Perspective

Small-Scale Free Surface Flows with Breakup: Drop Formation and Emerging Applications

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Introduction

A number of seemingly unrelated applications as ink jet printing, DNA arraying, deposition of reagents on diagnostic strips, automatic pipetting of fluids in massively parallel drug discovery, and manufacture of particles and microcapsules rely on the formation of drops either directly or from jet breakup. What these diverse operations (as printing a document and creating a DNA microarray) have in common are that the drops be monodisperse, the process be repeatable and fast, and the product be free of defects. Moreover, given the current importance of MEMS and microfluidics, they should also be amenable to miniaturization. The four images on the righthand side of the front cover make these points well. At four instances, they capture water being ejected from a piezoelectric (piezo), drop-on-demand (DOD) ink jet nozzle at 1,000 Hz. The images have been obtained using a strobe and a standard CCD camera so that each image is actually a superposition of tens of successive drops. Each image looks sharp as the dynamics is identical from drop to drop. The bottom two images show that a satellite, which is always undesirable, merges with the main drop. A satellite left alone may create a stray mark on a printed page or ruin a DNA sequencing experiment. Ink jet printers from Hewlett-Packard (HP), Canon, Epson, and Lexmark incorporate hundreds of such nozzles and cost less than $100. Each nozzle can produce 1,000 to 10,000 identical drops per second, with drop volumes (radii) ranging from 4 to 11 pL (9.8 to 13.8 μm) (see Web sites of these and other companies). Despite the low cost of each unit and that most of the profit is made from selling ink and media, such printers are large revenue generators. For example, 20% of HP's annual revenues of 10 billion dollars come from sales of ink jet printers (Lee, 2001). In contrast, a four-head DNA arrayer costs about $100,000 (Packard Bioscience Corporation).

This article will discuss recent and emerging techniques that produce a monodisperse population of drops. Whether a millimeter-sized drop drips from the kitchen tap once per second or a stream of micron-sized drops are ejected from an ink jet nozzle at 5 kHz, drop formation is a complex free boundary problem exhibiting interface rupture. Scientists and engineers are drawn to the study of drop breakup because of the formation of finite time singularities and self-similar behavior near pinch-off, as highlighted by the four figures on the lefthand side of the front cover. They are also attracted to the problem because it entails large changes in interface topology and the creation of several disconnected masses from an initially single connected mass. Visualization of drop breakup is equally challenging given the micrometer and microsecond length and time scales of interest near pinch-off. Recent advances in fluid mechanics of drop formation will be highlighted, as well as some exciting applications of drop dynamics.

Methods for making drops

Figure 1 shows some common and certain recently developed methods for producing drops. Figures 1a–1c depict some of the simplest methods. All three involve flowing a liquid at a constant flow rate Q through a cylindrical tube of radius R. The ambient fluid is typically air, but can be another liquid. The dynamics in the method of Figure 1a, dripping, is governed by three dimensionless groups: Reynolds number $Re^* \equiv \rho R U/\mu$, where ρ is density, $U \equiv Q/(\pi R^2)$ is average velocity, and μ is viscosity; capillary number $Ca \equiv \mu U/\sigma$, where σ is surface tension; and gravitational Bond number $G \equiv \rho g R^2/\sigma$, where g is gravitational acceleration. In lieu of (Re^*, Ca, G), one can use $(We, \mathrm{Oh}{=}Re^{-1}, G)$. Here, $We \equiv (Re^*)(Ca) = \rho U^2 R/\sigma$ is Weber number, $\mathrm{Oh} \equiv (Ca/Re^*)^{1/2} = \mu/(\rho R \sigma)^{1/2}$ is Ohnesorge number, and $Re = (\rho R \sigma)^{1/2}/\mu$ is the property-based Reynolds number. Dripping requires that We is not too large and that G is not too small. It is difficult to make drops much smaller than about 1 mm in radius using this technique. As We increases, dripping ultimately gives way to jetting, the basis of the method depicted in Figure 1b. In contrast to dripping, drops can be generated by jetting even in microgravity. The radii of drops resulting from jet breakup are on the order of $2R$. Both dripping and jetting can be profoundly affected by the application of an electric field $\mathbf{E}$. If the drop liquid is a perfect conductor and the ambient fluid is a dielectric or insulator of permittivity ε, a fourth dimensionless group, the electric Bond number $Ne \equiv \varepsilon E^2 R/\sigma$, enters the problem (Zhang and Basaran, 1996). However, most ordinary liquids, such as corn or silicone oil, are semi-insulators or leaky dielectrics. If the physical properties of such liquids fall in a certain range and $We \ll 1$, an operating state known as electrohydrodynamic (EHD) jetting can be achieved, as shown in Figure 1c (Cherney, 1999). In this case, the meniscus attached to the tube takes on a conical profile—the Taylor cone and a fine jet, which subsequently breaks up into drops, emanates from the cone's tip. Although EHD jetting places stringent requirements on both physical properties and operating conditions, it is attractive because, unlike the methods of Figures 1a–1b and many others, it can generate micron-size drops from a millimeter-size tube.

Figures 1d–1f depict three methods that are collectively referred to as ink jet printing. There are two primary methods of ink jet printing: continuous ink jet (CIJ), depicted in Figure 1d, and DOD, depicted in Figures 1e and 1f. The DOD methods can be further subdivided as piezo and thermal ink jet (TIJ) or bubble jet (Le, 1998). As the names imply, CIJ printers produce drops continuously, while DOD printers produce drops only when needed.

First, in CIJ printing, jet breakup is carried out in the presence of external forcing to suppress formation of satellites (cf. Figure 1b) and to generate equal-sized drops. Unfortunately, one can merely draw lines and curves on a substrate using drops generated from jet breakup and moving the nozzle and the substrate relative to each other. However, Sweet (1965) developed an ingenious technique that became the first ink jet printing method. In this approach, one selectively charges some of the drops as they form from the breaking jet. By using a set of electrodes downstream of the breakup point, one can then deflect the charged drops, as shown in Figure 1d. Since printing requires spaces between characters, not all the drops generated can be utilized. In the method known as binary CIJ printing, one uses deflected drops for printing and sends undeflected drops to a gutter for recycling. CIJ printers have been around since the 1970s and are clearly among the first MEMS devices to be successfully commercialized. However, they are exclusively used today in high-end printing applications and have not gained acceptance in the home-market. Electrostatic CIJ printers can operate at speeds exceeding 100 kHz, but are expensive and difficult to maintain. They also require that inks used in them can be charged. A recent development (Chwalek et al., 2002) appears to overcome many of these drawbacks. These authors report that a liquid jet can be deflected by asymmetrically heating a microscopic nozzle manufactured using standard silicon processing technology. By turning on and off heat pulses of microsecond duration, both deflected and undeflected drops of equal size can be generated sans satellites.

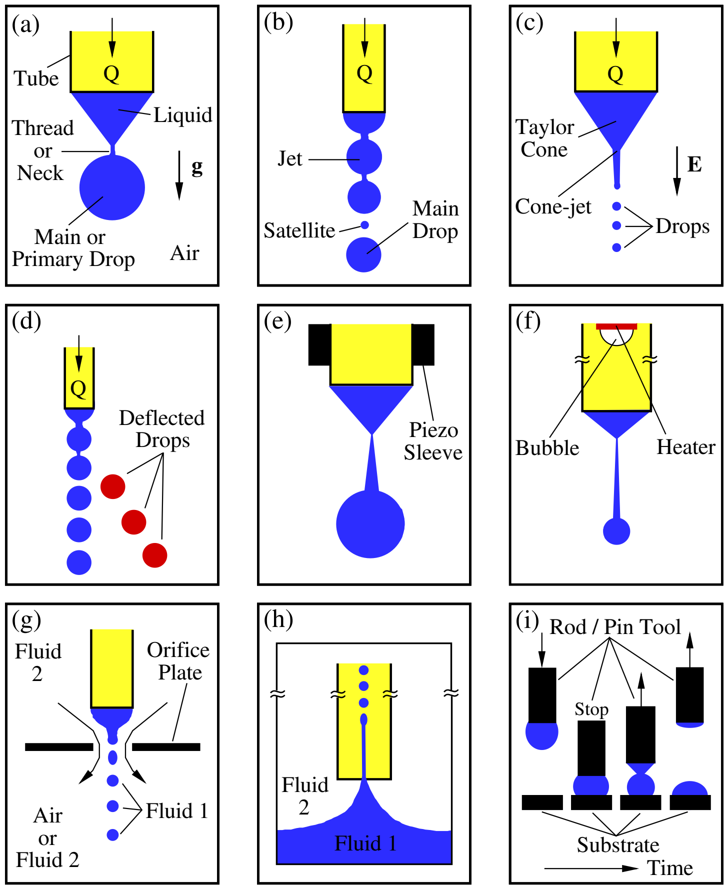

Figure 1. Popular and recently developed methods of drop formation.

Piezo was the first DOD technology to be developed (Zoltan, 1972; Kyser and Sears, 1976). In its simplest form, a piezo DOD nozzle can be made by taking a glass capillary tube and bonding a piezoelectric (PZT) transducer or sleeve outside it, as shown in Figure 1e. The PZT sleeve contracts (expands) when a positive (negative) voltage is applied to it and thereby squeezes (relaxes) the tube. Glass tubes having radii of just under a micron (Kung et al., 1999) to tens of microns have been used (Le, 1998; Chen and Basaran, 2002). A single drop can be ejected from a piezo-DOD nozzle by judicious application of a suitable voltage pulse. Figures 2a–2c show a water drop being ejected from a DOD nozzle by application of a positive square wave, the most commonly used type of voltage pulse which is hereafter called waveform 1. A minor drawback of waveform 1 is that a great deal of experimentation is required to arrive at the right values of the waveform parameters, such as amplitude or duration, to ensure that no satellites are formed (cf. Figure 2c). By using a negative square wave followed by a positive square wave, hereafter called waveform 2, the satellite can be eliminated, as shown in Figures 2d–2f (Chen and Basaran, 2002).

TIJ DOD technology was developed independently by Canon (Kobayashi et al., 1981) and HP (Vaught et al., 1984). In a TIJ DOD printer, a drop is ejected from a nozzle upon the expansion of a (set of) vapor bubble(s) on the surface of a heating element located near the nozzle exit, as shown in Figure 1f. Different versions of both piezo and TIJ DOD printers are described in the review article by Le (1998).

Decreasing drop volume V has been a goal of researchers since the invention of the DOD method due to the desire to increase resolution in printing and array densities in DNA arraying. Unfortunately, virtually all publications and patents on DOD ink jet printing to date have found that $R_d \approx R$, where R_d is the drop radius, as shown in Figures 2c and 2f. Thus, the only reliable way to reduce V, or R_d, until quite recently, has been to reduce R. However, very small nozzles are difficult to manufacture and are prone to clogging and damage. Chen and Basaran (2002) have shown that a voltage pulse consisting of a negative, a positive, and a second negative square wave, hereafter called waveform 3, can be used to form drops that are significantly smaller than the nozzle radius, as shown in Figures 2g–2i. Volume of drops obtained with waveform 3 of Figure 2i is more than an order of magnitude smaller than that obtained with waveform 2 of Figure 2f.

Making small drops from a large nozzle, either using EHD jetting as in Figure 1c or waveform 3 in DOD ink jet printing as in Figure 1e, is exciting from the standpoints of ease of manufacturing and applications (see Applications section). Two other recently developed methods depicted in Figures 1g and 1h also make possible production of small drops from large nozzles. Gañán-Calvo (1998) has developed a technique called flow focusing, which is shown in Figure 2g. Here a liquid, labeled as fluid 1, emerges as a jet from a tube of radius R whose outlet is located near the opening of an orifice plate. The jet of fluid 1 flows through the orifice surrounded by a coflowing gas stream, labeled as fluid 2. Fluid 2 focuses the tip of the meniscus of fluid 1 into a cusp-like profile and enables production of drops of fluid 1 with $R_d \ll R$. This technique has been demonstrated to be capable of making drops with radii of 35–40 μm from tubes of radii of 200 μm. Gañán-Calvo (1998) has also shown that a compound jet, which can be used in encapsulation applications, can be formed with a flow focusing apparatus by replacing fluid 2 with a second liquid. An idea similar to Gañán-Calvo's has been exploited by Umbanhowar et al. (2000) who have created monodisperse emulsions by use of a coflowing stream. Gañán-Calvo and Gordillo (2001) have generalized flow focusing to produce both micron-size gas bubbles by expelling both fluid 1 (gas) and fluid 2 (liquid) into fluid 2 and gas filled microcapsules by expelling the fluids into air. Figure 1h depicts the method of selective withdrawal (Cohen et al., 2001), where the initially flat interface of fluid 1 is sucked as a fine jet into a tube of large radius when the flow rate at which fluid 2 overlying fluid 1 is drawn into the tube exceeds a threshold. Whereas the piezo DOD method depicted in Figure 1e can be used to form one drop or many small drops in sequence from a large nozzle, the methods of Figures 1c, 1g, and 1h have only been demonstrated to generate drops continuously.

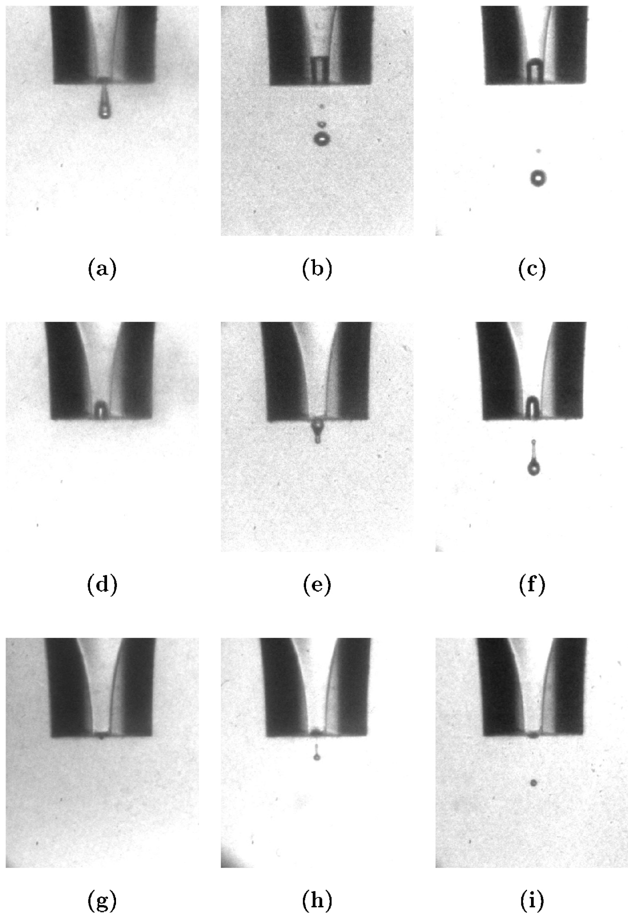

Figure 2. Drop formation from an ink jet nozzle.
(a)–(c): Water drops formed using waveform 1. 50% glycerol-water drops formed using waveform 2, (d)–(f), and waveform 3, (g)–(i). In all cases, the rate of drop formation is 1 kHz. Images have been obtained using an exposure time of 80 ns. Photos courtesy of A. U. Chen and O. A. Basaran, Purdue University.

The final method of drop formation is that shown in Figure 1i. A liquid drop is held pendant from a rod, which is sometimes called a pin tool in DNA arraying. The tool is first moved downward to close proximity of a substrate and a liquid bridge is created. The pin tool is then moved upward to break the bridge and leave a volume of liquid behind on the substrate as a sessile drop. Stretching liquid bridges are used in extensional rheometry. They also arise in gravure coating, where the substrate and the rod undergo relative motion with respect to each other horizontally, as well as vertically.

Drop breakup and interface rupture

Study of drop formation has remained an active research area for over a century because it is a challenging problem for theoreticians, computational scientists, and experimentalists alike. As shown on the righthand side of the front cover and in Figure 2, drop breakup exhibits finite time singularities. A casual examination of these figures may lead one to incorrectly conclude that the dynamics drastically differs from one situation to the next. A closer examination, however, reveals that the dynamics near pinch-off ought to exhibit self-similar behavior due to the orders of magnitude difference between local length and time scales and corresponding global scales. In simple terms, the dynamics in the vicinity of the pinch point should be identical from one situation to the next regardless of the global conditions imposed in an experiment.

Keller and Miksis (1983) were first to propose a scaling theory governing interface rupture. They took the liquid within a thinning axisymmetric thread to be inviscid and the motion to be irrotational. They further took the ambient fluid to be a passive gas like air and neglected its dynamics. If the interface shape is a single valued function of the axial coordinate, it can be represented as $h=h(r,z;t)$, where r and z are radial and axial coordinates in cylindrical coordinates and t is time. Here h, r, and z are made dimensionless using a global length scale such as tube radius. Time is nondimensionalized using capillary time $t_c \equiv (\rho R^3/\sigma)^{1/2}$. Keller and Miksis (1983) showed that the interface thickness varies as the 2/3 power of time $\tau \equiv t - t_b$ remaining to breakup, where t_b is the breakup time, as summarized in Figure 3 under the heading "Inviscid Thread." Numerical solutions of pinch-off using the boundary element method (BEM) (Day et al., 1998) later showed that axial and radial lengths in the pinch region scale in the same manner. As the thread pinches, i.e., as $h \rightarrow 0$, pressure p, which varies as $1/h$, and axial velocity v blow up. One would expect the inviscid thread analysis to be applicable if $Re \gg 1$.

A similar analysis was carried out by Papageorgiou (1995), but at the opposite extreme where $Re \ll 1$. He thereby obtained the scalings summarized in Figure 3 under the heading "Viscous Thread," where $\beta \leq 0.175$.

If the previously obtained scalings are used to calculate a local Reynolds number Re_{loc}, it is found that $Re_{loc} \to 0$ (∞) as $\tau \to 0$ for an inviscid (viscous) thread (Lister and Stone, 1998). In other words, viscous (inertial) force becomes important during pinch-off of a liquid of small (high) viscosity once the minimum thickness of the thread h_{min} becomes sufficiently small. Local analysis of pinch-off accounting for viscosity, inertia, and capillarity was carried out by Eggers (1993), who obtained the scalings shown in Figure 3 under the heading "Viscous-Inertial Thread."

However, Lister and Stone (1998) later showed that once h_{min} becomes sufficiently small, the dynamics of the outer fluid may no longer be neglected and the motion thereafter proceeds as both the inner and the outer fluids locally undergo Stokes flow. In Figure 3, this situation is found under the heading "Viscous Thread With Ambient Fluid," where m equals the viscosity of the outer fluid divided by that of the inner fluid. Figure 3 summarizes transitions that can occur from one scaling regime to another as pinch-off nears and builds on an earlier figure reported by these authors.

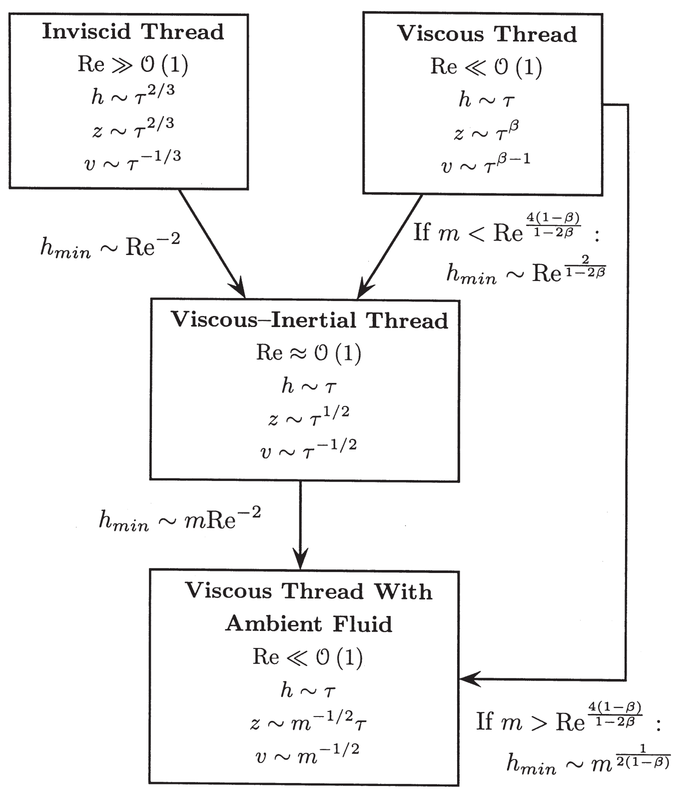

Figure 3. Scaling theories and transitions between scaling regimes during interface rupture.

For a 140 μm water drop breaking in air, Re=100. Pinch-off of the interface of this drop would therefore initially follow the inviscid thread scaling law. According to Figure 3, viscous effects would come into play when the minimum thickness of the interface falls below 12 nm, a value too small to be observed visually in experiments.

Ink jet nozzles are unique MEMS devices in that they do not entail low Reynolds number flow despite the smallness of length scales involved. For a typical Newtonian ink of 5 cp viscosity emanating from a 10 μm radius nozzle at a typical value of the velocity of 5 m/s, Re^*=10. Therefore, algorithms for analyzing drop formation in general have to be able to solve the full nonlinear Navier-Stokes equations in a free boundary setting. Such algorithms must be tested against both scaling theories and experiments.

When $Re^* \ll 1$ or $\gg 1$, well established BEM algorithms are available for analyzing the dynamics. When Re^* is finite, most of the work to date has relied on algorithms based on: (a) solving a set of one-dimensional equations based on the slender-jet approximation; (b) the volume of fluid (VOF) method; and (c) the finite-element method (FEM). One-dimensional algorithms solve approximations to the Navier-Stokes equations and, hence, are not discussed here (Shi et al., 1994; Ambravaneswaran et al., 2000). VOF methods are easy to use, but do not capture well local details of pinch-off (Zhang, 1999). The four figures on the lefthand side of the front cover show FEM simulations carried out in our group (Chen et al., 2002). To date, only FEM algorithms (Wilkes et al., 1999; Chen et al., 2002) have been able to demonstrate interface overturning in low-viscosity systems (top two frames) and formation of microthreads (bottom two frames), features that are observed in experiments (Shi et al., 1994; Chen et al., 2002). Moreover, FEM algorithms have been shown to accord with scaling analyses and be capable of predicting transitions between different scaling regimes.

A variety of imaging tools exists for studying drop dynamics. If the phenomenon is repeatable, it can be observed using a setup consisting of a standard CCD camera and a strobe, which can be assembled for ~$1,000. With a fast strobe, one can obtain high-quality images of even ink jet drops using this technique, as shown on the front cover. Digital video cameras, capable of recording ~1,000 frames per second, today cost ~$10,000. Such systems are adequate for studying phenomena like dripping but are too slow for studying ink jet drops. Most versatile are ultrafast digital imaging systems that can record multiple frames at rates up to 100 million frames per second (cf. Figure 2). Such systems are ideal for studying fast, nonperiodic phenomena, but cost ~$200,000.

Applications

The diversity of applications of drop formation is dumbfounding. A partial appreciation of this diversity can be gained by doing a search on ink jets on the Science Citation Index (SCI). Whereas most publications on ink jets even 10 years ago were devoted to printing, the number of papers on nonprinting applications are now a significant fraction of the total.

One branch of science in which drop formation has played a major role is analytical chemistry. Miller and Synovec (2000) reviewed 112 references on drop-based analytical measurements. Some of the widely used methods include measurement of equilibrium and dynamic surface tension and viscosity. Because one can repeatedly make micron-size drops at rates ranging from 1 Hz (or lower) to 10 kHz using DOD technology, analytical techniques that take advantage of the method have proven to be a boon in single-molecule detection. For example, Kung et al. (1999) have developed a method for real-time detection of single-molecule fluorescence in a guided stream of 1.5-2 μm water droplets. Single molecules confined in such small drops can then be manipulated using electric fields.

Use of DNA microarrays in genomics and other types of microarrays in various applications has experienced explosive growth recently. Creation of a DNA microarray typically involves delivery of nucleotide monomers and reagents to selected locations on a biochip and *in situ* synthesis of oligonucleotides. In other situations, presynthesized oligonucleotides are delivered to the biochip. One nondrop-based microarray technology involves photolithography, a technique popularized by Affymetrix (Schena et al., 1998). The other two primary microarray delivery methods utilize drops (Schena et al., 1998). The more primitive of these two methods, popularized by Patrick Brown and Ronald Davis, uses pin tools shown in Figure 1i and is sometimes referred to as mechanical microspotting. The other drop-based method relies on DOD ink jet technology shown in Figure 1e. Ink jet technology is superior to pin tools because it can create smaller spot sizes, can achieve higher rates of throughput, and is a noncontact delivery method. However, ink jet technology is both more expensive and complex compared to pin tools.

Because ink jet technology (cf. Figures 1d–1f) can handle ultrasmall quantities of fluids at high speeds, it is ideal for fluid dispensing applications that arise in massively parallel or combinatorial drug discovery and material synthesis (Lemmo et al., 1997).

An exciting application is to use molten microdrops drop-by-drop to microfabricate complex 3-D objects (Gao and Sonin, 1994). Orme and Smith (2000) have used CIJ technology to form molten aluminum drops and then deployed them for rapid prototyping of components. Shah et al. (1999) have used a commercial HP TIJ DOD printer to print metal circuit lines.

In certain applications, the use of drops does not merely result in a more efficient process, but enables a manufacturing process not possible by other means. A recent example comes from light emitting diodes (LEDs) made from organic polymers. Such materials are used in color flat panel displays. If the material is deposited by spin coating or evaporation, only devices of a single color can be readily fabricated. Hebner et al. (1998) have modified a commercial Canon ink jet printer to directly deposit drops that contain different color emitters in a single step.

Drop-based techniques also enable low-cost fabrication alternatives to existing processes. For example, ink jet technology has been used to directly print transistors (Sirringhaus et al., 2000). Another example comes from optics where arrays of microlenses have been fabricated using ink jet printing (Danzebrink and Aegerter, 2001).

Drop-based techniques can be used to create patterned functional micro- and nanostructures (Fan et al., 2000). The patterning process relies on using an ink which upon evaporation undergoes self assembly to form the desired structures. The ink can be delivered to a substrate by ink jet printing. Using this method, one can create channels with pores of or features having micron-size or smaller dimensions.

Drop-based methods are ideal for applications involving the production of polymer particles and microcapsules especially for use in biomedical applications. Numerous techniques including emulsion polymerization and spraying can be used to make small particles and microcapsules, but resulting size distributions are broad or difficult to control. Berkland et al. (2001) describe several drop-based techniques for making small poly(D,L-lactide-co-glycolide) (PLG) spheres. They use CIJ technology to make monodisperse spheres of radii down to 15 μm by using nozzles of comparable radii. They also describe a technique based on flow focusing (cf. Figure 1g) that can produce 2.5 μm-radius spheres by using a nozzle of 50 μm radius. Cohen et al. (2001) use selective withdrawal (cf. Figure 2h) to coat small particles with a thin polymer film.

Some applications of method 1c fall in categories that have already been discussed above but are grouped here for convenience. Method 1c forms the basis of electrospray mass spectrometry for studying single large biomolecules (Fenn et al., 1989). The method has also gained much attention recently because of applications in materials science such as electrospinning (Gibson et al., 1999), making particles (Amsden and Goosen, 1997), and microencapsulation (Loscertales et al., 2002).

Outlook

Many unsolved problems remain with regard to both scientific aspects of drop formation and its applications. Due to their training and the nature of the field, chemical engineers have played and will continue to play a major role in it.

Although a great deal has been learned in the past decade about drop breakup through scaling and computational analyses and experiments, much remains to be done. Most previous analyses of drop formation have been restricted to simple Newtonian fluids. The influence of non-Newtonian rheology and dynamic surface tension have been inadequately studied despite that fluids in many applications are non-Newtonian and/or contain surface-active ingredients. However, complex fluids are beginning to draw increasing attention. For example, Renardy (2002) has determined similarity solutions governing pinch-off without inertia of filaments of liquids described by several viscoelastic models. Christanti and Walker (2002) have explored experimentally varying fluid relaxation times to control drop size distributions and to suppress satellite formation during breakup of jets of polymer solutions.

The most accurate algorithms for analyzing drop formation, which use the FEM, employ either elliptic mesh generation (Christodoulou and Scriven, 1992) or pseudo-solid mapping (Cairncross et al., 2000) for domain discretization. Virtually all detailed calculations to date have been axisymmetric, i.e., 2-D. There are many practical situations where 3-D effects are important, including nonaxisymmetric formation of drops, problems with wetting, deflection of jets, and deposition of drops on substrates. Existing scaling analyses reveal that as the interface thickness becomes vanishingly small, pressure and axial velocity blow up. However, nature abhors singularities. Thus, it would be worthwhile to investigate whether another scaling regime exists where apparent singularities are removed during the final stages of pinch-off (Shikhmurzaev, 2000).

The use of gradients in surface tension and other physical properties to promote drop formation and manipulate small-scale flows involving drops is likely to receive increasing attention in coming years. Exciting applications include the use of light to cause changes in surface tension to induce drop pinch-off (Shin and Abbott, 1999) and heat to cause surface tension and viscosity gradients to induce microjet deflection and breakup (Chwalek et al., 2002).

Another area of future research is drop breakup in liquid-liquid systems. Many of the emerging applications of drop formation such as particle production (Berkland et al., 2001), microencapsulation (Loscertales et al., 2002), and generation of emulsions (Umbanhowar et al., 2000) involves two-fluid breakup. Once again, scaling analyses and computational studies of two-fluid drop formation are in their infancy compared to work that has been done on single-fluid drop formation.

Analysis of the so-called dripping faucet, where a simple Newtonian fluid issues at constant flow rate from a tube into air (cf.

Figure 1a), has long fascinated the scientific community (Ambravaneswaran et al., 2000). In contrast, little is known about nonlinear dynamic phenomena that can occur with two-fluid systems, complex fluids, and more complicated drop generators. An interesting recent study is that by Thorsen et al. (2001) where the authors demonstrate experimentally the formation of dynamic patterns in a microfluidic device.

When Lord Rayleigh and other giants of science were laying down the foundations of fluid dynamics of drops in the 19th century, they could not have imagined that the subject would still be of great interest in the 21st century. The fascinating responses that drops exhibit and their technological usefulness are no doubt some of the reasons why the subject resides at the frontiers of research and technology after more than 100 years.

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