Stabilizing liquid drops in nonequilibrium shapes by the interfacial cross-linking of nanoparticles

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1. Droplet formation with 10 mM HTA$^+$, or 1 mM La^{3+} alone

SI Figure 1 Shows the extrusion of diethyl phthalate (DEP) with 20 vol % of ethanol at 15 ml/hr flowrate in an aqueous dispersion of 5 wt % nanoparticles with either 10 mM hexyltrimethylammonium bromide (HTAB) or 1 mM La^{3+}. In both cases, no tubule formation is not observed only drops are formed with slightly oblate shapes.

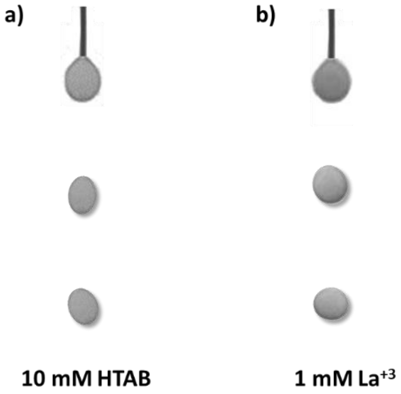

Figure SI1: diethylphthalate (DEP) with 20 vol % of ethanol at 15 ml/hr flowrate in aqueous dispersion of 5 wt % nanoparticles a) 10 mM HTAB b) 1mM La^{3+}.

2. Pendant droplet volume reduction with La^{3+} alone

SI Figure 2 depicts the control experiment to check the effect of La^3+ ions alone on interfacial aggregation. A drop of the same volume was exposed to an aqueous suspension of 5 wt % nanoparticle with 1 mM La^{3+}. Subsequently, the area was reduced by 50% by withdrawing the oil in one step. No change in shape or wrinkles were observed in this case and the drop seems to be quite spherical same as in the case of HTAB.

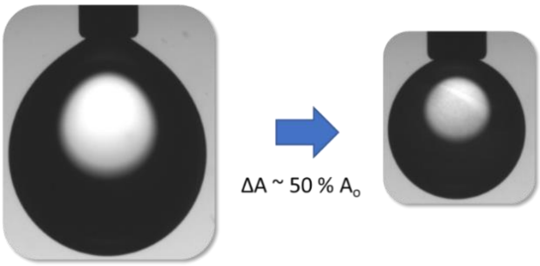

Figure SI2: Optical image of 50 % area compression of oil drop in water with 5 wt % NPs and 1 mM La^{3+}.

3. Critical force determination for droplet pinch-off

SI Figure 3 shows drop size reduction as a function of increasing ethanol vol % (0-20) in DEP. The threshold size (*Dc*) of the drop decreases gradually from 2 mm to 1.6 mm before pinching from the extrusion nozzle or forming fiber. This can be understood with the analysis of net force balance on the drop. We assume the density of the drop to be constant and calculate the gravitational force acting against the surface tension. SI figure 3 (ii) shows a schematic of the force balance between surface tension and the gravitational pull on the drop. As we increase the ethanol vol % in DEP interfacial tension decreases and less gravitational force is required to pinch off or elongate the droplet. Critical force (Fc) is defined as the force acting on the drop of critical diameter and causes pinching or elongation. Above 12 vol% of ethanol continuous liquid tubule generation was observed.

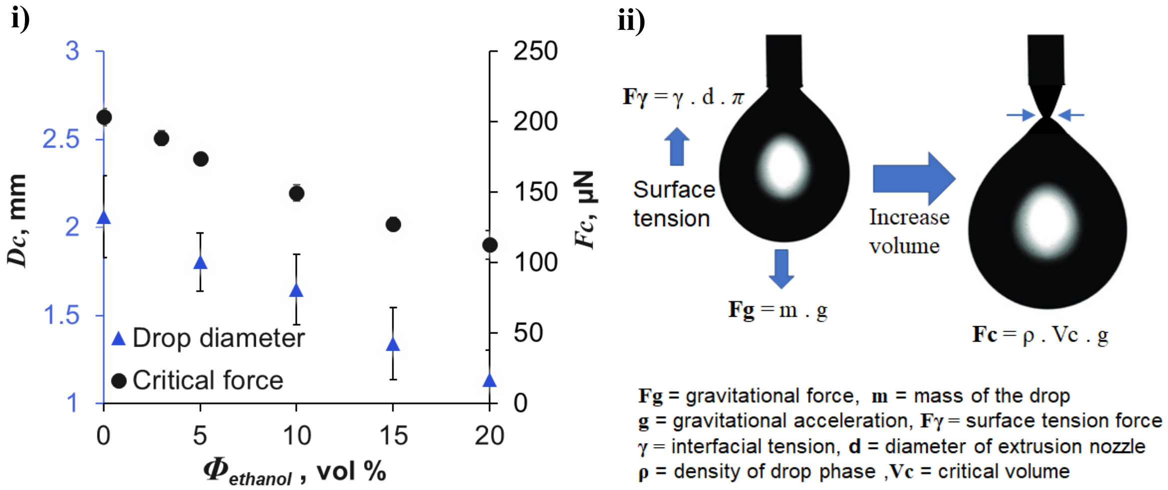

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Figure SI3: i) shows the variation of critical drop size (*Dc*) and force (*Fc*) acting on the drop at the point of detachment from the extrusion nozzle with various $\varphi_{\mathrm{ethanol}}$. The concentration of silica particles (5 wt %), C_6TAB (10 mM) and La^{3+} ion (1 mM) are kept constant for all the experiments. ii) Depicts a schematic of force balance in pendant drop experiments.

4. Interfacial tension measurements in dependence of the ethanol concentration

SI Figure 4 Increasing the ethanol volume % in water from 0 to 40 reduces the interfacial tension between pure DEP and water from ~15 mN/m to ~ 2 mN/m. All the measurements were recorded at room temperature.

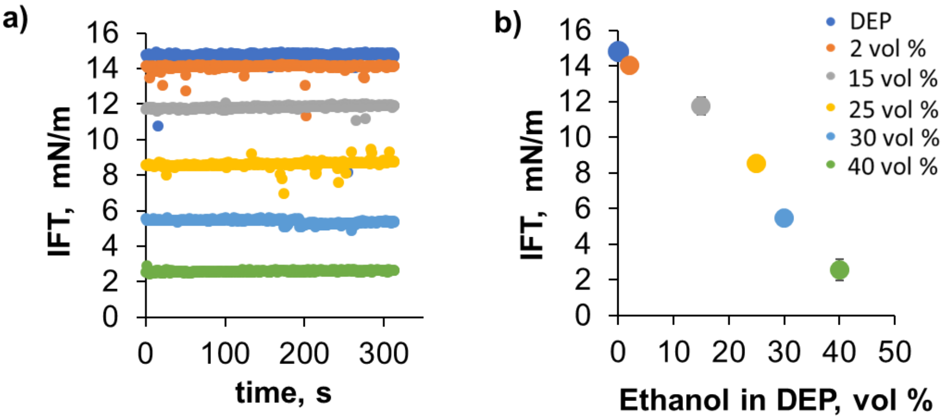


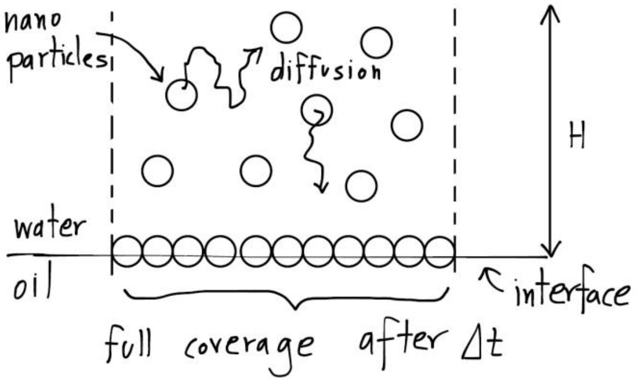
Figure SI4: Depicts the effect of surface tension on liquid fiber formation. a) Time dependant measurement of interfacial tension (γ) of DEP-water interface with different ethanol volume % (φ_{ethanol}). b) Equilibrium interfacial tension measurement with varying φ_{ethanol}.

The interfacial tension is constant because for the experiment in SI Figure 4 we have added ethanol to the surrounding water phase, not the DEP droplet phase. If ethanol would have been added to the droplet phase, the diffusion of ethanol would have caused the interfacial tension to change over time. Because of the limited reproducibility of this experiment, we have decided to measure the interfacial tension with a constant ethanol concentration in the surrounding water.

5. Estimation of the nanoparticle deposition rate

The goal of the following calculation is to estimate the time it takes for nanoparticles in a dispersion to form a monolayer on an oil/water interface. We consider transport by diffusion from a liquid column above the interface as depicted below.

The suspension has a particle weight fraction w. How high must H be to provide enough particles for full coverage of the interface? We assume that half of the particles diffuse upwards away from the interface and the other half downward to the interface. The particles cover the surface in hexagonal packing with an area coverage of 91%.



coverage : $A \cdot \xi$, A - area $[m^2]$, ξ - coverage fraction 0.91

cross sect particle $a = \frac{\pi}{4} d^2$

maximum number of attached particles $N_{P,A} = \frac{A \cdot \xi}{a} = \frac{A \cdot \xi \cdot 4}{\pi \cdot d^2}$

volume of suspension above interface $V = \underset{[m^2]}{A} \cdot \underset{[m]}{H}$

volume fraction of particles in suspension $\varphi = w \cdot \rho \cdot 1/\rho_p \quad \left[\frac{ml\ part}{ml}\right]$

w - weight fraction $\quad$ ρ - suspens density $\quad$ ρ_p - particle density $\quad$ $\left[\frac{\cancel{g\ part}}{\cancel{g\ tot}} \cdot \frac{\cancel{g\ tot}}{ml\ tot} \cdot \frac{ml\ Part}{\cancel{g\ Part}}\right]$

volume of one particle $V_{P,i} = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi \left(\frac{d}{2}\right)^3 = \frac{1}{6}\pi d^3$

volume of particles in suspension $V_P = V \cdot \varphi = A \cdot H \cdot \varphi$

number of particles in suspension $N_{P,V} = \frac{V_P}{V_{P,i}} = \frac{A \cdot H \cdot \varphi \cdot 6}{\pi d^3} = \frac{A \cdot H \cdot 6 \cdot w \cdot \rho}{\pi \cdot d^3 \cdot \rho_p}$

2 times as many particles in suspension (half diffuse up) as there will be on the surface $\frac{1}{2} \cdot N_{P,V} = N_{P,A}$

$$\frac{\cancel{A} \cdot H \cdot \overset{3}{\cancel{6}} \cdot w \cdot \varrho}{2 \cdot \cancel{\pi} \cdot d^{\cancel{3}} \cdot \varrho_p} = \frac{\cancel{A} \cdot \xi \cdot \cancel{4}^{2}}{\cancel{\pi} \cdot \cancel{d^2}} \qquad \frac{3 H w \varrho}{d \, \varrho_p} = 2 \xi \qquad \boxed{H = \frac{4}{3} \, \frac{\xi \cdot d \cdot \varrho_p}{w \cdot \varrho}}$$

5 wt% ($w = 0.05$), $\varrho_p = 2.2 \, \frac{g}{ml}$ (silica density),
$\varrho = 1.03 \, g/ml$ (density of silica suspension)
$d = 20$ nm (Ludox TM particle size)

$$\underline{H = 1033 \text{ nm}}$$

That means, if half of the particles from the volume V = H*A diffuse to the interface, the longest distance to travel is 1033 nm. On average, the particles diffuse a distance of H / 2 = 516 nm.

Next, we determine the time it takes for a particle to diffuse the average distance H / 2. To this end, we first calculate the diffusion coefficient of the particles with the Stokes-Einstein relationship.

$$D = \frac{kT}{6 \pi \eta r}$$

k - Boltzmann const $= 1.3806 \cdot 10^{-23} \, \frac{m^2 \, kg}{s^2 \cdot K}$
T - Temperature $= 298$ K
η - dynamic viscosity $= 10^{-3}$ Pa·s
r - particle radius $= 10^{-8}$ m

$$\underline{D = 2.18 \cdot 10^{-11} \, \frac{m^2}{s}}$$

The mean square displacement for diffusion in 1D calculates to (https://en.wikipedia.org/wiki/Mean_squared_displacement):

$$\langle (x(t) - x_0)^2 \rangle = 2 D t$$

$$(H/2)^2 = \langle (x(t) - x_0)^2 \rangle$$

$$\rightsquigarrow \quad t = \frac{H^2}{8D} = \frac{(1033 \, nm)^2 \cdot m^2}{8 \cdot 2.18 \cdot 10^{-11} \, \frac{m^2}{s} \cdot (10^9 \, nm)^2} = 0.006 \text{ sec}$$
$$= 6 \text{ msec}$$

The dependence of H and t on the mass fraction of the nanoparticles is shown in Figure SI5a.

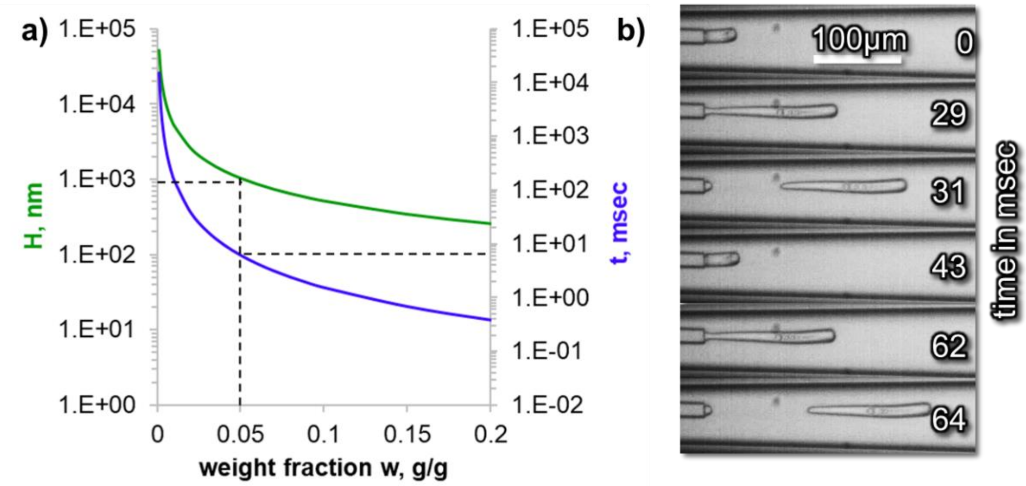


Figure SI5. Comparison of approximated nanoparticle diffusion time and droplet formation time. **a)** Height of aqueous column above the interface with sufficient particles for stabilization and diffusion time t over the average height H/2. **b)** High-speed video micrographs of the droplet pinch-off in the microfluidic device.

We can now compare the diffusion time with the droplet pinch-off time. Figure SI5b shows high-speed video microscopy of the droplet pinch-off. The pinch-off time for the cylindrical droplet is on the order of a few tens of milliseconds. The approximation of the diffusion time and the drop formation process have roughly the same order of magnitude. It seems, that the particles have just enough time to stabilize the interface. According to Figure SI5a, lowering the particle concentration will result in a significantly longer diffusion time, thus there must be a threshold concentration below which the out of equilibrium droplet shapes cannot be stabilized.

6. Extended experimental section

6.1 Experimental procedure for the pendant drop measurements.

A rectangular glass container (see image on the side) is filled with an aqueous dispersion of 5 wt-% Ludox TM particles, 10 mM HTA+ and variable concentrations of La^{3+}. The glass cuvette is placed on the stage of a pendant drop tensiometer ThetaPhysics OCA. A 1 mL glass syringe with a 20 gauge dispensing needle (OD 0.908 mm, ID 0.603) is filled with diethylphthalate (98%, Sigma Aldrich). The syringe is mounted in the motorized dispensing unit of the pendant drop tensiometer and the needle is submerged in the Ludox dispersion. The camera is focused on the needle and the pixel to millimeter ratio is determined for the CMOS camera at the specific zoom level. A droplet of 15 microliter DEP is formed through the automatic dispensing unit. Based on the shape analysis of the droplet, the software determines the interfacial tension, the droplet volume and the droplet surface area. The volume of the droplet is reduced by 10 – 11 microliter at a rate of 2 microliter/s, resulting in an area reduction of the droplet of ~ 50%, as indicated by the droplet analysis. During this, the interfacial tension is perpetually measured at a camera frame rate of 40 – 110 Hz.

6.2 Microfluidic device fabrication and experiments.

A cylindrical glass capillary (OD 1 mm, ID 0.6 mm) is tapered with a Sutter P-1000 Micropipette puller. With the help of a ceramic scoring tile (Sutter), the tapered capillary ends are opened to obtain orifices of 25 µm and 70 µm, respectively. The tapered capillaries are submerged in a saturated solution of KOH in 2-propanol for 12hrs. Next, the capillaries are rinsed with water and ethanol. Then, the capillaries are thoroughly dried with a stream of Nitrogen and under vacuum to remove water. The capillaries are then placed in a desiccator and a few droplets of Trichloro(1H,1H,2H,2H-perfluorooctyl)silane are added in a petri dish next to the capillaries. A vacuum is applied for 2 hours through a vacuum pump to partially evaporate the Trichloro(1H,1H,2H,2H-perfluorooctyl)silane and coat the glass capillaries from the gas phase. After rinsing and drying, the two tapered capillaries are inserted into a square capillary (ID 1.05 mm), interdigitated and aligned under a microscope (see SI Figure 6). Dispensing needles are glued at the ends of the square capillary with 5-minute epoxy glue (12 hrs curing time) and connected with plastic tubing. A mixture of 50 vol-% ethanol in DEP is flown out of the 25 µm capillary orifice, supplied at a pressure of 2.7 atm. The aqueous phase is flown at variable rates controlled by a syringe pump. A high-speed camera (Phantom Miro C110) is used to visualize the droplet formation on an inverted Nikon Diaphot microscope.

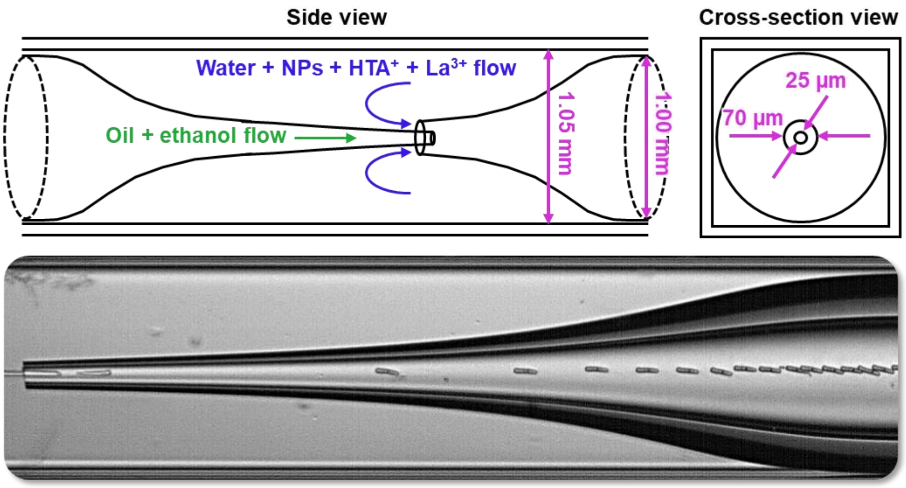


Figure SI6. Schematic drawing and micrograph of glass capillary microfluidic device.

7. DLS of Ludox TM in dependence La3+ and HTA+ concentrations

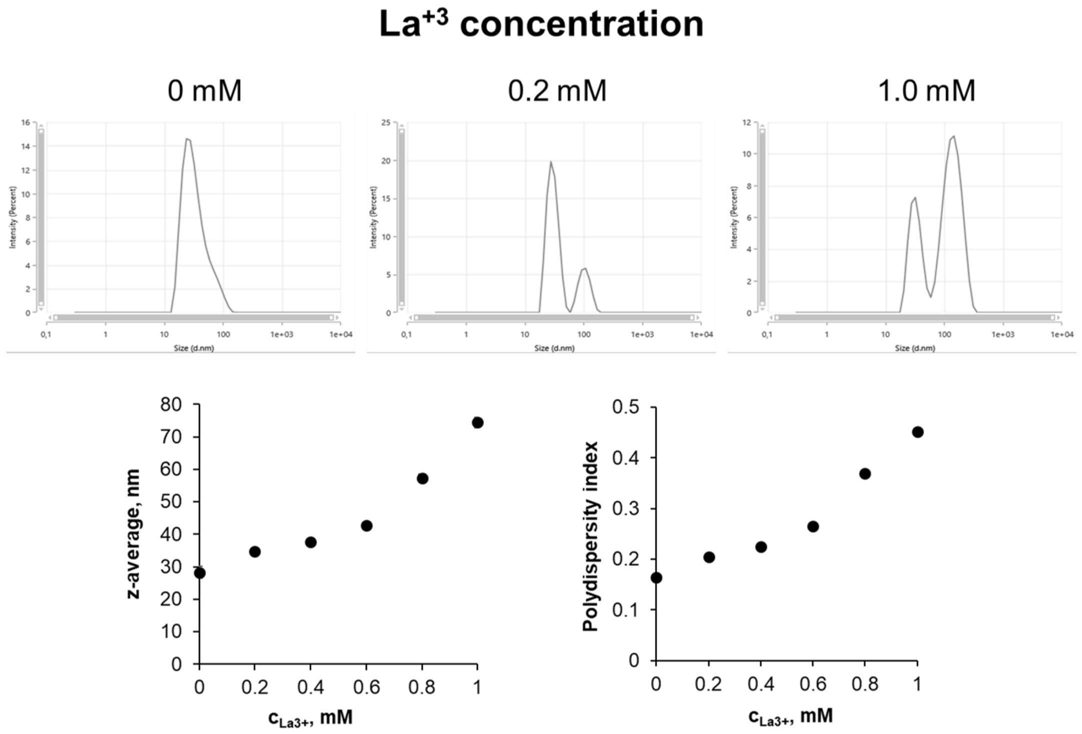


Figure SI7. Dynamic light scattering of Ludox TM particles at different La3+ concentrations.

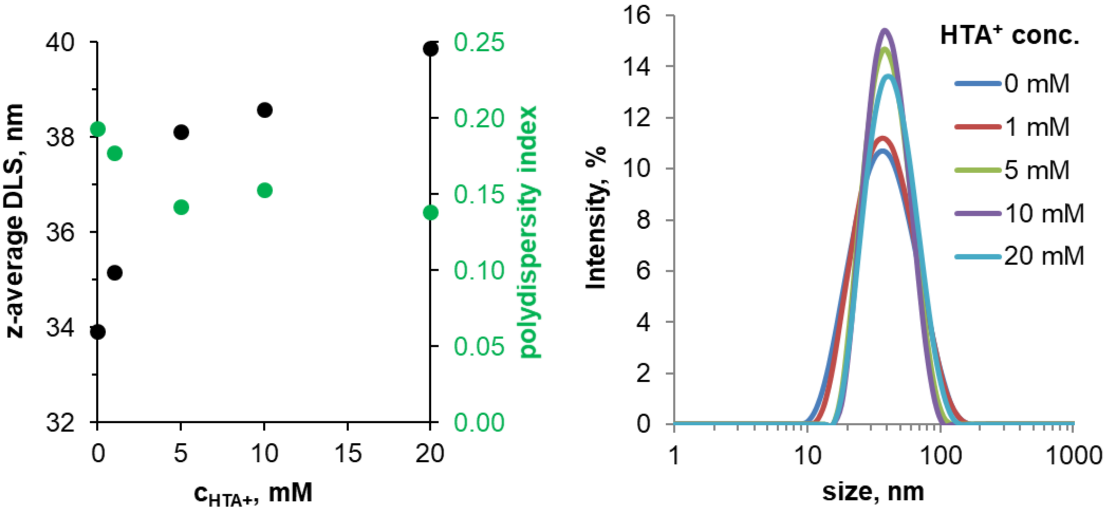


Figure SI8. Dynamic light scattering measurements of Ludox TM particles (5 wt-%) at different HTA$^+$ concentrations.

The intensity averaged size increases from 34 nm to 40 nm, as the HTA$^+$ concentration is raised from 0 to 20 mM. Thus, HTA+ only results in minor aggregate formation. In contrast, increasing the La3+ concentration from 0 to 1 mM results in an increase in the intensity averaged size from 34 to 75 nm. We have included the new Figure SI8 in the supporting info.

8. Apparent interfacial tension change measurements for different droplet aging times

The apparent interfacial tension change does not depend on the age of the droplet, at least not for the accessible age in our experimental setup. We can conclude, the coating of the droplet with the nanoparticles and their interfacial cross-linking occurs on time scales smaller than 18 seconds (time needed to inflate the droplet for Figure SI9).

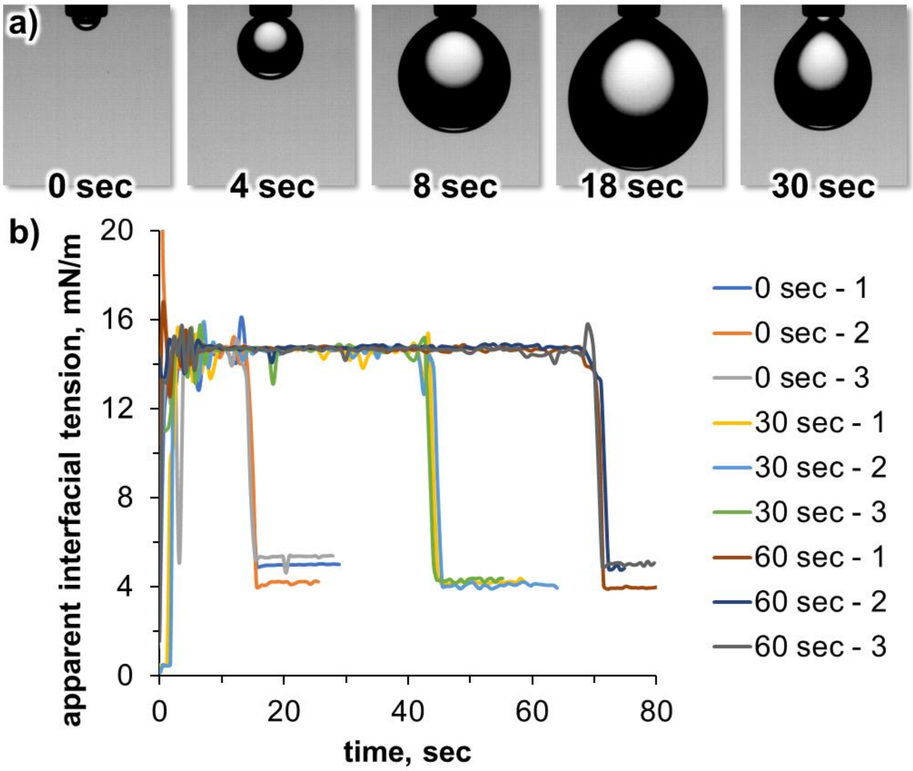


Figure SI9. Droplet shrinking experiment for different droplet aging times. **a)** Photograph time series showing the inflation of a droplet over a duration of ~18 seconds (final volume 15 µl), followed immediately by volume reduction (10 µl) for ~10 seconds. **b)** Measurement of the apparent interfacial tension for different droplets. The legend shows the aging time of the droplet after completion of the inflation before the volume reduction is initialized.

9. Shear stress equation

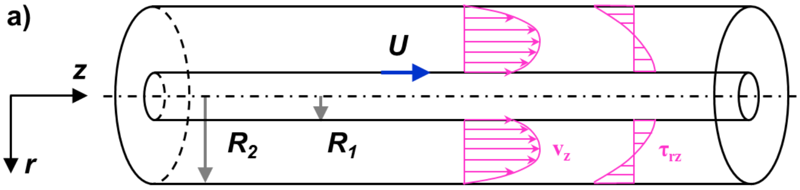


Figure SI10. Cylindrical annulus approximation of a cylindrical droplet in a cylindrical capillary. Water flows around the droplet with a volumetric flow rate Q_w. The cylindrical droplet moves with the velocity U (determined by high speed video microscopy). The droplet has a radius of R1 and the inner radius of the capillary is R2.

A detailed derivation of the following equations can be found in the supporting info of Haase, M. F., Sharifi-Mood, N., Lee, D., & Stebe, K. J. (2016). In situ mechanical testing of nanostructured bijel fibers. *ACS nano*, *10*(6), 6338-6344.

The radial velocity profile of the water around the cylindrical droplet calculates to

$$u_z(r) = -\frac{dp}{dz}\frac{\left({R_2}^2 - r^2\right)}{4\mu} + \left\{U + \frac{dp}{dz}\frac{\left({R_2}^2 - {R_1}^2\right)}{4\mu}\right\}\frac{ln(R_2/r)}{ln(R_2/R_1)}$$

with

$$\frac{dp}{dz} = \frac{2\mu\, ln(\frac{R_2}{R_1})}{\pi J}\left\{Q_w + \frac{2\pi U}{ln(\frac{R_1}{R_2})}[\frac{R_1^2}{2}ln(\frac{R_1}{R_2}) + \frac{R_2^2}{4} - \frac{R_1^2}{4}]\right\},$$

J is a geometrical parameter and calculates to

$$J = \left(\frac{R_1^4}{4} - \frac{R_2^4}{4}\right) ln\left(\frac{R_2}{R_1}\right) + \left(\frac{R_2^2}{2} - \frac{R_1^2}{2}\right)^2$$

The shear stress on the surface of the droplet calculates to

$$\tau_{rz}|_{R_1} = \mu\frac{(U_0 - U)}{R_1}\frac{1}{ln(R_2/R_1)}$$

With the parameter U0 (the velocity of the droplet where it experiences 0 shear stress).

$$U_0 = \frac{dp}{dz}\frac{R_1^{\ 2}}{2\mu}\ln\frac{R_2}{R_1} - \frac{dp}{dz}\frac{(R_2^{\ 2} - R_1^{\ 2})}{4\mu}$$