Supplementary Information

Shrinking, Growing, and Bursting: Microfluidic Equilibrium Control of Water-in-Water Droplets

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1. Calculation of droplet volume

We calculate the segment of the droplet volume by the following equations. The volume of an undeformed spherical shape droplet is given by $V = 4/3\pi R^3$, where R is the radius (Fig. S1 (a)), the volume of the spherical cap segment is then given by $V_C = 1/3\ \pi h_d'^2\ (3R - h_d')$, where h_d' is the height of the spherical cap segment (Fig. S1 (b)). Since the height of the discoid droplet $h = 2\ (R - h_d')$, we can calculate the discoid droplet volume, $V_{discoid} = (\pi/12)\ [2D^3 - (D - h_d)^2\ (2D + h_d)]$, where D and h_d is the diameter of the discoid and height of the droplet, respectively, (Fig. S1 (c)).[1] We assume that the droplet height h_d, is the same as the height of the channel, h.

For non-axisymmetric discoid shape droplets, we simplify the equation, $V_{disk} = h_d A$, where, A is the cross-sectional area of the droplet (Fig. S1 (d)). The area is manually selected using ImageJ™ software.

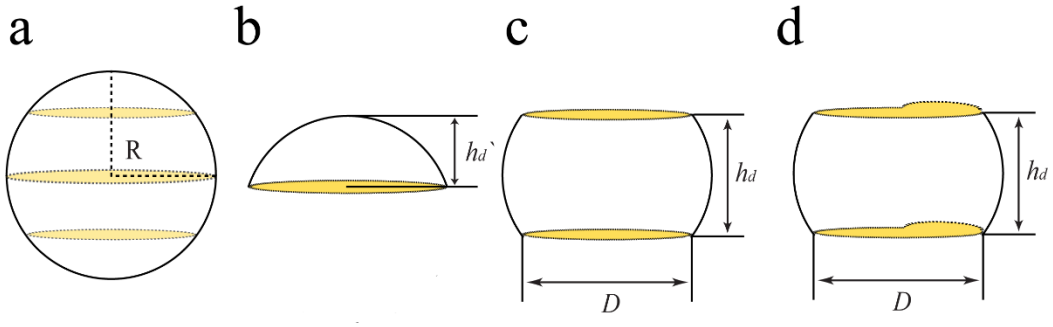

Figure S1: Schematic diagram of discoid and non-axisymmetric discoid droplets.

2. Using tie lines to estimate the size of droplets

The model for ATPS droplet shrinking and growing is developed by utilizing tie lines. Tie lines are useful tools for estimating the exchange of water during an ATPS re-equilibrium process. To predict the final size of re-equilibrated system, we make three assumptions, as described below. First, we assume that no exchange of PEG and DEX polymers occurs during re-equilibrium. Second, we assume that the PEG_b phase that enters at the second cross junction only mixes with the PEG_a phase, and does not interact directly with the DEX droplets. Third, we assume that water is the only substance that enters or exits the droplets during the re-equilibrium process.

Figure S2 shows an illustration of the phase diagram for droplet shrinking. At above the binodal curve (long dashes) of a given ATPS mixture, the solution phase separates into a lower density PEG-rich phase, and a higher density DEX-rich phase. For example, an initial ATPS 1 mixture (point A on Fig. S2), which is composed of 2.43 % (w/w) PEG and 7.78 % (w/w) DEX, phase-separates into two phases.[2] The equilibrated PEG phase has 6.01 % (w/w) PEG and 0.65 % (w/w) DEX (point B on Fig. S2). The equilibrated DEX phase has 0.03 % (w/w) PEG and 12.55 % (w/w) DEX (point C on Fig. S2). The equilibrated state forms a tie line indicated by BC. The tie line BC is described by the expression, $y = -0.5026\,x + 6.3407$, where x and y corresponds to DEX and PEG concentrations on the phase diagram, respectively.

In the microfluidic channel, the PEG_a phase (indicated by point B in Fig. S2) mixes with the PEG_b phase (indicated by point D in Fig. S2) at the second cross junction at a mixing ratio of 1:3, respectively. The mixture of the two PEG solutions leads to a new PEG phase, PEG_{ab} (indicated by point E in Fig. S2). This new continuous phase, PEG_{ab}, causes the disperse DEX phase (originally indicated by point C in Fig. S2) to become out-of-equilibrium. By mainly water-exchange the droplet DEX_a phase (point C) becomes the DEX_{ab} (point F), keeping the same slope of the original tie line. The new tie line, EF, is describes the final equilibrium state of the PEG continuous phase, and DEX droplets.

The process of re-equilibrating the DEX droplet, from a lower concentration DEX_a phase (point C) to a higher concentration DEX_{ab} phase (point F) is possible by water exchange out of the droplet. This is the reason why the DEX droplet shrinks when PEG_b has a higher concentration than PEG_a. The concentration change is calculated as $M_0/M = V/V_0$ where, M_0 and V_0 are the initial droplet polymer concentration and volume, respectively, and M and V are the instantaneous droplet polymer concentration and volume, respectively.

Figure S3 shows the predicted tie lines corresponding to different concentrations of PEG_b. We obtain these tie lines by demanding that the slope of each tie line remain the same as that for the original ATPS 1 mixture.

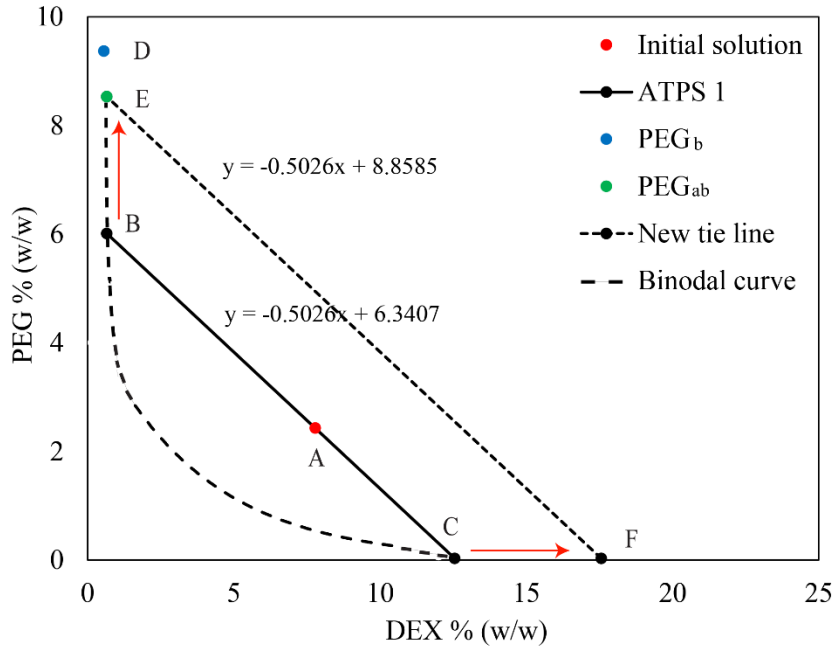

Figure S2: Phase diagram of tie line used for the droplet shrinking model.[2]

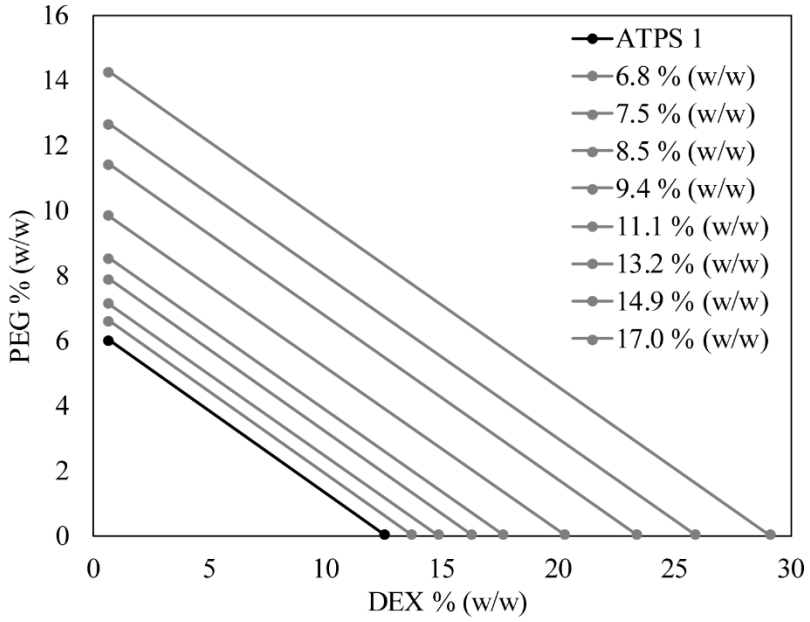

Figure S3: Predicted tie lines for different concentrations of PEG solutions.

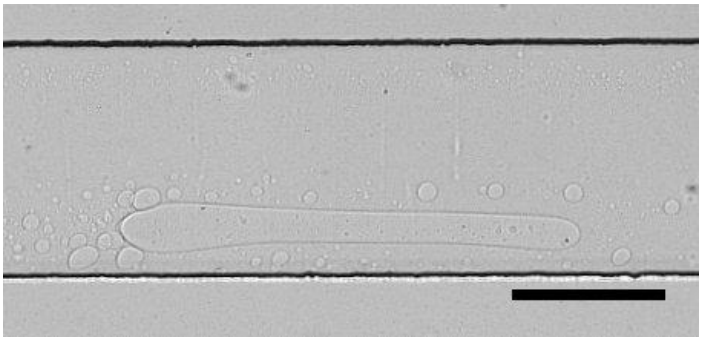

Figure S4: Droplet elongation and satellite droplet formation. We observe that at below a critical concentration of PEG in the PEG_{ab} phase, the drop does not form a single discoid shape, but elongates and breaks up into several satellite droplets. Here, a drop that was first formed using DEX and PEG phases from ATPS 4 begins to dissolve after the second cross-junction, where PEG_b, a 3 % (w/w) PEG solution, is introduced. Scale bar 200 µm.

References

1 N. Zhihong, M. Seo, X. Shengquing, P. C. Lewis, M. Mok, E. Kumacheva, G. M. Whitesides, P. Garstecki and H. A. Stone, *Microfluid. Nanofluidics*, 2008, **5**, 585–594.

2 E. Atefi, J. A. Mann and H. Tavana, *Langmuir*, 2014, **30**, 9691–9699.

Supplementary Information Movies Legend:

Supplementary Information Movie 1:
Video shows shrinking of ATPS droplets at the second junction. The inner ATPS 1 DEX and the intermediate ATPS 1 PEG solutions are introduced at applied pressures 0.29 and 0.28 kPa, respectively, while the outer ATPS 4 PEG solution is supplied at a pressure of 0.48 kPa. Here, the video is recorded at a frame rate of 50 fps, and played back at 2 x the actual speed

Supplementary Information Movie 2:
Video shows growing of a single ATPS droplet along the channel. The inner ATPS 4 DEX and the intermediate ATPS 4 PEG solutions are introduced at applied pressures 0.34 and 0.35 kPa, respectively, while the outer ATPS 1 PEG solution is supplied at a pressure of 0.46 kPa. Here, the video is recorded at a frame rate of 50 fps, and played back at 2 x the actual speed.

Supplementary Information Movie 3:
Video shows dissolving of ATPS drops. The inner ATPS 4 DEX and the intermediate ATPS 4 PEG solutions are introduced at applied pressures 0.33 and 0.34 kPa, respectively, while the outer DI water enters at 0.33 kPa. Here, the video is recorded at a frame rate of 100 fps, and played back in real time.

Supplementary Information Movie 4:
Video shows dissolving of ATPS drops. The inner ATPS 4 DEX with FITC-dextran and the intermediate ATPS 4 PEG solutions are introduced at applied pressures 0.34 and 0.39 kPa, respectively, while the outer DI water burst is supplied at 0.24 kPa. Here, the video is recorded at a frame rate of 50 fps, and played back at 2 x the actual speed.

Supplementary Information Movie 5:
Video shows single MCF-7 breast cancer cell encapsulation and release in ATPS drops. Here, ATPS 2 DEX and PEG phases are used to encapsulate a cell, and DI water is introduced at the second junction to release the cell. The video is recorded at a frame rate of 100 fps, and played back in real time.