

Dripping, Jetting, Drops, and Wetting: The Magic of Microfluidics

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Abstract

The following article is based on the Symposium X presentation given by David A. Weitz (Harvard University) on April 11, 2007, at the Materials Research Society Spring Meeting in San Francisco. The article describes how simple microfluidic devices can be used to control fluid flow and produce a variety of new materials. Based on the concepts of coaxial flow and hydrodynamically focused flow, used alone or in various combinations, the devices can produce precisely controlled double emulsions (droplets within droplets) and even triple emulsions (double emulsions suspended in a third droplet). These structures, which can be created in a single microfluidic device, have various applications such as encapsulants for drugs, cosmetics, or food additives.

Introduction

The use of microfluidic devices provides an excellent way to mix and precisely control fluids at the length scales of the structures being made.¹ Here, we will focus primarily on how fluids can be mixed together to make new types of structures or materials, taking advantage of the ability to structure the channels in which the fluids flow at the desired length scales. This presentation centers mainly on multiphase fluid mixtures—primarily droplets and emulsions—and demonstrates what can be done through the control of emulsions.

The standard way to make an emulsion is to take two fluids that are immiscible (think of oil and vinegar, as an example), add a little surfactant (mustard, for example, is a good surfactant), and shake it up. When the fluids are shaken, there is enormous shear, and the result is a good emulsion. What is missing is the fine control required for studying individual droplets.

We will demonstrate how microfluidics can provide this fine control, and how it

can be used to make emulsions, one drop at a time, with exquisite precision. At the end, we will address the possibility of scaling up this process to make many droplets, in either large or small batches, for various applications.

Microfluidic Droplet Formation

First, let's discuss droplet formation in general. How do droplets form? Anyone can make droplets simply by turning on a faucet. If the water is turned on to flow very slowly, a series of single drops are formed. If the tap is turned up a little, no drops are seen, and instead a steady stream, or jet, of water is formed. However, this stream ultimately breaks into drops,²⁻⁵ as can be seen, for example, if a hose is used to create a stream of water; it ultimately breaks into drops as it moves farther away from the hose.

Coaxial Flow

Microfluidics provides a means to form drops in a controlled fashion, taking advantage of a hydrodynamic instabil-

ity.^{2,4,5} To explain this, we will start not with the traditional form of microfluidics, but with another class. Traditional microfluidic devices, as found in the literature, are all made using some variant of semiconductor technology—etching channels in glass or in Si; or more recently and very importantly, using silicone rubber of poly(dimethylsiloxane) (PDMS) through the use of soft lithography, which was pioneered at Harvard by our colleague George Whitesides.⁶

Here, we will describe a different way of making microfluidic devices that offers several advantages.⁷ The most critical advantage is the ability to make truly three-dimensional flows, which is important for the work discussed here. This way of making droplets is different from turning on a faucet. The water dripping from the tap is flowing into air—a fluid flowing into a gas. With our process, one liquid flows into a second immiscible liquid to make an emulsion consisting of drops in a second liquid.

To accomplish this, we use capillaries similar to those used in neuroscience to make patch clamps (capillaries that form a tight seal with a cell membrane). These glass capillaries can be heated and pulled to create a finely controlled structure for making droplets. This process begins with a glass capillary that has been heated and pulled to a fine point. To achieve the level of control we are seeking, we add a second capillary, one through which the outer fluid flows, the second through which the inner fluid flows.

We align the two capillaries precisely, using a concept that many of us are familiar with—trying to put a round peg into a square hole. Think, for example, of a popular toy from childhood—a wooden block with pieces cut out of it in the shapes of circles, squares, triangles, and so forth. The goal is to fit the pieces back in, the square inside the square, the circle inside the circle. Trying to put the circle into the square never works. In our droplet-making device, however, the circle can fit within the square. If the outer dimension of the circle exactly matches the inside of the square, it can be easily aligned. Moreover, if the circle and square are long tubes, the alignment is perfect. One fluid flows through the inner circular capillary, while the other fluid flows on the outside of the circular capillary through the outer, square one, as shown in Figure 1. The circular capillary is tapered at its end, restricting the flow inside it. The result is a coaxial flow of the two fluids.

With this setup, it is easy to make drops. If, for example, there is oil flowing through the center round capillary, and

water flowing outside it, perfectly controlled drops can be formed by this co-flow, in a process we call dripping.⁸⁻¹⁰ This is exactly analogous to the drip, drip, drip from a faucet. If we increase the flow of either the inner fluid or the outer fluid sufficiently, the result is a jet, a long stream of oil, with drops forming downstream. A typical production rate for most of the examples I am going to show is several thousand drops per second.

Dripping-to-Jetting Transition

To better understand how dripping occurs, think back to the analogy of the faucet. When the flow is very slow, a drop begins to form and gets larger and larger, but is held in place by the surface tension force. Ultimately, the weight of the water gets large enough to overcome the surface tension force and a drop is formed which falls from the faucet. In the example of a tap, drop formation results from a balance between surface tension forces and the weight of the drop. In the case of the microfluidic device, drop formation involves a balance between surface tension forces and the viscous drag of the coaxial fluid pulling on the drop.¹⁰

Similarly, a stream or jet of fluid is always unstable to the formation of drops because the surface energy is decreased when the cylindrical jet breaks into drops. The principle behind this drop formation can be understood in terms of the Rayleigh-Plateau instability.^{4,5} Any perturbation in the jet will result in a slightly thinner region, leading to an increase in the Laplace pressure within this thinner region of the jet. The Laplace pressure is the increase in the internal pressure of the water due to the curvature of the interface, and this higher pressure pushes the fluid within the jet to either side, causing the thin region to become even thinner; ultimately, the stream breaks into drops. The dynamics of this drop pinch-off reflects a balance between the surface tension driving the fluid away from the perturbation and the viscous drag of the fluid that resists this flow.

By understanding this instability, we can make it work for us—that is, we can control drop formation using this instability. How can drop formation during jetting be understood? The fluid is flowing downstream. As the jet begins to pinch off, the break-up point is being pulled downstream by the flow of the outer fluid. The length of the jet then depends on the time it takes for the drop to pinch off, due to the flow induced by the Laplace pressure and the downstream velocity of the interface. The length is the downstream velocity of the interface multiplied by the pinch-off time.

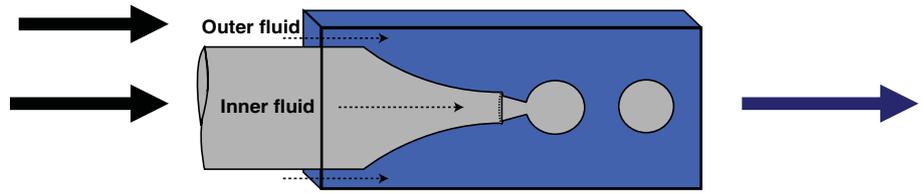


Figure 1. Schematic illustration of a co-flow microcapillary device for making droplets.

This argument allows us to determine the transition between dripping and jetting.^{8,9} This transition is determined by the balance between how long it takes to fill a drop and the time required for the drop to be pulled downstream. The dripping-to-jetting transition depends on the capillary number, which is a dimensionless number that reflects the balance between force due to the viscous drag and force due to surface tension.

There is another class of jetting, where something different happens. If the drop is filled much more rapidly, and the viscous drag on the drop is relatively low, the result is very large drops. A perturbation occurs and travels with the drop. The perturbation increases in size, eventually leading to pinch off. In this case, the inner fluid flows much faster than the outer fluid, as can be seen if colloidal particles are added to the fluids to help visualize the flow. The inner fluid flows very rapidly, filling the drop, but the flow of the

outer fluid is slow, and its viscous drag is so small that it takes quite a while before the drop is large enough for it to actually break off.

These processes can be combined and plotted on a single phase diagram, shown in Figure 2.¹¹ The behavior is determined by two numbers: the capillary number and the Weber number. The capillary number reflects the balance between the drag of the outer fluid pulling the drop downstream and surface tension forces that resist the flow in the jet as pinch-off occurs. The Weber number reflects a balance between inertial and surface tension forces. It becomes important in describing the behavior when there is very little viscous drag, and so the capillary number is low. Then, it is the inertial force of the fluid that must overcome surface tension forces and ultimately lead to pinch-off, creating the drop. The boundary between dripping and jetting occurs when the sum of these two numbers is approximately equal to 1.

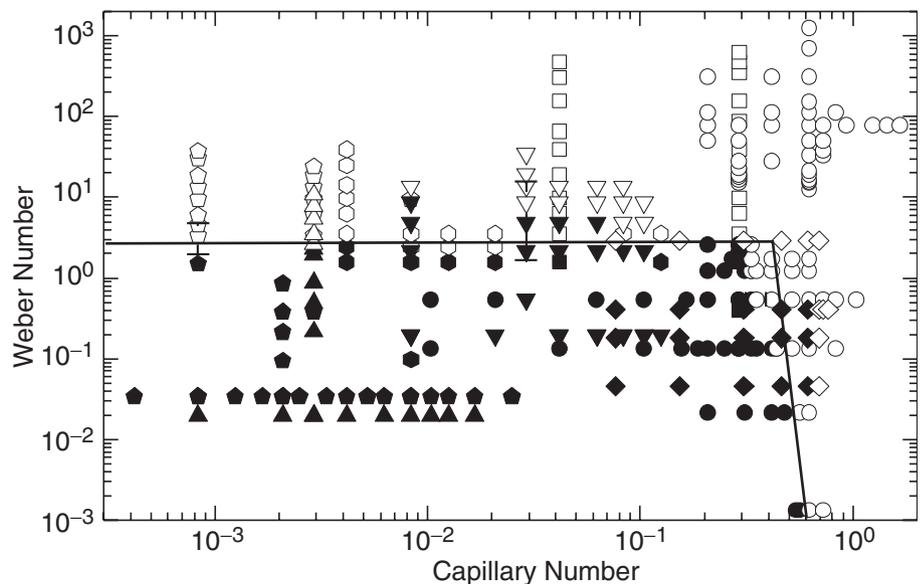


Figure 2. Dependence of the transition between dripping and jetting on the capillary number of the outer flow and the Weber number of the inner flow of a co-flow microcapillary device. Squares and diamonds, $\eta_{\text{in}}/\eta_{\text{out}} = 0.01$, with slightly different geometries; hexagons and circles, $\eta_{\text{in}}/\eta_{\text{out}} = 0.1$, with slightly different geometries; pentagons, $\eta_{\text{in}}/\eta_{\text{out}} = 1$; triangles, $\eta_{\text{in}}/\eta_{\text{out}} = 10$.

The phase diagram is a plot of the Weber number as a function of the capillary number and shows that the boundary between dripping and jetting occurs approximately where the sum of the two numbers is 1.

Hydrodynamic Focusing

An understanding of how these drops are formed enables us to create very uniform drops. The standard co-flow geometry described earlier is similar to what happens when the tap is turned on. We can also use an alternate method to create drops, hydrodynamic flow-focusing of the inner fluid by the outer one.^{12,13} A schematic illustration of this device is shown in Figure 3. The outer fluid is introduced in the standard way. The inner fluid, however, is introduced from the opposite side. Instead of the inner fluid being introduced into the capillary, both fluids are collected and exit through the capillary. The drops are then formed at the orifice, in the dripping regime, and a jet and drops are formed farther downstream, in the jetting regime. The basic process is the same as the first geometry, but one fluid is flowing in the opposite direction. It is then hydrodynamically focused through the narrow orifice by the second, outer fluid.

A major advantage of this method is that it produces a narrower stream compared to the orifice size, so there is less likelihood of clogging for a given drop size. Flow-focusing works very well, and we can create drops in both the dripping and the jetting regimes.

Controlled Multiple Emulsions

The co-flow and flow-focusing geometries can be combined in a manner that provides the basis for producing a variety of new materials.⁷ Starting with the hydrodynamic flow-focusing geometry, we use the extra space on the other side of the outer square capillary and add a second circular, tapered capillary, allowing the co-flow and hydrodynamic focusing processes to operate together. This combination requires the capillaries to be perfectly aligned.

A schematic illustration of this device in Figure 4 shows two round glass capillaries lying end to end within a square glass tube. The inner fluid, an oil, is pumped through the tapered end of one round capillary into the other round capillary (the collection tube). A middle fluid, water, moves through the outer capillary in the same direction as the inner fluid in a coaxial flow. The outermost fluid, an oil, moves through the outer capillary from the opposite direction, hydrodynamically flow-focusing the

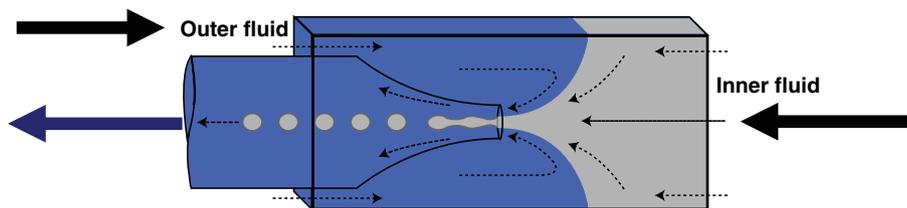


Figure 3. Schematic illustration of a flow-focusing microcapillary device for making droplets.

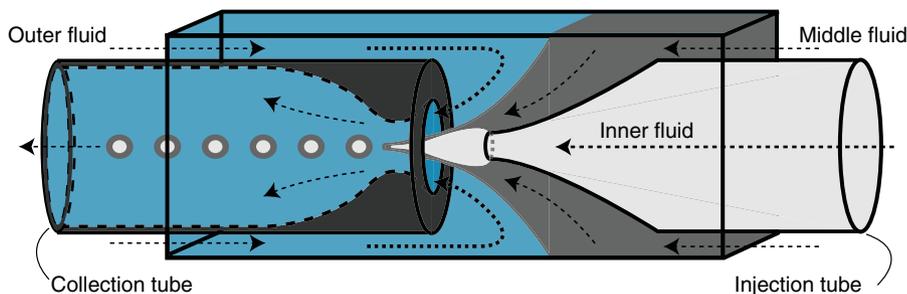


Figure 4. Schematic illustration of a microcapillary device that combines co-flow and flow-focusing to create double emulsions.

coaxial stream. When the three fluids enter the collection tube, a double emulsion is formed, consisting of oil droplets within larger drops of water, contained in a second, continuous oil phase. Thus, drops are made at the orifice not from a single fluid, but from a coaxial flow of two fluids. The result is a perfect double emulsion of uniform droplets within larger uniform drops. Such uniformity cannot be achieved with traditional approaches to making double emulsions, which require two separate emulsification steps, each introducing polydispersity. Such double emulsification processes usually result in more than one small drop within each larger drop. We can achieve the same result as the double emulsification process and obtain a controlled number of inner drops in the larger drop simply by allowing more drops from the innermost fluid to form before the formation of one larger drop.

This highlights the importance of understanding the dripping and jetting regimes. There are now two drop formation events, and each can be either dripping or jetting. By adjusting each individually, different drop structures are formed, as shown in Figure 5. Perhaps the most useful form is that containing a single inner drop, creating a core-shell structure. This occurs most controllably when both drops are formed in the dripping regime, leading to very uniform drops and very uniform shells. Moreover, the thickness of the shell can

be precisely controlled. Control of the dripping-to-jetting transition in microfluidic devices will allow the creation of different kinds of new and useful structures.

New Materials from Droplets

While the combination of the co-flow and flow-focusing geometries affords many possibilities for creating new materials, a different geometry offers other advantages. This is formed by a double co-flow geometry: drops formed with one co-flow device are introduced into the entry of a second device, and the third fluid is flowed around only the second co-flow capillary. This separates each drop formation step and enables control of each separately, allowing both the size and number of the inner drops to be precisely controlled, while still maintaining perfect monodispersity of each drop.

The double emulsions just described—one droplet of fluid surrounded by a shell of a second fluid, inside a third fluid—have many uses. Consider, for example, a droplet of water surrounded by oil within a continuous phase of water. Inside the oil we put a surfactant, for example, a phospholipid or a diblock copolymer. Upon formation of the double emulsion, the surfactant will go to the two interfaces, the inner and outer oil interfaces. If a volatile oil is used, however, the intermediate oil phase can be evaporated, leaving just a bilayer of surfactant. The resultant structure would be a liposome or

a polymerosome, a closed container consisting of a bilayer of the surfactant. However, since each of the fluid streams are separate, precious materials such as drugs or other active ingredients can be efficiently encapsulated in the innermost phase. The result is a perfect encapsulant.

Variety of Polymerosome Structures

An example is polymerosomes made from diblock copolymers. Polymerosomes were first made by a group from the University of Pennsylvania, in collaboration with a group from the University of Minnesota.¹⁴ They are liposome-like structures, fabricated with diblock copolymers. In our experiments,^{15,16} we first produce a double emulsion with a core-shell geometry. As the oil evaporates, the optical contrast is lost when observing the drop with bright-field optical microscopy, as shown in Figure 6. However, when observed with phase contrast, the structure of the nascent polymerosome is again visible as the middle oil phase evaporates, as shown in Figure 6d. We are left with a polymerosome. However, the inner fluid comes from a completely different fluid stream than that of the outermost fluid. Thus, if the structure is used to encapsulate fluids, it can be loaded very efficiently. This is confirmed by the 70- μ m-diameter polymerosome shown in Figure 7a. A dye is encapsulated in the innermost drop, and the structure is viewed with fluorescent microscopy in Figure 7c. We can also encapsulate more hydrophobic materials within the bilayer, as shown in Figure 7b, where quantum dots are encapsulated in the shell.

How can we verify that what has been made actually has the structure of a polymerosome? First, the structure should be somewhat flexible. If an osmotic pressure is exerted on the outside, it should collapse. We verify this by adding sugar to the outermost fluid to apply an osmotic pressure. The structure does indeed collapse and buckle, as shown by the images in Figure 8, confirming that it is flexible, as expected for a polymerosome.

An additional means to verify that the structure is a polymerosome is to determine its permeability. This can be done by measuring the rate of the decrease of the radius as a function of time, which demonstrates the permeability, or how fast the water goes in or out. When the measured value of the permeability is compared with those in the literature, the result is exactly the same as that of bilayer structures. This confirms that we have made a polymerosome consisting of a bilayer of diblock copolymers. This structure can be optimized by adding the exact

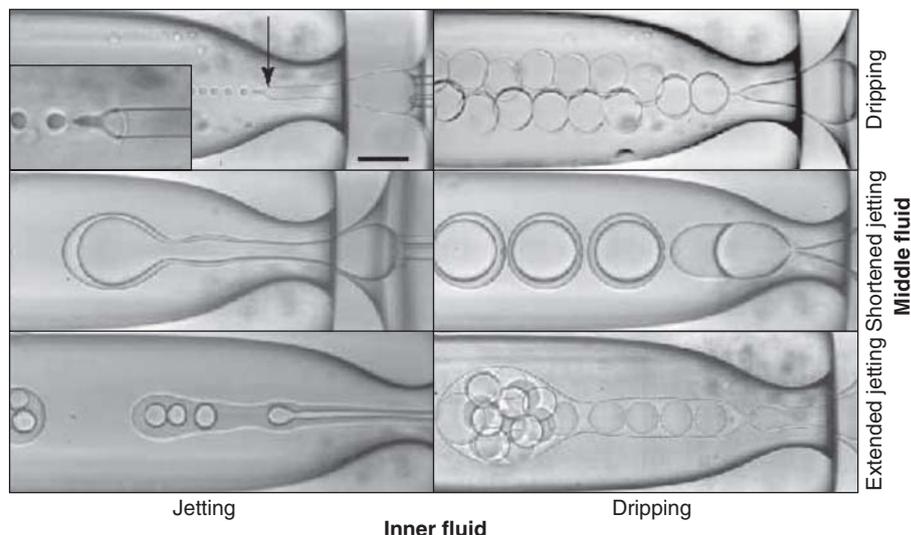


Figure 5. Different morphologies of double emulsions produced with a microcapillary device. Scale bar is 200 μ m and applies to all micrographs in the figure.

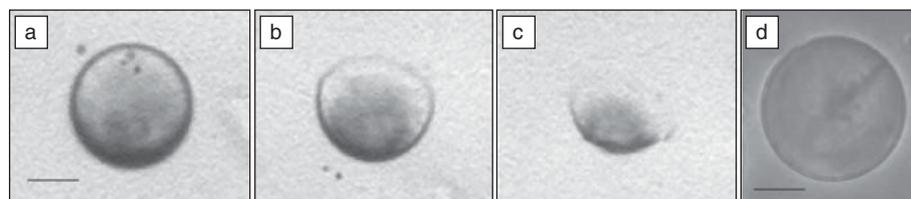


Figure 6. Polymerosome formed with a microcapillary device. (a)–(c) As the oil in the middle phase evaporates, optical contrast is lost and the drop begins to disappear when viewed with bright-field microscopy. (d) The polymerosome structure is clearly visible when viewed with phase contrast. Scale bar in (a) is 40 μ m and applies to (b) and (c) as well; scale bar in (d) is 30 μ m.

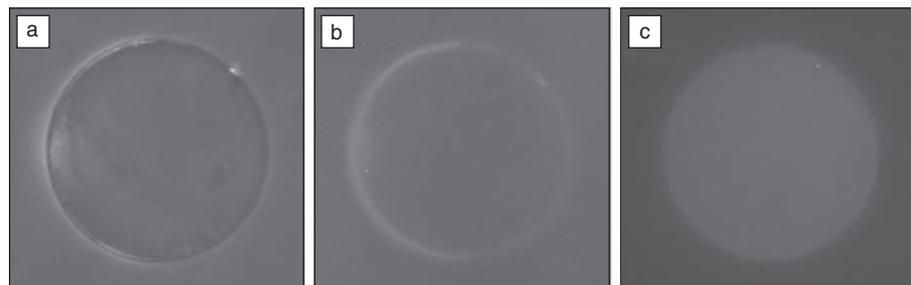


Figure 7. Encapsulation of quantum dots in a 70- μ m-diameter polymerosome, shown with fluorescent microscopy. (a) Phase-contrast microscopy image of the polymerosome. (b) Fluorescent microscopy image of the polymerosome with quantum dots in the hydrophobic shell. (c) Fluorescent microscopy image of the polymerosome with dye molecules encapsulated within the core.

amount of diblock copolymer needed to cover the surface, with perhaps a bit extra.

As these structures are being made, the bilayer of the diblock copolymer forms a shell as the oil begins to evaporate, and a distinct drop of oil forms on one side of the shell; this results from a dewetting

transition caused by the small excess diblock copolymer, which is added to ensure that the interface is completely covered.¹⁶ This creates a depletion interaction, leading to the dewetting and resulting in the formation of the shell and the distinct drop of oil.

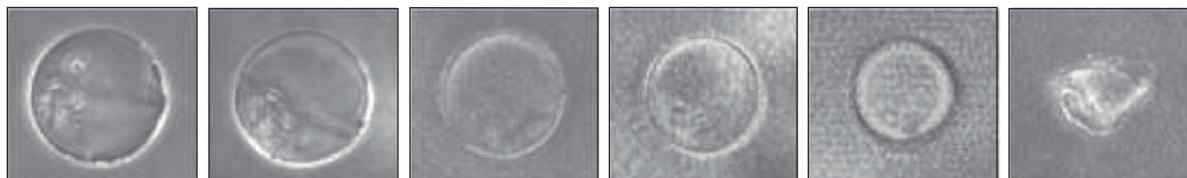


Figure 8. Optical microscopy images showing the evolution of a polymerosome being compressed by osmotic pressure. The initial diameter of the polymerosome is 70 μm .

Eventually, everything evaporates and there remains only a small dot of excess diblock. This is exactly the way the process was designed—to make a bilayer structure with only the small amount of extra diblock. Thus, we can precisely control both the size and the filling of these structures.

These examples are only a few of the many possible variations that can be made from these structures. For example, they can be made into a foam by evaporating the oil from a drop containing several inner drops. They can be made into solid shells by adding resin and hardening it or by adding monomer inside the shell and polymerizing it. For example, we used a UV-curable resin to make solid structures. We can verify that they are solid structures by crushing them and observing that they break open, as shown by the broken shells in Figure 9.

Shells of Liquid Crystals

We are also able to create shells of liquid crystals. We make the middle fluid a liquid crystal mixed with chloroform, to lower its viscosity and make it isotropic. After the shell is formed, the chloroform evaporates, leaving a shell of liquid

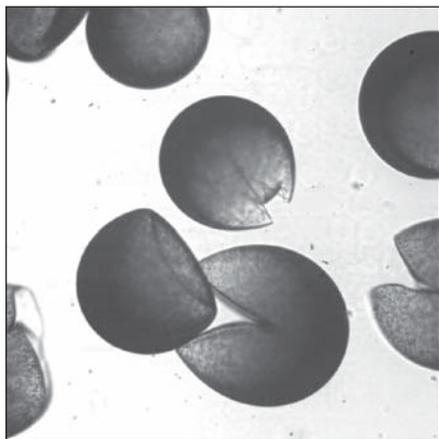


Figure 9. Cracked solid shells, 200 μm in diameter, made by solidifying the outer fluid of a core-shell double emulsion, then cracking the shell by squeezing it between two glass slides.

crystal. The inspiration for doing this came from my colleague, David Nelson, who had predicted that a variety of different defect structures would result from making a shell of liquid crystal.¹⁷ We have been able to identify some of these defect structures.

Hydrogels from Double Emulsions

We have developed a technology to create shells of liquid crystal easily, something that we had been trying to accomplish for several years. Carlos Martinez, one of the postdocs in my group, also uses this technology, but for a different purpose. He uses double emulsions to create monodisperse alginate hydrogels which encapsulate living cells to protect them from hostile environments. Basically, this involves encapsulating alginate hydrogels within a drop of mineral oil.¹⁸

Materials from Triple Emulsions

The process by which we make double emulsions is completely scalable. Any desired number of layers can be added downstream simply by repeating the “focus and co-flow” procedure. As an example, we have made triple emulsions. Triple emulsions are even more difficult to produce than double emulsions. Nevertheless, we are now able to make triple emulsions with exquisitely precise control. This process is highly adjustable; the size and number of drops can each be controlled, as shown in Figure 10.

Thermosensitive Gels

One of the materials we have made by means of a triple emulsion is droplets of water inside a drop of oil encased within a thermosensitive gel. Taking advantage of the fine control that we have in mixing fluids, we have been able to create a gel that shrinks in response to heat. Our purpose in making this type of gel is to build structures that provide precision-controlled release. As the gel shrinks upon raising the temperature, it contracts. However, since the inner fluid is incompressible, the shell ultimately tears apart. This releases the inner water drops into the continuous oil phase. Simply changing the temperature can control this process. This strategy for

controlled release can also be adapted to many other materials and applications. Again, the control we have through microfluidics makes this material possible.

Asymmetric Encapsulants

A material we are currently developing is a variation on a triple emulsion. It begins with a polymerosome structure, but uses two slightly different volatile oils, with two different kinds of diblock copolymers, one in each oil. Each polymer will predominantly go to the nearest interface. The result will be a polymerosome structure, but it will be asymmetric, with the inside leaflet different from the outside leaflet. The same experiment could also be done with different phospholipids to make an asymmetric liposome. An asymmetric lipid membrane is a highly desirable structure that is commonly found in cells, but is almost impossible to make in the lab.

Scale-Up for Materials Fabrication

We have shown that it is possible to make elegant emulsion structures and controlled release structures, but in the end, the process we are using can produce only one particle at a time. Can we scale it up?

The answer is yes. We are unlikely to be able to make huge quantities of materials, say tons per day, with the devices we have discussed. In many cases, however, making tons of material per day would not be necessary. The primary applications for such encapsulation materials would likely be for high-value-added materials, which would require rather low treatment rates and thus require much smaller volumes. Therefore, a more likely scenario is a much smaller materials requirement of perhaps something in the range of a few kilograms per day. This would, for example, likely be the case when encapsulating drugs or flavors.

Scaling up the fabrication can be done in a variety of ways. One way, of course, is to use a large number of the aligned capillaries, operating in parallel. The advantage of the capillaries is that they are effective in producing truly three-dimensional structures, enabling precise control of wettability.

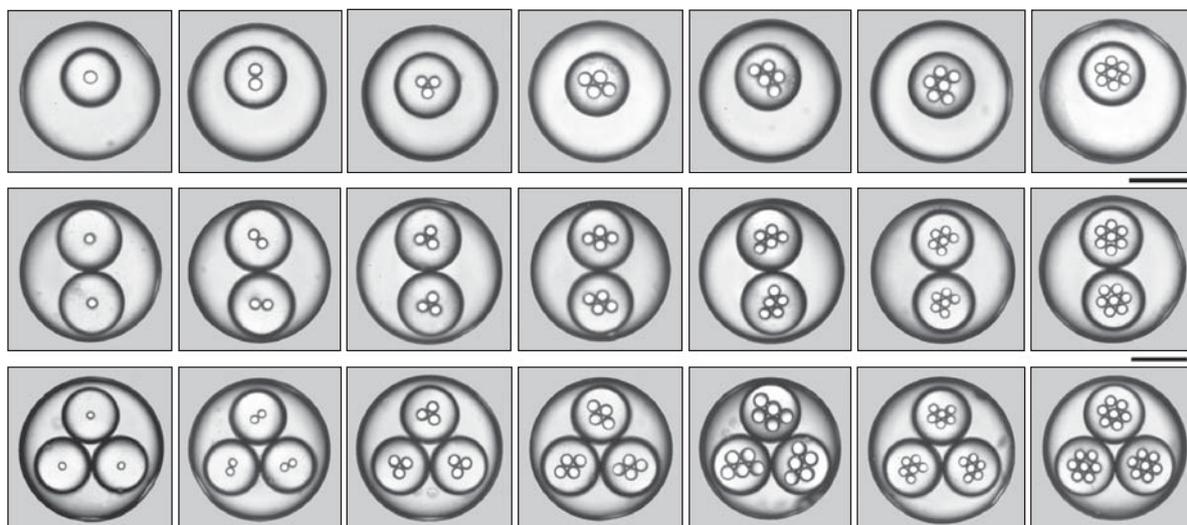


Figure 10. Examples of monodisperse triple emulsions made with cascaded microcapillary devices. Both the number and size of each of the sets of inner drops can be precisely controlled. Scale bars are 200 μm and apply to all images.

A more efficient way is through the more standard microfluidics device fabrication technique of stamping, using soft lithography. The key to being able to employ this technique is the ability to precisely control the different surface wettabilities—a difficult feat, but one that we and others are working to perfect.

An example of our work in this area involves using the same hydrodynamic focusing geometry but shrinking it down and making it into a stamped device. This technique was first done by our colleague, Howard Stone,¹³ another member of our MRSEC. Using this method, we have been able to make thousands of drops per second. To make it work, however, we must continually develop a variety of different surfactants, which is the key to keeping the drops stable.

Chemistry in Drops

Another important application of our microfluidic drop technologies is the use of the drops as isolated microreactors for chemical reactions. Most typically, we make aqueous drops, so water-based reactions are the most common. These are particularly important for bio-assays. However, we are also investigating non-aqueous reactions. As the continuous-phase fluid, we can use a fluorocarbon oil. In this case, we can make drops from a wide range of hydrocarbon-based chemicals, given that they are immiscible in the continuous phase. Moreover, emulsions in fluorocarbon oils provide us with a system of droplet microreactors suitable for reactions that must avoid

the presence of any water. As an example of what is feasible using this system, we have made polyurethane particles, which demand the absence of water for the reactions.

An important requirement for using these drops as microreactors is a surfactant, which must stabilize the drops against coalescence while also preventing any of the contents of the drops from becoming soluble in the continuous phase. Surfactants for fluorocarbon oils are less common than those for hydrocarbon oils, and thus we have been synthesizing block copolymers for use as surfactants. Optimizing these surfactants remains a challenge that we continue to address.

Controllable Microgels

In another adaptation of this technology, we have made thermoresponsive microgel particles. We create the particles from emulsion droplets using our basic flow-focusing technology. Then we add another fluid input downstream, where we introduce an activator or accelerator for the gelation reaction to produce different kinds of gels. For example, we have made poly(*N*-isopropylacrylamide) (PNIPAM) microgels in this fashion. We add the monomer, *N*-isopropylacrylamide (NIPAM); the initiator, ammonium persulfate (APS); and the cross-linker, *N,N'*-methylenebisacrylamide (BIS), to the aqueous phase, and make drops out of this. The accelerator, *N,N,N',N'*-tetramethylethylenediamine (TEMED), is introduced to the continuous phase down-

stream, after the emulsion drops are formed. It diffuses into the drops to induce the gelation.

While most of this discussion has focused on microfluidic devices made from microcapillaries, it is also possible to do many of the same things using devices stamped in PDMS. The advantage of this is that once the drops are made, they can be manipulated downstream within the channels in the PDMS. We have developed techniques to facilitate this manipulation through the addition of electric fields to steer the drops and to aid in their coalescence on demand. This technology will enable the drops to be used for combinatorial chemistry, allowing us to probe large numbers of individual chemical reactions. This will be of great value in high-throughput screening applications in biology. It will also be of value in formulating new materials. In fact, Darren Link, a former postdoc in my group, has used this capability to start a company, Raindance Technologies (www.raindancetechnologies.com), which makes devices that provide a platform for droplet-based microfluidics. He sees a promising future for using microfluidic techniques to make new materials.

Ultimately, the successful application of these fabrication techniques will depend on how well the process can be scaled up to produce larger quantities. This will likely be accomplished through massive parallelization. This might be achieved using microcapillaries. However, more likely, this will be achieved using devices fabricated from PDMS or other materials

that allow many droplet makers to be produced on each device. The key to being able to successfully accomplish this is the precise control of the wettability of the surfaces. This is easy to achieve in microcapillary devices but is much more difficult to control in stamped devices. Nevertheless, once that is achieved, scale-up will be possible. Then, these microfluidic methods for making new materials will become much more practical and should become an important new way of synthesizing colloidal-scale structures with richer and more complex geometries.

Indeed, we are still in the early stages of finding ways to apply microfluidic techniques. I hope that this presentation has illuminated some of the challenges we face, some of the work we are now engaged in, and some of the promising advances that can be achieved by using the elegant simplicity and precise control offered by microfluidics.

Acknowledgments

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References

1. T.M. Squires, S.R. Quake, *Rev. Mod. Phys.* **77**, 977 (2005).
2. T.R. Powers, D. Zhang, R.E. Goldstein, H.A. Stone, *Phys. Fluids* **10**, 1052 (1998).
3. S. Tomotika, *Proc. R. Soc. London, Ser. A* **150**, 322 (1935).
4. J. Plateau, *Acad. Sci. Brux. Mem.* **23**, 5 (1849).
5. L. Rayleigh, *Proc. R. Soc. London* **29**, 71 (1879).
6. G.M. Whitesides, A.D. Stroock, *Phys. Today* **54**, 42 (2001).
7. A.S. Utada, E. Lorenceau, D.R. Link, P.D. Kaplan, H.A. Stone, D.A. Weitz, *Science* **308**, 537 (2005).
8. B. Ambravaneswaran, H.J. Subramani, S.D. Phillips, O.A. Basaran, *Phys. Rev. Lett.* **93**, 034501 (2004).

9. C. Clanet, J.C. Lasheras, *J. Fluid Mech.* **383**, 307 (1999).
10. P.B. Umbanhowar, V. Prasad, D.A. Weitz, *Langmuir* **16**, 347 (2000).
11. A.S. Utada, A. Fernandez-Nieves, H.A. Stone, D.A. Weitz, *Phys. Rev. Lett.* (2007) accepted.
12. A.M. Gañán-Calvo, J.M. Gordillo, *Phys. Rev. Lett.* **87**, 274501 (2001).
13. S.L. Anna, N. Bontoux, H.A. Stone, *Appl. Phys. Lett.* **82**, 364 (2003).
14. B.M. Discher, Y. Won, D.S. Ege, J.C.-M. Lee, F.S. Bates, D.E. Discher, and D.A. Hammer, *Science* **284**, 1143 (1999).
15. E. Lorenceau, A.S. Utada, D.R. Link, G. Cristobal, M. Joanicot, and D.A. Weitz, *Langmuir* **21**, 9183 (2005).
16. R.C. Hayward, A.S. Utada, N. Dan, D.A. Weitz, *Langmuir* **22**, 4457 (2006).
17. D.R. Nelson, *Nano Lett.* **2**, 1125 (2002).
18. C. Martínez, J.-W. Kim, M. Marquez, D. Weitz, "Encapsulation of Yeast Cells in Alginate Hydrogels Created from Monodisperse Double Emulsion Drops," presented at MRS Spring 2007 Meeting (San Francisco, April 11, 2007) paper P5.1.



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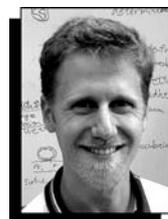
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