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An "Off-the-shelf" Capillary Microfluidic Device that Enables Tuning of the Droplet Breakup Regime at Constant Flow Rates

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Abstract

The fabrication of glass capillary microfluidic devices is technically challenging, often hampering use of the design. We describe a new technique, based on commercially available components, for assembling flow focusing capillary devices that can readily be taken apart and cleaned between uses. This design strategy allows for generation of both water-in-oil and oil-in-water emulsions in the same device after an ethanol rinse. The modularity of the device enables the adjustment of the tip separation between the two inner capillaries during droplet generation, which enables tuning of the age of the interface. Time-dependent surfactant diffusion to the interface changes the interfacial tension, thus providing an approach for adjusting the capillary number in addition to the usual method of changing flow rates. This design enables the tuning of the mode of breakup and the droplet size.

Keywords

Glass Capillary Microfluidics; Droplet Microfluidics; Dynamic Surface/Interfacial Tension; Simple Microfluidic Device; Off-the-shelf Microfluidics

Glass capillary microfluidics are an important tool in many different fields, including complex emulsion and particle generation[1–6], drug delivery[7–9], particle sorting[10], protein dynamics[11], and even tissue engineering[12]. Due to their axisymmetric flow and ability to withstand organic solvents, when compared with their lithographically fabricated polydimethylsiloxane (PDMS) counterparts, glass capillary devices possess advantages for microfluidic applications. In particular, a circular tube is inserted into a square outer flow channel, which greatly simplifies alignment and centering of these devices.[1, 2, 8] Recently designs have been introduced to simplify this fabrication process using commercially available components to set up co-flowing systems.[13–15] These devices can produce large droplets, typically hundreds of microns in diameter, but lack the ability to generate the O(10 μm) size droplets that can be produced using a flow focusing device.[16, 17] A summary of current devices used, including their construction and typical applications, is shown in Table 1.

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Associated content

Electronic supplementary information is included with this manuscript. Formation of double emulsions using our microfluidic device is shown in Figure S1. Wetting of pulled capillary tips, due to lack of chemical functionalization, is shown in Figure S2. Images of experiments used to build the graph in Figure 4 are shown in Figure S3. One-step generation of double emulsion droplets using our device is shown in Supplemental Video 1.

However, limitations exist with the current design of capillary microfluidics. Conventional glass capillary devices for flow focusing microfluidic droplet generation are typically built in a manner similar to that shown in Figure 1(a).[7, 8] The devices are assembled on a glass slide and needles are epoxied over the capillaries in order to interface the device with tubing that injects the fluids. This fabrication method is technically challenging, and reproducibility in fabrication is more difficult than with lithographically produced devices.[18] For both conventional capillary devices and PDMS devices, cleaning can only be accomplished by flushing and not by device disassembly. We have found this to be a significant problem for polymerizing fluids and in high-solids droplet generation.[7]

In this technical innovation, we present a flow focusing glass capillary device based on commercial chromatography components that can be assembled easily, can be disassembled for cleaning, and can be switched from oil-in-water to water-in-oil drop formation after rinsing with ethanol. A specific advantage of the design is that the separation between the capillary inlets can be adjusted during operation. This feature allows tuning of the “age” of the interface at the point of drop breakup. As a consequence of time-dependent surfactant diffusion to the interface, the interfacial tension can be varied to control the breakup regime. The device is shown in Figure 1(b), with a schematic of the components in Figure 1(c). Briefly, the device includes two PEEK chromatography tees (IDEX Health & Science, P-713). The central square capillary (Vitrocom, 8290-050) bridges the two tees and ensures concentric alignment of the two round capillaries (Vitrocom, CV7087) that define the breakup zone (Figure 1(c)). The two orifices, one for injection of the inner fluid phase and one for the focusing of the flow, are created by flaming the ends of the glass capillaries, so that “art-dependent” capillary pulling and breaking using expensive equipment is not required.[1, 2] Alternatively, the focusing capillary can have a tapered tip to produce a different geometry for droplet generation. The sealing of the square and round capillaries in the chromatography tees is accomplished by sliding a 10 mm section of soft PVC tubing (Tygon, R-3603 1/8” OD) over the glass tubing. The compression by the chromatography ferrules provides a pressure-tight seal. The continuous phase flows into the device from both directions in order to prevent the dispersed phase from interacting with the square capillary tube. Alternatively, three immiscible phases can be injected to create double emulsions (see Figure S1 and Supplemental Video 1 in ESI).

Due to the use of a flamed tip design for injection of the dispersed phase into the microfluidic device, a favorable contact angle is created for both water and oil that allows us to use a glass capillary without chemical functionalization. Most capillary microfluidic devices using pulled-tip glass capillaries have very small outside tip diameters. They require chemical functionalization in order avoid wetting by water along the injection tip,[19] which affects droplet breakup (see Figure S2 in ESI). However, by using a flamed injection tip, the relatively flat interface that is perpendicular to the flow direction (Figure 1(c) insert) effectively pins the water/oil contact line. This result is shown by the red arrow in Figure 2(a). Using this feature, combined with the ability to disassemble and clean the device, both water-in-oil and oil-in-water emulsions can be produced in the same device after quickly rinsing the glass with ethanol.

To demonstrate this concept, we first used a pure water and mineral oil system with Span 80 surfactant at 2% (v/v) in the oil to produce droplets of water-in-oil as shown in Figure 2(a). After operating the device, it was disassembled by removing the outer screw on the tees and removing the round capillary tubes. The individual components were washed with ethanol, dried by nitrogen, and reassembled. Injecting pure water as the continuous phase and mineral oil with 2% (v/v) Span 80 as the dispersed phase produced the oil-in-water emulsion shown in Figure 2(b).

The importance of the ability to adjust the distance between orifices is shown in Figure 3. The two orifices are easily adjusted manually under a microscope during device operation, without any leakage occurring, by pushing or pulling the ends of the round capillaries. The orifices can be precisely positioned with an error of 20 microns or less. By changing the distance between the injection and collection orifices, the surface area of the dripping liquid drop can be increased. As shown in Figure 3(a-f), by holding the flow rates constant, we can change the droplet generation regime of our system. We used a pure water-in-mineral oil system containing 2% (v/v) ABIL EM 90 (Evonik Industries) as the surfactant and kept the continuous phase constant at 20 μL/min and the dispersed phase at 0.2 μL/min. We slowly adjusted the collection orifice distance and waited for the flow to become stable again after a few minutes. As we increased the collection orifice distance, the droplet generation regime of our system changed. This observation is due to the increased "age" of the interface at larger separations. The longer time enables surfactant diffusion to the interface to reduce the interfacial tension. This effect leads to transitions from geometry controlled dripping to tip streaming, then to dripping and finally jetting. Droplets around 20 microns in size were produced by dripping and are shown in Figure 3(e). It has been described elsewhere that changing of the droplet generation regime of the microfluidic system is caused by a change in the capillary number (Ca) of the system.[4, 20] The capillary number, Ca, is defined,

$$Ca = \frac{\mu_c V_c}{\gamma},$$

where μ_c is the viscosity of the continuous phase, V_c is the characteristic velocity of the flow through the orifice, which is a function of the orifice size and volumetric flow rate, and γ is the interfacial tension. The capillary number determines the conditions for breakup in a particular breakup regime.[16, 20] Normally, the capillary number is changed by adjusting the continuous or dispersed phase flow rates. We see that adjusting the tip spacing, and therefore the age of the interface, enables variation in the capillary number by varying the effective interfacial tension. This new device enables more flexible control of the capillary number and drop breakup than can be achieved with flow rate control alone. We also ran a similar experiment using 2% (v/v) Span 80 as the surfactant, and it showed a similar trend towards an increase in Ca. The images of these experiments are shown in Figure S3 in the ESI.

To ensure that the observed phenomenon was due to the surfactant in the system, a control experiment was performed using just water and mineral oil. The results of this experiment are shown in Figure 3(g-i). The continuous phase flow rate was considerably higher (ten-fold) in order to produce droplets by dripping. As the separation distance increased, the dripping does not change to jetting but instead transitions to geometry controlled dripping. This control of the interfacial tension, using diffusion controlled surfactant tuning by tip separation, demonstrates a unique capability of this new device.[21, 22]

In an attempt to gain some knowledge about the dynamic interfacial tension of a water-in-mineral oil system containing 2% (v/v) Span 80 as the surfactant, we varied the collection distance for three different flow rate ratios to learn how it affected the transitions between droplet generation regimes. Figure 4 is a graph of the droplet generation regimes for different orifice separations (l_c) that have been normalized to the collection orifice diameter (d_c) of 100 microns. The continuous phase flow rate (q_c) was maintained constant and the dispersed phase flow rate (q_d) was reduced to maintain a constant continuous phase capillary number that only changed due to changes in the dynamic interfacial tension. The results show that as the flow rate ratio is increased, the transition between different droplet

generation regimes occurs at a shorter separation distance. This result supports the argument that the age of the interface controls the effective interfacial tension; a lower interfacial tension produces a larger capillary number. Therefore, changing droplet generation regimes by tip separation is also dependent on the flow rate ratio of the system.

Through these proof-of-concept experiments, we have shown that using this easily assembled and reconfigured glass capillary microfluidic device allows precise control of drop breakup during droplet generation. A user can adjust both flow rates as well as the dynamic interfacial tension of the system in order to find the optimum operating conditions for droplet production.

In this technical innovation, we have described an easy-to-fabricate, reusable microfluidic device for the production of monodisperse droplets down to 20 microns in size. The orifices produced by flaming relatively large glass capillaries avoid the more complex capillary pulling and scoring required for conventional flow focusing glass capillary devices. Moreover, the flat ends of the capillary tip effectively pin the oil/water contact line and enable oil-in-water or water-in-oil operation without functionalized glass surfaces. We have shown that we can tune the tip separation in an operating microfluidic device, which leads to changes in the droplet generation regime. We believe that this device, with its simple design and assembly, will be useful to the community that builds and experiments with glass capillary microfluidics. The inherently serial nature of capillary devices compared with PDMS molded devices is still an issue. Scaling-up will require multiple devices to be fabricated individually. However, by shortening and simplifying the fabrication process with commercial materials, our device is an attractive alternative for these applications. A quantitative understanding of the role of surfactant diffusion to the interface, the axisymmetric flow field, and surfactant dynamics on the interface will require modeling and simulations. These further investigations would help more fully define the processes at play in this work. By using this device, we hope to further the understanding of the role of surfactants and dynamic interfacial tension in microfluidic droplet generation.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References

1. Utada AS, Lorenceau E, Link DR, Kaplan PD, Stone HA, Weitz DA. Science. 2005; 308:537–541. [PubMed: 15845850]
2. Duncanson WJ, Lin T, Abate AR, Seiffert S, Shah RK, Weitz DA. Lab Chip. 2012; 12:2135–2145. [PubMed: 22510961]
3. Panizza P, Engl W, Hany C, Backov R. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2008; 312:24–31.
4. Nunes JK, Tsai SSH, Wan J, Stone HA. J Phys D Appl Phys. 2013; 46
5. Adams LLA, Kodger TE, Kim SH, Shum HC, Franke T, Weitz DA. Soft Matter. 2012; 8:10719–10724.
6. Shum HC, Lee D, Yoon I, Kodger T, Weitz DA. Langmuir. 2008; 24:7651–7653. [PubMed: 18613709]

7. Wan JD, Shi L, Benson B, Bruzek MJ, Anthony JE, Sinko PJ, Prudhomme RK, Stone HA. Langmuir. 2012; 28:13143–13148. [PubMed: 22934976]
8. Vladisavljević GT, Duncanson WJ, Shum HC, Weitz DA. Langmuir. 2012; 28:12948–12954. [PubMed: 22860633]
9. Windbergs M, Zhao Y, Heyman J, Weitz DA. J Am Chem Soc. 2013; 135:7933–7937. [PubMed: 23631388]
10. Terray A, Hart SJ. Lab Chip. 2010; 10:1729–1731. [PubMed: 20376381]
11. Burke KS, Parul D, Reddish MJ, Dyer RB. Lab Chip. 2013
12. Onoe H, Okitsu T, Itou A, Kato-Negishi M, Gojo R, Kiriya D, Sato K, Miura S, Iwanaga S, Kuribayashi-Shigetomi K, Matsunaga YT, Shimoyama Y, Takeuchi S. Nat Mater. 2013; 12:584–590. [PubMed: 23542870]
13. Steinbacher JL, Lui Y, Mason BP, Olbricht WL, McQuade DT. Journal of Flow Chemistry. 2012; 2:56–62.
14. Chang Z, Serra CA, Bouquey M, Prat L, Hadziioannou G. Lab Chip. 2009; 9:3007–3011. [PubMed: 19789758]
15. Wang W, Xie R, Ju XJ, Luo T, Liu L, Weitz DA, Chu LY. Lab Chip. 2011; 11:1587–1592. [PubMed: 21461409]
16. Christopher GF, Anna SL. J Phys D: Appl Phys. 2007; 40
17. Jeong WC, Lim JM, Choi JH, Kim JH, Lee YJ, Kim SH, Lee G, Kim JD, Yi GR, Yang SM. Lab Chip. 2012; 12:1446–1453. [PubMed: 22402819]
18. Anderson JR, Chiu DT, Wu H, Schueller OJA, Whitesides GM. Electrophoresis. 2000; 21:27–40. [PubMed: 10634468]
19. Kim SH, Nam J, Kim JW, Kim DH, Han SH, Weitz DA. Lab Chip. 2013; 13:1351–1356. [PubMed: 23380918]
20. Anna SL, Mayer HC. Physics of Fluids. 2006; 18
21. Xu JH, Dong PF, Zhao H, Tostado CP, Luo GS. Langmuir. 2012; 28:9250–9258. [PubMed: 22650368]
22. Peng L, Yang M, Guo SS, Liu W, Zhao XZ. Biomed Microdevices. 2011; 13:559–564. [PubMed: 21484446]

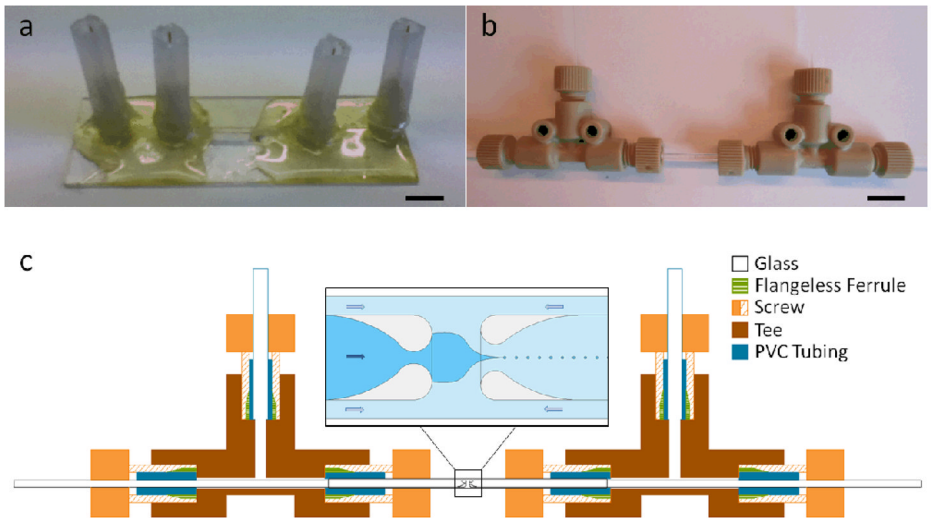

Figure 1. Design of a modular glass capillary flow focusing device

a) Image of common, non reusable glass capillary device. **b)** Image of modular, reusable microfluidic device built from commercial materials in minutes. **c)** Schematic of the construction of the modular glass capillary device. Scale bars are 1 cm.

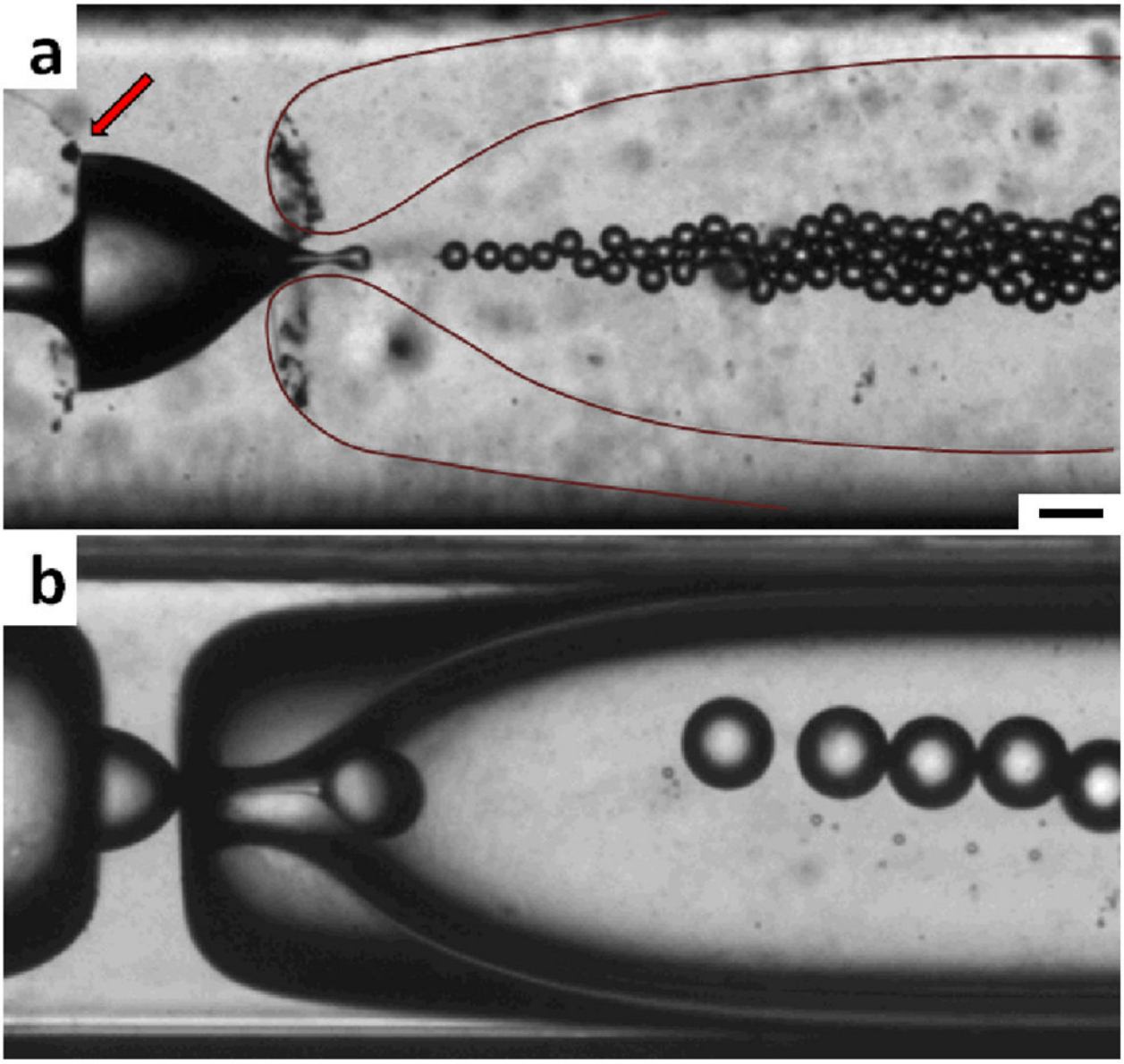

Figure 2. Unfunctionalized microfluidic device being used to produce water-in-oil and oil-in-water emulsions

a) Water-in-oil emulsion created by microfluidics. The arrow indicates the three-phase contact angle. Outline of the glass was added for visualization. **b)** Oil-in-water emulsion generated in the same device after disassembly, ethanol rinsing, and reassembly. Shadowing from the water continuous phase makes the capillaries appear differently. Scale bar is 100 μm.

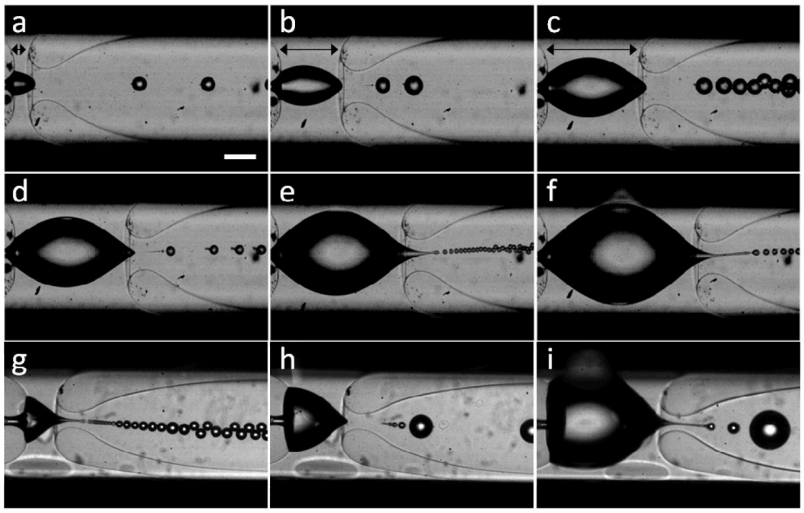

Figure 3. Changing droplet breakup regime by adjusting the collection orifice difference

Water in mineral oil with 2% (v/v) ABIL EM 90 as surfactant, q_c = 20 μL/min and q_d = 0.2 μL/min. **a)** Geometry controlled breakup. **b-d)** Droplet breakup by tip streaming. **e)** Breakup by dripping. **f)** Breakup by jetting. **g-i)** Water in mineral oil with no surfactant, q_c = 200 μL/min and q_d = 20 μL/min to produce dripping. Breakup transitioned into geometry controlled dripping. Scale bar is 200 μm.

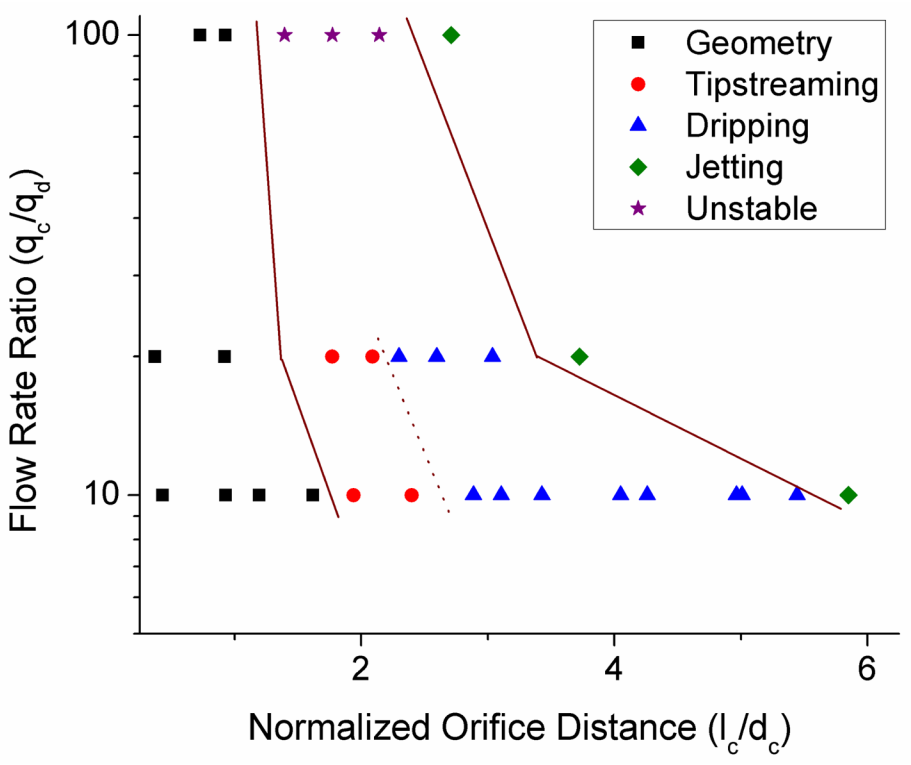

Figure 4. Mapping the change in droplet generation regime as the collection orifice distance (l_c) increases at a constant continuous phase flow rate (q_c) of 20 μL/min and a constant collection orifice diameter (d_c) of 100 μm

As the ratio of continuous phase flow rate to dispersed phase flow rate (q_d) is increased, more surfactant can reach the interface, thus reducing the interfacial tension faster and leading to a larger capillary number. Solid lines have been added to the graph to show major droplet generation regime transitions and the dotted line shows the more subtle transition from tipstreaming to dripping.

Table 1

Comparison of different glass capillary microfluidics devices and our current design using commercial tees.

Fluid Flow	Capillary Interface	Reusable	Adjustable Tips	Application
Co-flow	1 Commercial Tee	Yes	No	Protein dynamics,[11] focusing particles[10]
	2 Commercial Tees	Yes	Yes	Polymeric double emulsions[14]
	2 Lithographically fabricated Tees	Yes	No	Cell-laden microtubes[12]
Flow Focusing	2 Epoxied needles	No	No	Double emulsions,[1] polymersomes,[5] liposomes,[6] particles for drug delivery[2]
	2 Commercial Tees	Yes	Yes	Dynamic interfacial tension tuning