UNDERSTANDING PROPAGATED COALESCENCE OF DROPS IN 2D MICROCHANNELS: A MONTE-CARLO APPROACH

MICROFLUIDICS MEETS EMULSION SCIENCE:

Droplet based microfluidics offers a technique to produce mono-disperse and tunable poly-disperse emulsions at a high rate [1]. The compartmentalization of a fluid of interest as a drop helps in conducting reactions and biological activities in a more controlled fashion [2,3]. Microfluidics allows a more sophisticated and controllable method to exploit the rich physio-chemical phenomena in emulsions [1], the design of complex emulsions: double emulsions [4], emulsions with anisotropic features [5], Janus particles [6]. Drops can be packed in a 2D microchannel to form complex concentrated emulsions [7]. Some of the important questions in these systems are: is this complex arrangement stable? What is the probability with which drops coalesce with its neighbors? Also from a fundamental view point it is interesting to understand phenomena like the phase inversion, which is commonly seen in macro systems [8], where the continuous phase becomes the discrete and vice versa. This is interesting because, the significant physics that results in phase inversion in a macro-system become insignificant in a microchannel due to the presence of wall close to the drop phase [9]. Recent experiments have shown a different route towards phase inversion: propagated coalescence [10]. This phenomenon may also result in large scale destabilization of emulsions. As a result, it becomes important to understand this complex behavior.

COALESCENCE MECHANISMS:

Two drops coalesce when the continuous phase between them drains off. The non-zero interfacial tension drives the coalescence when two drop surfaces meet each other. Let us consider the case where two drops approach each other. The associated film drainage results in a very high pressure that resists the approach of the drop. This pressure is due to the thin film lubrication flow of the continuous phase and the drop-surface immobility [11,12]. Recently it was found that separating two drops instead of pushing them together can also lead to coalescence [14]. Though the phenomenon sounds counter-intuitive, the mechanism is straight forward. Low pressure is formed when two drops are pulled apart. This low pressure pulls the drop interfaces towards each other, which results in a liquid bridge [15,16] following which they instantly coalesce because of interfacial tension. Experimental observations show that this mechanism has the potential to result in a cascade of coalescence events [10,14]. This is because; coalescing pair pull themselves away from its neighbors during coalescence. This retraction can result in a low pressure that can induce another coalescence event and so on.

PROPAGATION DYNAMICS

Lai et al proposed conditions under which the drop decompression would lead to coalescence [16]. But Bremond et al observed the coalescence propagation to have a probabilistic nature. They were able to quantify this probability of coalescence as a function of the spatial orientation of the drops [10]. It becomes clear from the previous work that the propagation of coalescence is a complicated function of the film thickness, mobility of interface, interfacial tension, viscosities and contact time. In a 2D concentrated emulsion, drop thicknesses may vary locally and possess a distribution. Considering all these factors in a deterministic simulation may mimic the seemingly stochastic experimental observations but its implementation would be difficult. This motivates the use of a stochastic Monte-Carlo framework where the probability of a coalescence event can be framed from the phenomenology associated with the mechanism of coalescence propagation.

PROPOSED STRATEGY:

It can be seen that the velocity of propagation of coalescence is at least an order of magnitude greater than the velocity of drops. Hence we consider a system of static drops closely packed (hexagonal packing). Coalescence of a random pair (i, j) is initiated. Now this event can trigger additional coalescence events. Propagation of coalescence is based only on the orientation of the neighboring drop with respect to the coalescing pair. Drops i and j can coalesce with their neighbors with probability described experimentally by Bremond et al [10]. Now these coalescence events can trigger more such events leading to an avalanche of size S. It is important to understand the probability of occurrence of such an event. Hence $O(10^5)$ independent simulations are carried out and a probability distribution for the avalanche size is obtained (see

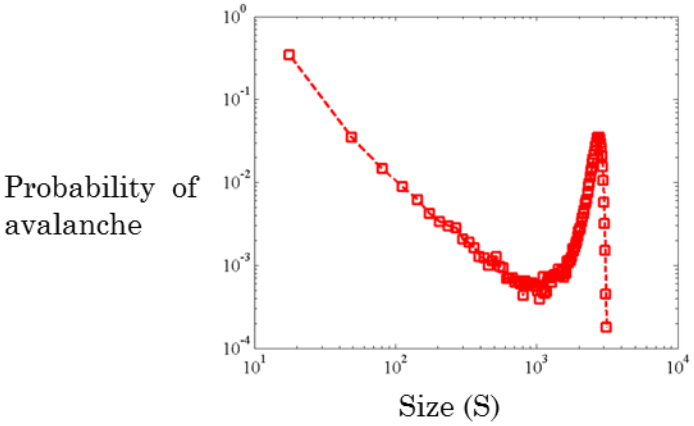


Figure 2 Probability of avalanche vs its size (S)

figure 1). Understanding the quenching of the coalescence propagation will shed light on the unusual shape of the avalanche probability curve. Because each of the coalescence events is probabilistic, quenching can happen when all the drops Q that can induce a coalescence event at a particular instant fail to do so. As the number of Q increases, the probability of quenching decreases, this increases the probability of propagation. Hence an avalanche of that size has a tendency to grow to a larger size. Now once the propagation covers the almost the whole of the system, the number of free drops per Q reduces and this eventually results in quenching of the propagation. These two effects result in a minima and a maxima in the probability curve respectively.

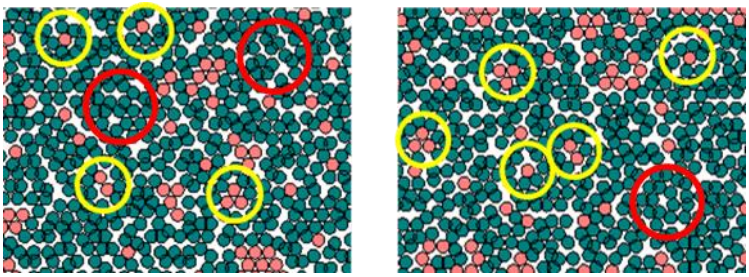


Figure 1 Evidence of formation of composite emulsions (yellow circles) and local phase inversion (red circles) through propagated coalescence

Double emulsions are complex emulsions where there are three phases: an outer continuous phase (L1), inner discrete phase (L2), another discrete phase (L1) inside L2 [4]. These are seen to occur during a coalescence propagation event (encircled regions). A cluster of coalescing drops (circularly placed) can trap both the continuous phase and the non-coalesced drops inside them possibly resulting in double emulsions. If a consistent double emulsion type can be synthesized, it can replace complicated techniques that exist in literature.

When drops coalesce to form closed clusters they have a high probability to entrap continuous phase liquid to result in a local **phase inversion** event, where the continuous phase becomes the drop and vice versa. This is frequently seen whenever the number of drops coalescing is over 1000 drops. Consider the regions marked by red closed curves in figure 2. Large groups of coalesced drops are to be found. When this event occurs, the continuous phase may be trapped within the coalesced cluster resulting in phase inversion.

REFERENCES

[1] N. Bremond and J. Bibette, Soft Matter **8**, 10549 (2012).
[2] H. Song, D. L. Chen, and R. F. Ismagilov, Angew. Chem. Int. Ed. Engl. **45**, 7336 (2006).
[3] B. T. Kelly, J.-C. Baret, V. Taly, and A. D. Griffiths, Chem. Commun. (Camb). 1773 (2007).
[4] S. Okushima, T. Nisisako, T. Torii, and T. Higuchi, Langmuir **20**, 9905 (2004).
[5] K. E. Sung, S. A. Vanapalli, D. Mukhija, H. A. Mckay, J. M. Millunchick, M. A. Burns, and M. J. Solomon, 1335 (2008).
[6] D. Dendukuri and P. S. Doyle, Adv. Mater. **21**, 4071 (2009).
[7] M. Hashimoto, P. Garstecki, and G. M. Whitesides, Small **3**, 1792 (2007).
[8] B. Hu, P. Angeli, O. K. Matar, and G. F. Hewitt, Chem. Eng. Sci. **60**, 3487 (2005).
[9] L. Shui, A. van den Berg, and J. C. T. Eijkel, Lab Chip **9**, 795 (2009).
[10] N. Bremond, H. Doméjean, and J. Bibette, Phys. Rev. Lett. **106**, 1 (2011).
[11] R. H. Davis, J. a. Schonberg, and J. M. Rallison, Phys. Fluids A Fluid Dyn. **1**, 77 (1989).
[12] L. G. Leal, *Advanced Transport Phenomena* (Cambridge University Press, Cambridge, 2007).
[13] D. Y. C. Chan, E. Klaseboer, and R. Manica, Soft Matter **7**, 2235 (2011).
[14] N. Bremond, A. Thiam, and J. Bibette, Phys. Rev. Lett. **100**, 1 (2008).
[15] D. Z. Gunes, X. Clain, O. Breton, G. Mayor, and A. S. Burbidge, J. Colloid Interface Sci. **343**, 79 (2010).
[16] A. Lai, N. Bremond, and H. a. Stone, J. Fluid Mech. **632**, 97 (2009).