Electronic Supplementary Information for:

Interaction of Sedimenting Drops in a Miscible Solution – Formation of Heterogeneous Toroidal-Spiral Particles.

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Materials and Methods

Materials and Reagents

Poly (ethylene glycol) diacrylate (PEG-DA) with a molecular weight of 700, glycerol, ethanol, 37% hydrochloric acid, malachite green carbinol base, ammonium molybdate IV tetrahydrate, and polyphosphate (with 45 repeating units) were purchased from Sigma-Aldrich (St. Louis, MO). Irgacure 2959 (2-hydroxy-1-[4-(2-hydroxyethoxy) phenyl]-2-methyl-1-propanone) (I-2959) was kindly provided by Ciba Specialty Chemicals (Basel, Switzerland). Water used in all experiments was de-ionized to 18.2 MΩ-cm (Nanopure II, Barnstead, Dubuque, IA.). All chemicals were purchased at standard grades and used as received.

Solution Viscosities

The viscosities of the polymer and bulk solutions were measured using a rheometer (Physica MCR 301, Anton Paar, Graz, Austria) and presented in **Table S1**. The composition of each bulk solution was chosen to approximately match the viscosity of the corresponding polymer solution and achieve a suitable density difference. Unit viscosity ratio was previously found to be advantageous for the formation of TS structure.[1] In the drop phase, the viscosity is mainly affected by the PEG-DA concentration; while in the bulk phase, the viscosity is mainly affected by the glycerol concentration. Ethanol and DI water were added in both phases to adjust the density difference.

Table S1. Measured viscosities of polymer and bulk solutions. The composition of each bulk solution was chosen to approximately match the viscosity of the corresponding polymer solution.

Polymer Solution	**Viscosity (Pa · s)**	**Corresponding Bulk Solution**	**Viscosity(Pa · s)**
83wt% PEG 17wt% ethanol	0.057	63wt% glycerol 37wt% ethanol	0.063
45wt% PEG 55wt% DI water	0.011	50wt% glycerol 30wt% ethanol 20wt% DI water	0.0098
35wt% PEG 65wt% DI water	0.0067	40wt% glycerol 25wt% ethanol 35wt% DI water	0.0059

Reaction Scheme of PEG-DA Cross-linking

Initiator, I-2959, dissolved in ethanol was added to PEG-DA to enable sub-second cross-linking with a high intensity (~10 W/cm^2) ultra violet (UV) lighting system (Bluewave 75, Dymax, Torrington, CT). In the experiments, UV light in the wave-length range of 280-450nm was used to initiate radical formation from I-2959 (**Fig. S1**). These free radicals cross-link the polymer into a dense matrix by breaking double bonds on the acrylated end groups of PEG-DA.[2]

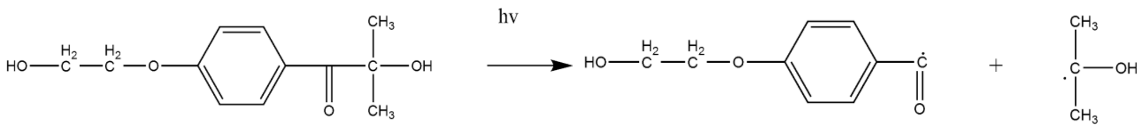

Fig. S1. Free radical formation from I-2959 due to UV light exposure, which can be used to cross-link acrylated polymers.

Experimental Setup for Generating Drops

A syringe pump (PHD 2000 programmable, Harvard Apparatus, Holliston, MA) and a 5 mL gastight glass syringe (Hamilton Company, Reno, Nevada) were used to infuse the polymer solution for the generation of polymer drops with controlled volume. To study the interaction of the two vertically displaced drops, the drops were generated sequentially. The size of the drops was determined by the balance of gravity and surface tension at the rim of needle. A flat-tip needle (22G PS3, Hamilton Company, Reno, Nevada) yielded drops of 1mm radius over a range of flow rates of 0.02 to 10 ml/min. The target volume of the syringe pump was adjusted to be 0.0195 mL in order to infuse exactly two drops. The flow rate determined the time interval between the two drops, and thereby their separation distance during sedimentation. To ensure that drops experienced the same surface impact when they entered the miscible bulk solution, the flat surface of the bulk solution was disturbed by pre-splashing a drop of bulk solution before the first drop entered the interface. In order to generate drops with different solution compositions and properties (such as in the cases of encapsulating polyphosphate into TS particles), two sets of syringe pumps, syringes, and needles were used. The trailing drops containing polyphosphate and PEG-DA (0 – 40 wt%) were smaller compared to the leading drops containing PEG-DA (83 wt%). To vary the sizes of the drops, two sizes of the needles were used: 22 gauge (with a targeting volume 0.011 mL) for the leading drop and 26 gauge (with a targeting volume 0.007 mL) for the trailing drop. Moreover, to align the drops horizontally, the 22 gauge needle was beveled and attached to the flat tipped 26 gauge needle at a slightly higher tip position. The polymer drop was infused from the 22 gauge needle first, then clung to the 26 gauge needle and eventually fell from the tip of the latter. Shortly there after, the polyphosphate drop was dispensed from the 26 gauge needle and fell at the same position.

The horizontally displaced drops were generated by using an array of glass capillaries (ID: 536.2 µm, OD: 658.3 µm). The glass capillaries were embedded in an epoxy plug inside one end of a section of polyurethane tubing (ID: 2.4 mm, OD: 4.0 mm). The other end of the tubing was connected to a gastight glass syringe. The device was assembled by fixing the position of the glass capillaries under the stereoscope. To ensure that the glass capillaries were completely parallel, they were tacked onto two plastic bars with epoxy (**Fig. S2**). The flow rate was set to be 15 ml/min. The glass capillaries were buried below the surface of the bulk solution. For a given device, the distance between the glass capillaries was fixed. However, the dimensionless distance could be varied by changing the sizes of the drops. Target volumes ranged from 0.02mL to 0.13mL to produce dimensionless distances from 2 to 4.5 as presented in **Fig. 5**.

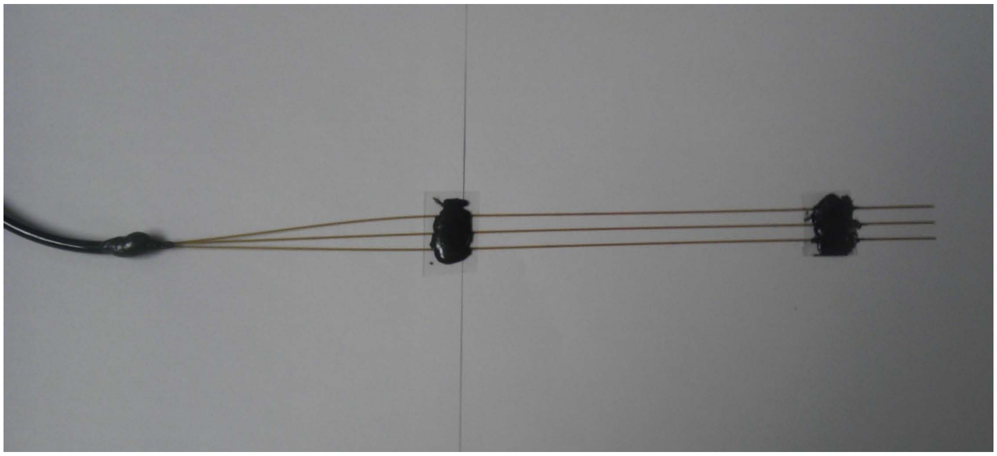

Fig. S2 Device consisting of three glass capillaries.

To illustrate that multiple compounds can be encapsulated into one TS particle, we placed four smaller drops surrounding a relatively bigger polymer drop. The injection device was constructed in a similar way as above, except with the capillaries in a five-spot pattern. The center capillary was fed by one syringe pump with target volume (0.03 mL), while the other four capillaries were fed by a pair of syringes driven by a second pump with target volume (0.003 mL). Therefore, the dispensed volume for each surrounding drop was 0.0015mL.

Acquisition of High-Speed Camera Images

All the time sequences of drops were obtained by using a high-speed camera (Prosilica GX 1050, Allied Vision Technology, Germany) with a magnification lens (MLH-10X, Computar, Commack, NY). The capture speed was set to a nominal speed of 67 frames per second. Exposure was set to 1 milli-second.

Definition of Dimensionless Groups

Reynolds number (*Re*) represents the ratio of inertial forces to viscous forces. It is calculated from the expression, $\mathrm{Re} = UR/\nu$, where U (m•s^{-1}) and R (m) are the velocity and radius of the sedimenting leading polymer drop (for vertically displaced drop interaction) or the center polymer drop(s) (for horizontally displaced drop interaction), and ν (m^{2}•s^{-1}) is the kinematic viscosity of the bulk solution. The radius of the polymer drop and its sedimentation distance were measured from the images captured by the high-speed camera. The time was measured by the number of frames and the recording speed of the camera. The average velocity of the sedimenting drop was then calculated by the distance divided by the time.

Weber number (*We*) represents the ratio of the kinetic energy to surface-tension energy during splashing impact. It was calculated from the expression, $We = \rho U^2 R/\sigma$, where ρ (kg•m^{-3}), U (m•s^{-1}), and R (m) are the density, velocity, and radius of the polymer drop, and σ (N•m^{-1}) is the surface tension at the interface between the bulk solution and air. By neglecting the air resistance, kinetic energy can be converted from potential energy and $\rho U^2 = 2\rho gh$, where h (m) is the height of the needle above the surface of the bulk phase and g (m•s^{-2}) is the gravitational acceleration.

Bond number (*Bo*) represents the ratio of gravitational forces to surface tension. It is defined as: $Bo = \Delta\rho g R^2 / \sigma$, where $\Delta\rho$ (kg•m^{-3}) is the density difference between the drop phase and the bulk phase, g (m•s^{-2}) is the gravitational acceleration, R (m) is the radius of the polymer drop and σ (N•m^{-1}) is the interfacial tension between the drop phase and the bulk phase.

The Flory-Huggins parameter (χ) represents the polymer/solvent solvation interaction. It is defined as: $\chi = z\Delta\omega / RT$, where z is the lattice coordination number, $\Delta\omega$ (J•mol^{-1}) is the change in the internal energy from mixing, R (J•mol^{-1}•K^{-1}) is the gas constant and T (K) is the absolute temperature.

In Vitro Release of Polyphosphate

TS particles encapsulating polyphosphate were generated by employing vertically displaced drop interaction. The leading drop solution containing 83wt% PEG-DA 700, 14.2wt% ethanol and 2.8wt% I-2959 formed the main body of the particle with dense pores. The trailing drop containing approximately 1 mg/mL polyphosphate was entrained to form the TS layer. The PEG-DA concentrations in the trailing drop were varied from 0 – 40 wt% to maintain different size pores in the TS layer, and thereby different release kinetics. Glycerol was also dissolved in the trailing drop to achieve a sufficiently high density for the trailing drop to catch up with the leading drop. Ethanol was added to dissolve the photoinitiator (I-2959) in it in order to crosslink the internal TS layer. Furthermore, DI water was needed to dissolve the polyphosphate in it. Various suitable compositions of the trailing drop are listed in **Table S2.**

Table S2. Various compositions of a trailing drop.

Solution	**Polyphosphate (wt%)**	**PEG-DA 700 (wt%)**	**Glycerol (wt%)**	**DI water (wt%)**	**Ethanol (wt%)**	**I-2959 (wt%)**
1	0.1	0	28	71.9	0	0
2	0.1	5	33	58.9	2.5	0.5
3	0.1	10	30	54.9	4.17	0.83
4	0.1	15	28	51.9	4.17	0.83
5	0.1	20	23	51.9	4.17	0.83
6	0.1	30	16	46.9	5.8	1.2
7	0.1	40	12	42.9	4.17	0.83

After solidification at various evolutionary stages, the release of polyphosphate was monitored by using malachite green assay as previously described.[1] The remaining unreleased polyphosphate trapped in the particles was measured by dissolving the particles in 12.1 M HCl for two weeks. In this way, we obtained the total amount of polyphosphate originally encapsulated. Thus, we could convert the cumulative release to a percentage release. Moreover, this measured value of phosphate encapsulated in TS particle compared reasonably with the estimated value based on the size of the trailing drop and its polyphosphate concentration.

Simulation

Computer simulations of drop sedimentation, deformation and interaction were based on the assumptions of viscous-dominated flow (low *Re*) and equal viscosities μ of all drops and the bulk liquid. Both assumptions were satisfied, at least approximately, in the experiments. Details of the numerical method and supporting references have been given before;[1] the following explanation focuses on those aspects most relevant to drop interactions. For a set of time-evolving volumetric domains $\mathcal{V}_1(t), \ldots, \mathcal{V}_N(t)$ representing N hydrodynamically interacting drops, the Stokes velocity field $\mathbf{v}(\mathbf{r}, t)$ is obtained from the convolution integral

$$\mathbf{v}(\mathbf{r}, t) \;=\; \sum_{n=1}^{N} \int\!\!\int\!\!\int_{\mathcal{V}_n(t)} (\Delta\rho)_n \mathbf{g} \cdot \mathsf{G}(\mathbf{r} - \mathbf{q})\, \mathrm{d}V[\mathbf{q}] \tag{1}$$

where $(\Delta\rho)_n$ is the density difference between the nth drop and the bulk liquid, $\mathbf{g}$ is the gravitational acceleration vector, and G is the Green's function for creeping flow (Stokeslet tensor field),[3]

$$\mathsf{G}(\mathbf{r}) \;=\; \Big(8\pi\mu\|\mathbf{r}\|\Big)^{-1}\Big(\mathsf{I} \,+\, \|\mathbf{r}\|^{-2}\mathbf{r}\mathbf{r}\Big) \tag{2}$$

As time progresses, the flow field (1) moves and deforms the drop domains $\mathcal{V}_n(t)$ that in turn determine it, resulting in nonlinear dynamics. For numerical computations, each drop domain $\mathcal{V}_n(t)$ is replaced with a statistically uniform swarm of many Lagrangian particles of the appropriate mass. The integral (1) is then approximated, in what amounts to a Monte Carlo method, with a sum over all particles from all drops.[4] This leads to a coupled, nonlinear system of ODEs for the coordinates of the particles, which is solved numerically with a fourth-order Runge-Kutta method.[5] If we use a total of M particles to represent the N drops, a direct summation over all M particles to calculate the velocity of each of these M particles leads to order M^2 operations. A particle-mesh method[6] is combined with the fast Fourier transform[7] to reduce the operation count to order $M \log M$ with only minor losses in accuracy.[8]

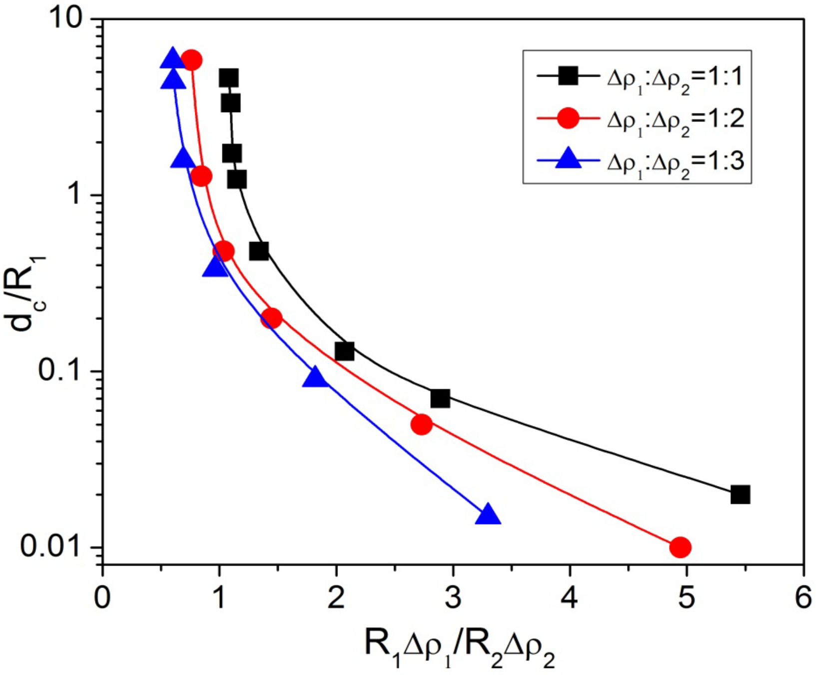

Fig. S3 Numerically simulated dependence of critical catch-up distance on $R_1\Delta\rho_1/R_2\Delta\rho_2$ and $\Delta\rho_1/\Delta\rho_2$.

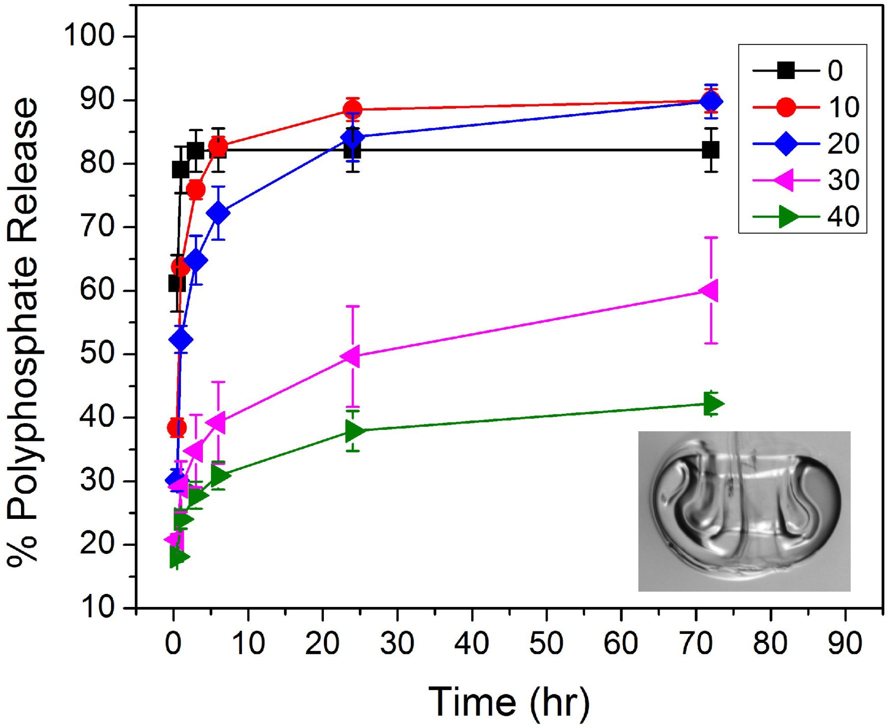

Fig. S4 Release kinetics of polyphosphate from early-stage TS particles with various concentrations of PEG-DA in the TS layer. Numbers 0-40 correspond to wt% of PEG-DA in the internal layer.

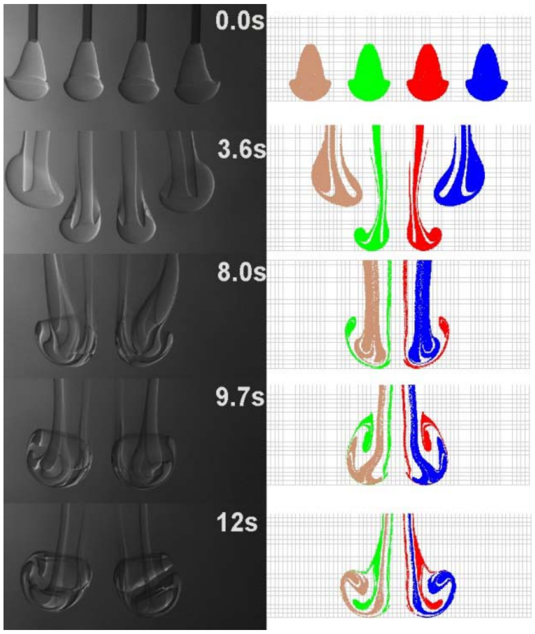

Fig. S5 Comparison of the experimental observation and numerical simulation of drop interaction for four parallel droplets sedimenting in a miscible solution.

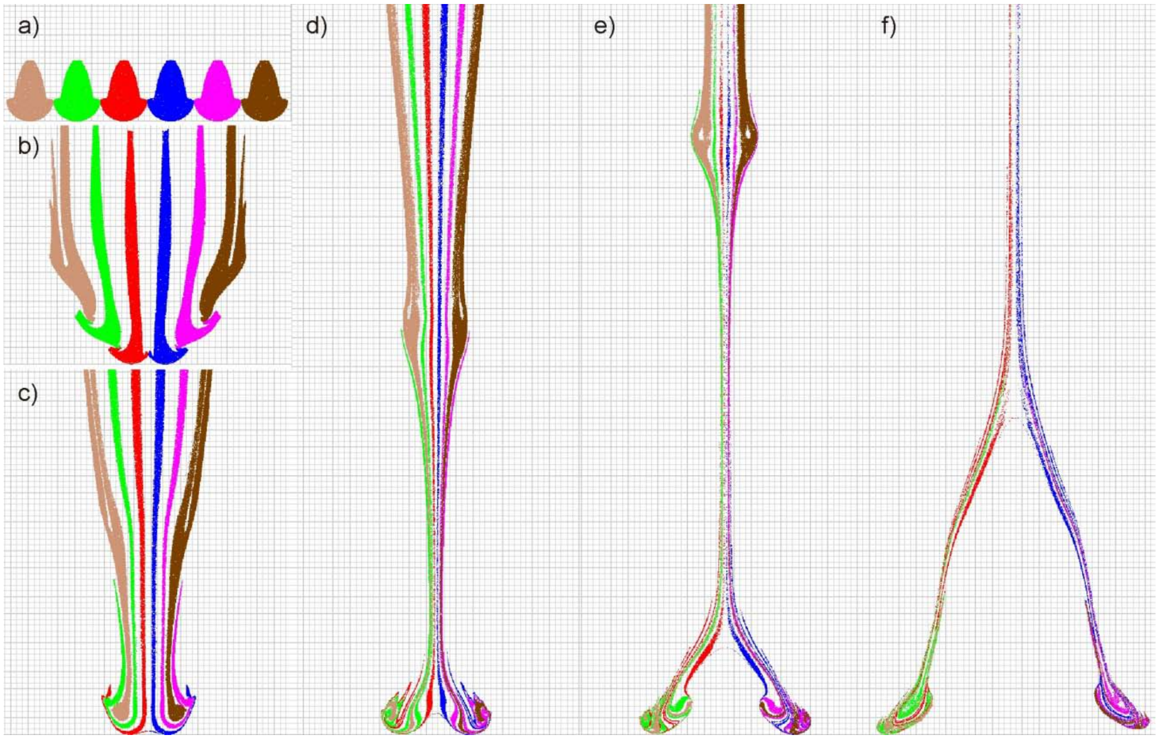

Fig. S6 Sedimentation of close packed six parallel drops investigated by simulation.

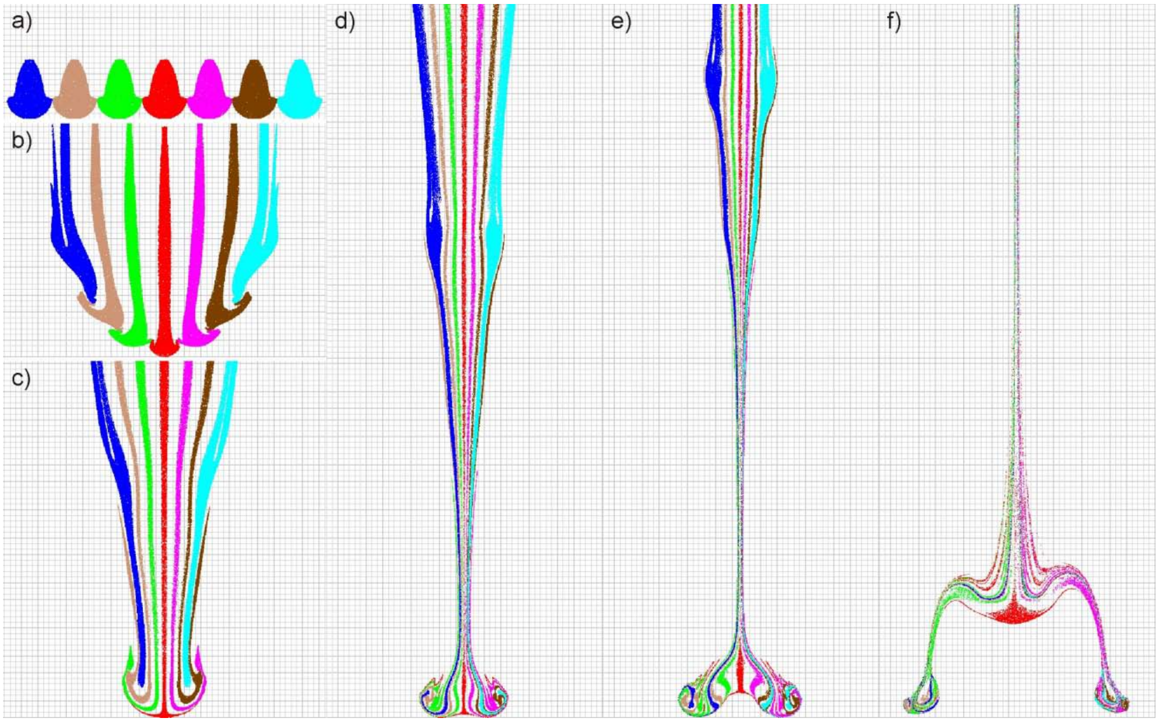

Fig. S7 Sedimentation of close packed seven parallel drops investigated by simulation.

References:

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