

Imperial College London
Department of Chemical Engineering

**Three-dimensional computational
fluid dynamics simulations of
complex multiphase flows with surfactants**

by
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Abstract

The breakup of an interface into a cascade of droplets is a phenomenon of central importance to a large number of industrial and biological/healthcare applications. Examples of these applications include the atomisation of propellants in engines, the formation of droplets in injectors, mixers and separators, and spray-formation that accompany environmental flows, as well as coughs and sneezes in biomedical settings. Multiphase flow dynamics are influenced by a range of multi-scale physics; this includes the interaction of turbulence with interfaces (creating cascades of motion featuring a large separation of scales), capillarity, viscosity (and complex rheology), gravity, and also heat transfer with phase change. The presence of surface-active agents (surfactants), either as contaminants, pathogens, or additives, also influences the flow dynamics adding layers of complexity. The multi-scale nature of many types of the flow, and the tremendously complex interfacial topology, however, complicates the scrutiny of multiphase flows.

In this thesis, I have worked on direct numerical simulations to elucidate the physics of vortex-surface interaction in turbulent multiphase jets for industrial mixing applications. The thesis topic focuses on understanding physics of interface breakup and coalescence, which exemplify situations wherein the interface undergoes topological transitions, e.g. filament breakup into drops, and merging of drops/bubbles due to coalescence, accounting for surfactant-induced effects. These transitions involve the development of singularities where interfacial distances vanish and velocity fields diverge, requiring highly-specialised numerical techniques.

Prior to this thesis, the vortex-surface interaction in the context of turbulent liquid jets has not been presented. Not to say, that this thesis accounts for the first time the effect of surfactant in such a complex phenomenon. Additionally, previous research was restricted either to flows pre-breakup/coalescence, or the study of these phenomena but within the constraints of axisymmetry, which is not reflective of real-life applications. By using a hybrid front tracking/level set method to treat the interfacial dynamics, this thesis has accounted not only for surface tension forces, but those arising from the presence of interfacial surfactant concentration gradients that lead to Marangoni stresses, to analyse a number of industrially-relevant phenomena post-break and within a three-dimensional framework. These phenomena include breakup and recoiling of liquid threads, bubbles undergoing bursting, and drops coalescing partially or completely with deformable interfaces.

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To my mother, my dad and my brothers

With infinite love

I have no idea. People who boast about their IQ are losers.

Stephen Hawking

Publications

During the duration of this PhD, I participated in the following publications:

Dynamics of retracting surfactant-laden ligaments at intermediate Oh number

C. R. Constante-Amores, L. Kahouadji, A. Batchvarov, S. Shin, J. Chergui, D. Juric and O. K. Matar.
Phys. Rev. Fluids **5**, 084007 (2020)

Rico and the Jets: turbulent liquid jets

C. R. Constante-Amores, L. Kahouadji, A. Batchvarov, S. Shin, J. Chergui, D. Juric and O. K. Matar.
Phys. Rev. Fluids **5** 110501 (2020)

Dynamics of a surfactant-laden bubble bursting through an interface.

C. R. Constante-Amores, L. Kahouadji, A. Batchvarov, S. Shin, J. Chergui, D. Juric and O. K. Matar.
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Effect of surfactant on elongated bubbles in capillary tubes at high Reynolds number.

A. Batchvarov, M. Magnini, L. Kahouadji, **C. R. Constante-Amores**, S. Shin, J. Chergui, D. Juric, R. Craster, O. K. Matar
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Three-dimensional dynamics of falling films in the presence of insoluble surfactants.

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Direct Numerical Simulations of transient turbulent jets: vortex-interface interaction.

C. R. Constante-Amores, L. Kahouadji, A. Batchvarov, S. Shin, J. Chergui, D. Juric and O. K. Matar.
J. Fluid Mech. (under review)

Dynamics of a surfactant-laden droplet coalescence with an interface.

C. R. Constante-Amores, A. Batchvarov, L. Kahouadji, S. Shin, J. Chergui, D. Juric and O. K. Matar.
J. Fluid Mech. (under review)

The transition to aeration in two-phase mixing

L. Kahouadji, **C. R. Constante-Amores**, A. Batchvarov, , J. Chergui, D. Juric, S. Shin and O. K. Matar
Int. J. Multiph. Flow (under review)

Conference presentations

I delivered the following conference presentations apart from those co-authored.

Nov 2020 (virtual): 73rd Annual Meeting of the APS Division of Fluid Dynamics, Chicago, USA

Contributed talks:

Direct numerical simulations of turbulent liquid jets

Dynamics of surfactant laden bursting bubbles through an interface

Benchmarking of solvers for the simulation of two-phase jets

Visualizing CFD data in 3D augmented reality as an extension of 2D figures in scientific publications

Effect of Marangoni parameter on three-dimensional wave dynamics of falling liquid film

The transition to aeration in a two-phase turbulent mixing system

Aug 2020 (postponed): 25th International Congress of Theoretical and Applied Mechanics, Milan, Italy - contributed talk: Dynamics of a surfactant-laden bubble bursting through an interface

Nov 2019: 72nd Annual Meeting of the APS Division of Fluid Dynamics, Seattle, USA

Contributed talks:

DNS of the Three Dimensional Dynamics of Surfactant Laden Bursting Bubbles

DNS of the Three Dimensional Dynamics of Surfactant Laden Retracting Ligaments

3D DNS of Annular Falling Film Wave Dynamics in the Presence of Soluble Surfactants

The effect of surfactant on the tail dynamics of elongated bubbles

Numerical Simulations of Drop Impact on Surfactant-Laden Interfaces

Two-dimensional direct numerical simulations of viscoelastic jets

Three-dimensional Numerical Simulations of Turbulent Surfactant-laden Jets

Nov 2019: BP-ICAM Conference. University of Manchester, UK - contributed talk: Three-dimensional Numerical Simulations of Turbulent Surfactant-laden Jets

Sep 2019: Droplets 2019. University of Durham, UK - contributed material to plenary speaker, Omar K Matar: Droplet generation via bursting, impacting, and jetting, with surfactants

Aug 2019: UK Fluids Conference 2019. University of Cambridge, UK - contributed talk: DNS of the Three Dimensional Dynamics of Surfactant Laden Bursting Bubbles

Jul 2019: Chemical Engineering PhD Symposium 2019. Imperial College London, UK - contributed talk: Complex multiphase flows in presence of surfactants

May 2019: 10th International Conference on Multiphase Flow, Rio Janeiro - contributed talk: Three-dimensional Numerical Simulations of Turbulent Surfactant-laden Jets

Nov 2019: 71st Annual Meeting of the APS Division of Fluid Dynamics, Atlanta, USA - contributed talk: Direct numerical simulation of three-dimensional liquid jet breakup with surfactant

Nov 2018: BP-ICAM Conference. University of Manchester, UK - contributed talk: Three-dimensional Numerical Simulations of Turbulent Surfactant-laden Jets

Jun 2018: CDT of TSM: Postgraduate Student day 2018. Imperial College London, UK - contributed talk: Complex multiphase flows in presence of surfactants

Nov 2017: 70th Annual Meeting of the APS Division of Fluid Dynamics, Denver, USA - contributed talk: Direct numerical simulation of three-dimensional liquid jet breakup

Nov 2017: BP-ICAM Conference. University of Manchester, UK - contributed talk: Three-dimensional Numerical Simulations of Turbulent Jets

Jun 2017 CDT Fluids Student Symposium 2017. Imperial College London, UK (poster)

Feb 2017 Thomas Young Centre Postgraduate Student day. Queen Mary University of London, UK (poster)

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2020: UK Fluids Network, Photo competition in Turbulence: Honourable mention (2nd place)

2019: Milton van Dyke Award from the American Physical Society, Division of Fluid Dynamics

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Notation

In this thesis, all symbols are defined where they first appear. For the reader's convenience, the principal meanings of the commonly used notations are presented in the lists below. The symbols are arranged based on the chapter where they are first introduced, so as to avoid confusion. Though many of the symbols are specific to the chapter where they are introduced, in certain cases, symbols introduced in previous chapters might be employed with the same meaning in following chapters.

General rules

- A ' on top of a symbol denotes the time derivative of the corresponding quantity.
- The subscripts $_l$ and $_g$ is used to refer to liquid and gas phases.
- The subscripts $_s$ and $_b$ are used to refer to the surface and bulk quantities of given parameters, respectively.
- A tilde symbol on top of a symbol denotes a non-dimensional quantity.

Abbreviations

2D,3D	Two-dimensional and three-dimensional respectively
LCRM	Level Contour Reconstruction method
VOF	Volume of fluid
HPC	High Performance Computing
CFD	Computational Fluid Dynamics
FDM	Finite Difference Methods
GMRES	Generalised Minimal Residual
MPI	Message Passing Interface
KH	Kelvin-Helmholtz
RP	Rayleigh-Plateau

Dimensionless quantities

Bi	Biot number
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Bo	Bond number
Fr	Froude number
k	Adsorption parameter
La	Laplace number
Oh	Ohnesorge number
Pe_b	Bulk Peclet number
Pe_s	Surface Peclet number
Re	Reynolds number
We	We number

Symbols used throughout

$\mathbf{x}$	Cartesian coordinate vector $[x, y, z]^T$
t	Time
$\mathbf{I}$	Identity matrix with dimension $n \times n$
$\mathbf{u}$	Velocity vector field $[u, v, w]^T$
p	Pressure field
ρ	Density field
$\mathbf{S}$	Symmetric strain rate tensor
g	Acceleration of gravity (dimensional)
ω	Vorticity field
β_s	Surfactant elasticity
Γ	Interfacial surfactant concentration
Γ_∞	Maximum packing of interfacial surfactant species
ρ	Density field
μ	Viscosity field
σ	Surface tension
σ_s	Surfactant-free surface tension
τ	Tangential stress
∇	Laplace operator
∇_s	Surface gradient operator
h	Film thickness
A	Area or Amplitude
A_e	Area of interfacial mesh element
C	Bulk surfactant concentration
C_s	Surfactant concentration in bulk sub-phase
D	Diameter

D_c	Surfactant bulk diffusion coefficient
D_s	Surfactant surface diffusion coefficient
$\mathbf{F}_n$	Term containing normal component of surface tension
$\mathbf{F}_s$	Term containing tangential component of surface tension
$\mathbf{G}$	Term containing gravitational forces
$\mathbf{H}$	Smoothed Heaviside function
r	Radius

Symbols introduced in chapter 3

ε	Kinetic energy viscous dissipation
η	Kolgomorov length-scale
l	Length-scale
f	Frequency
U	Inlet velocity
θ	Azimuthal component of vorticity
d_m	Mean diameter

Symbols introduced in chapter 5

L_o	Initial length of the ligament
R	Initial radius of the thread
E_k	Kinetic energy
θ	Azimuthal component

Symbols introduced in chapter 6

P_o	Pressure underneath of the bubble
P_b	Pressure inside of the bubble
P_{atm}	Pressure in the surrounding medium
h_∞	Height of the bubble tail
R_{cap}	Radius of the spherical cap
a	Large semi-axes of the ellipse
b	Small semi-axes of the ellipse

Chapter 1

Introduction: Multiphase flows

1.1 Challenges of Multiphase flows

The physical understanding of gas-liquid multiphase flows has received significant interest due to their occurrence in a multitude of natural and industrial applications (e.g., breaking waves, raindrops or disease transmission via droplet-formation). Examples of these applications include the atomisation of propellants in engines, the formation of droplets in injectors, mixers, separators, and the generation of droplets in two- and multiphase flow regime transitions (Eggers, 1993; Eggers and Villermaux, 2008; Tryggvason et al., 2011; Pope, 2000).

This thesis focuses on surface-tension-driven-flows, and consequently, I would introduce the concept of *surface tension* which can be explained as the force existing on the surface of a liquid as a result of the asymmetries in the cohesive (i.e., strong) and adhesive (i.e., weak) forces between surface molecules. The surface molecules are partially surrounded by other liquid molecules, and therefore, they exhibit a stronger attractive forces in comparison to the molecules which are in the liquid bulk. On this basis, the net effect is an inward force which minimises the interfacial area for a given volume. Surface tension is described by units of force/length (or energy/area) which can also be thought as a negative surface pressure (or as a line tension which acts in all the directions parallel to the interface).

The elucidation of the physics behind gas-liquid multiphase flows is challenging and most of the available information have come from experimental work or scaling analysis. Analytical solutions for multiphase systems are only available for simplified problems (such as the motion of bubbles in Stokes flows) due to the nonlinear term in the governing equations and the need for the the prediction of the interface location as part of the solution. Some of the challenges associated with two-phase flows are:

- (i) Multiphase flows are discontinuous in nature.

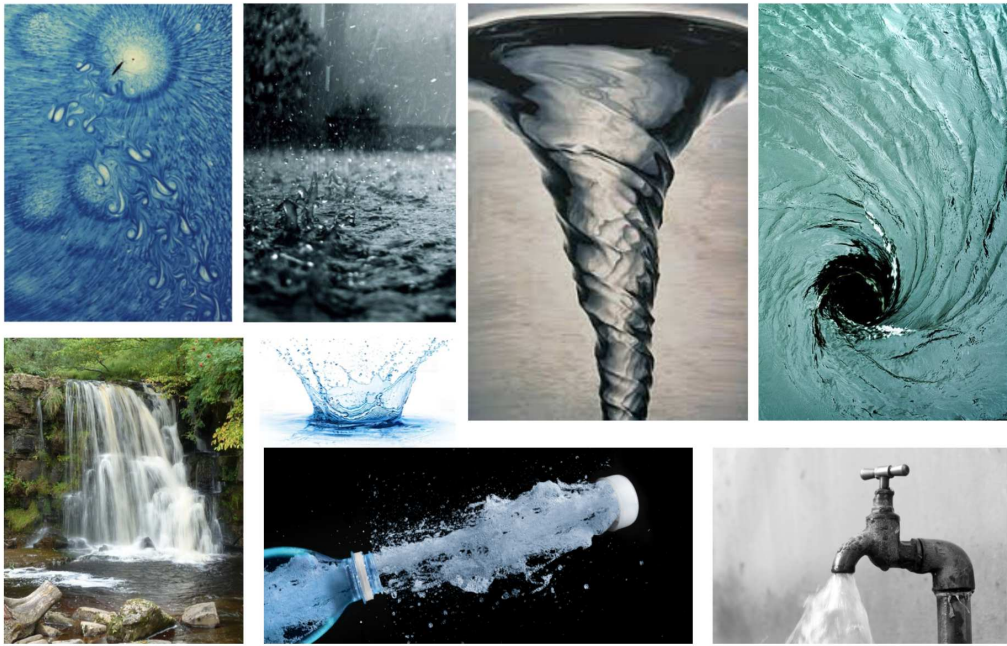


Fig. 1.1. The beauty and complexity of multiphase flows in nature: insect walking on a water surface, drop fragmentation as a result of falling rain or droplet splash, jet dynamics for tap water falling into a sink or during the explosion of a liquid-pressurised, and whirlpools.

- The interface is extremely thin and exhibits a singular surface tension force.
 - Fluid properties vary significantly across the interface.
- (ii) Multiphase flows are strongly multi-scale.
- From microscopic droplets to even meters in many flows (e.g., atomisation or oceanic flows).
 - Complex topological changes (e.g., coalescence and capillary breakup).
 - Turbulence (creating cascades of motion featuring a large separation of scales).
- (iii) Multiphase flows are generally multi-physics.
- Surfactants may be present, whose concentration variations lead to surface tension gradients (e.g., Marangoni stresses).
 - Thermal variation along the interface and phase change.
 - Electric and magnetic fields.
 - Complex rheological effects (i.e., viscoelastic fluids).

The multi-scale nature of the flow, and the tremendously complex interfacial topology, make difficult the scrutiny of multiphase flows experimentally even in the absence of additives. Thus, elucidat-

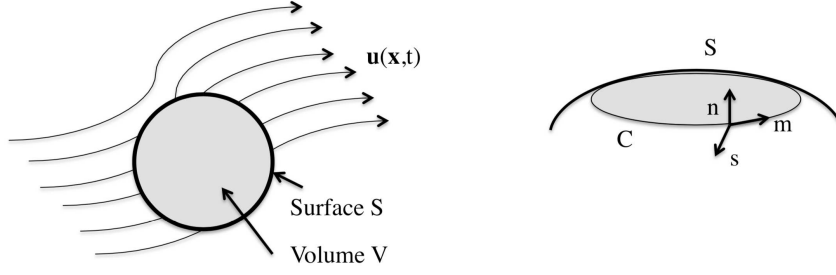


Fig. 1.2. A stationary control volume V surrounded by a surface S (left figure). A surface S separating two fluids and bounding contour C on the interface between two fluids (right figure).

ing the influence of additives on these flows requires the development of theoretical and computational tools to enable high-fidelity simulations to be deployed to drive experiment design and understand the delicate interplay among the different physical mechanisms across scales.

Since the experimental characterisation is a challenging process, the natural movement of the multiphase research community has been to use the growing computational resources in the search for numerical solutions as a discovery tool to elucidate the physics behind the complex phenomena. These numerical simulations can generate data to help the understanding of the physical mechanisms at play.

1.2 Governing equations

The governing equations of fluid mechanics are based on the principles of conservation of mass, and momentum in a stationary control volume V , surrounded by a surface S (see figure 1.2). The mass conservation states that mass cannot be created or destroyed in V , and the change of mass is due to mass flowing in and out through S . Therefore, the principle of mass conservation, in an integral form is

$$\frac{d}{dt} \int_V \rho dv = - \int_S \rho \mathbf{u} \cdot \mathbf{n} ds \quad (1.1)$$

where $\mathbf{u}$ stands for the velocity, t denotes time, ρ stands for density and $\mathbf{n}$ refers to the unit normal vector pointing outwards. By applying the divergence theorem to the integral of the fluxes through the boundary, the previous equation becomes

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (1.2)$$

For incompressible flows (e.g., a constant value of density), the previous equation becomes:

$$\nabla \cdot \mathbf{u} = 0 \quad (1.3)$$

The equation of fluid motion can be obtained from a the momentum-conservation principle: the rate of change of momentum in a control volume V is the difference in the momentum flux which goes through the surface boundary S , plus the net forces acting on the control volume. Mathematically, this is expressed as

$$\frac{d}{dt} \int_V \rho \mathbf{u} dv = - \int_S \rho \mathbf{u} (\mathbf{u} \cdot \mathbf{n}) ds + \int_V \mathbf{f} dv + \int_S \mathbf{n} \cdot \mathbf{T} ds \quad (1.4)$$

here, the tensor $\mathbf{T}$ is a symmetric stress tensor constructed in such a way that $\mathbf{n} \cdot \mathbf{T} ds$ is the force on a surface element ds with a normal $\mathbf{n}$. The first term of the right-hand side (RHS) stands for the momentum flux going through the boundary of the control volume. The second term of the RHS stands for body forces on V (e.g., gravitational, electric or magnetic forces). Finally, the last term of the RHS refers to the total surface force.

By applying the divergence theorem to the integral of the fluxes through the boundary, the previous equation becomes

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = \mathbf{f} + \nabla \cdot \mathbf{T}, \quad (1.5)$$

The stress tensor $\mathbf{T}$ is characterised by being a linear function of the rate of strain $\mathbf{S}$

$$\mathbf{T} = (-p + \lambda \nabla \cdot \mathbf{u}) \mathbf{I} + 2\mu \mathbf{S} \quad (1.6)$$

where, p stands for pressure, μ represents the viscosity, $\mathbf{I}$ is an identity tensor and $\mathbf{S} = 1/2(\nabla \mathbf{u} + \nabla \mathbf{u}^T)$ refers to the rate-of-strain or deformation tensor whose components are

$$S_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \quad (1.7)$$

Equation 1.5 together with 1.6 are known as the Navier-Stokes equations (NS).

Additionally to the mass and momentum governing equations, it is necessary to introduce the interface conditions which couple the fluid motion across the interface. By assuming that the interface thickness vanishes (i.e., no fluid accumulation in the interface is allowed) and no phase-change, the velocity across the interface satisfies the following condition

$$[\mathbf{u}_s] = 0 \quad (1.8)$$

The attention is now turned towards the normal and tangential stress boundary conditions at a fluid-fluid interface (shown in figure 1.2b). Performing a force balance in the control volume enclosing the interface, results in

$$\int_V \frac{D\mathbf{u}}{Dt} dV = \int_V \mathbf{f} dV + \int_S \mathbf{n} \cdot \mathbf{T} dS + \int_C \sigma \mathbf{s} dl \quad (1.9)$$

where the left-hand side of the equation corresponds to the force associated to the fluid-acceleration inside of the control volume. The second term corresponds to the jump in $\mathbf{T}$ across the interface. In the limit of the interfacial thickness tending to zero, the previous equation becomes

$$-[\mathbf{T}_s] \cdot \mathbf{n} = \sigma \kappa \mathbf{n} + \nabla_s \sigma \quad (1.10)$$

This condition can be split into normal and tangential stress boundary conditions as

$$-[-p + 2\mu \mathbf{n} \cdot \mathbf{S} \cdot \mathbf{n}]_S = \sigma \kappa \quad (1.11)$$

$$-[2\mu \mathbf{t}^k \cdot \mathbf{S} \cdot \mathbf{n}]_S = \mathbf{t}^k \cdot \nabla_s \sigma \quad (1.12)$$

1.2.1 Navier-Stokes equations: the scaling of surface tension

Multiphase flows are usually described by dimensionless variables which take into account the material properties of the fluids (i.e., density ρ , viscosity μ), and with an interface characterised by a surface tension σ . In the simplest system, the flow motion is described by a length- and velocity-scales (or time-scale) of a and U , respectively. Additionally, the system may also be influenced by the presence of gravitational forces $\mathbf{g} = -g\mathbf{z}$. Therefore, the simplest multiphase phenomenon is entirely defined by six variables (i.e., $\rho, \mu, \sigma, a, U, g$) depending on three fundamental units (i.e., mass, length and time). Through Buckingham's Theorem, solely three non-dimensional groups are needed to characterise physically the system:

$$Re = \frac{\rho U a}{\mu}, \quad We = \frac{\rho U^2 a}{\sigma}, \quad Fr = \frac{U^2}{ga} \quad (1.13)$$

where Re , We and Fr stand for Reynolds, Weber and Froude numbers, respectively. Re represents the ratio of inertial to viscosity forces, We represents the ratio of inertial to surface tension forces,

and Fr represents the ratio of inertial to gravitational forces. Additionally, three other dimensional parameters will be used through this thesis, which can be obtained from combination of the previous dimensionless groups:

$$Oh = \frac{\sqrt{We}}{Re} = \frac{\mu}{\sqrt{\rho\sigma a}}, \quad La = \frac{1}{Oh^2} = \frac{\rho\sigma_s R_o}{\mu^2}, \quad Bo = \frac{\rho g a^2}{\sigma} \quad (1.14)$$

where the Ohnesorge number Oh , measures the relative importance of viscous to surface tension forces, La is the Laplace number (e.g., it is the inverse of Oh ; La is widely used in France), and Bo stands for Bond number representing the ratio of gravity to surface tension forces.

The previous nondimensional groups arise naturally from the non-dimensionalisation of Navier-Stokes equations by choosing the right scalings. If all variables are rendered non-dimensional by using the following scalings (where the tildes designate dimensionless quantities):

$$\tilde{x} = \frac{x}{a}, \quad \tilde{t} = \frac{t}{a/U}, \quad \tilde{\mathbf{u}} = \frac{\mathbf{u}}{U}, \quad \tilde{p} = \frac{p}{\rho U^2}, \quad (1.15)$$

the nondimensionalising of the Navier-Stokes equations yields

$$\nabla \cdot \tilde{\mathbf{u}} = 0, \quad (1.16)$$

$$\left(\frac{\partial \tilde{\mathbf{u}}}{\partial \tilde{t}} + \tilde{\mathbf{u}} \cdot \nabla \tilde{\mathbf{u}} \right) + \nabla \tilde{p} = \frac{1}{Fr} \mathbf{i}_z + \frac{1}{Re} \nabla \cdot [(\nabla \tilde{\mathbf{u}} + \nabla \tilde{\mathbf{u}}^T)] + \frac{1}{We} \mathbf{F}_s \quad (1.17)$$

For simplicity, the tildes are dropped henceforth.

1.3 Surfactant effects - Marangoni flows

Surfactants are surface-active-agents which affect the dynamics of the flow as they absorb at free-interfaces due to their chemical structure (e.g., hydrophobic tail and a hydrophilic head). Surfactants can live either on the free surface (known as insoluble surfactants) or also stay in the liquid bulk (known as soluble surfactants) adding layers of complexity as a result of the interplay between the interface and the bulk. Surfactants reduce the local surface tension value until a critical micelle concentration (CMC) is reached, beyond this point no further dependence between the surfactant concentration and surface tension is observed (Manikantan and Squires, 2020).

Since the surface tension is dependent on the surfactant concentration, the presence of surfactants leads to gradients in surface tension, and subsequently, the formation of Marangoni-induced flow

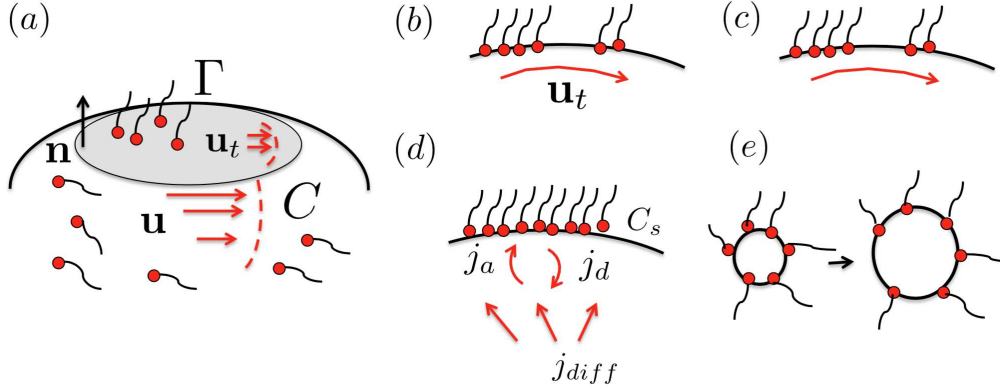


Fig. 1.3. Schematic representation of the different mechanisms associated to surfactant transport in a surfactant-laden interface: (a) surfactant transport on the interface and the bulk; (b) surfactant convection as a result of Marangoni-induced flow (c) surfactant transport as a result of the interfacial concentration diffusion (d) adsorption/desorption of surfactant from the adjacent bulk concentration C_s (e) change of surfactant concentration due to interfacial topological change.

from regions of high to low concentration. Marangoni flows are a classical fluid mechanics problem, observed for example in the so-called ‘tears of wine’ phenomenon (Hosoi and Bush, 2001). In a glass of wine, the alcohol concentration in the free surface changes as a result of its evaporation. A lower alcohol concentration is found in the thin-film layer close to the glass-walls in comparison to the liquid bulk owing to the enhanced surface area to volume ratio. Thus, the resulting Marangoni stresses drive flow upwards from the liquid bulk towards the edges of the glass forming a thin-film layer. The film will thicken forming a rim which undergoes a gravitational destabilization (Rayleigh-Plateau type) to roll down and form the well known ‘tears of wine’.

Mathematically, the transport of chemical species in the bulk and on the interface, with concentrations C and Γ , respectively, are expressed by a set of convection-diffusion equations:

$$\frac{\partial C}{\partial t} + \mathbf{u} \cdot \nabla C = \nabla \cdot (D_c \nabla C), \quad (1.18)$$

and

$$\frac{\partial \Gamma}{\partial t} + \nabla_s \cdot (\Gamma \mathbf{u}_t) = D_s \nabla_s^2 \Gamma + J, \quad (1.19)$$

where $\mathbf{u}_t = (\mathbf{u}_s \cdot \mathbf{t}) \mathbf{t}$ is the tangential velocity on the interface in which $\mathbf{u}_s$ represents the surface velocity; D_s and D_c denote the surfactant interfacial and bulk diffusivities, respectively, and J is the sorptive flux, which provides a relationship between C and Γ that connects the bulk and interfacial concentrations. The left-hand-side of Eq. (1.19) represents the transient and convective transport of surfactant at the interface, and its right-hand side models interfacial diffusion and bulk-interface mass

exchange. The flux J is expressed by

$$J = k_a C_s (\Gamma_\infty - \Gamma) - k_d \Gamma, \quad (1.20)$$

where k_a and k_d stand for the kinetic constants for adsorption and desorption, respectively, and C_s denotes the surfactant concentration in the sub-phase adjoining the interface.

The equation of state describing the variation of the surface tension as a function of the local interfacial surfactant concentration is given by the Langmuir relation Shin et al. (2018)

$$\sigma(\Gamma) = \sigma_s + RT\Gamma_\infty \ln \left(1 - \frac{\Gamma}{\Gamma_\infty} \right), \quad (1.21)$$

where σ_s is the surface tension in the absence of surfactant, and Γ_∞ is interfacial concentration at maximal packing.

1.3.1 Non-dimensionalisation of the surfactant equations

The non-dimensionalisation of the previous equations will give rise to several non-dimensional groups describing the physical-chemical properties of the surfactants. All variables are rendered non-dimensional by using the following scaling where the tildes designate dimensionless quantities:

$$\tilde{x} = \frac{x}{a}, \quad \tilde{t} = \frac{t}{a/U}, \quad \tilde{\mathbf{u}} = \frac{\mathbf{u}}{U}, \quad \tilde{\sigma} = \frac{\sigma}{\sigma_s}, \quad \tilde{\Gamma} = \frac{\Gamma}{\Gamma_\infty}, \quad \tilde{C} = \frac{C}{C_\infty}, \quad \tilde{C}_s = \frac{C_s}{C_\infty} \quad (1.22)$$

As a result of this scaling, the equations 1.18-1.20 become

$$\frac{\partial \tilde{C}}{\partial \tilde{t}} + \tilde{\mathbf{u}} \cdot \nabla \tilde{C} = \frac{1}{Pe_b} \nabla \cdot (\nabla \tilde{C}), \quad (1.23)$$

$$\frac{\partial \tilde{\Gamma}}{\partial \tilde{t}} + \nabla_s \cdot (\tilde{\Gamma} \tilde{\mathbf{u}}_t) = \frac{1}{Pe_s} \nabla_s^2 \tilde{\Gamma} + \tilde{J}, \quad (1.24)$$

$$\tilde{J} = Bi (k\tilde{C}(1 - \tilde{\Gamma}) - \tilde{\Gamma}), \quad (1.25)$$

$$\tilde{\sigma} = 1 + \beta_s \ln (1 - \tilde{\Gamma}), \quad (1.26)$$

The dimensionless parameters appearing in equations (1.23-1.26) are given by

$$Bi = \frac{k_d R}{u_R}, \quad \beta_s = \frac{\Re T \Gamma_\infty}{\sigma_s}, \quad Pe_s = \frac{u_R R}{D_s}, \quad Pe_b = \frac{u_R R}{D_b}, \quad (1.27)$$

where Bi is the Biot number representing the ratio of characteristic desorptive to convective time-scales, β_s is the elasticity number, which measures the sensitivity of the surface tension to changes

in surfactant interfacial concentration; Pe_s and Pe_b are the interfacial and bulk Peclet numbers and compare the ratio of convective to diffusive time-scales in the plane of the interface and the bulk, respectively. Finally, k_d refers to the surfactant desorption coefficient, $\mathfrak{R}$ the ideal gas constant, T the temperature, D_s and D_b the surfactant interfacial and bulk diffusivities, respectively.

At equilibrium, equation (1.25) reduces to the Langmuir adsorption isotherm

$$\chi = \frac{\Gamma_{eq}}{\Gamma_\infty} = \frac{k}{1+k}, \quad k = \frac{k_a C_\infty}{k_d}, \quad (1.28)$$

where χ stands for the fraction of surface covered by adsorbed surfactant, k is the adsorption parameter, which represents the ratio of adsorption to desorption time scales. Here, k_a refers to the adsorption coefficient. The equation of state describing the variation of the surface tension as a function of the local interfacial surfactant concentration is given by the Langmuir relation shown in Eq. (1.26). Marangoni stress, τ , arises due to the surface tension gradients and they can be expressed in terms of gradients in Γ as follows:

$$\tilde{\tau} \equiv \nabla_s \tilde{\sigma} \cdot \mathbf{t} = -\frac{\beta_s}{1-\tilde{\Gamma}} (\mathbf{t} \cdot \nabla_s \tilde{\Gamma}). \quad (1.29)$$

For simplicity, the tildes are dropped henceforth.

1.4 Role of capillary singularity in hydrodynamics

The foundation of modern fluid mechanics lays on the Navier-Stokes equations, which are characterised by being nonlinear partial differential equations. A fundamental problem of the nonlinear nature is the rise of singularities in which the velocity fields diverge (e.g., one-dimensional inviscid Burger equation or the case of Kirchhoff's flow past a body).

This thesis considers interfacial singularities associated with three-dimensional free-surfaces, where interfacial length scales vanish and velocity fields diverge. Considering a liquid thread whose radius decreases, and once the radius becomes zero locally i.e., the original liquid thread separates, and the mathematical description of the thread-radius breaks down. This behaviour leads to a singularity of the NS equations at the point of disconnection (pinch-off). Figure 1.4 shows different interfacial singularities in multiphase phenomena associated with the formation of droplets from a jet or from the bursting of a bubble.

When a liquid thread approaches to its capillary singularity (i.e., $r_{min} \rightarrow 0$, and velocity fields diverge) the relevant interfacial length and velocity scales are governed entirely by the fluid material

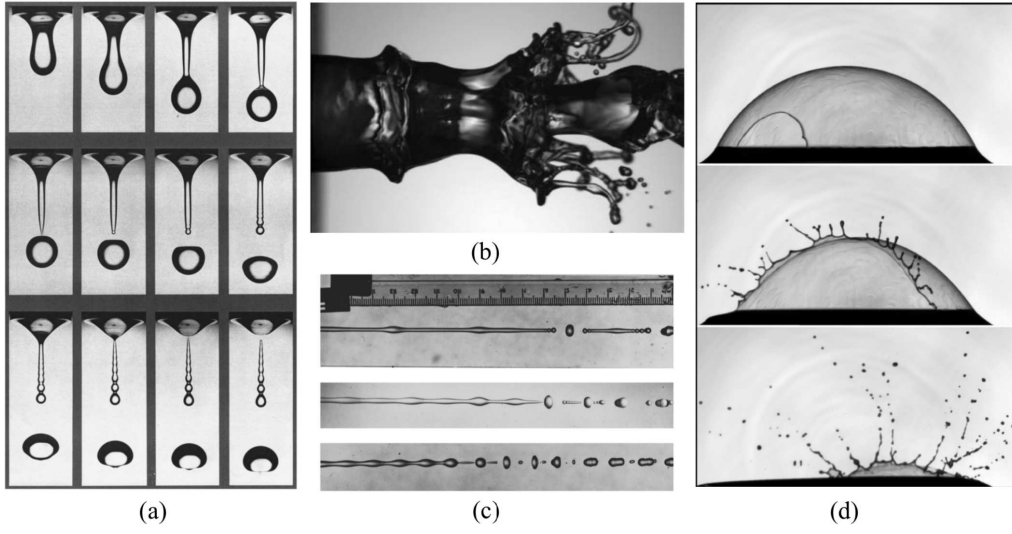


Fig. 1.4. Examples of interfacial capillary singularity. (a) Waterdrop formation leading to the generation of a liquid thread which retracts due to capillarity (Shi et al., 1994); (b) Cascade mechanism for droplet formation: from the growth of linear modes (through a Kelvin-Helmholtz instability) to the development of nonlinearities leading to primary and then secondary breakup events (through long filament pinch-off modulated by a Rayleigh-Plateau instability), and the formation of a cascade of droplet sizes (Villermaux et al., 2004); (c) Rayleigh-Plateau instability of a jet (Rutland and Jameson, 1971); (d) Bursting of a bubble leading to the formation of droplets from the rim retraction due to RP instability (Lhuissier and Villermaux, 2012)

properties, including the competition between viscous and surface tension, and inertial forces. Therefore, the interfacial dynamics of the thread is independent from initial or boundary conditions. This behaviour implies two key simplifications: (i) close to vicinity of the thread breakup, the dynamics of the thread becomes ‘universal’, and solely depend on the length scale (i.e., $l = v^2 \rho / \sigma$) which accounts for the internal material properties of the fluid thread (Peregrine et al., 1990; Eggers and Dupont, 1994); (ii) by performing asymptotics to the NS, Eggers (1993) proved that the motion close to capillary singularity is self-similar, with the thread radius diminishing its size at a faster rate than the longitudinal dimension. Therefore, the flow motion near the breakup point can only be described in terms of its radius $h(z, t)$ (where z describes the position along the axis of symmetry), and the axial velocity $u(z, t)$. Thus, it is possible to predict the size of the neck at a given time in function of the breakup time τ

$$h_{min} = 0.03 \frac{\sigma}{\rho v} (t - \tau) \quad (1.30)$$

The previous equation has been experimentally confirmed by Kowalewski (1996). The dynamics of a cylindrical thread follows the Rayleigh-Plateau instability (Rayleigh (1879), see also Brenner et al. (1996)). As time evolves and the neck decreases, the formation of a secondary neck from

the primary neck has been observed, which again obeys the previous self-similar equation (see for example Brenner et al. (1994)). After the singularity point, the interface retracts driven by capillarity, and eventually forms satellite drops, noticed for the first time by Guthrie (1864). Thus, formation of satellite drops can be seen as an universal feature as a result of the interfacial breakup (see figure 1.4).

Considering the effect of surfactants in the capillary singularity, Craster et al. (2002, 2009) show that surfactants do not alter the scalings for the minimum neck radius and axial velocity as the capillary singularity is approached. Thus, the scalings are the same as the ones derived by Eggers (1993) (e.g., the surfactants are swept away from the thinning region).

To conclude, the Rayleigh-Plateau instability governs the onset of the breakup of thin water threads, in which the growth of non linear modes triggers the nonlinear effect of the equations to produce the interfacial singularity to form droplets.

1.5 Thesis overview

The overarching theme of this thesis is the study of capillary singularities as a result of changes in interfacial topology in the absence and in the presence of surfactants. As such, this thesis tries to answer questions regarding turbulence, fluid mechanics and applied-maths. The fundamental questions explored in this dissertation are: **What is the role of vorticity in the interfacial dynamics of turbulent jets? What is the effect of surfactants on the system?**

Chapter 2 presents the state-of-the-art of the computational techniques for multiphase flows with interfaces. The increase of computational capabilities has led to the use of numerical methods in the search of solutions for previously inaccessible problems. An in-depth analysis of the numerical method employed throughout this thesis, the level contour reconstruction method (LCRM) is given here.

Chapter 3 introduces the direct numerical simulations of turbulent liquid jets focusing on the surface-vortex interaction to explain the spatio-temporal interfacial dynamics. A careful state-of-the-art of the field is presented first. Liquid atomisation processes are widely used to break down a liquid stream into smaller droplets to enhance its mixing with a stagnant phase. These streams may be contaminated with surfactants, whose concentration variations lead to surface tension gradients and Marangoni stresses. In **Chapter 4**, I present the effect of surfactant on the complex interfacial dynamics associated with a turbulent jet. A larger droplet size distribution is found in the presence of surfactant, although the surface tension is reduced making the interface more susceptible to fragmentation.

I hypothesised the effect of surfactant, and consequently, the formation of Marangoni stresses on the place of the surface rigidifies the interface and the tangential stresses prevent the capillary breakup of the liquid threads. To test this hypothesis, I have isolated three single events observed in the jet: recoiling of liquid threads, droplets undergoing bursting, and drops coalescing partially or completely with deformable interfaces and they have been studied in detail in the following chapters of this thesis. The effect of surfactants for the previous scenarios have not been reported for a generic air-water system, therefore, I have generalised those problems for air-water, and the chosen density and viscosity ratios corresponds to $\rho_g/\rho = 1.2 \times 10^{-3}$ and $\mu_g/\mu = 0.018$, respectively, which are representative of an air-water system.

Chapter 5: In this chapter, I describe the effect of surfactants on the dynamics of retracting liquid threads. The key results from this chapter resides to the inhibition of the ‘end-pinching’ mechanism brought by Marangoni stresses. This is a remarkable outcome whereby the presence of contaminants inhibits flow singularities. This chapter concludes with a parametric study with respect to the governing dimensionless parameters.

Chapter 6: In this chapter, the effect of surfactants in the dynamics of bursting bubbles through an interface is described in detail. I have shown the detrimental effect of the Marangoni-induced flow in the final number of droplets, explain the reason of the fewer number of droplets for the surfactant-laden cases.

Chapter 7: In this chapter, I present the effect of surfactants in a drop-interface coalescence. The key finding is linked to the reopening of the neck as a result of the Marangoni stresses, and consequently the inhibition of the interfacial singularity.

Conclusions: In this section, the main contributions made with this work are summarised, putting all the individual results in a broader context, and suggesting pathways for future work.

Chapter 2

Fluid mechanics with interfaces: computational modelling

Summary

Predicting multiphase flow dynamics is extremely difficult by the multi-scale nature of the flow, and the tremendously complex interfacial topology. The position of the interface must be also predicted as part of the solution, adding layers of complexity to the numerical simulations. On this basis, interface-tracking methods (e.g., front tracking method) treat the interface as a sharp boundary whose motion is tracked by using marker points, forming an additional Lagrangian grid. On the other hand, interface-capturing methods, in which the volume-of-fluid (VOF) method is the most representative of this group, solves all the fields in a solely Eulerian-grid, and subsequently, the interface is not tracked as a sharp boundary, but instead, it is determined by knowing the amount of a colour function (which determines the amount of interface) in each cell.

2.1 Advecting the fluid interface

The direct numerical simulations of multiphase flows are based on the assumption of the single field-formulation of the NS equations, in which a single set of governing equations describes the motion of all individual phases. The identification of the different fluids is done by the use of a marker function. This marker function is a Heaviside (step) function $H(x, t)$, which is zero in one phase and unity in the other phase. Therefore, the density and viscosity are given by

$$\rho = \rho_1 + (\rho_2 - \rho_1)H(\mathbf{x}, t) \quad (2.1)$$

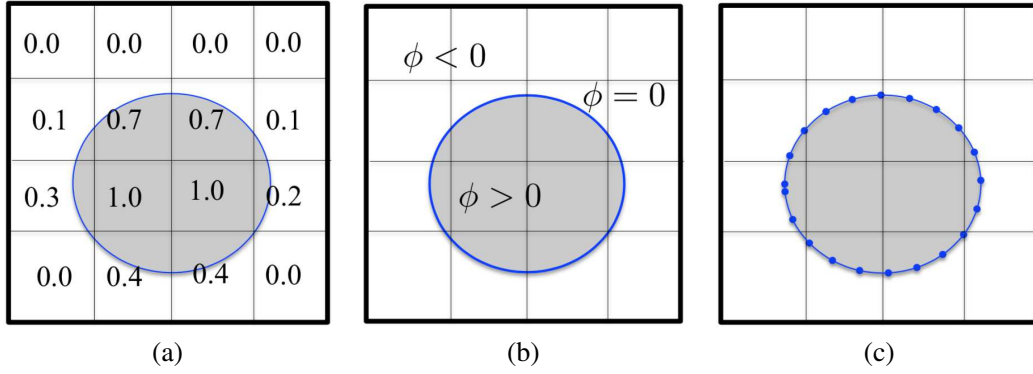


Fig. 2.1. A schematic representation of a bubble or droplet in a computational domain. Illustration of three different interface transport methods to advect the interface: (a) volume-of-fluid; (b) level-set-method, and (c) front-tracking method.

$$\mu = \mu_1 + (\mu_2 - \mu_1)H(\mathbf{x}, t) \quad (2.2)$$

while subscripts ‘1’ and ‘2’ designate the individual phases, respectively. The marker function moves with the flow according to

$$\frac{\partial H}{\partial t} + \mathbf{u} \cdot \nabla H = 0 \quad (2.3)$$

The advection of the previous marker function by standard numerical methods leads to numerical oscillations or excessive smearing for high- and low-order methods, respectively. For this reason, it has been necessary to develop more specialised methods for the advection of the marker function, such as the VOF, level-set or front tracking methods. In the last two methods, the marker function is reconstructed from the knowledge of the interface location.

2.1.1 Volume-of-Fluid method

The VOF method is one of the oldest and widely used in the fluid mechanics community (Hirt and Nichols, 1981; Lafaurie et al., 1994; Renardy and Renardy, 2002; Liovic et al., 2006). The method is based on the use of a color function C which is defined as the average value of the Heaviside function in each computational cell, and it is described as

$$C = \frac{1}{V} \int_V H(x, y) dV \quad (2.4)$$

The color function has a value of either one or zero depending on whether cells are filled with fluid

‘1’ or ‘2’. However, if the interface is located in a computational cell, the color function will have a fractional value. A schematic representation of this concept is shown in figure 2.1a

The VOF method consists of two independent steps: the reconstruction of the interfacial surface and its advection. The reconstruction of the interface is done by the knowledge of the value of the color function in each computational cell. The method is based on finding a geometrical shape which best approximates to the fluid interface, for example, in the Piecewise linear interface calculation (PLIC) reconstruction, the surface is approximated by straight lines (2D) or planes (3D) whose orientation is determined by taking into consideration the value of the color function in the neighbouring cells (Tryggvason et al., 2011; Liovic et al., 2006). The reconstruction allows one to compute the necessary geometrical information (e.g., the local unit normal vector) from the interface which allows the calculation of the surface tension forces. Once the interface has been reconstructed, the interface is advected according to the velocity field. The advection can be done either by using geometrical techniques (e.g., the end points of each of each segment of the interface are advected by the flow) or by fluxing techniques (e.g., computing the internal phase fluxes across the computational cell boundary) (Scardovelli and Zaleski, 1999; Gueyffier et al., 1999; Lopez and Hernandez, 2008; Renardy and Renardy, 2002).

The main advantage of the VOF method is its mass conservation as a result of its mathematical formulation. However, the method has a tendency to smear the fluid interface over time because of the discretisation of the convective term of the transport equation of the color function (Tryggvason et al., 2011; Ferziger and Perić, 1999). Additionally, due to the discontinuous nature of the color function, problems in the calculation of the surface tension forces have been reported leading to parasitic currents (e.g., nonphysical fluid motion) (Tryggvason et al., 2011).

2.1.2 Level-set method

The level-set method is another popular method to advect the interface (Sussman et al., 1994; Olsson and Kreiss, 2005; Desjardins et al., 2008). It is based on a continuous distance function $F(x, t)$ which is positive in one fluid, negative in the other, and vanishes in the interface (a schematic representation of this concept is shown in figure 2.1b). The distance function is advected by the fluid velocity, and evolves according to

$$\frac{\partial \phi}{\partial t} + \mathbf{u} \cdot \nabla \phi = 0 \quad (2.5)$$

The use of distance function which varies smoothly across the interlace let the calculation of the geometrical information accurately. However, as the distance function is not part of the conserva-

tive equations, the level set method faces problems with mass conservation (Tryggvason et al., 2011; Ferziger and Perić, 1999).

2.1.3 Front-tracking method

In the front-tracking method (FT), the interface separating different fluids is represented by a Lagrangian grid (i.e., connected marker points) which is advected with the fluid (Unverdi and Tryggvason, 1992). As the interfacial location is tracked, it yields accurate predictions of the geometrical information for the surface tension forces (Tryggvason et al., 2001).

The geometrical information, the pressure and velocity variables are exchanged between the adaptive Lagrangian mesh and the fixed Eulerian grid following the general Immersed Boundary Method of Peskin Peskin (1977), where surface tension forces are calculated on the Lagrangian grid and this information is added to the fluid equations calculated in the fixed grid). The transfer of information is done by approximating the interface as a smooth distribution that can be represented on the Eulerian fixed grid (Tryggvason et al., 2011).

The main downside of this method is the difficulty to handle complex topological changes, such as rupture of films or capillary break-up, as the marker points are locally connected and need to be updated (i.e., deleted or added). The process of ‘addition/deletion’ of points results in mass loss, but improvements are possible through adaptive mesh refinement or through the use of level-set method to reconstruct the interface Shin and Juric (2002).

2.2 The Level Contour Reconstruction Method

The hybrid front-tracking/level-set technique known as Level Contour Reconstruction Method, (LCRM) was proposed by Shin and Juric (Shin and Juric, 2002; Shin et al., 2005, 2018) to predict the location of the interface. The LCRM is capable of predicting accurately the surface tension, and of handling deforming interfaces with topological changes.

The governing equations for incompressible and immiscible two-phase fluid systems in a three-dimensional Cartesian domain $\mathbf{x} = (x, y, z)$ are expressed by a single field formulation for the continuity and the momentum balance equation:

$$\nabla \cdot \mathbf{u} = 0, \quad (2.6)$$

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \nabla \cdot \mu (\nabla \mathbf{u} + \nabla \mathbf{u}^T) + \mathbf{F}, \quad (2.7)$$

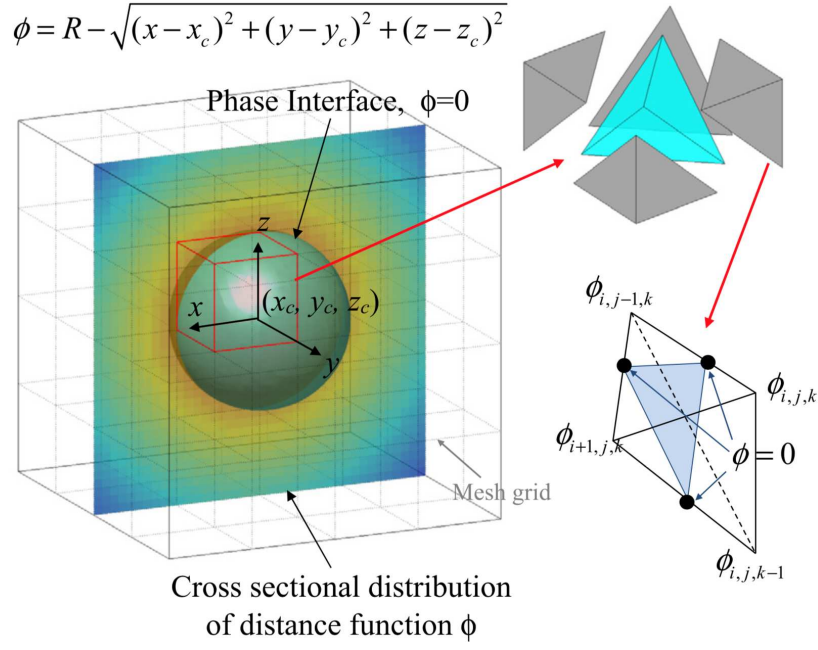


Fig. 2.2. Schematic representation of the level reconstruction method, showing the interface location in which the distance function is equal to zero (i.e., $\Phi = 0$). Additionally, a computational cell is represented, which has been divided into tetrahedra, and the use of the distance function to identify the zero isocontour surface of the distance function field (Shin et al., 2018).

The last term in (2.7) represents the surface tension force, which is decomposed into its normal component ($\mathbf{F}_n$) for the normal stress jump across the interface, and its tangential component ($\mathbf{F}_s$), which is associated with the surface gradient of the surface tension $\nabla_s \sigma$:

$$\mathbf{F} = \mathbf{F}_n + \mathbf{F}_s = \int_c \sigma \mathbf{p}' dl = \int_{A_e} \sigma \kappa \mathbf{n} \delta(\mathbf{x} - \mathbf{x}_f) dA + \int_{A_e} \nabla_s \sigma \delta(\mathbf{x} - \mathbf{x}_f) dA \quad (2.8)$$

here, κ and $\mathbf{n}$ denote the curvature and the outward-pointing unit normal, respectively, and the surface gradient operator is given by $\nabla_s = [\mathbf{I} - \mathbf{n}\mathbf{n}] \cdot \nabla$ wherein $\mathbf{I}$ is the identity tensor. In these formulae, $\mathbf{x}_f$ is an interface parameterisation, A , and $\delta(\mathbf{x} - \mathbf{x}_f)$ is a Dirac distribution that is non-zero only when $\mathbf{x} = \mathbf{x}_f$.

The foundation of the LCRM resides in taking advantage of the best parts of the front-tracking and the level-set methods. The interfacial elements (i.e marker points) are tracked over time (front tracking method), but they are not logically connected, and the interface is reconstructed using an additional distance function field (level set method). The reconstruction of the interface avoids the ‘addition/deletion’ of connected elements. By using both techniques, the method can handle complex interfacial systems with no mass loss. The level-set method is only used in the reconstruction of the interface, and not in the advection of the interface as the distance function is never advected.

The LCRM is capable of predicting accurately $\mathbf{F}_n$ and $\mathbf{F}_s$, and of handling deforming interfaces with topological changes. Figure 2.2 shows the conceptual idea behind the LCRM in a three-dimensional framework. The distance function is generated from the Lagrangian grid. The reconstruction of the interface takes place in the Eulerian grid in which velocity and pressure are calculated. In order to connect the Eulerian and the triangular-Lagrangian elements, the Eulerian grid is subdivided into tetrahedra elements. The idea behind the reconstruction is to identify the zero isocontour surface of the distance function (given by the FT method) and identify the interception of this surface with the tetrahedra. This procedure makes sure that only one isocontour surface can be identified for each cell during the interface reconstruction. The objective of this reconstruction is to handle complex topological changes and keep an uniform element size, and subsequently, avoiding the concentration of elements in a region or the formation of large elements due to motion of the interface. The main difference with respect to the original FT method is the marker points are physically linked but not logically connected (Shin et al., 2017, 2018).

2.2.1 Transfer of information between the Eulerian and Lagrangian grids

Communication between the Eulerian and Lagrangian grid (e.g., needed for the transfer of information regarding the interfacial geometric, velocity, and pressure) is done by using a discrete delta function and the immersed boundary method, proposed by Peskin (1977). By using this method, the interface is assumed to be a smooth distribution function which distributes sources terms at several grid points located near the interface. In the same way, this smooth distribution function allows the exchange of information from the Eulerian fixed grid to the Lagrangian grid. On this basis, the interface or front has a thickness on the order of the computational mesh size providing with stability and smoothness. As the front has a finite value, there is no interfacial numerical diffusion which is the main downside of the volume-of-fluid method.

The source terms which appear in the equation 2.7 can be written as

$$\Phi = \int_{\Gamma(t)} \phi \delta(\mathbf{x} - \mathbf{x}_f) ds \quad (2.9)$$

where ϕ represents the discrete interfacial sources which can be distributed to the fixed grid; R_{ij} can be transferred from the fixed grid to the interface by the discrete summations

$$\Phi_{ij} = \sum_p \phi_p D_{ij}(\mathbf{x}_p) \Delta s \quad (2.10)$$

$$R_p = \sum_{ij} h_x h_y R_{ij} D_{ij}(\mathbf{x}_p) \quad (2.11)$$

here Δs represents the length or area of the element depending on the system is 2d or 3d, respectively. Equation 2.10 is the discretised form of 2.9 and the Dirac function has been approximated by D_{ij} . For $\mathbf{x}_p = (x_p, y_p)$, it uses the following distribution function (Peskin and McQueen, 1995)

$$D_{ij}(\mathbf{x}_p) = \frac{\delta(x_p/h_x - i)\delta(y_p/h_y - j)}{h_x h_y} \quad (2.12)$$

where

$$\delta(r) = \begin{cases} \delta(r), & |r| \leq 1 \\ 1/2 - \delta_1(2 - |r|), & 1 < |r| < 2 \\ 0 & |r| \geq 2 \end{cases} \quad (2.13)$$

and

$$\delta_1(r) = \frac{3 - 2|r| + \sqrt{1 + 4|r| - 4r^2}}{8} \quad (2.14)$$

2.2.2 Integration of the Navier–Stokes Equations

The NS equations are solved by the Chorin’s projection method (Chorin, 1968b). Its main numerical steps are briefly presented below.

The momentum equation, at the current time step n , can be discretised as follows

$$\frac{(\rho \mathbf{u})^{n+1} - (\rho \mathbf{u})^n}{\Delta t} = \mathbf{A}^n + \mathbf{F}_\sigma^{n+1} - \nabla_h P \quad (2.15)$$

where the term $\mathbf{A}$ collects the gravitational, advection and diffusion terms from equation 2.7, $\mathbf{F}_\sigma$ stands for the surface tension force, and h stands for a numerical approximation.

To calculate the next time level $n + 1$, the momentum equation (equation 2.15) is divided into two parts. The first part corresponds to a ‘prediction-step’, in which the effect of the pressure is neglected to estimate $\mathbf{u}^*$ (so-called, ‘predicted velocity’):

$$\frac{\rho^{n+1} \mathbf{u}^* - (\rho \mathbf{u})^n}{\Delta t} = \mathbf{A}^n + \mathbf{F}_\sigma^{n+1} \quad (2.16)$$

The second step is the ‘correction-step’, in which the pressure gradient is added

$$\frac{\rho^{n+1} \mathbf{u}^{n+1} - \rho^{n+1} \mathbf{u}^*}{\Delta t} = -\nabla_h p \quad (2.17)$$

The pressure field is computed in such way that the velocity $\mathbf{u}^{n+1}$ meets the mass conservation constraint (i.e., divergence free) at the next time step:

$$\nabla_h \cdot \mathbf{u}^{n+1} = 0 \quad (2.18)$$

Therefore, the pressure field is computed by combination of equations 2.17-2.18, resulting in

$$\nabla_h \frac{1}{\rho^{n+1}} \cdot \nabla_h p = \frac{1}{\Delta t} \nabla_h \cdot \mathbf{u}^* \quad (2.19)$$

leaving the final expression for the velocity as:

$$\mathbf{u}^{n+1} = \mathbf{u}^* - \Delta t \frac{\nabla_h p}{\rho^{n+1}} \quad (2.20)$$

Because the density is not a constant, the previous equation cannot be solved with tradition Poisson solvers. Therefore, a multigrid iterative method is used for solving the elliptic pressure Poisson equation, which is based on the work of Kwak and Lee (2004). This multigrid approach lets the numerical method handle systems with large density ratios.

Reverting back to the spatial derivatives of the quantities, once more a second-order centered differences scheme was used for all except the advection term $(\mathbf{u} \cdot \nabla \mathbf{u})$, which has the from:

$$\mathbf{u} \cdot \nabla \mathbf{u} = \frac{u_{i,j,k}(\mathbf{u}_{i+1/2,j,k} - \mathbf{u}_{i-1/2,j,k})}{\Delta x} + \frac{v_{i,j,k}(\mathbf{u}_{i,j+1/2,k} - \mathbf{u}_{i,j-1/2,k})}{\Delta y} + \frac{w_{i,j,k}(\mathbf{u}_{i,j,k+1/2} - \mathbf{u}_{i,j,k-1/2})}{\Delta z}. \quad (2.21)$$

here, an essentially non-oscillatory (ENO) method is used to obtain face values of $\mathbf{u}_{i,j+1/2,k}$, $\mathbf{u}_{i,j-1/2,k}$, etc. More details of this methodology can be found in the work of Shu and Osher (1989).

In all simulations carried out in this work, the temporal integration scheme is based on a second-order Gear method, with implicit solution of the viscous terms of the velocity components. Each time step is computed by an adaptive time step-size criterion:

$$\Delta t = \min \{ \Delta t_{cap}, \Delta t_{vis}, \Delta t_{CFL}, \Delta t_{int} \} \quad (2.22)$$

where Δt_{cap} , Δt_{vis} , Δt_{CFL} , and Δt_{int} represent the capillary time step, the viscous time step, the Courant-Friedrichs-Lewy (CFL) time step, and interfacial CFL time step, respectively. Those terms are defined by

$$\begin{aligned}\Delta t_{cap} &= \frac{1}{2} \sqrt{\frac{(\rho_l + \rho_g) \Delta x^3}{\pi \sigma_s}}, & \Delta t_{vis} &= \frac{\rho_g \Delta x^2}{6\mu_l} \\ \Delta t_{CFL} &= \frac{\Delta x}{|u_{max}|}, & \Delta t_{int} &= \frac{\Delta x}{|V_{int}|}\end{aligned}\quad (2.23)$$

where Δx refers to the minimum cell size, u_{max} and V_{int} are the maximum fluid and interface velocities, respectively. More details of the numerical method are provided in Shin et al. (2018, 2017).

In summary, the Navier-Stokes equations are solved by a finite volume method on a staggered grid (Harlow and Welch, 1965). The computational domain is discretised by a fixed regular grid (i.e. Eulerian grid) and the spatial derivatives are approximated by standard centred difference discretisation, except for the non-linear term, which makes use of a second-order essentially non-oscillatory (ENO) scheme (Shu and Osher, 1989). In the case of the viscous term, a second-order centred difference scheme is used. The projection method is used to treat the incompressibility condition (Chorin, 1968a).

With respect to the treatment of the free surface, the interface is tracked with an additional Lagrangian grid by using the FT method together with the reconstruction of the interface by using the level-set method (Shin and Juric, 2002, 2009). Communication between the Eulerian and Lagrangian grid (for the transfer of the geometric information of the interface) is done by using the discrete delta function and the immersed boundary method of Peskin (1977). The advection of the Lagrangian interface is done by integrating $d\mathbf{x}_f/dt = \mathbf{V}$ with a second-order Runge-Kutta method, where $\mathbf{V}$ stands for the interfacial velocity which has been calculated by interpolation from the Eulerian velocity. The code is parallelised through an algebraic domain-decomposition technique and the communication between subdomains for data exchange is managed by the Message Passing Interface (MPI) protocol.

2.2.3 Discretisation of surfactant equations

As a result of the nature of the system, the surfactant transport equation is solved at the interface, where the information of the surfactant concentration is located on the centre of the triangular front elements. In the convective-diffusive equations, the time is integrated by a first order explicit scheme. The surface surfactant gradients in the interface are computed by using a probing technique introduced by Udaykumar et al. (1999). A sharp boundary condition for the bulk surfactant concentration equation is implemented to treat the source term at the interface.

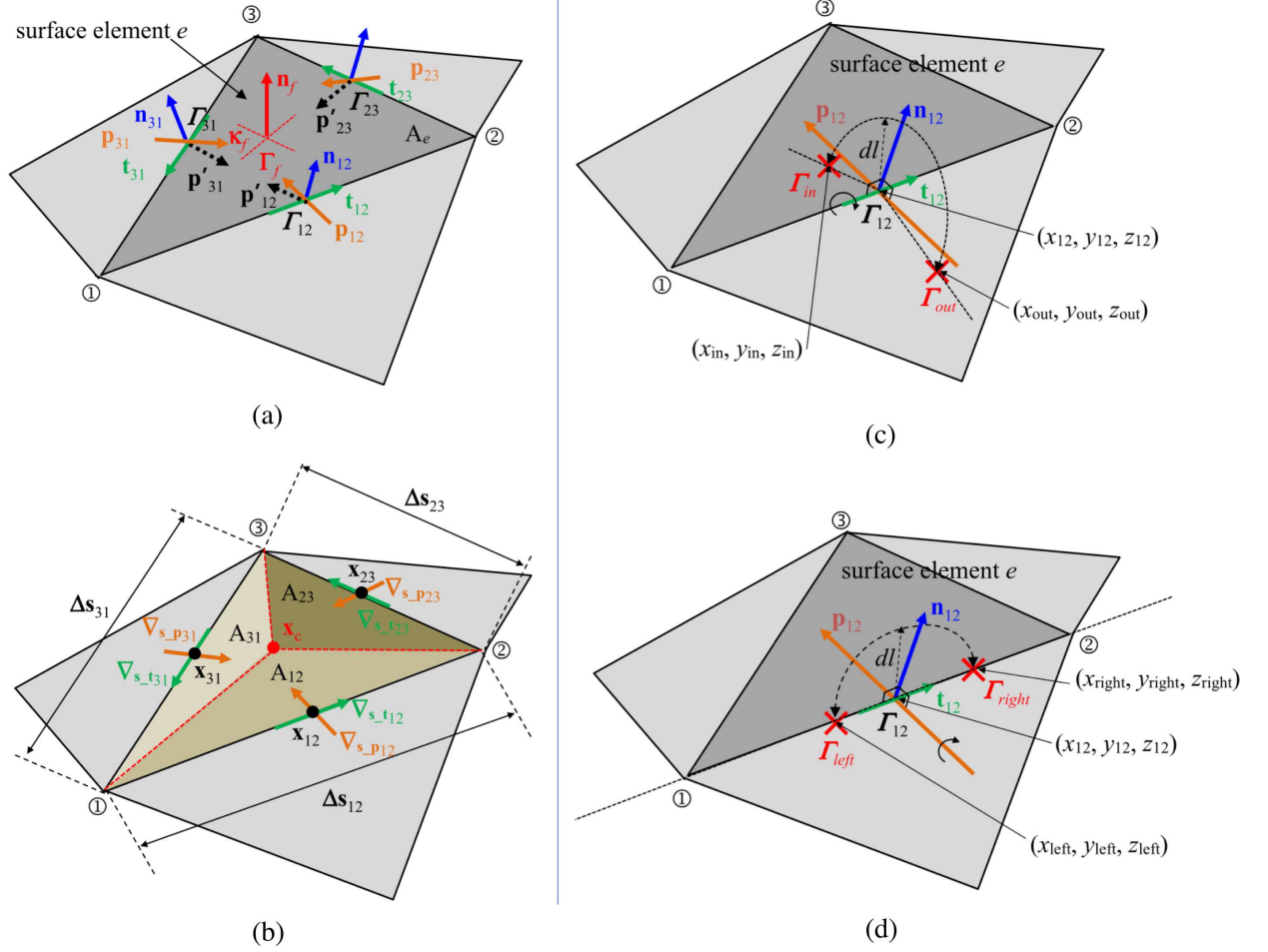


Fig. 2.3. Left panels represent a schematic representation of the geometrical information for an individual interface element, showing: (a) interface unit vectors which are computed at the edges of each elements, while the interface normal is calculated at the center of the individual element; (b) the direction of the surface gradient along the edge of the interface element. Right panels show the probing technique for computing surface gradient quantities of (c) binormal components, $\mathbf{p}$, (d) tangential components $\mathbf{t}$. Adapted from Shin et al. (2018)

A brief summary of the numerical discretisation of the convective-diffusion equations related to the surfactant transport (equations 1.18-1.21) is provided below. The discretisation is explained for an element 'e' of the Lagrangian interface, which is characterised by a surface A_e and its unit normal vector is computed from its element-centre (see figure 2.3). As before, n represents the current time step and $n + 1$ the next time step. The notation for the vertices of a Lagrangian element is ①, ② and ③, and subsequently the edges of an element are $\overline{①②}$, $\overline{②③}$ and $\overline{③①}$. Therefore, the area of the element and the local unit vector are represented by

$$A_e = \frac{1}{2} \left| \mathbf{x}_{①②} \times \mathbf{x}_{①③} \right| \quad (2.24)$$

$$\mathbf{n}_f = \frac{\mathbf{x}_{①②} \times \mathbf{x}_{①③}}{|\mathbf{x}_{①②} \times \mathbf{x}_{①③}|} \quad (2.25)$$

The left-hand side of equation 1.19 can be discretised by using the Leibniz formula as

$$\int_{A_e} \left[\frac{\partial \Gamma}{\partial t} + \nabla_s (\Gamma \mathbf{U}_s) \right] dA_e \approx \frac{(\Gamma A_e)^{n+1} - (\Gamma A_e)^n}{\Delta t} \quad (2.26)$$

The right-hand side of equation 1.19 (i.e., surface gradient concentration and source terms) can be discretised as

$$\begin{aligned} \int_{A_e} (D_s \nabla_s^2 \Gamma + J) dA &= \\ \delta \Gamma_{De}^n + (J A_e)^n &= \\ D_s \int \int_{A_e} \nabla_s^2 \Gamma dA + (J A_e)^n &= \\ D_s \int_C \nabla_s \Gamma \cdot \mathbf{p} ds + (J A_e)^n \end{aligned} \quad (2.27)$$

The discretised form of the surface gradient concentration term (e.g., first term of equation 2.27) can be represented by

$$\begin{aligned} \delta \Gamma_{De}^n &= D_s \sum_{k=1}^3 (\nabla_s \Gamma)_k \cdot \mathbf{p}_k \Delta s_k = \\ D_s \{ (\nabla_s \Gamma)_{12} \cdot \mathbf{p}_{12} \Delta s_{12} + (\nabla_s \Gamma)_{23} \cdot \mathbf{p}_{23} \Delta s_{23} + (\nabla_s \Gamma)_{31} \cdot \mathbf{p}_{31} \Delta s_{31} \} &= \\ D_s \{ (\nabla_s \Gamma)_{p12} \cdot \Delta s_{12} + (\nabla_s \Gamma)_{p23} \cdot \Delta s_{23} + (\nabla_s \Gamma)_{p31} \cdot \Delta s_{31} \} \end{aligned} \quad (2.28)$$

where Δs_{ij} represents the edge length between vertices ① and ②. Equation 2.27 makes use of the binomial vectors $\mathbf{p}_{12}$, $\mathbf{p}_{23}$ and $\mathbf{p}_{31}$. These normals are calculated by the cross product of the other unit vectors ($\mathbf{n} \times \mathbf{t}$).

The information of Γ is stored in the centre of each element, and is used to calculate the surface gradient ∇_s . The calculation of the surface gradient is performed on the centre of edge elements. The interfacial surfactant gradient from equation 2.28 is the last missing information up to this point.

Here, I consider the calculation of the interfacial surface gradient in the $\mathbf{p}$ direction between the vertices ① and ② $(\nabla_s \Gamma)_{p12}$. The numerical method defines an additional point (x_{12}, y_{12}, z_{12}) , and a distance dl . Therefore, the interfacial surfactant gradient in the $\mathbf{p}$ direction is interpolated as

$$(\nabla_s \Gamma)_{p12} = \frac{\Gamma_{out} - \Gamma_{in}}{2dl} \quad (2.29)$$

Similarly, the interfacial surfactant gradient in the $\mathbf{t}$ direction (see Figure 3b) is calculated by

$$(\nabla_s \Gamma)_{t12} = \frac{\Gamma_{right} - \Gamma_{left}}{2dl} \quad (2.30)$$

The total mass of surfactant on the surface of each element can be computed by

$$\int_{A_e} \Gamma \delta(\mathbf{x} - \mathbf{x}_f) dA \quad (2.31)$$

here $\mathbf{x}_f$ is the parametrisation of the interface and $\delta(\mathbf{x} - \mathbf{x}_f)$ is a delta function which vanishes everywhere except at the interface. The discretised version of the previous equation is

$$M_{sijk} = \sum_f \Gamma_f D_{ijk}(\mathbf{x}_f) \Delta A \quad (2.32)$$

where D_{ijk} represents a Dirac function, and has been described previously in equation 2.12

The total mass of surfactant is obtained by integrating the previous equation over the entire interface

$$Q = \int_{A_e} \delta(\mathbf{x} - \mathbf{x}_f) dA \quad (2.33)$$

Thus, the final surfactant distribution in the domain is given by

$$\Gamma(\mathbf{x}) = \frac{\int_{A_e} \Gamma \delta(\mathbf{x} - \mathbf{x}_f) dA}{\int_{A_e} \delta(\mathbf{x} - \mathbf{x}_f) dA} = \frac{M_{sijk}}{Q_{ijk}} \quad (2.34)$$

Using the traditional Peskin immersed boundary technique is possible to redistribute the surface surfactant concentration to the neighbouring cells.

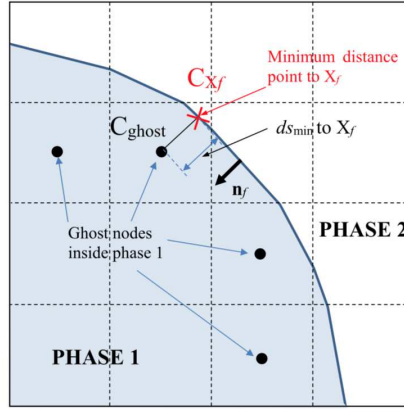


Fig. 2.4. Sharp boundary method for implementing source term in bulk concentration equation.

Taking into consideration all the previous equation, the discretised version of equation 1.19 over time is represented by

$$\frac{(\Gamma A_e)^{n+1} - (\Gamma A_e)^n}{\Delta t} = \delta \Gamma_{De}^n + J^n (A_e)^{n+1} \quad (2.35)$$

which can be arranged to the next equation to calculate the interfacial surfactant concentration at the next time step

$$\Gamma^{n+1} = \Gamma^n \frac{A_e^n}{A_e^{n+1}} + \Delta t \left[\frac{\delta \Gamma_{De}^n}{A_e^{n+1}} + J^n \right] \quad (2.36)$$

2.2.3.1 Sharp boundary condition for bulk surfactant concentration equation

The equation governing the surfactant motion in the bulk is a typical convective-diffusion equation, except for the presence of a ‘source term’ which connects the surfactant transfer between the interface and the bulk. To account for this source term, the numerical method makes use of the sharp boundary method which uses ghost nodes close to the interface. The numerical method assumes that surfactant is solely soluble in phase ‘2’, therefore, the ghost nodes are only located in phase ‘1’. Thus, the concentration gradient on the interface can be expressed by

$$\frac{\partial C}{\partial n}|_f = \frac{C_{ghost} - C_{xf}}{ds_{min}} = \frac{-J}{D_{c2}} \quad (2.37)$$

where C_{ghost} is the concentration in the ghost node, C_{xf} is the surfactant concentration on the interface element and ds_{min} is the minimum distance from the ghost node to the interface (graphical definitions are shown in figure 2.4).

2.2.4 Implementation of surface tension forces

The surface tension term of the momentum equation is represented by its normal and tangential components. The normal component of the surface tension force can be described from the mean curvature

$$\mathbf{F}_n = \int_{A_e} \sigma \kappa \mathbf{n} \delta(\mathbf{x} - \mathbf{x}_f) dA = \sigma \kappa_H \nabla \mathcal{H} \quad (2.38)$$

where κ represents the curvature, which is assumed to be twice the mean interface curvature and is calculated from the the Eulerian grid by using

$$\kappa_H = \frac{\mathbf{F}_L \cdot \mathbf{G}}{\sigma \mathbf{G} \cdot \mathbf{G}} \quad (2.39)$$

$$\mathbf{F}_L = \int_{A_e} \sigma \kappa \mathbf{n} \delta(\mathbf{x} - \mathbf{x}_f) ds \quad \mathbf{G} = \int_{A_e} \mathbf{n} \delta(\mathbf{x} - \mathbf{x}_f) ds \quad (2.40)$$

here $\mathbf{x}_f$ is the parametrisation of the interface, $\Gamma(t)$ and $\delta(\mathbf{x} - \mathbf{x}_f)$ is a delta function which vanishes everywhere except at the interface, $\mathbf{n}$ the outward-pointing unit normal vector to the interface and ds is the length of the surface element.

The tangential component of the surface tension force in the hybrid formulation is defined as

$$\mathbf{F}_s = \int_{A_e} \nabla_s \sigma \delta(\mathbf{x} - \mathbf{x}_f) dA \quad (2.41)$$

The interfacial gradient of surface tensions $\nabla_s \sigma$ is formed by $\mathbf{p}$ and $\mathbf{t}$ components as

$$\nabla_s \sigma = (\nabla_s \sigma)_p \mathbf{p} + (\nabla_s \sigma)_t \mathbf{t} \quad (2.42)$$

Therefore, the final expression for the tangential component for the surface tension forces is described by

$$\begin{aligned} \mathbf{F}_s = & [(\nabla_s \sigma)_{p12} \mathbf{p}_{12} + (\nabla_s \sigma)_{t12} \mathbf{t}_{12}] \delta(\mathbf{x} - \mathbf{x}_{12}) A_{12} + \\ & [(\nabla_s \sigma)_{p23} \mathbf{p}_{23} + (\nabla_s \sigma)_{t23} \mathbf{t}_{23}] \delta(\mathbf{x} - \mathbf{x}_{23}) A_{23} + \\ & [(\nabla_s \sigma)_{p31} \mathbf{p}_{31} + (\nabla_s \sigma)_{t31} \mathbf{t}_{31}] \delta(\mathbf{x} - \mathbf{x}_{31}) A_{31} \end{aligned} \quad (2.43)$$

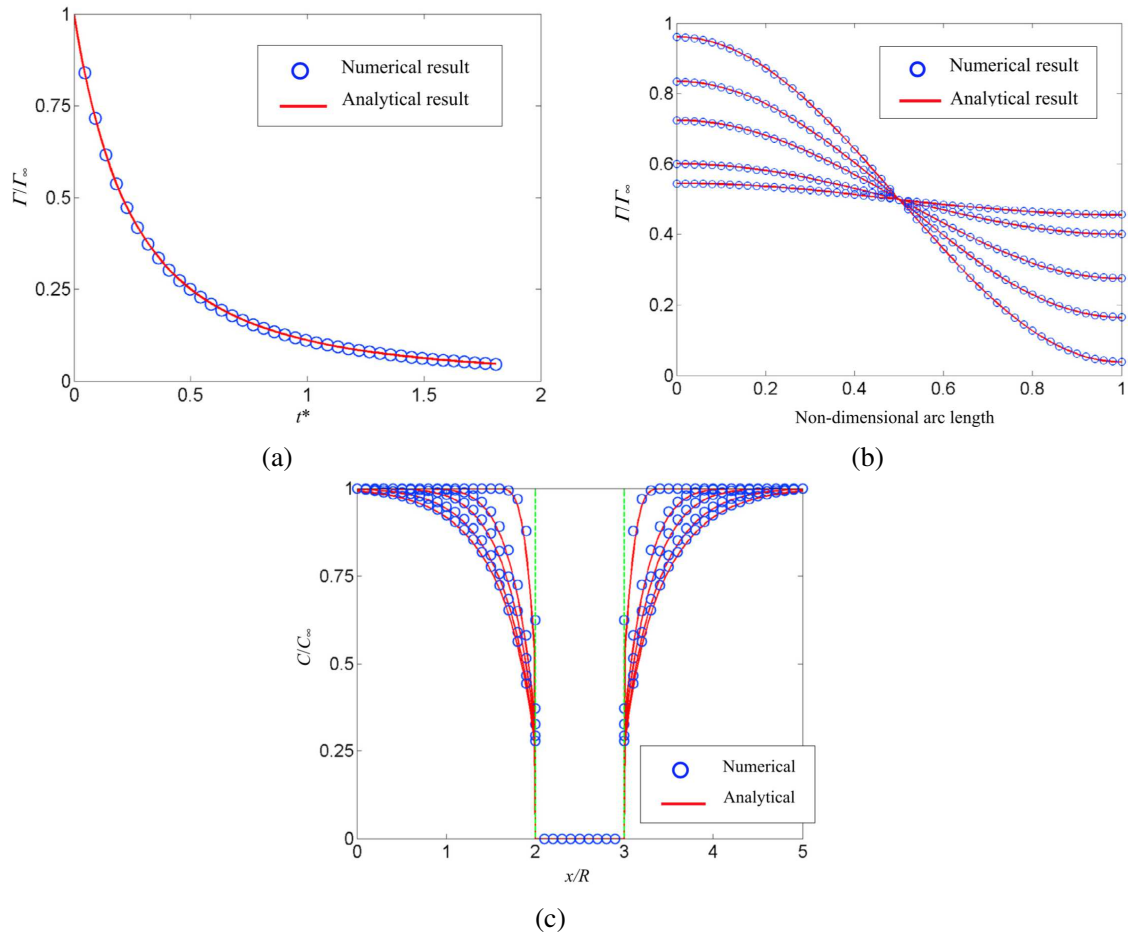


Fig. 2.5. Benchmarking of the surfactant equations for: (a) Surfactant mass conservation for an expanding sphere; (b) interfacial diffusion; (c) bulk diffusion. Adapted from Shin et al. (2018)

2.2.5 Benchmarking of the surfactant equations

This section presents some test cases done to check the accuracy of the numerical implementation of the surfactant equations.

- The mass conservation when changing the area of the interface is checked by the uniform expansion of a sphere contaminated with insoluble surfactant. Figure 2.5a shows an excellent agreement between the numerical prediction together the analytical solution. The latter is given by

$$\frac{\Gamma(t)}{\Gamma_\infty} = \frac{A_o}{A(t)} \frac{\Gamma_o}{\Gamma_\infty} \quad (2.44)$$

- The benchmarking of the diffusion term from the interfacial surfactant concentration equation is done by using a stationary droplet with a non-uniform interfacial concentration $((1 - \cos \theta)/2$, where θ is the polar angle measured from the axis of symmetry). Figure 2.5b shows an excellent agreement between the numerical prediction and the analytical solution. The latter is given by

$$\frac{\Gamma(\theta, t)}{\Gamma_\infty} = \frac{1}{2} (1 + e^{-\frac{t}{2D_s D^2}} \cos \theta), \quad (2.45)$$

- The accuracy of the boundary condition provided by equation 2.36 is tested by initialising a sphere with uniform bulk surfactant concentration, where the source term only depends on the adsorption parameter (i.e., desorption parameter is switched off). Figure 2.5c shows an excellent agreement between the numerical prediction together the analytical solution. The latter is given by

$$\frac{C_\infty - C}{C_\infty} = \frac{k_a \sqrt{\pi D_s t} / D_s}{1 + \frac{\sqrt{\pi D_s t}}{D/2} (1 + \frac{k_a D}{2 D_s})} \frac{D}{2r} \operatorname{erfc} \left(\frac{r - (D/2)}{2\sqrt{D_s t}} \right). \quad (2.46)$$

2.3 Conclusions

In this chapter, I have presented a brief summary of the state-of-the-art computational methods for multiphase fluids. Part of this thesis deals with multiphase systems contaminated with chemical surfactants which behave as a surface-active components to generate surface tension gradients. Therefore, the discretisation of the convection-diffusion equation for the surfactant concentration at the free surface and the liquid bulk were also presented. At the end of the chapter, attention was turned towards the level contour reconstruction method, which is a hybrid front-tracking/level set method, as it is used throughout. The hybrid nature takes advantage of both methods allowing one to handle phenomena with complex topological changes.

Chapter 3

Turbulent jets

Related publication: Rico and the jets: Direct numerical simulations of turbulent jets. *C. R. Constante-Amores*, L. Kahouadji, A. Batchvarov, S. Shin, J. Chergui, D. Juric and O. K. Matar. *Phys. Rev. Fluids* **5**, 110501 (2020)

Related publication: Direct Numerical Simulations of transient turbulent jets: vortex-interface interaction. *C. R. Constante-Amores*, L. Kahouadji, A. Batchvarov, S. Shin, J. Chergui, D. Juric and O. K. Matar. *J. Fluid Mech* (under review)

Summary

The breakup of an interface into a cascade of droplets and their subsequent coalescence is a generic problem of central importance to a large number of industrial settings such as mixing, separations, and combustion. I study the breakup of a liquid jet which is introduced through a cylindrical nozzle into a stagnant viscous phase by employing a hybrid interface-tracking/level-set method to account for the surface tension forces in a three-dimensional Cartesian domain. Numerical solutions are obtained for a range of Reynolds (Re) and Weber (We) numbers. I have found that the interplay between the azimuthal and streamwise components of the vorticity leads to different interfacial features and flow regimes in $Re - We$ space. I show that the streamwise vorticity plays a critical role in the development of the three-dimensional instabilities on the jet surface. In the inertia-controlled regime at high Re and We , I expose the details of the spatio-temporal development of the vortical structures affecting the interfacial dynamics. A mushroom-like structure is formed at the leading edge of the jet inducing the generation of a liquid sheet in its interior that undergoes rupture to form droplets. These droplets rotate inside the mushroom structure due to their interaction with the prevailing vortical structures. Additionally, Kelvin-Helmholtz vortices that form near the injection point deform in the streamwise

direction to form hairpin vortices, which, in turn, trigger the formation of interfacial lobes in the jet core. The thinning of the lobes induces the creation of holes which expand to form liquid threads that undergo capillary breakup to form droplets.

3.1 Introduction

The breakup of a dispersed fluid in a stagnant phase is a classical problem in multiphase flows, as it encompasses a multitude of interfacial singularities, which exemplify situations wherein the interface undergoes topological transitions, e.g., liquid-threads breakup into drops, and merging of drops/bubbles due to coalescence. These transitions involve the development of singularities where interfacial distances vanish and velocity fields diverge, and the system is controlled by a combination of capillary, inertial, and viscous forces. The complex topological nature of the jet phenomenon has fascinated the scientific community for decades which has led to numerous, comprehensive reviews, see for example Lin and Reitz (1998); Eggers and Villermaux (2008); Lasheras and Hopfinger (2000).

Jet breakup is influenced by a range of multi-scale physics; these include the interaction of turbulence with interfaces (creating cascades of motion featuring a large separation of scales), capillarity, potentially complex rheology, the presence of fields (e.g. gravitational, electromagnetic), as well as heat transfer and phase change. Reitz and Bracco (1986) proposed four jet breakup regimes depending on the appearance of the jet far downstream from the injection point. In the ‘Rayleigh regime’, the onset of breakup is the Rayleigh-Plateau instability, in which the growth of the linear modes on the jet-surface leads to the formation of large droplets with respect to the jet-nozzle. In the ‘first/second wind-induced’ regime the resulting droplets have roughly the same scale or smaller as the jet-nozzle. Finally, in the ‘atomisation regime’, the generated turbulence helps to create spatio-temporal chaos resulting in droplets which are up to four orders of magnitude smaller than the size of the injection nozzle. The physics of droplet generation in turbulent jets remains partially-understood despite the significant scientific attention it has received over the years (Dombrowski et al., 1954; Hoyt and Taylor, 1977; Lasheras and Hopfinger, 2000; Marmottant and Villermaux, 2004; Villermaux et al., 2004; Eggers and Villermaux, 2008). The rest of this introduction aims to provide an up-to-date summary of the experimental and numerical efforts to study the jet breakup phenomenon.

The ground-breaking experiments of Hoyt and Taylor (1977) and Taylor and Hoyt (1983) showed the complex topological features of the surface waves formed on the jet. They revealed that these waves are responsible for the transition from laminar to turbulent flow, and found underlying similarities of the occurring instabilities to inviscid linear theory. Marmottant and Villermaux (2004) with their pioneering experiments scrutinised the various stages of the jet dynamics: from the growth of

linear modes (through a Kelvin-Helmholtz instability) that characterises the early-time dynamics, to the development of nonlinearities leading to ‘primary’ and subsequent ‘secondary’ breakup events (through long filament pinchoff modulated by a Rayleigh-Taylor instability), and the formation of a cascade of droplet sizes. These authors found that mean droplet-size is proportional to the wavelength selected during the Rayleigh–Taylor instability (also observed by Varga et al. (2003)). In the same premise, Kooij et al. (2018a) showed that the droplet size distribution is also a function of the nozzle geometry and the surrounding pressure. More recently, Ibarra et al. (2020) presented the results of an experimental study of the spatial evolution of turbulent immiscible liquid-liquid jets; however, a detailed account of the spatio-temporal development, and critical mechanisms leading to droplet generation remains outstanding.

The multi-scale nature of the flow, and the complex interfacial topology complicate the experimental scrutiny of the different physical mechanisms occurring across the scales. Thus, elucidating the fundamental physics of this problem has also relied on high-fidelity simulations exemplified by the work of Ménard et al. (2007); Desjardins et al. (2008); Gorokhovski and Herrmann (2008); Desjardins and Pitsch (2010); Shinjo and Umemura (2010); Herrmann (2011); Chenadec (2012); Desjardins et al. (2013); Jarrahbashi et al. (2016); Ling et al. (2017); Agbaglah et al. (2017); Zandian et al. (2018); Ling et al. (2019); Zandian et al. (2019). The first step towards the use of numerical simulations to understand the physical mechanisms at play was conducted by Desjardins and Pitsch (2010), who were able to identify a sequence of essential steps during the spatio/temporal interfacial development of a planar liquid jet-segment: the formation of initial corrugations on the surface, followed by the development of ligaments whose capillary instability leads to droplet formation. They also showed that the early interfacial corrugations are a consequence of the turbulent eddies which carry enough kinetic energy to overcome capillary forces.

Using a similar approach to Desjardins and Pitsch (2010), but for a cylindrical liquid jet-segment surrounded by an outer gas phase, Jarrahbashi et al. (2016) provided a comprehensive study of the flow structures in terms of the vortex-surface interaction. They showed that ‘hole formation’ of a liquid-sheet is an essential requirement to trigger the formation of droplets, and the thinning of the liquid-sheet is driven by the superposition of hairpin-vortices near the interface rather than by capillarity action. Similar findings have been reported for a planar liquid jet-segment surrounded by an outer gas phase Zandian et al. (2018), and for the transient dynamics of a cylindrical liquid jet surrounded by a coaxial air phase Zandian et al. (2019). Ling et al. (2017, 2019) performed simulations of a two-phase mixing layer between parallel gas and liquid streams to investigate the interfacial dynamics, and the statistics for the multiphase turbulence. They also observed that the formation of ligaments, and subsequently-formed droplets, are triggered by the hole-induced perforation of the liquid sheets.

In the previous numerical studies, interface-capturing capabilities were used to account for the sur-

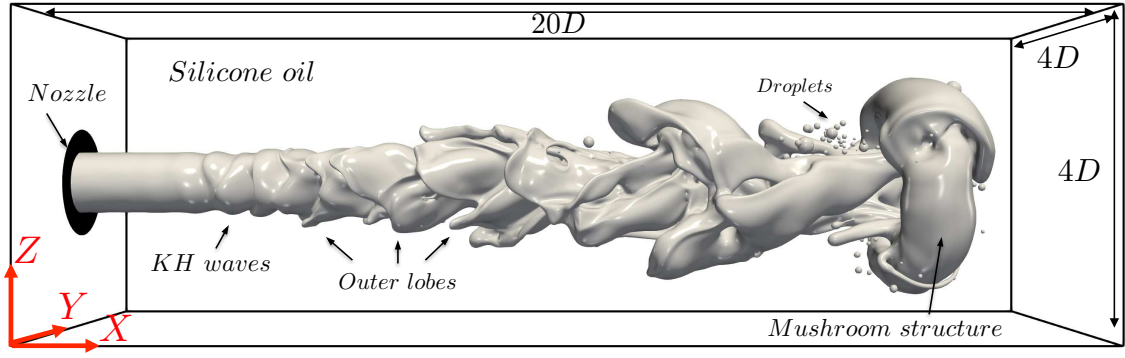


Fig. 3.1. Injection of a turbulent water jet into a stagnant silicone-oil phase. Three-dimensional representation of the interfacial shape for case-4 (i.e., $Re = 6530$ and $We = 303$) at $t = 28.97$ with definitions of particular regions and specific features discussed in this work.

face tension forces in the absence of intermolecular forces (i.e., disjoining pressure). For static sheets, the disjoining pressure is neglected as the minimum computational cell is larger than the film sheet thickness in which the intermolecular forces will drive its perforation. Therefore, the hole formation is an outcome of the numerical cut-off interfacial length scale, i.e., minimum mesh size ($O(10^{-6})\text{m}$). Nevertheless, recent experiments (Kooij et al., 2018a; Marston et al., 2016; Néel and Villerraux, 2018) demonstrate the existence of hole formation in dynamic sheets with a characteristic film thickness on the order of microns.

In this study, I aim to provide a comprehensive explanation of the physical mechanisms governing the interfacial dynamics of turbulent jets focusing on the less well-studied liquid-liquid systems. We will perform high-resolution three-dimensional direct numerical simulations using a hybrid interface-tracking/level-set approach to resolve the interfacial dynamics. I will demonstrate how the interaction between the vortical structures, which accompany the development of the flow, and the interface influence the mechanisms underlying droplet generation over a wide range of Reynolds and Weber numbers.

The rest of this chapter is organised as follows. In Sections 3.2-3.4, I present the problem formulation, numerical configuration, mesh considerations, and validation in terms of the RP instability. In Section 3.5, I begin with the presentation of a regime map in $Re - We$ space, classifying jet spatio-temporal development, followed by an in-depth discussion of the vortex-surface interactions linked to the topological changes; in addition, I elucidate the role of hole formation as a precursor to droplet generation. Finally, concluding remarks are provided in Section 3.6.

Table 3.1. Density and viscosity of the fluids used throughout this work (Ibarra, 2017).

ρ_w	ρ_{so}	μ_w	μ_{so}
kg/m ³	kg/m ³	mPa.s	mPa.s
998	824	1.0	5.4

3.2 Numerical configuration and physical parameters

Figure 3.1 shows a three-dimensional representation of the interface highlighting several specific features that are discussed in detail in the present work: Kelvin Helmholtz (KH) waves close to the injection nozzle, outer lobes formed on the main body of the jet, a leading edge ‘mushroom’-like structure, and droplets resulting from the atomisation process.

Figure 3.1 shows the three-dimensional computational domain, which is a rectangular box of the size $20D \times 4D \times 4D$, where D stands for the inner diameter of the nozzle (e.g., 4mm). The jet is produced when water leaves the cylindrical nozzle to enter progressively into the stagnant silicone oil. The physical properties of the fluids are given in table 3.1. An inflow boundary condition is applied to nozzle on the left of the domain, i.e., at $(x = 0)$, which follows a simplified power-law turbulent velocity profile:

$$u(r, t) = \frac{15}{14}U \left(1 - \left(\frac{r}{D/2} \right)^{28} \right) (1 + A \sin(2\pi ft)). \quad (3.1)$$

Here, U , A , f , and $r = \sqrt{(y - y_0)^2 + (z - z_0)^2}$ stand for the injected average velocity, amplitude, frequency, external perturbation, and the radial component of the jet, respectively. The values for A and f are informed by the previous work of Ling et al. (2015) (e.g., $A = 0.05$ m/s and $f = 20$ Hz). The numerical setup closely follows other computational studies; for example, we impose a free boundary condition on the walls of the computational domain to let the fluid freely enter or leave the boundaries (Taub et al., 2013; Ling et al., 2015, 2019). A pressure outflow boundary condition is applied on the right surface of the domain to allow the fluid to exit the domain. The solid nozzle is treated as a no-slip surface (Asadi et al., 2018).

The distance $\mathbf{x}$, velocity $\mathbf{u}$, time t , and pressure p in Navier Stokes equation are rendered dimensionless using the following characteristic scales, D , U , D/U , and $\rho_w U^2$, respectively. Hence, the dimensionless control parameters governing the phenomena we will study are given by:

$$Re = \frac{\rho_w U D}{\mu_w}, \quad We = \frac{\rho_w U^2 D}{\sigma}, \quad (3.2)$$

where Re stands for the Reynolds number (i.e. the ratio of inertial to viscous forces), and We represents

Table 3.2. The Reynolds-Weber number combinations for the four cases studied in detail with the M3-mesh (see table 3.4).

Case	Re	We
1	1000	30
2	1000	100
3	3260	75
4	6530	303

the Weber number (i.e. the ratio of inertial to capillary forces). All the variables appearing in the equations and boundary conditions are rendered dimensionless using the aforementioned scalings, unless stated otherwise.

The first part of the results section corresponds to a discussion of a regime map of jet dynamics in the $Re - We$ space. In this instance, I have used the M2-mesh (see table 3.4) to perform the fully three-dimensional simulations. The selection of this mesh is dictated by the need to map out parameter space relatively rapidly before focusing on elucidating the details of the dynamics using the M3-mesh, which provides higher resolution, for four cases; the $Re - We$ combinations for these cases are listed table 3.2.

3.3 Mesh study and resolution considerations

Solving the small scales of the atomisation phenomenon is a challenging process, and in order to ensure the physical validity of the results, we have assessed the grid dependence nature of our results by performing a mesh study for case-4 (see table 3.4). The appropriate choice for the minimum grid length-scale will depend on either the vanishing interfacial singularity or the smallest turbulence length-scale (i.e., Kolmogorov-length-scale).

For single-phase jets, Pope (2000) suggested that the Kolmogorov-length-scale η is resolved if $\Delta x/\eta \leq 2.1$, where Δx represents the minimum computational cell size, and η is estimated by $\eta = Re^{-3/4}l$, where l is the length scale. Previous computational studies of temporal and spatial multiphase jets are presented in table 3.3, showing the current state-of-the-art in terms of Pope's criterion. It is evident that Pope's criterion is difficult to meet due to the high computational costs of the simulations. In their recent work, Ling et al. (2017, 2019) performed simulations of two-phase mixing layer between parallel gas and liquid streams to investigate the interfacial dynamics and the statistics of the multiphase turbulence, estimating the Kolmogorov length scale to be $\eta \sim 0.945\mu m$, which leads to $\Delta x/\eta \sim 3$. Through their simulations, they estimated that $\eta = 3 - 4.5\mu m$ and also showed that their

Table 3.3. List of computational studies of atomisation showing compliance with Pope’s criterion (Pope, 2000).

Study	Configuration	Type of study	Re	$\Delta x/l$	$\Delta x/\eta$
Desjardins and Pitsch (2010)	Planar	Temporal	2000 – 3000	0.015	$\sim 5 - 6$
Herrmann (2011)	Round	Spatial	5000	0.031/0.0078	$\sim 5 - 19$
Jarrahbashi et al. (2016)	Round	Temporal	1600 – 16000	0.0125	$\sim 3 - 18$
Zandian et al. (2016, 2018)	Planar	Temporal	2500 – 5000	0.025	$\sim 9 - 15$
Zandian et al. (2019)	Round	Spatial	2000 – 3200	0.01	$\sim 3 - 4$
Ling et al. (2019)	Planar	Temporal	8000	0.0039	~ 3
Current study	Round	Spatial	1000 – 6530	0.0065	$\sim 1 - 4.5$

lower resolution mesh, i.e., $\Delta x/\eta \sim 6$ (see their figure 19d), was capable of predicting similar results in terms of turbulence dissipation.

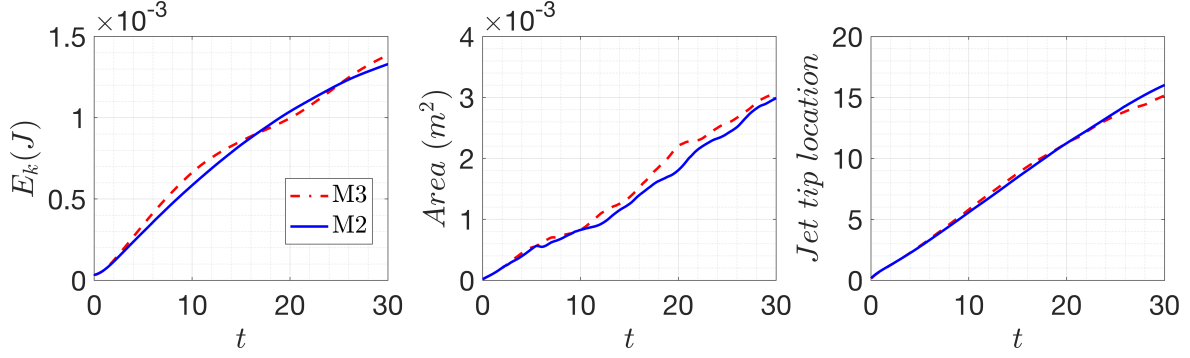
For our highest Reynolds number (case-5), our simulation does not meet the Pope’s criterion. But as shown by Ling et al. (2019), the actual η could be larger. Additionally, the atomisation of the injected phase in a stagnant viscous phase alleviates the range of relevant physical scales.

The second biggest challenges of computational atomisation is the ‘numerical breakup’ of liquid threads. A coarse grid would trigger the formation of thicker numerical threads, and consequently the formation of larger droplets (this problem has been previously reported by Shinjo and Umemura (2010), Herrmann (2011), Gorokhovski and Herrmann (2008), and Jarrahbashi and Sirignano (2014)). Shinjo and Umemura (2010) stated that the mesh should be refined up to the point where the dynamics of the thread are solely governed by surface tension forces. These forces would trigger the formation of capillary waves during the retraction of these ligaments, giving rise to the onset of the Rayleigh-Plateau instability (i.e., the ‘end-pinching’ mechanism). After those mechanisms are initialised, the thread-dynamics enter in an asymptotic behaviour towards the interfacial singularity (i.e., a refined mesh would not affect the size of the resulting droplets). On this basis, the numerical resolution regarding the interfacial length scales will be assessed following the methodology proposed by Ménard et al. (2007) and Desjardins and Pitsch (2010), who used a ‘grid-based Weber number’, defined by $We_{\Delta x_{min}} = \rho_w U^2 \Delta x_{min} / \sigma$. This equation provides us with the smallest interfacial length scale that the simulation is capable of resolving by assuming that the smallest interfacial structure is equal to the minimum mesh size of the computational domain. Ménard et al. (2007) suggested that no further breakup is observed for values under 10. For a Reynolds number corresponding to $Re \sim 10^4$ and M3-type mesh, the grid-based Weber number is $We_{\Delta x_{min}} \sim 4.12$, which meets the above criterion, suggesting that all capillary singularities would be resolved.

Therefore, we have proved that M3 mesh is capable of resolving turbulent-scales and interfacial singularities, and consequently detailed analysis of interfacial and vortical structures is performed

Table 3.4. Characteristics of different mesh sizes used to study the jet dynamics in this study.

Run	Global mesh size (number of cells)	Number of parallel process threads	Minimum mesh size (μm)	Total Comput. hours
M1	$768 \times 192 \times 192$	$12 \times 3 \times 3 = 108$	104.1	180
M2	$1536 \times 192 \times 192$	$24 \times 6 \times 6 = 864$	58.5	100
M3	$3072 \times 384 \times 384$	$48 \times 6 \times 6 = 1728$	26.1	500

**Fig. 3.2.** Mesh study for case-4 ($Re = 6530$ and $We = 303$). The panels highlight the temporal evolution of the kinetic energy E_k (left panel), the interfacial area (middle panel) and the maximum axial location of the jet tip (right panel).

using a M3 mesh-type (unless stated otherwise). Figure 3.2 shows the temporal evolution of the kinetic energy, $E_k = \int_V (\rho \mathbf{u}^2)/2 dv$, the interfacial area and the maximum axial location of the jet tip (i.e., leading edge) for different meshes. Additionally, the vorticity profiles were checked between M2- and M3-mesh, and no significant difference were found.

3.4 Scalings laws for the capillary breakup of liquid threads

As we have presented in the introduction, the direct numerical simulations must be capable of predicting the developing two-phase fluid interfacial dynamics featuring interface breakup, and droplet coalescence. In light of this, we aim to show the capabilities of our numerical framework in the prediction of the scalings laws for the capillary singularity of liquid threads. As the point of singularity approaches, the system is driven locally by the large interfacial curvature, and its interfacial dynamics depends solely upon the physical properties of the liquid. Lister and Stone (1998) have suggested that the pinchoff of a viscous thread (of radius $r(z, t)$, density ρ , viscosity μ and surface tension σ) surrounded by another viscous fluid transits between different dynamical regimes as $r(t) \rightarrow 0$ towards the breakup time τ (see figure 1 of Lister and Stone (1998)). The thinning of a water thread, surrounded by air, transitions from an inertial-capillary regime ($r \sim \tau^{2/3}$ and $u \sim \tau^{-1/3}$) to an inertial-viscous regime ($r \sim \tau$ and $u \sim \tau^{-1/2}$), more details can be found in Day et al. (1998), Eggers (1993) and Lister and Stone (1998).

Table 3.5. Characteristics of different mesh sizes used to study the capillary breakup of a water thread.

Run	Global mesh size (number of cells)	Number of parallel process threads	Pinchoff time (s)	Total Comput. hours
V1	$64 \times 64 \times 256$	16	0.375	~ 2
V2	$96 \times 96 \times 384$	54	0.372	~ 20
V3	$192 \times 192 \times 768$	432	0.369	~ 48

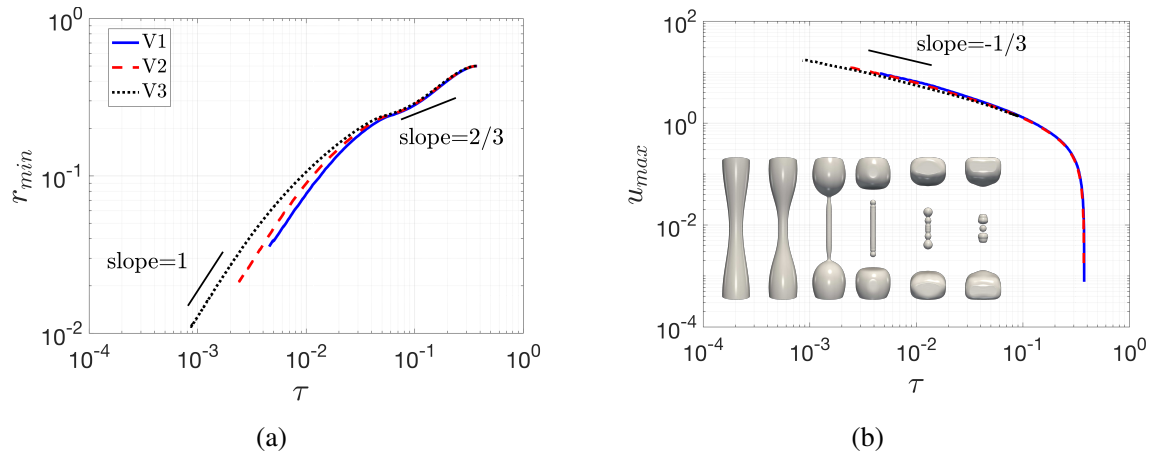


Fig. 3.3. Scaling laws for the capillary singularity of a water-thread surrounded by air for different numerical resolutions (see table 3.5). Here, the Ohnesorge number is 1.178×10^{-3} . The minimum thread radius, (a), and the maximum streamwise velocity, (b), versus the remaining time to breakup τ , agree with the inertial-capillary and inertial-viscous regimes presented by Eggers (1993); Day et al. (1998). Additionally, a three-dimensional representation of the interface is shown to depict the retraction of the satellite ligament to produce daughter droplets via the ‘end-pinching’ mechanism (in agreement with Notz and Basaran (2004)).

Therefore, we consider the capillary singularity of a water thread (of initial radius R) surrounded by air in absence of gravity as the interfacial dynamics are locally driven by a balance of viscous-capillary and inertial forces, which can be expressed by the Ohnesorge number $Oh = \mu/(\rho\sigma R)$. As time evolves, the thinning of the thread is driven by capillarity, and the predicted thread radius towards the singularity agrees with the theoretical scalings (see figure 3.3) as the thread transits between different regimes (i.e., $r(t) \rightarrow 0$). After the singularity point, the formation of satellite ligament is observed which has an initially cylindrical shape (with $Oh = 2.62 \times 10^{-3}$ and $L_o = 11.55$); however, it undergoes retraction driven by capillarity to form more spherical droplets. This process known as ‘end-pinching’ has been previously well described by Notz and Basaran (2004). By performing this analysis we have proved the capability of our numerical technique to predict the dynamics of the capillary singularity of a liquid thread and its post-breakup events (table 3.5 shows a summary of the different meshes evaluated for this study).

Additionally, the accuracy and validation of the numerical method has been previously addressed to other complex interfacial phenomena. These phenomena include breakup and recoiling of liquid threads (Constante-Amores et al., 2020a), falling film flows (Batchvarov et al., 2020a), propagation of elongated bubbles in channels (Batchvarov et al., 2020b), bubbles undergoing bursting (Constante-Amores et al., 2020b), and drops coalescing partially or completely with deformable interfaces.

3.5 Results

3.5.1 Interfacial dynamics: phase diagram in $Re - We$ space

We start the discussion of the results by presenting a phenomenological picture of the interfacial dynamics in a phase diagram in the $Re - We$ space. The Reynolds and Weber numbers range between $10^3 - 10^4$ and $30 - 900$, respectively. Figure 3.4 shows the regime map in terms of the interfacial dynamics predicted from our numerical simulations. Several features emerge from this figure, which we have divided into four phenomenological regions based on the appearance of the interfacial structures. We aim to quantify the different jet behaviours by close inspection of the interplay between the vorticity field, $\boldsymbol{\omega} = \nabla \times \mathbf{u}$, and the interface. Such in-depth analysis is carried out following the introduction of each region, utilising the higher resolution M3-mesh examples, as shown in table 3.2.

Region ‘A’ in figure 3.4 is characterised by low Reynolds and Weber numbers and defined by the dominance of the capillary over inertial forces, yielding an axisymmetric behaviour of the jet. The formation of neither a leading mushroom-like structure nor interfacial lobes is observed. Figure 3.5 shows the interplay between the azimuthal and streamwise vorticity components, ω_θ and ω_x , respec-

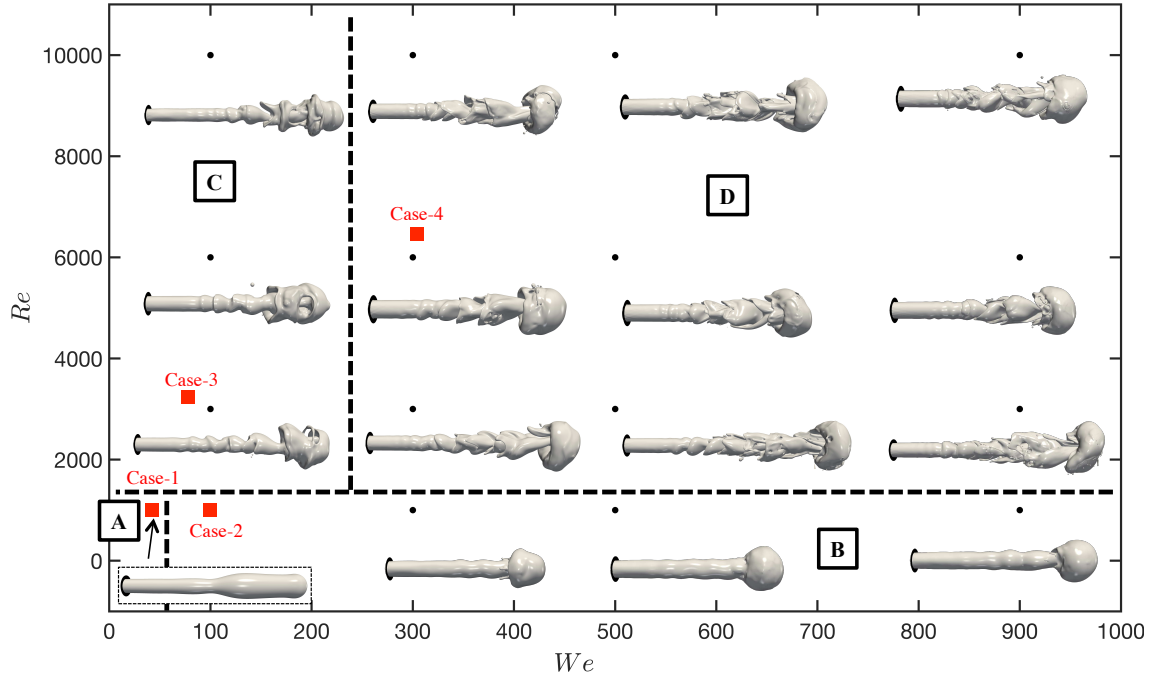


Fig. 3.4. Regime map of the phenomenological interfacial dynamics in the Re - We space using the $M2$ -mesh (see table 3.4 for mesh details). Four different regimes and their boundaries are identified. A snapshot of the flow corresponding to the three-dimensional representation of the interface for each simulated point (i.e., black marker) is shown. The red squares refer to the cases presented in table 3.2.

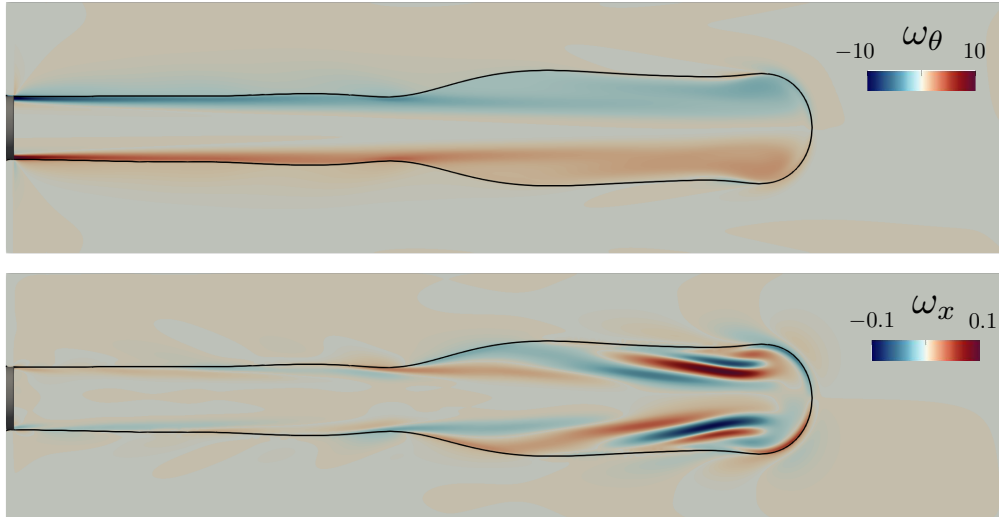


Fig. 3.5. Two-dimensional representation of the interfacial location together with ω_θ (top panel) and ω_x (bottom panel) in the x - z plane ($y=2$) for Case 1 in table 3.2 ($Re = 1000$ and $We = 30$) at $t = 24.38$. The colour represents the respective vorticity field, where appropriate scales are shown in each panel.

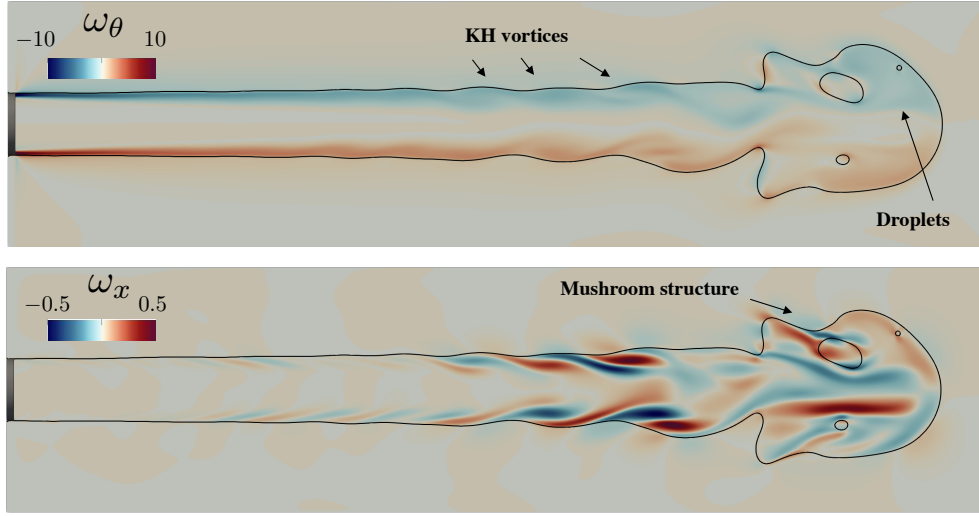


Fig. 3.6. Two-dimensional representation of the interfacial location together with ω_θ (top panel) and ω_x (bottom panel) in the $x-z$ plane ($y=2$) for Case 2 in table 3.2 ($Re=1000$ and $We=100$) at $t=26.87$. The colour represents the respective vorticity fields, where appropriate scales are shown in each panel.

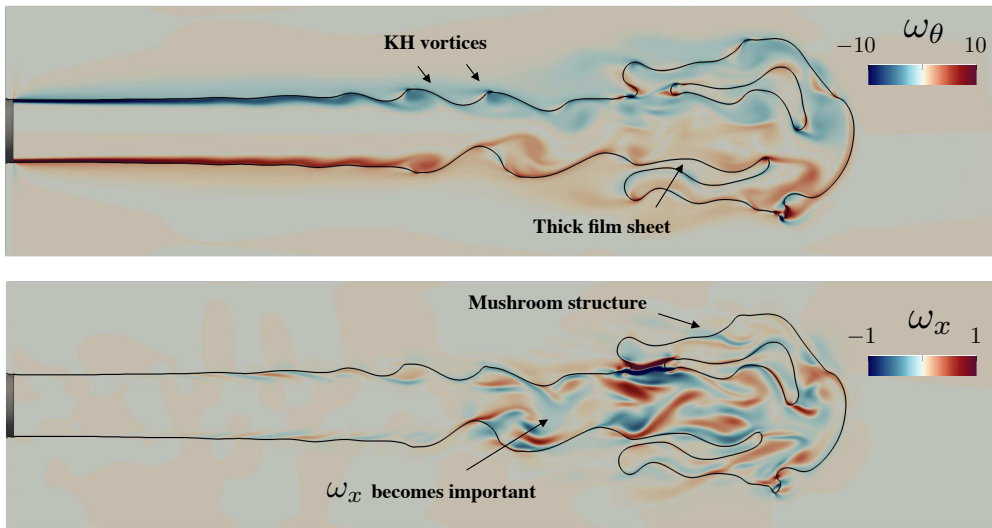


Fig. 3.7. Two-dimensional representation of the interfacial location together with ω_θ (top panel) and ω_x (bottom panel) in the $x-z$ plane ($y=2$) for Case 3 in table 3.2 ($Re=3260$ and $We=75$) at $t=24.65$. The colour represents the respective vorticity fields, where appropriate scales are shown in each panel.

tively for Case 1 (see table 3.2). We observe that ω_θ exceeds ω_x by two orders of magnitude for the entirety of the jet, which explains the lack of deformation of the jet-core, and its axisymmetric shape.

Region ‘B’ is defined by low Reynolds and high Weber numbers. As shown in figure 3.4, the snapshots of the interface in this region of parameter space reveal the development of interfacial waves as well as the formation of a ‘mushroom’-like structure at the jet leading edge. This is due to the large capillary pressure generated as a result of the interfacial curvature at this leading edge, which induces radial flow that is retarded by the viscous resistance from the stagnant phase. Figure 3.6 shows that although the magnitude of ω_θ exceeds that of ω_x by almost two orders of magnitude for Case 2, the relative significance of ω_x has increased in comparison with Case 1. This is correlated with the corrugations which are observed on the main body of the jet in Case 2 that appear to be largely absent in Case 1. These corrugations are related to the development of Kelvin-Helmholtz (KH) instabilities that arise from the velocity difference between the injected jet and the surrounding, initially stagnant phase. As shown in figure 3.6, the mushroom structure is also accompanied by the formation of droplets within it. More information regarding the mechanisms which induce droplet formation is provided in Section 3.5.3.

Region ‘C’ is characterised by low Weber and high Reynolds numbers. To elucidate the mechanisms at play in this region, we refer to Case 3 (see table 3.2), as shown in figure 3.7. It is seen clearly that the magnitude of ω_θ is an order of magnitude larger than that of ω_x . The higher levels of inertia in Case 3, in comparison to Case 2, leads to formation of pronounced KH instabilities with vortical rings close to the interface, yielding spanwise interfacial deformations. Close inspection of figure 3.7 reveals that the mushroom structure, which is also present in Case 3, undergoes significant deformation leading to the formation of a toroidal sheet, which envelopes that main body of the jet.

In region ‘D’, the flow is characterised by both high Reynolds and Weber numbers. Here, it is seen from the snapshots of the interface in figure 3.4 that the interfacial dynamics in this region of $Re - We$ space are the most complex. The mushroom structures suffer severe deformation as does the main body of the jet which also features the formation of lobes arising from the KH-induced corrugations. It is also evident that flow in region D is also accompanied by droplet generation. In Section 3.5.2 below, we focus on Case 4 in figure 3.4 and provide an extensive explanation of the mechanisms linking droplet formation to vortex-interface interaction.

3.5.2 Interfacial-dynamics explained through vortex-surface interaction

This section focuses on the inertia-controlled Region D and Case 4 as a principal exemplar of the flow in this region. In figure 3.8, we examine the spatio-temporal interfacial dynamics overlaid with the

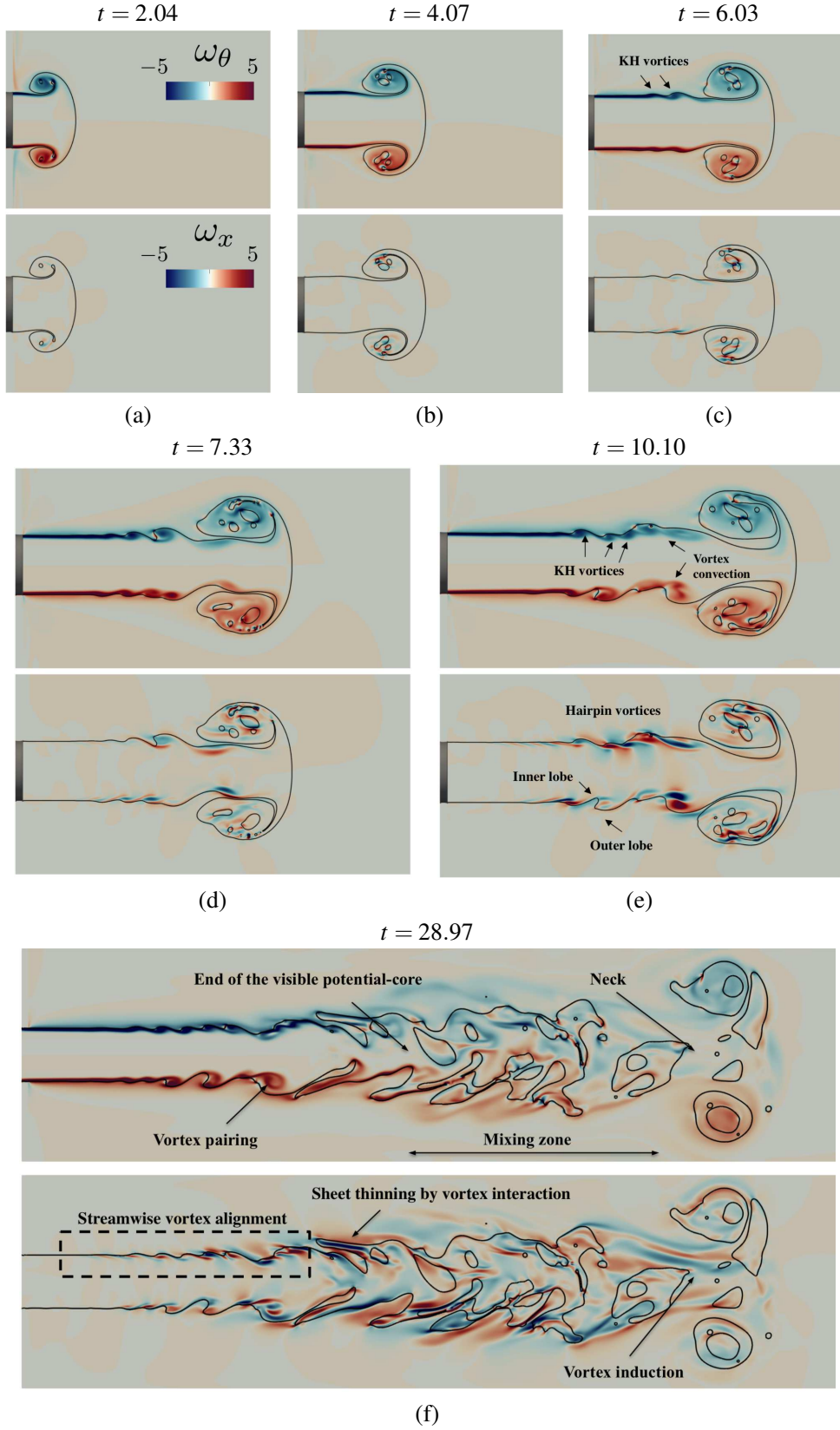


Fig. 3.8. Two-dimensional representation of the spatio-temporal evolution of the interface for Case 4 in table 3.2 ($Re = 6530$ and $We = 303$) together with ω_θ (top panel of each sub-figure) and ω_x (bottom panel of each sub-figure) in the $x-z$ plane ($y = 2$) for the dimensionless times shown in each panel. The colour represents the respective vorticity fields, where appropriate scales are shown in each panel.

magnitude of ω_θ and ω_x in the $x - z$ plane. During the early stages of the injection, the mushroom-shape structure develops due to the capillary-driven radial flow arising from the large interfacial curvature at the jet leading edge, which is resisted by the stagnant phase. As time evolves, the entrainment and formation of a toroidal liquid sheet of stagnant phase are observed inside the mushroom structure (see for example figure 3.8a,b). Upstream of the mushroom, it is seen that the KH instability develops (see figure 3.8c) amplified by the pulsatile-injection into waves which cause a local adverse pressure gradient by virtue of the local interfacial curvature (see figure 3.8d). With increasing time, we observe the formation of outer lobes as a result of the entrainment of the stagnant phase in the jet-core (see figure 3.8e).

Figure 3.8 also highlights the spatio-temporal development of the azimuthal and streamwise components of the vorticity. At early times, vorticity generation coincides with the velocity boundary layer attached to the interface, which corresponds to strong tangential flow near the interface. The roll-up of the shear layers, and subsequently, the vortex roll-up gives rise to the formation of KH vortex rings close to the interface (see figure 3.8c). As time increases, the vorticity boundary layer is convected towards the jet-core (see figure 3.8e). Additionally, vorticity dissipates strongly in the stagnant phase due to the damping effect of the viscosity.

Attention is now turned towards the competition between ω_θ and ω_x . In the region adjacent to the injection point, the azimuthal vorticity component dominates over its streamwise counterpart by two orders of magnitude; this dominance is reflected by the fact that the KH vortex rings shown in figure 3.8c are essentially axisymmetric. As the flow develops downstream (see figure 3.8d,e), ω_x becomes comparable in magnitude to ω_θ leading to streamwise stretching of the KH vortex rings to form hairpin-shaped vortices. Hairpin vortical or ‘horseshoe’ structures were proposed by Theodorsen (1952) to describe the features of turbulence dynamics related to the existence of a shear or boundary layer near a wall. A hairpin vortex is made from a ‘vortex-head’ which is the arched region farther away from the boundary layer. The head is connected to the free surface or wall by its ‘vortex-legs’. The hairpin-head orientation results from a balance between the effect of shear flow and the local velocity.

Interestingly, the streamwise alignment of hairpin vortices near the surface (see figure 3.8e,f) has been reported previously by Jarrahbashi et al. (2016) and Zandian et al. (2018) for coaxial round and planar jets, respectively. In spite of the absence of a coaxial phase in our case, we observe the same phenomenon. Additionally, we observe the successive alignment of opposite-signed vortices, where the angle between each vortex pair is determined by the induction effect of the opposite-signed ‘neighbour’ vortex. Similar arrangement of vortices has been reported previously by Jeong et al. (1997) for boundary layer turbulence, and Davoust et al. (2012) for compressible homogeneous jets. Further details about the specific alignment of the vortical structure is provided below.

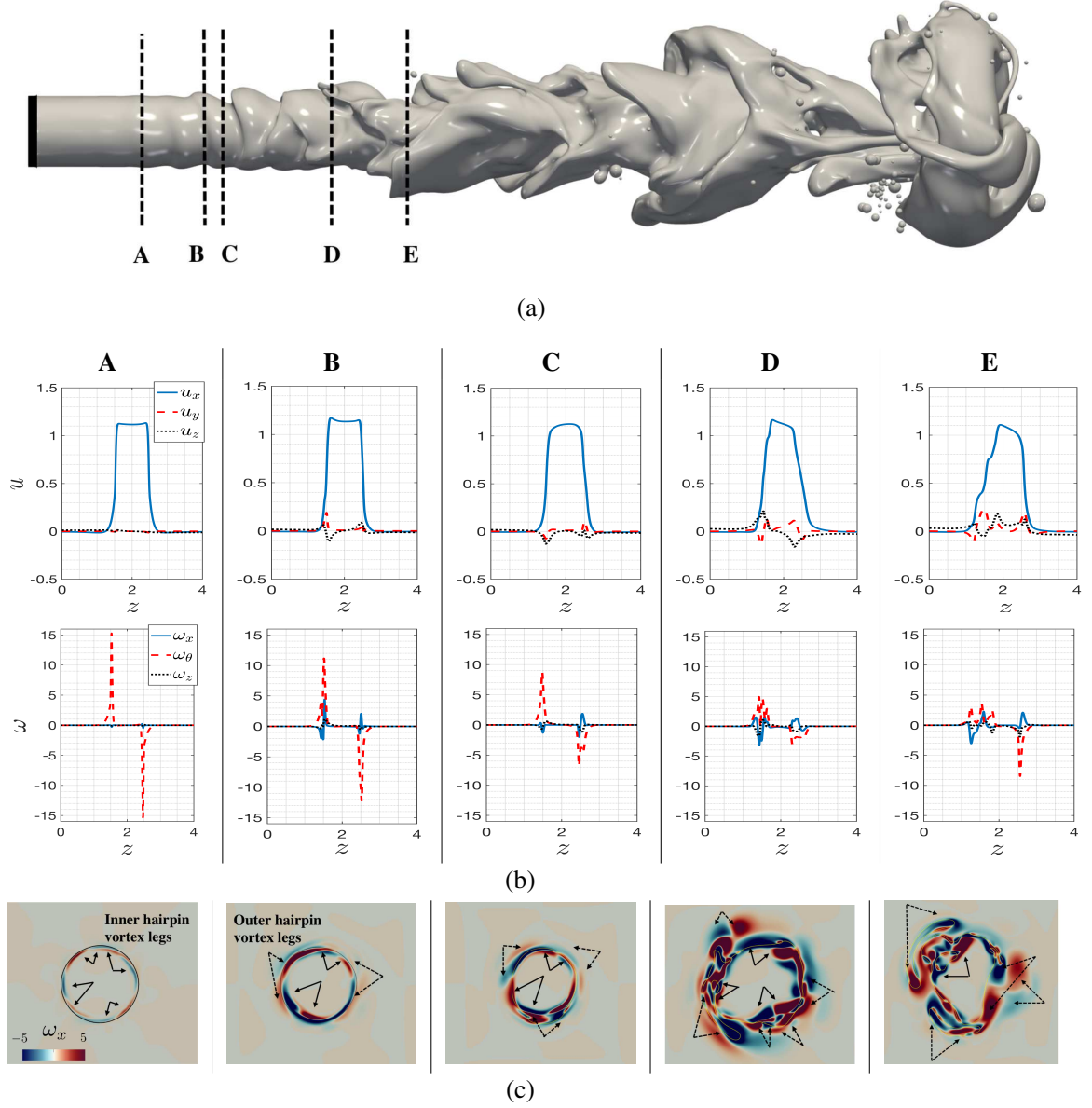


Fig. 3.9. Three-dimensional representation of the interface for case-4 ($Re = 6530$ and $We = 303$) at $t = 28.97$, showing the spatial locations ‘A’-‘E’, (a). The streamwise location of the ‘A’-‘E’ probe lines correspond to $x = (1.50, 2.50, 2.75, 4.25, 5.25)$, respectively. (b) Velocity (top panel) and vorticity profiles (middle panel) in the $y = 2$ plane for each probe location. (c) Streamwise vorticity in the $y - z$ plane for each sampling location. The arrows show examples of identified hairpin-vortex legs. Solid and dashed arrows correspond to inner and outer hairpin vortex legs, respectively. The colour represents the streamwise vorticity field, ω_x .

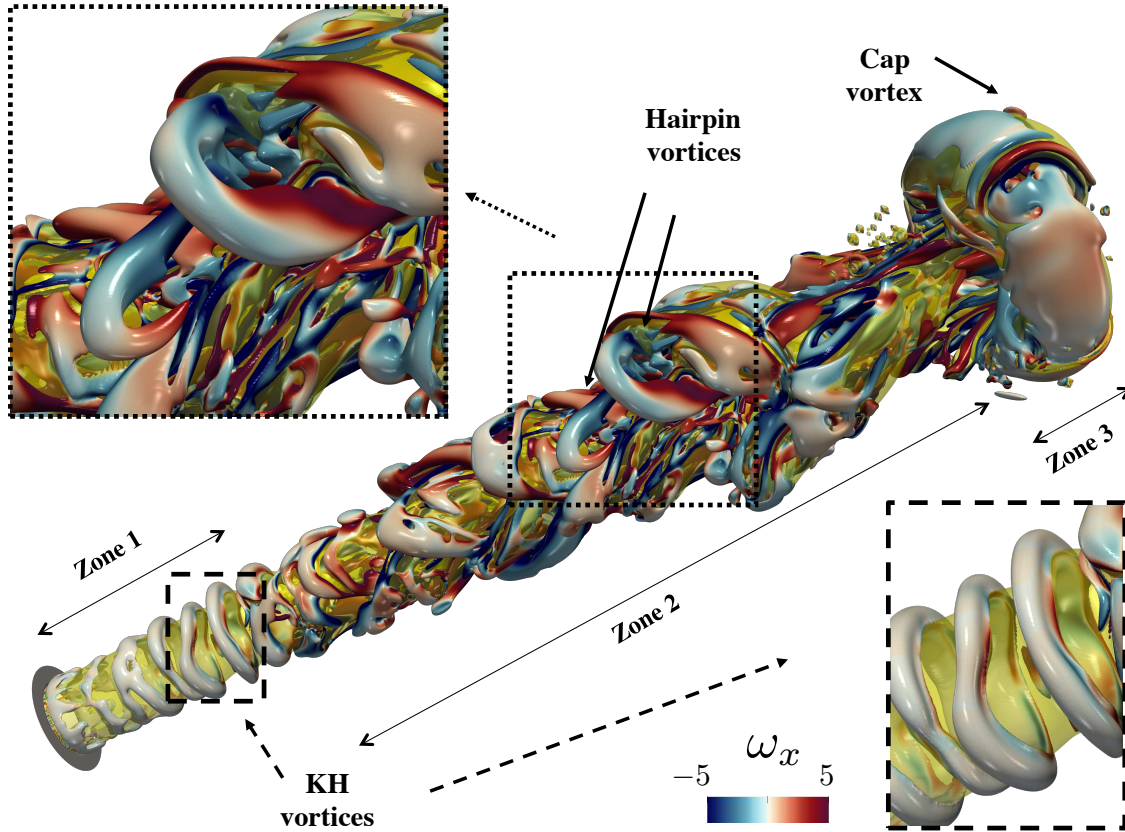


Fig. 3.10. Illustration of the coherent vortical structures close to the interface for case-4 ($Re = 6530$ and $We = 303$) at $t = 28.97$. The coherent vortical structures are visualised by the Q -criterion with a value of $Q = 0.1$, where the colour represents the streamwise vorticity field, ω_w . Magnified views of the KH-vortex rings near the injection point, and the hairpin-vortical structures in the jet core are also shown.

Figure 3.9a presents a three-dimensional representation of the jet at $t = 28.97$ alongside five spatial locations which will be used to show the evolution of vorticity and velocity across the jet core. The specific locations were chosen as follows: panel ‘A’ is representative of the dynamics near the injection point, where there is little disturbance to the interface; panel ‘B’ displays the cross-section of the jet in a jet-ring (i.e., the part of the interface where we observe the capillary wave crest), whereas panel ‘C’ depicts a jet-braid (i.e., the capillary wave trough); panels ‘D’ and ‘E’ portray the jet core dynamics where lobe formation is present. Figure 3.9b shows the velocity and vorticity line profiles at the $y = 2$ plane alongside the streamwise vorticity in the $y - z$ plane for each of those locations. Near the injection point (location ‘A’), $\omega_\theta \gg \omega_x$, which is in agreement with the lack of deformation of the vortical structures in the streamwise direction (see also figure 3.8f). The tangential motion of the fluid close to the surface results in the emergence of the velocity boundary layer. In turn, this causes the formation of two large peaks of opposite signs for ω_θ . As the flow evolves downstream, ω_θ still dominates the physics, although, its value has been reduced in favour of an increase in ω_x , and consequently the local formation of corrugations on the jet-core (location ‘B’). Additionally, the ω_θ peaks have widened in their base due to the growth of the velocity boundary layer as the jet moves downstream (Liepmann and Gharib, 1992). Further downstream (location ‘D’ and ‘E’), the interface has lost its cylindrical shape due to the entrainment of the stagnant phase as ω_x becomes comparable in magnitude to ω_θ . Several peaks can be seen in the vorticity profiles as the probe line passes through several lobes. By inspecting the instantaneous velocity-fields in locations ‘D’ and ‘E’, we observe that the main component of velocity is associated with the direction of injection, where there is a decay of its mean centreline value as flow evolves downstream, which is in agreement with Pope (2000) for single-phase jets. The velocity decay leads to a reduction in the velocity difference between the injected and stagnant phases, which attenuates the interfacial shearing, supporting the development of the vortical rings close to the surface of the jet. Notice that the y and z velocity-components are positive or negative close to the surface, showing the entrainment of injected fluid towards the stagnant viscous phase or vice versa.

Next our attention is turned towards the physical mechanisms which lead to the alignment of the hairpin-like vortical structures along the free-surface. Figure 3.9c shows cross-section panels with ω_x of the jet at the streamwise locations shown in figure 3.9a. As depicted in panel ‘A’, ω_x is mainly confined inside of the injected stream, where hairpin vortex legs are observed (see first panel of figure 3.9c). In panel ‘B’, the outer layer of vorticity comes from the braid located immediately downstream, which starts to roll-up around the ring. Further analysis of panel ‘B’ shows the existence of additional pairs of vortex legs which are 180° out-of-phase with respect to the inner layer, and subsequently they correspond to a second hairpin vortex layer with opposite direction (e.g., upstream direction). Similarly, in panel ‘C’ we observe that the inner layer of the vorticity comes from the ring located upstream, whereas the outer layer comes from the ring located immediately downstream. Therefore, we

can conclude that the alignment of the hairpin vortices is a result of the existence of a vortex-induction mechanism which causes the reorientation of vortical structure within the ring and braid skeleton. This phenomenon is in agreement with Brancher et al. (1994) for homogeneous jets, Jarrahbashi et al. (2016) for the coaxial atomisation of a round liquid jet, Zandian et al. (2018) for coaxial atomisation of planar jets, and Bernal and Roshko (1986) for plane mixing layers. The analysis between the panels ‘B’ and ‘C’, can be extended to other locations of the jet where the core has undergone further interfacial development. For example, in panels ‘D’ and ‘E’ we observe the same distribution of inner and outer layer of hairpin vortex legs. The alignment of vortical structures has a detrimental effect on the interfacial dynamics, which will be shown in section 3.5.3.

Additionally, we have used the Q -criterion to present a three-dimensional visualisation of the vortices in the present study. The Q -criterion was described by Hunt et al. (1988) as a quantity which measures the dominance of vorticity ω over strain s , $Q = 1/2(\|\omega\|^2 - \|s\|^2)$. Figure 3.10 shows the spatial development of the coherent structures for $Q = 0.1$. Near the injection point, axisymmetric KH vortex rings are located close to the surface (a magnified view is shown). As explained previously, when ω_x and ω_θ are of comparable magnitude, the KH vortices are stretched downstream or upstream. The topological shape of these vortical structures resembles the instantaneous hairpin-like vortical structures reported in experiments and numerical simulations by Head and Bandyopadhyay (1981); Zhou et al. (1999); Zandian et al. (2018). Outer hairpin vortices (a magnified view is also shown) are observed clearly and the inner hairpin vortices not as clearly as they are localised underneath of the interface. Further downstream, we observe the presence of a ‘cap-vortex’ covering the mushroom-like structure. Inside of this structure, the vortices are unstable and break down.

To conclude, we have identified three different zones in the transient flow field which are associated with different vortical dynamics. We present the different regions at $t = 28.97$ (see figure 3.10). Zone 1 starts from the injection point and extends up to the deformation of the free-surface ($x \sim 1.8$). This zone is characterised by the dominance of ω_θ . Zone 2, which extends from $x \sim 1.8$ up to $x \sim 11.5$ (e.g., behind the mushroom-like structure). This region is characterised by the interfacial deformation of the jet-core by KH vortex rings and their posterior deformation by the competition between ω_x and ω_θ . As the flow moves downstream, ω_x becomes responsible for the entrainment of the stagnant phase to form interfacial lobes (this agrees with Liepmann and Gharib (1992) for homogeneous jets). In this region, vortex rings pair up and merge together. Additionally, the ending of the visible-potential core of the jet and the beginning of the mixing region is also observed. Zone 3, expands from the end of zone 2 up to the leading edge of the mushroom-like structure. A large vortex-ring dominates the dynamics in this region (so-called ‘cap-vortex’, Zandian et al. (2019)), wherein its interaction with upstream vortex structures via means of velocity induction leads to the formation of the neck, connecting the mushroom-like structure with the cylindrical body of the jet. The narrowing of the neck as a result of

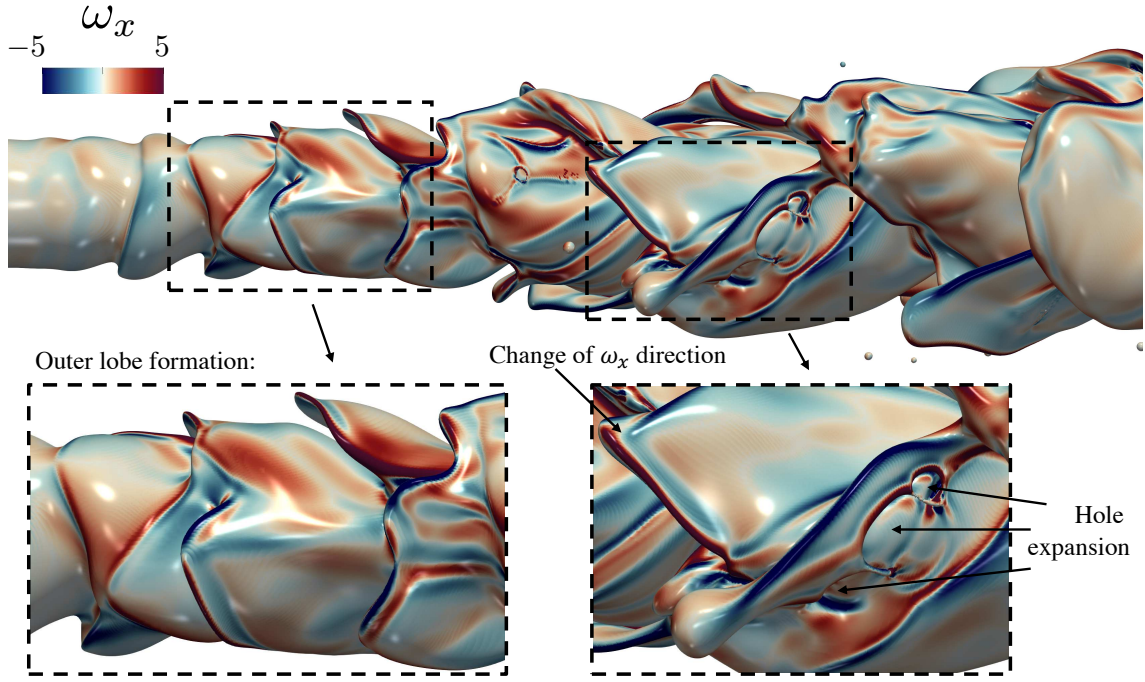


Fig. 3.11. Three-dimensional representation of the surface of the jet for case-4 ($Re = 6530$ and $We = 303$) at $t = 28.97$ showing the spatial formation of outer lobes. The colour represents the streamwise vorticity field, ω_x .

the streamwise convection of vortical structures is in agreement with the work of Asadi et al. (2018).

3.5.3 Cascade mechanism for droplet formation: hole-formation genesis

In the previous section, we discussed the vortex dynamics of the transient jet. This section focuses on the effect of vortices on the formation of inner/outer lobes, the thinning of which leads to genesis of droplets.

Figure 3.11 shows a close view of the interfacial jet dynamics where outer lobes are present. The formation of lobes is observed along the spanwise direction of the jet. Close inspection of the interface shows it has assumed the shape of the surrounding hairpin vortical structures, where a change of the vorticity-direction is observed for subsequent lobes (similar observations have been made by Jarrahbashi et al. (2016); Zandian et al. (2018)). Consequently, the alignment of the hairpin vortices induces the thinning of the outer lobes, leading to formation of holes, which expand and eventually give rise to droplets.

Figure 3.12 shows the temporal stretching of an outer lobe to form a ligament, and eventually droplets. The ligament orientation is linked to the vortical structures, as suggested above. A bulbous-tip is formed in the edge of the ligament driven by capillarity. The ligament posterior breaks by its base

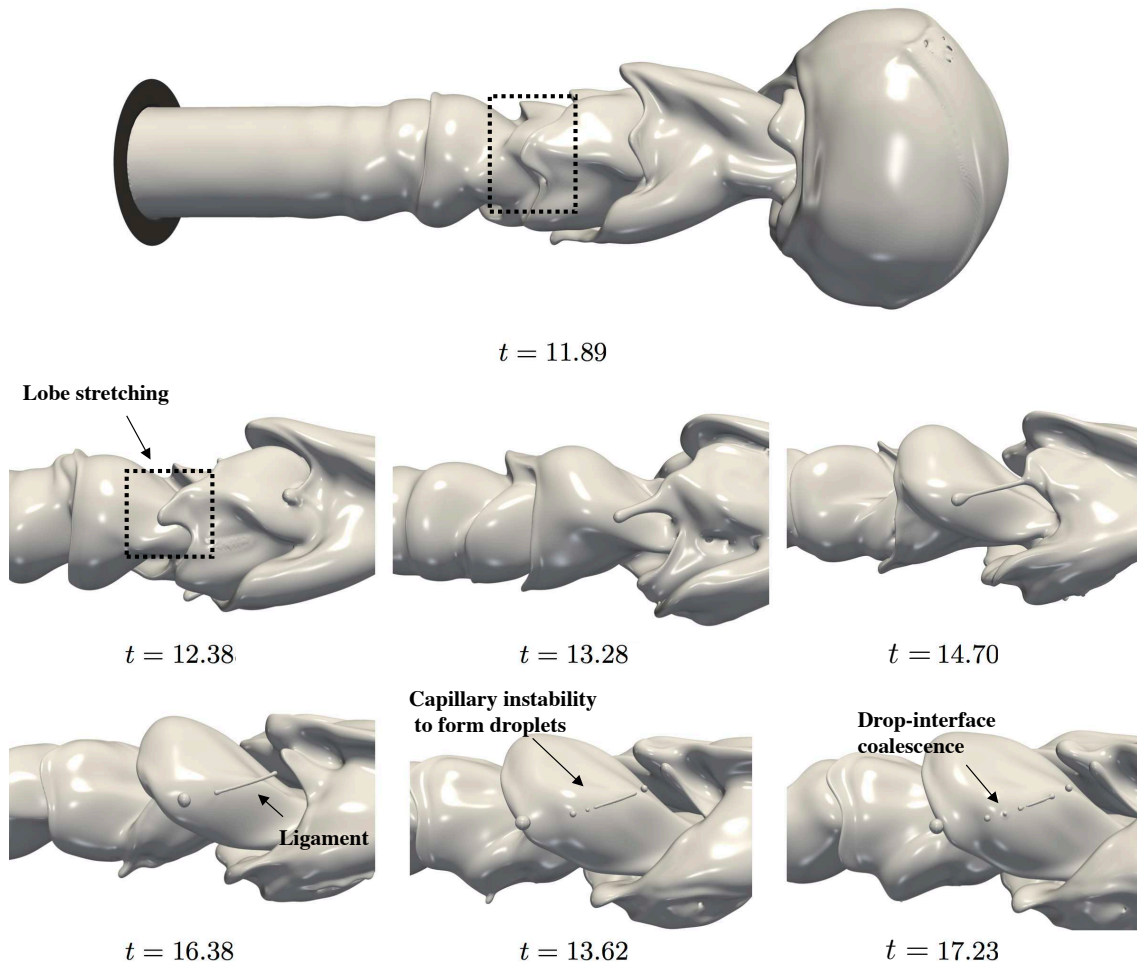


Fig. 3.12. Three-dimensional representation of the interface showing the spatio-temporal evolution of the formation of droplets via the stretching of the outer lobe for case-4 ($Re = 6530$ and $We = 303$). Dimensionless times are shown in each panel.

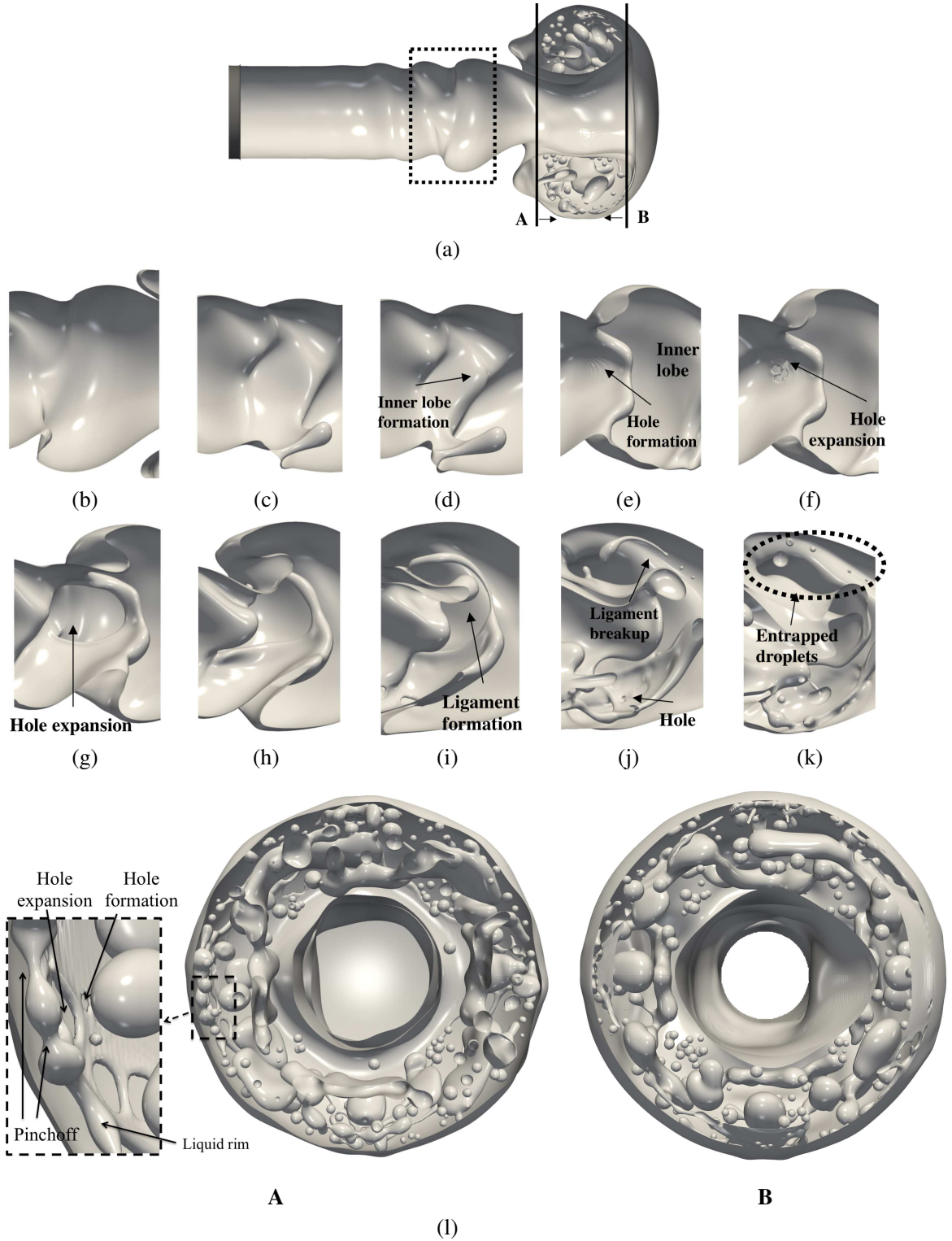


Fig. 3.13. (a) Three-dimensional representation of the interface for case-4 ($Re = 6530$ and $We = 303$) at $t = 7.33$ showing a selected region in the jet core where inner lobes will form, together with two probe locations in the leading-edge structure, where the arrows indicate the direction of the view. (b-k) Cascade mechanism for the formation of entrapped droplets within the jet core at $t = (8.84, 9.96, 10.10, 10.92, 11.36, 11.41, 12.06, 13.61, 16.38)$, respectively. (l) Illustration of the entrapped-droplets inside of the mushroom-like structure at $t = 7.33$ from the back (probe 'A') and front (probe 'B') of the structure, respectively. A magnified region of the structure is also shown to illustrate the hole-formation behind the rim-edge.

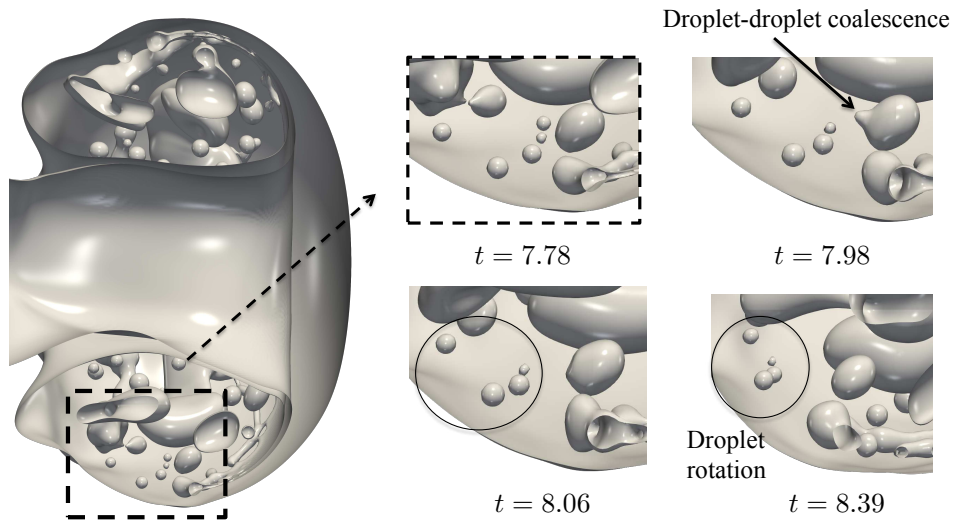


Fig. 3.14. Three-dimensional representation of the interface for case-4 ($Re = 6530$ and $We = 303$) at dimensionless times shown in each panel. A magnified region of the structure is also shown to illustrate droplet-droplet coalescence and the droplet-rotation inside of the leading-edge structure.

due to thinning (e.g., as the jet is moving downstream), leaving a long ligament which retracts under the action of surface tension forces to form droplets from both sides via the end-pinching mechanism Notz and Basaran (2004). The characteristic length of the ligament (their thickness) is influenced by the external velocity field, the ratio of densities, and the surface tension. The ligament is characterised by having a small thickness previous to its detachment from the base. However, the droplets formed after the breaking process have a larger length scale (in agreement with Villermaux (2007)).

Figure 3.13 shows the formation of droplets inside of the jet core, and the mushroom structure. Specifically, figures 3.13b-k depict the formation and elongation of the inner lobe in the streamwise direction. As before, the stretching of the interface gives rise to a thin sheet as a result of the mutual induction of neighbouring hairpin-vortices. The hairpin vortex located above the liquid sheet induces flow downwards, whereas the vortex located under the sheet induces flow upwards. Under the joint action of the vortical structure, the liquid sheet thins until it is perforated (see figure 3.13e). Following the formation of the hole, retraction of the liquid sheet is radially driven by capillarity (see figures 3.13f and 3.13g), and as shown in figure 3.13i, it subsequently gives rise to the formation of a curved liquid thread or ligament. Once more, ligament retraction is driven by capillarity where bulbous ends that form initially undergo ‘end-pinching’ to form smaller droplets, as shown in figures 3.13j-k. The inertia-induced mechanism for the sheet-thinning presented here has been previously reported by Jarrahbashi et al. (2016).

The analysis will now focus on the dynamics underneath the mushroom-like structure. Figure 3.13l shows entrapped droplets inside of the leading-edge structure. The formation of these droplets is also

linked to the interfacial rupture of the toroidal liquid sheet. The liquid sheet retracts driven by surface tension to accumulate liquid in a rim at its edge. The rim experiences a spanwise destabilisation (i.e., Rayleigh-Plateau type), which leads to a non-uniform rim-radius. The film retraction is also accompanied by the formation of interfacial capillary waves that precede the rim. The capillary waves vary the film thickness, and consequently induce the perforation of the film adjacent to the rim in regions where the film thickness is sufficiently small (in agreement with Mirjalili et al. (2018)) The radial expansion of multiple holes yields the formation of liquid threads which experience a capillary instability to produce droplets. Following their formation, the entrapped droplets rotate inside of the leading structure due to their interaction with the vorticity field (not shown here). The rotation leads to complex interfacial phenomena such as coalescence or collision (similar to the reported by Desjardins and Pitsch (2010)). The coalescence has been observed not only between droplets, but also between droplets and ligaments or droplets and the jet core (see figure 3.14).

Next, we aim to explain the validity of the hole formation mechanism as a result of liquid film thinning. Our numerical method does not consider the destabilising effect brought about by the Van der Waals attractive forces as the film thickness tends to zero. Churaev et al. (1987) reported that while the thinning takes place, the dynamics of the film enters in an asymptotic behaviour leading to its rupture, depending only on a balance between viscous, van der Waals, and surface tension forces. After the film-puncture, the circular hole expansion is driven by capillarity, and fluid is accumulated in a circular rim which grows in size as it moves away from the puncture point. The retraction can be predicted by the classic ‘Taylor-Culick’ retraction speed $V_{TC} = (2\sigma/\rho h)^{1/2}$, where h is the film thickness. Prior to the puncture $h \sim 40\mu$, which means $V_{TC} = 1.18m/s$. The measured retraction speed of the holes in our simulations ranges from 0.75 m/s to 1.2 m/s. This ensures that although our simulations cannot predict the exact location of the puncture, and their formation is mesh-dependent, its expansion is well predicted, ensuring that the physics are fully resolved following the formation of the hole. Additionally, the film thickness of the sheet prior to its rupture is on the order of $h \sim 10^{-6}m$, which agrees with the findings from Marston et al. (2016); Lhuissier and Villermaux (2009); Néel and Villermaux (2018), who observed the interface rupture for film sheets of the same order of magnitude.

3.5.3.1 Droplet size distribution

This section draws attention to the size distribution of the droplets, formed as a result of the ruptures of the liquid threads. At early stages, the formation of droplets is only observed inside of the leading-edge structure, owing to the film rupture via hole formation. At larger times, both entrapped and dispersed droplets coexist in the computational domain. I have identified all the droplets inside of the entire domain, and each droplet diameter is calculated through the knowledge of its volume, and the assumption of a spherical shape.

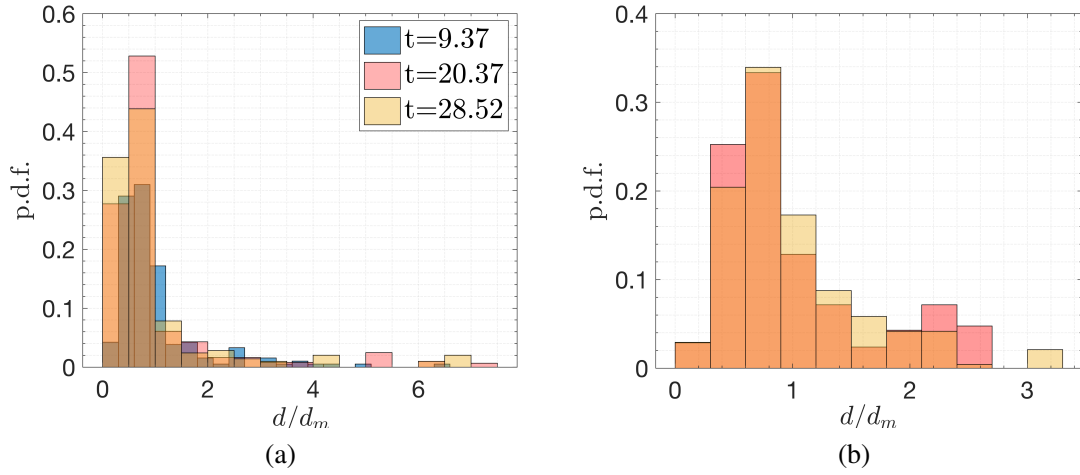


Fig. 3.15. Probability density function for the entrapped and injected droplets for case-4 ($Re = 6530$ and $We = 303$) at $t = 9.37$, 20.37 , and 28.52 shown in panels (a) and (b), respectively. The distributions are normalised by the calculated mean diameter for each time.

Figure 3.15 shows the probability density function (i.e., p.d.f.) normalised by the mean droplet diameter at different temporal stages $t = (9.37, 20.37, 28.52)$. Their distribution keeps roughly the same shape with a higher number of smaller droplets at longer times. The reason for this lies in the breakup of ligaments into smaller size droplets, as explained previously. Some characteristics of the sampling corresponding to the entrapped droplets under the mushroom shape at $t = 9.37$: mean droplet-diameter equal to $341.69\mu\text{m}$, median droplet-value equal to $246.41\mu\text{m}$, standard deviation of the sample is $296.36\mu\text{m}$. Figure 3.15b shows a similar histogram for the injected phase where the distribution remains nearly identical for both times.

3.6 Conclusions

Three-dimensional numerical simulations were carried out for turbulent water jets entering a stagnant and more viscous silicon oil phase. Particular attention has been paid to the temporal interfacial dynamics that arise as a result of the vortex-surface interaction. Using less computationally expensive simulations, I have explored the $Re - We$ physical space, identifying four distinct regions based on the appearance of the interfacial structures. On this basis, I have carried out high fidelity simulations representative of each region. I have shown that the streamwise vorticity plays a major role in the development of the three-dimensional instabilities on the jet surface. At low Re and We numbers (i.e., capillary-controlled region), the jet interface remains axisymmetric and no surface corrugations are observed due to strong capillarity. Moreover, this region is also characterised by values of azimuthal vorticity such that the streamwise vorticity, ω_x , never becomes comparable to the azimuthal vorticity, ω_θ . The azimuthal vorticity always remains two orders of magnitude larger than the streamwise

vorticity. At low Re and high We numbers, the reduction of capillarity enhances the formation of a mushroom structure at the leading edge of the jet, and the formation of corrugations in the jet core; however, ω_x is still almost two orders of magnitude smaller than ω_θ . At high Re and low We numbers, streamwise vorticity starts becoming important, resulting in further deformation of the jet core. Finally, in the inertia-controlled region (i.e., high Re and We numbers), the streamwise vorticity becomes comparable to the azimuthal vorticity triggering the streamwise deformation of KH vortices. We show the formation of hairpin vortices near the interface, which are aligned in the streamwise direction forming layers of inner- and outer- hairpin-vortices. The formation of inner and outer lobes in the jet core are closely linked to their neighbouring hairpin-vortices. The alignment of vortices enhances the perforation of the lobes to form holes which expand radially by capillarity, and ultimately give rise to the formation of droplets. Another main feature of the inertia-controlled regime is the creation of a thin toroidal sheet inside of the leading-edge structure. The thinning of this sheet yields its perforation to form droplets. The droplets rotate as a result of their interaction with the vorticity field, and further topological transitions occur (e.g., coalescence).

While in the present study I have focused on the spatial and temporal development of the interfacial dynamics as a result of the vortex-surface interaction, further investigations should be carried out on the statistical response of the turbulent multiphase flow, similar to the work presented by Ling et al. (2019) for a mixing layer between parallel gas and liquid streams. Additionally, our study assumes a constant value of surface tension, but it is known that streams are usually contaminated with deliberately places or naturally occurring surfactants, which reduce surface tension and give rise to surface tension gradients (i.e., Marangoni stresses). As shown recently by Constante-Amores et al. (2020a), surfactants are capable of inhibiting capillary singularities and rigidifying the interface, subsequently changing the fate of the atomisation. Hence, the presence of surfactants may change the present results, providing us with an exciting avenue of future research.

Chapter 4

Surfactant-laden turbulent jets

Summary

This chapter explores the effect of surfactant on the interfacial dynamics of turbulent jets. The motivation behind this chapter resides in the fact that most industrial or naturally occurring streams are contaminated with chemical components whose concentration variations lead to surface tension gradients, and subsequently the generation of Marangoni stresses on the plane of the interface. The interface-tracking nature of the numerical method employed facilitates the faithful modelling and simulation of the spatio-temporal evolution of the surfactant concentration field on the interface and in the bulk. Interestingly, a larger droplet size distribution is found for the surfactant-laden case rather than the surfactant-free case, although the surface tension is reduced (i.e., weaker capillary forces), which would normally make the interface more susceptible to its fragmentation.

4.1 Introduction

Multiphase flow dynamics are influenced by a range of multi-scale physics. The presence of chemical surfactants (i.e., contaminants, pathogens, or additives) which act as surface-active agents could have a detrimental effect on the flow dynamics, adding new layers of complexity. The multi-scale nature of the flow and the tremendously complex interfacial topology complicate the scrutiny of multiphase flows experimentally even in the absence of additives. Thus, elucidating the influence of additives on these flows requires the development of theoretical and computational tools to enable high-fidelity simulations to be deployed to drive experiment design and to understand the delicate interplay among the different physical mechanisms across scales.

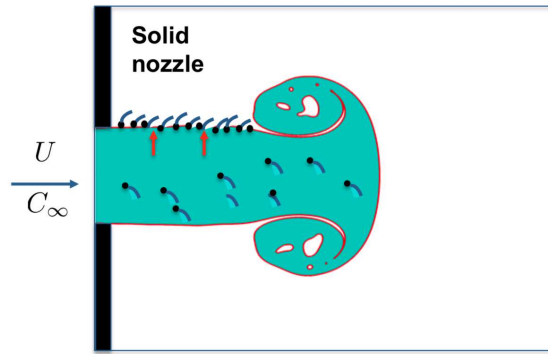


Fig. 4.1. Two-dimensional representation of the numerical set-up, with a schematic view of the migration of surfactant towards the interface.

Chapter 3 discussed in detail the state-of-the-art of atomisation field. In many industrial applications, liquid streams may contain impurities or any chemical components which behave as surface-active agents affecting the dynamics of the system. These surface-active agents lower the interfacial surface tension, and triggers the generation of surface tension gradients, and ultimately Marangoni stresses on the plane of the interface. These Marangoni stresses add rigidity to the interface, acting from regions of higher to lower concentration, and consequently modifying the dynamics of the phenomenon.

Recently, Kooij et al. (2018b) and Sijs et al. (2019) studied experimentally the effect of surfactants on the atomisation phenomenon. Kooij et al. (2018b) showed that the lowering of surface tension via surfactants is ‘completely ineffective’ on the resulting droplet size distribution, in a posterior study, Sijs et al. (2019) showed that the physical mechanisms for droplet formation are qualitatively identical to those described for surfactant-free cases, and they also concluded that the mean-droplet size slightly decreases in the presence of surfactants (similar findings were also made by Sanderson et al. (1997)). On the other hand, other researchers have found that the addition of surfactant can lead to the increase of the mean droplet size (Oliveira et al., 2013; Stainier et al., 2006). However, a complete understanding of what is the reason behind either the increase or reduction of the mean droplet size is still lacking.

To the best of my knowledge, no computational studies regarding surfactant-laden turbulent jets have been reported in literature. Therefore, this chapter tries to understand for the first time the effect of surfactant on the dynamics of the jet. This chapter will leave some open questions which will be addressed in the following chapters.

4.2 Set-up and dimensionless parameters

Figure 4.1 shows a schematic representation of the numerical configuration considered in this chapter. The computational configuration (e.g. size, boundary conditions, inlet velocity profile and nozzle) is identical to the one described in chapter 3. Jin and Stebe (2007) reported that the surfactant effects are more predominant when $\mu_{inj}/\mu_{ext} < 1$, therefore, I consider the case in which chemical surfactants enter the computational domain together with the injected stream.

For the considered case, the dimensionless parameters governing the surfactant equations are given by

$$Pe_s = \frac{u_R R}{D_s}, \quad Pe_b = \frac{u_R R}{D_b}, \quad \beta_s = \frac{\Re T \Gamma_\infty}{\sigma_s}, \quad Bi = \frac{k_d R}{u_R}, \quad \chi = \frac{\Gamma_{eq}}{\Gamma_\infty} = \frac{k}{1+k}. \quad (4.1)$$

The parameters have been chosen carefully to formulate the problem in a more realistic experimental framework.

- The non-dimensional Biot number $Bi = k_d R_0 / U$ represents the ratio of characteristic desorptive to convective timescales. For $Bi \ll 1$, the sorptive timescales are much larger than those associated with interfacial effects. Therefore, the dynamics are more dominated by capillarity and Marangoni stresses, and are expected to be similar to those observed for an insoluble surfactant case. The first part of the manuscript aims to study the delicate interplay between the surfactant and the interfacial dynamics when the surfactant behaves as though it were insoluble. The Biot number contains the desorption rate constant k_d , which can range between $10^{-4} < k_d < 10^2 \text{ s}^{-1}$. The lower value in the previous range corresponds to $C_{12}E_6$, while the upper value is associated with surfactants that have short-chain alcohols. On this basis, all Bi values that are used in the manuscript are based on these realistic values of the desorption parameter k_d .
- The elasticity number β_s measures the sensitivity of the surface tension to variations in interfacial surfactant concentration Γ . This parameter depends on the interfacial concentration at saturation, Γ_∞ , which, in turn, is related to the critical micelle concentration (CMC) that is of $O(\sim 10^{-5}) \text{ mol/m}^2$.
- Pe_s and Pe_b are the interfacial and bulk Peclet numbers, respectively, comparing the ratio of convective to (interfacial and bulk) diffusive timescales. Bulk diffusion coefficients on the interface are similar in magnitude to the superficial diffusion coefficients (see Agrawal and Neuman (1988)). Typical values of diffusivity D_s for SDS, SB12, and other monomers in aqueous solution are within the range $10^{-9} < D_s < 10^{-7} \text{ m}^2/\text{s}$, when the concentration is below the critical

micelle concentration (see Siderius et al. (2002)). Therefore, the Peclet number lies in the range $10^1 < Pe_s < 10^5$, which means that influence of surface diffusion is greater compared to the convection.

Therefore, the dimensionless parameters are chosen to be agreement with aforementioned experimental values, leading to: $Pe_s = Pe_b = 1000$, $\beta_s = 0.7$, $\chi = 0.9$ and $Bi = 0.1$.

4.3 Results

The discussion of the results will start by turning the attention towards the spatio-temporal interfacial surfactant concentration (see figure 4.2). The interfacial dynamics of the surfactant-laden case resembles the surfactant-free case with the formation of a mushroom-like structure at its leading edge. Figure 4.2 also shows the entrainment of the stagnant phase in the leading structure. This is as a result of the same mechanisms of hole formation discussed in chapter 3. The capillary retraction of multiple holes leads to the formation of ligaments, and subsequently, droplets via capillary instability. As time evolves, the free surface behind the leading structure adopts the shape of a ‘cylinder’ which undergoes a Kelvin-Helmholtz instability (KH) to give the formation of initial corrugations (i.e, capillary waves) on the surface.

The interfacial dynamics of the jet can also be explained by coupling the vorticity $\omega = \nabla \times \mathbf{u}$ with the interfacial location. During the early stages, and close to the injection point, the streamwise vorticity field ω_x is characterised by values which are two orders of magnitude smaller than the azimuthal vorticity ω_θ . As flow evolves downstream, ω_x becomes comparable in magnitude with ω_θ , leading to the deformation of axisymmetric KH vortex rings in the streamwise direction adopting a new hairpin shape. These hairpin vortices trigger the formation of interfacial lobes which are stretched downstream (from outer hairpin vortices) and upstream (from inner hairpin vortices) to eventually obtain a hairpin shape (these mechanisms were explained in detailed in chapter 3).

Figure 4.2 shows that surfactant accumulates in the high-curvature interfacial regions (e.g., in the edges of the inner lobes and droplets). Surfactant is swept or displaced towards the edges of the inner lobes, and subsequently, surface tension is reduced, enhancing lobe entrainment and eventual droplets creation (see figure 4.2). Attention is now turned towards the mushroom-like structure, surfactant is swept towards its rear, where it accumulates (which agrees with the concept of flow passing through a surfactant-laden droplet). Inside of the jet, a higher surfactant concentration is located in the droplet/ligaments as the adsorption of surfactant is enhanced in high curvature regions. Regions with high change in the topological shape are characterised by high-velocity gradients. This can also be observed by tracking the interfacial concentration for the imminent droplet-surface coalescence. As

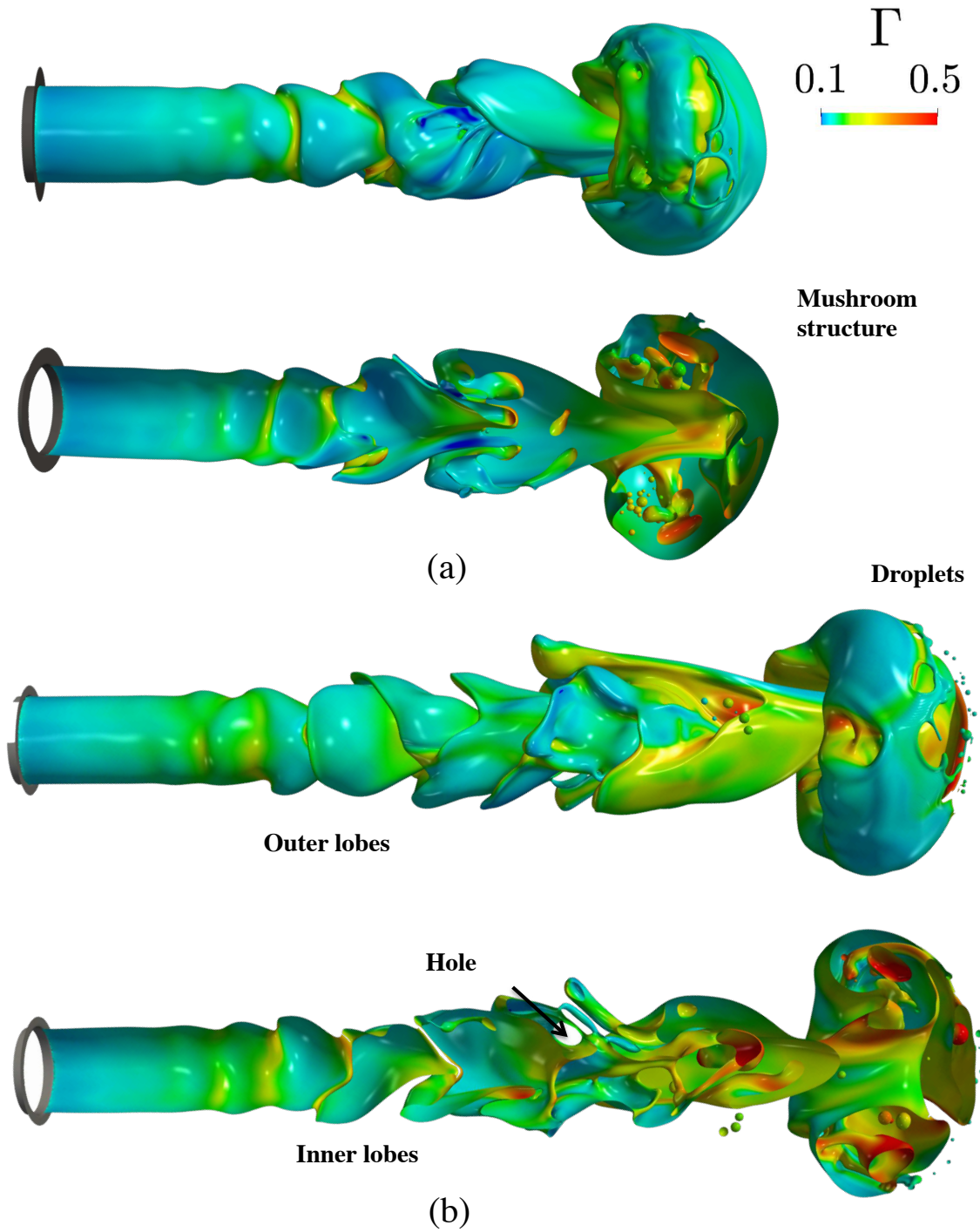


Fig. 4.2. Three dimensional representation of the interface at $t = 12.59$ and $t = 19.96$, corresponding to (a) and (b), respectively. In each sub-panel, a transversal cut of the interface in the plane $y = 2$ is shown to ease the visualisation of the jet interior (i.e, entrapped droplets and inner-lobe formation). The colour represents the respective interfacial concentration field, where appropriate scales are shown at the top of the figure.

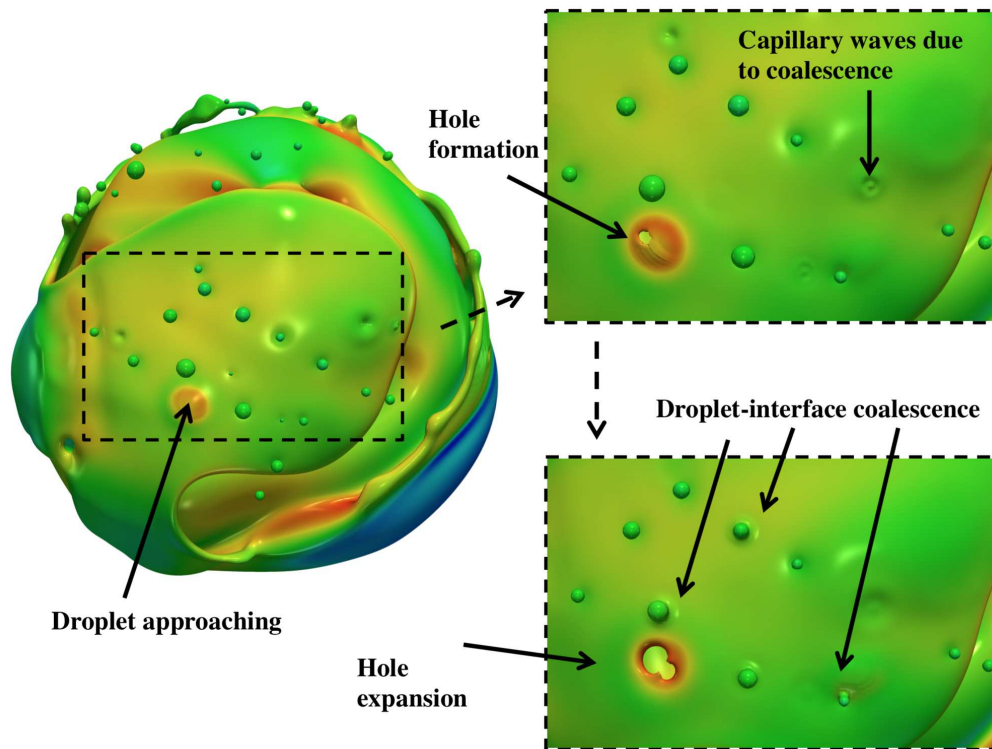


Fig. 4.3. Three dimensional representation of the interface showing complex interfacial topological events such as droplet-surface coalescence or the so-called ‘bursting-bubble’ mechanism.

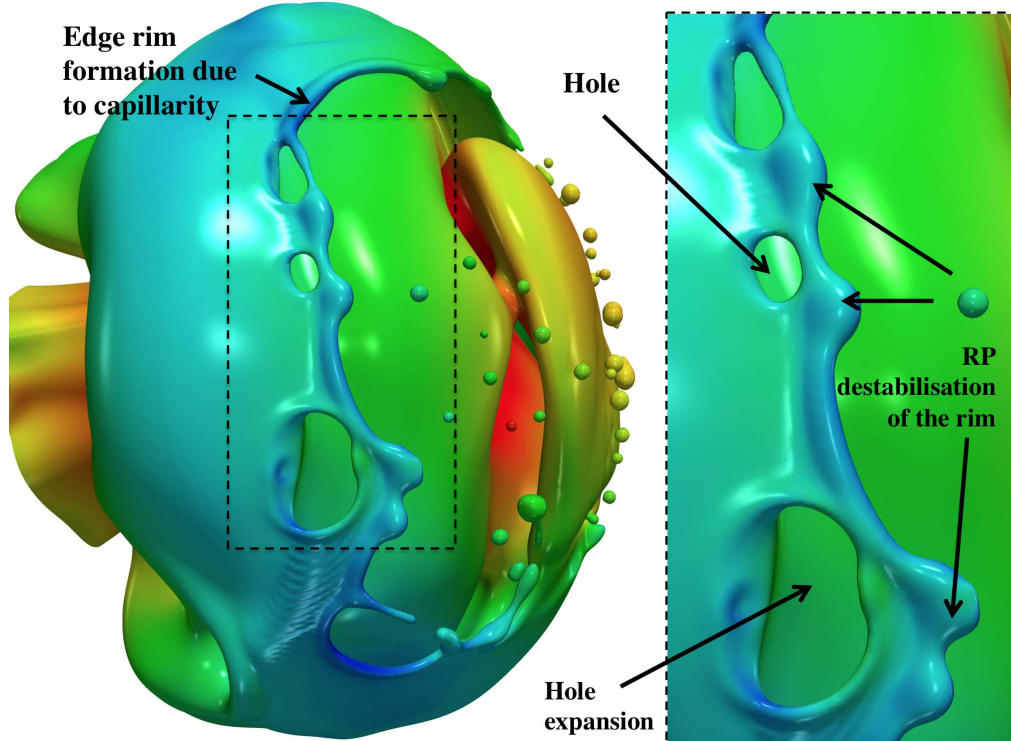


Fig. 4.4. Three dimensional representation of the rim-edge formation as a result of capillarity. The rim-edge undergoes a capillary destabilisation via RP yielding hole formation behind the rim-edge.

the distance between the droplet and the jet-core reduces in size, a higher liquid drainage takes places in the region between interfaces, and subsequently an increase of the velocity is observed, enhancing the adsorption of surfactant in this region. Eventually, the droplet-interface coalescence takes place, giving the creation of a hole, which leaves an open and unstable cavity, which collapses following the ‘bursting-bubble mechanism’ (see figure 4.3).

The mechanisms for droplet formation, explained in chapter 3, as a result of the formation and expansion of holes can be extrapolated for the surfactant-laden case. In the lobes, we observe their inertial-induced thinning via alignment of hairpin vortices. When the interfacial distance in a film sheet vanishes over time, the formation of a hole is observed as the film thinning dynamics enter in an asymptotic behaviour. The radial expansion of multiple holes lead to the formation of ligaments which breakup as a result of capillary instabilities. Figure 4.4 shows the formation of a hole behind the destabilised-rim sheet as a result of the capillary retraction resulting in the variation of the film thickness. Additionally, we observe the destabilisation of the rim due to Rayleigh-Plateau instability (I again refer to Chapter 3)

Figure 4.5 considers the effect of surfactant on the resulting droplet size distribution. Figure 4.5a shows a three dimensional representation of the interface inside of the mushroom structure for both surfactant-free and surfactant-laden cases at the same non-dimensional time. For both cases, we observe the formation of droplets inside of the leading-edge; however, by a qualitative inspection of the droplet size and number, it is observed a higher number of smaller droplets for the surfactant-free case. The probability density function for the droplet size distribution for both sets of data (i.e., surfactant free and surfactant-laden cases) is presented in figure 4.5b. The larger droplet size distribution for the surfactant-laden case is an unexpected behavior, as it was hypothesised that the addition of surfactants would lower the surface tension value, and subsequently, capillary forces would enhance the interfacial breakup to form smaller droplets. However, the generation of Marangoni stresses on the plane of the interface brought via surface tension gradients on the surface seams to inhibit the capillary singularity of threads, or any other kind of interfacial singularity phenomena (e.g., partial coalescence). **To find an answer to this hypothesis, chapters 5-7 focus on the study of the effect of surfactants in recoiling of liquid threads, bubbles undergoing bursting, and drops coalescing partially or completely with deformable interfaces.**

Finally, in figure 4.6, we show the influence of surfactants on the kinetic energy, defined as $E_k = \int_V (\rho \mathbf{u}/2)^2 dV$, the interfacial area, and the location of the maximum location of the interface in the axial and streamwise location. By observing the kinetic energy plot, surfactant acts to decrease the overall value of kinetic energy, as a result of the hypothesised interface rigidification, and subsequent reduction of the interfacial velocity. Following the inspection of the interfacial area, it is observed that surfactants reduce the overall available area. This finding implies the formation of larger droplets,

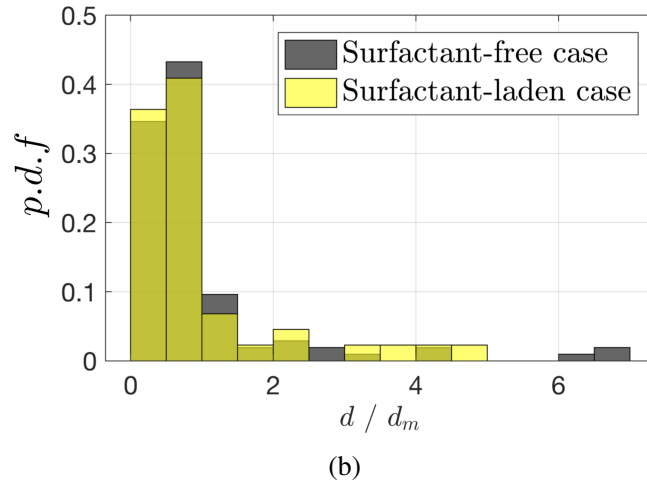
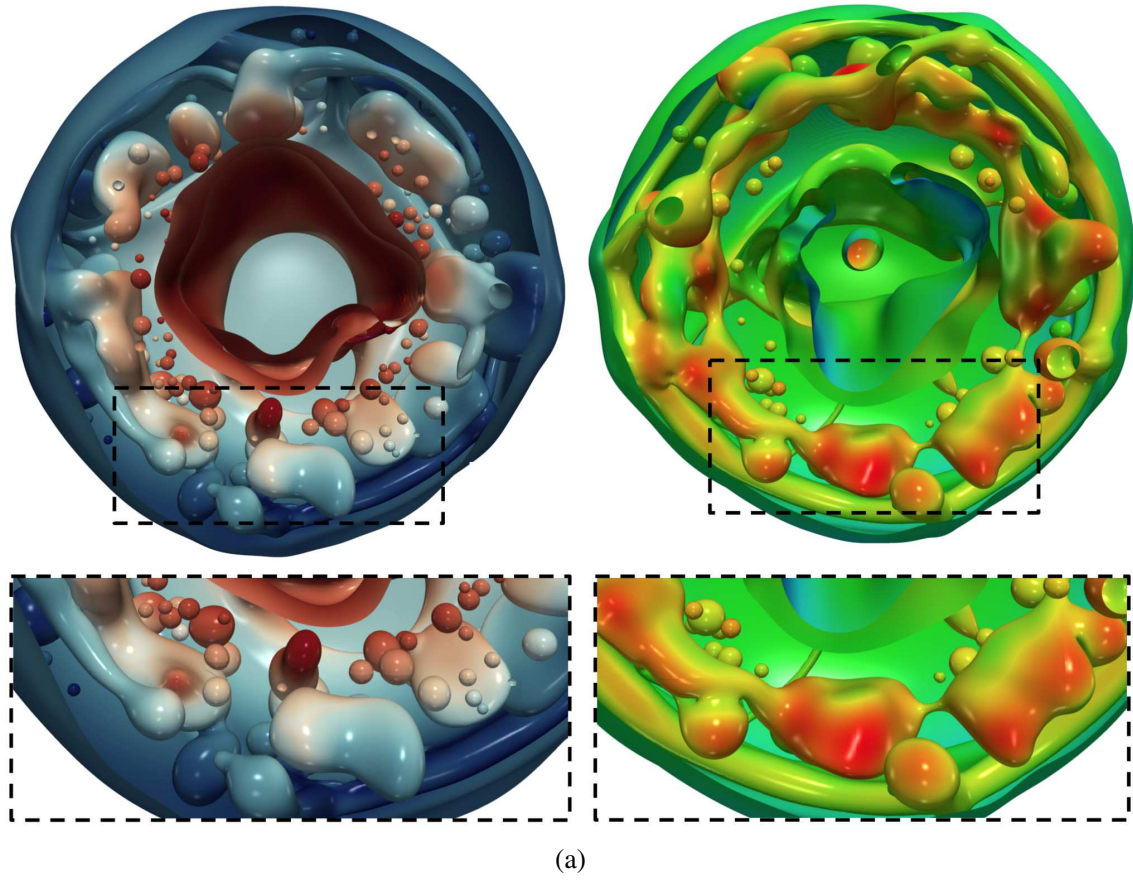


Fig. 4.5. (a) Three dimensional representation of the interface for the surfactant free and laden-base cases inside of the mushroom structure. For both figures, the dimensionless time is identical $t = 12.22$. (b) Probability density function for the droplet size distribution. The distributions are normalised by the calculated mean diameter for each time.

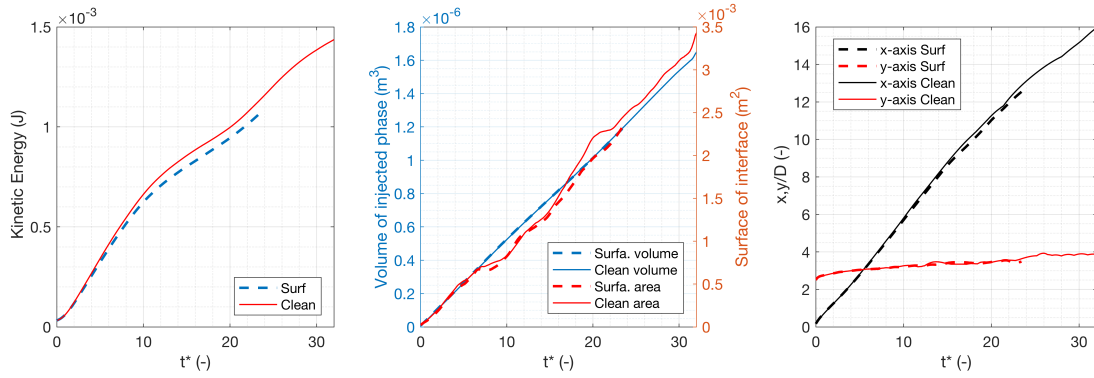


Fig. 4.6. The panels represent the temporal variation of the kinetic energy (left panel), relative variation of the liquid volume and interface area (middle panel) and the maximum location of the interface in the axial and streamwise location (right panel), for the surfactant-free and the surfactant-laden base cases.

and consequently the reduction of the effective interfacial area. Unsurprisingly, figure 4.6 shows that surfactants barely affects the maximum axial and streamwise interfacial location as the flow in this regime is highly controlled by inertia.

4.4 Conclusions

Three-dimensional numerical simulations were carried out for turbulent jets entering a stagnant and more viscous silicon oil phase in the presence of surfactant. It has been shown that the presence of surfactants has a detrimental effect on the interfacial dynamics. Particular attention has been paid to the resulting mechanism which leads to droplet formation and the resulting droplet size distribution. Surprisingly, a higher droplet size distribution has been found for the surfactant-laden case; however, surfactant reduction should lead to a smaller droplets as a result of the reduction of the mean value of surface tension. Thus, I have hypothesised the following question: **Can Marangoni stresses acting on the plane of the interface prevent interfacial singularities yielding larger droplets?** The search of the answer to this question has triggered the following chapters:

- Chapter 5: Effect of surfactants in retracting ligaments.
- Chapter 6: Effect of surfactants in bursting bubbles.
- Chapter 7: Effect of surfactants in the coalescence of a drop/flat-interface.

Chapter 5

Ligament retraction

Related publication: Dynamics of retracting surfactant-laden ligaments at intermediate Ohnesorge number. *C. R. Constante-Amores*, L. Kahouadji, A. Batchvarov, S. Shin, J. Chergui, D. Juric and O. K. Matar. *Phys. Rev. Fluids* **5**, 084007 (2020)

Summary

The dynamics of ligaments retracting under the action of surface tension occurs in a multitude of natural and industrial applications; these include inkjet printing and atomisation. Direct, fully three-dimensional, two-phase numerical simulations of the retracting process over a range of system parameters that account for surfactant solubility, sorption kinetics, and Marangoni stresses are performed. The results indicate that the presence of surfactant inhibits the ‘end-pinching’ mechanism and promotes neck re-opening through Marangoni-flow; this is induced by the formation of surfactant concentration gradients that drive flow-reversal towards the neck. The vortical structures associated with this flow are also analysed in detail. We also show that these Marangoni stresses lead to interfacial rigidification, observed through a reduction of the retraction velocity and ligament kinetic energy.

5.1 Introduction

Interfacial breakup is often accompanied by the formation of satellite droplets (Plateau, 1873; Rayleigh, 1879; Eggers and Villermaux, 2008). Following breakup, the interface assumes the shape of liquid threads or ligaments which undergo further capillary breakup if their lengths exceed their perimeters

(Plateau, 1873; Rayleigh, 1879); if not, then they retract into a single spherical drop or a multitude of droplets. Both the breakup and retraction processes are driven by surface tension in order to minimise interfacial energy. These phenomena are observed in multiple applications, such as, atomisation or spray formation (Marmottant and Villermaux, 2004; Eggers and Villermaux, 2008), ink-jet printing or micro-encapsulation (Eggers, 1997; Basaran, 2002; Hoath et al., 2013).

In the absence of surfactant, the retracting dynamics of a Newtonian liquid thread surrounded by a passive ambient gas has been studied by Schulkes (1996), and Notz and Basaran (2004) using a Galerkin finite element approach under a two-dimensional axisymmetric assumption in the azimuthal direction, and by also assuming another symmetry through the ligament mid-plane in the longitudinal direction; the flow is parameterised by the ligament aspect ratio, $L_o = L/R$, and Ohnesorge number, $Oh = \mu / \sqrt{\rho \sigma R}$, where L and R are the initial half length and radius of the ligament, while ρ , μ , and σ are the density, dynamic viscosity, and surface tension, respectively.

Schulkes (1996) has simulated the ligament retraction towards a minimum radius of $r \sim 0.8R$, where r is the radial coordinate, while Notz and Basaran (2004) were able to reach $r \sim 10^{-4} \times R$. Notz and Basaran (2004) have also presented the temporal evolution of a retracting ligament of aspect ratio $L_o = 15$ for three different regimes depending on the magnitude of Oh : (i) low Oh values ($Oh \sim 10^{-3}$), where capillarity is more dominant than viscous forces, the outcome is the formation of two bulbous regions at both ends of the ligament that pinchoff eventually leading to the formation of a smaller, secondary ligament; (ii) intermediate Oh values ($Oh \sim 10^{-2}$), where there is a balance between viscous and capillary forces, a situation that culminates in the breakup of the ligament into three droplets; (iii) at higher Oh values ($Oh \sim 10^{-1}$), which reflects the dominance of viscous forces and for which the retraction is not accompanied by breakup but by the formation of a single spherical drop.

Notz and Basaran (2004) have also presented a regime map of the ligament evolution prior to its eventual breakup, varying both L_o and Oh . Castrejón-Pita et al. (2012) performed experiments on retracting ligaments beyond breakup, and, more recently, Anthony et al. (2019) extended the work of Notz and Basaran (2004), considering all possible ranges of fluid properties ($Oh = 10^{-3} - 10^0$) and aspect ratios ($L_o = 5 - 10^3$). Hoepffner and Paré (2013) have shown that a cylindrical ligament undergoes capillary-driven ‘end-pinching’ at low values of Ohnesorge number (below $Oh \sim 0.002$). As Oh increases, a viscous boundary layer is localised in the region of the neck, due to its high curvature, which may detach leading to the formation of a jet inside the thread, reopening the neck and, subsequently, inhibiting the end-pinching mechanism. This jet is the onset of formation of a vortex ring inside the bulbous ends of the ligament.

Wang et al. (2019) have performed both experimental and two-dimensional axisymmetric computations to determine the influence of capillary waves on the ligament stability at low viscosities (i.e.,

low Oh numbers). They have shown that the end-pinching mechanism always takes place for large L_o (i.e., $L_o > 14$ for $Oh < 0.03$). At intermediate L_o (i.e., $5 \leq L_o \leq 14$ for $Oh < 0.03$), the retraction time is too short for the neck to lead to an end-pinching mechanism, and the dynamics are induced by the interaction of the superficial capillary waves. This capillary wave interaction provides another mechanism to generate equal-sized droplets. Recently, Contò et al. (2019) have analysed the capillary retraction of Newtonian ligaments identifying three distinct regions in the system: the body of the ligament, the growing spherical bulbous end regions, and the intermediate region which connects the bulbous ends to the ligament body.

The studies summarised in the foregoing have shown that the ligament dynamics are characterised by a longitudinal retraction followed by one or possibly several breakup events (Eggers, 1993, 1997; Day et al., 1998; Lister and Stone, 1998; Castrejón-Pita et al., 2015) which lead to satellite droplet formation. The presence of surfactants, either as an additive or a contaminant, influences the interfacial dynamics via reduction of the mean surface tension, and the creation of Marangoni stresses. Craster et al. (2002) showed that insoluble surfactant retard thread pinchoff but do not alter the breakup scalings; this is because the surfactant is convected away from the thread neck by the capillary-driven flow.

McGough and Basaran (2006) observed the formation of microthreads, which connect drops during the thinning of surfactant-covered threads. This thinning towards the breakup singularity follows the scalings predicted by Eggers (1993). Kamat et al. (2018) performed both experiments and simulations of pendant droplets covered by insoluble surfactant and showed that Marangoni stresses are responsible for microthread formation. These stresses act near the pinch point giving rise to reduced rates of thread thinning. Kamat et al. (2018) further observed that as the thread thins, a stagnation point is formed leading to surfactant accumulation at this point resisted by Marangoni-induced flow.

Surfactant solubility provides additional complexity due to its influence on Marangoni-driven transport along the interface, which influences the stability and dynamics of a number of flows driven by capillary instabilities. Liao et al. (2004) observed experimentally that the addition of a soluble surfactant at high concentrations enhances the asymmetric behaviour of a liquid bridge. Jin et al. (2006) and Jin and Stebe (2007) studied the detachment of a viscous drop in the presence of soluble surfactant. They have shown that solubility alters the drop dynamics in terms of neck thinning. For slow adsorption-desorption kinetics, characterised by a large, suitably-defined Biot number, Bi , solubility does not influence the neck dynamics since surfactant behaves as an insoluble additive leading to the formation of primary and secondary necks, and the capillary breakup of the former. For faster adsorption-desorption kinetics (i.e. increasing Bi), the neck dynamics can transition through different regimes such as the existence of only one neck, the thinning of the secondary neck, or the inhibition of neck thinning. As the Biot number increases, the mean interfacial concentration approaches its

equilibrium value, as the rate of mass transfer between the bulk and the interface becomes comparable to, and eventually, exceeds the convection rates which give rise to the formation of Marangoni stresses. Craster et al. (2009) have studied the breakup of a viscous thread in the presence of soluble surfactant at concentrations that are potentially above the critical micelle concentration and have shown that Marangoni stresses cause the formation of large satellites. This prediction was observed experimentally by Kovalchuk et al. (2016, 2018) where the satellite drop size increased by up to three times when soluble surfactant was added; the diffusion from the bulk to the interface has also been studied experimentally by Roche *et al* (2009). Craster et al. (2009) have also shown that the scalings for the minimum neck radius and axial velocity as the breakup singularity is approached are the same as the ones derived by Eggers (1993) as surfactant is swept away from the thinning region.

In this chapter, direct numerical simulations of the Navier-Stokes equations coupled to transport equations for the interfacial and bulk surfactant species in order to analyse the effect of soluble surfactant on the dynamics of retracting ligaments. This study accounts for surfactant solubility, sorption kinetics, bulk and interfacial diffusion, and Marangoni stresses. The results of these simulations allow to elucidate the delicate interplay between the flow dynamics and the surfactant physico-chemical effects that underlies the mechanisms responsible for several phenomena of interest; these include ligament retraction with and without breakup, and, in the latter case, subsequent re-coalescence.

The rest of this chapter is organized as follows. Section 5.2 presents problem formulation, numerical configuration and mesh study. Section 5.3 presents a discussion of the results focusing on the effect of surfactant on the dynamics of the thread, a parametric study with respect to the governing surfactant parameters, and a detailed analysis of the vorticity. Finally, concluding remarks are provided in Section 5.5.

5.2 Problem formulation and numerical configuration

The numerical simulations are performed by solving the two phase Navier-Stokes equations in a three-dimensional Cartesian domain $\mathbf{x} = (x, y, z)$. Surfactant transport was resolved in both the liquid bulk and on the interface by convection-diffusion equations describing the transport of surfactant species in the bulk and on the interface, with concentrations C and Γ , respectively. The source term of the momentum related to the surface tension forces is treated by using a hybrid interface-tracking/level-set method presented by Shin et al. (2017). The surface force is decomposed into its normal component for the normal stress jump across the interface, and its tangential component, which is associated with the surface gradient of the surface tension due to the presence of surfactants (Shin et al., 2018). All variables are rendered non-dimensional. The dimensionless parameters appearing in the governing

equations are given by

$$Oh = \frac{\mu_l}{\sqrt{\rho_l \sigma_s R}}, \quad Bi = \frac{k_d R}{u_R}, \quad \beta_s = \frac{\Re T \Gamma_\infty}{\sigma_s}, \quad Pe_s = \frac{u_R R}{D_s}, \quad Pe_b = \frac{u_R R}{D_b}, \quad (5.1)$$

where Oh denotes the Ohnesorge number and measures the relative importance of viscous to surface tension forces, Bi is the Biot number representing the ratio of characteristic desorptive to convective time-scales, β_s is the elasticity number, which measures the sensitivity of the surface tension to changes in surfactant interfacial concentration; Pe_s and Pe_b are the interfacial and bulk Peclet numbers and compare the ratio of convective to diffusive time-scales in the plane of the interface and the bulk, respectively. Finally, k_d refers to the surfactant desorption coefficient, $\Re$ the ideal gas constant, T the temperature, D_s and D_b the surfactant interfacial and bulk diffusivities, respectively.

At equilibrium, Eq. (1.25) reduces to the Langmuir adsorption isotherm

$$\chi = \frac{\Gamma_{eq}}{\Gamma_\infty} = \frac{k}{1+k}, \quad k = \frac{k_a C_\infty}{k_d}, \quad (5.2)$$

where χ stands for the fraction of surface covered by adsorbed surfactant, k is the adsorption parameter, which represents the ratio of adsorption to desorption time scales. Here, k_a refers to the adsorption coefficient. The equation of state describing the variation of the surface tension as a function of the local interfacial surfactant concentration is given by the Langmuir relation shown in Eq. (1.26). Marangoni stress, τ , arises due to the surface tension gradients and they can be expressed in terms of gradients in Γ as follows:

$$\tilde{\tau} \equiv \nabla_s \tilde{\sigma} \cdot \mathbf{t} = -\frac{\beta_s}{1-\tilde{\Gamma}} (\mathbf{t} \cdot \nabla_s \tilde{\Gamma}). \quad (5.3)$$

For simplicity, the tildes are dropped henceforth.

The viscosity and density ratios, ρ_g/ρ_l and μ_g/μ_l , are set to 1.2×10^{-3} and 1.8×10^{-2} , respectively, corresponding to values for a water ligament in air. The time scale associated with the Marangoni flow is determined from a balance between Marangoni stresses and viscous retardation, $\tau \sim \Delta\sigma/R \sim \mu_l/t_M$, hence $t_M = \mu_l R/\Delta\sigma$, and is of order 10^{-3} s. However, the capillary breakup time is of order 10^{-2} s, and the time scale associated with the retraction of the ligament is also of order 10^{-2} s. For the soluble cases, we consider the properties of n-alcohols (such as n-propanol, n-butanol and n-pentanol) or dicarboxylic acid type (such as adipic and pimelic acid) as surfactants, which are characterised by desorptive time scales of 10^{-2} s (Bleys and Joos, 1985; Joos, P. and Serrien, G., 1989; Joos, P. et al., 1982). Therefore, for both soluble and insoluble surfactant configurations, Marangoni stress is expected to play a major role in the ligament retraction dynamics.

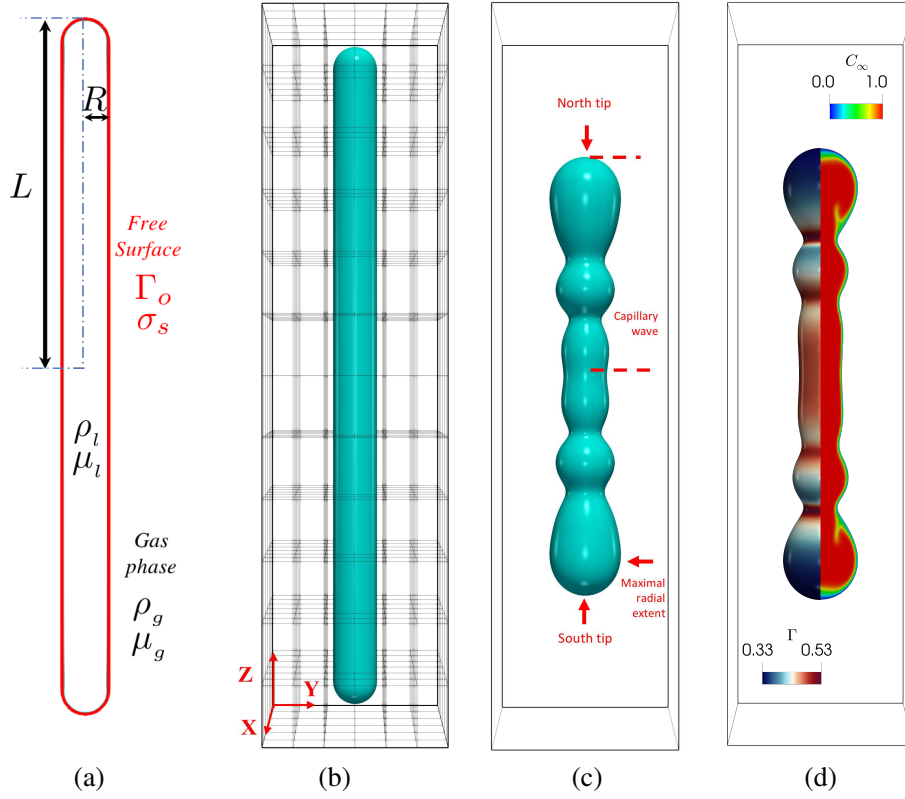


Fig. 5.1. Schematic representation of the initial shape of the ligament, (a), highlighting the fluid quantities and non-dimensional parameters of the system, (b), initial shape of the ligament with the computational domain of size $8R \times 8R \times 32R$ in a three-dimensional Cartesian domain $\mathbf{x} = (x, y, z)$ and divided into $6 \times 6 \times 12$ sub-domains; the Cartesian resolution is set to $32 \times 32 \times 64$ per sub-domain, and the global resolution is $192 \times 192 \times 768$. Typical interfacial shape for a surfactant-free case at $t = 7$ for $L_o = 15$ and $Oh = 10^{-2}$, (c), with definitions of particular locations and features whose dynamics will be discussed in the present work. (d) Typical interfacial shape for a surfactant-laden case at $t = 7$ with $L_o = 15$, $Oh = 10^{-2}$, $Bi = 1$, $Pe_s = 10$, and $\chi = 0.9$ with colour bars indicating the magnitude of the surfactant interfacial and bulk concentrations in the left and right halves of the ligament, respectively.

5.2.1 Numerical configuration

As introduced in the beginning of this section, the liquid ligament is initialised as a cylindrical thread of length $2L$ with an aspect ratio $L_o = L/R = 15$ and hemispherical caps at its two ends, as shown in figure 5.1-(a). The size of the three-dimensional computation domain is $8R \times 8R \times 32R$ where the z -coordinate is aligned with the height of the ligament while x and y are along its width. Hence a radial component is defined as $r = \sqrt{(x - x_o)^2 + (y - y_o)^2}$, where x_o and y_o are the abscissa and ordinate ligament position, respectively. The simulation is initialised with fluids at rest in the absence of gravity. A no-slip boundary condition is imposed on the fluid velocity at the walls of the computational domain and a Neumann condition is imposed for the pressure ($\partial p / \partial \mathbf{n} = 0$), where $\mathbf{n}$ here refers to the normal vector at the boundaries of the computational domain. At the free surface, we set

$$\mathbf{n} \cdot \nabla \tilde{C} = -Pe_b Bi (k \tilde{C}_s (1 - \tilde{\Gamma}) - \tilde{\Gamma}), \quad (5.4)$$

as a condition on $\tilde{C}$. The entire domain is discretised into an Eulerian fixed regular mesh. The surfactant-free simulation was carried out on three different meshes, referred to here as M1, M2, and M3, to ensure mesh-independent results. The results presented in the study correspond to the M2 mesh, unless stated otherwise. The code was benchmarked against the ligament profiles of Notz and Basaran (2004) (see figure 5.3) on the dynamics of the surfactant-free simulation and the pinchoff time. The validation of the surfactant solver has been presented previously by Shin et al. (2018), where the authors ensured mass conservation of the surfactant. More information of the validation, mesh refinement studies, and numerical method can be found in subsection 5.2.2.

5.2.2 Mesh study

Filament profiles (characterised by $L_o = 15$ and $Oh = 10^{-2}$) are compared against Notz and Basaran (2004), from which data was extracted by image analysis. They used a Galerkin finite element approach under a two-dimensional axisymmetric assumption in the azimuthal direction. As shown in figure 5.3, the ligament profiles show a good qualitative agreement with the predicted by the numerical method. The second check is the predicted time for the capillary breakup for the surfactant-free case between the two methods (Notz and Basaran's pinchoff time is 11.114 and the pinchoff time for different meshes are shown in Table 5.1), which shows a good quantitative agreement between the two methods. These two checks allow it to proceed with caution.

The next question is to ensure that our numerical results are mesh-independent. To this end, the dynamics of the retracting ligament for the surfactant free (i.e., $L_o = 15$ and $Oh = 10^{-2}$) and surfactant laden base cases (i.e., $L_o = 15$, $Oh = 10^{-2}$, $\beta_s = 0.3$ and $Pe_s = 10$) are tested for different mesh

resolutions (see figure 5.2) in terms of the temporal evolution of the tips location, E_k and the relative variation of the liquid volume. The main characteristics of the meshes are summarised in Table 5.1 including the number of elements, and the predicted pinchoff time for the surfactant-free case. As for the time $t \approx 12 - 12.5$, the resulting three droplets coalesce with each other to form a single droplet (shown in figure 5.2-a). The volume of the liquid is conserved with a loss of less than 0.2% during the topological changes (displayed in figure 5.2e,f). Because the curves for the kinetic energy and the location of the tips overlap for M2 and M3 meshes, we conclude that M2 is sufficiently refined to ensure mesh-independent results while providing a good compromise with the computational cost of the simulation. The results presented in this chapter correspond to the M2 mesh. Additionally, the accuracy of the surfactant mass conservation in all the simulations has been carefully checked. The numerical framework conserves surfactant moles with a relative error of 0.062% for the surfactant-laden base case. Moreover, the code conserves surfactant moles with a relative error of 0.08% for a soluble case (e.g., $L_o = 15$, $Oh = 10^{-2}$, $\beta_s = 0.3$, $Pe_s = 10$, $Pe_b = 10$, $\chi = 0.9$ and $Bi = 0.1$).

Table 5.1. Retracting ligament mesh study for the surfactant free case ($L_o = 15$ and $Oh = 10^{-2}$).

Run	Global mesh size (number of cells)	Number of parallel process threads	Pinchoff time (s)
M1	$96 \times 96 \times 384$	54	11.1151
M2	$192 \times 192 \times 768$	432	11.1158
M3	$384 \times 384 \times 1536$	3456	11.1167

5.3 Results

In this section, I present a discussion of our results, beginning by comparing our predictions with previous work on retracting surfactant-free ligaments. This serves the purpose of validating the numerical method and provides a benchmark against which to highlight the effects associated with the presence of surfactant.

5.3.1 Surfactant-free ligament retraction and capillary-breakup

I have studied the retraction of a surfactant-free ligament with $L_o = 15$ and $Oh = 10^{-2}$ previously examined by Schulkes (1996) and Notz and Basaran (2004) paying particular attention to interfacial breakup and post-pinchoff dynamics. In order to inspire confidence in the reliability of the numerical method used to carry out the computations, figure 5.3 shows a comparison between our numerical predictions and those from Notz and Basaran (2004) which reveals a good agreement. Figure 5.4 depicts time-space plots of the interface, pressure, and the axial velocity; for the latter two, spatial variations are shown with respect to the ligament centreline. The initially motionless, cylindrical

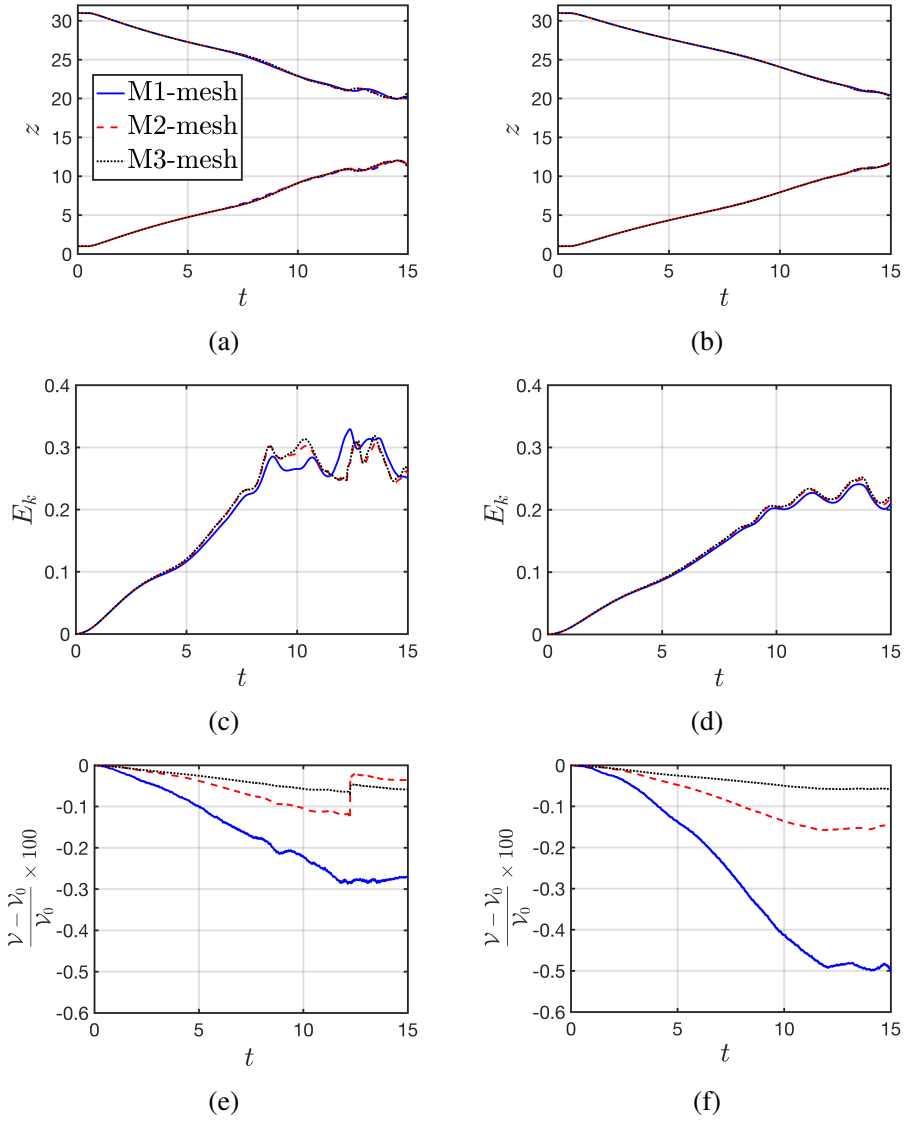


Fig. 5.2. Mesh study for ‘surfactant-free’ (panels (a),(c), and (e) on the left) when $L_o = 15$ and $Oh = 10^{-2}$, and ‘surfactant-laden base case’ (panels (b), (d) and (f) on the right) when $L_o = 15$, $Oh = 10^{-2}$, $\beta_s = 0.3$ and $Pe_s = 10$. The panels highlight the temporal evolution of the north and south tips location (a-b), the kinetic energy E_k (c-d), and the relative variation of the liquid volume (e-f).

ligament undergoes retraction due to the pressure gradient between the two bulbous ends and the rest of its body, which drives flow from these regions towards its centre in the form of a capillary wave; this dominates the early stages of the dynamics.

The retraction velocity results from a force balance between capillary and inertial forces, the latter being proportional to the rate of change of momentum of the bulbous ends. Extending the Taylor-Culick expression for the retraction of a two-dimensional axisymmetric planar liquid sheet to a cylindrical thread, $V = (2\sigma_s/\rho_l\pi R)^{1/2}$, which gives a value for the vertical velocity of retraction 0.079 m/s. This is in good agreement with the retraction velocity predicted by our simulations, ~ 0.0789 m/s and

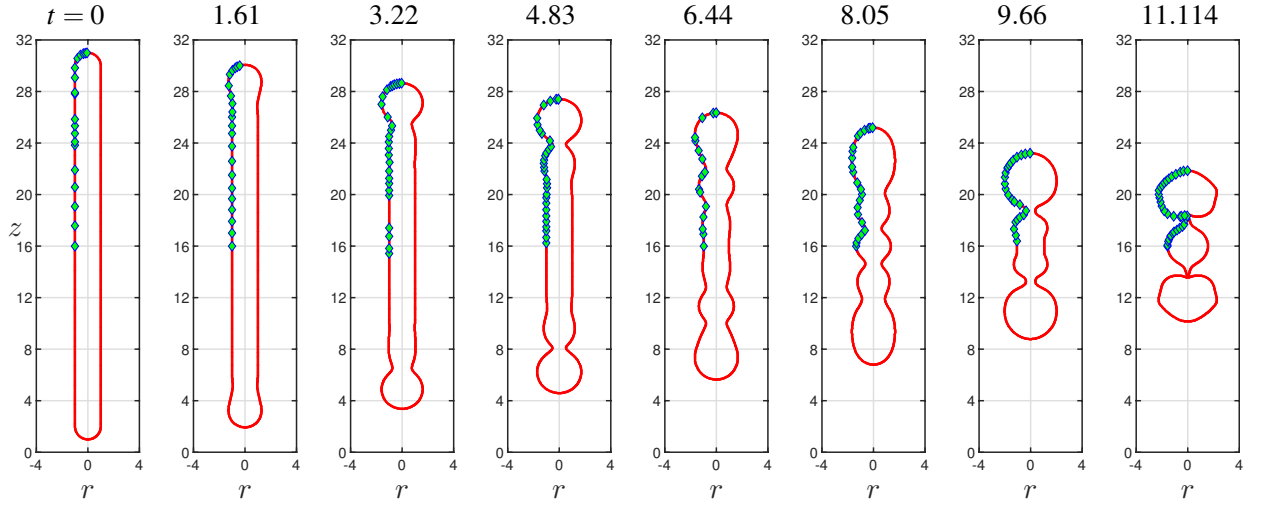


Fig. 5.3. Spatio-temporal evolution of a retracting ligament for $L_o = 15$ and $Oh = 10^{-2}$. The solid lines correspond to the results of the present study and the diamonds are collected from Notz and Basaran (2004).

provides further validation of the accuracy and reliability of our numerical method.

The retraction motion and associated capillary waves form neck regions near the two ends of the ligament connecting the bulbous regions with the rest of the ligament. The pressure under these neck regions is large and drives flow away from them on time scales shorter than those related to retraction, dominating the intermediate stage of the dynamics, and promoting further necking and an even larger pressure gradient that eventually leads to a double pinchoff event for the set of parameters used to generate these results; the profiles for the interface, pressure, and axial velocity associated with this event are highlighted in red in figures 5.4d,f.

Figure 5.4a, which highlights the temporal evolution of the north and south tips of the bulbous ligament ends during retraction, also shows that the pinchoff, which takes places at $t \sim 11.11$, is followed by the formation of three droplets (see figure 5.4a for $t = 11.4$). These droplets are sufficiently close that a double coalescence takes place simultaneously at $t = 12.1$ generating capillary waves that travel up and down the ligament (see figure 5.4a for $t = 12.6, 14$, and 15.2). These waves decelerate giving way to decaying oscillations between a spherical and an ellipsoidal ligament shape that are the main features of the late-time dynamics (see figure 5.4a for $t = 28$ and 37).

It is also instructive to perform an analysis of the temporal variation of the system energy. The total energy E_T must be constant over time and its constituents are the surface energy, $E_s = S\sigma_s$, where S is the superficial area of the ligament, the kinetic energy, $E_k = \int_V (\rho \mathbf{u}^2)/2 dv$, and the energy dissipated, $E_D = -\int_V (\tilde{\tau} : \nabla \mathbf{u}) dv$, where $\tilde{\tau}$ refers to a viscous stress tensor. As highlighted in figure 5.4b, all energies are normalised by the surface energy of a motionless spherical droplet with a volume similar

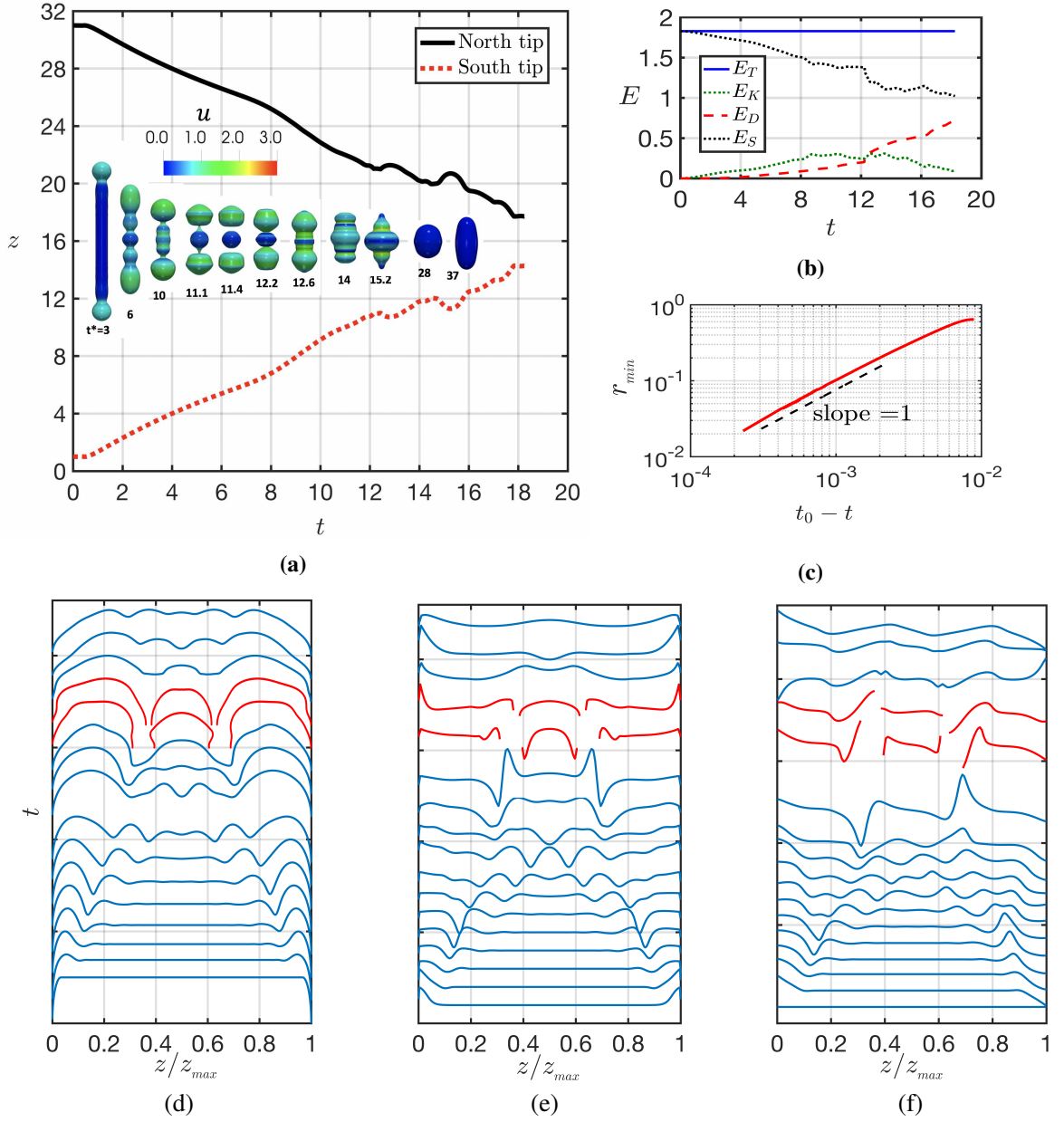


Fig. 5.4. Surfactant-free ligament retraction for $L_o = 15$ and $Oh = 10^{-2}$: (a) Temporal evolution of the location of both ligament tips, and a three-dimensional representation of the interface for the dimensionless times shown in the panel in which the colour bar depicts the velocity magnitude; (b) temporal evolution of the total, kinetic and surface energies, E_T , E_K and E_S , respectively, and the energy dissipated, E_D ; (c) scaling of the minimum radius with respect to the pinchoff time $t_o = 11.115$, which agrees with that predicted by inertio-viscous scaling theory of Eggers (1993); (d)-(f) time-space plots of the interface, p , and u_z , respectively, with snapshots shown between $t = 0 - 13.5$, with time intervals of 1 between $t = 0 - 11$ and 0.5 between $t = 11 - 13.5$; here, the red profiles are associated with $t = 11.5$ and $t = 12$, the instances at which pinchoff occurs.

to that of the ligament of aspect ratio $L_o = 15$. Initially, the total energy is solely represented by the surface energy E_s . When the ligament retracts, part of the surface energy is transferred into kinetic energy. During the coalescence of the three droplets (at $t \sim 12.1$) the total area of the system changes significantly and a fraction of the surface energy is dissipated (see figure 5.4b). At longer times, $E_s \rightarrow 1$ and $E_k \rightarrow 0$, as the ligament tends towards a steady, spherical shape.

5.3.2 Surfactant-laden ligament retraction: escape from capillary-breakup

In this section, the effect of insoluble surfactant on the dynamics of a retracting ligament with $L_o = 15$, $Oh = 10^{-2}$, $Pe_s = 10$, $\beta_s = 0.3$, and $\Gamma_o = \Gamma_\infty/2$ is presented. Figure 5.5 depicts the spatio-temporal evolution of the interface and Γ together with the pressure and axial velocity along the ligament centreline. Similar to the surfactant-free case, retraction is accompanied by the formation of capillary waves that dominate the dynamics leading to the collapse of the initially-cylindrical ligament towards a spherical one. The surfactant concentration Γ , which is coupled to the interfacial dynamics through the dependence of σ on Γ , is redistributed along the interface, and achieves a maximal value around $t \sim 15$ since the ligament area decreases as it approaches a spherical shape. As shown clearly in figure 5.5a,b, the presence of surfactant retards ligament retraction as evidenced by the slower temporal evolution of the ligament tips and lower kinetic energy in comparison to the surfactant-free case; the retraction speed is ~ 0.070 m/s as compared to ~ 0.0789 m/s in the ‘clean’ case. This is due to the surfactant-induced interfacial rigidification brought about by the Marangoni stresses, which, in turn, are caused by gradients in Γ .

In order to elucidate the coupling between interface and surfactant concentration, it is considered the interface, Γ , p , and u_z , at $t = 10$ shown in red dashed lines in panels (c)-(f) of figure 5.5. The retraction capillary waves are characterised by regions of radially-diverging and converging motion and associated higher and lower interfacial areas and therefore reduced (i.e. increased) and increased (i.e. reduced) Γ (σ) locally, respectively. These concentration gradients lead to Marangoni stresses that drive flow from the higher-tension radially-diverging to the lower-tension converging regions, which act to retard the interfacial motion. To further illustrate the retarding effect of the Marangoni stresses, three distinct regions are also highlighted, as shown in figure 5.6a. In Region ‘A’, the interfacial flow diverges away from point ‘1’, at the ligament tip, driving surfactant away from this location leading to the lowest Γ value along the interface. There is an overall increase in Γ from the tip towards the centre reaching a maximal value at location ‘3’ where the interface exhibits a local minimum. The Γ profile then undergoes oscillations in response to the wavy shape of the interface, with a local minimum and maximum in Γ at locations ‘4’ and ‘5’ that coincide with a local interfacial maximum and minimum, respectively. It is clear from figure 5.6a that $\tau < 0$ in Region ‘A’ suggesting that the direction of

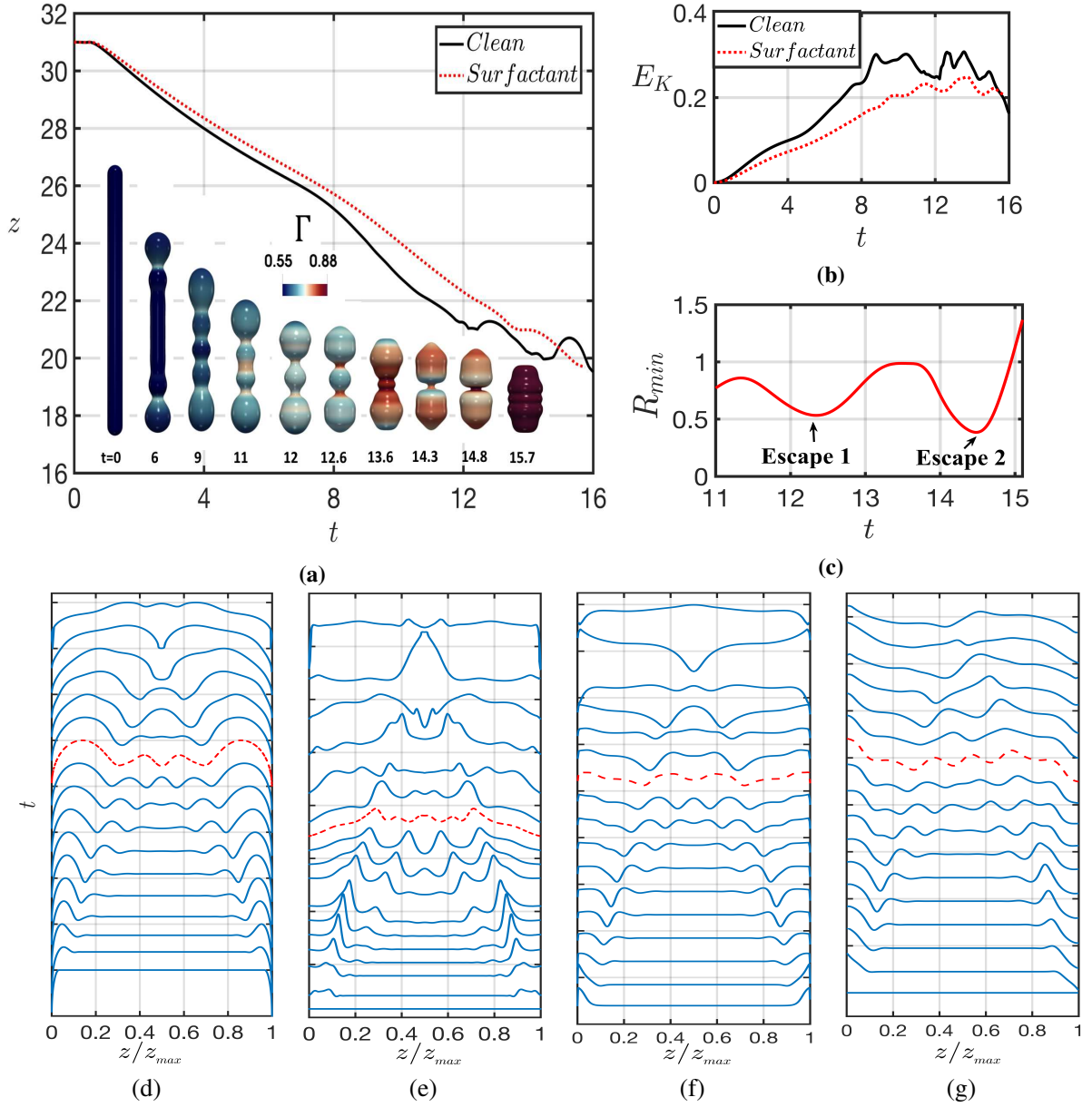


Fig. 5.5. Ligament retraction with an insoluble surfactant for $L_o = 15$, $Oh = 10^{-2}$, $Pe_s = 10$, $\beta_s = 0.3$ and $\Gamma_o = \Gamma_\infty/2$: (a) temporal evolution of the north tip location for the surfactant-free and surfactant-laden cases, and a three-dimensional representation of the interface for the dimensionless times shown in the panel in which the colour bar depicts the magnitude of the surfactant interfacial concentration, Γ ; (b) temporal evolution of the Kinetic energy E_K for the surfactant-free and surfactant-laden cases; (c) temporal evolution of the neck radius highlighting the two escapes of pinchoff; (d)-(g) time-space plots of the interface, Γ , p , u_z with snapshots shown between $t = 0 - 16$ at equal time intervals; here, the red profiles are associated with $t = 10$.

the Marangoni flow is towards the ligament tip, which acts to retard the capillary-driven flow from the tip towards the centre; this retarding effect in Region 'A' manifests itself through a decrease in the tangential velocity along the interface, u_t , as shown in figure 5.6b. In Region 'B', $\tau > 0$, thus

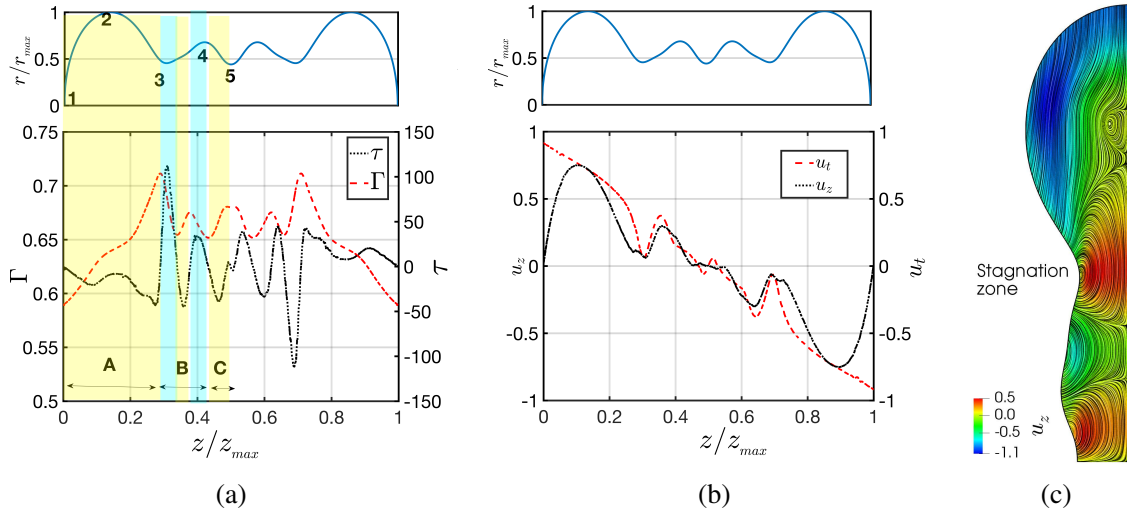


Fig. 5.6. Spatial variation of the interfacial shape, Γ , and τ , (a), the tangential interfacial velocity, u_t , for the surfactant-free and surfactant-laden cases, (b), and the streamline structure within the retracting ligament, (c); the parameter values are the same as in figure 5.5 with $t = 10$.

Marangoni-driven flow is towards the ligament centre, which is counter to the capillary flow away from this necking region. As also indicated in figure 5.6b, u_t , which was negative in Region ‘B’ in the surfactant-free, becomes positive in the surfactant-laden case.

It is also evident that using similar mechanisms, the Marangoni-driven flow reduces substantially the magnitude of u_t in Region ‘C’. Figure 5.6c shows the structure of the streamlines, which characterise the flow within the ligament. It is clearly seen that the formation of several stagnation points occurs along the interface reflecting the competition between the capillary- and Marangoni-driven flows an example of which is provided by the stagnation point close to the neck region. The formation of the stagnation zone is similar to what Kamat et al. (2018) have described, reporting the deceleration of the fluid by the action of the Marangoni stress during the thinning of the fluid thread. This force competition reverses the flow direction, leading to the genesis of the stagnation zone.

In order to separate the effects of mean surface tension and Marangoni stresses induced by surface tension gradients, it is considered a case in which the surface tension value is reduced and given by Eq. (1.26) using the initial interfacial concentration, but where no Marangoni stresses are supported. Figure 5.7 shows that the reduction in surface tension leads to a delay in the ligament retraction but does not prevent breakup; very similar behaviour to the surfactant-free case is observed in terms of the formation of three droplets, which eventually coalesce, and temporal evolution of the kinetic energy which undergoes a slightly delayed rise due to the slower capillary-driven flow, as expected. These results demonstrate that the prevention of the breakup is due to the formation of Marangoni stresses rather than the reduction in surface tension.

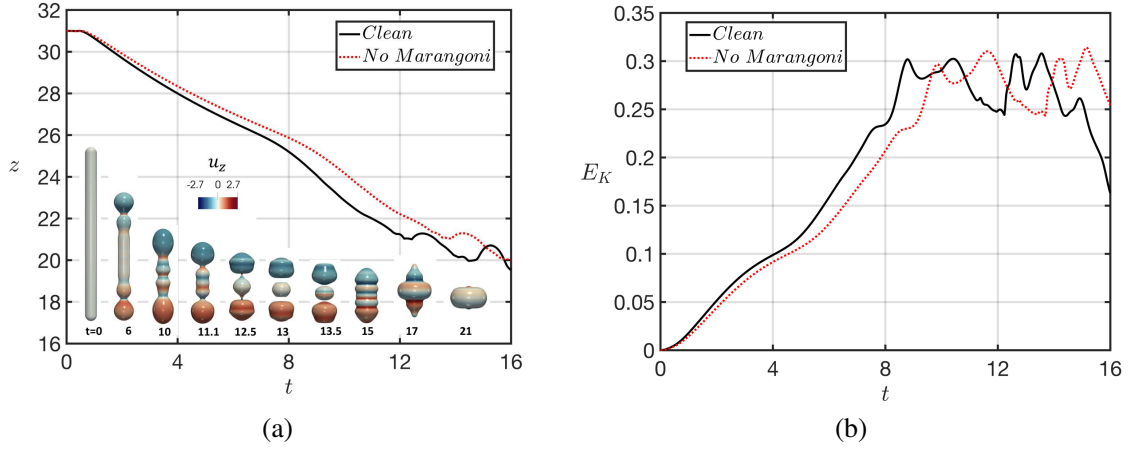


Fig. 5.7. Dynamics of a retracting, surfactant-covered ligament with isolating the Marangoni effect: (a) temporal evolution of the north tip location for the surfactant-free and surfactant-laden cases, and a three-dimensional representation of the interface for the dimensionless times shown in the panel in which the colour bar depicts the magnitude of the surfactant interfacial concentration, Γ ; (b) temporal evolution of the kinetic energy E_K for the surfactant-free and surfactant-laden cases.

In figure 5.5-(c), it is observed two escapes from breakup at $t \sim 12.3$ and $t \sim 14.3$. The interfacial shape prior to the first escape resembles that of the surfactant-free case before its breakup, shown in figure 5.4-(a). Hence, we will compare the flow fields of these two cases to determine the effect of surfactant on the onset of suppression of the capillary breakup for the surfactant-laden case.

The first row of figure 5.8-(a) shows the flow behaviour through the azimuthal vorticity, ω_θ , the instantaneous streamlines, and a three-dimensional representation of the velocity vector field for the surfactant-free case before pinchoff. Two stagnation points shown in figure 5.8a at $t = 10.6$ are also observed on either side of the neck, for which there is a change in direction of the flow rotation. By inspecting ω_θ , the highest vorticity production is located on the neck of the ligament promoted by the large interfacial curvature in that region. A thin vorticity boundary layer is detached from the neck of the ligament and diffuses into the bulk of the bulbous region (see figure 5.8a at $t = 11.0$). As the interfacial singularity is approached, the axial velocity component through the neck increases due to the associated rise in the capillary pressure, which pumps liquid rapidly away from the neck towards the bulbous region. The velocity achieves its maximum value at the moment of singularity as can be seen in figure 5.8a.

The second row of figure 5.8b shows the flow behaviour for the surfactant-laden case prior to the first escape from pinchoff. Inspection of ω_θ reveals the formation of a vortex ring also located at the neck, as shown at $t = 12.0$. However, the vorticity production is not as strong as in the surfactant-free case due to the rigidification of the interface brought about by the presence of Marangoni stresses. In comparison to the surfactant-free case, an additional stagnation point between the neck and the center of the ligament is observed as shown in figure 5.8b at $t = 12.0$. The presence of this stagnation

point has an associated vortex ring which interacts with the interface. As time increases, the mutual interaction of the two vortices leads to a vortex-pairing process, as shown at $t = 12.3$. This pairing up reverses the flow direction towards the neck ultimately leading to its reopening. The framed regions of the ligament show a magnified view of the flow direction and the flow reversal towards the neck. As the flow re-enters through the neck, the formation of a jet towards the bulbous region is observed, which gives rise to a vortex ring that eventually detaches towards the centre of the bulbous region, as shown at $t = 12.4$. This behaviour is similar to the phenomenon explained by Hoepffner and Paré (2013) (see their figure 6) where they showed that the formation of a vortex ring plays the primary role in the escape from breakup of viscous ligaments in the absence of surfactant.

Figure 5.9a shows the coupling between the interface, u_z , and p for the surfactant-free case as the neck evolves towards its capillary breakup. The fields have been limited to the framed region shown at the top of figure 5.9, due to the axisymmetric behaviour of the system. As the neck reduces its size, capillary pressure drives the flow, pumping fluid towards the neck, and, consequently, u_z increases over time.

Similarly, figure 5.9b shows the coupling between Γ , τ , u_z , p and the interface for the surfactant-laden base case. At $t = 11.8$, u_z has a qualitatively similar behaviour to that associated with the surfactant-free case though the competition between Marangoni stresses and the capillary pressure determines the direction of the flow. Inspection of τ at $t = 11.8$ reveals the presence of two Marangoni peaks of opposite sign is observed; it has been labelled the positive and negative peaks ‘P1’ and ‘P2’, respectively. It has also been labelled with red and blue arrows the direction associated with Marangoni-induced and capillary-driven flow.

In the region where P2 is located (see figure 5.9b at $t = 11.8$), Marangoni stresses and capillary pressure drive flow towards the neck and the centre of the ligament, respectively. Hence, both mechanisms act in opposing directions. The induced τ decelerates the flow caused by the capillary pressure (observe that u_z at $t = 11.8$ and $t = 12.0$ is equal to 0.18 and 0.05, respectively). At $t = 12.0$, an additional stagnation point appears, as already discussed in connection with figure 5.8-(b) and the deceleration continues until flow-reversal occurs at $t = 12.1$ with the merging of two stagnation points. Furthermore, the τ peak P1 also decelerates the flow which passes through the neck though the neck size reduces over time in this case. After this point, the flow behaviour follows that described previously in the discussion of figure 5.8b. It is also noteworthy that a comparison of the pressure p for the clean and surfactant-laden cases reveals that a reduction of the capillary pressure is observed in the latter case due to the reduction in surface tension.

Finally, the flow field associated with the second reopening of the neck, $t \sim 14.5$, depicted in figure 5.5c is examined. As shown at $t = 13.8$ in figure 5.10, a large counter-clockwise rotating vortex is

located at the neck, which drives flow from the neck towards the centre of the bulbous region as shown through the representation of the velocity vector fields. At $t = 13.8$, the displacement of the vortical ring from the neck towards the bulk is observed. This vortex moves flow from the neck to the bulk triggering the reopening of the neck. Comparing the neck size at $t \geq 14.8$, the neck does not stretch further and resists capillary breakup.

Figure 5.10 shows simultaneously a snapshot of the interface, Γ , and u_z at $t = 13.8$ in which two stagnation points are observed; the highest value of Γ is located close to the neck that links the neck with the bulbous region while its lowest value is at the centre of the ligament. Subsequently, Marangoni stresses induce flow towards the second stagnation point (see the strong magnitude peak of τ ; a red arrow has been added to highlight the induced flow due to the concentration gradients). In this region, the flow induced by τ competes with that driven by the capillary pressure in the opposite direction (shown with the blue arrow). As time evolves, Γ is convected towards the centre of the ligament which becomes a point of convergence and τ acts to oppose the surfactant accumulation (see $t = 14.4$ and $t = 14.5$); τ decelerates the flow induced by the capillary pressure and triggers flow-reversal, which is highlighted by the merging of the two stagnation points at $t = 14.5$. The flow reversal is due to the decrease in magnitude of the capillary pressure because of the surfactant-induced local reduction in surface tension; consequently, the capillary-driven flow is not strong enough to overcome that due to Marangoni stresses. With the suppression of one of the stagnation points, the vortex ring is displaced towards the bulk of the bulbous region.

5.3.3 Parametric study

Here, the fate of the ligament on system parameters such as the dimensionless elasticity parameter, β_s , the surface Peclet number, Pe_s , the Biot number, Bi , and the adsorption parameter, χ is investigated. Unless stated otherwise, the parameters remain fixed to their ‘base’ values: $Lo = 15$, $Oh = 10^{-2}$, $\beta_s = 0.3$, and $Pe_s = 10$.

By examining the effect of parameter β_s , which characterises the relative significance of Marangoni stresses. As highlighted above, the redistribution of surfactant along the interface gives rise to concentration gradients and Marangoni stresses that act to retard retraction and prevent ligament pinchoff. Further evidence for this is provided in figure 5.11a,b, which show the temporal evolution of the ligament tip location, and the kinetic energy, respectively, for $\beta_s = 0.1$ and 0.5 . Figure 5.11 show a three-dimensional representation of the interface for these β_s values. With increasing β_s , the Marangoni stresses are strengthened leading to a larger reduction in the retraction velocity and highlighting their retarding effect on the dynamics. As can also be seen clearly from figure 5.11a,b, for sufficiently large β_s values, Marangoni stresses dominate the flow preventing ligament breakup. In panels (c) and (e),

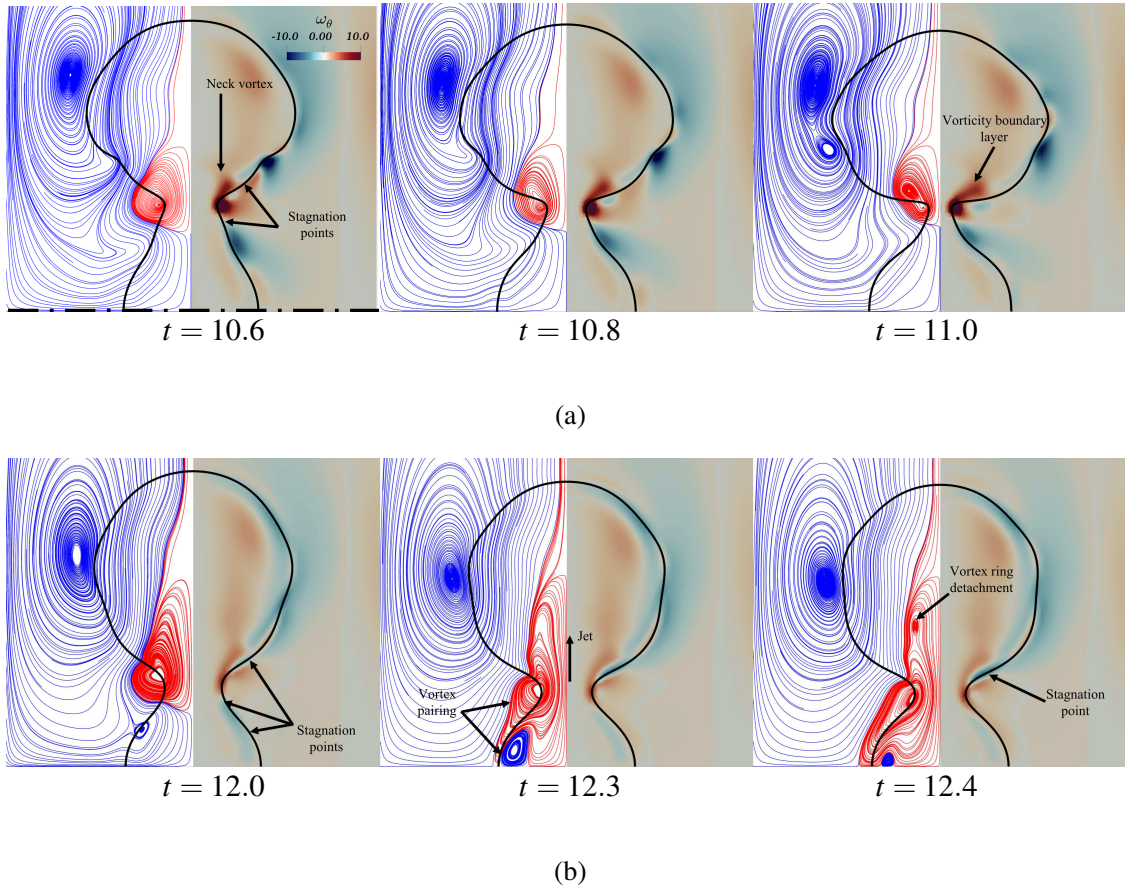


Fig. 5.8. Illustration of the surfactant-mediated mechanism underlying the first escape from pinchoff in figure 5.5c depicting a three-dimensional representation of the velocity vector field, together with ω_θ and streamlines for the surfactant-free case at $t = 10.6$, 10.8 , and 11 , (a), and the surfactant laden base case, (b) at $t = 12.0$, 12.3 , and 12.4 , with the same parameters as in figure 5.5. The framed regions of the ligament show a magnified view of the flow direction at every snapshot.

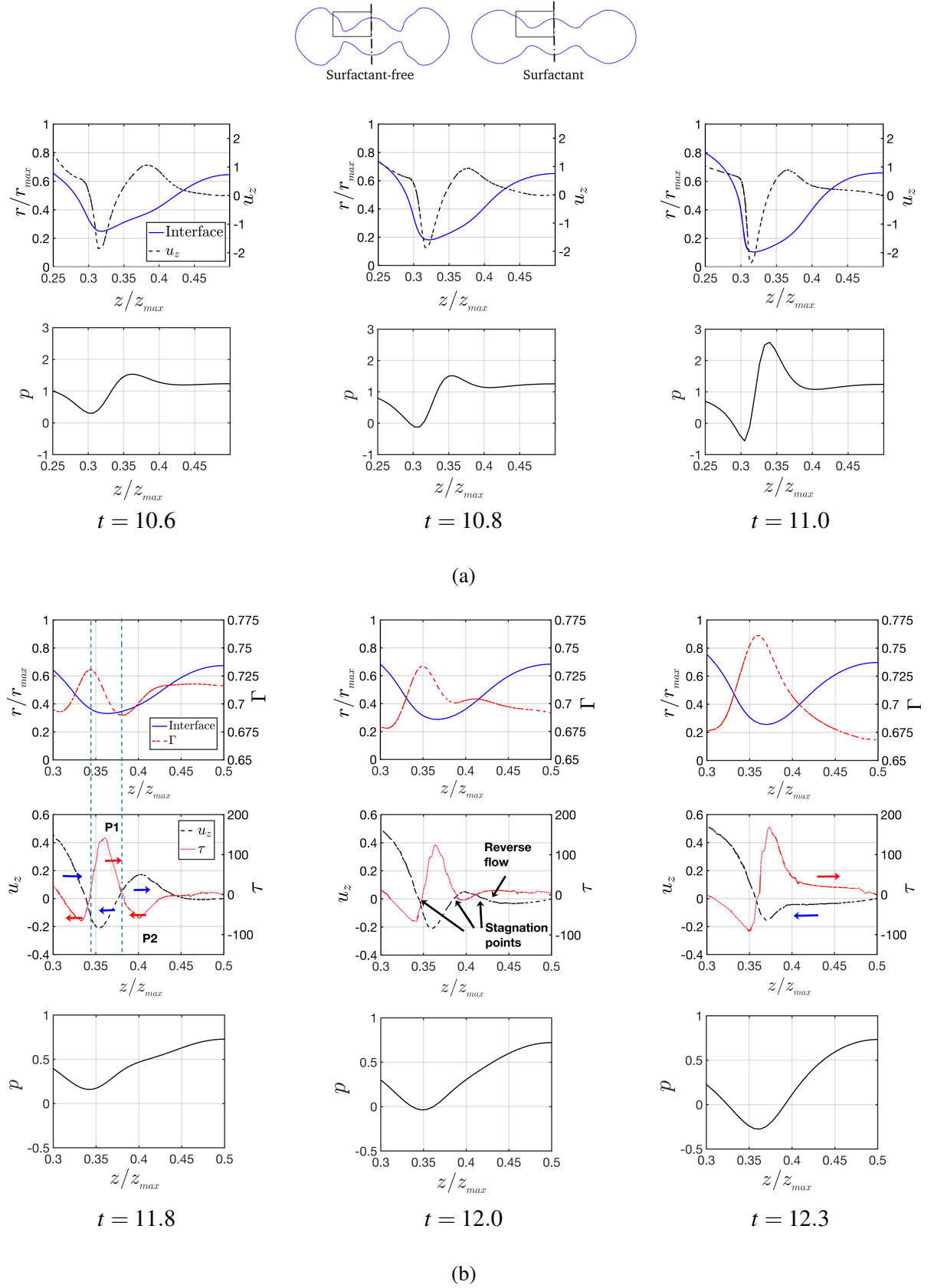


Fig. 5.9. Spatio-temporal evolution of the interfacial shape, u_z , and p for the surfactant-free case, (a), and the surfactant-laden case, (b), for the same parameters as those used to generate figure 5.8. In (b), the evolution of Γ and τ have also been plotted, and labelled the the direction of the Marangoni-induced and capillary-driven flows with red and blue arrows, respectively. The dimensionless times are shown in each panel.

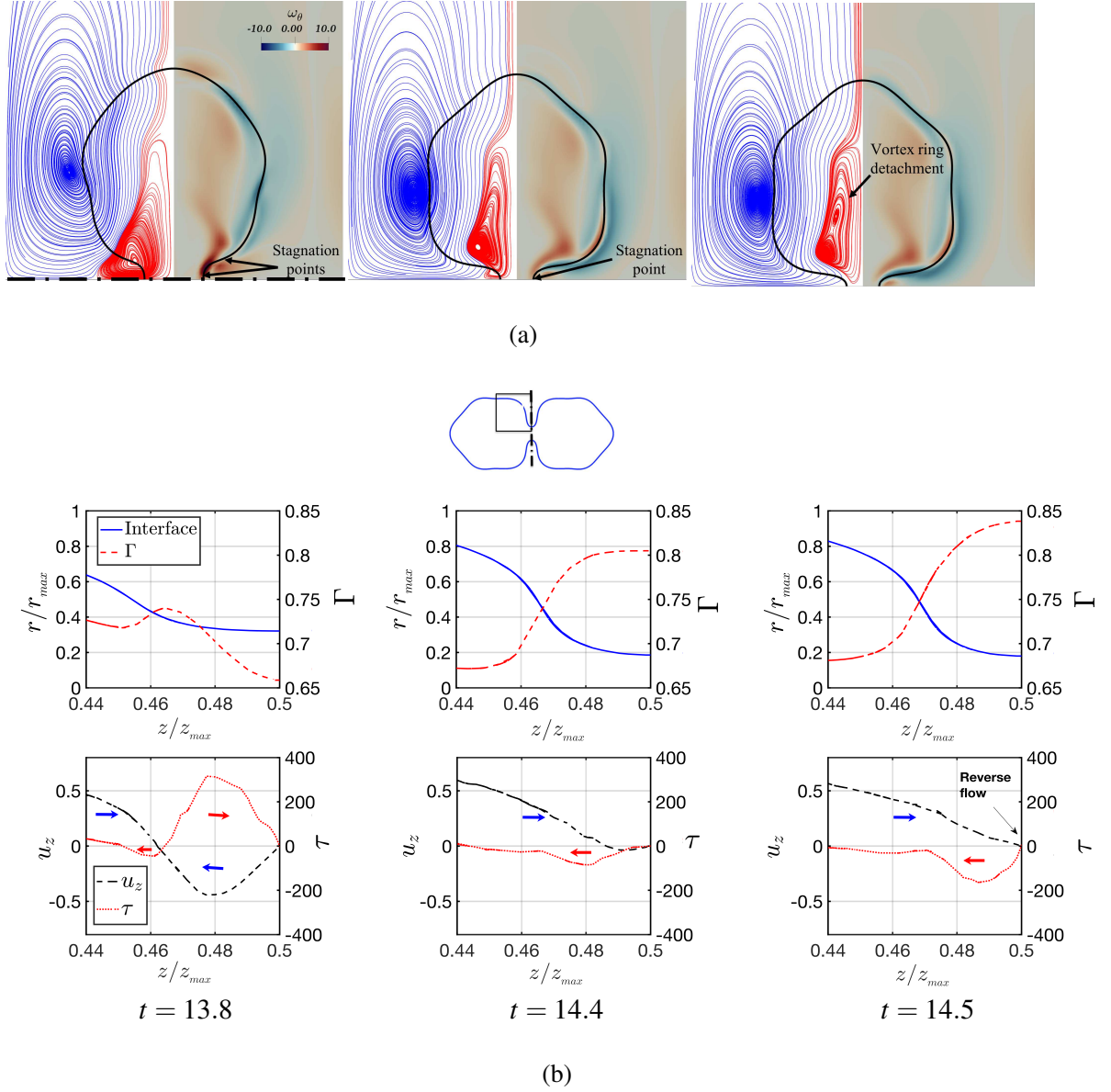


Fig. 5.10. Illustration of the surfactant-mediated mechanism underlying the second escape from pinch-off in figure 5.5c depicting a three-dimensional representation of the velocity vector field, together with ω_θ and streamlines, (a), at $t = 13.8$, 14.4 , and 14.5 . The framed regions of the ligament show a magnified view of the flow direction at each time. In (b), it has been plotted the spatio-temporal evolution of the interfacial shape, Γ , u_z , and τ and labelled the direction of the Marangoni-induced and capillary-driven flows with red and blue arrows, respectively.

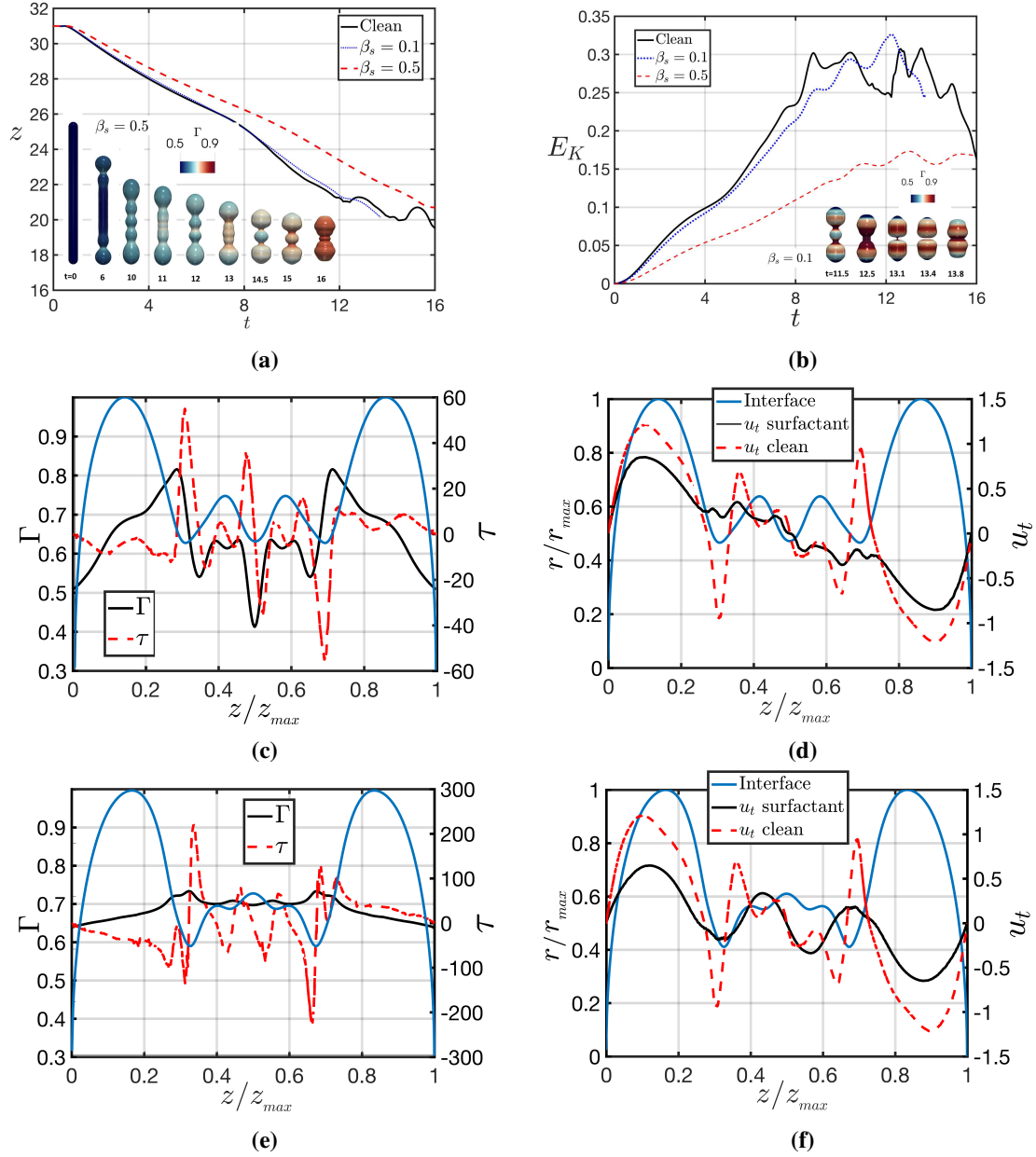


Fig. 5.11. Effect of β_s on the retraction dynamics for $L_o = 15$, $Oh = 10^{-2}$, $Pe_s = 10$, and $\Gamma_o = \chi\Gamma_\infty/2$: (a) and (b) temporal evolution of the north-tip location, and the kinetic energy, E_k , respectively; (a) and (b) also show three-dimensional representations of the interface for $\beta_s = 0.5$ and 0.1 , respectively, and for the dimensionless times shown in the panels in which the colour bar depicts the magnitude of the surfactant interfacial concentration, Γ . Panels (c) and (e), and (d) and (f) show the spatial variation of the interfacial shape, Γ , and τ , and the tangential interfacial velocity, u_t , for the surfactant-free and surfactant-laden cases, respectively, at $t = 10$. In (c) and (e), and (d) and (f), $\beta_s = 0.1$ and 0.5 , respectively. Note: in (c) interface location is superimposed, however, axis is not shown.

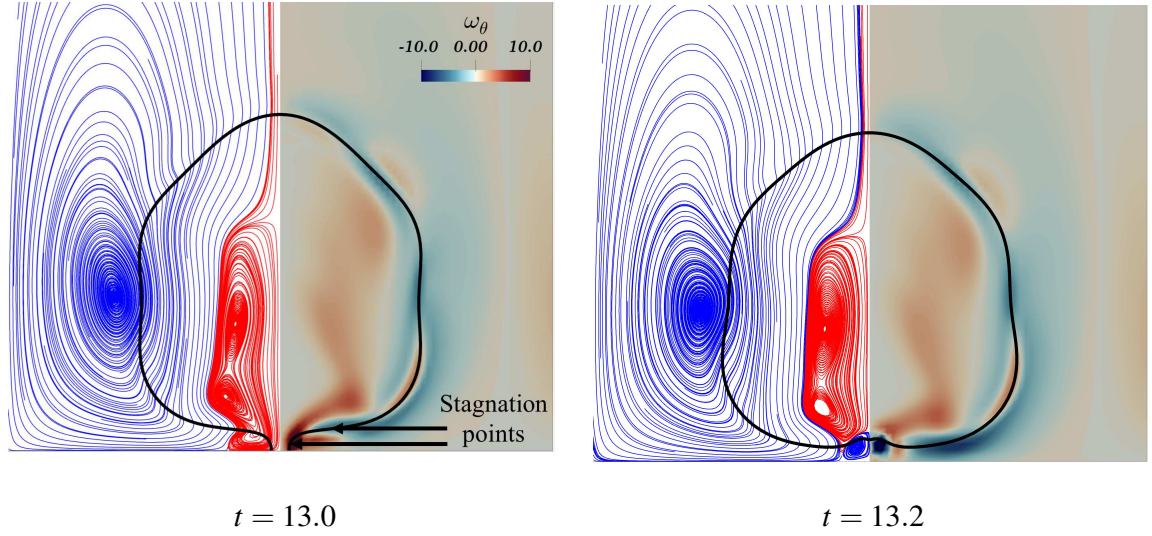


Fig. 5.12. Illustration of the no-escape from pinchoff for $\beta_s = 0.1$ at $t = 13$ and 13.2 . The rest of the parameters are the same as in figure 5.11.

and (d) and (f) of figure 5.11, which plot a snapshot of the interfacial shape, Γ , τ and u_t (for the clean and surfactant-laden cases), for $\beta_s = 0.1$ and 0.5 , respectively, it is shown that for the higher β_s value, the larger Marangoni stresses lead to a more uniform distribution of surfactant along the interface and a greater degree of interfacial rigidification; this is illustrated further through the overall reduction in u_t and E_K (see figure 5.11b) with increasing β_s .

For $\beta_s = 0.5$, the escape from the end-pinching mechanism is observed as described in the previous section. For $\beta_s = 0.1$, however, the relative importance of Marangoni stresses is smaller (see τ magnitude on figure 5.11c) which does not lead to prevention of the capillary breakup of the ligament (see interface at $t = 13.4$). Figure 5.12 shows that τ is not sufficiently large to reverse the flow and the merging of the stagnation points does not occur here. Due to the existence of these two stagnation points close to the neck, the vortex ring close to the neck is not displaced towards the bulk (similar to figure 5.10 at $t = 14.4$), which is the genesis of the escape of pinchoff. Therefore, two different regimes with respect to β_s are identified, and the transition region between the two regimes is located between $\beta_s = 0.1$ and $\beta_s = 0.3$.

In figure 5.13, the effect of varying Pe_s is shown, which reflects the influence of surfactant diffusion effects along the interface, on the retraction dynamics. Inspection of this figure reveals that the promotion of diffusive effects through a decrease in Pe_s leads to a more uniform interfacial distribution of Γ and a reduction in the magnitude of surface tension gradients. It can also be seen that the retraction speed and ligament kinetic energy are weakly-dependent on Pe_s : they exhibit quantitatively similar dynamics over a three orders of magnitude variation in Pe_s . Therefore, keeping the other parameters fixed, the inhibition of the end-pinching mechanism (see 5.13a at $t = 12.8$) is expected for cases when

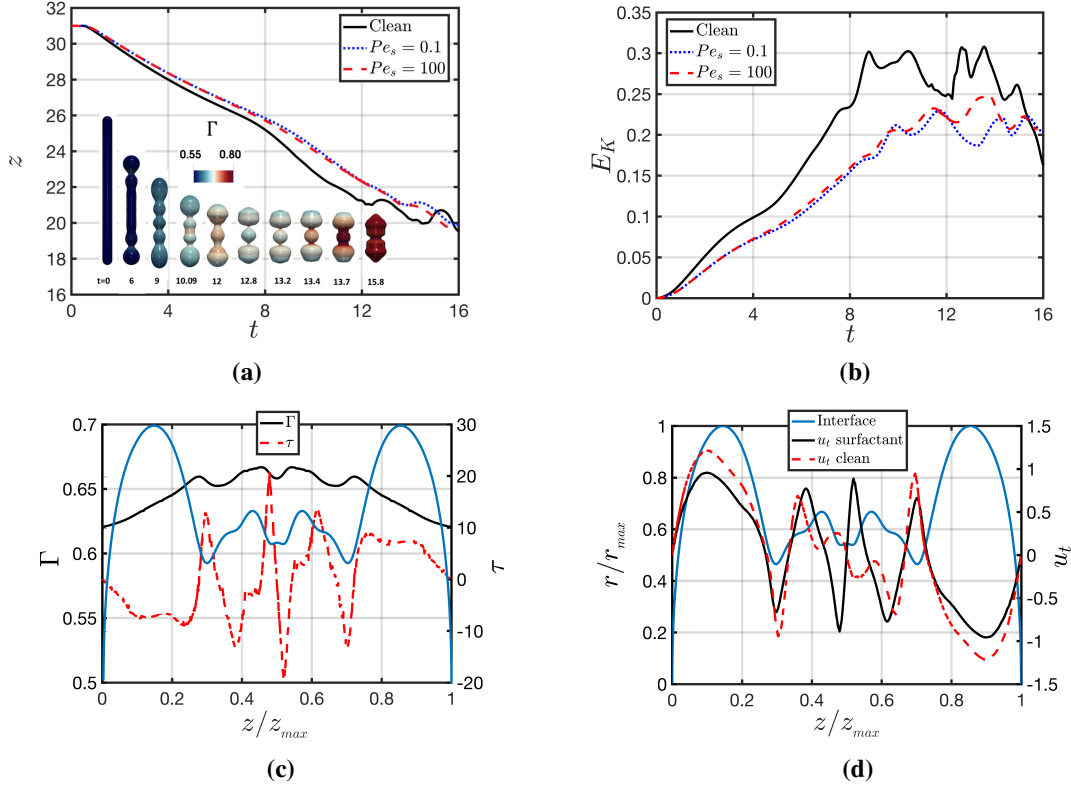


Fig. 5.13. Effect of Pe_s on the retraction dynamics for $L_o = 15$, $Oh = 10^{-2}$, $\beta_s = 0.3$, $\chi = 0.9$ and $\Gamma_o = \chi\Gamma_\infty/2$: (a) temporal evolution of the north-tip location and three-dimensional representations of the interface for $Pe_s = 0.1$ and for the dimensionless times shown in the panels in which the colour bar depicts the magnitude of the surfactant interfacial concentration, Γ ; (b) temporal evolution of the kinetic energy, E_k . respectively; (a) and (b) also show $\beta_s = 0.5$ and 0.1 , Panels (c) and (d) show the spatial variation of the interfacial shape, Γ , and τ , and the tangential interfacial velocity, u_t , for the surfactant-free and surfactant-laden cases, respectively, for $Pe_s = 0.1$ and at $t = 10$. Note: in (c) and (e) interface location is superimposed, however, axis is not shown.

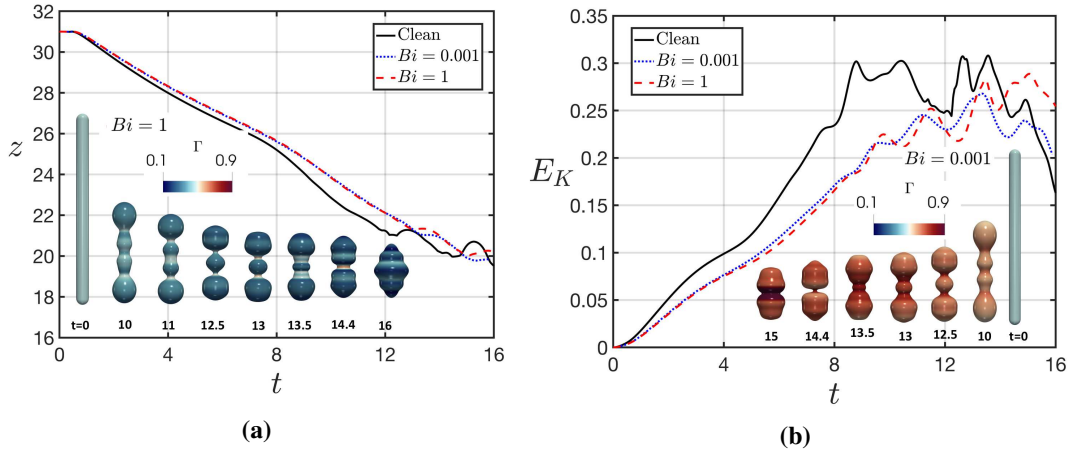


Fig. 5.14. Effect of Bi on the retraction dynamics for $L_o = 15$, $Oh = 10^{-2}$, $\beta_s = 0.3$, $Pe_s = 10$, $Pe_b = 10$ and $\Gamma_o = \chi\Gamma_\infty/2$: (a) and (b) temporal evolution of the north-tip location, and the kinetic energy, E_k , respectively; (a) and (b) also show three-dimensional representations of the interface for $Bi = 1$ and 10^{-3} , respectively, and for the dimensionless times shown in the panels in which the colour bar depicts the magnitude of the surfactant interfacial concentration, Γ . Panels (c) and (e), and (d) and (f) show the spatial variation of the interfacial shape, Γ , and τ , and the tangential interfacial velocity, u_t , for the surfactant-free and surfactant-laden cases, respectively, at $t = 10$. In (c) and (e), and (d) and (f), $Bi = 10^{-3}$ and 1, respectively.

$Pe_s > 0.1$.

Up to this point, the fate of the ligament in presence of insoluble surfactants has been analysed; here, it is investigated the effect of surfactant solubility on the dynamics by a fixed value of the fractional coverage to $\chi = 0.9$ and exploring the range $Bi = 10^{-3} - 1$. At the lower end of this range, the sorptive time scales are much larger than those associated with interfacial effects; consequently, the dynamics are dominated by capillarity and Marangoni stresses and are expected to be similar to those observed in the insoluble surfactant case. For $Bi = O(1)$, the sorptive time scales are comparable to their capillary and Marangoni counterparts and the flow will reflect the delicate interplay amongst these effects. Inspection of figure 5.14a,b, however, shows that, contrary to expectations, Bi has a relatively minor effect on the retraction speed and the ligament kinetic energy. From the three-dimensional representations of the interface, it can be seen that the ligament escapes its breakup for all Bi . For $Bi = 1$, it is observed the escape from breakup at $t \sim 12.4$ and $t \sim 14$. The radius of the neck prior to its escape also increases with Bi . Therefore, keeping the other parameters the same, the inhibition of the end-pinching mechanism (e.g. see 5.14-(a) at $t = 12.5$) is observed for three orders of magnitude of Bi .

By investigating the effect of the fractional coverage, represented by χ on the dynamics with $Bi = 0.1$ and the rest of the parameters set to their base values. Figure 5.15a,b shows that whereas the low χ dynamics resemble that of the surfactant-free case, at high χ , for which adsorption effects

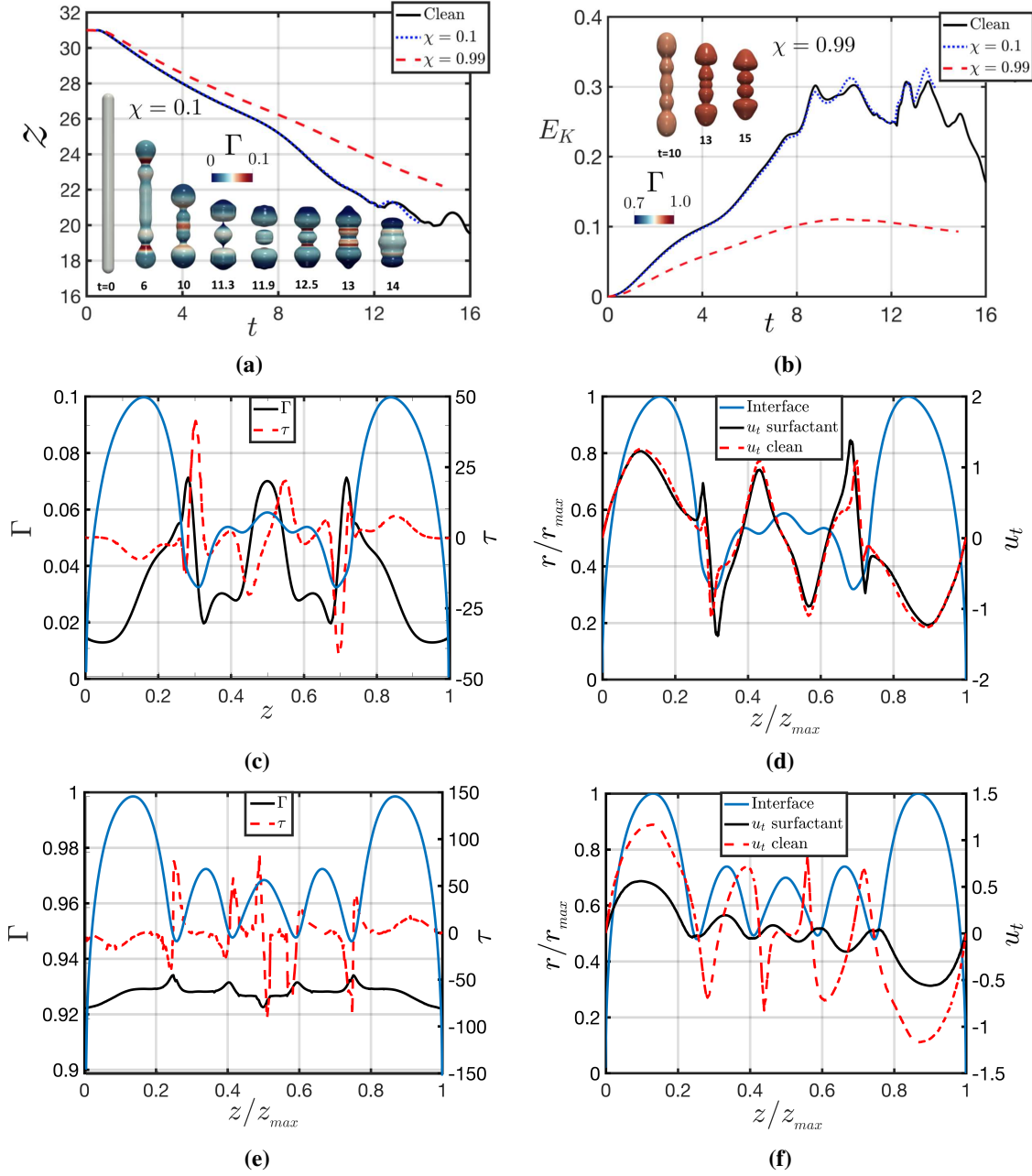


Fig. 5.15. Effect of χ on the retraction dynamics for $L_o = 15$, $Oh = 10^{-2}$, $\beta_s = 0.3$, $Pe_s = 10$, $Pe_b = 10$ and $Bi = 0.1$: (a) and (b) temporal evolution of the north-tip location, and the kinetic energy, E_k , respectively; (a) and (b) also show three-dimensional representations of the interface for $\chi = 0.1$ and 0.99 , respectively, and for the dimensionless times shown in the panels in which the colour bar depicts the magnitude of the surfactant interfacial concentration, Γ . Panels (c) and (e), and (d) and (f) show the spatial variation of the interfacial shape, Γ , and τ , and the tangential interfacial velocity, u_t , for the surfactant-free and surfactant-laden cases, respectively, at $t = 10$. In (c) and (e), and (d) and (f), $\chi = 0.1$ and 0.99 , respectively. Note: in (c) and (e) interface location is superimposed, however, axis is not shown.

are dominant, a significant reduction in the retraction velocity and kinetic energy is observed. Furthermore, as can be seen in figure 5.15c,f, for large χ , interfacial gradients of the surfactant concentration, and therefore of surface tension, are small, which implies that Marangoni stresses play a minor role in this case. Thus, the reduction in ligament retraction velocity must be related to the significant reduction in surface tension, which acts to diminish the magnitude of capillary effects. Therefore, for a low χ , the relative importance of Marangoni stresses is very small (see τ magnitude in figure 5.15c) which does not lead to the prevention of capillary breakup (see interface at $t = 11.3$).

5.4 Future research

Future research avenues involve performing numerical simulations of curved ligaments to breakup the symmetry behaviour. The liquid ligament thread is initialised as a curved cylindrical thread of length $2L$ with a constant radius of curvature R_θ , and also with a similar aspect ratio $L_o = L/R = 15$ bounded by two hemispherical caps at its two ends. A schematic representation of this curved ligament shape is shown in figure 5.16-(a). Here, the radius of curvature is set to $R_\theta = 10L_o/\pi$. If the value $R_\theta \rightarrow \infty$, a straight ligament could be obtained.

The simulation of a curved thread implies that the axi-symmetric-assumption is no longer valid. But, the presence of a symmetric plane still exists about the mid-plane $z = 16$. The simulation is initialised with fluids at rest in the absence of gravity. Similar to what was reported in subsection 5.2.1, no-slip boundary conditions are imposed on the fluid velocity at the walls of the computational domain and Neumann-type conditions for the pressure ($\partial p / \partial \mathbf{n} = 0$), where $\mathbf{n}$ here refers to the normal vector at the boundaries of the computational domain.

In Figure 5.17, I present the spatio-temporal dynamics of the surfactant-free ligament when $L_o = 15$ and $Oh = 10^{-2}$. The initially motionless, cylindrical ligament undergoes retraction due to the pressure gradient between the two bulbous ends and the rest of its body. At $t \sim 11.25$, the capillary breakup of the thread occurs with the formation of three droplets. Interestingly, the droplet positions are inverted in the $y - z$ plane with respect to the initial state. These droplets are sufficiently close and a double coalescence takes place simultaneously at $t \sim 11.75$. The resulting ligament oscillates over time in the three directions.

Figure 5.18 shows a three-dimensional representation of the interfacial dynamics in the presence of insoluble surfactant when $L_o = 15$, $Oh = 10^{-2}$, $Pe_s = 10$, $\beta_s = 0.9$, and $\Gamma_o = \Gamma_\infty/2$. I observe the inhibition of the capillary breakup, and subsequently the reopening of the neck via Marangoni stresses.

The three dimensional dynamics of the system lead to a non-uniform distribution of surfactants in the streamwise direction. The presence of surface tension gradients leads to a change of the fate of the

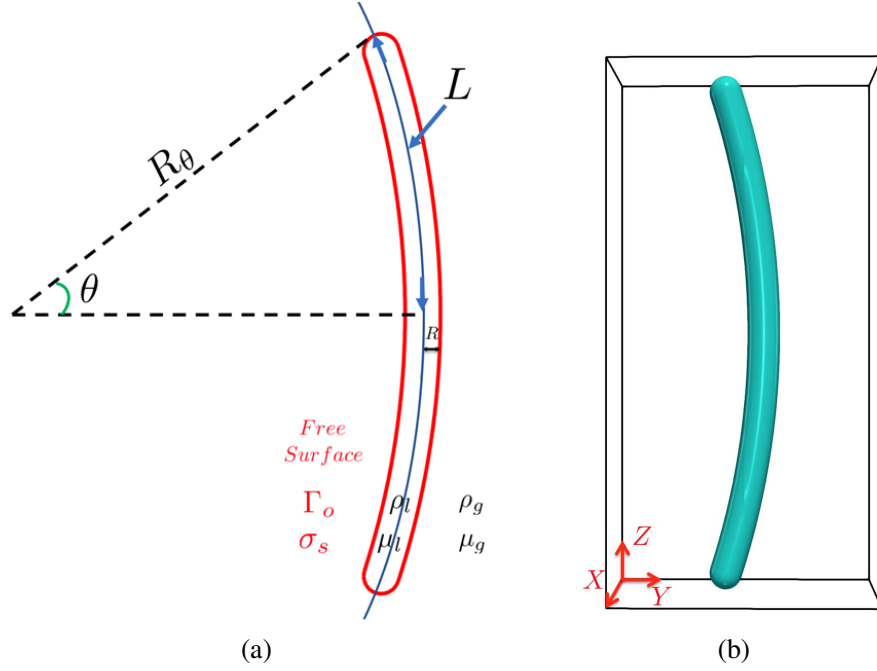


Fig. 5.16. Schematic representation of the initial shape of the ligament, (a), highlighting the fluid quantities and non-dimensional parameters of the system, (b), initial shape of the ligament with the computational domain of size $8R \times 16R \times 32R$ in a three-dimensional Cartesian domain $\mathbf{x} = (x, y, z)$ and divided into $6 \times 12 \times 12$ sub-domains with global resolution $192 \times 384 \times 768$.

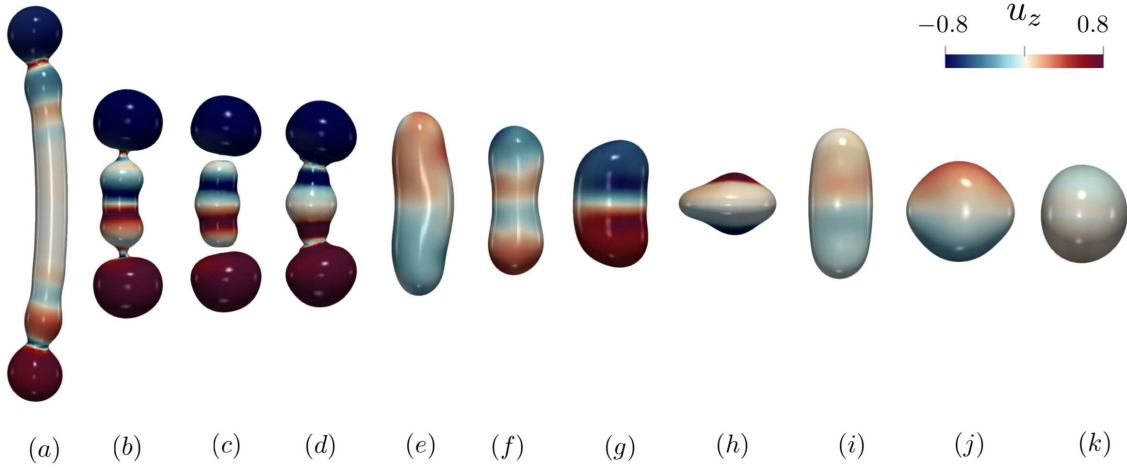


Fig. 5.17. Surfactant-free ligament retraction for $L_o = 15$, $Oh = 10^{-2}$, $\theta = L_o/R_\theta$ and $R_\theta = 10L_o/\pi$. at $t = (5, 11, 11.5, 12, 25, 30, 35, 40, 75, \text{ and } 125)$ respectively .

ligament with the entrapment of stagnant phase at $t \approx 30$. Further analysis are necessary to understand the physical mechanisms that lead to air-entrapment inside the ligament.

Figure 5.19 shows the temporal evolution of the north/south tip location and kinetic energy E_K for the surfactant-free and surfactant-laden cases. The interfacial rigidification brought about by

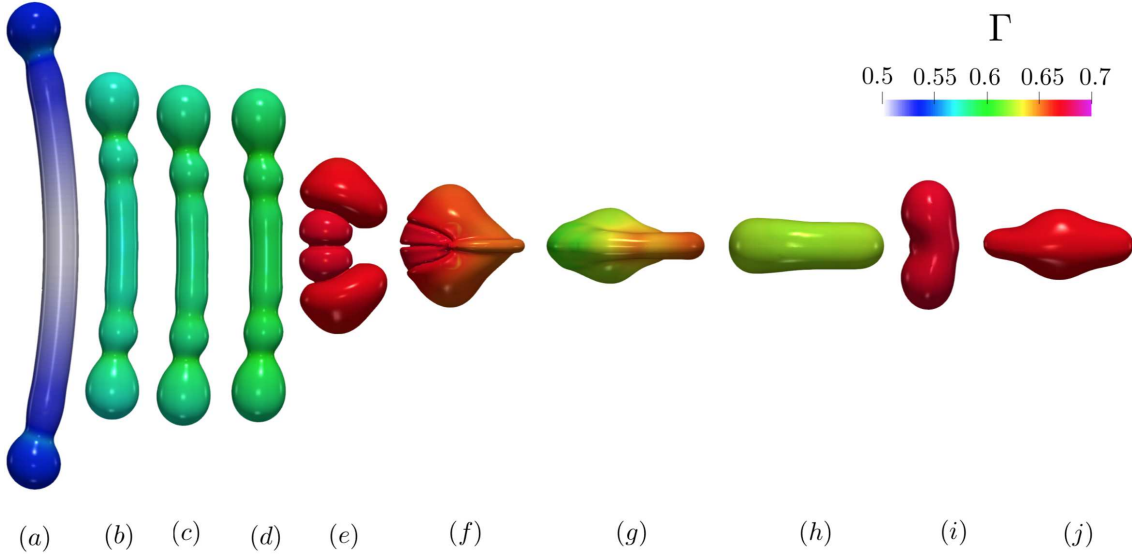


Fig. 5.18. Ligament retraction with an insoluble surfactant for $L_o = 15$, $Oh = 10^{-2}$, $\theta = L_o/R_\theta$, $R_\theta = 10L_o/\pi$, $Pe_s = 10$, $\beta_s = 0.9$ and $\Gamma_o = \Gamma_\infty/2$ for $t = 5, 11, 11.5, 12, 25, 30, 35, 40, 75$, and 125 respectively.

Marangoni stresses can be observed through the slower temporal evolution of the ligament tips. As time evolves, E_k tends to zero as the ligament tends towards a steady spherical shape. Interestingly, we observe that the presence of surfactant reduces significantly the kinetic energy and the oscillatory dynamics. To gain further insight into the oscillatory dynamics, further examination of the vortical structures should be done.

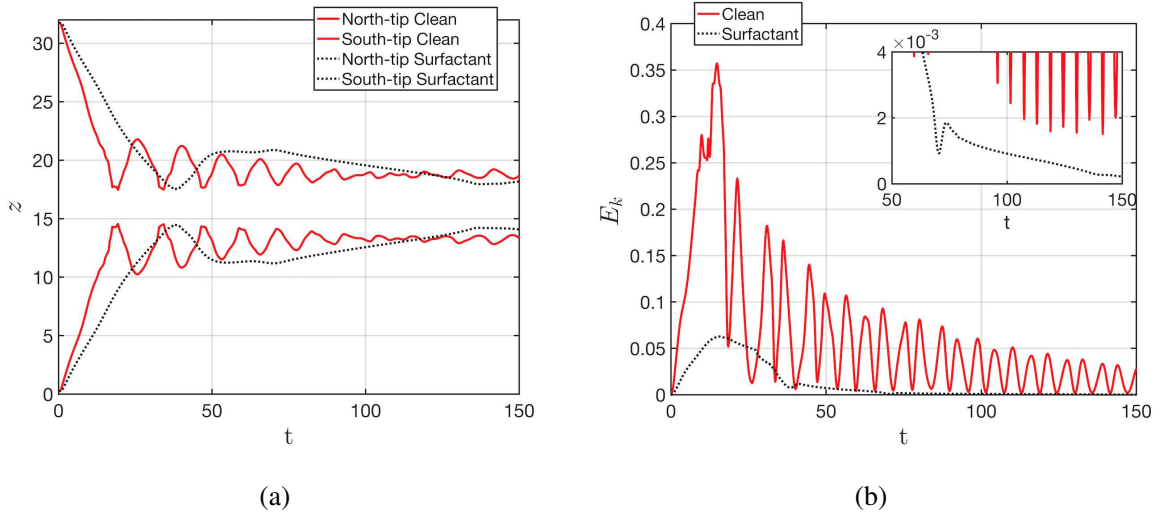


Fig. 5.19. Temporal evolution of the north/south tip location (a) and Kinetic energy E_K (b) for the surfactant-free and surfactant-laden cases.

5.5 Conclusions

It has presented the effect of surfactant on ligament retraction of an aspect ratio $L_0 = 15$ and for intermediate Ohnesorge numbers, $Oh \sim 10^{-2}$. I have performed fully three-dimensional numerical simulations of the retracting process over a range of system parameters that account for the surfactant solubility and sorption kinetics and Marangoni stresses. The numerical method has been validated against the work of Notz and Basaran (2004) for a surfactant-free case. The results indicate that the presence of surfactant inhibits the end-pinching mechanism and promotes the neck re-opening through Marangoni-flow, induced by the formation of surfactant concentration gradients, and not via lowering of the mean surface tension. The induced Marangoni stresses decelerate the flow caused by the capillary pressure until flow-reversal occurs close to the neck. As the flow re-enters through the neck, the formation of a jet towards the bulbous region is observed, which gives rise to a vortex ring that eventually detaches towards the centre of the bulbous region. This behaviour is similar to the phenomenon explained by Hoepffner and Paré (2013) in the escape from breakup of viscous ligaments in the absence of surfactant. Therefore, the presence of surfactants avoids the ‘end-pinching’ mechanism because of the existence of Marangoni stresses that suppress the mechanism of the Rayleigh-Plateau instability. This inhibition of the flow singularities is a remarkable outcome in the presence of a contaminant. It has also been demonstrated that the pinchoff inhibition cannot happen by simply reducing the value of the surface tension, but only by the introduction of the Marangoni stresses. The presence of Marangoni stresses also leads to interfacial rigidification, which is observed through reduction of the ligament retraction velocity and the ligament kinetic energy. I have also discussed the detrimental effect of the variation of the key surfactant parameters in the fate of the ligament. At $\beta_s = 0.1$, Marangoni stresses are insufficiently large to influence the flow close to the neck and do not prevent the capillary breakup of the ligament. I have also found that for the whole studied range of Pe_s and Bi , the suppression of the ‘end-pinching’ mechanism is predicted; thus, the neck reopens. Additionally, I have showed that solubility, contrary to expectations, has a relatively minor effect on the retraction speed and the ligament kinetic energy. Finally, the adsorption effects were studied via variation of χ , where at $\chi = 0.1$, Marangoni stresses do not lead to the prevention of capillary breakup.

This research is of importance for many applications that aim to produce equal-sized droplets, which is a desired outcome for improving efficiency in technologies such as ink-jet printing. An interesting future line of research would be to study the one-dimensional free-surface slender cylindrical flow on the Navier-Stokes equations coupled with a set of equations describing the surfactant interfacial transport on a Newtonian liquid thread. This analysis could provide insights into the relationship between the classic Taylor-Culick retraction velocity and interfacial rigidification brought by the surface-active agents. Future research avenues involve performing numerical simulations of curved ligaments to breakup the symmetry behaviour and of non-Newtonian ligaments, including visco-plastic and visco-

elastic types, with a large range of Ohnesorge numbers and ligament aspect ratios. The retraction dynamics of non-axisymmetric ligaments may lead to the formation of ‘entrapped bubbles’ inside the ligament and a three-dimensional oscillatory dynamics of the formed droplet.

Chapter 6

Dynamics of surfactant-laden bubble bursting through an interface

Related publication: Dynamics of a surfactant-laden bubble bursting through an interface. *C. R. Constante-Amores*, L. Kahouadji, A. Batchvarov, S. Shin, J. Chergui, D. Juric and O. K. Matar. *J. Fluid Mech* (2021) (accepted, under production)

Summary

I study the effect of surfactant on the dynamics of a bubble bursting through an interface. I perform fully three-dimensional direct numerical simulations using a hybrid interface-tracking/level-set method accounting for surfactant-induced Marangoni stresses, sorption kinetics, and diffusive effects. I select an initial bubble shape corresponding to a large Laplace number and a vanishingly small Bond number in order to neglect gravity, and isolate the effects of surfactant on the flow. Our results demonstrate that the presence of surfactant affects the dynamics of the system through Marangoni-induced flow, driving motion from high to low concentration regions, which is responsible for the onset of a recirculation zone close to the free surface. These Marangoni stresses rigidify the interface, delay the cavity collapse, and influence the jet breakup process.

6.1 Introduction

When a bubble is resting close to a liquid-gas interface, its rupture gives rise to the formation of a central jet. This jet breaks up into small droplets, which could transport biological material, toxins,

salts, surfactants or dissolved gases (Woodcock et al., 1953; MacIntyre, 1972; Veron, 2015; Zenit and Rodríguez-Rodríguez, 2018; Séon and Liger-Belair, 2017; Poulain and Bourouiba, 2018). It is unsurprising therefore that the bursting bubble phenomena have received significant interest due to their occurrence in a multitude of natural and industrial applications. In the absence of contaminants, the physical mechanisms of surfactant-free bursting bubbles on the ejection of droplets have been widely studied experimentally (Woodcock et al., 1953; Ghabache et al., 2014; Ghabache and Séon, 2016; Séon and Liger-Belair, 2017), numerically (Deike et al., 2018; Gordillo and Rodríguez-Rodríguez, 2019; Singh and Das, 2019), and through theoretical approaches (Zeff et al., 2000; Gañán-Calvo, 2017; Lai et al., 2018; Blanco-Rodríguez and Gordillo, 2020).

This previous work has shown that when a nucleated bubble rises through the liquid and then rests close to a free surface, its static resting shape results from a balance between gravitational and surface tension forces. The bubble shape may be characterised by a submerged interface, a liquid layer/cap above the bubble, and an interface, which extends away from the bubble cap (Toba, 1959; Ghabache, 2015). The cap is characterised by a length scale $\delta/R_o \sim O(10^{-6})$, where δ and R_o refer to the liquid layer thickness and the initial bubble radius, respectively. The layer curvature creates over-pressure relative to the liquid bulk below it. The fluid within the layer drains over time enabling van der Waals forces to rupture the interface when $\delta \rightarrow 0$ forming a hole (Lhuissier and Villermaux, 2012). The hole leaves an open, unstable cavity that collapses to form a vertical jet whose dynamics are governed by inertial, viscous, and capillary forces.

Surfactants can affect the dynamics of surface-tension driven flows by the reduction of the local surface tension and capillary pressure, and by the formation of Marangoni stresses brought about by gradients in interfacial surfactant concentration. In a recent study, Constante-Amores et al. (2020a) reviewed the state-of-the-art of the effect of surfactant in the dynamics of capillary singularities due to topological change. Craster et al. (2002) have shown that the presence of insoluble surfactant during the thinning of threads does not alter the well known breakup scalings predicted by Eggers (1993) as the capillary singularity is such a violent event which convects surfactant away from the pinchoff point. Both McGough and Basaran (2006) and Kamat et al. (2018) have reported that the presence of surfactant changes the fate of the thinning of threads as surfactant enhances the formation of micro-threads, whose thinning dynamics also follow Eggers (1993). Constante-Amores et al. (2020a) showed that the presence of surfactant can suppress the ‘end-pinching’ mechanism in the retracting dynamics of ligament threads due to the suppression of stagnation points, and subsequent flow reversal. Most of chemical surfactants are soluble in the bulk liquid, adding a layer of complexity to the phenomena as Marangoni stress can also be regulated by the surfactant sorption kinetics between the bulk and interface. Liao et al. (2004) observed experimentally that high concentrations of soluble surfactant favour an asymmetric breakup of a liquid bridge. Jin et al. (2006), and Jin and Stebe (2007) showed

that solubility affects the dynamics of drop formation in terms of thinning. Craster et al. (2009) have shown that similar to their previous work Craster et al. (2002), the addition of solubility does not affect the scaling predicted by Eggers (1993), but it does lead to the formation of larger satellite droplets, which was confirmed experimentally by Kovalchuk et al. (2016, 2018).

As revealed by the foregoing review, studies involving surfactant effects on interfacial flows have received considerable attention, however, to the best of our knowledge, the influence of surfactants on the dynamics of bursting bubbles has not been explored, and this is the subject of the present article. Here, we use three-dimensional numerical simulations to account for surfactant solubility, diffusion, sorption kinetics, and Marangoni stresses on the bursting phenomena. The rest of this chapter is structured as follows: in Section 6.2, the equations describing the bubble resting shape are presented, in Section 6.3 the governing dimensionless parameters, problem configuration, and validation, are introduced. Section 6.4 presents the results. Finally, future work and concluding remarks are introduced at the end of the chapter.

6.2 Bubble shape

The shape of the bubble before its rupture is determined by the characteristic size of the bubble R in respect of the capillary length scale $a = \sqrt{\sigma/\rho g}$. The comparison of the two previous length scales will elucidate whether the capillary pressure σ/R dominates the gravitational forces $\rho g R$. For the theoretical calculation of the shape of a bubble resting on a free-surface, the interfacial shape can be decomposed into three independent regions (shown in figure 6.1): the submerged cavity (I), the cap of the bubble (II) and the tail of the bubble (III). The previous three regions have a common point C , in which the interface has an effective surface tension 2σ due to the existence of two interfaces. Through the Laplace's law, each region can be described by the following equations

$$\begin{aligned} (I) \quad & P_b - (P_o - \rho g z) = \sigma \kappa \\ (II) \quad & P_b - P_{atm} = \frac{4\sigma}{R_{Cap}} \\ (III) \quad & P_{atm} - (P_{atm} - \rho g(h - h_\infty)) = \sigma \kappa \end{aligned}$$

here, P_b , P_{atm} and h_∞ stand for the pressure inside of the bubble, the pressure in the surrounding air and the height of the bubble tail, respectively. P_o denotes the pressure underneath of the bubble at $(0,0)$ in which the curvature of the bubble is described by $\kappa = 1/(R_1 + R_2)$, where R_1 and R_2 stand for the two main curvature radius. The previous set of equations neglects the liquid film entrapped between the bubble-cap and the free surface (i.e., weight of the liquid layer) under the assumption that the film thickness vanishes towards zero.

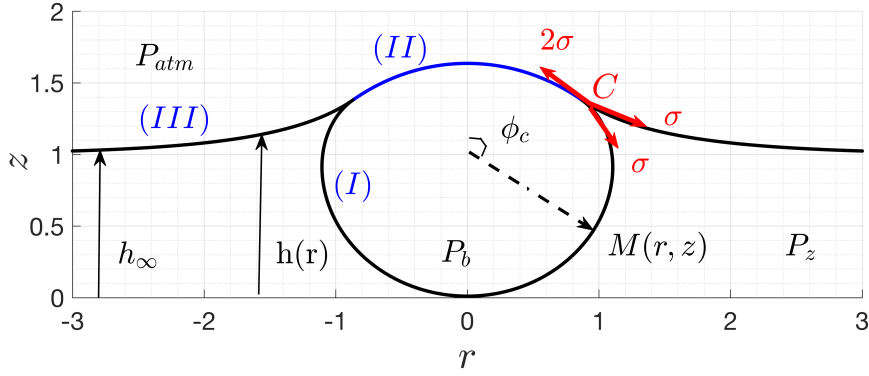


Fig. 6.1. Schematic representation of the interfacial shape of a bubble resting on an interface when $Bo = 1$. Additionally, it also highlights parameters of the system need for the calculation of its resting shape.

For the numerical solution of the previous set of equations, I followed the approach presented by Toba (1959), Boulton-Stone and Blake (1993), Duchemin et al. (2002), Lhuissier and Villiermaux (2012), and mainly, Ghabache (2015). The numerical solution is summarised briefly, and full details can be found in Ghabache (2015). The method consists of estimating a value for ' ϕ ' to predict the interfacial profile of the region (I) when $0 < \phi < C$.

The use of the equation describing the interfacial shape from the region (I) at $(0,0)$, it results in $P_b - P_o = 2\sigma/R_o$, where R_o is the curvature radius at $(0,0)$. Therefore, equation (I) can be modified to $2\sigma/R_o + \rho g z = \sigma \kappa$. Considering a point $M(r, z)$ as any interfacial location in region (I) described by cylindrical coordinates. Then, the interfacial curvature can be expressed as

$$\kappa = \frac{\sin\phi}{r} + \frac{d\sin\phi}{dx} \quad (6.1)$$

By scaling the other length scales with R_o (i.e., r and z as $r = \tilde{r}R_o$ and $z = \tilde{z}R_o$, respectively), the dimensionless Bond number appears

$$Bo_{num} = \frac{\rho g R_o^2}{\sigma} \quad (6.2)$$

Therefore, the interfacial bubble shape in the region (I) can be described by the following equation when $0 < \phi < C$ for a given R_o

$$\begin{cases} \frac{d\tilde{r}}{d\phi} = \frac{\tilde{r}\cos\phi}{\tilde{r}(2+Bo_{num}\tilde{z})-\sin\phi} \\ \frac{d\tilde{z}}{d\phi} = -\frac{d\tilde{r}}{d\phi}\tan\phi \end{cases} \quad (6.3)$$

The previous equation helps to calculate the curvature radius in point C, which is also the radius of the spherical cap R_{cap} of the bubble

$$\tilde{R}_{cap} = \frac{\tilde{r}}{\sin\phi_c} \quad (6.4)$$

The equation which describes the radius of the spherical cap is described by

$$\begin{cases} r = R_{cap}\sin\phi \\ z = h_c - R_{cap}\cos\phi_c + R_{cap}\cos\phi \end{cases} \quad (6.5)$$

As we have fixed R_o for (I) and R_{cap} is now known, h_∞ can be determined next by combining the equations of regions (I) and (II) at (0,0):

$$Bo_{num}\tilde{h}_\infty = \frac{4}{\tilde{R}_{cap} - 2} \quad (6.6)$$

At this point, the interfacial shape of the region (III) is the outstanding element. In this region, the interfacial shape is described by a surface $h(r) = z$, whose curvature is described by

$$\tilde{\kappa} = \frac{\tilde{h}'}{\tilde{r}(1 + \tilde{h}'^2)^{1/2}} + \frac{\tilde{h}''}{(1 + \tilde{h}'^2)^{3/2}} \quad (6.7)$$

Therefore, taking into account the previous definition for the curvature, the equation describing the interfacial shape of the region (III) becomes

$$Bo_{num} \left(h(\tilde{r}) - \tilde{h}_\infty \right) = \frac{\tilde{h}'}{\tilde{r}(1 + \tilde{h}'^2)^{1/2}} + \frac{\tilde{h}''}{(1 + \tilde{h}'^2)^{3/2}} \quad (6.8)$$

The previous equation is integrated subjected to the next boundary conditions: $\tilde{h}(\tilde{r}_c) = \tilde{h}_c$ and $\tilde{h}'(\tilde{r}_c) = -\tan\phi_c$. The iteration of ϕ_c continues until the following constraint is satisfied: $h(r) \xrightarrow{r \rightarrow \infty} h_\infty$

The previous Bo_{num} differs from the Bo defined in chapter 1. The former Bo_{num} is defined in terms of R_o , meanwhile the real Bo uses the actual shape of the bubble, and therefore should use $R = (a^2b)^{1/3}$, in which a and b stand for the large and small semi-axes of an ellipse, respectively. Therefore, the actual Bond number Bo is calculated as

$$Bo = \frac{(a^2b)^{1/3}}{R_o^2} Bo_{num} \quad (6.9)$$

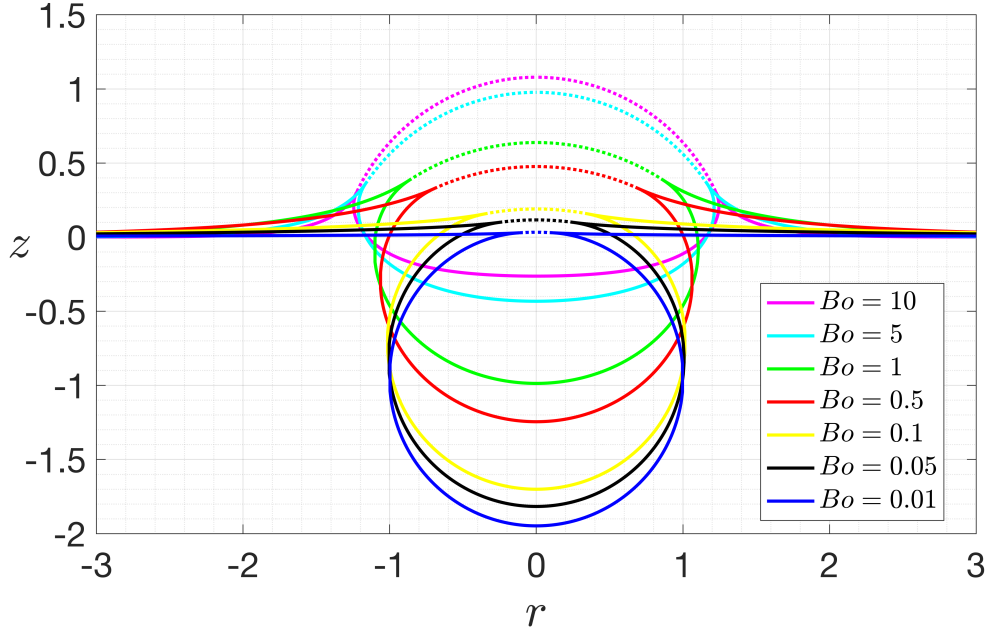


Fig. 6.2. Numerical prediction of the interfacial shape for the bubble for increasing Bond numbers (i.e., increasing radius values). The cap of the bubbles, region (II), is represented with dashed-lines.

Figure 6.2 shows the interfacial bubble shape for several Bond numbers predicted by the previous equations. The interfacial profiles have been validated against the experimental profiles from Ghabache (2015). As it was expected, the bigger the Bond number (i.e., the bigger the size of the bubble), the more important the gravitational forces are, and subsequently, the bubble loses its characteristic spherical shape. At high Bond numbers (i.e., $Bo > 0.1$) the free-surface is deformed, and the bubble-cap increases. At low Bond numbers (i.e., $Bo < 0.01$), the bubble stays underneath of the interface without deformation.

6.3 Problem formulation and numerical configuration

The numerical simulations were performed by solving the two-phase Navier-Stokes equations in a three-dimensional Cartesian domain $\mathbf{x} = (x, y, z)$ (see figure 6.3). A hybrid front-tracking/level-set method was used to treat the interface, where surfactant transport was resolved both in the bulk and on the interface (Shin et al., 2018). Here, and in what follows, all variables will be made dimensionless (represented by tildes) using

$$\tilde{\mathbf{x}} = \frac{\mathbf{x}}{R_o}, \quad \tilde{t} = \frac{t}{T}, \quad \tilde{\mathbf{u}} = \frac{\mathbf{u}}{U}, \quad \tilde{p} = \frac{p}{\rho U^2}, \quad \tilde{\sigma} = \frac{\sigma}{\sigma_s}, \quad \tilde{\Gamma} = \frac{\Gamma}{\Gamma_\infty}, \quad \tilde{C} = \frac{C}{C_\infty}, \quad \tilde{C}_s = \frac{C_s}{C_\infty}, \quad (6.10)$$

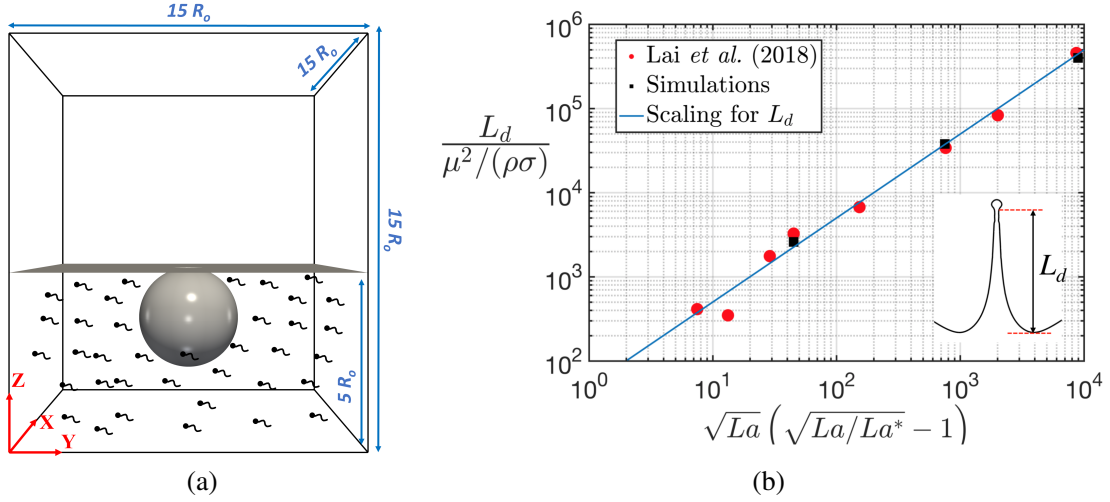


Fig. 6.3. (a) Initial shape of the bubble resting close to the interface, highlighting the computational domain of size $(15R_o)^3$ (not-to-scale) in a three-dimensional Cartesian domain $\mathbf{x} = (x, y, z)$, where Cartesian resolution is 768^3 ; (b) comparison of surfactant-free simulations from the current study (squares) with scaling argument of the length of the jet (solid line) and numerical simulations (dots) proposed by Lai et al. (2018).

where, t , $\mathbf{u}$, and p stand for time, velocity, and pressure, respectively. The physical parameters correspond to the liquid density ρ , viscosity, μ , surface tension, σ , surfactant-free surface tension, σ_s , and gravitational acceleration, g ; $T = \sqrt{\rho R_o^3 / \sigma_s}$ is the capillary time scale, hence the velocity scale is $U = R_o / T = \sqrt{\sigma_s / (\rho R_o)}$. The interfacial surfactant concentration, Γ , is scaled on the saturation interfacial concentration, Γ_∞ , whereas the bulk and bulk sub-phase (immediately adjacent to the interface) surfactant concentrations given by C and C_s , respectively, are scaled on the initial bulk surfactant concentration, C_∞ . As a result of this scaling, the dimensionless equations read, the dimensionless groups that appear in the above equations are defined as

$$Bo = \frac{\rho g R_o^2}{\sigma_s}, \quad La = \frac{1}{Oh^2} = \frac{\rho \sigma_s R_o}{\mu^2}, \quad (6.11)$$

$$Bi = \frac{k_d R_o}{U}, \quad k = \frac{k_a C_\infty}{k_d}, \quad Pe_s = \frac{U R_o}{D_s}, \quad Pe_b = \frac{U R_o}{D_b}, \quad \beta_s = \frac{\Re T \Gamma_\infty}{\sigma_s}, \quad (6.12)$$

where Bo stands for the Bond number and represents the ratio of gravitational to capillary forces; $Oh = \mu / \sqrt{\rho \sigma_s R_o}$ is the Ohnesorge number that measures the relative importance of viscous to surface tension forces, and La is the Laplace number; Bi denotes the Biot number representing the ratio of characteristic desorptive to convective time-scales; k is the ratio of adsorption to desorption time scales; Pe_s and Pe_b are the interfacial and bulk Peclet numbers, respectively, and represent the ratio of convective to diffusive time-scales in the plane of the interface and the bulk, respectively; and β_s is the surfactant elasticity number, which measures the sensitivity of the surface tension to the

surfactant concentration. The chosen density and viscosity ratios, $\rho_g/\rho = 1.2 \times 10^{-3}$ and $\mu_g/\mu = 0.018$, respectively, are representative of an air-water system.

The Marangoni stress, $\tilde{\tau}$, is expressed as a function of $\tilde{\Gamma}$:

$$\tilde{\tau} \equiv \nabla_s \tilde{\sigma} \cdot \mathbf{t} = -\frac{\beta_s}{1 - \tilde{\Gamma}} \nabla_s \tilde{\Gamma} \cdot \mathbf{t}, \quad (6.13)$$

where $\mathbf{t}$ is the unit tangent to the interface; tildes are dropped henceforth. The Marangoni time-scale, $\mu R_o / \Delta \sigma = O(10^{-5})$ s, as compared to the capillary and sorptive time-scales, which are of order $O(10^{-4})$ s and $O(10^{-3} - 10^{-5})$ s, respectively; thus Marangoni stresses will play a key role in the dynamics.

The dimensionless computational domain size is chosen as $(15R_o)^3$, which is found to be sufficiently large to render boundary effects negligible. Hence a radial component is defined as $r = \sqrt{(x - x_o)^2 + (y - y_o)^2}$ where x_o and y_o are the abscissa and ordinate bubble position, respectively. Solutions are sought subject to Neumann boundary conditions on all variables at the lateral boundaries, $p = 0$ at the top boundary $z = 15R_o$, and no-slip at $z = 0$. At the free surface, we impose $\mathbf{n} \cdot \nabla \tilde{C} = -BiPe_b (k\tilde{C}_s(1 - \tilde{\Gamma}) - \tilde{\Gamma})$ as a condition on $\tilde{C}$. Simulations are initialised as a bubble resting immediately beneath the free surface before its rupture. Its initial shape is determined by solving the Young-Laplace equation for $Bo = 10^{-3}$, which is sufficiently small to avoid the effect of gravity on the bubble bursting process. To initialise bursting, the top spherical cap of the bubble is removed, leaving only a bubble cavity (see figure 6.3a). The relevant time scale associated with the cap-retraction, $t_{CR} = R_o / \sqrt{2\sigma/\rho\delta} = O(10^{-6})$ s, is too short to affect the dynamics. A similar approach has been used by Boulton-Stone and Blake (1993), Garcia-Briones et al. (1994), Duchemin et al. (2002) and Deike et al. (2018). Our numerical simulations have been validated against the work of Eggers (1993) and Lai et al. (2018) in terms of liquid thread breakup, and the scaling of the ejected jet length, L_d , with La (see figure 6.3b), respectively. Solving the small-scales of the bursting dynamics is a challenging process. We have assessed the grid dependence of our results ensuring their convergence for grids larger than 768^3 .

The selection of bubble bursting configuration with such a small value of Bond number ($Bo = 10^{-3}$) is motivated by the fact that gravity can be neglected for this type of configuration, especially during the ejection process that involves many interfacial singularities such as breakup into tiny droplets. Therefore, gravity will not disturb any dynamics resulting from Marangoni stress. Moreover, the assumption of an open cavity with a perfect spherical-bubble before the film rupture is valid for all bubbles with $Bo \leq 10^{-2}$ (see figure 6.2). At higher values of Bo , the initialisation of the bubble requires taking into a consideration the shape of its “cap”, “cavity” and “meniscus” (see figure 6.2 for higher Bo values). Therefore, the presence of surfactant will not alter the initial spherical bubble

shape.

In terms of the applicability and relevance of the selected parameters, for Bond number $Bo = 10^{-3}$, the bubble radius is $R_o \approx 85 \mu\text{m}$. In breaking waves or ship wakes, a large number of microbubbles ($10 - 100 \mu\text{m}$) are generated. They have an impact on oceanic environments (such as gas transfer or heat absorption) and traceability of ship wakes.

6.4 Results

6.4.1 Bursting bubble dynamics of the surfactant-laden base case

The spatio-temporal evolution of the interfacial dynamics, shown in figure 6.4, is considered for the case characterised by $La = 2 \times 10^4$, $Bo = 10^{-3}$, $Pe_s = 1$, $\beta_s = 0.9$, $Bi = 0.01$, $k = 1$, and $\Gamma_o = k/4$. At early times, a large capillary pressure is generated near the nucleated hole due to the high curvature of the interface joining the spherical bubble and the horizontal free surface. This capillary pressure leads to rapid expansion of the hole and the creation of a toroidal capillary wave, which travels toward the bottom of the bubble. The convergence of this wave on the bubble rear leads to the formation of a cusp-like region, which is relieved via the detachment of downward-moving conical bubbles, and the formation of a vertical, upward-directed, high-speed, Worthington jet. Small droplets are subsequently ejected from the tip of the jet, triggered by a Rayleigh-Plateau instability. A pinchoff event is also seen to occur at the base of the Worthington jet that leads to retraction of the emitted ligament into a spheroidally-shaped drop.

In figure 6.5, we show snapshots of the interface, the interfacial concentration, Γ , the Marangoni stress, τ , the interfacial tangent velocity component, u_t , that provides a measure of mobility, and the azimuthal component of the vorticity, ω_θ . These snapshots, which are taken at $t = 0.360, 0.539, 1.239$, and 1.760 , corresponding to the framed panels in figure 6.4, reflect the strong coupling between these flow variables. Figure 6.5a,b illustrates that the collapsing cavity, and the accompanying capillary wave, transport surfactant towards the bottom of the bubble giving rise to a local decrease in surface tension. It is also instructive to separate figure 6.5b into four regions due to the existence of stagnation points. In region ‘A’, $\tau < 0$ and $u_t < 0$, indicating that the direction of the Marangoni flow is towards the bottom of the bubble, which aids cavity collapse and surfactant transport in this direction. In region ‘B’, $\tau > 0$ and $u_t > 0$, thus the Marangoni flow is directed away from the origin, which retards the collapse process. A similar behaviour is seen in regions ‘C’ and ‘D’ in which the trailing edge of the capillary wave has a similar Γ distribution, albeit with a smaller magnitude, to its leading edge. As a result, $\tau < 0$ and $\tau > 0$, and $u_t < 0$ and $u_t > 0$ in regions ‘C’ and ‘D’, which drives flow towards the bottom of the bubble and its tail, respectively. Figure 6.5b,c also shows the existence of an interfacial

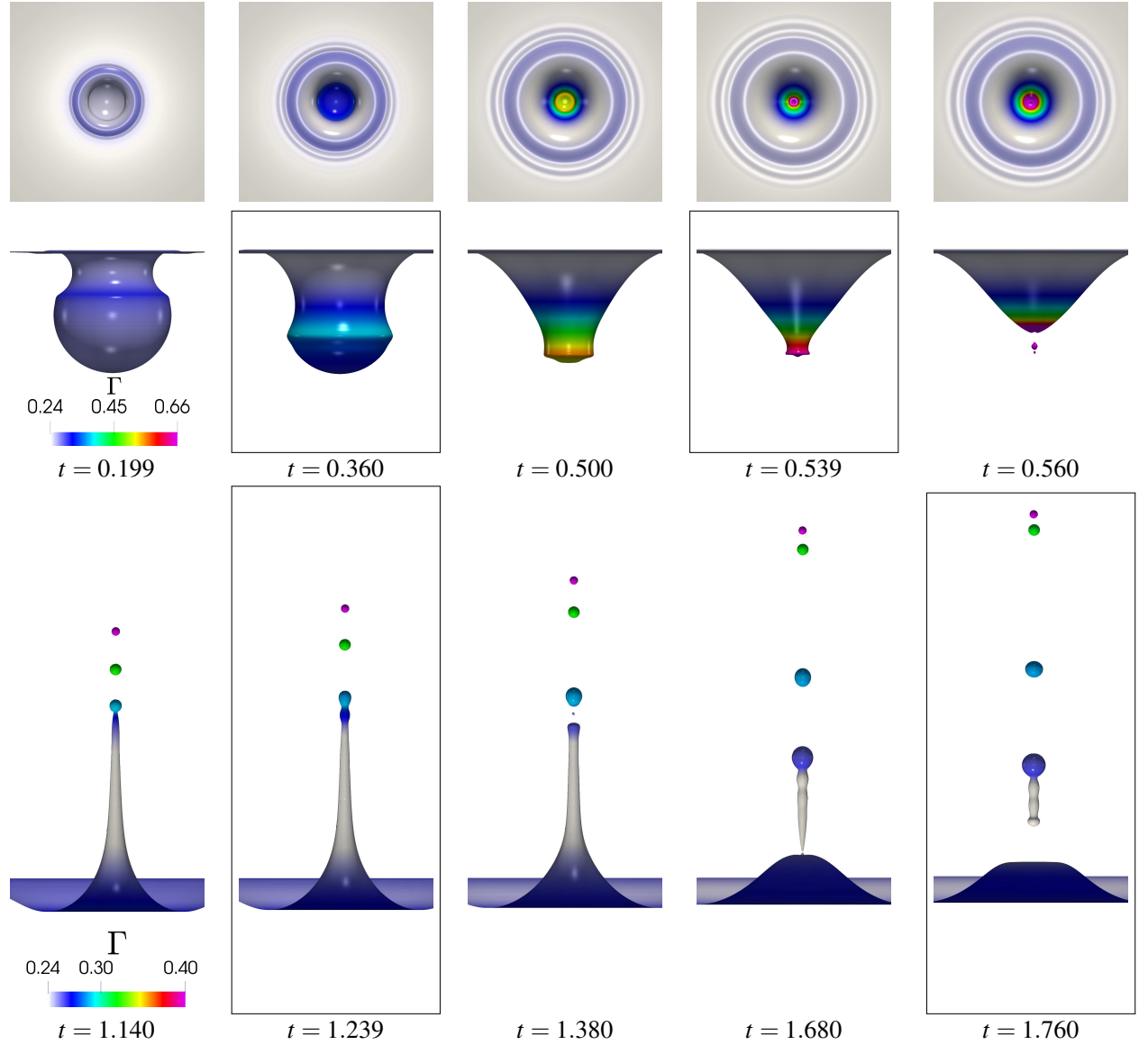


Fig. 6.4. Spatio-temporal evolution of the dynamics of the interface and of the interfacial surfactant concentration, Γ , with $La = 2 \times 10^4$, $Bo = 10^{-3}$, $Pe_s = 1$, $\beta_s = 0.9$, $Bi = 0.01$, $k = 1$, and $\Gamma_o = k/4$. The colour bars indicate the magnitude of Γ . Top row: top-view of the interface; middle row: side-view of cavity collapse; bottom row: Worthington jet (entrapped bubble is not shown).

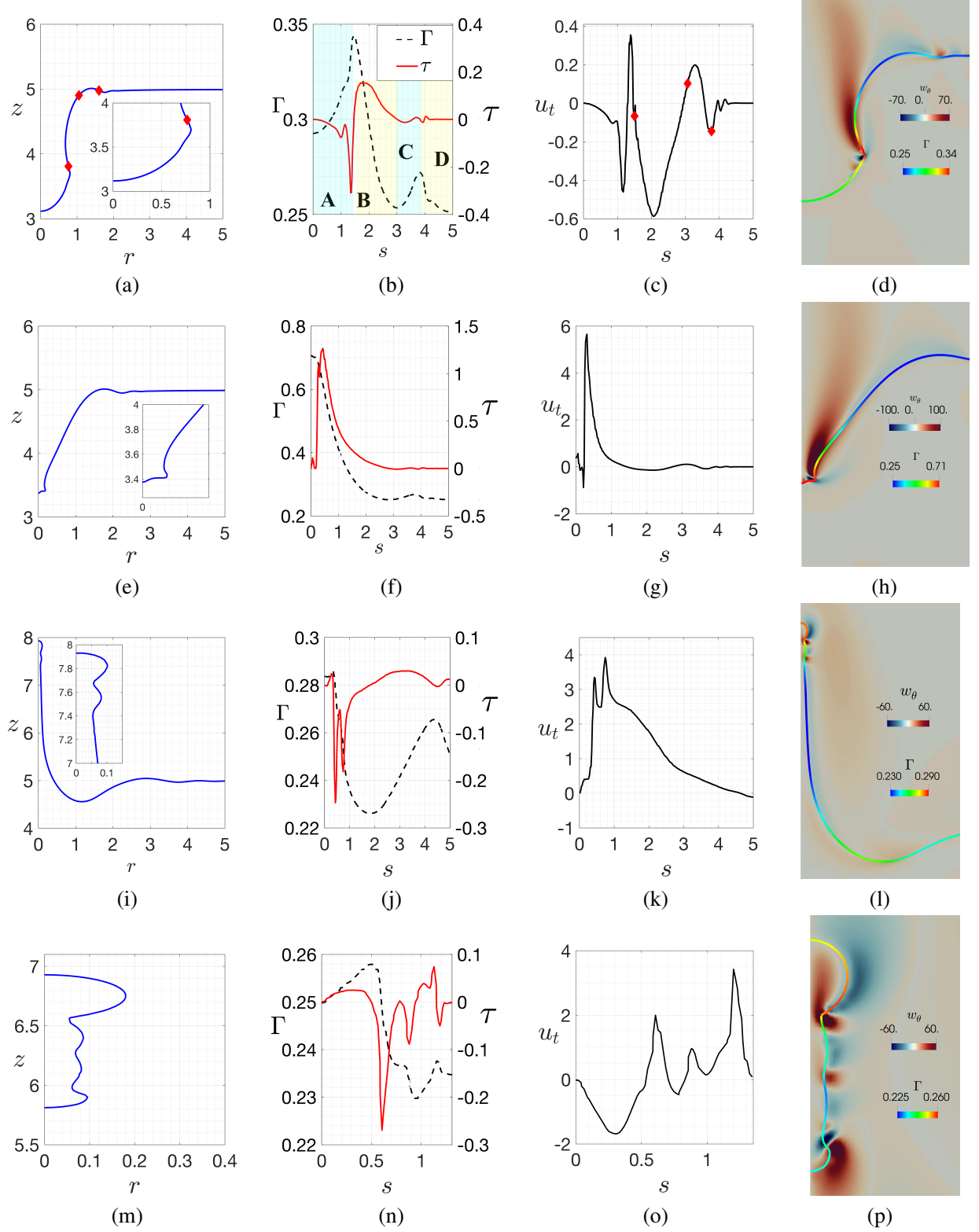


Fig. 6.5. Interface location, Γ and τ , u_t , and ω_θ are shown in columns one to four, respectively. In columns 1,4 and 2,3, the variation is with respect to the dimensionless radial coordinate, r , and arc length, s , respectively. Panels (a)-(d), and (e)-(h) show the cavity collapse dynamics $t = 0.360$ and $t = 0.539$, respectively, (i)-(l) the Worthington jet at $t = 1.239$, and (m)-(h) the retracting ligament at $t = 1.760$. The insets in (e) and (i) respectively focus on the bottom of the collapsing cavity, and the oscillations at tip of the Worthington jet that will eventually lead to its breakup. A description of regions 'A'-'D' in (b) is provided in the text. The parameter values are the same as in figure 6.4.

stagnation point ($s \sim 1.4$), where surfactant accumulates, Γ is highest, and the magnitude of τ is largest. This occurs in the region where ω_θ changes sign as the stagnation point is created (see figure 6.5d) corresponding to the capillary wave moving towards the bottom of the bubble.

Figure 6.5e-h shows the dynamics at $t = 0.539$ prior to the cavity collapse. The stagnation point where the surfactant accumulates has moved downward to the bottom of the cavity and the magnitude of ω_θ has increased in comparison to that in figure 6.5d. The interfacial surfactant concentration reaches its maximum value as the surfactant-laden capillary wave converges on the flow origin. The Marangoni stresses drive motion from high to low Γ regions and therefore act to oppose the flow, as indicated by the fact that both $\tau > 0$ and $u_t > 0$ over the majority of the spatial domain except in the close vicinity of the bottom of the cavity.

Figure 6.5i shows a snapshot of the jet for $t = 1.239$ in a situation of pinch-off ‘escape’ with a bulbous region formed at its tip. From figure 6.5j, we observe that Γ has two peaks: one at the jet tip, and a lower one far upstream. Figure 6.5l also shows that the change in the sign of ω_θ is linked to the Γ distribution in the bulbous region. The associated τ distribution is such that $\tau < 0$ between the bottom of the jet and close to the bulbous region at the jet tip (that is for $0.4 < s < 1.9$), and $\tau > 0$ elsewhere including in the bulbous region. Flow is driven by capillarity from this region towards the quasi-cylindrical jet body and, from figure 6.5k, it is seen that $u_t > 0$ over the whole domain. This suggests that Marangoni stresses oppose this capillary-induced motion driving flow from the bottom of the jet towards the bulbous region. When these stresses are not sufficiently strong to overcome the Rayleigh-Plateau instability, an ejection of a droplet occurs after the pinch-off of the jet tip. The first drops detached from the tip are characterised by high interfacial concentration while successive droplet detachments have lower Γ , as demonstrated in figure 6.4 for $t \geq 1.114$.

At $t = 1.680$ (see figure 6.4), the Worthington jet pinches off from its base forming an elongated ligament thread. Capillary waves develop on the ligament surface, leading to interfacial oscillations as the detached ligament transitions to a spherical drop. In figure 6.5m-p, we have isolated the retracting ligament shown at $t = 1.760$ from the rest of the flow. In figure 6.5o, we observe the formation of four stagnation points at $s = 0.55, 0.7$, and 0.84 , which are connected to the change in the distributions of Γ and τ . From figure 6.5n,o, it is also seen that the Marangoni stresses oppose ligament pinchoff since $\tau > 0$ and $u_t < 0$ ($\tau < 0$ and $u_t > 0$) for $0 \leq s \leq 0.55$ ($0.55 \leq s \leq 0.7$). For $0.7 \leq s \leq 0.84$ ($s > 0.84$), the Marangoni stresses oppose (aid) the stretching of the ligament as $\tau < 0$ and $u_t > 0$ ($\tau > 0$ and $u_t > 0$). Close inspection of ω_θ (see figure 6.5p) reveals that high vorticity production is observed close to the first stagnation point, which corresponds to the ligament ‘neck’. As shown by Constante-Amores et al. (2020a), the presence of such high vorticity regions near the neck is a requirement for the Marangoni-driven inhibition of capillary-induced ‘end-pinching’ of retracting surfactant-laden ligaments.

Figure 6.6a shows the temporal evolution of the jet-tip from the moment after the ejection of a jet-droplet to its next capillary singularity. The formation of a bulbous edge on the jet-tip is driven by capillarity (at $t = 1.120$). The estimated Oh number for the tip, using the jet radius as a reference, is $Oh \approx 0.02$. Therefore, we are still in the region of low Oh number, and consequently, the inhibition of the ‘end-pinching’ mechanism, identified by Constante-Amores et al. (2020a) can be invoked in order to rationalise the flow behaviour in this case. By close inspection of τ and u_{tr} (the radial component of the tangential velocity u_t), it is possible to identify that Marangoni-induced flow prevents the capillary breakup and reopens the neck of the jet-tip ($t = 1.140$). The reason behind the reopening of the neck is the suppression of the stagnation point close to the neck due to the Marangoni-induced flow brought about by the surfactants (see figure 6.6d). As was shown by Constante-Amores et al. (2020a), two stagnation points close to the neck are necessary for capillary breakup to occur (see figure 6.6e).

In order to isolate the surface tension-reducing effects of surfactants from those associated with Marangoni stress-formation, we show in figure 6.7a snapshots of the interface at $t = 0.44$, 0.496 , and 0.500 for the surfactant-free, surfactant-laden but Marangoni-suppressed, and full-Marangoni cases, respectively, prior to cavity-collapse for the same parameters as in figure 6.5. These times were chosen at identical spatial locations of the bubble rear in the axis of symmetry ($z \sim 3.28$). For the Marangoni-suppressed case, the reduced surface tension value is calculated via replacing Γ by Γ_o in equation 1.26. The presence of surfactant has been shown to enhance capillary wave-damping by Asaki et al. (1995) due to the interfacial rigidification brought about by τ , and this is seen clearly in figure 6.7a: the size of the cavity is largest for the full-Marangoni case, at the same stage of the dynamics for the three cases considered.

The capillary pressure field shown in figure 6.7b,c for the surfactant-free and full-Marangoni cases is influenced heavily by the capillary pressure and, therefore, the local interfacial curvature and surface tension. From panels (b) and (c) of figure 6.7, it is seen that the pressure is highest immediately upstream of the capillary wave peak and this pressure gradient drives flow towards the lower-pressure region located at bottom of the cavity that coincides with the axis of symmetry. Furthermore, Marangoni stresses induce a recirculation zone close to the free surface as shown in figure 6.7c. In figure 6.7d, we also show the axial distribution of the pressure at the axis of symmetry and this displays a peak at the interface due to capillarity. Owing to the presence of surfactant, the surface tension is reduced, which leads to a concomitant fall in the pressure, as illustrated via comparison of figure 6.7b,c. The pronounced reduction in capillary pressure, due primarily to the accumulation of surfactant at the bottom of the cavity, is shown in figure 6.7d.

As mentioned above, the convergence of the capillary wave on the bottom of the cavity leads to the formation of a Worthington jet (Gordillo and Rodríguez-Rodríguez, 2019), which is shown in figure 6.7e for the surfactant-free, Marangoni-suppressed, and full-Marangoni cases for $t = 0.507$,

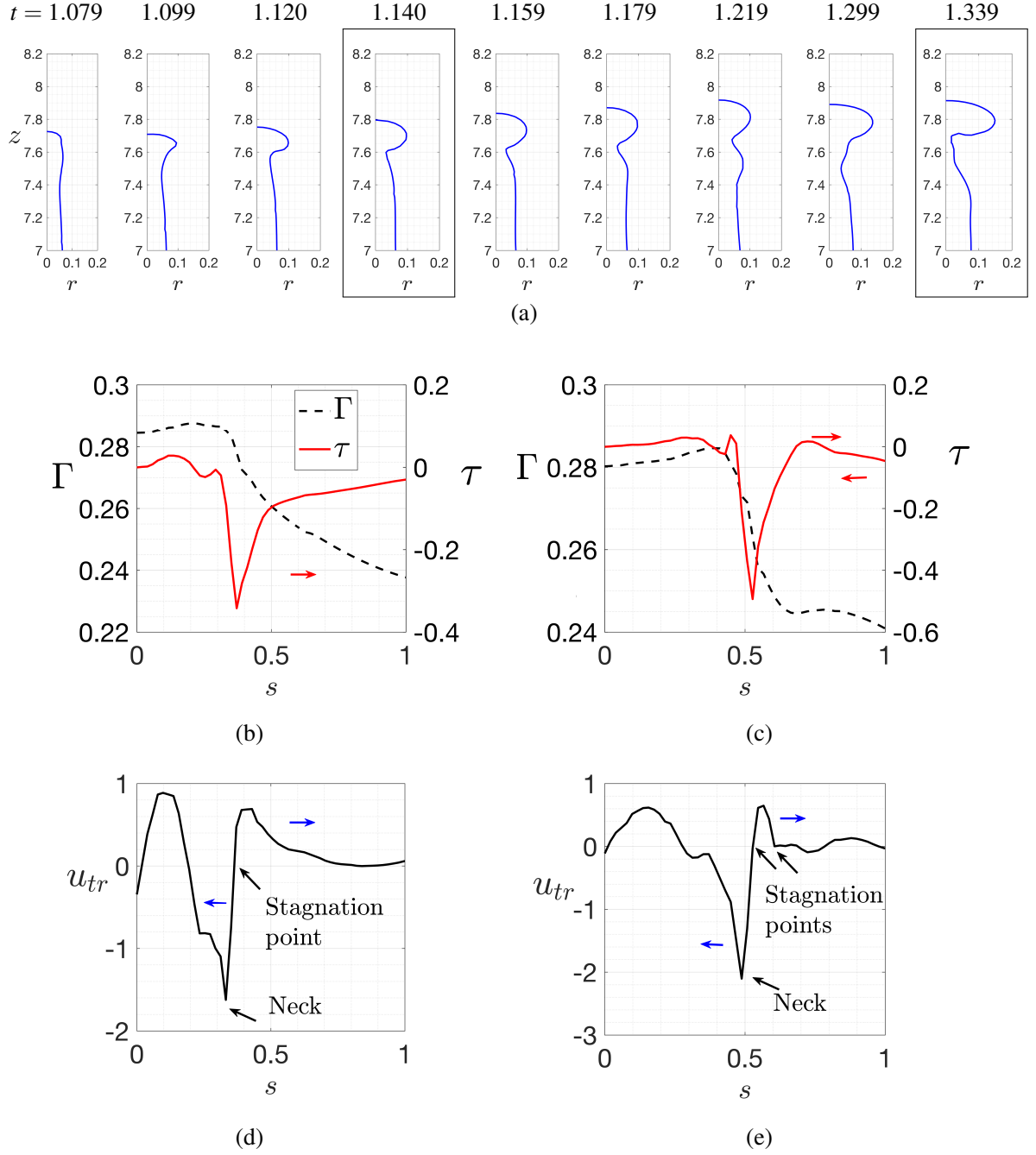


Fig. 6.6. (a) Spatio-temporal evolution of the jet-tip and its escape from pinchoff for the surfactant-laden base case. Panels (b) and (c) represent Γ and τ on the arc length s for time $t = 1.140$ and 1.339 , respectively; (d) and (e) represent the radial component of the tangential velocity u_{tr} as a function of the arc length s , respectively. The red arrows in (b) and (c) represent the direction of Marangoni-induced flow, and the blue arrows in (d) and (e) highlight the direction of the flow driven by capillarity. The value $s = 0$ corresponds to the tip of the jet at $r = 0$. The parameter values are the same as in figure 6.4.

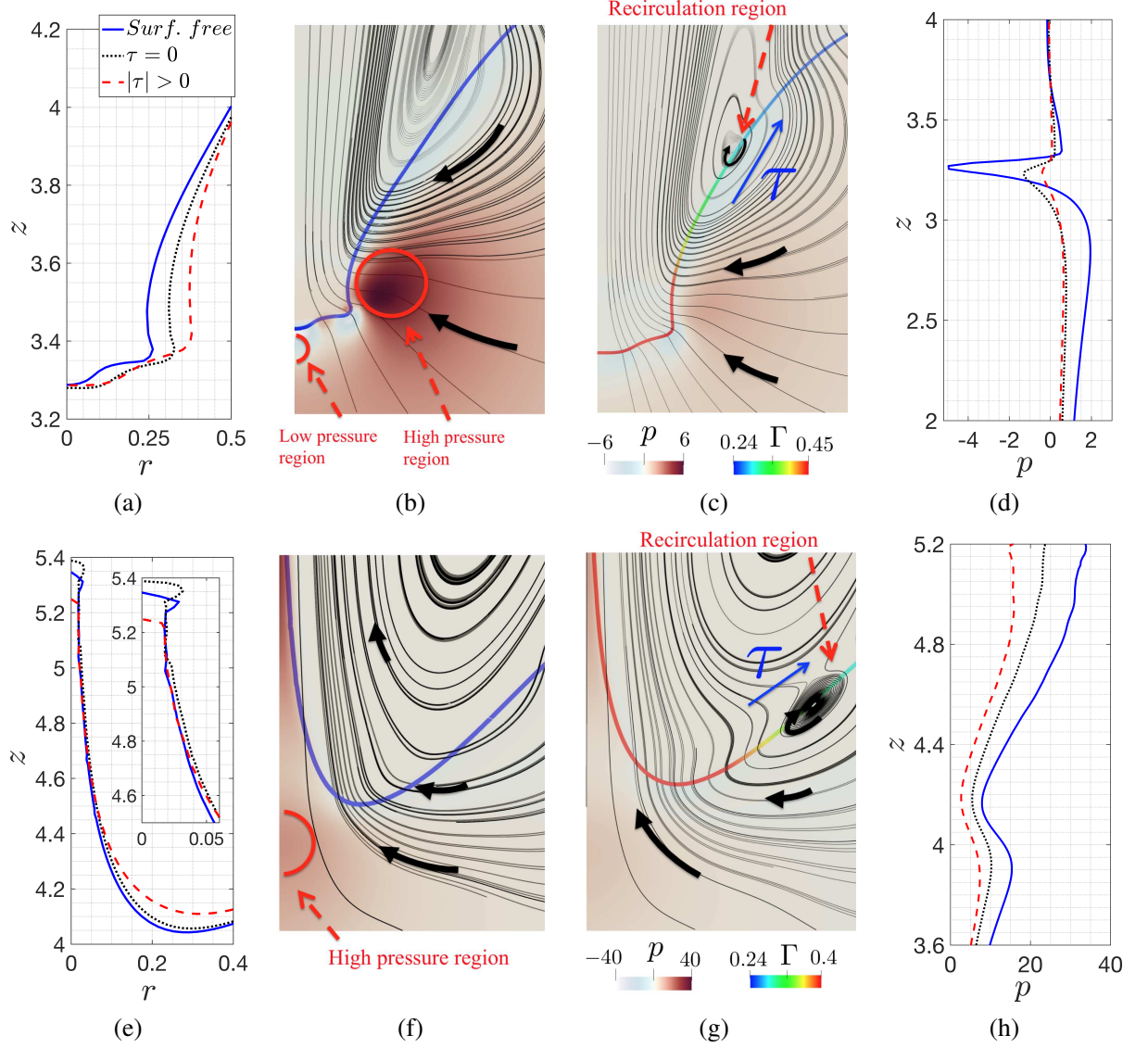


Fig. 6.7. Interface location, pressure field together with a representation of the streamlines for the surfactant-free and full-Marangoni ($|\tau| > 0$) cases, and pressure on the axis of symmetry, are shown in columns one to four, respectively. Panels (a-d) and (e-h) show the cavity collapse dynamics (at $t = 0.440, 0.496$, and 0.500 , for the surfactant-free, no-Marangoni $|\tau| = 0$, and full-Marangoni cases) and the Worthington jet (at $t = 0.507, 0.594$, and 0.619 , for the surfactant-free, $\tau = 0$, $|\tau| > 0$ cases), respectively. The parameter values are the same as those used to generate figure 6.4

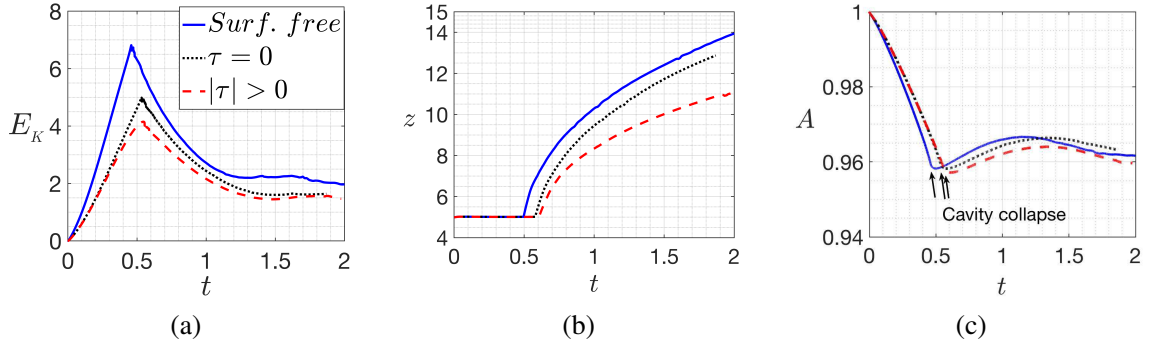


Fig. 6.8. Temporal evolution of kinetic energy, the maximal vertical interface location, and interfacial area (normalised by its initial value), (a)-(c), respectively, for the surfactant-free, full-Marangoni, and no-Marangoni cases, for the same parameters as in figure 6.4.

$t = 5.94$, and $t = 0.619$, respectively; again, these times are chosen at nearly identical spatial locations of the jet tip in the axis of symmetry. The larger pressure gradient associated with the surfactant-free case, discussed above, leads to longer jets, with more pronounced bulbous regions at their tips, in comparison to the full-Marangoni case where the retarding Marangoni stresses induce a recirculation zone close to the jet-base. Close inspection of figure 4e also reveals that the longest jets are associated with the $\tau = 0$ (rather than the surfactant-free) case wherein there is no Marangoni-induced retardation and for which La is lowest. As shown previously (Lai et al., 2018), decreasing La leads to faster, and thinner jets, with a greater propensity for breakup. As a result, a reduction in the number of ejected droplets is observed for the shorter, and slower, full-Marangoni jets: four (see figure 6.4), seven, and nine droplets (the latter two not shown) for the full-Marangoni, surfactant-free, and Marangoni-suppressed cases, respectively. The droplet numbers for surfactant free and Marangoni-suppressed cases agree with Berny et al. (2020). Finally, as shown in figure 6.7h, there is an adverse pressure gradient in all cases, since capillarity drives flow from the bulbous region towards the jet base, which is largest for the surfactant-free case.

The immobilising effect of the Marangoni stresses can be seen in figure 6.8a in which we plot the kinetic energy, defined as $E_k = \int_V (\rho \mathbf{u}^2 / 2) dV$, where Marangoni stresses reduce the maximal and asymptotic values of E_k in comparison to the surfactant-free and no-Marangoni cases. In figure 6.8b, we observe further that the motion of the interface is retarded maximally when Marangoni stresses are enabled fully. Inspection of figure 6.8c also reveals that the interfacial area A , normalised by its initial value, A_o , reduces over time leading to large Γ at the moment of interfacial vertical collapse at $t \sim 0.550$.

I have measured the droplet characteristics, in terms of their volume and their average interfacial surfactant concentration, at time $t = 1.76$, as shown in figure 6.4, and summarised the results in the table 6.1. The droplets are numbered depending on the order of ejection from the tip of the jet (i.e. the

Table 6.1. Droplet characteristics of surfactant-laden case

Droplet Number	V/V_o	Γ
1	2.374×10^{-4}	0.406
2	6.643×10^{-4}	0.307
3	2.279×10^{-3}	0.285
4	8.875×10^{-3}	0.247

highest droplet in the computational domain corresponds to the first ejected droplet). The volume of each droplet is normalised with the initial volume of the spherical bubble. This shows the multi-scale nature of the phenomenon. Moreover, the size of the first droplet, $r_d/R_o \sim 6\%$, which agrees with the experimental observations of Blanchard and Woodcock (1957) and Tedesco and Blanchard (1979), the empirical power law-dependence of Lewis and Schwartz (2004), and the theoretical scaling relationship proposed by Gañán-Calvo (2017). The predicted surfactant concentration of the ejected droplets is higher in value than the concentration of the liquid reservoir. This agrees with the experimental studies of Blanchard and Syzdek (1972) which were carried out within the context of examining bacterial concentrations in bursting bubbles.

6.4.2 Parametric study

Here, I have investigated the effect of system parameters on the dynamics of the bursting phenomenon beginning with the influence of β_s which controls the relative strength of Marangoni stresses. As shown previously, the presence of surfactant tends to rigidify the interface and delays the cavity collapse (see figure 6.9a). By increasing β_s , Marangoni stresses are strengthened leading to greater rigidification of the interface, and consequently, higher retardation of the cavity collapse (see figure 6.9a). This collapse-retardation is also accompanied by a lower surfactant convection towards the point of singularity (see figure 6.9c). Moreover, the strengthening of Marangoni stresses via increase in β_s leads to dampening of the tangential velocity along the interface (see figure 6.9e), thinner jets, and fewer ejected droplets (e.g. seven and four droplets for the lower and upper ends of the elasticity parameter β_s).

I have also analysed the effect of surfactant solubility on the bursting dynamics by varying the value of the Biot number, Bi . For the lower Bi values, the sorptive time-scales are larger than those associated with the interfacial dynamics and the Marangoni stresses, and consequently, the system behaves as if the surfactant were effectively insoluble. From the representation of the interfacial location of the cavity, we see that the desorptive time-scales dominate the system and, consequently, a reduction of Γ is observed as Bi increases (see figure 6.10a) with a concomitant weakening of the Marangoni stresses which oppose cavity collapse. The increase in interfacial mobility, characterised by a rise in

the magnitude of u_t is also seen in figure 6.10e.

I also examine the effect of solubility on the jet dynamics whereupon we observe that at the lower end of the Biot number, the jet is slowest due to interfacial rigidification brought about by τ , as can be seen via the damping of u_t , shown in figure 6.10f. Higher gradients in Γ are observed for weakly-soluble case (see figure 6.10d), which leads to the highest strength of τ . With increasing Bi more interfacial surfactants migrate to the bulk and as a result gradients in Γ are reduced, leading to an overall weakening of the Marangoni stresses. Finally, we study the effect of solubility on the number of ejected droplets. As before, the desorption of surfactant from the interface as Bi increases yields weakening of τ and, subsequently, the surfactant does not prevent ‘end-pinching’ of the jet-tip from which a larger number of droplets are ejected than in the low Bi case; for $Bi = 1$, seven droplets are ejected in comparison with the four droplets produced by the weakly-soluble case characterised by $Bi = 0.01$.

6.5 Future research

By conducting 3D simulations obviates the need for symmetry assumptions and accommodates naturally the occurrence of possible symmetry-breaking events, for instance, as breakup is approached, or during the post-breakup re-coalescence of satellite droplets. Although the results of the simulations presented in the previous section are axisymmetric in nature, it would not be the case across the ranges of parameters studied (e.g., for large Bond numbers).

Future research avenues for study are to perform numerical simulations featuring three dimensional behaviours occurring for large Bond numbers ($Bo \geq 0.5$). It has been shown by Ghabache (2015) that at large values of Bo , the bursting outcome can be either axisymmetric or purely three-dimensional producing an inclined Worthington jet. Thus, the bubble initialisation requires taking into account the entirety of the bubble: the immersed cavity, the cap, and the meniscus. If the hole formation is located at the extreme top of the cap, an axisymmetric outcome can be expected; whereas, if the hole is located anywhere else on the cap, three-dimensional cap retraction will certainly affect the behaviour of the collapsing cavity to finally culminate in an inclined Worthington jet, and subsequently a complex droplet detachment. An example of a non-axisymmetric bubble bursting is shown in figure 6.11 in which an additional capillary singularity in the side of the bubble is predicted to form another entrapped bubble.

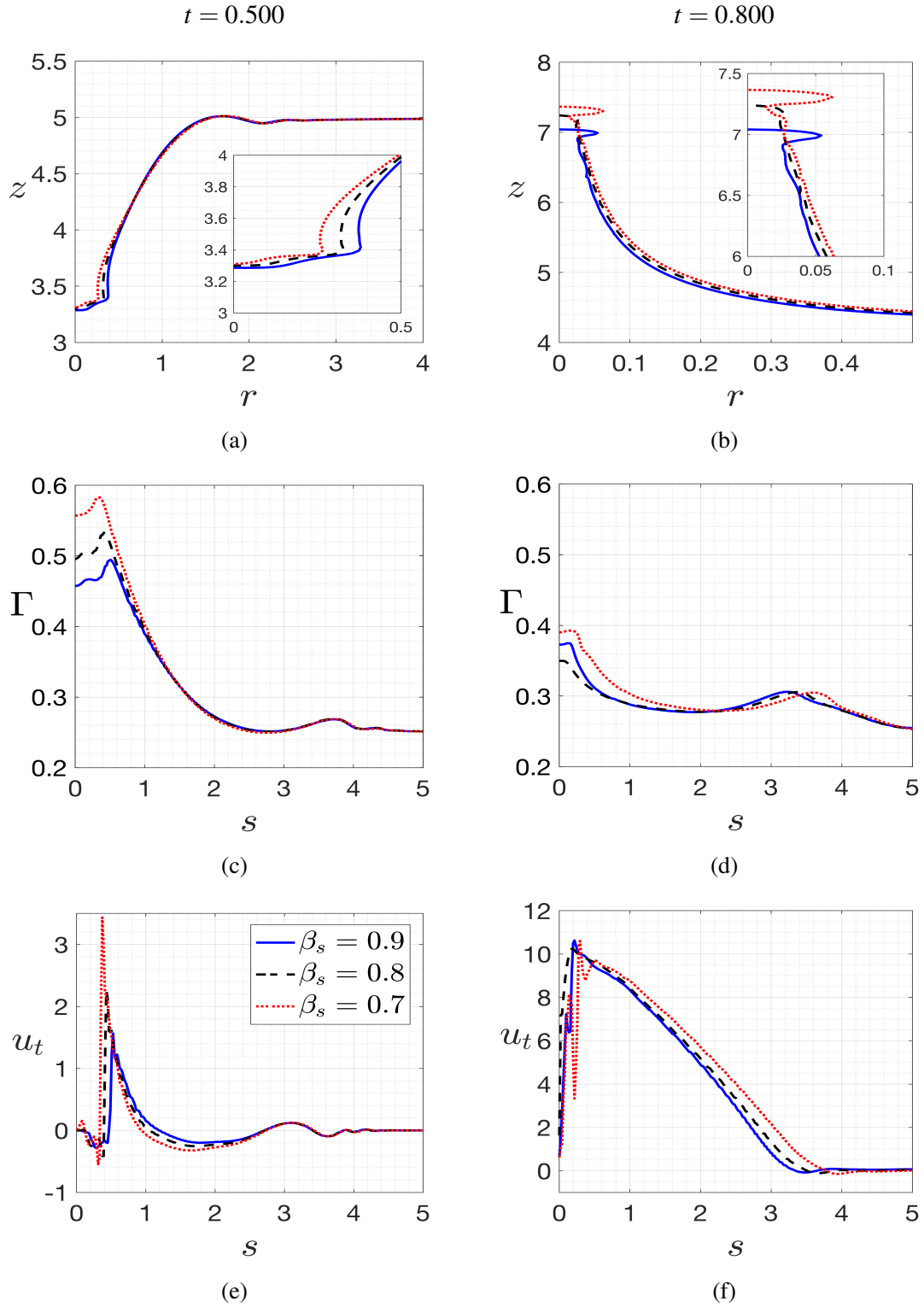


Fig. 6.9. Effect of the elasticity number, β_s , on the bursting dynamics for $La = 2 \times 10^4$, $Bo = 10^{-3}$, $Pe_s = 1$, $Bi = 0.01$, $k = 1$ and $\Gamma_o = 1/4$. Panels (a) and (b) represent the interfacial shape, (c) and (d) the interfacial surfactant concentration Γ along the arc length s , and (e) and (f) the tangential velocity u_t along s , during the cavity collapse at $t = 0.500$ and the Worthington jet at $t = 0.800$, respectively.

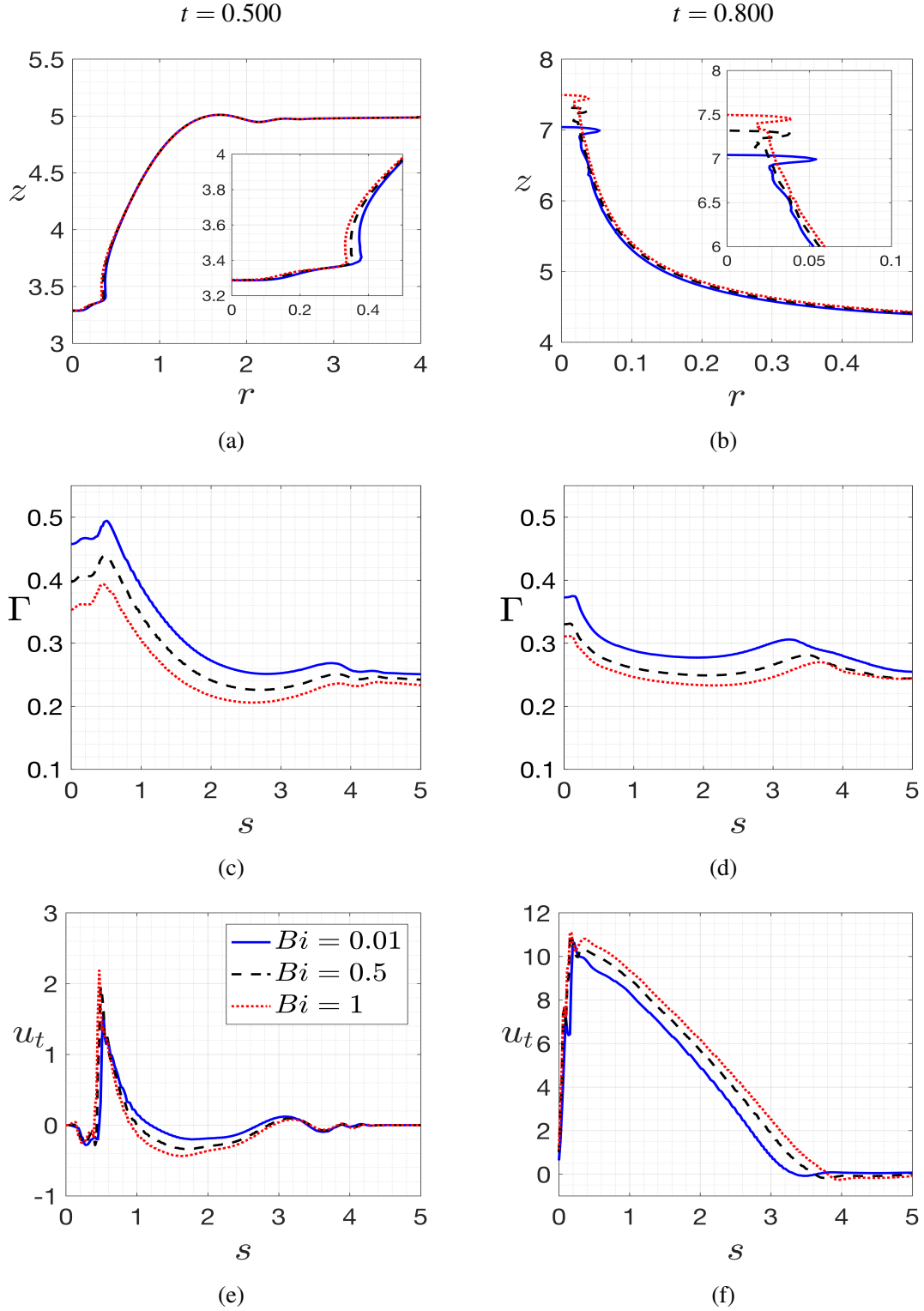


Fig. 6.10. Effect of the Biot number, Bi , on the bursting dynamics for $La = 2 \times 10^4$, $Bo = 10^{-3}$, $Pe_s = 1$, $\beta_s = 0.9$, $k = 1$ and $\Gamma_o = 1/4$. Panels (a) and (b) represent the interfacial shape, (c) and (d) the interfacial surfactant concentration Γ along the arc length s , and (e) and (f) the tangential velocity u_t along s , during the cavity collapse at $t = 0.500$ and the Worthington jet at $t = 0.800$, respectively.

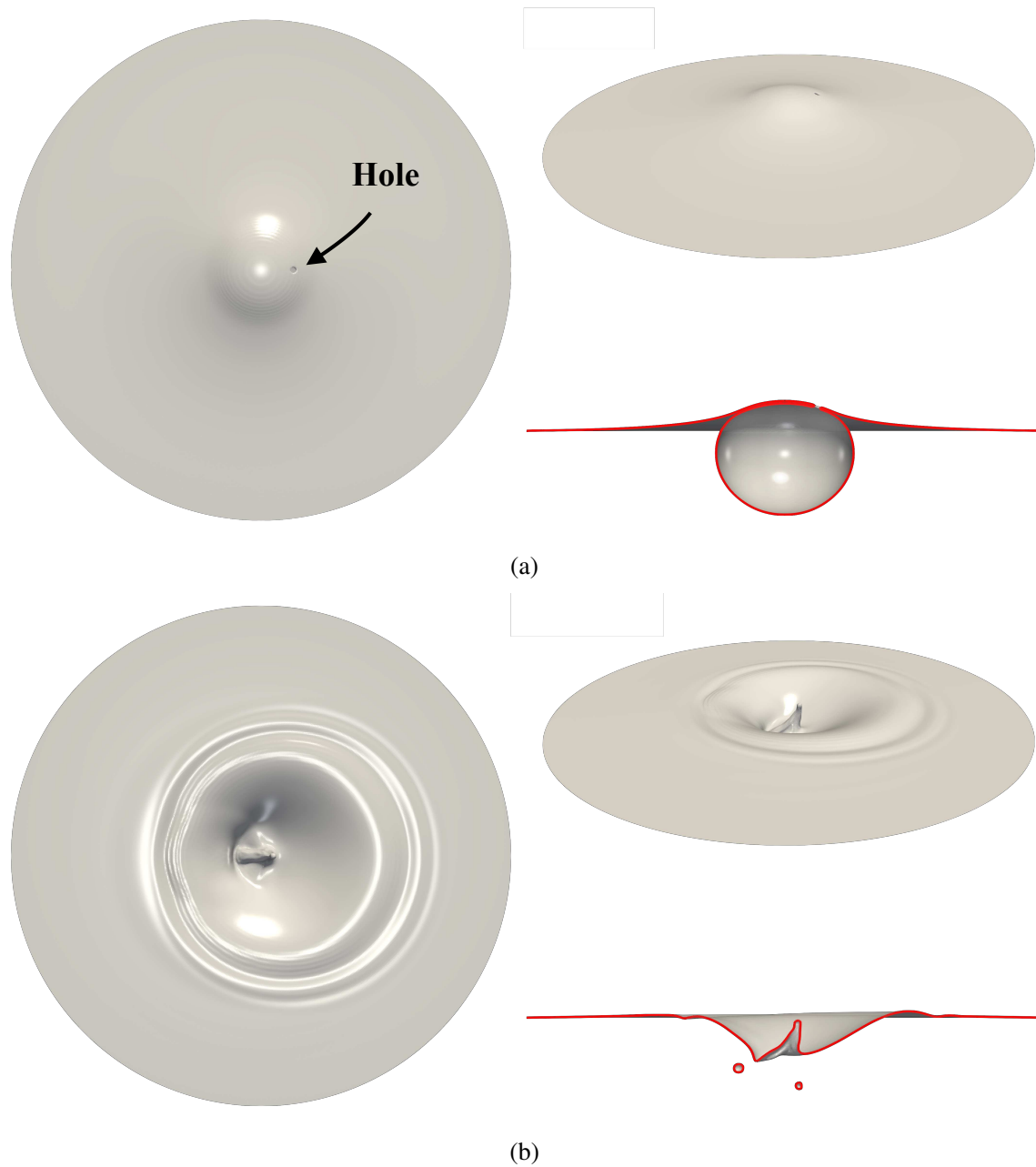


Fig. 6.11. (a) Initialisation of resting bubble with an artificial hole on its cap side, when $Bo = 0.5$. (b) After its cavity collapse, the non-axisymmetric capillary waves culminate in the formation of an inclined Worthington jet (at $t = 2$).

6.6 Concluding remarks

The effect of Marangoni-induced flow, brought about by the presence of surfactant, on the dynamics of a bubble bursting through an interface was studied using a hybrid front-tracking/level-set method. Our results indicate that a surfactant-covered toroidal capillary wave forms, following the collapse of the cavity, whose motion is retarded by the surfactant-induced Marangoni stresses; these stresses drive flow from regions of high surfactant concentration (low surface tension) to low concentration (high tension) regions. The immobilising effect of the surfactants due to the Marangoni stresses is also observed via the marked reduction in the system kinetic energy and the generation of shorter, and slower, Worthington jets. The breakup of these jets is accompanied by the formation of fewer droplets in comparison to the surfactant-free case. This behaviour is associated with the ‘end-pinching’ mechanism of the jet-tip and the presence of surfactant promotes the neck re-opening through Marangoni-flow, induced by the formation of surfactant concentration gradients, and not only via lowering of the mean surface tension value. Finally, we have examined the role of the elasticity number β_s which is an important parameter that controls the strengthening or weakening of Marangoni stresses along the interface. In a similar way, the surfactant solubility, via the variation of Biot number Bi , was also examined in this study.

This chapter is of great importance for breaking waves phenomenon in which the entrainment of air leads to bubble creation, in which the smallest bubbles dissolve entirely, and the largest bubbles get back to the gas-liquid interface where their bursting generates jet-droplets. The ocean surface is composed by a microlayer with the presence of biological material, toxins, salts, organic components or oil (linked to ocean oil-spill) which change the dynamics of the system, and subsequently affecting the droplet size distribution. Future research avenues involve performing numerical simulations accounting for collective effects of bubbles bursting at the same time or the study of film-droplets from the thin interlayer from the bubble cap at higher Bond numbers.

Chapter 7

Drop-interface coalescence in the presence of surfactants

Related publication: Drop-interface coalescence in the presence of surfactants. *C. R. Constante-Amores*, A. Batchvarov, L. Kahouadji, S. Shin, J. Chergui, D. Juric and O. K. Matar. *J. Fluid Mech* (under review).

Summary

The phenomenon of a coalescence of drops at a flat interface is a canonically singular problem in two-phase fluid mechanics as a result of the associated topological change, and subsequently the elucidation of the physical mechanisms has received a significant interest. In this chapter, I have proved that Marangoni-induced flow is the responsible for the inhibition of the partial coalescence, and consequently the reopening of the neck. Additionally, a parametric study considering the strength, and sorption and desorption kinetics have been performed.

7.1 Introduction

The occurrence of coalescence of a droplet with a flat interface has been observed in a wide range of natural phenomena and industrial applications, such as emulsification processes (Ziegler and Wolf, 2005), rain/cloud formation (Raes et al., 2000) and atomisation (Villermaux, 2007). Since, the groundbreaking experiments from Charles and Mason (1960) over half a century ago, the coalescence of droplets has driven a high research interest. However, its physical understanding did not come until the

development of the high-speed photography and computational methods (Thoroddsen and Takehara, 2000; Blanchette and Bigioni, 2006).

The draining of the fluid between the droplet and the bulk leads to the formation of a thin fluid layer connecting the droplet with the free surface. When the thickness of this layer is sufficiently small, van der Waals forces trigger its rupture with the formation of a hole. Then, the hole retracts driven by capillarity (Eggers et al., 1999; Kavehpour, 2015; Thoroddsen and Takehara, 2000), and the interfacial dynamics is solely governed by the Ohnesorge number Oh , which measures the importance of viscous and capillary forces. The interfacial dynamics of the coalescence phenomenon could be divided into three regimes depending on its order of magnitude: the inertial/capillary coalescence regime ($Oh \ll 1$) which is characterised by nearly inviscid liquid and the dynamics are surface-tension-driven; the viscous/capillary regime ($Oh > 1$) in where the viscous forces play a major role, and control the coalescence dynamics, and an intermediate regime which bridges the previous two ones (e.g., competition between viscous and nor surface tension forces).

Thoroddsen and Takehara (2000) observed the ‘coalescence-cascade of a drop’ in which the drop coalescence leads to the generation of a daughter droplet which results in a cascade of self-similar events until the coalescence process is completed. The process of formation of a secondary droplet or a daughter droplet is known as ‘partial coalescence’, and its physical understanding came from Blanchette and Bigioni (2006), who showed that the fate of the dynamics depends solely on the competition between the vertical and horizontal pulls (i.e., the former aids the total coalescence and the later aids the capillarity singularity), and its capillary singularity is not caused by a Rayleigh–Plateau instability. They also provided with an extensive phase diagram depending on Bo - Oh showing the boundaries where partial and total coalescence are expected.

The situation when the droplet and the liquid reservoir are made of different fluids has also been considered over the past decades. The situation is characterised by the formation of surface tension gradients triggering the generation of Marangoni stresses on the plane of the interface. The presence of Marangoni stresses change the fate of the coalescence as a result of the flow-induced from low to high surface tension regions. In the coalescence of a water-droplet into an ethanol-reservoir, Blanchette et al. (2009) and Sun et al. (2018) observed the ejection of a secondary droplet from the summit of the system (during the vertical stretching of the droplet), which is driven by Marangoni-induced flow. The variation of surface tension can also be triggered by chemical surfactants, as it was shown by Teng et al. (2019), who performed experimental work for the coalescence of an aqueous drop with an organic/aqueous interface. Their findings agreed qualitatively with the numerical work performed by Martin and Blanchette (2015). Shim and Stone (2017) observed that the presence of surfactant leads to the ‘damped-coalescence-cascade mechanism’, in which the time for air-drainage between the droplet and the interface is reduced, as a result of the Marangoni-induced flow enhancing the air drainage.

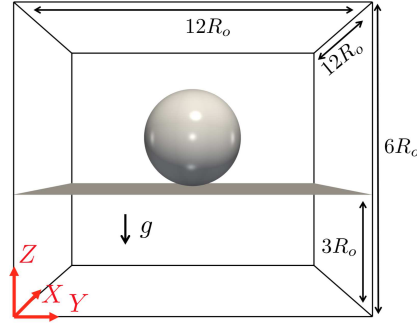


Fig. 7.1. Initial shape of the droplet resting close to the interface, highlighting the computational domain of size $(12R_o \times 12R_o \times 6R_o)$ (not-to-scale) in a three-dimensional Cartesian domain $\mathbf{x} = (x, y, z)$; the Cartesian resolution is 386^3 .

Although, it was demonstrated by Martin and Blanchette (2015) that surfactant is the responsible for the inhibition of the partial coalescence, a lack of explanation as to the cause of this inhibition, and other significant insights into the flow fields close to the pinch-off were missing in Martin and Blanchette (2015), and this is the main scope of this chapter. Additionally, this chapter overcomes the numerical difficulties presented by Martin and Blanchette (2015) in terms of taking into account the non-linear relation between Γ and σ which has a central importance in non-diluted systems, and taking the density and viscosity ratios corresponding to water-air (their ratios were limited to ten). Recently, Houssainy et al. (2020) showed that the viscosity of the surrounding fluid plays a major role in the size of the secondary droplet. The numerical predictions are benchmarked against the experimental observations from Blanchette and Bigioni (2006). On this basis, the chapter is organised as follows: Section 7.2 shows the problem formation and numerical setup, Section 7.3 presents the Results which are focused on the genesis of the inhibition of the capillary breakup, and a parametric study accounting for solubility is presented at the end of the chapter.

7.2 Problem formulation and numerical configuration

The numerical simulations were performed by solving the two-phase Navier-Stokes equations in a three-dimensional Cartesian domain $\mathbf{x} = (x, y, z)$ (see figure 7.1). A hybrid front-tracking/level-set method was used to treat the interface, where surfactant transport was resolved both in the bulk and on the interface (Shin et al., 2018). Here, and in what follows, all variables will be made dimensionless (represented by tildes) using

$$\tilde{\mathbf{x}} = \frac{\mathbf{x}}{R_o}, \quad \tilde{t} = \frac{t}{T}, \quad \tilde{\mathbf{u}} = \frac{\mathbf{u}}{U}, \quad \tilde{p} = \frac{p}{\rho U^2}, \quad \tilde{\sigma} = \frac{\sigma}{\sigma_s}, \quad \tilde{\Gamma} = \frac{\Gamma}{\Gamma_\infty}, \quad (7.1)$$

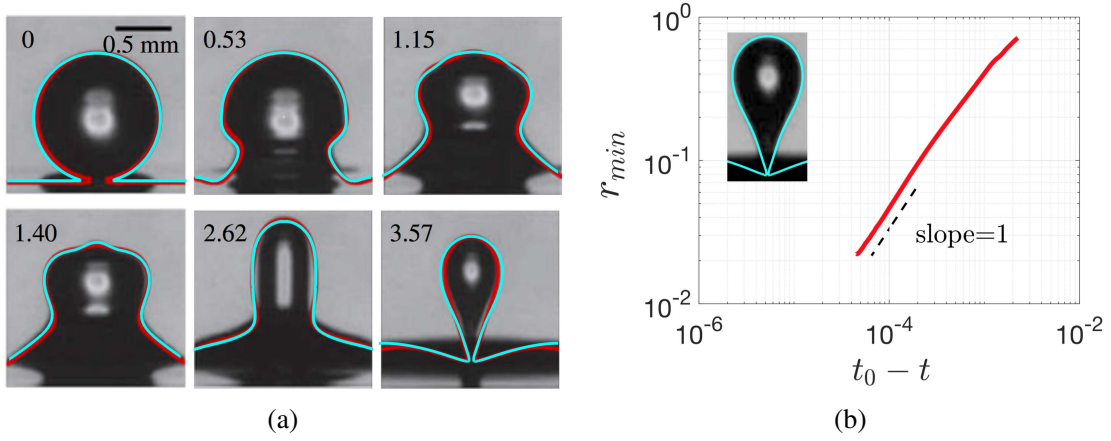


Fig. 7.2. (a) Comparison of surfactant-free simulation from our numerical method (blue line) with experimental results reported by Blanchette & Bigioni (2006) of an ethanol droplet in air prior to its interfacial singularity. Red contours correspond to the numerical predictions by Deka et al. (2019). (b) Additionally, we show the temporal evolution of the radius neck depending on the capillary breakup time t_0 which agrees with the inertial-viscous scaling theory (Eggers, 1993).

where, t , $\mathbf{u}$, and p stand for time, velocity, and pressure, respectively. The physical parameters correspond to the liquid density ρ , viscosity, μ , surface tension, σ , surfactant-free surface tension, σ_s , and gravitational acceleration, g ; $T = \sqrt{\rho R_o^3 / \sigma_s}$ is the capillary time scale, hence the velocity scale is $U = R_o / T = \sqrt{\sigma_s / (\rho R_o)}$. The interfacial surfactant concentration, Γ , is scaled on the saturation interfacial concentration, Γ_∞ . As a result of this scaling, the dimensionless groups that appear in the governing equations are defined as

$$Bo = \frac{\rho g R_o^2}{\sigma_s}, \quad Oh = \frac{\mu}{\sqrt{\rho \sigma R}}, \quad (7.2)$$

$$Bi = \frac{k_d R_o}{U}, \quad k = \frac{k_a C_\infty}{k_d}, \quad Pe_s = \frac{U R_o}{D_s}, \quad Pe_b = \frac{U R_o}{D_b}, \quad \beta_s = \frac{\Re T \Gamma_\infty}{\sigma_s}, \quad \chi = \frac{\Gamma_{eq}}{\Gamma_\infty} = \frac{k}{1+k}, \quad (7.3)$$

where Bo stands for the Bond number and represents the ratio of gravitational to capillary forces; Oh is the Ohnesorge number that measures the relative importance of viscous to surface tension forces; Bi denotes the Biot number representing the ratio of characteristic desorptive to convective time-scales; k is the ratio of adsorption to desorption time scales; Pe_s and Pe_b are the interfacial and bulk Peclet numbers, respectively, and represent the ratio of convective to diffusive time-scales in the plane of the interface and the bulk, respectively; β_s is the surfactant elasticity number, which measures the sensitivity of the surface tension to the surfactant concentration; and χ stands for the fraction of surface covered by adsorbed surfactant.

The Marangoni stress, $\tilde{\tau}$, is expressed as a function of $\tilde{\Gamma}$:

$$\tilde{\tau} \equiv \nabla_s \tilde{\sigma} \cdot \mathbf{t} = -\frac{\beta_s}{1 - \tilde{\Gamma}} \nabla_s \tilde{\Gamma} \cdot \mathbf{t}, \quad (7.4)$$

where $\mathbf{t}$ is the unit tangent to the interface; tildes are dropped henceforth. The Marangoni time-scale, $\mu R_o / \Delta \sigma = O(10^{-4})$ s, as compared to the capillary and sorptive/desorptive time-scales, which are of $O(10^{-3})$ s and $O(10^{-3} - 10^{-4})$ s, respectively; thus Marangoni stresses will play a key role in the dynamics.

The dimensionless computational domain size is chosen as $(12R_o \times 12R_o \times 6R_o)$, which is found to be sufficiently large to render boundary effects negligible (same as Sun et al. (2018), and Martin and Blanchette (2015)). Hence a radial component is defined as $r = \sqrt{(x - x_o)^2 + (y - y_o)^2}$ where x_o and y_o are the abscissa and ordinate bubble position, respectively. Solutions are sought subject to Neumann boundary conditions on all variables at the lateral boundaries, $p = 0$ at the top boundary $z = 6R_o$, and no-slip at $z = 0$. Simulations are initialised as a droplet resting immediately above the free surface before its rupture. Its initial shape is determined by solving the Young-Laplace equation for $Bo = 10^{-3}$, which is sufficiently small to avoid the effect of gravity on the coalescence process. Therefore, gravitational effects will not disturb any dynamics resulting from the Marangoni stresses. To initialise the coalescence, the droplet is connected to the liquid bulk by a narrow neck (see figure 7.1). A similar approach has been used by Blanchette and Bigioni (2006), Blanchette and Bigioni (2009) and Martin and Blanchette (2015). For the soluble cases, the interfacial surfactant concentration is initialised as its equilibrium surfactant concentration given by χ , $\Gamma_o = \Gamma_{eq} = \Gamma_\infty \chi$

Figure 7.2 shows the validation of the numerical configuration and scaling-laws in terms of temporal evolution of the neck-radius. The numerical simulations have been benchmarked against the experimental results of Blanchette and Bigioni (2006) in terms of the spatio-temporal interfacial dynamics of the coalescence phenomena of an ethanol drop in air (see figure 7.2a). Additionally, I have included the interfacial dynamics predicted by Deka et al. (2019). The numerical results are given as snapshots of the interface location at times corresponding to the given by Blanchette and Bigioni (2006). It is evident from figure 7.2a that the numerical method is capable of predicting the spatio-temporal dynamics with good accuracy. Additionally, figure 7.2b shows the temporal evolution of the radius neck depending on the capillary breakup time t_o which is in good agreement with the inertial-viscous scaling theory proposed by Eggers (1993).

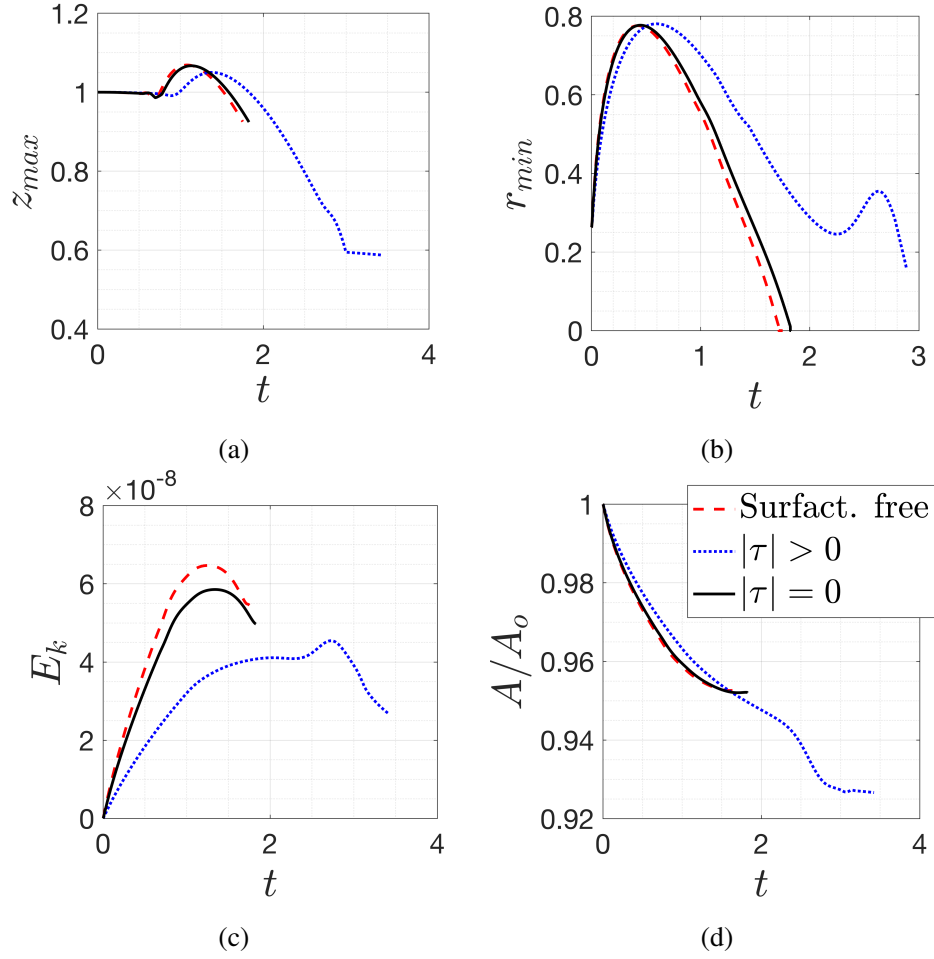


Fig. 7.3. Temporal evolution of the maximum vertical displacement of the interface, neck radius, kinetic energy and interfacial area; (a)-(d), respectively, for the surfactant-free, full-Marangoni, and no-Marangoni cases, for $Oh = 0.02$, $Bo = 10^{-3}$, $\beta_s = 0.5$, $Pe_s = 100$ and $\Gamma_o = 0.5\Gamma_\infty$

7.3 Results

I start the discussion of the results by presenting the immobilising effect of the surface-active agents through the analysis of the temporal dynamics of the maximum vertical stretching of the droplet, the neck radius, the kinetic energy and the interfacial area for the surfactant-laden case, which is characterised by $Oh = 0.02$, $Bo = 10^{-3}$, $\beta_s = 0.5$, $Pe_s = 100$, $\Gamma_o = \Gamma_\infty/2$.

Figure 7.3 shows the temporal dynamics of the previous parameters for the surfactant-free, surfactant-laden but Marangoni-suppressed and surfactant laden case when Marangoni stresses are enabled fully. The two-former simulations have been stopped after the capillary singularity, as the scope of this chapter is to elucidate the fundamental physics behind the escape of pinch-off. Turning attention towards the vertical stretching of the droplet (see figure 7.3a), the presence of surfactant retards and damps its maximum stretching in comparison to the Marangoni-suppressed or surfactant-free cases. The lower displacement of the interface in the axial direction for the surfactant-laden case is a result of the Marangoni stress inducing a downward pulling force (e.g., high surfactant concentration is accumulated on the summit of the droplet, see for example the τ -direction on 7.4 at $t = 1.028$).

Figure 7.3b shows the temporal evolution of the droplet-neck. As time evolves, the expansion of the droplet-neck is observed driven by capillarity as a result of the large interfacial curvature. For the three cases, the maximum horizontal stretching of the neck-radius happens up to $r \sim 0.75$; however a delay of the dynamics to get its maximum value is predicted for the surfactant laden case. For the surfactant-free case, the droplet-neck reduces its size yielding the horizontal collapse (i.e., capillary singularity) producing a daughter droplet. For the Marangoni-suppressed-case, it is observed that the mean reduction of the surface tension (i.e., reduction of capillary pressure) does not prevent the horizontal collapse of the droplet to its completion. Interestingly, when Marangoni stresses are enabled fully, a change of the fate of the coalescence is predicted: the inhibition of the capillary singularity, and subsequent the reopening of the droplet-neck. Therefore, it can be concluded that the reduction of the mean surface tension value is not the reason behind the escape from its capillary singularity, rather than the presence of tangential Marangoni stresses on the plane of the interface.

Figure 7.3c shows the kinetic energy, which is defined as $E_k = \int_V (\rho \mathbf{u}^2 / 2) dV$, where the density ρ is calculated with the help of a smoothed Heaviside function (i.e., is zero in the gas phase and unity in the liquid phase). The inspection of the kinetic energy plots show that the Marangoni-suppressed and surfactant-free cases have almost identical behaviour; however when Marangoni stresses are fully enabled, a strong decrease of the overall value of E_k is observed. The reduction of the kinetic energy is a result of the rigidification of the interface brought by Marangoni stresses (e.g., reduction of the interfacial tangential velocity).

Finally, figure 7.3d shows the normalised area, the normalised area tends to tail at lower values for the surfactant-free case. The surfactant-free and Marangoni-suppressed cases have similar behaviour.

Figure 7.4 displays the spatio-temporal interfacial dynamics for the surfactant-laden base case. At early times, a large capillary pressure is generated near the nucleated hole due to the high curvature of the interface joining the spherical droplet with the horizontal free surface. This capillary pressure leads to a rapid expansion of the hole (see $t = 0.137$) and the creation of a toroidal capillary wave, which travels toward the summit of the droplet (see $t = 0.685$). As time evolves, the topological changes lead to gradients in Γ (as it is observed at $t = 0.685$), the direction of τ has been drawn through arrows to show the direction of the Marangoni-induced flow. In the second row, the flow snapshots are related to the escape of pinch-off of the neck and its reopening. The highest concentration of surfactant has been displaced towards the neck at $t = 2.255$, which triggers an interfacial vertical pulling of τ towards the summit of the droplet, and an interfacial horizontal pulling towards the interface tail. The horizontal pulling overcomes the vertical one and prevents the pinch-off or capillary singularity, and subsequently the inhibition of the horizontal collapse of the droplet or the merging of the droplet with the bulk reservoir. Surprisingly, the generation of surface tension gradients on the plane of the interface triggers the formation of an interfacial cavity where the reverse of the curvature takes place, (similar behaviour as the bursting bubble phenomenon). Surfactant is accumulated at the bottom of the cavity (see for example $t = 3.180$).

The elucidation of fundamental physics related to the genesis of the capillary-breakup inhibition requires to depict the interplay between azimuthal vorticity w_θ with the surface. On this basis, figure 7.5 represents the vortex-surface interaction.

Figure 7.5 represents the vortex-surface interaction for the surfactant-laden and surfactant-free cases (corresponding to the top and row panels, respectively). The chosen snapshots of the surfactant cases correspond to the frames times from figure 7.4, whereas the surfactant free case snapshots correspond to their equivalent surfactant-free case in terms of the radius-neck size. For the surfactant-free case, the vorticity is confined mainly on the neck region as a result of the imminent interfacial singularity. This observation is similar to the findings presented for the ligament retraction prior to its capillary singularity in chapter 5. By comparing the vorticity field between the surfactant laden and the surfactant-free cases, a change in the vorticity-field pattern is observed, with a higher generation of vorticity near the interface for the surfactant-laden case as a result of the presence of surfactants. The generation of vorticity starts further up from the neck location rather than solely confined on the neck as the surfactant-free case. We observe that the vorticity is separated from the free surface and advected into the fluid bulk (this is in agreement with Ananthakrishnan and Yeung (1994)). The reason behind the vorticity separation is a result of w_θ which has shifted its direction close to the surface. The generation of secondary vorticity underneath of the free surface close to the neck is in agreement with

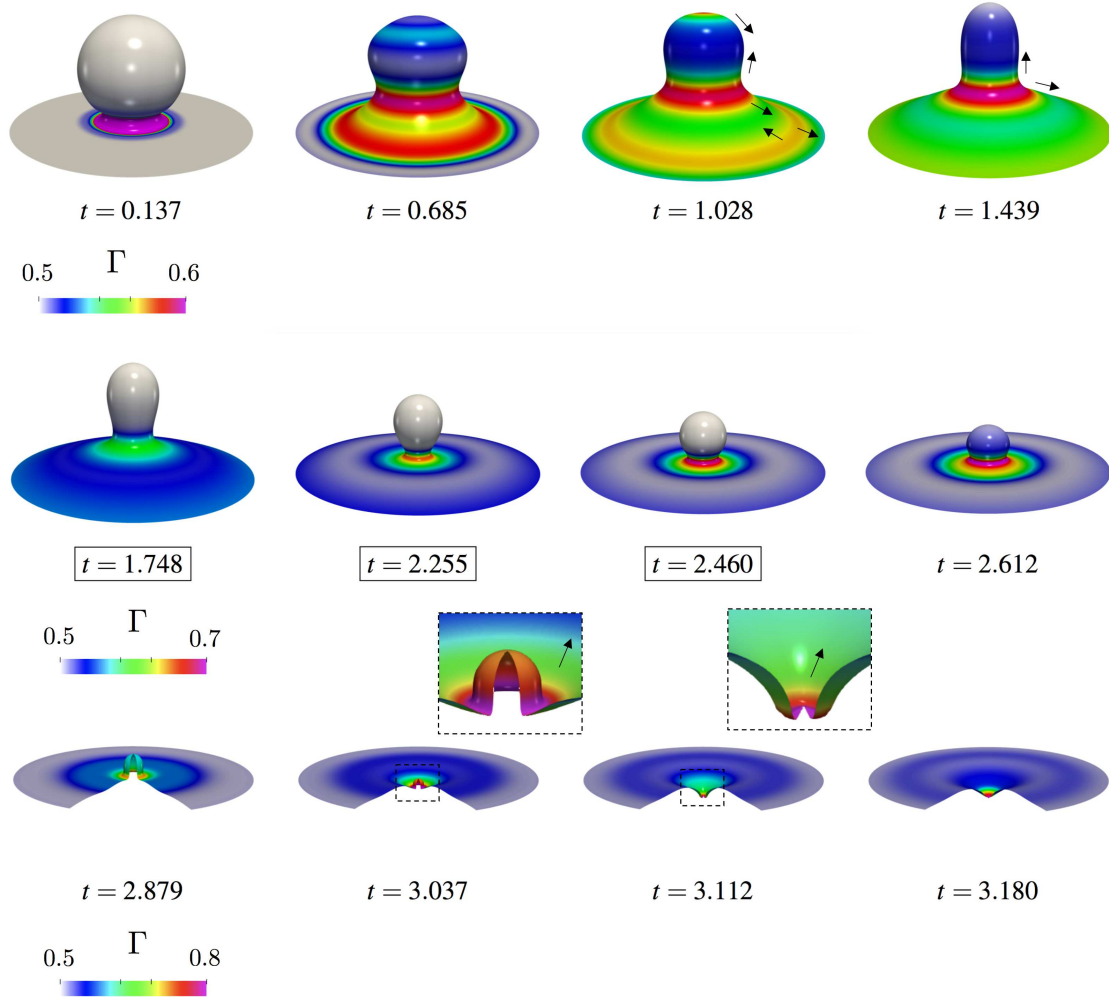


Fig. 7.4. Three dimensional representation of the Spatio-temporal interfacial dynamics when $Oh = 0.02$, $Bo = 10^{-3}$, $\beta_s = 0.5$ and $Pe_s = 100$. The colour represents the respective magnitude of Γ field, where appropriate scales are shown in each row. Solid arrows correspond to the direction of the Marangoni stresses τ . Magnified views of the interfacial cavity are also shown.

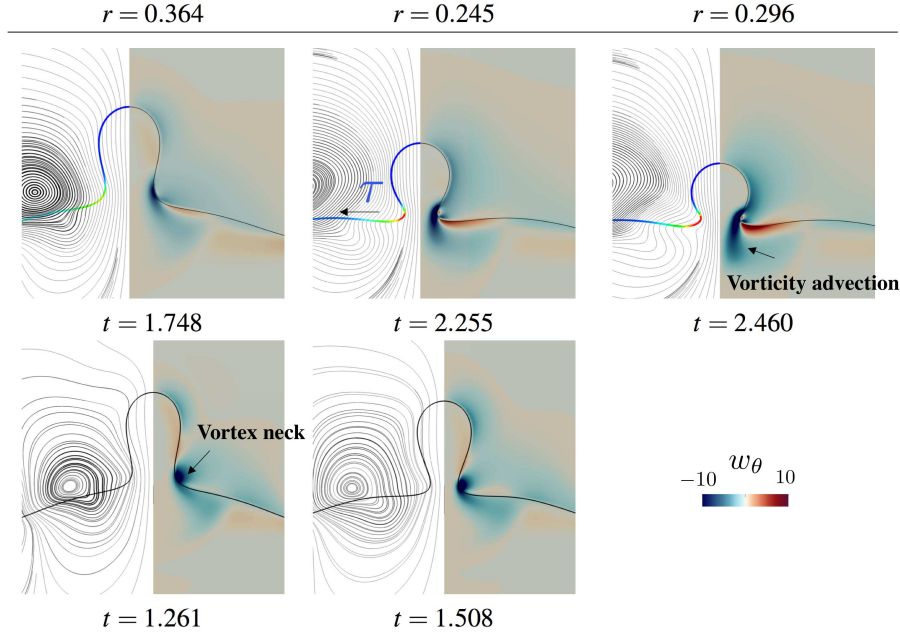


Fig. 7.5. Two dimensional representation of the vortex-surface interaction (i.e., w_θ) for the surfactant-laden (top row) and surfactant-free cases (bottom row). Columns correspond to equivalent neck radius size for both cases: $r = 0.364$, $r = 0.245$ and $r = 0.296$ for columns one to three, respectively. The colour represents the respective vorticity field.

Hirsa and Willmarth (1994). Therefore, it can be concluded that the higher vorticity production, and subsequently its advection towards the bulk triggers the reopening of the neck. On this basis, attention is turned towards the role of the Marangoni stresses for the production of vorticity.

Figure 7.6 has the purpose to identify the origin of the onset of the inhibition of the capillary singularity by depicting the close interplay between τ , Γ , and the vertical tangential velocity u_{tz} and radial tangential velocity u_{tr} at the same times shown in figure 7.5, for both surfactant-free and surfactant-laden base cases.

Figure 7.6a-d correspond to the surfactant-free and laden cases when $r = 0.364$. The first evident observation is the lower vertical stretching of the interface for the surfactant-laden case, as a result of the horizontal and vertical pulling by τ (see figure 7.6b), as the highest Γ is located underneath of the droplet-neck $s \sim 1.9$. The concentration gradient causes τ to act towards the top of the droplet (e.g., reducing the vertical downward pulling) and towards the tail of the droplet (e.g., opposing the horizontal pull towards the capillary singularity). The effect of Marangoni-induced flow in the coalescence dynamics can be observed in the streamlines (see figure 7.5 at $t = 2.460$). For the surfactant-laden case, the horizontal pull of τ towards the droplet tail induces the change of the streamlines pattern, in comparison to the surfactant-free case.

Figure 7.6e-h show the same interfacial fields (e.g., τ , Γ , u_{tz} , u_{tr}) at $r = 0.245$. As time evolves, the maximum value of Γ is displaced towards the neck of the droplet (see figure 7.6f), and τ induces flow-motion vertically and horizontally to aid the gradients of surfactant concentration. Figure 7.6f shows the existence of two peaks of different direction for τ . Prior to the neck $\tau > 0$, therefore τ acts towards the droplet-top retarding the collapse of the system; after the neck radius, $\tau < 0$, therefore τ acts towards the tail of the droplet (this horizontal pull can also be observed in the streamlines from figure 7.5 at $t = 2.460$). Additionally, by turning attention towards figure 7.6g and 7.6h, lower overall values of u_{tz} are predicted for the surfactant-laden case due to the rigidification of the interface. The minimum value of u_{tz} for both surfactant-free and surfactant-laden base cases are always located in the droplet-neck. Therefore, the interfacial rigidification brought by Marangoni can be observed in the oscillatory damping of the tangential velocity close to the tail of the droplet.

Finally, turning attention towards the effect of Marangoni stresses in the radial component of the tangential velocity. u_{tr} (see figure 7.6h), the surfactant-free case is characterised by the presence of a velocity peak ($P1$) close to the droplet-neck, and two stagnation points (e.g., the neck is located between these two stagnation points). The two stagnation points aid the fluid recirculation enhancing the vorticity generation mainly confined on the droplet-neck for the surfactant free-case (see figure 7.5). As time evolves, the peak $P1$ thins (i.e., increase of the vorticity) which yields the interfacial capillary singularity. Contrastingly, the inspection of the u_{tr} plot for the surfactant-laden case also shows the presence of a velocity peak; however, only one stagnation point is depicted near the neck (see figure 7.6h). Therefore, Marangoni-induced flow is capable of suppressing one stagnation point (figure 7.6h) close to the neck which yields the detachment of the vorticity boundary layer from the neck, and its advection towards the bulk of liquid reservoir. This behaviour is similar to the phenomenon explained in chapter 5 for the escape of capillary singularity during the capillary retraction of a liquid thread, and Hoepffner and Paré (2013), where they showed that the formation of a vortex ring plays the primary role in the escape from breakup of viscous ligaments in the absence of surfactants.

7.3.1 Parametric study

Here, I investigate the fate of the partial coalescence on system parameters related to solubility to make the problem more experimental friendly. Unless stated otherwise, the parameters remain fixed to their ‘base’ values: $Oh = 0.02$, $Bo = 10^{-3}$, $\beta_s = 0.5$, and $Pe_s = Pe_b = 100$.

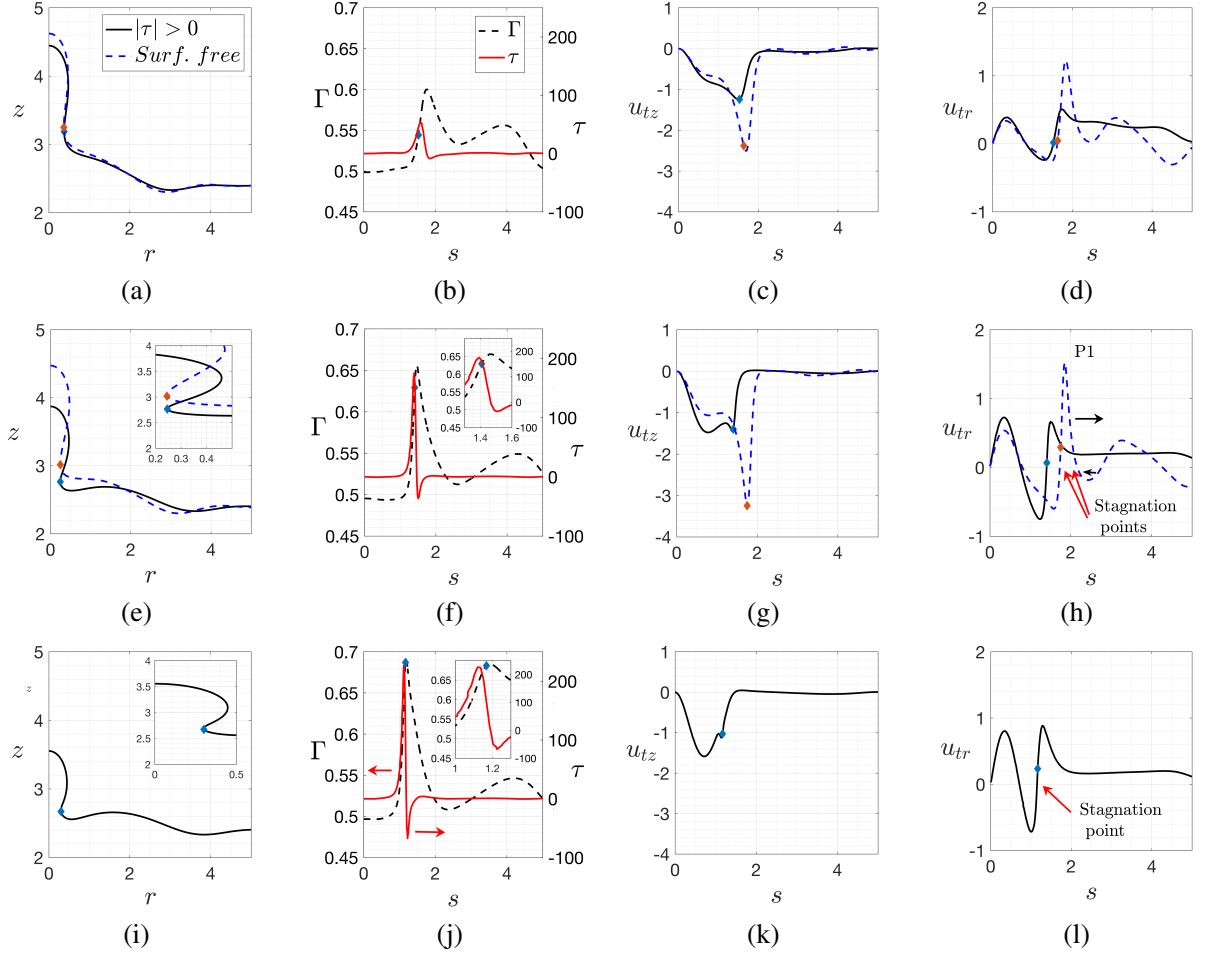


Fig. 7.6. Interface location, Γ and τ , u_{tz} and u_{tr} are shown in columns one to four, respectively, for the surfactant-free and surfactant-laden cases. In columns 1 and 2-4 the variation is with respect to the dimensionless radial coordinate and s , r , and arc length, s , respectively. The neck radius is $r = 0.364$, $r = 0.245$ and $r = 0.296$ for (a-d), (e-h) and (i-l), respectively. The parameter values and the times for the radius are the same as in Fig 7.4. The location of the neck has been marked with red and blue dots for the surfactant free and surfactant cases, respectively.

7.3.2 Effect of the solubility

Figure 7.7 shows the effect of the solubility on the temporal coalescence dynamics for some metric parameters (e.g., kinetic energy, vertical stretching of the interface, and droplet-neck radius) by a fixing value of $k = 1$, and exploring the range of $Bi = 0.1 - 10$. At the lower end of this range, the surfactant tends to act as insoluble, whereas at the upper end, surfactant tends to desorb from the interface, and the dynamics behave as a surfactant-free case. Initially, the surfactant concentration is uniformly distributed on the interface, and equal to $\Gamma_o = 0.5\Gamma/\Gamma_\infty$.

Turning attention towards figure 7.7a, which shows the kinetic energy of the system, the presence of surfactant leads to a reduction of the overall value of the kinetic energy. As the Biot number increases, the mass transfer between the bulk and the interface increases to reduce the Marangoni stress of the interface, and recover the clean interface behaviour. In fact, the profiles are bounded between the surfactant-free and insoluble surfactant cases. The higher the value of Biot, the more desorption of surfactant, and subsequently the less rigidification of the interface is predicted. The reduction of the grade of interfacial rigidity implies in the increase of the interfacial tangential velocity (i.e., increase of the kinetic energy), as Biot increases.

Turning attention towards figure 7.7b, which shows the vertical stretch of the interface on the axial direction. For the surfactant-free case, the higher vertical stretching of the interface is observed, In the presence of surfactant, there is a reduction in the vertical stretch via Marangoni-induced flow, which induces motion from the droplet summit towards its base droplet. Additionally, figure 7.7b also depicts that the higher the value of solubility, the sooner the initialization of the droplet stretching as a consequence of the strength of Marangoni stresses. Finally, it is also observed a non-monotonic response in this parameter (e.g, the less vertical stretching of the droplet is predicted for $Bi = 1$).

Finally, turning attention towards the effect of solubility on the temporal development of the neck (see figure 7.7c). The presence of surfactant changes the fate of the coalescence dynamics, and for the studied range of parameters $Bi = 0.1 - 10$, Marangoni-induced flow yields the inhibition of the capillary singularity (e.g., reopening of the droplet-neck). The profile for the surfactant cases are bounded between the insoluble and the surfactant-free cases, with a monotonical behaviour of the neck profile depending on the solubility value.

Figure 7.8 has the purpose to analyse the effect of solubility (i.e., Bi) on the coalescence dynamics with respect to the interfacial shape, τ , Γ , and tangential radial velocity u_{tr} at an identical temporal reference $t = (1.200, 1.680)$. Evidence of the interface rigidification is observed in figures 7.8a and 7.8b, in which surfactant delays the dynamics of the system. Figures 7.8c and 7.8d show confirmation regarding the higher desorption of surfactant as Bi increases, and the Γ field shows a more uniform

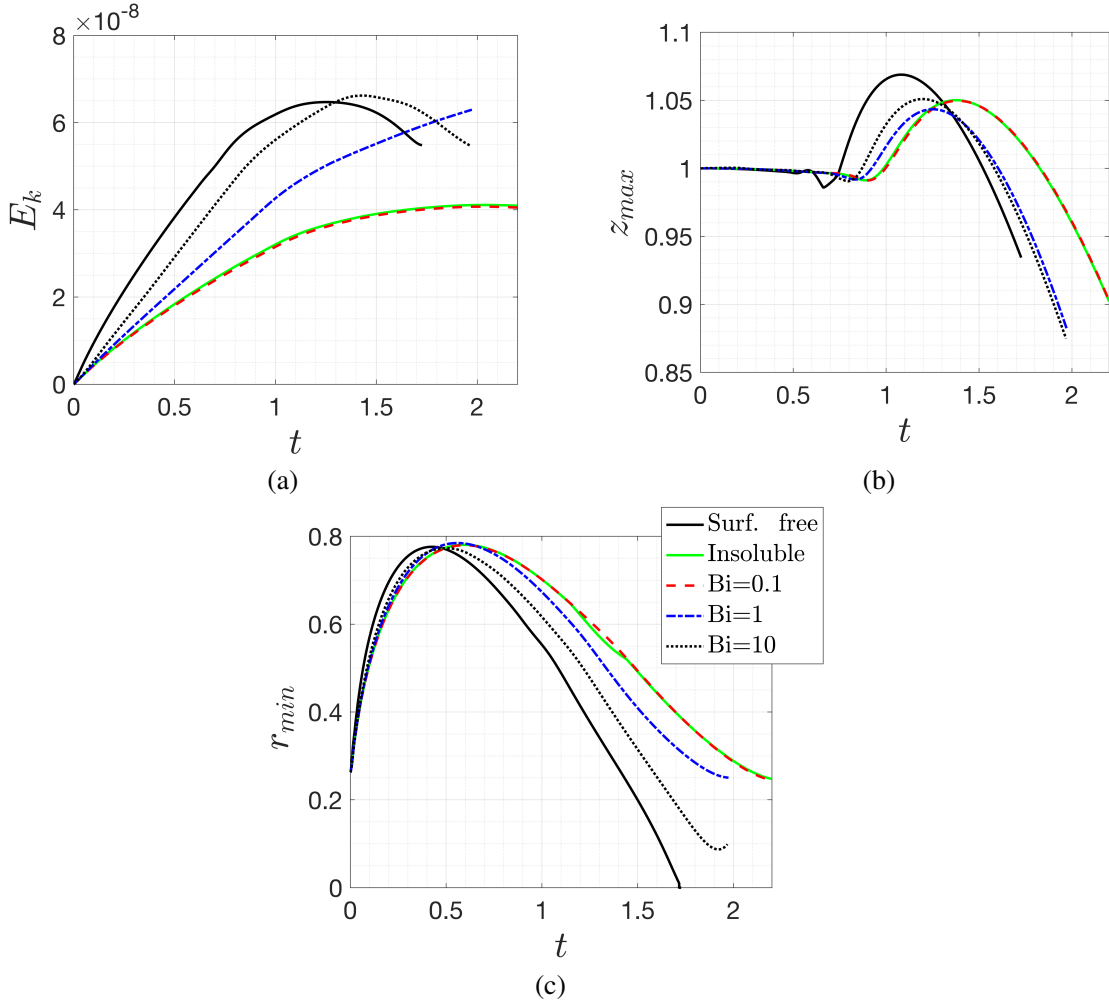


Fig. 7.7. Effect of Bi on the coalescence dynamics for $Oh = 0.02$, $Bo = 10^{-3}$, $\beta_s = 0.5$, $Pe_s = Pe_b = 100$, $\Gamma_o = 0.5\Gamma_\infty$ and $k = 1$. (a) Kinetic energy; (b) Maximum stretching of the interface; (c)

distribution. The reduction of the interfacial surfactant is driven by the mass transfer between the interface and bulk to reduce the strength of τ . For the most soluble case $Bi = 10$, the τ -profile has almost flatten up. Interestingly, for the intermediate Biot number $Bi = 0.1$, τ is the bigger which justifies the higher suppression of the vertical stretching of the interface described figure 7.7b. Finally, the inspection of the radial tangential velocity shows again the dampening of the tangential velocity and the suppression of one of the stagnation point for $Bi = 0.1$ and $Bi = 1$.

7.3.3 Effect of the adsorption parameter

Figure 7.9 shows the effect of the adsorption parameter k on the temporal coalescence dynamics for some metric parameters (e.g., kinetic energy, vertical stretching of the interface and droplet-neck radius) by a fixing value of $Bi = 1$, and exploring the values of $k = (0.01, 1, 5)$. The values of k cor-

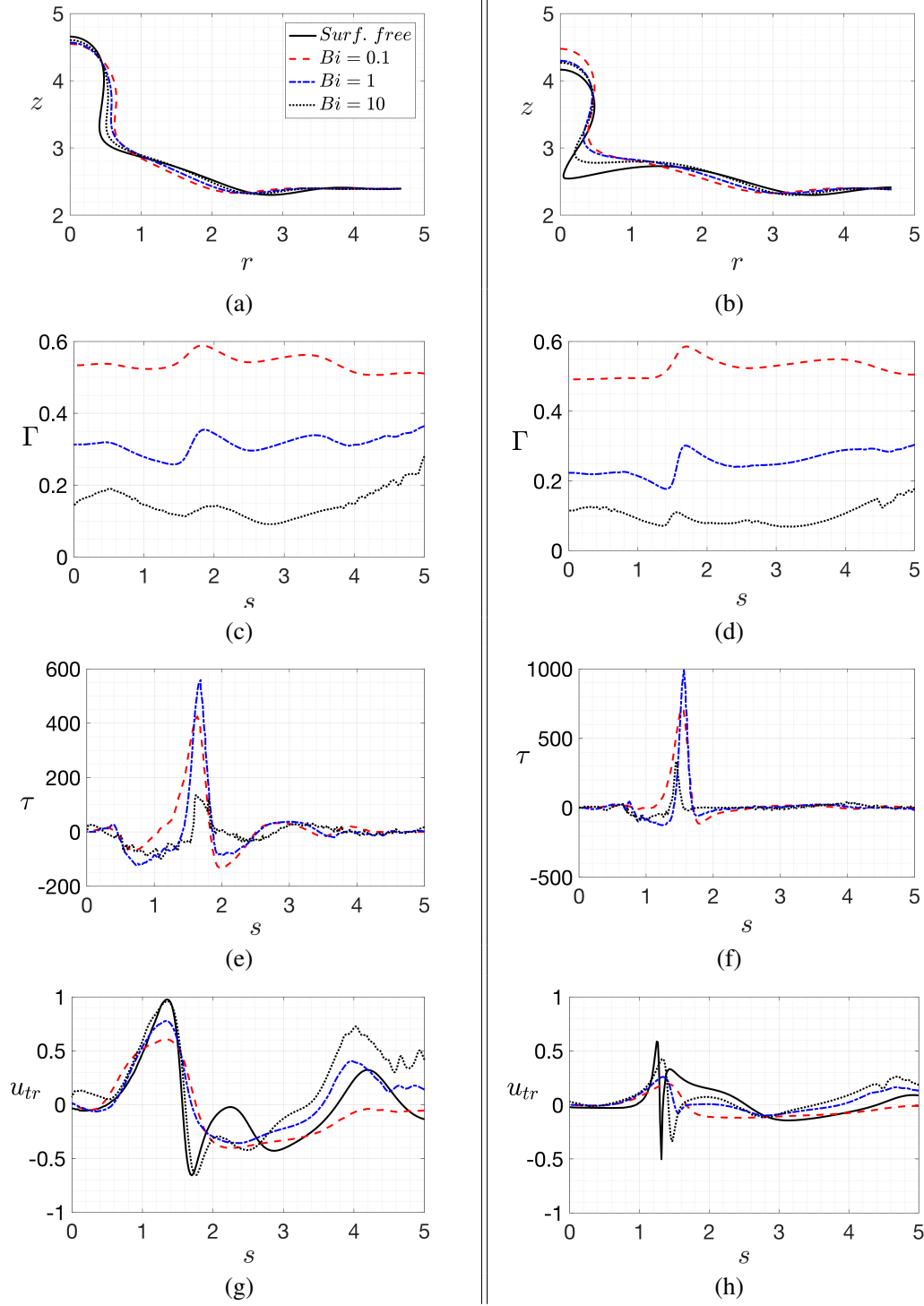


Fig. 7.8. Effect of Biot parameter Bi on the interfacial dynamics. Interface location, Γ , τ and u_{tr} are shown in rows one to four, respectively. In column 1 and 2, the dimensional times correspond to $t = 1.200$ and $t = 1.680$, respectively. In rows 1 and 2-4 the variation is with respect to the dimensionless radial coordinate and, r , and arc length, s , respectively.

respond to $\chi = (0.09, 0.50, 0.83)$, where χ represents the fraction of surface covered by adsorbed surfactant. The interfacial surfactant concentration is initialised as its equilibrium surfactant concentration, given by χ , $\Gamma_o = \Gamma_{eq} = \Gamma_{\infty}\chi$

Turning attention towards figure 7.9a, which shows the kinetic energy of the system, the presence of surfactant leads to a reduction of the overall value of the kinetic energy. As the k parameter reduces, the mass transfer from the bulk to the interface reduces to reduce the Marangoni stress of the interface, and recover the clean interface behaviour. The higher the value of k , the more adsorption of surfactant, and the higher interfacial rigidification. The increase of interfacial rigidity implies a dampening of the tangential velocity (i.e., dampening of kinetic energy).

Figure 7.7b shows the maximum vertical stretching of the interface on the axial direction. By inspection of their plot profiles, it is observed that the lower the value of the adsorption parameter, the system tends to behave as the surfactant-free case, with a similar vertical stretching. It is also observed a monotonic response in this parameter (e.g, the less stretching is observed for increasing k).

Finally, turning attention towards the effect of the adsorption parameter on the temporal dynamics of the droplet-neck radius (see figure 7.7c). For high adsorption parameters, the presence of surfactant changes the fate of the coalescence dynamics, as Marangoni-induced flow yields the inhibition of the capillary singularity (e.g., with the reopening of the droplet-neck). However, for the lower value of k studied in this chapter, the Marangoni stresses are not sufficiently large to prevent the capillary singularity.

Figure 7.10 has the purpose to analyse the effect of the k parameter on the coalescence dynamics with respect to the interfacial shape, τ , Γ , and tangential radial velocity u_{tr} at an identical temporal reference $t = (1.200, 1.680)$. Evidence of the interface rigidification is observed in figures 7.10a and 7.10b, in which surfactant delays the dynamics of the system. figures 7.10c and 7.10d show confirmation regarding the higher adsorption of surfactant as k increases, and the Γ field shows a more uniform distribution. The reduction of the interfacial surfactant is driven by the mass transfer between the interface and bulk to reduce the strength of τ . Interestingly, the τ -profile has almost flatten up for the upper-end case of the studied parameter. Finally, the inspection of u_{tr} shows again the dampening of the tangential velocity and the suppression of one of the stagnation points for $k = 1$ and $k = 5$. The suppression of this stagnation point yields the reopening of the neck, and therefore, the inhibition of the capillary singularity.

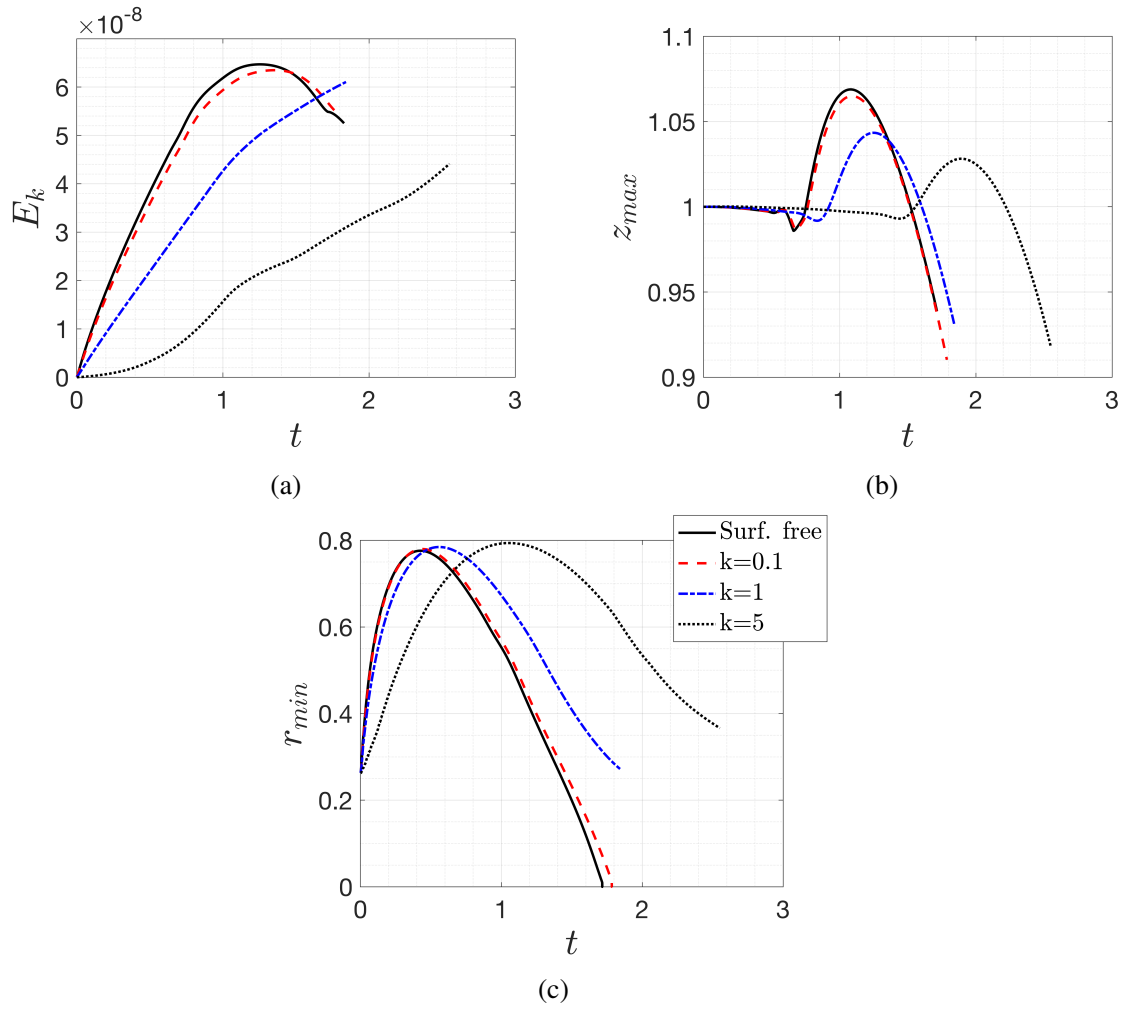


Fig. 7.9. Effect of adsorption parameter k on the coalescence dynamics for $Oh = 0.02$, $Bo = 10^{-3}$, $\beta_s = 0.5$, $Pe_s = Pe_b = 100$, $\Gamma_o = 0.5\Gamma_\infty$ and $Bi = 1$. (a) kinetic energy; (b) maximum stretching of the interface; (c) neck radius

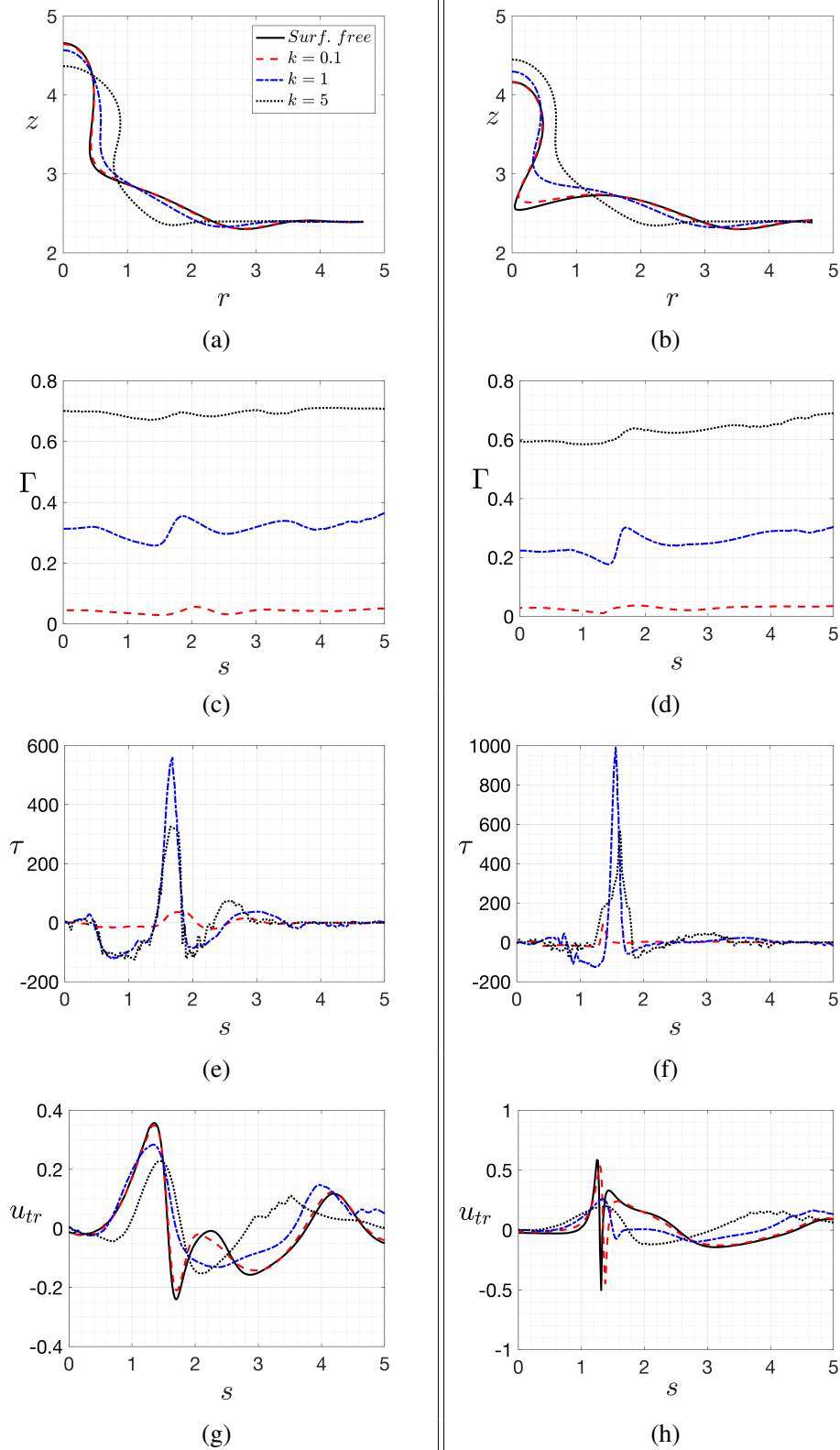


Fig. 7.10. Effect of adsorption parameter k on the interfacial dynamics. Interface location, Γ , τ and u_{tr} are shown in rows one to four, respectively. In column 1 and 2, the dimensional times correspond to $t = 1.200$ and $t = 1.680$, respectively. In rows 1 and 2-4 the variation is with respect to the dimensionless radial coordinate and, r , and arc length, s , respectively.

7.4 Conclusions

In this chapter, I have studied the effect of Marangoni-induced flow, brought about by the presence of surfactant, on the dynamics of droplet-interface coalescence using a hybrid front-tracking/level-set method. The numerical framework has been validated against the groundbreaking experimental work presented by Blanchette and Bigioni (2006) for the coalescence dynamics, and Eggers (1993) for the scaling regarding the temporal evolution towards the capillary singularity.

It has been shown that Marangoni stresses drive motion from regions of high surfactant concentration (low surface tension) to low concentration (high tension) regions, resulting in a delaying of the interfacial dynamics. The immobilising effect of the surfactants due to the Marangoni stresses is also observed via the marked reduction in the system kinetic energy and the maximum vertical stretching of the interface. The presence of surfactants yields the capillary inhibition with the reopening of the neck. One of the most important findings of this chapter is the physical explanation which leads to the reopening of the neck. The condition for the capillary singularity is the existence of two stagnation points close to the droplet neck, which leads to the generation of vorticity in this area. In the presence of surfactants, Marangoni-induced flow suppresses one of the stagnation points, which leads to the reopening of the droplet-neck. Additionally, the suppression of one of the stagnation points yields the advection of vorticity towards the liquid bulk.

Additionally, we have considered the role of soluble surfactants on the interfacial dynamics by analysing its sorptive kinetics (i.e., Bi and k parameters). For the studied range of Bi number (e.g., $0.1 < Bi < 10$), the presence of surfactants is capable of inhibiting the capillary break-up, and subsequently changing the outcome of the surfactant-free system. By altering the k parameter, we observe a competition between the adsorption-desorption and hydrodynamics time scales which implies the change of the rate of mass transfer from/to the interface to weaken the effect of the Marangoni stresses, and consequently changing the fate of the drop-interface coalescence.

Future directions are related to the performance of numerical simulations featuring three dimensional behaviours occurring for large Bond numbers. Recently, the groundbreaking experimental work performed by Dong et al. (2017) suggested that the presence of surfactants induces the rupture of the interface (i.e., hole formation) in a off-axis location at high Bond numbers. Thus, a fully three-dimensional retracting capillary wave will certainly affect the behaviour of the system rising a more complex coalescence dynamics, and constitute a fruitful area of future research for the fluid mechanics community.

Conclusions

Synthesis

This thesis has been motivated by the desire to understand the interfacial dynamics of multiphase jets. The breakup of an interface into a cascade of droplets is a phenomenon of central importance to a large number of industrial and biological/healthcare applications. Examples of these applications include the atomisation of propellants in engines, the formation of droplets in injectors, mixers and separators, and spray-formation that accompany environmental flows, as well as coughs and sneezes in biomedical settings. Multiphase flow dynamics are influenced by a range of multi-scale physics; this includes the interaction of turbulence with interfaces (creating cascades of motion featuring a large separation of scales), capillarity, viscosity (and complex rheology), and gravity, as well as heat transfer and phase change. The presence of surface-active agents (surfactants), either as contaminants, pathogens, or additives, also influences the flow dynamics adding layers of complexity. The multi-scale nature of the flow, and the tremendously complex interfacial topology, however, complicates the scrutiny of multiphase flows experimentally even in the absence of additives. Thus, elucidating the influence of additives on these flows requires the development of theoretical and computational tools to enable high-fidelity simulations to be deployed to drive experiment design and understand the delicate interplay among the different physical mechanisms across scales.

The framework of this thesis is based on the use of a novel numerical methods in an attempt to canvas the fundamental physics governing multiphase flows. Most of the numerical investigations in surface-tension-dominated flows have been based on the use of interface-capturing capabilities to account for the surface tension forces; meanwhile, a hybrid interface-tracking/level-set method was used to account for the effect of capillarity. The formulation of the numerical approach makes it very suitable to handle highly deforming interfaces with complex topology changes. Additionally, it is possible to account for Marangoni stresses on the plane of the interface, which arise from gradients of surfactant concentrations.

Following the definition of the numerical approach in Chapter 2, the presentation of the results of

this thesis starts in Chapter 3. The comprehensive literature search on turbulent jets highlighted that the physical mechanisms governing the interfacial dynamics on liquid-liquid systems was still lacking. Temporal instabilities and the resulting spatio-temporal interfacial structures are predicted by solving the full three-dimensional two-phase Navier-Stokes system. I consider a cylindrical nozzle which let a water jet enter progressively into the computational domain, initially filled with a stagnant viscous oil. We have carefully considered mesh resolution which is sufficiently small to resolve the relevant turbulent length scales and interfacial singularities (e.g., pinch-off and coalescence).

Three-dimensional numerical simulations were carried out for turbulent water jets entering a stagnant and more viscous silicon oil phase. Particular attention has been paid to the temporal interfacial dynamics that arise as a result of the vortex-surface interaction. Using less computationally expensive simulations, we explore the $ReWe$ physical space, identifying four distinct regions based on the appearance of the interfacial structures. On this basis, I carry out high fidelity simulations representative of each region. I show that the streamwise vorticity plays a major role in the development of the three-dimensional instabilities on the jet surface. At low Re and We numbers (i.e., capillary-controlled region), the jet interface remains axisymmetric and no surface corrugations are observed due to strong capillarity. Moreover, this region is also characterised by values of azimuthal vorticity the fact that streamwise vorticity never becomes comparable to the azimuthal vorticity, which are two order of magnitude bigger than the streamwise vorticity. At low Re and high We numbers, the reduction of capillarity enhances the formation of a mushroom structure at the leading edge of the jet, and the formation of corrugations in the jet core; however, the streamwise vorticity is still almost two orders of magnitude smaller than azimuthal vorticity. At high Re and low We numbers, streamwise vorticity starts becoming important, resulting in further deformation of the jet core. Finally, in the inertia-controlled region (i.e., high Re and We numbers), the streamwise vorticity becomes comparable to the azimuthal vorticity triggering the streamwise deformation of KH vortices. I show the formation of hairpin vortices near the interface, which are aligned in the streamwise direction forming layers of inner- and outer- hairpin-vortices. The formation of inner and outer lobes in the jet core are closely linked to their neighbouring hairpin-vortices. The alignment of vortices enhances the perforation of the lobes to form holes which expand radially by capillarity, and ultimately give rise to the formation of droplets. Another main feature of the inertia-controlled regime is the creation of a thin toroidal sheet inside of the leading-edge structure. The thinning of this sheet results in its perforation to form droplets. The droplets rotate as a result of their interaction with the vorticity field, and further topological transitions occur (e.g., coalescence).

The turbulent jets presented in Chapter 3 assumed a constant value of surface tension, but it is known that streams are usually contaminated with deliberately places or naturally occurring surfactants, which reduce surface tension and give rise to surface tension gradients (i.e., Marangoni stresses)

Manikantan and Squires (2020). Chapter 4 studies the effect of Marangoni-induced flow as a result of the presence of surfactants for a liquid jet in the inertia-dominated regime. The addition of surfactants in the interfacial dynamics have not received the attention they deserve in the literature. The recent experimental study by Kooij et al. (2018b) suggested that the addition of surfactants leads to a reduction of the mean diameter of the droplet size distribution due to the reduction of the mean value of surface tension, which makes the interface more susceptible to fragmentation. However, the numerical simulations carried out in the chapter show the formation of larger droplets in the presence of surfactants as a result of the formation of Marangoni stresses. I hypothesised that surfactant is capable of inhibiting capillary singularities and rigidifying the interface, and consequently changing the fate of the atomisation. To test this hypothesis, I have studied the effect of surfactants in three single events observed in the jet phenomenon: the retraction of liquid threads, the bursting bubble phenomenon, and the partial/total drop-interface coalescence.

Chapter 5 focuses on the study of the effect of surfactants on the dynamics of retracting ligaments at low values of viscosity. The simulation is initialised with fluids at rest in the absence of gravity to study closely the interplay between viscous and capillary forces, and Marangoni stresses on the plane of the interface. I closely validated the simulation against Notz and Basaran (2004), and numerical results proved to be independent of the mesh quality. Contrary to the surfactant free-case, the presence of surfactants avoids the ‘end-pinching’ mechanism as a result of the Marangoni-induced flow which induce flow-reversal close to the ligament-neck, and yielding its reopening. This behaviour is similar to the phenomenon explained by Hoepffner and Paré (2013) in the escape from breakup of viscous ligaments in the absence of surfactant. I have also demonstrated that the pinch-off inhibition cannot happen by simply reducing the value of the surface tension. In this Chapter, I have also studied the competition between the capillary-induced flow and the Marangoni-induced flow. The latter overcomes the former resulting in the inhibition of one of the stagnation points in the vicinity of the bulbous neck forcing the reopening of the neck (i.e., two stagnation points close to the neck are the requirement for the capillary breakup). Additionally, I have studied the dynamics in a range of controlling parameters such as the surface diffusion, sorptive kinetics and strength of the surfactant and surfactant solubility.

Chapter 6 focuses on the study of the effect of surfactants on the bubble bursting dynamics. This chapter is of great importance not only for jet dynamics but also for environmental flows (e.g., breaking waves). Bubbles generated after breaking waves rest close to a liquid-gas interface prior to their rupture. The rupture of the intervening liquid layer, and the subsequent bursting dynamics can be the source of hundreds of droplets (so-called film droplets) whereas the collapse of the bubble gives rise to the formation of a central jet to form jet-droplets. In the absence of contaminants, the physical mechanisms of surfactant-free bursting bubbles on the ejection of droplets have been widely studied exper-

imentally, numerically, and through theoretical approaches. The effect of surfactant in the jet-droplets of an isolated bubble has been described in detail in this Chapter. On this basis, I have performed for the first time, direct numerical simulations accounting for surfactant-induced Marangoni stresses on bursting bubbles. The main results demonstrate that the presence of surfactant affects the dynamics of the system through Marangoni-induced flow, which is responsible for the onset of a recirculation zone close to the free surface. These Marangoni stresses rigidify the interface, delay the cavity collapse, and influence the jet breakup process (i.e., production of fewer droplets). The jet droplets are formed due to a capillary singularity, which is affected by the presence of surfactant as surfactant inhibits the 'end-pinching' mechanism in jet-dynamics due to the suppression of stagnation points, and subsequently the reverse of the flow (similar to the finds showing in Chapter 5). I have measured the characteristics of the droplets resulting from the breakup of the Worthington jet in terms of their volume and average interfacial surfactant concentration. Furthermore, the size of the first droplet, $r_d/R_o \sim 6\%$, agrees with the experimental observations of Blanchard and Woodcock (1957) and Tedesco and Blanchard (1979), the empirical power law-dependence of Lewis and Schwartz (2004), and the theoretical scaling relationship proposed by Gañán-Calvo (2017). Finally, I have studied the effect of solubility and surfactant strength to formulate the problem in a more experimental framework.

Finally, Chapter 7 studies in detail the effect of surfactants on the dynamics of drop-interface coalescence. This type of coalescence is one of the most studied problems in multiphase flow dynamics as it represents a canonical example of an interfacial singularity. A hole is formed in the liquid sheet separating both interfaces (e.g., drop-flat-interface or two drops) which retracts by capillarity. I have started the chapter by validating the numerical predictions with the experimental work of Blanchette and Bigioni (2006) and Eggers (1993) in terms of the spatio-temporal evolution of the interface and the temporal evolution of the neck prior of its breakup, respectively. This Chapter shows that the addition of surfactants can prevent the capillary singularity of the interface. I have analysed in detail the role of Marangoni stresses on the interfacial dynamics, and I have concluded that they are responsible for the flow-reversal in the vicinity of the neck, which results in the suppression of one stagnation point in that location. The suppression of the stagnation point also translates in a change of the vorticity field close to the interface, whereby for the surfactant-laden case a higher vorticity-generation advected towards the liquid bulk is observed. Those findings are in agreement with Chapter 5 and Chapter 6 for the capillary ligament retraction and bursting phenomena, respectively. Finally, the coalescence dynamics are analysed for several control parameters to study their effect on the reopening of the neck.

Future research pathways

This thesis has made major contributions on the vortex-surface interaction of turbulent jets, and the effect of surfactants in hydrodynamics singularities of canonical fluid dynamics problems. Possible research pathways using the same numerical methods structure are suggested below.

Turbulent jets

In Chapter 3, I have focused on the spatial and temporal development of the interfacial dynamics as a result of the vortex-surface interaction, further investigations should be carried out on the statistical response of the turbulent multiphase flow, similar to the work presented by Ling et al. (2019) for a mixing layer between parallel gas and liquid streams. This analysis will allow to better estimate the turbulent scales (i.e., Kolmogorov and Hinze scales) associated with the system.

Other avenues worth exploring would be:

- Effect of the viscosity and density ratios. The increase of those ratios implies a larger range of physical length scales that need to be resolved, which leads to very expensive computational simulations. Figure 7.11 highlights a change in the interfacial dynamics in comparison to results in Chapter 3 when the density and viscosity ratios have been fixed to 20.
- Effect of the nozzle-geometry in the jet dynamics.

Chapter 4 has shown that the gradients of surface tension, as a result of the presence of surfactants, change the fate of the atomisation. However, there are still many open questions that deserve to be explored: What is the effect of the elasticity number on the atomisation? What would happen to interfacial dynamics when the adsorption kinetics control the system? What is the effect of surfactants on the regime map drawn in Chapter 3?

Ligament retraction

Chapter 5 has isolated a perfect straight ligament, future research avenues involve performing numerical simulations of curved ligaments to break up the symmetry behaviour, and therefore take advantage of the numerical set-up used in this thesis.

Additionally, another interesting future avenue of research would be to use lubrication theory analysis on ligament retraction with surfactants. This type of analysis could provide insights into the

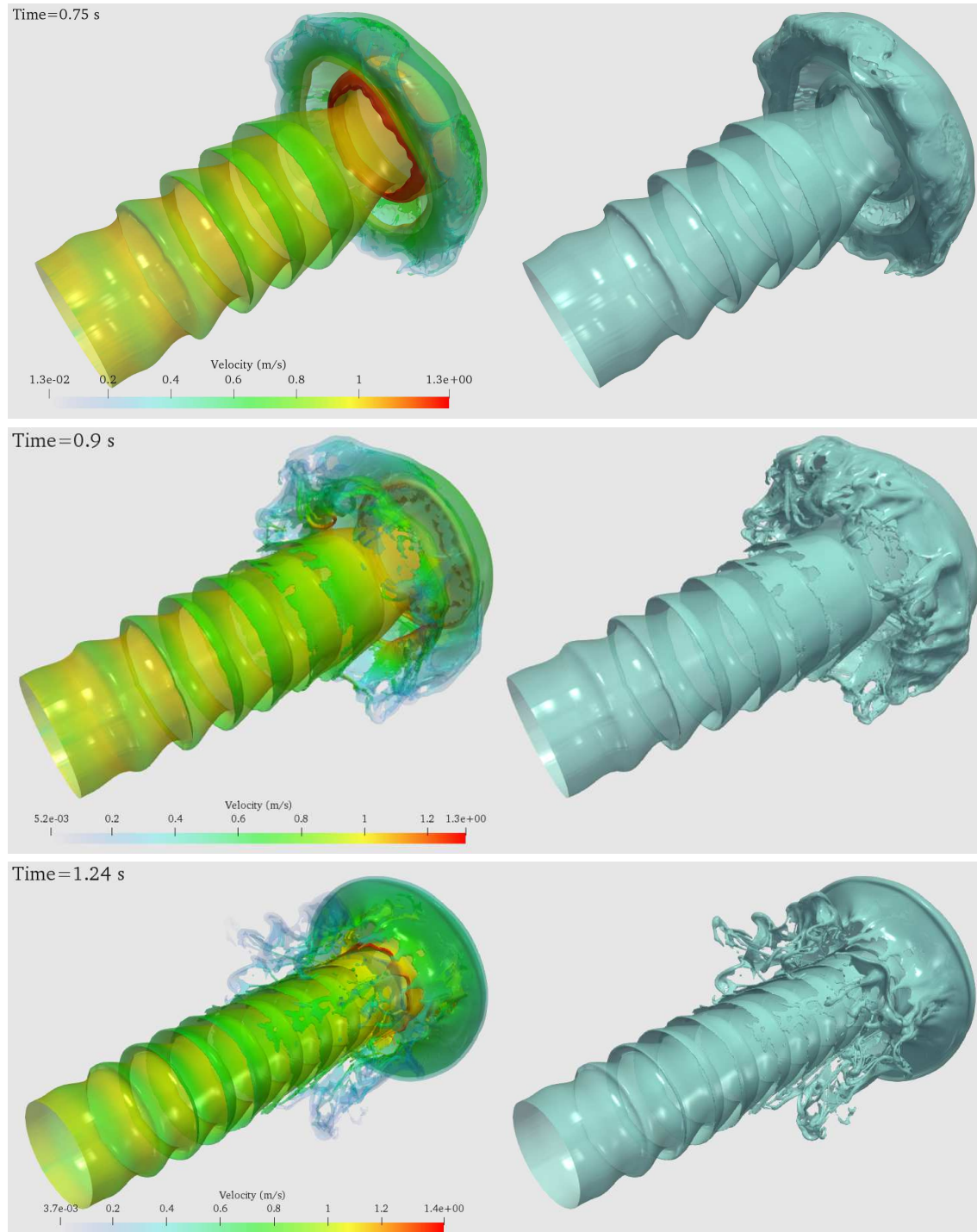


Fig. 7.11. Spatio-temporal development of the interfacial dynamics of jet atomisation with $Re = 800$, $We = 4000$ $\rho_l/\rho_g = 20$, $\mu_l/\mu_g = 20$. Non-dimensional values correspond to the work from Ling et al. (2015). The jet was performed in 4096 cores.

relationship between the classic Taylor-Culick retraction velocity and interfacial rigidification brought on by the surface-active agents.

Bursting bubble

The bursting bubble chapter can be extrapolated to breaking waves contaminated with surfactants. Approximately, between 1-4 large spills (> 700 tons) and between 2-3 medium spills (7-700 tons) of oil into the ocean per year have been observed in the 21st century.

After the bursting of a bubble, the bursting dynamics can be the source of hundreds of droplets (so-called film droplets) whereas the collapse of the bubble gives rise to the formation of a central jet to form jet-droplets. Chapter 6 focused entirely on jet-droplets in the absence of gravity. However, there are still many unanswered questions regarding single events, and subsequently, the numerical simulations should be geared to answer: What is the size distribution of the film droplets? What is the surfactant-load in film droplets? What is the surfactant capillary-wave-damping effect in the capillary section during the cavity-collapse? What is the typical speed of the ejected droplets?

Additionally, the presence of the neighbouring bubbles would certainly affect the dynamics of the upwards jet as the retracting capillary waves are no longer axisymmetric, leading to the formation of inclined jets. Therefore, the numerical simulations will be driven to improve the understanding of the role of surfactants and neighbouring bubbles on the interfacial dynamics of the vertical jet, and their subsequent breakup into droplets.

Surfactant effects on the thinning of liquid sheets

A question that this thesis has not addressed, and deserves attention, is the effect of surfactants in the thinning dynamics of liquid sheets. How does the presence of surfactants prevent the nucleation of the hole? This study could show how Marangoni stresses can heal the interface to prevent its interfacial rupture.

Concluding remarks

This thesis has demonstrated the importance of the use of well-resolved numerical simulations to elucidate the close interplay of physical mechanisms in surface-tension-driven phenomena. I hope that this thesis shows the importance of numerical methods as a discovery tool to explore rich interfacial systems involving capillary singularities.

References

- Agbaglah, G., Chiodi, R., and Desjardins, O. (2017). Numerical simulation of the initial destabilization of an air-blasted liquid layer. *J. Fluid Mech.*, 812:1024–1038.
- Agrawal, M. and Neuman, R. D. (1988). Surface diffusion in monomolecular films: II. experiment and theory. *Journal of Colloid and Interface Science*, 121(2):366 – 380.
- Ananthakrishnan, P. and Yeung, R. W. (1994). Nonlinear interaction of a vortex pair with clean and surfactant-covered free surfaces. *Wave Motion*, 19(4):343 – 365.
- Anthony, C. R., Kamat, P. M., Harris, M. T., and Basaran, O. A. (2019). Dynamics of contracting filaments. *Phys. Rev. Fluids*, 4:093601.
- Asadi, H., Asgharzadeh, H., and Borazjani, I. (2018). On the scaling of propagation of periodically generated vortex rings. *J. Fluid Mech.*, 853:150–170.
- Asaki, T. J., Thiessen, D. B., and Marston, P. L. (1995). Effect of an insoluble surfactant on capillary oscillations of bubbles in water: observation of a maximum in the damping. *Phys. Rev. Lett.*, 75(14):2686.
- Basaran, O. A. (2002). Small-scale free surface flows with breakup: Drop formation and emerging applications. *AIChE Journal*, 48(9):1842–1848.
- Batchvarov, A., Kahouadji, L., Constante-Amores, C. R., Gonçalves, G. F. N., Shin, S., Chergui, J., Juric, D., and Matar, O. K. (2020a). Three-dimensional dynamics of falling films in the presence of insoluble surfactants.
- Batchvarov, A., Kahouadji, L., Magnini, M., Constante-Amores, C. R., Craster, R. V. ., Shin, S., Chergui, J., Juric, D., and Matar, O. K. (2020b). Effect of surfactant on elongated bubbles in capillary tubes at high reynolds number. *Phys. Rev. Fluids*, 5:093605.
- Bernal, L. P. and Roshko, A. (1986). Streamwise vortex structure in plane mixing layers. *J. Fluid Mech.*, 170:499–525.

- Berny, A., Deike, L., Séon, T., and Popinet, S. (2020). Role of all jet drops in mass transfer from bursting bubbles. *Phys. Rev. Fluids*, 5:033605.
- Blanchard, D. C. and Syzdek, L. D. (1972). Concentration of bacteria in jet drops from bursting bubbles. *Journal of Geophysical Research (1896-1977)*, 77(27):5087–5099.
- Blanchard, D. C. and Woodcock, A. H. (1957). Bubble formation and modification in the sea and its meteorological significance. *Tellus*, 9(2):145–158.
- Blanchette, F. and Bigioni, T. P. (2006). Partial coalescence of drops at liquid interfaces. *Nature Physics*, 2(4):254–257.
- Blanchette, F. and Bigioni, T. P. (2009). Dynamics of drop coalescence at fluid interfaces. *J. Fluid Mech.*, 620:333–352.
- Blanchette, F., Messio, L., and Bush, J. W. M. (2009). The influence of surface tension gradients on drop coalescence. *Physics of Fluids*, 21(7):072107.
- Blanco-Rodríguez, F. J. and Gordillo, J. M. (2020). On the sea spray aerosol originated from bubble bursting jets. *J. Fluid Mech.*, 886:R2.
- Bleys, G. and Joos, P. (1985). Adsorption kinetics of bolaform surfactants at the air/water interface. *The Journal of Physical Chemistry*, 89(6):1027–1032.
- Boulton-Stone, J. M. and Blake, J. R. (1993). Gas bubbles bursting at a free surface. *J. Fluid Mech.*, 254:437–466.
- Brancher, P., Chomaz, J. M., and Huerre, P. (1994). Direct numerical simulations of round jets: Vortex induction and side jets. *Phys. Fluids*, 6(5):1768–1774.
- Brenner, M. P., Lister, J. R., and Stone, H. A. (1996). Pinching threads, singularities and the number 0.0304... *Phys. Fluids*, 8(11):2827–2836.
- Brenner, M. P., Shi, X. D., and Nagel, S. R. (1994). Iterated instabilities during droplet fission. *Phys. Rev. Lett.*, 73:3391–3394.
- Castrejón-Pita, A. A., Castrejón-Pita, J. R., and Hutchings, I. M. (2012). Breakup of liquid filaments. *Phys. Rev. Lett.*, 108:074506.
- Castrejón-Pita, J. R., Castrejón-Pita, A. A., Thete, S. S., Sambath, K., Hutchings, I. M., Hinch, J., Lister, J. R., and Basaran, O. A. (2015). Plethora of transitions during breakup of liquid filaments. *Proceedings of the National Academy of Sciences*, 112(15):4582–4587.

- Charles, G. and Mason, S. (1960). The coalescence of liquid drops with flat liquid/liquid interfaces. *Journal of Colloid Science*, 15(3):236 – 267.
- Chenadec, V. (2012). A stable and conservative framework for detailed numerical simulation of primary atomisation. *Stanford University*, PhD Thesis.
- Chorin, A. J. (1968a). Numerical solution of the Navier-Stokes equations. *Mathematics of Computation*, 22(104):745–745.
- Chorin, A. L. (1968b). Numerical solution of the navier-stokes equations. *Mathematics of Computation*, 22(104):745–762.
- Churaev, N. V., Derjaguin, B., and Muller, V. (1987). *Surface Forces*. Springer.
- Constante-Amores, C. R., Kahouadji, L., Batchvarov, A., S., S., Chergui, J., Juric, D., and Matar, O. K. (2020a). Dynamics of retracting surfactant-laden ligaments at intermediate ohnesorge number. *Phys. Rev. Fluids*, 5:084007.
- Constante-Amores, C. R., Kahouadji, L., Batchvarov, A., Shin, S., Chergui, J., Juric, D., and Matar, O. K. (2020b). Dynamics of a surfactant-laden bubble bursting through an interface.
- Contò, F. P., Marín, J. F., Antkowiak, A., Castrejón-Pita, J. R., and Gordillo, L. (2019). Shape of a recoiling liquid filament. *Scientific Reports*, 9(1):15488.
- Craster, R. V., Matar, O. K., and Papageorgiou, D. T. (2002). Pinchoff and satellite formation in surfactant covered viscous threads. *Phys. Fluids*, 14(4):1364–1376.
- Craster, R. V., Matar, O. K., and Papageoriorou, D. T. (2009). Breakup of surfactant-laden jets above the critical micelle concentration. *J. Fluid Mech.*, 629:195–219.
- Davoust, S., Jacquin, L., and Leclaire, B. (2012). Dynamics of $m = 0$ and $m = 1$ modes and of streamwise vortices in a turbulent axisymmetric mixing layer. *J. Fluid Mech.*, 709:408–444.
- Day, R. F., Hinch, E. J., and Lister, J. R. (1998). Self-similar capillary pinchoff of an inviscid fluid. *Phys. Rev. Lett.*, 80:704–707.
- Deike, L., Ghabache, E., Liger-Belair, G., Das, A. K., Zaleski, S., Popinet, S., and Séon, T. (2018). Dynamics of jets produced by bursting bubbles. *Phys. Rev. Fluids*, 3:013603.
- Deka, H., Biswas, G., Sahu, K. C., Kulkarni, Y., and Dalal, A. (2019). Coalescence dynamics of a compound drop on a deep liquid pool. *J. Fluid Mech.*, 866:R2.
- Desjardins, O., McCaslin, J., Owkes, M., and Brady, P. (2013). Direct numerical and large-eddy simulation of primary atomization in complex geometries. *Atomiz. Sprays*, 23(11):1001–1048.

- Desjardins, O., Moureau, V., and Pitsch, H. (2008). An accurate conservative level set/ghost fluid method for simulating turbulent atomization. *J. of Comp. Phys.*, 227(18):8395 – 8416.
- Desjardins, O. and Pitsch, H. (2010). Detailed numerical investigation of turbulent atomization of liquid jets. *Atomiz. Sprays*, 20(4):311–336.
- Dombrowski, N., Fraser, R. P., and Newitt, D. M. (1954). A photographic investigation into the disintegration of liquid sheets. *Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences*, 247(924):101–130.
- Dong, T., Weheliy, W. H., Chausset, P., and Angeli, P. (2017). An experimental study on the drop/interface partial coalescence with surfactants. *Phys. Fluids*, 29(10):102101.
- Duchemin, L., Popinet, S., Josserand, C., and Zaleski, S. (2002). Jet formation in bubbles bursting at a free surface. *Phys. Fluids*, 14:3000.
- Eggers, J. (1993). Universal pinching of 3d axisymmetric free-surface flow. *Phys. Rev. Lett.*, 71:3458–3460.
- Eggers, J. (1997). Nonlinear dynamics and breakup of free-surface flows. *Rev. Mod. Phys.*, 69(3):865–929.
- Eggers, J. and Dupont, T. F. (1994). Drop formation in a one-dimensional approximation of the navier–stokes equation. *J. Fluid Mech.*, 262:205–221.
- Eggers, J., Lister, J. R., and Stone, H. A. (1999). Coalescence of liquid drops. *J. Fluid Mech.*, 401:293–310.
- Eggers, J. and Villermaux, E. (2008). Physics of liquid jets. *Reports on Progress in Physics*, 71(3):036601.
- Ferziger, J. H. and Perić, M. (1999). *Computational Methods for Fluid Dynamics*. Springer, Berlin, 2nd edition.
- Gañán-Calvo, A. M. (2017). Revision of bubble bursting: Universal scaling laws of top jet drop size and speed. *Phys. Rev. Lett.*, 119(204502).
- Garcia-Briones, M. A., Brodkey, R. S., and J.Chalmers, J. (1994). Computer simulations of the rupture of a gas bubble at a gas-liquid interface and its implications in animal cell damage. *Chem. Eng. Sci.*, 49(14):2301–2320.
- Ghabache, E. (2015). *Out of equilibrium free surface : from cavity collapse to stretched jets*. PhD thesis, Université Pierre et Marie - Paris VI.

- Ghabache, E., Antkowiak, A., Josserand, C., and S  on, T. (2014). On the physics of fizziness: How bubble bursting controls droplets ejection. *Phys. Fluids*, 26:121701.
- Ghabache, E. and S  on, T. (2016). Size of the top jet drop produced by bubble bursting. *Phys. Rev. Fluids*, 1:051901(R).
- Gordillo, J. M. and Rodr  guez-Rodr  guez, J. (2019). Capillary waves control the ejection of bubble bursting jets. *J. Fluid Mech.*, 867(556–571).
- Gorokhovski, M. and Herrmann, M. (2008). Modeling primary atomization. *Annu. Rev. Fluid Mech.*, 40(1):343–366.
- Gueyffier, D., Li, J., Nadim, A., Scardovelli, R., and Zaleski, S. (1999). Volume-of-fluid interface tracking with smoothed surface stress methods for three-dimensional flows. *J. of Comp. Phys.*, 152(2):423 – 456.
- Guthrie, C. (1864). On drops. *Proc. R. Soc. London* 0370-1662, 13(44).
- Harlow, F. H. and Welch, J. E. (1965). Numerical calculation of time-dependent viscous incompressible flow of fluid with free surface. *Phys. Fluids*, 8(12):2182–2189.
- Head, M. R. and Bandyopadhyay, P. (1981). New aspects of turbulent boundary-layer structure. *J. Fluid Mech.*, 107:297–338.
- Herrmann, M. (2011). On simulating primary atomization using the refined level set grid method. *Atomiz. Sprays*, 21(4):283–301.
- Hirsa, A. and Willmarth, W. W. (1994). Measurements of vortex pair interaction with a clean or contaminated free surface. *J. Fluid Mech.*, 259:25–45.
- Hirt, C. and Nichols, B. (1981). Volume of fluid (vof) method for the dynamics of free boundaries. *J. of Comp. Phys.*, 39(1):201 – 225.
- Hoath, S. D., Jung, S., and Hutchings, I. M. (2013). A simple criterion for filament break-up in drop-on-demand inkjet printing. *Phys. Fluids*, 25(2):021701.
- Hoepffner, J. and Par  , G. (2013). Recoil of a liquid filament: escape from pinch-off through creation of a vortex ring. *J. Fluid Mech.*, 734(183–197).
- Hosoi, A. E. and Bush, J. W. M. (2001). Evaporative instabilities in climbing films. *J. Fluid Mech.*, 442:217–239.
- Houssainy, S., Kabachek, S., and Kavehpour, H. P. (2020). Closed-form theoretical model of the secondary drop size in partial coalescence-capturing pertinent timescales and viscous forces. *Physics of Fluids*, 32(5):052101.

- Hoyt, J. W. and Taylor, J. J. (1977). Waves on water jets. *J. Fluid Mech.*, 83(1):119–127.
- Hunt, J., Wray, A., and Moin, P. (1988). Eddies, streams, and convergence zones in turbulent flows. *Studying Turbulence Using Numerical Simulation Databases*, 1:193–208.
- Ibarra, E., Shaffer, F., and Savaş, O. (2020). On the near-field interfaces of homogeneous and immiscible round turbulent jets. *J. Fluid Mech.*, 889:A4.
- Ibarra, R. (2017). Horizontal and low-inclination oil-water flow investigations using laser-based diagnostic techniques. *Imperial College London*, PhD Thesis.
- Jarrahbashi, D. and Sirignano, W. A. (2014). Vorticity dynamics for transient high-pressure liquid injection. *Phys. Fluids*, 26(10):101304.
- Jarrahbashi, D., Sirignano, W. A., Popov, P. P., and Hussain, F. (2016). Early spray development at high gas density: hole, ligament and bridge formations. *J. Fluid Mech.*, 792:186–231.
- Jeong, J., Hussain, F., Schoppa, W., and Kim, J. (1997). Coherent structures near the wall in a turbulent channel flow. *J. Fluid Mech.*, 332:185–214.
- Jin, F., Gupta, N. R., and Stebe, K. J. (2006). The detachment of a viscous drop in a viscous solution in the presence of a soluble surfactant. *Phys. Fluids*, 18(2):022103.
- Jin, F. and Stebe, K. J. (2007). The effects of a diffusion controlled surfactant on a viscous drop injected into a viscous medium. *Phys. Fluids*, 19(11):112103.
- Joos, P. and Serrien, G. (1989). Adsorption kinetics of lower alkanols at the air/water interface: Effect of structure makers and structure breakers. *J. Colloid Interface Sci.*, 127(1):97 – 103.
- Joos, P., Bleys, G., and Petre, G. (1982). Adsorption kinetics of nonanediol and nonane dicarbonic acid at the air/water interface. *J. Chim. Phys.*, 79:387–393.
- Kamat, P. M., Wagoner, B. W., Thete, S. S., and Basaran, O. A. (2018). Role of marangoni stress during breakup of surfactant-covered liquid threads: Reduced rates of thinning and microthread cascades. *Phys. Rev. Fluids*, 3:043602.
- Kavehpour, H. P. (2015). Coalescence of drops. *Annual Review of Fluid Mechanics*, 47(1):245–268.
- Kooij, S., Sijs, R., Denn, M. M., Villiermaux, E., and Bonn, D. (2018a). What determines the drop size in sprays? *Phys. Rev. X*, 8:031019.
- Kooij, S., Sijs, R., Denn, M. M., Villiermaux, E., and Bonn, D. (2018b). What determines the drop size in sprays? *Phys. Rev. X*, 8:031019.

- Kovalchuk, N. M., Jenkinson, H., Miller, R., and Simmons, M. J. (2018). Effect of soluble surfactants on pinch-off of moderately viscous drops and satellite size. *J. Colloid Interface Sci.*, 516:182 – 191.
- Kovalchuk, N. M., Nowak, E., and Simmons, M. J. H. (2016). Effect of soluble surfactants on the kinetics of thinning of liquid bridges during drops formation and on size of satellite droplets. *Langmuir*, 32(20):5069–5077.
- Kowalewski, T. (1996). On the separation of droplets from a liquid jet. *Fluid Dynamics Research*, 17(3):121 – 145.
- Kwak, d. and Lee, J. (2004). Multigrid algorithm for the cell-centered finite difference method ii: Discontinuous coefficient case. *Numer Methods Partial Differ Equ*, 20:742 – 764.
- Lafaurie, B., Nardone, C., Scardovelli, R., Zaleski, S., and Zanetti, G. (1994). Modelling merging and fragmentation in multiphase flows with surfer. *J. of Comp. Phys.*, 113(1):134 – 147.
- Lai, C.-Y., Eggers, J., and Deike, L. (2018). Bubble bursting: Universal cavity and jet profiles. *Phys. Rev. Lett.*, 121:144501.
- Lasheras, J. C. and Hopfinger, E. J. (2000). Liquid jet instability and atomization in a coaxial gas stream. *Annu. Rev. Fluid Mech.*, 32(1):275–308.
- Lewis, E. R. and Schwartz, S. E. (2004). Sea salt aerosol production: Mechanisms, methods, measurements and models—a critical review. *Washington DC American Geophysical Union Geophysical Monograph Series*, 152:3719–.
- Lhuissier, H. and Villermaux, E. (2009). Soap films burst like flapping flags. *Phys. Rev. Lett.*, 103:054501.
- Lhuissier, H. and Villermaux, E. (2012). Bursting bubble aerosols. *J. Fluid Mech.*, 696:5–44.
- Liao, Y. C., Subramani, H. J., Franses, E. I., and Basaran, O. A. (2004). Effects of soluble surfactants on the deformation and breakup of stretching liquid bridges. *Langmuir*, 20(23):9926–9930.
- Liepmann, D. and Gharib, M. (1992). The role of streamwise vorticity in the near-field entrainment of round jets. *J. Fluid Mech.*, 245:643–668.
- Lin, S. P. and Reitz, R. D. (1998). Drop and spray formation from a liquid jet. *Annual Review of Fluid Mechanics*, 30(1):85–105.
- Ling, Y., Fuster, D., Tryggvason, G., and Zaleski, S. (2019). A two-phase mixing layer between parallel gas and liquid streams: multiphase turbulence statistics and influence of interfacial instability. *J. Fluid Mech.*, 859:268–307.

- Ling, Y., Fuster, D., Zaleski, S., and Tryggvason, G. (2017). Spray formation in a quasiplanar gas-liquid mixing layer at moderate density ratios: A numerical closeup. *Phys. Rev. Fluids*, 2:014005.
- Ling, Y., Zaleski, S., and Scardovelli, R. (2015). Multiscale simulation of atomization with small droplets represented by a lagrangian point-particle model. *Int. J. Multiph. Flow*, 76:122 – 143.
- Liovic, P., Rudman, M., Liow, J.-L., Lakehal, D., and Kothe, D. (2006). A 3d unsplit-advection volume tracking algorithm with planarity-preserving interface reconstruction. *Computers Fluids*, 35(10):1011 – 1032.
- Lister, J. R. and Stone, H. A. (1998). Capillary breakup of a viscous thread surrounded by another viscous fluid. *Phys. Fluids*, 10(11):2758–2764.
- Lopez, J. and Hernandez, J. (2008). Analytical and geometrical tools for 3d volume of fluid methods in general grids. *J. of Comp. Phys.*, 227(12):5939 – 5948.
- MacIntyre, F. (1972). Flow patterns in breaking bubbles. *J. Geophysical Sci.*, 77(27):5211–5228.
- Manikantan, H. and Squires, T. M. (2020). Surfactant dynamics: hidden variables controlling fluid flows. *J. Fluid Mech.*, 892:P1.
- Marmottant, P. and Villermaux, E. (2004). On spray formation. *J. Fluid Mech.*, 498:73 – 111.
- Marston, J. O., Truscott, T. T., Speirs, N. B., Mansoor, M. M., and Thoroddsen, S. T. (2016). Crown sealing and buckling instability during water entry of spheres. *J. Fluid Mech.*, 794:506–529.
- Martin, D. W. and Blanchette, F. (2015). Simulations of surfactant effects on the dynamics of coalescing drops and bubbles. *Physics of Fluids*, 27(1):012103.
- McGough, P. T. and Basaran, O. A. (2006). Repeated formation of fluid threads in breakup of a surfactant-covered jet. *Phys. Rev. Lett.*, 96:054502.
- Ménard, T., Tanguy, S., and Berlemont, A. (2007). Coupling level set/vof/ghost fluid methods: Validation and application to 3d simulation of the primary break-up of a liquid jet. *Int. J. Multiph. Flow*, 33(5):510 – 524.
- Mirjalili, S., Chan, W. H. R., and Mani, A. (2018). High fidelity simulations of micro-bubble shedding from retracting thin gas films in the context of liquid-liquid impact.
- Notz, P. K. and Basaran, O. A. (2004). Dynamics and breakup of a contracting liquid filament. *J. Fluid Mech.*, 512:223–256.
- Néel, B. and Villermaux, E. (2018). The spontaneous puncture of thick liquid films. *J. Fluid Mech.*, 838:192–221.

- Oliveira, R., Antuniassi, U., Mota, A., and Chechetto, R. (2013). Potential of adjuvants to reduce drift in agricultural spraying. *Engenharia Agrícola*, 33:986–992.
- Olsson, E. and Kreiss, G. (2005). A conservative level set method for two phase flow. *J. of Comp. Phys.*, 210(1):225 – 246.
- Peregrine, D. H., Shoker, G., and Symon, A. (1990). The bifurcation of liquid bridges. *J. Fluid Mech.*, 212:25–39.
- Peskin, C. and McQueen, D. (1995). A general method for the computer simulation of biological systems interacting with fluids. *Symposia of the Society for Experimental Biology*, 49:265–276.
- Peskin, C. S. (1977). Numerical analysis of blood flow in the heart. *J. of Comp. Phys.*, 25(3):220 – 252.
- Plateau, J. (1873). *Experimental and Theoretical Statics of Liquids Subject to Molecular Forces Only*, volume 1. Gand et Leipzig: F. Clemm.
- Pope, S. B. (2000). *Turbulent Flows*. Cambridge University Press.
- Poulain, S. and Bourouiba, L. (2018). Biosurfactants change the thinning of contaminated bubbles at bacteria-laden water interfaces. *Phys. Rev. Lett.*, 121:204502.
- Raes, F., Dingenen, R. V., Vignati, E., Wilson, J., Putaud, J.-P., Seinfeld, J. H., and Adams, P. (2000). Formation and cycling of aerosols in the global troposphere. *Atmospheric Environment*, 34(25):4215 – 4240.
- Rayleigh, L. (1879). On the capillary phenomena of jets. *Proc. of the Royal Society of London*, 29:71–97.
- Reitz, R. D. and Bracco, F. V. (1986). *Mechanisms of breakup of round liquid jets*, chapter 3. Number 233–249. Encyclopedia of Fluid Mechanics, Gulf Pub, Houston, TX.
- Renardy, Y. and Renardy, M. (2002). Prost: A parabolic reconstruction of surface tension for the volume-of-fluid method. *J. of Comp. Phys.*, 183:400–421.
- Rutland, D. F. and Jameson, G. J. (1971). A non-linear effect in the capillary instability of liquid jets. *J. Fluid Mech.*, 46(2):267–271.
- Sanderson, R., Hewitt, A., Huddleston, E., and Ross, J. (1997). Relative drift potential and droplet size spectra of aerially applied propanil formulations. *Crop Protection*, 16(8):717 – 721.
- Scardovelli, R. and Zaleski, S. (1999). Direct numerical simulation of free-surface and interfacial flow. *Annual Review of Fluid Mechanics*, 31(1):567–603.

- Schulkes, R. M. S. M. (1996). The contraction of liquid filaments. *J. Fluid Mech.*, 309:277–300.
- Séon, T. and Liger-Belair, G. (2017). Effervescence in champagne and sparkling wines: From bubble bursting to droplet evaporation. *Eur. Phys. J. Special Topics*, 226:117–156.
- Shi, X. D., Brenner, M. P., and Nagel, S. R. (1994). A cascade of structure in a drop falling from a faucet. *Science*, 265(5169):219–222.
- Shim, S. and Stone, H. A. (2017). Damped coalescence cascade of liquid drops. *Phys. Rev. Fluids*, 2:044001.
- Shin, S., Abdel-Khalik, S. I., Daru, V., and Juric, D. (2005). Accurate representation of surface tension using the level contour reconstruction method. *J. Comput. Phys.*, 203(2):493 – 516.
- Shin, S., Chergui, J., and Juric, D. (2017). A solver for massively parallel direct numerical simulation of three-dimensional multiphase flows. *J. Mech. Sci. Tech.*, 31:1739–1751.
- Shin, S., Chergui, J., Juric, D., Kahouadji, L., Matar, O. K., and Craster, R. V. (2018). A hybrid interface tracking – level set technique for multiphase flow with soluble surfactant. *J. Comp. Phys.*, 359:409–435.
- Shin, S. and Juric, D. (2002). Modeling three-dimensional multiphase flow using a level contour reconstruction method for front tracking without connectivity. *J. of Comp. Phys.*, 180:427–470.
- Shin, S. and Juric, D. (2009). A hybrid interface method for three-dimensional multiphase flows based on front tracking and level set techniques. *Int. J. Num. Meth. Fluids*, 60:753–778.
- Shinjo, J. and Umemura, A. (2010). Simulation of liquid jet primary breakup: Dynamics of ligament and droplet formation. *Int. J. Multiph. Flow*, 36(7):513 – 532.
- Shu, C.-W. and Osher, S. (1989). Efficient implementation of essentially non-oscillatory shock-capturing schemes, ii. *J. of Comp. Phys.*, 83(1):32 – 78.
- Siderius, A., Kehl, S. K., and Leaist, D. G. (2002). Surfactant diffusion near critical micelle concentrations. *Journal of Solution Chemistry*, 31(8):607–625.
- Sijs, R., Kooij, S., and Bonn, D. (2019). How surfactants influence the drop size in sprays.
- Singh, D. and Das, A. K. (2019). Numerical investigation of the collapse of a static bubble at the free surface in the presence of neighbors. *Phys. Rev. Fluids*, 4:023602.
- Stainier, C., Destain, M.-F., Schiffers, B., and Lebeau, F. (2006). Droplet size spectra and drift effect of two phenmedipham formulations and four adjuvants mixtures. *Crop Protection*, 25(12):1238 – 1243.

- Sun, K., Zhang, P., Che, Z., and Wang, T. (2018). Marangoni-flow-induced partial coalescence of a droplet on a liquid/air interface. *Phys. Rev. Fluids*, 3:023602.
- Sussman, M., Smereka, P., and Osher, S. (1994). A level set approach for computing solutions to incompressible two-phase flow. *J. of Comp. Phys.*, 114(1):146 – 159.
- Taub, G. N., Lee, H., Balachandar, S., and Sherif, S. A. (2013). A direct numerical simulation study of higher order statistics in a turbulent round jet. *Phys. Fluids*, 25(11):115102.
- Taylor, J. J. and Hoyt, J. W. (1983). Water jet photography techniques and methods. *Exp. Fluids*, 1(3):113–120.
- Tedesco, R. and Blanchard, D. (1979). Dynamics of small bubble motion and bursting in freshwater. *J. Rech. Atmos.*, 13(215).
- Teng, D., Hashi, W., and Panagiota, A. (2019). Laser induced fluorescence studies on the distribution of surfactants during drop/interface coalescence. *Physics of Fluids*, 31(1):012106.
- Theodorsen, T. (1952). Mechanism of turbulence. *Proceedings of the Midwestern Conference Fluid Mechanics*, 1-19.
- Thoroddsen, S. T. and Takehara, K. (2000). The coalescence cascade of a drop. *Physics of Fluids*, 12(6):1265–1267.
- Toba, Y. (1959). Drop production by bursting of air bubbles on the sea surface (ii) theoretical study on the shape of floating bubbles. *J. of the Oceanographical Soc. of Japan*, 15(3):121–130.
- Tryggvason, G., Bunner, B., Esmaeeli, A., Juric, D., Al-Rawahi, N., Tauber, W., Han, J., Nas, S., and Jan, Y.-J. (2001). A front-tracking method for the computations of multiphase flow. *J. of Comp. Phys.*, 169(2):708 – 759.
- Tryggvason, G., Scardovelli, R., and Zaleski, S. (2011). *Direct Numerical Simulations of Gas–Liquid Multiphase Flows*. Cambridge University Press.
- Udaykumar, H., Mittal, R., and Shyy, W. (1999). Computation of solid–liquid phase fronts in the sharp interface limit on fixed grids. *J. of Comp. Phys.*, 153(2):535 – 574.
- Unverdi, S. O. and Tryggvason, G. (1992). A front-tracking method for viscous, incompressible, multi-fluid flows. *J. Comput. Phys.*, 100(1):25 – 37.
- Varga, C. M., Lasheras, J. C., and Hoepfinger, E. J. (2003). Initial breakup of a small-diameter liquid jet by a high-speed gas stream. *J. Fluid Mech.*, 497:405–434.
- Veron, F. (2015). Ocean spray. *Ann. Rev. of Fluid Mech.*, 47:507–538.

- Villermaux, E. (2007). Fragmentation. *Ann. Rev. of Fluid Mech.*, 39:419–446.
- Villermaux, E., Marmottant, P., and Duplat, J. (2004). Ligament-mediated spray formation. *Phys. Rev. Lett.*, 92:074501.
- Wang, F., Contò, F. P., Naz, N., Castrejón-Pita, J. R., Castrejón-Pita, A. A., Bailey, C. G., Wang, W., Feng, J. J., and Sui, Y. (2019). A fate-alternating transitional regime in contracting liquid filaments. *J. Fluid Mech.*, 860:640–653.
- Woodcock, A. H., Kientzler, C. F., Arons, A. B., and Blanchard, D. C. (1953). Giant condensation nuclei from bursting bubbles. *Nature*, 172:1144–1145.
- Zandian, A., Sirignano, W. A., and Hussain, F. (2016). Three-dimensional liquid sheet breakup: vorticity dynamics. *54th AIAA Aerospace Sciences Meeting*.
- Zandian, A., Sirignano, W. A., and Hussain, F. (2018). Understanding liquid-jet atomization cascades via vortex dynamics. *J. Fluid Mech.*, 843:293–354.
- Zandian, A., Sirignano, W. A., and Hussain, F. (2019). Vorticity dynamics in a spatially developing liquid jet inside a co-flowing gas. *J. Fluid Mech.*, 877:429–470.
- Zeff, B. W., Kleber, B., Fineberg, J., and Lathrop, D. P. (2000). Singularity dynamics in curvature collapse and jet eruption on a fluid surface. *Nature*, 403:401–404.
- Zenit, R. and Rodríguez-Rodríguez, J. (2018). The fluid mechanics of bubbly drinks. *Phys. Today*, 71(11):44.
- Zhou, J., Adrian, R. J., Balachandar, S., and Kendall, T. M. (1999). Mechanisms for generating coherent packets of hairpin vortices in channel flow. *J. Fluid Mech.*, 387:353–396.
- Ziegler, V. E. and Wolf, B. A. (2005). Bimodal drop size distributions during the early stages of shear induced coalescence. *Polymer*, 46(22):9265 – 9273.