Final Technical Report:
Electrohydrodynamic Tip Streaming

Osman A. Basaran, Principal Investigator
School of Chemical Engineering, Purdue University, W. Lafayette, IN 47907
Email: obasaran@purdue.edu;
Web: https://engineering.purdue.edu/ChE/People/ptProfile?id=4239

Overall research goals:

When subjected to strong electric fields, liquid drops and films form conical tips and emit thin jets from their tips. Such electrohydrodynamic (EHD) tip streaming or cone-jetting phenomena, which are sometimes referred to as electrospraying, occur widely in nature, e.g., in ejection of streams of small charged drops from pointed tips of raindrops in thunderclouds, and technology, e.g., in electrospray mass spectrometry or electric field-driven solvent extraction. More recently, EHD cone-jetting has emerged as a powerful technique for direct printing of solar cells, micro- and nano-particle production, and microencapsulation for controlled release. In many of the afore-mentioned situations, of equal importance to the processes by which one drop disintegrates to form several drops are those by which (a) two drops come together and coalesce and (b) two drops are coupled to form a double droplet system (DDS) or a capillary switch (CS). The main objective of this research program is to advance through simulation, theory, and experiment the breakup, coalescence, and oscillatory dynamics of single and pairs of charged as well as uncharged drops.

Summary of significant achievements:

Drops subjected to strong electric fields emit charged jets from their pointed tips (Figure 1). The disintegration of such tip streaming jets into a spray consisting of charged droplets is common to electrospray ionization mass spectrometry, electric field-driven solvent extraction, printing and coating processes, and raindrops in thunderclouds. Despite being one of the oldest and most celebrated problems in science, there exist conflicting theories and measurements on the size and charge of these small electrospray droplets. We have used theory and simulation (Collins et al. 2013) to show that conductivity can be tuned to yield three distinct scaling regimes for droplet radius and charge. The amount of charge Q that electrospray droplets carry determines whether they are Coulombically stable and charged below the Rayleigh limit of stability Q_R, or are unstable and hence prone to further explosions once they are formed. Previous experiments have reported droplet charge values ranging from 10% to in excess of Q_R. We have shown unequivocally through simulations that electrospray droplets are Coulombically stable when they are created and that there exists a universal scaling law for droplet charge, $Q = 0.44Q_R$. A number of challenges and outstanding problems remain and can form the basis of future work. First, as the conductivity of the liquid increases, the sizes of the emitted drops decrease. Second, if the parent drops bear net charge, the emitted jets are longer than those in situations in which the parent drops are uncharged. Both of these issues exacerbate the multi-scale nature of the problem being tackled. Moreover, drop size and charge appear to follow different scaling laws when the parent drop is uncharged and when it is.

An important scientific question is the relationship between tip streaming in EHD and tip streaming in other physical problems. We had already investigated this relationship earlier in the case of dripping-jetting transitions when two liquids flow out of two concentric nozzles. We have recently discovered and have started studying a yet closer analog to EHD tip streaming than a two-liquid coflow. This closer analog is referred to as the transition from selective withdrawal (SW) to viscous entrainment (VE). As in EHD tip streaming, the SW to VE transition is also replete with multiple scaling laws. We have already discovered that some of the heretofore theoretically predicted scaling laws may in fact be suspect.

Drop coalescence is central to diverse processes involving dispersions of drops in industrial and scientific realms. During coalescence, two drops first touch and then merge as the liquid neck connecting them grows from initially microscopic scales to a size comparable to the drop diameters (Figure 2.). The curvature of the interface is infinite at the point where the drops first make contact, and the flows that ensue as the two drops coalesce are intimately coupled to this singularity in the dynamics. Conventionally, this so-called post-coalescence process has been thought to have just two dynamical regimes: a viscous and an inertial regime with a crossover region between them. We have used experiments and simulations to reveal that a third regime, one that describes the initial dynamics of coalescence for all drop viscosities, has been missed. An argument based on force balance has led to the construction of a new coalescence phase diagram (Paulsen et al. 2012). This work has been extended to analyze the coalescence singularity that arises when two bubbles touch and begin to merge (Munro et al. 2015). Equally important is the dynamics that takes place as two drops or bubbles approach one another. A key issue in this pre-coalescence process is the thinning of the thin film that separates the two drops or bubbles. We have carried out the first theoretical and computational study to elucidate the thinning and rupture of a thin film separating two bubbles when the film liquid exhibits non-Newtonian power-law rheology (Thete et al. 2015).

Thinning and breakup of liquid filaments are central to dripping of leaky faucets, inkjet drop formation, and raindrop fragmentation. As the filament radius decreases, curvature and capillary pressure, both inversely proportional to radius, increase and fluid is expelled with increasing velocity from the neck. As the neck radius vanishes, the governing equations become singular and the filament breaks. In slightly viscous liquids, thinning initially occurs in an inertial regime where inertial and capillary forces balance. By contrast, in highly viscous liquids, initial thinning occurs in a viscous regime where viscous and capillary forces balance. As the filament thins, viscous forces in the former case and inertial forces in the latter become important, and theory shows that the filament approaches breakup in the final inertial-viscous regime where all three forces balance. However, previous simulations and experiments reveal that transition from an initial to the final regime either occurs at a value of filament radius well below that predicted by theory or is not observed. In this research program, we have used new simulations and experiments, and have shown that a thinning filament unexpectedly passes through a number of intermediate transient regimes, thereby delaying onset of the inertial-viscous regime. The new findings have practical implications regarding formation of undesirable satellite droplets and also raise the question as to whether similar dynamical transitions arise in other free surface flows such as coalescence that also exhibit singularities (Castrejon-Pita et al. 2015).

Inkjet printers eject drops from microscopic nozzles and deposit them on substrates. For a number of years after its initial development, inkjet printing remained a method for visualizing computer output and printing documents. Beginning in the late 1990s, a number of researchers realized that inkjet printers can be employed as robotic pipettes that can be used to create microarrays, manufacture three-dimensional parts, print electrical devices, manufacture spherical particles, and facilitate combinatorial chemistry. While most inks are low viscosity Newtonian fluids, liquids in new applications are often complex fluids. At the same time that these new applications were emerging, replacement of traditional photography by digital imaging and the quest for ever faster printing speeds resulted in the development of novel printing methods. Whereas most previous reviews of the field have focused on evaluation of well known printing methods, we were invited to write a review (Basaran et al. 2013) that instead presented a critical analysis from a fluid mechanics perspective of the recent developments in nonstandard printing techniques and the increasingly widespread use of nonstandard inks of complex fluids (Bhat et al. 2012).

It is now well known that a pendant or a sessile drop that is subjected to an electric field elongates in the field direction and ultimately becomes unstable at a turning point in field strength. Upon loss of stability, an EHD tip streaming jet is emitted from the conical tips of such drops. What happens, however, if a pendant drop is connected to a sessile drop through a cylindrical hole in a plate from which a pendant drop hangs and a sessile drop protrudes? During the course of this research, we have successfully began a systematic study of the equilibrium shapes and stability of such electrified double droplet systems (DDSs) or capillary switches (CSs) and the oscillatory responses of uncharged DDSs (Ramalingam and Basaran 2010, Ramalingam et al. 2012, Sambath and Basaran 2014). We are now poised to study the dynamics of electrified DDSs, including EHD tip streaming from their tips and how they may be used as liquid grabbers in applications in microfluidics and analytical chemistry.

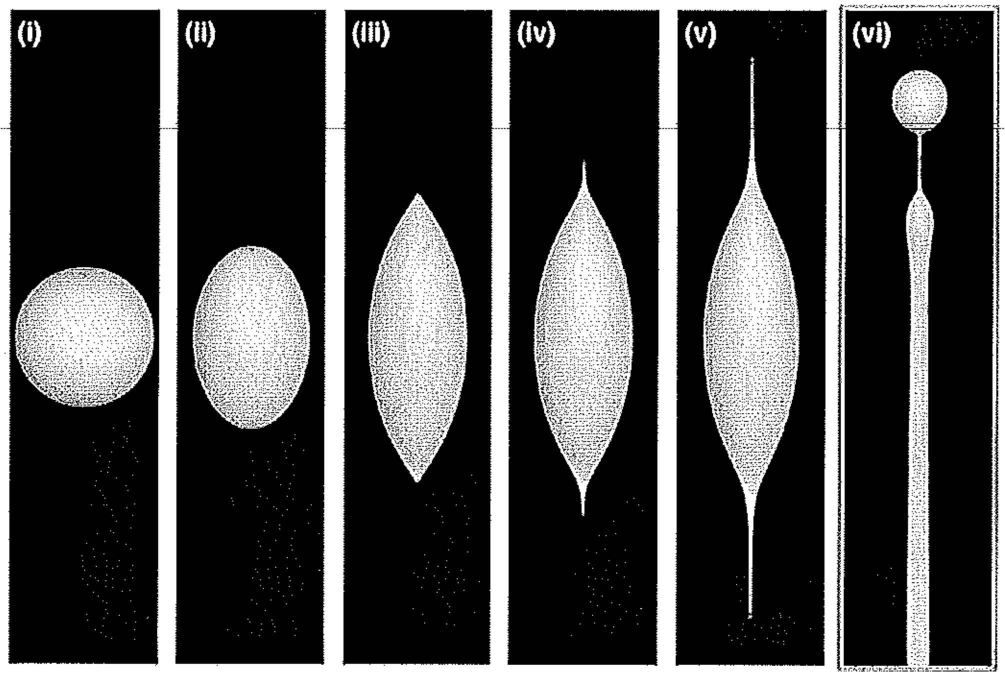

Figure 1. EHD tip streaming from an uncharged, slightly conducting liquid drop subject to a uniform electric field. (i) Initially spherical drop. (ii) Shortly after the imposition of the electric field, the drop takes on a nearly spheroidal shape. (iii) Later, the drop develops two Taylor cones at its opposing ends. (iv) Onset of tip streaming from the opposing ends. (v) Emission of fully develop tip streaming jets and the incipience of the pinch-off of two small electrospray droplets. (vi) Blow-up of one of the tip streaming jets in (v) detailing the about-to-form electrospray droplet and microthread connecting the droplet to the jet. (From Collins et al. 2013.)

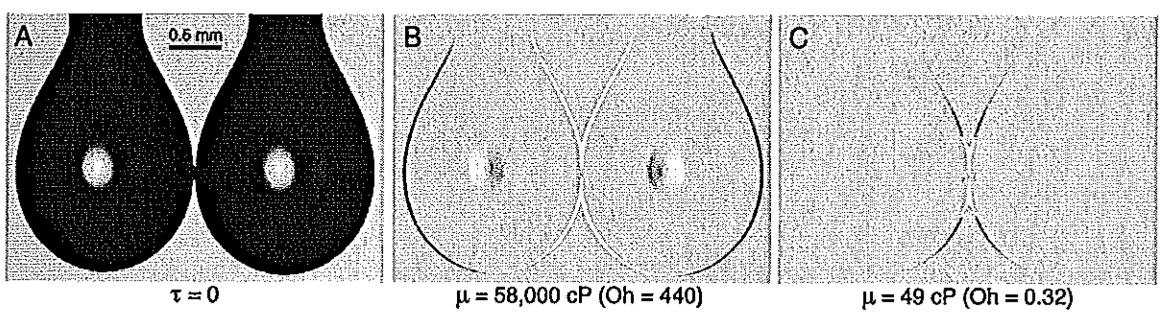

Figure 2. Coalescence of silicone oil drops with viscosities $\mu = 58{,}000$ cP (Oh = 440) and 49 cP (Oh = 0.32). (A) Two pendant drops at the instant they contact, $\tau = 0$. (The two bright spots are from back-lighting.) We subtract an image taken after the neck has grown to a size $r_{min} = 0.25A$ from the one at $\tau = 0$ for (B), $\mu = 58{,}000$ cP and (C), 49 cP. Here, A is the drop radius and Oh is the Ohnesorge number (ratio of viscous to inertial force). (From Paulsen et al. 2012.)

Publication resulting from this DOE funded program of research:

1. Ramalingam, S. and Basaran, O. A. 2010 Axisymmetric oscillation modes of a double droplet system. *Phys. Fluids* **22**, 112111.

2. Paulsen, J. D., Burton, J. C., Nagel, S. R., Appathurai, S., Harris, M. T., and Basaran, O. A. 2012 The inexorable resistance of inertia determines the initial regime of drop coalescence. *PNAS* **109**, 6857-6861.

3. Ramalingam, S., Ramkrishna, D., and Basaran, O. A. 2012 Free vibrations of a spherical drop constrained at an azimuth. *Phys. Fluids* **24**, 082102. (A highlight paper.)

4. Bhat, P. P., Appathurai, S., Harris, M. T., and Basaran, O. A. 2012 On self-similarity in the drop-filament corner region formed during pinch-off of viscoelastic fluids. *Phys. Fluids* **24**, 083101.

5. Basaran, O. A., Gao, H, and Bhat, P. P. 2013 Nonstandard inkjets. *Ann. Rev. Fluid Mech.* **45**, 85-113. (Invited review article.)

6. Collins, R. T., Sambath, K., Harris, M. T., and Basaran, O. A. 2013 Universal scaling laws for the disintegration of electrified drops. *PNAS* **110**, 4905-4910.

7. Sambath, K. and Basaran, O. A. 2014 Electrohydrostatics of capillary switches. *AIChE J.* **60**, 1451-1459. (Published in Founder's Issue honoring R. B. Bird.)

8. Castrejon-Pita, J. R., Castrejon-Pita, A. A., Thete, S. S., Sambath, K., Hutchings, I. M., Hinch, E. J., Lister, J. R., and Basaran, O. A. 2015 A plethora of transitions during breakup of liquid filaments. *PNAS.* **112**, 4582–4587.

9. Munro, J. P., Anthony, C. R., Basaran, O. A., and Lister, J. R. 2015 Thin-sheet flow between coalescing bubbles. *J. Fluid Mech.* **773**, R3-1-R3-12.

10. Thete, S. S., Anthony, C. R., Basaran, O. A., and Doshi, P. 2015 Self-similar rupture of thin free films of power-law fluids. *Phys. Rev. E* **92**, 023014.