Electronic Supplementary Material (ESI) for Soft Matter

Supplemental Information

1. Interferometry

A Michelson interferometer configured in our laboratory, shown in Fig. S1, is used to characterize the shape of the interface around a microparticle. Briefly, light from a light emitting diode (λ_{LED} = 532 nm) is filtered by a narrow-band-pass filter (not shown) of bandwidth \Delta\lambda = 3 nm to give a coherence length of about 40 microns in air. The light beam is then collimated before it is split into two orthogonal beams by a 50/50 beam splitter. One beam is projected onto a reference mirror using a 10x objective. The other beam is projected onto the sample using an identical 10x objective, and it is reflected off the air-water interface. The two reflected beams interfere as they recombine through the beam splitter. The resulting interferograms are recorded on the camera sensor.

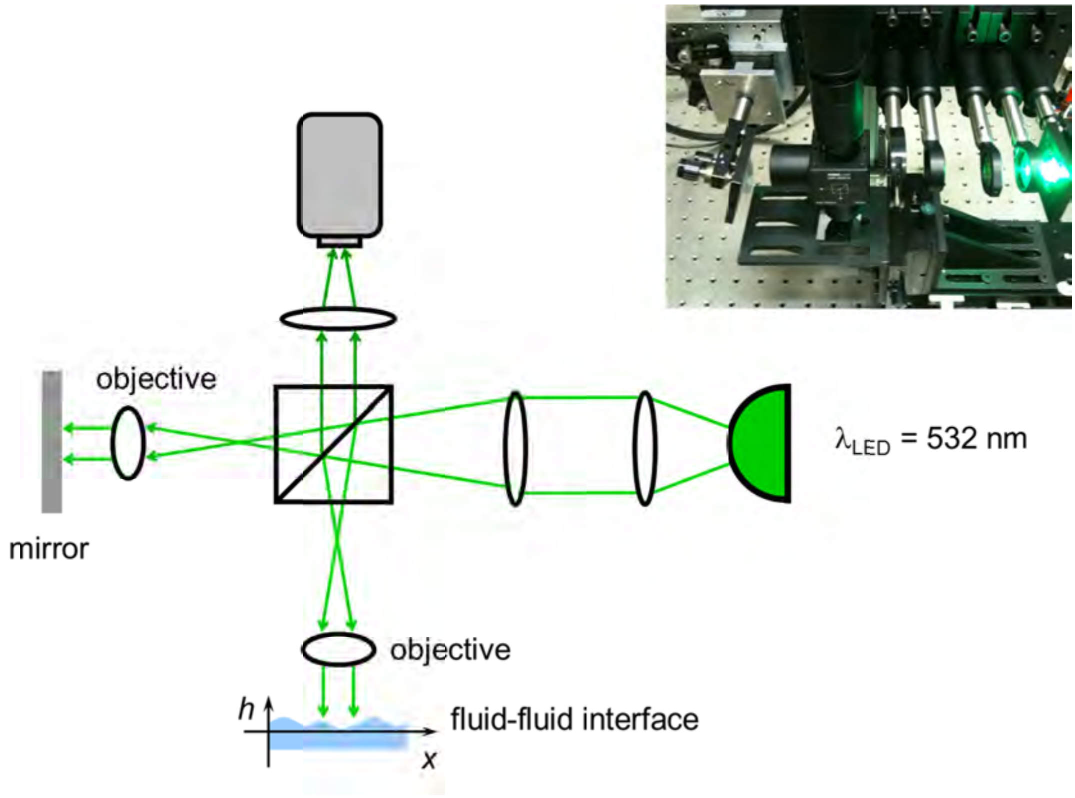


Figure S1. Schematic of the microinterferometer. Inset: An image of the instrument

2. Analytical Solution for Planar Microparticles with Corrugations of Differing Wavelength

Here we adopt the simplified model proposed by Lucassen[1] to understand capillary interaction energies between two microparticles close to contact. The particles are modeled as two vertical, infinitely long, parallel plates partially immersed in a liquid phase. The particles are separated by a distance *L*. The height of the liquid vapor interface is given by $z=h(x,y)$. The contact line where

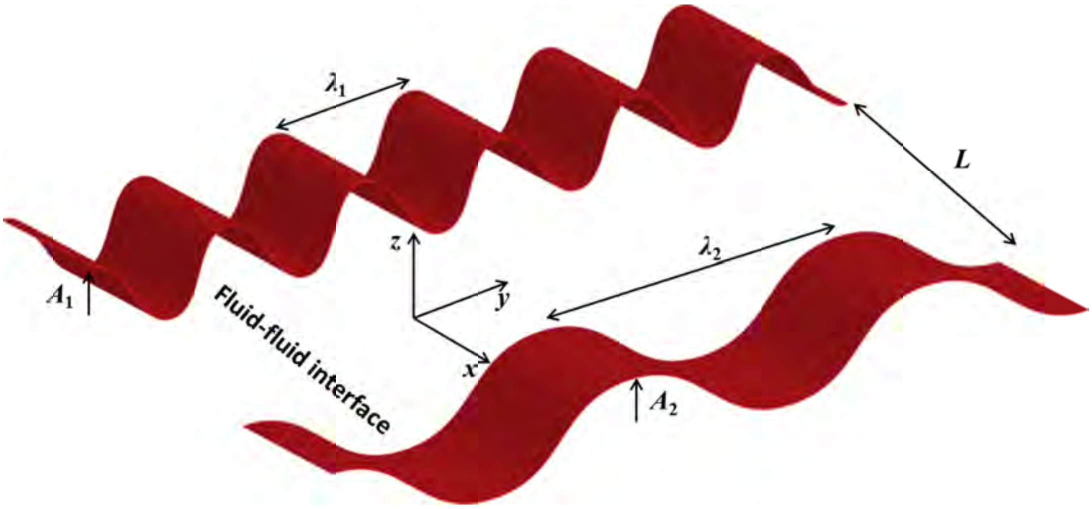


Figure S2. Schematic of Lucassen's model particles and the fluid-fluid interface between them. The interface is in the *x*-*y* plane and is pinned at the sinusoidal corrugations of the model particles.

plate, fluid and vapor meet is pinned on each plate, and has a sinusoidal shape (See Fig. S2). The area of the liquid interface between the particles can be described by

$$A = A_1 \frac{\sinh\left[k_1\left(\frac{L}{2}-x\right)\right]}{\sinh(k_1 L)}\cos(k_1 y) + A_2 \frac{\sinh\left[k_2\left(\frac{L}{2}+x\right)\right]}{\sinh(k_2 L)}\cos(k_2 y+\phi) \qquad (1.1)$$

where ϕ denotes the phase angle between corrugation of amplitudes A_1 and A_2, wave number k_1 and k_2 and the plates are located at $x = L/2$ and $x = -L/2$ respectively. For small amplitudes, the interaction free energy between the particles due to the surface deformation is:

$$E = \gamma S = \gamma \iint \left[\frac{1}{2}\left(\frac{\partial A}{\partial x}\right)^2 + \frac{1}{2}\left(\frac{\partial A}{\partial y}\right)^2\right] dxdy \qquad (1.2).$$

Lucassen evaluated this energy for the case where $k_1=k_2$ for arbitrary ϕ. Here, we evaluate this expression for arbitrary wavenumber, and find the interaction energy to be:

$$E=\frac{2A_1A_2k_1k_2\cos(\phi)\gamma}{\sinh(k_1L)\sinh(k_2L)}\frac{\left(\begin{array}{l}\sin\left(\frac{k_2y_o}{2}\right)\cos\left(\frac{k_1y_o}{2}\right)\sinh(k_2L)\\-\cos\left(\frac{k_2y_o}{2}\right)\sin\left(\frac{k_1y_o}{2}\right)\sinh(k_1L)\end{array}\right)}{\left(k_1^2-k_2^2\right)}$$
$$+\frac{A_1^2k_1}{8\sinh^2(k_1L)}\left(2L\sin(k_1y_o)+y_o\sinh(2k_1L)\right) \quad (1.3)$$
$$+\frac{A_2^2k_2\cos(2\phi)}{8\sinh^2(k_2L)}\left(2L\sin(k_2y_o)+y_o\sinh(2k_2L)\right)$$

for x = [-L/2, L/2] and y = [-y_o/2, y_o/2]. In Fig. S3 we plot ΔE, the energy difference between particles at finite separation distance and particles at an infinite distance from each other for $k_1=\frac{2\pi}{0.6};k_2=\frac{2\pi}{0.36}$, $A_1=A_2=0.1$, $y_o=2.7$ (i.e., w = 2.7), $\phi=0$, corresponding to interactions between aligned model particles with $\lambda_1=0.6;\lambda_2=0.36$.

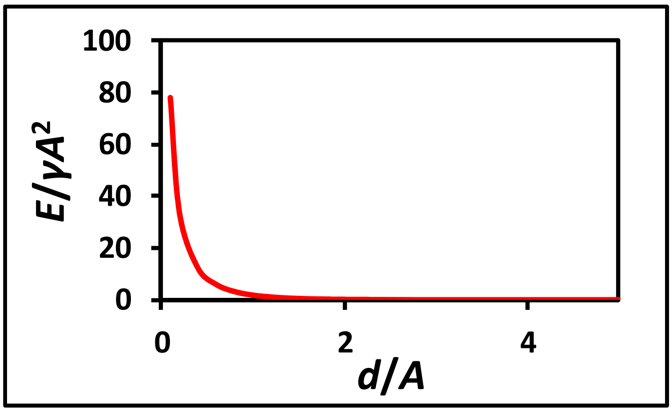


Figure S3. Normalized energy against distance of separation between the corrugated ends of the microparticles according to Eq. 1.3

3. Microparticles at Oil-Water Interface

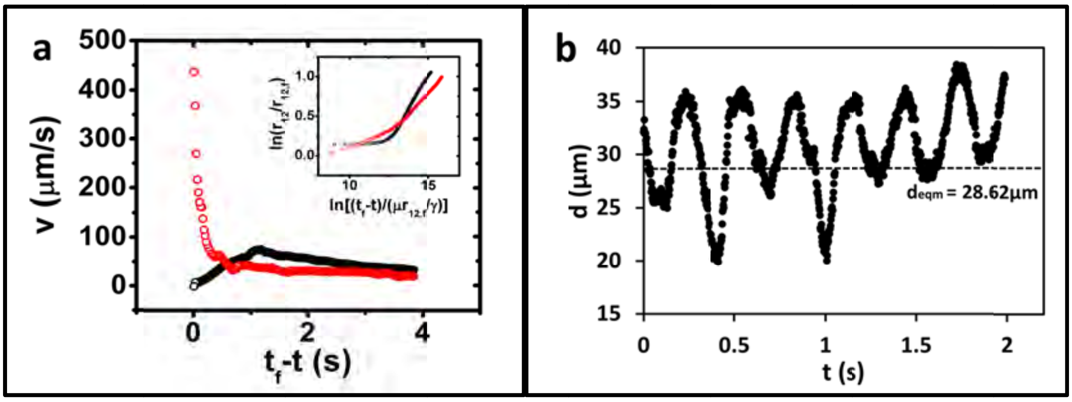
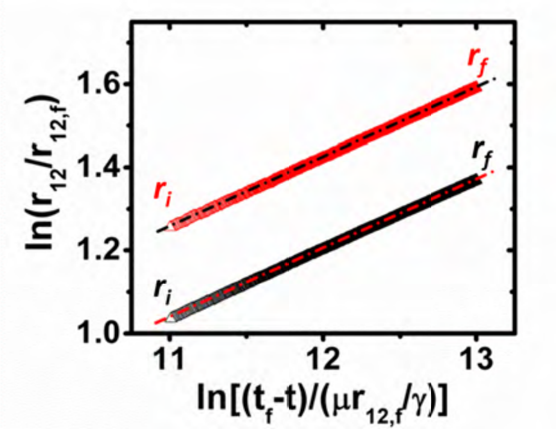


Figure S4. (a) Rate of approach for a pair of matching corrugated microparticles (λ = 36 μm; red-colored symbols in both the main figure and inset) and a pair of differing corrugated microparticles λ = 36 μm and 60 μm; black-colored symbols). Inset: Trajectories of the same pairs of particles over time. (b) End-to-end separation distance between two microparticles with differing wavelengths (λ = 36 μm and 60 μm) on an unbounded oil-water interface, when the pair was subject to forced perturbations in the direction of the major axis.

4. Estimating H_p from the velocity-time graph



5.

Figure S5. Normalized center-to-center separation distance versus normalized time to contact for microparticles with matching wavelengths (red triangles) and with differing wavelengths (black triangles). The data were extracted from Figure 4(a) in the manuscript. r_f and r_i are the final and initial separation distances between the microparticles. The dashed lines overlaying the data points have slope of -1/6.

In order to determine the actual deflection of the contact line around the corrugated microparticle, H_p, we extracted the data of center-to-center separation distance against time from Figure 4(a) for particle pairs with matching wavelengths (red triangles) and differing wavelengths (black triangles). The data points extracted represent the range over which the interactions between the microparticles are entirely owing to the capillary quadrupoles, i.e., the slope of the logarithmic graph is exactly -1/6 (-0.1666). The dashed lines in Fig. S5 are guide lines with -1/6 slopes.

For two particles that are in motion at fluid interfaces, the sum of the viscous drag on the particle, F_{drag} and the capillary force between two quadrupoles, F_{cap} is zero.

$$F_{drag} + F_{cap} = 0 \tag{1.4}$$

where $F_{drag} = 6\pi\mu a v C_D$, μ is the viscosity at the fluid interface, a is the characteristic length of the particle, v is the velocity and C_D is the unknown drag coefficient of order unity. As a result, between two reference positions on the interface, the sum of the dissipation energy due to viscous drag and the attractive quadrupolar interaction between the particles is also zero.

$$\Delta E_{diss} + \Delta E_{cap} = 0 \tag{1.5}$$

Here, $\Delta E_{diss} = 6\pi\mu a C_D \int_{r_i}^{r_f} v(r)dr$, r_f and r_i are the final and initial separation distances between the microparticles as shown in Fig. S5. The integral can be calculated with velocity data from Fig. 4(b) over the range of r_f and r_i.

From Fig. S5, r_f = 875.1 μm and r_i = 1222.5 μm for particles with matching wavelengths and r_f = 1095.5 μm and r_i = 1533.7 μm for particles with differing wavelengths. At the air-water interface, assuming C_D = 1, a = w = 270 μm, μ = 0.001 Pa·s (since the particles are mostly immersed in water), $\Delta E_{diss} = 1.78\times 10^8 kT$ for particles with matching wavelengths and $\Delta E_{diss} = 1.15\times 10^8 kT$ for particles with differing wavelengths.

Subsequently, capillary interaction energy due to quadrupoles is given by

$$\Delta E_{cap} = -12\pi\gamma H_p^{\,2}\cos\left(2(\phi_A - \phi_B)\right)\left(\left(\frac{a}{r_f}\right)^4 - \left(\frac{a}{r_i}\right)^4\right) \tag{1.6}$$

where γ is the surface tension, H_p is the amplitude of the quadrupole mode excited by the particle, φ_A and φ_B are the orientations of the particles on the interface.

At the air-water interface, γ = 0.072 mN/m. ϕ_A = ϕ_B = 0 for two particles that have their long axes aligned in tandem, we have H_p = 6.4 μm for particles with matching wavelengths and H_p = 8.0 μm for particles with differing wavelengths. The deflection of the interface is therefore approximately comparable to that in the experiment (5.0 μm).

Videos

1. Video for the formation of oblique assembly on unbounded oil-water interface (SI-M1).
2. Video for an elastic capillary bond on unbounded oil-water interface (SI-M2).
3. Video for formation of assembly between microparticles with out-of-phase corrugations. (SI-M3)
4. Particles with weakly differing widths, or with wavelengths comparable to the particle width can form angled assemblies, similar to the angled assemblies (capillary arrows) formed by ellipsoids of different aspect ratios. (SI-M4)

References

1. J. Lucassen, *Colloids and Surfaces*, 1992, **65**, 131-137.