study on compound drops helps in predicting the temporal rate of deformation and the estimation of rupture time. Furthermore, a novel methodology is proposed for analyzing the separation of water-ethanol solutions inside CNTs by the application of external electric fields.

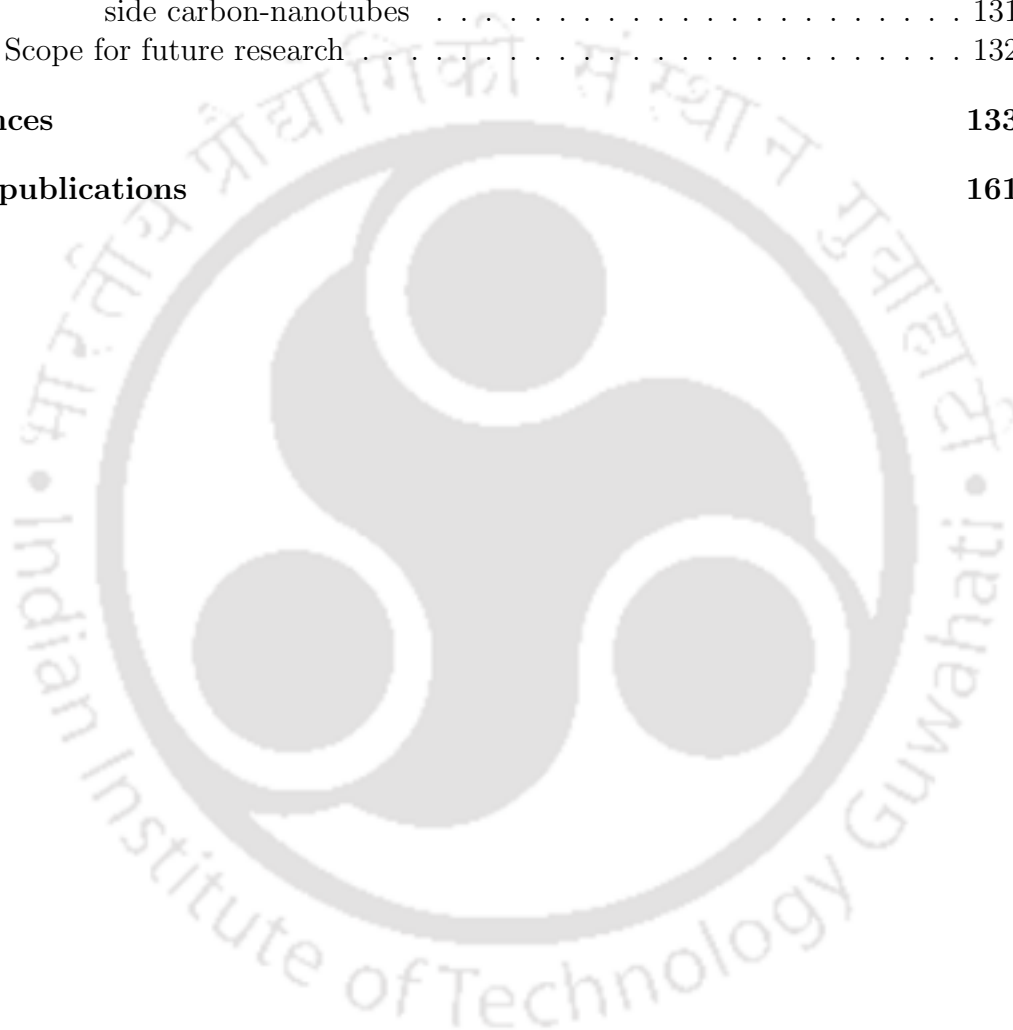
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Chapter 1

Introduction

The interaction of multiple fluid components is ubiquitous in a wide range of flow problems. Examples include water dropped in oil, milk poured in coffee, ink diffused in water, and so on. The fluid components may be mutually immiscible or miscible. The term miscible refers to the property of various substances, that allows them to be mixed together and form a single homogeneous phase. For example, water and ethanol are miscible in all proportions. In contrast, substances are said to be immiscible if they cannot be mixed together, for example, oil and water. The immiscible fluids in a multi-fluid system are characterized by sharp interfaces, which separate the fluid components. Due to the inherent complexities associated with the interactions between the multiple fluid components, numerical simulations of multi-fluid flow systems remain an attractive as well as challenging area of research.

One of the most commonly encountered classes of multi-fluid flow systems is the two-component flow wherein the number of fluid components (immiscible or miscible) present is two. In the case of immiscible fluids, the two fluid components are separated by a sharp interface. The interface between the fluids is held together by the surface tension force and such flows are often termed as interfacial flows. In contrast to the immiscible fluids, the two-component miscible fluid flow configuration is characterized by the absence of a separating interface thereby leading to a homogeneous mixture. Due to the absence of fluid-fluid interfaces, capillary forces are absent in miscible fluid systems.

The present dissertation is aimed at the analysis of fluid flow configurations consisting of two immiscible and miscible fluids by performing extensive numerical simulations. The studies pertaining to the immiscible fluid configuration are consid-

ered in the first part of the thesis. The dynamics corresponding to the formation, growth and breakup of liquid drops and jets emanating from an orifice under a variety of flow conditions are explored herein. Furthermore, the thesis investigates the hydrodynamic behavior of compound droplets or double emulsions migrating inside capillary tubes. In the second part of the thesis, the two-component miscible fluid flow configuration is considered. The present dissertation examines the dynamics of equimolar water-ethanol solutions in nano-confinement under the influence of an applied electric field. A novel electric field induced methodology is proposed for analyzing the separation of water and ethanol inside carbon nanotubes integrated to nanoporous graphene membranes.

1.1 Motivation and objectives

The motivation to study different immiscible and miscible two-component fluid flow systems is firstly to understand the rich underlying physics associated with such flows and secondly to numerically model the systems in detail. Each attribute is discussed in the following sections.

1.1.1 Formation and breakup of drops and jets

The formation and breakup of liquid drops and jets is a generic phenomenon, concomitant to almost any free-surface flows. They are encountered in a large variety of situations, spanning a broad range of physical length scales and having myriad applications in daily life and industry. A host of industrial processes employ the formation of drops or jets at a nozzle or an orifice, as observed in inkjet printing [1], spray coating [2], spray drying [3], separation and extraction processes [4], among others. The recurrent questions pertaining to drops and jets that are encountered commonly in the aforesaid applications are related to the breakup length and time. The sensitivity of the jet breakup to the inflow rate, or to the presence of a dense outer medium is a topic of deeper understanding. A few other heretofore unanswered questions are as follows. How does viscosity affect the pinch-off of the droplets? How can the dynamics be tuned by application of external fields?

A liquid injected through an orifice will eventually break into drops through one of the two mechanisms. At low inflow conditions, the emanating liquid drips from the orifice, whereas at higher inflows, the liquid forms a thin column that breaks into

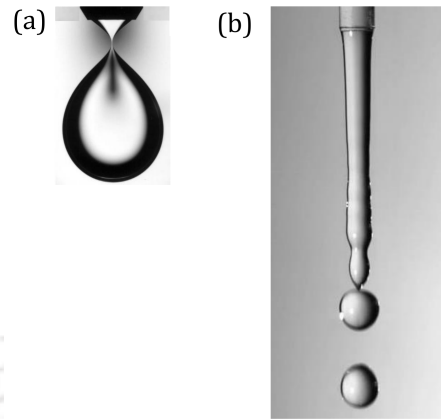


Figure 1.1: Photographic snapshots showing the formation of drops at a nozzle in the (a) dripping regime [5] and (b) jetting regime [6].

drops away from the orifice; these are classified as the dripping and jetting regimes, respectively. Figure 1.1 (a) and (b) illustrates the dripping and jetting regimes of drop formation, respectively [5,6]. The drop formation has rich dynamics that are affected by a host of parameters, such as the average liquid injection rate, density and viscosity of both fluids, magnitude of surface tension, device geometry and surface chemistry [2, 7, 8]. A number of theoretical, computational and experimental studies have been carried out in literature to shed light on the critical interplay of the operating parameters on the dynamics in the dripping and jetting regime [9–27]. A detailed description of the fascinating aspects pertaining to liquid drops and jets can be found in the comprehensive review of Eggers and Villermaux [2].

In spite of the wealth of information available about the dynamics of liquid drops and jets, a clear picture about the influence of many operating parameters on the formation and breakup processes is still lacking in literature. For instance, the interfacial morphology can be radically altered by the manipulation of the drop viscosity. When the viscosity of the drop fluid is sufficiently less, the interface folds on itself with an internal angle greater than 90° , thereby making the interface a multivalued shape function, and this phenomenon is called overturning. Wilkes *et al.* [28] investigated the overturning phenomenon in an attempt to uncover the hydrodynamics associated with such flow conditions. However, the critical conditions, by means of which, the interface overturning can be ensured or arrested, are not fully clear. Additionally, the effect of gravity on the dynamics of liquid jets injected perpendicular to gravity is a relatively unexplored subject. The jet trajectory and breakup

characteristics are fundamentally disparate between a liquid jet injected parallel and perpendicular to gravity [29] and require more investigations. Furthermore, the external electric fields have shown promising potential for manipulating the formation and breakup of drops [30–32]. The assistance of electric field in controlling the drop volume and breakup time has found use in diverse technologies, such as electropainting [33], electro-hydrodynamic ink-jet printing [34] and atomization processes [35], to name a few. Nonetheless, a complete understanding of the electro-hydrodynamic coupling and its associated impact on the dynamics of drop formation and breakup is heretofore unknown in open literature. The present thesis aims to analyze some of these long standing questions and attempts to shed light on a number of fascinating features pertaining to the dynamics of drop and jet formation employing different flow configurations.

1.1.2 Compound droplets inside micro-channels

The term ‘compound droplets’ refers to two (or more) immiscible fluid drops that share an interface with one another, surrounded by a third, mutually immiscible fluid. Figure 1.2 (a) and (b) illustrate different configurations of compound droplets obtained by the interaction of multiple immiscible fluids inside microchannels. With the recent advancement in microfluidic technologies, compound droplets have shown tremendous potential for encapsulation and release of active materials in diverse applications, such as, targeted drug delivery [36, 37], advanced materials processing [38, 39], phase separation [40, 41] and handling of hazardous materials [42]. In some microfluidic technologies, the breakup of the compound droplet is desirable for controlled release whereas in other applications, it is necessary to prevent the droplet from rupturing in order to allow further processing steps. It is thus of utmost importance to understand the hydrodynamic behaviour of compound droplets inside microchannels in order to accurately predict and manipulate the deformation and subsequent breakup of the droplets.

The growing interest in the generation and manipulation of compound droplets has lead to extensive studies on novel methods for fabrication [43, 44], enhanced deformation through external actuation [45] and controlled breakup inside microchannels [46, 47]. However, the transient characteristics of compound drops migrating inside microchannels are relatively less explored. Song *et al.* [48] developed an analytical solution for the motion of a compound drop in a long circular tube, based

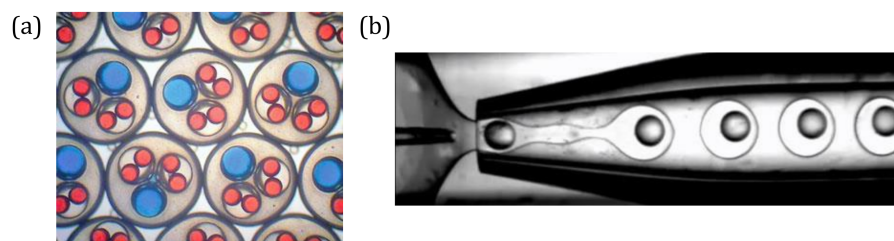


Figure 1.2: (a) Photographic snapshot showing a complex sextuple-component triple emulsion [43]. The different colours represent different components. The red colour represents oil and blue represents water. The bigger encapsulating drop consists of another immiscible oil. (b) Snapshot showing the formation of a double emulsion droplet inside a microchannel [51].

on the low Reynolds number Stokes flow theory. Mandal *et al.* [49] demonstrated the impact of surfactant on the motion and deformation of compound droplets in unbounded Stokes flows. Recently, the complex flow structure and shape of the compound drop inside microchannels was studied by Che *et al* [50]. Nevertheless, the detailed hydrodynamic effects on the transient deformation and breakup of the compound drops translating inside a capillary tube are yet to be investigated comprehensively. The present thesis explores the various hydrodynamic attributes and provides insight into the mechanism of temporal deformation and breakup of compound droplets in microfluidic flows.

1.1.3 Separation methodologies of water-ethanol solution

Ethanol, also known as ethyl alcohol, is a chemical compound having complete miscibility with water. The mixture of water and ethanol forms a two-component miscible configuration and is often encountered in a variety of industrial processes. Pure ethanol is a promising alternative for commercial biofuel technologies and serves to effectively reduce the dependence on fossil fuels thereby inhibiting the greenhouse effect [52, 53]. In addition, it can be added to gasoline as an oxygenate, which has been used as a fuel in several countries [54]. Furthermore, pure ethanol is an essential ingredient for the production of a host of medical and scientific products [55].

The conventional method of bio-ethanol production involves an inevitable step, i.e. ethanol dehydration. The separation of ethanol from water is commonly performed by heating processes, pervaporation or distillation, which consumes a large amount of energy and forms the bulk of the production cost. Consequently, a re-

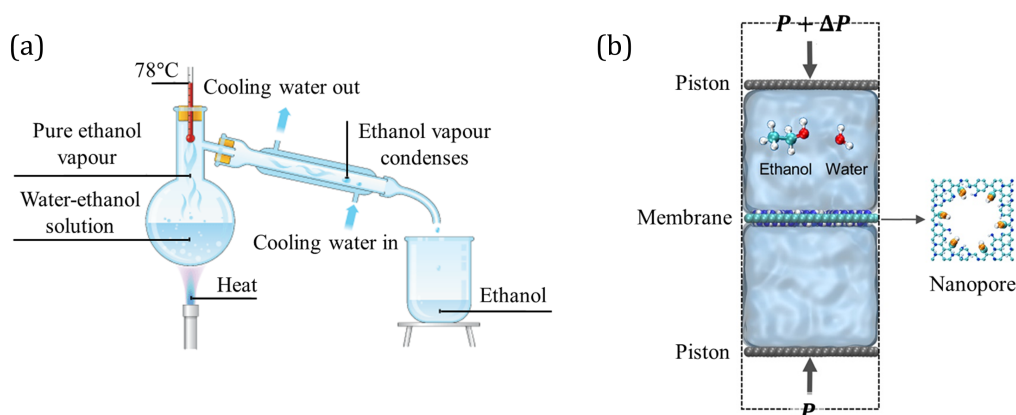


Figure 1.3: (a) Schematic of the distillation setup conventionally used for separation of water-ethanol solution and (b) nanoscale separation of water-ethanol solution employing graphene oxide membranes [56].

duction of the cost of ethanol dehydration is imperative for increased global usage of bio-ethanol. A broad range of solutions exist for the dehydration of ethanol, for instance, ordinary distillation, azeotropic distillation, extractive distillation, liquid-liquid extraction-fermentation hybrid, adsorption, and membrane separation technologies [57]. Figure 1.3 illustrates two diverse methodologies for production of pure ethanol from water-ethanol mixture. Presently, pervaporation, which consists of partial vaporization of the liquid through a membrane, is considered as one of the most effective and energy-saving processes for the separation of ethanol and water [58]. However, the method of pervaporation requires heating of the water-ethanol solution and thereby suffers from the disadvantage of a high energy penalty.

On the other hand, membrane-based separation methods, such as ultra-filtration and reverse osmosis (RO), have attained considerable importance in the recent years owing to superior treatment at modest cost, high stability and efficiency, and low energy requirement [59, 60]. The membrane separation is thus seen as a viable and effective technology at both laboratory and industrial scales. However, the applicability of the membrane separation is not obvious when it comes to two species that are neutral and have very similar size, such as ethanol and water. Hou *et al.* [61] presented direct computational evidence that nanoporous graphene can serve as a potential sieving membrane for the separation of water-ethanol solutions, with ethanol permeability several orders of magnitude higher than current pervaporation membranes. Subsequently, Shi *et al.* [62] and Gravelle *et al.* [57] demonstrated the separation of water and ethanol employing functionalized nanoporous graphene

membranes and carbon nanotubes, respectively. Interestingly, recent studies have revealed that the properties of fluids can be radically altered by applying external electric fields under nano-confinement. A recent study by Takaiwa *et al.* [63] explored the influence of electric field on water-methanol mixtures. In the present thesis, the effect of electric field orientation on water-ethanol solutions are investigated. A novel electric field induced methodology for separation of the water and ethanol inside a carbon nanotube is proposed in the present study.

1.1.4 Objectives

The objectives of the present work have been formulated in an attempt to understand and address some of the issues enumerated earlier.

1. To study the dynamics of formation, growth and breakup of liquid drops and jets emanating from orifices.
2. To investigate the evolution and disintegration of a liquid jet arched by gravity.
3. To understand the influence of electric field on the drop formation from submerged orifices.
4. To study the spatiotemporal deformation and pinch-off of compound drops migrating inside a capillary tube.
5. To propose a novel methodology for separation of water-ethanol solution in carbon nanotubes with graphene membranes using electric field.

1.2 Layout of the thesis

The present chapter provides a glimpse of the salient features pertaining to immiscible and miscible two-fluid flow systems and discusses the objectives of the current work. The detailed numerical methodology adopted for simulating interfacial flow problems is described in the second chapter. The third chapter provides a brief overview of the methodology adopted for molecular dynamics simulations. The fourth chapter presents an extensive study on the dynamics of liquid drops and jets emanating from an orifice. In the fifth chapter, the formation and breakup of a liquid jet curved by the gravity is explored in detail. The sixth chapter elucidates the influence of an external electric field on the dynamics of drop formation

from a submerged orifice. The investigation of the hydrodynamics of a migrating compound droplet inside a capillary tube is reported in the seventh chapter. In the eighth chapter, a novel methodology for separation of water-ethanol solutions by the application of external electric field inside a carbon nanotube is proposed. Finally, the contributions from the present research are summarized and potential areas for future exploration are proposed in the ninth chapter.



Chapter 2

Numerical modelling of interfacial flows

2.1 Introduction

The numerical simulation of interfacial flow systems remain a highly challenging problem owing to the complex topological changes as well as sharp discontinuities across the fluid interfaces. Numerous methods have developed over the years to handle the inherent transient nature of interfacial flow systems. The numerical approaches can be broadly classified into two groups, viz., Eulerian and Lagrangian methods. In the Eulerian approach, the mesh remains stationary with the flow moving through it. The location of the interface is identified using a scalar function. On the other hand, the Lagrangian approach treats the interface as a sharp boundary and employs markers to follow the evolving interface. Furthermore, hybrid Lagrangian-Eulerian methods are available wherein the nodes of the mesh can be moved in Lagrangian fashion, or be held fixed in Eulerian manner.

In the present thesis, the Eulerian approach has been adopted for simulating a multitude of interfacial flow systems. An ‘inhouse’ developed coupled level-set and volume-of-fluid (CLSVOF) method is employed for simulating the dynamics of drops and jets emanating from an orifice in chapter 4. Subsequently, an open source solver *Gerris* and its successor *Basilisk*, which are based on the volume-of-fluid (VOF) methodology, have been adopted for simulating the various interfacial flow systems presented in chapters 5 to 7.

2.2 CLSVOF method

The volume-of-fluid (VOF) method of Hirt and Nichols [64] forms the building block of computations involving two fluids separated by a sharp interface. In this approach, the mesh is fixed spatially and the interface is approximated within each ‘two-fluid’ cell. The preliminary method deployed for this purpose is known as SLIC (Simple Line Interface calculation) where the interface was identified by piecewise-constant line segments in each cell containing the interface. Subsequently, the interface representation was significantly improved by the piecewise-linear interface calculation (PLIC) of Youngs [65] and the least square volume interface reconstruction (LVIRA) method of Puckett et al [66]. The VOF method satisfies the compliance of mass conservation extremely well. However, it is sometimes difficult to capture the geometric properties employing the VOF method due to spatial discontinuity near the interface. An efficient interface capturing method, known as the level-set method was introduced by Osher and Sethian [67]. The level set method allows accurate computation of the geometric properties of the interface. However, the violation of mass conservation may occur if the level set method is improperly implemented. The CLSVOF method blends the advantages of both the volume-of-fluid and the level set method. In the CLSVOF method of Sussman and Puckett [68], the level set function is used only to compute the geometric properties at the interface while the volume fraction is advected using the VOF approach. A few variants of the CLSVOF method are available in literature [69, 70]. The CLSVOF methodology adopted for the present thesis is described in detail in the following subsections.

2.2.1 Governing equations

The governing equations for mass and momentum conservation for the incompressible Newtonian two fluid system can be expressed by a single fluid continuum as follows:

$$\nabla \cdot \mathbf{v} = 0, \quad (2.1)$$

$$\rho \left[\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right] = -\nabla p + \nabla \cdot [\mu(\nabla \mathbf{v} + \nabla \mathbf{v}^T)] + \rho \mathbf{g} + \mathbf{f}_{sv}, \quad (2.2)$$

where $\mathbf{v} = (u, v)$ is the velocity field, t is the time, p is the pressure, $\mathbf{g}$ is the gravitational acceleration, ρ and μ are the density and viscosity, respectively, and $\mathbf{f}_{\text{sv}}$ is the surface tension force. The surface tension term $\mathbf{f}_{\text{sv}}$ is defined by the continuum surface model of Brackbill *et al.* [71] and is detailed in Section 2.2.6. The marker-and-cell algorithm (MAC) is employed to solve the single set of governing equations on a staggered grid arrangement of Harlow and Welch [72]. A uniform grid is used where the grid size in both the directions is considered to be the same, i.e. $\Delta x = \Delta y$. The scalar variables are defined at the cell centers and the vector quantities are located at the center of the cell faces.

2.2.2 Volume-of-fluid advection

The scalar function α , denoted as the volume fraction, is used to locate the fluid interface inside the domain. The value of α is assigned as,

$$\alpha = \begin{cases} 1 & \text{if it is a fluid 1 cell,} \\ 0 & \text{if it is a fluid 2 cell,} \\ 0 < \alpha < 1 & \text{if it is a cell containing both fluids,} \end{cases} \quad (2.3)$$

where fluid 1 and fluid 2 are the two immiscible fluids separated by a sharp interface.

The motion of the moving interface is computed by solving an advection equation for volume fraction α . As the fluid type remains constant along particle paths, the volume fraction α is advected by

$$\frac{\partial \alpha}{\partial t} + \mathbf{v} \cdot \nabla \alpha = 0. \quad (2.4)$$

Using the continuity equation (Eq. 2.1), it can be written as

$$\frac{\partial \alpha}{\partial t} + \nabla \cdot (\mathbf{v} \alpha) = 0. \quad (2.5)$$

By using finite difference scheme, Eq. 2.5 can be discretised as

$$\alpha_{i,j}^{n+1} = \alpha_{i,j}^n + \frac{\Delta t}{\Delta x} (\delta G_{i-1/2,j} - \delta G_{i+1/2,j}) + \frac{\Delta t}{\Delta y} (\delta G_{i,j-1/2} - \delta G_{i,j+1/2}), \quad (2.6)$$

where $\delta G_{i+1/2,j} = (u\alpha)_{i+1/2,j}$ is the amount of liquid volume fraction fluxed through the right cell face. The superscript n and $(n+1)$ denotes the values at the current

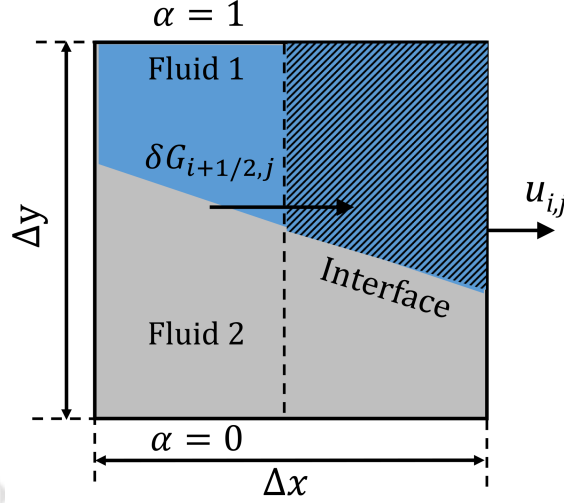


Figure 2.1: Schematic representation of a single cell containing the interface. The fluid to the right of the dotted line is advected into the neighboring cell on the right.

and next time step and $\Delta t, \Delta x$ and Δy are the time step and grid spacing in x and y direction, respectively. Eq. 2.6 is solved by applying operator split approach resulting in two equations:

$$\alpha_{i,j}^* = \alpha_{i,j}^n + \frac{\Delta t}{\Delta x} (\delta G_{i-1/2,j} - \delta G_{i+1/2,j}) + \frac{\Delta t}{\Delta x} \alpha_{i,j}^* (u_{i+1/2,j} - u_{i-1/2,j}), \quad (2.7)$$

$$\alpha_{i,j}^{n+1} = \alpha_{i,j}^* + \frac{\Delta t}{\Delta y} (\delta G_{i,j-1/2}^* - \delta G_{i,j+1/2}^*) + \frac{\Delta t}{\Delta y} \alpha_{i,j}^* (v_{i,j+1/2} - v_{i,j-1/2}). \quad (2.8)$$

The star (*) terms represent the intermediate values after sweep in first direction. To increase the accuracy, the modified equation $\partial \alpha / \partial t + \nabla \cdot (\mathbf{v} \alpha) = \alpha \nabla \cdot \mathbf{v}$ is solved instead of Eq. 2.5 by adding “divergence correction” terms on the right-hand side of Eqs. 2.7 and 2.8.

The volume flux δG can be obtained using a geometrical interpretation of flux as shown in Fig. 2.1. Considering the right face of a cell containing the interface, a portion $(u_{i+1/2,j} \Delta t h)$ can be calculated whose fluids will be fluxed into the neighboring cell, provided that $u_{i+1/2,j} \Delta t h$ is positive. Knowing the interface position and the velocity, the fluxed volume from this face to the neighboring cell can be

calculated as,

$$\delta G_{i+1/2,j} = \frac{u_{i+1/2,j} G_{i+1/2,j}}{u_{i+1/2,j} \Delta t \Delta y} = \frac{G_{i+1/2,j}}{\Delta t \Delta y}. \quad (2.9)$$

Equation. 2.7 can be solved after calculating δG from Eq. 2.9 and the interface is reconstructed based on $\alpha_{i,j}^*$. The vertical fluxes are then determined using a geometric calculation analogous to the horizontal fluxes and the updated volume fractions $\alpha_{i,j}^{n+1}$ are finally obtained from Eq. 2.8. To obtain second order accuracy, the sweep directions are swapped at each time step and the first sweep is differenced implicitly whereas the second sweep is differenced explicitly [73].

2.2.3 Level set advection

In the CLSVOF method, the level set function is used only to calculate the geometric properties of the interface. The level set function ϕ is maintained as the signed distance from the interface. Hence the level set function is defined as,

$$\phi(\mathbf{r}, t) = \begin{cases} +d & \text{in the fluid 1 region,} \\ 0 & \text{at the interface,} \\ -d & \text{in the fluid 2 region,} \end{cases} \quad (2.10)$$

where $d = d(t)$ is the shortest distance of the interface from point $\mathbf{r}$.

Using the initially known position of the interface, the interface is captured by solving the advection of the level set function as,

$$\frac{\partial \phi}{\partial t} + \mathbf{v} \cdot \nabla \phi = 0. \quad (2.11)$$

The convective term of Eq. 2.11 is discretized using the essentially non-oscillatory (ENO) scheme [74]. The level set function is reinitialized to the exact signed normal distance after each time step. The reinitialization of the level set function is done from the reconstructed interface by coupling level set function with the volume fraction.

2.2.4 CLSVOF algorithm

The CLSVOF method is an attempt to combine the advantage of both the level set and volume-of-fluid approaches. The algorithm for the interface advection in the CLSVOF method is described below.

1. The intermediate volume fraction $\alpha_{i,j}^*$ is calculated by solving the Eq. (2.7) in the first sweep direction (say x-direction).
2. After $\alpha_{i,j}^*$ is obtained, ϕ is advected in the same sweeping direction by solving the split form of Eq. (2.11). Hence, for the x-direction sweep, the equation is,

$$\frac{\partial \phi}{\partial t} + u \frac{\partial \phi}{\partial x} = 0. \quad (2.12)$$

The discretisation of the convective term in Eq. (2.12) is done by employing a second order ENO scheme [69, 74].

3. As the level set function is smooth, the interface normal can be easily calculated by using a central finite-differencing scheme for discretisation of,

$$\hat{\mathbf{n}} = \frac{\nabla \phi}{|\nabla \phi|}, \quad (2.13)$$

in every cell containing the interface [75]. The length l (perpendicular distance

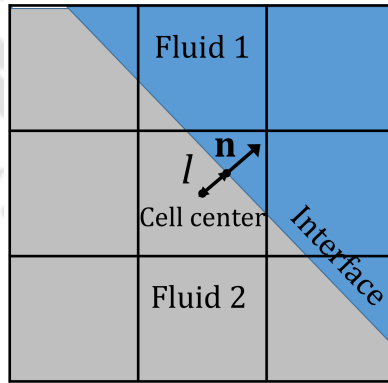


Figure 2.2: Interface normal n and length l

between cell centre and interface) as shown in Fig. 2.2, is adjusted to match the given volume fraction with that of the reconstructed interface to locate the interface.

4. The next sweep in the y-direction (Eq. 2.8) is performed leading to the final distribution of volume fraction field $\alpha_{i,j}^{n+1}$. Also, the intermediate level set function is advanced in the y direction by solving,

$$\frac{\partial \phi}{\partial t} + v \frac{\partial \phi}{\partial y} = 0. \quad (2.14)$$

The discretisation scheme is the same as outlined in step 2.

5. The interface is again reconstructed based on the newly obtained values of volume fraction and level set function as described in step 3.
6. With the advancement in time, ϕ loses the signed normal distance property. Therefore, the level set function is reinitialised after each time step based on the reconstructed interface by following the algorithm of Sussman *et al.* [68].

The solution methodology can be made second order accurate by alternating the sweep direction in each time step [73].

2.2.5 Interface reconstruction and smoothing

The advection of the volume fraction demands the interface position to be known at each time step. Hence, the interface has to be reconstructed at each time step from the calculated normal vector and the volume fraction. Geometrical approximation of the interface can be based on either piecewise constant segments, piecewise linear segments or some parabolic fit as in PROST [76].

In the CLSVOF approach, the interface is represented by the piecewise linear segments. In order to locate the interface, the interface normal $\hat{\mathbf{n}}_{i,j}$ and the offset distance $l_{i,j}$ are required to be known for each interfacial cell (i, j) . Due to the smoothness of level set function across the interface, the normal vector $\hat{\mathbf{n}}_{i,j}$ can be simply obtained by taking the gradient of the level set function as given by Eq. (2.13). Once the interface normal is calculated, the value of $l_{i,j}$ is obtained by means of a standard root-finding method (like secant method) such that the approximation of the interface reproduces the updated volume fraction $\alpha_{i,j}$ in each cell exactly.

Due to the sharp change of properties across the interface, normal finite difference schemes may lead to unwanted numerical diffusion. To alleviate these problems, the interface is given a fixed thickness that is proportional to the spatial mesh size. The

smoothness of the level set function allows in defining a smoothed volume fraction field using a Heaviside function $H(\phi)$ as,

$$\tilde{\alpha} = H(\phi) = \begin{cases} 0 & \text{if } \phi < -\epsilon, \\ \frac{1}{2} + \frac{\phi}{2\epsilon} + \frac{1}{2\pi} \left[\sin\left(\frac{\pi\phi}{\epsilon}\right) \right] & \text{if } |\phi| \leq \epsilon, \\ 1 & \text{if } \phi > \epsilon, \end{cases} \quad (2.15)$$

where, the thickness of the interface is taken as 2ϵ , which generally varies from $2\epsilon = 3\Delta r$ to $7\Delta r$, Δr is the size of the computational cell. The normal vector can be calculated following Sussman *et al.* [76] as,

$$\mathbf{n} = \nabla H(\phi). \quad (2.16)$$

The curvature κ is then given by,

$$\kappa = -\nabla \cdot \hat{\mathbf{n}}. \quad (2.17)$$

In order to allow the fluid properties to change smoothly from the value on one side of the interface to the value on the other side, the smoothed volume fraction field is used for calculation of density and volume fraction as

$$\rho(\tilde{\alpha}) = \rho_1 \tilde{\alpha} + \rho_2 (1 - \tilde{\alpha}), \quad (2.18)$$

$$\mu(\tilde{\alpha}) = \mu_1 \tilde{\alpha} + \mu_2 (1 - \tilde{\alpha}), \quad (2.19)$$

where, the subscripts 1 and 2 denote the properties of fluid 1 and 2, respectively.

2.2.6 Surface tension model

The efficient modelling of surface tension effect is very important for accurate numerical modelling of interfacial flows. In the present solver, the continuum surface force model (CSF) of Brackbill *et al.* [71] is incorporated wherein, the interfacial force is treated as a surface volume force $\mathbf{f}_{sv}$ (force per unit volume) given by,

$$\mathbf{f}_{sv} = \mathbf{f}_{sa} \delta_s, \quad (2.20)$$

where δ_s is the Dirac delta function, which is zero everywhere except at the interface and $\mathbf{f}_{sa}$ is the surface tension force per unit interfacial area, given as,

$$\mathbf{f}_{sa} = \sigma \kappa \hat{\mathbf{n}} + \nabla_s \sigma, \quad (2.21)$$

where σ is the surface tension coefficient, κ and $\hat{\mathbf{n}}$ are the curvature and unit normal to the interface and ∇_s is the surface gradient. Due to absence of temperature and concentration gradient along the surface, $\nabla_s \sigma$ can be neglected. The surface tension force per unit volume can be defined as,

$$\mathbf{f}_{sv} = \sigma \kappa \hat{\mathbf{n}} \delta_s. \quad (2.22)$$

The Dirac delta function can be written as,

$$\delta_s = |\mathbf{n}|. \quad (2.23)$$

Thus, the surface tension force added in the momentum equation (Eq. 2.2) has the form,

$$\mathbf{f}_{sv} = \sigma \kappa \mathbf{n}, \quad (2.24)$$

where the calculation of κ and $\mathbf{n}$ has been described in Section 2.2.5.

2.2.7 Discretisation scheme

The spatial discretisation of the governing equations is performed on a staggered grid arrangement with the scalars located at the cell centres and velocities at the face centres. The Marker-in-Cell (MAC) method is employed for solution of the momentum equations.

The continuity and momentum equations are discretised in time as,

$$\nabla \cdot \mathbf{v}^{n+1} = 0, \quad (2.25)$$

$$\begin{aligned}
\mathbf{v}^{n+1} = & \mathbf{v}^n + (-\nabla \cdot (\mathbf{v}^n \mathbf{v}^n)) \Delta t + (\mathbf{g}) \Delta t \\
& + \left(\frac{[-\nabla p^{n+1} + \nabla \cdot 2\mu(\phi^n) \mathbf{D}_v^n] + \sigma \kappa(\phi^n) \nabla H(\phi^n)}{\rho(\phi^n)} \right) \Delta t,
\end{aligned} \tag{2.26}$$

where $\mathbf{D}_v = \frac{1}{2} \{(\nabla \mathbf{v}) + (\nabla \mathbf{v})^T\}$ is the rate of deformation tensor and Δt is the time step.

The convective terms in the momentum equation are discretised using a second order essentially non-oscillatory (ENO) scheme as described by Chang *et al.* [74] and the remaining space derivatives are discretised using central differencing. The discretised momentum equations are solved explicitly for known values of volume fraction α and level set function ϕ at time t^n resulting in a provisionally predicted velocity field $\tilde{\mathbf{v}}$. The provisional velocity field may not be divergence free as the pressure gradient is discretised using the values at the earlier time step t^n . Hence, to enforce continuity, a pressure Poisson equation is solved using the preconditioned biconjugate gradient (BI-CGSTAB) method to obtain the pressure correction p' ($= p^{n+1} - p^n$). Using the pressure correction, the provisional velocities are corrected to obtain the final updated values at t^{n+1} . Using the updated velocity field, the updated volume fraction α^{n+1} and level set ϕ^{n+1} values are obtained followed by reconstruction of the interface.

2.2.8 Time step restriction

The employed solution procedure has accuracy of second order in space and first order in time. The explicit updation of convective, viscous, surface tension and gravity terms places restrictions on the maximum allowable time step size in order to ensure stability of the solution.

The convection time step restriction is given by,

$$\Delta t_{conv} \left(\frac{|u|_{max}}{\Delta x} + \frac{|v|_{max}}{\Delta y} \right) \leq 1. \tag{2.27}$$

The viscous time step restriction is given by,

$$\Delta t_{visc} \left\{ \frac{\mu_l}{\rho_l} \right\} \left(\frac{2}{\Delta x^2} + \frac{2}{\Delta y^2} \right) \leq 1. \tag{2.28}$$

The restriction on timestep due to surface tension terms is given by

$$\frac{C_\phi \Delta t_s}{\Delta x} < \frac{1}{2}, \quad (2.29)$$

where C_ϕ is the capillary wave velocity given by,

$$C_\phi = \left[\frac{\sigma \pi}{\Delta x (\rho_l + \rho_v)} \right]^{1/2}. \quad (2.30)$$

Thus, the capillary time step limit can be given by,

$$\Delta t_s < \left[\frac{(\rho_l + \rho_v) \Delta x^3}{4\pi\sigma} \right]^{1/2}. \quad (2.31)$$

Finally, the stability restriction due to gravity can be expressed as,

$$\frac{v_g \Delta t_g}{\Delta x} \leq 1, \quad (2.32)$$

where v_g is the gravity induced velocity $v_g = g \Delta t_g$.

The minimum value of Δt_{conv} , Δt_{visc} , Δt_s and Δt_g is deployed as the timestep for all the calculations.

2.3 Gerris and Basilisk solvers

Apart from the ‘inhouse’ CLSVOF solver used for the computations of chapter 4, the open source solver *Gerris* [77,78] and its successor *Basilisk* [79] have been adopted for the results presented in chapters 5 to 7. *Gerris* is a programming paradigm, developed by Popinet, for the solution of the partial differential equations describing fluid flow. *Basilisk* is designed to be the successor of *Gerris* and is under active development by the same group. A few salient features pertaining to these solvers are described in the following section.

The *Gerris* and *Basilisk* solvers consist of a highly parallelized finite volume code, which combines a quad/octree discretisation scheme, a projection method and a multilevel Poisson solver, for solution of the time-dependent incompressible Navier-Stokes equations. The domain is spatially discretised using square (cubic in 3D) finite volumes organised hierarchically as a quadtree (octree in 3D). All the variables (components of the momentum, pressure and passive tracers) are collocated at

the centre of each square in 2D (cubic in 3D) discretisation volume. Consistent with a finite-volume formulation, the variables are interpreted as the volume-averaged values for the corresponding discretisation volume. In order to avoid the classic problem of decoupling the pressure and velocity field, an approximate projection method is used for the spatial discretisation of the pressure correction equation and the associated divergence in the Poisson equation. The advection terms are discretised using the robust second-order upwind scheme of Bell et al [80]. The implemented numerical schemes ensure second order accuracy in space and time.

The classical piecewise-linear geometrical VOF scheme is generalised to work on the quad/octree in order to allow variable spatial resolution along the interface. The accurate estimation of the surface tension terms is ensured by employing a combination of a balanced-force CSF approach [76,81], and a height-function based curvature estimation [82,83]. The detailed methodology and code validations are available in the comprehensive reports of Popinet [77–79].

In addition to the aforesaid attributes, the powerful adaptive mesh refinement (AMR) capability enables the mesh to be locally refined or coarsened during the course of the simulations. The AMR feature enhances the computational efficiency and maintains the necessary accuracy of the simulations. A dynamic load balancing algorithm is incorporated in the solvers to efficiently distribute the computational load across the processors during a parallelized simulation. Furthermore, the solvers are equipped with an electro-hydrodynamic toolbox in the code architecture to model the influence of an external electric field. The basic programming paradigm related to the electro-hydrodynamic simulations have been discussed in detail together with the specific problem wherein we have involved the influence of the applied electric fields on the dynamics of the flow.

In context of the aforementioned features, the selected solvers are considered to be ideal choices for our computational requirements and have been accordingly adopted for performing the simulations pertaining to chapters 5 to 7. These solvers have been extensively used in prior literature to simulate a wide range of complex fluid flow problems [32,84,85].

Chapter 3

Molecular dynamics simulation

3.1 Introduction

Molecular dynamics (MD) is a computer simulation technique for studying the time evolution of a set of interacting atoms or molecules by integrating their equations of motion. It is basically a N-body simulation where a set of atoms or molecules are allowed to interact for a certain period of time thereby providing a glimpse of the dynamical evolution of the system.

Molecular dynamics simulations are based on Newton's second law of motion given by,

$$\mathbf{F}(\mathbf{r}_i) = m_i \mathbf{a}_i = m_i \frac{d\mathbf{v}_i}{dt} = m_i \frac{d^2 \mathbf{r}_i}{dt^2}, i = 1, 2, \dots, N, \quad (3.1)$$

where, F is the force, m_i , $\mathbf{a}_i$, $\mathbf{v}_i$, $\mathbf{r}_i$ are the mass, acceleration, velocity and position of particle i , respectively; t is the time and N is the total number of particles in the system. If the forces are conservative, they can be written as a derivative of a scalar potential U as follows,

$$\mathbf{F}(\mathbf{r}_i) = -\nabla_i U(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N). \quad (3.2)$$

The basis of molecular dynamics simulation is the solution of Eq. 3.1 by performing step-by-step numerical integration to obtain the position and velocities over time.

3.2 Integrators

Integrators are used to advance the positions and velocities of the atoms over time. Some of the popular algorithms are central difference (Verlet, velocity Verlet and leap-frog), predictor-corrector and symplectic integrators. In this work, the velocity Verlet algorithm is employed due to its compatibility with the Nosé-Hoover thermostat described later in Section 3.4.

The velocity Verlet algorithm [86] consists of a truncated Taylor series expansion for updating the position of a particle from the current timestep t to next timestep $t + \delta t$ as shown below [87],

$$\mathbf{r}_i(t + \delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\delta t + \frac{1}{2}\mathbf{a}_i(t)\delta t^2, \quad (3.3)$$

where $\mathbf{r}_i(t)$, $\mathbf{v}_i(t)$ and $\mathbf{a}_i(t)$ are the position, velocity and acceleration of the particle i at time t . The velocity for the subsequent timestep is calculated in a similar manner:

$$\mathbf{v}_i(t + \delta t) = \mathbf{v}_i(t) + \frac{1}{2}\delta t [\mathbf{a}_i(t) + \mathbf{a}_i(t + \delta t)]. \quad (3.4)$$

This operation is performed in two stages. First, the velocity is updated (over half timestep) along with the position update giving,

$$\mathbf{v}_i\left(t + \frac{1}{2}\delta t\right) = \mathbf{v}_i(t) + \frac{1}{2}\delta t\mathbf{a}_i(t). \quad (3.5)$$

Subsequently, the forces are calculated based on the updated position at time $t + \delta t$. The velocity update is then completed by advancing over another half timestep:

$$\mathbf{v}_i(t + \delta t) = \mathbf{v}_i\left(t + \frac{1}{2}\delta t\right) + \frac{1}{2}\delta t\mathbf{a}_i(t + \delta t). \quad (3.6)$$

3.3 Force field selection

A force field represents the basic functional form and set of parameters that is used to calculate the total potential energy of the system in molecular dynamics simulations. The general form for the total energy in an additive force field can be written as,

$$E_{total} = E_{bonded} + E_{nonbonded}, \quad (3.7)$$

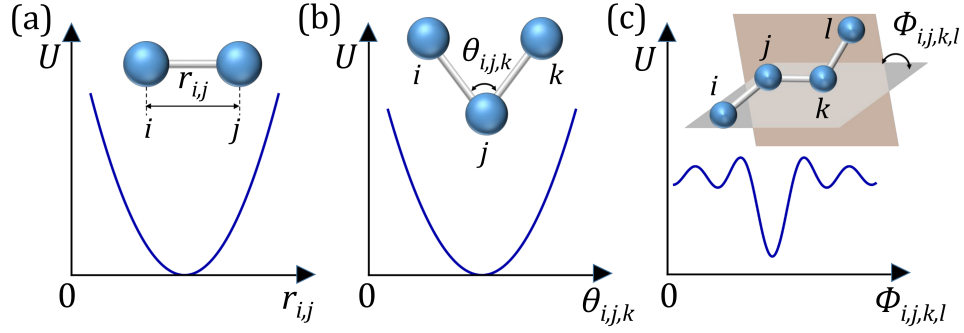


Figure 3.1: Schematic representation of the (a) bond potential, (b) angle potential and (c) dihedral potential for bonded interactions.

where E_{bonded} represents the interaction between atoms linked by covalent bonds and $E_{nonbonded}$ describes the electrostatic and van der Waals interactions. Generally, the functional forms and parameters in a force field are empirically determined from experimental properties or obtained from quantum mechanical calculations. The relevant functional forms and parameters of the force field employed in this work are presented below.

3.3.1 Bonded interactions

The bonded interactions represent the intramolecular effects between the covalently bonded atoms of a molecule. These are used to model the energy contributions from the bonds, angles and dihedral in a molecule. A schematic representation of the bond, angle and dihedral potentials are shown in Figs. 3.1 (a), (b) and (c), respectively. The functional form of the bonded potentials are shown below:

$$U_{bond} = \frac{1}{2} \sum_{bonds} k^b (r_{i,j} - r_{eq})^2, \quad (3.8)$$

$$U_{angle} = \frac{1}{2} \sum_{angles} k^\theta (\theta_{i,j,k} - \theta_{eq})^2, \quad (3.9)$$

$$\begin{aligned} U_{dihedral} = & \frac{1}{2} k_1^d [1 + \cos(\phi_{i,j,k,l})] + \frac{1}{2} k_2^d [1 - \cos(2\phi_{i,j,k,l})] \\ & + \frac{1}{2} k_3^d [1 + \cos(3\phi_{i,j,k,l})] + \frac{1}{2} k_4^d [1 - \cos(4\phi_{i,j,k,l})], \end{aligned} \quad (3.10)$$

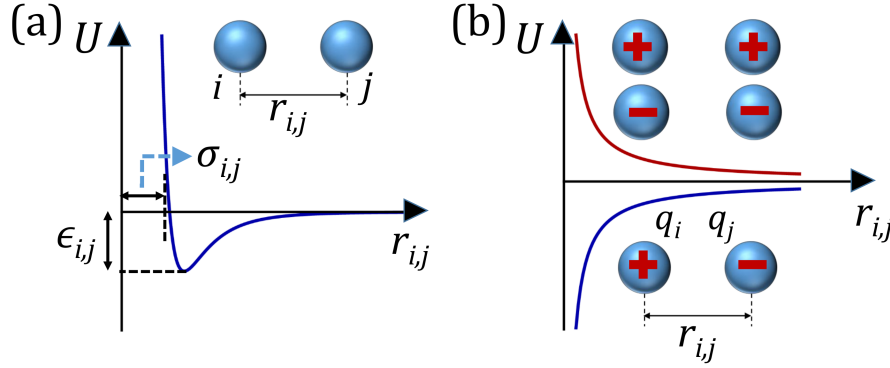


Figure 3.2: Schematic representation of the (a) Lennard-Jones (LJ) potential and (b) Coulombic potential for non-bonded interactions.

where $r_{i,j} = |r_i - r_j|$ represents the distance between two adjacent pairs of atoms, r_{eq} is the equilibrium bond length, $\theta_{i,j,k}$ is the angle between successive bond vectors $r_{i,j}$ and $r_{j,k}$. θ_{eq} is the equilibrium bond angle and $\phi_{i,j,k,l}$ is the dihedral angle. k^b , k^θ , k_1^d , k_2^d , k_3^d , k_4^d are the respective force constants.

3.3.2 Non-bonded interactions

The non-bonded interactions generally refers to the van der Waals and electrostatic interactions, which are described by Lennard-Jones (LJ) potential and Coulombic potential, respectively. A schematic representation of the Lennard-Jones (LJ) and Coulombic potentials are shown in Figs. 3.2 (a) and (b), respectively. The mathematical form of these potentials are given as,

$$U_{LJ} = \sum_{i,j \neq i}^N 4\epsilon_{i,j} \left[\left(\frac{\sigma_{i,j}}{r_{i,j}} \right)^{12} - \left(\frac{\sigma_{i,j}}{r_{i,j}} \right)^6 \right], \quad (3.11)$$

$$U_{Coulomb} = \sum_{i,j \neq i}^N \frac{q_i q_j}{4\pi\epsilon_0 r_{i,j}}, \quad (3.12)$$

where, U_{LJ} and $U_{Coulomb}$ are the Lennard-Jones and Coulombic potentials, respectively. $\sigma_{i,j}$ is the length parameter and $\epsilon_{i,j}$ is the energy parameter for the LJ potential between particles i and j . ϵ_0 is the permittivity of free space, q_i and q_j are the charges and $r_{i,j}$ represents the distance between particles i and j .

The calculation of the non bonded interactions is the most time consuming part

of the computation as they account for pair interactions between all particles in the system. The LJ interactions decay with increasing distances and hence they are usually truncated beyond a certain cutoff distance in order to save computational time. For long range Coulomb interactions, special algorithms like particle-particle particle-mesh (PPPM) method [88] are used to break them into two contributions: a short ranged interactions plus a smooth, field like interaction, both of which can be computed efficiently in separate ways.

3.4 Thermostat

A key concept in statistical thermodynamics is the notion of ensemble. An ensemble is a collection of all possible states of a system, which have different microstates but possess an identical macroscopic or thermodynamic state. Here, the term ‘microstate’ refers to the complete specification of positions and momenta of all atoms in the system whereas ‘thermodynamic state’ entails specification of few parameters, e.g. pressure, temperature, density and total mass. Depending on the nature of system under study, different ensembles can be considered. In classical molecular dynamics, simulations are done in a microcanonical ensemble (NVE) where the number of particles N , total volume V and energy E remains constant. However, in experiments, the temperature is generally controlled instead of energy. Therefore, a thermostat is employed to maintain constant temperature in the system by performing the simulations in a canonical NVT ensemble. Another reason of using a thermostat is to avoid steady energy drifts caused by the accumulation of numerical errors during long MD simulations.

The NVT simulations can be performed by either maintaining a constant temperature at every step of the simulation or ensuring the average temperature constant over the course of simulation. The former method is achieved by Velocity Rescaling thermostats. However it prevents the fluctuations in temperature, which are actually present in a canonical ensemble and as a result, the dynamics may be inaccurate. The Nosé-Hoover thermostat provides a more ‘gentle’ effect by ensuring that the average temperature over the course of simulations remains constant [89]. The idea is to couple a heat bath to the system as an integral part by addition of an artificial variable s associated with mass $Q > 0$ as well as velocity $\dot{s}$. The magnitude of Q determines the degree of coupling between the heat bath and real system and

hence influences the temperature fluctuations whereas s behaves like a time scaling parameter. The Lagrangian for the extended system is given as [87],

$$\mathcal{L} = \sum_{i=1}^N \frac{m_i}{2} \dot{\mathbf{r}}_i^2 - U(\mathbf{r}^N) + \frac{Q}{2} \dot{s}^2 - \frac{L}{\beta} \ln s. \quad (3.13)$$

The first two terms represent the kinetic and potential energy of the real system and additional terms are the kinetic and potential energy of s . The Hamiltonian in the real variable formulation can be derived as, [90]

$$\mathcal{H} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}^N) + \frac{\xi^2 Q}{2} + \frac{L}{\beta} \ln s, \quad (3.14)$$

where $L = 3N$ represent the total degrees of freedom in real space and ξ is the thermodynamic friction coefficient described as $\xi = \frac{d(\ln s)}{dt}$. From a practical viewpoint, the time evolution of position and velocity is modified as follows:

$$\mathbf{r}_i(t + \delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\delta t + \frac{\delta t^2}{2} [\mathbf{a}_i(t) - \mathbf{v}_i(t)\xi(t)], \quad (3.15)$$

$$\mathbf{v}_i(t + \delta t) = \mathbf{v}_i(t) + \frac{1}{2}\delta t [\mathbf{a}_i(t) - \mathbf{v}_i(t)\xi(t)] + \frac{1}{2}\delta t [\mathbf{a}_i(t + \delta t) - \mathbf{v}_i(t + \delta t)\xi(t + \delta t)]. \quad (3.16)$$

It can be seen in Eq. 3.16 that $\mathbf{v}_i(t + \delta t)$ appears both on the left and right hand sides. Thus, the Nosé-Hoover method is always implemented using a predictor-corrector method or solved iteratively. Alternatively, Martyna *et al.* [91] have proposed a set of explicit reversible integrators for such extended systems.

3.5 Periodic boundary conditions

The simulation of bulk liquids using a small number of atoms can introduce significant surface effects due to nature of forces at surface of simulation box compared to the bulk. This is handled by employing the technique of periodic boundary conditions. Using this method, a particle that tends to move out through one face of the simulation box at time $t + dt$ will in fact re-enter through the opposite face at the next timestep. Thus, the simulation effectively considers an infinite periodic lattice of replicates of the simulation box. In order to calculate the interaction between

two particles A and B , the nearest periodic image of B is considered.

3.6 Properties measurement

The initial system is allowed to equilibrate by running the MD simulations for a certain period of time. After equilibrium is reached, the properties can be calculated by taking time average as:

$$\langle A \rangle_{time} = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_{t=0}^{\tau} A [\mathbf{p}^N(t), \mathbf{r}^N(t)] dt \approx \frac{1}{M} \sum_{i=1}^M A_i [\mathbf{p}^N(t_i), \mathbf{r}^N(t_i)], \quad (3.17)$$

where τ is the simulation time, M is the number of timesteps over which averaging is performed, A_i is the instantaneous value of A expressed as function of momentum p and position r of the N atoms in the system. The ergodic hypothesis assumes that time averaged $\langle A \rangle_{time}$ is equal to ensemble average $\langle A \rangle$.



Chapter 4

Formation of liquid drops at an orifice and dynamics of pinch-off in liquid jets

The dynamics of formation and breakup of liquid drops and jets during injection of a liquid through an orifice into another fluid are investigated by performing direct numerical simulations. In the dripping regime, the growth and breakup rate of a drop are corroborated with theoretical predictions. During the growth stage of the drops, a self-similar behavior of the drop profile is identified over a relatively short duration of time. The phenomenon of interface overturning is explored and the variation of overturning angle as a function of drop viscosity is computed. A novel transition from dripping to jetting regime is demonstrated by varying the viscosity of the ambient medium. The breakup of jets in Rayleigh mode is explored and the breakup length obtained from our computations shows excellent agreement with the theoretical predictions owing to Rayleigh's analysis. The increased participation of the ambient medium is observed at higher inflow rates.

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4.1 Introduction

The dynamics of droplet formation and breakup of liquid jets have been studied extensively owing to its rich underlying physics and importance in many industrial applications. A variety of applications involve formation of drops from a nozzle or an orifice, as observed in inkjet printing [1], spray coating [2], separation and extraction processes [4] and others [34]. The success of such crucial technologies rely strongly on the accurate and reliable computation of dynamics related to liquid column breakup as well as subsequent drop formation.

The formation of drops from vertical capillary tubes has been studied experimentally [9–13, 92, 93] and numerically [10–12, 15, 27, 94–99] by many researchers. The process of drop formation is widely classified into two categories - dripping and jetting. In the dripping regime, which occurs at low flow rates, the drops form periodically near the mouth of the orifice. As the flow rate is slowly increased, the nonlinear effects come into picture resulting in a quasi-periodic pattern of drop formation characterized by regularly repeating multiple detached drop volumes and limiting drop lengths. At sufficiently high flow rates, the system transitions into jetting mode, where the inertia force becomes a dominating factor. The drops breakup from the end of a long jet of liquid, which is inherently unstable. The dynamics of growth and breakup in the dripping mode has been explored experimentally by several researchers [9–13, 13, 14, 92, 93, 97, 100]. Besides experimental investigations, numerical studies on drop formation in air has been conducted using one-dimensional (1D) slender jet approximations [10, 12, 15, 94], boundary integral methods [95, 96] and solution of full Navier-Stokes equations [27, 98, 99, 101]. The pioneering work by Savart [16], Plateau [17] and theoretical analysis of Rayleigh [102, 103] provided a basic understanding of the instability of jets and predictions of important parameters, such as the breakup length and drop diameter. Subsequently, many investigations have been performed theoretically [104–111], experimentally [18–22, 112–114] and numerically [23–27, 115] to uncover the fascinating aspects of the jetting mode and its associated dynamics.

The present study is an attempt to analyze a few salient features of drop formation in both dripping and jetting regimes by solving the full Navier-Stokes equations under axisymmetric conditions. For this purpose, we have used an inhouse interface capturing code based on the coupled level-set and volume-of-fluid method (CLSVOF). The code has been previously successfully applied to simulate two phase

flows [116–122]. In the dripping mode, the growth and breakup of the drop have been computed and a self similarity of the drop profile during the initial expansion stage has been proposed, which serves as an addition to the self similarity near the collapse stage previously shown in literature [98]. The thinning behavior of the liquid neck shows a transition from an inertia dominated regime to an inertia-viscous regime when the liquid neck falls below a critical minimum radius. A detailed parametric study of the overturning phenomenon has been carried out to quantify the overturning angle with variation of liquid viscosity, which has not been reported earlier. The transition from dripping to jetting regime has been simulated and two distinct jetting regimes has been observed depending of the dominance of inertia or viscous forces. Finally breakup of jets in Rayleigh mode has been explored by comparing the breakup length with theoretical predictions and entrainment of ambient air is demonstrated for jets moving at high velocity.

4.2 Formulation of the problem

4.2.1 Computational domain

A representative diagram of the computational domain adopted is shown in Fig 4.1. The drop liquid of density ρ_i and viscosity μ_i is injected through an orifice of radius R on a horizontal wall at a constant flow rate, $\dot{Q}_d$ into a quiescent ambience at density ρ_o and viscosity μ_o . The surface tension σ is assumed to be spatially uniform and constant with time. A cylindrical coordinate system (r, z, θ) is adopted considering the dynamics to be axisymmetric so that the problem is independent of θ where (r, z, θ) are the radial coordinate, axial coordinate, and azimuthal angle, respectively. The origin is chosen at the center of the orifice and gravity aligns in the direction of the z axis. The domain size is decided by carrying out domain independence tests. The size of the computational domain is taken as $5R$ in the radial direction and $30 - 60R$ in the axial direction. It is found that the results obtained from the simulations become insensitive to further increase in the domain size. In order to optimize the computational cost, we have adopted the aforementioned domain size in the present study. Furthermore, the size of the computational domain in our study is similar to previous investigations on drop formation [123]. The three phase contact circle where the drop base, outer ambience and orifice rim meet, remains pinned to the sharp edge of the orifice and hence no contact angle needs to be

specified in this problem.

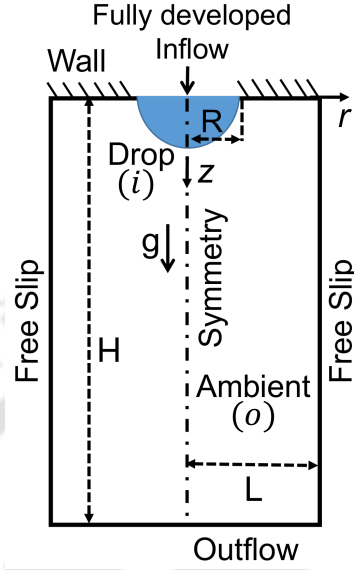


Figure 4.1: Schematic diagram (not to scale) showing the computational domain and boundary conditions in cylindrical coordinate system (r, z, θ) . A fully developed flow is imposed at the orifice inlet of radius R initialized with a hemispherical drop. Gravity acts along positive z axis. The size of the domain is taken as $5R$ in radial (r) direction whereas $30 - 60R$ in axial (z) direction.

4.2.2 Numerical methods

In the present study, a Newtonian liquid drop is injected into another Newtonian liquid and both fluids are considered immiscible and incompressible. The problem is governed by the single set of continuity and Navier-Stokes equations for treating a single fluid continuum. The two-dimensional axisymmetric setup has been considered by solving the same set of governing equations as described in Section. 2.2.1. The ‘inhouse’ CLSVOF solver, described extensively in Sec. 2.2, is employed for performing the numerical simulations. The aforementioned CLSVOF method has been used by many researchers successfully for solving a variety of interfacial flow problems of scientific interest [116–120].

4.2.3 Boundary conditions

At the orifice inlet, a parabolic velocity profile is imposed satisfying the conditions of desired liquid injection rate.

$$u(r) = 0, \quad v(r) = 2v_{avg} [1 - (r/R)^2], \quad \alpha = 1 \text{ for } 0 \leq r \leq R, \quad (4.1)$$

where u and v are the radial and axial velocity components, respectively. For the outflow boundary, it is assumed that influence of upstream is minimum, i.e., there is no change in axial direction.

$$\frac{\partial u}{\partial z} = \frac{\partial v}{\partial z} = \frac{\partial \alpha}{\partial z} = \frac{\partial \phi}{\partial z} = 0, \quad P = P_0. \quad (4.2)$$

Due to the axisymmetric nature of the problem, the normal components of velocity and the viscous shear stress vanish along the axis of symmetry.

$$u = 0, \quad \frac{\partial v}{\partial r} = \frac{\partial \alpha}{\partial r} = \frac{\partial \phi}{\partial r} = 0. \quad (4.3)$$

At the solid wall, liquid obeys conditions of no-slip and no-penetration.

$$u = v = 0 \text{ for } R \leq r \leq L. \quad (4.4)$$

4.2.4 Initial conditions

The drop is initially assumed to be a hemisphere of radius equal to that of the orifice radius. The initial state of the static drop can be defined as,

$$r^2 + z^2 = R^2. \quad (4.5)$$

Both the drop and ambience are considered to be initially quiescent and at uniform pressure.

$$u = v = 0, \quad P = \text{const}, \text{ at } t = 0. \quad (4.6)$$

4.2.5 Non-dimensional parameters

The non-dimensional parameters pertinent to our problem are the Weber number, Bond number and Ohnesorge number given as:

$$We = \frac{\rho_i v_{avg}^2 R}{\sigma}, \quad (4.7)$$

$$Bo = \frac{\rho_i g R^2}{\sigma}, \quad (4.8)$$

$$Oh = \frac{\mu_i}{\sqrt{\rho_i R \sigma}}. \quad (4.9)$$

The Weber number, We , measures the importance of inertia force relative to the surface tension force; the Bond number, Bo , measures the importance of gravity force relative to surface tension force; and the Ohnesorge number, Oh , measures the relative importance of viscous force over inertia and surface tension forces.

Two other non-dimensional parameters, the density ratio λ and viscosity ratio η are introduced to account for the dynamic effect of surrounding medium on the drop formation.

$$\lambda = \frac{\rho_o}{\rho_i}, \quad (4.10)$$

$$\eta = \frac{\mu_o}{\mu_i}. \quad (4.11)$$

The following dimensionless characteristic variables are introduced:

$$z^* = \frac{z}{R}, \quad r^* = \frac{r}{R}, \quad v^* = \frac{v}{v_{avg}}, \quad P^* = \frac{P}{\rho_i v_{avg}^2}, \quad t^* = t \frac{v_{avg}}{R}, \quad (4.12)$$

where, the orifice radius R is the characteristic length scale and the average velocity of liquid at inlet $v_{avg} = \dot{Q}_d / \pi R^2$, is the characteristic velocity scale.

4.2.6 Fluid properties

The drop fluid is chosen to be an aqueous solution of glycerine in varying concentrations. Depending on different cases, the surrounding medium is either considered as organic oil or air.

4.3 Validation of current numerical approach

4.3.1 Comparison with experiments

Figure 4.2 presents a comparison of the drop shape at the incipience of breakup predicted by our current computations with the experimental results of Subramani *et al.* [10]. The comparison shows excellent qualitative agreement of our computational results with experimental observations. The values of dimensionless limiting length

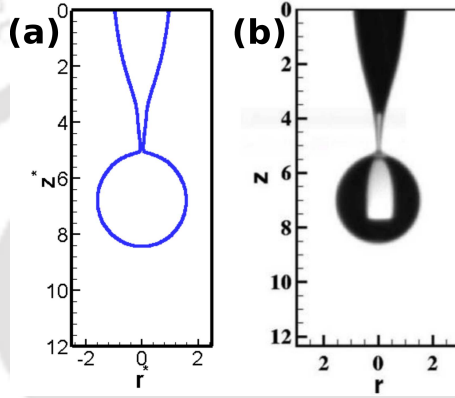


Figure 4.2: Qualitative comparison of drop formation between (a) current computations and (b) experimental results of Subramani *et al.* [10] under conditions of $Oh = 0.13$, $Bo = 0.33$, $We = 0.119$, $\lambda = 0.001$ and $\eta = 0.0005$.

($L_d^* = L_d/R$) and dimensionless detached volume ($V_d^* = V_d/R^3$) depicted in Fig. 4.2 are calculated in order to make a quantitative comparison with Subramani *et al.* [10]. The experimentally obtained values of L_d^* and V_d^* are $L_{d,exp}^* = 8.6 \pm 0.1$ and $V_{d,exp}^* = 17.4 \pm 0.3$. The corresponding values obtained from our computations are $L_{d,comp}^* = 8.45$ and $V_{d,comp}^* = 17.44$, which are in excellent agreement with the experiments.

Table 4.1: Quantitative comparison of drop formation between current computations and experimental results of Subramani *et al.* [10] under conditions of $Oh = 0.13$, $Bo = 0.33$, $We = 0.119$, $\lambda = 0.001$ and $\eta = 0.0005$.

Parameters	Experimental	Present Computation
Limiting length L_d^*	8.6 ± 0.1	8.45
Drop Volume V_d^*	17.4 ± 0.3	17.44

4.3.2 Grid convergence studies

To ensure that the results obtained from our computations are independent of grid resolution, we chose five grid sizes $[25 \times 150, 50 \times 300, 80 \times 480, 100 \times 600, 125 \times 750]$. The test was conducted under conditions of $Oh = 0.003$, $Bo = 0.18$, $We = 0.8$, $\lambda = 0.001$ and $\eta = 0.02$. The dimensionless drop volume V_d^* is compared for the five chosen grids as tabulated in Table 4.2. It was observed that the difference

Table 4.2: Comparison of dimensionless drop volume V_d^* for different grid sizes $[25 \times 150, 50 \times 300, 80 \times 480, 100 \times 600, 125 \times 750]$. The relevant conditions are $Oh = 0.003$, $Bo = 0.18$, $We = 0.8$, $\lambda = 0.001$ and $\eta = 0.02$.

Grid Points	Drop volume (V_d^*)	Percent change (%)
25×150	29.74	-
50×300	30.44	2.35
80×480	30.98	1.77
100×600	31.20	0.71
125×750	31.24	0.12

of V_d^* between grids 25×150 and 50×300 is around 2 % whereas the difference between grids 100×600 and 125×750 is less than 0.1 %. Arising out of computational experiments, we have chosen grid size of 100×600 for our present computations to optimize computational time without compromising the accuracy of the results.

4.4 Results and discussion

The following section presents the results from our simulations to uncover the dynamics of formation and breakup of liquid drops and jets injected in a quiescent medium from an orifice. The range of values for the governing dimensionless numbers explored in the simulations are listed in Table 4.3.

4.4.1 Drop growth

The temporal evolution of the drop is termed as drop growth history. Due to continuous injection of the liquid through the orifice, the size of the drop increases with time and finally detaches under the action of gravity. Figure 4.3 shows the drop growth history as a function of time. Here, D_d^* and t^* represent the nondimensional

Table 4.3: Range of dimensionless numbers employed for the numerical simulations.

Dimensionless parameter	Range
We	0.1 - 9.5
Bo	0.18
Oh	0.002 - 0.2
λ	0.001 and 0.74
η	0.0001-15.0

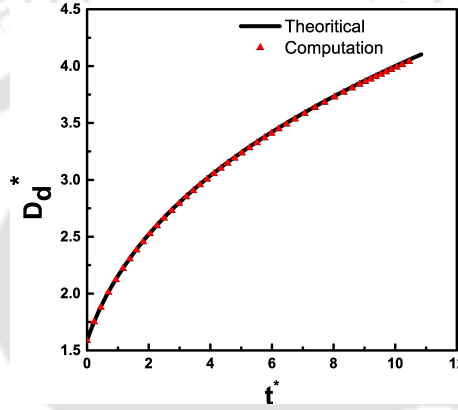


Figure 4.3: Numerical prediction of dimensionless drop diameter D_d^* as a function of dimensionless time t^* and comparison with analytical expression Eqn. 4.13 for $Oh = 0.003$, $Bo = 0.18$, $We = 0.2$, $\lambda = 0.001$ and $\eta = 0.02$.

drop diameter and time, respectively, where $D_d^* = D_d/R$. For a constant flow rate of the liquid through the nozzle, $V_d = V_o + \dot{Q}_d t$, where V_d and V_o are the instantaneous and initial drop volumes and $\dot{Q}_d$ is the constant rate of liquid injection. Assuming the drop remains spherical throughout the growth process, the drop volume is given by $V_d = (\pi/6)D_d^3$ and hence the dimensionless drop diameter is calculated from the growth law using Eqn. 4.13. The growth law from our numerical simulation is found to be $D_d^* = (4.009 + 5.940t^*)^{1/3}$, which is in excellent agreement with the theoretical prediction of Eqn. 4.13.

$$D_d^* = [4 + 6t^*]^{1/3}. \quad (4.13)$$

Considering the initial stage of the drop growth, a self similarity analysis of the profile of the growing drop is performed. The fitting function used is of the form $z^*/t^{*\alpha} = ar^*t^{*\beta}$ where z^* and r^* are the non-dimensional quantities defined earlier

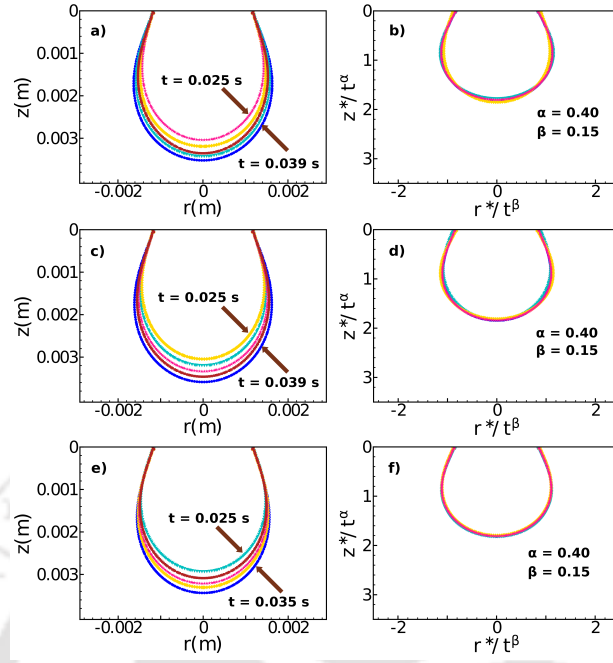


Figure 4.4: (a) Instantaneous interface profiles and (b) collapsed profiles during drop growth stage from $t = 0.025$ s to $t = 0.039$ s for $Oh = 0.002$, $Bo = 0.18$, $We = 0.2$, $\lambda = 0.001$, $\eta = 0.02$ (c) Instantaneous interface profiles and (d) collapsed profiles during drop growth stage from $t = 0.025$ s to $t = 0.039$ s for $Oh = 0.014$, $Bo = 0.18$, $We = 0.2$, $\lambda = 0.001$, $\eta = 0.004$ (e) Instantaneous interface profiles and (f) collapsed profiles during drop growth stage from $t = 0.025$ s to $t = 0.035$ s for $Oh = 0.1$, $Bo = 0.18$, $We = 0.2$, $\lambda = 0.001$, $\eta = 0.0006$. The axes has been rescaled following $z^*/t^{\alpha} = ar^{\beta}t^{\beta}$.

and α and β are the exponents [124]. The relationship between α and β is followed as $\alpha = 4\beta$. The constant a is considered as unity and the values of α and β are 0.40 and 0.15, respectively. The results obtained from simulation of drops of different viscosities are presented in Fig. 4.4. For values of $Oh = 0.002$ and 0.014 shown in Figs. 4.4 (a)-(b) and 4.4 (c)-(d), respectively, the growing drop profile collapse on a single curve between time instants $t = 0.025$ s and $t = 0.039$ s. The higher magnitude of α over β is indicative of the fact that the growth of the drop in the axial direction is faster than the radial direction due to the constant inflow imposed at the orifice. However, at a higher value of $Oh = 0.1$ shown in Fig. 4.4 (e)-(f), the growth follows self similarity but for a smaller time range between $t = 0.025$ s and $t = 0.035$ s. This demonstrates that the increasing drop viscosity accelerates the growth of the drop due to reduced surface tension forces compared to viscous forces at higher Oh .

4.4.2 Drop breakup

A salient feature of drop formation is the occurrence of a slender neck that connects the about-to-form drop with the rest of the fluid attached to the orifice. It is interesting to analyze the relation between the minimum radius of the neck ($r_{min}^* = r_{neck}^*$) and time before drop pinch-off takes place where $r_{min}^* = r_{min}/R$. The temporal decrease of the neck radius r_{min}^* with time t^* can be characterized by the power law expression $r_{min}^* \sim \tau^\alpha$ where τ is the time before drop pinch-off ($\tau = (t_{pinch} - t)/t_c$). Here, $t_c = \sqrt{\rho R^3/\sigma}$ is the capillary time scale and α is the effective exponent of power law. In our present computations, the drop is assumed to pinch-off when r_{min}^* falls below 0.001, i.e. the size of a single grid cell. Basaran [34] suggested that a thinning filament undergoes transition from either an initial inertia or viscosity

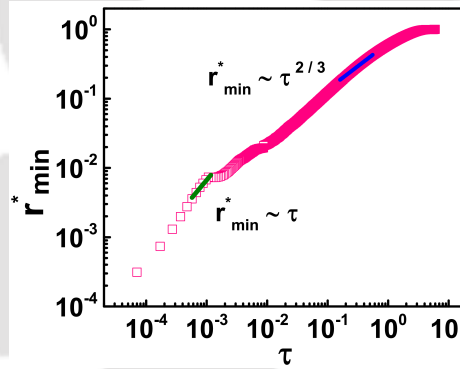


Figure 4.5: Relation between minimum neck radius r_{min}^* and time before pinchoff τ during collapse stage. The solid line represents $r_{min}^* \sim \tau^{2/3}$. Parameters are $Oh = 0.003$, $Bo = 0.18$, $We = 0.2$, $\lambda = 0.001$ and $\eta = 0.02$.

dominated regime to an inertia-viscous regime near the moment of pinch-off. In our present computations, $Oh = 0.003$, which signifies that viscous forces are weak and hence initial breakup is under an inertia dominated regime. The results from Fig. 4.5 clearly indicate the value of α to be $2/3$ in the inertia dominated regime, which agrees well with the predictions of Basaran [34]. However, as the neck radius r_{min}^* falls below 0.008, the viscous effects come into picture and the thinning transitions into an inertia-viscous regime with $r_{min}^* \sim \tau$. The results closely matches the transitional phenomenon reported earlier by Chen *et al.* [98] and Rothert *et al.* [125]

The shape of the interface at the moment of pinch-off is critically dependent

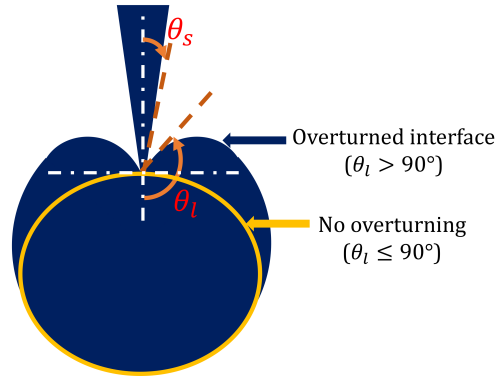


Figure 4.6: Schematic representation of the overturning phenomenon during droplet breakup. The droplet in blue undergoes interface overturning, while the yellow line represents a drop wherein overturning does not occur. The overturning is quantified in terms of the large angle (θ_l) and small angle (θ_s), measured from the axis of symmetry.

on the viscosity of drop liquid. For drops of low viscosity, the interface folds on itself with an internal angle greater than 90° thereby making the interface a multivalued shape function and this phenomenon is called overturning. However, the interface overturning ceases to occur for highly viscous drops. Figure 4.6 presents a schematic representation of the overturning phenomenon observed during droplet breakup. The overturning is quantified in terms of the large angle (θ_l) and small angle (θ_s), measured from the axis of symmetry. For the case of a droplet undergoing overturning, the value of $\theta_l > 90^\circ$. In contrast, $\theta_l \leq 90^\circ$, when overturning ceases to occur during droplet breakup.

The overturning of the drop interface can be explained by studying the velocity field inside the drop just prior to breakup as shown in Fig. 4.7. As the neck collapses, the fluid is expelled rapidly into the drop hanging below and the velocity increases along the centerline. For a low viscous drop such as pure water, the dissipation of this shear stress arising out of rapid fluid movement near the centerline is very poor. This results in a velocity gradient across the drop with the fluid velocity decreasing progressively towards the outer periphery. The drop interface thus folds onto itself as it approaches the moment of pinch-off. However, for a highly viscous drop, the velocity profile resembles that of a plug flow with an almost negligible velocity gradient across the drop. Accordingly, the interface maintains its smooth curvature and does not overturn. These results from our computations corroborate the findings of Wilkes et. al [28].

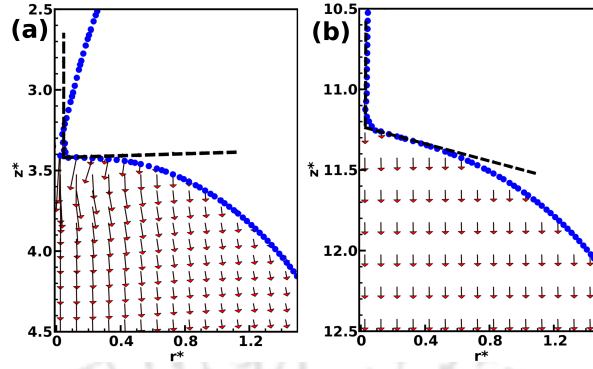


Figure 4.7: Velocity field inside drop of (a) pure water (b) 91% glycerine. Only selected velocity vectors are plotted to maintain clarity. It is seen that interface overturning occurs for a pure water drop whereas it vanishes for highly viscous drops.

A parametric study of the overturning phenomenon is carried out by varying

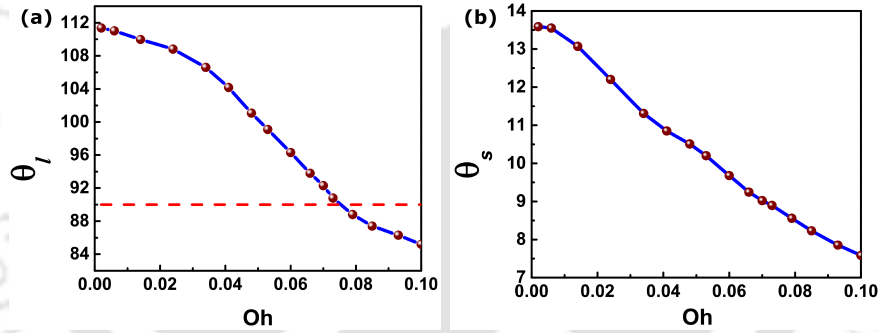


Figure 4.8: Effect of Oh on the overturning angles at pinch-off (a) large angle (b) small angle. The dashed line represents the limit when overturning vanishes ($\theta_l = 90^\circ$). The other relevant parameters are $Bo = 0.18$, $We = 0.2$, $\lambda = 0.001$ and $\eta = 0.02 - 0.0006$.

Oh in order to reveal the critical value of Oh at which overturning vanishes. Day *et al.* [126] and Casterjón-Pita *et al.* [127] showed that the drop interface at breakup for low Oh adopts a unique double cone shape with large and small angles of 112.8° and 18.1° , respectively. They proposed that the breakup remains self-similar with the interface approaching these unique angles irrespective of initial flow conditions or type of breakup. However, these studies were carried out for either inviscid or low viscosity drops. In our present simulations, the variation of large (θ_l) and small (θ_s) angles due to increasing viscosity of the drops is captured and presented in Fig. 4.8. It can be clearly observed that both the angles deviate significantly from the

theoretically predicted values of 112.8° and 18.1° and show a decreasing trend with increasing Oh . The value of θ_l ranges between 111.3° and 85.3° whereas θ_s varies between 13.5° and 7.6° when Oh is altered from 0.002 to 0.1. The overturning phenomenon vanishes when θ_l falls below 90° and this occurs at a critical value of $Oh = 0.075$. It is to be noted that values of θ_l and θ_s at the near-inviscid limit of 0.002 show slight deviation from the predictions of Day *et al.* [126]. This deviation may be attributed to the small yet finite effects of viscosity at $Oh = 0.002$.

4.4.3 Inertia driven dripping-to-jetting transition

The effect of inflow rate on the drop formation process is studied in detail. The Weber number signifies the increase of inertia force relative to surface tension force. At low We , the drop forms periodically close to the orifice and this regime is called dripping. With increasing We , the higher inertia force pushes the pendant drop further downwards producing a long elongated liquid column and the system finally transits into a jetting regime. Also, the increased inertia force reduces drop formation time and subsequently the drop volume.

Figure 4.9 illustrates the effect of increasing Weber number on the dynamics of the droplet formation process. At $We = 0.2$, the drop formation that occurs in the dripping regime is characterized by a very short liquid column and almost constant limiting length of breakup (L_d) as shown in Figure 4.9 (a)-(d). The drop volume and time period between two successive drop breakup is almost constant suggesting a periodic formation process. As We is increased to 1.0, the time period between successive drop breakups becomes slightly irregular and gets significantly reduced. Although the limiting length of breakup (L_d) is almost constant, the drops formed are of unequal volume and the process can be characterized as a quasi-periodic dripping process. It can be noted from Figs. 4.9 (e)-(h) that due to reduced drop formation time, multiple drops can be observed within an axial distance of $z^* = 30$ considered as the length of our computational domain. However, the slow formation process at $We = 0.2$ ensures that the previously released drop crosses the entire computational domain before another drop gets detached as observed in Figs. 4.9 (a)-(d). On the other hand, the drop formation at $We = 2.0$ clearly falls under a jetting regime where a long column of liquid finally breaks into drops often in an aperiodic manner. Figure 4.9 (i)-(l) demonstrates the breakup of a liquid column and subsequent drop formation in the jetting regime. It can be clearly perceived

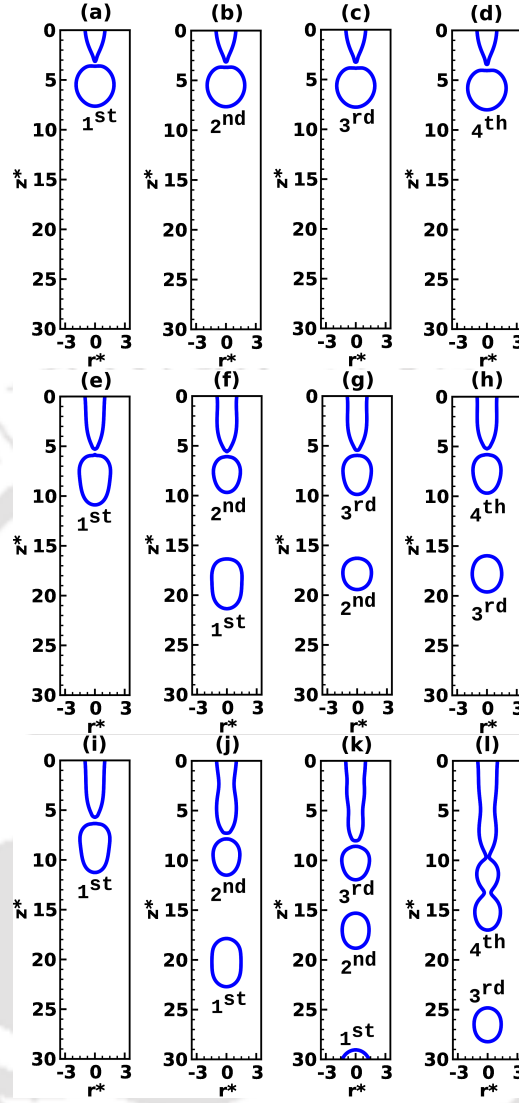


Figure 4.9: Effect of Weber number on the droplet formation process. (a)-(d) shows the drop formation for $We = 0.2$ at time $t^* = 10.90, 20.83, 30.92$ and 41.30 , respectively. (e)-(h) shows the drop formation for $We = 1.0$ at time $t^* = 11.50, 16.89, 22.22$ and 27.50 , respectively. (i)-(l) shows the drop formation for $We = 1.2$ at time $t^* = 11.05, 17.15, 21.30$ and 28.82 , respectively. Other parameters remain fixed at $Oh = 0.003$, $Bo = 0.18$, $\lambda = 0.001$ and $\eta = 0.02$.

that the jet length at breakup fluctuates with time and drop formation occurs with unequal time intervals. Axisymmetric wave like perturbations are seen developing on the surface of the liquid jet as it moves downstream. Infact this results in a big drop being disintegrated as shown in Figure 4.9 (l). The dynamics of jetting are further discussed in Section 4.4.5.

The important parameter of interest is the critical Weber number at which the system transitions from dripping to jetting regime. In order to understand the mechanistic reasons for this transition, we apply some of the scaling laws proposed by Ambravaneswaran *et al.* [12]. It was proposed that the transition can be explained in terms of the relevant characteristic time scales of the dynamics. For low Oh drops, the time scale for capillary breakup scales as $t_c \sim \sqrt{\rho R^3 / \sigma}$ whereas the time scale for flow scales as $t_f \sim R/U$. The flow time scale can also be termed as advection time scale. It is expected that the transition occurs when the advection time scale jumps the capillary breakup scale. In our present computations, parameters are fixed as $Oh = 0.003$ and $Bo = 0.18$. This gives a capillary time scale of $t_c = 4.656 \text{ ms}$, which does not vary with Weber number. However, the advection time scale varies with increasing We . For $We = 0.2$, $t_f = 10.41 \text{ ms}$, which is greater than t_c whereas for $We = 2.0$, $t_f = 3.29 \text{ ms}$, which is smaller than t_c . Thus, the transition of the system from dripping to jetting occurs as the time scale of flow t_f decreases below the capillary time scale for breakup of a given particular system. By equating the advection time scale with capillary time scale for the system of interest in our study, we obtain the critical Weber number for transition as $We \sim 1.0$, which seems to be in perfect agreement with our computational results reported herein. This criterion can hence be very useful to understand and correctly predict the system response at varying conditions of Weber numbers.

4.4.4 Viscosity driven dripping-to-jetting transition

Another class of dripping-to-jetting transition is driven by the viscous interaction of the outer ambient fluid. When the surrounding medium is filled with a viscous fluid like organic oil, the interface of the liquid column emanating from the orifice experiences a very high drag force from the ambient fluid, which tends to pull it downstream whereas the surface tension force tends to hold the liquid close to the orifice. At lower values of viscosity ratio η , the surface tension force is strong enough to maintain a dripping mode of drop formation. However, as η increases beyond a critical value, the viscous drag starts dominating and finally transitions into a long jet. The entire transition from dripping to jetting driven by viscosity of ambient medium is presented in Fig. 4.10, which to the authors knowledge has not been reported earlier.

It can be clearly observed from Figs. 4.10 (a) and (b) that when $\eta \leq 14.0$,

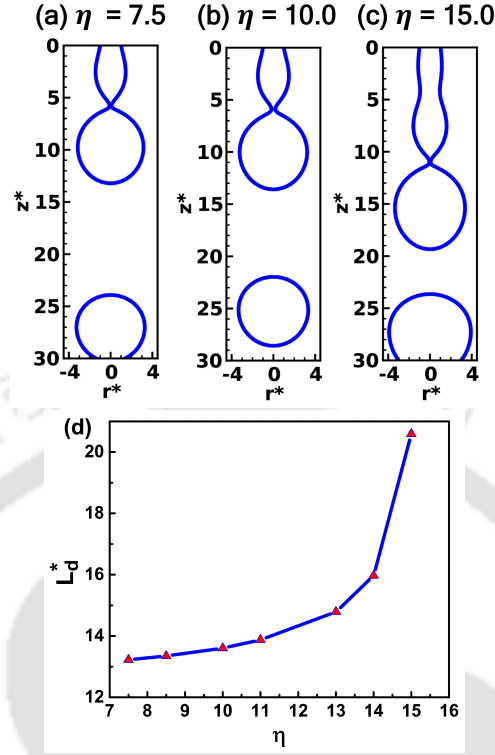


Figure 4.10: Transition from dripping to jetting regime with variation of viscosity ratio η . (a) and (b) shows the drop formation in dripping mode for $\eta = 7.5$ and 10.0 , respectively. (c) shows the jetting regime at $\eta = 15.0$ (d) shows the variation of limiting length at breakup L_d^* with increasing η . Other parameters remain fixed at $Oh = 0.02$, $Bo = 0.18$ and $\lambda = 0.74$.

the drop formation occurs in dripping mode with a small liquid neck connecting the drop to the orifice. The limiting length at breakup L_d^* shown in Fig. 4.10 (d) increases by $\sim 19\%$ when η is varied from 7.5 to 14.0 . However, as η increases from 14.0 to 15.0 , L_d^* abruptly increases by almost $\sim 30\%$ thereby signaling transition to a jetting mode. Udata *et al.* [128] studied dripping to jetting transitions in coflowing conditions using liquid-liquid systems. They demonstrated that transition to jetting mode can be triggered by increasing the flow rate of either the inner or outer fluid. The transition was thus categorized as inertia or viscosity driven similar to our observations. However, the viscosity driven transition demonstrated in our results shows an entirely different behavior from that reported in Utada *et al.* [128]. The liquid jet in their results shows a progressively thinning behavior as it moves downstream and the drops formed are comparable to the orifice diameter. In our present computations, the shape of the liquid jets in the jetting regime donot thin

as they move downstream. The drops formed are also much bigger than the orifice diameter. Although the transition occurs due to dominance of viscous effects in both our results and Utada *et al.* [128]., the effect of inertia of the ambient fluid is negligible in our case and hence the jet shows a profoundly different behavior from the previous results.

4.4.5 Jet breakup

A liquid jet emanating from a nozzle is inherently unstable and finally breaks up into small droplets to minimize its surface tension. The stability of a jet is influenced by a host of parameters such as the properties of the liquid, inflow rate and ambient conditions among others. A series of transitions occurs between different instability regimes that profoundly affect the evolution and breakup of a jet. Four major breakup regimes of jets have been established [129] and are named as Rayleigh regime, the first wind-induced regime, the second wind-induced regime, and the atomization regime. The Rayleigh instability regime [102] is initiated by the growth of small amplitude perturbations on the liquid surface leading to varicose deformation of the jet. As the inflow rate is increased, the breakup mode shifts to first wind-induced regime where the ambient medium starts interacting leading to asymmetric disturbances in the form of sinuous deformation. Further increase of inflow condition causes the formation of ligaments and smaller drops that breakup from the liquid jet. The diameters of these fragments are comparable with the jet diameter in the second wind-induced regime. Finally, transition to atomization occurs where fine drops are formed due to further breakup of ligaments and drops. These ligaments have undulated surfaces. The undulations (usually varicose) grow and breakup of the ligaments is brought about by the Rayleigh-Plateau instability mechanism entailing creation of droplets of even smaller sizes.

The present computations are performed for jet breakup in the Rayleigh mode as the axisymmetric assumption remains valid in this regime. The limiting length of the jet at breakup (L_d) serves as a convenient parameter for studying the dynamics in jetting regime. As the inflow rate is increased, L_d keeps increasing due to higher inertia of the jet. The criterion for predicting different breakup regimes have been reviewed by Chigier and Reitz [130]. It was suggested that breakup under Rayleigh

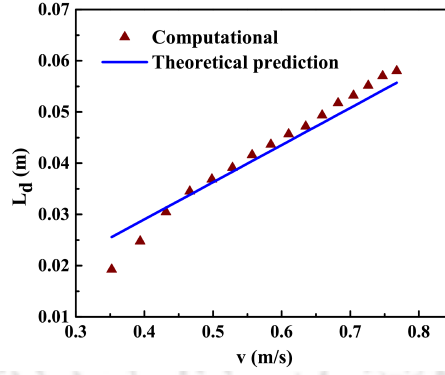


Figure 4.11: Variation of computed jet breakup length along with predictions from theory (Eqn. 4.16) as a function of inflow velocity. The breakup length show good agreement with the analytical results of Rayleigh's theory.

regime occurs when

$$We_l > 8 \text{ and } We_g < 0.4, \quad (4.14)$$

where $We_l = \rho_l v_{avg}^2 2R / \sigma$ and $We_g = \rho_g v_{avg}^2 2R / \sigma$ are the liquid and gas Weber numbers, respectively.

The pioneering work of Plateau and Rayleigh [17, 102] on jet instability can be summarized in the form of a dispersion equation that captures the dependence of growth rate of disturbance ω on the wave number k as [131]

$$\omega^2 = \frac{\sigma}{\rho_l R^3} k R \frac{I_1(kR)}{I_0(kR)} (1 - k^2 R^2) \quad (4.15)$$

Here, $I_0(kR)$ and $I_1(kR)$ are the modified Bessel functions of the first kind of zeroth and first order, respectively and R is the radius of the cylindrical jet. It can be clearly understood from Eqn. 4.15 that disturbances will amplify when the growth rate is real and positive thereby requiring $kR < 1$ and the maximum growth rate ω_{max} occurs for $kR = 0.697$. Substituting all the known parameters in Eqn. 4.15, ω_{max} comes out to be 73.016 s^{-1} . Having obtained ω_{max} , a relationship can be obtained to predict the breakup length as a function of inflow velocity as [114]

$$\begin{aligned} L &= v_{avg} t \\ t &= C / \omega_{max} \\ L &= C v_{avg} / \omega_{max} \end{aligned} \quad (4.16)$$

where L is the breakup length of jet, t is the breakup time and C is a constant defined as $C = \ln(R/a)$, a being the amplitude of perturbation applied to the interface.

In our present study, Bo and Oh are fixed at 0.18 and 0.003 while We is progressively increased by varying the inflow velocity. The breakup of the jets occurs experimentally as a result of naturally occurring perturbations. Homma *et al.* [132] reported that a source of disturbance is generated during the early stages of jet formation when the interface evolves from the initially assumed shape to a liquid column in the numerical simulations. Thus the hypothesis of Rayleigh that growth of infinitesimal disturbances leads to breakup is satisfied without any externally imposed perturbations. However the precise magnitude of this disturbance is not known. As such, a temporal sinusoidal perturbation of amplitude a and angular frequency ω was introduced in the inflow velocity. The angular frequency is obtained from Eqn. 4.15 corresponding to maximum growth rate and the amplitude a is taken as $0.005R$. The limiting length of jet at breakup L_d computed from our simulations is plotted along with the theoretical predictions from Eqn. 4.16 as a function of average inlet velocity v_{avg} and shown in Fig. 4.11. The value of constant C is found to be 5.98 from our present computations. The theoretical value of C corresponding to an externally applied perturbation of amplitude $a = 0.005R$ is 5.2, which is close to the numerically obtained value of 5.98. The constant C has an inverse relationship with the applied amplitude of disturbance. As the perturbation amplitude increases, the value of C decreases and hence the breakup length decreases. García *et al.* [133, 134] also reported that the breakup length decreases with increase in the amplitude of the disturbance, which agrees well with our current observations. It can be obviously discerned that values of L_d obtained from our computations agree well with the predictions owing to Rayleigh's theory given by Eqn. 4.16 for $v_{avg} > 0.53$ m/s, which corresponds to $We > 4.5$. It is to be noted from Eqn. 4.7 that We for our study is defined based on the orifice radius whereas in Eqn. 4.14, We has been defined based on the orifice diameter. Hence, the effective value of We_l above which good agreement with Rayleigh's theory is observed in our computations occurs at $We_l > 9$. The result matches closely with the criterion given in Eq. 4.14. Due to very small density of air, We_g remains less than 0.4 for our entire range of computations.

A snapshot is arbitrarily taken from the simulation of jet breakup under the conditions of $Oh = 0.003$, $Bo = 0.18$ and $We = 3.0$ as depicted in Fig. 4.12 (a). No

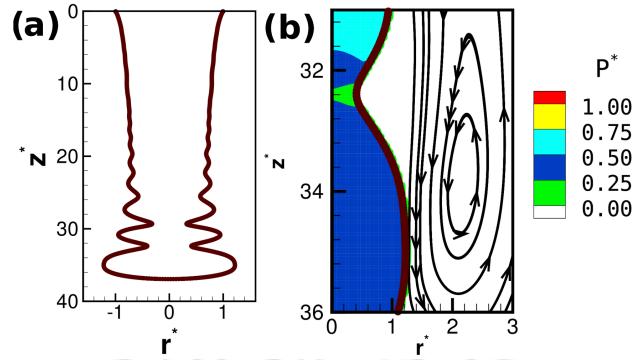


Figure 4.12: (a) Instantaneous jet radius as a function of downstream distance showing varicose undulations on its surface. The radial direction has been magnified for clear visualization of the perturbations. (b) Closeup view of the jet between $z^* = 31$ and $z^* = 36$ showing pressure contours and also streamlines in the ambient air. A vortex is seen developing just outside the jet indicating air entrainment. The relevant parameters are $We = 3.0$, $Oh = 0.003$ and $Bo = 0.18$.

external perturbations are applied in this case. Similar observations were reported by Pan and Suga [27] during simulation of jet breakup in the Rayleigh regime without applying any external perturbations. The radial coordinate has been magnified to clearly display the surface oscillations present on the liquid jet. These varicose shaped undulations emerge from upward wave propagation on the jet surface after drops pinch-off from it. It may be noted that Taylor [135] also studied waves on a fluid sheet where surface tension effects are dominant compared to gravity and aerodynamic effects. He showed that these capillary waves are of two types - symmetrical waves in which displacement of opposite surfaces are in opposite directions and antisymmetrical waves in which displacements at corresponding points of opposite surfaces are in same direction. As the inertia effects become more and more dominant with increasing We , the interaction with the ambient medium can no longer be neglected. A jet injected into quiescent air has a liquid-air interface on the surface of the column that can result in perturbations to a quasi-stable flow situation owing to aerodynamic drag, friction and flow turbulence. Figure. 4.12 (b) presents a closeup view of the jet showing the contours of nondimensional pressure P^* and also the streamlines in the ambient medium. It can be easily observed that a sharp jump of pressure exists between the outer medium and the inside of the jet. Also, a gradient of pressure exists as we move downstream towards the neck region, which facilitates drop breakup. Additionally, a closer look at the streamline plot

in the ambient air reveals a vortical structure on the side of the jet. This growing vortex signifies that the ambient air is entrained as the jet elongates downstream and this air entrainment increases with increasing We . The growing interaction of the ambient air with the liquid jet will finally cause transition from the Rayleigh regime to first wind- induced regime where sinuous waves start appearing on the jet surface thereby deviating from axisymmetric flow behavior. Hence, we limit our computations to the Rayleigh regime and the flows with higher throughput fall beyond our scope of study.

4.5 Summary

The present chapter explores the formation of drops and breakup of liquid jets from an orifice using CLSVOF method under axisymmetric conditions. The profile of the drop during the initial growth stage is shown to be self-similar. A transition is observed during the thinning of the drop neck from an inertia dominated regime to an inertia-viscous regime beyond a critical minimum radius. It is observed that interface overturning occurs when drop viscosity is low whereas it is arrested for highly viscous drops. A detailed parametric study of the overturning phenomenon reveals a critical value of Oh above which overturning stops. The transition from dripping to jetting regime has been simulated and two distinct jetting regimes has been observed depending of the dominance of inertia or viscous forces. Another class of transition occurs due to the increasing viscosity of the outer ambient fluid, which leads to higher drag force on the interface thereby leading to jetting. The jet length at breakup, computed from our simulations, corroborates the predictions from Rayleigh's theory in the jetting regime. The high inertia of the moving jet causes entrainment of ambient air resulting in a vortical structure just outside the liquid jet.

Chapter 5

Dynamics of an arched liquid jet under the influence of gravity

The formation and breakup of an arched liquid jet in air is investigated by conducting extensive three-dimensional numerical simulations. The dynamics of the jet issuing from an orifice are compared between the conditions of liquid injection in parallel and perpendicular directions to gravity. For the case of liquid injected parallel to gravity, symmetric perturbations develop on the surface of the liquid jet. In contrast, under the condition of liquid injected perpendicular to gravity, asymmetric perturbations are observed on the liquid surface, thereby deviating from the theoretical predictions of Rayleigh's analysis. The trajectory of the jet follows a parabolic path and the horizontal distance traversed is critically dependent on the value of Weber number. The horizontal distance of the liquid jet released from the same vertical height increases with increasing the value of the Weber number. Increasing the Bond number significantly increases the curvature of the jet trajectory. The detached drops from the main jet exhibit rolling motion as well as shape oscillations while migrating along their trajectories. The velocity field inside the drop have both the horizontal and vertical components, which manifest in the form of the rolling motion as well as shape oscillations of the falling drop.

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5.1 Introduction

The dynamics of a liquid jet is not only fundamentally interesting but also relevant to several industrial applications, such as ink-jet printing, particle sorting, atomization, mixing, combustion, separation and spraying technologies, to name a few [2]. A liquid jet issued from an orifice is inherently unstable due to the propagation of surface perturbations and finally culminates in the breakup leading to formation of droplets. This phenomenon is called the Rayleigh-Plateau instability [17]. The work of Plateau [17], Savart [16] and theoretical study of Rayleigh [102] provided fundamental understanding of the jet instabilities. The dynamics of a liquid jet from a vertical capillary tube or orifice has been studied extensively and many aspects of the jet formation and breakup were observed. A brief review of the literature on this subject is provided below.

The study of Rayleigh [102] was extended by Weber [136], who incorporates the influence of liquid viscosity and gas density on jet breakup. Goedde and Yuen [113] investigated the capillary instability of water-glycerine jets and found that non-linear effects dominate the jet breakup process leading to formation of ligaments and satellite droplets. Kitamura and Takahashi [137] found that nozzle characteristics can affect the breakup length of the jet occurring due to the Rayleigh instability. A set of non-linear evolution equations developed by Papageorgiou [138] to predict the appearance of satellite droplets. A simple one-dimensional model was developed by Ahmed *et al.* [139] to predict the evolution and breakup of viscous liquid jets. While most of the aforementioned studies employed circular liquid jets, the dynamics associated with elliptical-orifice liquid jets was also investigated by Kashyap *et al.* [140] and Farvardin and Dolatabadi [141].

As the liquid injection rate is increased, corresponding to different combinations of surface tension, inertia and aerodynamic interactions, four distinct breakup regimes can be observed, namely (i) the Rayleigh breakup regime (varicose perturbations), (ii) the first wind-induced breakup (sinuous perturbations), (iii) the second wind-induced breakup, and (iv) the atomization (spray) regime [129, 142–144]. In the Rayleigh breakup regime, the growth of long-wavelength, small-amplitude varicose disturbances on the liquid surface initiates the liquid breakup process. As the liquid injection rate is increased, the first wind-induced breakup regime is attained, wherein sinuous perturbations appear on the liquid surface, promoted by the interaction between the liquid and ambient gas. The detached drop sizes are of the order

of the jet diameter in the Rayleigh and first wind-induced regimes. For high-speed liquid jets, the breakup results from the unstable growth of short wavelength disturbances, namely in the second wind-induced breakup regime. The breakup starts some distance downstream of the orifice and the detached drops are smaller than the jet diameter. Further increase of injection rate leads the system into atomization regime, wherein the drop sizes are much smaller than the jet diameter. The liquid jet breakup in this regime starts at the orifice exit. The numerical simulations of liquid jets was conducted by Pan and Suga [26,27] to investigate the characteristics of breakup. The breakup length of a turbulent liquid jet was studied by Lafrance [145]. Chigier and Reitz [130] and Lin and Reitz [129] provide extensive review of this subject.

As the above review suggests, the dynamics and subsequent breakup of a liquid jet falling due to gravity vertically in a gaseous medium have been studied extensively; however, much less attention has been given to the dynamics of liquid columns injected orthogonal to gravity. The formation of curved liquid jets commonly arises when liquid is injected from a circular orifice located on the outer surface of a rapidly rotating cylindrical container. This process is known as prilling and is widely used in industry for the manufacture of fertilizers, magnesium, and aluminium pellets [146,147]. In recent years, curved slender jets have been employed in the production of nanofibres from centrifugal spinning [148–150]. The flow of liquid jets injected perpendicular or inclined to gravity also find application in water sprinklers and fountains, irrigation systems and propulsion technologies for liquid jets in cross-flow conditions [29, 151, 152]. The success of such technologies rely strongly on the precise and reliable prediction of dynamics related to the formation as well as the subsequent breakup of liquid jets curved by gravity.

Uddin and Decent [153] carried out a theoretical investigation on the instability of liquid jets injected perpendicular to gravity. They performed a linear instability analysis to explore the nature of the most unstable wavenumber and the growth rate of an infinitesimally small perturbation at the liquid surface. Suñol and González-Cinca [154] carried out an experimental investigation to capture the trajectory and breakup of liquid jets falling perpendicular to gravity. It was observed that the droplet size distribution was wider for perpendicular injection in comparison to parallel injection of a liquid jet with respect to direction of gravity. To the best of our knowledge, numerical study of the dynamics of jets injected perpendicular to gravity has not been reported in literature so far. Due to the inherently complex

and three dimensional nature, numerical simulations for such systems demand high computational cost and accuracy. A detailed analysis of the jet behaviour under parametric variations of important governing parameters has heretofore been unknown. Furthermore, understanding the underlying disparity between a liquid jet injected parallel and perpendicular to gravity requires a comprehensive comparison between the two modes of jet formation, which is still lacking in literature. In the present study, we conduct three dimensional numerical simulations to capture the dynamics of a liquid jet injected perpendicular to the direction of gravity. A comparison between the jet formation and breakup in perpendicular and parallel injections to gravity is presented in order to shed light on the underlying dissimilarity between the two systems. A parametric study is conducted by varying the dimensionless numbers associated with this problem, such as the Weber number, We and the Ohnesorge number, Oh . The effects of these dimensionless numbers on length of the jet at the breakup and jet trajectories are investigated in detail.

5.2 Formulation of the problem

5.2.1 Computational domain

The dynamics of a Newtonian liquid jet (density ρ_l and viscosity μ_l) is injected in initially quiescent air (density ρ_a and viscosity μ_a) is investigated via three-dimensional numerical simulations. The fluids are considered to be mutually immiscible and incompressible. A Cartesian coordinate system (x, y, z) with its origin at the center of the orifice is used to model the flow dynamics. The gravitational acceleration, g acts in the negative y direction. A schematic diagrams showing the computational domain for jets injected along (in negative y direction) and perpendicular (positive x direction) to gravity are shown in Fig. 5.1(a) and (b), respectively; they are termed as parallel and perpendicular injections, respectively. The main objective of the present study is to investigate the liquid jet dynamics when the jet is injected perpendicular to the gravity (Fig. 5.1(b)). The situation presented in Fig. 5.1(a) (when the jet is injected along the gravity) is considered in order to contrast the dynamics observed in both the injections. The size of the computational domain is $24D \times 12D \times 12D$, where D is the diameter of the orifice. In the case of parallel injection, the orifice is placed at the centre of the top face of the computational domain, whereas in the case of perpendicular injection, it is placed on the left side

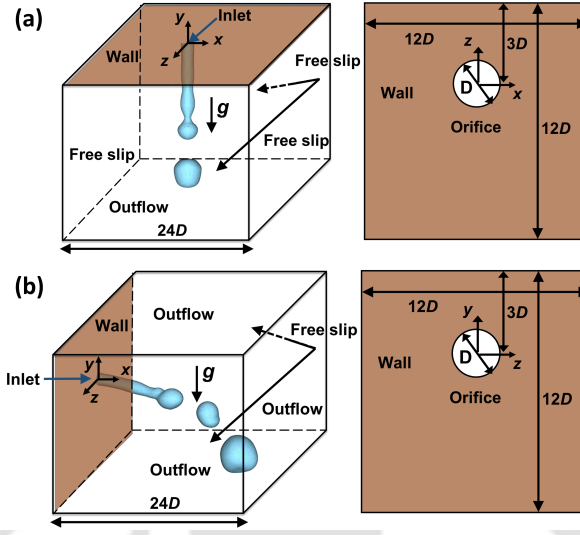


Figure 5.1: Schematic diagrams showing the computational domain (not to scale) and boundary conditions for (a) jet injected along gravity (parallel injection), and (b) jet injected in the direction perpendicular to gravity (perpendicular injection). The left panels present the front views, whereas the right panels present the top views of the computational domain for both the configurations. A fully developed flow is imposed at the orifice inlet of diameter D initialised with a hemispherical drop. The gravitational acceleration g acts along negative y direction.

wall at a distance $3D$ below the top face. The choice of the computational domain size is made by conducting a domain dependency test. It is observed that increasing the domain size in the y and z directions, does not alter the jet dynamics, such as the jet breakup length, significantly. Thus, to optimise the computational cost, we have adopted a domain of size $24D \times 12D \times 12D$ in the present study. A fully developed flow is imposed with a hemispherical drop at inlet of the orifice inlet.

A constant surface tension, σ acts at the interface separating the liquid jet and air. The boundary condition used in the numerical simulations are as follows. The flow of the liquid jet occurs in the $x - y$ plane only and hence outflow conditions are applied at the right, bottom and top faces of the computational domain. The front and back faces are maintained at a sufficiently large distance from the jet with no flow occurring in the z direction thereby allowing the usage of free slip conditions. The three phase contact line remains pinned at the sharp edge of the orifice. This is a common simplification used for simulating drop formation at an orifice and has been often used in prior literature [123, 155].

5.2.2 Numerical methods

The governing equations describing the problem considered in the present study are the continuity and the conservation of momentum equations. In order to track the interface, an advection equation for the volume fraction of the injected fluid, α is solved using the Volume-of-Fluid (VOF) approach. The governing equations, described in detail in Section. 2.2.1, are solved using an open source code *Gerris* [77]. The salient features pertaining to *Gerris* are mentioned in Section 2.3 and described extensively in ref. [77, 78].

5.2.3 Non-dimensionalisation

The governing equations are non-dimensionalized by adopting the following scaling parameters,

$$x^* = \frac{x}{D}, \quad y^* = \frac{y}{D}, \quad z^* = \frac{z}{D}, \quad \mathbf{u}^* = \frac{\mathbf{u}}{v_{avg}}, \quad P^* = \frac{P}{\rho_l v_{avg}^2}, \quad t^* = t \frac{v_{avg}}{D},$$

$$\mu^* = \frac{\mu}{\mu_l}, \quad \rho^* = \frac{\rho}{\rho_l}. \quad (5.1)$$

Here, the orifice diameter D and the average velocity of liquid at inlet $v_{avg} = 4Q/(\pi D^2)$ are used as the characteristic length and velocity scale, respectively; Q being the constant volumetric flow rate. The superscript (*) represents dimensionless quantities.

The non-dimensional parameters pertaining to the problem are the Weber number (We), the Bond number (Bo) and the Reynolds number (Re), which are given by

$$We = \frac{\rho_l v_{avg}^2 D}{\sigma}, \quad Bo = \frac{\rho_l g D^2}{\sigma}, \quad Re = \frac{\rho_l v_{avg} D}{\mu_l}. \quad (5.2)$$

The Weber number (We) signifies the importance of inertia over the surface tension force, the Bond number (Bo) highlights the importance of gravity over the surface tension force, and the Reynolds number (Re) depicts the relative importance of inertia force over viscous force. Additionally, $\lambda (\equiv \rho_a/\rho_l)$ and $\eta (\equiv \mu_a/\mu_l)$ are the density and viscosity ratios, respectively. As we consider an air-liquid system, the density and viscosity ratios are fixed at $\lambda = 10^{-3}$ and $\eta = 1.8 \times 10^{-2}$ in the present study. It is to be noted that previous studies on jet breakup in air [10, 26, 155]

considered the Ohnesorge number, which can be defined as $Oh = \sqrt{We}/Re = \mu_l/\sqrt{\rho_l D \sigma}$. Hence, for the sake of uniformity, the Ohnesorge number is used to present the results instead of the Reynolds number in the present study. Also note that all the variables, such as the jet breakup length (L_d), the volumes of the droplet (V_d) and time, used in the presentation of the results in the following sections are dimensionless.

5.3 Validation and grid convergence

We present a comparison of the results obtained using the present solver with those of Subramani *et al.* [10]. The dynamics of dripping of an incompressible Newtonian liquid drop from a vertical circular tube is considered in this test case. The values of the dimensionless parameters are $Oh = 0.75$, $Bo = 0.31$ and $We = 6.5 \times 10^{-2}$. It is to be noted that in order to facilitate comparison with the experimental observations, here alone, the dimensionless numbers are defined using the orifice radius as the characteristic length scale, instead of orifice diameter used in the present study. It can be seen that the result obtained from our simulation is in excellent agreement with that of Subramani *et al.* [10]. A quantitative comparison of the volumes of the drop after detachment (V_d) obtained from our numerical simulations for different values of the Weber number with the experimental and computational results of Subramani *et al.* [10] is presented in Fig. 5.3. It can be seen that the results from our computations agree well with the experimental observations of Subramani *et al.* [10].

We perform a grid convergence test in order to ensure that the grid resolution is appropriate. The dimensionless parameters considered for this test are $Oh = 0.13$, $Bo = 0.33$ and $We = 0.12$. The grid density near the interfacial region is increased while maintaining a relatively coarse mesh in the rest of the computational domain. In Fig. 5.4 (a), (b) and (c), the typical snapshots of the drop along with the main jet obtained using the smallest mesh size, $\Delta = 9.3 \times 10^{-2}$, 4.6×10^{-2} and 2.3×10^{-2} , respectively are shown. We found that the droplet volume V_d obtained using $\Delta = 9.3 \times 10^{-2}$ and 4.6×10^{-2} differs by 5.0%, whereas this difference is less than 1% when we compare the result obtained using $\Delta = 4.6 \times 10^{-2}$ and 2.3×10^{-2} . In view of this finding and to optimize the computational resources with solution accuracy, $\Delta = 4.6 \times 10^{-2}$ is selected to generate the rest of the results in our study.

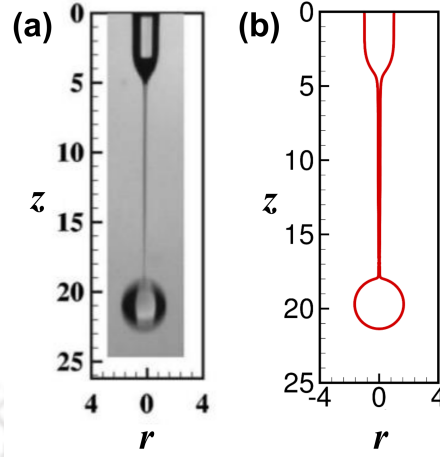


Figure 5.2: Qualitative comparison of drop formation in the dripping regime for $Oh = 0.75$, $Bo = 0.31$ and $We = 6.5 \times 10^{-2}$. (a) Experimental result of Subramani *et al.* [10], and (b) the result obtained from the present simulation.

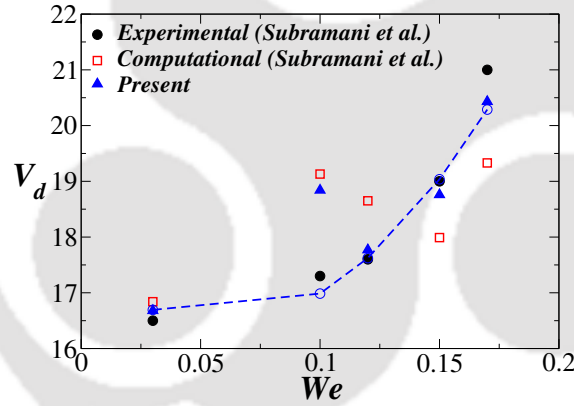


Figure 5.3: Quantitative comparison of the volumes of the drop after detachment (V_d) for different values of the Weber number (We) obtained from the present computations with those reported by Subramani *et al.* [10]. The other parameters are $Oh = 0.13$ and $Bo = 0.33$.

5.4 Results and discussion

We begin the presentation of our results by showing the contrast between the dynamics of a jet injected along and perpendicular to the direction of gravity, which are

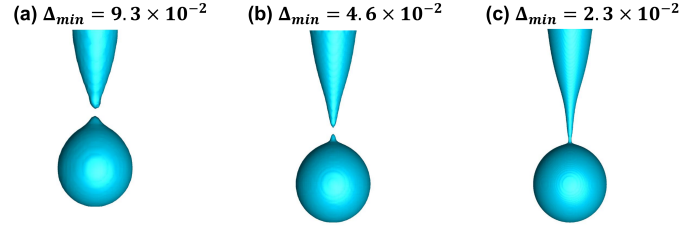


Figure 5.4: Grid convergence test showing the dripping of a drop of an incompressible Newtonian liquid from a vertical circular tube obtained using different mesh sizes, Δ_{min} . The dimensionless numbers are $Oh = 0.13$, $Bo = 0.33$ and $We = 0.12$.

termed as “parallel” and “perpendicular” injections, respectively. The evolutions of jet, breakup and subsequent droplet formation in case of parallel and perpendicular injections are shown in Fig. 5.5(a) and (b), respectively. The dimensionless parameters considered to generate these plots are $Oh = 4 \times 10^{-3}$, $Bo = 0.06$ and $We = 4.0$. The dynamics of a liquid jet in air is influenced by several parameters, namely, the fluid properties, inflow rate and the interfacial tension. As discussed in the introduction, the parallel injection jets are well studied. In this case, when the flow rate is low, small amplitude perturbations appear on the liquid surface, which grow to form the varicose deformation (commonly known as the Rayleigh mode [103]). This amplifies further and ultimately leads to pinch-off, thereby causing droplet formation. This process can be clearly seen in Fig. 5.5(a). As the jet starts to move in the downward direction (along gravity), the small amplitude disturbance can be seen at $t = 3.7$, subsequently the first varicose mode develops at $t = 8.7$. As the jet continues to elongate, at $t = 15.0$ the second varicose mode appears. At a later time, the bottom one, pinched off to form a droplet (see $t = 21.2$). The phenomena of pinch-off and breakup continues leading to the subsequent droplet formation (see the formation of second droplet at $t = 40.0$) for this set of parameters.

In case of perpendicular injection (in Fig. 5.5(b)), the prevailing symmetry is disturbed due to the influence of gravity, which is now acting orthogonal to the direction of injection. The dynamics is much more complex as compared to that of the parallel injection discussed above. For the case of parallel injection to gravity, the characteristic varicose perturbations associated with the Rayleigh instability engenders the breakup of the jet. In contrast, the perturbations developing on the jet are asymmetrical under the condition of perpendicular injection to gravity. Although the breakup occurs in the Rayleigh mode, the asymmetric nature of the

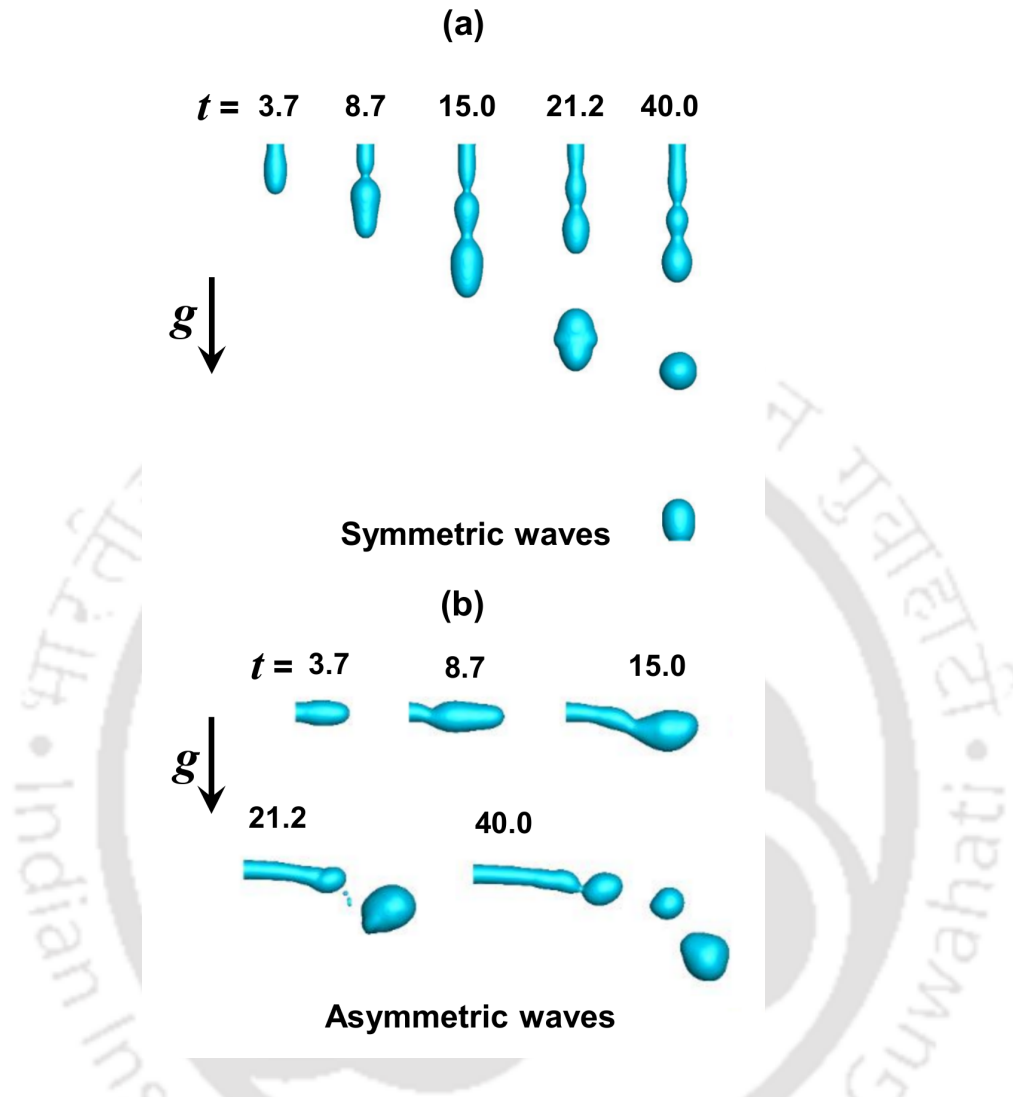


Figure 5.5: Spatiotemporal evolutions of the jet and subsequent breakup for (a) parallel injection and (b) perpendicular injection. The dimensionless parameters are $Oh = 4 \times 10^{-3}$, $Bo = 0.06$ and $We = 4.0$.

disturbances leads to fundamental differences in the breakup characteristics of the jet. The predictions of the breakup length, droplet spacing and droplet volume from Rayleigh theory are based on the assumption that the disturbances are symmetrical. Additionally, the trajectory of the jet is considered to be straight in the theoretical calculations. Due to the inherent asymmetry of the perturbations in case of perpendicular injections and the curved trajectory of the jet, the prediction obtained from the theory deviates from the actual observation. In order to get a precise estimate

of the breakup length and droplet characteristics, a three dimensional linear stability analysis can be performed to examine the exact behavior of the most unstable wavenumber and the growth rate of instabilities for a liquid jet curved by gravity. However, such a rigorous study falls beyond the scope of the present work.

For the case of perpendicular injection to gravity, the asymmetry in the jet

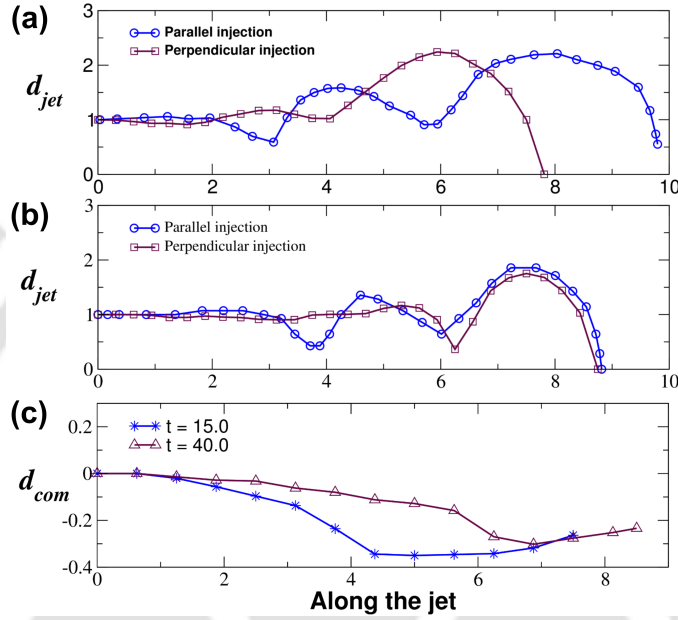


Figure 5.6: The variation of jet diameter (d_{jet}) along length for the parallel and perpendicular injections at (a) $t = 15$ and (b) $t = 40$. (c) The distance of the instantaneous center-of-mass of the jet (d_{com}) from the orifice center ($y = 0$) along the length of the jet. The results corresponds to the case of perpendicular injection for time instances $t = 15.0$ and 40.0 . The negative value of d_{com} indicates that the jet center-of-mass lies below the orifice center ($y = 0.0$) along the length of the jet. The rest of the dimensionless parameters are $Oh = 4 \times 10^{-3}$, $Bo = 0.06$ and $We = 4.0$.

is visible even at an early time ($t = 3.7$), which increases faster (as gravity starts to dominate) and a curved jet is clearly seen at $t = 8.7$ for this set of parameters. Due to the effect of gravity, the jet trajectory is curved, i.e. the jet bends in the downward direction. In contrast to the parallel injection (Fig. 5.5(a)), the droplets are released in an aperiodic manner. The variation of jet diameter along length for the parallel and perpendicular injections at $t = 15.0$ and $t = 40.0$ are shown in Fig. 5.6(a) and (b), respectively. Inspection of these figures also reveals that the pinch-up occurs early, and the size of the released droplets are smaller in the case

of perpendicular injection as compared to those in the parallel injection. Figure 5.6 (c) presents the distance of the instantaneous center-of-mass of the jet (d_{com}) from the orifice center ($y = 0.0$) along the length of the jet. The plot corresponds to the case of perpendicular injection for time instances $t = 15.0$ and 40.0 . It can be observed that the center-of-mass of the jet lies below the orifice center as indicated by negative values of d_{com} along the length of the jet. However, the trend of d_{com} is non-monotonic due to the presence of asymmetric perturbations on the jet surface. It is to be noted that for the case of parallel injection to gravity, the center-of-mass always lies along the orifice axis ($d_{com} = 0.0$) as the perturbations are symmetric in nature (varicose) under such conditions.

5.4.1 Jet breakup length

The jet breakup length, L_d is defined as the length of the jet from the orifice to the pinch-off location. This is an important parameter in the study of the jet dynamics. As the jet breakup length is dependent on both the inertia (inflow rate) as well as the viscosity of the liquid jet, in this section, we investigate the effects of the Weber number (We) and the Ohnesorge number (Oh) on the jet dynamics. The variations of L_d with We and Oh are shown in Fig. 5.7(a) and (b), respectively.

First, we discuss the influence of inertia or inflow rate. By increasing the inflow rate, i.e. the value of We is increased and the simulations are performed by keeping the rest of the dimensionless parameters fixed at $Oh = 4 \times 10^{-3}$ and $Bo = 0.06$. The results are compared between the conditions of parallel and perpendicular injection to gravity. In Fig. 5.7(a), it can be seen that with the increase in the value of We , the jet breakup length, L_d increases for both the cases of parallel and perpendicular injection to gravity. This is due to the increase in momentum (as We increases), which allows the jet to traverse a larger horizontal distance before undergoing breakup due to Rayleigh-Plateau instability. The breakup times indicated on the Fig. 5.7(a) demonstrate that the jet breakup occurs earlier at higher We for both systems under consideration. The jet breakup is highly accelerated with increase in We for the case of parallel injection as depicted by the significantly smaller breakup times. This can be attributed to the fact that the inertia and gravity are perfectly aligned (downwards) under the condition of parallel injection and act to destabilize the jet leading to early breakup. However, under the condition of perpendicular injection, inertia and gravity are not aligned (act perpendicular to each

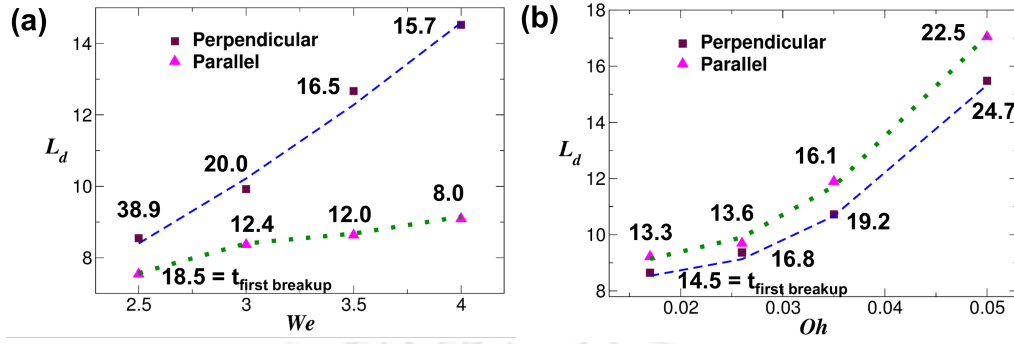


Figure 5.7: (a) The jet breakup length, L_d versus Weber number (We) for both perpendicular and parallel injection to gravity under the conditions of $Oh = 4 \times 10^{-3}$ and $Bo = 0.06$. The dashed lines represent best fitted curves given by $L_d = 2.9 + We + 0.4 We^2$ and $L_d = -31.1 + 34.5 We - 10.1 We^2 + We^3$ for perpendicular and parallel injection, respectively. (b) The jet breakup length, L_d versus Ohnesorge number (Oh) for both perpendicular and parallel injection to gravity under the conditions of $We = 4$ and $Bo = 0.06$. The dashed lines represent best fitted curves given by $L_d = 10 - 1.8 \times 10^2 Oh + 5.8 \times 10^3 Oh^2$ and $L_d = 10.5 - 1.9 \times 10^2 Oh + 6.4 \times 10^3 Oh^2$ for perpendicular and parallel injection, respectively. The time at which the first breakup occurs are also shown.

other). Nonetheless, the resultant effect destabilizes the jet, albeit in a diminished way, as demonstrated by the longer breakup times for perpendicular injection. The longer breakup time for perpendicular injection enables the jet to traverse a larger distance before breakup thereby leading to higher magnitude of L_d in comparison to parallel injection. By conducting a linear stability analysis, Biswas *et al.* [110] showed that for large values of Weber number defined based on the ambient fluid, a liquid sheet breaks down due to the unstable axisymmetric disturbance. In the case of parallel injection, Chigier and Reitz [130] suggested that the Weber number, We_o , with respect to the ambient fluid, defined as $We_o = \rho_a v_{avg}^2 D / \sigma$ should be less than 0.4 for the breakup to occur in the Rayleigh regime. In the present study, due to the low density of the surrounding fluid (air) as compared to the jet fluid, We_o for breakup remains much less than 0.4. The asymmetric deformation on the jet surface observed in case of the perpendicular injection provides a qualitatively different picture from that of varicose deformation observed in the case of the parallel injection in the Rayleigh regime.

It is to be noted that changing the magnitude of We modulates both the surface tension term and the gravitational term in the governing equations (Section.

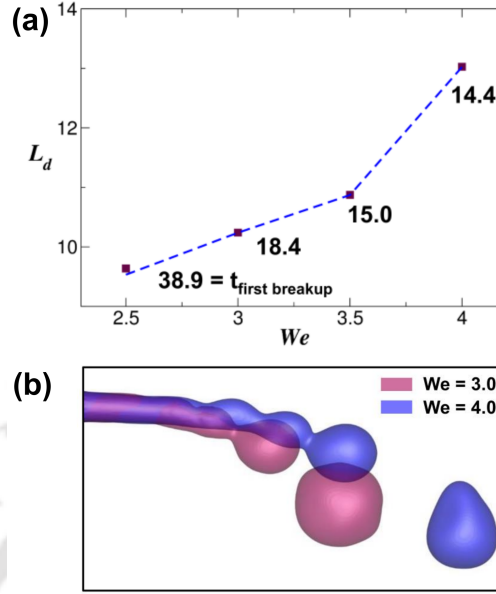


Figure 5.8: (a) The jet breakup length, L_d versus Weber number (We) for perpendicular injection to gravity under the conditions of $Oh = 4 \times 10^{-3}$ and $Fr = 6.4$. The dashed lines represent a best fitted curve given by $L_d = -45.0 + 54.0 We - 17.8 We^2 + 1.9 We^3$. The time at which the first breakup occurs are also shown. (b) Instantaneous snapshots showing the the jet profile for $We = 3.0$ and 4.0 keeping Fr fixed at 6.4 .

2.2.1). The Froude number, Fr , denotes the relative importance of inertia force over gravitational force and is defined as $Fr = \frac{V}{\sqrt{gD}} = \sqrt{\frac{We}{Bo}}$. In order to isolate the influence of inertia from the effect of gravitational force during the variation of We , we perform additional simulations by increasing We keeping Fr fixed at 6.4 . The results from the computations are presented in Fig. 5.8 (a) and (b). It can be clearly observed that as We is increased, the jet traverses a longer distance before undergoing breakup. This can be attributed to the fact that at higher We , the influence of inertia dominates over the surface tension force, while the gravitational force is held constant for fixed Fr . The higher inertia enables the jet to migrate across a larger horizontal distance with increasing We . The breakup length monotonously increases while the jet breakup is accelerated as the magnitude of We is increased, keeping Fr fixed at 6.4 .

Next we discuss the effect of the viscosity of the liquid jet, which is varied via the Ohnesorge number (Oh) in our computations. In other words, increasing the value of Oh signifies the intensity of dominance of viscous force over the inertia and

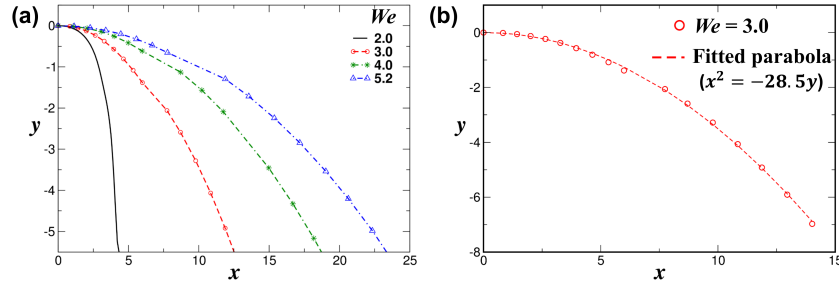


Figure 5.9: (a) The jet trajectories obtained for different values of the Weber number, We . The rest of the dimensionless parameters are $Oh = 4 \times 10^{-3}$ and $Bo = 0.06$. (b) A curve fitted to the trajectory corresponding to $We = 3.0$ showing the parabolic nature of the path traversed by the jet as given by $x^2 = -28.5y$.

the surface tension forces. In Fig. 5.7(b), the variation of the jet breakup length, L_d versus Oh is shown for both parallel and perpendicular injection to gravity under the conditions of $We = 4.0$ and $Bo = 0.06$. It can be seen that increasing the value of Oh increases the length of the liquid jet, thereby increasing the value of L_d for both the systems under consideration. Thus, we can conclude that the breakup phenomenon is delayed as the value of Oh is increased. As discussed above, this can also be observed from the first breakup times shown in Fig 5.7 (b). This behaviour can be explained as follows. As the inertia of the liquid jet is constant (which is ensured by fixing the value of We), increasing the value of Oh (increasing the liquid viscosity) increases viscous dissipation, which suppresses the developing perturbations (short waves) on the jet surface, thereby increasing the wavelength of the resulting deformation. For high Oh , the effect of surface tension force is minimum, which in turn allows the jet to travel a long distance before undergoing breakup to form droplets.

5.4.2 Jet trajectory

In the case of perpendicular injection, due to the influence of gravity the liquid jet follows a parabolic trajectory (path followed by the tip of the jet). In Fig. 5.9 (a), we investigate the effect of We on the jet trajectory with the rest of the dimensionless numbers fixed at $Oh = 4 \times 10^{-3}$ and $Bo = 0.06$. The liquid jet is injected from the same vertical height (at $y = 0.0$) for all the cases. The nature of the trajectory followed by the jet is characterized by fitting a polynomial to the trajectory at

$We = 3.0$ as shown in Fig. 5.9 (b). The equation of the curve from the polynomial fitting comes out to be $x^2 = -28.5y$ thereby confirming the parabolic nature of the trajectory. It can be seen that the Weber number significantly influences the jet trajectory. Increasing the value of We (inflow rate) increases the horizontal distance covered by the jet. For low value of We (see the trajectory for $We = 2.0$ in Fig. 5.9), the jet travels a short distance in the horizontal direction, before falling almost in the vertical direction (as in case of the parallel injection). The inertia force is not strong enough to significantly alter the jet trajectory resulting in an almost vertical trajectory. As We is increased, the inertia starts to dominate over the surface tension force, resulting in a larger distance being covered in the horizontal direction. As expected, this finding reveals that inertia plays a critical role in the jet dynamics and its trajectory.

There are three dominating forces (inertia, gravitational and surface tension),

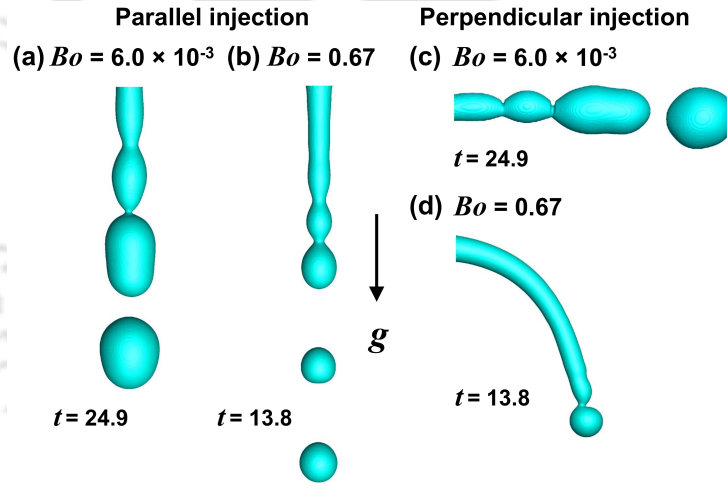


Figure 5.10: Temporal snapshots showing the effect of Bond number on the jet trajectories. (a) and (b) correspond to the condition of parallel injection with $Bo = 6 \times 10^{-3}$ and 0.67 , respectively. (c) and (d) correspond to the condition of perpendicular injection with $Bo = 6 \times 10^{-3}$ and 0.67 , respectively. The rest of the dimensionless parameters are $Oh = 4 \times 10^{-3}$ and $We = 3.0$.

which influence the dynamics of jet via its trajectory and breakup. We investigated the effect of inertia over surface tension force by keeping the rest of the parameters fixed in Fig. 5.9. Next, we discuss the effect of Bond number on the jet dynamics. The effect of Bo on the jet trajectory for $Oh = 4 \times 10^{-3}$ and $We = 3.0$ is investigated in Fig. 5.10 for both the case of perpendicular and parallel injection. For a fixed

value of We and for the same pair of fluids as considered in the present study, increasing Bo signifies the increase in the influence of the gravitational force over the surface tension force. In the case of parallel injection as shown in Fig. 5.10 (a) and (b), the trajectory of the jet is aligned with the direction of gravity. The increasing magnitude of Bo manifests in the form of a higher body force, which tries to pull the jet in the downwards direction thereby accelerating the breakup of the jet. As a consequence of the earlier pinch-off at higher Bo , the volume of the drops formed become smaller with increasing Bo . However, under the condition of perpendicular injection, the magnitude of Bo dictates both the volume of the drops formed as well as the curvature of the trajectory. The gravitational pull on the jet acts perpendicularly in the downwards direction. For $Bo = 6 \times 10^{-3}$ (see Fig. 5.10 (c)), the influence of the downwards pull of gravity is less and hence the curvature of the trajectory is less. In contrast, for higher value of Bo (see Fig. 5.10 (d)), the jet trajectory becomes significantly curved under the influence of higher gravitational force.

5.4.3 Drop oscillations

The jet breakup leads to the formation of droplets. In case of perpendicular injection, the detached droplets from the jet show random shape oscillations (mostly asymmetrical) as they migrate in the surrounding air (see Fig. 5.11). Moreover, it is also observed that these droplets roll about the horizontal axis. The complex motion of a detached droplet is shown in the supplemental video 1. In order to understand this phenomenon, the flow fields inside the detached droplets for parallel and perpendicular injections are depicted in Fig. 5.12 (a) and (b), respectively. The flow field inside the droplet under parallel injection remains symmetrical about the vertical axis, whereas, the velocity field becomes asymmetrical in case perpendicular injection. We observed that the magnitude of the horizontal velocity component (u) is significantly greater in case of the perpendicular injection as compared to the parallel injection. This imparts a rolling motion to the droplet in case of perpendicular injection, while the droplet undergoes asymmetrical shape oscillations during the migration along its trajectory.

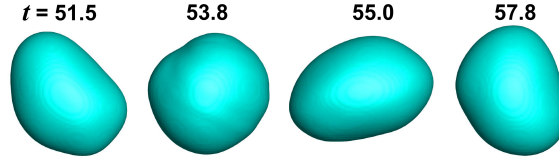


Figure 5.11: Evolutions of the shape of a detached droplet from the main jet for $Oh = 4 \times 10^{-3}$, $Bo = 0.06$ and $We = 4.0$.

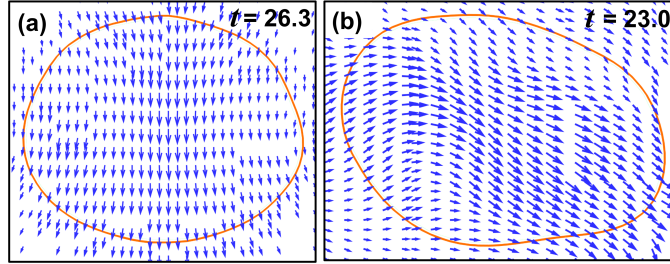


Figure 5.12: The velocity fields inside the detached droplets from the main liquid jets. (a) Parallel injection (at $t = 26.3$), and (b) perpendicular injection (at $t = 23$). The parameters are $Oh = 4 \times 10^{-3}$, $Bo = 0.07$ and $We = 5.0$.

5.4.4 Transition to wind induced regime

The dynamics discussed so far in this study (small We) falls under the Rayleigh regime. As the flow rate is increased significantly (for very high We), the jet dynamics enters into another regime, known as wind-induced regime. In this regime, the aerodynamic interaction with the surrounding medium (air) becomes important. In order to understand the jet dynamics, we conduct numerical simulation for $We = 6 \times 10^2$, $Oh = 4 \times 10^{-3}$ and $Bo = 0.06$. The spatio-temporal evolution of the liquid jet is presented in Fig. 5.13. For this set of parameters, it can be seen that a jet with a neck develops at $t = 3.0$. The deformation becomes asymmetrical and the neck becomes thinner at a later time, $t = 7.0$. A Kelvin-Helmholtz type instability (screw pattern) appears and the jet disintegrates into small droplets (much smaller than the jet diameter) near the jet tip at $t = 16.0$. A similar instability pattern was observed by Redapangu *et al.* [156,157] in case of a displacement flow of one fluid by another immiscible fluid in a three-dimensional channel. The breakup observed in this regime is thought to be due to the unstable growth of short wavelength waves. In this case, as the inertia is the most dominant force as compared to the gravitational

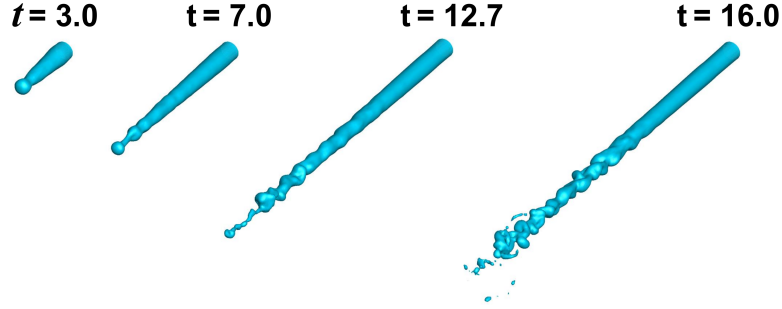


Figure 5.13: Spatiotemporal evolutions of the jet in the wind-induced regime. The dimensionless parameters used are $We = 6 \times 10^2$, $Oh = 4 \times 10^{-3}$ and $Bo = 0.06$.

force, the jet travels in the straight horizontal direction till its breakup. Herrmann and co-workers [158–160] and Kim *et al.* [161] conducted extensive studies on the primary atomization of jets in coaxial and crossflow configurations. In contrast, the dynamics reported in the present study corresponds to the low inflow (gravity dominated) Rayleigh regime. Also in our study the surrounding medium (air) is considered to be initially quiescent. In future, the present study can be extended to get more insight into the breakup modes in the wind-induced and atomization regimes.

5.5 Summary

The formation and breakup phenomena of a liquid jet injected parallel and perpendicular to the direction of gravity are investigated via three-dimensional numerical simulations. The study uncovers that the surface perturbations appearing on the liquid jet surface due to the interfacial instability are symmetrical in nature for the case of the liquid injected parallel to gravity. In contrast, the perturbations on the interface becomes asymmetrical when liquid is injected perpendicular to gravity. The jet exhibits a parabolic trajectory and the length of the horizontal distance traversed increases with increase in the Weber number. The jet breakup length is dependent on the magnitude of the Weber number and Ohnesorge number. The detached droplets undergo rolling motion along with the asymmetrical shape oscillations. The asymmetry of the velocity field inside the droplet is responsible for the rolling motion observed in the present study.



Chapter 6

Dynamics of drop formation from submerged orifices under the influence of an electric field

The influence of an external electric field on the dynamics of drops formed at the orifice inside a quiescent pool of another liquid are explored by conducting electrohydrodynamic simulations. The simulations reveal that only prolate shaped drops are formed in the case of perfect dielectric fluids. In contrast, for leaky dielectric fluids, the drops formed can be either prolate or oblate in nature depending on the relative combination of the electrical permittivity and conductivity of the fluids. The deformation, breakup time and volume of the drops formed can be effectively tuned by varying the applied electric field strength. The local electric field intensity inside the drop is significantly altered due to the permittivity contrast between the fluids. The nature of the electric forces acting at the interface plays a crucial role in deciding the dynamics of formation as well as breakup of the droplets. The flow behavior inside the droplet is decided by the combination of the electrical conductivity and permittivity ratios of the fluids under the influence of the applied electric field.

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6.1 Introduction

The formation and breakup of drops in immiscible liquid-liquid systems is a ubiquitous phenomenon with widespread applications in pharmaceutical, chemical and food processing industries [162–164]. A host of technologies involve formation of a liquid drop from a nozzle or orifice in a pool of another immiscible liquid; for example, extraction, coating, separation and emulsification processes [155, 165]. The generation of drops in immiscible liquid-liquid systems has been studied extensively in recent literature [166–168]. The imposition of an external electric field provides a tunable and facile way of controlling the motion, deformation and breakup of the fluid interfaces [30–32, 169–171]. The addition of the electro-hydrodynamic (EHD) force due to the applied electric field enables active control over the interfacial dynamics and has shown promising potential for several applications, such as electro-hydrodynamic atomization [35, 172], enhanced coalescence and demixing in emulsions [173], ink-jet printing [34], electrowetting [174], sorting and separation technologies [175–177], to name a few.

The formation of drops from vertical tubes or capillaries in the presence of an electric field has been studied experimentally and computationally by previous researchers. The equilibrium shapes and stability of pendant drops in an electric field was studied by Joffre *et al.* [178] and later by Basaran and Scriven [179]. Harris and Basaran [180] studied the behavior of both conducting and non-conducting pendant drops from a metal capillary in the presence of an electric field. The transition from dripping to EHD jetting for a pendant drop under low values of flow rate and electric field strength was investigated by Cloupeau and Prunet-Foch [181]. Sato [165] demonstrated the controlled production of monodispersed droplets issuing from an electrified jet. Zhang and Basaran [182] carried out experimental investigations of the influence of an axial electric field on drop formation in the dripping regime. A number of theoretical attempts to study the dynamics of drop formation with electric field were made by Vu and Carlson [183], Byers and Perona [184] and Grigor'ev *et al.* [185] by employing approximate expressions based on macroscopic balances of the relevant forces acting on the drop. The influence of electric field on the dynamics of a perfectly conducting drop surrounded by insulating air was explored by Notz and Basaran [186]. Weidner [187] studied the drop formation using magnetic fluids in the presence of an axial electric current. Cavalli *et al.* [188] performed experimental as well as numerical investigations to shed light on the detachment of

liquid drops through electrical actuation. A recent study by Hokmabad *et al.* [169] demonstrated that the liquid jet is deflected under the application of a transverse electric field, which in turn affects the breakup behaviour of the jet.

There are relatively few studies on the drop growth from a submerged orifice under the influence of an externally applied electric field. Sato [165] performed extensive experiments to study the formation of drops of kerosene, benzene and n-hexane in distilled water under the effect of an alternating electric field. He *et al.* [189] observed that the drop volume and velocity after detachment are significantly influenced by the applied electric field for distilled water drops injected into viscous oil. The presence of the surrounding liquid medium, as opposed to an insulating gaseous medium considered in most previous studies, fundamentally alters the dynamics of the drop formation and breakup process. Recently, Sharma *et al.* [30] and Timung *et al.* [190] studied the formation of oil droplets in water inside a “T” shaped microchannel and demonstrated that the size, shape and frequency of the droplets can be effectively tuned by varying the relevant parameters pertaining to the electric field.

In the present study, we perform numerical investigations to explore the dynamics of droplet formation under the influence of an externally applied electric field for pairs of dielectric and leaky dielectric fluids. A fluid medium is considered to be perfect dielectric when the presence of free charge carriers is neglected. In contrast, if the presence of small but finite amount of free charges are considered, such fluids are categorized as leaky dielectric fluids. Our study elucidates the contrasting dynamics of drop formation for dielectric and leaky dielectric fluids by conducting a host of numerical simulations for both classes of fluids under consideration. We first present detailed investigations of drop formation considering the fluids to be perfect dielectrics. Subsequently, the fluids are regarded as leaky dielectrics and the dynamics of the drop formation process are investigated over a wide range of pertinent input parameters.

6.2 Formulation of the problem

6.2.1 Computational domain

A representative diagram of the computational domain adopted for the present study is shown in Fig. 6.1. The drop fluid is introduced through an orifice of radius R_o

on a horizontal wall at a constant flow rate $\dot{Q}_d$ into a pool of another quiescent liquid. The fluids are considered Newtonian, incompressible and immiscible and the interface separating the fluids has surface tension γ , which is assumed to be spatially uniform and constant with time. The dynamics of the problem are considered to be axisymmetric and a cylindrical coordinate system (r, z) is adopted, where r and z are the radial and axial coordinates, respectively. The center of the orifice is selected as the origin of the coordinate system and gravity (g) acts in the direction of the z axis. The computational domain is taken as $L = 16R_o$ in the radial direction and $H = 48R_o$ in the axial direction. The size of the computational domain is determined keeping in mind previous studies on drop and bubble formation under electric field [186, 191, 192]. Also, we have explored with different domain sizes

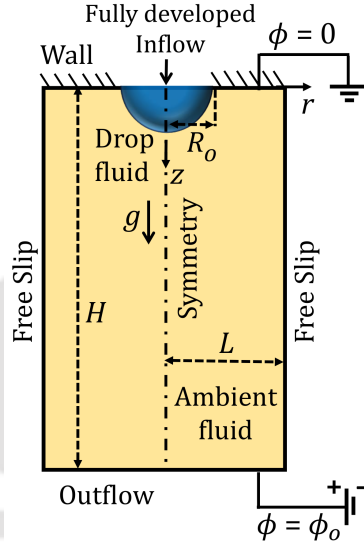


Figure 6.1: Schematic diagram (not to scale) showing the computational domain and boundary conditions in axisymmetric cylindrical coordinate system (r, z) . A parabolic flow is imposed at the orifice inlet initialized with a hemispherical droplet and submerged in a pool of another quiescent liquid. Gravity acts along the positive z axis. An electric field is applied by maintaining the lower boundary at a constant electric potential whereas the upper boundary is grounded.

and found the dynamics to be insensitive to any further increase in the domain size. An electric field is applied by maintaining the lower boundary at a constant electric potential whereas the upper wall is grounded. The orifice wall is considered to be perfectly non-wetting. The three-phase contact circle where the drop base, surrounding fluid and orifice rim meet, remains pinned to the sharp edge of the

orifice. This is a common simplification used by many previous studies on drop formation from orifices [155, 191].

6.2.2 Governing equations

The hydrodynamics are governed by the incompressible Navier-Stokes and continuity equations and an EHD model is used to describe the electric field effects. The governing equations of the problem are,

$$\nabla \cdot \mathbf{V} = 0, \quad (6.1)$$

$$\rho \left[\frac{\partial \mathbf{V}}{\partial t} + (\mathbf{V} \cdot \nabla) \mathbf{V} \right] = -\nabla p + \nabla \cdot [\mu(\nabla \mathbf{V} + \nabla \mathbf{V}^T)] + \gamma \kappa \mathbf{n} \delta + \rho \mathbf{g} + \mathbf{F}_e, \quad (6.2)$$

$$\frac{\partial \alpha}{\partial t} + \nabla \cdot (\mathbf{V} \alpha) = 0, \quad (6.3)$$

where $\mathbf{V} = (u, v)$ represents the velocity field. The pressure is denoted by p and α represents the drop liquid fraction with values of 1 and 0 inside the drop and surrounding fluid, respectively. The effect of surface tension γ is incorporated into the momentum equations employing the continuum surface force (CSF) model of Brackbill *et al.* [71], where κ is the curvature of the interface given as $\kappa = -\nabla \cdot \mathbf{n}$ wherein $\mathbf{n}$ is the unit normal to the interface. The gravitational acceleration is given by $\mathbf{g} = (0, g)$ and $\mathbf{F}_e$ denotes the volumetric electric force due to the application of the electric field.

The Gauss law of electrodynamics can be written in terms of the electric displacement ($\mathbf{D} = \epsilon \mathbf{E}$) as $\nabla \cdot \mathbf{D} = \nabla \cdot (\epsilon \mathbf{E}) = q$. Here ϵ and q represent the absolute permittivity of the fluid and the volume density of free charges inside the domain, respectively. Also, the irrotational ($\nabla \times \mathbf{E} = 0$) electric field $\mathbf{E}$ can be expressed in terms of the electric potential ϕ as $\mathbf{E} = -\nabla \phi$. Hence, Gauss law can be rewritten in terms of electric potential as $\nabla \cdot (\epsilon \nabla \phi) = q$. The charge conservation equation for volumetric charge density is given as,

$$\frac{\partial q}{\partial t} + \nabla \cdot (q \mathbf{V}) = -\nabla \cdot (\sigma \mathbf{E}). \quad (6.4)$$

Here, σ represents the electrical conductivity of the fluids. In perfect dielectrics, no free charge carriers exist and the Gauss law simplifies to $\nabla \cdot (\epsilon \mathbf{E}) = \nabla \cdot (\epsilon \nabla \phi) = 0$. For leaky dielectric fluids, the electrical relaxation time scale is smaller than the

time scale of fluid motion and hence the charge accumulates at the interface almost instantaneously. Hence, Eq. 6.4 can be simplified with a quasi-static assumption and expressed as $\partial q/\partial t = -\nabla \cdot (\sigma \mathbf{E}) = \nabla \cdot (\sigma \nabla \phi)$. The Maxwell stress tensor ($\mathbf{M}$) is a symmetric second-order tensor used to represent the interaction between electromagnetic forces and mechanical momentum. The definition of $\mathbf{M}$ is given as, $\mathbf{M} = \epsilon[\mathbf{E} \otimes \mathbf{E} - \frac{1}{2}(\mathbf{E} \cdot \mathbf{E})\mathbf{I}]$. Hence, the electrostatic force ($\mathbf{F}_e$) acting on the fluids for the perfect dielectric assumption can be written as,

$$\mathbf{F}_e = \nabla \cdot \mathbf{M} = -\frac{1}{2}\mathbf{E} \cdot \mathbf{E} \nabla \epsilon, \quad (6.5)$$

and for the leaky dielectric assumption can be written as,

$$\mathbf{F}_e = \nabla \cdot \mathbf{M} = -\frac{1}{2}\mathbf{E} \cdot \mathbf{E} \nabla \epsilon + q\mathbf{E}. \quad (6.6)$$

The fluid properties are volume averaged as,

$$\begin{aligned} \rho &= \rho_d \alpha + \rho_s (1 - \alpha), \\ \mu &= \mu_d \alpha + \mu_s (1 - \alpha), \\ \epsilon &= \epsilon_d \alpha + \epsilon_s (1 - \alpha), \\ \sigma &= \sigma_d \alpha + \sigma_s (1 - \alpha). \end{aligned} \quad (6.7)$$

where subscripts d and s refer to the drop and surrounding fluid, respectively.

6.2.3 Initial and boundary conditions

To solve the governing equations, the following initial and boundary conditions are implemented. The simulations are initialized by placing a hemispherical drop of radius R_o at the orifice and both the drop and surrounding fluids are considered to be initially quiescent. At the orifice inlet, a parabolic velocity profile is imposed satisfying the conditions of the desired injection rate. No-slip and no penetration conditions are imposed at the horizontal wall ($z = 0$) and outflow conditions are prescribed at the lower boundary ($z = H$). The horizontal wall is considered to be perfectly non-wetting with liquid fraction $\alpha = 0$ at the wall surface. Additionally, the lower boundary is set at a constant electric potential ($\phi = \phi_o$) whereas the upper boundary is grounded ($\phi = 0$). The left boundary of the computational domain

($r = 0$) is considered to be the axis of symmetry, whereas free-slip conditions are applied at the right boundary, i.e. $v = 0$, $\frac{\partial u}{\partial r} = 0$, $\frac{\partial p}{\partial r} = 0$ and $\frac{\partial \phi}{\partial r} = 0$ at $r = L$.

6.2.4 Scaling

The results from the numerical simulations are presented in terms of dimensionless parameters. Lengths are scaled by the orifice radius R_o , velocities by the average velocity of injection $v_{avg} = \dot{Q}_d / \pi R_o^2$ and time by R_o / v_{avg} . The material properties of the drop fluid are taken as reference values. This leads to the following non-dimensional groups describing the flow,

$$Re = \frac{\rho_d v_{avg} R_o}{\mu_d}, We = \frac{\rho_d v_{avg}^2 R_o}{\gamma}, Bo = \frac{\rho_d g R_o^2}{\gamma}, Re_E = \frac{\epsilon_d v_{avg}}{\sigma_d R_o}, \eta = \frac{\rho_s}{\rho_d}, \lambda = \frac{\mu_s}{\mu_d},$$

$$S = \frac{\epsilon_s}{\epsilon_d}, R = \frac{\sigma_s}{\sigma_d}, E^* = \frac{E}{v_{avg} \sqrt{\rho_d / \epsilon_d}}. \quad (6.8)$$

The parameters in Eqn. 6.8 correspond to Reynolds number, Weber number, Bond number, electric Reynolds number, density, viscosity, permittivity and conductivity ratios and a dimensionless electric field, respectively. Here, $E_c = v_{avg} \sqrt{\rho_d / \epsilon_d}$ is the characteristic scale for electric field strength. The seemingly uncommon scaling for electric field is motivated by numerical work such that the dimensionless parameter associated with the Maxwell stresses is unity [193]. The associated scaling for electric potential $\phi^* = \frac{\phi}{v_{avg} L} \sqrt{\frac{\epsilon_d}{\rho_d}}$ and charge $q^* = \frac{qL}{\sqrt{\rho_d v_{avg}^2 \epsilon_d}}$ are established due to the choice of the electric field scale parameter. The asterisk (*) represents dimensionless variables. For the sake of convenience, E^* is represented as E , ϕ^* as ϕ and q^* as q for the rest of the paper and denotes the dimensionless values of the field strength, electric potential and charge, respectively.

6.2.5 Numerical methods

The governing equations, described in detail in Section. 6.2.2, are solved using an open source code *Gerris* [77]. The salient features pertaining to *Gerris* are mentioned in Section 2.3 and described extensively in ref. [77, 78]. We also utilize the EHD toolbox available in the code architecture in order to model the influence of the applied electric field. The execution time is also greatly accelerated by the implementation of a parallelized framework and efficient processor load control. We

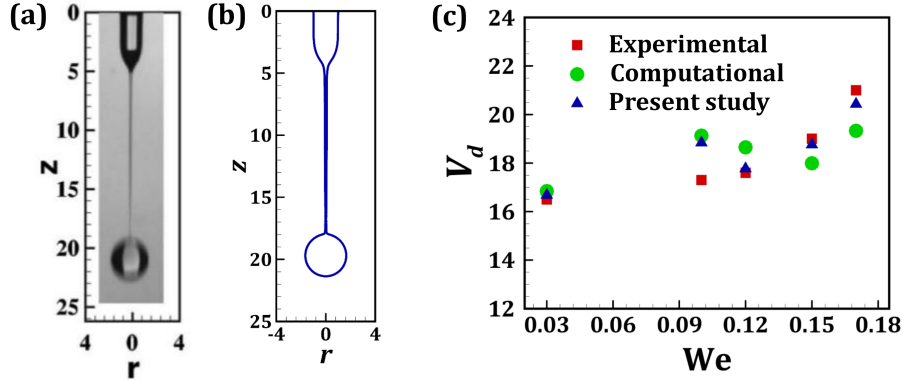


Figure 6.2: (a) Qualitative comparison of drop formation between the (a) experimental results of Subramani *et al.* [10] and (b) present computations, under conditions of $We = 0.065$, $Bo = 0.31$ and $Re = 0.34$. (c) Quantitative comparison of the volumes of the drop after detachment (V_d) for different values of We obtained from the present computations with those reported by Subramani *et al.* [10].

consider the selected solver to be the ideal choice for our model by customizing the code to include all requisite components of a well-designed multi-phase EHD platform. The solver has been used earlier by the researchers for simulating a wide range of complex fluid flow problems [32, 193, 194].

6.3 Validation of the solver

The numerical methodology adopted in this study is thoroughly validated by comparing our results with previous investigations. Figures 6.2 (a) and (b) presents a comparison of the drop shape at the incipience of breakup obtained from our numerical simulations with the experimental results of Subramani *et al.* [10]. A good qualitative agreement can be observed between our computed prediction and the experimental observation. In order to gain more confidence on the accuracy of the adopted solver, a quantitative comparison is made with the experimental as well numerical results of Subramani *et al.* [10]. The volumes of the detached drops are compared over a wide range of We and the results shown in Fig. 6.2 (c) demonstrate good quantitative agreement with the previous observations. Additionally, we validate our EHD model by computing the deformation of a stationary droplet placed in a uniform electric field [195]. The analytical solution for the deformation parameter, $D = \frac{z_{max} - z_{min}}{r_{max} - r_{min}}$, for a spherical droplet under electric field is given

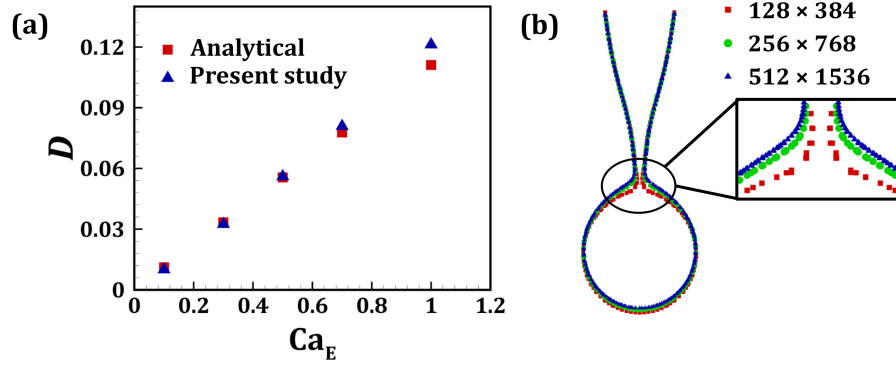


Figure 6.3: (a) Comparison of drop deformation parameter D obtained from the present simulations with analytical predictions [195] for varying Ca_E . (b) Grid resolution test showing drop profile at $t = 7$ for three different grid-meshes (128×384 , 256×768 and 512×1536). The values of R , S and E are 0.5, 2.0 and 0.0.

as [195], $D = \frac{9}{16} \frac{2R^2 + 3R + 2 - 7S}{2(2+R)^2} Ca_E$, where Ca_E is the electric capillary number. It can be discerned from Fig. 6.3 (a) that the deformation obtained from the present computations agree well with the analytical predictions thereby confirming the accuracy of the adopted EHD model for the current simulations.

In order to ensure that the results are independent of grid resolution, we plot the drop profile at the same time instant $t = 7$ using three different grid resolutions (128×384 , 256×768 and 512×1536) as depicted in Fig. 6.3 (b). The non-dimensional size of the grid cells corresponding to the three chosen grids are 0.12, 0.06 and 0.03, respectively. It is to be noted that Gerris is enabled with adaptive mesh refinement (AMR) technique for local mesh refinement during the simulation. However, we have not employed the AMR technique and a static mesh has been used throughout the entire study. It can be observed from Fig. 6.3 (b) that the drop profiles converge with the increasing grid refinement. Additionally, the difference of the detached drop volume between grid-meshes having 256×768 and 512×1536 is less than 1%. Based on the computational experiments, we have chosen the grid-mesh with 256×768 cells to optimize computational time without compromising the accuracy of the results.

6.4 Results and discussion

We initiate the study on the dynamics of drop formation in liquid-liquid systems under an applied electric field with the assumption of perfect dielectric fluids. Sub-

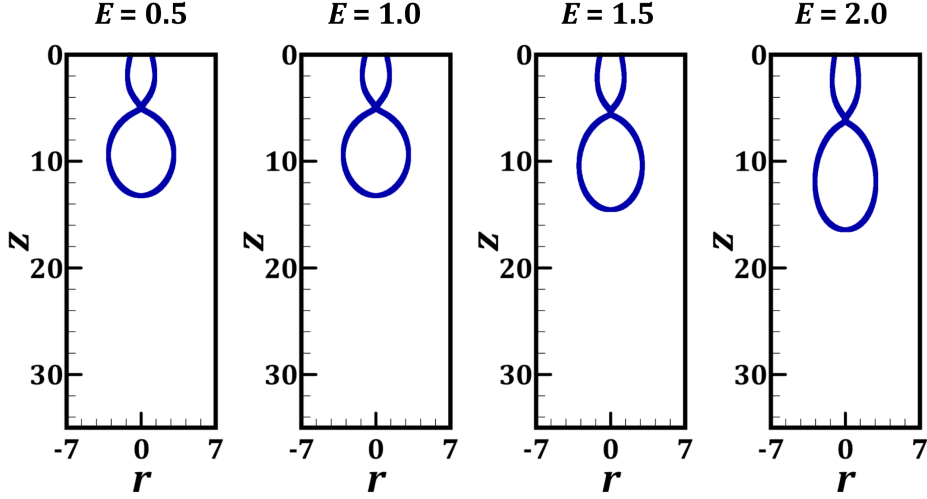


Figure 6.4: Instantaneous interface profiles at the incipience of drop breakup with variation of applied electric field strength. The fluids are considered as perfect dielectrics. The value of permittivity ratio S is fixed at 2.0.

sequently, we extend the study by considering the fluids to be leaky dielectrics. A large set of parameters are to be taken under consideration and in the results that follow, we have fixed the values of We , Re , Bo , η and λ at 0.4, 30.0, 0.2, 0.8 and 7.5 throughout the entire study. These parameters have been adopted from our previous investigation on drop formation [155] and they ensure that drop formation occurs in the dripping regime in the absence of an electric field. The influence of the variation of these parameters on the dynamics of drop formation have been investigated by a host of researchers [10, 13, 28, 155]. In the present study, we focus on the electro-hydrodynamics of the simulated system and study in detail the impact of the electrical properties as well as the applied electric field on the flow behavior and its associated dynamics. The deformation parameter (D), defined in Sec. 6.3 is used to characterize the shape of the drop profile. A value of D greater than unity ($D > 1.0$) implies a prolate shaped droplet whereas $D < 1.0$ indicates an oblate shaped droplet. The volume of the detached droplet is denoted as V_d . The time leading to the breakup of the droplet is represented as t_b whereas the length of the liquid thread connecting the drop with the orifice at the moment of pinch-off is defined as the limiting length at breakup (L_b).

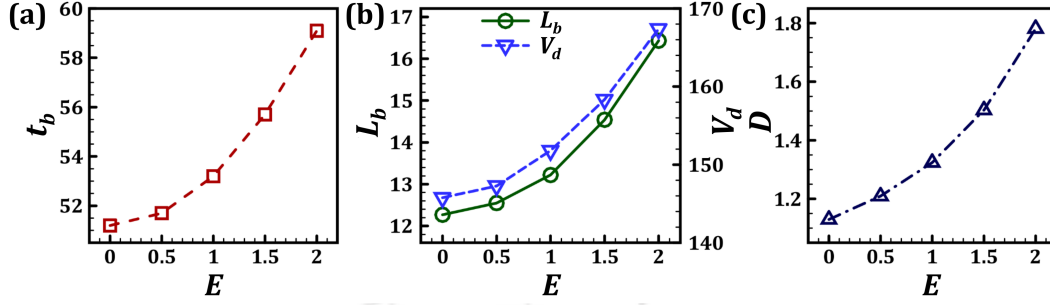


Figure 6.5: Effect of the applied electric field strength E on the (a) time leading to the breakup of the droplet t_b , (b) limiting length at breakup L_b and detached drop volume V_d and (c) deformation parameter D of the drop. The value of permittivity ratio S is fixed at 2.0.

6.4.1 Perfect dielectric fluids

We investigate the influence of the applied electric field strength (E) on the interface morphology of the drops. Figure 6.4 presents the interface profiles at the incipience of drop breakup for different magnitudes of E keeping the permittivity ratio (S) fixed at 2.0. It can be observed that in the presence of the imposed electric field, the drops elongate along the z axis attaining a prolate shape. The deformation parameter D is always greater than unity for such prolate shaped drops. The extent of elongation is enhanced as the electric field strength is gradually increased. In order to provide a quantitative picture of the influence of the electric field strength on the droplet dynamics, we compute the variation of t_b , L_b , V_d and D with increasing magnitude of the applied field strength E as depicted in Fig. 6.5. It can be observed that t_b , L_b , V_d and D monotonically increase with increasing E . The imposed electric field generates stresses, known as Maxwell stresses, which act in addition to the influence of surface tension, viscous stress and gravity. The magnitude of the polarization forces, arising out of the Maxwell stresses, is proportional to the contrast of permittivity existing between the two phases and squared magnitude of the electric field strength and acts perpendicular to the interface. The polarization force is directed from the medium of higher permittivity to the medium of lower permittivity and acts only on the interface separating the phases as the permittivity gradient exists only across the interface. For a fixed value of S , the polarization force acting at the interface increases with the increase in E . Sunder *et al.* [191] investigated bubble formation under an electric field and observed that Maxwell stresses compress the bubble laterally and lead to its elongation along the axis of

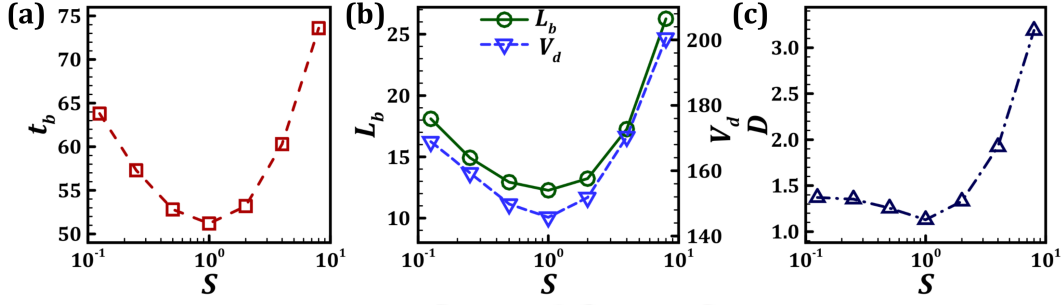


Figure 6.6: Effect of the permittivity ratio S on the (a) time leading to the breakup of the droplet t_b , (b) limiting length at breakup L_b and detached drop volume V_d and (c) deformation parameter D of the drop. The value of E is fixed at 1.0.

symmetry. A similar analogy can be drawn to explain the deformation behavior of the drops under the influence of an electric field thereby leading to the prolate shape. Moreover, the direction of electric force at the tip of the drop is opposite to that of gravity for $S > 1.0$, which results in an additional balancing force acting on the drop along with surface tension. As a consequence, the polarization force effectively delays the drop breakup time t_b . The longer breakup time enables more amount of fluid to accumulate inside the drop leading to enhanced drop volume V_d and larger L_b at higher magnitudes of E .

We now explore the impact of the fluid permittivity ratio S on the deformation dynamics. Figure 6.6 presents the variation of t_b , L_b , V_d and D over a wide range of S keeping E constant at 1.0. It can be inferred from Fig. 6.6 that for $S = 1$, the values of t_b , L_b , V_d and D match with the scenario when the electric field is absent. This can be attributed to the fact that when no permittivity contrast exists between the two phases, the polarization force vanishes at the interface. However, irrespective of S being smaller or greater than unity, the trend of t_b , L_b and V_d remain similar and depict an increasing response as the relative constant of permittivity between the fluids increases. In contrast, the deformation of the drop D is less sensitive to S for $S < 1$.

In order to highlight the primary difference in the dynamics brought about by the change of S , we compare the polarization forces acting across the fluid interface for $S = 0.125$ and $S = 8.0$ under a constant field strength $E = 2.0$ as presented in Fig. 6.7. The magnitude of the electric forces acting at the interface depend on the relative contrast of permittivity existing between the two phases. As such, the electric forces increase when either S is increased or decreased beyond unity.

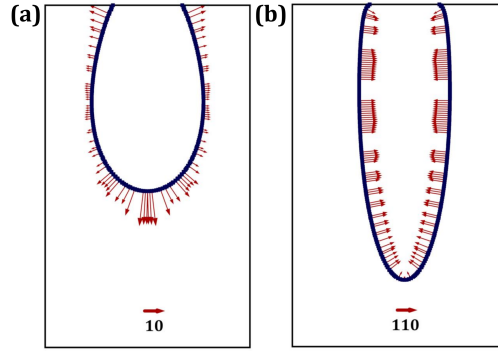


Figure 6.7: The electric forces acting on the drop interface for (a) $S = 0.125$ and (b) $S = 8.0$ under an applied electric field of $E = 2.0$. Only selected force vectors are plotted to maintain clarity.

However, the direction of the electric forces are different between the conditions of $S > 1$ and $S < 1$ as shown in Fig. 6.7 (a) and (b). For $S > 1$, the nature of electric forces are compressive and the direction of the electric forces at the tip of drop are opposite to that of gravity. As such, the electric forces effectively act as a balancing force along with surface tension and delays the pinch-off of the droplet. The delayed pinch-off allows more fluid to accumulate inside the drop before breakup occurs and hence the detached drop volume increases with increase in S beyond unity. In contrast, the electric forces are tensile under the condition of $S < 1$. Interestingly, the breakup time and drop volume also increases for $S < 1$. However, the seemingly counterintuitive observation may be explained by closely examining the magnitude as well as direction of the electric forces near the base of the drop attached to the orifice. The electric forces at the drop base have a net upward component and the tensile nature of the forces may oppose the inward collapse of the interface during necking. As a result, the pinch-off of the drop is delayed leading to longer breakup times and consequently larger drop volume as S is reduced below unity. Additionally, the local intensity of the electric forces are maximum near a small region around the drop tip for $S = 0.125$. However, for the condition of $S = 8.0$, the maximum intensity of electric forces acts along a considerable interfacial length close to the equatorial region of the drop. As a result, the deformation of the drop is more pronounced when the permittivity ratio $S > 1$.

The inhomogeneity of the polarization forces can be explained by considering the local variation of the electric field strength. In the absence of the drop phase, a spatially uniform electric field with lines of constant potential parallel to the

electrodes is generated. Due to the presence of the drop phase, the uniform electric field is disturbed due to the disparity in the dielectric permittivity between the two phases. Figure 6.8 (a) depicts the variation of electric potential ϕ along the vertical

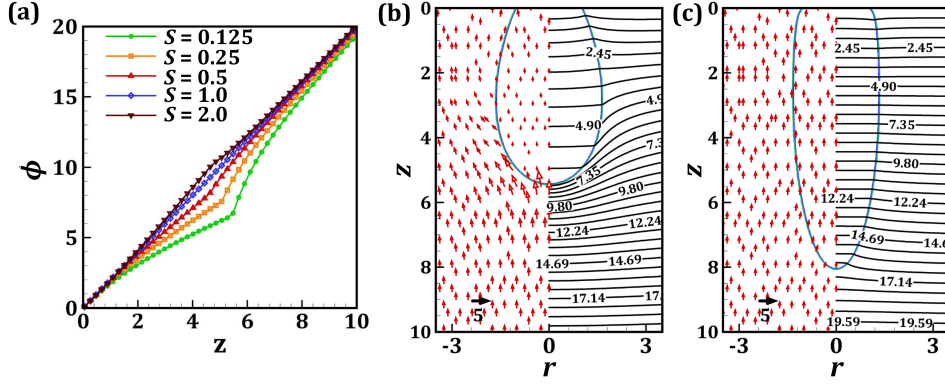


Figure 6.8: (a) The influence of permittivity ratio S on the vertical distribution of electric potential ϕ along the drop centerline ($r = 0$). Electric field vectors (left half) and iso-potential lines (right half) around the region of the growing drop for (b) $S = 0.125$ and (c) $S = 8.0$, respectively. The value of E is fixed at 1.0.

(z) coordinate plotted at the centerline of the drop (axis of symmetry). The values of S are indicated on the figure and several interesting features can be observed. Firstly, the sharp change in the slope of equipotential lines indicates a change of the electric field strength and corresponds to the location of the interface. In addition, the field intensity inside the drop is augmented as S is increased, which can be inferred from the rising slope of the potential drop at larger values of S . The increase in field strength is also corroborated by the images in Fig. 6.8 (b) and (c) wherein the electric field vectors and iso-potential lines are plotted for $S = 0.125$ and 8.0. The density of the iso-potential lines is less inside the drop for $S = 0.125$ representing a lower field strength. The electric field vectors plotted alongside the iso-potential lines also depict the lower field strength inside the drop. In contrast, the magnitude of the local field is higher inside the drop for $S = 8.0$ thereby demonstrating the contradictory influence of permittivity ratio S on the electro-hydrodynamics of the droplet.

6.4.2 Leaky dielectric fluids

In this section, we present the results from our computations based on the leaky dielectric model. Taylor [196] studied the deformation of stationary spherical drops

in an uniform electric field and derived an analytical relation that discriminates between prolate and oblate shape of the drop based on the ratios of fluid permittivity S as well as its conductivity R . The leaky dielectric model supports the presence of tangential electric stresses due to the small but finite electrical conductivity of the liquids and hence we anticipate differences in the dynamics of the droplets between the leaky and the perfect dielectric systems. The electric Reynolds number defined as, $Re_E = \frac{\epsilon_d V_{avg}}{\sigma_d R_o} = \frac{(\epsilon_d/\sigma_d)}{(R_o/V_{avg})} = \frac{t_E}{t_f}$, is the ratio of time scale of charge relaxation (electric time scale t_E) to the flow time scale t_f . For $t_E < t_f$, volumetric charge does not exist in the bulk and the charges instantly accumulate at the interface satisfying the assumption of leaky dielectric fluids. In our present investigations, we have considered a fixed value of $Re_E = 0.1$ for the entire study using leaky dielectric fluids. The chosen value of Re_E is similar to the typical values used by Mandal *et al.* [170]. Additionally, we have explored with different values of Re_E and observed that the dynamics remain insensitive to the value of Re_E for $Re_E < 1.0$.

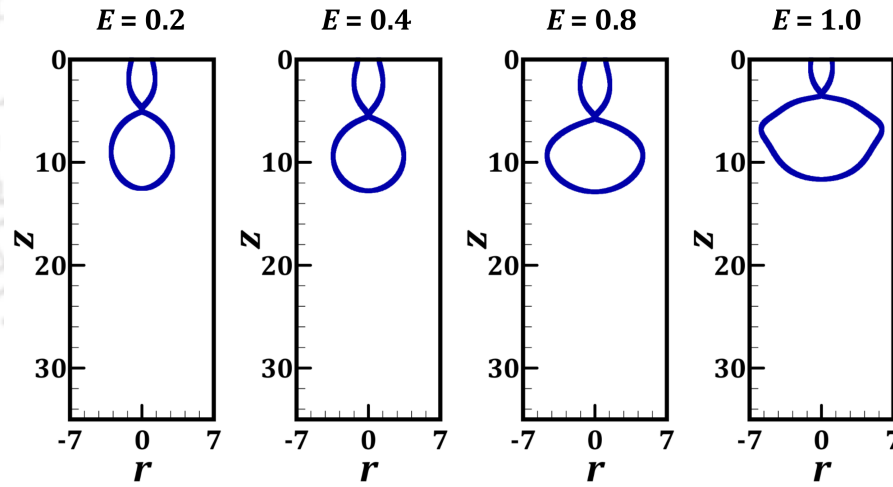


Figure 6.9: Instantaneous interface profiles at the incipience of drop breakup with variation of applied electric field strength. The fluids are considered as leaky dielectrics. The values of R and S are fixed at 2.0 and 0.5, respectively and represent system A.

We consider two (R, S) pairs of leaky dielectric fluids with values of (2.0, 0.5) and (0.5, 2.0). These are denoted as systems A and B, respectively. System A represents a drop whose conductivity is lower but permittivity is higher than the surrounding fluid, while system B represents a drop whose conductivity is higher but permittivity is lower than the surrounding fluid. Figure 6.9 and 6.10 presents

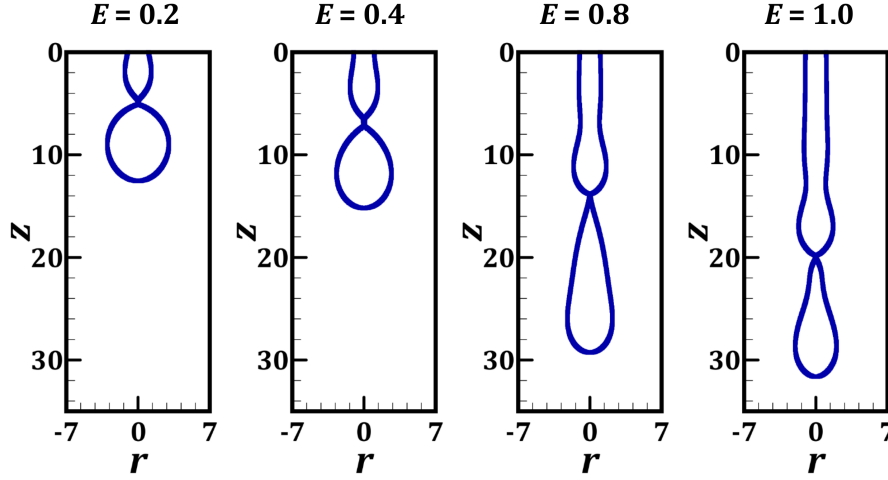


Figure 6.10: Instantaneous interface profiles at the incipience of drop breakup with variation of applied electric field strength. The fluids are considered as leaky dielectrics. The values of R and S are fixed at 0.5 and 2.0, respectively, and represent system B.

the influence of the applied electric field strength on the morphology of the drop profile close to the onset of pinch-off for system A and B, respectively. It can be clearly observed that the electric field yields a profoundly diverging behavior of the droplet dynamics for the two systems under consideration. For system A, the droplet is increasingly deformed along the horizontal direction at higher magnitudes of E leading to an oblate shaped droplet ($D < 1.0$), whereas, for system B, the droplet is stretched towards the electrodes leading to a prolate shape ($D > 1.0$). Additionally, a transition from dripping to jetting can be observed for system B in Fig. 6.10 when the field strength is sufficiently increased.

In order to provide a quantitative picture of the influence of the electric field on the two systems under consideration, we compute the variation of t_b , L_b , V_d and D with increasing magnitude of the applied field strength E as presented in Figs. 6.11 and 6.12. For system A, the values of t_b and V_d show a monotonous increase with increasing field strength, whereas D shows a monotonic decrease at higher E . The breakup length L_b is less sensitive to the variation of E . The analogous results for system B are presented in Fig. 6.12, wherein a non-monotonous increasing trend can be observed for t_b and V_d with increasing field strength. The non-monotonic variation of the droplet breakup time can be attributed to the transition of the flow dynamics from a dripping pattern to a jetting pattern as E is increased beyond 0.4.

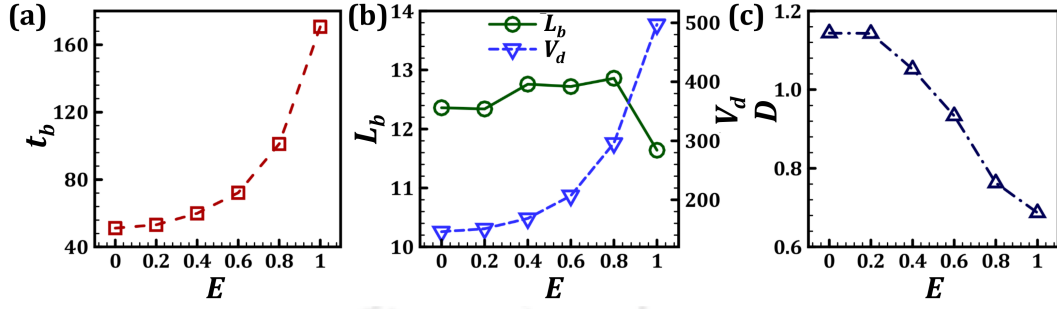


Figure 6.11: Effect of the applied electric field strength E on the (a) time leading to the breakup of the droplet t_b , (b) limiting length at breakup L_b and detached drop volume V_d and (c) deformation parameter D of the drop. The fluids are leaky dielectrics and represent system A ($R = 2$ and $S = 0.5$).

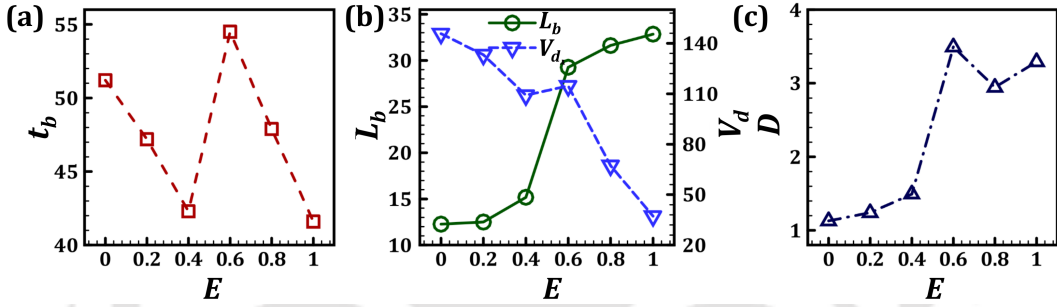


Figure 6.12: Effect of the applied electric field strength E on the (a) time leading to the breakup of the droplet t_b , (b) limiting length at breakup L_b and detached drop volume V_d and (c) deformation parameter D of the drop. The fluids are leaky dielectrics and represent system B ($R = 0.5$ and $S = 2.0$).

The transition can be clearly visualized in the profiles presented in Fig. 6.10 for $E = 0.4$ and 0.6 . The drop breakup occurs in the dripping regime for $E \leq 0.4$. However, the drop breakup occurs in the jetting regime for $E \geq 0.6$. The transition is characterized by a sharp increase in the jet breakup length, which can be observed in Fig. 6.12 (b). Although the breakup time increases during the transition, the longer breakup length for $E = 0.6$ results in more amount of liquid to be contained inside the fluid column than the detached drop. Hence, the volume of the drops does not differ much between $E = 0.4$ and $E = 0.6$. The drops formed in the jetting regime are smaller than those in the dripping regime and V_d further diminishes with increase in the field strength E .

The differing behavior of the drops for system A and B can be understood by closely examining the charges accumulated at the interface as illustrated in Fig. 6.13

(a) and (b). For system A, the drop tip facing the lower (positive) electrode becomes positively charged. In contrast, for system B, negative charges accumulate at the tip of the forming drop. The resultant effect of this differential charge accumulation between the two systems manifests in the opposing nature of Coulombic forces acting at the tip of the drop interface. The net electric forces for leaky dielectrics can be

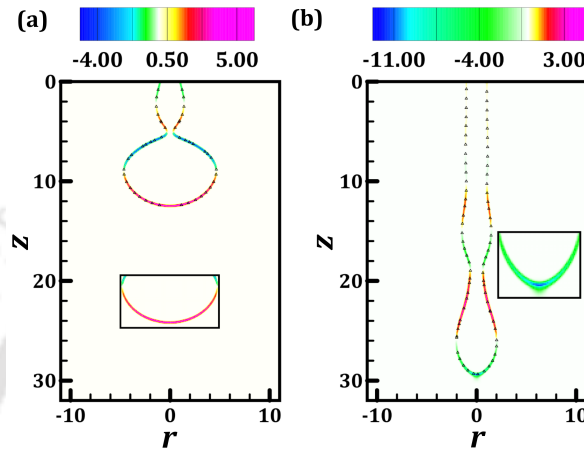


Figure 6.13: The distribution of charge accumulated at the interface for (a) system A and (b) system B. The value of E is fixed at 0.8.

classified into the polarization component acting on the dipoles ($-\frac{1}{2}\mathbf{E} \cdot \mathbf{E}\nabla\epsilon$) and the Coulombic component ($q\mathbf{E}$) exerted on the free charges. The polarization forces are directed from the medium of higher permittivity to lower permittivity and act only at the interface. The Coulombic forces point in the direction of the applied field when the accumulated charge is positive whereas they are directed opposite to the field when the accumulated charge is negative. Furthermore, the assumption of leaky dielectric fluids ensure that the charges are accumulated only at the interface and the bulk remains free of charges. As a consequence, the Coulombic forces also act only at the drop interface. Figure 6.14 compares the electric forces acting on the interface for the two systems under consideration. It can be clearly discerned from Fig. 6.14 that the Coulombic component dominates over the polarization component near the drop tip for both the systems, A and B. In addition, the nature of the Coulombic force is compressive for system A, whereas it is tensile in nature for system B. The Coulombic force vary spatially along the interface due to the local variation of the charge density and electric field strength. The magnitude of the Coulombic force is higher over a significant portion near the tip of the drop for both systems A and B. As a result, a net upward force is generated at the drop tip

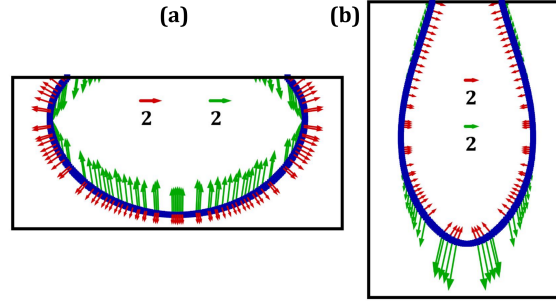


Figure 6.14: The electric forces acting on the drop interface for (a) system A and (b) system B under an applied electric field of $E = 0.8$. The Coulombic forces acting on the free charges ($q\mathbf{E}$) are depicted in green colour whereas the polarization forces acting on the dipoles ($-\frac{1}{2}\mathbf{E} \cdot \mathbf{E}\nabla\epsilon$) are shown in red colour. Only selected force vectors are plotted to maintain clarity.

for system A, whereas a net downwards force is generated at the drop tip for system B. Accordingly, the drop deforms into a oblate and prolate shape for systems A and B, respectively. The magnitude of the Coulombic force is augmented at higher values of E and hence, the deformation of the drop is significantly enhanced with increasing E for both the systems, albeit in a contrasting way. For system A, the net upward Coulombic force is amplified with increasing E , which aids the action of the surface tension force and delays the drop breakup. The delayed breakup allows more fluid to accumulate thereby increasing the droplet volume at higher E . However, for system B, the net downward Coulombic force counteracts the influence of surface tension and hastens the drop breakup thereby reducing the detached drop volume. Furthermore, in the case of system B, the system transits from a dripping to a jetting regime, characterized by an abrupt change in the breakup length L_b and time t_b . The transition can be attributed to the significantly enhanced Coulombic forces as the applied field strength E is increased leading to a strong pulling effect on the drop interface in the downward direction.

Figures 6.15 (a) and (b) present the flow fields around the drop for both systems A and B together with variation of pressure in the domain. The local pressure is significantly higher near the tip of the drop for system B, which can be ascribed to the smaller curvature of the interface in comparison to system A. The tangential electric stresses acting on the interface of the leaky dielectric fluids bring about a strong recirculation inside the drop. The magnified view of the tip region for system A and B are shown in Fig. 6.15 (c) and (d), respectively, with streamlines drawn

in the frame of reference of the drop. Interestingly, the circulation patterns differ radically between the two systems. For system A, the fluid flows in a circulation

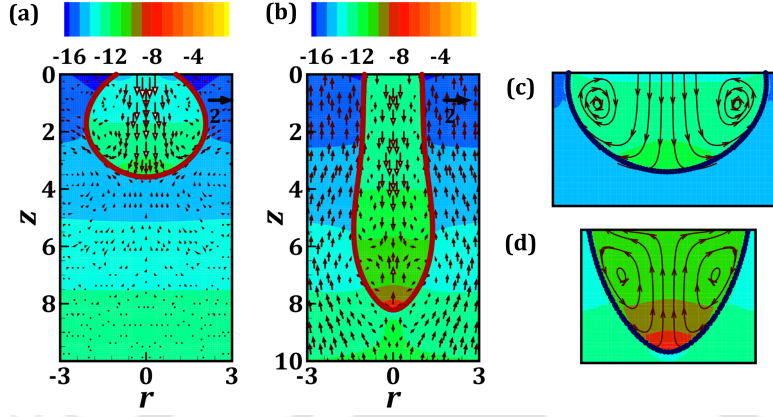


Figure 6.15: Contour plot of pressure variation superimposed on the velocity vectors depicting the flow field around the drop at $t = 10.0$ for (a) system A and (b) system B. The magnified view of the drop tip region shown in (a) and (b) with streamlines (drawn in the frame of reference of the drop) for (c) system A and (d) system B, respectively. The value of E is fixed at 1.0.

pattern inside the drop from the tip region to the equatorial region along the drop surface resulting in the formation of an oblate shaped droplet. In contrast, for system B, the flow occurs from the equatorial region to the drop tip along the interface thereby promoting the formation of prolate shaped droplets.

We now explore the impact of the fluid conductivity ratio R on the deformation dynamics under an applied field of $E = 0.5$. The permittivity ratio S is considered as unity and the polarization forces vanish under such circumstances. Figure 6.16 illustrates the variation of breakup time t_b , breakup length L_b , detached drop volume V_d , deformation parameter D and charge at the tip q with increasing R . The charges accumulating at the drop tip are positive in nature when $R > 1$, whereas negative charges are concentrated at the tip when $R < 1$. As a consequence, the drop assumes an increasingly prolate shape when R is progressively reduced below unity, while an increasingly oblate shaped drop is formed when R is further raised above unity. The breakup time increases with increase in R thereby delaying the drop breakup. As a consequence, the volume of the detached drops also monotonically increases at higher R . For $R < 1.0$, the breakup length is significantly enhanced as R is progressively reduced, which can be attributed to the higher negative charge accumulation at the drop tip. However, for $R > 1.0$, the breakup length is less

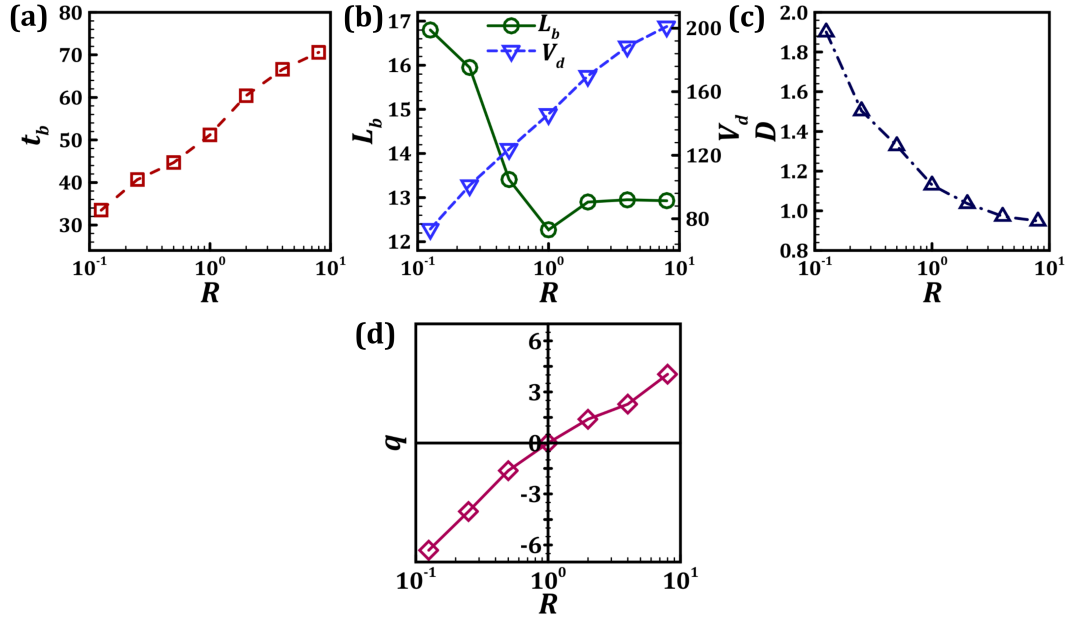


Figure 6.16: Effect of the conductivity ratio R on the (a) time leading to the breakup of the droplet t_b , (b) limiting length at breakup L_b and detached drop volume V_d , (c) deformation parameter D of the drop and (d) accumulated charge at the tip of the drop q . The value of E is fixed at 0.5.

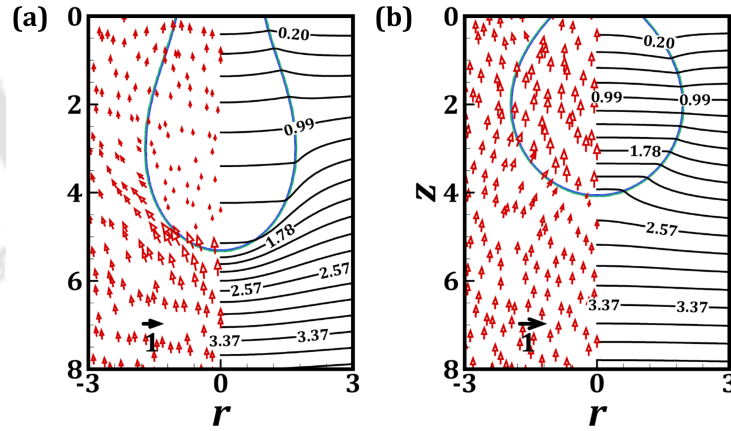


Figure 6.17: Electric field vectors (left half) and iso-potential lines (right half) around the region of the growing drop for (a) $R = 0.125$ and (b) $R = 8.0$. The value of S and E are fixed at 1.0 and 0.5, respectively.

sensitive to the change in R .

The local field intensity inside the drop is also modulated by varying the conductivity ratio R . The iso-potential lines around the drop are plotted for $R = 0.125$

and 8.0 in Fig. 6.17 (a) and (b) keeping the values of S and E fixed at 1.0 and 0.5, respectively. The electric field lines diverge while entering the drop for $R = 0.125$ whereas a converging pattern is observed for $R = 8.0$. As the strength of the electric field can be inferred from the density of the iso-potential lines ($\mathbf{E} = -\nabla\phi$), the local electric field intensity inside the drop is lower when R is less than unity, whereas the field intensity is amplified in the drop interior when R is more than unity. The variation of the local electric field strength with R modulates the intensity of the EHD forces acting at the interface thereby significantly altering the dynamics of the droplets.

6.5 Summary

The present chapter investigates the dynamics of formation and breakup of drops at a submerged orifice under the influence of an external electric field. The electrohydrodynamic problem is solved by considering the fluids as either perfect dielectrics or leaky dielectrics. The study reveals that under the influence of electric field, prolate shaped drops are formed in the case of perfect dielectric fluids. Systems of leaky dielectric fluids have also been studied and in particular two cases have been computed in detail. The first system consists of a drop which is less conducting but has higher permittivity than the surrounding fluid, whereas in the second system, the drop is more conducting but has a lower permittivity than the suspending fluid. In complete contrast to the case of perfect dielectrics, the drop which is less conducting but has higher permittivity than the surrounding medium, deforms into an oblate shape. However, the drop deforms into a prolate shape when the second system of fluids is considered. The breakup time and volume of the drops jettisoned from the orifice are dependent on the combination of fluid properties as well as the applied field strength E . The nature of the electric forces acting at the interface plays a crucial role in deciding the dynamics of formation as well as breakup of the droplets.

Chapter 7

Dynamics of deformation and pinch-off of a migrating compound droplet in a tube

The deformation and breakup of a migrating compound droplet inside a capillary tube are analyzed through direct numerical simulations. The investigations reveal that the deformation of the inner and outer interfaces are opposing in nature; the outer drop deforms to a prolate shape whereas the inner drop attains an oblate shape at steady state. The inner drop migrates away from the initial concentric configuration and finally attains a constant eccentricity. The magnitudes of the capillary number and viscosity ratio are found to have significant influence on the temporal evolution of the interfacial deformations as well as the eccentricity of the droplets. Furthermore, the migrating compound droplet can undergo an uncommon breakup stimulated by a rather irregular pinch-off of the outer shell. The breakup is initiated with the thinning of the outer shell followed by the pinch-off. The thinning of outer shell is found to follow two distinct power-law regimes - a swiftly thinning stage at the onset followed by a rate limiting stage before pinch-off.

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7.1 Introduction

The controlled production of monodisperse droplets using microchannels or capillary tubes has become an important process of late owing to their frequent appearance in cutting-edge applications such as the aerosol detection [197], spray atomizers [198], single cell analysis [199, 200], PCR studies [201, 202], microreactors [203, 204] and emulsifiers [205], among others. In particular, the production of stable compound droplets or double emulsions has become one of the major area of research owing to their capacity in the continual release of active ingredients in the various products and processes such as cosmetics, food, agriculture, and pharmaceuticals [36, 206]. The compound droplets are in general composed of a primary large droplet impregnated with a single or a collection of smaller droplets. The configuration ensures that the smaller liquid droplets can be loaded with a specialty chemical inside the encapsulating larger droplet and kept isolated from the surroundings with the help of the wrapping of the outer immiscible fluid [207]. The size of the compound droplets vary typically in the range from a few micrometers to a few millimeters [208]. In general, a large collection of such droplets are synthesized inside fluidic medium through various emulsification processes [44, 209–212]. Recent studies suggest that these droplets can be employed for next-generation targeted drug delivery [36, 37], advanced materials processing [38, 39], phase separation [40, 41] and handling of hazardous materials [42], among others.

The prior art indicates that while in some of the applications the breakup of the compound droplet decides their performance, in other applications the stability of them ensure the viability. It is thus of paramount importance to understand the spatiotemporal hydrodynamic behavior of the compound droplets moving inside a tube to track and control the deformation and subsequent breakup of them. Importantly, the formation and breakup of compound droplets can be very different from the same of the single droplets flowing inside a cylindrical tube. For example, a number of previous theoretical [213–215], numerical [216–222], and experimental [223–225] investigations show the various deformation and break up features of the single droplet flows inside a tube. These behaviors are found to be very different from the response of the compound droplets under a variety of flow conditions [44, 209–212]. In particular, the uniqueness of the interfacial deformations and subsequent pinch-off mechanisms during the extensional and shear flows [226–231], spreading [232–238], under the effects of surfactants [170, 239] and constrictions [47, 240], and also under confine-

ment [47, 240] have been explored so far in a greater detail. Importantly, while most of the afore stated studies have explored the concentric compound drops, a handful of studies have also focused on the dynamics of eccentric compound droplets [241–243].

However, there are hardly any studies that explore the transient evolution and the subsequent hydrodynamics of compound drops moving inside a capillary tube. In such a scenario, the physics associated with the interplay between the surface tension forces at the deforming interfaces alongside the frictional influence of the fluids inside and of the deforming compound droplet can be an interesting subject for fundamental study. A recent work [48] has attempted to provide an analytical solution for the motion of a compound drop in a long circular tube in the Stokes flow limit at the low Reynolds number. However, the detailed spatiotemporal dynamics of the coupled twin-deformable interface of the compound drops translating inside a tube is yet to be explored in detail. In the present work, we make an attempt to uncover the spatiotemporal dynamics of a compound droplet migrating inside a tube. We employ the computational fluid dynamic framework to solve the axisymmetric Navier- Stokes equations and unveil the influence of the various thermodynamic and kinetic parameters on the deformation and breakup of such droplets. In particular, starting with a configuration shown in Fig. 7.1, we focus on the positions of the inner and outer droplets in the unsteady and steady regimes of the dynamics, which helps in predicting the kinetics of the deformation of the interfaces and the conditions for the pinching-off of the outer shell of the droplet. Interestingly, the kinetics of the thinning of outer droplet is found to follow distinct power-law regimes in which the onset is associated with a swiftly thinning stage followed by a rate limiting stage before pinch-off. The study shows that controlling of the later stage decides the formation of stable or unstable compound droplets wherein the inner drop is either protected or exposed to the surroundings. The results reported can be of significance for the microfluidic prototypes that targets using stable or unstable compound droplets useful for drug delivery, microreactor, cosmetic and pharmaceutical applications.

7.2 Formulation of the problem

7.2.1 Computational domain

A representative diagram of the computational domain adopted is presented in Fig. 7.1. We consider a two component compound droplet placed inside a capillary tube of radius R and length L . The inner drop fluid and the ambient fluid are considered to be the same thereby simplifying the dynamics to a two-phase interfacial flow system. This configuration typically represents water-oil-water (W/O/W) or oil-water-oil (O/W/O) compound droplets [244, 245]. Initially, the outer and inner interfaces are considered as concentric spheres of radius R_1 and R_2 , respectively. The fluids are considered Newtonian, incompressible and mutually immiscible. A fully developed inflow of the ambient fluid is imposed at the inlet of the capillary tube. A cylindrical coordinate system (r, z, θ) is adopted considering the dynamics to be axisymmetric so that the problem is independent of θ where (r, z, θ) are the radial coordinate, axial coordinate and azimuthal angle, respectively. The length of the computational domain is taken as $30R$ in the axial direction so as to ensure that the results are not influenced by outflow boundary conditions.

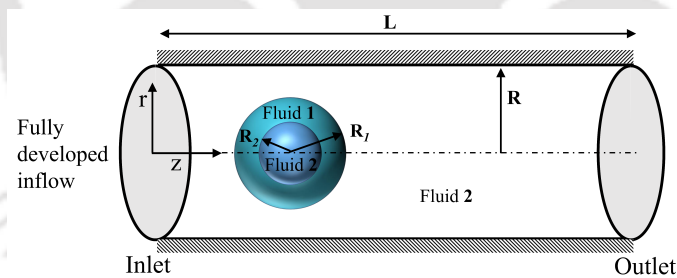


Figure 7.1: Schematic diagram showing the computational domain (not to scale) and boundary conditions in cylindrical coordinates system (r, z, θ) .

7.2.2 Numerical methods

The governing equations of the problem correspond to the conservation of mass and momentum, respectively, as described in Section. 2.2.1. The axisymmetric, incompressible Navier-Stokes equations are solved using an open source code Basilisk [246]. Basilisk is the successor to popular open source solver Gerris [77] and has been extensively benchmarked on a wide range of problems involving interfaces [79, 247, 248].

A brief description of the Basilisk solver is provided in Section 2.3. Furthermore, extensive details on the implemented methods and convergence studies are available in ref. [79].

7.2.3 Initial and boundary conditions

In order to solve the governing equations, the following initial and boundary conditions are implemented. The simulations are initialized by placing a concentric compound droplet in a parabolic flow inside the tube. The drop is placed at a distance of $2.5R$ from the inlet location. Although the initialization of the concentric drop is somewhat artificial, we expect the steady state deformation and droplet eccentricity to remain invariant to the initial conditions. This approach of initializing a circular droplet in a flowing fluid inside a tube has been adopted earlier, by many researchers [220, 222, 249]. A fully developed velocity is imposed at the inlet of the capillary tube ($z = 0$) given by $u(r) = 2V_{avg} \left(1 - \frac{r^2}{R^2}\right)$ and $v(r) = 0$, where V_{avg} is the average velocity of the imposed inflow. The walls of the capillary tube are modeled as rigid surfaces with no-slip and no-penetration conditions, i.e. $u = v = 0$ at $r = R$. At the tube outlet, Neumann conditions for velocity and a fixed pressure is applied for the outflow condition as $\partial u / \partial z = \partial v / \partial z = 0$ and $p = p_0$ at $z = L$. The computations are stopped when the drop is at a distance of $2R$ from the outlet. This ensures that the flow disturbances produced by the drop do not reach both the inlet and the outlet.

7.2.4 Scaling

The radius of the tube, R , and average velocity of imposed flow at inlet V_{avg} are taken as the characteristic length and velocity scales. The corresponding time scale comes out as R/V_{avg} . The properties of shell fluid, ρ_1 and μ_1 are employed as the density and viscosity scales, respectively. The results obtained from our computations are presented in terms of non-dimensional parameters. The relevant dimensionless numbers pertinent to our problem are the capillary number $Ca = \mu_1 V_{avg} / \sigma$, Reynolds number $Re = \rho_1 V_{avg} R / \mu_1$, density ratio $\lambda = \rho_2 / \rho_1$, viscosity ratio $\eta = \mu_2 / \mu_1$, drop aspect ratio $a = R_1 / R$ and the shell thickness ratio $k = R_2 / R_1$. The capillary number represents the ratio of viscous force over surface tension force. In our study, the Reynolds number, which represents the relative magnitude of inertia over viscous

forces, is maintained at unity ($Re = 1$) for the entire range of our computations. Furthermore, as we concentrate on the dynamics of neutrally buoyant drops ($\gamma = 1$), the influence of gravity can be safely neglected.

7.2.5 Fluid properties

The inner drop fluid and the outer ambient fluid are considered to be same thereby the problem is simplified as the study of a two-fluid system. The shell fluid is chosen to be an aqueous solution of glycerine. The ambient fluid (and inner core fluid) is considered as different grades of silicone oil [250]. The density contrast for the chosen fluid combinations is negligible and hence in our entire study, we consider the density ratio γ to be unity.

7.3 Validation of numerical approach

7.3.1 Comparison with literature

The numerical solver adopted for the present study is thoroughly validated by comparing our results with earlier investigations. Figure 7.2 (a), (b) and (c) presents the steady shapes of a droplet migrating inside a capillary tube as observed by Olbritch and Kung [251] for three different Ca . The corresponding shapes from the present computations are superimposed on top of the experimental images. It can be seen that the drop profile shows good agreement for $Ca = 0.05$ and 0.10 . However, a slight deviation is seen for $Ca = 0.16$. Additionally, we reproduce the shapes obtained by Tsai and Miksis [252] for droplets approaching breakup inside capillary tubes (Fig. 7.2 (d)). The results from our simulations, as shown in Fig. 7.2 (e), demonstrate good qualitative agreement with the reported shapes of Tsai and Miksis [252] for the time instants $t^* = 0, 2, 4$ and 6 .

In order to gain more confidence on the numerical solver, we compare the drop shapes and average drop velocity obtained from the analytical solutions of Nadim and Stone [253] with the results from our present computations. The theoretical

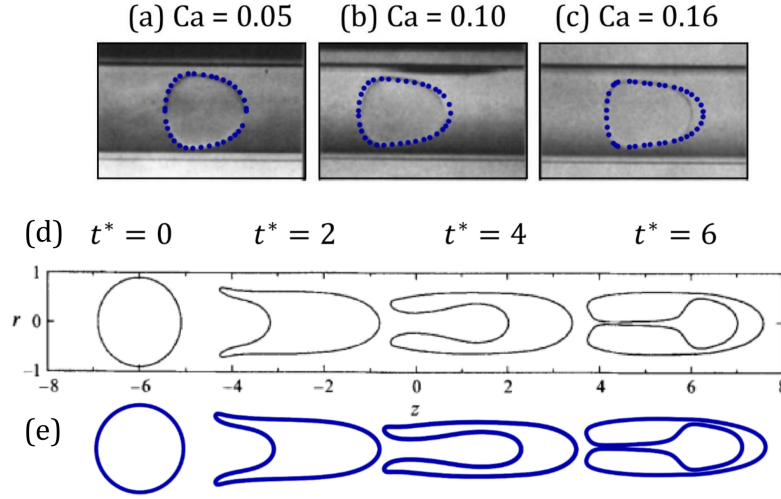


Figure 7.2: Comparison of experimental results of Olbritch and Kung [251] with present computations (blue line) for steady shapes of a droplet migrating inside a capillary tube at (a) $Ca = 0.05$, (b) $Ca = 0.10$ and (c) $Ca = 0.16$. The operating parameters are $\eta = 1.01$ and $a = 0.95$. (d) Temporal evolution of droplet shapes obtained by Tsai and Miksis [252] (e) The shapes obtained from the present computations using the same configuration of Tsai and Miksis [252]. The corresponding time instants are $t^* = 0, 2, 4$ and 6 .

solutions of drop shapes and average velocity are given as [253],

$$s = 1 + Ca \left(\frac{R_1}{R} \right)^2 \frac{10 + 11\eta}{8(1 + \eta)} (\cos^3 \theta - \frac{3}{5} \cos \theta)$$

$$u_{avg}^* = 2.0 \left[1 - \frac{2\eta}{2 + 3\eta} \left(\frac{R_1}{R} \right)^2 \right] \quad (7.1)$$

where s and θ describe the drop interface relative to its center and u_{avg}^* denotes the average drop translation velocity. The results from our computations presented in Fig. 7.3 demonstrate good agreement with the theoretical predictions of Nadim and Stone [253].

7.3.2 Grid convergence studies

In order to ensure that the results are independent of grid resolution, we chose four grid meshes (8×240 , 16×480 , 32×960 and 64×1920). The test was conducted for a compound drop migrating under conditions of $Ca = 0.5$, $\eta = 0.2$, $a = 0.6$ and $k = 0.5$ and the average dimensionless velocity of the drop u_{avg}^* was compared as

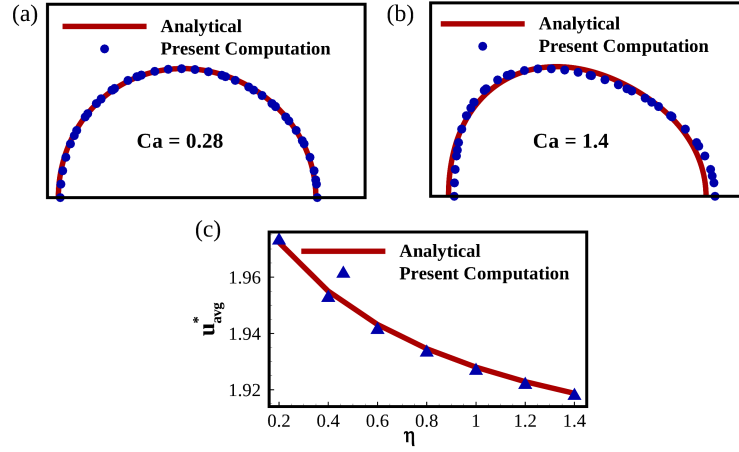


Figure 7.3: Quantitative comparison of drop shapes and average droplet velocity between theoretical solutions of Nadim and Stone (Eq. 7.1) and present computations. (a) and (b) shows the drop shapes for $Ca = 0.28$ and 1.4 , respectively, while other parameters are fixed at $\eta = 1$ and $a = 0.3$. (c) demonstrates the variation of u_{avg}^* with η keeping Ca and a fixed at 0.2 and 0.3 , respectively.

a function of dimensionless time t^* for the chosen grids as shown in Fig. 7.4. The steady velocities of the drop obtained are 1.526 , 1.569 , 1.584 and 1.588 for the four chosen grids, respectively. The difference of u_{avg}^* between grids 8×240 and 16×480 is around 2.8% whereas the difference between the grid-meshes 32×960 and 64×1920 is less than 0.3% . Based on this, the grid-mesh of 32×960 has been adopted for this study to optimize the computational time without compromising the accuracy of the obtained results. The smallest dimensionless cell size for the chosen grid is 0.031 . However, in Section 7.4.4, the breakup of compound droplets is explored, which is more sensitive to the grid resolution and requires further refinement. The numerical convergence of our results for drop breakup is demonstrated by performing additional grid resolution tests and are presented in Section 7.4.4.

7.4 Results and discussion

The following section presents a detailed study of the motion of the compound drops traversing inside a capillary tube and their associated dynamics. We initiate our study by considering the deformation dynamics of a compound droplet and exploring the hydrodynamics during its motion inside the capillary. Subsequently we investigate the dynamics of breakup of the compound droplet. A large set of

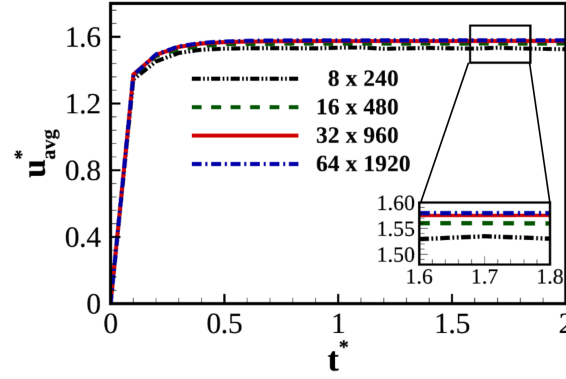


Figure 7.4: Comparison of the average drop velocity for different grid sizes (8×240 , 16×480 , 32×960 and 64×1920) as a function of dimensionless time t^* . The operating parameters are $Ca = 0.5$, $\eta = 0.2$, $a = 0.6$ and $k = 0.5$.

parameters are to be taken under consideration and in the results that follow, we have fixed the drop aspect ratio a at 0.6. The size of the inner drop has been taken to be half of the outer drop, i.e. $k = 0.5$.

The simulations are initialized by introducing a concentric drop in the cap-

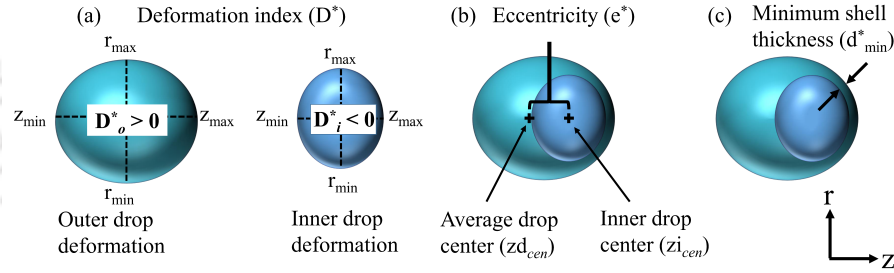


Figure 7.5: The computed parameters used to describe the dynamics of compound droplets, (a) Deformation index (D_i and D_o) corresponding to inner and outer drop interfaces, (b) Drop eccentricity (e^*), (c) Minimum shell thickness d_{min}^* .

illary tube where a fully developed flow persists. The parabolic flow imposed at the tube inlet propels the drop to migrate across the tube. The video suggests that during the flow, both the inner and outer interfaces deform in which the outer one elongates in the direction of the flow while the inner one does the same in the normal direction of the flow. Fig. 7.5 presents the variables which are employed to quantitatively estimate the variation in the shapes of the interfaces during the motion. For example, the deformation index $D^* = (z_{max} - z_{min}) / (r_{max} - r_{min})$ can be employed to evaluate the change of shape of a droplet along the flow direction

(towards z-axis) where $D^* = 0$ as well as along the normal to the flow direction (towards r-axis) where $D^* < 0$. Additionally, the inner drop moves away from the initial concentric position, which can be quantified in terms of an eccentricity index $e^* = z_{i_{cen}} - z_{d_{cen}}$, where $z_{i_{cen}}$ is the area averaged center of the inner drop and $z_{d_{cen}}$ is the area averaged center of the entire drop. Owing to the drop eccentricity e^* , the outer shell thickness of a compound drop does not remain spatially uniform. In what follows, the temporal evolution of deformation index D^* and eccentricity index e^* have been explored for a wide range of parameters to uncover the steady and unsteady deformation dynamics of the compound droplets, as shown in Sections 7.4.2 and 7.4.3. Further, the minimum distance between the inner and outer interfaces is defined as d_{min}^* , which helps in identifying the zone of pinching-off of the outer shell. Thus, the temporal variation of d_{min}^* unveils the breaking and pinch-off kinetics of the compound droplets, as shown in Section 7.4.4.

7.4.1 Temporal evolution of compound droplets

We consider the dynamics of a compound droplet and analyze its temporal evolution under conditions of $Ca = 0.5$ and $\eta = 0.2$. Figures 7.6 (a)-(b) present snapshots of the compound droplet during its unsteady and steady states of evolution. The temporal evolution of the deformation parameter D^* and drop eccentricity e^* are shown in Fig. 7.6 (c) and (d). The figures suggest that at the onset, the outer drop starts deforming with time in the direction of the flow, which generates a non-uniform curvature of the outer interface to compensate for the interfacial shear stresses. Figure 7.6 (a) depicts the pressure field across the interfaces of a moving compound drop, which suggests that the pressure drop across the interfaces is inversely related to the curvature radius, as defined by the Young-Laplace equation. The minimum curvature radius of the deformed outer droplet interface at the front and rear ends corresponds to the regions of maximum pressure drops. Further, the minimum pressure drop occurs approximately normal to the flow direction where the interfaces are rather flat and the curvature radius is maximum. Interestingly, the reduction in pressure in the normal direction of the flow stimulates the inner drop to deform perpendicular to the flow direction. It can be clearly observed from Fig. 7.6 (c) that the deformation index D^* for the outer drop increases with time in the unsteady domain of evolution and attains a constant magnitude thereby in-

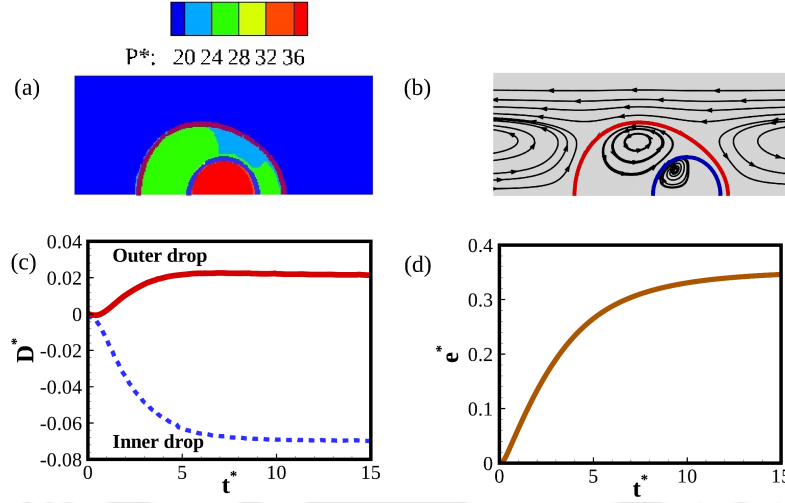


Figure 7.6: Temporal evolution of the compound droplet under conditions of $Ca = 0.5$ and $\eta = 0.2$. (a) represents the pressure field inside the compound droplet (b) shows the streamline patterns inside the drop at steady state (c) shows the variation of deformation index D^* with time for the inner and outer drop (d) presents the evolution of drop eccentricity with time.

indicating a steady state with constant elongation axially. However, the magnitude of D^* is negative for the inner drop signifying an unsteady deformation along the perpendicular axis at the initial stages of evolution. As time progresses, the inner drop also reaches a steady state with constant deformation normal to the flow direction. Figure 7.6 (b) presents the streamline patterns inside the compound droplet after it has attained steady state. The flow streamlines represent a set of circulation loops demonstrating the pattern of momentum transfer between the inner and outer interfaces of the compound droplet. Certainly, the temporal variation in the strength of the vorticities of these recirculations in the unsteady and steady domain of evolution decide the extent of mass, heat, and momentum transport across the interfaces. Additionally, it can be clearly perceived that the inner drop moves away from its concentric position and finally stabilizes near the ‘nose’ of the outer drop. This can be attributed to the fact that the inner drop experiences lower drag due to its smaller size whereas the outer drop encounters higher drag force due to its larger size and proximity to the tube walls. This allows the smaller inner drop to migrate faster as compared to the larger outer drop thereby leading to an eccentric configuration with time. The evolution of the drop eccentricity e^* plotted in Fig. 7.6 (d) demonstrates that the drop eccentricity initially rises sharply and saturates

to a steady value with time. The faster moving inner drop is counteracted by the viscous drag of the thin shell fluid near the ‘nose’ thereby reducing its velocity with time and hence the drop attains a fixed e^* after migrating for some period inside the capillary.

7.4.2 Effect of capillary number

In order to understand the influence of capillary number on the dynamics of compound droplets, we perform simulations by varying Ca from 0.3 to 0.6 while keeping η fixed at 0.2. The evolution of D^* and e^* with variation of capillary number is presented in Fig. 7.7 (a) and (b), respectively. With increase in the capillary number, the dominance of capillary force over viscous resistance is reduced. In consequence, the deformations of both the inner and outer increases. Additionally, under these circumstances, the inner drop undergoes significantly higher deformation than the outer drop. This can be elucidated by considering the smaller curvature of the inner drop compared to the outer drop, which demands a larger interfacial strength to maintain the curvature of the inner drop. Importantly, Fig. 7.7 (b) shows that the steady state eccentricity of the compound drop is hardly influenced by the variation of Ca .

Figure 7.8 presents the pressure field in the region around the compound drop

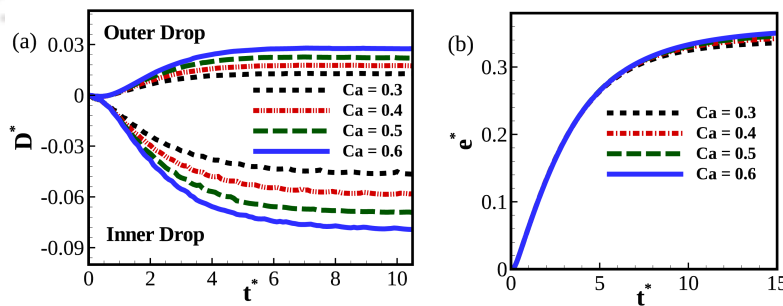


Figure 7.7: Effect of capillary number on the (a) deformation of inner and outer drop and (b) eccentricity of the drop. The viscosity ratio η is kept fixed at 0.1.

obtained at $t^* = 8.0$ for $Ca = 0.3$ and 0.6. It can be clearly observed from Fig. 7.8 that the pressure inside the inner core drop is higher for $Ca = 0.3$ in comparison to 0.6. The reduction of pressure inside the inner core with increasing Ca can be anticipated upon consideration of the discontinuity in normal stress at the interface

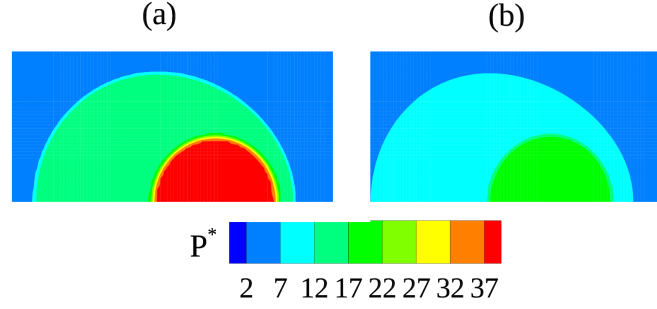


Figure 7.8: Contour of pressure (zoomed in the region of the compound drop) at time $t^* = 8.0$ under condition of (a) $Ca = 0.3$ and (b) $Ca = 0.6$. The viscosity ratio η is kept fixed at 0.1.

as described by the Young-Laplace equation. The dominating effect of surface tension is strong when the capillary number is small and the pressure difference acting across the interface is proportional to $O(\sigma/R_2)$. The major influence of increasing Ca is to raise the level of pressure inside the drop in comparison to the pressure exterior to the drop.

7.4.3 Effect of viscosity ratio

In this section, we explore the impact of the relative viscosity contrast between the shell and ambient fluid on the deformation and steady shape of the compound droplet. Figure 7.9 (a) and (b) show the evolution of D^* and e^* , respectively, for varying η . A decrease in the viscosity ratio leads to significant decrease in the drop deformation as well as eccentricity. This implies that a compound drop traversing in a more viscous ambience tends to deform more significantly as demonstrated in Fig. 7.9. Furthermore, the magnitude of η controls the temporal rate of evolution of droplet eccentricity. A compound drop with higher η evolves into an eccentric configuration faster than the one with lower η .

In order to explain the dependence of D^* and e^* on the relative viscosity contrast between the fluids, we analyze the temporal evolution of the average velocities of the inner and outer drops for $\eta = 0.05$ and 0.2 as shown in Fig. 7.10. It can be clearly discerned that the velocity of the drops for both values of η remains less than the tube centerline velocity in a Poiseuille flow. In the frame of reference of the outer drop, the tube walls move opposite to the drop motion, dragging the fluid at the interface of the drop. The outer drop thus experiences shear imposed by

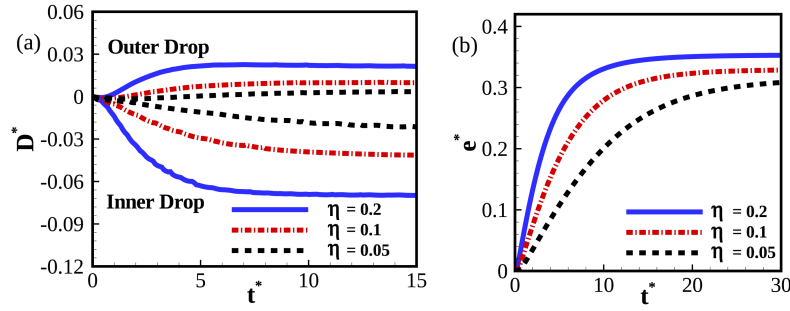


Figure 7.9: Effect of viscosity ratio on the (a) deformation of inner and outer drop and (b) eccentricity of the drop. The capillary number is kept fixed at 0.5.

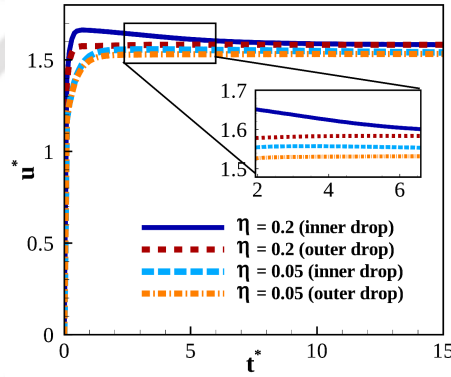


Figure 7.10: Temporal evolution of inner and outer drop velocities under varying η . The capillary number is kept fixed at 0.5.

the walls of the capillary tube. As the ambience becomes more viscous, the drag force on the interface increases thereby increasing the deformation of the outer drop at higher η . It can also be noted from the inset to Fig. 7.10 that the inner drop moves faster than the outer drop during the initial moments of migration inside the capillary due to its smaller volume and proximity to the centerline. This relative velocity difference between the inner and outer drop increases at higher η and serves as the root cause for the significantly greater deformation of the inner drop due to the large amount of shear acting at the inner interface. The compound droplet undergoes larger deformation if the viscosity of the inner droplet is more or the outer droplet is less viscous.

7.4.4 Breakup of compound droplets

The deformation of the inner and outer interfaces of the compound drop depends on the delicate balance between hydrodynamic stresses and interfacial tension. However, this balance may fail under certain conditions leading to breakup of the droplet. We investigate the rupture of the compound droplet during the course of its deformation inside the tube. Figure 7.11 presents a qualitative picture of the evolution of a compound droplet leading to its eventual breakup. Owing to the opposing nature of deformation of the inner and outer interfaces, the shell thickness becomes non-uniform spatially with increasing eccentricity of the droplet configuration during its temporal evolution. A rapidly thinning region can be clearly observed wherein both the interfaces close in on each other. Eventually, the gap between the two interfaces becomes negligible and the outer shell ruptures to release the inner fluid.

The drop breakup phenomenon is sensitive to the resolution of the numerical

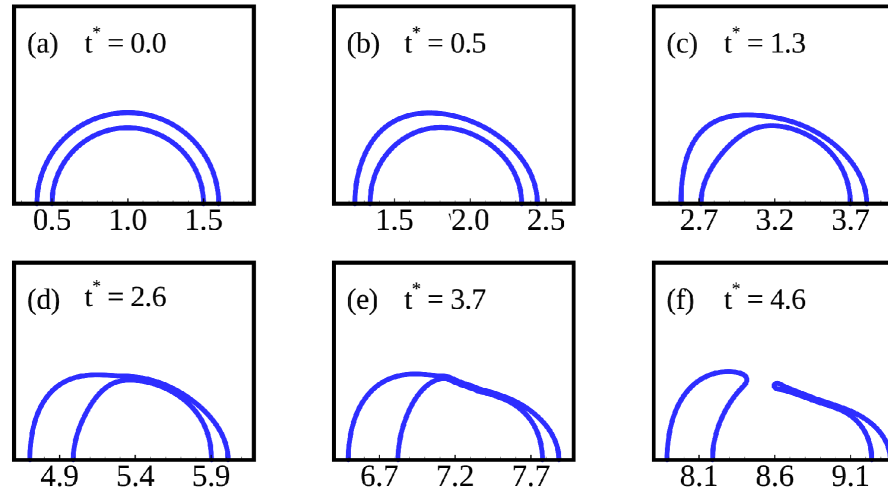


Figure 7.11: Snapshots showing the temporal evolution of a compound droplet leading to breakup.

grid. In order to check the convergence of our results, additional grid tests are performed and presented in Fig. 7.12. We measure the minimum distance between the inner and outer interfaces d_{min}^* (defined in Fig. 7.5) as the drop proceeds towards breakup and plot the drop profile for $d_{min}^* = 0.05$ and 0.01 for two levels of refinement. The upper and lower half of the drop profile in Fig. 7.12 (a) corresponds to grid-meshes 128×3840 and 256×7680 , respectively. It can be clearly observed that the drop profiles are almost identical for the grid sizes 128×3840 and 256×7680

thereby showing convergence of our results. The volume of the primary and secondary drop formed after breakup is computed using different grids and presented in Fig. 7.12 (b). The difference in primary drop volume between grids 32×960 and 64×1920 is $\sim 15\%$ whereas the difference between grid-meshes 128×3840 and 256×7680 is less than 4% . Based on this, the grid-mesh of 128×3840 is used for computing the dynamics of compound drop breakup. The smallest dimensionless cell size for the chosen grid is 0.0078. Here, we note that the final rupture of the thin liquid sheet will be essentially numerical as the physics that governs the final breakup is molecular and requires multiscale modelling, which hopefully will be possible in the near future. The error introduced due to numerical clipping of the interface is of the order of the smallest grid cell. The present computations shed light on the mechanism of compound droplet breakup and its dependence on relevant parameters.

In order to gain deeper understanding about the breakup process, we vary

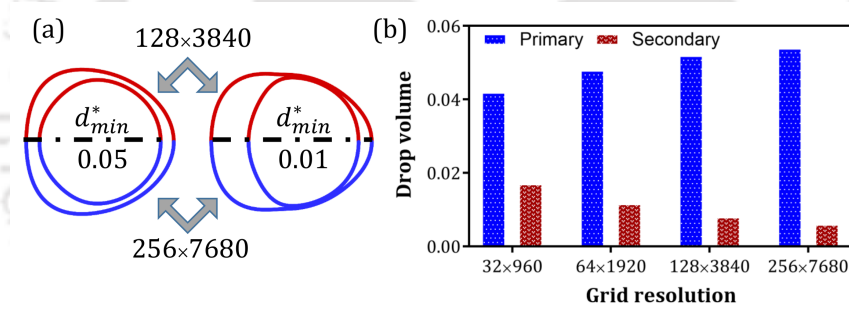


Figure 7.12: Grid resolution test for drop breakup. (a) Comparison of drop profile using grid sizes of 128×3840 (upper half) and 256×7680 (lower half). The profiles are plotted for two values of d_{min}^* , 0.05 and 0.01, as the drop proceeds towards breakup. (b) The variation of the volume of primary and secondary drops formed after breakup with different grid resolutions. The capillary number is kept fixed at 0.5.

the thickness of the shell and examine its effect on the breakup phenomenon. The evolution of d_{min}^* with t^* is presented in Fig. 7.13 (a) for compound droplets with different shell thickness ratio k . Note that a higher value of k denotes a compound drop with smaller shell thickness ($k = R_2/R_1$). A compound drop with higher value of k ruptures in a shorter time due to the smaller distance separating the inner and outer interfaces. In order to quantify the thinning rate of the shell, we analyze the relation between the minimum distance between the interfaces d_{min}^* and the time leading to rupture of the shell for $k = 0.73$ and 0.83 . The temporal decrease of d_{min}^*

with time t^* can be characterized by a power law expression [155] $d_{min}^* \sim \tau^\alpha$, where τ is the time leading to rupture ($\tau = t_{rupture}^* - t^*$) and α is the exponent of power law.

Figure 7.13 (b) depicts the thinning behavior of a compound droplet with

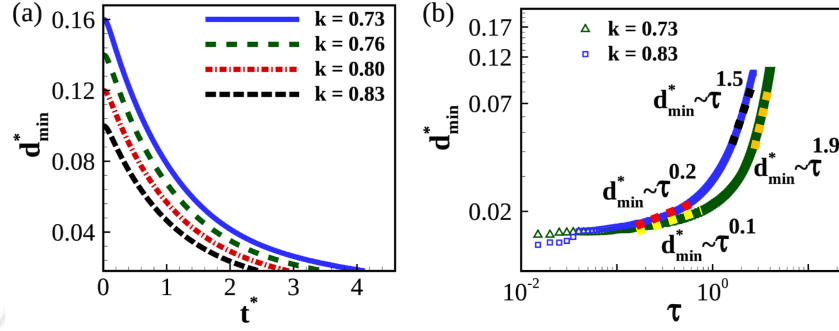


Figure 7.13: (a) The temporal evolution of minimum distance between the inner and outer interfaces d_{min}^* for different drops with $k = 0.73, 0.76, 0.80$ and 0.83 . (b) Relation between d_{min}^* and time before rupture τ near the breakup of the droplet for $k = 0.73$ and 0.83 . The dotted lines in black, orange, red and yellow represents $d_{min}^* \sim \tau^{1.5}$, $\tau^{1.9}$, $\tau^{0.2}$ and $\tau^{0.1}$, respectively. The other operating parameters are $Ca = 0.5$ and $\eta = 1.0$.

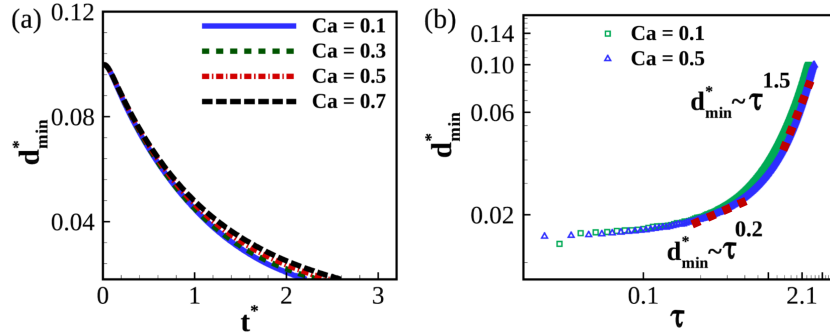


Figure 7.14: (a) The temporal evolution of minimum distance between the inner and outer interfaces d_{min}^* for $Ca = 0.1, 0.3, 0.5$ and 0.7 . (b) Relation between d_{min}^* and time before rupture τ near the breakup of the droplet for $Ca = 0.1$ and 0.5 . The dotted lines represents $d_{min}^* \sim \tau^{1.5}$ and $d_{min}^* \sim \tau^{0.2}$. The other operating parameters are $\eta = 1.0$ and $k = 0.83$.

$k = 0.73$ and 0.83 . During the initial stage of droplet motion, the thinning proceeds at a rapid rate with $\alpha = 1.9$ and 1.5 for $k = 0.73$ and 0.83 , respectively. This can be attributed to the high velocity of the inner droplet during the initial moments of

the flow, which leads to a significant increase of the drop eccentricity. As the inner and outer interfaces approach each other, a thin film is formed near the ‘nose’ of the drop with spatially non-uniform thickness. The flow in this annular thin region is highly squeezed leading to strong viscous stresses. This also explains the higher magnitude of α witnessed for a thicker shell ($k = 0.73$) during the initial duration of thinning in comparison to a thinner shell ($k = 0.80$). Beyond a critical minimum thickness of the film, the thinning rate diminishes with α taking a value of 0.1 and 0.2 for $k = 0.73$ and 0.83, respectively thereby transitioning into a slowly thinning regime. The influence of Ca on the thinning rate is presented in Fig. 7.14. It can be observed that the thinning rate is insensitive to the variation of Ca . This can be elucidated by considering the evolution of eccentricity e^* for different Ca as shown in Fig. 7.7 (b). The temporal evolution of e^* is unaffected by the change of Ca , which in turn makes the thinning rate insensitive to Ca . As the magnitude of d_{min}^* decreases, the typical distance separating the interfaces becomes very small compared to the compound drop radius. The pressure inside this small gap is very large, which significantly diminishes the thinning speed as reflected by the rate limiting stage. Eventually, both the interfaces make contact and the film ruptures. The rupture of the thin film can lead to entire draining of the inner core fluid into the surrounding ambient fluid or result in the formation of a smaller compound droplet along with a separate drop of the shell fluid. It may be noted here that herein we attempted only to capture the pinch-off dynamics because the actual breaking of a compound droplet and the post breakup dynamics require the use of full three dimensional simulations, which falls beyond the scope of the current study.

7.5 Summary

The present chapter investigates the temporal evolution of a compound droplet inside a tube and analyzes its deformation history and interface morphology. It is observed that under the action of an imposed flow, the outer drop deforms along the flow direction attaining a prolate shape. The inner drop however deforms perpendicular to the flow direction and reaches an oblate shape at steady state. The inner drop moves away from the initial concentric position and finally attains a constant eccentricity at steady state. The magnitudes of the capillary number and viscosity ratio have profound influence on the interfacial deformations as well as the

eccentricity. The breakup of the compound droplet is studied and it is observed that a thin film of the shell fluid forms near the nose the drop as the inner drops departs from its concentric configuration. The thickness of the shell has profound influence on the stability of the drop thereby determining the time before rupture occurs. Interestingly, the rate of thinning of the outer shell thickness follows a power law criterion with one initial stage of swiftly thinning regime to a slowly thinning regime before the pinch-off.





Chapter 8

Electric field mediated separation of water-ethanol mixture in carbon-nanotubes integrated to nanoporous graphene membrane

The present study demonstrates the separation of ethanol-water solutions inside carbon nanotubes (CNTs) under the influence of applied electric field using molecular dynamics simulations. Starting from an equimolar mixture of water and ethanol, a tuneable separation of the mixture into the individual constituents is demonstrated by varying the orientation of the electric field to the axis of the carbon nanotube. The separation manifests owing to the contrasting effect of the axial ($\theta = 0^\circ$) and orthogonal ($\theta = 90^\circ$) electric fields on the preferred occupancy of water and ethanol in the CNT. The orientation of the electric field controls the molecular ordering of the water and ethanol molecules thereby modulating the hydrogen bonding and average interaction energy of the molecules. The separation efficiency is found to improve with the increase in intensity of the externally applied electric field.

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8.1 Introduction

Transport of water molecules in nanoscale systems have been extensively studied in the recent years owing to their appearance in various important scientific and technological processes. While the carbon nanotube (CNT) based nano-devices are envisioned to meet the ever increasing demand of purified water by desalinating the abundant sea-water resources [254–260], a number of fundamental theoretical and experimental works have predicted abnormally high rate of water transport inside the atomically smooth and hydrophobic CNTs [261,262]. The essential scientific details on the transport of fluids inside the nanotubes are expected to enrich the generation of power converters [263–265], ion-exchange purifiers [266], nanorobotics [267], targeted drug delivery, biomedical therapies [268,269] and pumping devices for atomic transportation [270,271].

Interestingly, the present decade has also experienced another important paradigm-shift in which the applications composed of metal, ceramic, polymer, or composite materials are expected to be replaced by carbon based materials. For example, the high mechanical strength, electrical and thermal conductivities, surface-to-volume ratio, and biocompatibility of graphene have been exploited to develop a number of futuristic nanotechnologies [272–276]. Thus, in the recent past, extensive research has been carried out in the field of transport and separation processes based on CNT and graphene devices [277]. In view of the above, in this study, we perform molecular dynamics simulations to attempt electric field induced separation of water-ethanol mixture inside a CNT integrated with graphene membrane.

It may be noted here that at the macroscopic level, the separation of the ethanol-water mixture has been one of the very important technological processes attempted for long. This is because, ethanol production is always associated with the formation of the by-product water. Pure ethanol is a promising alternative for commercial biofuel technologies along with widespread application in medical and scientific products [52, 53, 55]. The conventional process of separating ethanol from aqueous solution is through distillation, which consumes a large amount of energy and forms the bulk of the production cost [278]. Although the newer technologies like membrane based separation [63,279–282] have been implemented successfully for desalination, the applicability of such systems are challenged when the two separating species are electro-neutral and have similar size, such as water and ethanol. Remarkably, in such a scenario, the effect of electric fields in biological membranes and

CNTs show promising potential for the nanofluidic applications [283–286]. Previous studies uncover that under the influence of an external electric field, water congregates into a variety of exquisite structures inside CNTs thereby radically altering its transport properties, suitable for the development of newer separation methodologies [63, 281, 283, 287]. However, a clear picture of the dynamics of separation of water-ethanol solutions in the presence of electric field is still lacking in literature and serves as a motivation for the present study.

In the present study, we perform a series of molecular dynamics (MD) simulations in order to demonstrate that external electric fields can be employed to efficiently separate water-ethanol solutions inside carbon nanotubes. Starting from an equimolar solution of water and ethanol, the MD simulations reveal that the direction of the applied electric field plays a crucial role in deciding the separation inside the CNT. The mole fraction of water inside the nanotube can be tuned by varying the field strength as well as the direction of the applied electric field with respect to the axis of the CNT. While an axially aligned electric field increases the concentration of water in the CNT, the orthogonal field enhances the concentration of ethanol inside the nanotube. The study showcases example where by varying the angle between the electric field and nanotube axis (θ), the concentration of water-ethanol solution in the CNT can be suitably controlled. Further, the separation efficiency can be significantly enhanced by increasing the strength of the externally applied electric field. The study elucidates the behaviour of water-ethanol mixtures confined inside CNTs under external electric field, which can be a promising alternative for ethanol dehydration during bio-ethanol production.

8.2 Methodology

The model system for the MD simulations consists of a rigid CNT, which connects two water-ethanol reservoirs at the ends, as schematically shown in the Fig. 8.1. Two rigid graphene sheets having a pore equal to the CNT diameter are placed at each end of the tube to act as separating membranes. The chosen CNT for the present study is of diameter, $D = 3.4$ nm, chirality (25, 25), and 0.142 nm carbon-carbon bond length. The origin of the coordinate system $(x, y, z) = (0, 0, 0)$ coincides with the CNT centre. The reservoirs are filled with equimolar water-ethanol solutions,

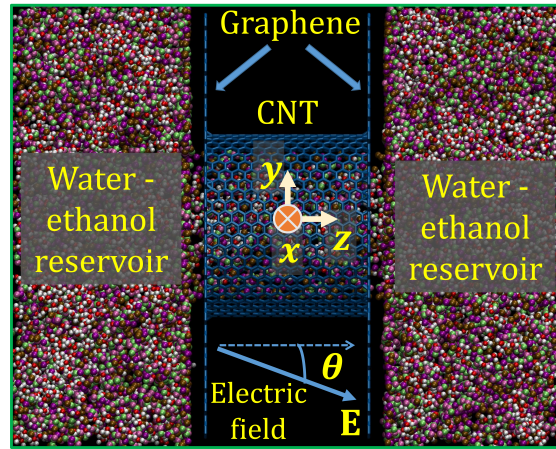


Figure 8.1: Schematic diagram of the molecular dynamics setup. The origin of the system coincides with the CNT centre. The vertical and horizontal axes are denoted by y and z , respectively. The x -axis points into the plane of the paper. Red and white represent the oxygen and hydrogen atoms of water molecules, respectively. The ethanol molecules are represented by brown, purple, green and pink for the methyl group, methylene group, oxygen and hydrogen atoms, respectively. The electric field is applied over the entire domain and the direction of the electric field is given by angle θ with respect to the positive z -axis.

i.e. $\chi_{water} = \chi_{ethanol} = 0.5$, where χ_{water} and $\chi_{ethanol}$ denote the mole fractions of water and ethanol, respectively. Periodic boundary conditions are applied in all directions (x, y , and z axes) thereby mimicking a system of infinitely large nanoporous graphene membranes having carbon nanotubes sandwiched between the pores.

We employ the TIP4P/2005 model for water molecules [288], which consists of four interaction sites, i.e. one oxygen (O), two hydrogen (H), and a massless site M near the oxygen atom along the bisector of the HOH angle. The ethanol molecules are described by the united atom optimized potentials for liquid simulations (OPLS-UA) [289, 290]. In the OPLS-UA model, each ethanol molecule is represented by four interaction sites, i.e. methyl group (CH₃), methylene group (CH₂), oxygen (O), and hydrogen (H). The carbon atoms in the system are considered as uncharged Lennard-Jones (LJ) particles and their parameters are taken from the previous literature [63].

The cross interaction LJ parameters are computed using the combination rule $\sigma_{ij} = (\sigma_i \sigma_j)^{1/2}$ and $\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2}$. The positions of the carbon atoms are considered fixed, which is a common simplification in MD simulations [57, 261]. We apply an external homogeneous static electric field vector, $\mathbf{E}$, on the entire unit cell and the

angle between the direction of the field and the CNT ($+z$ -axis), denoted as θ , which is varied from 0° to 90° . The electric field is implemented as an additional electrohydrodynamic force vector, $\mathbf{F}_i = q_i \mathbf{E}$, to all the atoms [291], where q_i is the partial charge on atom i . This is a valid representation of the electromotive force exerted by a voltage difference between two electrodes and has been commonly employed in the previous studies [63, 291, 292].

The MD simulations are performed using open source solver LAMMPS [293]. The equations of motion are integrated with the velocity-Verlet algorithm [86]. A cut-off of 1.2 nm is employed for the short range van der Waals interactions, while the long range Coulomb forces are treated using particle-particle particle-mesh (PPPM) method [88] with the real space cut-off also set to 1.2 nm. The simulations are performed in an NPT ensemble and the temperature of the system is kept at 300 K using a Nosé-Hoover thermostat [89]. The pressure in the axial direction (z -axis) is maintained at 0.1 MPa using a Nosé-Hoover barostat [294]. The length of the chemical bonds of water and ethanol molecules as well as the angles between them are kept constant using SHAKE algorithm [295]. The time step of integration is set to 2 fs and the simulations are performed for a total duration of 50 ns out of which the first 10 ns are considered for equilibration. The simulated system is well equilibrated within 10 ns and a production run of 40 ns is adequate to capture the dynamics. Three separate runs are carried out starting from different sets of initial condition for each configuration. The computed results are averaged over the three sets to ensure that the quantities reported are well converged.

8.3 Results and discussion

In this section, we demonstrate the separation of ethanol-water mixture in the CNT under the influence of electric field. A detailed examination has been carried out to uncover the underlying mechanism for the separation of water-ethanol solutions. The strength of the electric field is varied upto a maximum of 2 V/nm, which is below the threshold limit at which dissociation of water molecules may occur due to electric field discharge [296].

In order to demonstrate the separation of water-ethanol solutions, we apply an electric field intensity of, $E = 1.5$ V/nm and vary the orientation angle θ from

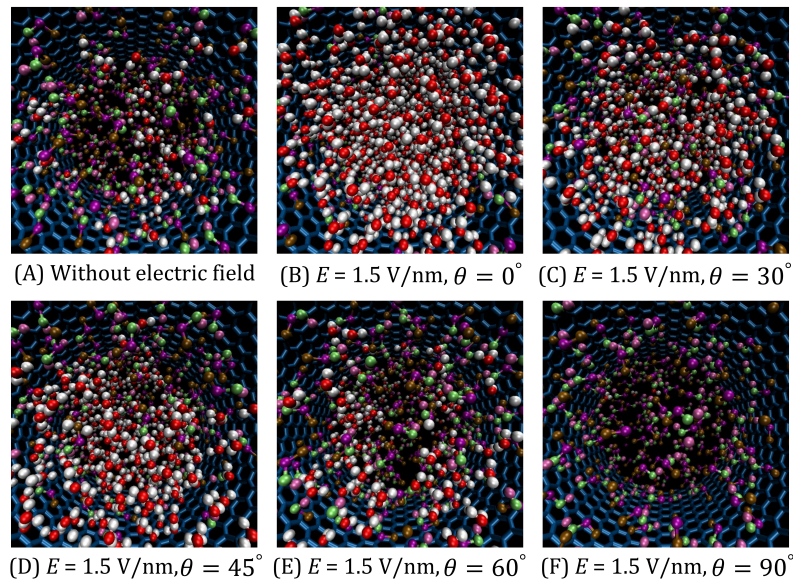


Figure 8.2: Snapshots of the molecular structure inside the CNT without an electric field (A) and under an imposed electric field of $E = 1.5 \text{ V nm}^{-1}$ (B)–(F). Red and white represent the oxygen and hydrogen atoms of water molecules, respectively. Ethanol molecules are represented by brown, purple, green and pink for the methyl group, methylene group, oxygen and hydrogen atoms, respectively.

0° to 90° . Figures 8.2 (A-F) presents snapshots of the molecular arrangements in the CNT with the variation in θ . The image in Fig. 8.2 (A) depicts the water-ethanol structure in the absence of an applied electric field. It can be observed that both water and ethanol molecules occupy the CNT. The magnitude of χ_{water} inside the CNT is 0.38, which is marginally less than the equimolar concentration in the reservoir. Thus, the figure shows a preferential occupancy of ethanol in the CNT when the electric field is not applied. However, in the presence of an electric field, the molecular arrangement undergoes significant change with variation of θ . For lower values of θ , water molecules show higher occupancy inside the CNT whereas at higher values of θ , ethanol preferentially fills the CNT.

To provide a quantitative picture of the variation of water-ethanol occupancy with electric field orientation, we plot the mole fractions of water and ethanol inside the CNT for $E = 1.5 \text{ V/nm}$ as shown in Fig. 8.3 (A). The figure suggests that for $\theta = 0^\circ$, the CNT is nearly filled with water having, $\chi_{water} = 0.93$, leading to a separation of water from ethanol. As θ is increased, the magnitude of χ_{water} decreases thereby signalling the increasing occupancy of ethanol molecules inside the CNT. The nanotube is almost entirely emptied of water molecules ($\chi_{water} = 0.06$) when

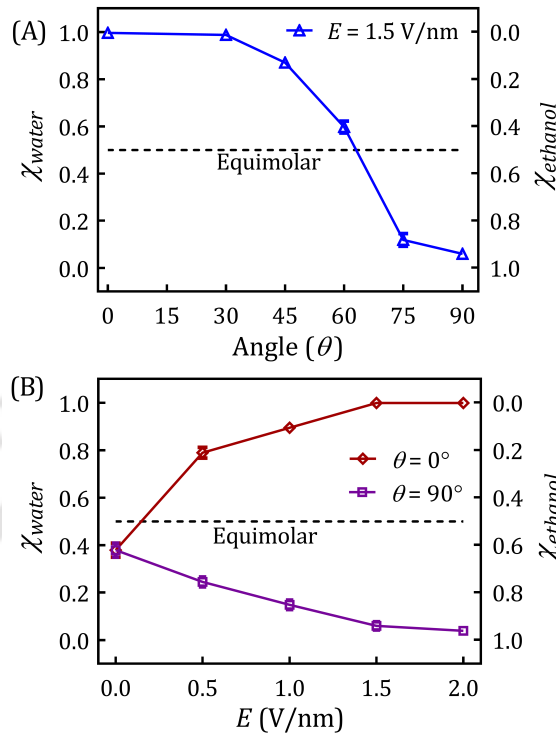


Figure 8.3: (A) The variation of the mole fraction with orientation angle θ inside the CNT under the influence of applied electric field of $E = 1.5 \text{ V nm}^{-1}$. (B) The variation of the mole fraction with electric field strength for $\theta = 0^\circ$ and 90° . The left vertical axis depicts the mole fraction of water molecules χ_{water} whereas the right vertical axis shows the mole fraction of ethanol molecules $\chi_{ethanol}$.

the applied field becomes orthogonal, i.e. $\theta = 90^\circ$, which again leads to segregation of ethanol from water. A deeper analysis suggests that the origin of the aforesaid separation lies in the contrasting effect of axial ($\theta = 0^\circ$) and orthogonal ($\theta = 90^\circ$) electric fields on the molecular arrangements inside the CNT. Figure 8.3 (B) presents the variation in mole fraction with increasing field strength for the limiting cases of $\theta = 0^\circ$ and 90° . It can be easily discerned that an axial electric field increases the water concentration inside the CNT whereas the orthogonal field enhances the ethanol concentration. Moreover, the separation effect is significantly augmented at higher magnitudes of applied field strength and almost complete separation of water-ethanol is observed at $E = 2.0 \text{ V/nm}$ for both $\theta = 0^\circ$ and 90° .

The influence of the applied electric field can be elucidated by examining the dipole orientation of water molecules inside the CNT. The water dipole angle, represented by ϕ , is defined as the angle between a water dipole (defined from the

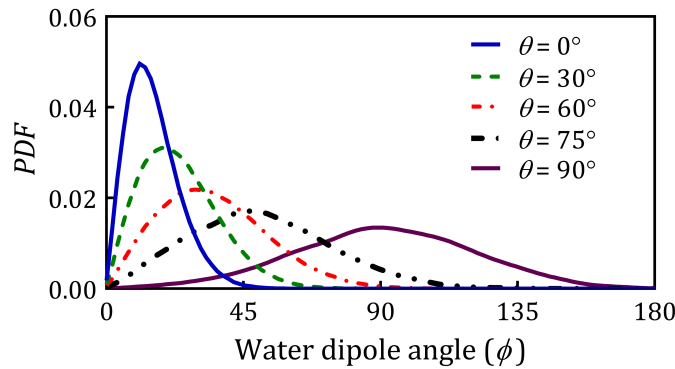


Figure 8.4: The probability distribution of water dipole angles ϕ inside the CNT under an imposed electric field of $E = 1.5 \text{ V nm}^{-1}$ oriented at $\theta = 0^\circ, 30^\circ, 60^\circ, 75^\circ$ and 90° . The water molecules existing inside an annular region of 1 nm from the CNT walls are only considered for the calculation.

oxygen atom to the centre of the two hydrogen atoms) and the CNT ($+z$) axis. For pure water flow inside a CNT, the formation of a dense ordered water layer has been reported with dipoles orienting parallel to the nanotube axis [261,287]. Figure 8.4 presents the probability distribution of the water dipole angle ϕ (within an annular region of 1 nm from the CNT wall) with variation in the electric field orientation angle θ . It can be clearly observed that an axially aligned ($\theta = 0^\circ$) electric field promotes an uniform orientation of the water molecules inside the CNT with the dipoles pointing towards the CNT axis. The ordered orientation of dipoles results in a stable water structure and leads to preferentially occupancy of water inside the CNT. As θ is increased, the ordered structure of water is diminished with water dipoles distributed over a large range. When the applied electric field becomes orthogonal ($\theta = 90^\circ$), the dipoles align perpendicular to the CNT axis and disrupt the water ordering inside the CNT. Under such circumstance, the hydrophobic nature of the CNT offers an advantage to the ethanol molecules leading to preferential partition. The nanotube is hence favourably occupied by ethanol molecules in place of water.

In order to understand the mechanism behind the separation phenomenon, we compute the radial density distributions of atoms inside the CNT. The nanotube is divided into a number of annular sections of equal spacing in the radial direction and the density distribution is obtained by time averaging the molecules contained within a thin annular section at radius r . Figure 8.5 (A) presents the density profiles of both water and ethanol along the radial direction of the CNT under an imposed

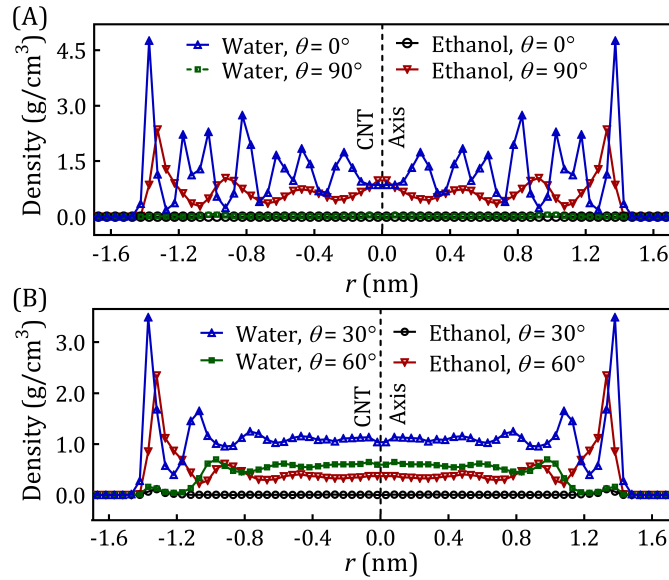


Figure 8.5: Radial density distribution inside the CNT for water and ethanol molecules under an imposed electric field of $E = 1.5 \text{ V nm}^{-1}$ oriented at (A) $\theta = 0^\circ$ and 90° and (B) $\theta = 30^\circ$ and 60° . The vertical dotted line at $r = 0$ denotes the CNT centreline and the CNT walls are located at $r = \pm 1.7 \text{ nm}$ (the ends of the horizontal axis).

electric field of $E = 1.5 \text{ V/nm}$ for the limiting cases of $\theta = 0^\circ$ and 90° . When the electric field is axially aligned ($\theta = 0^\circ$), the water density profile resembles sharp oscillatory waves throughout the entire cross section of the CNT. A dense layer of water molecules is observed adjacent to the CNT wall at a distance of 0.32 nm which agrees well with previous literature [261]. The strong oscillatory profile indicates the formation of an ordered water structure with multiple layers of water in an ice-like configuration. The density profile of water corroborates the observations of Fig. 8.4 wherein the dipole distribution predicted an uniform arrangement of the water molecules for $\theta = 0^\circ$. The ethanol presence is negligible under this circumstance. On the other hand, when the applied field is orthogonal to the CNT ($\theta = 90^\circ$), the water structure is completely disrupted thereby making it unfavourable inside the CNT. Interestingly, the ethanol density profile for this field orientation exhibits similar oscillatory nature albeit in a diminished way. It can be thereby inferred that an orthogonal field promotes the formation of a uniform multi-layered structure of ethanol inside the CNT with negligible presence of water molecules.

Apart from the limiting conditions of $\theta = 0^\circ$ and 90° , the density profiles of

water and ethanol for $\theta = 0^\circ$ and 60° are presented in Fig. 8.5 (B). For $\theta = 30^\circ$, the dense layer of water molecules is observed adjacent to the CNT wall at a distance of 0.32 nm with a reduced magnitude in comparison to an axially aligned field. Moving inwards, additional peaks are observed signifying existence of multiple layers of water molecules. However, the water molecules gradually lose memory of the wall and tends to assume a bulk-like structure near the CNT centreline. This is in contrast to the observation in Fig. 8.5 (A) wherein the oscillatory behaviour of water density persists throughout the entire cross-section of the CNT. The relative disruption in the ordered arrangement of water molecules, when θ is increased from 0° to 30° , significantly alters the density pattern and results in a bulk-like structure of water rather than an ice-like configuration inside the CNT. However, the presence of ethanol molecules remains negligible for $\theta = 30^\circ$.

On the other hand, for $\theta = 60^\circ$, the ethanol molecules are concentrated in an annular layer at a distance of 0.37 nm from the CNT wall. Towards the centreline of the CNT, a bulk-like structure persists with the ethanol density being lower than the bulk density for an orthogonal electric field. In contrast to $\theta = 30^\circ$, the presence of water molecules in the bulk region is non-trivial. However, the water peak near the wall is absent under this condition indicating the favoured residence of ethanol molecules inside the CNT for $\theta = 60^\circ$.

The molecular arrangements inside the CNT and their transport properties are closely linked to the interaction of water and ethanol molecules. We compute the average interaction potential energy per molecule of water and ethanol within the CNT region. The probability distribution function (PDF) of the interaction potential for water (U_w) and ethanol (U_e) under an applied electric field intensity of, $E = 1.5$ V/nm is presented in the Fig. 8.6. The plot in Fig. 8.6 (A) depicts that for, $\theta = 30^\circ$, the interaction energy per water molecule is highest with a maximum of $U_w = -46$ kJ/mol. The distribution of the energy is concentrated in a rather narrow band. As the orientation angle θ is increased, the interaction energy of water monotonically decreases wherein the distribution of energy spread over a wider range. In contrast, the average interaction energy of ethanol in Fig. 8.6 (B) continuously increases with increase in θ . The maximum interaction energy per ethanol molecule for $\theta = 60^\circ$ is around $U_e = -15.6$ kJ/mol. The distribution of energy also remains confined over a narrow band at higher magnitude of θ . The electric field orientation thus exert a completely contrasting influence on the interaction of water and ethanol, which ultimately manifest in the preferential occupancy of water or ethanol at lower or

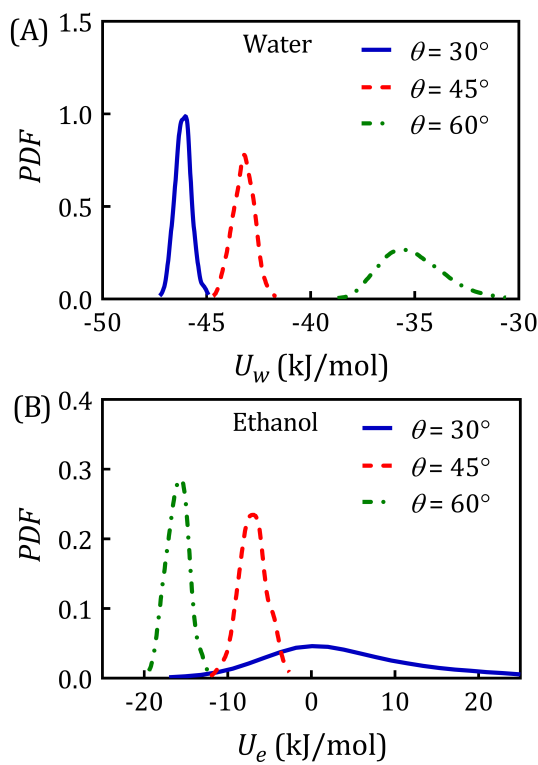


Figure 8.6: The probability distribution of the average interaction energy of each molecule inside the CNT under an imposed electric field of $E = 1.5 \text{ V nm}^{-1}$ oriented at $\theta = 30^\circ$, 45° and 60° for (A) water molecules and (B) ethanol molecules.

higher values of θ , respectively.

In order to further explain the interaction of water and ethanol inside the CNT, we analyse the average number of hydrogen bonds (N_{hb}) formed per molecule of water and ethanol for varying θ under an imposed field of $E = 1.5 \text{ V/nm}$. We note here that no ‘absolute’ definition of hydrogen bonding exists in literature. In the present work, we employ a geometric criterion by considering a hydrogen bond to be formed when the distance between the donor and acceptor oxygen atoms (O—O) is less than 0.35 nm and simultaneously, the H—O—O angle is smaller than 30° [292]. The water molecules existing inside an annular region of 1 nm from the CNT walls are considered for the calculation. Additionally, the average number of water and ethanol molecules (N) residing inside the CNT is computed. The variation of N_{hb} and N with θ is presented in the Fig. 8.7. It is seen from Fig. 8.7 (A) that N_{hb} for both water and ethanol is strongly dependent on the angle of the applied field. The figure suggests that a lower value of θ promotes the formation of hydrogen bonds

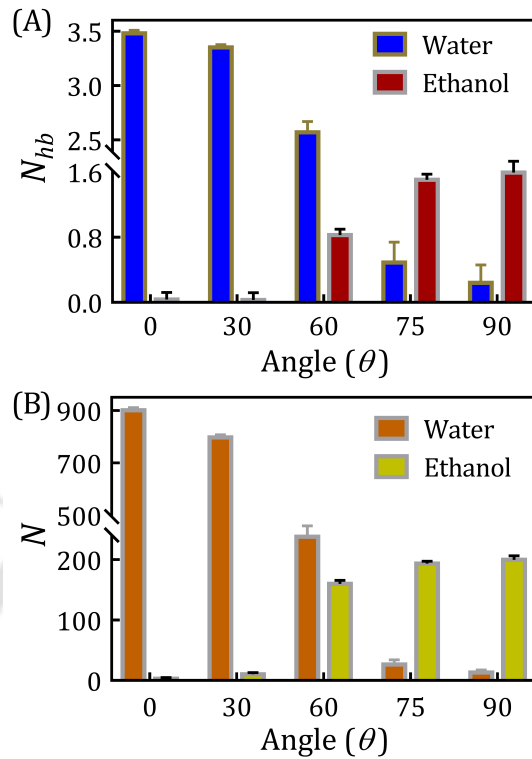


Figure 8.7: The variation of (A) the number of hydrogen bonds N_{hb} formed by water and ethanol molecules inside the CNT and (B) the number of molecules N of water and ethanol occupying the CNT with an electric field orientation angle θ . Water molecules existing inside an annular region of 1 nm from the CNT walls are considered for the calculation.

between water molecules while diminishes the same between ethanol molecules. On the contrary, at higher values of θ , the hydrogen bonded structure of water is depleted and ethanol forms a strongly bonded network. This is corroborated by Fig. 8.7 (B) wherein it is observed that the number of water molecules decreases whereas ethanol molecules increases with continuous raising of θ from 0° to 90°. As the number of water molecules decreases, the average separation distance between the water molecules decreases and hence the interaction between water molecules is reduced.

On the other hand, ethanol molecules come closer due to increasing occupancy inside the CNT and hence the ethanol-ethanol molecular interaction increases upon varying θ from 0° to 90°. The increase (decrease) of hydrogen bonding for ethanol (water) owing to the variation of the electric field orientation thus plays a crucial role in deciding the separation of water and ethanol inside the carbon nanotube. The separation of water and ethanol inside the CNT under the influence of applied

electric field can lead to a selective membrane under the flow conditions. Recently, Gravelle *et al.* [57] demonstrated the separation of water-ethanol in an osmotic flow setup using carbon nanotubes. In the case of osmotic separation systems, an external electric field can be used to tune the selectivity of the CNT-membrane configuration towards a specific species (water or ethanol) thereby enhancing the efficiency of membrane based separation systems.

8.4 Summary

The present chapter investigates the influence of an externally applied electric field on the separation of water-ethanol solution inside a carbon nanotube employing molecular dynamics simulations. Starting from an equimolar mixture of water and ethanol, a tuneable separation of the mixture into the individual constituents is demonstrated by varying the orientation of the electric field to the axis of the carbon nanotube. The separation manifests owing to the contrasting effect of the axial ($\theta = 0^\circ$) and orthogonal ($\theta = 90^\circ$) electric fields on the preferred occupancy of water and ethanol in the CNT. For lower values of θ , water molecules show higher affinity towards the CNT whereas at higher magnitude of θ , ethanol molecules show preferred occupancy in the CNT. The separation is augmented by increasing the strength of the applied electric field. The molecular ordering and arrangement inside the CNT is significantly altered by variation of θ resulting in the separation effect for water and ethanol.



Chapter 9

Conclusions and scope for future research

9.1 Conclusions

The present thesis attempts to shed light on the dynamics of fluid flow configurations consisting of two immiscible and miscible fluids by performing extensive numerical simulations. In this chapter, we summarize the important findings from our research work. The concluding remarks are categorized into three groups based on the broad research domains and are listed below.

9.1.1 Formation, growth and breakup of liquid drops and jets emanating from orifices

Numerical simulations of formation of drops and break-up of liquid jets from an orifice are performed using CLSVOF method under axisymmetric conditions. The study focuses on the growth history of a drop under constant inflow conditions and presents a quantitative match with a theoretically predicted growth law. The profile of the drop during the initial growth stage is showed to be self-similar, which serves as an addition to the self similarity near the collapse stage previously reported in literature. The thinning behavior of the liquid neck shows a transition from an inertia dominated regime to an inertia-viscous regime when the liquid neck falls below a critical minimum radius. It is observed that interface overturning occurs when drop viscosity is low whereas it is arrested for highly viscous drops. A detailed paramet-

ric study of the overturning phenomenon reveals a critical value of Oh above which overturning stops. The values of large and small cone angles of the interface deviate significantly from the theoretically predicted values of 112.8° and 18.1° as the drop viscosity is increased. The transition from dripping to jetting regime has been simulated and two distinct jetting regimes has been observed depending of the dominance of inertia or viscous forces. Increasing the injection rate of drop liquid causes a transition to jetting regime, which can be explained in terms of the dominance of inertia over capillary forces. Another class of transition occurs due to the increasing viscosity of the outer ambient fluid, which leads to higher drag force on the interface thereby leading to jetting. The drops formed in this regime are significantly larger than the jet radius. The jetting profile under the dominance of viscous effects shows a profoundly different behavior compared to previously reported results and thus serves as an addition to the existing literature on dripping-jetting transition. The jet length at break-up, computed from our simulations, corroborates the predictions from Rayleigh's theory in the jetting regime. Varicose perturbations are observed on the surface of the liquid column as the jet moves downstream. The high inertia of the moving jet causes entrainment of ambient air resulting in a vortical structure just outside the liquid jet. The entrainment increases as the We is increased signifying the influence of the ambience on the dynamics of break-up at higher inflow rates.

The formation and breakup of a curved liquid jet in air is investigated by conducting extensive three-dimensional numerical simulations. The liquid is injected from an orifice perpendicular to the direction of gravity and the trajectory of the flowing jet follows a parabolic pattern. The jet breakup mode is compared between liquid injected parallel and perpendicular to gravity. The simulations reveal that the perturbations growing on the jet surface are asymmetric in nature for perpendicular injection whereas the perturbations remains symmetric for parallel injection. As the Weber number is increased, the limiting length of the jet at breakup L_d^* increases due to higher inertia of the jet. Increasing the Ohnesorge number allows the jet to breakup at higher value of L_d^* . The trajectory of the jet follows a parabolic path and the horizontal distance traversed is critically dependent on the value of Weber number. A higher value of Weber number enables the jet to cover larger horizontal distance. Additionally, the magnitude of the Bond number dictates the path followed by the jet and the curvature of the trajectory is significantly enhanced with increase in the Bond number. The drops detached after pinch-off undergo rolling

motion with shape oscillations, which is in stark contrast to the periodic oblate-prolate oscillations observed in parallel injection. The asymmetry of the velocity field inside the drop manifests in the form of a rolling motion as well as results in the shape oscillations of the falling drop.

The dynamics of drop formation from a submerged orifice under the influence of an external electric field are explored in detail. The study focuses on the interfacial morphology of the droplet formed at the orifice inside a quiescent pool of another liquid and analyzes the effect of the applied electric field on the droplet characteristics. The electro-hydrodynamic problem is solved by considering the fluids as either perfect dielectrics or leaky dielectrics. The study reveals that under the influence of electric field, prolate shaped drops are formed in the case of perfect dielectric fluids. The deformation of the drops is enhanced as the applied electric field strength E is increased. The electric field increases the volume of the detaching drops and delays the drop breakup. The polarization force generated by the electric field acts normal to the interface and the direction of the force is governed by the permittivity ratio S between the fluids. The local intensity of the polarization forces are maximum near the drop tip when S is less than unity, whereas the maximum polarization forces are concentrated near the equatorial region when S is greater than unity. The disparity of electric permittivity across the interface disturbs the applied uniform electric field. The electric potential lines diverge while entering the drop for $S < 1$ thereby indicating the lower electric intensity inside the drop under such conditions. Systems of leaky dielectric fluids have also been studied and in particular two cases have been computed in detail. The first system consists of a drop which is less conducting but has higher permittivity than the surrounding fluid, whereas in the second system, the drop is more conducting but has a lower permittivity than the suspending fluid. In complete contrast to the case of perfect dielectrics, the drop which is less conducting but has higher permittivity than the surrounding medium, deforms into an oblate shape and the magnitude of deformation is amplified when the field strength E is increased. However, the drop deforms into a prolate shape when the second system of fluids is considered. The prolate deformation is enhanced owing to the higher magnitude of applied field and a dripping-jetting transition is observed for sufficiently high field strength. The breakup time and volume of the drops jettisoned from the orifice are dependent on the combination of fluid properties as well as the applied field strength E . Interestingly, the charge accumulation at the drop tip presents a contradictory behavior for both the systems, which fun-

damentally alters the direction of the Coulombic forces for the two systems under consideration. The fluid motion reveals a circulation pattern inside the drop from either the tip region to the equatorial region or from the equatorial region to the tip, alongside the interface, depending on the fluid systems of interest. The conductivity ratio R decides the sign of the charge accumulated at the drop tip and modulates the local electric field intensity inside the drop.

9.1.2 Deformation and pinch-off of a migrating compound droplet in a tube

The hydrodynamic behavior of compound droplets traversing inside a capillary tube under axisymmetric conditions are investigated by performing direct numerical simulations. The study focuses on the temporal evolution of a compound droplet and analyzes its deformation history and interfacial morphologies. The study uncovers an unsteady evolution of a compound droplet under the action of an imposed flow in which the outer droplet progressively deforms along the flow direction attaining a distorted prolate shape. The inner drop however gradually deforms perpendicular to the flow direction in the unsteady regime and reaches a distorted oblate shape at steady state. The inner drop moves away from the initial concentric position thereby increasing the drop eccentricity and finally saturates to a constant value with time. The deformation of both the inner and outer interfaces depends on the magnitude of Ca with the inner drop undergoing significantly larger deformation at higher values of Ca . In addition, the viscosity ratio plays a critical role in deciding the magnitude of interfacial deformations and drop eccentricity. The inner drop is found to migrate faster than the outer drop during the initial stage of motion inside the capillary and the relative velocity difference between the drops increases at higher η . The spatio-temporal evolution of the inner drop towards the front of the compound drop and the deformations of the inner and outer interfaces normal to each other forms a thin film near the nose of the moving compound droplet, which eventually causes the breakup of the outer shell of the compound droplet. The thickness of the shell is found to have substantial influence on the stability of the drop thereby determining the time before the outer shell pinches-off. However, the rate of thinning is found to be independent of the initial thickness of the shell. Importantly, the rate of thinning of the outer shell thickness follows a power law criterion with one initial stage of swiftly thinning regime to a slowly thinning regime

before the pinch-off. The findings from the present study may help in predicting the temporal rate of deformation of compound drops traversing inside a capillary. The estimation of rupture time can also be attempted by applying the power-law criterion proposed for compound droplet breakup.

9.1.3 Electric field induced separation of water-ethanol mixture inside carbon-nanotubes

A systematic investigation has been carried out to reveal the influence of an externally applied electric field on the separation of water-ethanol solution inside a carbon nanotube. Starting from an equimolar mixture of water and ethanol, a tuneable separation of the mixture into the individual constituents is demonstrated by varying the orientation of the electric field to the axis of the carbon nanotube. The separation manifests owing to the contrasting effect of the axial ($\theta = 0^\circ$) and orthogonal ($\theta = 90^\circ$) electric fields on the preferred occupancy of water and ethanol in the CNT. For lower values of θ , water molecules show higher affinity towards the CNT whereas at higher magnitude of θ , ethanol molecules show preferred occupancy in the CNT. The separation is augmented by increasing the strength of the applied electric field. An in depth analysis uncover that the molecular arrangement inside the CNT is significantly altered by variation of θ . The water dipoles are favourably aligned with the CNT axis for smaller values of θ and points towards the CNT walls at higher magnitude of θ . For lower values of θ , multiple layers of water are observed around the CNT walls, which diminish with increasing θ . In contrast, the ethanol concentration is amplified at higher values of θ thereby demonstrating the contrasting influence of the electric field orientation on the molecular interactions in the CNT. The simulations suggest that the interaction energies of water molecules decrease whereas the same for the ethanol molecules increase when θ is increased from 0° to 90° . The change of interaction energy can be attributed to the promotion (retardation) of hydrogen bonding for ethanol (water) molecules at larger magnitudes of θ . The findings from the present work provide insight into the influence of an external electric field and its orientation on the separation of water-ethanol solution into the constituents.

9.2 Scope for future research

In the context of the present investigations, several aspects can be identified that would benefit from further examination. Some of the potential areas that may form the basis for future research are listed below:

The studies on drop and jet formation can be extended beyond the axisymmetric regime by carrying out full three-dimensional simulations. The increase in the fluid inertia at higher inflow rates as well interaction with the ambient medium initiates multiple transitions, which offer rich underlying dynamics for more detailed analysis.

The fluids considered in the present thesis are assumed to have Newtonian characteristics. However, many commonly used fluids exhibit non-Newtonian behaviour. The effective viscosity of non-Newtonian fluids is dependent on the shear rate or shear rate history. As the consequence, it can be envisaged that drops and jets of non-Newtonian fluids may describe a large number of interesting features during formation as well as the subsequent breakup.

In the present thesis, the influence of direct current electric field on the dynamics of formation and breakup of drops have been investigated. Interestingly, the usage of an alternating current electric field has shown promising potential for controlling the dynamics of bubble formation [192]. The present study can be further enriched by analyzing the effect of alternating current electric field on the droplet dynamics.

The controlled breakup of translating compound drops is a challenging task due to its related applications in encapsulation and targeted drug delivery. The application of an external electric field for non-invasive control over the deformation and breakup of the compound droplets may be considered as an interesting avenue for future exploration.

Finally, the present thesis has proposed a novel methodology for simulating the separation of water-ethanol solution at the nanoscale. However, extensive studies are required to analyze the feasibility and efficiency of the proposed method. The separation effect may be analyzed employing a large array of aligned carbon nanotubes to increase the throughput of the process. The rapid advancement of nanofabrication technologies may pave the way for realistic experimentation to provide a quantitative estimation of the performance of the proposed methodology in the near future.

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List of publications

Journal publications

1. **M.P. Borthakur**, G. Biswas and D. Bandyopadhyay, Formation of liquid drops at an orifice and dynamics of pinch-off in liquid jets, *Physical Review E* 96, 013115, 2017.
2. **M.P. Borthakur**, G. Biswas and D. Bandyopadhyay, Dynamics of deformation and pinch-off of a migrating compound droplet in a tube, *Physical Review E* 97, 043112, 2018.
3. **M.P. Borthakur**, D. Bandyopadhyay and G. Biswas, Electric field mediated separation of water-ethanol mixture in carbon-nanotubes integrated to nanoporous graphene membrane, *Faraday Discussions* 209, 259-271, 2018.
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1. **M.P. Borthakur**, B. Nath, G. Biswas and D. Bandyopadhyay, Formation and Breakup of Liquid Jets Curved by Gravity, *ASME 2017 International Mechanical Engineering Congress and Exposition*, Tampa, Florida, 3rd - 9th November, 2017.
2. **M.P. Borthakur**, B. Nath, G. Biswas and D. Bandyopadhyay, Numerical Simulation of Break-Up of Liquid Jets Curved by Gravity, *The Asian symposium on computational heat transfer and fluid flow (ASCHT)*, IIT Madras, 10th - 13th December, 2017.
3. **M.P. Borthakur**, D. Bandyopadhyay and G. Biswas, The modelling and enhancement of water hydrodynamics: general discussion, *Artificial Water Channels*, University of Strathclyde, Glasgow, 25th - 27th June, 2018.

