Insights into mechanisms of capillary assembly

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1 Electronic Supplementary Information

PDMS Template

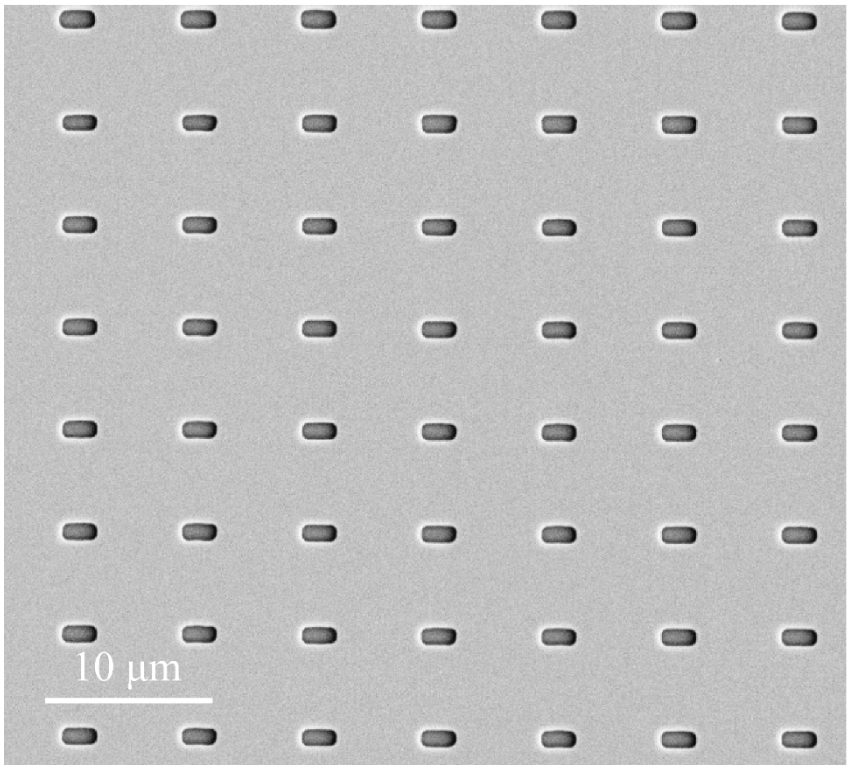

Figure S1. SEM image of cuboid-like templates. Various lateral dimensions and depths are prepared for the different experiments that are detailed in the manuscript.

Visualization of assembly by confocal microscopy

Movie 1. A confocal movie of the assembly process. The pairs of brighter particles within the particle accumulation zone (AZ) illustrate that the particles are already inside the traps before the arrival of the meniscus. Only one particle is trapped when the meniscus moves away.

First-order estimate of the deformation of the PDMS template

In the Figure 4 of the manuscript we indicate the possibility that the PDMS template is deformed by the force F_{cy} and by adhesive Van der Waals forces when particle 2 is pressed downwards and is in close contact with the substrate. By modelling the contact with the Hertz model (i.e. sphere on flat surface), we can estimate the vertical displacement *m* on the PDMS template.

$$F = \frac{4}{3} \cdot E^* \cdot \sqrt{r \cdot m^3} \qquad (Hertz\ model)$$

With $\frac{1}{E^*} = \frac{1 - v_S}{E_S} + \frac{1 - v_F}{E_F}$, where V_s and V_F are the Poisson's ratios for the substrate and the indenter, respectively and E_s and E_F are the Young's moduli for the substrate and the indenter, respectively. Then one can derive the deformation m by solving the equation below:

$$\frac{4}{3} \cdot E^* \cdot \sqrt{r \cdot m^3} = F_{cy} + \frac{H(rD + 2mr)}{6D^3} \qquad (1)$$

The deformation receives two contributions: one is from the vertical component of the capillary force F_{cy}, and the other is from Van der Waals forces $\frac{H(rD + 2mr)}{6D^3}$,[1] with *H* the Hamaker constant, *r* the particle radius and *D* the distance between the particle and the template. All the values for the calcuation can be found in the Table/Appendix S1. The estimated deformation for both particles with the radius of 450 nm and 500 nm is shown in Figure S2. Figure S2a shows that the vertical displacement *m* varies with the pinning angle for the given surface tension of 22 mN/m corresponding to the solvent S1, as reported in Table 1 of the mani text. Figure S2b shows that the vertical displacement *m* varies with the reduced depth of the traps (*d* - *r*)/*r* for the same surface tension. For the data in Figure S2b, the pinning angle is approximated to be equal to the receding angle, which is 30° for the surface tension of 22 mN/m. *D* is set to be 1 nm in the calculations, assuming that the particle is pressed down by the capillary force into close contact with the template. The displacment *m* is in the range of a few tens of nanometers.

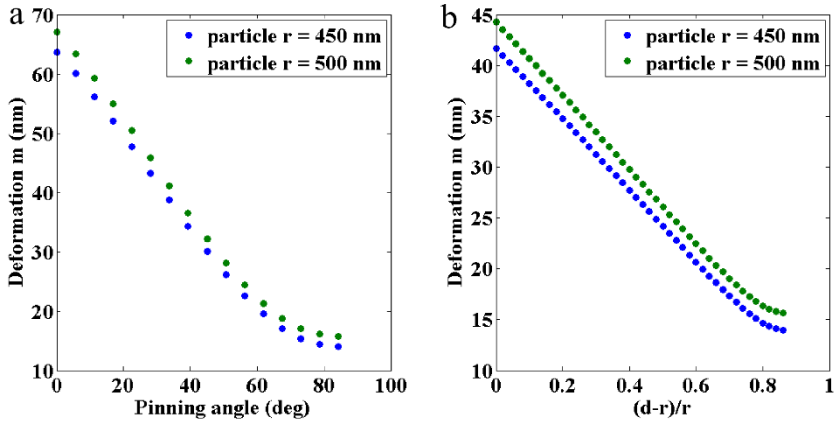

Figure S2. First-order estimation of the vertical displacement *m* for both types of particles (radius: 450 nm and 500 nm). a): the vertical displacement *m* as a function of pinning angle. b): the vertical displacements *m* as a function of the reduced depth *(d-r)/r*.

First-order estimate of the opposing force (osmotic pressure + adhesion)

We use an approach based on the Wigner-Seitz cell to calculate the osmotic pressure in the highly concentrated suspension present in the AZ.[2, 3] In this approach, the osmotic pressure can be regarded as the sum of three contributions: entropic interactions, Van der Waals interactions, and electrostatic interactions. The equations below describing those interactions are found in literature.[2, 3] All the values for the calcuation can be found in the Table/Appendix S1.

Entropic interactions Π_{en}:

$$\Pi_{en} = \frac{3kT}{4\pi r^3} \cdot \phi \cdot \frac{1 + \phi + \phi^2 - 0.67825\phi^3 - \phi^4 - 0{,}5\phi^5 - X\phi^6}{1 - 3\phi + 3\phi^2 - 1.04305\phi^3} \qquad (2)$$

With $X = 6.2028exp^{[(\phi cp - \phi) \cdot \{7.9 - 3.9(\phi cp - \phi)\}]}$, $\phi cp = \frac{\sqrt{2}}{6}\pi$, r is particle radius, and ϕ is the volume fraction.

Van der Waals interactions Π_{VdW}:

$$\Pi_{VdW} = -\frac{Z_n \cdot H}{48\pi r^3} \cdot \frac{\phi^3}{\left(\phi cp - \phi cp^{\frac{1}{3}}\phi^{\frac{2}{3}}\right)^2} \qquad (3)$$

Where Z_n is the number of the nearest particles (12 in hexagonal packing). H is the Hamaker constant.

Electrostatic interactions Π_e:

$$F_e = \frac{1}{3} \cdot S_{cell} \cdot N_A \cdot c_0 kT \left(\cosh \frac{ze\Psi_{r_{cell}}}{kT} - 1 \right) \qquad (4)$$

With r_{cell} is the radius of Wigner-Seitz cell: $r_{cell} = (2r + D_1)(\frac{3}{4\pi\sqrt{2}})^{1/3}$. The lattice constant in the cystal is $2r + D_1$. D_1 is the inter-particle distance. Then the osmotic pressure contribution from electrostatic forces can be derived as:

$$\Pi_e = F_e \cdot \frac{\sqrt{6}}{S_h} = F_e \cdot \frac{\sqrt{6}}{2\sqrt{3}(r + 0.5D_1)^2} \qquad (5)$$

With S_h is the effective area occupied per one particle in the crystal[2] ($S_h = 2\sqrt{3}(r + 0.5D_1)^2$). Π_e can be calculated once ψ_{rcell} is known. We calculated it according to the solution from reference [2].

The total osmotic pressure can then be written as:

$$\Pi_{osmotic} = \Pi_{en} + \Pi_{VdW} + \Pi_e \qquad (6)$$

Since the entropic pressure is negligible in this case using microspheres, the osmotic pressure can be approximately converted into the force:[2]

$$F_{osmotic} = \Pi_{osmotic} \cdot \frac{S_h}{\sqrt{6}} \qquad (7)$$

The adhesion between the particle and the template is generated by Van der Waals attraction. The Van der Waals force here is estimated based on the model of sphere on flat surface.[1]

$$F_{adhesion} = -\frac{Hr}{6D^2} \qquad (8)$$

H is the Hamaker constant. The Hamaker constant (1.3 x 10^{-20} J) for PS - PS is used in calculation of PS - PDMS attaction in the absence of the specific value of H in for the latter materials pair in the literature. D is the distance between the particles and the template.

In a closely packed AZ with a high osmotic pressure (Figure S3a and b), we assume that D is equal to the interpacticle distance in the AZ. Therefore, the force due to the osmotic pressure and the adhesion force can be plotted with the volume fraction of the particles in the AZ for both particles with the radius of 450 nm and 500 nm (Figure S3c and d). In the volume fraction interval 0.6 – 0.7, the total opposing force on particle 1 is in the range of 0.05 nN – 0.1 nN.

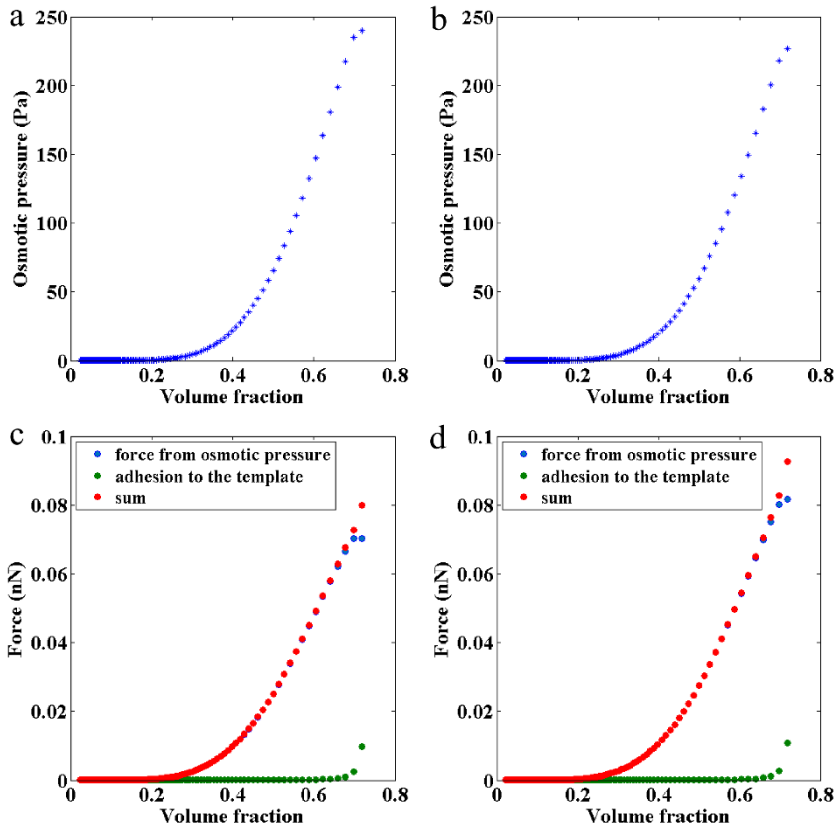

Figure S3. Osmotic pressure is plotted with the volume fraction of the particles in AZ, for particles with a radius of 450 nm (a) and 500 nm (b), respectively. Opposing force from the osmotic pressure and the adhesion between the particles and the template, is plotted with volume fraction of the particles in AZ, for particles with a radius of 450 nm (c) and 500 nm (d), respectively.

Effects from the depth of the traps and the surface tension

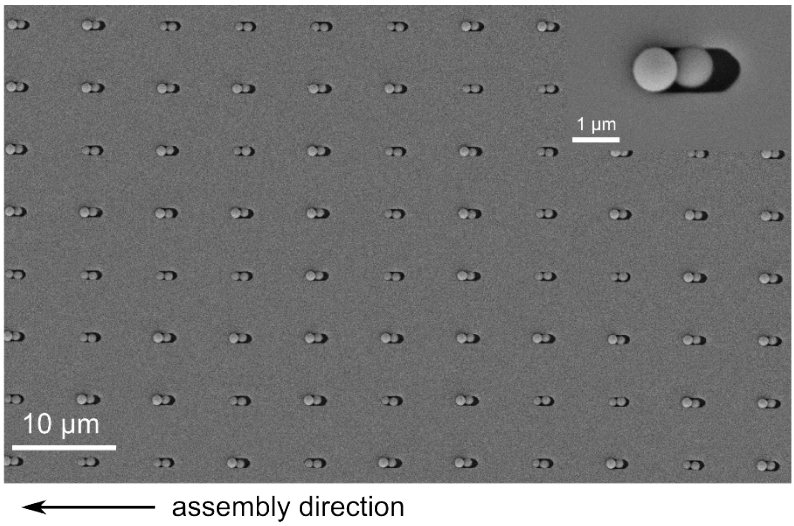

Figure S4. SEM image of assembled particles in the cuboid-like traps. The particles are 450 nm in radius. The depth of the traps is 612 ± 5 nm. The inset shows that two particles are assembled in the trap, with one particle staying on top of the other.

Formation of asymmetric dimers

Movie 2. A confocal movie of the assembly process elucidating the formation of the asymmetric dimers. The blue particles are assembled previously. In the second assembly, the red particles are trapped next to the blue particles. The blue particles stick to the template during the second assembly.

Symbol	Name	Value for calculation
r	Particle radius	500, 450 nm
H	Hamaker Constant	$1.3 \times 10^{(-20)}$ J
N_A	Avogadro constant	6.022×10^{23} mol^{-1}
κ^{-1}	Debye length	100 nm
I	Ionic strength in mol/m^3	0.01 mol/m^3
c_o	Ion concentration in mol/m^3	0.01 mol/m^3
e	elementary charge	1.602×10^{-19} C
ε	dielectric constant of the solvent	80 (value from water at 20°C)
ε_0	vacuum permittivity	8.854×10^{-12} CV^{-1}m^{-1}
ζ	Zeta potential	60 mV
z	Charge number of an ion	1
D_{ohp}	Distance from Helmholtz outer plane to the particle surface	$0.55 \times 10^{(-9)}$ m

γ_{lg}	Liquid-gas interfacial tension	22 mN/m
E_s	Young's modulus of PDMS	12 MPa
E_F	Young's modulus of Polystyrene	3300 MPa
v_s	Possion's ratio of PDMS	0.5
v_F	Possion's ration of Polystyrene	0.35

Table/Appendix S1. Values for the calculations.

Reference

1 S. Alvo, P. Lambert, M. Gauthier and S. Régnier, *J. Adhes. Sci. Technol.*, 2010, **24**, 2415–2428.
2 W. R. Bowen and F. Jenner, *Chem. Eng. Sci.*, 1995, **50**, 1707–1736.
3 P. Bacchin, D. Si-Hassen, V. Starov, M. . Clifton and P. Aimar, *Chem. Eng. Sci.*, 2002, **57**, 77–91.