Droplet microfluidics for studying surfactant-rich interfaces found in aerosols, emulsions and foams

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Droplet microfluidics for studying surfactant-rich interfaces found in aerosols, emulsions and foams

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Abstract

The presence of droplets suspended in a liquid or gas is known to play an essential role in fields ranging from materials to atmospheric science. Often, the dispersed phase is stabilized by surface active compounds and surfactants, resulting in complex chemical composition and material properties at the fluid-fluid interface. In this talk, recent advancements in use of microscale flow fields will be highlighted for measuring properties of aqueous multiphase, interface-rich systems. Systems studied will include atmospheric aerosol droplets and liquid-liquid emulsions. Microfluidic contractions, traps, and wells are used to measure surface-bulk partitioning and temperature-dependent liquid-liquid phase separation of aqueous droplets, towards better understanding of suspensions of aerosol droplets in our atmosphere. Advanced measurements of droplet shape deformations and coalescence will also be presented for both water-in-fuel and oil-in-water emulsions, for improved treatment and separation of emulsions. Dynamic interfacial tensions measurements were performed using a microfluidic tensiometer, demonstrating a dependence on if the surfactant approaches the interface from inside (dispersed) versus outside (continuous), implying phase dependent surfactant transport to curved interfaces at the microscale. Droplet coalescence and film drainage experiments are also performed in a microfluidic Stokes trap across a range of viscosity ratios and surfactant concentrations. Results are used to explore the influence of interfacial mobility and Marangoni stresses on film stability with soluble surfactants.

Keywords
Droplet microphysics, Phase separation, Surfactant transport, Dynamic interfacial tension, Interfacial rheology, Droplet coalescence

Figures and tables

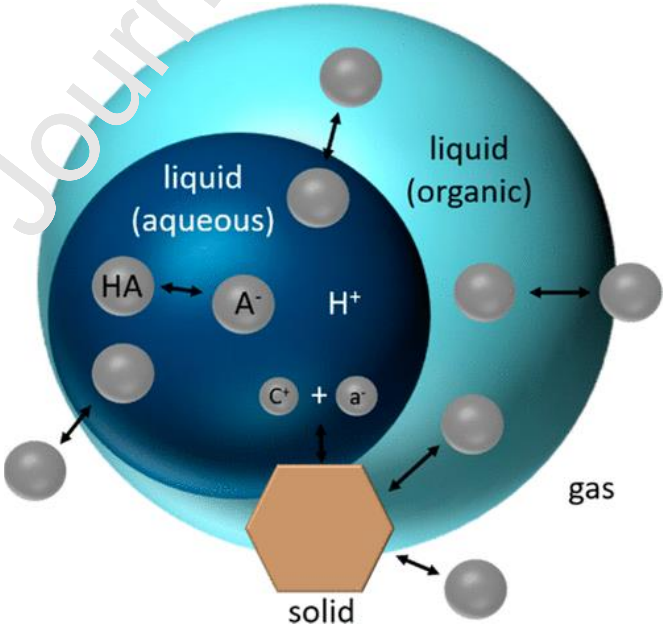


Figure 1. Schematic of possible aerosol particle chemical phase partitioning (not to scale), including liquid-liquid phase-separation (LLPS) into water-rich (‗aqueous‘) and water-poor

(‗organic‘) phases. Adapted with permission from [1]. Copyright 2017 American Chemical Society.

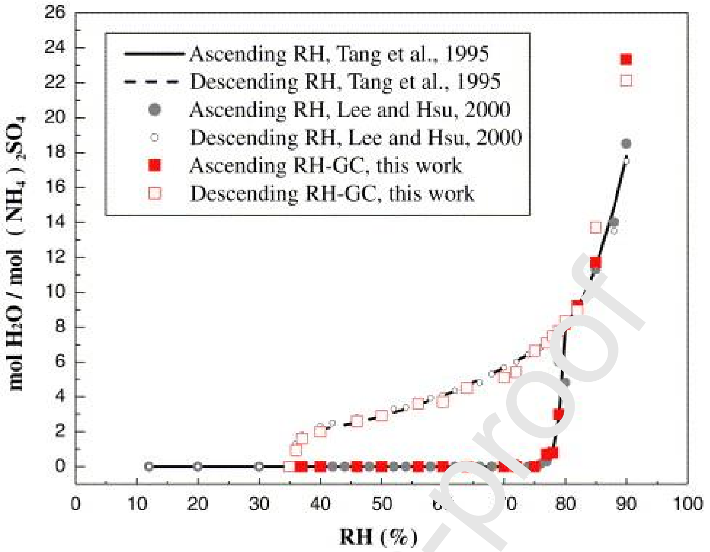


Figure 2. Hysteresis of deliquescence/ efflorescence curves for ammonium sulfate salt. Deliquescence (water uptake) follows the lower curve, and occurs during relative humidity (RH) changes from a low RH to a high RH value. Efflorescence (water loss) follows the upper curve, and occurs during RH changes from high RH to low RH, and. Figure reprinted from [2], with permission from Elsevier; ‗this work‘ refers to that from Tsai and Kuo [2].

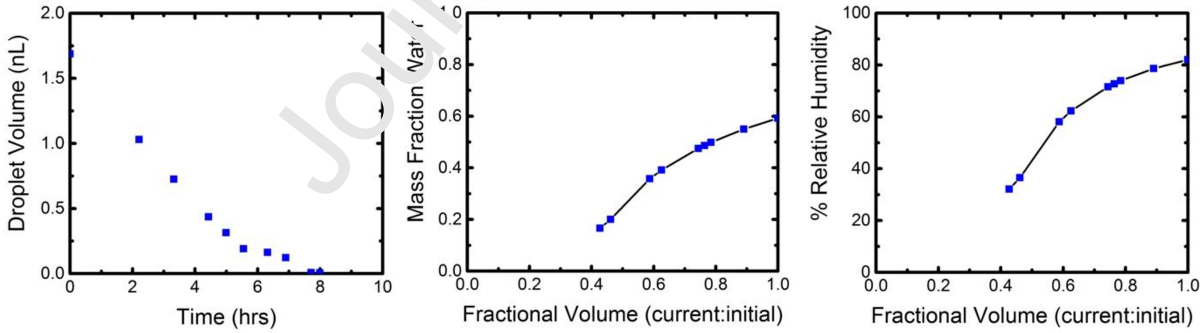


Figure 3. (left) Change in droplet volume of ammonium sulfate solution with time. (middle, right) Change in mass fraction of water and % RH, corresponding to the water activity within the droplet phase, as a function of fractional droplet volume during drying. Adapted with permission from [3]. Copyright 2018 American Chemical Society.

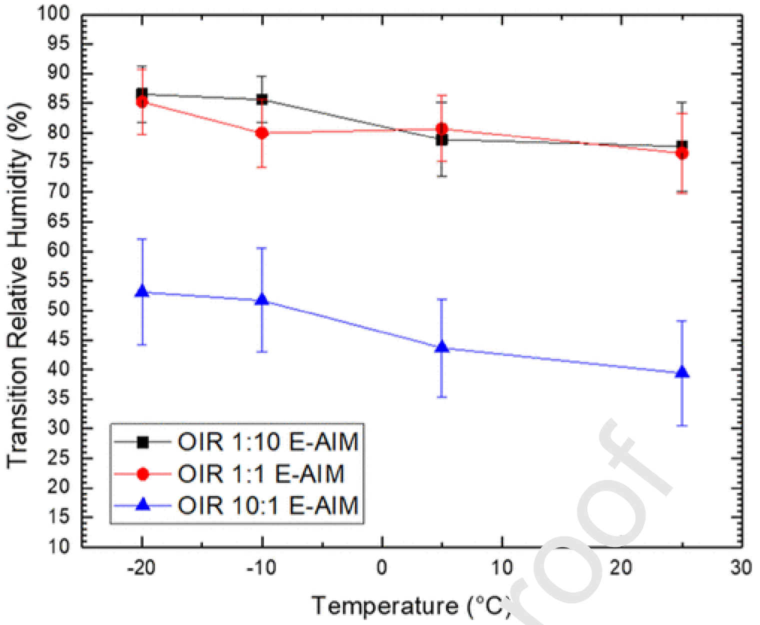


Figure 4. RH of phase transitions at different organic to inorganic ratios and at different temperatures for ammonium sulfate + 3-methylglutaric acid aqueous droplets. The phase transition refers is LLPS for OIR 1:10 and 1:1 and efflorescence for OIR 10:1. Reprinted with permission from [4]. Copyright 2020 American Chemical Society.

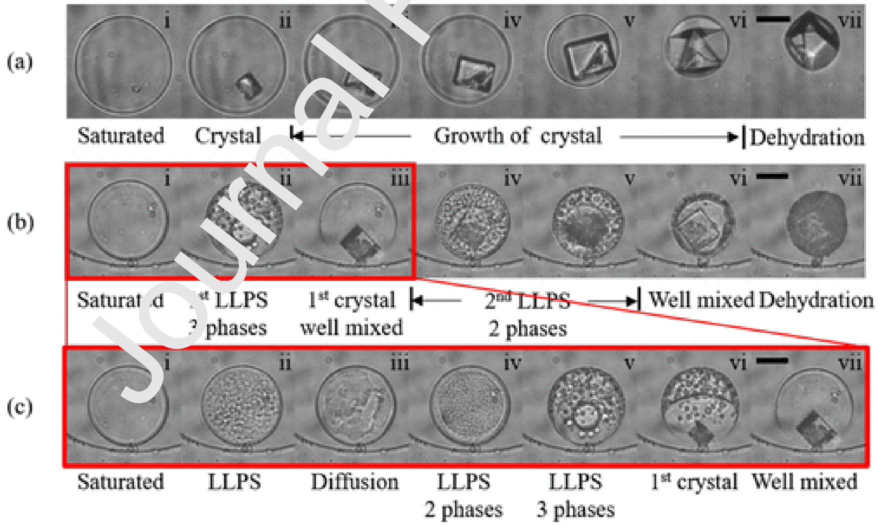


Figure 5. Microscopy images of phase transitions in time observed for (a) NaCl + $MgCl_2$ + Na_2SO_4 aqueous droplet, and (b, c) in 3-methylglutaric acid + NaCl + $MgCl_2$ + Na_2SO_4 aqueous droplet. Scale bar is 50 μm. Reprinted with permission from [5]. Copyright 2019 American Chemical Society.

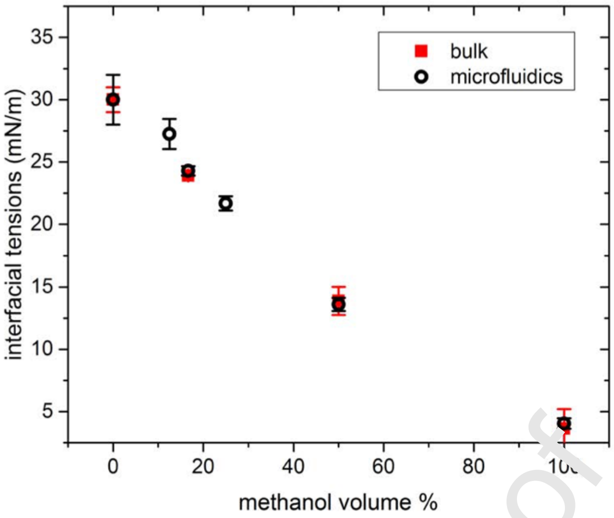


Figure 6. Example of interfacial tension between an oil and aqueous methanol solutions, measured using pendant drop (“bulk”) and microfluidic method, showing good agreement between the two methods for simple surfactant-free mixtures. For more information, see ref [6].

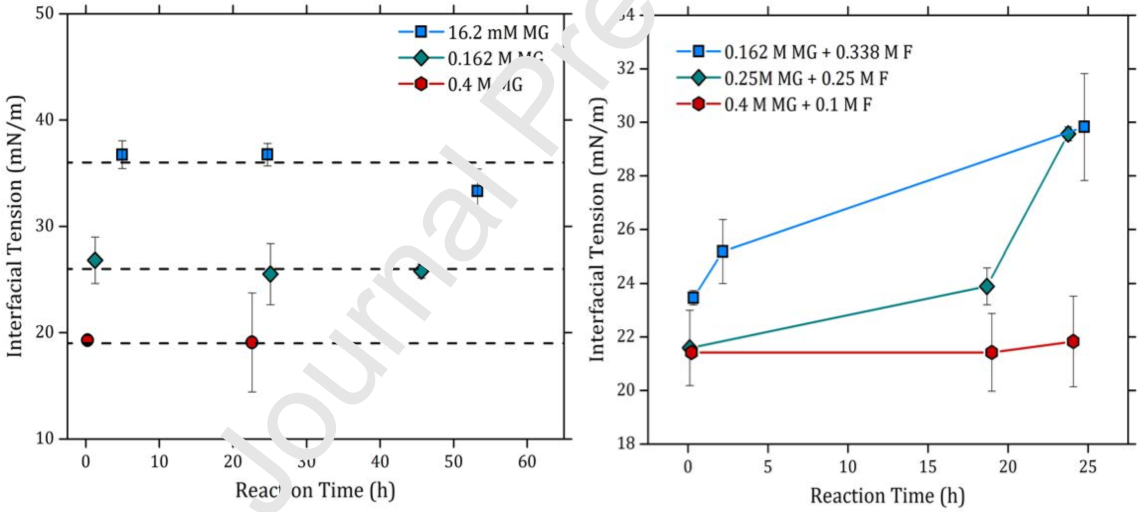


Figure 7. Microfluidic measurements of interfacial tensions of aqueous ammonium sulfate and (left) methylglyoxal (MG) and (right) methylglyoxal (MG) + formaldehyde (F) solutions. Adapted with permission from ref [7]. Copyright 2016, American Chemical Society.

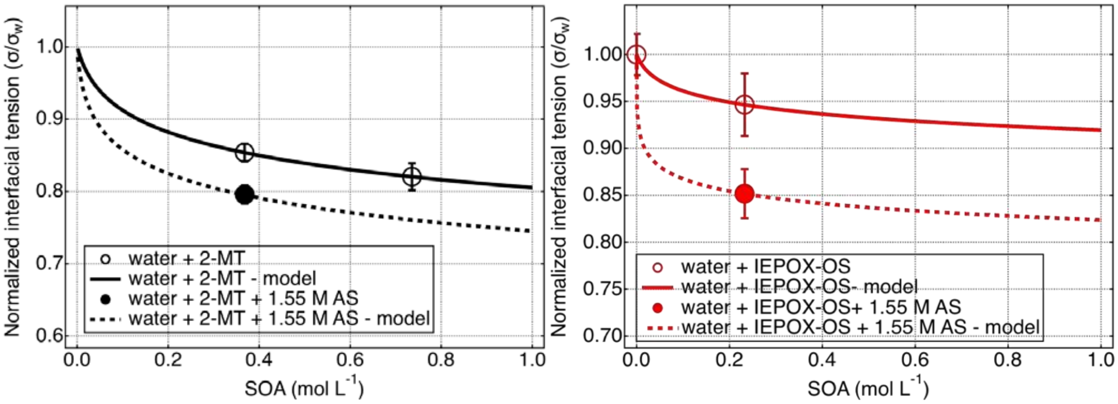


Figure 8. Microfluidic measurements and modeled values of interfacial tensions of (left) 2-methyltetrols and (right) IEPOX-OS, without and with ammonium sulfate (AS). Reprinted with permission from ref [8]. Copyright 2019, American Chemical Society.

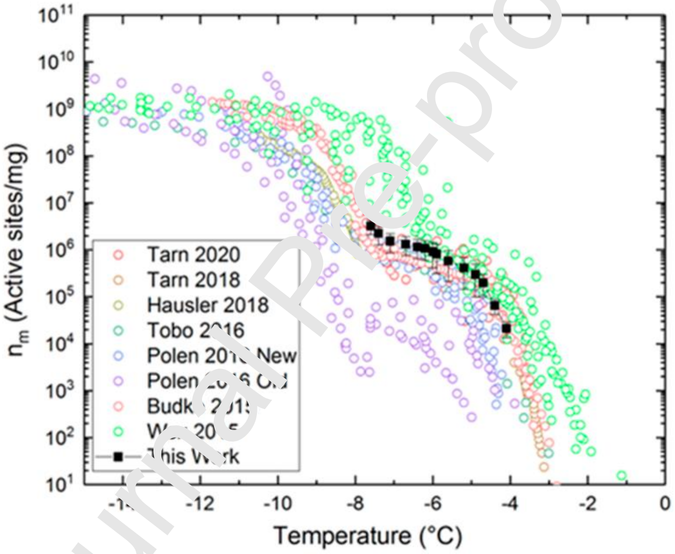


Figure 9. Ice nucleation site density per unit mass of Snomax® in aqueous droplets using a microfluidic platform ("This Work"), along with comparison to literature data obtained from others (see ref [9] for more information). Reprinted with permission from ref [9], open access Creative Common CC BY license.

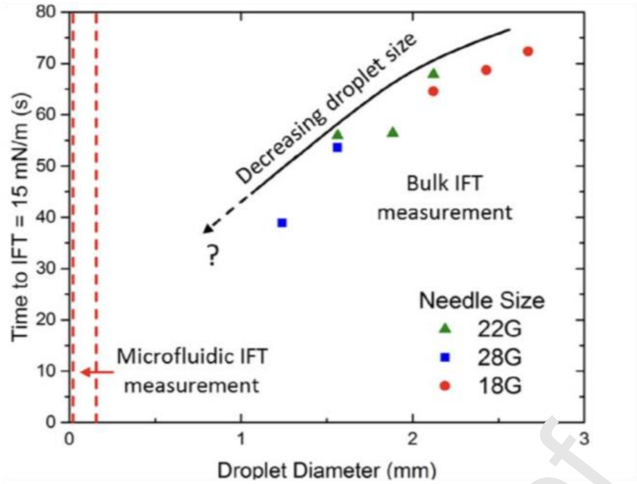


Figure 10. Time required to reach a dynamic interfacial tension IFT value of 15 mN/m millimeter-sized water droplet in surfactant-containing fuel as a function of droplet size, using a pendant drop method. For the same chemical composition, less time is needed as the droplet size decreases. Adapted with permission from ref [10]. Copyright 2018 American Chemical Society.

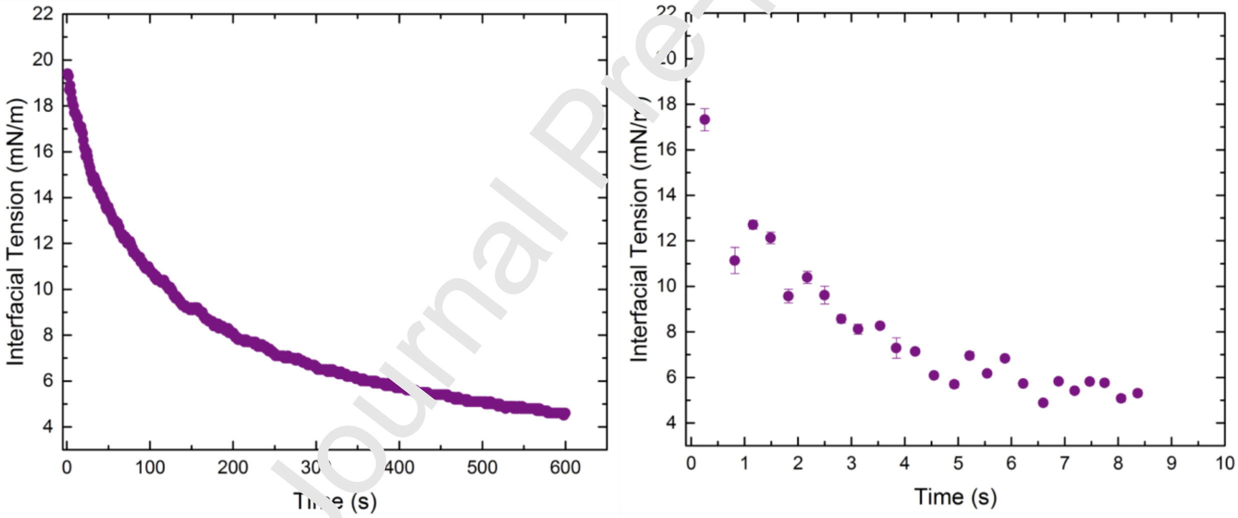
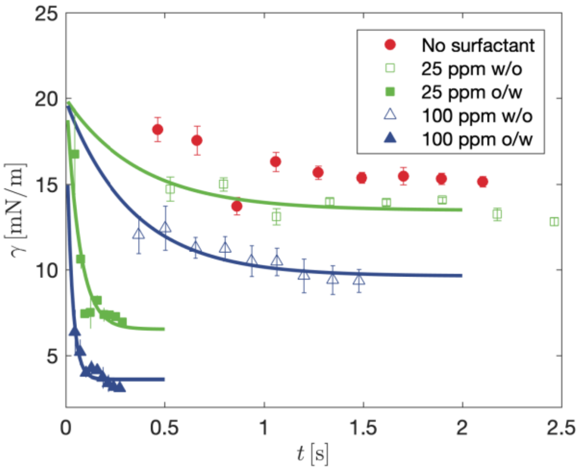


Figure 11. Dynamic interfacial tension measurements using (left) pendant drop and (right) microfluidic for water – fuel interface, in the presence of a fuel-phase surfactant. Droplet size dependent kinetics are evident, with the microfluidic approach reaching an IFT of 5 mN/m much faster than the pendant drop method for the same chemical system. Adapted with permission from ref [10]. Copyright 2018 American Chemical Society.



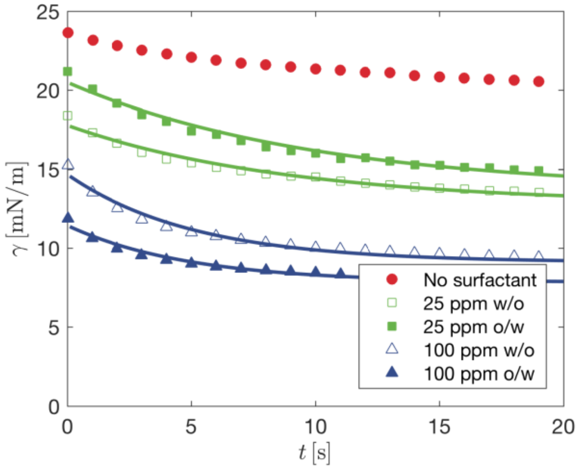


Figure 12. Dynamic interfacial tension of both water-in-oil (w/o) and oil-in-water (o/w) droplets using (left) pendant drop and (right) microfluidic platform. Note that some surface-active additives are already present in the complex oil mix used here, and “No surfactant” simple refers to a case where no additional surfactant was added. Figure adapted from Refs. [11] and [12], with permission from the Royal Society of Chemistry.

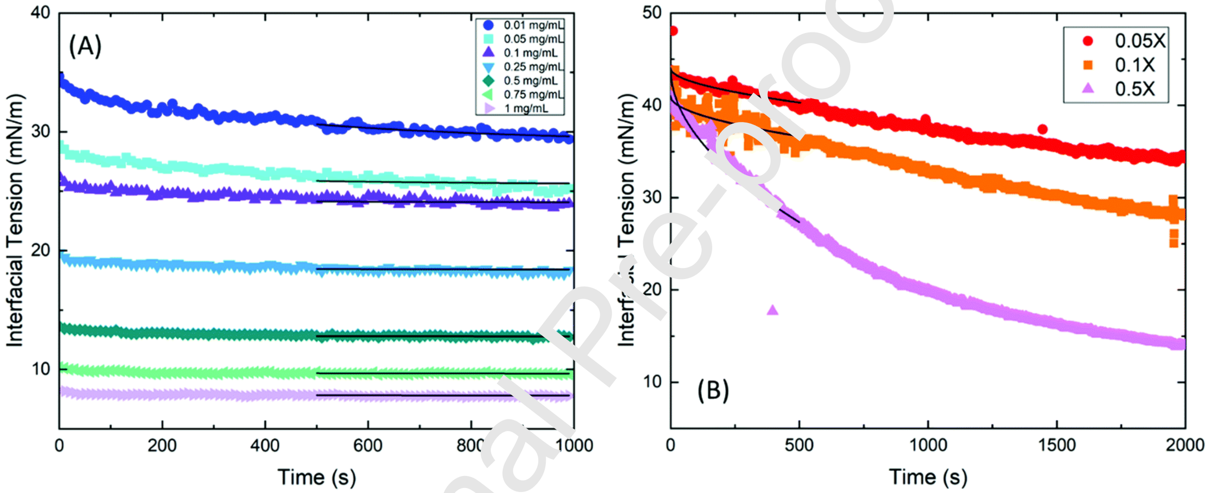


Figure 13. Dynamic interfacial tension using pendant drop tensiometry for water – fuel systems contain (A) mono-olein and (B) PIBSI surfactants. Solid black lines are fits to either the (A) late or (B) early time solutions to the Ward and Tordai equation [43]. Panel (A) uses results from Ref. [10]. Reproduced from Ref. [13] with permission from the Royal Society of Chemistry.

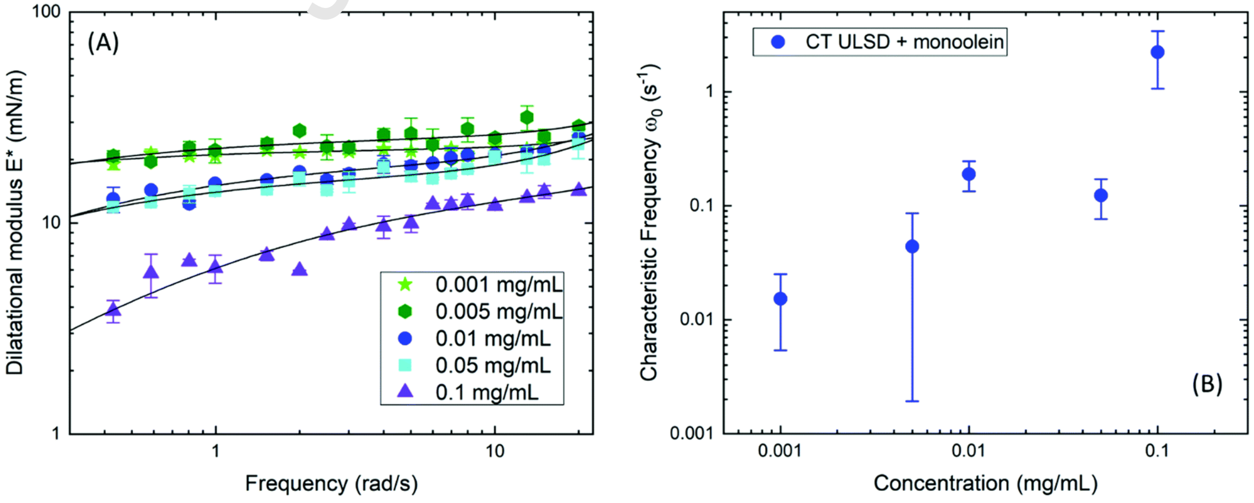


Figure 14. (A) Magnitude of the interfacial dilatational modulus for water – fuel interface, at varied fuel phase surfactant concentrations, as a function of frequency. (B) Characteristic frequency of surfactant exchange with the subphase obtained from the fits to the data in (A), as a function of surfactant concentration. Reproduced from Ref. [13] with permission from the Royal Society of Chemistry.

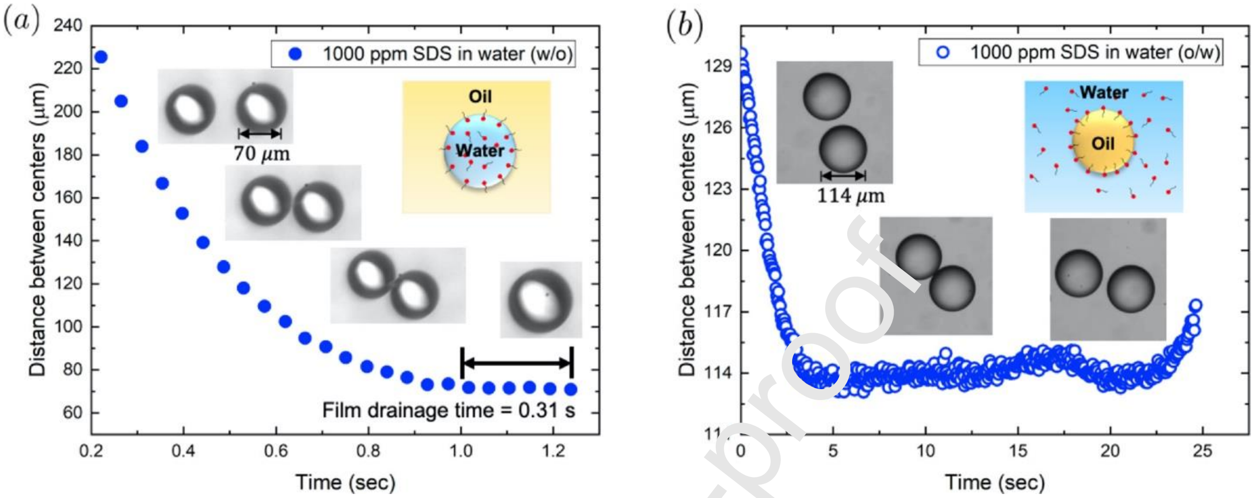


Figure 15. (a) Distance between the two approaching droplets for (a) water in light mineral oil (w/o) and (b) light mineral oil in water (o/w), with a water-soluble surfactant. For the same chemical system, the film drainage time is less than a second for the w/o and did not coalescence for the o/w. In general, the dynamics after droplet impact depend on a range of factors, including droplet size, viscosity ratio, surfactant type, concentration, and phase, and velocities and angles of impact. Reprinted from Ref. [14].

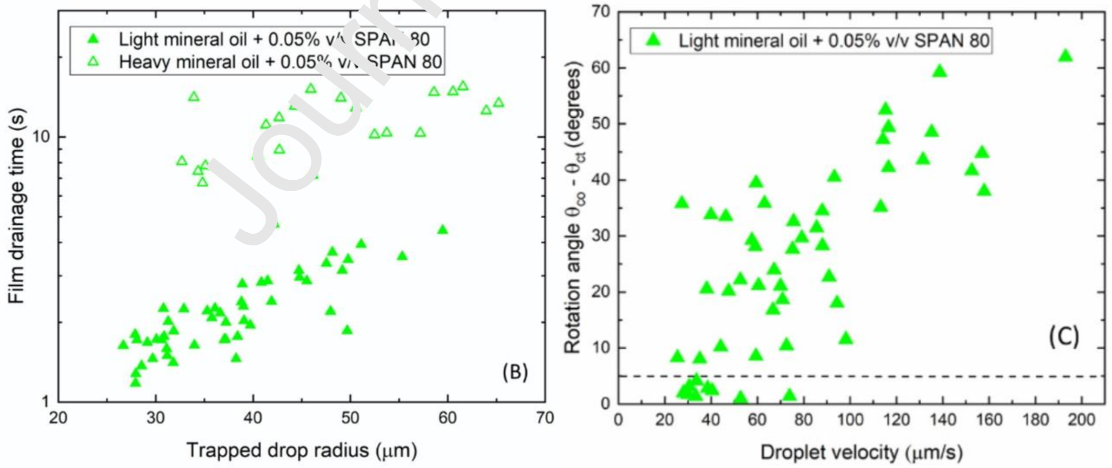


Figure 16. (left) Film drainage time during water droplet coalescence in a microfluidic platform, as a function of trapped droplet radius, for continuous phases of light mineral oil (closed triangles) and heavy mineral oil (open triangles) with an oil phase SPAN 80 surfactant. (right) Degree of droplet rotation (equal to angle of coalescence minus angle of impact) as a function of the velocity of the incoming droplet. Reproduced with permission from ref [15]. Copyright 2020 American Chemical Society.

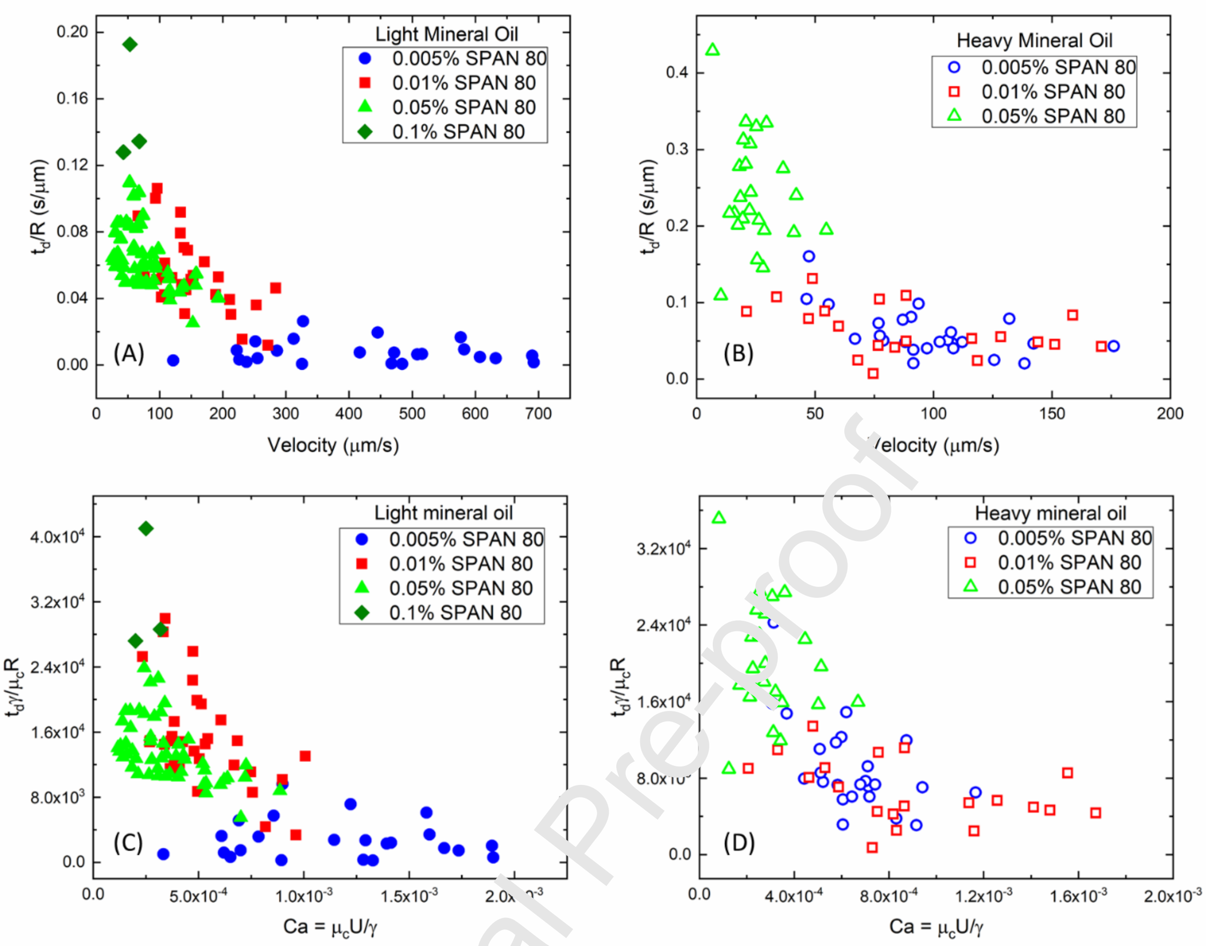


Figure 17. Characterization of film drainage times for two coalescing water droplets in light or heavy mineral oil. (A, B) Film drainage time normalized by mean radius, as a function of droplet velocity at various concentrations of SPAN 80 in (A) light and (B) heavy mineral oil. (C,D) Dimensionless film drainage time as a function of capillary number at various concentrations of SPAN 80 in (C) light and (D) heavy mineral oil. Reproduced with permission from refs [15] and [16]. Copyright 2020 and 2022 American Chemical Society.

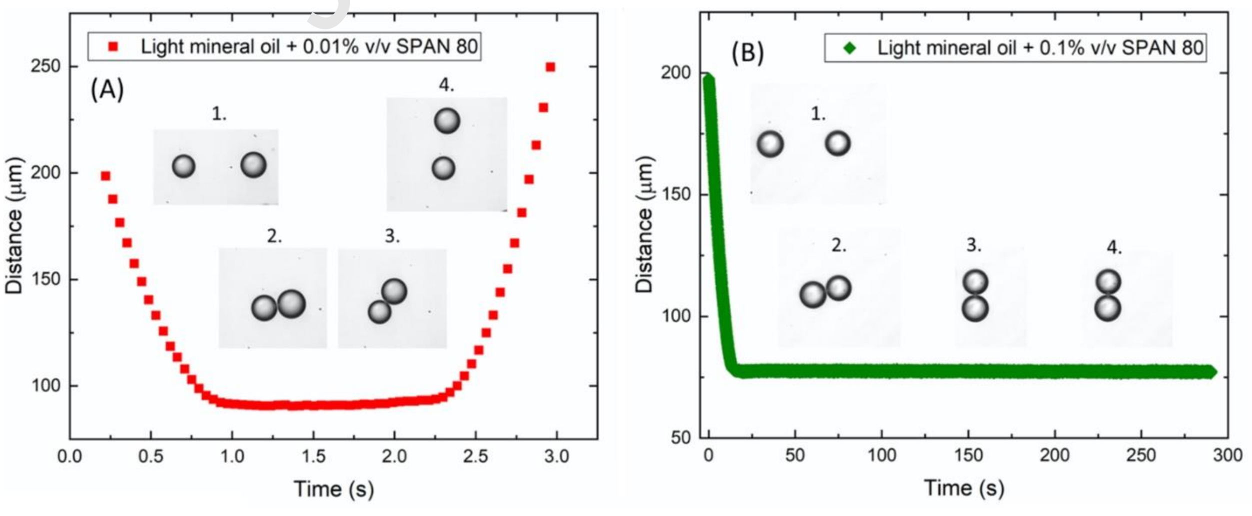


Figure 18. Beyond coalescence, droplets can also experience other dynamics, such as (A) bounce-off or (B) flocculation, depending on factors such as impact velocity and surfactant concentration. Here the center-to-center distance between water droplets as a function of time in light mineral oil + SPAN 80 systems demonstrate of two non-coalescing events. Reproduced with permission from ref [15]. Copyright 2020 American Chemical Society.

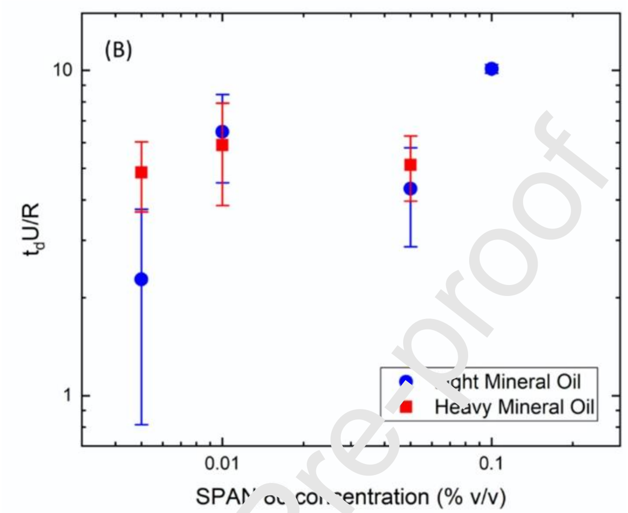


Figure 19. Film drainage time between two water droplets scaled by velocity and mean drop radius as a function of oil phase SPAN 80 concentration with light (blue circles) and heavy (red squares) mineral oils in the continuous phase. Adapted with permission from ref [15]. Copyright 2020 American Chemical Society.

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Declaration of interests

*Please **tick** the appropriate statement below and declare any financial interests/personal relationships which may affect your work in the box below.*

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
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References

[1]. Boyer, H.C. and Dutcher, C.S. Atmospheric Aqueous Aerosol Surface Tensions: Isotherm-based Modeling and Biphasic Microfluidic Measurements. *Journal of Physical Chemistry A*, 121 (25), 4733 - 4742 (2017). DOI: 10.1021/acs.jpca.7b03189

[2]. Tsai, Y.I. and Kuo, S-C. PM2.5 aerosol water content and chemical composition in a metropolitan and a coastal area in southern Taiwan, Atmospheric Environment, 39, 4827-4839 (2005). DOI 10.1016/j.atmosenv.2005.04.024.

[3]. Nandy, L. and Dutcher, C.S. Phase Behavior of Ammonium Sulfate with Organic Acid Solutions in Aqueous Aerosol Mimics Using Microfluidic Traps. *Journal of Physical Chemistry B*, 122 (13), 3480-3490 (2018). DOI: 10.1021/acs.jpcb.7b10655

[4]. Roy, P., Mael, L., Makhnenko, I., Martz, R., Grassian, V., Dutcher, C. Temperature-dependent phase transitions of aqueous droplet systems in microfluidic traps, *ACS Earth and Space Chemistry* (2020). DOI: 10.1021/acsearthspacechem.0c00114

[5]. Nandy, L., Liu, S., Gunsbury, C., Wang, X., Pendergraft, M., Prather, K., Dutcher, C.S, Multistep Phase Transitions in Sea Surface Microlayer Droplets and Aerosol Mimics using Microfluidic Wells. *ACS Earth and Space Chemistry*, 3(7), 1260-1267 (2019). DOI: 10.1021/acsearthspacechem.9b00121.

[6]. Boyer, H.C. Atmospheric Aqueous Aerosol Interfaces: Thermodynamic Modeling and Biphasic Microfluidic Flows with Fluid-Fluid Interfaces, PhD thesis, University of Minnesota, Minneapolis, MN, 2017

[7]. Metcalf, A.R., Boyer, H.C., and Dutcher, C.S. Interfacial Tensions of Aged Organic Aerosol Particle Mimics using a Biphasic Microfluidic Platform. *Environmental Science and Technology*, 50 (3), pp 1251-1259 (2016). DOI: 10.1021/acs.est.5b04880

[8]. Riva, M., Chen, Y., Zhang, Y., Lei, Z., Olson, N.E., Boyer, H.C., Narayan, S., Yee, L., Green, H., Cui, T., Zhang, Z., Baumann, K., Fort, M., Edgerton, E., Budisulistiorini, S.H., Rose, C., Ribeiro, I., e Oliveira, R., dos Santos, E., Machado, C., Szopa, S., Zhao, Y., Alves, E.G., de Sá, S.S., Hu, W., Knipping, E.M., Shaw, S.L., Duvoisin, S., de Souza, R., Palm, B.B., Jimenez, J.L., Glasius, M., Goldstein, A.H., Pye, H., Gold, A., Turpin, B.J., Vizuete, W., Martin, S.T., Thornton, J.A., Dutcher, C.S., Ault, A., Surratt, J.D. Increasing Isoprene Epoxydiol-to-Inorganic Sulfate Aerosol (IEPOX:Sulfinorg) Ratio Results in Extensive Conversion of Inorganic Sulfate to Organosulfur Forms: Implications for Aerosol Physicochemical Properties. *Environmental Science & Technology*, 53(15), 8682-8694 (2019). DOI: 10.1021/acs.est.9b01019

[9]. Roy P., House, M. and Dutcher, C.S. A Microfluidic Device for Automated High Throughput Detection of Ice Nucleation of Snomax. *Micromachines* (2021). DOI: 10.3390/mi12030296

[10]. Narayan, S., Moravec, D. B., Hauser, B. G., Dallas, A. J., Dutcher, C.S. Removing water from diesel fuel: Understanding the impact of droplet size and surfactant transport on liquid-liquid separation of water-in-fuel microemulsions, *Energy and Fuels*, 32 (7), 7326-7337 (2018) DOI: 10.1021/acs.energyfuels.8b00502

[11]. Dutcher, C.S., Understanding Shipboard Oil/Water Emulsions Using Macro- and Micro-scale Flows, SERDP Project WP18-C1-1031 Final Report, December, 2020.

[12]. Chen, Y. and Dutcher, C.S., Size dependent droplet interfacial tension and surfactant transport in liquid–liquid systems, with applications in shipboard oily bilgewater emulsions, *Soft Matter*, 16, 2994-3004 (2020). DOI: 10.1039/C9SM01892A

[13]. Narayan, S., Sourav, B., Moravec, D.B., Hauser, B.G., Dallas, A.J. Zasadzinski, J.A, Dutcher, C.S. Dilatational rheology of water-in-diesel fuel interfaces: Effect of surfactant concentration and bulk-to-interface exchange. *Soft Matter* (2021). DOI: 10.1039/D1SM00064K

[14]. Chen, Y., Narayan, S., and Dutcher C.S., Phase-dependent surfactant transport on the microscale: Interfacial tension and droplet coalescence. *Langmuir* (2020). DOI: 10.1021/acs.langmuir.0c02476

[15]. Narayan S., Makhnenko, I., Moravec, D.B., Hauser, B.G., Dallas, A.J. and Dutcher C.S, Insights into the microscale coalescence behavior of surfactant-stabilized droplets using a microfluidic hydrodynamic trap, *Langmuir* 36, 33, 9827-9842 (2020). DOI: 10.1021/acs.langmuir.0c01414

[16]. Narayan S., Makhnenko, I., Moravec, D.B., Hauser, B.G., Dallas, A.J. and Dutcher C.S, Correction to Insights into the microscale coalescence behavior of surfactant-

stabilized droplets using a microfluidic hydrodynamic trap, *Langmuir* 38, 8, 2749–2750 (2022). DOI 10.1021/acs.langmuir.1c02591

[17]. Smitt, Y. (updated Aug 24, 2018) “Just another day on aerosol earth” (https://www.nasa.gov/image-feature/just-another-day-on-aerosol-earth)

[18]. Heintzenberg, Raes, Schwart, Chapter 4: Tropospheric Aerosols, pp. 125-156 from Brasseur, G.P., Prinn, R.G., Pszenny, A.A.P. (eds) Atmospheric Chemistry in a Changing World. Global Change - The IGBP Series. Springer, Berlin, Heidelberg (2003). DOI: 10.1007/978-3-642-18984-5_4

[19]. You, Y., L. Renbaum-Wolff, M. Carreras-Sospedra, S.J. Hanna, N. Hiranuma, S. Kamal, M.L. Smith, X.L. Zhang, R.J. Weber, J.E. Shilling, D. Dabdub, S.T. Martin and A.K. Bertram, *Proc. Nat. Acad. Sci. USA*. 109, 13188 (2012). DOI: 10.1073/pnas.1206414109

[20]. Kreidenweis, S.M. and Petters, M.D. A single parameter representation of hygroscopic growth and cloud condensation nucleus activity. *Atmos. Chem. Phys*. 7, 1961-1971 (2007). DOI: 10.5194/acp-7-1961-2007

[21]. Freedman, M. A. Phase separation in organic aerosol. *Chem. Soc. Rev.* 46, 7694–7705 (2017). DOI: 10.1039/C6CS00783J

[22]. Bzdek, B.R., Reid, J.P., Malila, J. and Prisle, N.L. The surface tension of surfactant-containing, finite volume droplets. *Proc. Nat. Acad. Sci. USA*., 117 (15), 8335-8343. DOI: 10.1073/pnas.1915660117

[23]. Kiselev, A., Bachmann, F., Pedevilla, P. Cox, S.J., Michaelides, A., Gerthsen, D. and Leisner, T., Active sites in heterogeneous ice nucleation—the example of K-rich feldspars, *Science*, 355, 6323, 367-371 (2017). DOI: 10.1126/science.aai8034

[24]. Roy P., Liu S.& Dutcher C.S. Droplet interfacial tensions and phase transitions measured in microfluidic channels. *Annual Review of Physical Chemistry*, 72, 3.1-3.25 (2021). DOI: 10.1146/annurev-physchem-090419-105522

[25]. Metcalf, A., Narayan, S. and Dutcher, C.S. A Review of Microfluidic Concepts for Atmospheric Aerosol Science, *Aerosol Science and Technology*, 52, 3, 310-329 (2018). DOI: 10.1080/02786826.2017.1408952

[26]. Bithi, S. S., Vanapalli, S.A. Behavior of a Train of Droplets in a Fluidic Network with Hydrodynamic Traps. *Biomicrofluidics*, *4* (4), 44110 (2010). DOI: 10.1063/1.3523053

[27]. Randall, G.C. and Doyle, P. Permeation-driven flow in poly(dimethylsiloxane) microfluidic devices. *Proc. Nat. Acad. Sci. USA*. 102 (31) 10813-10818 (2005). DOI: 10.1073/pnas.0503287102

[28]. Laliberte, M., Cooper, W. E. Model for Calculating the Density of Aqueous Electrolyte Solutions. *J. Chem. Eng. Data*, *49* (5), 1141–1151 (2004). DOI: 10.1021/je0498659

[29]. Nandy, L, Ohm, P.B., and Dutcher, C.S. Isotherm-Based Thermodynamic Models for Solute Activities of Organic Acids with Consideration of Partial Dissociation. *Journal of Physical Chemistry A*, 120 (24), pp 4147 - 4154 (2016). DOI: 10.1021/acs.jpca.6b01904

[30]. Nandy, L. and Dutcher, C.S. Isotherm-Based Thermodynamic Model for Solute Activities of Asymmetric Electrolyte Aqueous Solutions. *Journal of Physical Chemistry A* 121 (37), 6957 - 6965 (2017). DOI: 10.1021/acs.jpca.7b03649

[31]. Taylor, G. I. The Viscosity of a Fluid Containing Small Drops of Another Fluid. *Proc. R. Soc. London. Ser. A, Contain. Pap. a Math. Phys. Character*, *138* (834), 41–48 (1932). DOI: 10.1098/rspa.1932.0169.

[32]. Taylor, G. I. The Formation of Emulsions in Definable Fields of Flow. *Proc. R. Soc. London. Ser. A, Contain. Pap. a Math. Phys. Character*, *146* (858), 501–523 (1934). DOI: 10.1098/rspa.1934.0169.

[33]. Rallison, J. M. The Deformation of Small Viscous Drops and Bubbles in Shear Flows. *Annual Review of Fluid Mechanics*, *16* (1), 45–66 (1984). DOI: 10.1146/annurev.fl.16.010184.000401.

[34]. Cabral, J. T., Hudson, S. D. Microfluidic Approach for Rapid Multicomponent Interfacial Tensiometry. *Lab Chip*, *6* (3), 427–436 (2006). https://doi.org/10.1039/b511976f

[35]. Hudson, S.D., Cabral, J.T., Goodrum, W.J., Beers, K.L., Amis, E.J. Microfluidic Interfacial Tensiometry. *Appl. Phys. Lett.*, *87* (8), 081905 (2005). DOI: 10.1063/1.2034098.

[36]. Martin, J. D., Hudson, S. D. Mass Transfer and Interfacial Properties in Two-Phase Microchannel Flows. *New J. Phys.*, *11* (11), 115005 (2009). DOI: 10.1088/1367-2630/11/11/115005.

[37]. Brosseau Q, Vrignon J, Baret JC. Microfluidic dynamic interfacial tensiometry (µDIT). *Soft Matter* 10(17):3066–76 (2014). DOI: 10.1039/c3sm52543k

[38]. Stan C.A., Schneider G.F., Shevkoplyas S.S., Hashimoto M., Ibanescu M., Wiley, B.J., and Whitesides, G.M. A microfluidic apparatus for the study of ice nucleation in supercooled water drops. *Lab Chip* 9(16):2293–2305 (2009). DOI: 10.1039/b906198c

[39]. Narayan, S., Metaxas, A. E., Bachnak, R. Neumiller, T. and Dutcher, C. S. Zooming in on the role of surfactants in droplet coalescence at the macro- and microscale, *Current Opinion in Colloid & Interface Science*, 50, 101385 (2020). DOI: 10.1016/j.cocis.2020.08.010.

[40]. Manikantan, H., Squires, T. M. Surfactant Dynamics: Hidden Variables Controlling Fluid Flows. *Journal of Fluid Mechanics*. 892 (2020). DOI: 10.1017/jfm.2020.170

[41]. Alvarez, N. J., Walker, L. M., Anna, S. L. A Microtensiometer to Probe the Effect of Radius of Curvature on Surfactant Transport to a Spherical Interface. *Langmuir*, *26* (16), 13310–13319 (2010). DOI: 10.1021/la101870m.

[42]. Jin, F., Balasubramaniam, R., Stebe, K.J. Surfactant Adsorption to Spherical Particles: The Intrinsic Length Scale Governing the Shift from Diffusion to Kinetic-Controlled Mass Transfer. *J. Adhes.*, 80 (8), 773–796 (2004). DOI: 10.1080/00218460490480770.

[43]. Ward, A. F. H., Tordai, L. Time-Dependence of Boundary Tensions of Solutions I. The Role of Diffusion in Time-Effects. *J. Chem. Phys.*, *14* (7), 453–461 (1946). DOI: 10.1063/1.1724167.

[44]. Eastoe, J., Dalton, J.S. Dynamic Surface Tension and Adsorption Mechanisms of Surfactants at the Air-Water Interface. *Advances in Colloid and Interface Science*. p103–144 (2000). DOI: 10.1016/S0001-8686(99)00017-2.

[45]. Kotula, A.P., Anna, S.L. Regular Perturbation Analysis of Small Amplitude Oscillatory Dilatation of an Interface in a Capillary Pressure Tensiometer. *J. Rheol.*, *59* (1), 85–117 (2015). DOI: 10.1122/1.4902546.

[46]. Barman, S., Davidson, M.L., Walker, L.M., Anna, S.L., Zasadzinski, J.A. Inflammation Product Effects on Dilatational Mechanics Can Trigger the Laplace Instability and Acute Respiratory Distress Syndrome. *Soft Matter* 16, 6890-6901 (2020). DOI: 10.1039/D0SM00415D.

[47]. Chesters, A.K. The Modelling of Coalescence Processes in Fluid-Liquid Dispersions: A Review of Current Understanding. *Chem. Eng. Res. Des.*, *69*, 259–270 (1991)

[48]. Ivanov, I.B., Danov, K.D., Kralchevsky, P.A. Flocculation and Coalescence of Micron-Size Emulsion Droplets. In *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Elsevier Science Publishers B.V., Vol. 152, pp161–182 (1999). DOI: 10.1016/S0927-7757(98)00620-7

[49]. Hudson, S.D., Jamieson, A.M., Burkhart, B.E. The Effect of Surfactant on the Efficiency of Shear-Induced Drop Coalescence. *J. Colloid Interface Sci.*, *265* (2), 409–421 (2003). DOI: 10.1016/S0021-9797(03)00396-5.

[50]. Jaensson, N., Vermant, J. Tensiometry and Rheology of Complex Interfaces. *Current Opinion in Colloid and Interface Science*. 37, 136–150 (2018). DOI: 10.1016/j.cocis.2018.09.005.

[51]. Jaensson, N., Anderson, P.D., Vermant, J. *Journal of Non-Newtonian Fluid Mechanics*, 290, 104507 (2021). DOI: 10.1016/j.jnnfm.2021.104507

[52]. Chatzigiannakis E., Jaensson, N. Vermant, J. Thin liquid films: Where hydrodynamics, capillarity, surface stresses and intermolecular forces meet. *Current Opinion in Colloid & Interface Science* .53, 101441 (2021). DOI: 10.1016/j.cocis.2021.101441

[53]. Shenoy, A., Rao, C.V., Schroeder, C.M. Stokes Trap for Multiplexed Particle Manipulation and Assembly Using Fluidics. *Proc. Natl. Acad. Sci. U. S. A.*, *113* (15), 3976–3981 (2016). DOI: 10.1073/pnas.1525162113.

[54]. Shenoy, A., Kumar, D., Hilgenfeldt, S., Schroeder, C.M. Flow Topology during Multiplexed Particle Manipulation Using a Stokes Trap. *Phys. Rev. Appl.*, *12* (5), 54010 (2019). DOI: 10.1103/PhysRevApplied.12.054010.

[55]. Yang, H., Park, C.C., Hu, Y.T., Leal, L.G. The Coalescene of Two Equal-Sized Drops in a Two-Dimensional Linear Flow. *Phys. Fluids*, *13* (5), 1087–1106 (2001). DOI: 10.1063/1.1358873.

[56]. Yoon, Y., Borrell, M., Park, C.C., Leal, L.G. Viscosity Ratio Effects on the Coalescence of Two Equal-Sized Drops in a Two-Dimensional Linear Flow. *J. Fluid Mech.*, *525*, 355–379 (2005). DOI: 10.1017/S0022112004002824.

[57]. Politova, N. I., Tcholakova, S., Tsibranska, S., Denkov, N.D., Muelheims, K. Coalescence Stability of Water-in-Oil Drops: Effects of Drop Size and Surfactant Concentration. *Colloids Surfaces A Physicochem. Eng. Asp.*, *531*, 32–39 (2017). DOI: 10.1016/j.colsurfa.2017.07.085.

[58]. Goel, S., Joshi, N., Uddin, M.S., Ng, S., Acosta, E., Ramachandran, A. Interfacial Tension of the Water-Diluted Bitumen Interface at High Bitumen Concentrations Measured Using a Microfluidic Technique. *Langmuir*, *35* (48), 15710–15722 (2019). DOI: 10.1021/acs.langmuir.9b02253.

[59]. Chan, D.Y.C., Klaseboer, E., and Manica, R. Film drainage and coalescence between deformable drops and bubbles. Soft Matter 7, 2235-2264 (2011). DOI: 10.1039/C0SM00812E

[60]. Chatzigiannakis E. and Vermant, J. Breakup of Thin Liquid Films: From Stochastic to Deterministic. *Physical Review Letters* 125, 158001 (2020). DOI: 10.1103/PhysRevLett.125.158001

[61]. Vrij, A. Possible mechanism for the spontaneous rupture of thin, free liquid films. Discussions of the Faraday Society, 42, 23-33 (1966). DOI: 10.1039/DF9664200023

[62]. Yoon, Y., Hsu, A., Leal, L.G. Experimental Investigation of the Effects of Copolymer Surfactants on Flow-Induced Coalescence of Drops. *Physics of Fluids*, *19* (2) (2007). DOI: 10.1063/1.2409735.

[63]. Hsu, A.S., Roy, A., Leal, L.G. Drop-size effects on coalescence of two equal-sized drops in a head-on collision, *Journal of Rheology* 52, 1291 (2008), https://doi.org/10.1122/1.2980013

[64]. Dai, B., Leal, L.G. The Mechanism of Surfactant Effects on Drop Coalescence. *Physics of Fluids*, *20* (4) (2008). DOI: 10.1063/1.2911700

Further reading

- [*Review article*] Metcalf, A., Narayan, S. and Dutcher, C.S. A Review of Microfluidic Concepts for Atmospheric Aerosol Science, Aerosol Science and Technology, 52, 3, 310-329 (2018). DOI: 10.1080/02786826.2017.1408952

- [*Review article*] Narayan, S., Metaxas, A. E., Bachnak, R. Neumiller, T. and Dutcher, C. S. Zooming in on the role of surfactants in droplet coalescence at the macro- and microscale, *Current Opinion in Colloid & Interface Science*, 50, 101385 (2020). DOI: 10.1016/j.cocis.2020.08.010.

- [*Review article*] Chen, Y., Narayan, S., and Dutcher C.S., Phase-dependent surfactant transport on the microscale: Interfacial tension and droplet coalescence. *Langmuir* (2020). DOI: 10.1021/acs.langmuir.0c02476

- [*Review article*] Roy P., Liu S.& Dutcher C.S. Droplet interfacial tensions and phase transitions measured in microfluidic channels. *Annual Review of Physical Chemistry*, 72, 3.1-3.25 (2021). DOI: 10.1146/annurev-physchem-090419-105522.

- [*Droplet phase*] Roy, P., Mael, L.E., Hill, T.C.J., Mehndiratta, L., Peiker, G. House, M.L., DeMott, P.J., Grassian, V.H., Dutcher, C.S., Ice nucleating activity and residual particle morphology of bulk seawater and sea surface microlayer, *ACS Earth and Space Chemistry*, 5, 8, 1916-1928 (2021). DOI: 10.1021/acsearthspacechem.1c00175

- [*Droplet deformation*] Narayan, S., Moravec, D.B., Dallas, A.J., and Dutcher, C.S. Droplet shape relaxation in a four-channel microfluidic hydrodynamic trap, *Physical Review Fluids*. 5, 113603 (2020). DOI: 10.1103/PhysRevFluids.5.113603

- [*Droplet coalescence*] Narayan S., Makhnenko, I., Moravec, D.B., Hauser, B.G., Dallas, A.J. and Dutcher C.S, Insights into the microscale coalescence behavior of surfactant-stabilized droplets using a microfluidic hydrodynamic trap, *Langmuir* 36, 33, 9827-9842 (2020). DOI: 10.1021/acs.langmuir.0c01414

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