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On the dispersion dynamics of liquid-liquid surfactant-laden flows in a SMX static mixer

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ABSTRACT

This study aims to elucidate, for the first time, the intricate fundamental physics governing the dispersion dynamics of a surfactant-laden two-phase liquid-liquid system in the well-known SMX static mixer. Following the analysis carried out in the preceding publication to this work [1], a comparative assessment of the most relevant and recurrent deformation and breakup mechanisms is conducted for a 3-drop scenario and then extrapolated to a more industrially-relevant multi-drop set-up. A parametric study on relevant surfactant physico-chemical parameters (i.e., elasticity, sorption kinetics) is undertaken, isolating each property by considering insoluble and soluble surfactants. In addition, the role of Marangoni stresses on the deformation and breakage dynamics is explored. High fidelity, three-dimensional direct numerical simulations coupled with a state-of-the-art hybrid interface capturing algorithm are carried out, which provides a wealth of information, previously inaccessible via volume-averaged or experimental approaches.


1. Introduction

Liquid-liquid (L-L) dispersions and emulsions are of central relevance to various modern industrial sectors, ranging from consumer and mass-produced goods (i.e., food, cosmetics) to processing applications (i.e., polymers, biotechnology, petro-chemical) [2]. Even though emulsions are thermodynamically unstable due to their inherent immiscibility, two criteria can be pursued to achieve a kinetic pseudo-stability: (i) addition of surface-active agents, and (ii) energy incorporation to induce drop breakage and disperse one phase into the other [2, 3]. It is well-known that surfactants play a major role in drop breakage/coalescence dynamics and the associated droplet size distribution (DSD) attained by lowering interfacial tension [4]. In turn, the dispersed phase concentration (i.e., number of drops) and DSD greatly influence, not only the emulsion physico-chemical attributes and stability, but also mixer design, operation and scale-up considerations in terms of energy requirements [2, 5].

Despite the fact that conventional high-energy methods (e.g., agitated tanks, rotor-stator mixers) remain as first choice for emulsification processes, static mixers have shown remarkable potential as an alternative to those methodologies. A static mixer consists of a series of inserts or *elements* arranged in a given configuration inside a pipe, channel, column or reactor [2]. These inserts are responsible for redistributing the flow sequentially in directions transverse to the main flow, thus inducing chaotic mixing [6, 7]. A broad range of these devices are available nowadays, and are classi-

fied according to their geometry and/or intended application, as summarized thoroughly in previous reviews [2, 7]. Static mixers are widely regarded as being more energy efficient than stirred tanks, since they guarantee a similar degree of mixing with shorter residence times, and lower capital costs and energy consumption [2, 7, 8]. These mixers have been found to distribute energy more efficiently and uniformly at a higher intensity than agitated tanks, as demonstrated experimentally by Theron et al. [9].

L-L static mixing has been extensively investigated over the past few decades, testing a broad scope of fluid properties, design and operational parameters [2]. In particular, the influence of the interfacial tension (σ), mainly through the addition of surface-active agents, has been of crucial interest given its key role in the dispersion dynamics and emulsion properties. Early works probed the effect of varying σ solely by testing different organic compounds (e.g., oils, benzene, cyclohexane), as is the case for pioneering experimental works by Middleman [10], Streiff [11], and Grace [12], who studied σ ranges between 5 - 46 mN/m, 24.7 - 46.0 mN/m, and 1 - 25 mN/m, respectively. Apart from Grace [12], who studied the physics underlying the flow and drop breakage mechanics, both Middleman [10] and Streiff [11] derived mean droplet size (D_{32}) correlations based on Kolmogorov's turbulence dispersion theory, where interfacial tension effects were accounted for through the inclusion of the Weber (We) number. Following a similar route, Berkman and Calabrese [13] studied different dispersing liquids in a Kenics mixer. Although the emphasis of this study lies in the dispersed phase viscosity, a semi-empirical D_{32} correlation was formulated, comparable to that proposed by Mid-

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60 dleman [10]. All these models derived a relation of the form
61 $D_{32} \sim We^{-n}$, implying that the droplet size scales with σ .

62 Numerous experimental works in the following years un-
63 dertook similar endeavours by proposing (semi)-empirical
64 correlations from parametric studies [14, 15, 16, 17]. Haas
65 [14] is among the first to report the use of surfactants in L-L
66 static mixing and recognize the inherent complications in-
67 volved, such as the possible biases when fitting coefficients
68 for D_{32} correlations whilst assuming σ to be constant. In ad-
69 dition, discrepancies between σ measured in controlled lab
70 environments vs. *in situ* values during the dispersion pro-
71 cess are addressed, acknowledging the fact that surfactant-
72 laden daughter droplets require a finite time to approach the
73 equilibrium interfacial tension measured in the lab. On the
74 other hand, Maa and Hsu [15], Legrand et al. [16] and Gin-
75 gras et al. [17] carried out parametric studies on multiple
76 fluid properties with different static mixers (e.g., SMX, heli-
77 cal, etc), aiming towards various applications such as micro-
78 encapsulation [15], general oil/water dispersions [16] and
79 bitumen emulsification [17], specifically targeting σ through
80 the surfactant concentration. All studies maintained the same
81 dependence of D_{32} on σ , albeit with different exponents and
82 assuming σ to be constant [2].

83 More exhaustive investigations ensued on the same sub-
84 ject. Fradette et al. [4] correlated surfactant concentration
85 and water-surfactant ratio with mean droplet diameter and
86 distribution span for different mixing techniques, showing
87 that there is not always a monotonic trend between these
88 parameters (higher surfactant concentrations do not always
89 lead to smaller mean diameters). In particular, it was demon-
90 strated that the same mean droplet size (albeit with a dif-
91 ferent distribution span) can be achieved with static mix-
92 ers and stirred vessels, despite the hydrodynamic differences
93 between the two processes, attributing surface generation
94 solely to the chemical formulation (i.e., surfactant content).
95 Lobry et al. [6] studied four different water/surfactant/oil sys-
96 tems in a SMV mixer, where a noticeable change in the DSD
97 was reported by only replacing the type of surfactant (PVA
98 and Tween 80). It became evident that the difference be-
99 tween σ values at equilibrium did not truly account for the
100 variation seen in the DSD leading to the proposition that
101 temporal gradients in σ should be considered in relation to
102 the residence time in the mixer. From this observation, it
103 was argued that slower PVA diffusion times caused a higher
104 σ during the dispersion which explained the changes in DSD
105 observed in the experiments of Lobry et al. [6].

106 Das et al. [8] explored L-L dispersions in a SMX mixer at
107 three levels of surfactant concentration, varying the superfi-
108 cial velocities and viscosity ratios. General trends exhibited
109 a mean diameter decrease for reduced interfacial tensions,
110 which was less apparent at low concentrations. A similar
111 explanation as those conveyed by Lobry et al. [6] and Haas
112 [14] was proposed, arguing that the dynamic σ would be
113 higher than its equilibrium value since the interfacial con-
114 centration at a moving surface is less than that at its equilib-
115 rium, given that the rate of surfactant adsorption at the in-
116 terface is diffusion-limited. Further details are given on the

DSD shape at high concentrations, correlating a departure
from Gaussian to log-shaped distributions with a shift in the
dominant breakage mechanisms, suggesting tip-streaming as
the primary one.

120
121 In addition to the studies summarised in the foregoing, an
122 extensive array of works exist on the fundamental dynamics
123 of surfactant-laden liquid drops in a liquid medium, mostly
124 exploring two canonical flows: simple shear and extensional
125 flows. In both cases, the focus is on drop deformation (in ex-
126 tensional [18, 19, 20] and simple shear flow [21, 22]), as well
127 as breakage (in extensional [23, 24, 25, 26, 27] and simple
128 shear flow [28, 29]), assuming (numerically) an insoluble
129 surfactant confined to the interface. A few studies have ac-
130 counted for surfactant solubility and scrutinized the effect of
131 surfactant transport dynamics on the same phenomena men-
132 tioned above [30, 31, 32, 33, 34]. A number of pertinent ref-
133 erences are cited here that have examined deforming, thin-
134 ning and breaking surfactant-laden liquid threads, bridges
135 and ligaments [35, 36, 37, 38, 39]. Although most of these
136 works deal with a liquid-air interface, the underlying mecha-
137 nisms discussed are also active in liquid-liquid systems. Es-
138 sentially, all of the aforementioned studies focus on isolated
139 and controlled scenarios where the fundamental physics can
140 be elucidated.

141 To the best of the authors' knowledge, no detailed nu-
142 merical studies on the intricate interfacial mechanics of surfactant-
143 laden L-L systems have been carried out in the context of an
144 industrially relevant operation like mixing, let alone static
145 mixing. Instead, most studies have targeted variations in σ
146 from a macroscopic perspective while disregarding key in-
147 terfacial and bulk surfactant transport dynamics. More im-
148 portantly, numerous studies have agreed on the crucial de-
149 ficiencies in models assuming a constant σ , and on the sub-
150 stantial deviation between equilibrium vs. dynamic σ , which
151 strongly depends on the surfactant physico-chemical prop-
152 erties and the dispersion process itself. Based on the above,
153 this study seeks to provide the first account of a more real-
154 istic depiction of a L-L surfactant-laden dispersion process
155 in a full-scale static mixing operation. For this, a frame-
156 work consisting of three-dimensional direct numerical sim-
157 ulations coupled with a high fidelity interface-tracking al-
158 gorithm will be deployed. This study will provide a wealth
159 of information on the complex interfacial dynamics unfold-
160 ing while accounting for surfactant transport at the inter-
161 face and in the bulk of the dispersing phase. Furthermore,
162 a parametric study of relevant variables, such as surfactant
163 strength, and different sorptive kinetic profiles, will be con-
164 ducted. The level of detail achieved with our numerical frame-
165 work provides complementary information to that obtained
166 via experimental studies, leading to a deeper understanding
167 of surfactant-laden L-L dispersions in static mixers.

2. Problem formulation

168
169 This paper builds upon the results previously published
170 by Valdes et al. [1]. Hence, the problem set-up and nu-
171 merical framework remain mostly unchanged, except for the

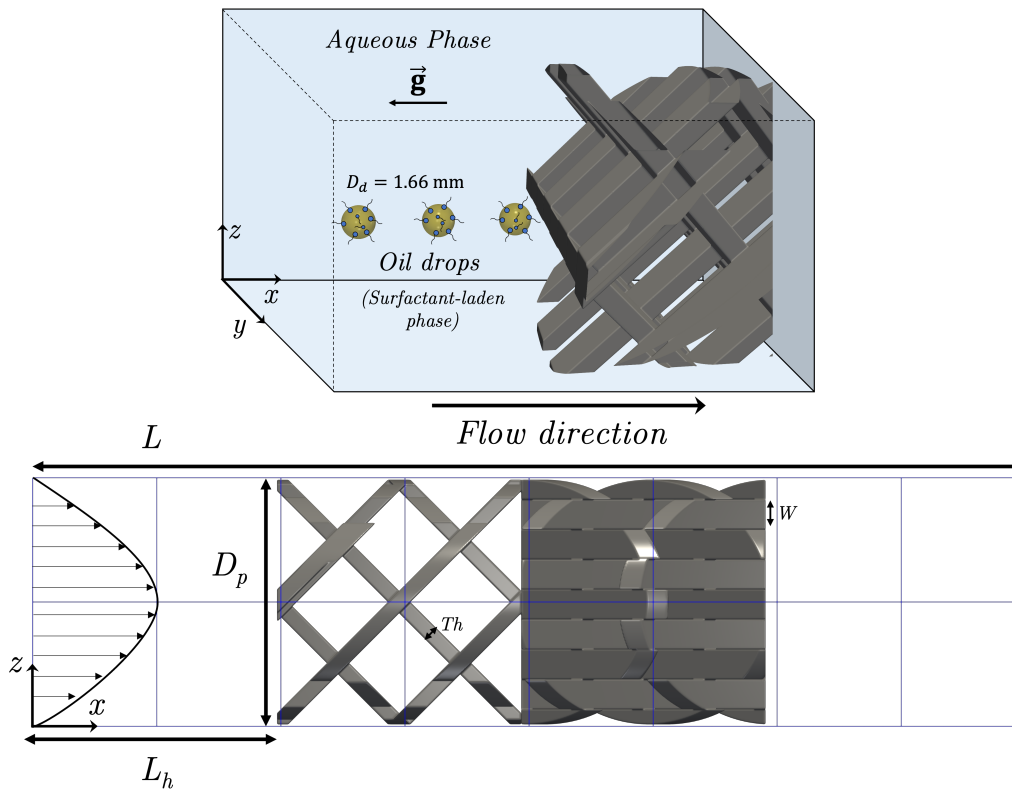


Figure 1: Problem formulation and computational domain. Top panel shows the set-up of the aqueous and oil (surfactant-laden) phases; bottom panel displays the mixer's geometry, labeling the relevant dimensions given in Table 1.

172 inclusion of transport equations dealing with the surfactant
 173 mass transfer dynamics. The following subsections will briefly
 174 recall the problem set-up from Valdes et al. [1] but will mostly
 175 focus on the details of the surfactant modelling. For an overview
 176 of the numerical framework employed in this study, the reader
 177 is referred to previous publications [1, 40, 41, 42].

178 2.1. Geometry, grid and simulation configuration

179 The static mixer studied herein is a 2-element standard
 180 Sulzer SMX (multi-layered) design. The mixer dimensions
 181 follow specifications given in Valdes et al. [1], which, in
 182 turn, are based on the experimental work of Liu et al. [43],
 183 as summarized in Table 1 and labeled in Fig. 1. Details of
 184 the estimation of the entrance length L_h and the numerical
 185 construction of the geometry can be found in our previous
 186 work [1]. The computational domain consists of a three-
 187 dimensional structured Cartesian grid, divided into $12 \times 6 \times$
 188 6 sub-domains. Each sub-domain is divided into another
 189 structured Cartesian grid with a $128 \times 64 \times 64$ configura-
 190 tion, rendering a global mesh size of $1536 \times 384 \times 384$.
 191 The domain size is $0.064 \times 0.016 \times 0.016 \text{ m}^3$ as specified
 192 in Valdes et al. [1]. Therefore, cells will have an approxi-
 193 mate volume of $7.0 \times 10^{-14} \text{ m}^3$, resulting in an average size
 194 of $4.12 \times 10^{-5} \text{ m}$. As detailed in Valdes et al. [1], and vali-
 195 dated through a grid independence study, this mesh resolu-
 196 tion was deemed to be reliable when capturing the droplet
 197 distortion and breakup, as it complies with the number of
 198 cells per drop diameter recommended for interface-tracking

199 algorithms [44]. Furthermore, the numerical framework used
 200 in this work naturally provides sub-grid resolution due to its
 201 front-tracking formulation (refer to § 2.2), which involves
 202 high-fidelity tracking of the interfacial dynamics occurring
 203 at smaller scales after the droplets' initial collision with the
 204 leading edge of the mixer [40].

205 Following the case studies mentioned in Valdes et al. [1],
 206 this paper will mostly focus on the three-drop "isolated" con-
 207 figuration for the dispersed phase, as depicted in Fig. 1. In
 208 this scenario, the oil droplets ($D_d = 1.66 \text{ mm}$ initial diame-
 209 ter) are at first set to be stationary and the continuous phase
 210 (denoted with subscript c) flowrate is set to $Q_c = 9.0 \times$
 211 $10^{-6} \text{ m}^3 \cdot \text{s}^{-1}$, which renders a $Re_c = 4\rho_c Q_c / \pi D_p \mu_c = 1.63$,
 212 as specified by Valdes et al. [1]. The flow is initiated by im-
 213 posing a fully-developed parabolic velocity profile at the on-
 214 set of the domain as shown in Fig. 1, and no-slip boundary
 215 conditions are defined at the mixer crossbars. In addition,
 216 more complex exploratory cases with a multi-drop inlet mor-
 217 phology will be included. These instances will adhere to the
 218 specifications given in Valdes et al. [1] for the "Coarse Pre-
 219 mix" case, namely 160 oil drops with a size range between
 220 $0.4 < D_d (\text{mm}) < 2$ and the same continuous flowrate Q_c .

221 Similarly, fluid properties are defined following the ex-
 222 perimental tests carried out by Liu et al. [43], namely: con-
 223 tinuous phase (aqueous solution) viscosity and density: $\mu_a =$
 224 $0.615 \text{ Pa} \cdot \text{s}$ and $\rho_a = 1364 \text{ kg} \cdot \text{m}^{-3}$, respectively; dispersed
 225 phase (silicon oil) viscosity and density: $\mu_o = 0.0984 \text{ Pa} \cdot \text{s}$
 226 and $\rho_o = 960 \text{ kg} \cdot \text{m}^{-3}$, respectively and a "clean" or surfactant-

Table 1

Geometrical specifications for the SMX mixer taken from Valdes et al. [1] and based on Liu et al. [43] tests.

Feature	
Pipe Diameter D_p (m)	0.01575
Number of Crossbars	8
Length L (m)	0.064
Aspect Ratio L_E/D_p	1
Bar Width W (m)	0.00193
Bar Thickness Th (m)	0.00102

free interfacial tension of $\sigma_{cl} = 0.036\text{N} \cdot \text{m}^{-1}$. The effects of gravity are considered acting in the negative x -direction opposite to the flow as portrayed in Fig. 1.

2.2. Governing equations

The governing equations considered in this study are presented in the context of the Level Contour Reconstruction Method (LCRM), explained in detail in previous works [1, 40, 41, 42]. Both liquid phases are treated as immiscible Newtonian and incompressible fluids. The continuity and momentum equations in a three-dimensional Cartesian domain $\mathbf{x} = (x, y, z) \in [0, 0.064] \times [0, 0.016] \times [0, 0.016]$ m can be written as follows using a single-field formulation:

$$\nabla \cdot \mathbf{u} = 0, \quad (1)$$

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \rho \mathbf{g} + \nabla \cdot \mu (\nabla \mathbf{u} + \nabla \mathbf{u}^T) + \int_A [\sigma \kappa \mathbf{n} + \nabla_s \sigma] \delta(\mathbf{x} - \mathbf{x}_f) dA, \quad (2)$$

where t , p , \mathbf{u} , and \mathbf{g} denote time, pressure, velocity, and gravity, respectively. The interfacial force term in Eq. 2 is decomposed into its normal ($\sigma \kappa \mathbf{n}$) and tangential components ($\nabla_s \sigma$), the former representing the mean interfacial tension and the latter arising as a consequence of interfacial tension gradients which lead to Marangoni stresses. Here, κ denotes the interface curvature, ∇_s stands for the surface gradient operator, and \mathbf{n} is the normal unit vector pointing away from the interface. The 3D Dirac delta function $\delta(\mathbf{x} - \mathbf{x}_f)$ takes a value of 0 at every point except at the interface, which is located at $\mathbf{x} = \mathbf{x}_f$.

The density ρ and viscosity μ are defined throughout the domain as:

$$\begin{aligned} \rho(\mathbf{x}, t) &= \rho_a + (\rho_o - \rho_a) \mathcal{H}(\mathbf{x}, t), \\ \mu(\mathbf{x}, t) &= \mu_a + (\mu_o - \mu_a) \mathcal{H}(\mathbf{x}, t). \end{aligned} \quad (3)$$

The Heaviside function $\mathcal{H}(\mathbf{x}, t)$ given above is generated by means of a vector distance function $\varphi(\mathbf{x})$ computed directly from the tracked interface [40]. $\mathcal{H}(\mathbf{x}, t)$ is defined as zero in the aqueous phase and unity in the oil phase, with subscripts a and o denoting the aqueous and oil phases, respectively. This function is solved numerically with a smooth transition across 3 to 4 grid cells [41].

Surfactant transport was resolved in both the liquid bulk and the interface by a set of convection-diffusion equations,

similar to those presented in previous works [39, 45]. It is important to mention that the surfactant is assumed to be soluble only in the oil phase, thus bulk diffusion is allowed only within the dispersed phase [42]. The surfactant concentration on the interface, Γ , is treated as follows:

$$\frac{\partial \Gamma}{\partial t} + \nabla_s \cdot (\Gamma \mathbf{u}_t) = D_s \nabla_s^2 \Gamma + \dot{S}_\Gamma, \quad (4)$$

where $\mathbf{u}_t = (\mathbf{u}_s \cdot \mathbf{t})\mathbf{t}$ stands for the tangential velocity vector in which \mathbf{u}_s is the surface velocity at the interface and \mathbf{t} is the unit vector tangent to the interface, and D_s is the surface diffusion coefficient. The sorptive flux accounting for the surfactant transfer between the interface and the bulk is estimated through the source term:

$$\dot{S}_\Gamma = k_a C_s (\Gamma_\infty - \Gamma) - k_d \Gamma, \quad (5)$$

where k_a and k_d are the adsorption and desorption coefficients, respectively, C_s is the surfactant's concentration in the region immediately adjacent to the interface (bulk "sub-phase" [45]), and Γ_∞ is the interfacial surfactant concentration at saturation. The equation dictating surfactant concentration in the bulk, C , is given as follows:

$$\frac{\partial C}{\partial t} + \mathbf{u} \cdot \nabla C = D_b \nabla^2 C, \quad (6)$$

where D_b stands for the surfactant diffusivity in the bulk. The relationship between the interfacial (Γ) and bulk (C) surfactant concentrations is governed by the source term \dot{S}_Γ , displayed in Eqs. 4 and 5, as shown in the expression below:

$$\mathbf{n} \cdot \nabla C|_{\text{interface}} = -\frac{\dot{S}_\Gamma}{D_b}. \quad (7)$$

As commonly defined in several previous works [42, 39, 45, 46], the Langmuir equation of state (EOS) is used to describe the relationship between the effective interfacial tension (σ) and the interfacial surfactant concentration (Γ);

$$\begin{aligned} \sigma &= \sigma_{cl} + \mathcal{R}T\Gamma_\infty \ln \left(1 - \frac{\Gamma}{\Gamma_\infty} \right) \\ &= \sigma_{cl} \left[1 + \frac{\mathcal{R}T\Gamma_\infty}{\sigma_{cl}} \ln \left(1 - \frac{\Gamma}{\Gamma_\infty} \right) \right], \end{aligned} \quad (8)$$

where \mathcal{R} is the ideal gas constant and T is the temperature. To appropriately identify the governing forces in the system studied, all variables are rendered dimensionless through the following scalings:

$$\begin{aligned} \tilde{\mathbf{x}} &= \frac{\mathbf{x}}{D_0}, \quad \tilde{\mathbf{u}} = \frac{\mathbf{u}}{U_r}, \quad \tilde{t} = \frac{t}{D_0/U_r}, \quad \tilde{p} = \frac{p}{\rho_o U_r^2}, \quad \tilde{\rho} = \frac{\rho}{\rho_o}, \\ \tilde{\mu} &= \frac{\mu}{\mu_o}, \quad \tilde{\sigma} = \frac{\sigma}{\sigma_{cl}}, \quad \tilde{\Gamma} = \frac{\Gamma}{\Gamma_\infty}, \quad \tilde{C} = \frac{C}{C_\infty}, \quad \tilde{C}_s = \frac{C_s}{C_\infty}, \end{aligned} \quad (9)$$

292 where the tildes designate dimensionless quantities. The length
 293 and velocity are normalised by the radius of the pipe D_0 ,
 294 and the corresponding average flow velocity U_r at the inlet
 295 corridors between crossbars, which is calculated from the
 296 simulations carried out in Valdes et al. [1]. The interfacial
 297 surfactant concentration is scaled against the interfacial con-
 298 centration at saturation (Γ_∞), whereas the concentrations in
 299 the bulk and bulk sub-phase are scaled against a reference
 300 bulk concentration (C_∞) set as an initial condition [39, 45].
 301 As a result of this procedure, Eqs. 1 - 8 become:

$$\nabla \cdot \tilde{\mathbf{u}} = 0, \quad (10)$$

$$\begin{aligned} \tilde{\rho} \left(\frac{\partial \tilde{\mathbf{u}}}{\partial \tilde{t}} + \tilde{\mathbf{u}} \cdot \nabla \tilde{\mathbf{u}} \right) = & -\nabla \tilde{p} + \frac{\tilde{\rho}}{\text{Fr}^2} \mathbf{e}_x + \frac{1}{\text{Re}} \nabla \cdot [\tilde{\mu}(\nabla \tilde{\mathbf{u}} + \nabla \tilde{\mathbf{u}}^T)] \\ & + \frac{1}{\text{We}} \int_{\tilde{A}} [\tilde{\sigma} \tilde{\mathbf{k}} \mathbf{n} + \nabla_s \tilde{\sigma}] \delta(\tilde{\mathbf{x}} - \tilde{\mathbf{x}}_f) d\tilde{A}, \end{aligned} \quad (11)$$

$$\begin{aligned} \tilde{\rho}(\mathbf{x}, t) &= \frac{\rho_a}{\rho_o} + \left(1 - \frac{\rho_a}{\rho_o} \right) \mathcal{H}(\mathbf{x}, t), \\ \tilde{\mu}(\mathbf{x}, t) &= \frac{\mu_a}{\mu_o} + \left(1 - \frac{\mu_a}{\mu_o} \right) \mathcal{H}(\mathbf{x}, t). \end{aligned} \quad (12)$$

$$\frac{\partial \tilde{C}}{\partial \tilde{t}} + \tilde{\mathbf{u}} \cdot \nabla \tilde{C} = \frac{1}{\text{Pe}_b} \nabla^2 \tilde{C}, \quad (13)$$

$$\frac{\partial \tilde{\Gamma}}{\partial \tilde{t}} + \nabla_s \cdot (\tilde{\Gamma} \tilde{\mathbf{u}}_t) = \frac{1}{\text{Pe}_s} \nabla_s^2 \tilde{\Gamma} + \text{Bi} [k \tilde{C}_s (1 - \tilde{\Gamma}) - \tilde{\Gamma}], \quad (14)$$

$$\mathbf{n} \cdot \nabla \tilde{C}|_{\text{interface}} = -\text{Pe}_b \text{DaBi} [k \tilde{C}_s (1 - \tilde{\Gamma}) - \tilde{\Gamma}], \quad (15)$$

$$\tilde{\sigma} = \max[\varepsilon_\sigma, 1 + \beta_s \ln(1 - \tilde{\Gamma})]. \quad (16)$$

304 Here, Marangoni stresses, which arise from gradients in sur-
 305 face concentration ($\tilde{\Gamma}$), are defined as:

$$\tau_M = \nabla_s \tilde{\sigma} \cdot \mathbf{t} = \frac{\partial \tilde{\sigma}}{\partial \tilde{\Gamma}} \nabla_s \tilde{\Gamma} \cdot \mathbf{t} = -\frac{\beta_s}{1 - \tilde{\Gamma}} \nabla_s \tilde{\Gamma} \cdot \mathbf{t}. \quad (17)$$

306 Eq. 16 has been slightly modified by adding $\varepsilon_\sigma = 0.05$ in
 307 order to avoid negative interfacial tension values ($\tilde{\sigma}$) at high
 308 surfactant interfacial coverage ($\tilde{\Gamma} \approx 1$), as proposed by Mu-
 309 radoglu and Tryggvason [46]. The minimum effective in-
 310 terfacial tension possible with $\varepsilon_\sigma = 0.05$ lies in the same
 311 order of magnitude as experimental interfacial tension val-
 312 ues reported for commonly used surfactants in liquid-liquid
 313 systems, such as Tween 80, PVA [6], ε -caprolactam [47],
 314 and SDS [48], in the context of static mixing applications.

315 The dimensionless groups appearing in the equations above
 316 are defined as follows:

$$\begin{aligned} \text{Re} &= \frac{\rho_o U_r D_0}{\mu_o}, \quad \text{Fr} = \frac{U_r}{\sqrt{D_0 g}}, \quad \text{We} = \frac{\rho_o U_r^2 D_0}{\sigma_{cl}}, \\ \text{Pe}_b &= \frac{U_r D_0}{D_b}, \quad \text{Pe}_s = \frac{U_r D_0}{D_s}, \quad \text{Bi} = \frac{k_d D_0}{U_r}, \end{aligned} \quad (18)$$

$$k = \frac{k_d C_\infty}{k_d}, \quad \text{Da} = \frac{\Gamma_\infty}{D_0 C_\infty}, \quad \beta_s = \frac{\mathcal{R} T \Gamma_\infty}{\sigma_{cl}},$$

317 where Re, Fr and We stand for the Reynolds, Froude, and
 318 Weber numbers, respectively. The competition between con-
 319 vective and diffusive surfactant transport in the bulk and at
 320 the interface is determined by the Peclet numbers Pe_b and
 321 Pe_s , respectively. The remaining parameters characterise sev-
 322 eral relevant physicochemical aspects of the surfactant species:
 323 the elasticity parameter, which acts as a measure of the "strength"
 324 of the surfactant on the effective interfacial tension exhib-
 325 ited, is given by β_s ; the competition between desorptive ca-
 326 pability vs. convective surface transport is accounted for
 327 through the Biot number (Bi); the ratio of adsorption to des-
 328 orption rates (sorption kinetics) is given by the adsorption
 329 number (k); and the relative importance of the bulk vs. sur-
 330 face concentration is given by the Damkohler number (Da),
 331 commonly referred to as the adsorption depth, which can be
 332 interpreted as the characteristic depth beneath the interface
 333 that gets diluted by surfactant adsorption [31].

2.3. Scalings and parametric study outline

334 It is important to establish the relative importance of the
 335 governing forces and validate the proposed scalings against
 336 available experimental data. Firstly, it is useful to examine
 337 the hydrodynamics at drop scale, with $D_d = 0.00166$ m
 338 and $U_d = 0.075$ m \cdot s $^{-1}$ (calculated from [1]). These es-
 339 timates generate values of $\text{Re}_d = 0.276$, $\text{Fr}_d = 0.587$, and
 340 $\text{We}_d = 0.353$, which imply a heavy dominance of viscous,
 341 buoyant, and interfacial tension forces over inertia, as ex-
 342 pected given the highly viscous and slowly flowing contin-
 343 uous phase through which the drops are traveling. It is worth
 344 highlighting the commanding influence of interfacial tension
 345 forces over inertia given by the low We_d obtained, as it sug-
 346 gests that surfactants will play a major role in the dynam-
 347 ics studied herein. The Re_d and We_d values obtained are
 348 well in agreement with data reported in Das et al. [8] for
 349 laminar L-L surfactant-laden dispersions in a SMX operat-
 350 ing at $\text{Re}_c < 210$ (as defined in §2.1), where the experi-
 351 ments conducted lie in a range of $0.01 < \text{We}_d < 1$ and
 352 $0.255 < \text{Re}_d < 10.13$. Surfactant-related scalings rely on
 353 the previously mentioned pipe scale utilized for normalizing
 354 the governing equations. This involves defining length and
 355 velocity scales as $D_0 = 0.0079$ m and $U_r = 0.159$ m \cdot s $^{-1}$,
 356 respectively.

357 Both Pe values at the interface and in the bulk were ex-
 358 cluded from the parametric study. Typical interfacial dif-
 359 fusion coefficients for frequently used surfactants in static
 360 mixing applications, such as SDS (Sodium Dodecyl Sulfate)
 361 [8, 48], are within a range of $10^{-12} < D_s < 10^{-8}$ m 2 \cdot s $^{-1}$
 362 [49, 50], thus yielding a surface Peclet range of $10^3 < \text{Pe}_s <$
 363 10^6 [51], which lowers further to $1 < \text{Pe}_s < 10^6$ for highly
 364 viscous solutions with dominating viscous forces (albeit as-
 365 suming the same D_s as for aqueous solutions) [38]. Previous
 366 studies dealing with similar surfactant-laden systems (i.e.,
 367 deforming/breaking [26] and coalescing liquid drops [51],
 368 retracting liquid ligaments [39], and liquid thread breakup
 369 [36, 37]) have hinted towards a negligible effect of increas-
 370

ing Pe_s any further than $\sim O(10)$, suggesting that the relative importance of diffusive vs. convective transport becomes negligible for $Pe_s \gg 1$ [36]. Furthermore, authors remark that the interfacial dynamics become weakly dependent on surface diffusion effects, reaching a saturation point at $Pe_s \sim O(10^2)$ [26, 39, 51]. Hence, Pe_s was set to 100, thus guaranteeing interfacial surfactant transport to be convection rather than diffusion-driven [19, 37].

The bulk Peclet Pe_b was set equal to Pe_s as suggested by Constante-Amores et al. [51] and in agreement with the numerical framework implemented in previous works [39, 45]. More importantly, setting $Pe_b = 100$ ensures the interface-bulk surfactant distribution to be kinetically-controlled by satisfying the condition $Pe_b \cdot Da \cdot Bi < 1$ [31] (except for case 9 in Table 2). Therefore, the sorption kinetics can be effectively isolated since, in this limit, the diffusive flux of surfactants onto or off the interface, driven by bulk concentration gradients, can be neglected. In other words, the diffusive timescale in the bulk will be significantly smaller than the sorptive timescales, thus instantly smoothing out bulk concentration gradients so that $C_s(t) \approx C_{bulk}$ [52]. Such a limit is appropriate for the present setup since our current grid resolution might not suffice in all cases to accurately resolve surfactant concentration gradients within the oil droplets.

The remaining surfactant-related variables included in the parametric study are grouped by the governing dimensionless parameters extracted in the previous subsection and shown in Eq. 17, namely: elasticity parameter (β_s), Biot number (Bi), adsorption number (k) and Damkohler number (Da). To effectively isolate the effect of each parameter, three sets of case studies at three levels are proposed, as summarized in Table 2. The first set (cases 1-3) corresponds to a fully insoluble scenario, where the surfactant species is effectively confined to the interface. In this way, only mean interfacial tension effects and Marangoni stresses can be appreciated at different strengths. The β_s values were selected following the ranges studied by previous relevant papers [19, 23, 39]. As a reference, in the context of this study, a $\beta_s \approx 0.7$ is representative of a system at room temperature ($T = 298.15\text{K}$) where the maximum packing concentration at the interface is $\Gamma_\infty \sim O(10^{-5}) \text{ mol} \cdot \text{m}^{-2}$, being on the same order of magnitude as experimental values reported for surfactants such as SDS [53, 54]. The concentration Γ_∞ was set to $1 \times 10^{-5} \text{ mol} \cdot \text{m}^{-2}$ and kept constant throughout all case studies, taking as a reference the order of magnitude assumed for Γ_∞ in previous relevant studies [36, 51].

The second and third sets (cases 4-6 and 7-9, respectively) encompass soluble surfactants transported throughout the interface and inside the oil bulk phase. The second set explores desorptive vs. convective effects by manipulating Bi. A base case at $Bi = 1$ was defined leading to a desorptive timescale in the same order of magnitude as the one measured for SDS, which is $t_D = 1/k_d \sim O(10^{-2}) \text{ s}$ [55, 56]. In addition, Da set for the base case ($Da = 0.001$) results in an initial bulk concentration of $C_\infty = 1.25 \text{ mol} \cdot \text{m}^{-3}$, being lower than the critical micelle concen-

Table 2

Parametric study outline for all surfactant-laden cases.

Case study	β	Bi	Da	k	$\Gamma_0 \times 10^{-5} [\frac{\text{mol}}{\text{m}^2}]$				
1	Insoluble	0.3	N/A	9	0.9				
2		0.6							
3		0.9							
4	Soluble	0.6	0.01	0.001	9	0.909			
5			0.1						
6			1	0.01	10				
7			0.1				0.1	1	0.5
8							0.1	1	0.0909
9				1	0.1		0.0909		

tration (CMC) estimated experimentally for SDS [8]. The additional Bi values shown in Table 2 represent scenarios where the desorption kinetics have been slowed down up to $t_D \sim O(1) \text{ s}$, thus exploring a system which loses less surfactant at the interface via desorption. These cases render values up to $k_d \sim O(10^{-1}) \text{ s}^{-1}$, which correspond to realistic desorption rates for surfactants such as lower alkanols and long-chain alcohols [55, 56, 57].

Finally, the third set explores the characteristic adsorption depth by varying Da. In order to avoid surface convection effects (constant Bi), both k and Da are varied simultaneously, adhering to the guidelines given in [45]. To achieve this, k_a and k_d are left constant, and instead, Da is conveniently modified through C_∞ and the initial interfacial concentration (see Γ_0 in Table 2). At larger Da values, C_∞ and k drop accordingly, which can be interpreted as a system with slower adsorption and/or faster desorption. The real k_a parameter defined is in the order of $O(10^3)$, and the theoretical values obtained from the k and Da numbers given in Table 2 range between $O(10^1) < k_d [\text{m}^3 \cdot \text{mol}^{-1} \text{ s}^{-1}] < O(10^3)$, which agree as well with measured values for both alcohols and non-ionic surfactants [56, 57].

An important feature to consider is the role of Marangoni stresses on the dispersion and breakage dynamics taking place. Their relevance can be assessed by comparing the macroscopic flow ($t_f = \dot{\gamma}^{-1}$ [23, 58]) and drop reference timescales ($t_R = D_d/U_d$) against the Marangoni flow timescale ($t_M = \mu_o D_d / (\sigma_{cl} - \sigma)$), which essentially comes from the competition between Marangoni stress and viscous retardation [39, 51]. For this comparison, σ is taken as the lowest possible value yielded by the EOS shown in Eq. 16 (i.e., $\sigma = \sigma_{cl} \epsilon_\sigma$), D_d, U_d are set as mentioned at the onset of this subsection, and $\dot{\gamma}$ is taken as the average value obtained in the gaps between crossbars ($\dot{\gamma} = 75 - 100 \text{ s}^{-1}$ [1]). In the context of this work, such comparison renders $t_f, t_R (\text{s}) \sim O(10^{-2})$ vs. $t_M (\text{s}) \sim O(10^{-3})$. Furthermore, the desorptive timescales introduced previously for the soluble cases lie in a range between $O(10^{-2}) < t_D (\text{s}) < O(1)$. Consequently, for both soluble and insoluble scenarios, Marangoni stresses will play a relevant role in the deformation and breakage dynamics since the Marangoni flow timescale can be smaller than other competing timescales in certain scenarios.

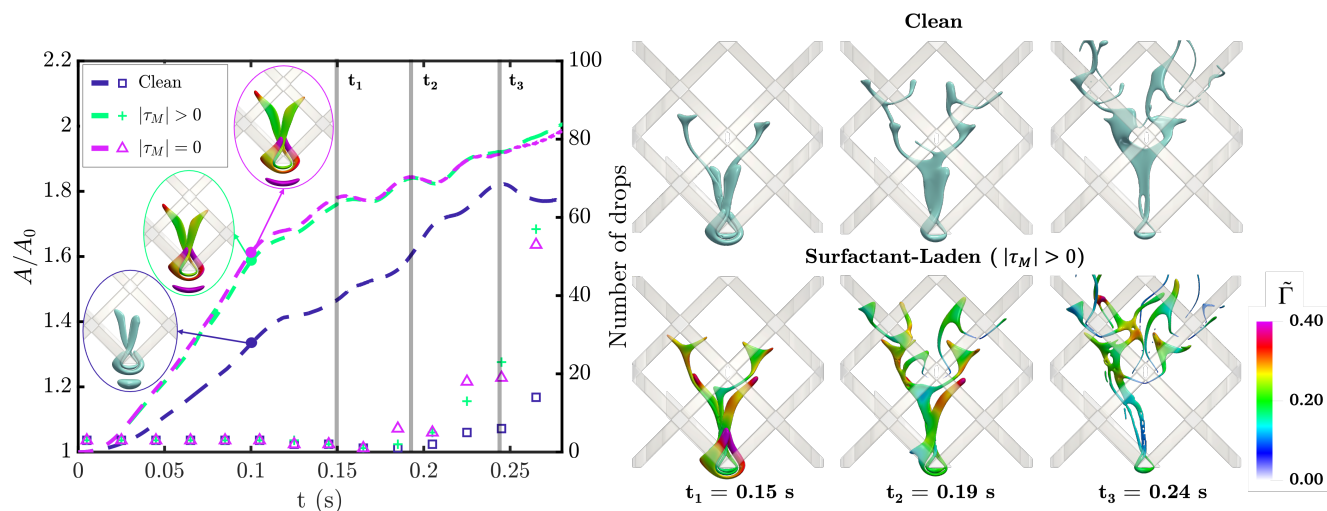


Figure 2: Comparative temporal evolution of the first stage dispersion dynamics [1] observed for the clean and surfactant-laden cases with ($|\tau_M| > 0$) and without ($|\tau_M| = 0$) Marangoni stresses. SL corresponds to Case 3 in Table 2 (insoluble surfactant with $\beta = 0.9$, $\tilde{\Gamma}_0 = 0.9$). Left axis corresponds to the dimensionless interfacial area A/A_0 , plotted with dashed lines, whilst the right axis represents the number of detached interfacial structures (labeled as drops for simplicity), plotted with markers. Interfacial morphological evolution is given to the right, colored by the dimensionless surfactant surface concentration ($\tilde{\Gamma}$).

3. Results and discussion

Our numerical framework has been successfully deployed to study complex mixing applications [59, 60], and has been validated experimentally and fine-tuned (i.e., via mesh-refinement studies) for the specific SMX studied herein [1]. Moreover, the surfactant transport module has been benchmarked against multiple analytical solutions: i) uniformly expanding spheres (mass conservation), ii) non-uniform surfactant distribution in spherical surfaces (surface diffusivity), iii) drop submersion in surfactant-laden phase (bulk surfactant transport), and iv) Marangoni-driven drop migration [42]. Also, our code has been proven to accurately handle the core physical mechanics studied here (e.g., ligament retraction [39], drop coalescence [51], capillary instabilities and breakup [61]).

3.1. Surfactant-laden dispersion and role of Marangoni stresses

It is well known that higher deformation is prompted by surfactant-induced lowered interfacial tension ($\tilde{\sigma}$), as this implies lower restoring interfacial forces resisting disruptive external stresses (e.g., viscous or inertial) [18, 23]. However, the possibility of an inhomogeneous surfactant distribution at the interface leads to Marangoni stresses (τ_M) [22] whose magnitude is sensitive to the dependence of $\tilde{\sigma}$ on the local surface concentration $\tilde{\Gamma}$ ($\frac{\partial \tilde{\sigma}}{\partial \tilde{\Gamma}}$ is modulated by β and $\tilde{\Gamma}$ as shown in Eq. 17), and the local hydrodynamics, resulting in enhanced or thwarted deformation [18, 20, 26]. To identify the role played by Marangoni stress, Case 3 in Table 2 was run in two separate instances, where the tangential component of the interfacial force ($\nabla_s \tilde{\sigma}$, refer to Eq. 11 in § 2.2) was neglected in one of them (this corresponds to a ‘Marangoni-free’ flow situation). For conciseness, we will refer to the normal surfactant-laden and Marangoni-free

cases as SL and MF, respectively. The distinct traits in the interfacial physics and breakage events unfolding between both scenarios can be directly attributed to the presence of Marangoni stresses. Selecting an insoluble configuration facilitates the analysis since only interfacial transport dynamics are involved. The upcoming discussion will be separated into two stages, as outlined in Valdes et al. [1].

3.1.1. First stage: Deformation mechanics

Fig. 2 quantifies the initial stage of the dispersion through the dimensionless interfacial area (A/A_0). Here, surfactant-laden cases are seen to adhere to the same behavior detailed in Valdes et al. [1] for a clean system: only interfacial distortion takes place at this stage, with essentially no breakage events being registered. As expected, surfactant-laden droplets experience a substantially larger interfacial area growth overall, quantified by the A/A_0 curves in Fig. 2, particularly at the beginning by nearly doubling the clean case stretching rate ($\frac{\Delta A/A_0}{\Delta t} \approx 6s^{-1}$ vs. $3.5s^{-1}$ @ $t = 0.1$ s, respectively). The initial wrapping, folding, and stretching motion at the leading edge, mostly governed by characteristic three-dimensional helical flows and extensional stresses [1], occurs in a similar manner for both clean and SL drops, spawning two elongating necks diverging in a v-shape (see inserts @ $t = 0.1$ s on the left-hand side plot in Fig. 2).

A surprising result at first glance comes from the nearly identical evolution of the A/A_0 up to $t = 0.1$ s for both SL and MF cases, suggesting that deformation mechanics at this point are not affected by Marangoni stresses, despite the elevated initial surface concentration ($\tilde{\Gamma}_0 = 0.9$). This seems to contradict previous studies [18, 20] dealing with highly tangentially-stressed drops via Marangoni stresses when exposed to extensional deformation. At a surface coverage close to saturation ($\tilde{\Gamma} \approx 1$), even with a nearly uniform sur-

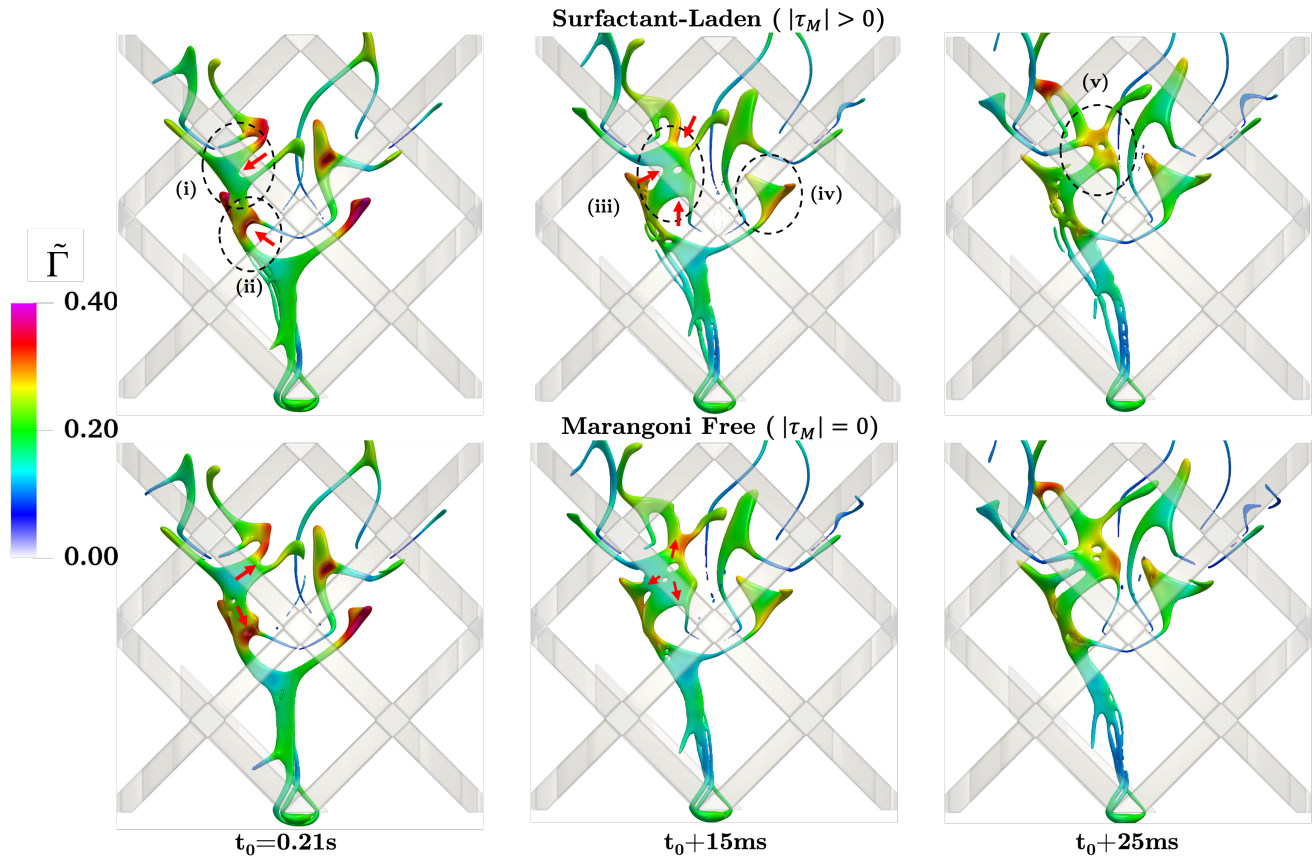


Figure 3: Comparative temporal evolution of the interface deformation with an insoluble surfactant, colored by the dimensionless surfactant surface concentration ($\tilde{\Gamma}$), for cases with ($|\tau_M| > 0$) and without ($|\tau_M| = 0$) Marangoni stresses at a constant elasticity number $\beta = 0.9$. Areas of interest highlighted in the top row to further address the role of Marangoni stresses on the deformation mechanics are presented in Figure 4.

535 factant distribution (i.e., small $\nabla_s \tilde{\Gamma}$) as is the case here initially, Marangoni stresses are expected to be very large in
 536 magnitude ($\tau_M \propto \nabla_s \tilde{\Gamma} \cdot \frac{\partial \tilde{\sigma}}{\partial \tilde{\Gamma}}$ with $\frac{\partial \tilde{\sigma}}{\partial \tilde{\Gamma}} \rightarrow \infty$ when $\tilde{\Gamma} \rightarrow 1$)
 537 [18, 20]. Strong τ_M implies that the deformation dynamics
 538 associated with the two cases should be at variance to some
 539 extent (e.g., τ_M can promote weak tip stretching or impede
 540 deformation by immobilizing the interface), and surfactant
 541 accumulation at the drop poles should be strongly restricted
 542 by Marangoni effects [18, 20, 23, 26]. Neither of these fea-
 543 tures are seen in the inserts at $t=0.1s$ in Fig. 2.

544 To probe the early-time dynamics further, we define the
 545 flow topology parameter Q ,
 546

$$Q = \frac{D^2 - \Omega^2}{D^2 + \Omega^2} \begin{cases} = -1, & \text{for rotational flow} \\ = 0, & \text{for shear flow} \\ = +1, & \text{for extensional flow,} \end{cases} \quad (19)$$

547 where $D^2 = \mathbf{D} : \mathbf{D}$ and $\Omega^2 = \mathbf{\Omega} : \mathbf{\Omega}$; \mathbf{D} and $\mathbf{\Omega}$ stand
 548 for the rate of deformation and rotation tensors, respectively
 549 [1, 60]. Converging extensional flows ($Q = 1$) have been
 550 established to drive the droplet folding motion at the lead-
 551 ing edge, triggering the formation of necks from the elongat-
 552 ing drop tips as they travel into the corridors between cross-
 553

554 bars [1]. Nonetheless, flows immediately adjacent to the
 555 leading edge are predominantly shearing in nature ($Q = 0$)
 556 [1]. This suggests a two-fold mechanism, where the drop is
 557 initially flattened and stretched via shearing stresses (up to
 558 $t \approx 0.05s$), followed by the drop tips elongating via exten-
 559 sional flows at the corridors.

560 As proposed in previous works [22, 28], Marangoni stresses
 561 exhibit limited participation in shear-induced deformation
 562 due to drop rotation, allowing significant interfacial veloci-
 563 ties to develop (even at high $\tilde{\Gamma}$) that permit surfactant accu-
 564 mulation at the tips. Consequently, the initial shearing here
 565 induces two effects: 1) drop in τ_M caused by surfactant di-
 566 lution as the drop expands ($\uparrow A/A_0$, $\downarrow \tilde{\Gamma}$), and 2) surfactant
 567 sweep towards the drop poles via convection [22], causing a
 568 normal stress jump (local drop in $\tilde{\sigma}$) which is compensated
 569 by an increase in curvature at the poles [20, 23]. Through
 570 this, the poles/tips elongate as they wrap around the leading
 571 edge, transitioning to the neck stretching dynamics.

572 Although neck stretching at $t = 0.05 - 0.1s$ is governed
 573 by extensional stresses converging at the corridor, the paral-
 574 lel SL-MF evolution up to this point can be tied to the rel-
 575 evant competing timescales estimated (i.e., Marangoni t_M
 576 vs. inertia/flow t_R, t_f). Considering the definitions given in

§2.3, this comparison renders a slower τ_M timescale ($t_M \sim O(10^{-2})$ with $D_d \approx 1.05$ mm and $\sigma = 0.75\sigma_{cl}$) compared to disruptive inertia and shear stress ($t_R, t_f \sim O(10^{-3})$), taking as reference the strain rate experienced at the leading edge ($\dot{\gamma} = 350\text{s}^{-1}$), and the neck peak width and interfacial velocity during elongation at the corridor ($@t = 0.08\text{s}$, $U_d \approx 0.13 \text{ m} \cdot \text{s}^{-1}$, $D_d \approx 1.05$ mm). From this observation, we can infer that Marangoni stresses, which tend to hinder deformation at high $\tilde{\Gamma}$ [20, 23], are not able to act fast enough against strong disruptive inertial forces, and are eventually overwhelmed as τ_M plummets at larger deformations due to surfactant dilution ($\uparrow A/A_0, \downarrow \tilde{\Gamma}, \downarrow \frac{\partial \tilde{\sigma}}{\partial \tilde{\Gamma}}$) [26]. Accordingly, neck lengthening driven by strong inertia (usually at the corridor center, resulting in a nearly unidirectional elongation [1]) unfolds closely for both SL and MF. Despite concentration gradients growing as surfactant accumulates at the tips, τ_M keeps decreasing initially since $\frac{\partial \tilde{\sigma}}{\partial \tilde{\Gamma}}$ falls sharply with increasing A/A_0 at higher $\tilde{\Gamma}$. These mechanisms will hold throughout the dispersion process where either shearing stresses at the crossbars, or strong inertia in the corridors, neutralize the influence of Marangoni stresses.

As surfactant is depleted from the necks and swept towards the bulbous heads via extensional flows, tip stretching is strongly favoured, leading to a faster and flatter neck elongation compared to the clean case, spawning highly curved tips [18, 23]. At first, τ_M is not strong or fast enough to effectively restrict surface flux and prevent tip stretching, given the lower $\tilde{\Gamma}$ ($\downarrow \frac{\partial \tilde{\sigma}}{\partial \tilde{\Gamma}}$) [20], and strong inertia pushing the neck at the center of the corridor, as discussed previously. However, a subtle deviation in A/A_0 can be noted at $t = 0.1 - 0.15\text{s}$, corresponding to a slight neck retraction in the SL case. During this time window, elongating necks approach low-velocity recirculation zones ($Q = -1$), induced by the mixer X-shaped geometry, before forking and switching direction at the upcoming cross-point [1]. Naturally, competing Marangoni stresses grow in relevance as inertial effects weaken at these low-velocity regions, particularly when extensional deformation continues to dominate. Moreover, steady elongation prompts $\nabla_s \tilde{\Gamma}$ to rise as surfactant accumulates at the tips, which at lower $\tilde{\Gamma}$ becomes the dominant term behind Marangoni stresses.

The signature A/A_0 undulations at $t = 0.10 - 0.25\text{s}$, identified primarily as forking/wrapping mechanisms [1], are maintained between SL and MF but amplified when compared with the clean case. Similarities in the former can be attributed to shear-induced deformation driving wrapping/forking events, and strong inertial flows commanding near-unidirectional elongation in the corridor, both diminishing the τ_M effect as explored before. In contrast, increased waviness compared to the clean case comes from a lowered, in-homogeneous $\tilde{\sigma}$ inducing a more unstable interface. As captured in Fig. 2 ($t_1 - t_3$ vignettes), the SL interface tends to split and wrap at more locations without breaking, forming additional branches ($\uparrow A/A_0$). In addition, a larger steady deformation takes place during wrapping thanks to a $\tilde{\Gamma}$ dilution effect at the point of contact ($\uparrow \tilde{\sigma}$), where surfactant is swept via convection towards the nascent necks (see (iv) in Fig. 4), thus

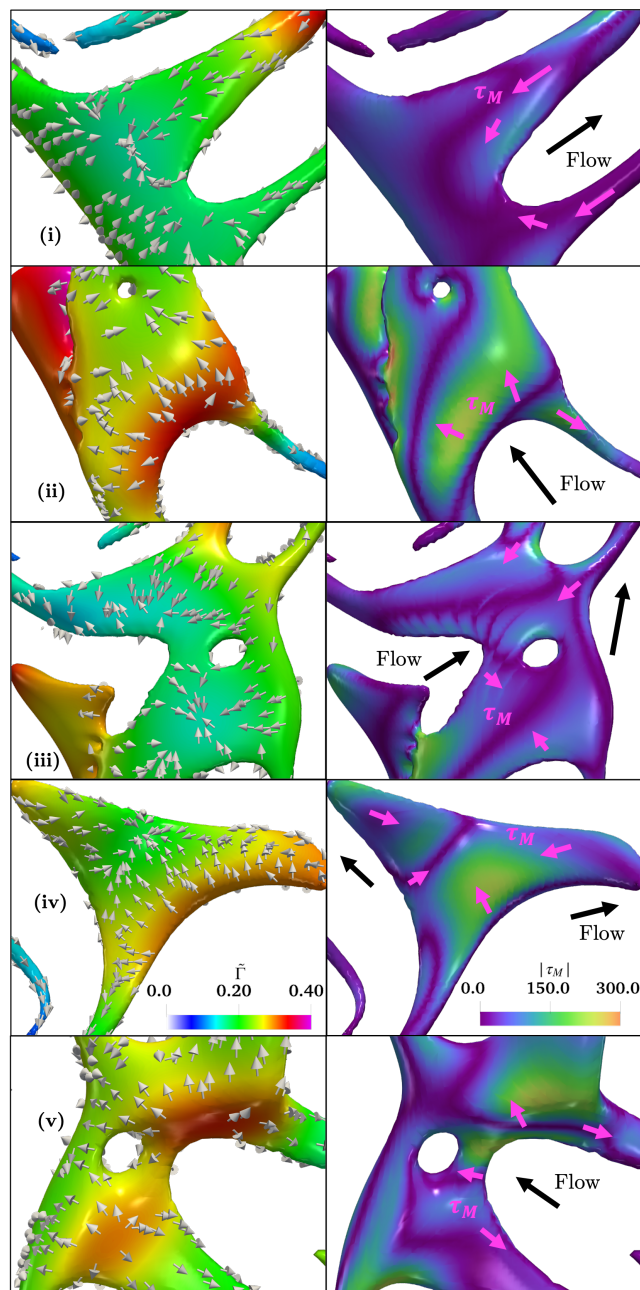


Figure 4: Closeups shown in Fig. 3. Left shows Marangoni flows through unit vectors on a $\tilde{\Gamma}$ colored interface, while right displays the magnitude of the Marangoni stresses $|\tau_M|$.

promoting further tip stretching [18, 23].

Even though the A/A_0 curves in the $t_2 - t_3$ window (Fig. 2) seem consistent between SL and MF cases, Fig. 3 highlights subtle yet key differences in the interface morphological evolution which will later impact the DSD attained (see §3.1.2). These variations arise in regions with governing extensional deformation and low flow inertial disruption (e.g., low velocity regions). Instances (i) and (iii) in Fig. 3 display an augmented interfacial retraction, where the elongating SL left branch seems tighter and less spread out, with thinner, longer, and more cylindrical necks developing. By

645 taking a closer look at these instances in Fig. 4, we notice
 646 that Marangoni stresses pulling inwards, opposite to the flow
 647 direction, are responsible for rigidifying the left branch tan-
 648 gentially as the flow attempts to stretch it, impeding nascent
 649 necks from spreading uncontrollably, but rather evolving as
 650 cylindrical columns. Deepening cavities (see red arrows in
 651 Fig. 3), absent in the MF case, progressively develop as a
 652 $|\tau_M| > 100$ threshold is surpassed around the rim of the
 653 indentation where the retraction motion ensues; τ_M here is
 654 induced by large concentration gradients promoted during
 655 early neck stretching dynamics, as analyzed above. These
 656 mechanisms help compact the expanding left branch, induc-
 657 ing the ‘jellyfish’ morphology seen in instance (v), where
 658 surfactant has been accumulated in the central ring by virtue
 659 of τ_M restricting surface flux towards the emerging branches
 660 during cavity formation (see Fig. 4 (i) and (iii)). The ‘tenta-
 661 cles’ are stabilized by reversed τ_M flows exhibited in Fig. 4
 662 (v), going from the center outwards into the necks, in agree-
 663 ment with the experimental phenomena captured by Zhao
 664 et al. [62].

665 Similarly, τ_M also enhances interfacial retraction when
 666 acting parallel to the flow, as conveyed by close-up (ii). Al-
 667 though being less relevant due to larger inertial effects (higher
 668 flow velocities close to the corridor’s center), Marangoni
 669 flows are sufficiently intense here (almost twice as large as
 670 instance (i)) to generate a strong surface flux that further re-
 671 tracts the interface, developing a more pronounced indenta-
 672 tion than in the MF case, as seen from Fig. 3. Marangoni
 673 stresses in Fig. 4 (ii) are seen to promote surfactant trans-
 674 port towards the central ring region, which eventually be-
 675 comes the ‘jellyfish’ structure described above. Neverthe-
 676 less, many examples of mirrored deformations between SL
 677 and MF cases can be devised from Fig. 3, as exemplified by
 678 closeup (iv). Marangoni flows in Fig. 4 (iv) pull steadily in-
 679 wards towards the center, opposite to the flow, and away from
 680 the forming poles as the wrapping motion progresses. De-
 681 spite exceeding the $|\tau_M|$ threshold identified, shearing flows
 682 in the vicinity of the crossbar are dominant enough to render
 683 Marangoni action negligible, thus evolving in a nearly iden-
 684 tical way between SL and MF. As established earlier, lower
 685 $\tilde{\sigma}$ at the tips instigates tip stretching, and the $\tilde{\Gamma}$ diluting effect
 686 at the center stabilizes the elongating structure, resulting in
 687 a larger area growth compared to the clean case. This sug-
 688 gests that shear-induced deformation is mostly governed by
 689 local imbalances in $\tilde{\sigma}$, prompted by $\tilde{\Gamma}$ re-distribution.

690 3.1.2. Second stage: breakup mechanics

691 The second stage of the dispersion encompasses break-
 692 age events via two mechanisms: geometrical (disruptive stress
 693 induced by the crossbars/cross-points) and hydrodynamical
 694 (capillary instabilities in ligaments) [1]. A larger number
 695 of daughter drops, as well as higher droplet birth rates, are
 696 seen for the surfactant-laden systems in Fig. 5a, akin to the
 697 A/A_0 growth rate trend discussed earlier in §3.1.1. In this
 698 case, the clean scenario production rate is nearly doubled in
 699 the presence of surfactants, with $\frac{\Delta n_{drop}}{\Delta t} \approx 1.37 \text{ drops}\cdot\text{ms}^{-1}$
 700 vs. $0.77 \text{ drops}\cdot\text{ms}^{-1}$, for the SL and clean respectively, as-

701 suming a linear trend up to t_5 . In addition, the SL DSD (vs.
 702 clean) carries a slightly more negative skewness (left-biased
 703 distribution with $s = -0.28$ vs. -0.16 , respectively), and
 704 higher excess kurtosis (heavier tails implying higher varia-
 705 tion from the mean with $k_{ex} = 0.49$ vs. 0.25 , respectively).
 706 Despite both cases being normally distributed, as verified by
 707 standard Kolmogorov-Smirnov (KS) and Anderson-Darling
 708 (AD) tests, the altered s and k_{ex} values hint towards a gener-
 709 ally increased production of small-sized drops with a higher
 710 degree of deviation from the mean, indicating a pivotal shift
 711 in the governing breakage physics when surfactant is added.
 712 This result is visually confirmed from the taller bars seen in
 713 the mid-to-small size range ($1 \times 10^{-6} < V/V_{cap} < 1 \times 10^{-4}$)
 714 vs. the clean case in Fig. 5b, and the left-shifted PDF and
 715 CDF curves in Fig. 5c. Even though SL and MF cases share
 716 similar trends, notable deviations in the DSD and droplet
 717 count attained can be identified in the absence of Marangoni,
 718 as we will explore further in this section.

719 A crucial factor influencing dispersion performance is
 720 the higher ligament population emerging in the SL case (re-
 721 fer to Fig. 2). Moreover, SL ligaments tend to experience a
 722 longer, more stable elongation at first, rendering them more
 723 susceptible to instabilities induced by disruptive stresses, given
 724 their larger aspect ratio (\tilde{L}_0) [1, 63], and naturally lower
 725 local $\tilde{\sigma}$ [21]. Deformation dynamics discussed in §3.1.1,
 726 such as increased splitting events via lower $\tilde{\sigma}$, and longer
 727 neck elongation due to a stabilized interface via $\tilde{\Gamma}$ dilution
 728 effects (e.g., during the wrapping motion), account for the
 729 surge in ligament formation with larger \tilde{L}_0 . The same hap-
 730 pens with the jellyfish structure generated via high exten-
 731 sional deformability ($\downarrow \tilde{\sigma}, Q = 1$) and rigidifying Marangoni
 732 forces. The ‘tentacles’, stabilized via τ_M [62], continue to
 733 elongate steadily without early breakages, thus producing
 734 large \tilde{L}_0 ligaments which will eventually yield more daugh-
 735 ter drops. This agrees with studies suggesting high droplet
 736 output breakup mechanisms (e.g., tip-streaming, capillary
 737 fragmentation) to be dominant in moderately concentrated
 738 SL systems [8, 27]. Even in clean systems, elevated liga-
 739 ment production has been linked with higher droplet counts,
 740 since multi-drop breakup modes (e.g., capillary fragmenta-
 741 tion) are more likely to occur at larger \tilde{L}_0 than binary breakups
 742 (e.g., cross-point necking or end-pinching) [1, 63, 64].

743 Recurrent deformation and breakup mechanisms, within
 744 the two main classifications defined at the onset of this sub-
 745 section (i.e., geometrical and hydrodynamical), can be iden-
 746 tified for the SL case in Fig. 6, and categorized as follows:

- 747 1. *Breakup via folding and necking*: Usually resulting
 748 in binary breakup, this mechanism consists of inter-
 749 facial structures folding and necking at a cross-point,
 750 thanks to the flow-induced elongation of the structure
 751 extremities, and the shear stress exposure at the point
 752 of contact, giving rise to a thinning/pinching region.
 753 Depending on the cross-point location, local flow fea-
 754 tures will vary, thus leading to different outcomes. Outer
 755 cross-points prompt a steady u-shaped interfacial elon-
 756 gation, generating parabolic or flow-oriented ligaments,
 757 given the absence of geometrical effects on the exiting

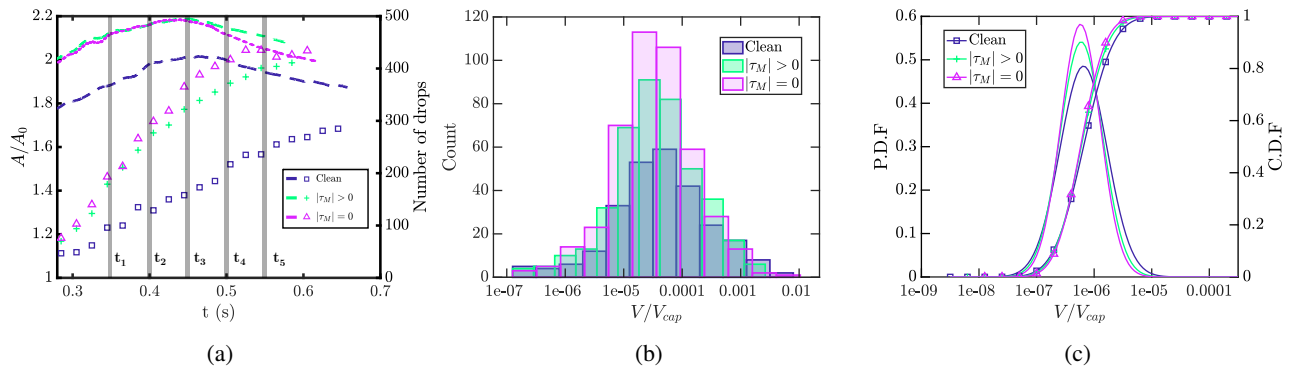


Figure 5: Comparative dispersion performance metrics for the clean and surfactant-laden case with ($|\tau_M| > 0$) and without ($|\tau_M| = 0$) Marangoni stresses, assuming an insoluble surfactant with an elasticity number of $\beta = 0.9$. a) Temporal evolution of the second stage dispersion dynamics as defined in Valdes et al. [1], b) overlapping dimensionless droplet size distribution (DSD) histograms, taking as a reference the capillary volume $V_c = 4\pi/3 \left(\sqrt{\sigma/g\Delta\rho}\right)^3$ as in Valdes et al. [1], and c) probability and cumulative density functions (PDF and CDF). Both b) and c) figures correspond to $t = 0.59s$.

758 flows (Quasi-poiseuille flow at the corridor’s outlet).
 759 Such is the case for ligaments #1 @ t_1 , #3 @ t_2 , and
 760 #4.2 @ t_3 . In contrast, inner cross-points feature local
 761 swirling flow currents diverging into adjacent crossbar
 762 corridors with opposite flow directions [1]. Hence,
 763 forming filaments are either caught by recirculating
 764 regions near the crossbars, thereby initiating a wrap-
 765 ping process, or pulled into a corridor and stretched
 766 towards the next cross-point. Examples of this are lig-
 767 ament #4 @ $t_1 - t_2$, and the preceding structure from
 768 which ligaments #2 and #3 originate (not shown).

769 2. *Breakup via crossbar wrapping:* Similar to the pre-
 770 vious item, this mechanism centers on the necking re-
 771 gion developing at the crossbar through the same stress
 772 imbalance described earlier, engendering only a few
 773 daughter structures. The main difference lies in the
 774 breakup outcome. Owing to the necking region loca-
 775 tion, emerging ligaments can only stretch through par-
 776 allel flow currents, as opposed to entering diverging
 777 swirling flows (i.e., at the cross-point), which could
 778 set-off further wrapping events. The wrapping struc-
 779 ture elongates asymmetrically, contingent upon local
 780 flow conditions and surfactant-related effects (e.g., $\bar{\sigma}$
 781 imbalances, see §3.1.1), commonly yielding a main
 782 head and tail filament, and satellite threads. This be-
 783 havior is portrayed by ligaments #2 @ t_1 , and #4.1 @ t_2 .

784 3. *Tip streaming/dropping:* Tip streaming occurs after a
 785 thread is drawn from a weakly deformation-resistant
 786 region ($\uparrow \tilde{\Gamma}$, $\downarrow \bar{\sigma}$). As surfactant gets swept towards
 787 the growing thread, local $\bar{\sigma}$ decreases, thus triggering
 788 a necking region at the leading end [25]. A daugh-
 789 ter drop, whose size depends on the initial $\tilde{\Gamma}$, is emit-
 790 ted from the pinching neck. At higher local $\tilde{\Gamma}$ and
 791 $Ca = \dot{\gamma}D_d\mu_a/2\sigma$, the thread can also neck and snap
 792 at the parent structure-thread juncture, transitioning to
 793 the tip-dropping phenomenon which results in larger

daughter drops [25, 28]. Specific examples are not 794
 captured in Fig. 6 but commonly occur at the ligament 795
 bulbous lobes, where $\tilde{\Gamma}$ tends to accumulate. 796

4. *General pinching and capillary instabilities:* The fate 797
 of a ligament is determined by its \tilde{L}_0 , prevailing forces 798
 acting on it (quantified through the Ohnesorge number, 799
 $Oh = \mu_o/\sqrt{\rho_o\sigma D_d}$, defined at the drop scale intro- 800
 duced at the onset of §2.3), as well as surfactant- 801
 related effects (e.g., Marangoni). In a capillary-dominated 802
 regime ($\downarrow Oh$), breakup most likely happens via end- 803
 pinching [65]. However, depending on \tilde{L}_0 and Oh , a 804
 transitional regime comprising complex shape oscilla- 805
 tions may appear, delaying or even precluding pinch- 806
 offs at the filament end, entering a middle-break mode 807
 variation [63]. In contrast, small enough ligaments (\downarrow 808
 \tilde{L}_0) entail short retraction times that inhibit instabil- 809
 ities from developing, thus inducing stable no-break 810
 modes [63, 65]. Filaments with sufficiently large \tilde{L}_0 811
 and viscous resistive forces ($\uparrow Oh$), experience breakup 812
 via surface capillary instabilities (i.e., capillary waves), 813
 which are triggered by varicose perturbations, mim- 814
 icking Rayleigh-Plateau instability [64]. Developing 815
 disturbances can be induced hydrodynamically (in tan- 816
 dem with inertia from the flow) or geometrically (i.e., 817
 mixer collisions). The implications of adding surfac- 818
 tants are manifold, as we will explore further on. Clean 819
 ligaments undergoing capillary fragmentation comply 820
 with a critical \tilde{L}_0 and perturbation wavelength λ thresh- 821
 old [1]. However, the resolution available in our simu- 822
 lations is not sufficient to delve further into the rami- 823
 fications of adding surfactant on these critical thresh- 824
 olds, but further study is encouraged. Multiple exam- 825
 ples of these phenomena can be recognized between 826
 times t_4 - t_5 essentially for all ligaments tracked. 827

Key relationships between the listed mechanisms include 828
 the evolution from inner to outer cross-point breakup. Lig- 829

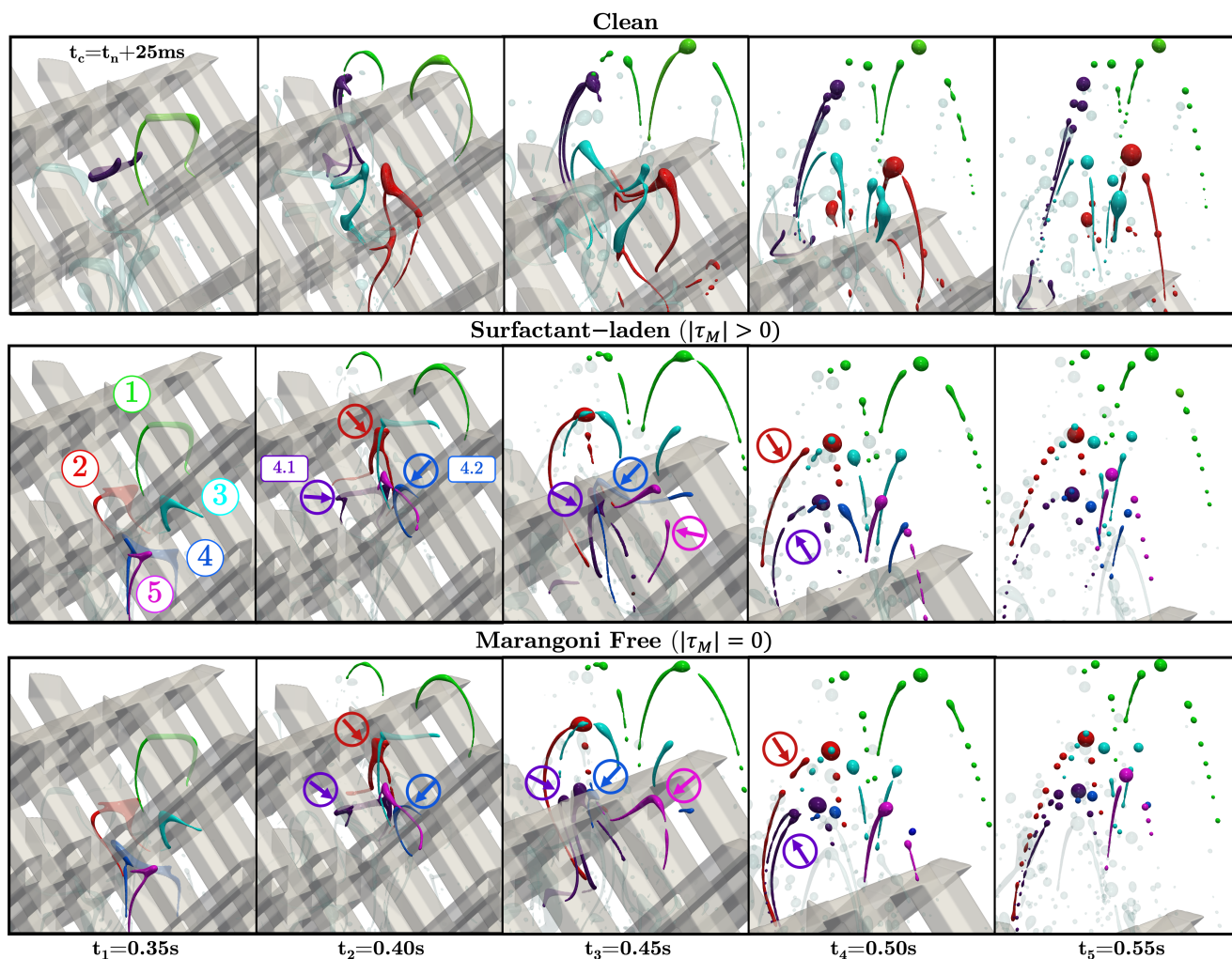


Figure 6: Comparative temporal evolution of the second stage for the clean (top), surfactant-laden ($|\tau_M| > 0$, middle) and Marangoni-free ($|\tau_M| = 0$, bottom) cases at constant $\beta = 0.9$. Five specific ligaments (color-coded) are tracked in the SL and MF scenarios to unravel recurrent breakage modes and the role of the Marangoni stresses in the breakage mechanics unfolding. Interfacial structures resembling those shown for the surfactant-laden case are highlighted for the clean with the same color code, albeit with a time delay of 25 ms to their respective counterparts. Relevant instances are pointed out through colored arrows for further discussion on particular breakage modes and their evolution, with additional detail provided in Figs. 7 and 8.

830 aments #3 and #4.2, both originating from an inner cross-
 831 point breakup (i.e., #4.2 spawning from #4 @ t_1), proceed
 832 to stretch into an inverted L-shape through the corridors at
 833 t_2 - t_3 , until they split at an outer cross-point, producing flow-
 834 oriented ligaments at t_3 - t_4 . Likewise, the succession from inner
 835 cross-point split to wrapping breakup can be pointed out,
 836 which incidentally connects with prime examples of frag-
 837 menting ligaments via capillary instabilities. This is the case
 838 for filaments #2 and #4.1, both emanating from an inner
 839 cross-point split. The wrapping breakages take place be-
 840 tween $t_1 - t_2$ and $t_2 - t_3$, respectively, creating similar head
 841 and tail ligaments with neighbouring detached threads. Tip-
 842 dropping can ensue from this process at the bulging heads,
 843 given the rapid curvature increase promoted by $\tilde{\Gamma}$ and inter-
 844 facial strain ($\dot{\gamma}$) accumulation ($\downarrow \tilde{\sigma}$, $\therefore \uparrow Ca$) [20, 25]. Ex-
 845 amples of snapped threads from the parent structure can be
 846 spotted at t_3 for ligament #4.1. Finally, elongating ligaments

at t_4 (red and purple arrows) exhibit wave-like disturbances,
 breaking into multiple daughter drops at t_5 . Ultimately, all
 filaments stemming from solid-interaction breakups undergo
 a myriad of the break or no-break modes from item 4.

Although the aforementioned physics resembles that iden-
 tified for the clean case (colour coded in Fig. 6 vs. SL lig-
 aments #1 through #3 and #4.1), multi-drop breakup modes
 are substantially less frequent since clean ligaments are in-
 trinsically more deformation-resistant ($\uparrow \tilde{\sigma}$). Therefore, early
 steady elongation gets inhibited ($\downarrow \tilde{L}_0$), which renders them
 less susceptible to fragmentation via capillary instabilities.
 Breakage dynamics by means of cross-point necking and
 crossbar wrapping unfold similarly for both systems (refer
 to $t_{c1} - t_{c3}$ in Fig. 6), albeit with a lesser A/A_0 growth due
 to the lack of local $\tilde{\sigma}$ imbalances (e.g., tip stretching or $\tilde{\Gamma}$
 dilution seen in §3.1.1). As a result, many nascent filaments
 from these events are significantly bulkier ($\downarrow \tilde{L}_0$) or struc-

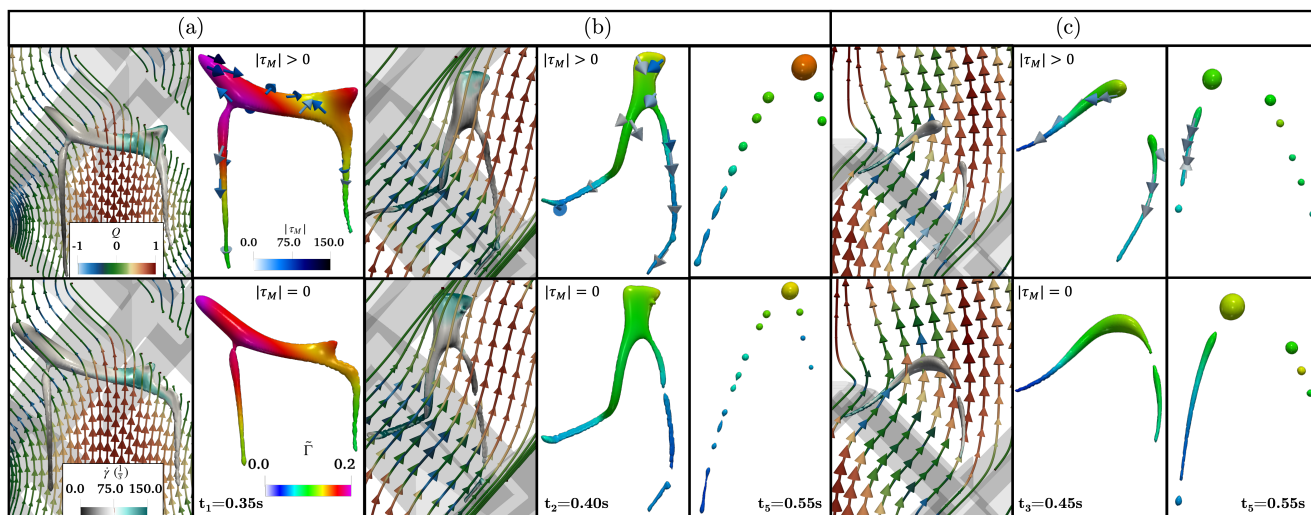


Figure 7: Comparative close-ups on several relevant ligaments at different times shown in Fig. 6 and their evolved states for surfactant-laden (top row) and Marangoni free (bottom row) cases. Per sub-figure: left view displays the deforming interface, coloured by the strain rate ($\dot{\gamma}$), embedded in flow streamlines with velocity-scaled glyphs coloured by the flow topology parameter Q . Right views depict the same interfacial structure (and its evolution when applicable) coloured by the surface concentration ($\tilde{\Gamma}$). Surfactant-laden case in the top row includes the direction and magnitude ($|\tau_M|$) of developing Marangoni flows. From left to right: a) ligament #4 (blue) at $t_1 = 0.35s$, b) ligament #2 (red) at $t_2 = 0.40s$, and its final state at $t_5 = 0.55s$, and c) ligament #5 (pink) at $t_3 = 0.45s$, and its final state at $t_5 = 0.55s$.

864 turally more unstable (higher capillary pressure due to $\uparrow \tilde{\sigma}$
 865 at the thinning lobe-tail liquid bridge), thus strongly favouring
 866 either retraction or end-pinching breakups. Such is the case for
 867 the cyan and red coloured ligaments at $t_{c4} - t_{c5}$ in Fig. 6. Despite
 868 there being exceptions (i.e., purple and green ligaments deriving
 869 from wrapping occurrences @ $t_{c1} - t_{c2}$), clean capillary fragmenta-
 870 tion tends to produce lower outputs of mostly uniform (and some-
 871 times sizeable) drops compared to the SL case. These variations in
 872 the predominant breakup modes in the presence of surfactants are
 873 reflected in the altered DSD features noted previously from Fig. 5.

875 Marangoni stress plays an influential role in the breakage
 876 phenomena examined, despite not being immediately evident from
 877 the comparable SL vs. MF structures depicted in Fig. 6. These simi-
 878 larities often stem from shear or inertia-dominated deformation
 879 where τ_M does not actively intervene, analogous to the scenarios
 880 exposed in §3.1.1. Such is usually the case for breakup mecha-
 881 nisms 1 and 2 (i.e., ligaments #1 and #3 @ $t_1 - t_3$). However,
 882 subtle morphological differences, akin to those highlighted from
 883 Fig. 3 by virtue of τ_M , can severely impact the course of a
 884 given breakup event, as well as future breakages triggered from
 885 it (example in Fig. 7 (a) discussed up next). This, in conjunction
 886 with breakups markedly regulated by τ_M (see Figs. 7 (b-c)),
 887 lead to the performance disparity observed in Fig. 5. The MF case
 888 carries a $\approx 15\%$ higher droplet count between $t_3 - t_5$, as shown
 889 in Fig 5a, and features higher excess kurtosis ($k_{ex} = 0.73$) and
 890 lower skewness ($s = -0.12$) overall, entailing a heavily-tailed
 891 distribution with no particular bias towards larger or smaller
 892 drops, as verified from Figs. 5b, 5c. This suggests a dual nature
 893 for the Marangoni effect, where τ_M can either act beneficially
 894 (augment small droplet for-

896 mation) or detrimentally (restrict droplet birth altogether).
 897 Inferring from previous discussion and further evidenced up
 898 next, Marangoni effects are simultaneously modulated by local
 899 Q , $|\tau_M|$ ($\frac{\partial \tilde{\sigma}}{\partial \tilde{\Gamma}}$, $\nabla_s \tilde{\Gamma}$) [18, 20], and $Oh - \tilde{L}_0$ [63, 65].

900 Fig. 7 (a) zooms in on ligament #4 at t_1 , exposed to vigorous
 901 extensional flows from below, and faint shear stresses in prox-
 902 imity to the cross-point, enabling active τ_M participation. Both
 903 SL and MF cases share locally equivalent restoring capillary forces
 904 ($\sim \tilde{\Gamma}$ profiles) at the point of contact. This leads to comparably
 905 high $\dot{\gamma}$ profiles in this region, heralding the onset of a necking
 906 region (inner cross-point breakup). Nonetheless, a distinctly
 907 asymmetrical elongation is captured on the left tip of the struc-
 908 ture in the absence of Marangoni, causing a left-skewed inner
 909 cross-point split that results in a vanishing #4.2 ligament, but
 910 a dual-necking #4.1 ligament, both marked at $t_2 - t_3$ in Fig. 6
 911 (blue and purple arrows). In contrast, strong $|\tau_M| > 100$ (over
 912 the threshold established in §3.1.1) restrict tip stretching in SL
 913 ligament #4, analogous to the retraction dynamics discussed from
 914 Fig. 4 (i-iii), leading to a middle section split. Hence, a single
 915 head and tail #4.1 filament develops at t_3 (and satellite threads),
 916 with the remaining mass going to filament #4.2, which adopts an
 917 inverted L-shape. This distinction reveals substantial implications
 918 of Marangoni effects on the fate of nascent ligaments since
 919 emerging structures akin to ligament #4.2 usually favour lower
 920 output breakup modes (i.e., outer cross-point breakup @ t_3 ,
 921 followed by end-pinching @ t_5). Instead, the MF case gener-
 922 ates $\approx 30\%$ more drops, given the extra capillary fragmentation
 923 coming from ligament #4.1.

924 Fig. 7 (b) shows ligament #2 at t_2 subjected to shearing
 925 crossbar flows on the left, and extensional currents on the right,
 926 dragging the front lobe into a corridor. As expected, 927

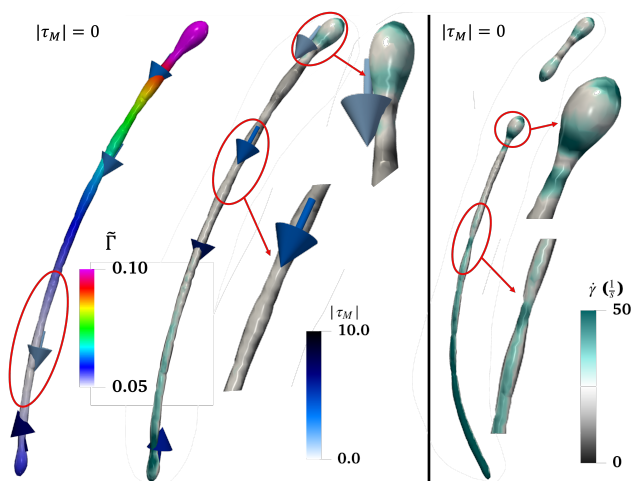


Figure 8: Close-ups on daughter ligaments at $t_4 = 0.50\text{s}$ in Fig. 6 (red arrow), evolving originally from ligament #2 (red) (see t_1 in Fig. 6). Left and right correspond to surfactant-laden ($|\tau_M| > 0$) and Marangoni-free ($|\tau_M| = 0$) cases, respectively. Left view shows interfacial strain rate ($\dot{\gamma}$) and surfactant concentration ($\tilde{\Gamma}$) profiles, with the direction and magnitude of Marangoni stresses (τ_M). Right view only shows interfacial $\dot{\gamma}$.

928 the left segment deforms evenly at first for both SL and MF in
 929 light of weakly influential τ_M (refer to $t_2 - t_3$ in Fig. 6). On
 930 the contrary, SL's right segment develops moderate $|\tau_M| <$
 931 75 opposing the flow, thereby diminishing strain buildup in
 932 areas exposed to extensional stress (e.g., leading head) with-
 933 out compromising filament elongation. This stabilizing ef-
 934 fect promotes a longer and more stable stretching right tail
 935 which escapes early breakups, abiding by the same physics
 936 described in §3.1.1 for the necks and tentacles in Fig. 4 (i,iii,v).
 937 In contrast, MF's right tail fragments prematurely when ex-
 938 posed to equivalent elongational flows despite exhibiting a
 939 similar morphology ($\sim \tilde{L}_0$), therefore attributing its breakup
 940 to the lack of τ_M . This observation is consistent with pre-
 941 vious studies arguing that surfactant depletion ($\uparrow \tilde{\sigma}$) from
 942 the thinning regions incentivizes τ_M that opposes capillary-
 943 pressure-driven flow [35], leading to reduced thread thinning
 944 rates which ultimately delay, or prevent filament pinch-off
 945 [36, 37]. Even though stabilizing Marangoni forces could
 946 favour drop production by supporting ligament lengthening
 947 ($\uparrow \tilde{L}_0$), they could also end up limiting subsequent breakups.

948 An example of the above comes from the evolution of
 949 ligament #2 between $t_2 - t_5$ (see Fig. 7 (b)). Marangoni two-
 950 pronged effect depends on its relative strength/activity against
 951 disruptive external stresses instigating either deformation or
 952 instability propagation. As hinted above, τ_M flows in the
 953 right tail are competitive enough radially vs. extensional
 954 stress to thwart wave perturbations, but sufficiently small and
 955 slow lengthwise to enable elongation. Analysis of the rele-
 956 vant interacting timescales supports this claim. Marangoni
 957 effects are on the same order of magnitude or faster ($t_M \sim$
 958 $O(10^{-3})$ with $D_d = 0.143\text{mm}$ and $\sigma = 0.9\sigma_{cl}$) than dis-
 959 ruptive inertia/shear stress from a radial perspective ($t_R \sim$
 960 $O(10^{-3})$, $t_f \sim O(10^{-2})$), taking $U_d \approx 0.073\text{m} \cdot \text{s}^{-1}$ and

961 $\dot{\gamma} \approx 30\text{s}^{-1}$ as the average interfacial velocity and strain rate,
 962 respectively. In contrast, they appear slower overall longi-
 963 tudinally ($t_M \sim O(10^{-1})$ vs. $t_f, t_R \sim O(10^{-2})$ with $D_d =$
 964 3.80mm), assuming the same U_d and $\dot{\gamma}$. However, once the
 965 right tail detaches from the parent structure and decelerates
 966 at the corridor exit, it becomes more sensitive to τ_M and less
 967 affected by external stress. Accordingly, capillary fragmen-
 968 tation is averted due to τ_M limiting capillary-pressure-driven
 969 flows as the filament recoils [35], which ultimately favours
 970 low drop output breakup modes ($\downarrow \tilde{L}_0$). Consequently, the
 971 SL tail yields two daughter threads at $t_2 - t_3$, whereas the
 972 early fragmented MF tail spawns three instead.

973 The same phenomenon is observed on the shear-disrupted
 974 left section of ligament #2 where τ_M , irrelevant at first, re-
 975 stricts emerging disturbances during extensional-governed
 976 prolongation at $t_3 - t_4$ (see Fig. 8). In this instance, the SL
 977 case generates over 20% less, yet slightly smaller drops (\approx
 978 10% on average) compared to MF, in agreement with the sta-
 979 tistical traits discussed for both distributions. The average
 980 difference in drop size derives from an interplay between
 981 capillary-driven tip swelling and Marangoni-delayed end-
 982 pinching [36, 37] (see red arrows @ $t_2 - t_4$ in Fig. 6). As
 983 filament #2 lengthens, its leading head bulges due to sur-
 984 factant accumulation, weakly opposed by modest $\tau_M < 50$.
 985 This prompts a rise in curvature that balances the normal
 986 stress jump provoked by lowering $\tilde{\sigma}$ [20, 23], resembling
 987 the neck stretching physics addressed in §3.1.1. While the
 988 same mechanism elapses in the MF ligament, its leading
 989 lobe swiftly pinches due to the absence of stabilizing τ_M
 990 stress, and growing capillary pressure as $\tilde{\sigma}$ plummets. In this
 991 way, the MF filament engenders more, slightly larger drops,
 992 whereas the Marangoni-delayed end-pinching in the SL case
 993 allows for further oil phase to be drawn into the swelling bul-
 994 bous head (reaching a higher $\tilde{\Gamma}$ as seen in Fig. 7 (b)), leading
 995 to less, but smaller nascent drops.

996 Fig. 8 sheds light on the nuances behind τ_M stabilizing
 997 action and its role hindering droplet birth. Thread thinning
 998 deceleration is reflected by the low $\dot{\gamma}$ profile ($< 25\text{s}^{-1}$) ex-
 999 tending through most of the SL ligament, in lieu of high
 1000 strain ($\approx 50\text{s}^{-1}$) necking regions, and varicose perturbations
 1001 developing in the MF filament. On top of its pinch-off retar-
 1002 dation effort, τ_M is also noted to expedite ligament retrac-
 1003 tion by inducing inwardly converging surface fluxes. These
 1004 flows arise from $\nabla_s \tilde{\Gamma}$ triggered by surfactant-depleted re-
 1005 gions mid-ligament (see Fig. 8). Therefore, critical \tilde{L}_0 -Oh
 1006 delimiting surfactant-free no-break modes (e.g., 'short lig-
 1007 ament' regime [63, 65]) may be altered by this effect. Kin-
 1008 dred examples of τ_M accelerated retraction are seen for cyan
 1009 and pink ligaments at t_5 , spawning from filaments #3 and #5
 1010 (refer to Fig. 6 and Fig. 7 (c)). Marangoni activity scales
 1011 proportionally with the local hydrodynamics, captured by $\dot{\gamma}$
 1012 (e.g., $|\tau_M| \approx 50$ influential at $\dot{\gamma} \approx 125\text{s}^{-1}$ in Fig. 7 (b), and
 1013 $|\tau_M| \approx 10$ at $\dot{\gamma} \approx 25\text{s}^{-1}$ in Fig. 8).

1014 On the other hand, Fig. 7 (c) showcases the opposite situ-
 1015 ation, where Marangoni-stabilized daughter filaments at t_3 ,
 1016 stemming from ligament #5, attain a longer elongation (\uparrow
 1017 \tilde{L}_0) vs. the MF case when subjected to vigorous extensional

1018 currents, thereby breaking into more drops at $t_4 - t_5$ via cap- 1070
 1019 illary fragmentation. It is worth mentioning that τ_M sets SL 1071
 1020 ligament #5 into a more symmetrical initial split at $t_2 - t_3$ by 1072
 1021 immobilizing the interface, akin to the physics explored in 1073
 1022 Fig. 7 (a). Both ligaments #5 and #2 at t_3, t_4 , respectively, 1074
 1023 exhibit an $\text{Oh} \sim O(1)$, implying strong enough viscous resist- 1075
 1024 tive forces precluding capillary-dominated breakup modes 1076
 1025 (e.g., end-pinching). However, the difference between them 1077
 1026 lies on their radial stability, quantified by the $\lambda > 2\pi R_d$ sta- 1078
 1027 bility criterion [1]. Ligament #5 features nearly half the radi- 1079
 1028 us estimated for ligament #2 ($R_{d,L5} = 0.66R_{d,L2}$), strongly 1080
 1029 suggesting a higher propensity for smaller λ oscillations to 1081
 1030 destabilize the filament. This accounts for the rapid break- 1082
 1031 age events seen in lieu of τ_M -enhanced retraction. 1083

1032 3.2. Parametric study

1033 This section delves into the influence of handling differ- 1084
 1034 ent types of surfactants by manipulating their physicochem- 1085
 1035 ical nature, as delineated in §2.3 (refer to Table 2). The met- 1086
 1036 rics selected to assess the mixer operation are the normal- 1087
 1037 ized interfacial area A/A_0 , the number of detached struc- 1088
 1038 tures or "drops" (N_d), and the DSD, represented via PDF 1089
 1039 and CDF curves. The DSD characterization is computed at 1090
 1040 $t = 0.59\text{s}$, corresponding to the earliest first drop exiting 1091
 1041 the computational domain amongst all cases (namely, case 1092
 1042 study 3 from Table 2). Accordingly, N_d is plotted between 1093
 1043 $0.2 < t(\text{s}) < 0.6$. Additionally, droplet count is fitted to a 1094
 1044 generalized logistic function of the form, 1095

$$1045 N_d(t) = \frac{M}{1 + e^{-k_g(t-t_{mid})}}, \quad (20)$$

1046 where M , k_g , and t_{mid} are fitting coefficients indicating the 1100
 1047 function maximum value, growth rate, and x-axis midpoint 1101
 1048 value, respectively. In this way, drop breakage and overall 1102
 1049 dispersion performance can be better quantified and compre- 1103
 1050 hensively analyzed for a diverse range of surfactants. 1104

1050 3.2.1. Effect of surfactant elasticity (β)

1051 This subsection encompasses cases 1-3 from Table 2 where 1105
 1052 surfactants are confined to the interface, thus isolating the 1106
 1053 impact of surfactant strength (σ dependency on Γ , see Eq. 8) 1107
 1054 on the interfacial dynamics and end performance. Fig. 9 (a) 1108
 1055 illustrates a monotonic trend that remains invariant through- 1109
 1056 out the dispersion: increasing β leads to larger interfacial ar- 1110
 1057 eas (A/A_0), which in turn implies higher A/A_0 growth rates. 1111
 1058 When surfactant is incorporated, regardless of its strength, 1112
 1059 the A/A_0 curves display similar undulations occurring be- 1113
 1060 tween $t = 0.15\text{--}0.25\text{s}$, although fainter at $\downarrow \beta$. As previously 1114
 1061 inspected from Fig. 2, these undulations ($@t_1 - t_3$) corre- 1115
 1062 spond to additional forking/wrapping events, and longer neck 1116
 1063 elongating dynamics vs. the clean case, which seem to be 1117
 1064 sustained for all β . Furthermore, the inflection point evident 1118
 1065 in the clean case around $t = 0.25\text{s}$ (see closeup in Fig. 9 1119
 1066 (a)) is absent for all surfactant-laden cases. This point de- 1120
 1067 notes the squeezing, thinning, and subsequent stretching of 1121
 1068 the initially flat and coalesced body of oil (see Fig. 2), which 1122
 1069 forks at the cross-point as the dispersion transitions to the 1123

1070 second stage [1]. This situation is averted in the SL case 1071
 1072 given the more divaricate, already stretched, and thinned- 1073
 1074 out interfacial morphology acquired at this stage (i.e., jelly- 1075
 1076 fish structure). Therefore, these observations suggest a gen- 1077
 1078 eralization of the core deformational mechanisms exposed 1079
 1079 in §3.1.1 for lower β , albeit with a less intense effect due to 1080
 1080 stronger restoring interfacial forces ($\uparrow \tilde{\sigma}$). 1081

1082 Two distinct and roughly linear A/A_0 growth rates $\left(\frac{\Delta A/A_0}{\Delta t}\right)$ 1083
 1084 can be estimated for all cases during the first stage, labeled 1084
 1085 as G1 and G2 in Fig. 9 (a), respectively. These rates are 1085
 1086 associated with either early tip/neck stretching and wrap- 1086
 1087 ping ($@t(\text{s}) \in [0, 0.15]$), or complex elongational distor- 1087
 1088 tion (i.e., forking/branching events) ($@t(\text{s}) \in [0.15, 0.25]$). 1088
 1089 For both time intervals, growth rates scale linearly with in- 1089
 1090 creasing β but in a contrasting fashion. On the one hand, 1090
 1091 G1 rates rise proportionally, following a linear trend $G1_\beta \approx$ 1091
 1092 $2.83\beta + G1_{clean}$, while G2 rates drop inversely proportional 1092
 1093 to rising β , obeying the form $G2_\beta \approx -1.61\beta + G2_{clean}$. 1093
 1094 These relationships denote a sharper positive increment for 1094
 1095 G1 rates as β rises, whilst G2 rates decline at a slower pace. 1095
 1096 This accounts for the rapidly widening gap between curves at 1096
 1097 $t \leq 0.2\text{s}$, and the ensuing slower narrowing as we approach 1097
 1098 the transition point at $t \approx 0.25\text{s}$. This behavior points to a 1098
 1099 stronger and favorable influence of β on the early interfacial 1099
 1100 deformation dynamics occurring at G1, primarily driven by 1100
 1101 inertial or shear stresses, and consequently governed by lo- 1101
 1102 cal $\tilde{\sigma}$ imbalances (e.g., enhanced splitting and wrapping me- 1102
 1103 chanics at $\downarrow \tilde{\sigma}$, see §3.1.1). Conversely, β becomes less im- 1103
 1104 pactful but detrimental in the latter stages, where Marangoni 1104
 1105 effects dominate over complex morphological changes (e.g., 1105
 1106 stronger τ_M rigidification at $\uparrow \beta$ suppresses interfacial spread 1106
 1107 in nascent tentacles). These trends are in agreement with 1107
 1108 several previous studies [18, 19, 23, 26] establishing two 1108
 1109 competing physical processes from the heightened $\tilde{\Gamma} - \tilde{\sigma}$ 1109
 1110 dependence ($\uparrow \frac{\partial \tilde{\sigma}}{\partial \tilde{\Gamma}}$) at elevated elasticities: greater interfa- 1110
 1111 cial distortion instigated by larger $\tilde{\sigma}$ gradients (at compara- 1111
 1112 ble $\nabla_s \tilde{\Gamma}$), and augmented τ_M stresses inhibiting surface ad- 1112
 1113 vection and therefore countering deformation. The A/A_0 1113
 1114 plateaus during the second stage ($t > 0.3\text{s}$) for all cases, 1114
 1115 reaching the same value after $\beta > 0.6$, evidently hinting to- 1115
 1116 wards droplet birth saturation. 1116

1117 Fig. 9 (b) reveals a seemingly linear growing trend in 1117
 1118 the droplet count (N_d), which flattens out after $\beta = 0.6$, as 1118
 1119 gauged from the M parameters displayed in Fig. 9 (b). In 1119
 1120 contrast, the N_d growth rate does not scale linearly with β , 1120
 1121 as settled for the A/A_0 , but rather jumps considerably when 1121
 1122 surfactant is added ($\uparrow \approx 40\%$ from the clean), and then re- 1122
 1123 mains essentially constant as β escalates, ranging between 1123
 1124 $19.14 < k_g < 19.58$. The stabilization of k_g can be verified 1124
 1125 by plotting the normalized drop count ($\tilde{N}_d = N_d/N_{max}$) 1125
 1126 against time ($\tilde{t} = t/t_f$), causing all curves to collapse to 1126
 1127 a logistic function of the form $\tilde{N}_d = \frac{0.9788}{1 + e^{-11.45(\tilde{t} - 0.6368)}}$ with 1127
 1128 a $R^2 = 0.9955$. These features indicate a marginal effect 1128
 1129 in the predominant breakage mechanisms when varying β , 1129
 1130 since k_g remains fixed, and suggest a droplet birth satura- 1130
 1131 tion at increasing elasticities. Initially, one might consider 1131

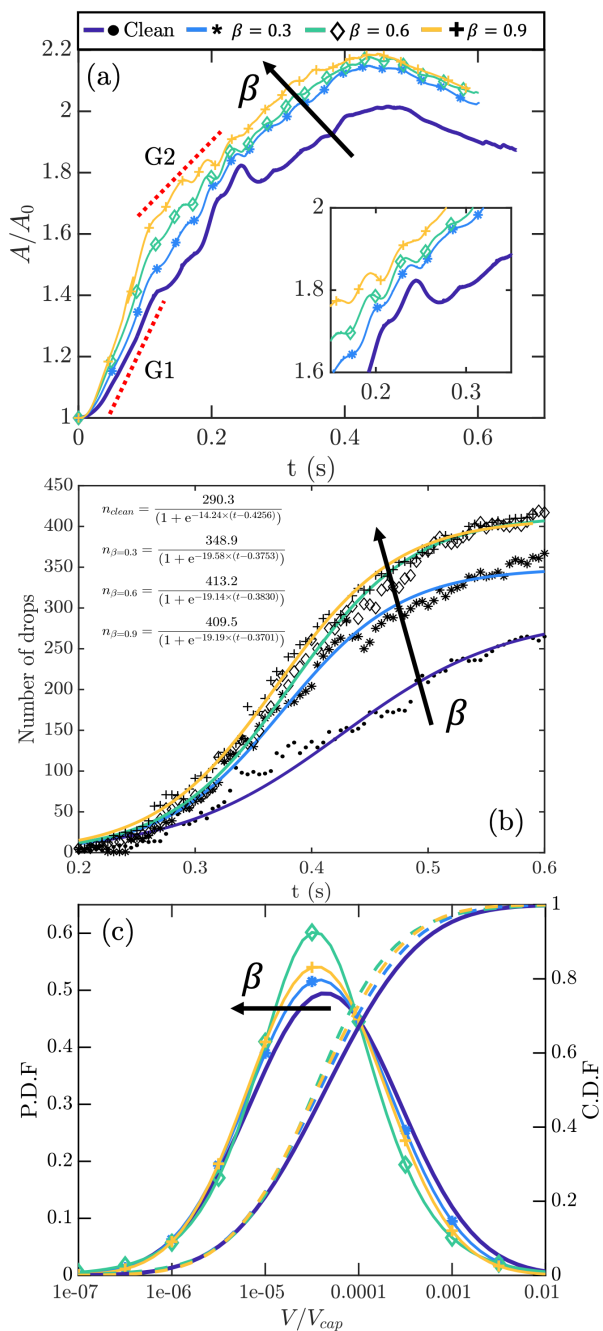


Figure 9: Comparative performance metrics for varying elasticity numbers (β). Temporal evolution of: (a) A/A_0 , and (b) number of drops (markers) with generalized logistic function fittings (solid curves adhering to Eq. 20) given in the top left; (c) dimensionless DSDs, calculated as V/V_{cap} following [1], with probability (left axis) and cumulative (right axis) density functions shown. All data sets are normally distributed apart from $\beta = 0.6$, which follows a logistic distribution.

1126 Marangoni stresses ascending in strength to be the root cause
 1127 behind saturation given their stabilizing action (e.g., pinch-
 1128 off retardation and escape [23, 36, 37], accelerated ligament
 1129 retraction, see §3.1.2). However, MF simulations at $\beta = 0.6$
 1130 and 0.9 saturated at the same N_{max} with nearly identical
 1131 DSDs, discarding a governing incidence of τ_M on this phe-

1132 nomena. A plausible explanation relies on the Ca_{crit} delimiting
 1133 drop stability, which lowers with $\downarrow \tilde{\sigma}$. After surpassing
 1134 a specific $\tilde{\sigma}$ threshold, the energy imparted by the SMX will
 1135 suffice to ensure breakage ($Ca_{\text{local}} > Ca_{\text{crit}}$), thus implying
 1136 that further lowering $\tilde{\sigma}$ will not benefit drop production, but
 1137 $\uparrow \beta$ could in turn negatively impact daughter drop sizes.

1138 DSDs in Fig. 9 (c) appear to have heavier left tails as surfactant
 1139 strength increases. Nevertheless, the skewness calculated conveys a
 1140 non-monotonic trend, where s rises from -0.16 to -0.39 between the
 1141 clean and $\beta = 0.6$ case, but then decreases to -0.28 at $\beta = 0.9$.
 1142 This is consistent with the pronounced left bias seen for the $\beta = 0.6$
 1143 PDF-CDF curves. In addition, the distributions variabilities conform
 1144 to a similar pattern, always indicating a leptokurtic shape with
 1145 generally wider spans at larger β , ranging between $0.19 < k_{\text{ex}} < 0.79$.
 1146 This denotes a higher drop production leaning toward smaller sizes
 1147 but exhibiting amplified variability with increasing surfactant strength,
 1148 aligning with the trends explored in Fig. 5. By dissecting the raw data,
 1149 $\beta = 0.6$ manifests a surge in medium-sized drops ($V/V_{\text{cap}} \sim O(10^{-4})$),
 1150 resulting in a substantially heavier left tail and thereby transitioning
 1151 to a logistic distribution. Instead, $\beta = 0.9$ reveals a comparatively
 1152 augmented population of large and small entities (i.e., normally
 1153 distributed). This suggests an adverse impact on the breakage dynamics
 1154 when β values exceed saturation, given that stronger τ_M stabilizing
 1155 effects would facilitate the preservation of larger drops. This agrees
 1156 with previous experimental observations [8], where a departure from
 1157 Gaussian-shaped distributions was attributed to a shift in the prevalent
 1158 breakup modes. Despite these discrepancies, a non-parametric
 1159 Kruskal-Wallis test (conducted due to the violation of normality and
 1160 homoscedasticity [1]) demonstrated no statistically significant
 1161 differences in the mean ranks between DSDs, thus hinting towards a
 1162 low impact of varying β in the governing breakup physics.

3.2.2. Effect of surfactant desorption vs. convection

1167 This subsection comprises cases 4-6 in Table 2, where surfactant
 1168 is no longer confined to the interface and can be transported freely
 1169 into the bulk (oil) phase. Its desorptive capability is manipulated
 1170 through k_d , and its characteristic timescale is compared against
 1171 surface convection through the Bi number, as addressed in §2.3. Similar
 1172 to the results given in §3.2.1, Fig. 10 (a) conveys a consistently
 1173 monotonic, although inversely proportional tendency: A/A_0 diminishes
 1174 as surfactant desorption is enhanced ($\uparrow \text{Bi}$). Unlike the insoluble
 1175 scenarios, the signature A/A_0 undulations (@ $t = 0.15 - 0.25$ s) are
 1176 drastically reduced with augmenting surfactant solubility, resembling
 1177 those seen for the clean case. Moreover, the inflection point established
 1178 at $t = 0.25$ s, signaling stage transition, is partially recovered at the
 1179 strongest desorptive capability simulated ($\text{Bi}=1$), as captured in the
 1180 closeup vignette in Fig. 10 (a). Both features indicate a pivotal
 1181 shift in the deformation dynamics unfolding in the first stage vs.
 1182 insoluble and weakly soluble surfactant-laden cases. As expected,
 1183 heightened desorption eliminates surface concentration gradients
 1184 ($\nabla_s \tilde{\Gamma}$) by preventing surfactant buildup

(e.g., at the leading lobes during neck stretching), thus rendering Marangoni effects negligible and consequently inhibiting τ_M -driven mechanisms (e.g., jellyfish formation via interfacial retraction and rigidification). The A/A_0 saturates during the first stage ($t < 0.25$ s) at $Bi \leq 0.1$, overlapping with the insoluble curve at $Bi=0.01$, suggesting that the impact of solubility on convection becomes negligible thereafter.

These observations are consistent with previous studies, confirming that elevated surfactant mass transfer into the bulk leads to deformations between those developed by clean and insoluble surfactant systems [30, 31]. This is attributed to the concurrent reduction of $\tilde{\Gamma}$ and $\nabla_s \tilde{\Gamma}$, suppressing both inhomogeneities in capillary forces ($\uparrow \tilde{\sigma}$) and Marangoni stresses, thereby mitigating many of the phenomena discussed throughout this work. These dynamics arise from the inherent compensating effect induced by solubility, where surfactant is adsorbed in regions of low $\tilde{\Gamma}$ and desorbed in regions of high $\tilde{\Gamma}$ [30] (modeled via Eq. 5). In addition, A/A_0 exhibits a monotonic descent with $\uparrow Bi$ given the constant adsorption-desorption ratio maintained through cases 4-6 (see k in Table 2), hence preventing preferential sorptive effects from counteracting the competition against surface convection (e.g., adsorption supplying surfactant-depleted regions faster than desorption removing $\tilde{\Gamma}$ accumulation, permitting greater distortions at high solubility due to $\downarrow \tilde{\sigma}$ [31]).

The A/A_0 growth rate linear approximations carried out in §3.2.1 (labeled as G1 and G2 in Fig. 9 (a)) can be replicated here. In contrast to the insoluble scenarios, growth rates G1/G2 do not scale linearly with varying desorption, but rather obey a quadratic dependence on the logarithm of Bi , expressed as $G_{Bi} = f(x^2) = f(\log(Bi)^2)$. Nonetheless, G1 and G2 retain a divergent behavior with respect to Bi , analogous to the correlation established for β but in an opposite manner given the inverse A/A_0 - Bi dependency. In this case, G1 rates diminish quadratically with rising $x = \log(Bi)$ at a rate of $\frac{dG1}{dx} = -0.4416x - 0.9548$, whilst G2 rates escalate in the same fashion at a rate of $\frac{dG2}{dx} = 0.3166x + 0.4902$. A sharper decline for G1 and a smoother rise for G2 can be inferred from the above ($|\frac{dG1}{dx}| > |\frac{dG2}{dx}|$), generating the same rapid gap widening at $t \leq 0.2$ s and subsequent slower narrowing detected in Fig. 9 (a). These trends point towards a substantial influence of desorptive kinetics on the early inertia/shear-governed deformational dynamics, given the fast-paced $\tilde{\sigma}$ homogenization that transpires as $\tilde{\Gamma}$ plummets. Neck formation is heavily limited at higher Bi , favoring early coalescence (i.e., after the leading edge) which leads to an interfacial structure resembling that of the clean system (see t_3 in Fig. 2). Latter distortion ($t > 0.15$ s) slightly intensifies at high Bi given the mostly uniform $\tilde{\Gamma}$ profiles attained early on. This homogeneity eliminates concentration gradients, thereby negating the effects of τ_M on interfacial spread, contrary to the findings discussed in §3.2.1 for $\uparrow \beta$.

Fig. 10 (b) portrays a lowering trend for the final droplet count with increasing Bi , starting from saturation at $Bi=0.01$ and holding a linear relationship against $\log(Bi)$. However, a larger gap ($\downarrow 23\%$) exists between $Bi=1$ and the clean case, hinting towards highly desorptive scenarios ($Bi > 1$) where

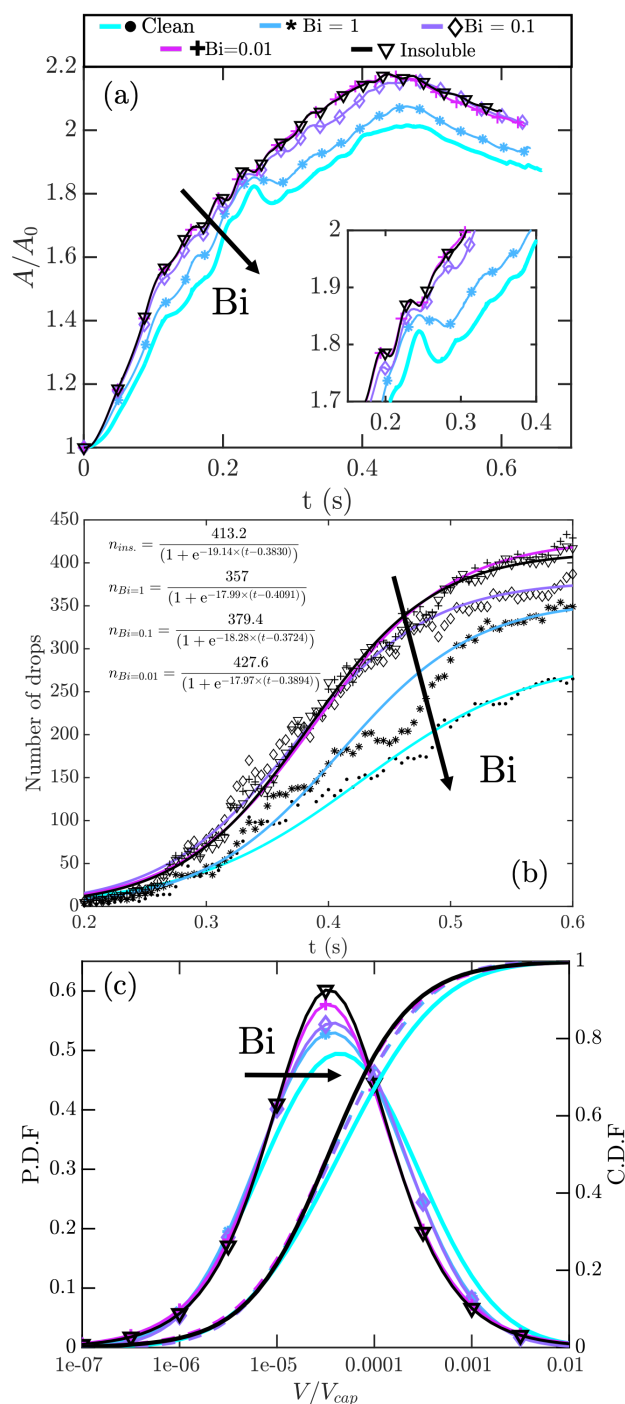


Figure 10: Comparative performance metrics for varying Bi . Same description given in Fig. 9 applies, with all cases being normally distributed, except the insoluble and $Bi=0.01$ case.

drop production could still surpass that of a clean system. The N_d growth rate rises when surfactant is added ($\uparrow \approx 26\%$) and remains stable for all soluble scenarios, with values amidst $17.97 < k_g < 18.28$. Nonetheless, breakage mechanisms can not be claimed to remain consistent at different Bi from the k_g invariability among cases, as concluded for the insoluble scenarios. An attempted collapse of \tilde{N}_d vs. \tilde{t} for all Bi values further clarifies this insight. This procedure yields a

logistic regression $\tilde{N}_d = \frac{0.9735}{1 + e^{-12.92(\tilde{r} - 0.6447)}}$, where $Bi=1$ con-
 forms with a higher level of deviation ($R^2_{Bi=1} = 0.96$ vs.
 $R^2 > 0.99$ for $Bi < 1$). This discrepancy appears at $t(s) \in$
 $[0.4, 0.5]$ in Fig. 10 (b), where N_d uncharacteristically falls
 below the logistic fit. To account for the possible variations
 in the breakage mechanisms, we must bring forth notions ex-
 plored in §3.1.2, such as restricted ligament formation and
 elongation due to $\uparrow \tilde{\sigma}$ and $\downarrow \tau_M$, which could potentially cas-
 cade into favouring low output breakup modes and also tam-
 per with developing capillary instabilities. Previous studies
 agree with these observations as they have demonstrated that
 neck formation and rate of thinning markedly fluctuates as a
 function of Bi and surfactant coverage [32]. Further detail
 into the altered deformation and breakup dynamics in these
 scenarios could certainly be dissected in future studies.

DSDs in Fig. 10 (c) generally indicate a left bias and
 wider span compared to the clean, regardless of the surfac-
 tant's desorptive activity. This is confirmed by the s and k_{ex}
 parameters, which often convey a more pronounced negative
 skewness ($-0.1093 < s < -0.4422$, with $Bi=0.1$ being the
 exception), and always confer leptokurtic shapes with larger
 k_{ex} ($0.4701 < k_{ex} < 0.6168$). Similar to the conclusions in
 §3.2.1, adding surfactant promotes the production of smaller
 daughter droplets but introduces a larger degree of variabil-
 ity. It is worth noting that even at the strongest solubility
 tested ($Bi=1$), surfactants continue to exert a significant in-
 fluence on the DSD attributes, resulting in the highest k_{ex}
 amongst all Bi cases. This comes from the interplay of com-
 peting breakup dynamics, alternating between those identi-
 fied for the clean and SL case in §3.1.2. On the other hand,
 a Kruskal-Wallis test unveiled statistically significant dif-
 ferences between the insoluble and highly desorptive cases
 ($Bi > 0.01$), whereas the clean and soluble showed no signif-
 icant differences except for the weakly soluble scenario at
 $Bi=0.01$. Furthermore, DSDs are seen to depart from Gaus-
 sian shapes as we approach the insoluble limit ($Bi=0.01$),
 confirming that rising desorption capability alters signifi-
 cantly the predominant breakup modes [8], drifting towards
 the mechanics elucidated for the clean case.

3.2.3. Effect of surfactant adsorption depth

This subsection encompasses cases 7-9 from Table 2,
 varying simultaneously Da and k as indicated in [45]. The
 solubility analysis here focuses on the surfactant sorption ki-
 netics, considering varying adsorption 'depths' below the in-
 terface from which surfactant can be retrieved from the bulk
 phase [31]. A higher solubility is given by $\uparrow Da$, $\downarrow k$, de-
 noting smaller adsorption depths and thereby comparatively
 weaker adsorption vs. desorption kinetics. As mentioned
 in §2.3, k_a is not varied directly, but rather Γ_0 and C_∞ for
 numerical convenience. This procedure generates systems
 where the actual feature being manipulated is the relative
 importance of Γ and C . Considering this approach, connec-
 tions to the underlying physics explored throughout §3.1 will
 not be emphasized as most come from the immediate effect
 of lowering or increasing $\tilde{\Gamma}$. Nonetheless, these cases can
 also be interpreted via Da and k as equivalent surfactant-

laden mixtures with varying sorptive natures. Consequently,
 the findings explored in this subsection can not be directly
 tied to the sorption kinetics but do provide insights on the
 possible behaviour of self-similar systems.

Fig. 11 (a) illustrates comparable trends to those addressed
 in §3.2.2, exhibiting the same monotonic and inversely pro-
 portional relationship between A/A_0 and Da . As discussed
 previously, higher surfactant solubility causes a severe re-
 duction of the A/A_0 undulations at $t = 0.15 - 0.25s$ and
 a recovery of the stage-transitioning inflection point at $t =$
 $0.25s$. However, rising Da and dropping k has a more dra-
 matic effect than elevating desorption through $\uparrow Bi$, as evi-
 denced by the highly soluble case at $Da = 1$, which closely
 aligns with the clean A/A_0 curve and fully restores the in-
 flexion point. Although these results are mostly due to the
 initially low surface concentration ($\Gamma_0 \approx \frac{\Gamma_\infty}{10}$ see Table 2),
 they can be interpreted as a more substantial influence of ad-
 sorption strength on $\tilde{\Gamma}$. This stems from k being lower than
 unity ($k = 0.1$ for $Da = 1$), representing a surfactant whose
 desorption rate is faster than its adsorption (weakly adsorp-
 tive). For this reason, regardless of other competing trans-
 port dynamics (e.g., surface convection or diffusion), surfac-
 tant pivots towards desorption and accumulation in the bulk
 phase, thus rendering a deformational profile closely resem-
 bling that of the clean case. In contrast, all Bi cases in §3.2.2
 maintained $k > 1$ (highly adsorptive), which could account
 for the less impactful effect of increasing desorption. A near
 saturated state is reached at $Da = 0.01$ (overlapping with the
 insoluble curve), hinting towards a negligible impact of fur-
 ther lowering Da / rising k thereafter.

The A/A_0 growth rates ($G1, G2$) adhere to a similar be-
 havior as the one settled for Bi in §3.2.2 by obeying a de-
 pendence, albeit linear in this case, against the logarithm
 of Da . $G1$ and $G2$ rates hold opposing behaviors against
 $\uparrow Da, \downarrow k$, with $G1$ rates decreasing at a faster pace com-
 pared to that at which $G2$ rates rise, following linear expres-
 sions of the form $G1_{Da} \approx -0.6272 \cdot \log(Da) + G1_{Da=1}$ and
 $G2_{Da} \approx 0.2475 \cdot \log(Da) + G2_{Da=1}$, respectively. Accord-
 ingly, rapidly declining $G1$ rates lead to a widening gap be-
 tween curves at $t \leq 0.2s$, whilst slowly ascending $G2$ rates
 provoke a narrower disparity. Nonetheless, these responses
 result marginally different than the ones identified in §3.2.2,
 given the linear nature at which growth rates scale. If we in-
 terpret these systems from an adsorptive profile perspective,
 the general deformation dynamics unfolding during the first
 stage will be analogously affected with increasing solubility
 as evaluated for the Bi cases (i.e., highly limited neck forma-
 tion and weak τ_M -driven retraction due to uniform $\tilde{\Gamma}$). How-
 ever, these mechanisms evolve slower than those in §3.2.2
 for $\uparrow Da$ given their linear scaling, rendering them independ-
 ent of the surfactant's sorptive profile.

Fig. 11 (b) depicts a flat droplet count profile for $Da \leq$
 0.1 and a sudden drop at $Da=1$. Even though the M pa-
 rameters do not converge between the clean and highly sol-
 uble case ($Da=1$), they do not exhibit a major jump akin to
 that calculated for $Bi=1$ in §3.2.2 ($\approx 15\%$ drop from $Da=1$).
 From this, we can safely estimate an upper bound of $Da \sim$

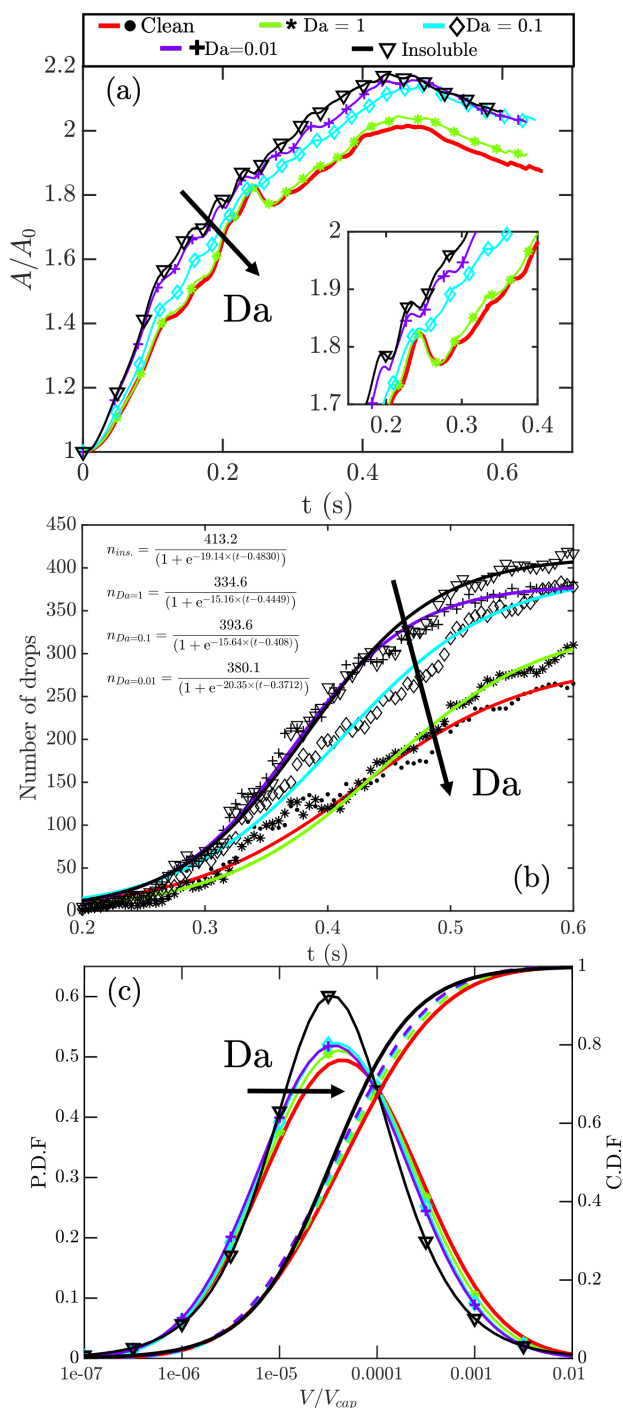


Figure 11: Comparative performance metrics for varying Da . Same description given in Fig. 9 applies here. All cases, except the insoluble case, are normally distributed.

1366 $O(10)$ where the generalized dynamics would collapse to
 1367 those unfolding in a clean mixture, specially since this would
 1368 yield a system with $k \sim O(10^{-2})$ where surfactant would be
 1369 essentially irreversibly lost to the bulk phase once it gets des-
 1370 orbed. Contrarily to §3.2.2, k_g values remain virtually un-
 1371 changed from the clean to the moderately soluble cases up
 1372 to $Da=0.1$. The abrupt spike occurs at $Da=0.01$, where k_g
 1373 surges by $\approx 30\%$, leveling with the insoluble case. This re-

1374 sult potentially reinforces the premise postulated from Fig. 11
 1375 (a), hinting that adsorption strength plays a highly influen-
 1376 tial role on Γ , thereby swiftly altering the mechanisms gov-
 1377 erning breakage. By performing the same N_d vs. t nor-
 1378 malisation at varying Da , a logistic regression of the form
 1379 $\tilde{N}_d = \frac{0.9749}{1 + e^{-13.12(\tilde{t} - 0.6456)}}$ is obtained, where $Da \geq 0.1$ cases fit
 1380 with a lower accuracy ($R^2_{Da=0.01} = 0.99$ vs. $R^2 < 0.97$ for
 1381 $Da > 0.1$). This deviation can't be clearly distinguished from
 1382 Fig. 11 (b), but emulates the behavior seen for $Bi=1$, where
 1383 the droplet count falls below the general logistic fit around
 1384 $t(s) \in [0.35, 0.55]$. These observations can be interpreted as
 1385 a sharper transition between clean and SL breakup modes at
 1386 different k , unlike the interplay between co-existing modes
 1387 proposed in §3.2.2 at different Bi .

1388 The PDFs shown in Fig. 11 (c) depict similar tendencies
 1389 to those explored in §3.2.2, with a generalized left-bias and
 1390 broader variability with decreasing solubility. The k_{ex} and s
 1391 parameters (estimated from the raw data) convey a slightly
 1392 different story. The system at $Da=1$ yields $|s| < |s_{clean}|$ and
 1393 a $k_{ex} < k_{ex, clean}$, indicating a near-normal DSD with a low
 1394 dispersion from the mean. This case remains uninteresting
 1395 as discussed before due to its close resemblance to the clean
 1396 system ($\Gamma_0 \ll \Gamma_\infty$). On the other hand, cases above $Da=0.1$
 1397 reveal a substantially different behaviour. The raw data un-
 1398 veils an abnormal surge in the production of medium-sized
 1399 interfacial structures ($V/V_{cap} \sim O(10^{-4})$) for the moder-
 1400 ately soluble scenario (similar to the insoluble $\beta = 0.6$ case),
 1401 whereas the weakly soluble system evenly distributes drops
 1402 among $O(10^{-5}) < V/V_{cap} < O(10^{-3})$, dragging the k_{ex}
 1403 and s features down. As postulated previously, this trend could
 1404 indicate a sharp transition in the governing breakup modes
 1405 when the adsorptive profile is modified, suggesting it has a
 1406 more commanding influence on the underlying physics than
 1407 enhancing desorption with a constant k profile.

1408 As a closure to §3.2, Fig. 12a displays the shape of se-
 1409 lected DSDs through a kernel density estimation (KDE), visu-
 1410 ally presented via violin plots. A weak bi-modal nature
 1411 of the clean DSD becomes immediately evident, with two
 1412 distinct peaks located in the interquartile range (IQR), prob-
 1413 ably due to dominant low output breakup modes of bulkier
 1414 structures (see §3.1.2). Interestingly, this feature is promptly
 1415 eliminated and the DSD characteristics are noticeably al-
 1416 tered when incorporating surfactant, even at the highest
 1417 solubility trialed ($Da=1$) despite producing a similar drop
 1418 count to the clean system. As surfactant activity increases,
 1419 either via higher β or weaker solubility, the IQR markedly
 1420 tightens and the mean lowers whilst maintaining relatively
 1421 long lower tails, indicating a pivotal shift in the predomi-
 1422 nant breakup modes, and accounting for the generally larger
 1423 k_{ex} and prominent left skewness detected in most SL cases.
 1424 Accordingly, the IQR could serve as a potential indicator
 1425 of surfactant activity in the system. Large interfacial struc-
 1426 tures ($V/V_{cap} > O(10^{-3})$) survive at moderate solubility
 1427 given the active competition with clean breakup modes (see
 1428 §3.1.2), whereas the upper tails shrink for the insoluble cases.

1429 Furthermore, Fig. 12b provides a summary of the overall
 1430 relationships dissected throughout §3.2 based on the max-

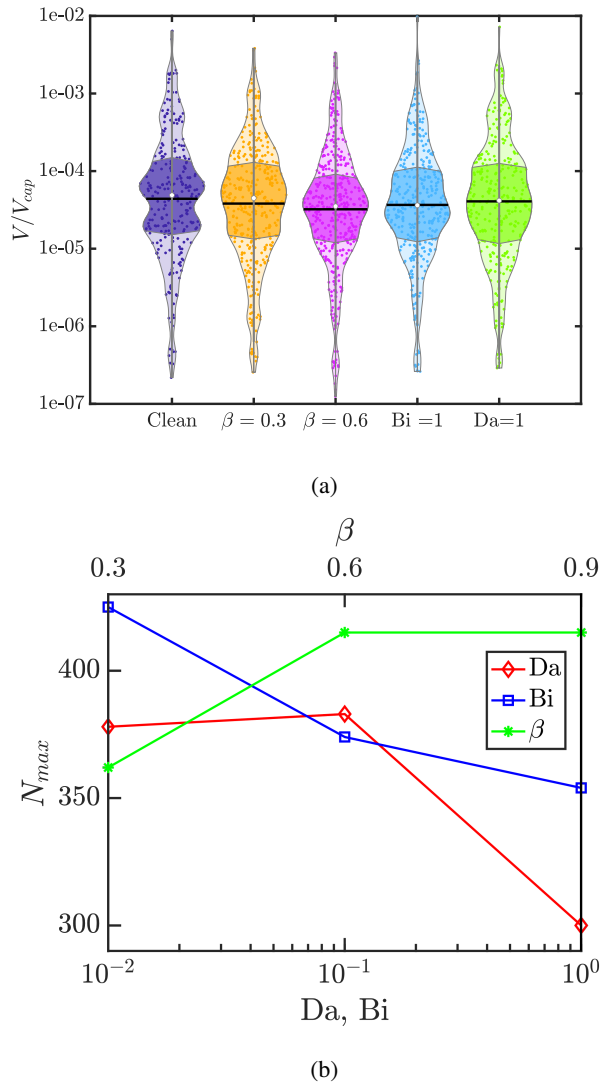


Figure 12: Global comparisons between selected cases. (a) Dimensionless DSD violin plots. Kernel density estimation considers a constant bandwidth, following the well-established Silverman [66] rule of thumb for normally distributed data-sets. Interquartile range (IQR) is given by the shadowed region in each violin. Mean and median values are depicted by black horizontal lines and white dots, respectively. Grey "whiskers" represent the $1.5 \times \text{IQR}$ limit, (b) global maximum drop count (N_{max}) attained by each case throughout the dispersion.

imum droplet count (N_{max}) attained. N_{max} increases until saturation with ascending elasticity, and decreases with strengthening solubility. However, the descending profile differs depending on the manipulation given to the sorption kinetics, with N_{max} exhibiting a convex and concave shape for increasing Bi and Da , respectively. These behaviors suggest a more dramatic effect of weakening adsorption kinetics through $k_a Da$ rather than increasing desorptive power via Bi .

3.3. Multi-drop surfactant-laden dispersion

In this brief exploratory section, we consider a short version of the parametric study conducted above for a more

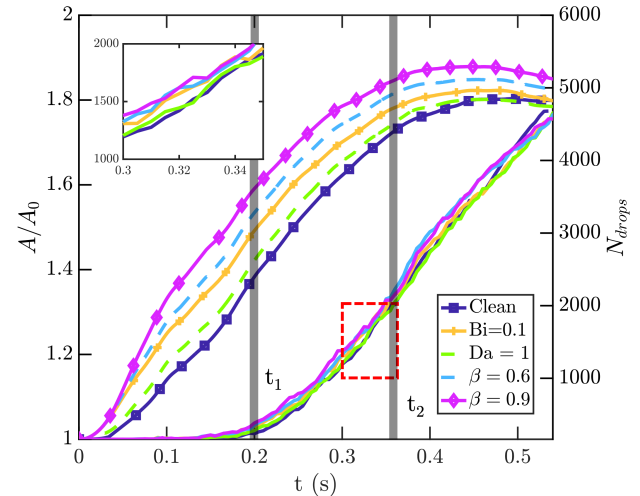


Figure 13: Comparative temporal evolution of the normalized interfacial area A/A_0 (left axis) and number of detached structures N_{drops} (right axis) for different surfactant physicochemical profiles considering a multi-drop set-up specified in §2.1. Highlighted times t_1 , t_2 refer to instances shown in Fig. 14.

industrially-relevant multi-drop inlet, as described in Valdes et al. [1] (coarse per-mix setup). To avoid redundancy, the main trends behind dispersion performance will be highlighted, while diving into physical mechanisms sparingly, as they can be directly extrapolated from the aforementioned dynamics.

Fig. 13 illustrates a clear distinction between the interfacial growth attained with different surfactant physicochemical profiles. Following the discussion given in §3.2, the insoluble cases exhibit the highest A/A_0 , which ultimately ascends at higher β , considering the intricacies behind competing processes stemming from $\uparrow \frac{\partial \tilde{\sigma}}{\partial \Gamma}$ (greater shear-driven deformation due to $\downarrow \tilde{\sigma}$ vs. augmented interfacial retraction from $\uparrow \tau_M$) [18, 19, 28]. The soluble scenarios lie between the insoluble and clean deformation profiles [30, 31], with the weakest adsorption kinetics aligning closer to the clean curve. The transition between stages (i.e., inflection point) and other distinctive features associated with specific deformational dynamics (i.e., undulations related to forking and wrapping) are smoothed out from the A/A_0 curves due to the layered configuration of incoming droplets, which causes several mechanisms to progress simultaneously (i.e., drops from different layers breaking, wrapping and elongating) [1].

By isolating sections where A/A_0 behaves quasi-linearly, the timeframe between $t(s) \in [0, 0.1]$ depicts quite rich variations between different systems. $\frac{\Delta A/A_0}{\Delta t}$ rises by $\Delta \approx 1.08s^{-1}$ from the clean to the $Bi=0.1$ case, namely from $G_{clean} \approx 1.42s^{-1}$ to $G_{Bi} \approx 2.50s^{-1}$, with $Da=1$ roughly in the middle at $G_{Da} \approx 1.83s^{-1}$. On the other hand, a higher increment of $\Delta \approx 1.37s^{-1}$ takes place between the clean and insoluble, with an even larger gap existing to the highest elasticity, spiking from $G_{\beta=0.6} \approx 2.79s^{-1}$ to $G_{\beta=0.9} \approx 3.34s^{-1}$. All cases seem to stabilize between $t(s) \in [0.1, 0.3]$ at an average rate of $\approx 2.32s^{-1}$, implying a saturation of the system

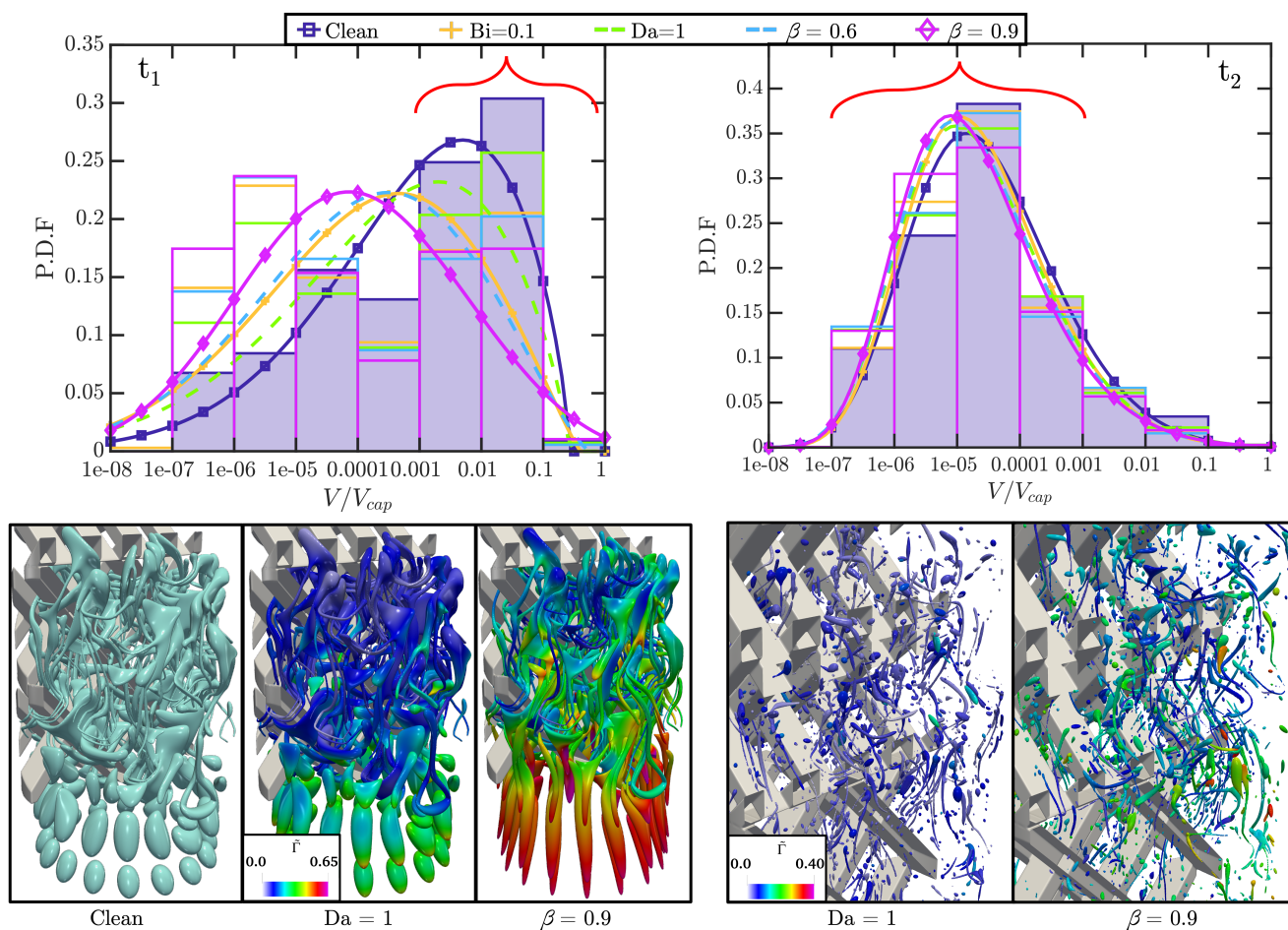


Figure 14: Comparative dimensionless DSDs in the top row for times t_1 (left) and t_2 (right) identified in Fig. 13. The DSDs are represented through a normalized probability histogram with a superimposed PDF curve. All multi-drop cases, at both t_1, t_2 , are fitted to a generalized extreme value distribution to better capture the sparsity of the data in the different size groups. Bottom row emphasizes on the dispersed phase's morphology of selected cases (clean, weakly adsorptive and insoluble) at each temporal instance. Drops shown correspond to a subset of the drop population marked with red brackets on the histogram plot.

1475 where modifying surfactant properties will no longer have a
1476 substantial effect on interfacial deformation.

1477 Fig. 13 also displays the evolution of the droplet count,
1478 which for all scenarios, including the clean, collapses to a
1479 dimensionless generalized logistic function, obeying the ex-
1480 pression $\tilde{N}_d = \frac{1.089}{1+e^{-7.231(\tilde{t}-0.6927)}}$ with an $R^2 = 0.9920$. More-
1481 over, fitting each case separately leads to a similar result,
1482 where the M and k_g parameters present minimal relative
1483 variation, ranging between $5153 < M < 5484$ and $12.33 <$
1484 $k_g < 13.27$. These outcomes reinforce the observation raised
1485 above on the saturated state of the dispersion after $t > 0.1$ s,
1486 since droplet births will not depend predominantly on the
1487 nature of the surfactant, but rather on the average energy im-
1488 parted by the mixer [1]. This phenomenon is an inherent
1489 consequence of the high oil phase volume fraction travelling
1490 through an insufficiently long mixer. As depicted in the 3D
1491 views in Fig. 14 @ t_1 , large drops promptly fill the SMX el-
1492 element as they elongate and wrap around crossbars, severely
1493 disrupting the internal hydrodynamics. This potentially in-
1494 tensifies the shear experienced by the drops, analogous to

1495 modifying the continuous phase's effective viscosity [2, 47],
1496 thus obscuring variations in the drop production stemming
1497 from the surfactant's properties. Nevertheless, the A/A_0 at
1498 the exit region ($t > 0.4$ s) plateaus at markedly different val-
1499 ues for each case, adhering to the trends established in §3.2.
1500 This indicates distinct degrees of interfacial distortion, de-
1501 pendent on the surfactant's nature, which could favour partic-
1502 ular breakup modes if the dispersion was to continue.

1503 Notwithstanding, heterogeneity in breakup events at dif-
1504 ferent physicochemical profiles can be identified throughout
1505 the dispersion, despite being concealed by the deceptively
1506 large drop count scale. The top-left close-up in Fig. 13 at
1507 $t(s) \in [0.3, 0.35]$ reveals a gap of $\sim 100+$ drops between
1508 the clean and $Bi=0.1$ system, which is doubled when compared
1509 against the $\beta = 0.9$ case, being consistent with the drop
1510 count deviations estimated in §3.2. In addition, substantial
1511 impact on the DSDs is captured in Fig. 14 at t_1 , in agree-
1512 ment with the A/A_0 disparities at $t < 0.1$ s. Considering the spar-
1513 sity of the data across different size groups at this early stage,
1514 DSDs were fitted to a generalized extreme value (GEV) dis-

tribution via Q-Q plot analysis, seeking to best represent the inhomogeneities in the distributions. Stronger and/or less soluble surfactants enhance the production of small-sized drops and prompt higher variability, thereby generating wider and left-shifted distribution bells with a faint yet positive skewness ($0.075 < s < 0.195$). On the contrary, the clean and highly soluble $Da=1$ case show an emphatic right-shift with a thin yet long left tail ($s_{clean} < s_{Da} = -0.18$), implying a greater population of unbroken large structures.

Due to the sparsity of the data, all distributions exhibit a platykurtic modality ($k_{ex} < 0$), indicating lighter, less populated tails. Therefore, the skewness features discussed in §3.2 are not directly comparable, given the dissimilar nature of the DSDs therein. Distributions at t_2 illustrate gentler contrasts, while still preserving the same trends. Systems with stronger surfactant activity induce heavier left-tails and wider distribution spans. The 3D bottom views @ t_2 show comparable drop populations with markedly different $\tilde{\Gamma}$, exemplifying the saturation effect but showcasing the underlying contrasts in surfactant content. These complex scenarios successfully extrapolate the main results gathered throughout this paper, clearly identifying the impact in performance of varying surfactant properties, even at highly saturated, hydrodynamically disrupted systems.

4. Conclusions

A numerical investigation of the fundamental physical mechanisms governing surfactant-laden L-L dispersions in a SMX mixer has been conducted using high fidelity, 3D direct numerical simulations coupled with an interface tracking algorithm. Furthermore, a parametric study was carried out to elucidate the effect of different surfactant physicochemical profiles in the dispersion performance, aiming to extrapolate the main trends to more realistic case studies.

Deformational mechanisms are dictated by two competing effects: 1) inhomogeneity in capillary forces induced by local $\tilde{\sigma}$ fluctuations, and 2) Marangoni stresses arising from surface concentration gradients ($\nabla_s \tilde{\Gamma}$), modulated by the sensitivity between $\tilde{\sigma} - \tilde{\Gamma}$ ($\frac{\partial \tilde{\sigma}}{\partial \tilde{\Gamma}}$). The importance of these effects greatly depends on the local hydrodynamics. Shearing type flows ($Q = 0$) developing at high strain regions near the crossbars/cross-points, and strong inertial flows mostly emerging at the center of corridors, nullify τ_M action since they grant sufficiently high interfacial velocities to allow for surface flux, even at high $\tilde{\Gamma} \gg 0.5$, thus enabling mechanisms contingent on surfactant accumulation to unfold (i.e., tip-stretching). Contrarily, Marangoni plays an influential role in prevailing extensional ($Q = 1$) and weakly inertial flows (e.g., recirculation regions).

Surfactant-induced effects reveal a dual nature:

- Prompting a more unstable interface susceptible to larger distortions. This effect is associated with weaker restoring interfacial forces ($\downarrow \tilde{\sigma}$), which enhance shear-driven splitting events spawning new necks, and accelerate elongation via tip-stretching due to surfactant accumulating at the forming lobes.

- Stabilizing deformational dynamics by limiting interfacial spread, and preventing early breakups. This effect comes two-fold, firstly from surfactant dilution during wrapping, being swept towards the nascent poles, thus triggering a rise in $\tilde{\sigma}$ at the point of contact; and secondly, Marangoni stresses retracting and rigidifying interfacial regions primarily subjected to extensional deformation, thereby restricting interfacial spread and generating thinner and longer ligaments.

These observations can translate to the breakage mechanisms, which, in conjunction with the local characteristics of the interfacial entity (i.e., \tilde{L}_0 , Oh, fluid-solid interaction), ultimately dictate the breakup mode occurring. Marangoni flows exhibit a two-pronged effect in relation to breakup events conditional to their relative strength/activity against disruptive external stresses. They can act beneficially and augment small drop formation (i.e., stabilizing ligament lengthening, hence favouring high output breakup modes), or detrimentally and restrict droplet birth altogether (i.e., delaying or precluding pinch-off and accelerating ligament retraction).

The parametric study reflected a consistent trend throughout: stronger surfactant activity, determined by either elevated elasticities (β) or weaker bulk solubility (highly adsorptive/weakly desorptive), yields a larger interfacial area growth and higher droplet count with a left-biased DSD, leaning towards small-sized droplets with a wider degree of variability. As dissected from the underlying physics, adding surfactant tends to promote sizeable populations of large \tilde{L}_0 ligaments, thus favouring high output breakup modes rendering more, smaller droplets. Variability is introduced via augmenting τ_M effects, which alters breakup mechanisms as mentioned prior. Solubility effects trigger a shift in the predominant breakup modes, which is detected by a deviation from the logistic evolution of the droplet count and a departure from a Gaussian distribution of the DSD. Weakening the adsorptive profile suggested a more dramatic effect compared to rising desorption relevance vs. surface convection.

The perspectives presented herein, to our knowledge, deliver a valuable first account of the complex governing interfacial dynamics behind an industrially-relevant surfactant-laden system by offering an unprecedented level of detail, currently inaccessible via numerical volume-averaged or experimental methods. These results can substantially benefit decision-making pipelines in operation and equipment design by providing a comprehensive physical understanding of the implications behind surfactant physicochemical properties, visualized from relevant dispersion performance metrics. Furthermore, the physical insights showcased can serve as building blocks for the development of more robust predictive models and correlations that can offer wider applicability and improved accuracy.

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