Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supplementary Information

Modulating photothermocapillary interactions for logic operations at the air-water interface

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Fabrication of Hydrogel nanocomposite disks (HND)

Chemicals: Azobisisobutyronitrile (AIBN), Poly-(vinyl alcohol) (PVA, 13 – 23 kg/mol, 87-89% hydrolyzed), diethylene glycol, gold chloride trihydrate, 1-propanol, and 4-methyl-2-pentanone (4MP) were purchased from Aldrich and used as received. *N*,*N*-diethylacrylamide (DEAM) and acrylic acid (AAc) were purchased from TCI America, and inhibitors were removed by passage through basic alumina. 1,4-dioxane was purchased from Thermo Fisher Scientific. Benzophenone acrylamide (AAmBP) and rhodamine B methacrylate (RhBMA) were prepared following procedures from literature [1,2].

Copolymer synthesis

We synthesized poly(diethylacrylamide-co-*N*-(4-benzoylphenyl)-acrylamide-coacrylic acid) (PDEAM) following an established protocol. Briefly, DEAM (3.0 g), AAmBP (0.45 g), AAc (0.037 g), RhBMA (0.01 g), and AIBN (0.01 g) were dissolved in 1,4-dioxane (20 mL) and added to a sealed vial. The vial, while protected from light, was kept at 80°C in inert atmosphere for 20 h, and then cooled to room temperature. The resulting polymer solution was precipitated into hexane and dried under vacuum.

Photolithography

We fabricated the HNDs using a two-step photolithographic method as reported previously [2,3]. First, we prepared a sacrificial layer of PVA on a Si wafer by spin coating 4 wt.% aqueous PVA solution at 3,000 rpm for 60 s. Then we prepared a copolymer solution to cast on the Si wafer. First, 50 mg of the PDEAM copolymer was dissolved in 500 µL of 1-propanol solution in a glass vial followed by sonication for 15 minutes. A stock solution of 1-propanol with diethylene glycol (DEG) was prepared by dissolving 100 µL of DEG in 7.5 mL of 1-propanol. Next, we dissolved 12-14 mg of gold salt ($AuCl_3 \cdot 3H_2O$) in 750 µL of the DEG/propanol mixture. The gold salt solution was then mixed with the copolymer solution and filtered through a 0.45 µm PTFE membrane.

A small volume of the resultant solution (30 - 35 µL) was then drop cast onto the PVA-coated Si wafer (1 cm × 1 cm) and dried for 12-24 h in a closed dark jar. To pattern the dried polymer film, we transfer the Si wafer to a microscope stage and expose it to patterned UV light (365 nm, 0.17 W/cm^2, 60 s) through an objective lens using a digital micromirror device (DMD) array (Texas Instruments DLP LightCrafter 6500 Evaluation Module). This patterning step crosslinks the polymer film in the exposed circle-shaped areas. We then performed another photo-exposure (400 nm, 2.0 W/cm^2, 700 s) to cause photocatalytic reduction that forms Au NPs inside the circular crosslinked polymer regions. Following the two exposures, we removed uncrosslinked polymers and unreacted salts by immersing the sample in a 9:1 (volume) mixture of 4MP : hexane for 2 - 2.5 min, and then by washing it in hexane for 30 s.

Marangoni trapping experiments

We immersed the Si wafer in ultrapure water (purchased from Fisher Scientific) to dissolve the sacrificial layer and to release the HNDs. We performed this procedure in a sterile petri dish (Fisher scientific, FB0875713A). After dissolving, we transferred the HNDs to another petri dish filled with fresh ultrapure water two times to remove any residual PVA or other impurities that affect the surface tension of water. We placed the petri dish with floating HNDs on the translational stage of an inverted microscope (Nikon

ECLIPSE Ti) equipped with a white light source (Lumencor Spectra light-emitting diode) and the DMD array. The experiments were performed by illuminating the HNDs with patterned light of intensity typically in the range of 0.6 – 1.3 W/cm^2. To limit the effects of spatial nonuniformity of the white light beam, we first measured the 2D intensity profile without modulation (Figure S1a) from the image collected by an sCMOS camera (Hamamatsu ORCA Flash) connected to the optical microscope. We then prepared a black and white 'speckle' pattern wherein each pixel is assigned to be "ON" (white) with a probability that is inversely proportional to the local intensity of the light source. Following this procedure, the modulated intensity profile is nearly uniform across the illuminated region (Figure S1b).

Visualizing thermocapillary flow

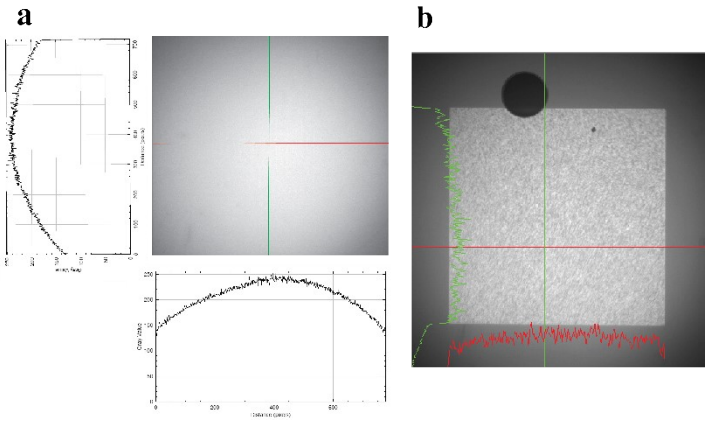

Figure S1 intensity profile (a) before, and (b) after modulation to reduce the spatial variation in light intensity.

Colloidal polystyrene microparticles (purchased from Thermo Fisher Scientific, CML latex beads) with a diameter of 5.9 µm was mixed with the water to visualize the thermocapillary flow, as shown in Figure S2

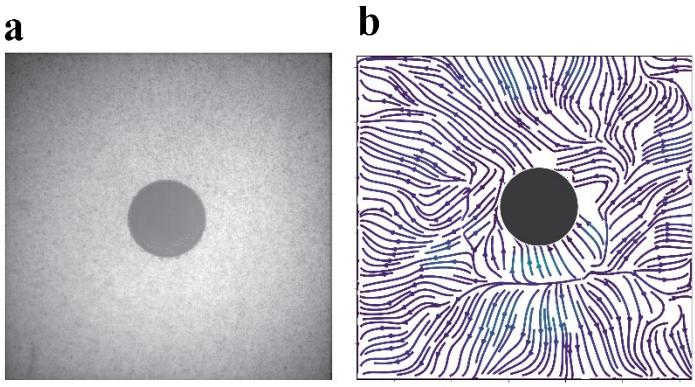

Figure S2 Thermocapillary flow around one particle in a trap. (a) Image of a particle in a trap in an aqueous solution mixed with tracer colloidal beads. (b) Thermocapillary flow around the particle, the direction of which is shown by the arrows. The flow generally points radially outward, away from the particle.

and S3. Particle image velocimetry algorithm was implemented to determine the direction of the flow.

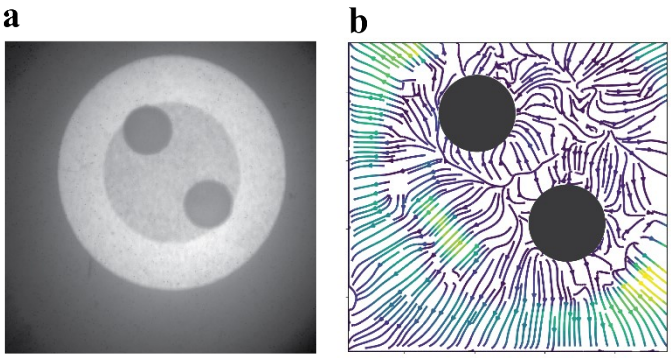

Figure S3 Thermocapillary flow around two neighboring particles (a) Image of two neighboring particles confined in a dimly illuminated region. (b) Thermocapillary flow around each particle points radially outward, causing a repulsive force on the neighboring particle.

Long-ranged repulsive interaction between two HNDs

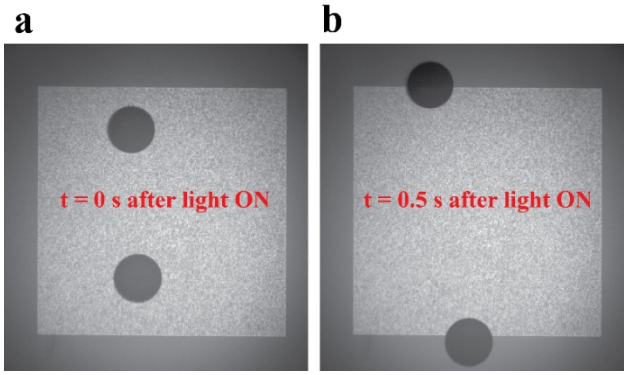

Figure S4 Initial separation distance between the two HNDs are set to be 3 times larger (1.1 mm) than the individual particle diameters. The particles experience long-ranged repulsive interaction and therefore move to the opposite sides of the frame within 0.5 s after illumination.

Modeling repulsive interactions between HNDs

We solved the coupled differential equations below to model particle displacements under thermal repulsion that originates from the Marangoni force.

Particle 1:
$$\ddot{x}_1 = \frac{1}{m_{eff}}\left(-\eta_{eff}\dot{x}_1 - \frac{\Lambda_{th}}{{d_{sep}}^2}\right)$$

Particle 2:
$$\ddot{x}_2 = \frac{1}{m_{eff}}\left(-\eta_{eff}\dot{x}_2 + \frac{\Lambda_{th}}{{d_{sep}}^2}\right)$$

Where m_{eff} and η_{eff} are effective mass and effective viscous drag coefficient, where we use values independently determined in our prior work by modeling the behavior of oscillatory partciles[3], d_{sep} is the

separation distance between the two particles, and $\Lambda_{th} = \frac{\gamma_T Q a^2}{2\pi k}$ is the thermal coupling co-efficient described in the main text.

In Figure S5 (a), we show the displacement of individual particles (x_1 and x_2: blue and red solid lines, respectively) achieved by numerically solving the coupled differential equations. We compare these results with experimentally measured displacements (blue and red open circles) and good agreement at short timescales, corresponding to separation distances relevant to the experiments throughout the manuscript. Deviations are seen at longer timescales, especially in the case of particle 1; their origin is unclear at present, but we speculate could arise from the increasing importance of fluid flows and resulting hydrodynamic effects (ignored here) at larger particle separations.

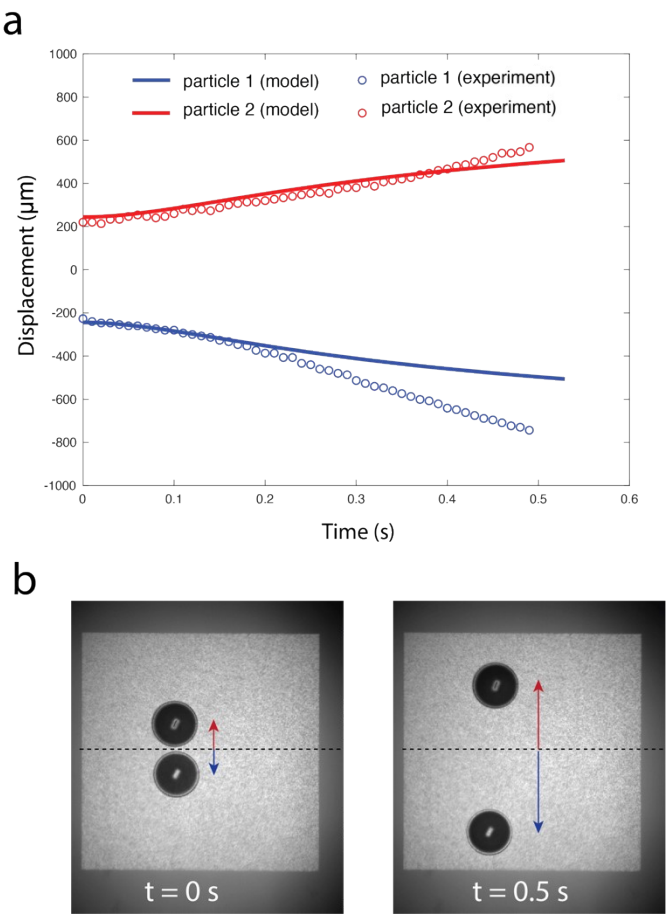

Figure S5 (a) Particle displacement over time under Marangoni thermal repulsion. Solid lines and open circles represent results from modeling and experiment, respectively. (b) Images of particle repulsion experiment used for the data presented in (a). Blue and red arrows show the displacement of the two particles at different times (t= 0 s and t = 0.5 s).

Failed operation of AND gate with (1,1) input

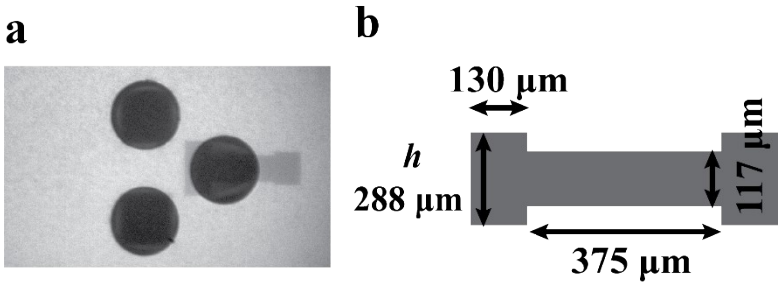

Figure S6 The AND gate fails to operate properly when both inputs are at 1 if the gate is designed with too large of a trap.

Supplementary movies:

Movie S1: One particle (located at the center of the frame) remains trapped as the stage moves from left to right (shown by the movement of the other four particles). Scale bar 500 µm.

Movie S2: Repulsion between two particles in an illuminated region without the presence of any trap, movie played slower (0.2x) than real time. Scale bar 500 µm.

Movie S3: Demonstration of OR logic gate for different inputs, movie played slower (0.2x) than real time. Scale bar 300 µm.

Movie S4: Demonstration of AND logic gate for different inputs, movie played slower (0.2x) than real time. Scale bar 300 µm.

Movie S5: Demonstration of NOT logic gate for different inputs, movie played slower (0.2x) than real time. Scale bar 300 µm.

Movie S6: Stability of trapped particles arranged in ring geometry for N=2,3,4,5,6. The diameter of the ring is slowly reduced to find at which neighboring distance the arrangement becomes unstable. Scale bar 500 µm.

References:

1. Kim, J., Hanna, J. A., Byun, M., Santangelo, C. D. & Hayward, R. C. Designing Responsive Buckled Surfaces by Halftone Gel Lithography. *Science* **335**, 1201–1205 (2012).
2. Kim, H. *et al.* Light-Driven Shape Morphing, Assembly, and Motion of Nanocomposite Gel Surfers. *Adv. Mater.* **31**, 1900932 (2019).
3. Kim, H. *et al.* Coupled oscillation and spinning of photothermal particles in Marangoni optical traps. *Proc. Natl. Acad. Sci.* **118**, e2024581118 (2021).