

DOCTORAL THESIS

Molecular Dynamics Simulation of the Coalescence of Freely Suspended and Sessile Droplets

Author: Soheil Arbabi Supervisor: Dr hab. Panagiotis THEODORAKIS

A thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy in Physics

> Division of Theoretical Physics Soft Matter and Fluids Physics Group

> > February 15, 2024

Abstract of thesis entitled

Molecular Dynamics Simulation of the Coalescence of Freely Suspended and Sessile Droplets

Submitted by

Soheil ARBABI

for the degree of Doctor of Philosophy at Institute of Physics, Polish Academy of Sciences

in February, 2024

 \mathbf{I} he coalescence of droplets is an everyday natural process, wherein raindrops combine as they descend, forming larger raindrops. Alternatively, they may unite upon the surface of a leaf, crafting a picturesque dew on a crisp early autumn morning. Furthermore, this phenomenon has numerous applications. For instance, in inkjet printing, achieving high-quality prints depends on the flawless coalescence of color drops on the paper's surface. In microfluidics, encapsulating bio-particles within droplets become feasible by adding surfactants to hinder coalescence. Numerous studies have attempted to explain coalescence through numerical and experimental approaches. However, these methods often suffer from a lack of resolution, particularly in the initial stages of coalescence, known as the 'pinching stage'. This stage remains inaccessible in terms of both length and time scales in continuum and experimental studies. It is where molecular dynamics can play a role by offering extremely fine resolution in time and space to capture the initial pinching. Following pinching, the formation of a bridge between two droplets occurs. The growth dynamics of this bridge takes place within different regimes, and various controversial explanations have been proposed about these different regimes involved in this process. Furthermore, describing the mass transport mechanism of surfactant molecules during coalescence presents another challenge. In continuum simulations, researchers can investigate the convection and diffusion of surfactants as a result of capillary forces, primarily arising from the curved interface of the bridge between two droplets. Additionally, Marangoni effects come into play, generating surface flows due to surface tension gradients in the presence of surfactants. The mathematical description of these processes involves various equations, each based on specific assumptions. However, a knowledge gap persists in the detailed description of surfactant mass transport with molecular resolution, particularly concerning the bridge and the initial stages of coalescence. In the case of coalescence of sessile droplets, much less is known, despite its relevance for microfluidics and coating technologies. Different types of substrate ranging from non-wettable to wettable substrate can affect the coalescence process and bridge growth dynamics.

The objective of this thesis is to offer a comprehensive explanation of droplet coalescence by utilizing the Molecular Dynamics method. This investigation encompasses three distinct types of surfactants and various concentrations. Additionally, polymer droplets with different chain lengths are taken into consideration. The presence of two distinct regimes within the dynamics of bridge growth has been observed in this study: the Thermal and Inertial regimes. Notably, it has been demonstrated that the transition between these two regimes becomes more pronounced when the surfactant concentration is well above the Critical Aggregation Concentration (CAC). Furthermore, a second objective of this thesis is to provide a comprehensive explanation of the mass transport mechanism. Here, the mass transport mechanism during coalescence is compared and investigated for surfactant concentrations both below and above the CAC, considering three different surfactants. The findings reveal that the coalescence process is initiated by surfactant pinching, followed by the formation of a surfactant film between the two droplets. In cases where the concentration exceeds the CAC, this film becomes continuous, thereby hindering the participation of water in the initial stages of coalescence. Moreover, large-scale molecular dynamics simulations are utilized to investigate the coalescence of surfactant-laden sessile droplets on substrates with varying wettability. Noteworthy, similarities are observed between the coalescence of sessile droplets with equilibrium contact angles exceeding 90° and that of freely suspended droplets. A significant shift in bridge dynamics and the mass transport mechanism becomes apparent below the 90° contact angle, where the initial contact point transforms into a small, line-like structure, exerting a pronounced influence on various aspects of the coalescence process. This configuration allows water to actively participate in the coalescence from the outset. Finally, the coalescence of sessile polymer droplets with different chain lengths is studied, considering the effects of substrate wettability and droplet viscosity on coalescence and bridge growth dynamics. The study reveals that the presence of the substrate and its wettability significantly influence bridge dynamics. In general, increasing the polymer chain length results in a reduction in the bridge growth rate and coalescence speed.

Thus, we anticipate that the present thesis provides a comprehensive account of droplet coalescence, which can play an important role in various applications requiring a detailed understanding of droplet coalescence behavior. This pertains to both freely suspended and sessile droplets, making it of primary interest. Additionally, this study has the potential to create new opportunities, such as advances in droplet research. For instance, it can offer innovative solutions in cases where both numerical and experimental methods face challenges in capturing minute scales, be it at the nano, micro, or smaller levels.

Streszczenie pracy doktorskiej pt Symulacja dynamiki molekularnej koalescencji swobodnie zawieszone i siedzące kropelki Instytut Fizyki PAN Przesłane przez Soheil ARBABI

Koalescencja kropelek jest codziennym, naturalnym procesem, podczas którego krople deszczu łączą się podczas opadania, tworząc większe krople deszczu. Alternatywnie mogą zjednoczyć się na powierzchni liścia, tworząc malowniczą rosę w rześki wczesny jesienny poranek. Co więcej, zjawisko to znajduje liczne zastosowania. Na przykład w druku atramentowym uzyskanie wysokiej jakości wydruków zależy od precyzyjnej koalescencji kropel farby na powierzchni papieru. W mikrofluidyce kapsułkowanie biocząstek w kropelkach staje się możliwe poprzez dodanie surfaktantów utrudniających koalescencje. W licznych badaniach próbowano wyjaśnić koalescencje zarówno metodami numerycznymi, jak i eksperymentalnymi. Jednakże metody te często charakteryzują się słabą rozdzielczością, szczególnie w początkowym stadium koalescencji, znanym jako "etap szczypnięcia". Etap ten pozostaje niedostępny zarówno pod względem rozdzielczości przestrzennych i czasowych, w symulacjach metodą kontinuum i eksperymentalnych. To właśnie tu rolę może odegrać dynamika molekularna, która zapewnia odpowiednio wysoką rozdzielczość w czasie i przestrzeni, aby uchwycić początkową fazę szczypnięcia. Po szczypnięciu następuje utworzenie mostu pomiędzy dwiema kropelkami. Dynamika wzrostu tego pomostu odbywa się w ramach różnych reżimów; zaproponowano dotychczas różne sporne wyjaśnienia dotyczące tego zjawiska. Ponadto opisanie mechanizmu transportu masy cząsteczek surfaktantu podczas koalescencji stanowi kolejne wyzwanie. W symulacjach ciągłych możliwe jest zbadanie konwekcji i dyfuzji surfaktantów pod wpływem sił kapilarnych, wynikających głównie z zakrzywionej powierzchni styku między dwiema kropelkami. Dodatkowo w grę wchodzą efekty Marangoniego, generujące przepływy powierzchniowe w wyniku gradientów napięcia powierzchniowego w obecności surfaktantu. Matematyczny opis tych procesów obejmuje różne równania, każde oparte na określonych założeniach.

Jednakże niejasne pozostają szczegóły opisu transportu masy surfaktantów w skali molekularnej, szczególnie w odniesieniu do pomostu i początkowych etapów koalescencji. W przypadku koalescencji kropelek osiadłych wiadomo jeszcze znacznie mniej, pomimo znaczenia tego przypadku dla mikroprzepływów i technologii powlekania. Różne rodzaje podłoża, od niezwilżalnego do zwilżalnego, mogą wpływać na proces koalescencji i dynamikę wzrostu mostka.

Celem tej pracy jest kompleksowe wyjaśnienie koalescencji kropel z wykorzystaniem metod dynamiki molekularnej. Badanie to obejmuje trzy różne typy surfaktantów i różne stężenia. Dodatkowo brane są pod uwagę kropelki polimerów o różnych długościach łańcucha. W niniejszej pracy zaobserwowano obecność dwóch odrębnych reżimów w dynamice wzrostu mostów: reżim termiczny i inercyjny. W szczególności wykazano, że przejście między tymi dwoma reżimami staje się bardziej wyraźne, gdy stężenie surfaktantu znacznie przekracza CAC (krytyczne stężenie agregacji). Ponadto drugim celem tej pracy jest kompleksowe wyjaśnienie mechanizmu transportu masowego. Tutaj porównany zostaje mechanizm transportu masy podczas koalescencji pod katem stężeń surfaktantu zarówno poniżej, jak i powyżej CAC, obejmujac trzy różne gatunki surfaktantu. Wyniki pokazują, że proces koalescencji rozpoczyna się od lokalnego wzrostu koncentracji surfaktantu, po czym następuje utworzenie warstwy pomiędzy dwiema kropelkami. W przypadkach, gdy stężenie przekracza CAC, film ten staje sie ciagły, utrudniając tym samym udział wody w początkowych etapach koalescencji. Ponadto wielkoskalowe symulacje dynamiki molekularnej są wykorzystywane do badania koalescencji kropelek pokrytych surfaktantem, osadzonych na powierzchniach o różnej zwilżalności. Na uwagę zasługują podobieństwa które obserwuje się pomiędzy koalescencją kropelek osadzonych o równowagowych kątach zwilżania przekraczających 90° a swobodnie zawieszonymi kropelkami. Znacząca zmiana dynamiki mostu i mechanizmu transportu masy następuje poniżej kąta zwilżania 90°, gdy początkowy punkt styku przekształca się w małą, liniową strukturę, wywierająca wyraźny wpływ na różne aspekty procesu koalescencji. Taka konfiguracja pozwala wodzie aktywnie uczestniczyć w koalescencji od samego początku. W końcu zbadano koalescencje osadzonych kropelek polimeru o różnych długościach łańcucha, biorac pod uwagę wpływ zwilżalności podłoża i lepkości kropel na dynamikę koalescencji i wzrostu mostka. Z przeprowadzonych badań wynika, że obecność podłoża i jego zwilżalność maja istotny wpływ na dynamike pomostu. Ogólnie rzecz biorac, zwiększenie długości łańcucha polimeru powoduje zmniejszenie szybkości wzrostu pomostu i szybkości koalescencji.

Podsumowując, niniejsza praca oferuje kompleksowy opis koalescencji kropel, co może odegrać ważną rolę w różnych zastosowaniach, w których szczegółowe zrozumienie zachowania koalescencji kropel, zarówno swobodnie zawieszonych jak i znajdujących się na powierzchniach (siedzących), jest przedmiotem zainteresowania. Ponadto badania te mogą na różny sposób przyczynić się do rozwoju dziedziny. Mogą na przykład zaoferować nowe rozwiązania w przypadkach, gdzie dotychczasowe metody numeryczne lub eksperymentalne nie umożliwiają badania zjawisk na odpowiednio małej skali, czy to na poziomie mikro, nano, czy mniejszym.

Molecular Dynamics Simulation of the Coalescence of Freely Suspended and Sessile Droplets

by

Soheil ARBABI

A Thesis Submitted in Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy

to

Institute of Physics, Polish Academy of Sciences February, 2024

Copyright ©2024, by Soheil Arbabi All rights reserved.

Declaration

I, Soheil ARBABI, declare that this thesis titled, "Molecular Dynamics Simulation of the Coalescence of Freely Suspended and Sessile Droplets", which is submitted in fulfillment of the requirements for the Degree of Doctor of Philosophy, represents my own work except where due acknowledgement have been made. I further declared that it has not been previously included in a thesis, dissertation, or report submitted to this University or to any other institution for a degree, diploma or other qualifications.

Signed: Soheil Arbabi

Date: February 15, 2024



"I'm immensely thankful to my mother, Mersa, and my father, Nasser, for their endless love and support."



Acknowledgements

I would like to express my heartfelt gratitude to Panagiotis Theodorakis and Piotr Deuar for their unwavering support and invaluable guidance throughout my Ph.D. journey. Without their support, it would have been impossible for me to have the opportunity to conduct this research. In fact, their support not only greatly facilitated my academic journey but also enriched my daily life in lovely Poland.

Moreover, I want to express my sincere gratitude to Rachid Bennacer and Zhizhao Che for their guidance and their valuable feedback throughout my PhD journey.

Additionally, I would like to express my gratitude for the support received from the European Union's Horizon 2020 Research and Innovation program, specifically under the Marie Skłodowska-Curie grant agreement number 778104. This support enabled me to collaborate with Elvesys SAS and Professor Rachid Bennacer from ENS Paris-Saclay and afforded me the opportunity to travel to France during my Ph.D. This experience was invaluable, and I gained valuable knowledge and experiences through my collaboration.

Soheil ARBABI Institute of Physics of the Polish Academy of Sciences February 15, 2024

Acknowledgements

This thesis was supported by the National Science Centre, Poland, under grant No. 2019/34/E/ST3/00232. I gratefully acknowledge Polish high-performance computing infrastructure PLGrid (HPC Centers: ACK Cyfronet AGH) for providing computer facilities and support within computational grants no. PLG/2020/014344, PLG/2022/015261, PLG/2022/015747, and PLG/2023/016608.

Soheil ARBABI Institute of Physics of the Polish Academy of Sciences February 15, 2024

List of Publications

JOURNALS:

- Soheil Arbabi, Piotr Deuar, Mateusz Denys, Rachid Bennacer, Zhizhao Che, Panagiotis E. Theodorakis; Coalescence of surfactant-laden droplets. <u>*Phys. Fluids*</u> 35 063329 (2023). https://doi.org/10.1063/5.0153676
- [2] Soheil Arbabi, Piotr Deuar, Mateusz Denys, Rachid Bennacer, Zhizhao Che, and Panagiotis E. Theodorakis. "Molecular dynamics simulation of the coalescence of surfactant-laden droplets." <u>Soft Matter</u> 19, 8070-8080 (2023). https://doi.org/ 10.1039/D3SM01046E
- [3] Soheil Arbabi, Piotr Deuar, Rachid Bennacer, Zhizhao Che, and Panagiotis E. Theodorakis, Coalescence of Sessile Aqueous Droplets Laden with Surfactant. *Phys. Fluids* 36, XXXXX (2024). https://doi.org/10.1063/5.0194816
- [4] Soheil Arbabi, Panagiotis E. Theodorakis, Coalescence of Sessile Polymer Droplets: A Molecular Dynamics Study. <u>Macromol. Theory Simul.</u> 32, 2300017 (2023). https: //doi.org/10.1002/mats.202300017

Contents

Al	bstrac	2t	i
D	eclara	ition	v
A	cknov	wledgements	vii
Li	st of]	Publications	xi
Li	st of]	Figures	xv
Li	st of '	Tables	xix
Li	st of .	Abbreviations	xxi
Li	st of S	Symbols x:	xiii
1 2	Intr 1.1 1.2 Bac	oduction Motivation Thesis Organization kground	1 1 3 5
	2.1	 Coalescence Mechanisms and Bridge Growth Dynamics 2.1.1 Bridge Growth Dynamics During Coalescence of Freely Suspended Droplets 2.1.2 Bridge Growth Dynamics of Sessile Droplets 2.1.2 Bridge Growth Dynamics of Sessile Droplets 2.1.2 Mass Transport Mechanism of Surfactant Molecules During Coalescence 	5 5 9
	2.2	 of Surfactant-Laden Droplets 2.2.1 MD Study on Mass Transport Mechanisms in the Coalescence of Freely-Suspended and Sessile Surfactant-Laden Droplets 	13 15
	2.3	2.2.2 Experimental Studies on Mass Transport Mechanism During Co- alescence of Droplets Summary Summary	17 19
3	Met 3.1 3.2	hodology Computer Simulation Methods Molecular Dynamics Method 2.2.1 All Atom Modeling	21 21 22
		3.2.1 All-Atom Modeling	23

		3.2.2	Coarse Grained Modeling	24
			Bottom-Up Approaches:	25
			Top-Down Approaches:	27
			MARTINI Force-Field	27
			SAFT γ -Mie Force-Field	28
	3.3	Sumn	nary	30
4	Res	ults: Sı	ammary of Publications	33
	4.1	Coale	scence of Surfactant-laden Droplets	33
		4.1.1	Summary of Key Findings of This Publication:	33
		4.1.2	Details of Publication	34
	4.2	Moleo	cular Dynamics Simulation of the Coalescence of Surfactant-Laden	
		Dropl	ets	58
		4.2.1	Summary of Key Findings of this Publication:	58
		4.2.2	Details of publication	60
	4.3	Coale	scence of Sessile Aqueous Droplets Laden with Surfactant	101
		4.3.1	Summary of Key Findings of this Publication:	101
		4.3.2	Details of Publication	103
	4.4	Coale	scence of Sessile Polymer Droplets: A Molecular Dynamics Study .	166
		4.4.1	Summary of Key Findings of this Publication:	166
		4.4.2	Details of Publication	167
5	Con	clusio	ns and Outlook	177
Bi	bliog	raphy		179

List of Figures

1.1	Coalescence of raindrops on a glass surface. ¹	3
2.1	Stages of coalescence of water droplets with equal size. (a) Initial con- figuration; (b) Beginning of the bridge formation (Pinching); (c) Bridge growth. The bridge is indicated with a dashed rectangle and a magnified bridge picture with radius b is shown. (d) Final equilibrium configura- tion after reshaping is completed; The snapshots of the systems were	ſ
22	obtained using Ovito software [86].	6
2.2	(θ_s) is shown and all three interfacial forces involving the solid (<i>s</i>), liquid	
• •	(<i>l</i>) and gas (<i>g</i>) are illustrated.	10
2.3	Bridge formation during coalescence of water droplets on substrates of different wettabilities. (a) Non-wettable substrate ($\theta_s > 90^\circ$); (b) Intermediate substrate ($\theta_s \simeq 90^\circ$); (c) Wettable substrate ($\theta_s < 90^\circ$) and top view of the droplets on wettable substrate. <i>b</i> represents bridge height, <i>w</i> is the bridge width θ_i is the angle formed at the bridge and <i>X</i> is the	
	distance between the centers of mass of the two droplets. The snapshot	
	of the systems were obtained using Ovito software [86]	11
2.4	(a) Schematic of an non-ionic surfactant. Red beads represent the hy- drophobic part and yellow beads represent the hydrophilic part; (b) Two surfactant-laden droplets with concentration below CAC; (c) Two surfactant laden droplets with concentration above CAC; (d) A surfactant monomer on the surface of a droplet; (e) A surfactant aggregate inside the droplet.	-
2.5	The snapshot of the systems were obtained using Ovito software [86] Mass transport of surfactant molecules of freely suspended droplets (a-b) and sessile droplets (c-f). In all figures a larger arrow-end indicates the dominant direction of surfactant transport and magnified views of the bridge and its cross section on the y–z plane (only hydrophobic beads of surfactant) are shown beside and above each figure (In panels e and f such snapshots are placed beside and below). (a,c,e) Initial stage during coalescence of freely suspended droplets, sessile droplets on a non-wettable, and sessile droplets on a wettable substrate, respectively. (b,d,f) Developed bridge of coalescence of freely suspended droplets on a wettable droplets on a wettable substrate, and sessile droplets on a wettable substrate.	14
	substrate, respectively.	16

- 2.6 Coalescence of surfactant-laden droplet and surfactant-free droplet under confinement [40]. (a) Penetration of surfactant-free droplet into surfactant laden droplet due to gradient of capillary pressure which causes asymmetric coalescence. (b) Moreover due to no slip boundary condition on channel walls two vortices are created inside the surfactant-free droplet. The figure is reproduced from Nina M. Kovalchuk and co-workers [40], which investigated the coalescence of surfactant-laden and surfactant-free drops in a microfluidic channel. Reproduced with permission of the publisher, Americal Chemical Society (https://pubs.acs.org/doi/10.1021/acs.langmuir.9b00843#). Further permission related to the material excerpted should be directed to the ACS.
- 3.2 (a) All-atom representation of a water molecule; (b) Coarse-grained representation of two water molecules by one SAFT bead; (c) Coarse-grained representation of four (MARTINI) water molecules; (d) All-atom representation of a C10E8 molecule [Source: Chemical Compounds Deep Data Source (CCDDS; https://www.molinstincts.com) based on 41 patented SQN and QN technology commercialized into Mol-Instincts database and ChemRTP, ChemEssen, Inc (2022)]; (e) Coarse-grained representation of a C10E8 molecule in SAFT force-field. A hydrophobic alkane CG 'C' bead represents a -CH₂ -CH₂ - CH₂ - group of atoms while a hydrophilic CG 'EO' bead represents -CH₂ - $O - CH_2$ group. 29 Surface tension isotherms as obtained by the simulations in the planar 3.3 limit for the (a) C10E4 and (b) C10E8 surfactants, using SAFT force field. The insets show slab of water laden with surfactant (above CAC). 30 Stages of Coalescence of surfactant-laden droplets, Reproduced from [So-4.1

18

23

4.2	Stages of Coalescence of surfactant-laden droplets, Reprinted from [So-	
	heil Arbabi, Piotr Deuar, Mateusz Denys, Rachid Bennacer, Zhizhao Che,	
	and Panagiotis E. Theodorakis, Molecular Dynamics Simulation of the Co-	
	alescence of Surfactant-Laden Droplets, Soft Matter, 19, 8070-8080 (2023)	
	https://doi.org/10.1039/D3SM01046E]	60
4.3	Coalescence of Sessile Aqueous Droplets Laden with Surfactant. Reprinted	
	from [Soheil Arbabi, Piotr Deuar, Rachid Bennacer, Zhizhao Che, and	
	Panagiotis E. Theodorakis, Coalescence of Sessile Aqueous Droplets Laden	
	with Surfactant. Phys. Fluids 36,(2024), https://doi.org/10.1063/5.	
	0194816]	.03
4.4	Coalescence of sessile polymer droplets. Reprinted from [Soheil Arbabi,	
	Panagiotis E. Theodorakis, Coalescence of Sessile Polymer Droplets: A Molec-	
	ular Dynamics Study, Macromol. Theory Simul. 32 , 2300017 (2023) https:	
	//doi.org/10.1002/mats.202300017, with permission of John Wiley and	
	Sons, Inc.]	.67

List of Tables

2.1	Summary of bridge growth dynamics within inertial regime in suspended	
	and sessile droplets in our Studies [4–7]	13
3.1	Different computer simulation methods with their typical time and length	
	scales to describe a fluid system.	22
3.2	Comparison of MARTINI versions 2.2 and 3.0, examining their surface	
	tension on pure water under various cut-offs. The surface tension of	
	water–air at 25° is 71.99±0.05 [62].	28

List of Abbreviations

MD	Molecular Dynamics	
SAFT	Statistical Associating Fluid Theory	
AA	All Atom	
CG	Coarse Grained	
TR	Thermal R egime	
VR	Viscous Regime	
IR	Inertial Regime	
DNS	Direct Numerical Simulation	
CAC	Critical Aggregation Concentarion	
DFT	Density Functional Theory	
DPD	Dissipative Particle Dynamics	
EoS	Equation of State	

List of Symbols

Global notations

σ_{ij}	Effective bead size
ϵ_{ij}	Interaction strength between any beads of type i and j
r _{ij}	Distance between two beads
τ	Time
т	Mass
$U^{Mie}(r)$	Mie potential
λ_a	Mie potential parameter
λ_r	Mie potential parameter
K_B	Boltzmann constant
Т	Absolute temperature

Chapter 2

Surface tension
Density
Time
Droplet radius
Initial droplet radius
Bridge radius
Bridge width
Reynolds number
Viscosity
Velocity

Chapter 3

Α	Helmholtz free energy
U(r)	Nonbonded potential
Γ	Surface excess concentration
Z	Partition function

Chapter 1

Introduction

1.1 Motivation

he coalescence of droplets is a common natural process found throughout nature and it plays a crucial role in processes like understanding how raindrops (Fig. 1.1) come together and their rate of merging [14, 19]. Furthermore, coalescence has numerous practical applications such as inkjet printing, microfluidics, and the purification of water in the separation of crude oil and natural gas [22, 89]. Adding surfactants to droplets can significantly influence coalescence behavior and is essential in various applications. Surfactants can be employed to enhance the stability of droplet boundaries, preventing the merging of tiny droplets and affect the droplet fusion and mixing in microfluidic devices. Furthermore, they can improve the compatibility of the system in biological contexts [12]. Despite considerable research efforts in this area, there are numerous aspects of this process that require further exploration. Until now, investigations involving the coalescence of droplets, whether through experimental, theoretical, or numerical approaches, have predominantly centered on scenarios where pure water or polymer droplets are present [1, 24, 39, 63, 68, 97].

From the perspective of continuum simulations, they have provided primarily explanations and representations of the overall and evolving characteristics of coalescence. However, they often suffer from a lack of adequate resolution at the initial contact point between two droplets, which is also referred to as the 'pinching point' [84]. At the pinching point, the dynamics of bridge and mass transport mechanisms have remained unexplored in numerical methods, primarily due to a singularity that poses challenges for standard numerical approaches. When it comes to experimental methods, high-speed imaging and particle-image velocimetry [21, 40, 61] have been utilized to study the coalescence of surfactant-laden droplets. These techniques have primarily concentrated on portraying the overall characteristics of this phenomenon, similar to numerical simulations. However, due to equipment constraints, capturing the initial stages of coalescence with great precision is a significant obstacle. Both experiments and continuum modeling cannot provide a detailed account of the molecular-level mass transport mechanism and bridge growth dynamics.

Hence, the main goal of this thesis is addressing such issues by using the molecular dynamics method. In particular, we employed a high-fidelity coarse-grained (CG) force-field enabling us to simulate with molecular dynamics the coalescence of surfactantladen droplets. Coarse-grained molecular dynamics enable us to target larger systems than All-Atom (AA) models, where one attempts to account for every single atom in simulations and which become highly computationally demanding when dealing with droplets and their macroscopic characteristics. Here, the CG methods come into play. In CG methods, each "bead" represents multiple atoms, making simulations computationally efficient compared to those using other MD methods, such as AA models, and allowing the consideration of larger droplets. The use of larger droplets enables the observation of mass transport mechanisms, while minimizing the effects attributable to the finite size of the system. However, the use of CG methods comes with a tradeoff, involving the sacrifice of some degrees of freedom and details. For example, in CG models where water molecules (H_2O) are considered, a single bead typically represents one or even more water molecules (depending on the CG method). Consequently, studying hydrogen bonds between individual water molecules becomes impossible in such CG models. Therefore, it's essential to exercise caution when selecting a force field that accurately represents important macroscopic properties. When it comes to droplet coalescence, it is crucial for a suitable CG force field to provide precise surface tension values and accurately depict the phase-behaviour of surfactant concentration. In this context, our chosen CG force field (SAFT γ -Mie CG force field) has undergone rigorous testing and has shown remarkable results [9, 10, 57, 58].

We investigate specific aspects, such as the bridge growth dynamics, mass transport, and water flow, during the coalescence of freely suspended droplets and sessile droplets at each phase of the process. This exploration involves contrasting systems with different types and concentrations of surfactant. Additionally, molecular dynamics methods allow for tracking the movement of each individual particle throughout the coalescence process. This offers exceptional resolution, especially when the bridge formation is observed in the early stages of coalescence, and it provides a comprehensive explanation of the mechanisms involved in mass transport. The investigation of the coalescence of sessile droplets containing surfactants, both below and above the CAC, is another aim of this research. Substrate wettability can have a significant impact on bridge dynamics and mass transport mechanisms. Coalescence on substrates holds substantial industrial applications, and our research aims to provide insights into various aspects of this phenomenon that have remained unclear and unexplored in the existing literature.

In another system, we conducted a study on the coalescence behaviour of polymer droplets with varying chain lengths on substrates that exhibit diverse degrees of wettability. The rationale for exploring different chain lengths is rooted in the fact that an increase in the polymer chain length results in higher viscosity. Therefore, we examined droplets with different chain lengths to investigate the impact of viscosity on the coalescence of sessile droplets.



Figure 1.1: Coalescence of raindrops on a glass surface. ¹

1.2 Thesis Organization

The content of the subsequent chapters is structured as follows:

Chapter 2: Background; In this section, a review of the literature is conducted on the growth dynamics of bridge and the mass transport mechanism during the coalescence of freely suspended and sessile droplets.

Chapter 3: Methodology; A summary of the Molecular Dynamics method, with a particular focus on the Coarse-Grained method is provided.

Chapter 4: Results: Summary of Publications; In this section the published papers are presented and key findings of each paper are highlighted.

Chapter 5: Conclusions and Future Work

¹Source: Photo by Soheil Arbabi on Unsplash https://unsplash.com/photos/JjIh_9AcVhg and https://unsplash.com/@soheil_rb

Chapter 2

Background

2.1 Coalescence Mechanisms and Bridge Growth Dynamics

Coalescence of droplets mainly takes place in three different stages:

1. Droplet Approach (Figs 2.1a,b): In the initial phase, two distinct droplets approach each other, coming close enough where they start experiencing inter-molecular forces.

2. Bridge Growth (Fig. 2.1c): Once the two droplets are positioned close enough, a thin liquid bridge forms between them. Surface tension is responsible for reducing the surface area and thus lowering the overall energy of the system. During the growth phase of the bridge, the liquid bridge passes through various growth regimes. Indeed, the rate of coalescence depends on the dynamics of bridge growth. An explanation of these regimes is one of the main goals of this research. Based on the development of the bridge radius (denoted as *b*), different regimes will be discussed in detail.

3. Final Reshaping Towards Equilibrium (Fig. 2.1d): In the final stage, the two droplets merge to form a single, larger droplet. Surface tension forces work to decrease the surface area. Gradually, the system reaches a state of equilibrium, achieving minimization of surface energy.

2.1.1 Bridge Growth Dynamics During Coalescence of Freely Suspended Droplets

When two droplets come into close contact without any relative velocity, the primary attractive forces between them are Van der Waals (VDW) forces and electrostatic forces. The VDW forces are the result of fluctuations in electron distributions and tend to bring the droplets closer together, whereas electrostatic forces can also influence their interaction, either attracting or repelling them depending on their charge distribution.



Figure 2.1: Stages of coalescence of water droplets with equal size. (a) Initial configuration; (b) Beginning of the bridge formation (Pinching); (c) Bridge growth. The bridge is indicated with a dashed rectangle and a magnified bridge picture with radius *b* is shown. (d) Final equilibrium configuration after reshaping is completed; The snapshots of the systems were obtained using Ovito software [86].

Viscous forces act as resistance to the coalescence of two liquid droplets at the very beginning of coalescence. Moreover, since the bridge is a highly curved meniscus it creates a capillary pressure gradient where higher pressure in the drop induces a flow towards the bridge. Capillary pressure will be discussed in more detail later in this chapter. Moreover, surface tension effectively maintains the smallest possible liquid-liquid interface between the droplets. The interplay between these attractive and repulsive forces can result in various outcomes, including coalescence, partial coalescence, or even rebounding and separation (in case of droplet collision). The specific behavior observed depends on the unique conditions and parameters of the system. In the context of coalescence, the emergence of a bridge between two droplets occurs within distinct regimes, each under the influence of physical forces and conditions.

The majority of studies on coalescence of droplets have been done on freely suspended droplets in vacuum, air, oil or other liquids [8, 34, 71]. When two droplets are floating inside another fluid in the initial stage of head-on coalescence, a film is created between the two droplets. Once the film thickness decreases to a critical point, VDW forces destabilize the film, leading to film rupture and drainage. The thinning rate depends on the radial pressure gradient within the film, where the Laplace pressure in the film is $\frac{2\gamma}{R}$, γ is surface tension and R is the droplet radius. After the rupture, a bridge connecting two droplets will emerge and grows following a specific power-law scaling, which will be discussed later in this thesis [35]. The dynamic interplay between the various forces involved contributes to the formation of the bridge. Consequently, we will review various studies that have been conducted to explain the dynamics of bridge growth.

Initial Thermal Regime: Molecular studies offer high resolution both in time and space, enabling the revelation of an initial regime primarily governed by the thermal fluctuations of molecules. However, this particular regime remains beyond the reach of experimental and continuum studies. Perumanath et al. [68] studied coalescence of two water droplets using an all-atom MD method, and have revealed the emergence of several preliminary bridges due to thermal fluctuations occurring on the droplet's surface. These initial bridges establish connections between the droplets and subsequently expand, thereby highlighting the presence of a thermal phase at the beginning of the coalescence process. In fact, inside the bridge there is a competition between hydrodynamic effects and molecular fluctuation at the pinching stage. Initially, the dominant effect is the thermal motion of molecules. Once a specific point is reached, where the size of the developing bridge exceeds a characteristic thermal length scale, $l_T \approx (k_B T/\gamma)^{1/4} R_0^{1/2}$, with R_0 denoting the initial drop radius, the hydrodynamic regime is recovered. The authors also found that after this initial linear thermal regime, there is a power-law scaling of $b \propto t^{0.5}$ for the entire bridge growth process.

In our studies [4–7], the presence of this initial thermal regime has been identified and characterized not only for pure water droplets, but, also, in the case of surfactantladen droplets. While Perumanath et al. [68] used an all-atom model to study coalescence of 2D (cylindrical water droplets), we have used a CG model to simulate 3D (spherical-cap droplets) water droplets with and without surfactant, which provides further confidence that this regime is indeed present in the coalescence. However, we were unable to observe linear behavior [68] within this regime, especially in the presence of surfactant [5, 6]. This may be attributed to the complexity introduced by considering 3D droplets, the used CG model, as well as the addition of surfactant molecules.

The Viscous Regime: This stage of coalescence corresponds to the Stokes-flow limit, where the dominant forces are macroscopic flows that draw the two droplets together. Gross et al. [28] mentioned that this regime is characterized by the competition between viscous forces and surface tension. To quantify the characteristic velocity in this regime, the parameter $u_c = \gamma/\eta$ is introduced, where γ represents surface tension and η is the viscosity of the fluid. The dimensionless Reynolds number, *Re*, is defined as $Re = \rho u_c b/\eta = \rho \gamma b/\eta^2$, where ρ is the fluid density, and *b* is the bridge radius. In the early stages of the process, the radius of the bridge, *b*, is exceedingly small, leading to a very low Reynolds number ($Re \ll 1$). This condition holds regardless of the specific values of γ and η . In summary, since Reynolds number is the ratio of inertial forces to viscous forces, when it is less than one, viscous forces play the main role and that is why this regime is called the viscous regime which can be described by the Stokes equations, in contrast to the inertial regime, $Re \gg 1$, where the Euler equations are valid [28].

However, there is an ongoing debate in the scientific community regarding the validity and significance of viscous regime. Hopper [32] provided an analytical solution for the process of two cylindrical droplets coalescing during viscous sintering. While sintering may differ from liquid droplets, it can still offer certain understanding. In particular, they revealed that the change in the radius, *b*, of the connecting bridge between the droplets can be approximated by the relation $t \sim -b \ln b^*$, where b^* is defined as b/R_0 with R_0 being the initial radius of cylindrical droplets. Eggers et al. [24] focused on viscous-dominated coalescence of 3D droplets and obtained $b^* \sim -t^* \ln t^*$ where $b^* < 0.03$ and $t^* = t/\tau_v$ where $\tau_v = \mu R_0/\gamma$ and for larger initial droplet radius (R_0) [94].

On the other hand, in experimental studies, a linear scaling is mostly suggested. For example, Thoroddsen et al. [90] found that the viscous behavior in their experiments could be accurately predicted by the linear relationship between the bridge radius (b) and time (t), expressed as $b \sim t$. Paulsen et al. [64, 65] provided a detailed examination of the coalescence process of droplets containing mixtures of glycerol, water, and NaCl. They employed an ultra-fast electrical method along with a high-speed camera to capture the coalescence events. In their research, they introduced a previously unaccounted-for phase referred to as the inertially limited viscous regime (ILV). They discovered that the initial stages of coalescence cannot be solely described by the traditional Stokes-flow limit. This is because, at the outset of coalescence, the inertia of the droplets plays a significant role and cannot be ignored. This deviation from the traditional Stokes-flow limit¹ occurs when the radius of the bridge is small. However, as the bridge expands, it eventually enters the Stokes regime. The authors highlighted that even when the bridge radius is small and the viscosity is finite (even if it's relatively low), the surface tension force, which is responsible for pulling the two droplets together, is not strong enough to overcome the inertia of the droplets. This observation led them to propose the existence of ILV regime to explain the initial stage of droplet bridging. In the ILV regime, various factors including surface tension, viscous forces, inertia, and the bridge radius was empirically observed to follow a linear scaling with time ($b \sim t$). Burton et al. [16, 94] suggested a crossover length scale from viscous to inertial regime $b_c = \mu (R_0 / \rho \gamma)^{0.5}$, which is confirmed by Paulsen and coworkers [63–66, 94], who also found a crossover time-scale as $t_c = \mu^2 (R_0 / \rho \gamma^3)^{0.5}$.

The Inertial Regime: During this phase, the dynamics are characterized by local deformations occurring near the growing bridge. Eggers et al. [24] argued that for $b/R_0 > 0.03$ the bridge flow goes beyond the viscous regime to the inertial and they considered balance between interfacial stress ($\gamma R/b^2$) and dynamic pressure (ρv^2), which leads to a power law of $b \sim (t/\tau_i)^{0.5}$, where $\tau_i = (\rho R_0^3/\gamma)^{0.5}$ [24, 94].

Aarts et al. [1] conducted a study on droplet coalescence within a molecular system characterized by variable viscosity and a colloid-polymer mixture with remarkably low surface tension. Their research challenged the notion that both viscous and inertial regimes are present in all liquids. Specifically, they successfully observed a phenomenon known as purely viscous coalescence, where the radius of the bridge between merging droplets increased linearly with time ($b \sim t$). They also mentioned that,

¹Stokes flow also referred to as creeping flow, characterizes a fluid flow in which the influence of advective inertial forces are small compared to viscous forces.
in the studied range, no signs of logarithmic correction were observed, as opposed to Hopper et al. [32]. Their findings revealed that the viscous regime characterized by a linear relationship ($b \sim t$) is observable when the Reynolds number is less than one ($Re = \frac{\rho\gamma b}{\eta^2} < 1$). Conversely, when Re exceeds 1, only the inertial regime ($b \sim t^{0.5}$) is detectable. As a result, by defining a crossover at Re = 1, they established characteristic length and time scales, experimentally verified as $R_{\eta} = \frac{\eta^2}{\rho\gamma}$ and $t_{\eta} = \frac{\eta^3}{\rho\gamma^2}$. Using typical values for pure water, these scales are estimated as $R_{\eta} = 15nm$ and $t_{\eta} = 10^{-10}s$. This analysis underscores that, in the case of water, observing the viscous regime is unlikely due to its small characteristic length and time scales. Consequently, the study suggests that witnessing both the viscous and inertial regimes is not a universal phenomenon and may not occur under all conditions in any given liquid.

Nowak et al. [60] studied the coalescence of a surfactant-laden droplet and a water droplet inside silicone oil of various viscosities. In all cases, the bridge growth was characterized by a power law with an exponent of approximately 0.5, and the specific pre-factors varied depending on surfactant concentration and the viscosity of the surrounding liquid. They found that a linear regime (viscous regime) can be observed in experiments only for highly viscous fluids, where the bridge grows linearly with time, represented as $b \sim \gamma/\eta t$. However, in low-viscosity fluids like water, only the inertial regime is observable, and the bridge growth follows a power law given by $b \sim (\frac{R\gamma}{\rho})^{1/4}t^{1/2}$. They also showed that when coalescence happens inside the viscous outer fluid (not in air or vacuum) this equation should be replaced by $b \sim (\frac{R\gamma}{\rho_{out}})^{1/4}t^{1/2}$ where ρ_{out} is the density of the surrounding fluid, while in the case that the inertia of the outer fluid is important, it can be written as $b \sim (\frac{R^3\gamma}{\eta_{out}})^{1/2}t^{1/2}$ where η_{out} is viscosity of surrounding fluid.

We were unable to identify any intermediate linear viscous regime in our studies [4–7]. However, adding surfactant leads to more pronounced transition from thermal regime to inertial regime and inertial regime is generally characterized by a power-law behavior with an exponent of 0.5. This transition was observed in all three surfactant types and at various concentrations, which will be presented in more detail in the results section (Chapter 4).

2.1.2 Bridge Growth Dynamics of Sessile Droplets

When a liquid droplet is placed on a flat substrate a contact angle, θ_s , is measured, which is the angle between the substrate and the tangent line to the droplet surface. From a macroscopic point of view (Fig. 2.2), force balance at equilibrium is given by the Young–Laplace equation:

$$\gamma_{sg} = \gamma_{lg} \cos \theta_s + \gamma_{sl} \tag{2.1}$$

which means:

$$\cos\theta_s = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}} \tag{2.2}$$



Figure 2.2: Schematic of a liquid droplet on a substrate at equilibrium. Contact angle (θ_s) is shown and all three interfacial forces involving the solid (s), liquid (l) and gas (g) are illustrated.

where γ_{lg} is surface tension between liquid and gas phases; γ_{sg} is the surface tension between substrate and gas, and γ_{sl} is the surface tension between substrate and liquid and they are all usually in the unit of mN/m. Measuring contact angles plays a vital role in the examination of wetting phenomena and how surfaces interact with liquids. The nature of the interaction between a liquid and a surface influences the contact angle and it can be categorized based on wettability as follows:

1. Non-Wettable: When the equilibrium contact angle exceeds 90° (Fig. 2.3a), in this scenario, the liquid has a tendency to gather into small 'spherical' shapes on the surface, and the substrate is less prone to being wetted by the liquid.

2. Intermediate Wettability: In this thesis in the context of the sessile droplets, we define intermediate wettability substrates as those on which the equilibrium contact angle of the droplet is about 90° (Fig. 2.3b).

3. Wettable: When the equilibrium contact angle is less than 90° (Fig. 2.3c). In this case, the liquid tends to spread out and wet the surface, forming a liquid film-like structure.

Droplet coalescence on a substrate also follows three main stages, much like what occurs with freely suspended droplets. However, the specific outcomes can vary depending on the substrate's wetting properties. In instances where the substrate is non-wettable by the liquid medium, the formation of a bridge between droplets begins at some distance from the substrate (as illustrated in Fig. 2.3a). In such cases, the dynamics of bridge growth closely resemble the coalescence of suspended droplets. For example, it is shown that the rate of change in the angle of the bridge (θ_b) over time (Fig. 2.3a) in the case of $\theta_s \simeq 140^\circ$ follows the same dynamics as that of the freely suspended droplets [4].

On the contrary, when the substrate is intermediately or highly wettable (as seen in Figs 2.3b and c), the pinching process initiates directly on the substrate. This leads to a distinct coalescence dynamics that is influenced by the presence of the substrate.

It is widely acknowledged that the growth dynamics of bridge width (*w* in Fig. 2.3c) follows a power-law relationship with an exponent of 0.5, expressed as $w \sim t^{0.5}$ [4, 45, 59, 73]. For instance Ristenpart et al. [73] studied experimentally and theoretically the



Figure 2.3: Bridge formation during coalescence of water droplets on substrates of different wettabilities. (a) Non-wettable substrate ($\theta_s > 90^\circ$); (b) Intermediate substrate ($\theta_s \simeq 90^\circ$); (c) Wettable substrate ($\theta_s < 90^\circ$) and top view of the droplets on wettable substrate. *b* represents bridge height, *w* is the bridge width, θ_b is the angle formed at the bridge and *X* is the distance between the centers of mass of the two droplets. The snapshot of the systems were obtained using Ovito software [86].

coalescence dynamics of two droplets on a highly wettable substrate. They showed that the width of the bridge scales as $w \sim t^{1/2}$. However, when it comes to bridge height (*b* in Fig. 2.3), there are varying arguments [26, 73].

When it comes to sessile water droplets, Eddi et al. [23] experimentally studied the coalescence of water drops on substrates with different wettabilities. They demonstrated that on a wettable substrate ($\theta_s < 90^\circ$), the bridge height is characterized by $b \propto t^{2/3}$. However, on intermediate or non-wettable substrates ($\theta_s \ge 90^\circ$), the dynamics shift to $b \propto t^{1/2}$, resembling the behavior of suspended droplets. The bridge dynamics in our MD study [4] on coalescence of sessile water droplets and surfactantladen droplets is in very good agreement with this experimental study.

The study of coalescence behavior extends beyond water droplets to encompass various other materials, as explored in the literature. For example, Sivasankar et al. [80, 81] conducted a study on the coalescence of microscopic polymeric drops with a density of 1250 kg/m³ on a wettable substrate characterized by $\theta_s = 25^{\circ}$. They employed a direct numerical simulation (DNS) approach to investigate the collision of droplets and its outcomes under different Weber numbers. The Weber number, denoted as We, serves as a dimensionless parameter for assessing the relative significance of inertial forces compared to surface tension forces in fluid systems. In the context of the collision of two droplets, the Weber number is calculated as $We = \frac{\rho V^2 R}{\gamma}$, where V represents the relative velocity of the droplets during impact. The study examined various Weber numbers, specifically We values of 0, 0.1, and 1, and identified two distinct regimes governing the growth dynamics of the bridge height during coalescence: an early stage and a late stage. In the early stage, the authors reported power-law scaling with exponents of 1/2, 2/3, and 3/1 for We values of 0, 0.1, and 1, respectively. In the late stage of coalescence, a consistent power-law exponent of 1/10 was observed across all cases. Additionally, they observed that the growth of bridge width (w) also followed a two-regime power-law pattern.

In another study by Lee et al. [45], coalescence behavior of macroscopic sessile oil droplets are studied. Authors experimentally studied coalescence of spherical drops (silicone oil) within a diameter range of $100-240 \mu m$. They considered varying contact angles of 10° , 24° , 27° , 56° and observed power-law scaling with corresponding exponents of 0.5061, 0.6435, 0.6719, and 0.8612, respectively.

In the scope of coalescence of sessile droplets, we considered the effect of viscosity and substrate on coalescence process. We studied coalescence of sessile polymer droplets [7] and we have found that as the length of the polymer chains increases, which indicates higher viscosity of polymer droplets, the coalescence process becomes significantly slower. We can identify two distinct regimes: an initial thermal regime and an inertial regime. Within the inertial regime, the growth of the bridge follows a power law, but with an exponent that is less than 1/2 for non-wettable surfaces and less than 2/3 for wettable surfaces. These exponents are different from those reported for the coalescence of water or surfactant-laden droplets [4]. Furthermore, in our study of bridge dynamics during the coalescence of sessile surfactant-laden droplets [4], we have confirmed a scaling law with an exponent of approximately 0.5 for bridge width ($w \simeq t^{0.5}$) for both water and surfactant-laden sessile droplets. It is demonstrated that the wettability of the substrate does not affect the growth dynamics of the bridge width. Regarding the bridge height (*b*), the results of our simulations indicate the presence of a power-law scaling relationship, which is influenced by the wettability of the substrate. Specifically, we observe a power-law with an exponent of about 0.5 for non-wettable and intermediate substrates, while for wettable substrates, our results reveal an exponent of $2/3 \simeq 0.7$. In Table. 2.1 our findings [4–7] on bridge dynamics for sessile and suspended droplets are summarized.

Table 2.1: Summary of bridge growth dynamics within inertial regime in suspended and sessile droplets in our Studies [4–7].

System	Bridge width (<i>w</i>)	Bridge height (b)
Suspended water and surfactant-laden droplets [5, 6]	$w \sim t^{0.5-0.6}$	$b \sim t^{0.5-0.6}$
Sessile water and surfactant-laden droplets ($\theta_s \ge 90^\circ$) [4]	$w \sim t^{0.5-0.6}$	$b \sim t^{0.5-0.6}$
Sessile water and surfactant-laden droplets ($\theta_s < 90^\circ$) [4]	$w \sim t^{0.5-0.6}$	$b \sim t^{0.6-0.8}$
Sessile polymer droplets ($\theta_s > 90^\circ$) [7]	Not studied	$b \sim t^{0.28 - 0.38}$
Sessile polymer droplets ($\theta_s < 90^\circ$) [7]	Not studied	$b \sim t^{0.29-0.45}$

2.2 Mass Transport Mechanism of Surfactant Molecules During Coalescence of Surfactant-Laden Droplets

In this section, we will review some studies on the mass transport mechanism during coalescence, primarily focusing on continuum and experimental methods. Among these studies, Marangoni flow, arising from the gradient of surface tension caused by the presence of surfactants, and capillary flow, predominantly driven by bridge curvature, emerge as the main flows within coalescence. In our studies [4–6], with molecularlevel resolution, we track each individual molecule across various regions, including the bulk and surface of each droplet and the bridge between them. By employing this approach, we can elucidate the mass transport mechanism with a very high resolution. Further details on these findings will be discussed in the results section of this thesis.

It is well-established that the addition of surfactants to droplets leads to a reduction in interfacial surface tension and, consequently, delay in the coalescence process [33, 42]. When surfactant is added to a water droplet, the hydrophobic part tends to position toward the droplet's surface. In turn, the surface of the droplet becomes coated with surfactant molecules as depicted in Fig. 2.4b. It is energetically preferable for surfactant to be on the droplet's surface, with some surfactant existing in the form of



Figure 2.4: (a) Schematic of an non-ionic surfactant. Red beads represent the hydrophobic part and yellow beads represent the hydrophilic part; (b) Two surfactant-laden droplets with concentration below CAC; (c) Two surfactant-laden droplets with concentration above CAC; (d) A surfactant monomer on the surface of a droplet; (e) A surfactant aggregate inside the droplet. The snapshot of the systems were obtained using Ovito software [86].

monomers in the bulk of the droplet as well (Fig. 2.4b). Then, when concentration increases and the droplet surface is fully covered, the CAC is reached. At this moment, the surfactant at the surface and the bulk are in a dynamic equilibrium and there is not sufficient space on surface to accommodate a higher amount of surfactant molecules. In such cases, after covering the surface, the remaining surfactant molecules within the bulk of the droplet aggregate together. The aggregation process entails the hydrophobic beads coming together to form a hydrophobic core. In this core, hydrophobic beads try to escape from water, leaving exposed the hydrophilic part of the surfactant (as illustrated in Fig. 2.4e).

While the methodology employed in this study is molecular dynamics, effective forces that are mainly in the scope of continuum methods are summarized below for an overall picture. Nevertheless, even within the continuum framework, accurately quantifying the impact of these effects and characterizing their relative importance alongside surface tension remains a challenge [26], while the mass transport mechanism during coalescence is often influenced by various flows.

Coalescence in this context involves two primary flows: Marangoni and capillary. Both Marangoni flow and capillary flow contribute to the mass transport mechanism during coalescence, influencing the dynamics and behavior of the merging droplets. Below, we will review these main flows and, subsequently, we will examine some experimental studies that visualized and studied the mass transport mechanism during coalescence.

Capillary Effect: In the early stages of coalescence, the curvature of the interface undergoes changes as two droplets merge. This alteration in curvature gives rise to capillary

pressure (Δp). This phenomenon is driven by the Laplace pressure, a pressure jump induced by the curvature of the interface (R_c). Consequently, as the droplets approach each other, the radius of bridge curvature decreases, and ΔP becomes more negative, leading to a capillary attraction force between them. the Laplace pressure is described below as follows:

$$\Delta p = \frac{2\gamma}{R_c} \tag{2.3}$$

or in the case that the curvature radii of the merging droplets (1 and 2) are different:

$$\Delta p = \gamma \left(\frac{1}{R_{c1}} + \frac{1}{R_{c2}} \right) \tag{2.4}$$

Surfactant-Induced Marangoni Stresses: Coalescence of surfactant-laden droplets involves a crucial phenomenon known as the Marangoni effect, driven by gradients in surface tension along the interface. When two such droplets come into contact, the presence of surfactants on their surfaces works to reduce the surface tension. However, the non-uniform distribution of surfactants creates a gradient in surface tension. This variation in tension induces tangential stresses on the liquid interfaces called Marangoni stresses.

During the coalescence process, surfactant molecules diffuse in the bulk, and they subsequently adsorb onto the surfaces. Continuum methods are unable to study the molecular-level diffusion of surfactants. However, they can generally explain flow and diffusion using the Advection–Diffusion equation as follows:

$$\rho(\frac{\partial c}{\partial t} + u \cdot \nabla c) = \nabla \cdot (\rho D \nabla c)$$
(2.5)

where D is the diffusion coefficient and c the concentration of the solute. This equation considers both convection (transport due to bulk fluid motion) and surfactant diffusion.

In summary, coalescence results in two distinct types of flow: Marangoni flow, which is driven by the gradient of interfacial tension between the droplets at the pinching point and the surface, and bulk flow toward the bridge, which originates from the difference in capillary pressure between the droplet and the curvature of the bridge. The following section will provide a concise summary of key findings from various relevant MD and experimental research papers.

2.2.1 MD Study on Mass Transport Mechanisms in the Coalescence of Freely-Suspended and Sessile Surfactant-Laden Droplets

In our studies, using the MD method [4–6], we have investigated the mass transport mechanism of surfactant molecules during the coalescence of surfactant-laden droplets, including both freely suspended droplets and sessile droplets. In the case of freely suspended droplets (Fig. 2.5a, b) [5, 6], pinching starts with surfactant beads, and in concentrations above CAC, a surfactant film between two droplets is created (Fig. 2.5a).



Figure 2.5: Mass transport of surfactant molecules of freely suspended droplets (a-b) and sessile droplets (c-f). In all figures a larger arrow-end indicates the dominant direction of surfactant transport and magnified views of the bridge and its cross section on the y–z plane (only hydrophobic beads of surfactant) are shown beside and above each figure (In panels e and f such snapshots are placed beside and below). (a,c,e) Initial stage during coalescence of freely suspended droplets, sessile droplets on a non-wettable, and sessile droplets on a wettable substrate, respectively. (b,d,f) Developed bridge of coalescence of freely suspended droplets, sessile droplets on a non-wettable substrate, and sessile droplets on a wettable substrate, respectively.

The dominant movement of surfactant molecules is from the bulk of the bridge towards the surface of the bridge. However, since there is not enough space on the liquid-gas (LG) surface of the bridge, the bridge surface cannot accommodate all surfactant molecules, resulting in the creation of new aggregates inside the bridge bulk (Fig. 2.5b).

Moreover, our study on sessile droplets [4] reveals that the wettability of the substrate has a significant influence on the mass transport mechanism. When the substrate is non-wettable ($\theta_s > 90^\circ$), pinching starts far from the substrate (Fig. 2.5c), and the coalescence dynamics are very similar to those of suspended droplets. Due to the limited space at the LG interface of the merged droplets (Fig. 2.5d), surfactant from the newly formed aggregates in the bridge bulk cannot be accommodated at the LG interface. Additionally, we observe surfactant transport away from the bridge from the solid-liquid (SL) interface toward the LG surface through the contact line.

The case $\theta_s < 90^\circ$ (Fig. 2.5e) shows a different behavior. The transport toward the LG surface is more pronounced as compared to cases where $\theta_s \ge 90^\circ$. Unlike the preceding instances, the coalescence process does not lead to the formation of new aggregates. This can be ascribed to several factors. Firstly, the smaller amount of surfactant at the bridge in the case of $\theta_s < 90^\circ$ is due to the higher curvature of the droplets. In this scenario, only a small portion of the droplet surfaces come into contact at the contact line. In contrast, for non-wettable substrates, a substantial portion of the surfaces of the two droplets comes into contact, forming a film. Secondly, there is considerably less space in the bridge for aggregates to form from any excess surfactant that does not originate at the bridge's LG surface.

In the results section of this thesis, various features of the coalescence of sessile

droplets will be discussed, including the velocity of approach measured by tracking the distance between the centers of mass of two droplets over time (Fig. 2.3b). Additionally, detailed discussions on bridge dynamics and the mass transport mechanism of surfactants will be presented.

2.2.2 Experimental Studies on Mass Transport Mechanism During Coalescence of Droplets

Hack et al. [29] studied coalescence and collision of two droplets with different surface tensions numerically and experimentally. They demonstrated that when the surface tensions of droplets differ, the process of merging droplets exhibits pronounced shape asymmetry in their shape evolution. They propose that capillary waves play a significant role in driving this distinctive shape behavior. Capillary waves are small amplitude, high-frequency oscillations that occur at the interface between two fluids due to surface tension effects. Furthermore, it has been observed that this asymmetry increases as the differences in surface tension between the droplets become more pronounced. In fact, the primary cause of this asymmetry lies in the variations in the amplitudes of the capillary waves on each individual droplet. It is worth noting that they have found that the Marangoni effect can dampen the capillary waves and consequently reduce the overall asymmetry of the merged droplets. This means that when the average surface tension of the droplets is lower, one can expect less asymmetry in the merging process. However, when the surface tension of both droplets are equal (identical droplets), the shape of the merging droplets remains symmetric because the amplitudes and propagation dynamics of the capillary waves on both droplets are identical.

Novak et al. [60, 61] conducted experimental research on the merging of droplets containing both surfactants and water within silicone oils of diverse viscosities. In one study [60], they reported interfacial Marangoni flows and a strong convective flow in case of the coalescence of a surfactant-laden and a surfactant-free water drop. They used dye in water droplet to visualize the bulk motion during the coalescence and the considerable bulk flow is only observed when droplets have different surface tensions. When water droplet is in contact with surfactant-laden droplets due to higher capillary pressure in water droplet the pressure difference drives bulk flow from water droplet to surfactant-laden droplet and at the same time Marangoni flow develops from surfactant-laden droplet to water droplet. The Marangoni flow moves surfactant from surface of surfactant-laden drop to the surface of water drop. Since there is no surfactant in the bulk of the water drop then surfactant will be absorbed from the surface of the water drop to its bulk. Simultaneously, they observed a convection flow that replenishes the surface of a surfactant-covered droplet with surfactant from the bulk of the surfactant-laden droplet. Furthermore, they examined how the viscosity of the surrounding fluid impacts the interfacial flow and confirmed that when a more viscous

17



Figure 2.6: Coalescence of surfactant-laden droplet and surfactant-free droplet under confinement [40]. (a) Penetration of surfactant-free droplet into surfactant laden droplet due to gradient of capillary pressure which causes asymmetric coalescence. (b) Moreover due to no slip boundary condition on channel walls two vortices are created inside the surfactant-free droplet. The figure is reproduced from Nina M. Kovalchuk and co-workers [40], which investigated the coalescence of surfactant-laden and surfactant-free drops in a microfluidic channel. Reproduced with permission of the publisher, Americal Chemical Society (https://pubs.acs.org/doi/10.1021/acs.langmuir.9b00843#). Further permission related to the material excerpted should be directed to the ACS.

surrounding fluid is present, the interfacial flow proceeds at a slower rate. Moreover, in case of two similar droplets no evidence of Marangoni flow was reported.

In a comparable investigation, Kovalchuk et al. [40] conducted experimental research on the mass transport mechanism during coalescence of a droplet containing surfactant and a pure water droplet within a microfluidic channel (Fig. 2.6). Their findings demonstrate that the surfactant-free droplet penetrates into the surfactant-laden droplet due to capillary pressure-driven flow, which is directed from the water droplet into the surfactant-laden droplet, with a maximum velocity along the axis connecting their centers. In addition, Marangoni flow is generated on the surface. The combination of these flows leads to formation of a film of surfactant-laden liquid spreading over the surfactant-free droplet. It is shown that the rate of penetration depends on various parameters such as drop order penetration inside the tube, where better penetration is observed when surfactant-laden droplet goes first inside the tube. Moreover, the rate of penetration is enhanced by increasing the interfacial tension difference between the two droplets. They demonstrated that increasing the surfactant concentration from $0.5 \times CAC$ to $1 \times CAC$ results in an interfacial tension difference ranging from 12 to 22 mN/m, leading to faster and deeper penetration. Due to the no-slip boundary condition on the channel wall, vortices are generated as depicted in Fig. 2.6b. When similar droplets, whether they are both water or both surfactant-laden, coalesce, both droplets equally contribute to the bridge formation. Consequently, four symmetrical convective vortices are generated. This symmetric configuration prevents any exchange of mass between them due to presence of vorticities. In the case of coalescence between droplets with different interfacial tensions, the outcome is influenced by the difference in surface tension and capillary pressure between them. The droplet with the higher capillary pressure or interfacial tension tends to occupy more space within the bridge and can even penetrate into the second droplet (Fig. 2.6). This leads to the formation of only two convective vortices. Notably, these two vortices are consistently located within the water droplet, as observed in the study. However, when the surfactant concentration exceeds the CAC, even transitioning from $1 \times CAC$ to $5 \times CAC$ does not significantly affect the kinetics of penetration. This is because the saturation of surfactant at the surface with the rest of surfactant remaining in the bulk as monomers and aggregates causes the surface tension to plateau with increasing surfactant concentration.

2.3 Summary

In this section, continuum and experimental representative highlights are discussed. Generally, such methods are unable to provide a detailed view of surfactant mass transport and bridge growth dynamics during the coalescence of surfactant-laden droplets. In Chapter 4 of this thesis, we will study the bridge growth dynamics and mass transport of surfactant during the coalescence of suspended and sessile droplets in great detail using the MD method [4–6].

Chapter 3

Methodology

3.1 Computer Simulation Methods

 ${
m T}$ o describe a fluid system, various approaches are available, covering a range of time and length scales. Table. 3.1 provides an overview of typical length and time scales for these methods at the time of writing. The time and length scales presented in this table are not strict boundaries. They serve as a general outline, typically reflecting common scenarios found in various studies. In practice, the achievable time and length scales can exhibit significant variability. It is important to recognize that as the size of the system under simulation increases, the computational demands also increase significantly. Consequently, researchers should carefully select the appropriate method, level of detail (electronic states, atomic-level detail, molecular interactions, coarse-grained models, mesoscale and macroscale) and length scale based on their scientific objectives and available computational resources. Moreover, there are combined methods, for example, coupling different methodologies offers a means to leverage the strengths of both methods. For example, Smith and Theodorakis [82] provided a perspective on multiscale simulation by combining Molecular Dynamics and Computational Fluid Dynamics (CFD) with a focus on the domain decomposition coupling approach. Each method is applied to a specific segment of the simulation domain in the case of domain decomposition coupling. This approach guarantees the inclusion of molecular detail only where it is essential.

In the case of *ab initio* methods, a complete electronic quantum mechanical description of matter is achieved by solving the wave equations associated with wave mechanics, such as Schrödinger's. However, it is crucial to acknowledge that an essentially exact numerical solution of the Schrödinger equation exists only for systems with a few number of atoms due to the complexity of the many-body wave function. Consequently, this method is impractical for describing the behavior of large droplets. By considering some simplifications, quantum Density Functional Theory (DFT) can provide reasonably accurate simulations for systems containing hundreds of atoms on standard computers or even thousands on large supercomputers. Nevertheless, DFT does have limitations when it comes to accurately describing Van Der Waals (VDW) forces [18]. This limitation makes it an unsuitable choice even for small droplets, as VDW forces play a pivotal role in coalescence processes. Continuum methods, on the other hand, offer valuable tools for describing the macroscopic behavior of droplets. However, despite numerous fruitful studies, they encounter limitations, particularly in the initial stages of coalescence and the detailed analysis of mass transport mechanisms during coalescence, due to their limited resolution. These limitations which are mentioned in Chapter. 1 encouraged us to consider MD methods, which offer molecular-level resolution of the initial stages of coalescence and can explain the mass transport mechanism of surfactant, which is indispensable in understanding the coalescence of surfactant-laden droplets.

Table 3.1: Different computer simulation methods with their typical time and length scales to describe a fluid system.

Method	Time	length
Ab initio	fs - ps	pm-nm
DFT	fs-ps	Å-nm
AA MD	ps-ns	nm - µm
CG MD	ps-s	nm-mm
Continuum methods	\geq ms	$\geq \mu m$

In this chapter, we provide a brief review of various molecular dynamics methods, with a specific focus on the chosen CG model, namely, the SAFT γ -Mie CG force field. Further technical details of the selected force field, such as the parameters, interactions, and bonds, will be provided in the results section (Chapter 4) of this thesis.

3.2 Molecular Dynamics Method

By defining the intermolecular interactions, one can calculate the forces acting between every pair of molecules within the system. This force field, in turn, allows for the simulation of the system's dynamic evolution with time. Such simulations provide valuable insights into the structural and thermodynamic characteristics of the system, which enhances our understanding of its behavior. A ubiquitous example of intermolecular interactions is the Lennard-Jones potential Eq. (3.1) [36]

$$U(r_{ij}) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right], \qquad (3.1)$$

where r is the distance between the center of mass of each molecule and σ and ϵ are parameters that represent the length scales and energy of the pair interaction, respectively. The force can be obtained through the negative derivative of potential (LJ potential in



Figure 3.1: (a) Lennard-Jones potential. U(r) is the potential energy between two particles at a distance r, σ is the distance at which the potential energy is zero, ϵ is the depth of the potential energy well, which characterizes the strength of the attractive interaction between particles. The cutoff determines the distance beyond which pairwise interactions between particles are truncated to reduce computational expense. (b) Schematic of a system of particles and forces acting between every pair of them (forces on particle 5 are shown as well as the counter-force on each of the other particles due to the presence of particle 5).

this case) w.r.t. the distance , which is (Eq. 3.2):

$$F(r) = \frac{24\epsilon}{\sigma} \left[2\left(\frac{\sigma}{r}\right)^{13} - \left(\frac{\sigma}{r}\right)^7 \right]$$
(3.2)

In molecular dynamics simulations, the cutoff serves as a significant parameter in the force-field parametrization. Particularly when dealing with non-bonded interactions like the Lennard-Jones potential. The cutoff for the potential is a parameter that defines the distance beyond which pairwise interactions between particles are truncated to accelerate calculations and reduce computational expense. In general, the choice of the cutoff is made as short as possible to minimize computational costs, as it involves considering a smaller number of nearest neighbor interactions.

3.2.1 All-Atom Modeling

In all-atom (AA) or atomistic modeling, each atom is generally considered as a point particle. The parameterization of these force fields based on different particle types involves defining the atom types, their masses, charges, and the potential energy functions that describe their interactions. All of these parameters, including atomic masses, charges, bond parameters, and non-bonded interactions, are collectively referred to as the force field. Several AA force fields exist, such as AMBER [20] which includes various versions such as AMBER94, AMBER96, AMBER99, AMBER14, etc., each with different parameters and refinements for simulating the behavior of amino acids and proteins, as well as CHARMM [15] which includes various versions, such as CHARMM22,

CHARMM27, CHARMM36, and more, each with different parameter sets and improvements to simulate the behavior of biomolecules and other chemical systems. Others include the GROMOS [72] and OPLS [30] family of force fields, which have been developed with their own parameter sets for various types of applications and molecular systems.

Each force field in molecular simulations employs its own unique parameterization method. However, researchers often rely on experimental data to inform the development of force field parameters. These data typically encompass a wide range of information, including structural details, bond lengths, bond angles, and dihedral angles. These experimental findings serve as a foundational basis for calibrating and refining force field parameters to ensure that the simulation accurately represents the behavior of molecules and materials in the real world. Moreover, from finer methods like other AA models, DFT or *ab initio* calculations they obtain accurate energy profiles and electronic properties of molecules and molecular interactions or even for calibrating bonds and angles. This approach provides a rich description of the physics at molecular level. However, several hydrodynamics related topics can hardly be captured by small time and length scales of all-atom models. Furthermore, it introduces numerous intricacies that are likely superfluous when studying the coalescence of droplets. For example, representing each water molecule with three beads (two hydrogen and one oxygen) leads to an abundance of water-water interactions that are not relevant for our research focus. Such unnecessary details can significantly increase computational complexity and impede our ability to simulate large droplets effectively.

3.2.2 Coarse Grained Modeling

The complete thermodynamic behavior of a system can be obtained once the Helmholtz free energy, A, of the system is determined. There is a direct relation between Helmholtz free energy and intermolecular interaction as it is shown in Eq. 3.3 [9].

$$\exp(-\beta A) = C \int_{V} \exp(-\beta U(r)) dr$$
(3.3)

U(r) is intermolecular potential and β represents $1/k_BT$, k_B is the Boltzmann constant, T is temperature, and C is a constant that incorporates the kinetic contribution. The goal of coarse-graining is to reduce the phase space of r to smaller one (r_{CG}) in such a way to be able to find an optimal solution to Eq.3.3 in a reduced phase space as Eq.3.4 [9]:

$$\exp(-\beta A) \simeq C' \int_{V} \exp[-\beta U_{CG}(r)] dr_{CG}$$
(3.4)

By removing certain details in all-atom modeling, we realise a smaller number of calculations, which allows us to access larger time scales and system size. Coarse-grained modeling can be very helpful in large macromolecules, polymer chains, complex fluids, and surfactants. The choice of the model is also influenced by the length and time scales of the phenomena we aim to study. For instance, in the case of coalescence, one could employ AA models; however, using such models would require waiting much longer than with CG models to observe a complete coalescence. Moreover, when large time scales are required, such as when studying the self-assembly of soft matter, the use of CG methods is crucial [79].

Within CG models, intermolecular potentials and parameterization are established by either adjusting them to data derived from molecular dynamics simulations involving AA, DFT or in general models at a higher level of theory in the case of simulations or from experimental observations. There are several examples of CG models, such as MARTINI [51, 83], which is widely used for the simulation of complex biomolecular systems, SAFT [9, 10, 41, 47, 55–57, 88] which is a CG force-field primarily used for simulating complex fluids, which can contain, for example, polymers and colloids. SPICA [38, 78, 95] which is an empirical CG force-field, was created with the specific aim of accurately replicating thermodynamic properties, including surface tension, density, and distribution functions. SPICA achieves this by drawing insights from all-atom molecular simulations rooted in the CHARMM force-field.

The process of developing a coarse-grained model consists of four key elements [77]: **1**. Selecting the model's level of detail (how coarse it should be); **2**. Determining the arrangement of CG sites based on the geometry/architecture of the molecules; **3**. Specifying the types of interactions to be incorporated; **4**. Fine-tuning these interactions to properly capture selected system properties. Typically, there are two primary approaches to incorporate information into a CG model: Bottom-Up and Top-Down approaches. In the following sections, these approaches will be briefly discussed.

Bottom-Up Approaches:

In these approaches, information is passed from any higher resolution model (such as AA, DFT, or *ab initio* methods) to the CG model. In such methods, a standard procedure for coarse-graining involves several key steps. It begins with the collection of data through system sampling; in most cases, coarse-graining requires sampling a reference (high-resolution) system. Subsequently, the collected data is analyzed using a coarse-graining method, resulting in the derivation of coarse-grained potentials. For iterative methods, additional steps may include running coarse-grained simulations and further refining the coarse-grained potentials through successive iterations.

Boltzmann inversion is a commonly applied technique for non-bonded and bonded interactions like bonds, angles, and torsions in molecular simulations. It relies on the structural information of the system and only necessitates the positions of the atoms. The idea in this approach comes from the fact that in canonical ensemble independent degrees of freedom obey the Boltzmann distribution (Eq.3.5) [75].

$$P(q) = Z^{-1} \exp\left[-\beta U(q)\right]$$
(3.5)

The symbol Z represents the partition function, which involves a sum or integral over all possible states of the system. Having known P(q), where q is the microscopic state of the system, coarse-grained potential can be defined by inverting the probability distribution of variable q denoted as P(q). The Boltzmann inversion formula is a method used to determine a potential energy function for CG models. It involves relating the potential energy to a desired distribution of a specific structural variable (order parameter, s), such as a bond length, bond angle, or torsion angle. The formula is generally expressed as Eq.3.6.

$$U(s) \approx -k_B T \ln(P(s)) \tag{3.6}$$

where normalization factor, Z, would enter the CG potential.

The Iterative Boltzmann Inversion (IBI) method [11, 13] represents a logical progression from the Boltzmann inversion technique. The primary objective of a coarsegrained model is to faithfully replicate distribution functions, such as the spatial distribution of particles, radial distribution functions, or other structural and thermodynamic properties of a reference system. This reference system is often a more detailed or atomistic model, serving as a benchmark for the properties we aim to capture with the coarse-grained model. Through this objective, a systematic enhancement of coarsegrained potentials becomes possible, achieved through an iterative numerical approach [75]. For instance Moore et al. [54] used the standard IBI method to match radial distribution function (RDF of centres of masses of molecules) to derive coarse-grained potentials.

Another approach that can be used in parameterizing a CG model is force matching [75]. In this method the primary goal is not to replicate a variety of distribution functions but rather to achieve a very close match of forces acting on coarse-grained components. This method does not involve iterations, making it computationally less intensive. First, we assume that forces on beads depend on M parameters that can be prefactors of analytical functions, tabulated values of the interaction potentials, or coefficients of splines used to describe these potentials. Then, we assume that the forces acting on the CG beads can be determined by appropriately adjusting the forces acting on individual atoms through a process of reweighting [75].

$$f_i^{ref} = M_i \left[\sum_a \frac{w_a f_a}{m_a} \right]$$
(3.7)

where M_i is the mass of the bead and *a* denotes number of atoms belonging to that bead and f_a is the force acting on the atom *a*. w_a are mapping coefficients used to obtain the position of the coarse-grained bead ($R_i = \Sigma_a w_a r_a$). By running simulations for a sufficiently extended duration, equations of the form $f_i^{CG}(g_1, g_2, g_3, ..., g_M) = f_i^{ref}$ are obtained for each run and this set of equations can be solved using a least-squares approach. f_i^{ref} represents force on bead *i* and g_i are parameters of this function that describe the interactions. They can be pre-factors of analytical functions or tabulated values of the interaction potentials. f_i^{CG} is CG representation of this force. Through validation and comparison, a set of forces acting on beads are obtained, which constitute the CG force-field.

Top-Down Approaches:

In these approaches, we consider macroscopic properties and we try to figure out what is the intermolocular potential that can produce these properties. While top-down approaches can be used for the intermolecular interactions, these can be combined with bottom-up approaches to determine intramolecular potentials for bonds and angles, as for example in the case of the MARTINI force-field [51, 83].

MARTINI Force-Field

MARTINI [51, 83] employs a top-down method involving thorough adjustment of the non-bonded interactions among chemical components based on experimental information, especially thermodynamic data like oil-to-water partitioning coefficients [52]. The mapping in MARTINI model in general is based on four-to-one approach where on average four heavy atoms and associated hydrogen atoms are represented as a unit interaction center (bead). Non-bonded interactions between beads in MARTINI are described by the Lennard-Jones (LJ) 12-6 potential (Eq.3.1).

This involves calculating the free energy of hydration, the free energy of vaporization, and the partitioning free energies between water and various organic phases for all 18 distinct coarse-grained particle types in MARTINI2 and 29 distinct coarsegrained particle types in MARTINI3 [83]. The MARTINI model for specific systems accurately replicates the expected patterns in free energies of hydration and vaporization [52]. Moreover, the MARTINI model particularly has been validated for several different lipids [50], peptides and proteins [27, 37, 53, 67], polymers [44, 74], sugars [93], DNA [91], RNA [96], various solvent [92], carbohydrates [49] and a wide range of other types of materials (mostly bio-materials).

In coalescence of droplets, surface tension plays a significant role that is why we compared the surface tension of pure water in MARTINI versions 2 and 3, and, also, explored the effect of the potential cutoff on the surface tension (Table. 3.2). In general, CG models tend to underestimate surface tension compared to all-atom and experimental measurements, primarily due to a smaller number of interactions. As a result, increasing the cutoff leads to larger surface tension. Our results (Table. 3.2) indicate that MARTINI version 2, using a cut-off of 35Å, closely approximates the experimental surface tension of water (71.99 \pm 0.05) at room temperature (25°*C*) [62]. However, the MARTINI force-field could not provide a satisfactory agreement with the experimental phase behavior of our selected surfactants. That is why we have opted to consider the

SAFT γ -Mie force-field, which has undergone evaluation for various properties, such as surface tension and phase behavior of our selected surfactants.

Table 3.2: Comparison of MARTINI versions 2.2 and 3.0, examining their surface tension on pure water under various cut-offs. The surface tension of water–air at 25° is 71.99±0.05 [62].

MARTINI version	Cut-off (Å)	Surface Tension (mN/m)
3.0	11	27.11 ± 0.81
3.0	25	50.20 ± 0.80
3.0	35	50.49 ± 0.78
2.2	11	31.02 ± 0.79
2.2	25	56.04 ± 0.84
2.2	35	85.80 ± 0.84

SAFT γ -Mie Force-Field

SAFT is a CG force field that maps the size, energy, and range of beads to expected macroscopic properties (it matches to macroscopic properties, first and also second derivatives of the free energy). It is a top-down approach where a molecular-based equation of state is employed to get an effective coarse-grained intermolecular potential that reproduces macroscopic thermodynamical properties [9, 10]. SAFT deals with the classical idea how to build an equation of state. The SAFT equation of state [17] is employed in the field of thermodynamics and the modeling of fluid phases to anticipate the actions of fluids, including polymers, colloids, and molecules that associate with one another. Moreover, SAFT also employs a more general LJ potential form, known as the Mie potential (Eq. 3.8), as it provides a greater number of parameters. This allows for a more effective fitting of the equation of state (EoS) to experimental data. In this approach, essentially, there is a cyclic process involving theory (Equation of State), experimental data, and simulations (MD or Monte Carlo), which is used to parameterize the Mie potential and refine the SAFT coarse-grained force field.

In the SAFT- γ Mie approach [9, 10, 56–58] interactions between two spherical segments can be represented with the Mie potential (Eq.3.8) [46].

$$u^{Mie} = C\epsilon \left[\left(\frac{\sigma}{r}\right)^{\lambda_r} - \left(\frac{\sigma}{r}\right)^{\lambda_a} \right]$$
(3.8)

where λ_r and λ_a are the exponents of the potential. λ_a is constant but λ_r is used as a fitting parameter and C is defined as follows:

$$C(\lambda) = \frac{\lambda_r}{\lambda_r - \lambda_a} \left(\frac{\lambda_r}{\lambda_a}\right)^{\frac{\lambda_a}{\lambda_r - \lambda_a}}$$
(3.9)



Figure 3.2: (a) All-atom representation of a water molecule; (b) Coarse-grained representation of two water molecules by one SAFT bead; (c) Coarse-grained representation of four (MARTINI) water molecules; (d) All-atom representation of a C10E8 molecule [Source: Chemical Compounds Deep Data Source (CCDDS; https://www.molinstincts.com) based on 41 patented SQN and QN technology commercialized into Mol-Instincts database and ChemRTP, ChemEssen, Inc (2022)]; (e) Coarse-grained representation of a C10E8 molecule in SAFT force-field. A hydrophobic alkane CG 'C' bead represents a $-CH_2 - CH_2 - CH_2 - group$ of atoms while a hydrophilic CG 'EO' bead represents $-CH_2 - O - CH_2$ group.

To parameterize the SAFT- γ force field, there are different parameters that are adjustable including the level of coarse-graining (how many atoms should represent each bead), ϵ , σ , λ_r and λ_a set to 6 (which is because this is a physical exponent that describes the dispersion interactions between particles). For this parameterization process, macroscopic data such as vapor-liquid densities and vapor pressures are commonly utilized, although other macroscopic properties can also be considered. By utilizing this macroscopic data, one can determine the parameters necessary for the EoS and the force field. Moreover, the validity of the force-field is checked in practice in the simulations and when the simulations are able to reproduce the target properties, then, the theory is in practice validated.

As mentioned, increasing the number of parameters in the Mie potential enhances its versatility compared to the Lennard-Jones 12-6 potential, which is employed in the MARTINI force field. The 12-6 LJ potential has demonstrated remarkable success in various applications, showcasing its outstanding versatility. In this thesis, for instance, when examining sessile polymer droplets [7], we employed a 12-6 LJ potential. We utilized a physics-based CG force field for polymer chains, implementing a standard bead–spring model. However, it is essential to acknowledge that, like any model, it may encounter challenges. For instance, it is reported that it cannot simultaneously reproduce saturated liquid densities and vapor pressure of n-alkanes [9, 69]. Moreover, it is mentioned that the Lennard-Jones 12-6 potential often struggles to accurately represent fluid-phase equilibria and is known to provide poor representations of vapor-pressure curves [85].

The force field selected for the study of surfactant-laden droplets in this thesis is based on the SAFT- γ Mie EoS, which has been demonstrated to provide convincing



Figure 3.3: Surface tension isotherms as obtained by the simulations in the planar limit for the (a) C10E4 and (b) C10E8 surfactants, using SAFT force field. The insets show slab of water laden with surfactant (above CAC).

agreement with experimental results, including phase diagrams, surface tension of the chosen surfactants, and other properties such as contact angles [87, 88]. In Figs 3.2 a-c, we present a comparison between the water models in atomistic and CG systems of MARTINI and SAFT. Additionally, we provide a comparison between the C10E8 surfactant in all-atom and SAFT models (Figs 3.2 d-e). C10E8 is a large molecule, and considering an atomistic model for it, would be computationally extremely expensive computationally. However, the SAFT CG model allows us to handle large systems with good accuracy and lower computational costs. In Fig. 3.3, we present examples of surface tension isotherms versus surface excess concentration (Γ [mol/m²]), with the latter being the area-related concentration of a surfactant at the surface or interface for a liquid-vapor (LV) interface. These data demonstrate a close agreement with experimental data [3, 43] and previously obtained simulation results [47, 48, 87, 88]. In addition, it has been demonstrated that the SAFT coarse-grained model is capable of accurately replicating the complex phase behavior of several different surfactants including C10E4, C10E8, Silwet-L77, spanning from extremely low concentrations to the formation of aggregates, and even extending to the presence of lamellar phases at higher concentrations.

3.3 Summary

In this section, we briefly reviewed CG MD methods and discussed different CG models. Using CG models make it possible to target large droplets to observe changes in shape of the droplet, avoiding effects that would be attributed to the small size of the droplets, and, also, be able to track the motion of surfactants at adequately large concentrations. Moreover among several existing successful CG methods checking surface tension and phase diagram of surfactant molecules convinced us that SAFT is the best possible choice to study coalescence of surfactant-laden droplets. The SAFT force-field has demonstrated successful testing not only in surface tension and surfactant phase diagrams of non-ionic surfactants but also in various studies involving different liquid and surface phenomena, as well as long-chain molecules and biomolecules. Examples of its application include liquid crystals [70], polymers [25], cryogenic fluids [2], water-oil interfacial tensions [31], super spreading surfactants [88]. Furthermore, it has been shown that this force field reproduces well the contact angles of water [76, 88].

Chapter 4

Results: Summary of Publications

4.1 Coalescence of Surfactant-laden Droplets

4.1.1 Summary of Key Findings of This Publication:

In this work, we studied coalescence of freely suspended surfactant-laden droplets. We considered a non-ionic surfactant (C10E4) with various concentrations below and above CAC. We presented the mass transport mechanism, bridge growth dynamics, and water flow during coalescence using molecular dynamics. The key findings of this work are summarized as follows:

- Demonstrating the initiation of pinching involves hydrophobic beads within surfactant molecules. After pinching, a hydrophobic film will be created between two droplets, which delays the participation of water molecules in the process.
- The dominant movement inside the bridge is the transport of surfactants from the bridge bulk to the bridge surface. However, since coalescence is a dynamic process there is not enough time and there is lack of enough space on bridge surfaces for all surfactants, which mainly come from the droplets' surfaces. Hence, some surfactant, previously part of the surfaces of the droplets, creates new aggregates inside the bridge bulk.
- The bridge initially undergoes growth within a Thermal Regime (TR), followed by a subsequent inertial regime characterized by a power law with an exponent of approximately 0.5. We have shown that higher concentration of surfactant leads to larger TR and the transition between TR and intertial regime (IR) is more pronounced in the presence of surfactant.
- Strong water flow towards the bridge is found in the case of coalescence of water droplets, which is hindered by adding more surfactant.



Coalescence of Surfactant-laden Droplets

Figure 4.1: Stages of Coalescence of surfactant-laden droplets, Reproduced from [Soheil Arbabi, Piotr Deuar, Mateusz Denys, Rachid Bennacer, Zhizhao Che, Panagiotis E. Theodorakis, *Coalescence of surfactant-laden droplets*, Phys. Fluids., **35** 063329 (2023) https://doi.org/10.1063/5.0153676], with the permission of AIP Publishing.

4.1.2 Details of Publication

Coalescence of Surfactant-laden Droplets

PDF version of this publication is reproduced from [Soheil Arbabi, Piotr Deuar, Mateusz Denys, Rachid Bennacer, Zhizhao Che, Panagiotis E. Theodorakis, Coalescence of surfactant-laden droplets, Phys. Fluids **35**, 063329 (2023). https://doi.org/ 10.1063/5.0153676], with the permission of AIP Publishing.



Soheil Arbabi

Institute of Physics, Polish Academy of Sciences (PAN)

Theoretical Physics Division (ON5),

Al. Lotników 32/46 02-668 Warsaw, Poland

arbabi@ifpan.edu.pl

STATEMENT

I declare that I am the co-author of the publication:

Coalescence of surfactant-laden droplets, Phys. Fluids., 35, 063329 (2023),

https://doi.org/10.1063/5.0153676

I contributed equally to the conceptualization. I took the lead role in data curation, analysis, investigation, methodology, simulations, validation, visualization and writing the draft. In addition, I played an equal part in review, and editing tasks.

signature:

Scheil Arbabi



dr hab. Piotr Deuar Head of the Quantum Noise group Institute of Physics, Polish Academy of Sciences (PAN) Theoretical Physics Division (ON5), Al. Lotników 32/46 02-668 Warszawa, Poland <u>deuar@ifpan.edu.pl</u>

STATEMENT

I declare that I am the co-author of the publication:

Coalescence of surfactant-laden droplets Phys. Fluids., **35**, 063329 (2023), https://doi.org/10.1063/5.0153676

My contributions included supporting mr Arbabi in analysis, conceptualization, as well as participation in discussions, reviewing and editing the draft, and co-supervision.

signature:



Dr.Mateusz Denys

Institute of Physics, Polish Academy of Sciences (PAN)

Theoretical Physics Division (ON5),

Al. Lotników 32/46 02-668, Warsaw, Poland

STATEMENT

I declare that I am the co-author of the publication:

Coalescence of surfactant-laden droplets, Phys. Fluids 35, 063329 (2023),

https://doi.org/10.1063/5.0153676

My contribution was supporting in Conceptualization and participation in discussions and reviewing the draft.

Signature:





Département Génie Civil et environnement e-mail : <u>rachid.bennacer@ens-Paris-Saclay.fr</u> www.dgc.ens-paris-saclay.fr

STATEMENT

I declare that I am the co-author of the publication:

Coalescence of surfactant-laden droplets, Phys. Fluids., 35, 063329 (2023),

https://doi.org/10.1063/5.0153676

My contributions included supporting conceptualization, participating in discussions, and reviewing/editing the draft.

Paris-Saclay le 07/12/2023



Tianjin University

Zhizhao Che, PhD, Professor State Key Laboratory of Engines, Tianjin University 135 Yaguan Road, Haihe Education Park, Tianjin, 300350, China Email: chezhizhao@tju.edu.cn

STATEMENT

I declare that I am the co-author of the publication:

Coalescence of surfactant-laden droplets, Phys. Fluids., 35, 063329 (2023),

https://doi.org/10.1063/5.0153676

My contribution involved supporting conceptualization, participating in discussions, and reviewing/editing the draft.

signature: Chark

Dr hab. Panagiotis Theodorakis Division of Theoretical Physics (ON5) Al. Lotników 32/46 02-668 Warsaw, Poland

STATEMENT

I declare that I am the co-author of the publication:

• Coalescence of surfactant-laden droplets S. Arbabi, P. Deuar, M. Denys, R. Bennacer, Z. Che, P. E. Theodorakis *Phys. Fluids* **35**, 063329 (2023), doi:10.1063/5.0153676

My contribution was supervising the project, helping in the interpretation of the results, and in manuscript writing.

Warsaw, 09.12.2023 Panagiotis Theodorakis

Coalescence of surfactant-laden droplets

Submitted: 11 April 2023 · Accepted: 31 May 2023 · Published Online: 20 June 2023

and Panagiotis E. Theodorakis^{1,2}

AFFILIATIONS

¹Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland ²Université Paris-Saclay, ENS Paris-Saclay, CNRS, LMPS, 4 Av. des Sciences, 91190 Gif-sur-Yvette, France ³State Key Laboratory of Engines, Tianjin University, Tianjin 300350, China

^{a)}Author to whom correspondence should be addressed: panos@ifpan.edu.pl

ABSTRACT

Droplet coalescence is an important process in nature and various technologies (e.g., inkjet printing). Here, we unveil the surfactant mass transport mechanism and report on several major differences in the coalescence of surfactant-laden droplets as compared to pure water droplets by means of molecular dynamics simulation of a coarse-grained model. Large-scale changes to bridge growth dynamics are identified, such as the lack of multiple thermally excited precursors, attenuated collective excitations after contact, slowing down in the inertial regime due to aggregate-induced rigidity and reduced water flow, and a slowing down in the coalescence rate (deceleration) when surfactant concentration increases, while at the same time, we also confirm the existence of an initial thermal, and a power-law, inertial, regime of the bridge growth dynamics in both the pure and the surfactant-laden droplets. Thus, we unveil the key mechanisms in one of the fundamental topological processes of liquid droplets containing surfactant, which is crucial in relevant technologies.

Published under an exclusive license by AIP Publishing. https://doi.org/10.1063/5.0153676

I. INTRODUCTION

Droplet coalescence plays an important role in many natural phenomena, for example, determining the size distribution of droplet rains,^{1,2} the dynamics of multiphase flows,^{3,4} and, also, in technological applications, such as inkjet printing⁵ or coating applications.⁶ The coalescence process depends on the interplay between viscous and inertial forces and surface tension, with the minimization of the latter driving this process. Experiments, theories, and simulations of the coalescence of droplets without additives have provided great insight into its mechanisms,^{/-} ⁵ but much less is known in the case of surfactant-laden droplets^{4,26–43} or droplets with other additives,^{44–51} despite their relevance in many areas, such as cloud formation,⁵² microfluidics,⁵³ coating technologies,⁵⁴ and water treatment during crude oil and natural gas separation.⁵⁵ Based on high-speed imaging and particle image velocimetry technology, experimental studies have investigated the coalescence of surfactant-laden droplets, mainly providing macroscopic descriptions of the coalescence process.^{35,2} ^{36,38,56–58} However, the initial fast stages of the coalescence process are impossible to observe in experiments due to device limitations.¹⁹ Moreover, conventional hydrodynamic models are only applicable in the later stages of coalescence,^{59–61} while the singularity at the initial contact point of the coalescing droplets continues to pose challenges for numerical modeling despite progress in this area.^{11,13,23,56} To address the latter

In this study, we report on large-scale MD simulations based on a high-fidelity coarse-grained (CG) force field,62-66 which allows for the faithful simulation of surfactant in water. With these, we uncover the mass transport mechanism of surfactant during coalescence,



issue, for example, continuum modeling may consider either the formation of a single body of fluid by an instant appearance of a liquid bridge that smoothly connects the two droplets and then evolves as a single body due to capillary forces, or a section of the free surface trapped between the bulk phases that gradually disappears.¹³ In the case of systems with surfactant, continuum simulation has suggested that an uneven contraction of the interface due to a nonuniform distribution of accumulating surfactant at the meniscus bridge that connects the droplets is an important factor that modulates the surface tension, which, in turn, drives the coalescence process.⁴ Still, numerical simulation is unable to analyze the mechanism of coalescence after the drops come into contact. Recent molecular-level simulations have clarified important aspects, such as the role of thermal capillary waves at the surface of water droplets,¹⁰ but the effect of surfactant on the physics involved in the coalescence has remained overwhelmingly unexplored. We know that surfactant effects must be large since they greatly change the surface tension, so the research reported here set out to clarify its role in the coalescence dynamics and other characteristics.

pubs.aip.org/aip/pof

elucidate the dynamics of the bridge growth process, resolve the flow, and analyze how the above depend on surfactant distribution. We find an unexpected lack of multiple thermally excited precursor bridges, attenuated collective flow after contact, formation of new aggregates inside the bridge from surfactant previously at the droplets' surface, and a slowing down in the inertial regime as surfactant concentration increases. In the following, we provide some background information in Sec. II. Then, we present our simulation model and methods in Sec. III and our results and relevant discussion in Sec. IV. Finally, we draw our conclusions and suggest possible directions for future work in Sec. V.

II. BACKGROUND

Droplet coalescence takes place in three different stages, namely, the droplet approach, when the two droplets are positioned close enough to "feel" intermolecular forces [Fig. 1(a)], the bridge growth stage [Figs. 1(b) and 1(c)],⁶⁸ and the final reshaping stage toward the equilibrium spherical droplet [Fig. 1(d)]. In the case of droplets without surfactant, the growth dynamics of the bridge has been investigated and in general, two different regimes have been assumed from the perspective of fluid dynamics:^{11,56} an initial viscous regime dominated by macroscopic flows that pull the droplets together, and a subsequent inertial regime, which involves the propagation of local deformations with higher Reynolds number excited near the bridge as it grows.

Even in the case without surfactant, the bridge growth dynamics has been under intense debate. In the viscous regime (VR), a linear scaling in time $b \propto t$ has been suggested for the bridge radius, *b*, as well as logarithmic corrections $t \ln t$,^{11,56} while a scaling $b \propto \sqrt{t}$ has been proposed for the inertial regime (IR).^{11,56} However, others have suggested scaling regimes that depend on the ratio of characteristic scales to the viscous length scale, including an additional inertially limited viscous (ILV) regime,^{69,70} which, according to numerical simulations, is only realized when the coalescing drops are initially separated



FIG. 1. Stages of coalescence of spherical surfactant-laden droplets with equal size and surfactant concentration (3.2 CAC). (a) Initial configuration; (b) beginning of the bridge formation; (c) bridge growth with a magnified view of the bridge region. *b* is the radius of the bridge; (d) final equilibrium configuration after reshaping; (e) coarse-grained representation of a C10E4 surfactant molecule. The surfactant's hydrophobic beads are in red, hydrophilic ones in yellow. Each cyan bead represents two water molecules. External or cross section views are shown to highlight the bulk, surface, and bridge structure of the droplets. Surrounding water vapor is omitted for the sake of clarity. The snapshots of the system were obtained using Ovito software.⁶⁷

by a finite distance.²¹ Another idea put forward has been the characterization of the viscous-inertia-regime transition via a modified Ohnesorge number in the case of immiscible droplets.⁷¹ Despite the advent of modern experimental techniques, such as electrical measurements with the resolution of a few micrometers,⁷² the bridge growth dynamics at the early stages still remains challenging for experimental studies. Instead, molecular dynamics (MD) simulation of an all-atom model for water droplets has provided insight into this initial stage of coalescence, suggesting the formation of multiple precursor bridges at the pinch point, due to thermal capillary waves at the droplet surfaces.¹⁰ These multiple bridges expand linearly in time, due to collective molecular jumps at the droplets' interface, and the transition to the classical hydrodynamics regime only takes place when the bridge radius becomes larger than a thermal length, $l_T \approx (k_B T / \gamma)^{1/4} R^{1/2}$, assuming that fluctuations on one droplet are not affected by the other and in the absence of instabilities.¹⁰ l_T describes the typical width of the contact points at droplet's interface at the initial stage of coalescence, k_B is Boltzmann's constant, T is the temperature, γ is the liquid-vapor (LV) surface tension, and R is the radius of the droplet. Since l_T depends on surface tension, it is expected to grow with surfactant concentration as γ decreases, saturating to a value, l_s , above the critical aggregation concentration (CAC) as γ reaches its plateau value.

In the presence of surfactant, there are many unknowns. Several studies have suggested that its presence would actually delay the coalescence process, due to the reduction in the surface tension,³⁷ ^{,57} while smaller droplets tend to show much faster equilibration of surfactant interfacial coverage.^{38,73} Moreover, it has been suggested that physical regimes could also depend on the diffusion and adsorption time scales of the surfactant, and their dependence on the surfactant concentration and the droplet size.⁷³ In addition, it has been pointed out that surfactant alters the properties of the droplets particularly in the bridge area.³⁹ For example, hydrodynamic instabilities, such as dimples, have been observed for concentrations larger than CAC,⁴¹ but surfactant might actually have a more global effect by affecting the overall size of the droplets.⁴⁰ Certain experiments have also highlighted the role of Marangoni flow that leads to local capillary pressure changes, which in turn affect the coalescence kinetics and result in a delay of the process.^{4,36} Despite these efforts, the mass transport mechanism of surfactants, the resulting dynamics and structure of the bridge, and other early time effects are not well understood. Molecular simulations allow for tracking the individual molecules, which goes beyond the reach of any continuum simulation or real experiment and is therefore crucial for unraveling the mass transport mechanism of surfactant. At present, the early time phenomena that are pivotal for the onset of coalescence can only be investigated in adequate detail by molecular-scale simulation.

III. MODEL AND METHODOLOGY

Our investigation covers all stages of coalescence for droplets of equal size and surfactant concentration. We have considered different surfactants, such as C10E8 and C10E4,⁶³ and a range of surfactant concentrations below/above CAC. The interactions between components of the system are obtained by the Mie- γ Statistical Associating Fluid Theory (SAFT Mie- γ).^{74–78} The MD simulations were carried out in the canonical ensemble using LAMMPS software.^{79,80} After the equilibration of each individual droplet, the droplets were placed next to each other for initiating their coalescence as illustrated in Fig. 1(a).

The force field has been validated for water-surfactant systems with particular focus on accurately reproducing the most relevant properties of the system, such as surface tension and phase behavior.^{62–66,81–83} Interactions between various types of CG beads are described via the Mie potential, which is mathematically expressed as

$$U(r_{ij}) = C\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{\lambda_{ij}^{r}} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{\lambda_{ij}^{a}} \right], \quad \text{for } r_{ij} \le r_{c}, \qquad (1)$$

where

$$C = \left(rac{\lambda_{ij}^{\mathrm{r}}}{\lambda_{ij}^{\mathrm{r}} - \lambda_{ij}^{\mathrm{a}}}
ight) \left(rac{\lambda_{ij}^{\mathrm{r}}}{\lambda_{ij}^{\mathrm{a}}}
ight)^{rac{\lambda_{ij}^{\mathrm{a}}}{2r_{ij}^{\mathrm{r}} - \lambda_{ij}^{\mathrm{a}}}}$$

Here, i and j are the bead types, σ_{ij} indicates the effective bead size, and ε_{ij} is the interaction strength between beads i and j. $\lambda_{ij}^a = 6$ and λ_{ij}^r are Mie potential parameters, while r_{ij} is the distance between two CG beads. A universal cutoff for all nonbonded interactions is set to $r_c = 4.583 \sigma$. Units are chosen for the length, σ , energy, ε , mass, m, and time, τ , which in real units would roughly correspond to: $\sigma = 0.43635$ nm, $\varepsilon/k_B = 492$ K, m = 44.0521 amu, and $\tau = \sigma(m/\varepsilon)^{0.5} = 1.4062$ ps. All simulations are carried out in the NVT ensemble by using the Nosé–Hoover thermostat as implemented in the LAMMPS package^{79,80} with an integration time step $\delta t = 0.005 \tau$. Moreover, simulations took place at room temperature; therefore, $k_B T/\varepsilon = 0.6057$, which corresponds to T = 25 °C.

Surfactants of type CnEm are considered, such as C10E8 and C10E4. A hydrophobic alkane CG "C" bead represents a $-CH_2-CH_2-CH_2-$ group of atoms, while a hydrophilic CG "EO" bead represents an oxyethylene group $-CH_2-O-CH_2$. Finally, a water CG "W" bead corresponds to two water molecules. In Table I, the nonbonded interactions between the different CG beads are listed, while the mass of each bead is reported in Table II.

Bonded interactions are taken into account via a harmonic potential, i.e.,

$$V(r_{ij}) = 0.5k(r_{ij} - \sigma_{ij})^2,$$
 (2)

where $k = 295.33 \varepsilon / \sigma^2$. Moreover, EO beads experience a harmonic angle potential,

$$V_{\theta}(\theta_{ijk}) = 0.5k_{\theta}(\theta_{ijk} - \theta_0)^2, \qquad (3)$$

where θ_{ijk} is the angle between consecutive beads i, j, and k. $k_{\theta} = 4.32 \epsilon / rad^2$, while $\theta_0 = 2.75$ rad is the equilibrium angle. Further discussion on the model can be found in previous studies.^{62,63}

TABLE I. Mie-potential interaction parameters between CG beads. $\lambda^a_{ij}=6$ for all cases.

i–j	$\sigma_{\mathrm{ij}}\left(\sigma ight)$	$arepsilon_{ m ij}\left(arepsilon/k_B ight)$	λ_{ij}^{r}
W-W	0.8584	0.8129	8.00
W-C	0.9292	0.5081	10.75
W-EO	0.8946	0.9756	11.94
C-C	1.0000	0.7000	15.00
C-EO	0.9653	0.7154	16.86
EO-EO	0.9307	0.8067	19.00

Phys. Fluids **35**, 063329 (2023); doi: 10.1063/5.0153676 Published under an exclusive license by AIP Publishing

TABLE II. Mass of CG beads.

Bead type	Mass (m)	
W	0.8179	
С	0.9552	
EO	1.0000	

To prepare the initial configuration of each system, individual droplets were first equilibrated in the NVT ensemble. The total number of beads in the simulations was 10⁵ per initial droplet, with approximately 5% evaporation into the gas. Droplet diameters were \sim 53 σ , which is about 23 nm. Careful consideration was given during the preparation not only to observing the energy of the system, but, also, making sure that the distribution of clusters has reached a dynamic equilibrium and that each cluster was able to diffuse a distance many times its size. After equilibration, the system size (volume of the simulation box) was doubled and droplets were placed next to each other in such a way to avoid interaction between mirror images of the droplets that could potentially occur due to the presence of periodic boundary conditions in all directions, if one was not careful. In this way, the same thermodynamic conditions for the system were approximately guaranteed in the system of a single droplet and in the systems of two droplets used for coalescence. Figure 1(a) illustrates a typical initial configuration of the system. Only the liquid state (droplets) is shown, which is identified by a cluster analysis,^{84,85} while the surrounding vapor has been removed for the sake of clarity. Finally, for our droplets, we have considered a range of different surfactant concentrations below and above the CAC and up to about 6.1 CAC. This covers the whole range of concentrations relevant for the mass transport and other phenomena discussed here.

To quantify the mass transport of surfactant, first a grid with the mesh size of 2σ is defined and surfactant and water particles are assigned to each grid cell. The grid size is chosen to guarantee adequate accuracy in the position of the grid cell while avoiding excessive technical randomness due to having a mesh finer than the size of single beads. Then, based on the density, one can identify the grid cells that belong to the droplets surface or the bulk. By following the grid locations of the surfactant beads, we are able to track the transport of surfactant between the different parts of the droplets. The central bead in a molecule determines whether it is counted as bulk or bridge, whereas if any bead of a molecule enters a surface grid cell, the molecule is counted as being on the surface.

To track the bridge growth, we need to define the bridge region. In our case, this is a slab whose width in the *X* direction is recalculated at each snapshot. The left and right limits of the slab are determined by analyzing the grid points on the *X*–*Z* plane after droplets have been aligned with the coordinate system as shown in Fig. 2. We fit a circle around each droplet and note the surface grid positions at the central X = 0 position, shown by the red points in Fig. 2. Horizontal lines are drawn in the *X* direction passing through these red points to touch the fitted circles, thus defining the rectangle in green. The vertical sides of the rectangle give the limits of the bridge slab in the *X* direction and its width. All molecules with centers having *X* coordinates inside these limits are labeled as belonging to the bridge in a given snapshot.



FIG. 2. Specifying the bridge (green rectangle). Orange and blue points are surface grids on left and right droplets, respectively. Red points are the location of highest and lowest beads on bridge. The solid black line is a best fit to the surface grid positions following Ref. 86.

On the other hand, the bridge radius, b (Fig. 1), is calculated using the distances between extrema of the positions of the beads belonging to the grids located at X = 0, i.e., this distance is first calculated separately for the *Z* coordinate to give a distance $2b_Z$, and then for the *Y* coordinate to give $2b_Y$. The final bridge radius estimate is then given by $b = (b_Z + b_Y)/2$.

IV. RESULTS AND DISCUSSION

The mass transport mechanism of surfactant molecules during coalescence is fundamental to understanding the role of surfactant in the dynamics of this process at all stages. Surfactant mass transfer mechanisms have been investigated in various processes, for example, superspreading,⁶³ emulsion films,⁴² and foam stabilization in lubricating oils.⁴³ For example, in the case of emulsion films, a fascinating

cyclic phenomenon has been observed where new dimples sequentially form with the surfactant redistribution driving this process through coupling to an interfacial hydrodynamic motion inside the films.⁴² In our system, coalescence starts with the formation of the contact point [Fig. 3(a)], where hydrophobic beads from the two droplets actively move to aggregate due to the favorable attractive interaction. In the case of surfactant-laden droplets, we have not observed the formation of multiple contact points (bridge precursors) for any of the systems, unlike what has been seen in pure water droplets.¹⁰ In fact, water molecules do not participate at this earliest stage in the bridge formation. The bridge growth process continues with the formation of a thin layer of surfactant between the droplets [Fig. 3(b)], whose origin is mostly from the initial surface coverage. To unveil these processes, we have monitored the transport of surfactant between different parts of the droplets, i.e., the interior, the bridge, and their surfaces, which sums up to 36 possible surfactant transport processes. The supplemental material (Table S3) provides the numbers for the probabilities of surfactant remaining at a certain place or moving to different parts of the droplets for all cases considered in our study. At this stage, the still small radius, b, of the bridge permits a high supply of surfactant at the contact surface [Fig. 3(b)], which is central to the coalescence of the droplets. However, as the bridge further grows, the surfactant from the initial contact and inflow to the bridge perimeter is not enough to fully supply the interior of the bridge with surfactant. The perimeter of the bridge grows proportionally to b, while its area (cross section) increases with b^2 . Therefore, the concentration of surfactant in the bridge, initially very high, reduces proportionally to 1/b as the bridge grows. Moreover, tracking the molecules shows that, as the bridge forms, less molecules end up in the bridge bulk than were on the approaching surfaces prior to contact. Surfactant transport toward the surface is favorable energetically, and only surfactant that cannot



FIG. 3. Mass transport mechanism of surfactant (C10E4 4.7 CAC) during the coalescence process. (a) Droplet pinching (precursor bridge) taking place through the aggregation of surfactant at the first contact point of the droplets ($t - t_c = 6.25 \tau$). Here, t_c is the time of first contact; (b) main surfactant transfer processes during the initial stage of coalescence as indicated by arrows on a droplet cross section in the x-y plane ($t - t_c = 32.5 \tau$). A larger arrow end indicates the dominant direction of surfactant transport between the different regions in the droplet. Magnified views of the bridge and its cross section on the y-z plane (only hydrophobic beads) are also shown above. At this stage, the bridge is dominated by the presence of surfactant molecules. (c)–(f) At times $t - t_c = 76.25 \tau$, $t - t_c = 233.75 \tau$, $t - t_c = 517.50 \tau$, $t - t_c = 1358.75 \tau$, respectively, show evolution in the inertial regime. The snapshots of the system were obtained using Ovito software.⁶⁷
escape to the exterior (surface) remains trapped in the interior of the bridge region. As a result, the engulfed surfactant forms separated aggregates within the bridge, especially for the cases above CAC [Fig. 3(d)]. These aggregates are characteristic of the bridge growth at later stages [Figs. 3(c)-3(e)], and, as we will see later by the analysis of the bridge growth, surfactant from the bulk can join the aggregates that formed at the bridge as it grows.

The relevant surfactant transport processes during the bridge growth that we have identified are the engulfment of surfactant from the contact surface of the droplets into the interior of the bridge (Tables S1 and S2 in the supplemental material give details), which increases with surfactant concentration, and to a smaller extent the transfer of surfactant in the bulk toward the bridge [Figs. 3(c) and 3(d)]. Coalescence is mainly affected by the transfer of surfactant in the region close to the bridge from the interior to the surfaces, while, in the other parts of the droplet, surfactant is rather in dynamic equilibrium and does not affect the coalescence process. After the bridge fully develops [Fig. 3(e)], a dynamic equilibrium of surfactant extends throughout and no dominant directions of adsorption/desorption processes remain, but only a slight surfactant transport from the surface toward the bulk as the surface area of the droplet becomes smaller. At this final stage, the droplet will reach its final spherical shape [Fig. 3(f), driven by the surface tension. We have also verified that the new aggregates emerging during the coalescence process consist of surfactant that was previously on the contact area (surfaces) between the two merging droplets. The latter observations are valid throughout a range of different concentrations and surfactants below and above the CAC. Data for other concentrations and surfactants than in Fig. 3 are reported in the supplemental material and show the same mechanism, while snapshots of the aggregate formation in the inertial regime are presented in Fig. 4.

To identify the various regimes and better understand the bridge growth dynamics, we have measured the bridge radius, b, over time for droplets with different surfactant concentrations (Fig. 5 here for



FIG. 4. Droplet interiors in the inertial regime showing the presence of new aggregates emerging during the coalescence process. Cross sections are shown at times corresponding to Fig. 3(d) for surfactant in different concentrations of C10E4 above the CAC: (a) 1.6 CAC, (b) 3.2 CAC, (c) 4.7 CAC, and (d) 6.1 CAC. The snapshot of the systems was obtained using Ovito software.⁶⁷



FIG. 5. Bridge growth dynamics (*b*, radius of the bridge) vs time, *t*, for droplets with different surfactant concentrations (C10E4), as indicated in the legend. CAC \approx 7.5 wt %. Power law fits are also shown, tentatively identifying the inertial (IR, $b = b_0 t^{\beta}$) regimes. The inset highlights the power law scaling in the inertial regime and the initial TR regime. I_w is the thermal length for pure water droplets and I_s for surfactant-laden droplets above CAC according to Ref. 10. Data for C10E8 and average growth rates are provided in the supplemental material.

C10E4 and Fig. S1 for C10E8 in the supplemental material). The regimes that follow after the initial bridge formation can be in principle identified by the bridge radius scaling. The inertial scaling with power law $b \sim \sqrt{t}$ is generally most conspicuous, although we see an apparent changeover from an initial thermal regime (TR) with little bridge growth to the IR power law (see fits in Fig. 5 and Fig. S1 of the supplemental material). Moreover, in Fig. 5, the values of the thermal lengths are marked with the horizontal lines for the cases of pure water and surfactant-laden droplets (above CAC) according to previous MD predictions.¹⁰ These values are of the same order as the TR regime bridge size that we observe in our data and express the range of the thermal length scale above which a persistent increase in the bridge radius, *b*, takes place.

Our findings also indicate that the growth speed of the bridge decreases as a function of surfactant concentration in both regimes. Tracking the simulation trajectories, we observe that the surfactant aggregates that are present in the bulk can slow the liquid flow and obstruct the strong water–water interactions. Upon a significant increase in the surfactant concentration far above CAC, aggregates merge in the bulk leading to an increased rigidity of the droplet. This then hinders the coalescence process by slowing down the rearrangement of the droplet toward its equilibrium spherical shape. This is explained by the interactions of water and hydrophobic beads (see Table I), which indicate a larger W–W (W: water beads) than C–C (C: hydrophobic surfactant beads) attraction and a strongly unfavorable (less attractive) C–W interaction in comparison with the interactions of all other components. The average bridge growth velocity, which includes both the TR and IR regimes together as an overview of the

pubs.aip.org/aip/pof

IABLE III. Average velocity of bridge growth in units σ/τ .						
Concentration (CAC)	0.8	1.6	3.2	4.7	6.1	
C10E4	0.2849	0.2204	0.1878	0.1605	0.1047	
C10E8	0.2794	0.2319	0.1871	0.1530	0.1115	
CAC = 7.5 wt %						

^aFor pure water droplets in the viscous regime (result from simulation): 0.3675 $\sigma/\tau.$

overall speed of growth, is reported for each surfactant for a range of concentrations in Table III. It is calculated over the time interval between the moment that the link between the droplets is established, t_c , at the beginning of the coalescence until the point at which the bridge radius is equal to the radius of the droplets in the *y* direction [for example, see Fig. 3(e)]. As surfactant concentration increases, the bridge growth process slows down in comparison with the simulated case of the pure water droplets. These data also show a slightly faster bridge growth in the case of the C10E8 surfactant (see Fig. S1 in supplemental material).

Furthermore, the flow field of water molecules during coalescence exhibits differences between droplets with and without surfactant. In Fig. 6, the color code indicates flow toward the bridge (red) and away from the bridge (blue). In the case of the water droplets without surfactant, the formation of the bridge at the very initial stages is accompanied by fluctuations of internal collective flow in the direction of the coalescence axis (x direction), which encompass the entire droplets [Figs. 6(a)and 6(b)]. This is due to the capillary waves produced by the energy release from the initial rupture of the surface when the droplets first touch.⁴⁴ The waves propagate and result in perturbations in the overall shape of the droplets and the flow patterns illustrated in Figs. 6(a) and 6(b). These flow patterns disappear as the bridge grows further and a robust contact between the two droplets establishes beyond the thermal regime. Moreover, an overall flow toward the bridge as the droplets further coalesce is observed [notice the dominance of red in Fig. 6(c)], while at the final equilibrium, only random thermal fluid flow patterns are seen [Fig. 6(d)]. We have not noticed any statistically significant flow patterns or Marangoni flow³³ (e.g., in the case of droplets with surfactant) toward any of the other directions (e.g., radial).

As surfactant is added to the droplets, the early time collective flow patterns of Figs. 6(a) and 6(b) gradually disappear, especially for all concentrations above the CAC (Fig. 7). Compare, for example, the flow patterns in Figs. 6(b) and 6(f), for the same bridge size. The suppression of the collective flow occurs through two routes: First, the surfactant at the surface reduces the surface tension (reducing energy input from the initial rupture of the surface) and, also, reduces the amplitude of thermal fluctuations, thus suppressing the formation of multiple thermal bridges.¹⁰ Second, the presence of aggregates in the bulk hinders the flow of the water molecules and disperses the momentum transfer before it enters deeper into the droplets.

V. CONCLUSIONS

In this study, the fundamental processes involved in coalescence of droplets containing surfactant have been described—including the initial rupture and bridge growth, which occur on time and length scales inaccessible to experiment. We have reported on the main adsorption processes (surfactant transport mechanism), characterized



FIG. 6. Flow field of water (*x* velocity component, v_x), in cross sections of droplets without (a)–(d) and with (e)–(h) surfactant (C10E4) at 4.7 CAC concentration, at different stages of coalescence. Side by side times correspond to similar stages of the coalescence process. Red reflects the intensity of flow (only water) motion toward the bridge, and blue away from the bridge. Time labels based on contact time (t_c) are added. Note that white space between the water areas (e.g., in the bridge) includes surfactant aggregates and surfactant on the surface. This can cause an illusion of multiple contact points, such as in panel f, which are in fact surrounded by surfactant forming an overall broad bridge.

the bridge growth dynamics of coalescence, and identified several important differences to the case of pure water droplets and those with surfactant. Notably, Fig. 5 suggests that if a slowdown of coalescence processes is desired industrially, more surfactant should be added, which confirms earlier suggestions.^{37,57} Moreover, we have identified early time collective flow patterns that are present in the case of aqueous droplets without surfactant, but are absent when appreciable surfactant is present. Surfactant also suppresses the multiple precursor bridges that are important at early times for pure water.¹⁰ The last appears to indicate that thermal fluctuations will be less important for topological changes of surfactant-laden droplets generally (splitting, merging, etc.). We anticipate that our results open new exploration

Physics of Fluids



FIG. 7. Water flow pattern for different concentrations [(a)-(f), 0-6.1 CAC] for C10E4 at the initial pinching stage. Above CAC (c)-(f), there is no observable pattern. Red color reflects the intensity of flow toward the bridge, while blue indicates the intensity of flow away from the bridge. Like in Fig. 6, empty space within/ between the water in the droplets (e.g., in the bridge) includes surfactant, and the contact point of the droplet surface is always single.

directions, which will be relevant for practical applications, and that they suggest the kind of effects that will be seen in other as yet unexplored processes, such as droplet break up and coalescence on substrates. An aspect that requires further consideration is the various effects that might be attributed to a larger surface-area-to-volume ratio as the size of the droplets decreases. For example, we saw that minor redistribution of surfactants from surface to bulk or vice versa can cause large fluctuations in the bulk, while such effects may become negligible in macroscale systems.²⁶ It would therefore be interesting to explore larger systems in the future as more computational resources become available, as well as employ a range of different simulation models to explore droplet coalescence in the presence of surfactant.

SUPPLEMENTARY MATERIAL

See the supplementary material for the details of the probabilities for the mass transport mechanism of surfactant molecules between the different regions in the droplets that reflect the arrows in Fig. 3. It also contains data on the bridge growth dynamics in the case of C10E8 surfactant.

ACKNOWLEDGMENTS

This research has been supported by the National Science Centre, Poland, under Grant No. 2019/34/E/ST3/00232. We gratefully acknowledge Polish high-performance computing infrastructure PLGrid (HPC Centers: ACK Cyfronet AGH) for providing computer facilities and support within computational Grant No. PLG/2022/015261.

AUTHOR DECLARATIONS **Conflict of Interest**

The authors have no conflicts to disclose.

ARTICLE

Author Contributions

Soheil Arbabi: Conceptualization (equal); Data curation (lead); Formal analysis (lead); Investigation (lead); Methodology (lead); Software (lead); Validation (lead); Visualization (lead); Writing review & editing (equal). Piotr Deuar: Conceptualization (supporting); Formal analysis (supporting); Methodology (supporting); Supervision (equal); Validation (supporting); Writing - review & editing (equal). Mateusz Denys: Investigation (supporting); Supervision (supporting); Writing - review & editing (equal). Rachid Bennacer: Conceptualization (supporting); Formal analysis (supporting); Investigation (supporting); Methodology (supporting); Resources (supporting); Supervision (supporting); Validation (supporting); Writing - review & editing (equal). Zhizhao Che: Conceptualization (supporting); Funding acquisition (supporting); Supervision (supporting); Writing - review & editing (equal). Panagiotis Theodorakis: Conceptualization (lead); Data curation (supporting); Formal analysis (supporting); Funding acquisition (lead); Investigation (supporting); Methodology (lead); Project administration (lead); Resources (lead); Supervision (lead); Validation (supporting); Writing - original draft (lead); Writing - review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

REFERENCES

- ¹E. G. Bowen, "The formation of rain by coalescence," Aust. J. Sci. Res., Ser. A 3, 193-214 (1950).
- ²E. X. Berry and R. L. Reinhardt, "An analysis of cloud drop growth by collection-Part 3: Accretion and self-collection," J. Atmos. Sci. 31, 2118-2126 (1974).
- ³D. Campana, J. D. Paolo, and F. A Saita, "A 2-D model of Rayleigh instability in capillary tubes-Surfactant effects," Int. J. Multiphase Flow 50, 431-454 (2004).
- ⁴J. Lu and C. M. Corvalan, "Coalescence of viscous drops with surfactants," Chem. Eng. Sci. 78, 9–13 (2012).
- ⁵M. Singh, H. Haverinen, P. Dhagat, and G. Jabbour, "Inkjet printing process and its applications," Adv. Mater. 22, 673–685 (2010). ⁶A. Frohn and N. Roth, *Dynamics of Droplets* (Springer, Berliln, 2000).
- ⁷J. D. Paulsen, R. Carmigniani, A. Kannan, J. C. Burton, and S. R. Nagel, "Coalescence of bubbles and drops in an outer fluid," Nat. Commun. 5, 3182
- (2014). ⁸Y. Yoon, F. Baldessari, H. D. Ceniceros, and L. G. Leal, "Coalescence of two momentatic flow" Phys. Fluids 19, equal-sized deformable drops in an axisymmetric flow," Phys. Fluids 19, 102102 (2007).

pubs.aip.org/aip/pof

- ⁹M. I. Khodabocus, M. Sellier, and V. Nock, "Scaling laws of droplet coalescence: Theory and numerical simulation," Adv. Math. Phys. **2018**, 1.
- ¹⁰S. Perumanath, M. K. Borg, M. V. Chubynsky, J. E. Sprittles, and J. M. Reese, "Droplet coalescence is initiated by thermal motion," Phys. Rev. Lett. **122**, 104501 (2019).
- ¹¹J. Eggers, J. R. Lister, and H. A. Stone, "Coalescence of liquid drops," J. Fluid Mech. **401**, 293–310 (1999).
- ¹²D. G. Aarts, H. N. Lekkerkerker, H. Guo, G. H. Wegdam, and D. Bonn, "Hydrodynamics of droplet coalescence," Phys. Rev. Lett. 95, 164503 (2005).
- ¹³J. E. Sprittles and Y. D. Shikhmurzaev, "Coalescence of liquid drops: Different models versus experiment," Phys. Fluids **24**, 122105 (2012).
- ¹⁴M. Dudek, D. Fernandes, E. Helno Herø, and G. Øye, "Microfluidic method for determining drop-drop coalescence and contact times in flow," Colloids Surf. A 586, 124265 (2020).
- ¹⁵M. M. Rahman, W. Lee, A. Iyer, and S. J. Williams, "Viscous resistance in drop coalescence," Phys. Fluids **31**, 012104 (2019).
- ¹⁶J. D. Berry and R. R. Dagastine, "Mapping coalescence of micron-sized drops and bubbles," J. Colloid Interface Sci. 487, 513–522 (2017).
- ¹⁷P. M. Somwanshi, K. Muralidhar, and S. Khandekar, "Coalescence dynamics of sessile and pendant liquid drops placed on a hydrophobic surface," Phys. Fluids **30**, 092103 (2018).
- ¹⁸P. K. Kirar, K. Alvarenga, P. Kolhe, G. Biswas, and K. Chandra Sahu, "Coalescence of drops on the free-surface of a liquid pool at elevated temperatures," Phys. Fluids **32**, 052103 (2020).
- ¹⁹S. Bayani, Y. Tabe, Y. T. Kang, S. H. Lee, and C. K. Choi, "Surface plasmon resonance imaging of drop coalescence at high-temporal resolution," J. Flow Visualization Image Process. 25, 191–205 (2018).
- ²⁰M. Brik, S. Harmand, and I. Zaaroura, "Relaxation and contact angle dynamics during the coalescence of different sized vertically aligned water drops in different silicone oil viscosities," Colloids Surf. A 629, 127429 (2021).
- ²¹C. R. Anthony, M. T. Harris, and O. A. Basaran, "Initial regime of drop coalescence," Phys. Rev. Fluids 5, 033608 (2020).
- ²²V. R. Kern, T. Saeter, and A. Carlson, "Viscoplastic sessile drop coalescence," Phys. Rev. Fluids 7, L081601 (2022).
- ²³M. Heinen, M. Hoffmann, F. Diewald, S. Seckler, K. Langenbach, and J. Vrabec, "Droplet coalescence by molecular dynamics and phase-field modeling," Phys. Fluids 34, 042006 (2022).
- ²⁴M. Geri, B. Keshavarz, G. H. McKinley, and J. W. M. Bush, "Thermal delay of drop coalescence," J. Fluid Mech. 833, R3 (2017).
- ²⁵M. Abouelsoud and B. Bai, "Bouncing and coalescence dynamics during the impact of a falling drop with a sessile drop on different solid surfaces," Phys. Fluids 33, 063309 (2021).
- ²⁶N. I. Politova, S. Tcholakova, S. Tsibranska, N. D. Denkov, and K. Muelheims, "Coalescence stability of water-in-oil drops: Effects of drop size and surfactant concentration," Colloids Surf. A 531, 32–39 (2017).
- ²⁷W. H. Weheliye, T. Dong, and P. Angeli, "On the effect of surfactants on drop coalescence at liquid/liquid interfaces," Chem. Eng. Sci. 161, 215–227 (2017).
- ²⁸G. Soligo, A. Roccon, and A. Soldati, "Coalescence of surfactant-laden drops by phase field method," J. Comput. Phys. **376**, 1292–1311 (2019).
- ²⁹T. Dong, W. H. Weheliye, P. Chausset, and P. Angeli, "An experimental study on the drop/interface partial coalescence with surfactants," Phys. Fluids **29**, 102101 (2017).
- ³⁰T. Dong, W. H. Weheliye, and P. Angeli, "Laser induced fluorescence studies on the distribution of surfactants during drop/interface coalescence," Phys. Fluids **31**, 012106 (2019).
- ³¹N. M. Kovalchuk, M. Reichow, T. Frommweiler, D. Vigolo, and M. J. H. Simmons, "Mass transfer accompanying coalescence of surfactant-laden and surfactant-free drop in a microfluidic channel," Langmuir 35, 9184–9193 (2019).
 ³²T. C. Botti, A. Hutin, E. Quintella, and M. S. Carvalho, "Effect of interfacial
- ³²T. C. Botti, A. Hutin, E. Quintella, and M. S. Carvalho, "Effect of interfacial rheology on drop coalescence in water-oil emulsion," Soft Matter 18, 1423-1434 (2022).
- ³³C. Constante-Amores, A. Batchvarov, L. Kahouadji, S. Shin, J. Chergui, D. Juric, and O. Matar, "Role of surfactant-induced Marangoni stresses in dropinterface coalescence," J. Fluid Mech. **925**, A15 (2021).
- ³⁴M. Kasmaee, F. Varaminian, P. Khadiv-Parsi, and J. Saien, "Effects of different surfactants and physical properties on the coalescence of dimethyl disulfide

- drops with mother phase at the interface of sodium hydroxide aqueous solutions," J. Mol. Liq. **263**, 31–39 (2018).
- ³⁵E. Nowak, Z. Xie, N. M. Kovalchuk, O. K. Matar, and M. J. Simmons, "Bulk advection and interfacial flows in the binary coalescence of surfactant-laden and surfactant-free drops," Soft Matter 13, 4616–4628 (2017).
- ³⁶E. Nowak, N. M. Kovalchuk, Z. Che, and M. J. Simmons, "Effect of surfactant concentration and viscosity of outer phase during the coalescence of a surfactant-laden drop with a surfactant-free drop," Colloids Surf. A 505, 124–131 (2016).
- ³⁷N. Jaensson and J. Vermant, "Tensiometry and rheology of complex interfaces," Curr. Opin. Colloid Interface Sci. 37, 136–150 (2018).
- ³⁸S. Narayan, A. E. Metaxa, R. Bachnak, T. Neumiller, C. S. Dutcher *et al.*, "Zooming in on the role of surfactants in droplet coalescence at the macro-and microscale," Curr. Opin. Colloid Interface Sci. **50**, 10385 (2020).
- ³⁹I. B. Ivanov, K. D. Danov, and P. A. Kralchevsky, "Flocculation and coalescence of micron-size emulsion droplets," Colloids Surf. A 152, 161–182 (1999).
- ⁴⁰S. Tcholakova, N. D. Denkov, and T. Danner, "Role of surfactant type and concentration for the mean drop size during emulsification in turbulent flow," Langmuir 20, 7444–7458 (2004).
- ⁴¹D. Langevin, "Coalescence in foams and emulsions: Similarities and differences," Curr. Opin. Colloid Interface Sci. **44**, 23–31 (2019).
- ⁴²O. D. Velev, T. D. Gurkov, and R. P. Borwankar, "Spontaneous cyclic dimpling in emulsion films due to surfactant mass transfer between the phases," J. Colloid Interface Sci. 159, 497–501 (1993).
- ⁴³V. C. Suja, A. Kar, W. Cates, S. M. Remmert, P. D. Savage, and G. G. Fuller, "Evaporation-induced foam stabilization in lubricating oils," Proc. Natl. Acad. Sci. U. S. A. 115, 7919–7924 (2018).
- ⁴⁴P. J. Dekker, M. A. Hack, W. Tewes, C. Datt, A. Bouillant, and J. H. Snoeijer, "When elasticity affects drop coalescence," Phys. Rev. Lett. **128**, 028004 (2022).
- ⁴⁵E. Calvo, E. de Malmazet, F. Risso, and O. Masbernat, "Coalescence of water drops at an oil-water interface loaded with microparticles and surfactants," Ind. Eng. Chem. Res. 58, 15573–15587 (2019).
- ⁴⁶S. Arbabi and P. E. Theodorakis, "Coalescence of sessile polymer droplets: A molecular dynamics study," Macromol. Theory Simul. 2300017 (2023).
- ⁴⁷S. C. Varma, A. Saha, and A. Kumar, "Coalescence of polymeric sessile drops on a partially wettable substrate," Phys. Fluids **33**, 123101 (2021).
- ⁴⁸V. S. Sivasankar, S. A. Etha, D. R. Hines, and S. Das, "Coalescence of microscopic polymeric drops: Effect of drop impact velocities," Langmuir 37, 13512–13526 (2021).
- ⁴⁹V. S. Sivasankar, D. R. Hines, and S. Das, "Numerical study of the coalescence and mixing of drops of different polymeric materials," Langmuir 38, 14084–14096 (2022).
- ⁵⁰M. R. Otazo, R. Ward, G. Gillies, R. S. Osborne, M. Golding, and M. A. K. Williams, "Aggregation and coalescence of partially crystalline emulsion drops investigated using optical tweezers," Soft Matter 15, 6383–6391 (2019).
- ⁵¹C. Vannozzi, "Effect of polymer-coated gold nanoparticle stabilizers on drop coalescence," Phys. Fluids 31, 082112 (2019).
- ⁵²A. Kovetz and B. Olund, "The effect of coalescence and condensation on rain formation in a cloud of finite vertical extent," J. Atmos. Sci. 26, 1060–1065 (1969).
- ⁵³S. Feng, L. Yi, L. Zhao-Miao, C. Ren-Tuo, and W. Gui-Ren, "Advances in micro-droplets coalescence using microfluidics," Chin. J. Anal. Chem. 43, 1942–1954 (2015).
- ⁵⁴W. Ristenpart, P. McCalla, R. Roy, and H. Stone, "Coalescence of spreading droplets on a wettable substrate," Phys. Rev. Lett. 97, 064501 (2006).
- droplets on a wettable substrate," Phys. Rev. Lett. 97, 064501 (2006).
 ⁵⁵M. Dudek, J. Chicault, and G. Øye, "Microfluidic investigation of crude oil droplet coalescence: Effect of oil/water composition and droplet aging," Energy Fuels 34, 5110–5120 (2020).
- ⁵⁶L. Duchemin, J. Eggers, and C. Josserand, "Inviscid coalescence of drops," J. Fluid Mech. 487, 167–178 (2003).
- 57 L. Leal, "Flow induced coalescence of drops in a viscous fluid," Phys. Fluids 16, 1833–1851 (2004).
- ⁵⁸M. Chinaud, V. Voulgaropoulos, and P. Angeli, "Surfactant effects on the coalescence of a drop in a Hele-Shaw cell," Phys. Rev. E 94, 033101 (2016).
- ⁵⁹L. Y. Yeo, O. K. Matar, E. S. P. de Ortiz, and G. F. Hewitt, "Film drainage between two surfactant-coated drops colliding at constant approach velocity," J. Colloid Interface Sci. 257, 93–107 (2003).

Phys. Fluids 35, 063329 (2023); doi: 10.1063/5.0153676

Published under an exclusive license by AIP Publishing

Physics of Fluids

pubs.aip.org/aip/pof

- ⁶⁰Y. Hu, D. Pine, and L. G. Leal, "Drop deformation, breakup, and coalescence with compatibilizer," Phys. Fluids **12**, 484–489 (2000).
- ⁶¹A. Mansouri, H. Arabnejad, and R. Mohan, "Numerical investigation of droplet-droplet coalescence and droplet-interface coalescence," in *Fluids Engineering Division Summer Meeting*, Vol. 46216 (American Society of Mechanical Engineers, 2014), p. V01AT05A006.
- ⁶²P. E. Theodorakis, E. A. Müller, R. V. Craster, and O. K. Matar, "Modelling the superspreading of surfactant-laden droplets with computer simulation," Soft Matter 11, 9254–9261 (2015).
- ⁶³P. E. Theodorakis, E. A. Müller, R. V. Craster, and O. K. Matar, "Superspreading: Mechanisms and molecular design," Langmuir 31, 2304–2309 (2015).
- ⁶⁴P. E. Theodorakis, E. R. Smith, R. V. Craster, E. A. Müller, and O. K. Matar, "Molecular dynamics simulation of the superspreading of surfactant-laden droplets. A review," Fluids 4, 176 (2019).
- ⁶⁵P. É. Theodorakis, E. A. Müller, R. V. Craster, and O. K. Matar, "Insights into surfactant-assisted superspreading," Curr. Opin. Colloid Interface Sci. 19, 283–289 (2014).
- ⁶⁶P. E. Theodorakis, E. R. Smith, and E. A. Müller, "Spreading of aqueous droplets with common and superspreading surfactants. a molecular dynamics study," Coll. Surf. A 581, 123810 (2019).
- ⁶⁷A. Stukowski, "Visualization and analysis of atomistic simulation data with OVITO—The open visualization tool," Modell. Simul. Mater. Sci. Eng. 18, 015012 (2010).
- ⁶⁸J. Jin, C. H. Ooi, D. V. Dao, and N.-T. Nguyen, "Coalescence processes of droplets and liquid marbles," Micromachines 8, 336 (2017).
- ⁶⁹J. D. Paulsen, J. C. Burton, S. R. Nagel, S. Appathurai, M. T. Harris, and O. A. Basaran, "The inexorable resistance of inertia determines the initial regime of drop coalescence," Proc. Natl. Acad. Sci. U. S. A. **109**, 6857–6861 (2012).
- 70 J. D. Paulsen, "Approach and coalescence of liquid drops in air," Phys. Rev. E 88, 063010 (2013).
- ⁷¹H. Xu, T. Wang, and Z. Che, "Bridge evolution during the coalescence of immiscible droplets," J. Colloid Interface Sci. 628, 869–877 (2022).
- ⁷²J. D. Paulsen, J. C. Burton, and S. R. Nagel, "Viscous to inertial crossover in liquid drop coalescence," Phys. Rev. Lett. **106**, 114501 (2011).
- ⁷³F. Jin, R. Balasubramaniam, and K. J. Stebe, "Surfactant adsorption to spherical particles: The intrinsic length scale governing the shift from diffusion to kinetic-controlled mass transfer," J. Adhes. 80, 773–796 (2004).
- ⁷⁴E. A. Müller and G. Jackson, "Force field parameters from the SAFT-γ equation of state for use in coarse-grained molecular simulations," Annu. Rev. Chem. Biomol. Eng. 5, 405–427 (2014).

- ⁷⁵O. Lobanova, C. Avendaño, T. Lafitte, E. A. Müller, and G. Jackson, "SAFT-γ force field for the simulation of molecular fluids. 4. A single-site coarse-grained model of water applicable over a wide temperature range," Mol. Phys. 113, 1228–1249 (2015).
- ⁷⁶T. Lafitte, A. Apostolakou, C. Avendaño, A. Galindo, C. S. Adjiman, E. A. Müller, and G. Jackson, "Accurate statistical associating fluid theory for chain molecules formed from Mie segments," J. Chem. Phys. **139**, 154504 (2013).
- ⁷⁷C. Avendaño, T. Lafitte, A. Galindo, C. S. Adjiman, G. Jackson, and E. A. Müller, "SAFT-y force field for the simulation of molecular fluids. 1. A single-site coarse grained model of carbon dioxide," J. Phys. Chem. B 115, 11154–11169 (2011).
- ⁷⁸C. Avendaño, T. Lafitte, A. Galindo, C. S. Adjiman, E. A. Müller, and G. Jackson, "SAFT-γ force field for the simulation of molecular fluids: 2. Coarse-grained models of greenhouse gases," J. Phys. Chem. B **117**, 2717–2733 (2013).
- ⁷⁹S. Plimpton, "Fast parallel algorithms for short-range molecular dynamics," I. Comp. Phys. **117**, 1–19 (1995).
- ⁸⁰A. P. Thompson, H. M. Aktulga, R. Berger, D. S. Bolintineanu, W. M. Brown, P. S. Crozier, P. J. in't Veld, A. Kohlmeyer, S. G. Moore, T. D. Nguyen, R. Shan, M. J. Stevens, J. Tranchida, C. Trott, and S. J. Plimpton, "LAMMPS—A flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales," Comput. Phys. Commun. 271, 108171 (2022).
- ⁸¹O. Lobanova, "Development of coarse-grained force fields from a molecular based equation of state for thermodynamic and structural properties of complex fluids," Ph.D. thesis (Imperial College London, 2014).
- 82O. Lobanova, A. Mejia, G. Jackson, and E. A. Müller, "SAFT-γ force field for the simulation of molecular fluids 6: Binary and ternary mixtures comprising water, carbon dioxide, and *n*-alkanes," J. Chem. Thermodyn. 93, 320–336 (2016).
- ⁸³P. Morgado, O. Lobanova, E. A. Müller, G. Jackson, M. Almeida, and E. J. Filipe, "SAFT-γ force field for the simulation of molecular fluids: 8. Heterosegmented coarse-grained models of perfluoroalkylalkanes assessed with new vapour-liquid interfacial tension data," Mol. Phys. **114**, 2597–2614 (2016).
- ⁸⁴P. E. Theodorakis, W. Paul, and K. Binder, "Pearl-necklace structures of molecular brushes with rigid backbone under poor solvent conditions: A simulation study," J. Chem. Phys. **133**, 104901 (2010).
- ⁸⁵P. E. Theodorakis, W. Paul, and K. Binder, "Analysis of the cluster formation in two-component cylindrical bottle-brush polymers under poor solvent conditions. A simulation study," Eur. Phys. J. E 34, 52 (2011).
- ⁸⁶K. Kanatani and P. Rangarajan, "Hyper least squares fitting of circles and ellipses," Comput. Stat. Data Anal. 55, 2197–2208 (2011).

Supplemental Material for "Coalescence of Surfactant-Laden Droplets"

Soheil Arbabi,¹ Piotr Deuar,¹ Mateusz Denys,¹ Rachid

Bennacer,
² Zhizhao Che,
³ and Panagiotis E. Theodorakis
1, *

¹Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland ²Université Paris-Saclay, ENS Paris-Saclay,

Laboratoire de Mécanique et Technologie, Gif-sur-Yvette 91190, France ³State Key Laboratory of Engines, Tianjin University, 300350 Tianjin, China (Dated: May 29, 2023)

CONTENTS

MASS TRANSPORT MECHANISM	1
BRIDGE GROWTH DYNAMICS	8
REFERENCES	8

MASS TRANSPORT MECHANISM

Firstly, in this supplemental material, we provide data on the overall mass transport of surfactant from the surface to the bulk. It is quantified by comparing the amount of surfactant at the beginning of coalescence (*e.g.* Fig 1a) to the amounts at the very end *e.g.* Fig. 1d). The data in Tables S1 and S2 indicate that although most of the molecules from the surfaces of the droplets at the contact area will be transported to the emerging bridge surface during coalescence, a certain amount of them will be trapped and will remain in the bulk of the formed droplet (notice the increased count in the bulk).

The relative contributions from surfactant transport processes from one part of a droplet to others over short time scales $\Delta t'$ are reported in Table S3 for two types of surfactant and a $\overline{* \text{ panos}@ifpan.edu.pl}$ range of concentrations. The arrows drawn in Fig. 3 of the manuscript are a consequence and illustrate the relative amount of mass transport during coalescence — in terms of absolute numbers of molecules transported over time.

TABLE S1. Number of surfactant molecules (C10E4) before pinching ("Initial snapshot", for example, see Fig. 1a) and at the end ("Last snapshot", for example, see Fig. 1d) of the coalescence process in the bulk and at the surface of the droplets.

Concentration (CAC):	0.8	1.6	3.2	4.7	6.1
Initial snapshot (two droplets)					
Bulk	0	202	2184	4096	5899
Surface	1428	2656	3530	4476	5529
Last snapshot (one droplet)					
Bulk	10	234	2229	4329	6167
Surface	1418	2624	3485	4243	5261

TABLE S2. Number of surfactant molecules (C10E8) before pinching ("Initial snapshot", for example see Fig. 1a) and at the end ("Last snapshot", for example, see Fig. 1d) of the coalescence process in the bulk and at the surface of the droplets.

Concentration (CAC):	0.8	1.6	3.2	4.7	6.1
Initial snapshot (two droplets)					
Bulk	0	379	1429	2514	3579
Surface	910	1439	2207	2940	3693
Last snapshot (one droplet)					
Bulk	11	400	1511	2603	3782
Surface	899	1418	2125	2851	3490

TABLE S3: Summary of the relative contributions from all relevant surfactant transport processes in the coalescing droplets. The table lists the relative frequency of transport from one region to another over a time interval $\Delta t' = 1.25\tau$ as a percentage of the mean number of surfactant molecules in source regions. Data was averaged over consecutive snapshots made at $\Delta t'$ intervals during the entire coalescence process which lasts $\mathcal{O}(1000 - 2000)\tau$. CAC ≈ 7.5 wt% for C10E4 and C10E8.

Probabilitie	Probabilities					
Concentration (CAC):	0.8	1.6	3.2	4.7	6.1	
Remaining at bridge bulk						
C10E4	0.8774	0.8098	0.8765	0.8647	0.8529	
C10E8	0.8728	0.8435	0.8693	0.8669	0.8741	
Movement from bridge bulk to left surface						
C10E4	0.0000	0.0000	0.0005	0.0003	0.0004	
C10E8	0.0000	0.0000	0.0001	0.0002	0.0004	
Movement from bridge bulk to left bulk						
C10E4	0.0066	0.0093	0.0648	0.0388	0.0388	
C10E8	0.0075	0.0472	0.0460	0.0419	0.0403	
Movement from bridge bulk to bridge surface						
C10E4	0.1092	0.1542	0.0326	0.0575	0.0685	
<u>C10E8</u>	0.1081	0.0642	0.0424	0.0504	0.0428	
Movement from bridge bulk to right surface						
C10E4	0.0000	0.0008	9.7 e-5	0.0004	0.0004	
C10E8	0.0000	0.0004	0.0004	9.7e-5	0.0007	
Movement from bridge bulk to right bulk						
C10E4	0.0066	0.0257	0.0252	0.0381	0.0388	
C10E8	0.0113	0.0444	0.0413	0.0402	0.0413	
Remaining at bridge surface						
C10E4	0.9398	0.9284	0.9360	0.9244	0.9099	
C10E8	0.9284	0.9428	0.9352	0.9249	0.9251	

Cont. next page...

Concentration (CAC):	0.8	1.6	3.2	4.7	6.1
Movement from bridge surface to left surface					
C10E4	0.0275	0.0305	0.0260	0.0237	0.0259
C10E8	0.0330	0.0256	0.0258	0.0278	0.0253
Movement from bridge surface to left bulk					
C10E4	0.0001	0.0001	5.5e-5	0.0001	0.0003
C10E8	0.0000	0.000	0.0001	0.0002	0.0003
Movement from bridge surface to bridge bulk					
C10E4	0.0042	0.0103	0.0098	0.0262	0.0373
C10E8	0.0057	0.0087	0.0129	0.0181	0.0235
Movement from bridge surface to right surface					
C10E4	0.0281	0.0304	0.0279	0.0251	0.0261
C10E8	0.0326	0.0226	0.0255	0.0284	0.0252
Movement from bridge surface to right bulk					
C10E4	0.0000	2.5e-5	4.1e-5	0.0003	0.0002
C10E8	8.7e-5	5.8e-5	0.0001	0.0002	0.0004
Remaining at left bulk					
C10E4	0.9332	0.9849	0.9894	0.9877	0.9835
C10E8	0.9074	0.9945	0.9870	0.9864	0.9803
Movement from left bulk to left surface					
C10E4	0.0046	0.0092	0.0052	0.0092	0.0138
C10E8	0.0092	0.0012	0.0095	0.0111	0.0158
Movement from left bulk to bulk bridge					
C10E4	0.0000	0.00021	0.0031	0.0012	0.0011
C10E8	0.0000	0.0019	0.0021	0.0008	0.0010
Movement from left bulk to surface bridge					_
C10E4	0.0000	0.0000	9.7e-6	4.9e-6	1.1e-5
C10E8	0.0000	0.0000	1.9e-5	9.8e-6	1.8e-5

Concentration (CAC):	0.8	1.6	3.2	4.7	6.1
Movement from left bulk to right surface					
C10E4	0.0000	0.0003	2.4e-5	3.5e-5	6.2e-5
C10E8	0.0000	0.0002	2.4e-5	2.7e-5	2.7e-5
Movement from left bulk to right bulk					
C10E4	0.0621	0.0052	0.0020	0.0018	0.0013
C10E8	0.0833	0.0020	0.0011	0.0015	0.0026
Remaining at left surface					
C10E4	0.9942	0.9922	0.9912	0.9863	0.9801
C10E8	0.9931	0.9948	0.9887	0.9859	0.9788
Movement from left surface to left bulk					
C10E4	2.1e-5	0.0008	0.0034	0.0094	0.0159
C10E8	5.9e-5	0.0003	0.0067	0.0104	0.0168
Movement from left surface to bridge bulk					
C10E4	0.0000	0.0000	1.6e-5	5.8e-6	1.4e-5
C10E8	1.2e-5	0.0000	3.4e-6	9.1e-7	1.7e-5
Movement from left surface to bridge surface					
C10E4	0.0032	0.0037	0.0029	0.0017	0.0018
C10E8	0.0045	0.0027	0.0032	0.0015	0.0014
Movement from left surface to right surface					
C10E4	0.0025	0.0031	0.0029	0.0024	0.0019
C10E8	0.0022	0.0020	0.0012	0.0020	0.0028
Movement from left surface to right bulk					
C10E4	0.0000	2.8e-5	1.1e-5	3.2e-5	6.5e-5
C10E8	1.2e-5	3.0e-5	2.4e-5	3.1e-5	1.7e-5
Remaining at right bulk					
C10E4	0.9251	0.9831	0.9900	0.9875	0.9831
C10E8	0.9103	0.9926	0.9871	0.9859	0.9808

Concentration (CAC):	0.8	1.6	3.2	4.7	6.1
Movement from right bulk to right surface					
C10E4	0.0000	0.0096	0.0068	0.0094	0.0142
C10E8	0.0373	0.0033	0.0097	0.0116	0.0153
Movement from right bulk to bulk bridge					
C10E4	0.0000	0.0018	0.0011	0.0011	0.0011
C10E8	0.0000	0.0018	0.0019	0.0007	0.0010
Movement from right bulk to surface bridge					
C10E4	0.0000	0.0000	2.4e-6	1.1e-5	1.4e-5
C10E8	0.0000	0.0000	2.8e-5	7.9e-6	1.9e-5
Movement from right bulk to left surface					
C10E4	0.0000	0.0001	1.9e-5	2.7e-5	5.0e-5
C10E8	0.0014	0.0001	1.9e-5	2.9e-5	2.7e-5
Movement from right bulk to left bulk					
C10E4	0.0748	0.0051	0.0019	0.0018	0.0013
C10E8	0.0508	0.0019	0.0011	0.0015	0.0026
Remaining at right surface					
C10E4	0.9940	0.9923	0.9898	0.9859	0.9795
C10E8	0.9932	0.9946	0.9884	0.9856	0.9793
Movement from right surface to right bulk					
C10E4	0.0000	0.0008	0.0045	0.0096	0.0165
C10E8	0.0002	0.0010	0.0069	0.0107	0.0163
Movement from right surface to bridge bulk					
C10E4	0.0000	0.0000	4.7e-6	9.9e-6	7.7e-6
C10E8	0.0000	0.0000	1.4e-5	3.6e-6	1.9e-5
Movement from right surface to bridge surface					
C10E4	0.0033	0.0036	0.0031	0.0019	0.0018
C10E8	0.0043	0.0023	0.0032	0.0015	0.0013

Concentration (CAC):	0.8	1.6	3.2	4.7	6.1
Movement from right surface to left surface					
C10E4	0.0025	0.0031	0.0024	0.0024	0.0019
C10E8	0.0021	0.0019	0.0013	0.0020	0.0028
Movement from right surface to left bulk					
C10E4	0.0000	2.2e-5	1.4e-5	3.3e-5	7.5e-5
C10E8	1.1e-5	3.6e-5	1.7e-5	2.5e-5	3.4e-5

BRIDGE GROWTH DYNAMICS



FIG. S1. Bridge growth dynamics (b, radius of the bridge) vs. time for droplets with different surfactant (C10E8) concentrations, as indicated in the legend. CAC ≈ 7.5 wt%. Power law fits are also shown, tentatively identifying the inertial (IR, $b = b_0 t^{\beta}$) regime (t_c is the time that the permanent contact between the droplets is established). l_w is the thermal length for pure water droplets and l_s for surfactant-laden droplets above CAC according to Ref. [1] (see main text for further details). The inset highlights the power law scaling in the inertial regime.

Figure S1 illustrates the bridge growth dynamics and gives the fit coefficients for the inertial regime (IR) for the C10E8 surfactant.

 S. Perumanath, M. K. Borg, M. V. Chubynsky, J. E. Sprittles, and J. M. Reese, Phys. Rev. Lett. 122, 104501 (2019).

4.2 Molecular Dynamics Simulation of the Coalescence of Surfactant-Laden Droplets

4.2.1 Summary of Key Findings of this Publication:

In this work, we studied coalescence of freely suspended surfactant-laden droplets. Considering three types of surfactant (C10E4 and C10E8 and Silwet-L77) in order to assess the effect of different surfactant types and concentrations on the coalescence process. These surfactants—C10E8, C10E4, and Silwet-L77—are all non-ionic. C10E8 is similar to C10E4 in its hydrophobic part but has a longer hydrophilic tail. Silwet-L77, known as a superspreading surfactant, has a hydrophilic part with the same number of beads as C10E8. However, it stands out due to variations in hydrophobic chemical units and overall molecular structure. We compared the mass transport mechanisms of all three types of surfactants at various concentrations. Additionally, in this study, we examined the mass transport mechanisms both below and above the CAC. Furthermore, we investigated the velocity of approach between two droplets and explored other geometric features of the system, such as its asphericity. The key findings of this work are summarized as follows:

- We demonstrated that pinching begins with the hydrophobic beads, and the main motion within the bridge occurs from the bulk of the bridge toward the bridge's surface. In this study, we have reaffirmed this observation for two additional types of surfactants at various concentrations. Through a comparative analysis of different surfactants, we have revealed that Silwet-L77 exhibits lower aggregate density, leading to slight variations in bridge dynamics and mass transport mechanisms.
- In scenarios with surfactant concentrations below the CAC, pinching still begins
 with the aggregation of hydrophobic beads. However, there is no continuous film
 present between the coalescing droplets, and we do not observe the formation of
 new aggregates inside the bridge due to the low surfactant concentration.
- The presence of both the thermal and inertial regimes is observed in all three types of surfactants. When surfactant is introduced into the system, it generally slows down the growth process. Furthermore, the transition from the thermal to the inertial regime takes longer in the case of surfactant-laden droplets compared to pure water droplets. We have also conducted a comparison of surfactants and demonstrated that above the CAC, the growth rate of the bridge is slower in the case of Silwet-L77 compared to other types.
- We elucidated the velocity of approach between two droplets during the coalescence process by measuring the system length along the axis that passes through the centre of mass of each droplet over time and calculated its derivative, which represents the velocity of approach. As the surfactant concentration increases, the velocity of approach decreases, and droplets containing surfactant consistently

exhibit a smaller maximum speed. Silwet-L77 displayed significantly slower growth in all aspects, particularly with a lower maximum velocity.



Figure 4.2: Stages of Coalescence of surfactant-laden droplets, Reprinted from [Soheil Arbabi, Piotr Deuar, Mateusz Denys, Rachid Bennacer, Zhizhao Che, and Panagiotis E. Theodorakis, *Molecular Dynamics Simulation of the Coalescence of Surfactant-Laden Droplets*, Soft Matter, **19**, 8070-8080 (2023) https://doi.org/10.1039/D3SM01046E].

4.2.2 Details of publication

Molecular Dynamics Simulation of the Coalescence of Surfactant-Laden Droplets

PDF of this publication is reproduced from [Soheil Arbabi, Piotr Deuar, Mateusz Denys, Rachid Bennacer, Zhizhao Che, and Panagiotis E. Theodorakis, *Molecular Dynamics Simulation of the Coalescence of Surfactant-Laden Droplets*, Soft Matter, **19**, 8070-8080 (2023). https://doi.org/10.1039/D3SM01046E]. According to the website of publisher: "If you are the author of this article, you do not need to request permission to reproduce figures and diagrams provided correct acknowledgement is given. If you want to reproduce the whole article in a third-party publication (excluding your thesis/dissertation for which permission is not required)".



Soheil Arbabi

Institute of Physics, Polish Academy of Sciences (PAN)

Theoretical Physics Division (ON5),

Al. Lotników 32/46 02-668 Warsaw, Poland

arbabi@ifpan.edu.pl

STATEMENT

I declare that I am the co-author of the publication:

Molecular dynamics simulation of the coalescence of surfactant-laden droplets, Soft Matter, **19**, 8070-8080 (2023), https://doi.org/10.1039/D3SM01046E

I contributed equally to the conceptualization. I took the lead role in data curation, analysis, investigation, methodology, simulations, validation, visualization and writing the draft. In addition, I played an equal part in review, and editing tasks.

signature:

Scheil Irbabi



dr hab. Piotr Deuar Head of the Quantum Noise group Institute of Physics, Polish Academy of Sciences (PAN) Theoretical Physics Division (ON5), Al. Lotników 32/46 02-668 Warszawa, Poland <u>deuar@ifpan.edu.pl</u>

STATEMENT

I declare that I am the co-author of the publication:

Molecular dynamics simulation of the coalescence of surfactant-laden droplets, Soft Matter, **19**, 8070-8080 (2023), https://doi.org/10.1039/d3sm01046e

My contributions included supporting mr Arbabi in analysis, conceptualization, as well as participation in discussions, reviewing and editing the draft, and co-supervision.

signature:



Dr.Mateusz Denys

Institute of Physics, Polish Academy of Sciences (PAN)

Theoretical Physics Division (ON5),

Al. Lotników 32/46 02-668, Warsaw, Poland

STATEMENT

I declare that I am the co-author of the publication:

Molecular dynamics simulation of the coalescence of surfactant-laden droplets, Soft Matter, **19**, 8070-8080 (2023), https://doi.org/10.1039/D3SM01046E

My contribution was supporting in Conceptualization and participation in discussions and reviewing the draft.

signature:





Département Génie Civil et environnement e-mail : <u>rachid.bennacer@ens-Paris-Saclay.fr</u> www.dgc.ens-paris-saclay.fr

STATEMENT

I declare that I am the co-author of the publication:

Molecular dynamics simulation of the coalescence of surfactant-laden droplets, Soft Matter, **19**, 8070-8080 (2023), https://doi.org/10.1039/D3SM01046E

My contributions included supporting conceptualization, participating in discussions, and reviewing/editing the draft.

Paris-Saclay le 07/12/2023



Zhizhao Che, PhD, Professor State Key Laboratory of Engines, Tianjin University 135 Yaguan Road, Haihe Education Park, Tianjin, 300350, China Email: chezhizhao@tju.edu.cn

STATEMENT

I declare that I am the co-author of the publication:

Molecular dynamics simulation of the coalescence of surfactant-laden droplets, Soft Matter, **19**, 8070-8080 (2023), https://doi.org/10.1039/D3SM01046E

My contribution involved supporting conceptualization, participating in discussions, and reviewing/editing the draft.

signature: Chell

Dr hab. Panagiotis Theodorakis Division of Theoretical Physics (ON5) Al. Lotników 32/46 02-668 Warsaw, Poland

STATEMENT

I declare that I am the co-author of the publication:

• Molecular dynamics simulation of the coalescence of surfactant-laden droplets S. Arbabi, P. Deuar, M. Denys, R. Bennacer, Z. Che, P. E. Theodorakis *Soft Matter* **19**, 8070 (2023), doi: 10.1039/d3sm01046e

My contribution was supervising the project, helping in the interpretation of the results, and in manuscript writing.

Warsaw, 09.12.2023 Panagiotis Theodorakis

Volume 19 Number 42 14 November 2023 Pages 8043-8276

Soft Matter

rsc.li/soft-matter-journal



ISSN 1744-6848



PAPER Panagiotis E. Theodorakis *et al.* Molecular dynamics simulation of the coalescence of surfactant-laden droplets

Soft Matter

PAPER



Cite this: Soft Matter, 2023, **19**, 8070

Received 7th August 2023, Accepted 2nd October 2023 DOI: 10.1039/d3sm01046e

rsc.li/soft-matter-journal

1 Introduction

While ubiquitous in nature, droplet coalescence is also an important process in various industrial applications, where the rate of coalescence can determine their performance. For example, in the context of bio-related microfluidic technologies, slowing down coalescence in bio-particle encapsulation on lab-on-chip devices is often desirable, and can be achieved by using various additives, such as surfactants.^{1,2} In contrast, speeding up the rate of coalescence by adding surfactant could be advantageous in applications, such as coatings³ and superspreading.4,5

Experimental, theoretical, and numerical studies of coalescing droplets have thus far mainly focused on cases without additives, e.g. water or polymer droplets.⁶⁻³⁰ From the point of view of numerical simulations, these have by and large provided descriptions of the macroscopic and dynamic properties of coalescence,^{7,8,20–22,31–33} but they generally continue to suffer from inadequate resolution at the pinching point between droplets at the initial stage of coalescence, despite progress in this area.¹² Moreover, a detailed molecular-level description

Molecular dynamics simulation of the coalescence of surfactant-laden droplets[†]

Soheil Arbabi, 💿 a Piotr Deuar, 💿 a Mateusz Denys, 💿 a Rachid Bennacer, b Zhizhao Che[©]^c and Panagiotis E. Theodorakis[®]*^a

We investigate the coalescence of surfactant-laden water droplets by using several different surfactant types and a wide range of concentrations by means of a coarse-grained model obtained by the statistical associating fluid theory. Our results demonstrate in detail a universal mass transport mechanism of surfactant across many concentrations and several surfactant types during the process. Coalescence initiation is seen to occur via a single pinch due to aggregation of surface surfactant, and its remnants tend to become engulfed in part inside the forming bridge. Across the board we confirm the existence of an initial thermal regime with constant bridge width followed by a later inertial regime with bridge width scaling roughly as the square root of time, but see no evidence of an intermediate viscous regime. Coalescence becomes slower as surfactant concentration grows, and we see evidence of the appearance of a further slowdown of a different nature for several times the critical concentration. We anticipate that our results provide further insights in the mechanisms of coalescence of surfactant-laden droplets.

> of the mass transport mechanism of surfactant is beyond the reach of any continuum model.^{10,34}

> Various attempts have been made to tackle this challenge. For example, numerical models based on advection-diffusion equations and chemical kinetic fluxes attempt to incorporate the mass transport of surfactant into the equations,³⁵ but these are only as good as the assumptions put into the model, while a detailed molecular description still remains out of reach for continuum simulation. When it comes to experimental techniques,^{34,36-44} high-speed imaging and particle-image velocimetry have been applied in investigating coalescence of surfactant-laden droplets, and have mainly focused on the macroscopic description of this phenomenon, much as in the case of numerical simulation. Due to device limitations, capturing with high resolution the early stages of coalescence during experiments poses a major challenge. Both experiments and continuum modelling are unable to provide a detailed description of the mass transport mechanism at the molecular level. In the case of molecular simulations, all-atom molecular dynamics (MD) has explained different microscopic aspects of coalescence, such as the role of the capillary waves on droplets' surface, but these have only been in the context of pure water droplets,9 except for one recent study which considered a few cases.45

> On the whole, though, the effect of surfactant in droplet coalescence has largely remained unexplored, with implications actually reaching beyond this, for example, in the context of surfactant-laden coalescence between micelle and bilayer.46



View Article Online

^a Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46,

⁰²⁻⁶⁶⁸ Warsaw, Poland. E-mail: panos@ifpan.edu.pl

^b Université Paris-Saclay, CentraleSupélec, ENS Paris-Saclay, CNRS,

LMPS - Laboratoire de Mécanique Paris-Saclay, 91190, Gif-sur-Yvette, France

^c State Key Laboratory of Engines, Tianjin University, 300350 Tianjin, China † Electronic supplementary information (ESI) available. See DOI: https://doi.org/

^{10.1039/}d3sm01046e

Paper

The initial work⁴⁵ suggests that it plays an important role, *e.g.* affecting the coalescence rate and dampening internal droplet dynamics. Reduction of the surface tension at the liquid–gas (LG) interface is usually expected, but the type of surfactant (*e.g.*, chemical groups and molecular architecture) and its concentration are also anticipated to differently affect the coalescence process. Differences are expected even when the concentration is higher than the critical aggregation concentration (CAC) and surface tension at the LG interface is expected to remain constant.^{47–51} On that account, unveiling the details of this phenomenon from a molecular-level perspective is key for fundamentally understanding the underlying mechanisms that can lead to tailor-made surfactant designs for applications.

Here we report on a more detailed and robust study of droplet coalescence using the methods of ref. 45, and a broader range of surfactants and their concentrations. We employed a high-fidelity coarse-grained force-field enabling us to simulate with MD the coalescence of surfactant-laden droplets. We discuss the details of coalescence at each stage of the process by comparing systems with different surfactant type and concentration. Our data indicate that the underlying mechanisms of coalescence are consistent between the different cases, which point to universal features of surfactant transport and droplet dynamics for the coalescence of water droplets with surfactant. Differences in the behaviour of different surfactants are also highlighted when relevant. The dynamic and static characteristics are unveiled by discussing both macroscopic- and molecular-level quantities, such as the bridge growth dynamics and the velocity of droplet approach, as well as describing the molecular transport of surfactant within the liquid phase. Thus, we anticipate that the present study lays a comprehensive account of the coalescence of surfactant-laden droplets.

In the following section, we provide background information for droplet coalescence. Then, Section 3 gives details on our model and methodology, while Section 4 presents and discusses the results of the coalescence simulations. Section 5, draws some broader conclusions.

2 Background

A macroscopic description of the droplet coalescence can generally be divided into three stages (see Fig. 1). The approach of the droplets, which leads to the initiation of the phenomenon (pinching) as a result of the inter-molecular interactions; the subsequent growth of the bridge formed between the droplets; and the final stage towards equilibrium, which manifests itself by the formation of a single spherical droplet. The system is driven towards the equilibrium state as it seeks to minimise the free-energy associated with the surface tension at the droplet boundary. Hence, on the coarsest level, the formation of larger droplets is energetically favourable. In particular, for a droplet with *N* beads, the droplet radius behaves as $R_0 \propto N^{1/3}$ (Fig. 1a) since the volume scales as *N*, while surface tension force as $\propto N^{2/3}$.



Fig. 1 Coalescence of droplets with C10E4 surfactant at low concentration (6.25 wt%, top of each panel) below CAC = 7.5 wt% and concentrations above CAC (24.18 wt%, bottom of each panel). Snapshots show the initial approach of the droplets (a), their pinching and initial formation of the bridge (b), see also ESI,† for a movie showing the pinching of the droplets, configurations with a partially (c) and fully (d) developed bridge, and the final equilibrium state (e). External or cross-section views are shown to highlight the bulk, surface, and bridge structure of the droplets. Magnified views of a micelle, a surfactant molecule, and a water bead are shown in panel (a). Water vapour surrounding the droplets is not shown for the sake of clarity.

The rate of bridge growth after the initial contact is key for characterising the coalescence process and can generally be described from the point of view of fluid dynamics by two successive regimes, namely the viscous regime (VR) and the inertial regime (IR).^{6,52} Moreover, recent MD simulations have uncovered the existence of a third, thermal regime (TR) during the droplet pinching at the very initial stage of the coalescence process,^{9,45} which will be discussed later in more detail. The characteristic velocity in the VR can be defined as $v_v = \gamma/\eta$, where γ is the surface tension and η the viscosity, which suggests that the capillary number Ca = $\eta v_v / \gamma \sim 1$, with the characteristic time scale for droplet-sized effects being $t_v = R_0 \eta / \gamma$,¹⁰ with R_0 the droplet radius as in Fig. 1. As coalescence proceeds to the subsequent IR, the bridge flow can be characterised by the Weber number, namely We = $\rho v_i^2 R_0 / \gamma \sim 1$ indicating the limit that inertia effects will take over the surface tension effects, while ρ is the density of the fluid. The bridge velocity is found to scale as $v_i \sim \sqrt{\gamma/\rho R_0}$, and thus the characteristic time scale is $t_i = \sqrt{\rho R_0^3 / \gamma}$. For many purposes, especially in the VR, the more relevant length scale is the radius of the bridge, b (Fig. 1), and the corresponding Reynolds number can be defined as Re = $\rho b/\eta$, which in the VR is $\rho \gamma b/\eta^2$. On the one hand, since the bridge radius is very small in the initial stage, the viscous forces are dominant regardless of the values of γ and η and Re \ll 1. On the other hand, Re \geq 1 reflects the IR.⁵³ Hence, it can be taken that the crossover between the viscous and the inertial regimes would take place for Ca ~ 1 or Re ~ 1 . Taking the IR expression $v_i \sim \sqrt{\gamma/b\rho}$ using bridge size, we obtain an estimate of the crossover bridge-radius, $b_c = \eta^2 / \rho \gamma$,

and a characteristic time $t_c = \eta^3 / \rho \gamma^2$, which for water droplets would roughly correspond to $b_c \sim 15$ nm and $t_c = 0.1$ ns, highlighting the fast time scales of coalescence.¹¹

In the VR, where inter-molecular forces are playing a dominant role in pulling the droplets together, a linear scaling has been proposed for the growth of the bridge radius with time, *i.e.* $b \propto t$, as well as logarithmic corrections, $b \propto t \ln t$.^{10,34} In the case of the IR, a power-law scaling law has been suggested for the bridge, namely $b \propto \sqrt{t}$.^{10,34} Experimental studies on the coalescence of water droplets are consistent with this and have shown that 0.7 ns after the first contact of the droplets, drag forces give way to the inertial ones and the bridge radius has been reported to scale with time as $b \propto$ $(R_0\gamma/\rho)^{1/4}t^{1/2}$ where R_0 is the initial droplet radius.^{10–12,53,54} Other works have proposed scaling regimes that depend on the ratio of characteristic scales to the viscous length scale $l_{\rm v}$ = $\eta^2/\rho\gamma.^{52,55}$ Moreover, it is argued that the inertia of the droplets cannot be neglected at the initial stage of coalescence. Then, the initial stage would be better described as inertially limited viscous (ILV) regime and a linear scaling with time for the bridge radius has been proposed, which, according to numerical simulations, is only realised when the coalescing drops are initially separated by a finite distance.²⁰ In the case of miscible and immiscible droplets, a similar viscous dominated regime has been suggested, but immiscible droplets seem to develop a bridge slower.56

All-atom molecular dynamics simulations of pure twodimensional (cylindrical) water droplets have found that multiple precursor bridges develop via thermal fluctuations at the droplet's surface, which initially connect the droplets and then grow, thus identifying a thermal regime at the onset of coalescence.9 After a certain threshold, when the radius of the growing bridge becomes larger than a thermal length scale, $l_{\rm T} \approx (k_{\rm B}T/\gamma)^{1/4} R_0^{1/2}$, the hydrodynamic regime is recovered, continuum models can describe the process, and one expects VR, IR, or ILV scaling. $k_{\rm B}$ is Boltzmann's constant and T the temperature. Since surface tension appears in the denominator, the addition of surfactant, which lowers the surface tension, is expected to lead to the increase of the thermal length, $l_{\rm T}$, towards an upper limit that is attained above the CAC. Moreover, these all-atom MD simulations have found that, in the TR, the bridge radius expands linearly in time with a velocity much faster than the viscous-capillary regime due to the thermal, molecular 'jumps' at the droplets' surface where multiple bridges are formed.9 The initial thermal regime has also been recently observed in the case of coarse-grained models for pure and surfactant-laden three-dimensional (spherical) droplets, without the formation of multiple thermal bridges but a single pinching point instead.45

The above considerations indicate that coalescence is still under intensive debate even in the case of pure water droplets. Moreover, only a few studies have dealt with droplet coalescence in the presence of surfactant.^{36–38,40–44,57–66} While it is generally expected that surfactant would decrease the surface tension of the droplets and a delay in the process would be potentially forecast,^{39,61} comprehensive understanding is currently lacking, which calls for a systematic investigation of different surfactants for a range of concentrations. It has been experimentally shown that the presence of surfactant would locally reduce the surface tension on the droplet surface and a nonuniform surfactant concentration would lead to surface tension gradients that would eventually lead to surface flow (Marangoni flow) and a rearrangement of the surfactant molecules to counteract the gradient would delay the coalescence process.³⁶ One might also attempt to see whether the diffusion and adsorption of surfactant at the droplets' LG interface would further affect the coalescence process, for example, by influencing the flow field of the water molecules,⁴⁵ especially when surfactant concentration is above the CAC and surfactant aggregates are present in large amounts within the liquid bulk. MD simulations based on a high-fidelity coarse-grained forcefield are capable of addressing these and other questions.

3 Model and methods

An important motivation for choosing the force-field for the problem at hand is the ability to simulate relatively large droplets that could allow for the investigation of the surfactant mass transport mechanism with MD. Based on the fact that coarse-grained force-fields would be a natural choice in this case, and our success in previous investigations on the mass transport mechanism of surfactant in the context of the superspreading phenomenon,^{4,5,67-69} we have embarked on carrying out our studies here by using MD simulations based on the SAFT (statistical associating fluid theory) force-field.⁷⁰⁻⁷⁵ More specifically, a force-field based on the SAFT- γ Mie theory⁷⁶ is used, which can accurately reproduce relevant key properties of water–surfactant systems, such as their phase behaviour and surface tension.^{5,67,77-79}

In the case of the SAFT force-field, interactions between different coarse-grained (CG) beads within a distance smaller than r_c are described *via* the Mie potential, which is mathematically expressed as

$$U(r_{ij}) = C \varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{\lambda_{ij}^{r}} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{\lambda_{ij}^{a}} \right], \quad r_{ij} \leq r_{c},$$
(1)

where

$$C = \left(\frac{\lambda_{ij}^{\mathrm{r}}}{\lambda_{ij}^{\mathrm{r}} - \lambda_{ij}^{\mathrm{a}}}\right) \left(\frac{\lambda_{ij}^{\mathrm{r}}}{\lambda_{ij}^{\mathrm{a}}}\right)^{\frac{\lambda_{ij}^{\mathrm{a}}}{\lambda_{ij}^{\mathrm{r}} - \lambda_{ij}^{\mathrm{a}}}}.$$
 (2)

i and *j* are the bead types, σ_{ij} indicates the effective bead size, and ε_{ij} is the interaction strength between any beads of type *i* and *j*. $\lambda_{ij}^{a} = 6$ and λ_{ij}^{r} are Mie potential parameters, while r_{ij} is the distance between two CG beads. Units are chosen for the length, σ , energy, ε , mass, *m*, and time τ , which in real units would correspond to: $\sigma = 0.43635$ nm, $\varepsilon/k_{\rm B} = 492$ K, m = 44.0521 amu and $\tau = \sigma(m/\varepsilon)^{0.5} = 1.4062$ ps. All simulations are carried out in the *NVT* ensemble by using the Nosé–Hoover thermostat as implemented in the LAMMPS package⁸⁰ with an integration time-step $\delta t = 0.005\tau$. Our simulations took place at room



Fig. 2 Coarse-grained representation of water and surfactant molecules. Surfactant's hydrophobic beads are shown in red, while the hydrophilic parts of the surfactant are in yellow. A cyan bead corresponds to two water molecules (a). C10E8 (b), C10E4 (c), and Silwet-L77 (d) CG surfactant models.

temperature (T = 25 °C), which in the simulation units corresponds to $T = 0.6057\varepsilon/k_{\rm B}$. Finally, a universal cutoff for all nonbonded (Mie) interactions is set to $r_{\rm c} = 4.583\sigma$.

We have considered surfactants of type CiEj, such as C10E8 and C10E4 (Fig. 2b and c) and a trisiloxane surfactant.^{4,48–51,67–69} In the case of CiEj surfactants, a hydrophobic alkane CG 'C' bead represents a $-CH_2-CH_2-CH_2-$ group of atoms, while a hydrophilic CG 'EO' bead represents an oxyethylene group $-CH_2-O-CH_2$. Silwet-L77 (Fig. 2d) is also considered as a trisiloxane surfactant with the same number of beads as in the case of C10E8, but different hydrophobic chemical units and architecture, where M type beads represent a chemical group $(-CH_3)_3$ -Si-O_{1/2} and D type O_{1/2}- (CH₃)₂-Si-O_{1/2}. Finally, a water CG 'W' bead corresponds to two water molecules (Fig. 2a). The nonbonded interaction parameters between the above chemical groups, which can be used in practice to simulate a wide range of surfactants with different molecular architecture are reported in Table 1, while the mass of each CG bead is documented in Table 2.

To tether beads together in the case of surfactant chains, a bond potential is required, which in the case of this model is harmonic, *i.e.*,

$$V(r_{ij}) = 0.5k(r_{ij} - \sigma_{ij})^2,$$
(3)

where the harmonic constant $k = 295.33 \ \varepsilon/\sigma^2$. Moreover, EO beads experience a harmonic angle potential,

Table 1	Summary of Mie interaction parameters (eqn (1)). $\lambda_{ij}^{a} = 6$				
i–j	$\sigma_{ij}\left[\sigma ight]$	$arepsilon_{ij}\left[arepsilon/k_{ m B} ight]$	$\lambda^{ m r}_{ij}$		
W–W	0.8584	0.8129	8.00		
W–C	0.9292	0.5081	10.75		
W-EO	0.8946	0.9756	11.94		
W-M	1.0491	0.8132	13.72		
W–D	0.9643	0.6311	10.38		
C–C	1.0000	0.7000	15.00		
C-EO	0.9653	0.7154	16.86		
M-M	1.2398	0.8998	26.00		
M-D	1.1550	0.7114	18.83		
M-EO	1.0853	0.8262	22.18		
D-D	1.0702	0.5081	13.90		
D-EO	1.0004	0.6355	16.21		
EO-EO	0.9307	0.8067	19.00		

View Article Online

Soft Matter

Bead type	Mass [m]
W	0.8179
С	0.9552
EO	1.0000
М	1.8588
D	1.6833

$$V_{\theta}(\theta_{ijk}) = 0.5k_{\theta}(\theta_{ijk} - \theta_0)^2, \qquad (4)$$

where θ_{ijk} is the angle between consecutive beads *i*, *j* and *k* (here, *i*, *j*, *k* indicate the order of EO beads instead of bead type), $k_{\theta} = 4.32\varepsilon \text{ rad}^{-2}$, and $\theta_0 = 2.75$ rad is the equilibrium angle. Further discussion on the model can be found in previous studies.⁶⁷⁻⁶⁹

To prepare the initial configuration of each system, individual droplets were first equilibrated in the NVT ensemble. The total number of beads in the simulations was 10⁵ per initial droplet, with approximately 5% evaporation into the gas. Droplet diameters were $\sim 53\sigma$, which is about 23 nm, similar to that of several previous studies.^{9,45} Careful consideration was given not only to observing the energy of the system, but, also, making sure that the distribution of surfactant clusters has reached a dynamic equilibrium and that each of them was able to diffuse a distance many times its size. After equilibration of the individual droplets, the volume of the simulation box was doubled and the two droplets (and the surrounding gas) were placed next to each other as shown in Fig. 1a. In this way, roughly the same thermodynamic conditions are maintained and further evaporation that would reduce the number of water molecules of the droplets is avoided. The final size of the simulation box is also chosen large enough to avoid the interaction of mirror images of the droplets over the periodic boundary conditions. Fig. 1 illustrates typical snapshots at different stages during coalescence for cases below and above CAC. For our study, we have considered a range of different surfactant concentrations up to about $6 \times CAC$, which cover the relevant span of phenomena. A summary of the mean values of various properties for our systems is given in Table 3. We can see that increasing surfactant concentration slightly increases the size of the droplet. Also, note that the CAC in the case of Silwet-L77 in terms of wt% is almost double that of C10E4 and C10E8 surfactants.

To obtain reliable estimates of the bridge growth dynamics and the mass transport mechanism, snapshots of the system are made frequently (every 250 MD time steps) for the initial 4×10^5 MD time steps, and cluster analysis is performed to identify the beads belonging to the liquid phase (droplets), which is used for our properties analysis. The bridge region is chosen to be a slab with a width in the *X* (approach) direction that is calculated for each configuration. In particular, the left and right limits of the slab are determined by analysing the grid points on the *X*–*Z* plane at position *Y* = 0 according to the procedure shown in Fig. 3b. We fit a circle around each droplet and note the surface grid positions at the central *X* = 0 position, shown by the red points in Fig. 3b. Horizontal lines are drawn

Table 3 Properties of individual droplets (equilibrium)

Concentration (wt%)	Diameter (σ)	Water beads ^a	# Molecule
C10E4			
6.25	53.08	90466.09	714
12.37	53.02	85496.45	1429
24.18	53.62	75572.27	2857
35.48	54.14	65746.73	4286
46.02	54.63	55966.55	5714
CAC \approx 7.5 wt%			
C10E8			
6.25	52.74	90519.09	455
12.37	52.98	85500.09	909
24.18	53.40	75722.36	1818
35.48	53.91	65862.36	2727
46.02	54.33	56488.91	3636
CAC \approx 7.5 wt%			
Silwet-L77			
7.6	52.62	90438.45	455
14.8	53.01	85574.64	909
28.2	53.89	75786.36	1818
40.3	54.78	66312.82	2727
51.2	55.71	56787.91	3636
CAC \approx 16.23 wt%			
-			

^{*a*} Indicates the average number of water beads.

in the *X* direction passing through these red points to touch the fitted circles, thus defining the rectangle in green. The vertical sides of the rectangle give the limits of the bridge slab in the *X* direction, and its width. All molecules with centres having *X* coordinates inside these limits are labelled as belonging to the bridge in a given snapshot. On the other hand, the bridge radius *b* shown in Fig. 1c and 3 is calculated using the distances between extrema of the positions of the beads belonging to the grids located at X = 0. That is this distance is first calculated



Fig. 3 Bridge analysis and domains for analysing the mass transport mechanism. Six different regions for the position of the molecules within the droplets are considered, namely, bridge bulk and surface, left and right surface and bulk. (a) A snapshot obtained by the MD simulation with a clearly developed bridge length. (b) Analysis of an X-Z projection for identifying the bridge based on the method described in Section 3. (c) Different regions of the droplets considered for analysing the mass transport mechanism of surfactants between these regions (see ESI† for further details).

separately for the *Z* coordinate to give a distance $2b_Z$, and then for the *Y* coordinate to give $2b_Y$. The final bridge radius estimate is then given by $b = (b_Z + b_Y)/2$.

We also describe the mass transport mechanism by tracking each surfactant molecule during the coalescence and then identifying the probability of adsorption of each molecule to different regions in the liquid phase, namely the left and right LG surfaces and the bulk, and the surface and interior of the bridge (Fig. 3b and c). Further discussion and details on the calculation of probabilities related to the mass transport mechanism can be found in the ESI.† Finally, we have calculated the density profiles of the water and surfactant molecules during coalescence, the flow field at different times, as well as the approach distance and velocity of approach of the droplets and their asphericity, for which further details are discussed in the ESI.†

4 Results and discussion

4.1 Coalescence mechanism

The initial stage of droplets' coalescence manifests itself *via* their pinching as illustrated by the snapshots of Fig. 4 and movies in the ESI.[†] In this early stage of the phenomenon, a previous study on coalescence with pure water droplets has shown *via* all-atom MD that multiple bridges form on the surface of the droplets and the overall radius of the affected region grows linearly over time.⁹ Here, we rather see that the droplet pinching initially involves only the surfactant molecules at the droplets' surfaces, particularly when the surfactant concentration is higher. Here and in those previous results the size of the droplets are about the same. Fig. 4 illustrates the single pinching of the droplets based on our model, whereby hydrophobic parts of the surfactants come together forming



Fig. 4 Pinching of droplets with C10E4 surfactant in the TR for concentration above (a, 35.4 wt%) and below (b, 6.25 wt%) CAC. For each case, a magnified view of the initial bridge formation is shown, as well as the distribution of surfactant (hydrophobic beads in red and hydrophilic in yellow colour) and water molecules (cyan colour). (a) $t = t_c + 8.75\tau$, (b) $t = t_c + 8.75\tau$.

Paper



Fig. 5 Density profiles of surfactant beads, C10E4 (46.2 wt%) (upper row) and water beads (lower row) on the mid plane (width of 6σ) at different stages after the time t_c at which a permanent contact between the droplets is established (a) $t = t_c \tau$, (b) $t = t_c + 71.25\tau$, (c) $t = t_c + 98.75\tau$.

aggregates, while water molecules remain further from the pinching point (Fig. 4). By inspecting the density profile of the droplets during coalescence and considering a cross-section on the X-Y plane passing through the centre of mass of the droplets for high-concentration droplets, we can better highlight the aggregates at the cross-section (Fig. 5). One can observe that the water density between the droplets is negligible (the grid used for the calculation of the density profile does not resolve the bead size), in contrast to the density of surfactant. Therefore, the latter is solely responsible for the droplet pinching. At later times and when the bridge has developed past the very initial pinching stage, water molecules become

part of the bridge (Fig. 5b). However, the bridge region is still dominated by the presence of surfactant, with surfactant density values similar to those inside aggregates. It is notable that surfactant continues to be present in the bridge in significant amounts even at later stages of coalescence, when the bridge has been almost fully developed (Fig. 5c). The reasons for this will become more apparent when further details on the surfactant mass transport are unveiled.

After the initial droplet pinching (Fig. 4), the contact between the droplet persists and the growth of the bridge, which manifests by the large change in curvature at the surface, takes place as shown in Fig. 6. Moreover, we analysed the surfactant mass transport mechanism during coalescence, and the main adsorption processes of surfactant were monitored. These processes are described by the probabilities of surfactant remaining at a particular region or moving between the different regions shown in Fig. 3c during coalescence. These are documented in the ESI⁺ for all surfactant types and concentrations considered in our study. On the basis of these probabilities we have indicated by arrows the main surfactant movements (Fig. 6). In particular, the concentration of surfactant is high at the initial contact of the droplets due to the preexisting surfactant at the droplet surfaces (Fig. 6a and d), which becomes trapped in between the droplets. As the bridge gradually grows, we observe that most of the surfactant, which was initially on the surfaces of the droplets, preferably moves towards the surface of the bridge, which is energetically more favourable. However, the bridge surface has limited place for



Fig. 6 Mass transport mechanism of surfactant (C10E8) during the coalescence process, for concentrations above (upper panel) and below (lower panel) CAC. The size of the arrows reflects the probabilities associated with surfactant transport to the different droplet areas (see Table S4 of the ESI† for further details). Above the CAC (a–c, 46.2 wt%) snapshots were obtained at times (a) $t_c + 22.5\tau$, (b) $t_c + 172.5\tau$, (c) $t_c + 480.0\tau$ while below the CAC (d–e, 6.2 wt%) times shown are (d) $t_c + 25.0\tau$, (e) $t_c + 66.3\tau$, (f) $t_c + 116.3\tau$, soon after the end of the thermal regime (a,d), the development of the bridge and the formation of new aggregates (b) or surfactant monomers remaining in the bridge region (e), and the full development of the bridge (c) and (f). Magnified views of the bridge region and its cross-section (showing only surfactant hydrophobic beads in the bridge region, red) are attached above and to the right of the snapshots, respectively. Fig. S4 in the ESI† illustrates results for the C10E4 surfactant.



Fig. 7 Density profiles of a *X*-*Y* cross-section (*X* and *Y* are the coordinates of the centre point of each grid voxel) passing through the centre of mass of the droplets with (a) C10E4 (46.2 wt%) $t = t_c + 288.75\tau$ and (b) Silwet-L77 (51.2 wt%), $t = t_c + 437.50\tau$. Upper panels show the number density of the surfactant beads, lower panels of the water.

accommodating all surfactant from the initial LG surfaces of the droplets, since in this area between the droplets the surface excess concentration is doubled at the initial approach. As a result, some surfactant remains in the bulk and forms new aggregates, which is most clearly seen in the case of higher surfactant concentrations (Fig. 6b, c and Fig. S1–S3 and movie in the ESI†). In contrast, when the concentration is lower than CAC, the bridge surface is able to accommodate surfactant molecules that existed on the LG surfaces before the coalescence (see Tables S1–S3, ESI† for detailed surfactant counts).

We observe that most of the surfactant activity takes place in the bridge area and that the dominant process is transport towards the bridge surface. We do not see any clear evidence of Marangoni flow in the studied system, possibly due to there not being enough space or time for it to develop. By analysing our data, we have verified that the qualitative features of the mass transport mechanism are independent of the surfactant type or concentration, while the largest quantitative differences were seen in the case of Silwet-L77. In particular, Silwet-L77 tends to form a larger number of aggregates but their overall density is lower than that of the C10E4 and C10E8 surfactants, which also implies that higher quantities of water molecules are found among surfactant in the case of droplets with Silwet-L77. To illustrate these effects, the density profiles of droplets with either C10E4 or Silwet-L77 with high surfactant concentration are plotted in Fig. 7. Finally, in terms of the mass transport (Table S4 in the ESI⁺ contains details), we find that Silwet-L77 have a higher tendency to move towards the surface of the bridge in comparison with C10E4 and C10E8 surfactants, which is in line with previous observations in systems with surfactant-laden droplets.⁶⁹ In turn, this results in the formation of fewer aggregates in the bridge in the case of droplets with Silwet-L77 surfactant.

4.2 Water flow

In a previous study,⁴⁵ we have shown that the coalescence of water droplets is characterised by intense internal flow variations during the thermal regime, which attenuate with the increase of surfactant concentration. Fig. 8 illustrates the flow of water in the case of water droplets and those with surfactant

View Article Online



Fig. 8 Flow field of water inside the droplets for the case without surfactant (a)–(c), with C10E4 (46.2 wt%, d–f), and with Silwet-L77 (51.2 wt%, g–i) surfactant. Cross-sections through the centre of mass are shown. Red reflects the intensity of flow motion (only water) toward the bridge X component of velocity, blue away from the bridge. The averaged data of red and blue grids indicating the total flow towards the bridge and away of it in the droplets and in the bridge region are reported in the ESI† and discussed further in the main text. Note that the white space between the water areas (e.g. in the bridge) includes surfactant aggregates and surfactant on the surface. The snapshots were obtained at times (a), (d) and (g) t_c , (b) $t_c + 90.75\tau$, (c) $t_c + 275.25\tau$, (e) $t_c + 183.75\tau$, (f) $t_c + 2446\tau$, (h) $t_c + 425\tau$, and (i) $t_c + 2437.5\tau$.

after the initial thermal regime and at the initial stages of the power-law (IR) regime. Firstly, as expected, the data suggest that there is an increased water flow toward the bridge (red colour) throughout the coalescence process. This is particularly visible in the bulk in the IR phase, as can be better seen in data included in Tables S6-S8 in the ESI.[†] These are separately averaged for the red and the blue grids and concern the pure water and surfactant-laden droplets at high concentration. Moreover, surfactant attenuates the free flow of water molecules toward the bridge, because it reduces the surface tension at the droplets' LG surface and moreover forms aggregates in the bulk that hinder the flow directly. The formation of aggregates at the pinching point is also seen, which manifests by the empty spots in the flow field of Fig. 8. These observations are valid for all of the different surfactants studied here and for the whole range of concentrations above CAC.

4.3 Bridge growth

The growth rate of the bridge radius, *b*, is a key parameter that characterises the dynamics of the coalescence process. From a fluid dynamics perspective, the VR and IR have mainly been proposed, where the former manifests itself through a linear dependence on time, $b \sim t$, while the latter is described by a slower power-law dependence, namely $b \sim t^{\beta \, 10,52,55,81}$ with expected $\beta \approx \frac{1}{2}$. In addition, all-atom molecular dynamics have identified a thermal regime at the very early stage of coalescence, which persists over the length scale $l_{\rm T}$ as

Paper

Soft Matter



Fig. 9 Bridge length *b* as a function of time from the first contact of the droplets at t_c for different concentrations of C10E4 surfactant, as indicated. Power-law fits $\sim t^{\beta}$ are shown, labeled "IR". l_s is the thermal length in the case of surfactant-laden droplets above CAC, while l_w is the thermal length in the case of pure water droplets.

mentioned in Section 1.9 Well beyond this length, the hydrodynamic description is considered valid. In view of the importance of b in describing the dynamics of coalescence and the various scenarios discussed thus far in the literature, we have embarked here on investigating the time evolution of b for a range of different surfactants and concentrations. Fig. 9 presents results for droplets with C10E4 surfactant at different concentrations, both below and above the CAC. In Fig. S6 in the ESI,† results for other surfactants and concentrations are shown. Overall, our model captures two different coalescence regimes, namely an initial TR and a subsequent power-law regime characterised by power law exponents β in the range 0.46–0.71, mean β = 0.57 close to those predicted by IR scaling. We observe different exponents for different surfactant concentration, with more or less random variation from case to case, which may be due to finite size effects and different internal aggregate configurations. Prefactors generally decrease with growing surfactant concentration, leading to a slowdown of growth. Hence, as in the case of all-atom water simulation,⁹ our CG model is also confirming the existence of a TR and an inertial-like power-law regime. The TR persists over a time $\mathcal{O}(10\tau)$ during which the length of the bridge is well described by the length $l_{\rm T}$ both for the pure and the surfactant-laden droplets. In Fig. 10, we compare the bridge growth for three different surfactants below and well above CAC to each other and pure water. Differences in the surface tension above CAC for the different surfactants are generally expected to be small, and our results for b(t) also differ a little, which agrees with the expectation that bridge size in this regime is determined by the thermal length $l_{\rm T} \propto \gamma^{-1/4}$.



Fig. 10 Comparison of bridge radius growth b(t) for different surfactants, below (a) and significantly above (b) CAC. Power-law fits $\sim t^{\beta}$ are shown, for times counted from the first contact of the droplets at t_{c} .

Following the TR, we observe the transition to the power-law regime. The time for the transition to occur is longer when droplets have a higher surfactant concentration. The power-law regime is characterised by exponents close and generally above 0.5. The mean over all cases is $\beta = 0.57$ and standard deviation 0.06, while the reference pure water case gives $\beta = 0.541$. It is also clearly seen that adding surfactant will lead to slower dynamics overall, regardless of exponent variability, as well as a delay in the start of the bridge growth – see ESI† Fig. S5. We can also see a trend that C10E8 clearly has higher β exponent than pure water and than C10E4 (Compare Fig. S6 in the ESI† with Fig. 9). Otherwise, the main variation lies in the reduction of

the growth prefactor as surfactant concentration grows, as can be seen by the progressive shifting of the evolution to the right in the logarithmic plots of Fig. 9, 10, and ESI† Fig. S6. This trend is broadly similar for all surfactants that we studied, with the addition that Silwet-L77 displayed a significantly slower growth in all respects, and in particular lower maximum velocity (see ESI,† Fig. S7 and S8).

4.4 Velocity of approach and asphericity

Soft Matter

A complementary measure of the coalescence dynamics is obtained by monitoring the total length of the droplets in the X direction, whence the velocity of approach $u = \dot{X}$ can be obtained.^{25,82} Data for droplets with C10E4 surfactant are presented in Fig. 11, and show that the fastest approach takes place in the middle of the process at a time about 150τ , which is similar for different surfactants. Although the exponents β of the bridge radius are roughly similar for all cases, we observe that the droplets with surfactant consistently exhibit a smaller maximum speed. Moreover, the process is shorter in time in the case of pure water droplets. A different behaviour appears well above CAC (e.g. four times above), when the process becomes significantly slower, sometimes rather suddenly. A conjecture is that this is due to increased internal rigidity of the aggregates present in the bulk. Monitoring the ratio of droplet radius to bridge radius $L_y/l_{\rm br} \approx R_0/b$ one finds that maximum coalescence velocity occurs for very broad bridges $L_{\rm y}/l_{\rm br} \approx 1.2$ when the surfactant concentration is low but earlier and for much smaller bridge size $L_{\rm y}/l_{\rm br} \approx 1.8$ when well above CAC. This would be consistent with the conjecture that a major



Fig. 11 System length, *X*, in the coalescence direction for different concentrations of C10E4. The inset shows the instantaneous velocity of approach u = dX/dt. The maximum speed occurs at droplet-to-bridge width ratios of $L_y/l_{br} = 1.22$ (0.0 wt%), 1.22 (6.2 wt%), 1.30 (12.3 wt%), 1.40 (24.2 wt%), 1.80 (35.4 wt%), 1.80 (46.2 wt%).

slowdown occurs once significant internal rearrangements, as necessitated by a broad bridge in high concentrations, become necessary. Further results for different surfactants and comparative plots are shown in the ESI[†] (Fig. S7 and S8).

Monitoring the asphericity of the two coalescing droplets (Fig. S9 and S10 in the ESI[†]), as a complimentary measure to monitor the lateral changes in the dimensions of the system, we can observe that this generally follows the behaviour of the velocity of approach. Pure water droplets complete the coalescing process obtaining the final spherical shape much faster than in the case of droplets with surfactant. As with approach velocity and system size, we see a change in behaviour when surfactant concentration increases, but the change is gradual and does not occur at the CAC but well above.

5 Conclusions

In this study, we have analysed various macroscopic and microscopic properties of droplets laden with surfactant and unveiled the surfactant mass transport mechanism during the process for different surfactants and a range of concentrations. We have demonstrated that the underlying mechanisms and flow patterns of coalescence are universal, qualitatively and often quantitatively independent of the type of surfactant. Particular differences between Silwet-L77 and *CiEj* surfactants have been noted in the bridge dynamics for concentrations below the CAC. We have also observed that water molecules are not part of the initial pinching process of coalescence at larger (above CAC) surfactant concentration, which is driven by surfactant aggregation at the droplet's surface.

Other features include the engulfment of part of the initial contact surface inside the forming bridge, the existence of an initial thermal regime, followed by a later power-law growth of the bridge radius with power exponents close to $\frac{1}{2}$, as expected in the inertial regime. We saw no evidence of an intermediate viscous regime. One possibility is that the droplets, despite being large computationally, were still too small for the VR to emerge out of the thermal regime before the IR is activated. Coalescence also universally becomes slower as surfactant concentration grows, and we see evidence of the appearance of a further slowdown with different qualities for several times the critical concentration, using several different indicators. We conjecture that this is due to the appearance of greater internal stiffness caused by closely-packed surfactant aggregates in the bulk. The range of concentrations studied here reflects the need in practical applications where surfactant concentration is usually above the CAC.⁸³ We anticipate that our results demonstrate the mechanisms of a fundamental process in nature and technological applications, which remain universal.

Conflicts of interest

There are no conflicts to declare.

Paper

Acknowledgements

This research has been supported by the National Science Centre, Poland, under grant No. 2019/34/E/ST3/00232. We gratefully acknowledge Polish high-performance computing infrastructure PLGrid (HPC Centers: ACK Cyfronet AGH) for providing computer facilities and support within computational grant no. PLG/2022/015747.

References

- 1 S. Feng, L. Yi, L. Zhao-Miao, C. Ren-Tuo and W. Gui-Ren, *Chin. J. Anal. Chem.*, 2015, **43**, 1942–1954.
- 2 J.-C. Baret, Lab Chip, 2012, 12, 422-433.
- 3 W. Ristenpart, P. McCalla, R. Roy and H. Stone, *Phys. Rev. Lett.*, 2006, **97**, 064501.
- 4 P. E. Theodorakis, E. A. Müller, R. V. Craster and O. K. Matar, *Curr. Opin. Colloid Interface Sci.*, 2014, **19**, 283–289.
- 5 P. E. Theodorakis, E. R. Smith, R. V. Craster, E. A. Müller and O. K. Matar, *Fluids*, 2019, 4, 176.
- 6 J. D. Paulsen, R. Carmigniani, A. Kannan, J. C. Burton and S. R. Nagel, *Nat. Commun.*, 2014, 5, 3182.
- 7 Y. Yoon, F. Baldessari, H. D. Ceniceros and L. G. Leal, *Phys. Fluids*, 2007, **19**, 102102.
- 8 M. I. Khodabocus, M. Sellier and V. Nock, *Adv. Math. Phys.*, 2018, **2018**, 4906016.
- 9 S. Perumanath, M. K. Borg, M. V. Chubynsky, J. E. Sprittles and J. M. Reese, *Phys. Rev. Lett.*, 2019, **122**, 104501.
- 10 J. Eggers, J. R. Lister and H. A. Stone, J. Fluid Mech., 1999, 401, 293–310.
- 11 D. G. Aarts, H. N. Lekkerkerker, H. Guo, G. H. Wegdam and D. Bonn, *Phys. Rev. Lett.*, 2005, **95**, 164503.
- 12 J. Sprittles and Y. Shikhmurzaev, *Phys. Fluids*, 2012, 24, 122105.
- 13 M. Dudek, D. Fernandes, E. Helno Herø and G. Øye, *Colloids Surf.*, A, 2020, 586, 124265.
- 14 M. M. Rahman, W. Lee, A. Iyer and S. J. Williams, *Phys. Fluids*, 2019, **31**, 012104.
- 15 J. D. Berry and R. R. Dagastine, J. Colloid Interface Sci., 2017, 487, 513–522.
- 16 P. M. Somwanshi, K. Muralidhar and S. Khandekar, *Phys. Fluids*, 2018, **30**, 092103.
- 17 P. K. Kirar, K. Alvarenga, P. Kolhe, G. Biswas and K. Chandra Sahu, *Phys. Fluids*, 2020, **32**, 052103.
- 18 S. Bayani, Y. Tabe, Y. T. Kang, S. H. Lee and C. K. Choi, J. Flow Visualization Image Process., 2018, 25, 191–205.
- M. Brik, S. Harmand and I. Zaaroura, *Colloids Surf.*, A, 2021, 629, 127429.
- 20 C. R. Anthony, M. T. Harris and O. A. Basaran, *Phys. Rev. Fluids*, 2020, **5**, 033608.
- 21 V. R. Kern, T. Sæter and A. Carlson, *Phys. Rev. Fluids*, 2022, 7, L081601.
- 22 M. Heinen, M. Hoffmann, F. Diewald, S. Seckler, K. Langenbach and J. Vrabec, *Phys. Fluids*, 2022, **34**, 042006.
- 23 M. Geri, B. Keshavarz, G. H. McKinley and J. W. M. Bush, *J. Fluid Mech.*, 2017, **833**, R3.

- 24 M. Abouelsoud and B. Bai, Phys. Fluids, 2021, 33, 063309.
- 25 S. Arbabi and P. E. Theodorakis, *Macromol. Theory Simul.*, 2023, **32**, 2300017.
- 26 P. J. Dekker, M. A. Hack, W. Tewes, C. Datt, A. Bouillant and J. H. Snoeijer, *Phys. Rev. Lett.*, 2022, **128**, 028004.
- 27 E. Calvo, E. de Malmazet, F. Risso and O. Masbernat, *Ind. Eng. Chem. Res.*, 2019, 58, 15573–15587.
- 28 V. S. Sivasankar, D. R. Hines and S. Das, *Langmuir*, 2022, 38, 14084–14096.
- 29 M. R. Otazo, R. Ward, G. Gillies, R. S. Osborne, M. Golding and M. A. K. Williams, *Soft Matter*, 2019, **15**, 6383–6391.
- 30 C. Vannozzi, Phys. Fluids, 2019, 31, 082112.
- 31 L. Y. Yeo, O. K. Matar, E. S. P. de Ortiz and G. F. Hewitt, J. Colloid Interface Sci., 2003, 257, 93–107.
- 32 Y. Hu, D. Pine and L. G. Leal, Phys. Fluids, 2000, 12, 484-489.
- 33 A. Mansouri, H. Arabnejad and R. Mohan, *Fluids Engineering Division Summer Meeting*, 2014, p. V01AT05A006.
- 34 L. Duchemin, J. Eggers and C. Josserand, J. Fluid Mech., 2003, 487, 167–178.
- 35 G. Karapetsas, R. V. Craster and O. K. Matar, *J. Fluid Mech.*, 2011, **670**, 5–37.
- 36 E. Nowak, N. M. Kovalchuk, Z. Che and M. J. Simmons, *Colloids Surf.*, A, 2016, 505, 124–131.
- 37 S. Narayan, A. E. Metaxas, R. Bachnak, T. Neumiller and C. S. Dutcher, *Curr. Opin. Colloid Interface Sci.*, 2020, 50, 101385.
- 38 E. Nowak, Z. Xie, N. M. Kovalchuk, O. K. Matar and M. J. Simmons, *Soft Matter*, 2017, 13, 4616–4628.
- 39 L. Leal, Phys. Fluids, 2004, 16, 1833-1851.
- 40 N. I. Politova, S. Tcholakova, S. Tsibranska, N. D. Denkov and K. Muelheims, *Colloids Surf.*, A, 2017, **531**, 32–39.
- 41 T. Dong, W. H. Weheliye, P. Chausset and P. Angeli, *Phys. Fluids*, 2017, **29**, 102101.
- 42 T. Dong, W. H. Weheliye and P. Angeli, *Phys. Fluids*, 2019, 31, 012106.
- 43 W. H. Weheliye, T. Dong and P. Angeli, *Chem. Eng. Sci.*, 2017, **161**, 215–227.
- 44 N. M. Kovalchuk, M. Reichow, T. Frommweiler, D. Vigolo and M. J. H. Simmons, *Langmuir*, 2019, **35**, 9184–9193.
- 45 S. Arbabi, P. Deuar, M. Denys, R. Bennacer, Z. Che and P. E. Theodorakis, *Phys. Fluids*, 2023, **35**, 063329.
- 46 S. Li, X. Zhang, W. Dong and W. Wang, *Langmuir*, 2008, 24, 9344–9353.
- 47 H. A. Ritacco, F. Ortega, R. G. Rubio, N. Ivanova and V. M. Starov, *Colloids Surf.*, *A*, 2010, **365**, 199–203.
- 48 H. A. Ritacco, V. B. Fainerman, F. Ortega, R. G. Rubio, N. Ivanova and V. M. Starov, *Colloids Surf.*, A, 2010, 365, 204–209.
- 49 N. Ivanova, V. Starov, R. Rubio, H. Ritacco, N. Hilal and D. Johnson, *Colloids Surf.*, A, 2010, 354, 143–148.
- 50 N. Ivanova, Z. Zhantenova and V. Starov, *Colloids Surf., A*, 2012, **413**, 307–313.
- 51 N. Ivanova, V. Starov, D. Johnson, N. Hilal and R. Rubio, *Langmuir*, 2009, **25**, 3564–3570.
- 52 J. D. Paulsen, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2013, **88**, 063010.

View Article Online

- 53 M. Gross, I. Steinbach, D. Raabe and F. Varnik, *Phys. Fluids*, 2013, **25**, 052101.
- 54 S. Thoroddsen, K. Takehara and T. Etoh, *J. Fluid Mech.*, 2005, **527**, 85–114.
- 55 J. D. Paulsen, J. C. Burton, S. R. Nagel, S. Appathurai, M. T. Harris and O. A. Basaran, *Proc. Natl. Acad. Sci. U. S. A.*, 2012, **109**, 6857–6861.
- 56 H. Xu, T. Wang and Z. Che, J. Colloid Interface Sci., 2022, 628, 869–877.
- 57 G. Soligo, A. Roccon and A. Soldati, J. Comput. Phys., 2019, 376, 1292–1311.
- 58 T. C. Botti, A. Hutin, E. Quintella and M. S. Carvalho, *Soft Matter*, 2022, **18**, 1423–1434.
- 59 C. Constante-Amores, A. Batchvarov, L. Kahouadji, S. Shin, J. Chergui, D. Juric and O. Matar, *J. Fluid Mech.*, 2021, 925, A15.
- 60 M. Kasmaee, F. Varaminian, P. Khadiv-Parsi and J. Saien, *J. Mol. Liq.*, 2018, **263**, 31–39.
- 61 N. Jaensson and J. Vermant, *Curr. Opin. Colloid Interface Sci.*, 2018, 37, 136–150.
- 62 I. B. Ivanov, K. D. Danov and P. A. Kralchevsky, *Colloids Surf.*, A, 1999, 152, 161–182.
- 63 S. Tcholakova, N. D. Denkov and T. Danner, *Langmuir*, 2004, 20, 7444–7458.
- 64 D. Langevin, Curr. Opin. Colloid Interface Sci., 2019, 44, 23–31.
- 65 O. D. Velev, T. D. Gurkov and R. P. Borwankar, *J. Colloid Interface Sci.*, 1993, **159**, 497–501.
- 66 V. C. Suja, A. Kar, W. Cates, S. M. Remmert, P. D. Savage and G. G. Fuller, *Proc. Natl. Acad. Sci. U. S. A.*, 2018, 115, 7919–7924.
- 67 P. E. Theodorakis, E. A. Müller, R. V. Craster and O. K. Matar, *Soft Matter*, 2015, **11**, 9254–9261.
- 68 P. E. Theodorakis, E. A. Müller, R. V. Craster and O. K. Matar, *Langmuir*, 2015, **31**, 2304–2309.

- 69 P. E. Theodorakis, E. R. Smith and E. A. Müller, *Colloids Surf.*, A, 2019, **581**, 123810.
- 70 W. G. Chapman, K. E. Gubbins, G. Jackson and M. Radosz, *Fluid Phase Equilib.*, 1989, **52**, 31–38.
- 71 E. A. Müller and K. E. Gubbins, *Ind. Eng. Chem. Res.*, 2001, **40**, 2193–2211.
- 72 C. Avendaño, T. Lafitte, A. Galindo, C. S. Adjiman, G. Jackson and E. A. Müller, *J. Phys. Chem. B*, 2011, 115, 11154–11169.
- 73 C. Avendaño, T. Lafitte, A. Galindo, C. S. Adjiman, E. A. Müller and G. Jackson, *J. Phys. Chem. B*, 2013, 117, 2717–2733.
- 74 D. Sergi, G. Scocchi and A. Ortona, J. Chem. Phys., 2012, 137, 094904.
- 75 E. A. Müller and G. Jackson, Annu. Rev. Chem. Biomol. Eng., 2014, 5, 405–427.
- 76 T. Lafitte, A. Apostolakou, C. Avendaño, A. Galindo, C. S. Adjiman, E. A. Müller and G. Jackson, *J. Chem. Phys.*, 2013, **139**, 154504.
- 77 O. Lobanova, PhD thesis, Imperial College London, 2014.
- 78 O. Lobanova, A. Mejia, G. Jackson and E. A. Müller, *J. Chem. Thermodyn.*, 2016, **93**, 320–336.
- 79 P. Morgado, O. Lobanova, E. A. Müller, G. Jackson, M. Almeida and E. J. Filipe, *Mol. Phys.*, 2016, 114, 2597–2614.
- 80 A. P. Thompson, H. M. Aktulga, R. Berger, D. S. Bolintineanu, W. M. Brown, P. S. Crozier, P. J. in't Veld, A. Kohlmeyer, S. G. Moore, T. D. Nguyen, R. Shan, M. J. Stevens, J. Tranchida, C. Trott and S. J. Plimpton, *Comput. Phys. Commun.*, 2022, **271**, 108171.
- 81 J. Frenkel, J. Phys., 1945, 9, 385.
- 82 C. Verdier and M. Brizard, Rheol. Acta, 2002, 41, 514-523.
- 83 I. M. Gonçalves, I. Castro, F. Barbosa, V. Faustino, S. O. Catarino, A. Moita, J. M. Miranda, G. Minas, P. C. Sousa and R. Lima, *Processes*, 2022, **10**, 2698.

Electronic Supplementary Information for "Molecular dynamics Simulation of the Coalescence of Surfactant-Laden Droplets"

Soheil Arbabi,¹ Piotr Deuar,¹ Mateusz Denys,¹ Rachid

Bennacer,
² Zhizhao Che,
³ and Panagiotis E. Theodorakis
1, \ast

¹Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland

²Université Paris-Saclay, CentraleSupélec, ENS Paris-Saclay, CNRS,

LMPS - Laboratoire de Mécanique Paris-Saclay, 91190, Gif-sur-Yvette, France

³State Key Laboratory of Engines, Tianjin University, 300350 Tianjin, China (Dated: September 27, 2023)

CONTENTS

MASS TRANSPORT MECHANISM	1
BRIDGE GROWTH DYNAMICS	13
WATER FLOW VELOCITY	16
VELOCITY OF APPROACH	17
ASPHERICITY OF THE DROPLETS	19
MOVIES	21
REFERENCES	22

MASS TRANSPORT MECHANISM

Figures S1, S2, and S3 illustrate droplet snapshots for different concentrations in the power-law regime for droplets with C10E4, C10E8, and Silwet-L77 surfactant, respectively,

^{*} panos@ifpan.edu.pl



FIG. S1. Droplet interiors in the inertial regime showing the presence of new aggregates emerging during the coalescence process. Cross-sections are shown at times roughly corresponding to Fig. 1c by bridge radius for C10E4 in different concentrations, as follows: (a) 6.2 wt%, $t_c + 45.00 \tau$; (b) 12.3 wt%, $t_c + 47.50 \tau$; (c) 24.2 wt%, $t_c + 48.75 \tau$; (d) 35.4 wt%, $t_c + 63.75 \tau$ (e) 46.2 wt%, $t_c + 92.5 \tau$.



FIG. S2. Droplet interiors in the inertial regime showing the presence of new aggregates emerging during the coalescence process. Cross-sections are shown at times roughly corresponding to Fig. 1c by bridge radius for C10E8 in different concentrations, as follows: (a) 6.2 wt%, $t_c + 50.00 \tau$; (b) 12.3 wt%, $t_c + 52.50 \tau$; (c) 24.2 wt%, $t_c + 70.00 \tau$; (d) 35.4 wt%, $t_c + 85.00 \tau$; (e) 46.2 wt%, $t_c + 92.50 \tau$.

which complement our data in Fig. 6 of the manuscript.

The information provided in Tables S1, S2, and S3 reveals that while a significant proportion of molecules from the surface of the droplets in the contact area are transported to the surface of the resulting bridge during coalescence, some of these molecules become trapped and remain within the bulk of the formed droplet (as evidenced by the increased count in the bulk).


FIG. S3. Droplet interiors in the inertial regime showing the presence of new aggregates emerging during the coalescence process. Cross-sections are shown at times roughly corresponding to Fig. 1c by bridge radius for Silwet-L77 in different concentrations, as follow: (a) 7.6 wt%, $t_c + 32.50 \tau$; (b) 14.8 wt%, $t_c + 53.75 \tau$; (c) 28.2 wt%, $t_c + 68.75 \tau$; (d) 40.3 wt%, $t_c + 81.25 \tau$; (e) 51.2 wt%, $t_c + 93.75 \tau$.

The relative contributions from surfactant transport processes from one part of a droplet to others over short time scales $\Delta t'$ are reported in Table S4 for three types of surfactant and the range of concentrations considered in our study. Fig. S4 shows cross-sections of the evolving droplets for C10E4, complementing also Fig. 6 of the manuscript.

TABLE S1.	Number of surfactant molecules (C10E4) before pinching ("Initial snapshot", for
example, see	Fig. 1a) and at the end ("Last snapshot", for example, see Fig. 1e) of the coalescence
process in the	e bulk and at the surface of the droplets.

Concentration (wt%):	6.25	12.37	24.18	35.48	46.09
Initial snapshot (two droplets)					
Bulk	0	202	2184	4096	5899
Surface	1428	2656	3530	4476	5529
Last snapshot (one droplet)					
Bulk	10	234	2229	4329	6167
Surface	1418	2624	3485	4243	5261

TABLE S2. Number of surfactant molecules (C10E8) before pinching ("Initial snapshot", for example see Fig. 1a) and at the end ("Last snapshot", for example, see Fig. 1e) of the coalescence process in the bulk and at the surface of the droplets.

Concentration (wt%):	6.25	12.37	24.18	35.48	46.09	
Initial snapshot (two droplets)						
Bulk	0	379	1429	2514	3579	
Surface	910	1439	2207	2940	3693	
Last snapshot (one droplet)						
Bulk	11	400	1511	2603	3782	
Surface	899	1418	2125	2851	3490	

TABLE S3. Number of surfactant molecules (Silwet-L77) before pinching ("Initial snapshot", for example see Fig. 1a) and at the end ("Last snapshot", for example, see Fig. 1e) of the coalescence process in the bulk and at the surface of the droplets.

Concentration (wt%):	7.6	14.8	28.2	40.3	51.2
Initial snapshot (two droplets)					
Bulk	0	8	939	2056	3122
Surface	910	1810	2697	3398	4150
Last snapshot (one droplet)					
Bulk	15	27	997	2221	3374
Surface	895	1791	2639	3233	3898

TABLE S4: Summary of the relative contributions from all relevant surfactant transport processes in the coalescing droplets. The table lists the relative frequency of transport from one region to another over a time interval $\Delta t' = 1.25\tau$ as a percentage of the mean number of surfactant molecules in source regions. Data was averaged over consecutive snapshots made at $\Delta t'$ intervals during the entire coalescence process which lasts $\mathcal{O}(1000 - 2000)\tau$. CAC ≈ 7.5 wt% for C10E4 and C10E8.

Probab	ilities				
Concentration (wt%)			C10E4 and C10E8		
	6.25	12.37	24.18	35.48	46.09
			Silwet-L77		
	7.61	14.82	28.21	40.25	51.19
Remaining at bridge bulk					
C10E4	0.8774	0.8098	0.8765	0.8647	0.8529
C10E8	0.8728	0.8435	0.8693	0.8669	0.8741
Silwet-L77	0.8915	0.8904	0.8814	0.8192	0.7958
Movement from bridge bulk to left surface					
C10E4	0.0000	0.0000	0.0005	0.0003	0.0004
C10E8	0.0000	0.0000	0.0001	0.0002	0.0004
Silwet-L77	0.0000	0.0015	9.1e-5	0.0002	0.0005
Movement from bridge bulk to left bulk					
C10E4	0.0066	0.0093	0.0648	0.0388	0.0388
C10E8	0.0075	0.0472	0.0460	0.0419	0.0403
Silwet-L77	0.0052	0.0068	0.0337	0.0392	0.0403
Movement from bridge bulk to bridge surface					
C10E4	0.1092	0.1542	0.0326	0.0575	0.0685
C10E8	0.1081	0.0642	0.0424	0.0504	0.0428
Silwet-L77	0.0912	0.0882	0.05551	0.1017	0.1254
Movement from bridge bulk to right surface					
C10E4	0.0000	0.0008	9.7e-5	0.0004	0.0004
C10E8	0.0000	0.0004	0.0004	9.7e-5	0.0007
Silwet-L77	0.0000	0.0000	9.1e-5	0.0002	0.0008

Concentration (wt%)			C10E4 and C10E8 $$		
	6.25	12.37	24.18	35.48	46.09
			Silwet-L77		
	7.61	14.82	28.21	40.25	51.19
Movement from bridge bulk to right bulk					
C10E4	0.0066	0.0257	0.0252	0.0381	0.0388
C10E8	0.0113	0.0444	0.0413	0.0402	0.0413
Silwet-L77	0.0119	0.0129	0.0290	0.0391	0.0370
Remaining at bridge surface					
C10E4	0.9398	0.9284	0.9360	0.9244	0.9099
C10E8	0.9284	0.9428	0.9352	0.9249	0.9251
Silwet-L77	0.9307	0.9494	0.9375	0.9083	0.9065
Movement from bridge surface to left surface					
C10E4	0.0275	0.0305	0.0260	0.0237	0.0259
C10E8	0.0330	0.0256	0.0258	0.0278	0.0253
Silwet-L77	0.0315	0.0227	0.0251	0.02893	0.0254
Movement from bridge surface to left bulk					
C10E4	0.0001	0.0001	5.5e-5	0.0001	0.0003
C10E8	0.0000	0.000	0.0001	0.0002	0.0003
Silwet-L77	9.4e-5	0.0000	3.4e-5	0.0001	0.0002
Movement from bridge surface to bridge bulk					
C10E4	0.0042	0.0103	0.0098	0.0262	0.0373
C10E8	0.0057	0.0087	0.0129	0.0181	0.0235
Silwet-L77	0.0077	0.0045	0.0110	0.0321	0.0417
Movement from bridge surface to right surface					
C10E4	0.0281	0.0304	0.0279	0.0251	0.0261
C10E8	0.0326	0.0226	0.0255	0.0284	0.0252
Silwet-L77	0.0298	0.02317	0.0260	0.0300	0.0257

Concentration (wt%)			C10E4 and C10E8		
	6.25	12.37	24.18	35.48	46.09
			Silwet-L77		
	7.61	14.82	28.21	40.25	51.19
Movement from bridge surface to right bulk					
C10E4	0.0000	2.5e-5	4.1e-5	0.0003	0.0002
C10E8	8.7e-5	5.8e-5	0.0001	0.0002	0.0004
Silwet-L77	0.0000	0.0000	3.4e-5	0.0002	0.0002
Remaining at left bulk					
C10E4	0.9332	0.9849	0.9894	0.9877	0.9835
C10E8	0.9074	0.9945	0.9870	0.9864	0.9803
Silwet-L77	0.9171	0.9210	0.9934	0.9913	0.9825
Movement from left bulk to left surface					
C10E4	0.0046	0.0092	0.0052	0.0092	0.0138
C10E8	0.0092	0.0012	0.0095	0.0111	0.0158
Silwet-L77	0.0213	0.0396	0.0027	0.0055	0.0150
Movement from left bulk to bulk bridge					
C10E4	0.0000	0.00021	0.0031	0.0012	0.0011
C10E8	0.0000	0.0019	0.0021	0.0008	0.0010
Silwet-L77	0.0000	0.0015	0.0009	0.0010	0.0011
Movement from left bulk to surface bridge					
C10E4	0.0000	0.0000	9.7e-6	4.9e-6	1.1e-5
C10E8	0.0000	0.0000	1.9e-5	9.8e-6	1.8e-5
Silwet-L77	0.0000	0.0000	0.00000	6.8e-6	1.3e-5
Movement from left bulk to right surface					
C10E4	0.0000	0.0003	2.4e-5	3.5e-5	6.2e-5
C10E8	0.0000	0.0002	2.4e-5	2.7e-5	2.7e-5
Silwet-L77	0.0000	0.0024	3.2e-5	5.2e-5	6.7e-5

Concentration (wt%)			C10E4 and C10E8		
	6.25	12.37	24.18	35.48	46.09
			Silwet-L77		
	7.61	14.82	28.21	40.25	51.19
Movement from left bulk to right bulk					
C10E4	0.0621	0.0052	0.0020	0.0018	0.0013
C10E8	0.0833	0.0020	0.0011	0.0015	0.0026
Silwet-L77	0.0615	0.035	0.0027	0.0020	0.0011
Remaining at left surface					
C10E4	0.9942	0.9922	0.9912	0.9863	0.9801
C10E8	0.9931	0.9948	0.9887	0.9859	0.9788
Silwet-L77	0.9947	0.9956	0.9954	0.9926	0.9840
Movement from left surface to left bulk					
C10E4	2.1e-5	0.0008	0.0034	0.0094	0.0159
C10E8	5.9e-5	0.0003	0.0067	0.0104	0.0168
Silwet-L77	0.0001	0.0004	0.0010	0.0037	0.0126
Movement from left surface to bridge bulk					
C10E4	0.0000	0.0000	1.6e-5	5.8e-6	1.4e-5
C10E8	1.2e-5	0.0000	3.4e-6	9.1e-7	1.7e-5
Silwet-L77	0.0000	0.0000	0.0000	5.7e-7	7.6e-6
Movement from left surface to bridge surface					
C10E4	0.0032	0.0037	0.0029	0.0017	0.0018
C10E8	0.0045	0.0027	0.0032	0.0015	0.0014
Silwet-L77	0.0033	0.0022	0.0015	0.0017	0.0019
Movement from left surface to right surface					
C10E4	0.0025	0.0031	0.0029	0.0024	0.0019
C10E8	0.0022	0.0020	0.0012	0.0020	0.0028
Silwet-L77	0.0017	0.0015	0.0019	0.0017	0.0012

Concentration (wt%)			C10E4 and C10E8		
	6.25	12.37	24.18	35.48	46.09
			Silwet-L77		
	7.61	14.82	28.21	40.25	51.19
Movement from left surface to right bulk					
C10E4	0.0000	2.8e-5	1.1e-5	3.2e-5	6.5e-5
C10E8	1.2e-5	3.0e-5	2.4e-5	3.1e-5	1.7e-5
Silwet-L77	0.0000	2.0e-5	1.0e-5	3.4e-5	5.2e-5
Remaining at right bulk					
C10E4	0.9251	0.9831	0.9900	0.9875	0.9831
C10E8	0.9103	0.9926	0.9871	0.9859	0.9808
Silwet-L77	0.9493	0.9155	0.9937	0.9912	0.9833
Movement from right bulk to right surface					
C10E4	0.0000	0.0096	0.0068	0.0094	0.0142
C10E8	0.0373	0.0033	0.0097	0.0116	0.0153
Silwet-L77	0.0059	0.0428	0.0025	0.0056	0.0143
Movement from right bulk to bulk bridge					
C10E4	0.0000	0.0018	0.0011	0.0011	0.0011
C10E8	0.0000	0.0018	0.0019	0.0007	0.0010
Silwet-L77	0.0000	0.0015	0.0008	0.0010	0.0010
Movement from right bulk to surface bridge					
C10E4	0.0000	0.0000	2.4e-6	1.1e-5	1.4e-5
C10E8	0.0000	0.0000	2.8e-5	7.9e-6	1.9e-5
Silwet-L77	0.0000	0.0000	2.7e-6	6.85e-6	2.0e-5
Movement from right bulk to left surface					
C10E4	0.0000	0.0001	1.9e-5	2.7e-5	5.0e-5
C10E8	0.0014	0.0001	1.9e-5	2.9e-5	2.7e-5
Silwet-L77	0.0000	0.0018	2.4e-5	5.4e-5	7.3e-5

Concentration (wt%)			C10E4 and C10E8		
	6.25	12.37	24.18	35.48	46.09
			Silwet-L77		
	7.61	14.82	28.21	40.25	51.19
Movement from right bulk to left bulk					
C10E4	0.0748	0.0051	0.0019	0.0018	0.0013
C10E8	0.0508	0.0019	0.0011	0.0015	0.0026
Silwet-L77	0.0447	0.0381	0.002	0.0020	0.0011
Remaining at right surface					
C10E4	0.9940	0.9923	0.9898	0.9859	0.9795
C10E8	0.9932	0.9946	0.9884	0.9856	0.9793
Silwet-L77	0.9948	0.9956	0.9954	0.9926	0.9845
Movement from right surface to right bulk					
C10E4	0.0000	0.0008	0.0045	0.0096	0.0165
C10E8	0.0002	0.0010	0.0069	0.0107	0.0163
Silwet-L77	8.10e-5	0.0004	0.0009	0.0037	0.0121
Movement from right surface to bridge bulk					
C10E4	0.0000	0.0000	4.7e-6	9.9e-6	7.7e-6
C10E8	0.0000	0.0000	1.4e-5	3.6e-6	1.9e-5
Silwet-L77	0.0000	0.0000	1.0e-6	3.4e-6	1.3e-5
Movement from right surface to bridge surface					
C10E4	0.0033	0.0036	0.0031	0.0019	0.0018
C10E8	0.0043	0.0023	0.0032	0.0015	0.0013
Silwet-L77	0.0032	0.0022	0.0015	0.0018	0.0019
Movement from right surface to left surface					
C10E4	0.0025	0.0031	0.0024	0.0024	0.0019
C10E8	0.0021	0.0019	0.0013	0.0020	0.0028
Silwet-L77	0.0017	0.0016	0.0019	0.0016	0.0012

Concentration (wt%)			C10E4 and C10E8		
	6.25	12.37	24.18	35.48	46.09
			Silwet-L77		
	7.61	14.82	28.21	40.25	51.19
Movement from right surface to left bulk					
C10E4	0.0000	2.2e-5	1.4e-5	3.3e-5	7.5e-5
C10E8	1.1e-5	3.6e-5	1.7e-5	2.5e-5	3.4e-5
Silwet-L77	0.0000	3.0e-5	9.2e-6	3.2e-5	4.9e-5



FIG. S4. Mass transport mechanism of surfactant (C10E4) during the coalescence process, for concentrations above (upper panels) and below (lower panels) CAC. The length of the arrows reflects the probabilities associated with surfactant transport to the different droplet areas as reported in Table S4. Above the CAC (a–e, 35.48 wt%) snapshots were obtained at times (a) t_c + 32.5 τ , (b) t_c + 76.25 τ , (c) t_c + 233.75 τ ,(d) t_c + 517.50 τ , (e) t_c + 1358.75 τ , while below the CAC (f–j, 6.25 wt%) times shown are (f) t_c + 20 τ , (g) t_c + 55 τ , (h) t_c + 100 τ , (i) t_c + 197.5 τ , (j) t_c + 283.75 τ Different stages of the coalescence process are shown: soon after the end of the thermal regime (a, f), the development of the bridge region (c, h), and the full development of the bridge (d, i) towards the final equilibrium state (e, j). Magnified views of the bridge region and its cross-section (showing only surfactant hydrophobic beads in the bridge region, red) are shown above and to the right of the snapshots, respectively.

BRIDGE GROWTH DYNAMICS

The average velocity (b/t) of bridge growth is reported in Table S5. It shows that adding surfactant reduces the average velocity in all cases. However, we see interesting behaviour for Silwet-L77, which is the fastest among surfactant-laden droplets in the lowest concentration but in higher concentrations Silwet-L77 is the slowest one. This behaviour also is confirmed when we compare later the velocities of approach. In low concentrations (below CAC), Silwet-L77 makes less aggregates and they have low density, which helps the droplets to coalesce faster. However, when it comes to higher concentrations, Silwet-L77 aggregates are more in quantity and surface tension is the smallest in Silwet-L77. Both of these properties make coalescence slower in higher concentrations for Silwet-L77.

In Fig. S5, the bridge growth rate of pure water and in the highest concentration (46.2 wt%) of C10E4 are plotted. In both curves the values of the thermal length scale $(l_{\text{Thermal}} = (k_B T/\gamma)^{1/4} R_0^{1/2})$ [1] are marked using horizontal lines which is $l_w = 4.0 \sigma$ for pure water and $l_s = 5 \sigma$ for surfactant-laden droplets. It is seen that this is an excellent match to the early non-changing bridge radius. This crossover takes more time and is more pronounced in case of surfactant-laden drops, presumably due to the reduction of surface tension due to presence of surfactant. We also report on the bridge growth dynamics for all concentrations in the case of C10E8 (Fig. S6a) and Silwet-L77 (Fig. S6b), in complement to Fig. 9 of the main manuscript.

Concentration (wt%)			C10E4 and C10E8		
	6.25	12.37	24.18	35.48	46.09
			Silwet-L77		
	7.61	14.82	28.21	40.25	51.19
C10E4	0.2849	0.2204	0.1878	0.1605	0.1047
C10E8	0.2794	0.2319	0.1871	0.1530	0.1115
Silwet-L77	0.2912	0.2029	0.1550	0.1034	0.0655
CAC(C10E4 and C10E8) $\simeq 7.5$) wt%					
$CAC(Silwet-L77) \simeq 16.23 \text{ wt}\%$					

TABLE S5. Average velocity of bridge growth in units σ/τ from t_c until the full development of the bridge (for example, see snapshots of Fig. 1d of the main manuscript).^a

^a For pure water droplets in the viscous regime (result from simulation): 0.3675 σ/τ



FIG. S5. a) Bridge growth rate in the case of pure water droplets. When the bridge radius, b, reaches the thermal length scale for pure water ($l_w = 4 \sigma$), hydrodynamics effect play the main role and a fast transition between thermal and inertial regimes occurs. b) Bridge growth rate of surfactant-laden droplets (C10E4, 46.2 wt%). When the bridge radius reaches the thermal length scale for surfactant-laden droplets ($l_s = 5 \sigma$), the transition occurs as well, but subsequent growth is slower than in pure water.



FIG. S6. Bridge growth rate in the case of a) C10E8 and b) Silwet-L77 for different concentrations in wt%, as indicated. Increasing the surfactant concentration makes the bridge growth slower and transition between thermal and inertial regime takes more time. Power-law fits $\sim t^{\beta}$ are shown, labeled 'IR'. l_s is the thermal length in the case of surfactant-laden droplets above CAC, while l_w is the thermal length in the case of pure water droplets. Notation like in Fig. 9 of the main manuscript, with b being the bridge radius and t_c the time of the establishment of the permanent contact between the droplets.

WATER FLOW VELOCITY

TABLE S6. Average velocity of water flow in the direction, X, of the droplets approach for pure water droplets in units σ/τ . The velocities are separately averaged for inward and outward flowing grids (colors in Fig. 8 of the manuscript) to show the relative importance of the difference between inflow and outflow.

$\frac{t(\tau)}{b(\sigma)}$	$t_c + [0, 7.5] \\ 3.2 < b < 5.4$	$\begin{array}{c} t_c + [8.25, 27.75] \\ 5.58 < b < 10.90 \end{array}$	$t_c + [28.5, 89.25]$ 11.00 < b < 20.11
Toward bridge (System)	$0.1946 {\pm} 0.0016$	$0.1926 {\pm} 0.0013$	0.2001 ± 0.0008
Away from bridge (System)	$0.1943 {\pm} 0.0018$	$0.1808 {\pm} 0.0019$	0.1660 ± 0.0011
Toward centre (In bridge)	0.298 ± 0.016	$0.257 {\pm} 0.009$	0.202 ± 0.004
Away from centre (In bridge)	0.27 ± 0.03	$0.193 {\pm} 0.010$	0.183 ± 0.004

TABLE S7. Data for C10E4 (46.2 wt%) droplets in the same convention as Fig. S6.

$\frac{t(\tau)}{b(\sigma)}$	$t_c + [0, 12.5] \\ 3.72 < b < 4.55$	$t_c + [13.75, 81.25] 4.87 < b < 10.33$	$t_c + [82.5, 360] \\ 11.00 < b < 22.00$
Toward bridge (System) Away from bridge (System)	$\begin{array}{c} 0.2634 \pm 0.0021 \\ 0.265 \pm 0.004 \end{array}$	$\begin{array}{c} 0.2684 \pm 0.0016 \\ 0.2642 \pm 0.0012 \end{array}$	$\begin{array}{c} 0.2710 \pm 0.0008 \\ 0.2593 \pm 0.0008 \end{array}$
Toward centre (In bridge) Away from centre (In bridge)	0.445 ± 0.024 0.40 ± 0.05	0.336 ± 0.010 0.325 ± 0.011	0.277 ± 0.003 0.272 ± 0.003

TABLE S8. Data for Silwet-L77 droplets (51.2 wt%) in the same convention as Fig. S6.

$t_c + [0, 12.5]$ 3.50 < b < 4.50	$t_c + [13.75, 86.25]$ 5.00 < b < 9.94	$t_c + [87.5, 598.75]$ 10.00 < b < 23.37
0.00 (0 (1.00	0.000 (0 (0.001	10.000 (0) (20.01
0.2625 ± 0.0027	0.2703 ± 0.0014	0.2705 ± 0.0005
0.2685 ± 0.0030	0.2614 ± 0.0014	0.2616 ± 0.0005
0.45 ± 0.04	0.341 ± 0.010	0.2756 ± 0.0017
0.37 ± 0.03	0.334 ± 0.010	0.2699 ± 0.0027
	$\begin{aligned} t_c + [0, 12.5] \\ 3.50 < b < 4.50 \end{aligned}$ $\begin{aligned} 0.2625 \pm 0.0027 \\ 0.2685 \pm 0.0030 \end{aligned}$ $\begin{aligned} 0.45 \pm 0.04 \\ 0.37 \pm 0.03 \end{aligned}$	$\begin{array}{c} t_c + [0, 12.5] \\ 3.50 < b < 4.50 \end{array} \begin{array}{c} t_c + [13.75, 86.25] \\ 5.00 < b < 9.94 \end{array}$ $\begin{array}{c} 0.2625 \pm 0.0027 \\ 0.2685 \pm 0.0030 \end{array} \begin{array}{c} 0.2703 \pm 0.0014 \\ 0.2614 \pm 0.0014 \end{array}$ $\begin{array}{c} 0.45 \pm 0.04 \\ 0.37 \pm 0.03 \end{array} \begin{array}{c} 0.341 \pm 0.010 \\ 0.334 \pm 0.010 \end{array}$

VELOCITY OF APPROACH

In the main manuscript, the velocity of approach of C10E4 for different concentrations is reported, using the length of system in the X direction and its derivative with time. Here, we present the analogous data for C10E8 (Figure S7a) and Silwet-L77 (Figure S7b). The dynamics are similar to C10E4, as explained in the main manuscript. We also compare all three types of surfactants for the lowest (Figure S8a) and highest concentrations (Figure S8b). The data show that Silwet-L77 has the smallest maximum absolute velocity both in low and high concentrations. The surface tension of Silwet-L77 is around 20.7 mN/m [2], while the values for C10E4 and C10E8 are about 27 mN/m and 36 mN/m, respectively [3, 4].



FIG. S7. System length X for droplets for different concentrations of a) C10E8 and b) Silwet-L77. Insets show the instantaneous velocity of approach u = dX/dt.



FIG. S8. comparison of velocity of approach in all three types of surfactants in a) low and b) high concentrations. When it comes to the maximum velocity, Silwet-L77 has the smallest.

ASPHERICITY OF THE DROPLETS

To characterise the structural features, we calculated the gyration tensor (Eq. 1) where N is the number of particles, x_i, y_i, z_i are coordinates of the particles and x_{cm}, y_{cm}, z_{cm} give the centre of mass of the system. Eigenvalues of the gyration tensor (Eq. 1) are found and sorted $(\lambda_1 \ge \lambda_2 \ge \lambda_3)$ to obtain the gyration tensor trace (Eq. 2), and calculate asphericity (Eq. 3) — which is zero for a perfect spherical symmetry — for each snapshot. Figure S9 illustrates the asphericity of C10E4, C10E8, and Silwet-L77 laden droplets during the coalescence for different concentrations. Adding more surfactant causes significant changes in structural features. Higher concentration of surfactant leads to delayed creation of a single equilibrated sphere $(a_s = 0)$. Moreover, comparison between all three types of surfactants in different concentrations are plotted in Figs S10a and b.

$$\frac{1}{N} \begin{pmatrix} \Sigma_{i}(x_{i} - x_{cm})^{2} & \Sigma_{i}(x_{i} - x_{cm})\Sigma_{i}(y_{i} - y_{cm}) & \Sigma_{i}(x_{i} - x_{cm})\Sigma_{i}(z_{i} - z_{cm}) \\ \Sigma_{i}(x_{i} - x_{cm})\Sigma_{i}(y_{i} - y_{cm}) & \Sigma_{i}(y_{i} - y_{cm})^{2} & \Sigma_{i}(y_{i} - y_{cm})\Sigma_{i}(z_{i} - z_{cm}) \\ \Sigma_{i}(x_{i} - x_{cm})\Sigma_{i}(z_{i} - z_{cm}) & \Sigma_{i}(y_{i} - y_{cm})\Sigma_{i}(z_{i} - z_{cm}) & \Sigma_{i}(z_{i} - z_{cm})^{2} \end{pmatrix}$$
(1)

$$TrS = \lambda_1 + \lambda_2 + \lambda_3 = R_g^2$$
⁽²⁾

$$a_s = \lambda_1 - \frac{1}{2}(\lambda_2 + \lambda_3) \tag{3}$$



FIG. S9. Comparison of Asphericity (a_s) during the coalescence process of surfactant types a) C10E4, b) C10E8, and c) Silwet-L77.



FIG. S10. comparison of Asphericity (a_s) in all three types of surfactants in a) low and b) high concentrations.

MOVIES

- File M1_coalescence.mp4: shows the coalescence of two surfactant-laden droplets (C10E4, 46.2 wt%)
- File M2_pinching.mp4: shows the pinching at the initial approach of the droplets (C10E4, 46.2 wt%)
- File M3_bridge_zoom.mp4: shows the bridge area of C10E4 (46.2 wt%, $t(\tau) = t_c + [0, 150]$) from the pinching point to a developed bridge. On the right, water beads and on the left surfactant beads during the coalescence are shown. It is evident that coalescence starts with surfactant beads (mainly the hydro phobic ones) and water joins much later.
- File M4_mass_transport.mp4: Here the inside of surfactant-laden droplets of C10E4 (46.2 wt%) are shown during the coalescence. The key points are surfactant movements inside the bridge (from bulk to surface) and the creation of new aggregates inside the bridge.

- S. Perumanath, M. K. Borg, M. V. Chubynsky, J. E. Sprittles, and J. M. Reese, Phys. Rev. Lett. 122, 104501 (2019).
- [2] X. Tang, J. Dong, and X. Li, J. Colloid Interface Sci. 325, 223 (2008).
- [3] Y.-C. Lee, H.-S. Liu, S.-Y. Lin, H.-F. Huang, Y.-Y. Wang, and L.-W. Chou, J. Chin. Inst. Chem. Eng. 39, 75 (2008).
- [4] D. Anghel, S. Saito, A. Băran, A. Iovescu, and M. Corniţescu, Colloid Polym. Sci 285, 771 (2007).

4.3 Coalescence of Sessile Aqueous Droplets Laden with Surfactant

4.3.1 Summary of Key Findings of this Publication:

In this paper, we explored the coalescence of sessile surfactant-laden droplets on various substrates, including wettable ($\theta_s < 90^\circ$), intermediate ($\theta_s \simeq 90^\circ$), and nonwettable ($\theta_s > 90^\circ$) substrates. We employed the SAFT CG force field to study sessile water droplets and surfactant-laden droplets both below and above the CAC. We compared the mass transport mechanism of surfactant molecules and bridge dynamics on three different substrates during the coalescence. Additionally, we studied the dynamics of the contact angle on the bridge (θ_b), density profile, and velocity of approach between the coalescing droplets. The key findings of this work are summarized as follows:

- Sessile droplets with θ_s ≥ 90° share similarities with freely suspended droplets. For contact angle of θ_s ≃ 140° our results show that coalescence behaves practically as if they were freely suspended. The pinching region and bridge formation begin at a distance from the substrate, and only later does the bridge region come into contact with the substrate. For instance, a comparison of the bridge angle (θ_b) with freely suspended droplets reveals very similar behavior. Moreover, mass transport mechanisms in this case exhibit similarities with freely suspended droplets, with the predominant movement of surfactant molecules from the bulk of the bridge to the surface of the bridge. The creation of a surfactant film in the pinching process (in the case of concentrations above the CAC) and the formation of new aggregates within the bridge bulk have been reported in this scenario. Regarding the bridge dynamics, the exponents for the power law (in the inertial regime) are approximately 0.5, consistent with observations in freely suspended droplets.
- In the case of an intermediate scenario ($\theta_s \simeq 90^\circ$), the bridge dynamics closely resemble those of non-wettable substrates; however, it grows slightly slower due to pinching initiating on the substrate. Concerning the mass transport mechanisms, the involvement of water in the pinching process is marginally higher, but overall, the mass transport mechanism of surfactant molecules within the bridge is akin to that of non-wettable substrates.
- Sessile droplets with $\theta_s < 90^\circ$, on the other hand, exhibit markedly different behavior in terms of mass transport mechanisms and bridge dynamics. We have investigated contact angles of approximately 50° and 70° for both water droplets and surfactant-laden droplets, both below and above CAC. Overall, it is demonstrated that when the contact angle is above 90°, the bridge height (*b*) grows with an exponent of 0.5 within the inertial regime. However, in the case of wettable

substrates ($\theta_s < 90^\circ$), an exponent of 2/3 is observed. Regarding the mass transport mechanism, wettable substrates exhibit increased water participation in the pinching process compared to non-wettable substrates. A notable result is the absence of newly formed aggregates as the bridge grows during coalescence in the case of wettable substrates.

• We calculated the velocity of approach between two droplets, and it was observed that the velocity is smaller when wettable substrates are used, irrespective of surfactant concentration.



Figure 4.3: Coalescence of Sessile Aqueous Droplets Laden with Surfactant. Reprinted from [Soheil Arbabi, Piotr Deuar, Rachid Bennacer, Zhizhao Che, and Panagiotis E. Theodorakis, Coalescence of Sessile Aqueous Droplets Laden with Surfactant. Phys. Fluids **36**,(2024), https://doi.org/10.1063/5.0194816].

4.3.2 Details of Publication

Coalescence of Sessile Aqueous Droplets Laden with Surfactant

PDF of accepted version of this publication is reproduced from [Soheil Arbabi, Piotr Deuar, Rachid Bennacer, Zhizhao Che, and Panagiotis E. Theodorakis, Coalescence of Sessile Aqueous Droplets Laden with Surfactant. Phys. Fluids **36**,(2024), https://doi.org/10.1063/5.0194816].



Soheil Arbabi

Institute of Physics, Polish Academy of Sciences (PAN)

Theoretical Physics Division (ON5),

Al. Lotników 32/46 02-668 Warsaw, Poland

arbabi@ifpan.edu.pl

STATEMENT

I declare that I am the co-author of the publication:

Coalescence of sessile aqueous droplets laden with surfactant, S. Arbabi,

P. Deuar, R. Bennacer, Z. Che, P. E. Theodorakis Fluid Phys. 36,(2024),

doi : 10.1063/5.0194816

I contributed equally to the conceptualization. I took the lead role in data curation, analysis, investigation, methodology, simulations, validation, visualization and writing the draft. In addition, I played an equal part in review, and editing tasks.

signature:

Scheil Irbabi



dr hab. Piotr Deuar, prof. IF PAN Head of the Quantum Noise group Institute of Physics, Polish Academy of Sciences (PAN) Theoretical Physics Division, Al. Lotników 32/46 02-668 Warszawa, Poland <u>deuar@ifpan.edu.pl</u>

STATEMENT

I declare that I am a co-author of the publication:

Coalescence of Sessile Aqueous Droplets Laden with Surfactant, Phys. Fluids, **36**, (2024) S. Arbabi, P. Deuar, R. Bennacer, Zhizhao Che, P. E. Theodorakis https://doi.org/10.1063/5.0194816

My contributions included support of Mr Soheil Arbabi in analysis, conceptualization participation in discussions, as well as reviewing and editing the draft.

signature:





Prof. Rachid BENNACER Univ. Paris-Saclay 4 Avenue des Sciences, 91190 Gif-sur-Yvette Mail: <u>rachid.bennacer@ens-paris-saclay.fr</u>

STATEMENT

I declare that I am the co-author of the publication:

Coalescence of Sessile Aqueous Droplets Laden with Surfactant., Phys. Fluids, **36**, (2024), https://doi.org/10.1063/5.0194816

My contributions included supporting conceptualization, participating in discussions, and reviewing/editing the draft.

signature:



Zhizhao Che, PhD, Professor

State Key Laboratory of Engines, Tianjin University

135 Yaguan Road, Haihe Education Park,

Tianjin, 300350, China

Email: chezhizhao@tju.edu.cn

STATEMENT

I declare that I am the co-author of the publication:

Coalescence of Sessile Aqueous Droplets Laden with Surfactant., Phys. Fluids, **36**, (2024), https://doi.org/10.1063/5.0194816

My contributions included supporting conceptualization, participating in discussions, and reviewing/editing the draft.

signature: 女よ剑

Dr hab. Panagiotis Theodorakis Division of Theoretical Physics (ON5) Al. Lotników 32/46 02-668 Warsaw, Poland

STATEMENT

I declare that I am the co-author of the publication:

• Coalescence of sessile aqueous droplets laden with surfactant S. Arbabi, P. Deuar, R. Bennacer, Z. Che, P. E. Theodorakis *Phys. Fluids* **36**, ... (2024), doi : 10.1063/5.0194816

My contribution was supervising the project, helping in the interpretation of the results, and in manuscript writing.

Warsaw, 06.02.2024 Panagiotis Theodorakis

Coalescence of Sessile Aqueous Droplets Laden with Surfactant

Soheil Arbabi^{*,1} Piotr Deuar,¹ Rachid Bennacer,² Zhizhao Che,³ and Panagiotis E. Theodorakis^{*1} ¹⁾Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland ²⁾Université Paris-Saclay, ENS Paris-Saclay, CNRS, LMPS, 4 Av. des Sciences, 91190 Gif-sur-Yvette, France ³⁾State Key Laboratory of Engines, Tianjin University, 300350 Tianjin, China

(*Electronic mail: panos@ifpan.edu.pl)

(*Electronic mail: arbabi@ifpan.edu.pl)

(Dated: 24 January 2024)

With most of the focus to date having been on the coalescence of freely suspended droplets, much less is known about the coalescence of sessile droplets, especially in the case of droplets laden with surfactant. Here, we employ large-scale molecular dynamics simulations to investigate this phenomenon on substrates with different wettability. In particular, we unravel the mass transport mechanism of surfactant during coalescence, thus explaining the key mechanisms present in the process. Close similarities are found between the coalescence of sessile droplets with equilibrium contact angles above 90° and that of freely suspended droplets, being practically the same when the contact angle of the sessile droplets is above 140°. Here, the initial contact point is an area that creates an initial contact film of surfactant that proceeds to break into engulfed aggregates. A major change in the physics appears below the 90° contact angle, when the initial contact point becomes small and line-like, strongly affecting many aspects of the process and allowing water to take part in the coalescence from the beginning. We find growth exponents consistent with a 2/3 power law on strongly wettable substrates but no evidence of linear growth. Overall bridge growth speed increases with wettability for all surfactant concentrations, but the speeding up effect becomes weaker as surfactant concentration grows, along with a general slowdown of the coalescence compared to pure water. Concurrently the duration of the initial thermally limited regime increases strongly by almost an order of magnitude for strongly wettable substrates.

I. INTRODUCTION

Many natural phenomena involve the coalescence of fluid droplets.^{1–20} For example, this is a fundamental process that determines the distribution and coalescence rate of raindrops in atmospheric aerosols.^{21–24} Apart from such natural processes, droplet coalescence is relevant for many industrial applications as well, such as inkjet printing,²⁵ microfluidics,^{26–29} and water treatment during crude oil and natural gas separation.^{30,31} Further control of the process may involve the use of various additives,^{32–39} such as surfactant,^{40–58} which can reduce surface tension at fluid interfaces, crucial in multi-phase systems. For example, surfactant can stabilize droplets' surface or prevent their coalescence, thus improving the bio-compatibility in certain systems⁵⁹ or affecting the fusion, mixing, and manipulation of droplets in microfluidic devices.⁶⁰ While many efforts have thus far been taken to understand coalescence phenomena at a fundamental level,^{1,3,61} there are still numerous aspects of this process that require further investigations, such as the coalescence of sessile droplets with surfactant.

In experiments,^{62–68} droplet coalescence has been studied for various conditions (*e.g.*, in the presence of applied electric fields) and geometries (*e.g.*, micro-channels, fibers, *etc.*), mainly by means of high-speed imaging and electrical sensing. Due to resolution limitations, the focus of these investigations has mainly been placed on unveiling macroscopic properties of the process.^{49,50,52,69–71} For example, the effect of surfactant concentration on droplet coalescence has been investigated by high-speed imaging.⁵⁰ When an asymmetry in surfactant concentration of the coalescing droplets is present, Marangoni flow was observed and the curvature on either side of the growing bridge was different. Numerical continuum approaches have also been employed to complement understanding of droplet coalescence.^{5,7,17,42,69,72–79} However, such methods suffer from inadequate resolution in capturing the mass transport mechanism of surfactant during coalescence or resolving the initial contact of the droplets. The singularity at the contact point still remains a challenge for continuum simulation.⁸⁰ On the other hand, molecular dynamics (MD) simulation can naturally resolve the contact region at the molecular level, to observe the start of the coalescence process.

In general, droplet coalescence is a non-equilibrium process that occurs in three stages. The first stage involves the initial approach of droplets, when they come close enough to interact (pinch-ing/contact) and form the so-called bridge (Figure 1a, e and pinching b, f). This is followed by a bridge-growth stage that leads to the reshaping (third stage) of the droplets (Figure 1c, g) and



FIG. 1. Different stages of coalescence of surfactant-laden droplets on non-wettable (a–d, $\theta_s \simeq 142^\circ$) and wettable (e–h, $\theta_s \simeq 49^\circ$) substrates, with surfactant concentration above CAC (35.48 wt%). *b* is the bridge height and *w* the bridge width. *X* is distance between the centers of mass of the two droplets in the *x*direction, while θ_s is the equilibrium contact angle of the droplet. θ_b is the angle formed at the bridge at the liquid–gas surface. The stages of coalescence shown here are: (a, e) Initial approach ($t = t_c$); (b, f) Moment of pinching ($t = t_c$); (c) Developed bridge ($t = t_c + 196.25 \tau$) and (d) final, equilibrium state of the system ($t = t_c + 1483.75$) in the case of the non-wettable substrate. (g) Developed bridge ($t = t_c + 1028.75 \tau$) and (h) final, equilibrium state of the system ($t = t_c + 3161.25 \tau$) in the case of the wettable substrate. The snapshots of the system were obtained using Ovito software.⁸¹

eventually the single spherical-cap shape for sessile droplets, which is the final equilibrium and minimum energy state of the system (Figure 1d,h). The time evolution of this process on substrates with different wettability is illustrated in Figure 2 (Multimedia view). The coalescence process is governed by the interplay of viscous, inertial and surface-tension forces, as the system tries to decrease the surface tension.⁸² In particular, from the perspective of fluid dynamics, viscous forces are expected to play an important role in the initial bridge growth, which is driven primarily by molecular interactions. At a later stage of the bridge growth, inertial effects are expected to take over. In the case of freely suspended droplets, a linear scaling of the bridge radius, *b*, in time $(b \propto t)$ and logarithmic corrections $b \propto t \ln t$ have been suggested for the viscous regime.^{6,83} For the inertial regime, a power law scaling $(b \propto t^{1/2})$ has been proposed.⁵ However, this classification



FIG. 2. (Multimedia view) Coalescence of droplets with surfactant concentration (35.48 wt%) on substrates with different wettability (upper row, non-wettable; middle row, intermediate; lower row, wettable).

is still under debate in the literature, and an inertially limited viscous (ILV) regime has also been reported.^{1,84} Moreover, an initial thermal regime, which is inaccessible to experiments has been identified by means of all-atom⁴ and coarse-grained (CG)^{85,86} MD simulation. This regime arises due to collective thermal motion of particles at the droplets' surface. Here, all-atom simulation has proposed a scaling law for a length scale characterizing the extent of the thermal fluctuations, namely $l_T \approx (k_B T / \gamma)^{1/4} R^{/1/2}$, where k_B is Boltzmann's constant, *T* the temperature, γ the surface tension, and *R* the droplet radius.⁴ When the bridge radius is smaller than this length scale ($b < l_T$), the bridge grows mainly due to thermal motion of particles, while later ($b > l_T$) hydrodynamic effects are expected to dominate. Recent MD simulations of a CG model have indicated the presence of the thermal regime and subsequent inertial scaling law ($b \propto t^{1/2}$) for the bridge growth for both aqueous droplets with and without surfactant.^{85,86}

In the case of the coalescence of sessile droplets,^{34,45,83,87–93} for water droplets on non-wettable substrates (contact angle $\theta_s \ge 90^\circ$, Figure 1) it has been suggested that the bridge grows with time as $b \propto t^{1/2}$, as has been observed in the case of freely suspended droplets. In contrast, for wettable substrates, namely $\theta_s < 90^\circ$, the bridge is predicted to grow with a new power law $b \propto t^{2/3}$.⁸⁸ Moreover, experiments of droplets with an equilibrium contact angle in the range $10^\circ - 56^\circ$ suggest that the bridge height roughly grows in time with power-law exponents between 0.50 and 0.86. Data was seen to follow the scaling law for the entire range of time in the case of 10° contact angle,

while the rest of the cases studied deviated from this law at longer times.⁶⁶ The bulk fluid properties also affect the bridge growth. For example, in the case of polymer droplets^{34,94,95}, their viscosity can result in a lower rate of coalescence in comparison with water droplets. One finds power-law exponents lower than 1/2 for nonwettable substrates (equilibrium contact angle greater than 90°) and power-law exponents lower than 2/3 for wettable substrates.³⁴ The bridge width, *w* (Figure 1), grows as $w \propto t^{0.5}$.^{66,89,90} However, a linear scaling $w \propto t$ has also been suggested for droplets of high viscosity.⁸³ To our knowledge, the regimes of applicability of the above findings have not been investigated in experiments nor in modeling that would include the early-time molecular level physics.

In view of the many unknowns in the coalescence of sessile surfactant-laden droplets, we embarked on investigating this phenomenon by using large-scale molecular dynamics simulations of a coarse-grained force-field, considering a comprehensive range of possible scenarios. Hence, our study includes a range of surfactant concentrations below and above the critical aggregation concentration (CAC) and substrates with different wettability, both wettable ($\theta_s < 90^\circ$) non-wettable ($\theta_s > 90^\circ$), and those with equilibrium contact angle of about 90°. In all these cases, we have explored the mass transport mechanism of surfactant, which provides insights into the details of the coalescence process, analyzed the dynamics of the bridge growth, which characterizes the rate of coalescence, as well as studied the bridge angle and the velocity of approach.⁹⁶ It turns out that while the coalescence of sessile surfactant-laden droplets on non-wettable substrates shares similarities with the coalescence of freely suspended droplets, significant differences in the mass transport mechanism and rate of coalescence appear for wettable substrates. The following section presents our MD simulation model and methods. Our results are discussed in Section III. Finally, the conclusions and possible suggestions for follow-up research are discussed in Section IV.

II. SIMULATION MODEL AND METHODS

Our system consists initially of two droplets placed close to each other as shown in Figure 1a,e, that is a distance below the cutoff range of the interactions between beads in order to initiate the coalescence of the droplets. We have considered concentrations above and below the CAC for C10E4 surfactants. The details of the model for the interactions between the different components and the validation for various surfactants are taken the same here as used in a number of previous related studies,^{97–103} and were obtained through the Mie- γ Statistical Associating Fluid Theory

(SAFT Mie- γ).^{100,104–107} The MD simulations were carried out in the canonical ensemble with the Nosé–Hoover thermostat as implemented in LAMMPS software.^{108,109} After equilibration of a single droplet on the specific substrate, it was cloned to produce the second droplet and the surrounding vapor for the start of the coalescence *in silico* experiment (Figures 1a,e).

The force-field has been validated for a range of water–surfactant systems with a focus on reproducing key properties, such as surface tension and phase behavior.^{97–99,101–103,110,111} In particular, interactions between the various CG beads representing different chemical units of the system are described via the Mie potential

$$U(r_{\rm ij}) = C \varepsilon_{\rm ij} \left[\left(\frac{\sigma_{\rm ij}}{r_{\rm ij}} \right)^{\lambda_{\rm ij}^{\rm r}} - \left(\frac{\sigma_{\rm ij}}{r_{\rm ij}} \right)^{\lambda_{\rm ij}^{\rm a}} \right], \text{ for } r_{\rm ij} \le r_{\rm c}, \tag{1}$$

where

$$C = \left(\frac{\lambda_{ij}^{r}}{\lambda_{ij}^{r} - \lambda_{ij}^{a}}\right) \left(\frac{\lambda_{ij}^{r}}{\lambda_{ij}^{a}}\right)^{\frac{\lambda_{ij}^{a}}{\lambda_{ij}^{r} - \lambda_{ij}^{a}}}$$

and i and j represent the bead types. Hence, σ_{ij} is an effective size of these beads, while ε_{ij} sets the interaction strength between beads of type i and j. One takes $\lambda_{ij}^a = 6$, which is connected to representing the dispersive interactions between the different particles, while λ_{ij}^r serves as a fitting parameter in the SAFT model and can vary. Finally, r_{ij} is the distance between any pair of beads, which interact when their distance is below a cutoff value set to $r_c = 4.583 \sigma$, where σ is the overall unit of length. The rest of the units are ε for the energy, *m* for the mass, while τ is the natural MD time unit $\tau = \sigma (m/\varepsilon)^{0.5}$. In real units, we consider the simulation to correspond to: $\sigma = 0.43635$ nm, $\varepsilon/k_B = 492$ K, m = 44.0521 amu and $\tau = 1.4062$ ps. The integration of the equations of motion was carried out with an integration time-step $\delta t = 0.005 \tau$, while the temperature was set to $k_B T/\varepsilon = 0.6057$, which would correspond to T = 25 °C in real units.

Here, we have chosen for our investigations the C10E4 surfactant, which has also been previously studied in the context of the coalescence of freely suspended droplets^{85,86} and superspreading.^{97–99} The above studies found other CmEn type surfactants to give similar behavior,^{85,86} so here we only consider C10E4 as representative of the whole family. Then, the CG representation of the C10E4 (Figure 3) uses hydrophobic alkane CG 'C' beads with each one representing a $-CH_2 - CH_2 - CH_2 - group$ of atoms. Hydrophilic CG 'EO' beads represent oxyethylene groups $-CH_2 - O - CH_2$. Finally, water CG 'W' beads correspond to two water molecules. The values of the nonbonded interaction parameters between CG beads are reported in Table S1 of the Supplementary Material (SM) and their masses in Table S2 of the SM.



FIG. 3. Description of model and notation. (a) Coarse-grained representation of water and C10E4 surfactant. (b–d) External and cross-section views are shown to highlight the bulk, interfaces, and contact line of the droplet ($\theta_s = 49^\circ$, with concentration above CAC). Surrounding water vapor is omitted for the sake of clarity. (b) Front view; (c) Top view; (d) Bottom view.

To link the alkane and oxyethylene beads together, each consecutive pair of beads along the surfactant chain interacts via a harmonic potential of the form

$$V(r_{ij}) = 0.5k(r_{ij} - \sigma_{ij})^2$$
⁽²⁾

where $k = 295.33 \varepsilon/\sigma^2$. In addition, each consecutive triad of EO beads along the chain experiences a harmonic angle potential, *i.e.*

$$V_{\theta}(\theta_{ijk}) = 0.5k_{\theta}(\theta_{ijk} - \theta_0)^2 \tag{3}$$

where θ_{ijk} is the angle between consecutive beads i, j=i+1 and k=j+1. Constants are $k_{\theta} = 4.32 \epsilon/\text{rad}^2$, and $\theta_0 = 2.75$ rad for the equilibrium angle.

The total number of beads per initial droplet in each simulation was 10⁵ and two different surfactant concentrations were considered, namely 6.25 wt%, which is below CAC, and 35.48 wt%, which is well above, with CAC roughly being 7.5 wt%.^{85,86} The latter concentration is taken as an average, since the number of water molecules in the liquid phase (droplet) fluctuates. The wettability of the smooth, unstructured substrate was also tuned, as described below, covering a range of wettable ($\theta_s < 90^\circ$) and non-wettable ($\theta_s > 90^\circ$) types of substrate (Figure 1). The exact values of the equilibrium contact angle of single droplets are reported in Table S3 of the SM along with the
corresponding droplet dimensions (Table S4 of the SM). Finally, to determine the beads belonging to the liquid phase (droplet), a cluster analysis has been performed.^{112,113}

To vary the wettability of the substrate, we need to define the interactions between the droplet beads and the substrate. This can be done by using the combining rules defined in SAFT γ -Mie¹⁰⁵:

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2},\tag{4}$$

$$\varepsilon_{ij} = \frac{\sqrt{\sigma_{ii}^3 \sigma_{jj}^3}}{\sigma_{ij}^3} \sqrt{\varepsilon_{ii} \varepsilon_{jj}}.$$
(5)

and start from the defined interactions for the liquid phases as given in Table S1 of the SM. By tuning the cross interaction ε_{ws} ("s" indicates the substrate), the empirical relationship between ε_{ws} and the contact angle of pure water droplets (Figure S1 of the SM) can be found, and is shown in Figure S2 of the SM. Then, by using the above combining rules, the parameter ε_{ss} corresponding to a given ε_{ws} can be obtained. We shall note here that the exact value of the σ_{ss} parameter is not important for our studies and is set to unity for simplicity. Similarly, $\lambda_{si}^r = 9$ is set for all interactions involving the substrate. Based on the knowledge of the latter parameters and the interactions σ_{ww} and ε_{ww} (Table S1 of the SM), the interaction of the substrate with the surfactant beads can be obtained as well, again using Equations 4-5. After obtaining all the interaction parameters, equilibrium simulations are run and the surfactant-laden droplet's contact angle is determined by using the method of Ref. 98 (see also text and Figure S1 of the SM) with data reported in Table S3 of the SM. It might be argued however that estimating the angles can in general be sensitive to the details of the definition of a sharp interface, as well as to the fitting procedure.^{114,115} Also, models that could take into account the disjoining pressure effects, very relevant in the context of droplets on solids substrates, might perform better than fitting spherical caps to nanodroplets.¹¹⁴ Moreover, according to a previous study,⁹⁸ the size of the droplet is large enough to guarantee that the equilibrium contact angle does not depend on the size of the droplet, which makes the interaction values valid for both larger and smaller droplets. Table S3 of the SM provides the exact values for all of the cross interactions between the beads and the substrate used in the simulations. Our choice here covers the relevant parameter space for surfactant concentration (above and below CAC) and substrate types (wettable, non-wettable, and about 90°).

The mass transport of surfactant molecules is investigated by tracking the motion of each individual molecule between the various parts of the droplet, which are illustrated in Figures 3c-d. These different parts are the liquid–gas (LG) surface for the left and right droplets (the center of the coordinate system is taken to be in the middle between the two droplets where the bridge forms), the bulk of the left and right droplets, the solid–liquid (SL) interface for the left and right droplets, the contact line for the left and right droplets, and the LG and SL interfaces, bulk, and contact line of the bridge as shown in Figure 3. Hence, this makes a total of twelve different regions where each surfactant molecule can belong. Further discussion and details on the calculation of the probabilities related to the motion of surfactant between these regions describing the mass transport mechanism of surfactants can be found in the SM. Finally, we have calculated the density profiles of the water and surfactant during coalescence, and the approach distance and velocity of the droplets³⁴, which will be further discussed in the following section.

III. RESULTS AND DISCUSSION

A. Surfactant mass transport mechanism

Our previous studies^{85,86} of the coalescence of freely suspended droplets have shown that surfactant plays an ever increasing role at the pinching point as its concentration in the droplets increases, while water has a smaller effect in initiating the coalescence process. Similar behavior is also observed in the case of $\theta_s > 90^\circ$ shown in Figure 4 for sessile droplets, since the bridge



FIG. 4. The pinching moment ($t \approx t_c$) in the case of (a) a non-wettable substrate ($\theta_s > 90^\circ$), (b) an intermediate case ($\theta_s \approx 90^\circ$), and (c) a wettable substrate ($\theta_s < 90^\circ$). Water participation in the coalescence process is more pronounced in the case $\theta_s < 90^\circ$, while the cases $\theta_s \ge 90^\circ$ behave very similarly to freely suspended droplets.^{85,86} Snapshots were obtained using Ovito software.⁸¹

formation starts far from the substrate (Figure 4a). For this reason, the bridge region initially is not affected by the presence of the substrate and the bridge angle is very steep ($\theta_b \approx 80^\circ$, for example, see Figure S6 of the SM) when pinching occurs. For the same reason, we find that the growth of the bridge occurs symmetrically in both the y and z directions (b, w, Figure 1). In contrast, in the case of wettable substrates, water molecules participate in the pinching process from its onset (Figure 4c).

To quantify mass transport, we count the surfactant molecule movements between the 12 regions identified in Figure 3. The raw numbers are reported in Table S5 of the SM. These set the intensity of the arrows in Figure 5, indicating the dominant direction of surfactant transport. Figures 5a–c present the dominant surfactant transport processes for the case $\theta_s > 90^\circ$. As in the case of freely suspended droplets, an interface film of surfactant initially forms consisting of surfactant from the LG surfaces of the droplets that come into contact. Figure 6 (Multimedia view) illustrates this in the case of non-wettable substrates, as well as the absence of this film when coalescence takes place on wettable substrates. The perimeter of the bridge is expected to linearly grow with b, while the area of the film increases as b^2 . Moreover, the data in Table S5 of the SM shows that the dominant movement of surfactant is towards the LG surface of the droplets, as in the case of freely suspended droplets. Since this movement towards the LG surface occurs and the area of contact between the droplet grows, the surfactant concentration in the film decreases, the film ruptures and some surfactant remains in the form of aggregates. Due to the lack of space at the LG interface of the merged droplets, surfactant from the newly formed aggregates in the bridge bulk cannot be accommodated at the LG interface. Also, we observe surfactant transport away from the bridge from the SL interface toward the LG surface through the contact line. Other transport processes away from the bridge are insignificant during coalescence in the case of non-wettable droplets. When the contact angle $\theta_s \approx 90^\circ$, the pinching is similar to the case of droplets with contact angle $\theta_s > 90^\circ$ (Figure 4) as well as the case of freely suspended droplets.^{85,86} Finally, θ_b has a value of around 90° at the pinching moment (for example, see Figure S6 of the SM).

The case $\theta_s < 90^\circ$ shows a somewhat different behavior. The transport toward the LG surface is higher than in the cases where $\theta_s \ge 90^\circ$, and unlike the previous cases, we do not see the formation of new aggregates as coalescence takes place [Figure 6 (Multimedia view)]. This can be attributed to several causes. Firstly, the amount of surfactant at the bridge is smaller in the case of $\theta_s < 90^\circ$, due to the higher curvature of the droplets. In this case, there is only a small portion of the droplet surfaces that come into contact, at the contact line of the droplets. In contrast, for non-wettable



FIG. 5. Snapshots of coalescing droplets with C10E4 surfactant and surfactant mass transport on substrates of different wettability. The surfactant concentration in the liquid phase is above CAC, namely 35.48 wt%. The size of the arrow heads reflects the probabilities associated with surfactant transport to the different droplet areas (see Table S5 of the SM for further details). (a–c) corresponds to the case $\theta_s \simeq 142^\circ$ with snapshots obtained at times (a) $t_c + 17.5 \tau$, (b) $t_c + 185.0 \tau$, and (c) $t_c + 1733.7 \tau$. (d–f) $\theta_s \simeq 94^\circ$, with snapshots shown at times (d) $t_c + 28.75 \tau$, (e) $t_c + 315.0 \tau$, and (f) $t_c + 1415.0 \tau$. (g–i) $\theta_s \simeq 49^\circ$ with snapshots at times (g) $t_c + 200.0 \tau$, (h) $t_c + 1358.7 \tau$, and (i) $t_c + 2200.0 \tau$. Snapshots in (a), (d), and (g) are soon after the end of the thermal regime. Snapshots (b) and (e) illustrate a clearly developed bridge with new aggregates formed in its bulk or additional monomers remaining at the bridge region. (h) shows a clearly developed bridge highlighting the absence of aggregates in the case $\theta_s < 90^\circ$. (c), (f), and (i) correspond to cases of a fully developed bridge. Magnified views of the bridge region and its cross-section (showing only surfactant hydrophobic beads in the bridge region, red) are attached above and to the right of the snapshots, respectively. Snapshots were obtained using Ovito software.⁸¹

substrates, a large portion of the surfaces of the two droplets come into contact forming a film. This major contact area difference may also explain the higher degree of participation of water molecules in the pinching process in the case of wettable substrates. Secondly, there is much less



FIG. 6. (Multimedia view) Cross-section of the bridge during coalescence on different substrates (first two columns, $\theta_s > 90^\circ$, middle two columns, $\theta_s \approx 90^\circ$, and last two columns, $\theta_s < 90^\circ$). Upper row shows the case of droplets with concentration lower than CAC (6.25 wt%), while the lower row with concentration above CAC (35.248 wt%). All beads (odd columns) or surfactant beads only (even columns) are shown at each cross-section at the bridge.

space in the bridge to form aggregates from any excess of surfactant that does not start at the bridge's LG surface. Finally, we note that surfactant transport from the contact line towards the SL and LG interface, is overall more pronounced than in the case of non-wettable substrates. This might be due to the immediate start of the decrease of the contact-line length as the droplets merge, resulting in a greater excess of surfactant in the contact-line region, and a greater migration to the LG and SL interfaces.

B. Bridge dynamics

In the case $\theta_s > 90^\circ$, the pinching of the two droplets takes place well above the substrate (Figure 1b), and only later does the bridge region make contact with the substrate (Figure 1c). In the case $\theta_s \leq 90^\circ$, the bridge starts to form on the substrate from the onset of the coalescence process, which affects the bridge dynamics. The rate of coalescence can generally be described by the pace of the bridge growth in the direction normal as well as parallel to the substrate. The size of the bridge in these directions is *b* and *w*, respectively, both defined as shown in Figure 1. Figure 7 plots *b* and *w* above the CAC as a function of time (see Figures S3 and S4 in the SM for pure water and concentration below CAC.) In the cases above CAC and for nonwettable substrates ($\theta_s > 90^\circ$), exponents for *b* are about 0.5, which are in line with the case of freely suspended droplets.^{85,86} In contrast, in the case of wettable substrates, the exponent is higher reaching values of about 0.72, which suggests a much faster dynamics in comparison with the nonwettable substrates. Similarly,

the parameter *w* shows a similar but weaker tendency for growth with exponents of about 0.5 for both freely suspended droplets^{85,86} and droplets on nonwettable substrates, up to about 0.65 for the wettable case. These higher values are agreeable with the 2/3 values seen for polymer droplets on wettable substrates.³⁴ In the case of water droplets, as a sanity check, exponents of *b* as well as *w* for both wettable and nonwettable substrates are in the range 0.60–0.66, which is in line with results reported in the literature,⁸⁸ where a power law of 2/3 has been suggested (see Figure S3a of the SM).

When surfactant concentration is below the CAC (Figure S3b of the SM), exponents for *b* are in the range 0.57–0.60 for non-wettable substrates (similar to pure water), but a significant increase of the exponent is noted for substrates reaching about 0.87, when the equilibrium contact angle of the droplet is about 52°. The exponents for *w* are in the range 0.55–0.68, with the highest exponents observed in the case of equilibrium contact angles close to 70°.

Finally, the initial thermal regime is well visible for sessile droplets as in the case of freely suspended droplets^{85,86} or sessile polymer droplets.³⁴ However, we notice both a decreasing extent



FIG. 7. Bridge height, *b*, as a function of time, *t*, starting from the pinching moment, t_c . Inset shows the bridge width, *w*. Results for droplets with surfactant concentration 35.48 wt% on substrates with different wettability, as indicated. The values of the power-law exponents for *b* and *w* are β_b and β_w , respectively, and are reported in the plot. Additional data for droplets without surfactant and with surfactant concentrations below CAC are reported in Figures S3 and S4 of the SM.



FIG. 8. (a) Rate of change of angle θ_b , $m = d\theta_b/d(t - t_c)$, as a function of the equilibrium contact angle, θ_s , that expresses the wettability of the substrates with $\theta_s > 90^\circ$ reflecting non-wettable cases. *m* is calculated from linear fits to the data of Figures S5 and S6 of the SM, where a linear change of θ_b with time is observed to a good approximation. The $\theta_s = 180^\circ$ data is for freely suspended droplets (no substrate). As an example here, panel b shows data for droplets with surfactant concentration 6.26 wt%.

of these fluctuations (smaller *b*, *w*) for sessile droplets when $\theta_s < 90^\circ$, due to the additional attraction and the contact with the substrate which suppresses these fluctuations, but also concurrently a strong lengthening of this regime in time, by almost an order of magnitude.

C. Angle formed at the bridge

We monitored the angle θ_b (Figure 1) as a function of time for all cases by employing the method of Ref. 98 (see Figure S1 and text in the SM). In particular, a layer parallel to the substrate at a distance *b* was considered, as indicated by the dashed line of Figure 1g. The dimensions of the spherical-cap liquid-phase above this layer were recorded in the *x* and *y* directions, as well as the distance of the apex from the layer, which are used as input to calculate θ_b .⁹⁸ The approach has been applied in both the right and the left parts of the merged droplets and the average was taken, resulting in the final values reported for θ_b . Time traces of θ_b are plotted in Figure S5 and S6 of the SM for all cases considered here, while an example is shown in Figure 8. We can

observe that θ_b exhibits to a large degree a linear behavior with time, which allows us to gather the slopes of the various curves and thus monitor the rate of change (dynamics) of this angle, *m*, during coalescence.

These rates of change data are plotted in Figure 8. The rate slows down as the substrate becomes more wettable, whether surfactant is present or not, but for $\theta_s \gtrsim 140^\circ$, the freely suspended behavior is already reached. This is also directly seen in Figure S5 of the SM. Greater surfactant concentration also slows down the process, as could be suspected from the earlier suspended droplet studies^{85,86}, with pure water droplets being the fastest. Hence, the use of surfactant facilitates the smoothing of the wedge formation at the bridge apex.

D. Velocity of approach

We calculated the coalescing system length, X, as defined in Figure 1, and done in our previous work in the context of sessile polymer droplets.³⁴ Its value is approximately one droplet diameter.



FIG. 9. The distance between the centers of mass of the two droplets in the *x*-direction, *X*, (see Figure 1) as a function of time, *t*, starting from the moment of first contact of the droplets, t_c , for surfactant-laden droplets of concentrations above CAC (35.48 wt%). The inset shows the instantaneous velocity, $u = \dot{X}$. Data for water droplets and surfactant-laden droplets with concentration below CAC are shown in Figure S7 of the SM.



FIG. 10. Surfactant density at the moment of pinching (upper panels) and at a time when the bridge has been clearly developed (bottom panels) for above droplets with surfactant concentration amounting to 35.48 wt%. Here, cases for substrates with different wettability are shown, namely, (a) $\theta_s \simeq 142^\circ$, snapshots taken at t_c and $t_c + 100 \tau$, (b) $\theta_s \simeq 90^\circ$, snapshots taken at t_c and $t_c + 412.5 \tau$, and (c) $\theta_s \simeq 50^\circ$, snapshots taken at t_c and $t_c + 1352.5 \tau$.

Its time derivative, $u = \dot{X}$, provides a measure of how fast the droplets approach each other. Figure 9 presents *X* for droplets above the CAC on various substrates with different wettability, while data for water droplets and droplets with surfactant with a concentration below CAC are given in Figure S7 of the SM. Overall, the velocity of approach is smaller in the case of wettable substrates, irrespective of surfactant concentration, paralleling what we saw with bridge sizes *b* and *w* and the angle formed at the bridge θ_b . This is also true for water droplets. The plots of Figure S8 of the SM show that an increase of surfactant concentration also significantly slows down the approach of the two droplets. This is mostly noticeable in the case of high concentrations, while surfactant-laden droplets with concentration below CAC show a similar behavior to pure water. Moreover, surfactant smooths the approach of the two droplets, as can be seen by the change of shape of the velocity of approach curves, particularly visible in Figure S8 of the SM. Finally, there is a clear shift in the moment of maximum velocity to later times for more wettable substrates at higher surfactant concentration, though this shift is much smaller in the latter case.

E. Density Profiles

The density of surfactant molecules on a cross-section parallel to the x - z plane and passing through the center of mass of the droplets is presented in Figure 10. Also, Figure S9 of the SM shows the corresponding density distribution of water molecules for various substrates. We observe the formation of surfactant aggregates during the coalescence for substrates with equilibrium contact angles larger than 90°, while it is absent for wettable substrates (see for example Fig. 5a–b and d–e versus g–h). Large concentrations of surfactant are distributed at the LG and SL interfaces. Interior to this lies an inner layer devoid of aggregates, which is particularly wide for the wettable droplets. Notably the wettable case has a much smaller number of aggregates, despite the fact that all cases shown have the same concentration. This is due to the larger area of the LG and SL interfaces on wettable substrates, which might suggest that the CAC has a higher value. The smaller thickness of the wettable droplets, also, hinders the accommodation of a larger number of surfactant aggregates.

IV. CONCLUSIONS

In this study, we have investigated the coalescence of sessile surfactant-laden droplets on substrates with different wettability, including those with equilibrium contact-angle higher as well as lower than 90°. We have explored the influence of surfactant concentration both below and above the CAC, and we juxtaposed our results with the case of pure water droplets. In particular, we have elucidated the mass transport mechanism in all these cases and explored the dynamics of the coalescence process by following the height and width of the bridge, the rate of change of the bridge angle, as well as the velocity of approach of the droplets.

Overall, sessile droplets with $\theta_s \ge 90^\circ$ share similarities with freely suspended droplets, and for $\theta_s \simeq 140^\circ$ already behave practically identically as if they were freely suspended. In this case, the influence of the substrate on the coalescence process is rather small. For example, the pinching region is mainly driven by the interaction of the surfactant molecules at the droplets' LG surface, as in the case of the freely suspended droplets. In contrast, in the case of wettable substrates $(\theta_s < 90^\circ)$, we see that water molecules are part of the pinching process, a significant departure from the physics of the freely suspended case. The mass transport of surfactant molecules during coalescence also shows some differences between wettable and nonwettable substrates, which mostly relates to their intensity. A more notable difference is the absence of newly formed aggregates as the bridge grows during coalescence in the case of wettable substrates. This is due to the lower amount of surfactant at the pinching region as the initial contact film has a far smaller area. In fact, the nature of the surface of first contact changes dramatically from a circular region to a thin contact line when the threshold of contact angle $\theta_s \approx 90^\circ$ is crossed. The smaller amount of space available in the bridge region between the LG and SL interfaces during later evolution also contributes. The latter is related to a still open question of identifying changes in CAC when the equilibrium contact angle of the droplets changes.

We also found that an increased wettability of the substrate leads to higher rate exponents for the growth of the bridge radius, *b*, and its width, *w*, but generally exponents for *w* are lower. We confirm the approach to a $\approx \frac{2}{3}$ rate exponent at low contact angles suggested by several previous studies,^{34,88} but see no evidence for the previously proposed linear growth.⁸³ Overall, surfactant will decelerate the coalescence of the sessile droplets, when above CAC, but we observed higher exponents in the case of concentration below the CAC for wettable substrates, which is not fully understood at the moment. Similarly, the bridge angle, θ_b , changes at a faster pace in the case of water droplets and low concentration and when the wettability of the substrate is lower (larger θ_s). Finally, by analyzing the velocity of approach of the two droplets, which is generally high at the initial stages of coalescence when the bridge forms, we found that more wettable substrates and a higher surfactant concentration will lead to smoother changes in the velocity, less acceleration. We anticipate that our study provides fundamental insights into the coalescence of sessile surfactant-laden droplets, an important phenomenon that has previously mostly remained unexplored at the molecular-scale level.

V. SUPPLEMENTARY MATERIAL

The SM contains: details on the estimation of the contact angle of a sessile droplet. Calibration of the dependence of the contact angle of a water droplet as a function of the droplet–substrate attraction parameter ε_{ws} . Table of the water–substrate and surfactant–substrate interaction parameters. Further data and methodology details on the mass transport mechanism along with the probabilities of surfactant moving between different areas of the droplets. Data on the bridge angle, the velocity of approach, and the density profiles of the droplets, for a wider set of parameters than shown in the main text.

ACKNOWLEDGMENTS

This research has been supported by the National Science Centre, Poland, under grant No. 2019/34/E/ST3/00232. We gratefully acknowledge Polish high-performance computing infrastructure PLGrid (HPC Centers: ACK Cyfronet AGH) for providing computer facilities and support within computational grant no. PLG/2022/015747.

REFERENCES

- ¹J. D. Paulsen, R. Carmigniani, A. Kannan, J. C. Burton, and S. R. Nagel, "Coalescence of bubbles and drops in an outer fluid," Nat. Commun. **5**, 3182 (2014).
- ²Y. Yoon, F. Baldessari, H. D. Ceniceros, and L. G. Leal, "Coalescence of two equal-sized deformable drops in an axisymmetric flow," Phys. Fluids **19**, 102102 (2007).
- ³M. I. Khodabocus, M. Sellier, and V. Nock, "Scaling laws of droplet coalescence: Theory and numerical simulation," Adv. Math. Phys. **2018**, 4906016 (2018).
- ⁴S. Perumanath, M. K. Borg, M. V. Chubynsky, J. E. Sprittles, and J. M. Reese, "Droplet coalescence is initiated by thermal motion," Phys. Rev. Lett. **122**, 104501 (2019).
- ⁵J. Eggers, J. R. Lister, and H. A. Stone, "Coalescence of liquid drops," J. Fluid Mech. **401**, 293–310 (1999).
- ⁶D. G. Aarts, H. N. Lekkerkerker, H. Guo, G. H. Wegdam, and D. Bonn, "Hydrodynamics of droplet coalescence," Phys. Rev. Lett. **95**, 164503 (2005).
- ⁷J. E. Spritles and Shikhmurzaev, "Coalescence of liquid drops: Different models versus experiment," Phys. Fluids **24**, 122105 (2012).
- ⁸M. Dudek, D. Fernandes, E. Helno Herø, and G. Øye, "Microfluidic method for determining drop-drop coalescence and contact times in flow," Colloids Surf. A: Physicochem. Eng. Asp. 586, 124265 (2020).
- ⁹M. M. Rahman, W. Lee, A. Iyer, and S. J. Williams, "Viscous resistance in drop coalescence," Phys. Fluids **31**, 012104 (2019).
- ¹⁰J. D. Berry and R. R. Dagastine, "Mapping coalescence of micron-sized drops and bubbles," J. Colloid Interface Sci. 487, 513–522 (2017).
- ¹¹P. M. Somwanshi, K. Muralidhar, and S. Khandekar, "Coalescence dynamics of sessile and pendant liquid drops placed on a hydrophobic surface," Phys. Fluids **30**, 092103 (2018).

- ¹²P. K. Kirar, K. Alvarenga, P. Kolhe, G. Biswas, and K. Chandra Sahu, "Coalescence of drops on the free-surface of a liquid pool at elevated temperatures," Phys. Fluids **32**, 052103 (2020).
- ¹³S. Bayani, Y. Tabe, Y. T. Kang, S. H. Lee, and C. K. Choi, "Surface plasmon resonance imaging of drop coalescence at high-temporal resolution," J. Flow Vis. Image Process. 25, 191–205 (2018).
- ¹⁴M. Brik, S. Harmand, and I. Zaaroura, "Relaxation and contact angle dynamics during the coalescence of different sized vertically aligned water drops in different silicone oil viscosities," Colloids Surf. A: Physicochem. Eng. Asp. **629**, 127429 (2021).
- ¹⁵C. R. Anthony, M. T. Harris, and O. A. Basaran, "Initial regime of drop coalescence," Phys. Rev. Fluids 5, 033608 (2020).
- ¹⁶V. R. Kern, T. Sæter, and A. Carlson, "Viscoplastic sessile drop coalescence," Phys. Rev. Fluids 7, L081601 (2022).
- ¹⁷M. Heinen, M. Hoffmann, F. Diewald, S. Seckler, K. Langenbach, and J. Vrabec, "Droplet coalescence by molecular dynamics and phase-field modeling," Phys. Fluids **34**, 042006 (2022).
- ¹⁸M. Geri, B. Keshavarz, G. H. McKinley, and J. W. M. Bush, "Thermal delay of drop coalescence," J. Fluid Mech. **833**, R3 (2017).
- ¹⁹M. Abouelsoud and B. Bai, "Bouncing and coalescence dynamics during the impact of a falling drop with a sessile drop on different solid surfaces," Phys. Fluids **33**, 063309 (2021).
- ²⁰L. Hilaire, B. Siboulet, S. Charton, and J.-F. Dufrêche, "Coalescence initiation in liquid–liquid systems: A stochastic model," Langmuir **39**, 14853–14858 (2023).
- ²¹E. G. Bowen, "The formation of rain by coalescence," Aust. J. Chem. **3**, 193–213 (1950).
- ²²M. Denys, P. Deuar, Z. Che, and P. E. Theodorakis, "A lagrangian particle-based numerical model for surfactant-laden droplets at macroscales," Phys. Fluids **34**, 095126 (2022).
- ²³E. X. Berry and R. L. Reinhardt, "An analysis of cloud drop growth by collection: part 3. accretion and self-collection," J. Atmos. Sci. **31**, 2118–2126 (1974).
- ²⁴A. Kovetz and B. Olund, "The effect of coalescence and condensation on rain formation in a cloud of finite vertical extent," J. Atmos. Sci. 26, 1060–1065 (1969).
- ²⁵M. Singh, H. Haverinen, P. Dhagat, and G. Jabbour, "Inkjet printing process and its applications," Adv. Mater. 22, 673–685 (2010).
- ²⁶S. Feng, L. Yi, L. Zhao-Miao, C. Ren-Tuo, and W. Gui-Ren, "Advances in micro-droplets coalescence using microfluidics," Chinese J. Anal. Chem. 43, 1942–1954 (2015).

- ²⁷M. Dudek, J. Chicault, and G. Øye, "Microfluidic investigation of crude oil droplet coalescence: effect of oil/water composition and droplet aging," Energy Fuels **34**, 5110–5120 (2019).
- ²⁸K. Choi, A. H. Ng, R. Fobel, and A. R. Wheeler, "Digital microfluidics," Annu. Rev. Anal. Chem. 5, 413–440 (2012).
- ²⁹R. B. Fair, "Digital microfluidics: is a true lab-on-a-chip possible?" Microfluid. Nanofluid. 3, 245–281 (2007).
- ³⁰T. Thomas and H. N. Unni, "Led-based opto-wetting and fluidic transport for droplet mixing," Microfluid. Nanofluid. 23, 1–12 (2019).
- ³¹H. Wijshoff, "The dynamics of the piezo inkjet printhead operation," Phys. Rep. **491**, 77–177 (2010).
- ³²P. J. Dekker, M. A. Hack, W. Tewes, C. Datt, A. Bouillant, and J. H. Snoeijer, "When elasticity affects drop coalescence," Phys. Rev. Lett. **128**, 028004 (2022).
- ³³E. Calvo, E. de Malmazet, F. Risso, and O. Masbernat, "Coalescence of water drops at an oil-water interface loaded with microparticles and surfactants," Ind. Eng. Chem. Res. 58, 15573–15587 (2019).
- ³⁴S. Arbabi and P. E. Theodorakis, "Coalescence of sessile polymer droplets: A molecular dynamics study," Macromol. Theory Simul., 2300017 (2023).
- ³⁵S. C. Varma, A. Saha, and A. Kumar, "Coalescence of polymeric sessile drops on a partially wettable substrate," Phys. Fluids **33**, 123101 (2021).
- ³⁶V. S. Sivasankar, S. A. Etha, D. R. Hines, and S. Das, "Coalescence of microscopic polymeric drops: Effect of drop impact velocities," Langmuir **37**, 13512–13526 (2021).
- ³⁷V. S. Sivasankar, D. R. Hines, and S. Das, "Numerical study of the coalescence and mixing of drops of different polymeric materials," Langmuir **38**, 14084–14096 (2022).
- ³⁸M. R. Otazo, R. Ward, G. Gillies, R. S. Osborne, M. Golding, and M. A. K. Williams, "Aggregation and coalescence of partially crystalline emulsion drops investigated using optical tweezers," Soft Matter 15, 6383–6391 (2019).
- ³⁹C. Vannozzi, "Effect of polymer-coated gold nanoparticle stabilizers on drop coalescence," Phys. Fluids **31**, 082112 (2019).
- ⁴⁰N. I. Politova, S. Tcholakova, S. Tsibranska, N. D. Denkov, and K. Muelheims, "Coalescence stability of water-in-oil drops: Effects of drop size and surfactant concentration," Colloids Surf. A: Physicochem. Eng. Asp. **531**, 32–39 (2017).

- ⁴¹W. H. Weheliye, T. Dong, and P. Angeli, "On the effect of surfactants on drop coalescence at liquid/liquid interfaces," Chem. Eng. Sci. **161**, 215–227 (2017).
- ⁴²G. Soligo, A. Roccon, and A. Soldati, "Coalescence of surfactant-laden drops by phase field method," J. Comput. Phys. **376**, 1292–1311 (2019).
- ⁴³T. Dong, W. H. Weheliye, P. Chausset, and P. Angeli, "An experimental study on the drop/interface partial coalescence with surfactants," Phys. Fluids **29**, 102101 (2017).
- ⁴⁴T. Dong, W. H. Weheliye, and P. Angeli, "Laser induced fluorescence studies on the distribution of surfactants during drop/interface coalescence," Phys. Fluids **31**, 012106 (2019).
- ⁴⁵N. M. Kovalchuk, M. Reichow, T. Frommweiler, D. Vigolo, and M. J. H. Simmons, "Mass transfer accompanying coalescence of surfactant-laden and surfactant-free drop in a microfluidic channel," Langmuir **35**, 9184–9193 (2019).
- ⁴⁶T. C. Botti, A. Hutin, E. Quintella, and M. S. Carvalho, "Effect of interfacial rheology on drop coalescence in water–oil emulsion," Soft Matter **18**, 1423–1434 (2022).
- ⁴⁷C. Constante-Amores, A. Batchvarov, L. Kahouadji, S. Shin, J. Chergui, D. Juric, and O. Matar,
 "Role of surfactant-induced marangoni stresses in drop-interface coalescence," J. Fluid Mech. **925**, A15 (2021).
- ⁴⁸M. Kasmaee, F. Varaminian, P. Khadiv-Parsi, and J. Saien, "Effects of different surfactants and physical properties on the coalescence of dimethyl disulfide drops with mother phase at the interface of sodium hydroxide aqueous solutions," J. Mol. Liq. **263**, 31–39 (2018).
- ⁴⁹E. Nowak, Z. Xie, N. M. Kovalchuk, O. K. Matar, and M. J. Simmons, "Bulk advection and interfacial flows in the binary coalescence of surfactant-laden and surfactant-free drops," Soft Matter **13**, 4616–4628 (2017).
- ⁵⁰E. Nowak, N. M. Kovalchuk, Z. Che, and M. J. Simmons, "Effect of surfactant concentration and viscosity of outer phase during the coalescence of a surfactant-laden drop with a surfactantfree drop," Colloids Surf. A Physicochem. Eng. Asp. **505**, 124–131 (2016).
- ⁵¹N. Jaensson and J. Vermant, "Tensiometry and rheology of complex interfaces," Curr. Opin. Colloid Interface Sci. **37**, 136–150 (2018).
- ⁵²S. Narayan, A. E. Metaxa, R. Bachnak, T. Neumiller, C. S. Dutcher, *et al.*, "Zooming in on the role of surfactants in droplet coalescence at the macro-and microscale," Curr. Opin. Colloid Interface Sci. **50**, 101385 (2020).
- ⁵³I. B. Ivanov, K. D. Danov, and P. A. Kralchevsky, "Flocculation and coalescence of micron-size emulsion droplets," Colloids Surf. A Physicochem. Eng. **152**, 161–182 (1999).

- ⁵⁴S. Tcholakova, N. D. Denkov, and T. Danner, "Role of surfactant type and concentration for the mean drop size during emulsification in turbulent flow," Langmuir 20, 7444–7458 (2004).
- ⁵⁵D. Langevin, "Coalescence in foams and emulsions: Similarities and differences," Curr. Opin. Colloid Interface Sci. 44, 23–31 (2019).
- ⁵⁶J. Lu and C. M. Corvalan, "Coalescence of viscous drops with surfactants," Chem. Eng. Sci.
 78, 9–13 (2012).
- ⁵⁷O. D. Velev, T. D. Gurkov, and R. P. Borwankar, "Spontaneous cyclic dimpling in emulsion films due to surfactant mass transfer between the phases," J. Colloid Interface Sci. **159**, 497– 501 (1993).
- ⁵⁸V. C. Suja, A. Kar, W. Cates, S. M. Remmert, P. D. Savage, and G. G. Fuller, "Evaporationinduced foam stabilization in lubricating oils," Proc. Natl. Acad. Sci. U.S.A. **115**, 7919–7924 (2018).
- ⁵⁹J.-C. Baret, "Surfactants in droplet-based microfluidics," Lab Chip. **12**, 422–433 (2012).
- ⁶⁰K. S. Elvira, F. Gielen, S. S. Tsai, and A. M. Nightingale, "Materials and methods for droplet microfluidic device fabrication," Lab Chip. 22, 859–875 (2022).
- ⁶¹R. W. Hopper, "Coalescence of two viscous cylinders by capillarity: Part i, theory," J. Am. Ceram. Soc **76**, 2947–2952 (1993).
- ⁶²M. A. Bruning, M. Costalonga, S. Karpitschka, and J. H. Snoeijer, "Delayed coalescence of surfactant containing sessile droplets," Phys. Rev. Fluids **3**, 073605 (2018).
- ⁶³H. Yi, T. Fu, C. Zhu, and Y. Ma, "Cascade coalescence of droplets in a sudden expansion microchannel," Chem. Eng. J. 442, 136240 (2022).
- ⁶⁴A. Schwarzwälder, J. Meyer, and A. Dittler, "Experimental analysis of droplet coalescence and transport mechanisms on a single vertical fiber," Exp. Fluids **64**, 103 (2023).
- ⁶⁵Y. Sun, D. Yang, H. Sun, H. Wu, Q. Chang, L. Shi, Y. Cao, Y. He, and T. Xie, "Experimental study on the falling and coalescence characteristics of droplets under alternating electric fields," Colloids Surf. A Physicochem. Eng. Asp. **603**, 125136 (2020).
- ⁶⁶M. W. Lee, D. K. Kang, S. S. Yoon, and A. L. Yarin, "Coalescence of two drops on partially wettable substrates," Langmuir **28**, 3791–3798 (2012).
- ⁶⁷S. Chen, J. Wang, C. Chen, and A. Mahmood, "Understanding the coalescence and non-coalescence of underwater oil droplets," Chem. Phys. **529**, 110466 (2020).

- ⁶⁸C. J. Park, J. Ha, J. H. Lee, and H.-Y. Kim, "Coalescence of oil drops and films on micropillared substrates enabled by enhanced water drainage through pillar gaps," Soft Matter **17**, 5888–5896 (2021).
- ⁶⁹L. Duchemin, J. Eggers, and C. Josserand, "Inviscid coalescence of drops," J. Fluid Mech. 487, 167–178 (2003).
- ⁷⁰L. Leal, "Flow induced coalescence of drops in a viscous fluid," Phys. Fluids 16, 1833–1851 (2004).
- ⁷¹M. Chinaud, V. Voulgaropoulos, and P. Angeli, "Surfactant effects on the coalescence of a drop in a hele-shaw cell," Phys. Rev. E **94**, 033101 (2016).
- ⁷²J. Shaikh, N. D. Patil, A. Sharma, and R. Bhardwaj, "Numerical simulations and experiments on droplet coalescence dynamics over a liquid–air interface: Mechanism and effect of dropletsize/surface-tension," SN Appl. Sci. 3, 292 (2021).
- ⁷³K. Gu, T. Gang, and L. Chen, "Numerical simulation of droplet coalescence based on the sph method," Theor. Appl. Mech. Lett. **12**, 100333 (2022).
- ⁷⁴L. Y. Yeo, O. K. Matar, E. S. P. de Ortiz, and G. F. Hewitt, "Film drainage between two surfactant-coated drops colliding at constant approach velocity," J. Colloid Interface Sci. 257, 93–107 (2003).
- ⁷⁵Y. Hu, D. Pine, and L. G. Leal, "Drop deformation, breakup, and coalescence with compatibilizer," Phys. Fluids **12**, 484–489 (2000).
- ⁷⁶A. Mansouri, H. Arabnejad, and R. Mohan, "Numerical investigation of droplet-droplet coalescence and droplet-interface coalescence," in *FEDSM*, Vol. 46216 (American Society of Mechanical Engineers, 2014) p. V01AT05A006.
- ⁷⁷J.-Y. Chen, P. Gao, Y.-T. Xia, E.-Q. Li, H.-R. Liu, and H. Ding, "Early stage of delayed coalescence of soluble paired droplets: A numerical study," Phys. Fluids **33**, 092005 (2021).
- ⁷⁸C. R. Anthony, M. T. Harris, and O. A. Basaran, "Initial regime of drop coalescence," Phys. Rev. Fluids 5, 033608 (2020).
- ⁷⁹F. Y. Leong and D.-V. Le, "Droplet dynamics on viscoelastic soft substrate: Toward coalescence control," Phys. Fluids **32**, 062102 (2020).
- ⁸⁰J. Sprittles and Y. Shikhmurzaev, "Coalescence of liquid drops: Different models versus experiment," Phys. Fluids 24, 122105 (2012).
- ⁸¹A. Stukowski, "Visualization and analysis of atomistic simulation data with ovito-the open visualization tool," Model. Simul. Mater. Sci. Eng. 18, 015012 (2010).

- ⁸²C. Verdier and M. Brizard, "Understanding droplet coalescence and its use to estimate interfacial tension," Rheol. Acta 41, 514–523 (2002).
- ⁸³J. Hernández-Sánchez, L. Lubbers, A. Eddi, and J. Snoeijer, "Symmetric and asymmetric coalescence of drops on a substrate," Phys. Rev. Lett **109**, 184502 (2012).
- ⁸⁴J. D. Paulsen, "Approach and coalescence of liquid drops in air," Phys. Rev. E 88, 063010 (2013).
- ⁸⁵S. Arbabi, P. Deuar, M. Denys, R. Bennacer, Z. Che, and P. E. Theodorakis, "Coalescence of surfactant-laden droplets," Phys. Fluids **35**, 063329 (2023).
- ⁸⁶S. Arbabi, P. Deuar, M. Denys, R. Bennacer, Z. Che, and P. E. Theodorakis, "Molecular dynamics simulation of the coalescence of surfactant-laden droplets," Soft Matter **19**, 8070–8080 (2023).
- ⁸⁷T. Li, "Molecular dynamics simulations of droplet coalescence and impact dynamics on the modified surfaces: A review," Comput. Mater. Sci. 230, 112547 (2023).
- ⁸⁸A. Eddi, K. Winkels, and J. Snoeijer, "Influence of droplet geometry on the coalescence of low viscosity drops," Phys. Rev. Lett. **111**, 144502 (2013).
- ⁸⁹W. Ristenpart, P. McCalla, R. Roy, and H. Stone, "Coalescence of spreading droplets on a wettable substrate," Phys. Rev. Lett. **97**, 064501 (2006).
- ⁹⁰R. Narhe, D. Beysens, and Y. Pomeau, "Dynamic drying in the early-stage coalescence of droplets sitting on a plate," EPL 81, 46002 (2008).
- ⁹¹N. Kapur and P. H. Gaskell, "Morphology and dynamics of droplet coalescence on a surface," Phys. Rev. E **75**, 056315 (2007).
- ⁹²P. Bazazi and S. H. Hejazi, "Retarding spreading of surfactant drops on solid surfaces: Interplay between the marangoni effect and capillary flows," Phys. Rev. Fluids 5, 084006 (2020).
- ⁹³P. Yatsyshin and S. Kalliadasis, "Surface nanodrops and nanobubbles: a classical density functional theory study," J. Fluid Mech. **913**, A45 (2021).
- ⁹⁴S. C. Varma, A. Saha, S. Mukherjee, A. Bandopadhyay, A. Kumar, and S. Chakraborty, "Universality in coalescence of polymeric fluids," Soft Matter 16, 10921–10927 (2020).
- ⁹⁵S. C. Varma, D. Dasgupta, and A. Kumar, "Elasticity can affect droplet coalescence," Phys. Rev. Fluids **34**, 028004 (2022).
- ⁹⁶C. Verdier, "Coalescence of polymer droplets: experiments on collision," C. R. Acad. Sci. Paris, Ser. IV, Phys. 1, 119–126 (2000).

- ⁹⁷P. E. Theodorakis, E. A. Müller, R. V. Craster, and O. K. Matar, "Superspreading: Mechanisms and molecular design," Langmuir **31**, 2304–2309 (2015).
- ⁹⁸P. E. Theodorakis, E. A. Müller, R. V. Craster, and O. K. Matar, "Modelling the superspreading of surfactant-laden droplets with computer simulation," Soft Matter **11**, 9254–9261 (2015).
- ⁹⁹P. E. Theodorakis, E. R. Smith, and Müller, "Spreading of aqueous droplets with common and superspreading surfactants. a molecular dynamics study," Colloids Surf. A: Physicochem. Eng. Aspects. **581**, 123810 (2019).
- ¹⁰⁰O. Lobanova, C. Avendaño, T. Lafitte, E. A. Müller, and G. Jackson, "SAFT- γ force field for the simulation of molecular fluids. 4. a single-site coarse-grained model of water applicable over a wide temperature range." Mol. Phys. **113**, 1228–1249 (2015).
- ¹⁰¹O. Lobanova, Development of coarse-grained force fields from a molecular based equation of state for thermodynamic and structural properties of complex fluids, Ph.D. thesis, Imperial College London (2014).
- ¹⁰²O. Lobanova, A. Mejia, G. Jackson, and E. A. Müller, "Saft-γ force field for the simulation of molecular fluids 6: Binary and ternary mixtures comprising water, carbon dioxide, and nalkanes," J. Chem. Thermodyn. **93**, 320–336 (2016).
- ¹⁰³P. Morgado, O. Lobanova, E. A. Müller, G. Jackson, M. Almeida, and E. J. Filipe, "Saft-γ force field for the simulation of molecular fluids: 8. hetero-segmented coarse-grained models of perfluoroalkylalkanes assessed with new vapour–liquid interfacial tension data," Mol. Phys. **114**, 2597–2614 (2016).
- ¹⁰⁴E. A. Müller and G. Jackson, "Force field parameters from the SAFT-γ equation of state for use in coarse-grained molecular simulations," Annu. Rev. Chem. Biomol. Eng. **5**, 405–427 (2014).
- ¹⁰⁵T. Lafitte, A. Apostolakou, C. Avendaño, A. Galindo, C. S. Adjiman, E. A. Müller, and G. Jackson, "Accurate statistical associating fluid theory for chain molecules formed from mie segments," J. Chem. Phys. **139**, 154504 (2013).
- ¹⁰⁶C. Avendaño, T. Lafitte, A. Galindo, C. S. Adjiman, G. Jackson, and E. A. Müller, "Saft-γ force field for the simulation of molecular fluids. 1. a single-site coarse grained model of carbon dioxide," J. Phys. Chem B **115**, 11154–11169 (2011).
- ¹⁰⁷C. Avendaño, T. Lafitte, A. Galindo, C. S. Adjiman, E. A. Müller, and G. Jackson, "Saft-γ force field for the simulation of molecular fluids: 2. coarse-grained models of greenhouse gases," J. Phys. Chem B **117**, 2717–2733 (2013).

- ¹⁰⁸S. Plimpton, "Fast parallel algorithms for short-range molecular dynamics," J. Comp. Phys. **117**, 1–19 (1995).
- ¹⁰⁹A. P. Thompson, H. M. Aktulga, R. Berger, D. S. Bolintineanu, W. M. Brown, P. S. Crozier, P. J. in 't Veld, A. Kohlmeyer, S. G. Moore, T. D. Nguyen, R. Shan, M. J. Stevens, J. Tranchida, C. Trott, and S. J. Plimpton, "LAMMPS a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales," Comp. Phys. Comm. **271**, 108171 (2022).
- ¹¹⁰P. E. Theodorakis, E. R. Smith, R. V. Craster, E. A. Müller, and O. K. Matar, "Molecular dynamics simulation of the superspreading of surfactant-laden droplets. a review," Fluids 4, 176 (2019).
- ¹¹¹P. E. Theodorakis, E. A. Müller, R. V. Craster, and O. K. Matar, "Insights into surfactant-assisted superspreading," Curr. Opin. Colloid Interface Sci. **19**, 283–289 (2014).
- ¹¹²J. Stillinger, Frank H., "Rigorous Basis of the Frenkel-Band Theory of Association Equilibrium," J. Chem. Phys **38**, 1486–1494 (1963).
- ¹¹³P. E. Theodorakis, W. Paul, and K. Binder, "Analysis of the cluster formation in two-component cylindrical bottle-brush polymers under poor solvent conditions. a simulation study," Eur. Phys. J. E 34, 52 (2011).
- ¹¹⁴P. Yatsyshin and S. Kalliadasis, "Surface nanodrops and nanobubbles: a classical density functional theory study," J. Fluid Mech. **913**, A45 (2021).
- ¹¹⁵F. Mugele, T. Becker, R. Nikopoulos, M. Kohonen, and S. Herminghaus, "Capillarity at the nanoscale: an afm view," J. Adhes. Sci. Technol. **16**, 951–964 (2002).

Supplemental Material for "Coalescence of Sessile Aqueous Droplets Laden with Surfactant"

Soheil Arbabi,^{1, *} Piotr Deuar,¹ Rachid Bennacer,² Zhizhao Che,³ and Panagiotis E. Theodorakis^{1,†}

¹Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland ²Université Paris-Saclay, ENS Paris-Saclay, CNRS, LMPS, 4 Av. des Sciences, 91190 Gif-sur-Yvette, France ³State Key Laboratory of Engines, Tianjin University, 300350 Tianjin, China (Dated: January 24, 2024)

CONTENTS

FORCE-FIELD PARAMETERS AND DROPLET PROPERTIES	2
MASS TRANSPORT MECHANISM	4
BRIDGE DYNAMICS	22
ANGLE FORMED AT THE BRIDGE, θ_b	23
VELOCITY OF APPROACH	24
DENSITY PROFILES	24
REFERENCES	29

^{*} arbabi@ifpan.edu.pl

[†] panos@ifpan.edu.pl



FIG. S1. Cross-section of a spherical droplet on a wettable substrate, where the macroscopic contact angle θ_s , the height *h* and the radius *r* are indicated.

FORCE-FIELD PARAMETERS AND DROPLET PROPERTIES

In Figure S1, a cross section of a spherical droplet is illustrated. Estimation of the contact angle of a droplet without the need for fitting is done by using the method of Ref. [1]. In this method, the average contact angle $(\langle \theta_s \rangle)$ is calculated from the average droplet height $(\langle h \rangle)$, (averaged over 100 snapshots) and the average droplet radius $(\langle r \rangle)$ under an assumption of circular cross-section. For wettable substrates, r > h, namely $\theta_s < 90^\circ$. However, for non-wettable substrates $\theta_s > 90^\circ$ since h > r. In particular,

$$\theta_s' = \arcsin\left(\frac{1}{\mu}\right),$$

where

$$\mu = \frac{1+\lambda^2}{2\lambda}$$

		5	
i–j	$\sigma_{ij}(\sigma)$	$\epsilon_{ij} (\epsilon/k_B)$	λ_{ii}^{r}
W–W	0.8584	0.8129	8.00
W–C	0.9292	0.5081	10.75
W-EO	0.8946	0.9756	11.94
C–C	1.0000	0.7000	15.00
C–EO	0.9653	0.7154	16.86
EO-EO	0.9307	0.8067	19.00

TABLE S1. Mie-potential interaction parameters between CG beads. $\lambda_{ij}^a = 6$ for all cases.

TABLE S2. Mas	s of CG beads.
---------------	----------------

Bead type	Mass (m)
W	0.8179
С	0.9552
EO	1.0000

with

$$\lambda = \frac{h}{r}.$$

Hence, for wettable substrates, $\theta_s = \theta'_s$, while for nonwettable substrates the contact angle will be $\theta_s = \pi - \theta'_s$.

The contact angle for pure water droplets is determined by the values of ε_{ww} and ε_{ws} . In Figure S2, the calculated equilibrium contact angle of a pure water droplet on substrates with different wettability is illustrated for a range of different ε_{ws} parameters. Then, one can obtain the resulting consistent self-interaction for the substrate ε_{ss} using Eqn. (5) in the main text. The latter can then be used for determining the cross-interactions ε_{Cs} and ε_{EOs} for the surfactant. There cross-interactions between the substrate and the water and the surfactant molecules, which are reported in Table S3, will then determine the equilibrium contact angle θ_s of the droplet with the surfactant molecules, which are reported in Table S4 of the manuscript along some other key geometrical parameters.



FIG. S2. Equilibrium contact angle of a water droplet on a smooth unstructured substrate as a function of ε_{ws} .

TABLE S3. Strength of interactions between the droplet components and the substrate for droplets of different wt% concentration, as indicated. The equilibrium contact angle θ_s for each case of the systems A, B, C, and D with a similar value of the contact angle θ_s are reported. The input control parameter is ε_{ws} .

		6.25 wt%		
System	A	В	С	D
θ_s°	142.97 ± 1.07	89.40 ± 5.04	68.68 ± 1.11	52.01 ± 0.91
$\overline{\boldsymbol{\varepsilon}_{ws}(\boldsymbol{\varepsilon})}$	0.500	2.200	2.800	3.200
$\boldsymbol{\varepsilon}_{Cs}(\boldsymbol{\varepsilon})$	0.475	2.090	2.660	3.041
$\epsilon_{EOs}(\epsilon)$	0.505	2.224	2.830	3.235
		35.48 wt%		
System	A	В	С	D
$ heta_s^\circ$	142.25 ± 1.17	94.61 ± 2.08	68.45 ± 1.00	49.35 ± 0.95
$\overline{\boldsymbol{\varepsilon}_{ws}(\boldsymbol{\varepsilon})}$	0.500	1.900	2.400	2.800
$\boldsymbol{\varepsilon}_{Cs}(\boldsymbol{\varepsilon})$	0.475	1.805	2.280	2.660
$\epsilon_{EOs}(\epsilon)$	0.505	1.920	2.426	2.830

TABLE S4. Average properties of one droplet after equilibrium on substrate with different wettabilities as defined through the angle θ_s . Notation as displayed in Figure S2.

		0.0 wt%		
$\overline{\theta_s}$ (°)	142.07 ± 0.85	91.95 ± 4.21	70.70 ± 0.92	49.82 ± 1.04
Average diameter of one drop $D(\sigma)$	52.57 ± 0.40	65.755 ± 0.50	77.80 ± 0.68	92.60 ± 1.02
Average height of one drop $h(\sigma)$	48.08 ± 0.44	32.58 ± 0.45	26.77 ± 0.34	20.70 ± 0.42
		6.25 wt%		
$\overline{\theta_{s}}(^{\circ})$	142.97 ± 1.07	89.40 ± 5.04	68.68 ± 1.11	52.01 ± 0.91
Average diameter of one drop $D(\sigma)$	53.13 ± 0.42	67.08 ± 0.59	80.16 ± 0.75	92.70 ± 1.09
Average height of one drop $h(\sigma)$	48.82 ± 0.82	32.79 ± 0.42	26.54 ± 0.46	21.70 ± 0.38
		35.48 wt%		
$\overline{\theta_{s}}(^{\circ})$	142.25 ± 1.17	94.61 ± 2.08	68.45 ± 1.00	49.35 ± 0.95
Average diameter of one drop $D(\sigma)$	54.60 ± 0.42	67.34 ± 0.51	81.46 ± 0.76	97.39 ± 1.18
Average height of one drop $h(\sigma)$	49.91 ± 0.60	34.18 ± 0.43	26.77 ± 0.38	21.51 ± 0.37
				· · · · · · · · · · · · · · · · · · ·

MASS TRANSPORT MECHANISM

We provide data on the mass transport of surfactant over 12 different regions of droplets on substrate in the same procedure as in Refs. [2, 3]. This gives a total of 144 categories of surfactant movement between these regions or remaining at the same place. Figure 3c-d of the manuscript

shows snapshots of the droplets with the regions annotated. The relative contributions from surfactant transport processes from one part of a droplet to others over short time scales $\Delta t'$ are reported in Table S5 for two concentrations of surfactant and a range of substrate wettabilities above and below 90° contact angle. The arrows drawn in Figure 5 of the manuscript are a consequence of these probabilities and illustrate the relative amount of mass transport during coalescence — in terms of absolute numbers of molecules transported over time. TABLE S5: Summary of the relative contributions from all relevant surfactant transport processes in the coalescing droplets. The table lists the relative frequency of transport from one region to another over a time interval $\Delta t' = 1.25\tau$ as a percentage of the mean number of surfactant molecules in source regions. Data was averaged over consecutive snapshots made at $\Delta t'$ intervals during the entire coalescence process which lasts $\mathcal{O}(1000 - 3000)\tau$. CAC ≈ 7.5 wt% for C10E4.

Probabilities				
System	А	В	С	D
stav left surface				
6.25 wt %	9.87e-01	9.91e-01	9.93e-01	9.92e-01
35.48 wt%	9.93e-01	9.94e-01	9.94e-01	9.92e-01
Movement from left surface to left bulk				
6.25 wt%	6.92e-05	3.35e-05	0.00e+00	0.00e+00
35.48 wt %	1.51e-03	7.28e-04	5.78e-04	1.29e-03
Movement from left surface to left contact				
6.25 wt%	2.36e-03	3.31e-03	3.98e-03	5.67e-03
35.48 wt%	2.69e-03	2.83e-03	3.36e-03	4.83e-03
Movement from left surface to left substrate				
6.25 wt%	2.03e-06	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	1.69e-06	0.00e+00	0.00e+00	0.00e+00
Movement from left surface to bridge surface				
6.25 wt%	3.80e-04	5.66e-04	4.00e-04	3.96e-04
35.48 wt%	4.11e-04	5.78e-04	3.00e-04	4.57e-04
Movement from left surface to bridge bulk				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	1.27e-06	0.00e+00	1.11e-06	2.03e-07
Movement from left surface to bridge contact				
6.25 wt%	2.03e-06	3.35e-06	0.00e+00	7.04e-06
35.48 wt %	1.27e-06	2.67e-06	1.11e-06	5.27e-06

System	А	В	С	D
Movement from left surface to bridge substrate				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
Movement from left surface to right surface				
6.25 wt%	1.03e-02	5.04e-03	2.84e-03	2.03e-03
35.48 wt%	2.27e-03	1.68e-03	1.62e-03	1.19e-03
Movement from left surface to right bulk				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	8.86e-06	1.07e-05	8.36e-07	2.03e-07
Movement from left surface to right contact				
6.25 wt%	2.03e-05	2.35e-05	1.05e-05	7.04e-06
35.48 wt%	5.06e-06	1.34e-06	2.79e-06	2.84e-06
Movement from left surface to right substrate				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
stay left bulk				
6.25 wt%	9.77e-01	9.57e-01	0.00e+00	0.00e+00
35.48 wt%	9.96e-01	9.97e-01	9.98e-01	9.94e-01
Movement from left bulk to left surface				
6.25 wt%	7.06e-03	1.47e-02	0.00e+00	0.00e+00
35.48 wt%	1.33e-03	7.76e-04	9.40e-04	3.93e-03
Movement from left bulk to left contact				
6.25 wt%	1.01e-03	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	2.25e-05	0.00e+00	9.07e-07	5.73e-05
Movement from left bulk to left substrate				
6.25 wt%	0.00e+00	1.47e-03	0.00e+00	0.00e+00
35.48 wt%	4.07e-06	1.29e-05	1.59e-04	2.03e-03

System	А	В	С	D
Movement from left bulk to bridge surface				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	2.96e-06	4.76e-07	0.00e+00	0.00e+00
Movement from left bulk to bridge bulk				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	1.71e-04	2.19e-04	0.00e+00	0.00e+00
Movement from left bulk to bridge contact				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	3.70e-07	0.00e+00	0.00e+00	1.85e-06
Movement from left bulk to bridge substrate				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
Movement from left bulk to right surface				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt %	7.02e-06	1.38e-05	1.36e-06	6.16e-07
Movement from left bulk to right bulk				
6.25 wt%	1.49e-02	2.64e-02	0.00e+00	0.00e+00
35.48 wt%	2.35e-03	1.51e-03	7.46e-04	3.45e-04
Movement from left bulk to right contact				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	0.00e+00	0.00e+00	3.70e-06
Movement from left bulk to right substrate				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	3.70e-07	0.00e+00	1.36e-06	6.16e-07
stay left contact				
6.25 wt%	9.25e-01	9.79e-01	9.81e-01	9.80e-01
35.48 wt%	8.88e-01	9.58e-01	9.65e-01	9.64e-01

System	А	В	С	D
Movement from left contact to left surface				
6.25 wt%	2.97e-02	1.54e-02	1.60e-02	1.70e-02
35.48 wt%	2.98e-02	2.21e-02	2.16e-02	2.17e-02
Movement from left contact to left bulk				
6.25 wt %	1.27e-04	0.00e+00	0.00e+00	0.00e+00
35.48 wt %	3.18e-04	0.00e+00	5.37e-06	0.00e+00
Movement from left contact to left substrate				
6.25 wt%	3.56e-02	1.05e-03	2.71e-04	1.74e-04
35.48 wt %	7.90e-02	1.78e-02	1.18e-02	1.26e-02
Movement from left contact to bridge surface				
6.25 wt%	2.54e-05	3.09e-05	0.00e+00	1.39e-05
35.48 wt%	1.87e-05	6.97e-06	1.43e-05	2.55e-05
Movement from left contact to bridge bulk				
6.25 wt %	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
Movement from left contact to bridge contact				
6.25 wt %	2.03e-04	1.01e-03	8.02e-04	1.15e-03
35.48 wt%	2.15e-04	7.28e-04	4.76e-04	7.30e-04
Movement from left contact to bridge substrate				
6.25 wt %	0.00e+00	3.09e-05	0.00e+00	0.00e+00
35.48 wt%	5.14e-05	4.53e-05	3.58e-06	1.64e-05
Movement from left contact to right surface				
6.25 wt%	2.29e-04	4.64e-05	2.08e-05	2.78e-05
35.48 wt%	6.54e-05	2.09e-05	2.15e-05	1.91e-05
Movement from left contact to right bulk				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	4.67e-06	0.00e+00	0.00e+00	0.00e+00

System	А	В	С	D
Movement from left contact to right contact				
6.25 wt%	9.11e-03	3.85e-03	1.67e-03	1.23e-03
35.48 wt%	2.70e-03	1.02e-03	1.00e-03	7.00e-04
Movement from left contact to right substrate				
6.25 wt%	4.32e-04	1.55e-05	1.04e-05	0.00e+00
35.48 wt%	3.41e-04	3.49e-05	5.37e-06	1.18e-05
stay left substrate				
6.25 wt%	8.87e-01	9.70e-01	9.69e-01	9.75e-01
35.48 wt%	8.79e-01	9.92e-01	9.95e-01	9.93e-01
Movement from left substrate to left surface				
6.25 wt %	7.00e-05	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	1.37e-05	0.00e+00	0.00e+00	3.35e-07
Movement from left substrate to left bulk				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	6.16e-05	2.83e-05	1.71e-04	1.08e-03
Movement from left substrate to left contact				
6.25 wt%	9.63e-02	1.20e-02	8.18e-03	6.18e-03
35.48 wt%	1.16e-01	5.35e-03	3.20e-03	4.62e-03
Movement from left substrate to bridge surface				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
Movement from left substrate to bridge bulk				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
Movement from left substrate to bridge contact				
6.25 wt%	1.40e-04	8.81e-04	0.00e+00	0.00e+00
35.48 wt %	4.79e-05	3.14e-06	1.46e-06	5.69e-06

System	А	В	С	D
Movement from left substrate to bridge substrate				
6.25 wt%	0.00e+00	1.76e-04	0.00e+00	9.89e-04
35.48 wt%	1.03e-04	4.82e-04	2.65e-04	4.13e-04
Movement from left substrate to right surface				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
Movement from left substrate to right bulk				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
Movement from left substrate to right contact				
6.25 wt%	9.10e-04	1.76e-04	2.92e-04	0.00e+00
35.48 wt %	5.27e-04	4.19e-06	2.92e-06	3.35e-06
Movement from left substrate to right substrate				
6.25 wt%	1.52e-02	1.69e-02	2.22e-02	1.78e-02
35.48 wt %	5.02e-03	2.11e-03	1.82e-03	1.36e-03
stay bridge surface				
6.25 wt%	9.61e-01	9.60e-01	9.54e-01	9.56e-01
35.48 wt%	9.45e-01	9.47e-01	9.57e-01	9.64e-01
Movement from bridge surface to left surface				
6.25 wt%	1.42e-02	1.51e-02	1.75e-02	1.44e-02
35.48 wt %	1.25e-02	1.23e-02	1.34e-02	1.35e-02
Movement from bridge surface to left bulk				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt %	1.17e-04	1.25e-04	2.46e-05	0.00e+00
Movement from bridge surface to left contact				
6.25 wt%	7.32e-05	1.61e-04	3.28e-04	1.57e-04
35.48 wt %	0.00e+00	2.88e-05	4.92e-05	1.23e-04

System	А	В	С	D
Movement from bridge surface to left substrate				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
Movement from bridge surface to bridge bulk				
6.25 wt%	4.68e-03	2.74e-03	0.00e+00	3.92e-04
35.48 wt%	2.75e-02	2.54e-02	9.88e-03	7.63e-05
Movement from bridge surface to bridge contact				
6.25 wt%	2.93e-03	5.81e-03	8.86e-03	1.07e-02
35.48 wt%	2.21e-03	3.02e-03	5.45e-03	8.42e-03
Movement from bridge surface to bridge substrate				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	3.91e-05	9.60e-06	2.83e-04	5.87e-06
Movement from bridge surface to right surface				
6.25 wt%	1.70e-02	1.60e-02	1.89e-02	1.77e-02
35.48 wt%	1.24e-02	1.16e-02	1.35e-02	1.36e-02
Movement from bridge surface to right bulk				
6.25 wt%	7.32e-05	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	1.43e-04	7.68e-05	0.00e+00	0.00e+00
Movement from bridge surface to right contact				
6.25 wt%	7.32e-05	0.00e+00	3.28e-04	3.14e-04
35.48 wt%	3.91e-05	4.80e-05	7.38e-05	1.17e-04
Movement from bridge surface to right substrate				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
stay bridge bulk				
6.25 wt%	9.38e-01	9.23e-01	0.00e+00	8.21e-01
35.48 wt%	9.15e-01	9.25e-01	8.53e-01	6.89e-01

System	А	В	С	D
Movement from bridge bulk to left surface				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	2.23e-04	0.00e+00	0.00e+00	0.00e+00
Movement from bridge bulk to left bulk				
6.25 wt%	5.74e-03	6.38e-03	0.00e+00	0.00e+00
35.48 wt%	1.41e-02	1.05e-02	2.15e-03	0.00e+00
Movement from bridge bulk to left contact				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	2.79e-05	0.00e+00	0.00e+00	0.00e+00
Movement from bridge bulk to left substrate				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt %	0.00e+00	0.00e+00	1.53e-04	0.00e+00
Movement from bridge bulk to bridge surface				
6.25 wt%	4.88e-02	6.60e-02	0.00e+00	1.43e-01
35.48 wt%	5.58e-02	5.17e-02	1.19e-01	2.03e-01
Movement from bridge bulk to bridge contact				
6.25 wt%	9.56e-04	2.13e-03	0.00e+00	0.00e+00
35.48 wt %	7.80e-04	6.11e-05	2.30e-03	1.35e-02
Movement from bridge bulk to bridge substrate				
6.25 wt%	1.91e-03	0.00e+00	0.00e+00	3.57e-02
35.48 wt %	8.36e-05	1.85e-03	1.96e-02	9.46e-02
Movement from bridge bulk to right surface				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt %	2.51e-04	2.04e-05	1.53e-04	0.00e+00
Movement from bridge bulk to right bulk				
6.25 wt%	4.78e-03	2.13e-03	0.00e+00	0.00e+00
35.48 wt %	1.34e-02	1.07e-02	3.53e-03	0.00e+00

System	А	В	С	D
Movement from bridge bulk to right contact				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
Movement from bridge bulk to right substrate				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt %	0.00e+00	0.00e+00	0.00e+00	0.00e+00
stay bridge contact				
6.25 wt %	8.60e-01	9.18e-01	9.34e-01	9.51e-01
35.48 wt%	8.41e-01	8.97e-01	9.02e-01	9.33e-01
Movement from bridge contact to left surface				
6.25 wt%	3.37e-03	2.07e-04	1.80e-04	0.00e+00
35.48 wt%	4.99e-04	5.16e-04	2.29e-04	1.83e-04
Movement from bridge contact to left bulk				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	2.50e-04	0.00e+00	0.00e+00	0.00e+00
Movement from bridge contact to left contact				
6.25 wt%	3.54e-02	1.37e-02	1.24e-02	1.34e-02
35.48 wt%	1.70e-02	1.21e-02	1.00e-02	1.11e-02
Movement from bridge contact to left substrate				
6.25 wt%	1.68e-03	2.07e-04	1.80e-04	0.00e+00
35.48 wt%	6.49e-03	3.22e-04	9.18e-05	2.54e-04
Movement from bridge contact to bridge surface				
6.25 wt%	2.53e-02	1.80e-02	1.93e-02	1.37e-02
35.48 wt%	2.77e-02	2.10e-02	2.29e-02	2.16e-02
Movement from bridge contact to bridge bulk				
6.25 wt%	0.00e+00	4.14e-04	0.00e+00	0.00e+00
35.48 wt %	3.49e-03	4.51e-04	5.51e-04	0.00e+00

System	А	В	С	D
Movement from bridge contact to bridge substrate				
6.25 wt%	3.87e-02	3.65e-02	2.05e-02	1.04e-02
35.48 wt%	8.41e-02	5.71e-02	5.31e-02	2.18e-02
Movement from bridge contact to right surface				
6.25 wt%	0.00e+00	2.07e-04	1.80e-04	2.55e-04
35.48 wt%	9.99e-04	1.29e-04	4.13e-04	2.82e-04
Movement from bridge contact to right bulk				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
Movement from bridge contact to right contact				
6.25 wt%	3.54e-02	1.22e-02	1.31e-02	1.17e-02
35.48 wt%	1.50e-02	1.14e-02	1.04e-02	1.17e-02
Movement from bridge contact to right substrate				
6.25 wt%	0.00e+00	2.07e-04	1.80e-04	0.00e+00
35.48 wt %	3.00e-03	4.51e-04	4.13e-04	1.55e-04
stay bridge substrate				
6.25 wt%	6.58e-01	9.32e-01	9.40e-01	9.63e-01
35.48 wt%	5.31e-01	9.57e-01	9.45e-01	9.62e-01
Movement from bridge substrate to left surface				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt %	0.00e+00	0.00e+00	0.00e+00	0.00e+00
Movement from bridge substrate to left bulk				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt %	0.00e+00	0.00e+00	2.41e-05	0.00e+00
Movement from bridge substrate to left contact				
6.25 wt%	1.32e-02	3.76e-04	0.00e+00	0.00e+00
35.48 wt%	1.43e-02	8.98e-05	4.82e-05	1.67e-04

System	А	В	С	D
Movement from bridge substrate to left substrate				
6.25 wt%	1.32e-02	4.51e-03	2.09e-03	5.28e-03
35.48 wt%	1.55e-02	1.15e-02	1.40e-02	1.17e-02
Movement from bridge substrate to bridge surface				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	1.12e-04	5.30e-04	9.29e-06
Movement from bridge substrate to bridge bulk				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	3.58e-03	1.77e-03	3.01e-03	8.36e-05
Movement from bridge substrate to bridge contact				
6.25 wt%	2.24e-01	5.87e-02	5.33e-02	3.14e-02
35.48 wt%	3.91e-01	1.82e-02	2.64e-02	1.39e-02
Movement from bridge substrate to right surface				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
Movement from bridge substrate to right bulk				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt %	0.00e+00	0.00e+00	0.00e+00	0.00e+00
Movement from bridge substrate to right contact				
6.25 wt %	5.26e-02	0.00e+00	0.00e+00	0.00e+00
35.48 wt %	1.19e-02	2.69e-04	7.22e-05	8.36e-05
Movement from bridge substrate to right substrate				
6.25 wt%	3.95e-02	4.89e-03	4.18e-03	5.86e-04
35.48 wt%	3.22e-02	1.07e-02	1.08e-02	1.20e-02
stay right surface				
6.25 wt%	9.87e-01	9.91e-01	9.93e-01	9.93e-01
35.48 wt%	9.93e-01	9.94e-01	9.94e-01	9.92e-01
System	А	В	С	D
---	----------	----------	----------	----------
Movement from right surface to left surface				
6.25 wt%	1.04e-02	5.05e-03	2.91e-03	2.08e-03
35.48 wt %	2.26e-03	1.68e-03	1.61e-03	1.20e-03
Movement from right surface to left bulk				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	7.13e-06	1.03e-05	0.00e+00	0.00e+00
Movement from right surface to left contact				
6.25 wt%	2.86e-05	2.70e-05	8.00e-06	2.37e-06
35.48 wt%	5.87e-06	3.59e-06	3.05e-06	2.64e-06
Movement from right surface to left substrate				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
Movement from right surface to bridge surface				
6.25 wt%	4.48e-04	5.93e-04	4.03e-04	5.17e-04
35.48 wt%	4.08e-04	5.62e-04	3.00e-04	4.55e-04
Movement from right surface to bridge bulk				
6.25 wt%	2.04e-06	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	3.77e-06	4.49e-07	0.00e+00	0.00e+00
Movement from right surface to bridge contact				
6.25 wt%	2.04e-06	3.37e-06	0.00e+00	7.11e-06
35.48 wt%	1.26e-06	1.80e-06	2.22e-06	4.26e-06
Movement from right surface to bridge substrate				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt %	0.00e+00	0.00e+00	0.00e+00	0.00e+00
Movement from right surface to right bulk				
6.25 wt%	5.32e-05	6.74e-06	0.00e+00	0.00e+00
35.48 wt%	1.51e-03	5.75e-04	6.95e-04	1.61e-03

System	А	В	С	D
Movement from right surface to right contact				
6.25 wt%	2.32e-03	3.27e-03	3.51e-03	4.76e-03
35.48 wt %	2.55e-03	2.73e-03	3.27e-03	4.95e-03
Movement from right surface to right substrate				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt %	3.36e-06	4.49e-07	0.00e+00	0.00e+00
stay right bulk				
6.25 wt%	9.56e-01	9.53e-01	0.00e+00	0.00e+00
35.48 wt %	9.96e-01	9.98e-01	9.98e-01	9.93e-01
Movement from right bulk to left surface				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	9.70e-06	1.23e-05	1.35e-06	2.45e-06
Movement from right bulk to left bulk				
6.25 wt%	3.13e-02	4.25e-02	0.00e+00	0.00e+00
35.48 wt%	2.38e-03	1.50e-03	7.43e-04	3.62e-04
Movement from right bulk to left contact				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	0.00e+00	0.00e+00	2.45e-06
Movement from right bulk to left substrate				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	3.73e-07	0.00e+00	4.51e-07	0.00e+00
Movement from right bulk to bridge surface				
6.25 wt%	4.06e-04	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	3.73e-06	4.74e-07	4.51e-07	0.00e+00
Movement from right bulk to bridge bulk				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	1.58e-04	2.26e-04	6.31e-06	0.00e+00

System	А	В	С	D
Movement from right bulk to bridge contact				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	0.00e+00	4.51e-07	1.84e-06
Movement from right bulk to bridge substrate				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
Movement from right bulk to right surface				
6.25 wt%	1.22e-02	4.72e-03	0.00e+00	0.00e+00
35.48 wt%	1.34e-03	6.00e-04	1.12e-03	4.87e-03
Movement from right bulk to right contact				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	2.31e-05	0.00e+00	2.25e-06	5.52e-05
Movement from right bulk to right substrate				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt %	8.58e-06	2.70e-05	1.38e-04	1.28e-03
stay right contact				
6.25 wt%	9.29e-01	9.79e-01	9.83e-01	9.83e-01
35.48 wt%	8.84e-01	9.57e-01	9.66e-01	9.63e-01
Movement from right contact to left surface				
6.25 wt%	2.92e-04	1.38e-04	1.05e-05	1.44e-05
35.48 wt%	8.00e-05	2.42e-05	1.42e-05	1.22e-05
Movement from right contact to left bulk				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt %	0.00e+00	0.00e+00	0.00e+00	0.00e+00
Movement from right contact to left contact				
6.25 wt%	8.34e-03	3.70e-03	1.70e-03	1.34e-03
35.48 wt%	2.57e-03	1.00e-03	9.90e-04	7.20e-04

System	А	В	С	D
Movement from right contact to left substrate				
6.25 wt%	3.40e-04	1.53e-05	0.00e+00	0.00e+00
35.48 wt%	3.67e-04	2.42e-05	7.12e-06	1.32e-05
Movement from right contact to bridge surface				
6.25 wt%	0.00e+00	0.00e+00	2.09e-05	1.44e-05
35.48 wt%	9.42e-06	1.38e-05	1.07e-05	1.97e-05
Movement from right contact to bridge bulk				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
Movement from right contact to bridge contact				
6.25 wt%	3.16e-04	8.75e-04	8.27e-04	1.04e-03
35.48 wt%	2.21e-04	7.30e-04	4.93e-04	8.56e-04
Movement from right contact to bridge substrate				
6.25 wt%	2.43e-05	0.00e+00	0.00e+00	0.00e+00
35.48 wt %	3.30e-05	2.08e-05	1.42e-05	1.13e-05
Movement from right contact to right surface				
6.25 wt%	2.89e-02	1.53e-02	1.40e-02	1.46e-02
35.48 wt %	2.89e-02	2.10e-02	2.10e-02	2.29e-02
Movement from right contact to right bulk				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt %	2.78e-04	0.00e+00	0.00e+00	9.40e-07
Movement from right contact to right substrate				
6.25 wt%	3.29e-02	9.67e-04	1.88e-04	9.36e-05
35.48 wt %	8.39e-02	1.98e-02	1.12e-02	1.24e-02
stay right substrate				
6.25 wt%	8.88e-01	9.74e-01	9.72e-01	9.86e-01
35.48 wt %	8.74e-01	9.92e-01	9.95e-01	9.93e-01

System	А	В	С	D
Movement from right substrate to left surface				
6.25 wt %	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
Movement from right substrate to left bulk				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	1.03e-06	9.81e-07	3.38e-07
Movement from right substrate to left contact				
6.25 wt%	1.56e-03	1.62e-04	2.81e-04	0.00e+00
35.48 wt%	5.38e-04	7.18e-06	3.92e-06	5.07e-06
Movement from right substrate to left substrate				
6.25 wt%	1.38e-02	1.54e-02	2.25e-02	1.16e-02
35.48 wt%	4.93e-03	2.08e-03	1.84e-03	1.36e-03
Movement from right substrate to bridge surface				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
Movement from right substrate to bridge bulk				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
Movement from right substrate to bridge contact				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	1.34e-05	6.16e-06	4.91e-07	3.38e-06
Movement from right substrate to bridge substrate				
6.25 wt%	0.00e+00	1.62e-04	0.00e+00	0.00e+00
35.48 wt%	1.14e-04	4.46e-04	2.04e-04	4.29e-04
Movement from right substrate to right surface				
6.25 wt%	0.00e+00	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	2.69e-05	1.03e-06	0.00e+00	0.00e+00

System	А	В	С	D
Movement from right substrate to right bulk				
6.25 wt%	7.10e-05	0.00e+00	0.00e+00	0.00e+00
35.48 wt%	1.28e-04	5.85e-05	1.51e-04	7.03e-04
Movement from right substrate to right contact				
6.25 wt%	9.67e-02	1.07e-02	5.05e-03	2.29e-03
35.48 wt%	1.20e-01	5.83e-03	3.06e-03	4.48e-03

BRIDGE DYNAMICS

Figure S3 displays the bridge dynamics for water and surfactant-laden droplets below CAC (6.25 wt%). These can be compared to concentrations above CAC (35.48 wt%), which are presented in Figure 7 of the main paper. Figure S4 contains plots that aim at highlighting differences between droplets with different surfactant concentration for each substrate.



FIG. S3. Bridge dynamics displayed to highlight the effect of substrate wettability. The bridge height, b, is plotted as a function of time, t, from the time of the first contact of the droplets, t_c . Insets show the bridge width, w. Results for (a) water droplets and (b) surfactant-laden droplets (below CAC) are shown. Figure 7 of the main paper shows results for concentration above CAC.



FIG. S4. Bridge dynamics displayed to highlight the effect of surfactant. As in Figure S3, we see bridge length, *b*, as a function of time, *t*, from the time of the first contract of the droplets, t_c . Insets show the bridge width, *w*. (a) Nonwettable substrate ($\theta_s > 90^\circ$) (b) Intermediate wettability substrate ($\theta_s \simeq 90^\circ$) (c) Wettable substrate with $\theta_s \simeq 70^\circ$ and (d) Wettable substrate with $\theta_s \simeq 50^\circ$. Data for different surfactant concentration are shown.

ANGLE FORMED AT THE BRIDGE, θ_b

Figure S5 presents data for the bridge angle (θ_b) for the coalescence of sessile water droplets, as well as for surfactant-laden droplets below and above CAC. In all three cases, a linear fit has been performed on the data to provide values used in Figure 8 of the main text. Figure S6 compares the



FIG. S5. Bridge angle, θ_b , for different substrate properties, as a function of time, *t*, starting from the contact moment, t_c for (a) pure water droplets, (b) surfactant-laden droplets below CAC, and (c) surfactant-laden droplets above CAC. The dashed lines are linear fits to the data, where $x = t - t_c$ (τ) and $y = \theta_b$ (deg). They are used in Figure 8 of the main paper, where the slope of the dashed line is denoted with the symbol *m*. Determination of θ_b was stopped when noise in the data became excessive.

behavior for three different surfactant concentrations for similar substrates.

VELOCITY OF APPROACH

The distance between the centers of mass of the two droplets in the *x*-direction, *X*, (Figure 1d,h of the main manuscript) is further monitored during the coalescence of sessile droplets. Moreover, its rate of change with time, $u = \dot{X}$, is also calculated from these data. Figure S7 compares the dynamics of approach of droplets (0 wt% and 6.25 wt%) and the one for above CAC (35.48 wt%) is presented in main paper. Figure S8 compares three concentrations on four different substrates from nonwettable to wettable cases.

DENSITY PROFILES

Figure S9 presents the density of water beads for the coalescence of sessile surfactant-laden droplets (above CAC, 35.48 wt%). In the main paper, the density profile of surfactant beads of the same snapshots are reported (Figure 10).



FIG. S6. Bridge angle, θ_b , as a function of time, t, starting from the time of first contact, t_c . This figure highlights the effect of surfactant concentration. (a) Non-wettable cases ($\theta_s > 90^\circ$), (b) intermediate wettability cases ($\theta_s \simeq 90^\circ$), (c) wettable case with $\theta_s \simeq 70^\circ$ and (d) $\theta_s \simeq 50^\circ$. As in Figure S5, determination of θ_b was stopped when noise in the data became excessive.



FIG. S7. The distance between the centers of mass of the two droplets in the *x*-direction, *X*, as a function of time, *t*, starting from moment of first contact of the droplets, t_c for (a) water droplets, and (b)surfactant-laden droplets of concentrations below CAC. The inset shows the instantaneous velocity, $u = \dot{X}$.



FIG. S8. The distance between the centers of mass of the two droplets in the *x*-direction, *X*, as a function of time, *t*, starting from moment of first contact of the droplets, t_c . The inset shows the instantaneous velocity, $u = \dot{X}$. (a) Nonwettable cases ($\theta_s > 90^\circ$), (b) intermediate wettability cases ($\theta_s \simeq 90^\circ$), (c) $\theta_s \simeq 70^\circ$ and (d) $\theta_s \simeq 50^\circ$.



FIG. S9. Water density at pinching (upper panels) and with a developed bridge (lower panels) for concentrations above CAC (35.48 wt%). (a) $\theta_s \simeq 142^\circ$, snapshots: t_c and $t_c + 100\tau$, (b) $\theta_s \simeq 90^\circ$, snapshots: t_c and $t_c + 412.5\tau$, (c) $\theta_s \simeq 50^\circ$, snapshots: t_c and $t_c + 1352.5\tau$

- [1] P. E. Theodorakis, E. A. Müller, R. V. Craster, and O. K. Matar, Soft Matter 11, 9254 (2015).
- [2] S. Arbabi, P. Deuar, M. Denys, R. Bennacer, Z. Che, and P. E. Theodorakis, Phys. Fluids 35 (2023).
- [3] S. Arbabi, P. Deuar, M. Denys, R. Bennacer, Z. Che, and P. E. Theodorakis, Soft Matter 19, 8070 (2023).

4.4 Coalescence of Sessile Polymer Droplets: A Molecular Dynamics Study

4.4.1 Summary of Key Findings of this Publication:

In this paper, we investigate the coalescence of sessile polymer droplets on various substrates, encompassing both wettable and non-wettable surfaces. In this study, we used a physics-based CG force field for polymer chains where a standard bead–spring model has been employed. Our primary goal is to elucidate the role of viscosity, where longer polymer chain lengths correspond to higher viscosity, through the use of molecular dynamics simulations. These droplets are deposited onto substrates with different levels of wettability, a characteristic determined by the equilibrium contact angles of individual droplets, ranging from angles above to below 90 degrees (i.e. with angles ranging from 78° to 118°). The key findings of this work are summarized as follows:

- The dynamics of the bridge height are notably slower in the case of polymer droplets when compared to what is observed for our study on sessile water and surfactant-laden droplets [4]. Additionally, the coalescence process decelerates significantly as the polymer chain length increases. Similar to surfactant-laden droplets, we can observe the presence of an initial thermal regime followed by an inertial regime. This inertial regime exhibits growth based on a power law with an exponent lower than 0.5 for non-wettable substrate and lower than 2/3 for wettable substrate (contact angle less than 90°), which are reported in the case of coalescence of sessile water droplets. Furthermore, it is demonstrated that increasing the polymer chain length results in a gradual decrease of the exponent.
- We explored the dynamics of bridge shape by measuring a quantity named the bridge angle, *θ*, (Fig. 1 in the paper). Overall, a steady decrease in the angle is observed across all polymer chain lengths. The decrease of the angle over time shows similar dynamics for polymer chain length over 80 beads. However, it decreases with a faster rate for the polymer chain length of 10 beads.
- The dynamics of coalescence were further explored by measuring the velocity of approach of two droplets on a substrate. For less wettable substrates, two different regimes with a noticeable transition between them were observed. This transition becomes more pronounced as the polymer chain length exceeds 40, and it appears smoother in the case of shorter chain lengths.



Figure 4.4: Coalescence of sessile polymer droplets. Reprinted from [Soheil Arbabi, Panagiotis E. Theodorakis, *Coalescence of Sessile Polymer Droplets: A Molecular Dynamics Study*, Macromol. Theory Simul. **32**, 2300017 (2023) https://doi.org/10.1002/mats. 202300017, with permission of John Wiley and Sons, Inc.].

4.4.2 Details of Publication

Coalescence of Sessile Polymer Droplets: A Molecular Dynamics Study

PDF of this publication is reprinted from [Soheil Arbabi, Panagiotis E. Theodorakis, *Coalescence of Sessile Polymer Droplets: A Molecular Dynamics Study*, Macromol. Theory Simul. **32**, 2300017 (2023). https://doi.org/10.1002/mats.202300017, with permission of John Wiley and Sons, Inc.].



Soheil Arbabi

Institute of Physics, Polish Academy of Sciences (PAN)

Theoretical Physics Division (ON5),

Al. Lotników 32/46 02-668 Warsaw, Poland

arbabi@ifpan.edu.pl

STATEMENT

I declare that I am the co-author of the publication:

Coalescence of Sessile Polymer Droplets: A Molecular Dynamics Study. Macromol. Theory Simul., **32**, 2300017 (2023). https://doi.org/10.1002/mats.202300017

I contributed equally to the conceptualization. I took the lead role in data curation, analysis, investigation, methodology, simulations, validation, and visualization. In addition, I played an equal part in review, and editing tasks.

signature: Soheil Arbabi

Dr hab. Panagiotis Theodorakis Division of Theoretical Physics (ON5) Al. Lotników 32/46 02-668 Warsaw, Poland

STATEMENT

I declare that I am the co-author of the publication:

• Coalescence of sessile polymer droplets: A molecular dynamics study S. Arbabi, P. E. Theodorakis *Macromol. Theory Simul.* **32**, 2300017 (2023), doi : 10.1002/mats.202300017

My contribution was supervising the project, helping in the interpretation of the results, and in manuscript writing.

Warsaw, 09.12.2023 Panagiotis Theodorakis

Check for updates

Coalescence of Sessile Polymer Droplets: A Molecular Dynamics Study

Soheil Arbabi and Panagiotis E. Theodorakis*

Droplet coalescence is ubiquitous in nature and, at the same time key to various technologies, such as inkjet printing. Herein, this study reports on the coalescence of polymer droplets with different chain lengths coalescing on substrates of different wettability. By means of molecular dynamics simulations of a coarse-grained model, it is found that the rate of bridge growth is higher in the case of droplets with smaller contact angles (more wettable substrates) and decreases with the increase of the chain length of the polymers. Different behavior is also identified in the dynamics of the approach of the two droplets during coalescence with the substrate wettability playing a more important role compared to the chain length of the polymers. While the dynamics of the droplet are greatly affected by the latter parameters, the density profile and flow patterns remain the same for the different cases. Thus, this study anticipates that it provides further insights into the coalescence of liquid polymer droplets on solid substrates with implications for relevant technologies.

1. Introduction

Droplet coalescence is ubiquitous in nature and at the same time much relevant for various technologies, such as spraying and printing,^[1,2] where the rate of this process can determine the efficiency of the application. The primary factor controlling coalescence is the interplay of viscous and inertial forces as droplets minimize their total surface-tension energy by coalescing.^[3] Despite research in this area,^[4–10] droplet coalescence remains a fascinating phenomenon with many of its aspects calling for further investigations to reach an adequate understanding of this phenomenon in various scenarios. $\ensuremath{^{[4-10]}}$ On the one hand, part of this knowledge gap is due to device limitations, since experiments cannot capture the initial fast stages of droplet coalescence. On the other hand, the singularity at the contact point during the initial stages of coalescence presents challenges for numerical modelling,^[8,10,11] despite progress in this area,^[10] while hydrodynamic models are only applicable at the later stages of coalescence.^[12-14] Apart from device and

S. Arbabi, P. E. Theodorakis Institute of Physics Polish Academy of Sciences Al. Lotników 32/46, Warsaw 02-668, Poland E-mail: panos@ifpan.edu.pl

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/mats.202300017

DOI: 10.1002/mats.202300017

methodology limitations, further understanding at molecular scales is much more desirable as applications often require greater control at nanoscale. Moreover, the role of a substrate in the coalescence of sessile droplets deserves further consideration despite research in this area by theory and experiment,^[15–19] especially in the context of complex liquids containing various additives, such as polymers and colloids.

Droplet coalescence takes place in three stages, with the first being the initial droplet approach when the droplets are close enough to interact with each other and form in between the so-called bridge. Then, the bridge-growth stage follows, which eventually results in the final reshaping of the two droplets toward the equilibrium state of a single spherical-cap droplet, which is the state of minimum energy. From the perspective of fluid dynamics, the initial

bridge growth is generally driven by viscous forces, as a result of the interactions between molecules, while inertial forces dominate the coalescence process at the later stage.^[8,11] In the case of the viscous regime, a linear scaling in time $b \propto t$ has been suggested for the bridge radius, b, or logarithmic corrections tln t, while a scaling $b \propto \sqrt{t}$ has been proposed for the inertial regime.^[8] However, the dynamics of the bridge growth is still under debate, for example, an inertially limited viscous regime has been $reported^{[20,21]}$ or the proposition of a modified Ohnesorge number in the case of immiscible droplets for coupling the linear and power-law scalings.^[22] All-atom molecular dynamics (MD) simulations^[7] have described the initial stage of the bridge growth for water droplets, not achievable by continuum simulation or experiment. In particular, the formation of multiple precursor bridges at the pinch point were observed, which result from thermal capillary waves that exist at the droplets' surface. In this case, simulations suggest that multiple bridges that expand linearly in time develop at the surface and the transition to the classical hydrodynamics regime only takes place when the bridge radius exceeds a thermal length defined as $l_T \approx$ $(k_{\rm\scriptscriptstyle B}T/\gamma)^{1/4}R^{/1/2}$, where $k_{\rm\scriptscriptstyle B}$ is Boltzmann's constant, *T* the temperature, γ the liquid–vapour (LV) surface tension, and R the radius of the droplets.

In the case of droplet coalescence on solid substrates, much less is known, despite the immediate implications for applications, for example, in coatings^[23] and microfluidics^[24] technologies. In particular, in the case of coalescence of low-viscosity droplets on a substrate it has been experimentally found that the





Figure 1. Evolution of the droplet coalescence on a solid substrate with a lower (a, $c_{pw} = 1.1 c$) and a higher (b, $c_{pw} = 2.5 c$) wettability as a function of time, *t*, from the first permanent contact of the droplets at time t_c , as indicated. Here, N = 10 beads. Moreover, the angle, θ , and the bridge length, *b*, are indicated. The implicit, smooth substrate modeled by the 9–3 LJ potential of Equation 3 is illustrated by a solid color.

the bridge height, *b*, grows with time as $t^{2/3}$ when the contact angle is below 90°, while a scaling $b \propto t^{1/2}$ has been observed for contact angles above 90°,^[16] which is the scaling found in the inertial regime for freely suspended drops.^[8,23] Moreover, a geometrical model that unifies the inertial coalescence of sessile and freely suspended drops and can capture the transition from the 2/3 to the 1/2 exponent in the case of sessile droplets has been proposed.^[16] In addition, in the case of asymmetric coalescence, that is droplets with different contact angles, the theory predicts that the shape of the bridge can be described by similarity solutions of the 1D lubrication theory, with the bridge growing linearly in time and exhibiting dependence on the contact angles.^[15] In earlier experimental studies, a power-law growth at early times as $t^{1/2}$ has been suggested for the symmetric case, while the growth rate appeared to be sensitive to both the radius and the height of the droplet with a scaling H/R, where H is the height of the droplet from the substrate to its apex and R its radius.^[23] Further experimental work on droplets with contact angles in the range 10°-56° has found that the bridge growth scales as a power law with exponents in the range 0.5061 to 0.8612 with data deviating from the power law at longer times during coalescence for contact angles larger than 24°. Moreover, a power law with an exponent 0.2901 has been found for the width of the bridge.^[17] Finally, further experimental work has focused on analysing the morphology and dynamics of droplet coalescence on substrates.^[25]

Despite previous study on the coalescence of sessile droplets, many aspects of this phenomenon require further investigation. One of them is the role of viscosity in the coalescence for substrates with different wettability. Viscosity is expected to play a role, especially in the context of polymer droplets studied here, where in addition to surface-tension-effects differences, and entanglement effects may also play a role for longer polymer chains or the polymer-polymer interactions close to the contact line in both the initial and later stages of coalescence. Here, we attempt to elucidate these points and fill in the gap in knowledge in this area by carrying out molecular dynamics simulations of a coarsegrained model for droplets comprised of polymer chains with different length on substrates of different wettability with equilibrium contact angles of individual droplets above and below 90°. We find that the bridge length dynamics are much slower in the case of polymer droplets than what is observed for water droplets. Moreover, the coalescence process considerably slows down with the increase in polymers chain length. Furthermore, more wettable substrates have consistently faster bridge growth dynamics in comparison with the less wettable substrates. The wettability of the substrate also affects significantly the dynamics of the bridge angle and the approach of the coalescing droplets, while the viscosity of the droplets appears to have a smaller effect. In the following, we describe our simulation model and method. Then, we discuss our results, while in the final section, we draw our conclusions.

2. Experimental section

This study's system consisted of two polymer droplets placed next to each other as shown in **Figure 1** to initiate their coalescence. Each droplet contained polymer chains with the same number of monomers (beads), *N*. The polymer chains were modeled by the

Theory and Simulations

www.mts-journal.de

ADVANCED SCIENCE NEWS _____ www.advancedsciencenews.com

standard bead–spring model,^[26–28] where all beads interact with a truncated and shifted Lennard-Jones (LJ) potential,

$$U_{\rm LJ}(r) = 4\varepsilon_{\rm ij} \left[\left(\frac{\sigma_{\rm ij}}{r} \right)^{12} - \left(\frac{\sigma_{\rm ij}}{r} \right)^6 \right]. \tag{1}$$

This interaction was applied for beads within the cutoff distance $r_c = 2.5 \sigma$, where σ is the length unit. The interaction between polymer beads is $\epsilon_{pp} = \epsilon$, where ϵ is the unit of energy. The temperature of the system is, $T = \epsilon/k_B$, where k_B is Boltzmann's constant. Moreover, consecutive beads along a polymer chain were tethered by the "finitely extensible nonlinear elastic" (FENE) potential,

$$U_{\rm FENE}(r) = -0.5 K_{\rm FENE} R_0^2 \ln \left[1 - \left(\frac{r}{R_0}\right)^2 \right],$$
 (2)

where r is the distance between two consecutive beads along the polymer chain, $R_0 = 1.5 \sigma$ expresses the maximum extension of the bond, and $K_{\text{FENE}} = 30 \epsilon / \sigma^2$ is an elastic constant. The length of the polymer chain in this model in effect varies the viscosity of the droplets.^[29] Here, the chain length was the same for both droplets in each system and was chosen in the range N = 10 - 640 beads. Since the total number of beads in each droplet was 57600, using longer chains would also require an increase in the overall size of the droplet, in order to ensure that the majority of the chains were not on the surface of the droplet, thus avoiding artifacts that might not apply to macroscopic droplets. Moreover, increasing N and the total number of beads in the droplets would result in longer times required for the equilibration of the initial droplets and the coalescence experiments to reach the final equilibrium stage. Still, it would be valuable to extend the range of N in future investigations and carry out a full scaling analysis of droplet properties on the chain length N and the overall droplet size. The wettability of the substrate by the droplet was controlled through the parameter ϵ_{nw} of the 9–3 LJ potential, which describes the interaction of the polymer beads with an implicit, smooth wall,^[30]

$$U_{\rm w}(z) = 4\varepsilon_{\rm pw} \left[\left(\frac{\sigma_{\rm s}}{z}\right)^9 - \left(\frac{\sigma_{\rm s}}{z}\right)^3 \right],\tag{3}$$

where *z* is the normal (vertical) distance of the beads from the substrate within a cutoff distance $z_c = 2.5 \sigma$. Here, $\sigma_s = \sigma$.

To evolve this study's system in time and control the temperature of the system, the Langevin thermostat was used as done previously.^[31] The equation of motion for the coordinates $\{r_i(t)\}$ of the beads of mass *m* (*m* is the unit of mass)

$$m\frac{d^{2}\mathbf{r}_{i}}{dt^{2}} = -\nabla U_{i} - \gamma \frac{d\mathbf{r}_{i}}{dt} + \Gamma_{i}(t).$$
(4)

was numerically integrated for each bead using the LAMMPS package.^[32] In Equation 4, *t* denotes the time, U_i is the total potential acting on the *i*th bead, γ is the friction coefficient, and $\Gamma_i(t)$ is the random force. As is well-known, γ and Γ are related by the usual fluctuation–dissipation relation

$$<\Gamma_{i}(t).\Gamma_{i}(t')>=6k_{B}T\gamma\delta_{ii}\delta(t-t').$$
(5)

Theory and Simulations www.mts-journal.de

Following previous study,^[31,33,34] the friction coefficient was chosen as $\gamma = 0.5 \tau^{-1}$. Equation 4 was integrated using an integration time step of $\Delta t = 0.01 \tau$, where the time unit is $\tau = (m\sigma^2/\epsilon)^{1/2}$. A single droplet was first equilibrated for an adequate time, so that the total energy had reached a minimum and properties, such as the mean contact angle and average shape of the droplet did not change with time. Then, the equilibrated droplet was cloned and positioned on the substrate as shown in Figure 1. In this case, the size of the box was chosen such as to accommodate the two droplets avoiding the interaction of mirror images of the droplets due to the presence of periodic boundary conditions in all Cartesian directions. Moreover, the use of polymer droplets led to the absence of vapor in the system,^[35] which greatly facilitated the analysis of the trajectories and maintaining the same thermodynamic conditions during the simulation of either the individual droplet or the two coalescing droplets. Different scenarios of substrate wettability were considered in this study, for which $\epsilon_{\rm pw}$ is 2.5 ϵ or 1.1 ϵ . In this case, the equilibrium contact angles of the individual droplets before coalescence were 78° and 118°, respectively. To estimate the contact angle of the droplet, a method that avoided a fitting procedure was used, which had been described in Reference.^[36] This study had also found that the equilibrium contact angles of the individual droplets did not show any statistically significant dependence on the length, N, of the polymer chains.

To analyze the bridge growth dynamics, snapshots of the system were frequently dumped, especially for the initial stage, typically every 250 integration time steps and beads were assigned to a 3D grid with size 2.5σ in all directions. For the analysis of each snapshot, the center of the bridge was located in the middle of the grid, corresponding to the position x = 0 in the x direction of the coordinate system and any rotation of the droplets around the *z* axis had been removed. This facilitates our analysis and guarantees that our measurements of the bridge radius and all other properties (e.g. density profiles) remain consistent as coalescence proceeds. The snapshots of Figure 1 had been taken after performing the above procedure, which was manifested by the perfect alignment of the droplets along their long axis in the x direction and the bridge was also placed in the middle of the substrate on the x - y plane. The 3D grid was also used to calculate the profile of the number density of the droplets by considering a slab along the x - z plane in the x direction that passed through the center of the bridge. Further details regarding the calculation of the various properties were provided later during the discussion of the respective results.

3. Results and Discussion

Figure 1 shows typical coalescence cases on substrates with different wettability, corresponding to contact angles of lower and greater than 90°. A key parameter for characterizing the dynamics of the coalescence process is the bridge length, *b*, which is indicated for each case in Figure 1. When the substrate is less wettable (contact angle greater than 90°), the bridge initially forms above the substrate at the contact point between the LV interface of the coalescing droplets, and later comes into contact with the substrate as the coalescence process proceeds (Figure 1a). In contrast, in the case of more wettable substrates (contact angles lower than 90°), the bridge grows onto the substrate from the beginning



Figure 2. Bridge length, *b*, as a function of time, *t*, counting from the time of first permanent contact of the coalescing droplets, t_c . Data for polymer droplets with different chain length are shown, *N*, as indicated. a) $\epsilon_{pw} = 1.1 \epsilon$; b) $\epsilon_{pw} = 2.5 \epsilon$. The power-law exponents $\approx t^{\beta_b}$) are reported for the bridge length with values of $\chi^2/ndf \approx 1$, where ndf indicates the number of degrees of freedom.

of the coalescence process. While the time that bridge is in contact with the substrate is expected to affect the dynamics of the droplets, in the case of more wettable substrates the interaction between the droplet and the substrate is also stronger.

SCIENCE NEWS _____ www.advancedsciencenews.com

Figure 2 presents our results for the dynamics of the bridge length, b, on the two different substrates. Apart from the initial thermal regime,^[7] we find that in terms of the bridge length the dynamics of coalescence on both substrates can be described by a power-law behavior ($\approx t^{\beta}$) with exponents that are clearly lower than 1/2 (contact angles greater than 90°) and 2/3 (contact angles lower than 90°), which have been reported for water droplets.^[16] Therefore, our results suggest that the rate of coalescence is slower in the case of polymer droplets compared to the case of water droplets. Moreover, the increase of the polymer chain length leads to gradually decreasing values of the powerlaw exponent for both types of substrates. However, exponents are clearly higher in the case of the more wettable substrate, which suggests that the coalescence process be faster when the attraction of the polymer chains to the substrate is stronger. Hence, an increased substrate wettability appears to accelerate the dynamics of the bridge growth, thus facilitating droplet coalescence throughout the range of N studied here. Moreover, we have identified the presence of a second regime at the final stages of the coalescence process and when almost the bridge has been fully developed in the case of less wettable substrates, an effect that is more pronounced for longer chain lengths N. In summary, we find that an increasing chain length of the droplets will slow down the coalescence of polymer droplets and more wettable substrates will exhibit faster dynamics than less wettable substrates with power-law exponents, β_b , significantly lower than what has been observed for sessile water droplets.

Figure 3 presents results for the angle θ at the bridge (see Figure 1). A symmetric angle is defined for the second droplet of Figure 1 and the average of the two angles for each snapshot is considered as the value of the angle θ . To calculate the angle θ , one considers a horizontal plane that passes through the top of the bridge. Then, the angle is calculated based on the curvature of the droplets, as discussed in a previous study, thus avoiding



Figure 3. Angle θ (see Figure 1 and main text for further details) as a function of time, *t*, counting from the time of first permanent contact of the coalescing droplets, *t_c*. Data for polymer droplets with different chain length, *N*, are shown, as indicated. The lines are a guide for the eye. Here, $\epsilon_{pw} = 2.5 \epsilon$ and $\epsilon_{pw} = 1.1 \epsilon$ (inset).

a fitting procedure.^[36] Estimating the angles can in general be highly sensitive to the details of the definition of a sharp interface, as well as the fitting procedure.^[37,38] Moreover, models that could account for the disjoining pressure effects, for example, in the context of droplets on solid substrates, might perform better than fitting spherical caps to nanodroplets.^[37] In general, our data for the angle θ appear noisier than the data referring to the bridge length. One of the main reasons for this is the larger fluctuations on the droplets shape during the coalescence process. Hence, a discussion here can only focus on the dynamics of the angle θ ,





Figure 4. Distance X in the x direction between the center of mass of coalescing droplets for cases of different chain length, N, as indicated. Insets show the instantaneous velocity of approach u = dX/dt. (a) $\epsilon_{pw} = 1.1 \epsilon$; (b) $\epsilon_{pw} = 2.5 \epsilon$.



Figure 5. Profiles of the number density along a cross-section in the *x* direction (x - z plane) of the coalescing droplets (N = 640 beads) at different stages (upper panels correspond to snapshots obtained at time t_c , when the droplets come into permanent contact). (a, b) $\epsilon_{pw} = 1.1 \epsilon$; (c, d) $\epsilon_{pw} = 2.5 \epsilon$.

which seems to greater be affected at the earlier times of coalescence in the case of more wettable substrates, while curves seem to saturate for chain lengths $N \ge 80$ beads. Moreover, a faster rate of change appears in the case of the less wettable substrates.

We have further explored the dynamics of the coalescence process by monitoring the distance *X* of the center of mass of the coalescing droplets, and, also, calculated its derivative with time, which reflects the instantaneous velocity of approach of the droplets (**Figure 4**). Our data for $\epsilon_{pw} = 1.1 \epsilon$ (less wettable substrate) show two different dynamics regimes with a transition between them that is more pronounced in the case of droplets

with longer polymer chains ($N \ge 40$ beads). This transition seems to become smoother as the chain length decreases. Moreover, the instantaneous velocity, u, of the approach of the droplets is higher at the initial stages of coalescence and then rather reaches a smaller value, which remains constant until the bridge has fully developed. This velocity appears to be similar for the different systems, independently of the chain length. In the case of the systems with $e_{pw} = 2.5 e$, a different behavior is observed. *X* steadily decreases, while the velocity, u, obtains small values over the entire coalescing process with the initial instantaneous velocity of the approach of the droplets to exhibit a slightly higher (more

Theory and Simulations

www.mts-journal.de

Data Availability Statement The data that support the findings of this study are available from the corresponding author upon reasonable request.

droplet coalescence, droplet dynamics, molecular dynamics simulation, polymer chains

> Received: March 30, 2023 Revised: May 10, 2023 Published online: May 23, 2023

- [1] J. Eggers, E. Villermaux, Rep. Prog. Phys. 2008, 71, 036601.
- [2] H. Wijshoff, Phys. Rep. 2010, 491, 77.

Keywords

- [3] C. Verdier, M. Brizard, Rheol. Acta 2002, 41, 514.
- [4] J. D. Paulsen, R. Carmigniani, A. Kannan, J. C. Burton, S. R. Nagel, Nat. Commun. 2014, 5, 3182.
- [5] Y. Yoon, F. Baldessari, H. D. Ceniceros, L. G. Leal, Phys. Fluids 2007, 19, 102102.
- [6] M. I. Khodabocus, M. Sellier, V. Nock, Adv. Math. Phys. 2018, 2018, 4906016.
- [7] S. Perumanath, M. K. Borg, M. V. Chubynsky, J. E. Sprittles, J. M. Reese, Phys. Rev. Lett. 2019, 122, 104501.
- [8] J. Eggers, J. R. Lister, H. A. Stone, J. Fluid Mech. 1999, 401, 293.
- [9] D. G. Aarts, H. N. Lekkerkerker, H. Guo, G. H. Wegdam, D. Bonn, Phys. Rev. Lett. 2005, 95, 164503.
- [10] J. E. Spritles, Shikhmurzaev, Phys. Fluids 2012, 24, 122105.
- [11] L. Duchemin, J. Eggers, C. Josserand, J. Fluid Mech. 2003, 487, 167.
- [12] L. Y. Yeo, O. K. Matar, E. S. P. de Ortiz, G. F. Hewitt, J. Colloid Interface Sci. 2003, 257, 93.
- [13] Y. Hu, D. Pine, L. G. Leal, Phys. Fluids 2000, 12, 484.
- [14] A. Mansouri, H. Arabnejad, R. S. Mohan, in Fluids Engineering Division Summer Meeting, 2014.
- [15] J. F. Hernández-Sánchez, L. A. Lubbers, A. Eddi, J. H. Snoeijer, Phys. Rev. Lett. 2012, 109, 184502.
- [16] A. Eddi, K. G. Winkels, J. H. Snoeijer, Phys. Rev. Lett. 2013, 111, 144502.
- [17] M. W. Lee, D. K. Kang, S. S. Yoon, A. L. Yarin, Langmuir 2012, 28, 3791.
- [18] W. D. Ristenpart, P. M. McCalla, R. V. Roy, H. A. Stone, Phys. Rev. Lett. 2006, 97, 064501.
- [19] N. Kapur, P. H. Gaskell, Phys. Rev. E 2007, 75, 056315.
- [20] J. D. Paulsen, J. C. Burton, S. R. Nagel, S. Appathurai, M. T. Harris, O. A. Basaran, Proc. Natl. Acad. Sci. U.S.A. 2012, 109, 6857.
- [21] J. D. Paulsen, Phys. Rev. E 2013, 88, 063010.
- [22] H. Xu, T. Wang, Z. Che, J. Colloid Interface Sci. 2022, 628, 869.
- [23] W. Ristenpart, P. McCalla, R. Roy, H. Stone, Phys. Rev. Lett. 2006, 97, 064501.
- [24] S. Feng, L. Yi, L. Zhao-Miao, C. Ren-Tuo, W. Gui-Ren, Chinese J. Anal. Chem. 2015, 43, 1942.
- [25] N. Kapur, P. H. Gaskell, Phys. Rev. E 2007, 75, 056315.
- [26] M. Murat, G. S. Grest, Phys. Rev. Lett. 1989, 63, 1074.
- [27] P. E. Theodorakis, S. A. Egorov, A. Milchev, J. Chem. Phys. 2017, 146, 244705.
- [28] P. E. Theodorakis, S. A. Egorov, A. Milchev, Europhys. Lett. 2022, 137, 43002.
- [29] R. Kajouri, P. E. Theodorakis, P. Deuar, R. Bennacer, J. Židek, S. A. Egorov, A. Milchev, Langmuir 2023, 39, 2818.
- [30] P. E. Theodorakis, Y. Wang, A. Chen, B. Liu, Materials 2021, 14, 9.

negative velocity, since the distance X decreases) velocity. Hence, although the bridge growth dynamics is faster in the case of the more wettable substrate, the approach of the two droplets appears

slower in the case of the more wettable substrate. Finally, we have calculated the density profiles of the droplets during coalescence. From the obtained results, we have not identified any noticeable changes in the density profiles for droplets of different chain length and substrates with different wettability. We have also analyzed the flow patterns and they have also not revealed any noticeable differences for the different systems. Typical density profiles for various cases are presented in Figure 5 at an initial stage of the coalescence process, when droplets come into contact, and at a later stage when the bridge has been clearly developed. Hence, while the dynamics of the coalescence process depends on the choice of the substrate and the chain length of the polymers, no noticeable changes in the patterns of the density and the flow are observed during coalescence for the various cases considered in our study.

4. Conclusion

In this study, we have characterized the dynamics of the coalescence of polymer droplets with different chain lengths on substrates with different wettability, where the contact angle of individual droplets is less and above 90°. The rate of coalescence is a key property and can be characterized by the growth rate of the bridge length. We find that polymer droplets overall show a slower rate of the bridge growth in comparison with what has been observed in the case of water droplets in experiments. Moreover, the dynamics are slower as the length of the polymer chains of the droplets increases. Also, we find that more wettable substrates will exhibit faster dynamics, which suggests that a stronger attraction between the droplet and the substrate will accelerate the bridge growth. In addition, we have characterized the dynamics of the approach of the two droplets based on the distance between the center of masses of the coalescing droplets. The behavior is different when the wettability of the substrate changes with two different regimes being more pronounced in the case of less wettable substrates. In this case, differences in the dynamics between droplets with different chain lengths have been also observed. While the dynamics of the coalescence can vary when the length of the polymer chains or the substrate wettability vary, the density, and velocity profile patterns do not reveal any dependence on these parameters. Thus, we anticipate that our study provides insights in the coalescence of liquid polymer droplets on solid substrates.

Acknowledgements

This research had been supported by the National Science Centre, Poland, under grant no. 2019/34/E/ST3/00232. The authors gratefully acknowledge Polish high-performance computing infrastructure PLGrid (HPC Centers: ACK Cyfronet AGH) for providing computer facilities and support within computational grant no. PLG/2022/015261.

Conflict of Interest

The authors declare no conflict of interest.

Theory and Simulations www.mts-journal.de

4DVANC SCIENCE NEWS www.advancedsciencenews.com



www.advancedsciencenews.com

- [31] P. E. Theodorakis, W. Paul, K. Binder, Eur. Phys. J. E 2011, 34, 52.
- [32] S. Plimpton, J. Comp. Phys. 1995, 117, 1.
- [33] G. S. Grest, M. Murat, *Macromolecules* **1993**, *26*, 3108.
- [34] M. Murat, G. S. Grest, *Macromolecules* **1991**, *24*, 704.
- [35] N. Tretyakov, M. Müller, Soft Matter 2013, 9, 3613.

Theory and Simulations www.mts-journal.de

[36] P. E. Theodorakis, E. A. Müller, R. V. Craster, O. K. Matar, Soft Matter

[38] F. Mugele, T. Becker, R. Nikopoulos, M. Kohonen, S. Herminghaus,

[37] P. Yatsyshin, S. Kalliadasis, J. Fluid Mech. 2021, 913, A45.

J. Adhes. Sci. Technol. 2002, 16, 951.

2015, 11, 9254.

15213919, 2023, 5, Downloaded from https://onlineibrary.wiley.com/doi/10.1002/mats.20230017 by University Of Athens, Wiley Online Library on [1909/2023]. See the Terms and Conditions (https://onlineibrary.wiley.com/doi/10.1002/mats.20230017 by University Of Athens, Wiley Online Library on [1909/2023]. See the Terms and Conditions (https://onlineibrary.wiley.com/doi/10.1002/mats.20230017 by University Of Athens, Wiley Online Library on [1909/2023]. See the Terms and Conditions (https://onlineibrary.wiley.com/doi/10.1002/mats.20230017 by University Of Athens, Wiley Online Library on [1909/2023]. See the Terms and Conditions (https://onlineibrary.wiley.com/doi/10.1002/mats.20230017 by University Of Athens, Wiley Online Library on [1909/2023].

2300017 (7 of 7)

Chapter 5

Conclusions and Outlook

This thesis has explored a broad spectrum of both macroscopic and microscopic characteristics during the coalescence of both freely suspended and sessile droplets. The primary focus has extended to surfactant-laden droplets with concentrations within the range relevant for applications and industrial use, typically exceeding the CAC. The thesis has demonstrated how surfactant mass transport and various geometrical features have operated during the process. This has included considerations of different types of surfactants, a range of concentration levels, and varying wettabilities, in the case of sessile droplets.

Considering the freely suspended droplets, this study has demonstrated that over a wide range of regimes the mass transport mechanism and flow patterns are generally unaffected by the type of surfactant used. It is observed that at higher concentrations (above CAC), water molecules do not participate in the initial stage of coalescence (pinching moment). The development of the initial pinching point, the process of bridge formation, and the creation of new aggregates within the bridge are investigated. When it comes to surfactant types, differences between Silewt-L77 and C_iE_j surfactants have been discussed within the bridge growth process. Furthermore, this research has revealed the presence of an initial thermal regime, followed by an inertial regime. This inertial regime exhibits growth patterns based on a power-law with an exponent close to 0.5, which is in agreement with macroscopic theories [24, 64]. Bridge growth dynamics and in general coalescence process become slower as surfactant concentration grows.

In the examination of coalescence in sessile surfactant-laden droplets on different substrates with varying wettabilities, it is demonstrated that, for non-wettable substrates ($\theta_s > 90^\circ$), the mass transport mechanism and bridge growth dynamics closely resemble those of freely suspended droplets. The process initiates far from the substrate, and after an initial thermal regime, it undergoes an inertial regime characterized by a power-law with an exponent of around 0.5. On the other hand, droplets on more wettable substrates ($\theta_s > 90^\circ$) exhibit distinct behavior. In this case, the bridge grows on the substrate, and after the initial thermal regime, it follows a power-law with an exponent close to 2/3. Coalescence begins with hydrophobic beads; however, a more significant involvement of water is observed on wettable substrates compared

to non-wettable substrates. One notable finding of this research is the absence of new aggregates inside the bridge bulk in the case of a wettable substrate ($\theta_s \simeq 50^\circ$).

To assess the impact of viscosity and substrate on coalescence, further study is conducted on the dynamics of coalescence of sessile polymer droplets with varying chain lengths. These droplets were placed on substrates with different levels of wettability, encompassing contact angles both below and above 90° . In general, polymer droplets exhibited slower rates of bridge development and coalescence compared to water and surfactant-laden droplets. Furthermore, an observed decrease in the speed of coalescence and bridge dynamics is correlated with the increased length of polymer chains. Moreover, the velocity of approach of polymer droplets by measuring the distance between center of masses of two droplets are further analyzed. In the case of a non-wettable substrate ($\theta_s > 90^\circ$), two distinct regimes are observed with a noticeable transition between them, this transition becomes more pronounced for droplets with longer polymer chain lengths. On the other hand, for wettable substrates ($\theta_s < 90^\circ$), the distance between droplets smoothly decreases within a single linear regime. Based on our studies, a possible extension might include the investigation of droplet coalescence under confinement, such as micro/nano-channels of varying wettability, where surfactant molecules are also present. For example, in bio-related studies and microfluidics, bio-particles are encapsulated within droplets, and the addition of surfactant can play a role in impeding the coalescence process.

Bibliography

- D. G. Aarts, H. N. Lekkerkerker, H. Guo, G. H. Wegdam, and D. Bonn. "Hydrodynamics of droplet coalescence". In: *Phys. Rev. Lett.* 95.16 (2005), p. 164503. DOI: 10.1103/PhysRevLett.95.164503.
- [2] A. Aasen, M. Hammer, Å. Ervik, E. A. Müller, and Ø. Wilhelmsen. "Equation of state and force fields for Feynman–Hibbs-corrected Mie fluids. I. Application to pure helium, neon, hydrogen, and deuterium". In: *J. Chem. Phys.* 151.6 (2019). DOI: 10.1063/1.5111364.
- [3] D. Anghel, S. Saito, A. Băran, A. Iovescu, and M. Corniţescu. "The aggregation of nonionic surfactants in the presence of poly (methacrylic acid)". In: *Colloid and Polymer Science* 285 (2007), pp. 771–779. DOI: 10.1007/s00396-006-1617-1.
- [4] S. Arbabi, P. Deuar, R. Bennacer, Z. Che, and P. E. Theodorakis. "Coalescence of Sessile Aqueous Droplets Laden with Surfactant". In: *Phys. Fluids* 36 (2024). DOI: 10.1063/5.0194816.
- [5] S. Arbabi, P. Deuar, M. Denys, R. Bennacer, Z. Che, and P. E. Theodorakis. "Coalescence of surfactant-laden droplets". In: *Phys. Fluids* 35 (2023), p. 063329. DOI: 10.1063/5.0153676.
- [6] S. Arbabi, P. Deuar, M. Denys, R. Bennacer, Z. Che, and P. E. Theodorakis. "Molecular dynamics simulation of the coalescence of surfactant-laden droplets". In: *Soft Matter* 19.42 (2023), pp. 8070–8080. DOI: 10.1039/D3SM01046E.
- S. Arbabi and P. E. Theodorakis. "Coalescence of Sessile Polymer Droplets: A Molecular Dynamics Study". In: *Macromol. Theory Simul.* n/a.n/a (2023), p. 2300017.
 DOI: 10.1002/mats.202300017.
- [8] N. Ashgriz and J. Poo. "Coalescence and separation in binary collisions of liquid drops". In: J. Fluid Mech. 221 (1990), pp. 183–204. DOI: 10.1017/S0022112090003536.
- [9] C. Avendaño, T. Lafitte, A. Galindo, C. S. Adjiman, G. Jackson, and E. A. Müller. "SAFT-γ Force Field for the Simulation of Molecular Fluids. 1. A Single-Site Coarse Grained Model of Carbon Dioxide". In: *J. Phys. Chem B* 115 (2011), pp. 11154– 11169. DOI: 10.1021/jp204908d.
- [10] C. Avendaño, T. Lafitte, A. Galindo, C. S. Adjiman, E. A. Müller, and G. Jackson. "SAFT-γ Force Field for the Simulation of Molecular Fluids: 2. Coarse-Grained Models of Greenhouse Gases". In: *J. Phys. Chem B* 117 (2013), pp. 2717–2733. DOI: 10.1021/jp306442b.

- [11] P. Banerjee, S. Roy, and N. Nair. "Coarse-grained molecular dynamics force-field for polyacrylamide in infinite dilution derived from iterative Boltzmann inversion and MARTINI force-field". In: *J. Phys. Chem. B.* 122.4 (2018), pp. 1516–1524. DOI: 10.1021/acs.jpcb.7b09019.
- [12] J.-C. Baret. "Surfactants in droplet-based microfluidics". In: *Lab Chip* 12.3 (2012), pp. 422–433. DOI: 10.1039/C1LC20582J.
- [13] V. Boţan, V. D. Ustach, K. Leonhard, and R. Faller. "Development and application of a coarse-grained model for PNIPAM by iterative Boltzmann inversion and its combination with lattice Boltzmann hydrodynamics". In: *J. Phys. Chem. B.* 121.45 (2017), pp. 10394–10406. DOI: 10.1021/acs.jpcb.7b07818.
- [14] E. G. Bowen. "The formation of rain by coalescence". In: Aust. J. Chem. 3.2 (1950), pp. 193–213. DOI: 10.1071/CH9500193.
- [15] B. R. Brooks, C. L. Brooks III, A. D. Mackerell Jr, L. Nilsson, R. J. Petrella, B. Roux, Y. Won, G. Archontis, C. Bartels, S. Boresch, et al. "CHARMM: the biomolecular simulation program". In: *J. Comput. Chem.* 30.10 (2009), pp. 1545–1614. DOI: 10. 1002%2Fjcc.21287.
- [16] J. Burton and P. Taborek. "Role of dimensionality and axisymmetry in fluid pinchoff and coalescence". In: *Phys. Rev. Lett.* 98.22 (2007), p. 224502. DOI: 10.1103/ PhysRevLett.98.224502.
- [17] W. G. Chapman, K. E. Gubbins, G. Jackson, and M. Radosz. "SAFT: Equation-of-state solution model for associating fluids". In: *Fluid Phase Equil.* 52 (1989), pp. 31–38. DOI: 10.1016/0378-3812(89)80308-5.
- [18] A. J. Cohen, P. Mori-Sánchez, and W. Yang. "Challenges for density functional theory". In: *Chem. Rev.* 112.1 (2012), pp. 289–320. DOI: 10.1021/cr200107z.
- [19] M. Denys, P. Deuar, Z. Che, and P. E. Theodorakis. "A Lagrangian particle-based numerical model for surfactant-laden droplets at macroscales". In: *Phys. Fluids* 34.9 (2022), p. 095126. DOI: 10.1063/5.0101930.
- [20] C. J. Dickson, B. D. Madej, Å. A. Skjevik, R. M. Betz, K. Teigen, I. R. Gould, and R. C. Walker. "Lipid14: the amber lipid force field". In: *J. Chem. Theory Comput.* 10.2 (2014), pp. 865–879. DOI: 10.1021/ct4010307.
- [21] L. Duchemin, J. Eggers, and C. Josserand. "Inviscid coalescence of drops". In: J. Fluid Mech. 487 (2003), pp. 167–178. DOI: 10.1017/S0022112003004646.
- [22] M. Dudek, J. Chicault, and G. Øye. "Microfluidic investigation of crude oil droplet coalescence: effect of oil/water composition and droplet aging". In: *Energy Fuels* 34.5 (2019), pp. 5110–5120. DOI: 10.1021/acs.energyfuels.9b03434.
- [23] A. Eddi, K. Winkels, and J. Snoeijer. "Influence of droplet geometry on the coalescence of low viscosity drops". In: *PRL* 111.14 (2013), p. 144502. DOI: 10.1103/ PhysRevLett.111.144502.
- [24] J. Eggers, J. R. Lister, and H. A. Stone. "Coalescence of liquid drops". In: J. Fluid Mech. 401 (1999), pp. 293–310. DOI: 10.1017/S002211209900662X.
- [25] M. Fayaz-Torshizi and E. A. Müller. "Coarse-Grained Molecular Simulation of Polymers Supported by the Use of the SAFT-γ γ Mie Equation of State". In: *Macromol Theory Simul* 31.1 (2022), p. 2100031. DOI: 10.1002/mats.202100031.

- [26] S. Feng, L. Yi, L. Zhao-Miao, C. Ren-Tuo, and W. Gui-Ren. "Advances in microdroplets coalescence using microfluidics". In: *Chin J Anal Chem*, 43.12 (2015), pp. 1942– 1954. DOI: 10.1016/S1872-2040(15)60886-6.
- [27] A. Gautieri, A. Russo, S. Vesentini, A. Redaelli, and M. J. Buehler. "Coarse-grained model of collagen molecules using an extended MARTINI force field". In: *J. Chem. Theory Comput.* 6.4 (2010), pp. 1210–1218. DOI: 10.1021/ct100015v.
- [28] M. Gross, I. Steinbach, D. Raabe, and F. Varnik. "Viscous coalescence of droplets: A lattice Boltzmann study". In: *Phys. Fluids* 25.5 (2013), p. 052101. DOI: 10.1063/ 1.4803178.
- [29] M. A. Hack, P. Vondeling, M. Cornelissen, D. Lohse, J. H. Snoeijer, C. Diddens, and T. Segers. "Asymmetric coalescence of two droplets with different surface tensions is caused by capillary waves". In: *Phys. Rev. Fluids* 6.10 (2021), p. 104002. DOI: 10.1103/PhysRevFluids.6.104002.
- [30] E. Harder, W. Damm, J. Maple, C. Wu, M. Reboul, J. Y. Xiang, L. Wang, D. Lupyan, M. K. Dahlgren, J. L. Knight, et al. "OPLS3: a force field providing broad coverage of drug-like small molecules and proteins". In: *J. Chem. Theory Comput.* 12.1 (2016), pp. 281–296. DOI: 10.1021/acs.jctc.5b00864.
- [31] C. Herdes Moreno, A. Ervik, A. Mejia, and E. Muller. "Prediction of the water/oil interfacial tension from molecular simulations using the coarse-grained SAFT-γ Mie force field". In: *Fluid Phase Equilibria* 476 (2018), pp. 9–15. DOI: 10.1016/j. fluid.2017.06.016.
- [32] R. W. Hopper. "Plane Stokes flow driven by capillarity on a free surface". In: J. *Fluid Mech.* 213 (1990), pp. 349–375. DOI: 10.1017/S002211209000235X.
- [33] N. Jaensson and J. Vermant. "Tensiometry and rheology of complex interfaces". In: *Curr. Opin. Colloid Interface Sci.* 37 (2018), pp. 136–150. DOI: 10.1016/j.cocis. 2018.09.005.
- [34] Y. Jiang, A. Umemura, and C. K. Law. "An experimental investigation on the collision behaviour of hydrocarbon droplets". In: *J. Fluid Mech.* 234 (1992), pp. 171– 190. DOI: 10.1017/S0022112092000740.
- [35] J. Jin, C. H. Ooi, D. V. Dao, and N.-T. Nguyen. "Coalescence processes of droplets and liquid marbles". In: *Micromachines* 8.11 (2017), p. 336. DOI: 10.3390/mi8110336.
- [36] J. E. Jones. "On the determination of molecular fields.—I. From the variation of the viscosity of a gas with temperature". In: *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* 106.738 (1924), pp. 441–462. DOI: 10.1098/rspa.1924.0082.
- [37] D. H. de Jong, G. Singh, W. F. D. Bennett, C. Arnarez, T. A. Wassenaar, L. V. Schäfer, X. Periole, D. P. Tieleman, and S. J. Marrink. "Improved Parameters for the Martini Coarse-Grained Protein Force Field". In: *J. Chem. Theory Comput.* 9.1 (2013), pp. 687–697. DOI: 10.1021/ct300646g.
- [38] S. Kawamoto, H. Liu, Y. Miyazaki, S. Seo, M. Dixit, R. DeVane, C. MacDermaid, G. Fiorin, M. L. Klein, and W. Shinoda. "SPICA force field for proteins and peptides". In: J. Chem. Theory Comput. 18.5 (2022), pp. 3204–3217.

- [39] M. I. Khodabocus, M. Sellier, and V. Nock. "Scaling Laws of Droplet Coalescence: Theory and Numerical Simulation". In: *Adv. Math. Phys.* 2018 (2018). DOI: 10. 1155/2018/4906016.
- [40] N. M. Kovalchuk, M. Reichow, T. Frommweiler, D. Vigolo, and M. J. H. Simmons. "Mass Transfer Accompanying Coalescence of Surfactant-Laden and Surfactant-Free Drop in a Microfluidic Channel". In: *Langmuir* 35.28 (2019), pp. 9184–9193. DOI: 10.1021/acs.langmuir.9b00843.
- [41] T. Lafitte, A. Apostolakou, C. Avendaño, A. Galindo, C. S. Adjiman, E. A. Müller, and G. Jackson. "Accurate statistical associating fluid theory for chain molecules formed from Mie segments". In: *J. Chem. Phys.* 139 (2013), p. 154504. DOI: 10. 1063/1.4819786.
- [42] L. Leal. "Flow induced coalescence of drops in a viscous fluid". In: *Phys. Fluids* 16.6 (2004), pp. 1833–1851. DOI: 10.1063/1.1701892.
- [43] Y.-C. Lee, H.-S. Liu, S.-Y. Lin, H.-F. Huang, Y.-Y. Wang, and L.-W. Chou. "An observation of the coexistence of multimers and micelles in a nonionic surfactant C10E4 solution by dynamic light scattering". In: *Journal of the Chinese Institute of Chemical Engineers* 39.1 (2008), pp. 75–83. DOI: 10.1016/j.jcice.2007.11.009.
- [44] H. Lee, A. H. de Vries, S.-J. Marrink, and R. W. Pastor. "A Coarse-Grained Model for Polyethylene Oxide and Polyethylene Glycol: Conformation and Hydrodynamics". In: *J. Phys. Chem. B* 113.40 (2009), pp. 13186–13194. DOI: 10.1021 / jp9058966.
- [45] M. W. Lee, D. K. Kang, S. S. Yoon, and A. L. Yarin. "Coalescence of two drops on partially wettable substrates". In: *Langmuir* 28.8 (2012), pp. 3791–3798. DOI: 10.1021/la204867c.
- [46] J. E. Lennard-Jones. "Cohesion". In: Proc. Phys. Soc. 43.5 (1931), p. 461.
- [47] O. Lobanova, C. Avendaño, T. Lafitte, E. A. Müller, and G. Jackson. "SAFT-fl force field for the simulation of molecular fluids. 4. A single-site coarse-grained model of water applicable over a wide temperature range." In: *Mol. Phys.* 113 (2015), pp. 1228–1249. DOI: 10.1080/00268976.2015.1004804.
- [48] O. Lobanova. "Development of coarse-grained force fields from a molecular based equation of state for thermodynamic and structural properties of complex fluids". PhD thesis. Imperial College London, 2014.
- [49] C. A. López, Z. Sovova, F. J. van Eerden, A. H. de Vries, and S. J. Marrink. "Martini Force Field Parameters for Glycolipids". In: *J. Chem. Theory Comput.* 9.3 (2013), pp. 1694–1708. DOI: 10.1021/ct3009655.
- [50] S. J. Marrink, A. H. De Vries, and A. E. Mark. "Coarse grained model for semiquantitative lipid simulations". In: J. Phys. Chem. B 108.2 (2004), pp. 750–760. DOI: 10.1021/jp036508g.
- [51] S. J. Marrink, H. J. Risselada, S. Yefimov, D. P. Tieleman, and A. H. De Vries. "The MARTINI force field: coarse grained model for biomolecular simulations". In: J. Phys. Chem. B 111.27 (2007), pp. 7812–7824. DOI: 10.1021/jp071097f.
- [52] S. J. Marrink and D. P. Tieleman. "Perspective on the Martini model". In: *Chem Soc Rev* 42.16 (2013), pp. 6801–6822. DOI: 10.1039/C3CS60093A.

- [53] L. Monticelli, S. K. Kandasamy, X. Periole, R. G. Larson, D. P. Tieleman, and S.-J. Marrink. "The MARTINI Coarse-Grained Force Field: Extension to Proteins". In: *J. Chem. Theory Comput.* 4.5 (2008), pp. 819–834. DOI: 10.1021/ct700324x.
- [54] T. C. Moore, C. R. Iacovella, and C. McCabe. "Derivation of coarse-grained potentials via multistate iterative Boltzmann inversion". In: *Chem. Phys.* 140.22 (2014). DOI: doi.org/10.1063/1.4880555.
- [55] E. A. Müller and G. Jackson. "Force field parameters from the SAFT-γ equation of state for use in coarse-grained molecular simulations". In: *Annu. Rev. Chem. Biomol. Eng.* 5 (2014), pp. 405–427. DOI: 10.1146/annurev-chembioeng-061312-103314.
- [56] E. A. Müller and K. E. Gubbins. "Molecular-based equations of state for associating fluids: A review of SAFT and related approaches". In: *Industrial & engineering chemistry research* 40.10 (2001), pp. 2193–2211.
- [57] E. A. Müller and G. Jackson. "Force-field parameters from the SAFT-γ equation of state for use in coarse-grained molecular simulations". In: *Annu. Rev. Chem. Biomol. Eng.* 5 (2014), pp. 405–427. DOI: 10.1146/annurev-chembioeng-061312-103314.
- [58] E. A. Müller and K. E. Gubbins. "Molecular-Based Equations of State for Associating Fluids: A Review of SAFT and Related Approaches". In: *Industrial & Engineering Chemistry Research* 40.10 (2001), pp. 2193–2211. DOI: 10.1021/ie000773w.
- [59] R. Narhe, D. Beysens, and Y. Pomeau. "Dynamic drying in the early-stage coalescence of droplets sitting on a plate". In: *EPL* 81.4 (2008), p. 46002. DOI: 10.1209/ 0295-5075/81/46002.
- [60] E. Nowak, N. M. Kovalchuk, Z. Che, and M. J. Simmons. "Effect of surfactant concentration and viscosity of outer phase during the coalescence of a surfactantladen drop with a surfactant-free drop". In: *Colloids Surf. A Physicochem. Eng. Asp.* 505 (2016), pp. 124–131. DOI: 10.1016/j.colsurfa.2016.02.016.
- [61] E. Nowak, Z. Xie, N. M. Kovalchuk, O. K. Matar, and M. J. Simmons. "Bulk advection and interfacial flows in the binary coalescence of surfactant-laden and surfactant-free drops". In: *Soft Matter* 13.26 (2017), pp. 4616–4628. DOI: 10.1039/C7SM00328E.
- [62] N. Pallas and Y. Harrison. "An automated drop shape apparatus and the surface tension of pure water". In: *Colloids Surf.* 43.2 (1990), pp. 169–194. DOI: 10.1016/ 0166-6622(90)80287-E.
- [63] J. D. Paulsen, R. Carmigniani, A. Kannan, J. C. Burton, and S. R. Nagel. "Coalescence of bubbles and drops in an outer fluid". In: *Nat. Commun.* 5 (2014), p. 3182. DOI: 10.1038/ncomms4182.
- [64] J. D. Paulsen. "Approach and coalescence of liquid drops in air". In: *Phys. Rev. E* 88.6 (2013), p. 063010. DOI: 10.1103/PhysRevE.88.063010.
- [65] J. D. Paulsen, J. C. Burton, S. R. Nagel, S. Appathurai, M. T. Harris, and O. A. Basaran. "The inexorable resistance of inertia determines the initial regime of drop coalescence". In: *Proc. Natl. Acad. Sci. U.S.A.* 109.18 (2012), pp. 6857–6861. DOI: 10.1073/pnas.1120775109.

- [66] J. D. Paulsen, J. C. Burton, and S. R. Nagel. "Viscous to Inertial Crossover in Liquid Drop Coalescence". In: *Phys. Rev. Lett.* 106 (11 2011), p. 114501. DOI: 10.1103/ PhysRevLett.106.114501.
- [67] X. Periole, M. Cavalli, S.-J. Marrink, and M. A. Ceruso. "Combining an Elastic Network With a Coarse-Grained Molecular Force Field: Structure, Dynamics, and Intermolecular Recognition". In: *J. Chem. Theory Comput.* 5.9 (2009), pp. 2531– 2543. DOI: 10.1021/ct9002114.
- [68] S. Perumanath, M. K. Borg, M. V. Chubynsky, J. E. Sprittles, and J. M. Reese. "Droplet coalescence is initiated by thermal motion". In: *Phys. Rev. Lett.* 122.10 (2019), p. 104501. DOI: 10.1103/PhysRevLett.122.104501.
- [69] J. J. Potoff and D. A. Bernard-Brunel. "Mie potentials for phase equilibria calculations: Application to alkanes and perfluoroalkanes". In: *J. Phys. Chem. B* 113.44 (2009), pp. 14725–14731. DOI: 10.1021/jp9072137.
- [70] T. D. Potter, J. Tasche, E. L. Barrett, M. Walker, and M. R. Wilson. "Development of new coarse-grained models for chromonic liquid crystals: insights from topdown approaches". In: *Liq. Cryst.* 44.12-13 (2017), pp. 1979–1989. DOI: 10.1080/ 02678292.2017.1342005.
- [71] J. Qian and C. K. Law. "Regimes of coalescence and separation in droplet collision". In: J. Fluid Mech. 331 (1997), pp. 59–80. DOI: 10.1017/S0022112096003722.
- [72] M. M. Reif, M. Winger, and C. Oostenbrink. "Testing of the GROMOS force-field parameter set 54A8: structural properties of electrolyte solutions, lipid bilayers, and proteins". In: J. Chem. Theory Comput. 9.2 (2013), pp. 1247–1264. DOI: 10. 1021/ct300874c.
- [73] W. Ristenpart, P. McCalla, R. Roy, and H. Stone. "Coalescence of spreading droplets on a wettable substrate". In: *Phys. Rev. Lett.* 97.6 (2006), p. 064501. DOI: 10.1103/ PhysRevLett.97.064501.
- [74] G. Rossi, L. Monticelli, S. R. Puisto, I. Vattulainen, and T. Ala-Nissila. "Coarsegraining polymers with the MARTINI force-field: polystyrene as a benchmark case". In: *Soft Matter* 7.2 (2011), pp. 698–708. DOI: 10.1039/C0SM00481B.
- [75] V. Ruhle, C. Junghans, A. Lukyanov, K. Kremer, and D. Andrienko. "Versatile object-oriented toolkit for coarse-graining applications". In: J. Chem. Theory Comput. 5.12 (2009), pp. 3211–3223. DOI: 10.1021/ct900369w.
- [76] E. E. Santiso, C. Herdes, and E. A. Müller. "On the calculation of solid-fluid contact angles from molecular dynamics". In: *Entropy* 15.9 (2013), pp. 3734–3745. DOI: 10.3390/e15093734.
- [77] M. G. Saunders and G. A. Voth. "Coarse-graining methods for computational biology". In: Annu. Rev. Biophys. 42 (2013), pp. 73–93. DOI: 10.1146/annurevbiophys-083012-130348.
- [78] S. Seo and W. Shinoda. "SPICA force field for lipid membranes: domain formation induced by cholesterol". In: *J. Chem. Theory Comput.* 15.1 (2018), pp. 762–774. DOI: 10.1021/acs.jctc.8b00987.

- [79] W. Shinoda, R. DeVane, and M. L. Klein. "Coarse-grained molecular modeling of non-ionic surfactant self-assembly". In: *Soft Matter* 4.12 (2008), pp. 2454–2462. DOI: 10.1039/B808701F.
- [80] V. S. Sivasankar, S. A. Etha, D. R. Hines, and S. Das. "Coalescence of Microscopic Polymeric Drops: Effect of Drop Impact Velocities". In: *Langmuir* 37.45 (2021), pp. 13512–13526. DOI: 10.1021/acs.langmuir.1c02337.
- [81] V. S. Sivasankar, D. R. Hines, and S. Das. "Numerical Study of the Coalescence and Mixing of Drops of Different Polymeric Materials". In: *Langmuir* 38.46 (2022), pp. 14084–14096. DOI: 10.1021/acs.langmuir.2c02029.
- [82] E. R. Smith and P. E. Theodorakis. "Multiscale simulation of fluids: coupling molecular and continuum". In: *Phys. Chem. Chem. Phys.* 26 (2 2024), pp. 724–744. DOI: 10.1039/D3CP03579D.
- [83] P. C. T. Souza, R. Alessandri, J. Barnoud, S. Thallmair, I. Faustino, F. Grünewald, I. Patmanidis, H. Abdizadeh, B. M. H. Bruininks, T. A. Wassenaar, P. C. Kroon, J. Melcr, V. Nieto, V. Corradi, H. M. Khan, J. Domański, M. Javanainen, H. Martinez-Seara, N. Reuter, R. B. Best, I. Vattulainen, L. Monticelli, X. Periole, D. P. Tieleman, A. H. de Vries, and S. J. Marrink. "Martini 3: a general purpose force field for coarse-grained molecular dynamics". In: *Nat. Methods* 18 (2021), pp. 382–388. DOI: 10.1038/s41592-021-01098-3.
- [84] J. Sprittles and Y. Shikhmurzaev. "Coalescence of liquid drops: Different models versus experiment". In: *Phys. Fluids* 24.12 (2012), p. 122105. DOI: 10.1063/1. 4773067.
- [85] S. Stephan and U. K. Deiters. "Characteristic curves of the Lennard-Jones fluid". In: *Int. J. Thermophys.* 41 (2020), pp. 1–24. DOI: 10.1007/s10765-020-02721-9.
- [86] A. Stukowski. "Visualization and analysis of atomistic simulation data with OVITO-the Open Visualization Tool". In: *Modelling Simul. Mater. Sci. Eng.* 18 (2010), p. 015012. DOI: 10.1088/0965-0393/18/1/015012.
- [87] P. E. Theodorakis, E. A. Müller, R. V. Craster, and O. K. Matar. "Modelling the superspreading of surfactant-laden droplets with computer simulation". In: *Soft Matter* 11.48 (2015), pp. 9254–9261. DOI: 10.1039/C5SM02090E.
- [88] P. E. Theodorakis, E. A. Müller, R. V. Craster, and O. K. Matar. "Superspreading: Mechanisms and Molecular Design". In: *Langmuir* 31.8 (2015), pp. 2304–2309. DOI: 10.1021/la5044798.
- [89] T. Thomas and H. N. Unni. "LED-based opto-wetting and fluidic transport for droplet mixing". In: *Microfluid Nanofluidics* 23 (2019), pp. 1–12. DOI: 10.1007% 2Fs10404-019-2273-3.
- [90] S. Thoroddsen, K. Takehara, and T. Etoh. "The coalescence speed of a pendent and a sessile drop". In: J. Fluid Mech. 527 (2005), pp. 85–114. DOI: 10.1017 / S0022112004003076.
- [91] J. J. Uusitalo, H. I. Ingólfsson, P. Akhshi, D. P. Tieleman, and S. J. Marrink. "Martini Coarse-Grained Force Field: Extension to DNA". In: *J. Chem. Theory Comput.* 11.8 (2015), pp. 3932–3945. DOI: 10.1021/acs.jctc.5b00286.

- [92] P. Vainikka, S. Thallmair, P. C. T. Souza, and S. J. Marrink. "Martini 3 Coarse-Grained Model for Type III Deep Eutectic Solvents: Thermodynamic, Structural, and Extraction Properties". In: ACS Sustain. Chem. Eng. 9.51 (2021), pp. 17338– 17350. DOI: 10.1021/acssuschemeng.1c06521.
- [93] J. Wohlert and L. A. Berglund. "A coarse-grained model for molecular dynamics simulations of native cellulose". In: J. Chem. Theory Comput. 7.3 (2011), pp. 753– 760. DOI: 10.1021/ct100489z.
- [94] X. Xia, C. He, and P. Zhang. "Universality in the viscous-to-inertial coalescence of liquid droplets". In: *Proceedings of the National Academy of Sciences* 116.47 (2019), pp. 23467–23472. DOI: 10.1073/pnas.1910711116.
- [95] H. O. Yadav, S. Harada, A.-T. Kuo, S. Urata, and W. Shinoda. "Hemimicelle formation of semi-fluorocarbon chains at air–water interface: coarse-grained molecular dynamics study with an extension of the SPICA force field". In: *Mol. Phys.* 119.19-20 (2021), e1910355. DOI: 10.1080/00268976.2021.1910355.
- [96] S. O. Yesylevskyy, L. V. Schäfer, D. Sengupta, and S. J. Marrink. "Polarizable Water Model for the Coarse-Grained MARTINI Force Field". In: *PLOS Comput. Biol.* 6.6 (June 2010), pp. 1–17. DOI: 10.1371/journal.pcbi.1000810.
- [97] Y. Yoon, F. Baldessari, H. D. Ceniceros, and L. G. Leal. "Coalescence of two equalsized deformable drops in an axisymmetric flow". In: *Phys. Fluids* 19.10 (2007), p. 102102. DOI: 10.1063/1.2772900.