Nanofluidic networks created and controlled by light

David A. Woods,[a] Christopher D. Mellor,[b] Jonathan M. Taylor,[c] Colin D. Bain[a]* and Andrew D. Ward[d]

[a] Department of Chemistry, Durham University, South Road, Durham DH1 3LE, UK

[b] Department of Chemistry, Oxford University, Mansfield Road, Oxford, OX1 3TA, U.K.

[c] Department of Physics, Durham University, South Road, Durham, DH1 3LE

[d] Lasers for Science Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon. OX11 0QX

*to whom correspondence should be addressed: e-mail c.d.bain@dur.ac.uk

Graphical Contents Entry: Optical tweezers have been used to create networks of micron-sized reservoirs of oil in water connected by stable threads of oil a few nanometres across and to pump liquid around the network.

Abstract: Nanofluidic networks have been fabricated in an oil-in-water emulsion. Micron-sized oil drops with ultralow interfacial tensions are connected by stable oil threads a few nm across. Lasers are used both to construct the nanofluidic network and to transport fluid from one drop to another. These networks form a platform for chemistry on the attolitre scale.

Microfluidic technology has reached a high level of sophistication over the past 20 years (*1*) but nanofluidic technology is still in its infancy (*2*). The best-developed approach to nanofluidics involves giant lipid vesicles that are immobilised on surfaces and then manipulated via micropipettes (*3,4,5*) Here we describe a radically different approach in which lasers are used to create and manipulate networks of oil droplets in water, connected by stable threads of oil of nanometric dimensions. Pumping of oil between the droplets is achieved entirely by light. These networks provide a platform for chemistry on the attolitre or single-molecule scale.

Droplets of oil in water can be readily trapped by a tightly focussed laser beam when the emulsion droplets are in the micron size range. Under normal conditions, the forces exerted by these optical traps ($k \sim 10^{-5}$ N m^{-1}) are orders of magnitude weaker than those due to surface tension ($\sigma \sim 10^{-2}$ N m^{-1}), which keeps the droplets spherical. Carefully chosen surfactants can be used to lower the oil-water surface tension to very near to a microemulsion phase transition, σ can reach values as low as 10^{-6} N m^{-1}.   At this point optical forces can compete with surface tension. We have shown that emulsion droplets with ultralow interfacial tensions can be deformed by optical tweezers into ellipses, triangles or squares as the number of traps is increased from two to three to four (*6*). Since this deformation can be achieved with oil drops composed of a polymerizable monomer, 'optical sculpting' offers a potential route into the fabrication of micron-sized rigid polymer objects.

If two optical traps are first superimposed in a single oil drop immersed in water and then gradually moved apart, the droplet deforms into a dumbbell and the neck between the two drops rapidly thins and appears to vanish even under a powerful optical microscope. Remarkably, this tenuous thread of oil connecting the two drops does not break: the two drops can be separated by large distances (>50 µm) and still these invisible threads remain intact.   Figure 1 shows a mother droplet connected to four daughter droplets; the nanothreads are too thin to be resolved by the microscope, but their presence can be inferred from the pinch points in the profiles of the droplets where the threads are attached. If one of the trapped droplets is released, it is rapidly drawn towards the parent droplet by

the surface tension acting around the perimeter of the thread (see Supplementary Video 1 in Supplementary Information). There is no discernable barrier to coalescence.
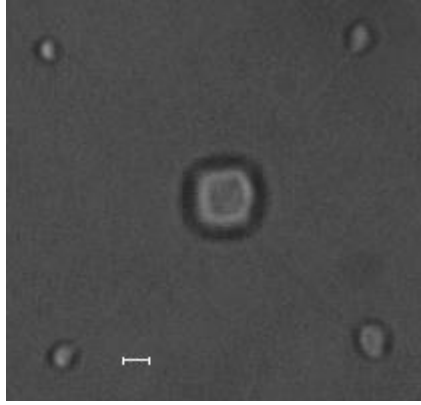

Figure 1. Four daughter droplets attached to a parent droplet by oil nanothreads < 100 nm thick. The scale bar is 2 μm long. A few drops of heptane were added to an aqueous solution of 0.05 M NaCl and 1.94 mM Aerosol OT (sodium 2-ethylhexyl sulfosuccinate) and dispersed by gentle shaking. The emulsion was held in a 100-μm deep temperature controlled cell, illuminated from above and observed through a water immersion objective (Leica HCX PL APO CS 63x/1.20 W CORR). A 1064 nm laser was focused through the same objective using acousto-optic deflectors to switch it rapidly between the different trap positions, effectively creating multiple simultaneous optical traps. Typical laser powers were 100–200 mW at the back aperture of the objective, shared between all the traps (*6*).

The persistence of the threads connecting the drops is surprising since cylindrical columns of liquid are not normally stable, but break up into string of spherical beads of lower surface area − a phenomenon famously studied by Rayleigh a century ago (*7*). On the nanometric scale, however, the resistance of an interface to bending provides a restoring force that opposes the thinning of a cylinder of liquid. The free energy, *G*, per unit length of a cylindrical surface is given by (*8*)

$$G = 2\pi R \left[\sigma + \frac{K}{2} \left(\frac{1}{R} - C_0 \right)^2 \right]$$

(1)

where R is the radius of the cylinder, σ is the surface tension, K is the bending modulus and C_0 is the spontaneous curvature of the interface. For the emulsion employed here, $C_0 = 0$ (9). Minimising the free energy then gives an expression for the radius of the thread:

$$R = \sqrt{K / 2\sigma} \qquad (2)$$

and for the free energy per unit length:

$$G = 2\pi\sqrt{2K\sigma} \qquad (3)$$

Binks and coworkers have measured the bending modulus of the heptane/AOT/brine interface to be $K = k_B T$, (10) which is one to two orders of magnitude less than in lipid vesicles. The surface tension varies with temperature with values in the range $\sigma = 10^{-4}–10^{-6}$ N m^{-1} at the temperatures in this study (9). Equation (2) then gives a diameter of the thread $2R = 10–100$ nm, which is below the resolution of an optical microscope. The force exerted by the thread on the oil droplets is predicted from equation (3) to be 200 fN for an interfacial tension of 10^{-5} Nm^{-1}. To establish the validity of equations (2) and (3), we have measured the recoil velocity when one of a pair of droplets connected by a nanothread is released from an optical trap (Figure 2(a) and Supplementary Video 1).
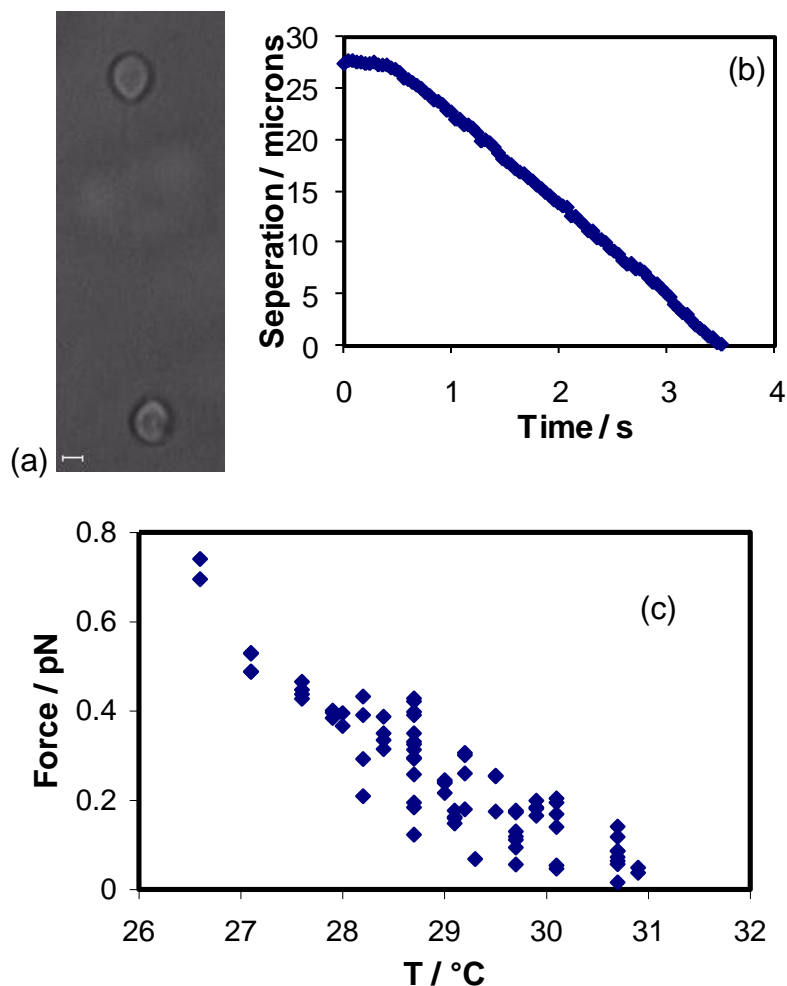
Figure 2. (a) Two droplets of oil connected by a nanothread. The upper droplet is released from the optical trap and is drawn towards the lower droplet by a force acting around the perimeter of the connecting thread. The scale bar is 2 μm. Supplementary Video 1 shows the recoil of the droplet in real time. (b) Separation between the surfaces of a pair of droplets as a function of time following the release of one droplet from the optical trap. (c) Recoil force of a released droplet as a function of temperature of the thermostatted liquid cell. The temperature is not corrected for small changes due to heating by the laser beam or cooling by the trapping objective. The calculated drag force neglects the effect of buoyancy; for the lowest interfacial tensions, the force exerted by the nanothread cannot overcome the buoyancy of the released droplet, which floats to the top of the sample cell.

Figure 2(b) shows that the recoil speed is constant until the separation between the droplets is comparable to the droplet diameter (*11*) as would be expected for a constant force acting around the perimeter of the thread: the thread does not behave like a spring. The drag on the droplet can be estimated from Stokes' Law: $F_{drag} = 6\pi\eta a$, where a is the droplet radius and η the viscosity of water. Figure 2(c) plots the drag force as a function of temperature. The force exerted by the thread is of the predicted magnitude (*9*), decreasing with increasing temperature as expected from the temperature dependence of the surface tension. The largest measured force (700 fN) corresponds to a thread diameter of only 10 nm (equation (2).

If droplets such as those shown in Figure 1 are observed over a period of a few minutes, the smaller droplets grow and the larger droplet shrinks. For separated droplets, no change in the sizes of the droplets is observed. It is well-known that as a result of surface tension, the pressure inside a drop or bubble is higher than that outside. This pressure, known as the Laplace pressure, is inversely proportional to the size of the drop and as a consequence small drops should shrink and large drops grow. The direction of flow that we observe – from large to small – is in the opposite direction to that expected from the Laplace pressure ($P = 2\sigma/a$). The physical origin of this flow is likely to be dielectrophoresis, that is, the force acting on an object of high dielectric constant (in this case, the oil) along the gradient in an electric field. Since the electric field at the surface of a small droplet in a tightly focussed laser beam is higher than that at the surface of a large droplet, the energy of the system is lowered if oil flows from the large to the small droplet. For droplets that are much larger than the wavelength of the light, this pressure is expected to scale as a^{-2} and therefore outweighs the Laplace pressure for sufficiently small droplets. For pairs of droplets of similar size, the direction of the flow can be controlled by variation of the laser power delivered to each droplet.

To establish the magnitude of the optical pressure, we computed the Maxwell stress tensor inside and outside a spherical heptane emulsion drop in a Gaussian trap using Mie scattering theory (*12–14*). We then used the difference between the stress tensors to compute the normal component of the force on the heptane-water interface and integrated

this force over the surface of the droplet. This approach combines both the scattering and gradient contributions to the optical pressure. The internal pressure is plotted against particle radius, a, in Figure 3.   The plot shows that the scaling prediction holds accurately down to a droplet radius of 0.5 µm.
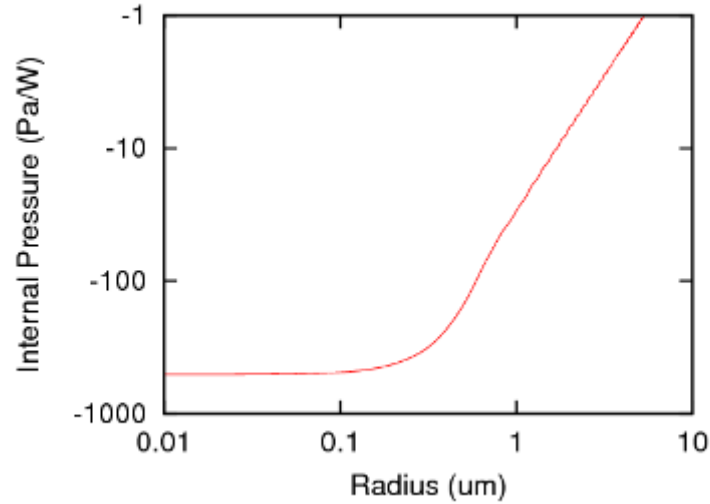

Figure 3. Computed mean pressure, per watt of laser power, inside a heptane droplet in water held in an optical trap as a function of the radius a of the droplet. The internal pressure is negative so that, in the absence of any competing forces, heptane would be drawn into the droplet from a large reservoir. The Mie scattering calculation assumes a perfect spherical droplet at the focus of a laser beam (numerical aperture = 1.1) with a vacuum wavelength of 1064 nm.   The mean pressure is obtained by dividing the integrated normal force by the surface area of the droplet ($4\pi a^2$). For $a > 0.5$ µm, the pressure scales with a^{-2}, but has a small modulation due to internal resonances within the spherical droplet. For a typical laser power of 50 mW incident on a 3-µm diameter droplet, the optical pressure would be –0.65 Pa. The calculation does not allow for the axial deformation of the droplet in the laser beam.

It is difficult to measure the flow rate through the nanothreads since we do not measure the deformation of the droplets in the direction of the laser beam and hence can not accurately determine the change in volume with time. Nevertheless, the flow rate predicted for pipe flow – less than 10^{-3} µm^3 s^{-1} (*15*) – is less than that observed experimentally (see, for

example, Figure 4) suggesting that the walls of the pipe move with the flow: the thread of oil emerges from one droplet and is consumed by the other.

Optical pressure also provides a means of creating junctions between nanothreads. Figure 4 and the accompanying Supplementary Video 2 show a sequence of images taken with four optical traps that are initially superimposed in a single oil droplet. One trap is fixed at the centre of the droplet and the other traps are moved outwards to create three daughter droplets connected to the parent droplet by nanothreads (fig. 4(b)). The central trap is then turned off, but the parent droplet cannot diffuse away since it is held weakly in place by the three threads from the daughter droplets (fig 4(c)). The negative pressure exerted by the optical traps on the three daughter droplets then drains the oil out of the central droplet (fig 4(d)–(e)) until the central droplet disappears leaving a Y-junction between the three nanothreads (fig 4(f)). Though the Y-junction is invisible, its existence can be deduced from the direction of motion of an oil drop if one trap is turned off. An alternative means to generate a Y-junction is to form a 'V' out of three droplets and then reduce the angle of the 'V' until the threads spontaneously rearrange into a Y, as has previously been demonstrated with lipid tubules (*3, 16*). The droplets can be moved around while retaining the integrity of the Y-junction. Pushing two oil droplets together with a pair of optical tweezers leads to droplet coalescence. Coalescence provides a means of creating closed circuits of droplets connected by nanothreads. For example, four droplets in a 'U' can be closed into a triangular network by coalescence of the two end droplets on the chain.

There is no physical reason why these nanofluidic networks should be restricted to two-dimensions. The acoustic optic deflectors we used to create multiple optical traps restrict the traps to a plane but holographic optical tweezers (*17*) permit the 3-D positioning of drops and would allow 4-way as well as 3-way junctions between nanothreads. In principle, it should also be possible to create networks of water droplets in oil, using suitable surfactants that stabilise oil-in-water microemulsions. Trapping of low index droplets (water) in a high index medium (oil) is more difficult than the converse demonstrated here and requires the use of doughnut-shaped 'bottle beams' (*18*).
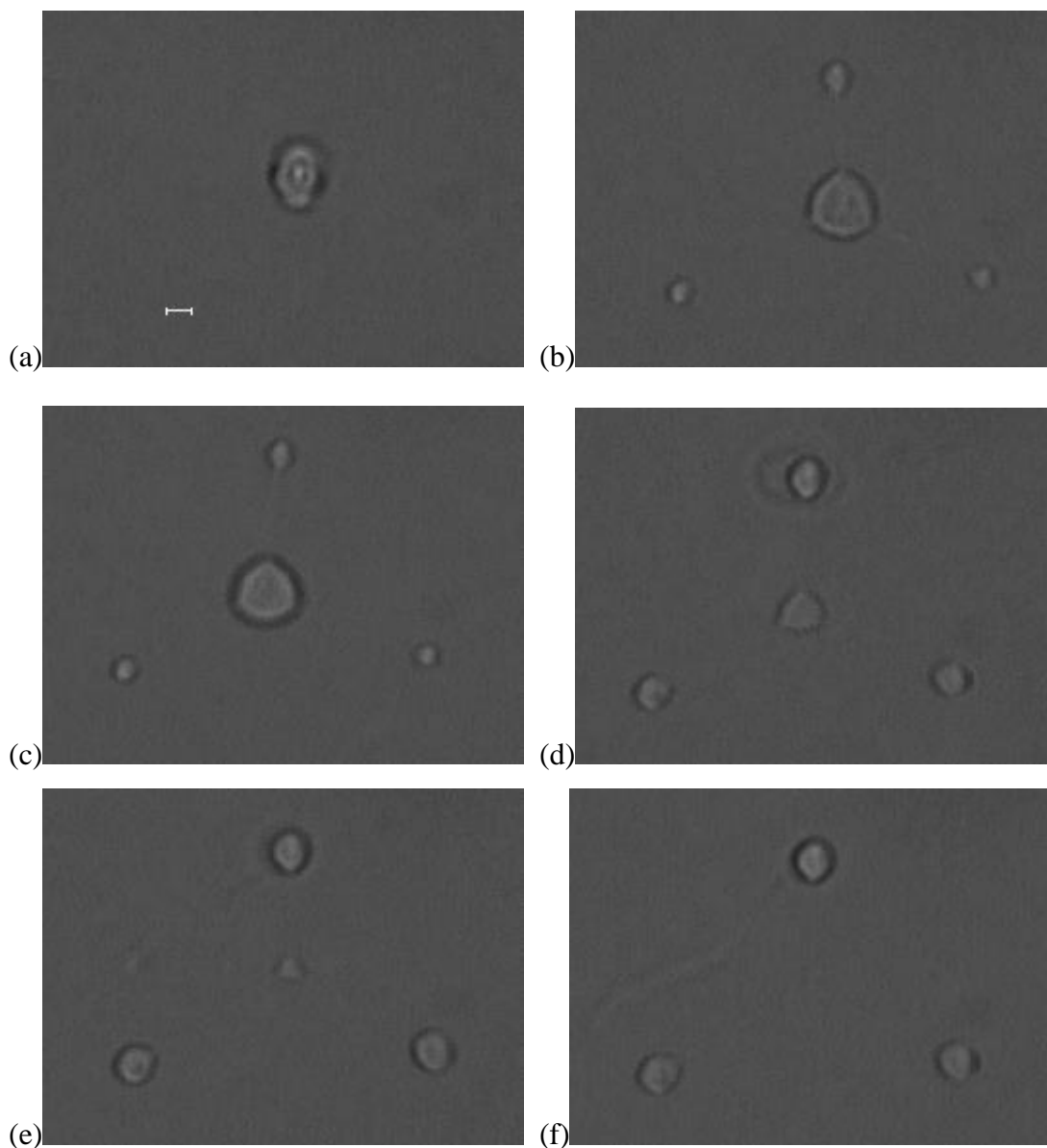
Figure 4. Creation of a Y-junction between nanothreads. (a) before separation of the traps, (b) after separation of the traps ($t = 0$ s), (c) after release of the central trap ($t = 18$ s), (d) $t = 720$ s, (e) $t = 900$ s , (f) $t = 920$ s. The released droplet is out of focus since it floats upwards until the downward component of the force exerted by the nanothreads counteracts the buoyancy force on the heptane droplet. The scale bar in (a) is 2 μm. The mean flow rate per thread is ~0.01 μm^3 s^{-1}.

In this paper, we have demonstrated the principles required to create networks of micron-sized reactors connected by conduits less than 100 nm in diameter and to transfer reagents

between them, entirely with lasers. First, a two or three-dimensional network of oil reservoirs in water connected by nanothreads is created by deformation and coalescence of emulsion droplets with ultralow interfacial tensions. Second, the reservoirs are filled by coalescence with a droplet containing the desired cargo (delivered, for example, via a microfluidic device). Third, the trapping powers on the droplets are varied to pump the contents of one reservoir into another through the nanothreads. These elementary operations can be combined to make nanofluidic networks of almost arbitrary complexity. Such networks provide a platform for carrying out chemical reactions in femtolitre reaction vessels and with attolitres of reagents and open a path to controlled chemical reactions between single molecules.

Acknowledgements

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Supplementary Information

Supplementary Video 1. Two oil droplets are connected by a nanothread of oil. The video shows the recoil of the upper oil droplet following release of one of the laser traps, and the instant coalescence of the two droplets when they touch.

Supplementary Video 2. Drainage of an oil droplet to form a Y-junction. Four traps, initially superimposed in a single droplet, are used to draw out three daughter droplet connected to the parent droplet by nanothreads. The central trap is then released and the negative pressure generated in the daughter droplets by the optical traps pumps the liquid out of the central droplet until only a junction between the threads remains. The video runs at normal speed until the central trap is released and is then accelerated 60-fold during the drainage process.