I. COMMENT ON THEORETICAL EXPRESSION OF DROPLET SEDIMENTATION IN A SPHERE WITH IMMOBILE BOUNDARIES

In our work the density difference between the oil and the inner water phase W1 was reduced by increasing the density of the oil phase to 0.960 *g/cm³* by the addition of Sucrose Acetate Isobutyrate (SAIB). As the density difference was not completely compensated, the inner water droplet W1 sank to the bottom of the oil droplet O due to gravity effects, resulting in a thinning of the oil layer. Mok & Kim[40] developed a first order estimation for calculating the sedimentation velocity of a sphere inside a concentric spherical liquid container,

$$\tilde{v} \rightarrow \frac{2}{9\eta_o} r_i^2 (\rho_o - \rho_{w1}) g \left[1 - \frac{9}{4}b + \frac{5}{2}b^3 - \frac{9}{4}b^5 + b^6 \right] (1 - b^5)^{-1} \tag{S1}$$

where $\tilde{v}$ is the steady state sedimentation velocity of the inner droplet, η_o the viscosity of the oil phase, r_i the inner droplet radius, ρ_o and ρ_{w1} the density of the oil and W1 phase, respectively, g the gravitational acceleration, and b the aspect ratio r_i/r_o. Equation S1 is valid under the assumptions that both fluids are Newtonian, and have constant thermodynamic and transport properties[41]. Moreover, it does not take into account swelling or deformation of the droplets. Furthermore, it has to be considered that Equation S1 describes the droplet sedimentation with a constant velocity and is only valid at the moment when the inner droplet is concentric embedded in the outer droplet[41]. Over the experimental time the inner droplet is not centered anymore and $\tilde{v}$ decreases with a power law behavior of b^6. Consequently, the sedimentation rate decelerates with time, which makes a calculation of the sedimentation velocities and thus the theoretical sedimentation times nonfeasible.

II. SWELLING KINETICS OF MULTIPLE DROP-IN-DROP W1/O/W2 EMULSIONS PREPARED BY MICROFLUIDICS

In addition to single drop-in-drop W1/O/W2 emulsions, emulsions with two and four identical inner W1 droplets were produced by microfluidics (Supplementary Figure 1). This was possible by using inner water phases W1 without the addition of sodium dodecyl sulfate (SDS). As a consequence W1/O droplets were created already at the first junction of the chip. They were subsequently pinched into defined multiple drop-in-drop emulsions at the second junction (Supplementary Figure 2). Due to an osmotic pressure gradient directed toward the W1 phase, the droplets swelled gradually with time (Supplementary Figure 1). Furthermore, small water droplets were spontaneously formed in the oil phase. This spontaneous emulsification was even more pronounced than in the case of one internal W1 droplet.

Following the swelling of the W1/O/W2 emulsions with more than one internal droplet resulted in the swelling kinetics curves illustrated in Supplementary Figure 3a. The measurements were performed in duplicate and show high reproducibility. This clearly illustrates the robustness of the experimental method. Similar to the single drop-in-drop emulsions, the curves show the characteristic two sequential stages. However, the distinction between the different stages is less sharply pronounced. As one reason for this the non-identical positioning of the inner droplets is assumed. A comparable sedimentation of the inner droplets W1 to the bottom of the oil droplet, as described for single drop-in-drop emulsions is not possible due to steric reasons. Thus, the minimal oil layer thickness differed between the internal W1 droplets and in comparison to the single drop-in-drop systems. The migration rates of water into the oil and the corresponding lag times are average values of the migration rates and the lag times of the single inner droplets, resulting in less sharply pronounced differentiation between the two stages.
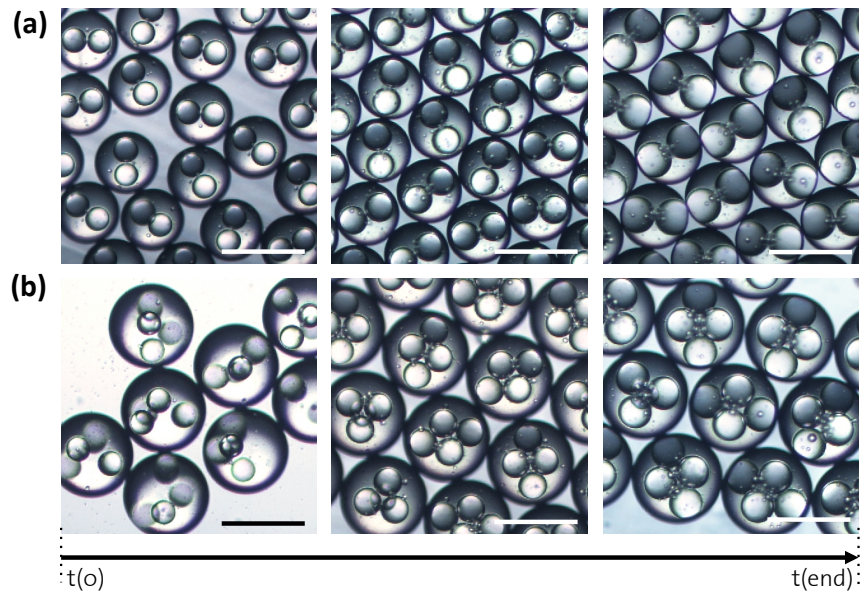
Supplementary Figure 1: Microscopic images of osmotically imbalanced W1/O/W1 emulsions with two (a) and four (b) internal W1 droplets produced by microfluidics. The images were taken after 0 *min*, 90 *min* and 180 *min* (from the left to the right). The oil phase contained SFO with 22 wt % SAIB and 2 wt % PGPR. The initial osmotic pressure gradient was set to 13.1 bar. (scale bar = 200 *μm*)
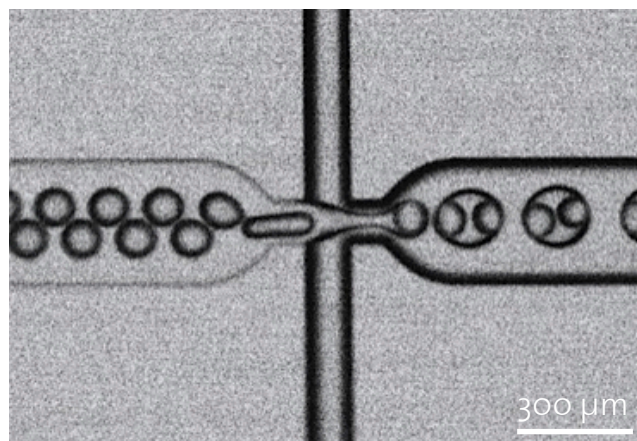

Supplementary Figure 2: Double drop-in-drop formation at the second junction of the microfluidic chip.

Comparing the swelling rates in Supplementary Figure 3a gives higher values for emulsion systems with four internal droplets. A normalization by the total inner W1/O interface results in the swelling curves shown in Supplementary Figure 3b. The total inner interface A_{tot} is defined as:

$$A_{tot} = n \, \pi \, d_{50}^2 \tag{S2}$$

with n the number of internal droplets and d_{50} the median inner droplet diameter. The normalized swelling curves of both systems overlap to a remarkable extent. Moreover, the degree of swelling is in the same range like for single drop-in-drop emulsions illustrated in Figure 2a. In summary, multiple emulsions with more than one internal W1 droplet follow the same mechanisms as described for single drop-in-drop emulsions. Consequently, it can be assumed that they obey the same driving forces.
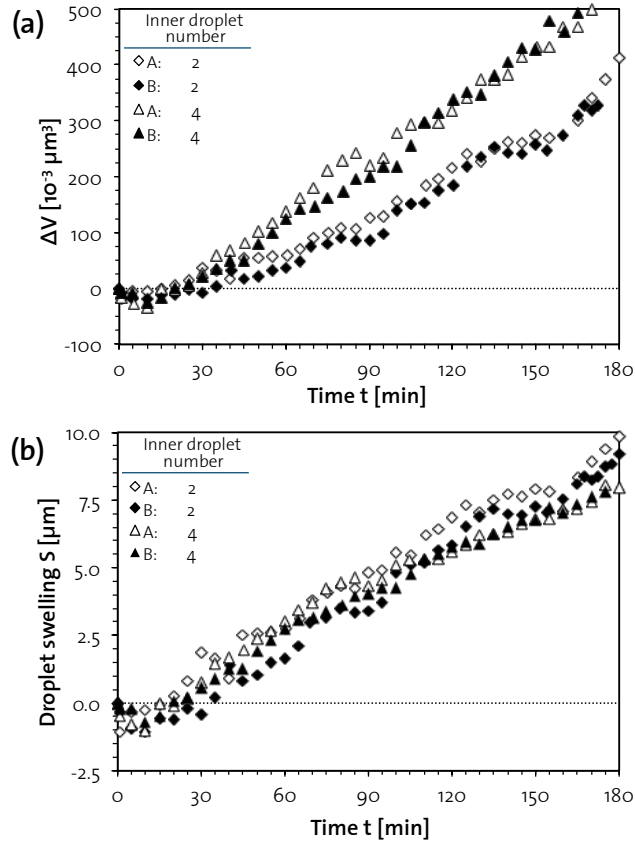
Supplementary Figure 3: Swelling kinetics of W1/O/W2 emulsions with two and four internal W1 droplets produced by microfluidics. The swelling is plotted as absolute (a) and normalized (b) volume increase of the inner droplets with time. The experiments were performed in duplicate (A and B). The oil phase contained SFO with 22 wt % SAIB and 2 wt % PGPR. The initial osmotic pressure gradient was set to 13.3 *bar*.