—Supporting Information—

Colloid Mobilization and Transport during Capillary Fringe Fluctuations

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Supporting information includes details on experimental setup, colloid properties, confocal microscopy, figures on experimental setup and additional confocal images. This information is available free of charge via the Internet at http://pubs.acs.org.

S1 Colloid Properties

Colloid properties are listed in Table S1. For the amine-modified colloids, we had to drop the pH to 3 to obtain a net positive electrophoretic mobility. According to the manufacturer (Molecular Probes Inc., Eugene, OR), the amine-modified colloids have both aliphatic amines as well as carboxyls on the surface, resulting in a zwitterionic colloid. We prepared the suspension of the amine-modified colloids at pH 3 to keep the majority of the surface charges positive. Moreover, in this case, the sulforhodamine B could not be added because the sulforhodamine rendered the colloids negative (Table S1). For the scenario 4, we therefore only used a 1 mM $CaCl_2$ solution.

S2 Glass Column

The glass column is shown in Figure S1. The column had an i.d. of 1.5 mm and a length of 7.5-cm. Two end-pieces were made of small sections of a 5-mm-long glass channel (same type as the column) to which we attached a 1-cm-long section of a sterile, stainless steel hypodermic needle (1.2 mm diameter, Monoject 250, Tyco) using epoxy (General Purpose Epoxy, PermaPoxy, Permatex Inc., Solon, OH). One end-piece was glued to the column with the epoxy, but the other end of the column was left open. We then inserted a piece of a 5-μm membrane filter (Lot Number 81831, Gelman Instrument Co., MI) through the column to cover the open needle hole, and then filled the empty column with glass beads. After filling with the glass beads, we inserted another piece of membrane, and then glued the second end-piece onto the column.

S3 Confocal Microscopy

Under the confocal microscope, we focused the magnification view to a setting of 4.5, which provided a representative view of the glass beads, and we scanned a fixed area (2000 μm $\times$ 2000 μm) throughout the interface displacement experiments. The image resolution was 512$\times$512 pixels. We set the confocal laser configuration to the proper range of excitation/emission wavelengths to cover the 505/515 nm of the yellow-green colloids and the 565/585 nm of the red aqueous solution. The glass beads had no fluorescence, so they appeared as gray. We used single, split, and combined modes during experimental visualization. During imbibition and drainage experiments, images were taken as time series in two second intervals.

We checked the field of view of the confocal microscope by taking images in 5 μm increments along the z-direction from the bottom to the top of the column. For this test, we saturated the glass bead-filled column with a colloid suspension. We could observe the same colloids within 19 z-increments, indicating that field of view for our setup was about 90 μm [(19-1) $\times$ 5 μm] in z-direction.

Table S1. Surface properties of colloids, glass bead, and glass channel.

Materials	Contact angle[a] (deg)	Surface charge[b] (meq/g)	pH (–)	Electrophoretic mobility[c] (μm/s)/(V/cm) $CaCl_2$[e]	Electrophoretic mobility[c] (μm/s)/(V/cm) $CaCl_2$ + SB[f]	ζ-potential [d] (mV) $CaCl_2$[e]	ζ-potential [d] (mV) $CaCl_2$ + SB[f]	Experiment
Carboxylate-modified colloids	35 ± 1	0.0175	5.5	-0.19 ± 0.02	-0.25 ± 0.02	-2.4 ± 0.2	-3.2 ± 0.3	Scenario 1 to 4
Sulfate-modified colloids	121 ± 1	0.0017	5.5	-0.21 ± 0.03	-0.42 ± 0.08	-2.7 ± 0.4	-5.6 ± 0.5	Scenario 4
Amine-modified colloids	34 ± 2	0.0143	3	3.17 ± 0.59	-0.99 ± 0.07	40.4 ± 7.5	-12.6 ± 0.9	Scenario 4
Glass bead[g]	19 ± 2	n.a.	5.5	-1.21 ± 0.11	-1.67 ± 0.06	-15.5 ± 1.4	-21.3 ± 0.8	Scenario 1 to 4
Glass bead[g]	19 ± 2	n.a.	3	-0.85 ± 0.08	-1.11 ± 0.05	-10.9 ± 1.0	-14.2 ± 0.6	Scenario 4
Glass channel[g]	15 ± 1	n.a.	5.5	-1.99 ± 0.09	-1.78 ± 0.04	-25.4 ± 1.1	-22.7 ± 0.6	Scenario 1 to 4
Glass channel[g]	15 ± 1	n.a.	3	-1.25 ± 0.18	-1.52 ± 0.10	-16.0 ± 2.2	-19.4 ± 1.3	Scenario 4

[a] Determined by the sessile drop method using a manual goniometer (Model 147 50-00-115, Rame-Hart Instrument Co., Netcong, NJ)

[b] Values provided by manufacturer.

[c] Measured by using Zetasizer Nano ZS (Malvern Instruments Ltd., Malvern, UK)

[d] Obtained from measured electrophoretic mobilities using the von Smoluchowski equation**?**

[e] 1 mM $CaCl_2$

[f] 1 mM $CaCl_2$ and 0.09 mM sulforhodamine B

[g] For electropholetic mobility measurements, glass beads and channels were ground with a mortar to a fine powder and dispersed in the aqueous solutions.

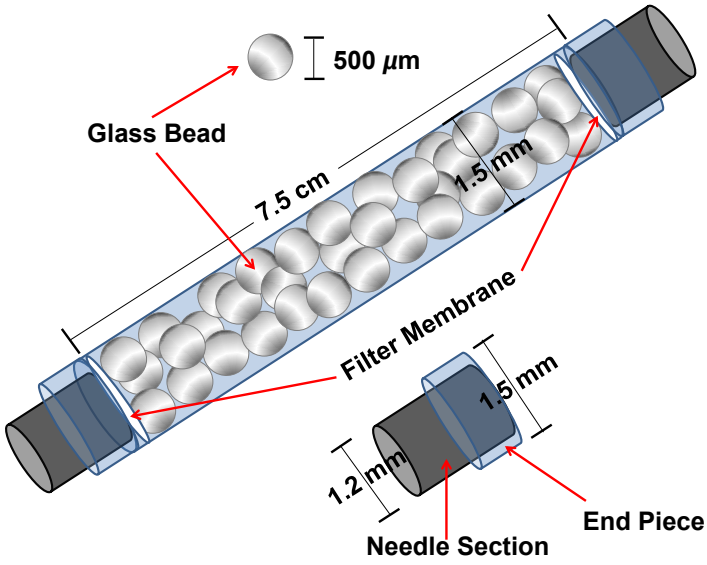

Figure S1. Schematic of the experimental channel filled with glass beads.

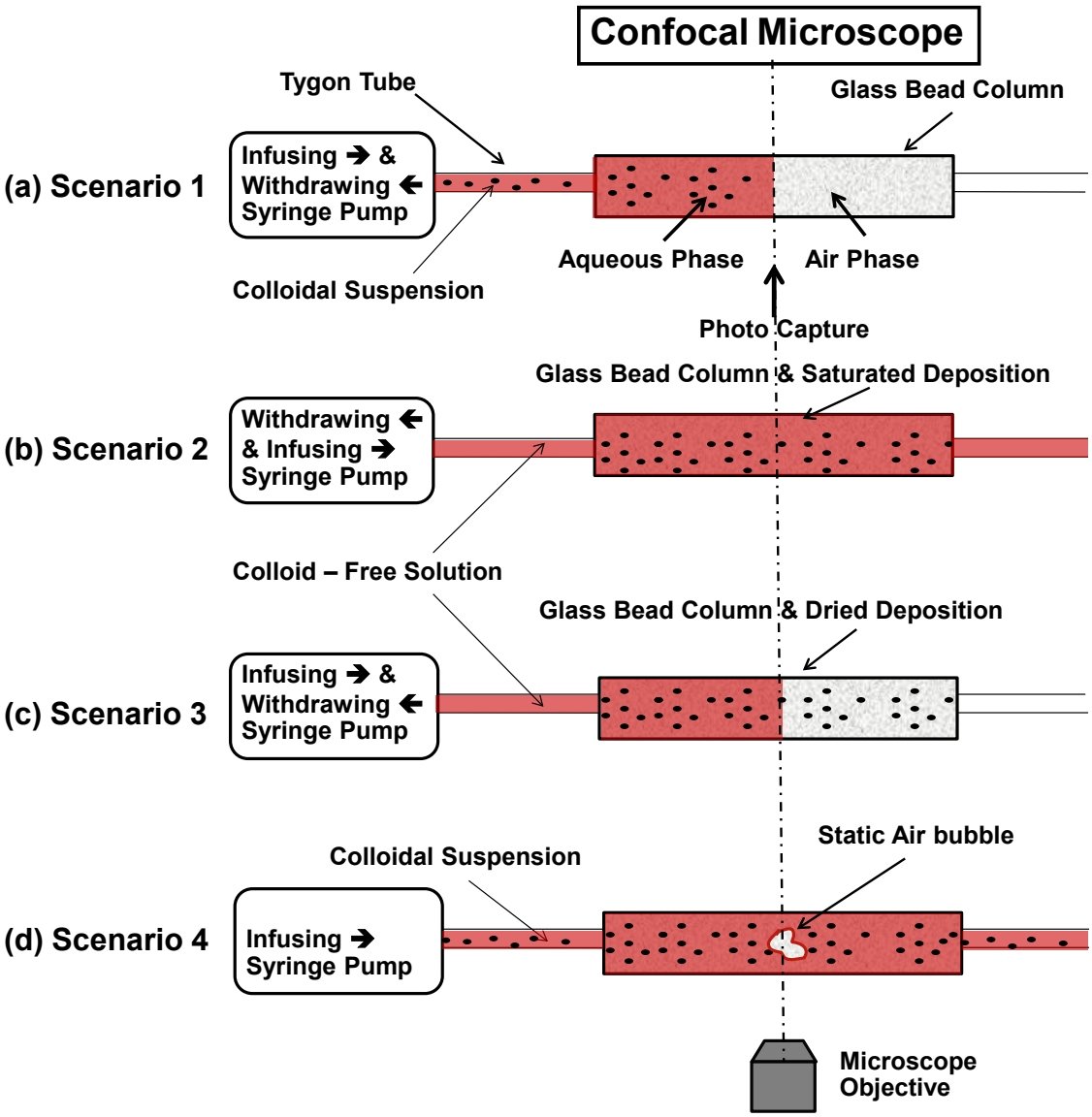

Figure S2. Schematic of capillary fringe fluctuation experiments under a confocal microscope: (a) Scenario 1: colloids suspended in aqueous phase; (b) Scenario 2: colloids attached to the glass beads in an initially wet porous medium; (c) Scenario 3: colloids attached to the glass beads in an initially dry porous medium; (d) Scenario 4: colloids suspended in aqueous phase in presence of a static air-water interface. The arrows in the syringe pump show the direction of infusing and withdrawing aqueous solution or colloidal suspension.

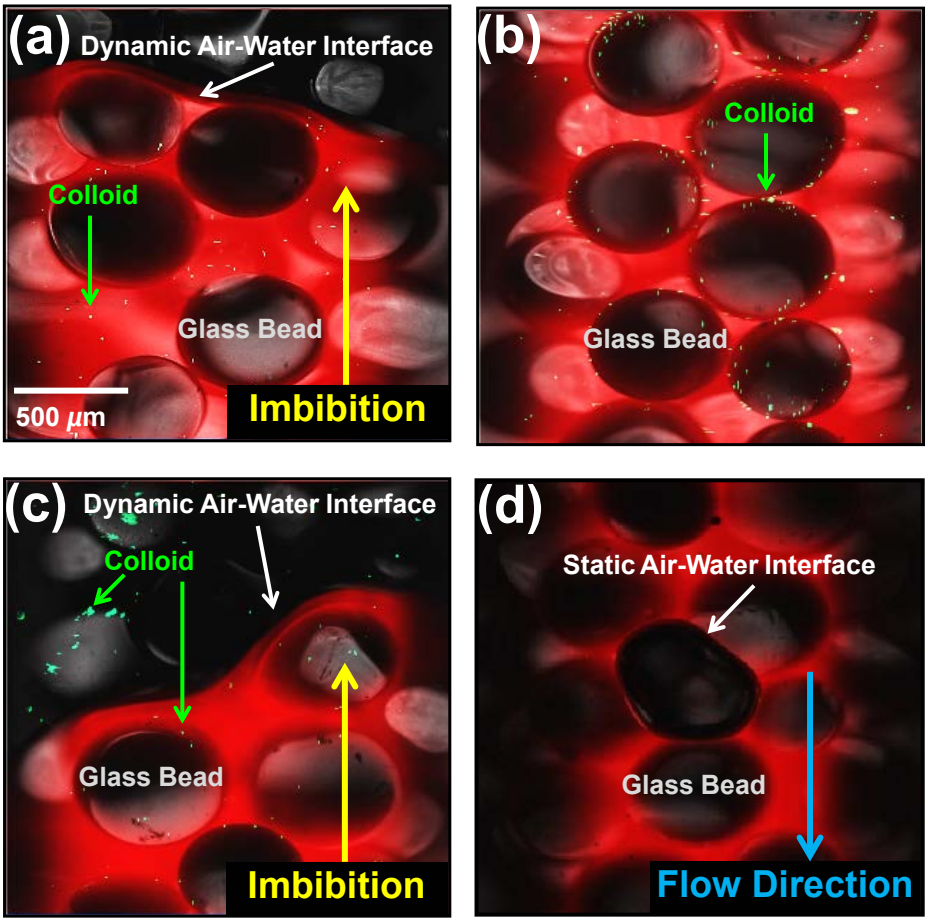

Figure S3. Confocal images of three initial conditions: (a) Scenario 1: colloids suspended in aqueous phase; (b) Scenario 2: colloids attached to the glass beads in an initially wet porous medium; (c) Scenario 3: colloids attached to the glass beads in an initially dry porous medium; (d) a static air-water interface. Yellow and blue arrows indicate the direction of imbibition and drainage fronts, respectively. (Scale bar: 500 μm)

(Note: this is a color figure)

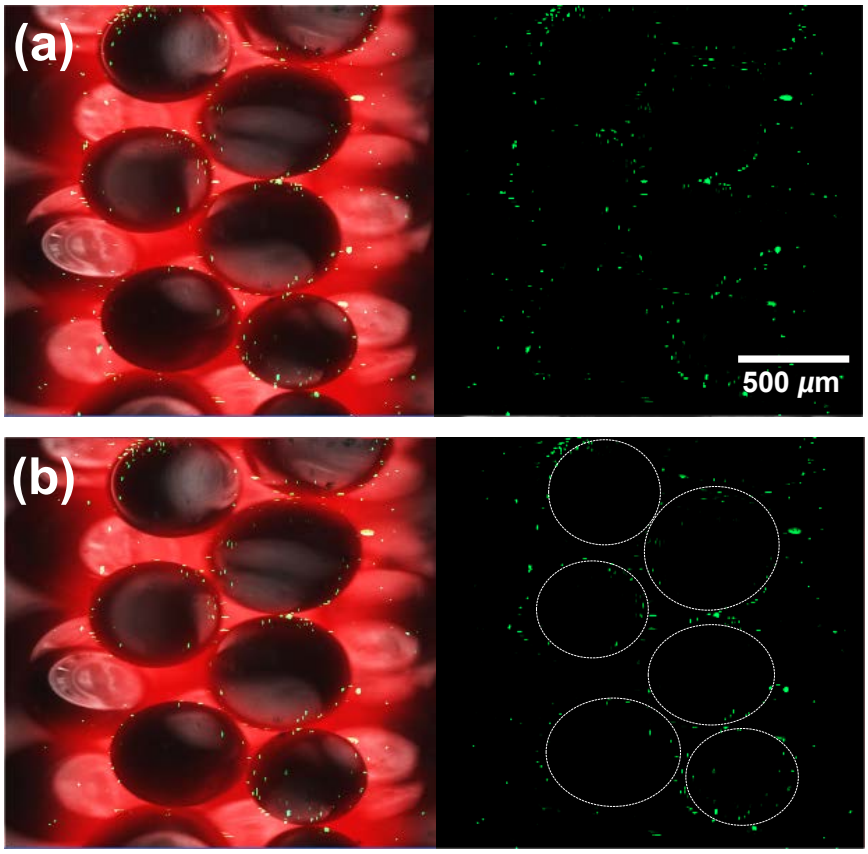

Figure S4. Confocal spilt images of initially wet deposited carboxylate-modified colloids on glass bead surfaces from Scenario 2: (a) before and (b) after flushing with a colloid-free solution for 10 min. The right column for (a) and (b) shows only colloid information. The white ovals in (d) indicate the positions of glass beads.

(Note: this is a color figure)

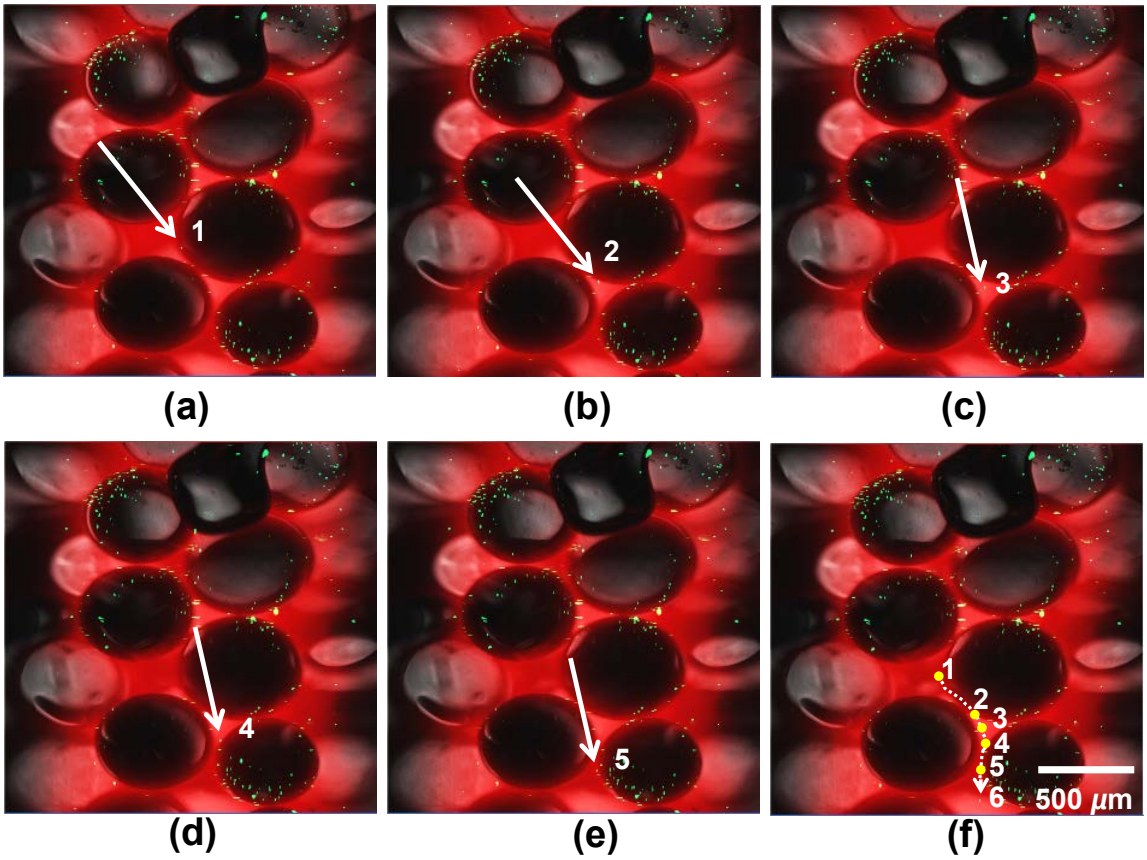

Figure S5. Positions and trajectory of carboxylate-modified colloids transported from one glass bead surface to another (Scenario 2). White arrows indicate the position of the colloid of interest. Highlighted yellow dots also represent the position where the colloid passes by. These figures are in a chronological sequence, taken at time = 0, 28, 32, 34, 48, and 54 s.

(Note: this is a color figure)

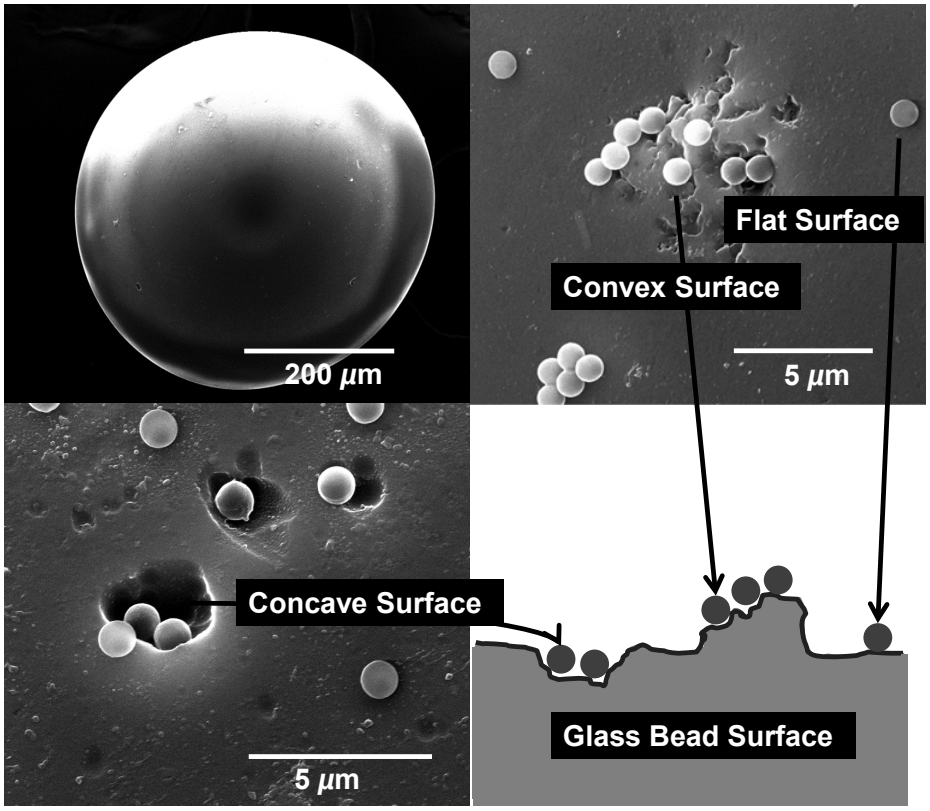

Figure S6. Scanning electron micrographs of a glass bead and deposited colloids showing colloids deposited at convex, concave, and flat topography.

Literature Cited

(1) Hiemenz, P. C.; Rajagopalan, R. *Principles of Colloid and Surface Chemistry*, 3rd ed.; Marcel Dekker: New York, 1997.