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## Dripping to jetting transitions observed from supercritical fluid in liquid microflows

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Dripping to jetting transition from liquid-liquid to liquid-gas systems has been widely studied in microfluidics. Recent developments have permitted the use of supercritical fluids at high pressure and various temperatures in microfluidic systems to develop sustainable processes. In this article, we use this strategy to demonstrate the possibility to generate stable droplets and reversible dripping to jetting transitions at microscale from supercritical carbon dioxide-liquid water microflows.

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Multiphase flow involving immiscible fluid systems at microscale have been known and studied for years.<sup>1</sup> Their uses include applications in emulsions, foams,<sup>2</sup> as well as droplets-based microfluidic approaches,<sup>3</sup> or the stabilization of jets.<sup>4</sup> Among the methods developed to generate segmented microflows, the case of immiscible fluids in coflow was particularly studied. Several works report detailed comprehensive modeling for the jetting to dripping transition observed in liquid-liquid and liquid-gas microsystems<sup>5</sup> for low Reynolds numbers [ $Re=(v \times \rho \times l)/\eta$ , where  $v$  is the fluid velocity,  $\rho$  the density,  $l$  the diameter of the channel, and  $\eta$  the viscosity].<sup>6</sup> The jetting to dripping transition is strongly dependent on the propagation of an absolute instability coming from a growing disturbance downstream, due to the Rayleigh-Plateau instability.<sup>7</sup> These regimes therefore depend on several factors such as inertia, interfacial tension, and viscosity ratio of the fluids.<sup>8</sup> These observations can be summarized considering two adimensional numbers: the Weber number of the inner phase ( $We_{in}$ ) and the Capillary number of the outer phase ( $Ca_{out}$ ),<sup>8</sup> defined, respectively, as  $We_{in}=(v_{in}^2 \times \rho_{in} \times l)/\sigma$ , and  $Ca_{out}=(v_{out} \times \eta_{out})/\sigma$ , where  $v_{in}$  and  $v_{out}$  are the fluids velocities of the inner and the outer phase, respectively,  $\sigma$  is the interfacial tension between the two fluids,  $\eta_{out}$  and  $\rho_{in}$  are the viscosity of the outer fluid and the density of the inner fluid, respectively. The recent development of pressure resistant microfluidic systems<sup>9</sup> offers the opportunity to study and to observe supercritical fluid (SCF)-liquid microflows. The particular interest of using SCFs stands in the possibility to tune their physical properties over a wide range of values, by small changes of pressure and/or temperature, unlike for liquid systems. This has driven their use in chemistry and physics.<sup>10</sup>

We present herein dripping and jetting regimes observed from SCF-liquid coflows, and their associated dynamic phase diagrams. We use supercritical carbon dioxide (scCO<sub>2</sub>)-liquid water as a model system. Indeed, CO<sub>2</sub> exhibits low critical coordinates and is essentially immiscible with water in the range of temperature investigated in this study (20–80 °C), although CO<sub>2</sub> can be dissolved in water as a

result of carbonate and hydrogen carbonate formation (0.8–1.2 mol/l at  $pH=7.7$  for  $20 < T < 80$  °C and  $8 \text{ MPa} < p < 12 \text{ MPa}$ ).<sup>11</sup> We demonstrate the possibility to tune reversibly the dynamic phase diagram simply by changing the pressure, without neither changing flow rates, nor fluids in use.

Similarly to previous studies,<sup>5,7</sup> we generate a coflow using a low cost and easy to use technique based on silica capillary tubing ( $\varnothing_{int}: 250 \pm 6 \mu\text{m}$ ; 1 m long), in which a second smaller capillary is inserted ( $\varnothing_{ext}: 150\text{--}200 \pm 6 \mu\text{m}$  and  $\varnothing_{int}: 50\text{--}100 \pm 3 \mu\text{m}$ ) all purchased from Polymicro, as shown in Fig. 1(a). We only discuss here the case where scCO<sub>2</sub> is the inner fluid and water is the outer fluid, although surface modification of the silica tubing with perfluoroalkyl trichlorosilane<sup>12</sup> allows scCO<sub>2</sub> to wet the surface, and permits the use of the reverse system: i.e., liquid water in scCO<sub>2</sub>. High pressure pumps for liquid and SCF chromatography (Agilent 1200 series isocratic and Jasco PU-2080-CO<sub>2</sub>, respectively) were used to deliver CO<sub>2</sub> and water, while a

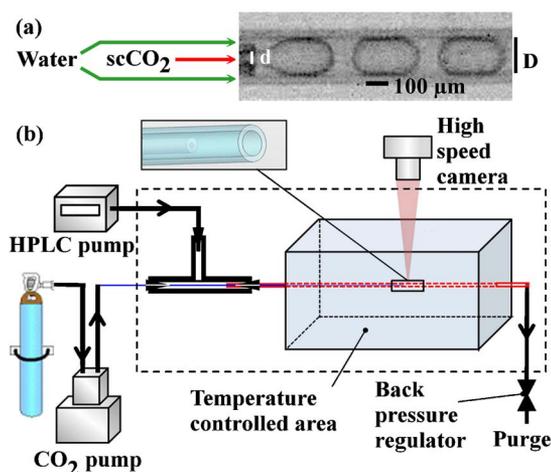


FIG. 1. (Color online) Coflowing setup developed for this study. (a) Typical observation of the flow with the insertion of a small diameter fused silica tubing in a larger one.  $D$  and  $d$  are the inner diameters of the large and the small tubing, respectively. (b) General setup including two high pressure pumps, a T connector for the insertion of the small silica tubing in the larger one, a temperature-controlled area and a back pressure regulator.

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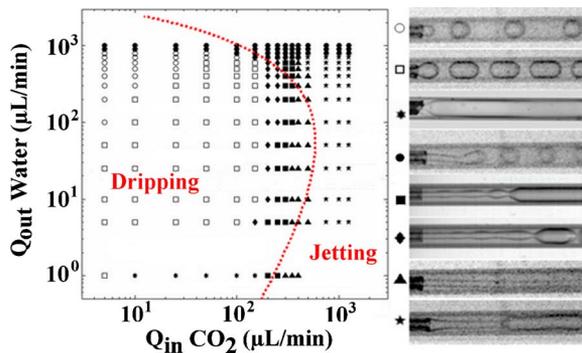


FIG. 2. (Color online) Dynamic phase diagram in the ( $Q_{in}$  and  $Q_{out}$ ) plane of the  $scCO_2$ -liquid water coflowing system. The dripping regime includes spherical droplets (open circle) and slugs (open square). Jets have been observed with various shapes: large straight jet (hexagon), thin jets breaking into droplets (filled circle), wavy jet (filled square), wavy jet breaking into slugs (diamond), thin straight jet (triangle), or more complicated shapes for flows with high Re. In this configuration,  $D=250 \mu m$ ,  $d=75 \mu m$ ,  $p=8 \text{ MPa}$ , and  $T=50 \text{ }^\circ\text{C}$ . The red dotted line corresponds to the dripping to jetting transition that should be obtained when considering a model developed for liquid-liquid microcoflows [see Ref. 5(a)].

back pressure regulator (Jasco BP-2080) allow to maintain the whole system under constant pressure ( $8 < p < 18 \text{ MPa}$ ). The capillary tubing was placed in a temperature-controlled area (water bath) and the behavior of the coflow was characterized using a high speed charge-coupled device camera (Phantom V4.2, Vision Research, Inc.) mounted on a binocular microscope, as shown in Fig. 1(b).  $CO_2$  turns supercritical when entering the water bath ( $40 < T < 80 \text{ }^\circ\text{C}$ ), i.e., above its critical point [ $T_c(CO_2) = 31 \text{ }^\circ\text{C}$  and  $p_c(CO_2) = 7.38 \text{ MPa}$ ], while  $H_2O$  remains liquid [ $T_c(H_2O) = 373 \text{ }^\circ\text{C}$  and  $p_c(H_2O) = 22.1 \text{ MPa}$ ].

Typical dynamic phase diagram from flow rate variations ( $Q_{scCO_2}$  and  $Q_{water}$ ) displays both dripping and jetting regimes,<sup>13</sup> similarly to either liquid-liquid or liquid-gas microcoflows (Fig. 2). Despite the absence of surfactants to stabilize the system, no coalescence of the  $scCO_2$  droplets was noticed in the dripping regime over the length of observation (30 cm). As mentioned previously, the dripping to jetting transition is strongly dependent on the values of the adimensional numbers ( $We_{in}$ ,  $Ca_{out}$ , or  $Re$ ). The main advantages of using  $scCO_2$  as one of the two immiscible flowing fluids stands in the possibility to tune the physical properties of the media—and therefore the value of the adimensional numbers—playing only with pressure. This results in dramatic changes in the map of the flow behavior. For instance, Fig. 3(a) presents the dynamic phase diagram obtained for

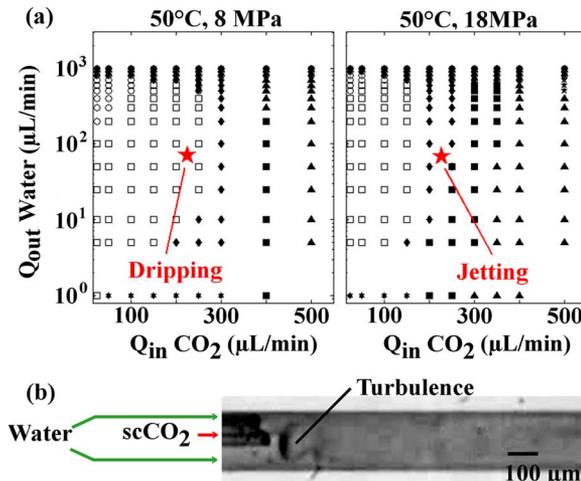


FIG. 3. (Color online) (a) Dynamic phase diagrams in the ( $Q_{in}$  and  $Q_{out}$ ) plane of the  $scCO_2$ -liquid water coflowing system, obtained at two different pressures, all other parameters being kept constant ( $D=250 \mu m$ ,  $d=75 \mu m$ , and  $T=50 \text{ }^\circ\text{C}$ ). (b) Turbulence observed from  $scCO_2$  high flow rate  $Q_{in}=1000 \mu l/min$ , in liquid water ( $Q_{out}=50 \mu l/min$ ), for  $D=250 \mu m$ ,  $d=50 \mu m$ ,  $T=50 \text{ }^\circ\text{C}$ , and  $p=8 \text{ MPa}$ , i.e., for the  $scCO_2$  flow:  $Re=4500$ .

the same system  $scCO_2$ -liq  $H_2O$  at  $T=50 \text{ }^\circ\text{C}$  at two different pressures (8 and 18 MPa), while Table I displays the physical properties and the values of the adimensional numbers of both phases in the same conditions, depending on flow rates. For the calculation, we have used  $5 \mu l/min < Q < 1000 \mu l/min$ ,  $D=250 \mu m$ , and  $d=75 \mu m$ .

In the studied conditions, the general properties of liquid water do not change much with the pressure, leading to stable adimensional numbers ( $Ca_{out}$  and  $Re$ ) for the outer fluid. However, by increasing pressure from 8 to 18 MPa, viscosity and density of  $scCO_2$  increase by a factor of 3.2 and 3.5, respectively. This results in a variation of  $We_{in}$  by a factor of 6, while  $Re$  remains quite stable (since the increase of  $\rho$  is compensated by the increase of  $\eta$ ). Note also the variation of the interfacial tension, in a smaller range, which can be obtained without any addition of surfactants.

The large range of values which can be obtained for  $We_{in}$  with  $scCO_2$  is of particular interest. Indeed, considering one particular coordinates [for instance,  $Q_{in}=225 \mu l/min$  and  $Q_{out}=75 \mu l/min$ , red stars on Fig. 3(a)], it is possible to switch from the dripping to the jetting regime playing only with pressure, all other experimental parameters being kept constant. Although dripping to jetting transition have been intensively studied and modeled,<sup>5,14</sup> none of these models

TABLE I. Physical properties and corresponding values for the adimensional numbers ( $We_{in}$ ,  $Ca_{out}$ , and  $Re$ ) of  $scCO_2$  and liquid water flows at  $T=50 \text{ }^\circ\text{C}$  for  $p=8$  and 18 MPa, respectively. Values of  $\sigma$  were estimated from pendant drop method data (see Ref. 15).

Pressure	8 MPa		18 MPa	
	$scCO_2$	Water	$scCO_2$	Water
$\sigma(\text{mN/m})$	37.1	37.1	28.8	28.8
$\eta(\mu\text{Pa s})$	20.5	548.3	64.4	550.16
$\rho(\text{kg/m}^3)$	219.2	991.5	757.1	995.7
$We_{in}$	$1.5 \times 10^{-4} - 6.3$	...	$7 \times 10^{-4} - 28$	...
$Ca_{out}$	...	$3.9 \times 10^{-5} - 7.8 \times 10^{-3}$	...	$5 \times 10^{-5} - 1 \times 10^{-2}$
$Re$	15-3025	1.1-240	17-3325	1.2-241

turn out to fit correctly our experimental results (Fig. 2 red dotted line). In fact, scCO<sub>2</sub> is a highly dilatible medium and every terms of the Navier–Stokes equation need to be taken into account. Moreover, high Re are to be considered ( $10 < \text{Re} < 3500$ , Table I). Therefore, further works need to be done to model these systems.

Another interesting aspect of these segmented scCO<sub>2</sub>-liq H<sub>2</sub>O microflows stands in the possibility to generate and to observe turbulence [Fig. 3(b)], even at very small scale. With scCO<sub>2</sub>, flows with high Re can be obtained (Table I), primarily due to the gaslike viscosity of SCFs, compared to liquids. The ability to generate turbulence in microsystems could be further used to improve mixing at microscale.

In conclusion, by using transparent microfluidic devices, we demonstrate one can easily generate stable and reversible SCFs droplets or jets in immiscible liquids. It opens several opportunities in chemistry by using these hydrodynamic structures as microreactors or mixers.<sup>9</sup> Further works are currently in progress in these ways.

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<sup>6</sup>The Reynolds number quantifies the relative importance of the inertial forces to the viscous forces and is typically in the range  $10^{-2}$ –1 for microfluidic flows.

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