1. Fluorinated oil background

The scattering signal of perfluoro-methylcyclohexane (labelled “F-oil”) as received from the supplier (Sigma) was been recorded in a standard Hellma cell (1 mm pathlength) at three detector distances: 1.4, 5.6 and 17 m and reported in Fig.S1. The averaged value is 0.02 cm$^{-1}$.

Since the fluorinated oil can retain some air, for consistency it is highly recommended to degas it (i.e. by heating it up and/or placing in vacuum oven) right before use.

2. Compositional averaging estimation

In the continuous flow, the effect of RTD and compositional averaging was calculated following the procedure detailed in our previous work [1]. In particular, the RTD was estimated according to the dispersion model [2] and calculated for each midpoint of the channels in the beam and contributes were summed. In order to calculate the step response, we numerically integrated the RTD(t) distribution.

In multiphase flow, we hypothesised an aqueous:carrier phase of 2:1 (which is the setup used in the H$_2$O/D$_2$O validation ramps, from the main paper). In this configuration, the aqueous plug is twice as
big as the carrier droplet. By knowing the area of the sample+carrier (which is 66.7 % of the beam footprint) we calculated the number of plugs which is always present in the control volume. The velocity is calculated as \( v = \frac{L}{FA} \) where \( L \) is the distance from the inputs, \( F \) the flowrate and \( A \) the cross section (where the width is 0.4 mm and the height is 0.25 mm). From the velocity, it is possible to estimate how many plugs enter (and exit) the control volume at each time. Supposing that the device starts in a steady condition at a concentration \( \phi_0 \), and that the input concentration is suddenly changed to \( \phi_1 \) at \( t=0 \), it is possible to calculate the percentage of area that is occupied by droplets of the new concentration. Supposing that at 100% \( \phi_0 \) the system does not scatter and at \( \phi_1 \) it scatters 100%, we proportionally link the number of droplets with a \( \phi_1 \) concentration (thus their projected area compared to the beam footprint) to the expected scattering intensity. The results are calculated every 1 s and can be integrated according to the experimental setup (1, 5, 10 s). The calculated step response has been numerically differentiated to calculate the actual compositional averaging, which is comparable to the RTD(t) distribution.

3. System stability

The stability of the system was studied by continuously injecting a mixture of water/D\(_2\)O at 5:95 (v/v) ratio. The total flowrate was 0.075 mL\,min\(^{-1}\) given by \( F_{\text{oil}} = 0.025 \,\text{mL\,min}^{-1} \) and \( F_{\text{sample}} = 0.05 \,\text{mL\,min}^{-1} \), the duration of the experiment was 600 s and the integration time 5 s. The detector was set at 5.6 m, covering a \( q \)-range of \( 0.009 \leq q \leq 0.131 \,\text{Å}^{-1} \). The data were corrected by empty cell and electronic background subtraction, and the intensity calibrated to absolute units by the direct neutron beam flux, then averaged for each time step over the whole \( q \)-range and plotted as a function of the time step (Fig. S2). Transmission (Fig. S3) has been calculated as the ratio of the transmitted signal when a sample was present by the empty cell (\( T = T_{\text{sample}}/T_{\text{empty}} \)).

**Figure S2** Scattering intensity \( I(q) \) at a fixed flowrate of 0.075 mL\,min\(^{-1}\) for the system 5:95 H\(_2\)O:D\(_2\)O. Each step corresponds to a \( I(q) \) pattern, where the intensity has been averaged over the scanned \( q \)-range.

**Figure S3** Sample transmission (\( T = T_{\text{sample}}/T_{\text{empty}} \)) at a fixed flowrate of 0.075 mL\,min\(^{-1}\) for the system 5:95 H\(_2\)O:D\(_2\)O.
4. Compositional averaging in droplets and continuous microfluidics

We report the expected output as the convolution between the step response $h(t)$ of the system and the applied input function $i(t)$, for an experiment time ($t_{exp}$) of 1 s. It has to be noticed that in case of an infinitesimal beam footprint, the output in the droplets system is identical to the input and shifted by a delay that is equal to the time needed to the fluids to travel from the input to the imaging point. If the beam footprint has a finite area, the effect of compositional averaging becomes not negligible. We report the effect of step number and duration at a total flowrate of $0.075 \text{ mL min}^{-1}$ (Fig.S4) and $0.05 \text{ mL min}^{-1}$ (Fig.S5) for a 1x1 cm$^2$ square beam footprint. For comparison, we report a response at 0.5 mL min$^{-1}$ with a concentration change rate $\Delta\Phi/\Delta t$ of 0.5 (10 steps in 200 s) in Fig.S6. In the latter, the continuous flow smears the steps into a ramp, whilst the multiphase flow allows to follow each imposed concentration.

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**Figure S4** Effect of step number and duration ($\Delta t$) on the response of the system in case of continuous and multiphase flow at a total flowrate of $0.075 \text{ mL min}^{-1}$. The selected data show a ramp of 120 steps with $t_{exp} = 5$ s (a), 60 s (b) and 600 s (c) and a ramp of 10 steps and $t_{exp} = 5$ s (d), 60 s (e) and 600 s (f).

**Figure S5** Effect of step number and duration ($\Delta t$) on the response of the system in case of continuous and multiphase flow at a total flowrate of $0.05 \text{ mL min}^{-1}$. The selected data show a ramp of 120 steps with $t_{exp} = 5$ s (a), 60 s (b) and 600 s (c).
5. Boundary conditions of the serial dilution

We recorded in droplet microfluidic SANS the two limit concentrations of the Ludox HS-40 in water (concentrated: 13 v/v %, diluted: 1.45 v/v %) at pH 9.7 that correspond to the end and start point of the dilution ramp, and compare the same concentrations in static cuvettes by the means of synchrotron SAXS. The results are shown in Fig.S7.

**Figure S6** Effect of step number and duration (Δt) on the response of the system in case of continuous and multiphase flow at a total flowrate of 0.5 mLmin⁻¹. The selected data show a ramp of 10 steps with t_{exp} = 20 s.

**Figure S7** Comparison between SANS (droplets SANS) and SAXS (static cuvettes) data at the maximum (1.43 v/v %) and minimum dilution (13 v/v %) for Ludox HS-40.
6. SANS from Ludox HS-40

We performed a static SANS experiment on 0.5 (v/v) % Ludox HS-40 in water at pH 9.7 in a 1 mm pathlength Hellma cell. The SANS data and the SASview fit are reported in Fig. S8 respectively as blue dots and a black line. We applied a spherical model with HMSA structure factor and polydispersity of 0.26 (Schulz). The particle radius was found to be 73.8 Å.

![SANS fit](image)

*Figure S8 SANS scattering intensity of 0.5 (v/v) % Ludox HS-40 in water*

7. Contrast variation of 120 nm colloidal silica

The contrast variation on 120 nm silica was been performed in standard Hellma cells (Fig. S9) and in the continuous flow cell (Fig. S10). For the first, we used three detector distances: 2m, 5.6 m and 17 m, whilst the scattering signal from the continuous flow was recorded at 11 m. The concentrations used correspond to the ones described in the main text.
Figure S 9 Contrast variation series of 120 nm silica in discrete measurements using Hellma cells

Figure S 10 Contrast variation series in continuous flow-SANS. Plots every 7.5 (v/v) % change in solvent concentration.

References
