

# Photo-actuation of liquids for light-driven microfluidics: state of the art and perspectives†

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Using light to control liquid motion is a new paradigm for the actuation of microfluidic systems. We review here the different principles and strategies to induce or control liquid motion using light, which includes the use of radiation pressure, optical tweezers, light-induced wettability gradients, the thermocapillary effect, photosensitive surfactants, the chromocapillary effect, optoelectrowetting, photocontrolled electroosmotic flows and optical dielectrophoresis. We analyze the performance of these approaches to control using light many kinds of microfluidic operations involving discrete pL- to  $\mu$ L-sized droplets (generation, driving, mixing, reaction, sorting) or fluid flows in microchannels (valve operation, injection, pumping, flow rate control). We show that a complete toolbox is now available to control microfluidic systems by light. We finally discuss the perspectives of digital optofluidics as well as microfluidics based on all optical fluidic chips and optically reconfigurable devices.

## 1. Introduction

Manipulating small amounts of liquids to perform reactions, analysis, or fundamental investigations in biology, physics or chemistry is a crucial challenge with great impacts on science, society and economy. In most cases, the manipulation of small amounts of fluids is achieved either by using microfluidic

devices,<sup>1</sup> where the fluids flow in micrometer sized channels,<sup>2</sup> or by manipulating pL- to  $\mu$ L-sized discrete droplets.<sup>3,4</sup> The success of such operations requires a fine control of fluid motion at the micro-scale, which is typically obtained through electrokinetic, mechanical, hydraulic, or pneumatic forces and usually relies on the implementation of external transducers, such as pumps, valves, or electrodes.<sup>5</sup> The viability of these approaches has been demonstrated. They have led to a very large number of fundamental and practical applications in chemistry, biology, physics, and at the frontiers between these disciplines. However, the necessity to implement external transducers tends to increase the complexity, cost, and the fragility of these devices. It can also raise some fabrication issues, especially when complex operations on very small volumes of liquid need to be performed in a parallel and high-throughput way. Contamination of, or by, the transducer can also limit device functionality. Finally, classical microfluidic devices are usually highly specific for a given operation and, once fabricated, they usually cannot be modified any further for new application purposes.

To overcome such limitations, a different paradigm consists of using an external stimulus to actuate fL- to  $\mu$ L-sized amounts of liquid, which can be either confined in an enclosed microfluidic channel or exposed to an open environment. Light is a particularly suitable stimulus as it can provide contactless stimulation, tunability of the excitation (wavelength and power) and excellent spatial ( $\sim\mu$ m) and temporal resolution ( $\sim$ ms or less). It is also biocompatible and has been used to elicit responses in biological systems in a non-invasive and highly precise manner.<sup>6–9</sup>

A particularly successful marriage between light and micro-scale fluids recently engendered a new research field called

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optofluidics,<sup>10</sup> which is the main topic of this special issue of *Lab on a Chip*. Up to now, optofluidics has mainly dealt with the use of microfluidic systems as new micro-scale optical elements. But the reciprocal approach, that is, the photo-actuation of fluids at the microscale, has also attracted a particular attention and this is what we review herein. Some recent reviews have already been devoted to specific aspects of this field. The use of radiation pressure and applications of the thermocapillary effect in microfluidic systems have been specifically reviewed by Delville *et al.*<sup>11</sup> The use of holographic optical tweezers for actuation and sensing purposes in microfluidic devices has been described in detail by Padgett and Di Leonardo.<sup>12</sup> However, other useful strategies to photo-actuate microfluidic systems, such as the use of photosensitive substrates or photosensitive surfactants, the application of the chromocapillary effect, light-induced electro-osmosis, or optoelectrowetting have never been reviewed. Moreover, the different strategies are usually discussed separately and their performances have seldom been compared. Here, we attempt to establish a comprehensive and comparative state of the art of the different existing methods to drive and manipulate micro-scale liquids by light.

This review is organized as follows. Firstly, we show how light energy can be converted into a liquid motion, by using optical forces (through radiation pressure and optical tweezers) and light-induced capillary forces or by combining optical and electrical effects. Then, we review how to achieve precise manipulation of discrete pL- to  $\mu$ L-sized droplets by light for digital microfluidic applications. We then focus on the photo-actuation inside microfluidic channels and enumerate the different microfluidic operations that can be controlled by light. We finally discuss some perspectives for the field.

## 2. Conversion of light energy into liquid motion

Fig. 1 shows the main strategies to directly convert light energy into liquid motion. Photons carry a momentum that can be directly transferred by radiation pressure to deform an interface. With optical tweezers, photon momentum transfer can be used to trap microparticles that can in turn be used as mobile elements to actuate liquids. Light-induced capillary forces can also be used to actuate liquids through the generation of a wettability gradient or a Marangoni effect. These effects rely on an interfacial energy

gradient that can be created by thermal or photochemical means. Finally, indirect light actuation can be obtained by modulating an electric actuation with a light stimulus. We describe all of these strategies in the following paragraphs.

### 2.1. Optical forces

**2.1.1. Radiation pressure.** When a laser beam passes through an interface separating two fluids of different refractive index, the photon momentum transfer induces a surface deformation toward the medium having the lower refractive index, regardless of beam propagation direction. This effect was experimentally demonstrated for the first time by Ashkin and Dziedzic in 1973.<sup>13</sup> However, for most fluid interfaces, the interfacial tension prevents large deformations and only very small deformations ( $\sim$ nm) can be observed. Later, Delville's group showed that a significant deformation (up to a few tens of  $\mu$ m) can be obtained at the interface of phase separated liquid mixtures near liquid–liquid critical point where interfacial tension was as low as  $10^{-7}$  mN m<sup>-1</sup>.<sup>14</sup> By increasing laser power, they observed the formation of a mm-long long microjet,<sup>15,16</sup> which could be destabilized into droplets due to Rayleigh–Plateau instability<sup>17</sup> or used as a liquid optical fiber.<sup>18</sup> Sakai *et al.* used similar radiation pressure-induced surface deformations to measure ultra-low surface tensions as well as rheological properties in bulk and at interfaces.<sup>19–21</sup> These approaches provide interesting systems for fundamental investigations of light–fluid interactions.<sup>11</sup> They are however ill-adapted for practical applications since a high laser power and very low interfacial tensions are necessary to achieve a significant liquid actuation.

**2.1.2. Optical tweezers.** Instead of directly transferring the momentum of photons impacting on a liquid interface, light momentum transfer can be applied to trap and manipulate  $\mu$ m-sized solid particles. These particles can be used as mobile elements to actuate liquids. In a breakthrough paper, Ashkin *et al.* described in 1986 the concept of optical tweezers where the gradient force generated by a strongly-focused laser coupled to the scattering force are able to create a stable trap and hold a microscopic particle.<sup>28</sup> Since that pioneering work, optical tweezers have been recognized as a revolutionary tool offering a large range of fundamental and practical applications in physics, chemistry, and biology.<sup>29–32</sup> Here, our focus is on converting the motion of a trapped solid particle into liquid motion. Let us consider a spherical particle with a diameter  $D = 1$   $\mu$ m immersed in water (viscosity  $\mu = 10^{-3}$  Pa s, density  $\rho = 10^3$  kg m<sup>-3</sup>). Moving this particle at a speed  $U = 1$   $\mu$ m s<sup>-1</sup> corresponds to a Reynolds number  $Re = DU\rho/\mu = 10^{-6} \ll 1$ . At such a low  $Re$ , inertia can be neglected and viscous forces are predominant. Assuming a non-slipping condition at the particle boundary, the viscous drag will induce a fluid flow around the particle, slowly decaying as the distance from the particle increases.<sup>33,34</sup> Note that the resulting flow profile strongly depends on boundary conditions, such as the presence of a solid wall in a microfluidic channel<sup>35</sup> or of other particles in the vicinity of the trapped particle.

Although the linear motion of a single trapped particle can induce some fluid flow around the particle, it is not really adequate for practical applications such as pumping or mixing. An interesting alternative consists in rotating the trapped particle

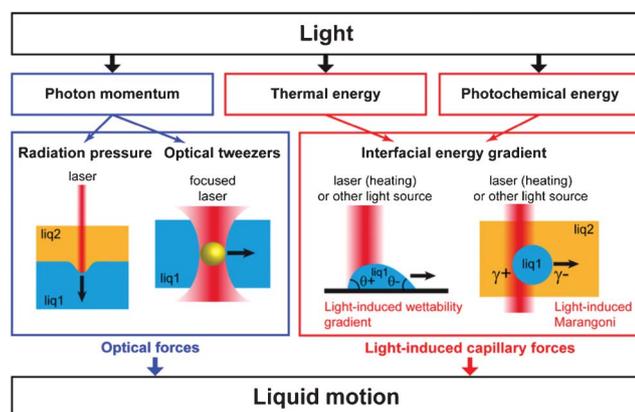


Fig. 1 Main strategies to convert a light stimulus into liquid motion.

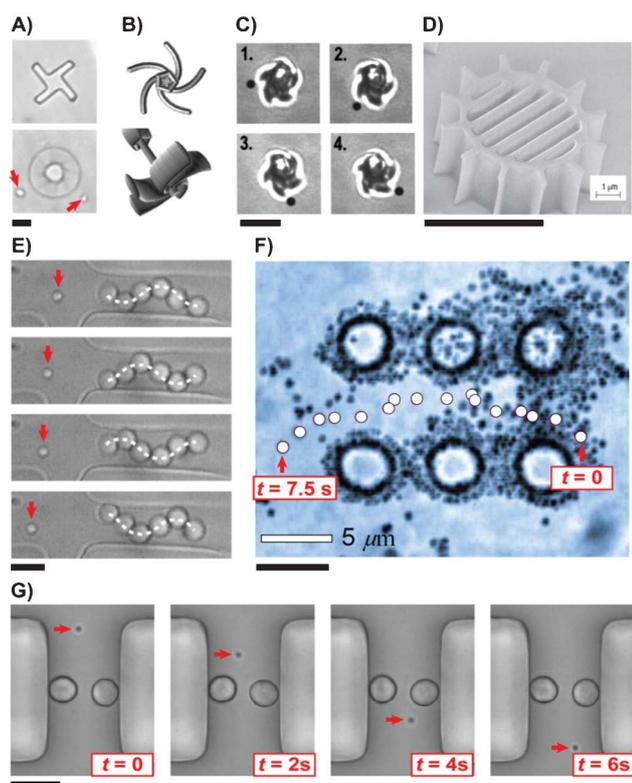
to generate a liquid flow. This can be achieved through different strategies. One solution is to trap a particle having an anisotropic shape and a rotational symmetry. This was demonstrated in the years 1994 to 1998 by Higurashi *et al.* who used different rotors fabricated using micromachining techniques (Fig. 2A).<sup>36,22,37</sup> The photon momentum transfer on these anisotropic rotors induced a net optical torque<sup>38</sup> on the trapped objects resulting in the rotation of 5–20  $\mu\text{m}$  objects at about 10–100 rpm with a 10–100 mW laser power. More sophisticated rotors were later proposed by Galajda

*et al.*<sup>39,23</sup> Two-photon polymerization techniques,<sup>40,41</sup> that can generate 3D polymeric objects of any arbitrary shape down to a 100 nm resolution,<sup>42</sup> allowed them to craft exquisite optically driven rotors (Fig. 2B, 2C) rotating at a few Hz with a 20 mW laser power, with a controllable direction of rotation,<sup>23</sup> and able to drive the rotation of engaged cogwheels.<sup>39</sup> Such strategies, which require complex microfabrication steps, have a low flexibility. An alternative is to transfer the angular momentum of light to induce the rotation of simpler colloids. One possibility consists in using a circularly polarized laser beam to induce the rotation of a trapped birefringent particle by transfer of spin angular momentum. This was demonstrated by Friese *et al.* in 1998 who induced the rotation of  $\mu\text{m}$ -sized vaterite particles at a rotation speed up to 350 Hz with a 300 mW laser power.<sup>43</sup> They later used the optically induced rotation of the trapped birefringent particle to actuate another trapped particle.<sup>44</sup> This approach is not limited to materials having an intrinsic birefringence such as vaterite. In 2005, Neale *et al.* reported the optically driven rotation of a trapped microgear with form-birefringence simply obtained by creating a photonic lattice with grooves and ribs inside the trapped particle (Fig. 2D).<sup>24</sup> The rotation speed increased from 10 to 100 rpm with an increase in laser power from 0.2 to 1 mW. Most of these strategies focused on the optimization of photon momentum transfer to achieve a maximal optical torque on the trapped rotor. These optically driven nanorotors have proven useful in micro-rheology.<sup>33,35,45–47</sup> Moreover, a few demonstrations of applicable liquid photo-actuation, such as microfluidic pumping, have been reported. In 2002, a remarkable work was published by Terray *et al.* who reported for the first time the motion of a liquid in a microchannel driven by optical tweezers.<sup>25</sup> The authors used a time-shared optical trap to actuate the collective motion of trapped particles working as a two-lobe gear pump or as a peristaltic pump (Fig. 2E). They obtained a maximum flow velocity of a few  $\mu\text{m s}^{-1}$  within a 6  $\mu\text{m}$  (width)  $\times$  3  $\mu\text{m}$  (height) channel and a maximum volume flow rate of about 17  $\text{pL min}^{-1}$ . Another approach of liquid actuation by optical tweezers was later proposed by Ladavac and Grier in 2004 who used holographic optical tweezers<sup>48</sup> to transfer orbital angular momentum<sup>49,50</sup> to rings of trapped particles generating a maximum flow velocity of about 6  $\mu\text{m s}^{-1}$  with a relatively high laser power (3 W) (Fig. 2F).<sup>26</sup> Unlike Terray *et al.*, this was done in bulk and not in a microchannel and no volume flow rate was measured. Finally, an interesting strategy was proposed by Leach *et al.* in 2006 to induce microfluidic pumping in a microchannel. They used a pair of counter-rotating birefringent particles actuated by spin angular momentum transfer using a circularly polarized laser (Fig. 2G).<sup>27</sup> By placing particles near the channel walls, the non-slip condition on the channel walls strongly limited the back flow and a net directional flow along the channel was obtained with a maximal flow velocity of about 8  $\mu\text{m s}^{-1}$  between the rotating particles in a 15  $\mu\text{m}$  (width)  $\times$  15  $\mu\text{m}$  (height) channel and a global volume flow rate of 12  $\text{pL min}^{-1}$ . Extensions of these pumping strategies as well as other microfluidic operations driven by optical tweezers will be described in more details in section 4.1.

## 2.2. Light-induced capillary forces

### 2.2.1. Light-induced wettability gradient.

Consider a surface with a solid/gas interfacial energy  $\gamma_{\text{S/G}}$ . When a droplet of liquid



**Fig. 2** Particle motion and liquid actuation by optical tweezers. For all pictures, a red arrow points to a tracer particle to allow visualization of the fluid motion. All black scale bars below pictures are 5  $\mu\text{m}$ . A) An anisotropic particle (top) enters into rotation when a strongly focused laser is turned on (bottom). Adapted with permission from [Ref. 22]. Copyright 1997, American Institute of Physics. B) Drawing of a rotor fabricated by two-photon polymerization. Adapted with permission from [Ref. 23]. Copyright 2002, American Institute of Physics. C) Timelapse observation of the rotor shown in B rotating under a strongly focused laser beam. Frames are separated by 40 ms and the black dot points to a specific tip of the rotor. Reprinted with permission from [Ref. 23]. Copyright 2002, American Institute of Physics. D) SEM picture of a form birefringent microgear that can rotate under circularly or linearly polarized laser beam. Adapted by permission from Macmillan Publishers Ltd: Nature Materials ([Ref. 24]), copyright 2005. E) Timelapse observation of a microfluidic peristaltic pump powered by a scanning laser actuating the collective motion of silica particles. Frames are separated by 2 s. Adapted with permission from [Ref. 25]. F) Timelapse composite image of the right-to-left pumping action of rotating rings of particles actuated by holographic optical tweezers. White disks indicate the position of a tracer particle taken every 0.5 s. Adapted with permission from [Ref. 26]. G) Longitudinal pumping in a microfluidic channel obtained by two counter-rotating birefringent particles actuated by a circularly polarized laser. Adapted from [Ref. 27].

is deposited on this solid surface, a solid/liquid interface is created with an interfacial energy  $\gamma_{S/L}$  as well as a liquid/gas interface with an interfacial energy  $\gamma_{L/G}$  (Fig. 3A). At equilibrium, the balance of these three capillary forces on the contact line of the droplet leads to a situation where the droplet lays on the surface with an equilibrium contact angle  $\theta_{\text{Young}}$  that obeys the Young equation:

$$\cos \theta_{\text{Young}} = (\gamma_{S/G} - \gamma_{S/L})/\gamma_{L/G} \quad (1)$$

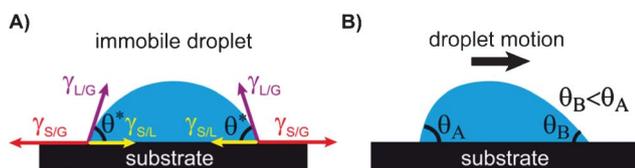
In most practical situations, an immobile droplet on a surface has a homogeneous contact angle  $\theta^*$  that is not equal to  $\theta_{\text{Young}}$  and can vary within a significant range of angles:

$$\theta_r < \theta^* < \theta_a \quad (2)$$

where  $\theta_r$  and  $\theta_a$  are the receding and advancing contact angles, respectively (Fig. 3A). The amplitude of the difference ( $\theta_a - \theta_r$ ), referred to as the hysteresis of contact angle, is attributed to surface inhomogeneities and pinning of the contact line on the surface.<sup>51</sup> This simple analysis implies a perfect contact between the liquid and solid, which is not the case when the liquid and the solid are separated by a film of imprisoned air,<sup>52–54</sup> a layer of vapour (leidenfrost state),<sup>55,56</sup> or by a colloidal skin (droplet marble).<sup>57</sup>

We now consider the situation of Fig. 3B, where two different contact angles  $\theta_A$  and  $\theta_B$  exist in a section of the droplet. We call this difference a wettability gradient. It can be due to a difference in  $\gamma_{S/G}$ ,  $\gamma_{S/L}$ , and/or  $\gamma_{L/G}$  between points A and B. This results in a Laplace pressure in the droplet larger in A (where the curvature is larger) than in B, generating a Poiseuille flow toward B. The droplet then moves if the unbalanced capillary forces on the contact line can overcome the contact angle hysteresis, *i.e.*, if  $(\theta_A - \theta_B)$  is larger than  $(\theta_a - \theta_r)$ . Note that, if  $\gamma_{L/G}$  differs between A and B, a Marangoni flow at the liquid/air interface of the droplet should also be taken into account.<sup>58,59</sup> This will be discussed in section 2.2.2.

In principle, a wettability gradient is thus able to induce droplet motion. This effect was experimentally demonstrated for the first time in 1992 by Chaudhury and Whitesides who reported the uphill motion of a 1  $\mu\text{L}$  water droplet on a silicon wafer that had been silanized in such a way as to possess a gradient in surface energy.<sup>60</sup> Other examples of liquid motion were later reported with different solid substrates having a static

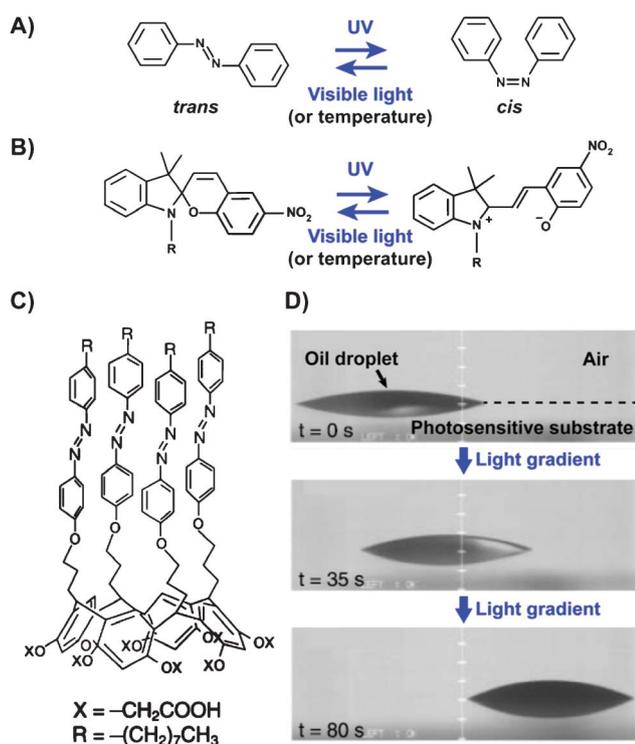


**Fig. 3** A) An immobile sessile droplet has a contact line, which is under three capillary forces corresponding to interfacial energies at solid/gas ( $\gamma_{S/G}$ ), solid/liquid ( $\gamma_{S/L}$ ) and liquid/gas ( $\gamma_{L/G}$ ) interfaces. The droplet has a contact angle  $\theta^*$  with the substrate. B) Example of a wettability gradient resulting in a difference of contact angles between the back and the front of the droplet, which creates a Laplace pressure gradient and a flow inside the droplet. The droplet moves in an A to B direction if  $\theta_A$  is sufficiently larger than  $\theta_B$  to overcome the contact angle hysteresis.

gradient in surface chemical composition.<sup>61–64</sup> Liquid motion was also observed when the wettability gradient was induced by a thermal,<sup>59</sup> electrical,<sup>65,66</sup> or electrochemical<sup>67</sup> effect; by the covalent<sup>68,69</sup> or noncovalent<sup>70,69</sup> deposition of molecules from the droplet; by noncongruent evaporation;<sup>71</sup> by crystallization;<sup>72</sup> and by the juxtaposition of two liquid droplets with different wetting properties on a homogenous surface.<sup>73,74</sup>

Following this principle, light can be used to generate droplet motion if a wettability gradient can be generated and controlled by light. Such a gradient can be created by partially illuminating a substrate with photosensitive wettability properties.<sup>75</sup> Such substrates can be categorized into two classes. The first one includes inorganic substrates with intrinsic photosensitive properties. This effect was first discovered for titanium dioxide ( $\text{TiO}_2$ ), whose photosensitive wetting property was reported in 1997 by Wang *et al.*,<sup>76</sup> and was observed later with zinc oxide ( $\text{ZnO}$ ).<sup>77</sup> The contact angle of water on  $\text{TiO}_2$  and  $\text{ZnO}$  equals  $\sim 70^\circ$  and  $\sim 110^\circ$ , respectively. Upon UV illumination at 365 nm, it drops to  $0\text{--}10^\circ$  for both substrates. The original contact angles can be slowly recovered by storing the substrates in the dark for a few days. The amplitude of UV-induced contact angle change was later increased by incorporating micro- and nano-scale surface structures.<sup>78</sup> By UV illumination of these photosensitive inorganic substrates through a photomask, it is thus possible to create surface patterns with different wettability properties. Although the motion of droplets on such patterns has been recently studied,<sup>79</sup> direct droplet manipulation by light on an inorganic substrate has not yet been reported.

The second class of solid substrates with photosensitive wettability properties includes substrates coated on their surface by an organic layer. The photosensitive wettability of this layer is usually achieved by the presence of a photochromic moiety<sup>80,81</sup> with photodependent polarity. Azobenzene is the most widely used photochromic group for this purpose (Fig. 4A). Under dark conditions, azobenzene is in a *trans*, apolar configuration. It photoisomerizes into a *cis*, more polar configuration upon UV illumination at 350–370 nm. Interestingly, *cis-trans* isomerization can be induced thermally or optically by illumination with visible ( $> 400$  nm), and more specifically blue ( $\sim 450$  nm), light. Both the kinetics of the thermal *cis-trans* conversion and the polarity change upon illumination strongly depend on the chemical groups that are attached to the azobenzene moiety. Azobenzene also offers several advantages such as stability and processivity, as many illumination cycles can be operated without degradation. The first incorporation of azobenzene in a solid surface composition to provide photodependent wettability was reported by Siewierski *et al.* in 1996.<sup>83</sup> They observed a decrease in water contact angle of up to  $9^\circ$  by illuminating a silicon wafer coated by a self-assembled monolayer (SAM) containing azobenzene. Similar results with a  $2\text{--}12^\circ$  decrease of water contact angle upon UV illumination were later reported with different azobenzene incorporations in a SAM<sup>82,84–86</sup> or in a polymeric layer.<sup>87–89</sup> With some specific modifications of the azobenzene providing a higher polarity in the *trans* than that in the *cis* configuration, water contact angle can be also observed to increase after UV stimulation.<sup>90</sup> Spiropyran<sup>91</sup> is another photochromic group, which has also been explored, though to a lesser extent, for light-induced wettability changes (Fig. 4B). Spiropyran undergoes, upon UV illumination, a ring-opening reaction from a non-polar closed form to a polar open



**Fig. 4** Photomanipulation on photosensitive solid substrates. A) The photochromic group azobenzene undergoes a *trans-cis* isomerization upon UV illumination. The reaction is reversible upon visible light illumination or heating. B) The photochromic group spiropyran undergoes a transition from an apolar to a polar form upon UV illumination. The reaction is reversible upon visible light illumination or heating. C) Example of an azobenzene-containing molecule that can be used to chemically treat a surface and render it photosensitive. Reprinted with permission from [Ref. 82]. D) An oil droplet is deposited on a surface coated with the molecule shown in C initially exposed under UV to get all azobenzene groups in *cis* form. The exposure of the droplet to a left-to-right gradient of blue light from  $t = 0$  leads to droplet motion to the right. Adapted with permission from [Ref. 82].

form. Like azobenzene, the reverse transition is possible by changing the temperature or by illumination at a higher wavelength. Spiropyran incorporated into SAM allowed an UV-induced decrease of water contact angle within the range of 5–14°. <sup>92–94</sup> For both azobenzene and spiropyran systems, the UV-induced change of contact angle was reversible and the amplitude of change was enhanced by the incorporation of microstructures on the substrate surface. <sup>88,89,93,94</sup> The photodimerization of thymine derivatives, which creates a reversible switch between neutral and ionized state upon 280 nm and 240 nm illumination, respectively, was also used to induce a reversible water angle contact change within the range of 10–25°. <sup>95,96</sup> Finally, the light-induced molecular motion of a macrocycle in a rotaxane molecule was used to expose variable density of fluoroalkane moieties on a substrate surface thus modulating its wettability properties. <sup>97</sup> Water contact angle on these substrates decreased by about 10° upon UV illumination. Although all of these substrates covered with an organic photosensitive layer displayed significant photodependent wettability properties, only a few demonstrations of droplet photomanipulation on such substrates have been provided. The first one was realized by Ichimura *et al.* in 2000. <sup>82</sup> The asymmetrical illumination of a  $\mu\text{L}$ -sized droplet

deposited on a substrate treated with an azobenzene-modified calixarene (Fig. 4C) induced the motion of the droplet for several liquids, including oil (Fig. 4D) and some liquid crystals, but not water. The motion was achieved on a 5 mm distance at a maximum speed of about  $50 \mu\text{m s}^{-1}$ . Similar results were later reported by Berná *et al.* who used a photosensitive rotaxane-modified substrate <sup>97</sup> and by Yang *et al.* who used an azobenzene-containing SAM. <sup>86</sup> For all of these examples, only linear droplet motions could be realized, on a distance comparable to the droplet size (1–5 mm) and this was achieved at a moderate speed ( $10\text{--}50 \mu\text{m s}^{-1}$ ). Moreover, complex photomanipulation of water droplets by this method has never been achieved. The main limitation comes from a too moderate change of water contact angle upon illumination that is usually insufficient to overcome the hysteresis of contact angles and contact line pinning. <sup>82,86</sup>

### 2.2.2. Light-induced Marangoni effects. The Marangoni effect.

A gradient of interfacial tension along an interface between two fluids (usually a liquid and a gas or two immiscible liquids) generates an interfacial flow in the direction of the gradient, that is, from the lower to the higher interfacial tension. This phenomenon, called Marangoni effect, <sup>98</sup> is responsible of many microscopic and macroscopic fluid movements. It is for instance involved in the formation of the “tears of wine”, which was first explained by Thomson in 1855. <sup>99</sup> When a film of wine is spread along the inner wall of a glass, the stronger evaporation of alcohol at the top of the film induces a local enrichment in water. This creates a vertical surface tension gradient between the bottom part of the film, rich in alcohol, with a low surface tension, and the upper part, rich in water, with a higher surface tension. This surface tension gradient induces an upward motion of liquid, which accumulates and forms a rim at the top of the film prior to destabilization into tear-like droplets. This is a clear demonstration that a Marangoni effect is able to drive micro- to macroscopic amounts of liquids. Several approaches have thus been proposed to manipulate liquids based on Marangoni effects by controlling the generation of a gradient of surface tension at a free interface. One strategy consisted in creating a concentration gradient in surface active molecules that was induced by asymmetric dissolution (such as in the “camphor boat” experiment), <sup>100</sup> electrochemical control, <sup>101,102</sup> interfacial chemical reaction, <sup>103</sup> pH gradient, <sup>104</sup> or chemical wave propagation. <sup>105</sup> It is however possible to modify interfacial tension without using surface active molecules. Interfacial energy is directly linked to the loss of cohesive energy when a molecule goes from bulk to interface. Since an increase in temperature is usually accompanied by a decrease in molecular cohesion, interfacial tension for simple liquid is usually observed to decrease with temperature at a rate of the order  $0.1 \text{ mN}^{-1} \text{ m}^{-1} \text{ K}^{-1}$  ( $d\gamma/dT < 0$ ). For complex fluids, for instance in the presence of some neutral surfactants, the opposite behaviour ( $d\gamma/dT > 0$ ) can be observed. Temperature gradients were thus exploited to generate interfacial gradients and induce interfacial liquid flow toward higher interfacial tension, that is, lower temperatures in the case  $d\gamma/dT > 0$ . <sup>106</sup> This special Marangoni case is usually referred to as the thermocapillary effect. A beautiful demonstration of the thermocapillary effect was realized in 1959 by Young *et al.* who could generate a thermocapillary force that was strong enough to prevent the ascension of a bubble in a liquid column. <sup>107</sup> Using a

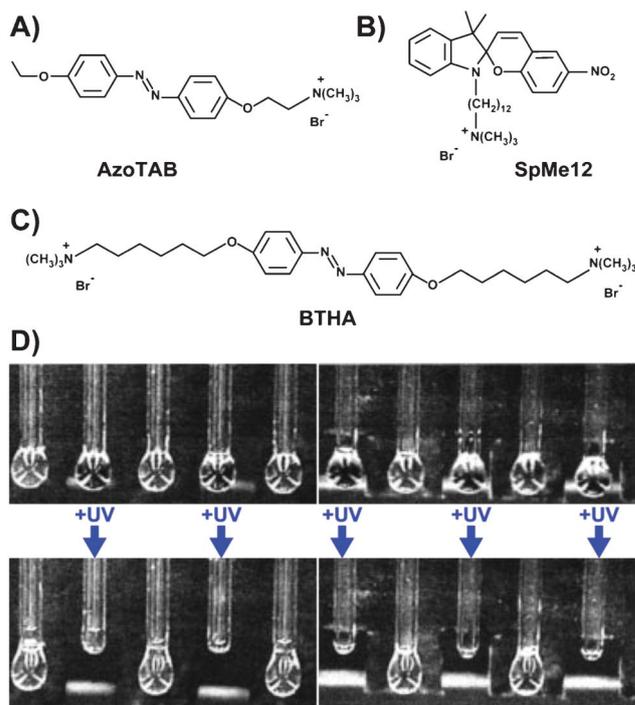
similar approach, Barton and Subramanian later induced the vertical ascension of droplets, which otherwise should fall.<sup>108</sup> In the case of a sessile droplet on a plate with a temperature gradient, an interesting situation can arise when the Marangoni flow tends to bring the droplet toward lower temperatures (higher  $\gamma_{LG}$ ) while a gradient of wettability favors the opposite motion toward higher temperatures and lower contact angles.<sup>59</sup>

**Laser-induced thermocapillary effect.** A natural way to induce Marangoni flows using light is to convert light into thermal energy to generate a light-induced thermocapillary effect. If the local illumination of a target liquid/liquid or liquid/gas interface can induce an increase in temperature sufficient to change interfacial tension (which usually decreases), this will result in a Marangoni flow from the illuminated area (lower interfacial tension) to the non illuminated region (higher surface tension). This principle was experimentally demonstrated for the first time by Garnier *et al.* in 2003 who created microflows in a thin liquid film by heating an absorbing substrate through a light illumination pattern.<sup>109</sup> As expected the fluid is moved away from illuminated areas but this approach only works for films that are thin enough to allow enough heat conduction from substrate to liquid/air interface. An improved heating efficiency through optical excitation of surface plasmons was later proposed by Farahi *et al.*<sup>110</sup> Recently, Lamhot *et al.* used a suspension of strongly absorbing quantum dots to heat the suspending liquid and control capillary rise.<sup>111</sup> Interestingly, if a tiny piece of a strongly absorbing solid is floating on a liquid surface, shining light at the rear of the object results in local heating beneath the object that will be transported forward by the resulting thermocapillary flow.<sup>113</sup> This modern version of the “camphor boat” has the advantage of being under precise light control and the laser can be used to push or to rotate the boat.<sup>113</sup>

In the case of a closed system, such as a gas bubble or a droplet either floating or immersed in an immiscible liquid, momentum conservation implies that the bubble (or the droplet) moves in the direction opposite to the interfacial flow, *i.e.*, the bubble (or the droplet) is attracted by the laser for usual systems ( $d\gamma/dT < 0$ ) and pushed by light in the opposite situation ( $d\gamma/dT > 0$ ). This was demonstrated in 2004 for two different systems. Rybalko *et al.* used a laser to attract a 5 mm oil droplet floating on a water bath.<sup>114</sup> As expected, the motion was reversed when the heating was located on the opposite side of the droplet.<sup>114</sup> The same year, Faris's group demonstrated the first manipulation of a discrete water droplet immersed in another liquid (in this case, dodecanol) using a light-induced thermocapillary effect at the liquid/liquid interface.<sup>115</sup> By focusing a laser on one droplet side, they observed that the droplet was pushed by the laser, which indicates a situation  $d\gamma/dT > 0$ . By moving the laser, they could push pL- to  $\mu$ L-sized droplets at a speed up to 3 mm s<sup>-1</sup>. By pushing a first droplet against a target droplet, they also demonstrated the possibility to use this method to fuse two droplets acting as micro-reactors. This constitutes the first demonstration that light can be used to manipulate discrete pL- to  $\mu$ L-sized water droplets, at relatively high speeds, and combine them in a way that is similar to digital fluidics. Later, the same group demonstrated some applications in this direction,<sup>116,117</sup> which will be discussed in section 3.3. Light-induced thermocapillary effects can also be combined with microfluidic

biphasic flows to control several microfluidic operations. This will be discussed in section 4.2.1.

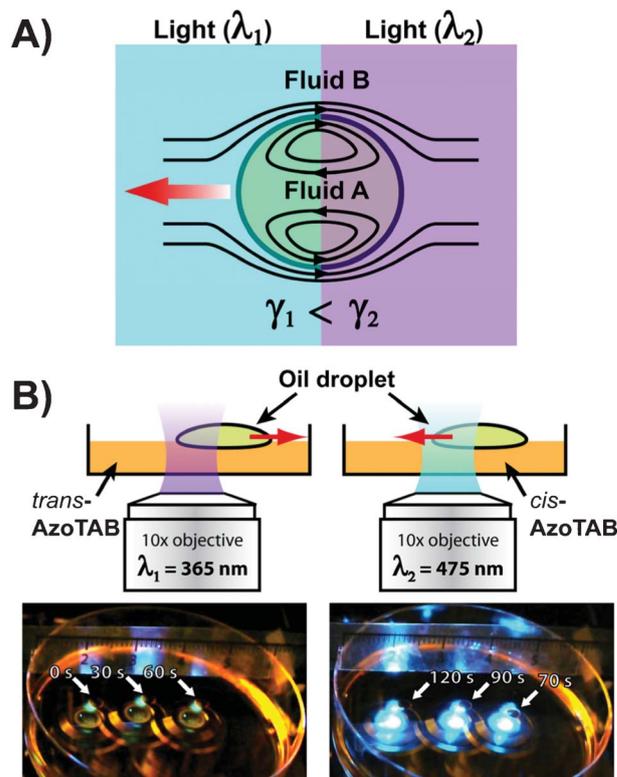
**Photosensitive surfactants.** The thermocapillary effect can be exploited to actuate liquid using light. However it requires a laser source, a strongly absorbing material (liquid or substrate) and the actuated liquid has to be heated to create a motion. To actuate a liquid in an isothermal way, an alternative is to use photosensitive surfactants. These surfactants allow for a photo-dependent and isothermal monitoring of interfacial energy. The synthesis of photosensitive surfactants started in the 1980s<sup>118</sup> with a real development starting in the middle of the 1990s.<sup>119</sup> Since then, a large variety of molecules have been synthesized and studied.<sup>120,121</sup> Most of them are composed of a single hydrophobic tail containing a photosensitive azobenzene moiety (Fig. 4A) and a cationic head<sup>122–126</sup> (Fig. 5A) although anionic<sup>127</sup> and neutral<sup>128,129</sup> photosensitive surfactants have also been studied. Some spiropyran-containing<sup>130</sup> molecules (Fig. 5B) as well as more complex structures such as bolaform<sup>112,131</sup> (Fig. 5C) and gemini<sup>132–135</sup> surfactants have also been developed. They have been applied for the photocontrol of different properties such as self-assembly,<sup>119,122,123,134,136</sup> solution viscosity,<sup>124,125,137</sup> or protein folding.<sup>126</sup> The photocontrol of interfacial tension in the presence of photosensitive surfactants has also been investigated.<sup>112,132,128–130</sup> The effect of light on interfacial tension is usually maximal at a surfactant concentration close to the critical micellar concentration (CMC). For both



**Fig. 5** Photosensitive surfactants. A) AzoTAB, an azobenzene-containing cationic surfactant. B) SpMe12, a surfactant containing spiropyran. C) BTHA, a bolaform azobenzene surfactant. D) Pending droplets of a water solution containing BTHA can be selectively released from capillaries by UV illumination due to the lowering of air–water interfacial tension of exposed droplets. Adapted with permission from [Ref. 112]. Copyright 1999 American Chemical Society.

azobenzene and spiropyran-containing linear surfactants, UV illumination induces a transition to a more polar form and therefore an increase in air–water interfacial tension of up to  $10 \text{ mN m}^{-1}$ . Due to the specific repartitioning of hydrophobic and hydrophilic moieties before and after illumination, more complex structures, such as bolaform or gemini surfactants, can induce a lowering of surface tension of up to  $25 \text{ mN m}^{-1}$  upon UV illumination.<sup>112,132</sup> Surprisingly, few studies have been devoted to the application of such light-induced surface tension changes for liquid actuation. Until recently, the only available example was a remarkable paper by Shin and Abbott who showed in 1999 that light could induce the release of water droplets pending from capillaries (Fig. 5D).<sup>112</sup> Ten years later, we proposed to use a simple cationic photosensitive surfactant, AzoTAB (Fig. 5A), to induce Marangoni flows using light and therefore actuate droplets in an isothermal way based on a phenomenon that we called the chromocapillary effect.<sup>138</sup>

**The chromocapillary effect.** AzoTAB (Fig. 5A), is a small cationic surfactant containing an azobenzene group in its hydrophobic tail. Due to the presence of azobenzene (Fig. 4A), two isomers can be obtained depending on illumination conditions: *trans*-AzoTAB, which has an apolar linear hydrophobic tail, and *cis*-AzoTAB, which has a more polar and bent tail. Due to this difference in polarity and geometry, CMC of *trans*-AzoTAB ( $12.6 \text{ mM}$ ) is lower than that of *cis*-AzoTAB ( $14.6 \text{ mM}$ ).<sup>139</sup> Similarly, at a given concentration, *trans*-AzoTAB induces a lower interfacial air–water or oil–water interfacial tension than *cis*-AzoTAB. Both isomers are stable under dark conditions for several hours and can be easily and quickly converted from *trans* to *cis* and from *cis* to *trans* upon UV ( $\sim 365 \text{ nm}$ ) and visible ( $>400 \text{ nm}$ ) light illumination, respectively. AzoTAB has been used for the photocontrol of nucleic acids (DNA, RNA),<sup>139–144</sup> gene expression,<sup>143–145</sup> and biomembrane stability<sup>146</sup>. Recently, we used it to realize the first demonstration of a chromocapillary effect, *i.e.*, a light-induced Marangoni flow, which was not due to a temperature gradient but to an isothermal light-induced change of interfacial tension.<sup>138</sup> Fig. 6A shows the principle of the chromocapillary effect. When the interface of a droplet or a bubble of a fluid A in contact with another fluid B is subjected to a gradient of interfacial tension, the resulting Marangoni flow induces a motion in a direction opposite to the gradient. This is the same principle as the thermocapillary effect, except for the fact that the gradient of interfacial tension is not due to temperature but to the presence of a photosensitive surfactant that changes the surface tension in an isothermal and wavelength-dependent manner. This strategy offers several advantages: i) heating of the sample is not necessary, which is particularly interesting for the manipulation of heat-sensitive or some biological materials; ii) there is no need for a strongly absorbing material; iii) a laser source is not needed and a standard illumination sources such as a microscope lamp or a LED can be used. The first demonstration was done with an oil droplet floating on a water bath containing AzoTAB initially in the *trans* configuration (Fig. 6B). Partial illumination with UV resulted in a higher surface tension in the illuminated area and the droplet was pushed by UV light (Fig. 6B, left). Conversely, by changing UV to blue light, partial illumination resulted in a gradient in the opposite direction and



**Fig. 6** The chromocapillary effect. A) Schematic principle. In the presence of a photosensitive surfactant, a one- or two-color illumination creates an interfacial tension gradient between two fluids. The resulting Marangoni flow from low to high interfacial tension, results in a motion of the droplet or bubble in the opposite direction, *i.e.*, toward lower interfacial tension. B) Experimental demonstration. Left, an oil droplet on a water bath containing the photosensitive surfactant *trans*-AzoTAB is partially illuminated by UV (365 nm), converting the surfactant into *cis*-AzoTAB and creating a higher interfacial tension in the illuminated zone. The droplet escapes from the illuminated area and can be pushed by UV light. Right, once the droplet has been pushed, the gradient of interfacial tension can be inverted by a blue illumination (475 nm), resulting in droplet attraction toward illumination. The droplet can then be pulled by blue light. Top schemes illustrate the experiment. Bottom pictures are superposition of images where white arrows indicate the position of a  $1.5 \mu\text{L}$  oil droplet moving forth and back under UV (left) and blue (right) illumination. Adapted with permission from [Ref. 138].

the droplet was pulled by blue light (Fig. 6B, right). Interestingly, several push-pull cycles could be achieved and the droplet could be manipulated in this way along several centimeters at a speed up to  $300 \mu\text{m s}^{-1}$ ,<sup>138</sup> which corresponded to a much longer distance and a much higher speed than what had been realized using photosensitive substrates.<sup>82,84,97,86</sup> Moreover, a two-color illumination was used to trap the droplet by the chromocapillary effect and further manipulate it with great precision.<sup>138</sup> This will be detailed in section 3.4.

### 2.3. Modulation of electrical actuation by light

We showed how light could directly actuate a liquid through optical or light-induced capillary forces. It is also possible to use light to modulate the actuation of a liquid by an electric field.

**2.3.1. Optoelectrowetting.** When a polar or conductive liquid droplet is resting on an electrode covered by a dielectric layer, the application of a potential difference between the droplet and the electrode usually results in a decrease in contact angle. This phenomenon, called electrowetting on dielectric (EWOD),<sup>147–149</sup> is applied for instance for the actuation of adaptive liquid lenses with a focal length that can be directly tuned with the applied voltage.<sup>150,151</sup> If an electrode array is used underneath the dielectric layer, it is possible to use EWOD effect to create a difference of contact angles along the droplet, which results, as explained previously (Fig. 3B), in a droplet motion toward the lower contact angle.<sup>65</sup> By finely addressing the electrode array, discrete nL- to  $\mu$ L-sized droplets can be precisely created, manipulated, combined, and sorted.<sup>152,153</sup> All these microfluidic operations are usually referred to as digital microfluidics and have opened a large number of applications.<sup>154–157</sup> Yet the precise control of the electrode array remains challenging for high-throughput droplet multiplexing. A breakthrough alternative, called optoelectrowetting, was proposed by Chiou *et al.* in 2003.<sup>158</sup> The authors inserted a photoconductive layer between the dielectric layer and the electrode array and applied an AC voltage between a water droplet resting on the dielectric layer and the electrodes. In the absence of light, the resistance in the photoconductive layer was large and the droplet had a high contact angle. Upon illumination, the resistance in the photoconductive layer dropped, which resulted in a decrease of the contact angle by up to 30°. As a result, focusing the laser on one side of the droplet led to a local decrease in contact angle and induced a motion of the droplet toward the illumination area. This effect was initially used to move a 2 mm-diameter water droplet at a speed of up to 7 mm s<sup>-1</sup> with a 4 mW laser.<sup>158</sup> The approach was later improved for the actuation of single droplets down to a volume of 10 pL<sup>159</sup> as well as for high-speed multidroplet manipulation.<sup>163</sup> An open version of this principle was proposed by Chuang *et al.*<sup>164,165</sup> Under some specific conditions, the droplet could also be pushed by light.<sup>166</sup>

**2.3.2. Photocontrol of electroosmotic flow.** When an electric field is applied along a microchannel having a charged wall, the motion of mobile counter-ions in the diffuse counter-ion layer near the channel wall induces through viscous forces a global liquid motion that is called electroosmotic flow.<sup>168</sup> This phenomenon, which is exploited to create microfluidic pumps,<sup>169,170</sup> is strongly sensitive to the zeta potential of the channel wall.<sup>171,172</sup> A first strategy to control electroosmosis by light thus consists in using a microchannel with a zeta potential which changes upon illumination. This was demonstrated by Moorthy *et al.* in 2001 using a microfluidic substrate coated with indium tin oxide (ITO).<sup>173</sup> The effect of light on electroosmotic flow rate depended on pH. Under optimal conditions (pH = 4.7), they could switch the flow from 0 (no light) to about 300 nL min<sup>-1</sup> (with light). Another strategy was later proposed by Oroszi *et al.* By using a microfluidic substrate coated with a photoconductive layer, light illumination resulted in a decreased electric field accompanied by a reduction of electroosmotic flow from about 54 nL min<sup>-1</sup> to 9.6 nL min<sup>-1</sup>.<sup>174</sup> The use of a patterned photoconductive layer resulted in the generation of complex flow profiles upon illumination.<sup>175</sup>

### 3. Photomanipulation of discrete droplets

Precise manipulation of discrete pL- to  $\mu$ L-sized droplets is a minimal requirement for digital microfluidics.<sup>176</sup> This is for instance achieved by using the electrowetting on dielectric (EWOD) effect,<sup>147–149</sup> where droplets deposited on an electrode array covered by a dielectric layer can be created, moved, combined, divided and sorted in a high-throughput and parallel manner.<sup>152,153</sup> The success of these operations rely on a precise addressing of the electrode array. In this section, we review how light can be used for precise manipulation of discrete droplets to achieve similar performances without any wiring issues. Table 1 summarizes the performances, advantages and drawbacks of the different strategies.

#### 3.1. Droplet manipulation with optical tweezers

Optical tweezers are usually inappropriate to trap water droplets immersed in an immiscible liquid because the refractive index of water is usually smaller than most of the possible surrounding media. However, Lorenz *et al.* demonstrated in 2007 that it was possible to trap and induce the fusion of pL- to nL-sized water droplets by using optical vortex traps.<sup>160</sup> This method enables precise droplet manipulation but i) the working distance is very limited ( $\sim 10 \mu\text{m}$ ); ii) parallel multidroplet manipulation seems difficult; and iii) it requires an optical vortex trap set-up.

#### 3.2. Droplet manipulation on photosensitive substrates

As described in section 2.2.1, light can induce the motion of droplets deposited on substrates that have been chemically rendered photosensitive (Fig. 4).<sup>82,84,86,97</sup> One advantage of this approach is that it does not require any specific optical set-up and a standard illumination source can be used. The motion of the droplet is limited however to a relatively short distance (usually comparable the droplet size) along simple linear trajectories and it is performed at a small speed (10–50  $\mu\text{m s}^{-1}$ ). Moreover, the need of a photosensitive substrate, possible problems of surface contamination, a too large contact angle hysteresis, or contact line pinning effects might be additional limitations. Although the fusion of two droplets has been demonstrated,<sup>84,86</sup> fast and parallel photomanipulation of a large number of individual droplets for digital microfluidic applications seems difficult with this method.

#### 3.3 Droplet manipulation by the thermocapillary effect

As explained in section 2.2.2, a laser-induced chromocapillary effect can be used to pull ( $d\gamma/dT < 0$ )<sup>114</sup> or push ( $d\gamma/dT > 0$ )<sup>115</sup> a pL- to  $\mu$ L-sized droplet at a relatively high speed (up to 3 mm s<sup>-1</sup>) over distances significantly larger than the droplet size ( $\sim \text{mm}$ ).

One advantage of this approach is that it can work with many kinds of liquids. It requires a strongly absorbing material to create local heating but this material can be put outside of the droplet containing the sample medium. Interestingly, some concrete applications of this photomanipulation strategy have already been demonstrated. In 2005, Kotz *et al.* used a laser to push a droplet containing a chromogenic substrate against another droplet containing a corresponding enzyme (in this case, horseradish peroxidase).<sup>116</sup> This resulted in the fusion of two

**Table 1** Performances, advantages and drawbacks of the different principles that can be used for discrete droplet manipulation by light

Basic principle	Main References	Specific requirement	Droplet volume	Working distance	Trajectory	Speed	Multidroplet capacity	Advantages	Drawbacks
Optical tweezers	160	Optical vortex trap set-up	fL–pL	~10 $\mu\text{m}$ (~droplet size)	Linear	n.a.	Fusion of two droplets <sup>160</sup>	- Compatibility with microfluidic chips- Very small droplet volume	- Heavy equipment- Small working distance
Light-induced wettability gradient on photosensitive substrate	82,84, 86,97	Photosensitive substrate	~ $\mu\text{L}$	1–5 mm (~droplet size)	Linear	10–50 $\mu\text{m s}^{-1}$	Fusion of two droplets <sup>84,86</sup>	- No specific optical set-up required- No laser required	- Photosensitive substrate needed- Low speed- Small working distance- No demonstration with water
Light-induced thermo-capillary effect	114–117, 161,162	Usually a laser and a light-absorbing material	pL– $\mu\text{L}$	~mm (> droplet size)	Linear	~ mm $\text{s}^{-1}$	- Fusion of two droplets for enzymatic <sup>116,161</sup> or gene expression <sup>161</sup> reactions- Parallel manipulation <sup>162</sup> - Contact between two droplets for bilayer formation <sup>117</sup>	- Applicable to different kinds of liquids, including oil and water- Fast manipulation	- Laser usually needed- Sample heating necessary
Chromo-capillary effect	138	Photosensitive surfactant	~ $\mu\text{L}$	~10 cm (>> droplet size)	Arbitrary	100–300 $\mu\text{m s}^{-1}$	Good potential yet to be demonstrated	- No specific optical set-up nor laser is required- Very precise and fast manipulation along arbitrary trajectories <sup>138</sup> - Low cost and portable- Isothermal	- Photosensitive surfactant required- No demonstration with water
Optoelectro-wetting	158,159, 163–167	Optoelectro-wetting device	pL– $\mu\text{L}$	~1 cm (> droplet size)	Arbitrary	7–70 mm $\text{s}^{-1}$	- Fusion of two droplets <sup>164</sup> - Droplet division <sup>163</sup> - Multidroplet manipulation <sup>163</sup> - Potential for massively parallel manipulation <sup>167</sup>	- Precise and very fast manipulation along arbitrary trajectories- Multidroplet manipulation	- Optoelectro-wetting device required

droplets in a single nL-sized droplet where the enzymatic reaction occurred (Fig. 7A). By absorption measurements, they followed the substrate conversion and could characterize the enzymatic activity in the droplet. In 2007, we followed a similar strategy to fuse phospholipid-coated droplets that were used as cell-mimicking microreactors.<sup>161</sup> We also performed an enzymatic reaction by mixing a droplet containing an enzyme with a droplet containing its substrate as well as a gene expression reaction by mixing a droplet containing a DNA template with droplet containing a gene expression medium.<sup>161</sup> In 2010, Dixit *et al.* used this method to put in contact two phospholipid-coated droplets and create a bilayer separating two aqueous compartments.<sup>117</sup> In 2011, Hu and Ohta used a projector to create a light pattern projected on an absorbing substrate to trap pL-sized water droplets.<sup>162</sup> They could manipulate up to four droplets in parallel and induce the fusion between two droplets. Although these experiments are at a proof-of-concept stage, they demonstrate the interest of manipulating individual  $\mu\text{m}$ -sized droplets using light and combine them to perform biochemical reactions in a confined biomimetic environment while strongly reducing the amount of reagents and waste. However, an important limitation has to be considered. The sample has to be heated to generate the surface tension gradient and therefore induce droplet motion. For the enzymatic assay described by Kotz *et al.*, the authors calculated a temperature rise of about  $10^\circ\text{C}$ .<sup>116</sup> For most chemical reactions, such an increase does not

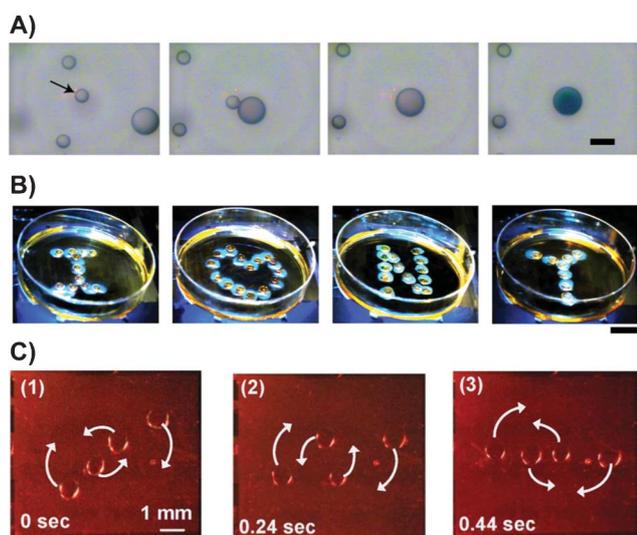
constitute an issue. However, some biological systems can be extremely sensitive to the temperature. The applicability for biological investigations will thus strongly depend on the biological system involved in the experiment.

#### 3.4. Droplet manipulation by the chromocapillary effect

As shown before, the chromocapillary effect is an alternative to the thermocapillary effect where there is no need for any laser nor sample heating. We explained that by using a photosensitive surfactant called AzoTAB, partial illumination of the droplet resulted in droplet attraction toward blue light and droplet repulsion from UV light. Hence, by illuminating the centre of the droplet with blue light while shining UV light around the droplet, we created a chromocapillary trap where the equilibrium position of the droplet was the centre of the two-color illumination trap. Interestingly, when the trap was moved, the droplet remained centred in the trap and could be moved along any desired, eventually complex trajectory.<sup>138</sup> Fig. 7B shows a superposition of images where a single droplet is moved along various trajectories at a speed of about  $300\ \mu\text{m s}^{-1}$ . This method offers several advantages: i) it enables fast and precise manipulation along any arbitrary trajectory; ii) it is isothermal (no sample heating is necessary); iii) it does not need any laser nor specific optical set-up. Moreover, since the droplet substrate is a simple water bath in a container (*e.g.*, a Petri dish), it shares with paper microfluidics<sup>177–179</sup> the advantages of being very cheap, portable, and applicable in any laboratory with no hardware needed except the illumination source. The precise and fast droplet manipulation allowed by the chromocapillary trap seems very promising for digital microfluidic applications. For example, parallel and complex manipulation of a large number of individual  $\mu\text{L}$ -sized droplets could be achieved by using a two-color dynamic light pattern. However, multidroplet manipulation has yet to be demonstrated. Two main limitations have to be mentioned. The first one is the need of a photosensitive surfactant, although a molecule such as AzoTAB is easy to synthesize. The second and more important one is the fact that this method has so far been limited to the manipulation of oil droplets. Oil droplets are interesting reactors to perform some organic reactions while the perspective of biological applications calls for the improvement of the photosensitive surfactants in order to move water droplets.

#### 3.5. Droplet manipulation by optoelectrowetting

Finally, we showed that optoelectrowetting could be used to induce droplet motion (section 2.3.1). When a droplet is deposited on an electrowetting device, illumination on one side of the droplet leads to a smaller contact angle on the illumination side resulting in a droplet motion toward the illuminated area. Chiou *et al.*, who pioneered this principle,<sup>158</sup> recently demonstrated that this approach allowed them to inject or divide a single droplet as well as to precisely manipulate several droplets at the same time at a high speed (up to  $78\ \text{mm s}^{-1}$ ) (Fig. 7C).<sup>163</sup> Optoelectrowetting was also used to fuse two target droplets.<sup>164</sup> By using projected images,<sup>167</sup> massively parallel manipulation of pL- to  $\mu\text{L}$ -sized droplets seems possible with performances comparable to digital microfluidics based on standard EWOD effects. Compared to other droplet photomanipulation



**Fig. 7** Photomanipulation of discrete droplets and applications. A) A focused laser beam (black arrow) is used to push a small water droplet containing a substrate to a bigger droplet containing the corresponding enzyme by the thermocapillary effect. After droplet fusion, the color change indicates that the enzymatic reaction has occurred. The scale bar is  $250\ \mu\text{m}$ . Adapted with permission from [Ref. 116]. Copyright 2005 American Chemical Society. B) Superposition of images showing various trajectories of a  $1.5\ \mu\text{L}$  oil droplet floating on an AzoTAB water solution and manipulated by a two-color UV-blue illumination using the chromocapillary effect. The scale bar is  $1\ \text{cm}$ . Adapted with permission from [Ref. 138]. C) Manipulation of four water droplets on an optoelectrowetting device by using four scanning laser beams to induce clockwise and anticlockwise trajectories of outer and inner droplets, respectively. © 2008 IEEE. Reprinted, with permission, from [Ref. 163].

strategies, the only limitation is the requirement of an optoelectrowetting device and a laser scanning set-up.

## 4. Photo-actuation in microfluidic channels

We review herein how light can be used to actuate liquids flowing in enclosed microfluidic channels. Table 2 and Table 3 summarize the different microfluidic operations that can be powered by light for monophasic and multiphasic flows, respectively.

### 4.1. Photocontrol of monophasic flows

**4.1.1. Optical pumps.** We showed in section 2.1.2 that optical tweezers could be used to trap and move microparticles to

generate a microflow of liquid. We focus herein on the integration of optical tweezer-driven microparticles inside microfluidic devices to generate a pumping action. Two main strategies have been proposed. The first one, pioneered by Terray *et al.*, consists in controlling the motion of simple colloidal particles within a microfluidic channel.<sup>25,187</sup> For instance, time-shared optical traps were used to control the collective motion of silica particles and create a peristaltic pump (Fig. 2E).<sup>25</sup> A circularly polarized laser beam was also used to control the rotation of birefringent particles and induce a longitudinal pumping action in a microfluidic channel (Fig. 2G).<sup>27</sup> The advantage of this approach is that it does not require any specific microparticle fabrication and that it can be easily adapted to any microfluidic device. It thus offers a quite large versatility. However, the particles usually have to be continuously trapped

**Table 2** Performance, advantages and drawbacks of light-controlled microfluidic operations in microchannels involving monophasic flows

Microfluidic operation	Strategy	Performance	Advantages	Drawbacks
Pumping	Optical tweezers + colloids <sup>25,27</sup>	Flow rates: 1–100 pL min <sup>-1</sup>	- High versatility- Precise actuation of small volumes	- The colloid needs to be continuously trapped- Very low flow rates
Pumping	Optical tweezers + integrated microrotor <sup>180–184</sup>	Flow rates: 1–100 pL min <sup>-1</sup>	- Microrotor integrated in the device- Precise actuation of small volumes	- Complex fabrication- High specificity- Very low flow rates
Pumping	Laser-induced bubble generation <sup>185</sup>	Flow rates: 100–500 nL min <sup>-1</sup>	- No fragile mobile element	- Heating of the sample- Perturbations by bubbles
Injection/filling	Laser + photothermal particles <sup>186</sup>	Flow rates: 10 pL min <sup>-1</sup> to 1 nL min <sup>-1</sup>	- No fragile mobile element- Precise injection and channel filling	- No continuous pumping- Local heating of the sample
Valve	Optical tweezers + colloids <sup>25,187</sup>	- ON/OFF- Flow redirection- Flow rate: 1–100 pL min <sup>-1</sup>	- Precise valve operation- High versatility	- Optical tweezers needed- Very low flow rates
Valve	Photocontrol of electroosmosis <sup>173–175</sup>	- ON/OFF- Flow rate modulation- Flow rate: 10–1000 nL min <sup>-1</sup>	- Simple- Control up to relatively high flow rates	- Only for devices driven by electroosmotic flows
Valve	Laser-induced bubble generation <sup>185</sup>	- Blockage of channel- Flow rates: 1–8 μL min <sup>-1</sup>	- No fragile mobile element	- Heating of the sample- Perturbations by bubbles

**Table 3** Performance, advantages and drawbacks of light-controlled microfluidic operations in microchannels involving multiphasic flows

Microfluidic operation	Strategy	Performance	Advantages	Drawbacks
Valve	Laser-induced thermocapillary effect <sup>188–190</sup>	- Blockage of a water phase for 0.1–10 s	- High precision- Possibility of modulation	- Limited time of blockage- Sample heating necessary
Droplet fusion	Laser-induced droplet fusion <sup>189,191</sup>	- Fusion of droplets in close contact	- Precise- Compatible with trapped droplets	- Droplet already in contact required- Sample heating necessary
Droplet deviation	Laser-induced thermocapillary effect <sup>188,189,192,193</sup>	- Switch of droplet direction for velocity up to 1.3 cm s <sup>-1</sup>	- Control of the direction of water-in-oil droplets, even for high velocity- Easy implementation	- Application to sorting requires an additional detection ( <i>e.g.</i> fluorescence)- Sample heating necessary
Droplet sorting	Optically induced dielectrophoresis <sup>167,194</sup>	- Separation of oil-in-water droplets by size with a 2.5 μm resolution	- Direct sorting by size using light	- Water-in-oil droplets yet to be demonstrated- Optodielectrophoretic setup required
Droplet generation	Laser-induced cavitation <sup>195</sup>	- Generation of droplets in the range 1–150 pL with less than 1% volume variation- Generation frequency up to 10 kHz	- Excellent control of droplet volume- Very high generation frequency	- Possible damage of the sample- No spatial selectivity
Droplet generation	UV-induced dewetting <sup>196</sup>	- Reversible generation of water-in-oil microdroplets- Spatial selectivity- Generation frequency up to 1 kHz	- Spatio-temporal resolution of droplet generation- High generation frequency- No sample heating	- Photosensitive surfactant required

by the laser beam to prevent them from being washed away by the flow or contaminating the sample. Another strategy consists of integrating a light-powered microrotor at the stage of the microfabrication of the microfluidic channel. Such microfluidic devices usually have a very complex geometry and are typically prepared by means of advanced microfabrication techniques such as two-photon polymerization. Different pump geometries have been proposed such as a two-lobed rotor,<sup>180</sup> a rotating disk (Fig. 8A, 8B),<sup>181</sup> a twin spiral microrotor,<sup>182</sup> or an Archimedes' micro-screw.<sup>183</sup> A step further in integration was also proposed by Kelemen *et al.* who developed a device containing an optical waveguide that delivered light *in situ* to power an integrated microrotor.<sup>184</sup> Although all of these devices have interesting pumping performances, their fabrication remains complex and they have a low degree of flexibility. All of the pumping strategies based on optical tweezers, either to actuate simple colloidal particles or to control sophisticated microrotors, enable pumping up to a maximum flow rate of a few tens of  $\text{pL min}^{-1}$ . These methods are thus suitable when very small volumes have to be manipulated, for example to perform a reaction under microbatch conditions. For applications requiring high-throughput manipulation and continuous flow rates in the range of  $\text{nL min}^{-1}$  to  $\mu\text{L min}^{-1}$ , other strategies have to be developed.

Zhang *et al.* recently showed that the generation of bubbles by local laser heating could be used to pump a fluid at a flow rate in the range of 100–500  $\text{nL min}^{-1}$ .<sup>185</sup> This interesting strategy however requires strong heating of the fluid sample as well as the creation of bubbles that can disturb the flows. A totally different pumping strategy was proposed by Liu *et al.* in 2006.<sup>186</sup> A laser light beam was focused at the air/water interface of a channel being filled by a water solution containing photothermal

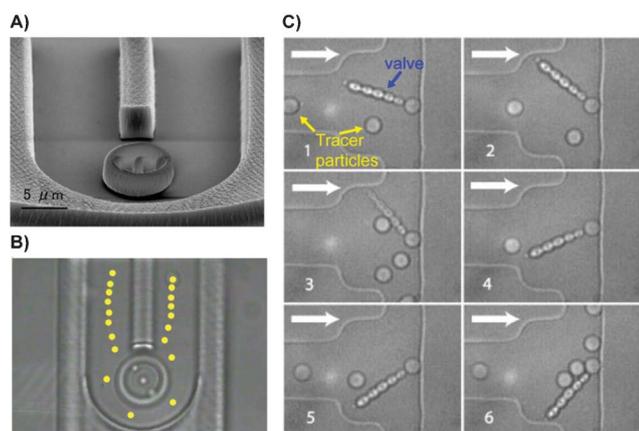
nanoparticles. The illumination generated local heating and a complex mechanism involving evaporation, droplet formation and coalescence, which resulted in a global liquid flow toward light. By moving the laser spot, they could drive the liquid inside the channel at a speed up to  $500 \mu\text{m s}^{-1}$  in a  $10 \mu\text{m}$  wide and  $5 \mu\text{m}$  high channel, corresponding to a flow rate of about  $1.5 \text{nL min}^{-1}$ . This interesting principle can also be used to mix different liquids. It unfortunately works only when there is an air/water interface in front of the liquid, *i.e.*, only during the filling of the channel. Since continuous pumping cannot be maintained once the channel has been filled, this strategy is mainly interesting as an injection strategy controlled by light rather than as a true optical pump.

**4.1.2. Optical valves.** The ability to open, redirect, or stop a flow is a key-operation in microfluidics that is usually achieved with valves.<sup>197,198</sup> The focus is here on how a valve-type operation can be set-up using light. One strategy consists of using optical tweezers to manipulate one or several microparticles to create moveable obstacles. This was first demonstrated by Terray *et al.* who could actuate a three-position valve to redirect a liquid at a flow rate of about  $30 \text{pL min}^{-1}$  (Fig. 8C).<sup>25,187</sup> Such a strategy is interesting because it can be easily adapted to different microfluidic configurations. However, since optical forces are typically on the order of piconewtons, it is difficult to apply such a strategy for many microfluidic applications where flow rates are on the order of  $\text{nL min}^{-1}$  to  $\mu\text{L min}^{-1}$  with a relatively high flow pressure. An alternative consists in using photocontrol of electroosmotic flow (see section 2.3.2). This effect is applicable to flow rates up to a few hundreds of  $\text{nL min}^{-1}$ . It allows a light-induced on/off switch<sup>173</sup> as well as a modulation<sup>173,174</sup> of the flow rate. Interestingly, it can be applied on a Y-shaped channel to dynamically control the flow distribution with light.<sup>174</sup> This strategy is inexpensive and simple to implement. It is however limited to microfluidic devices driven by electroosmotic flows. Another strategy was proposed recently by Zhang *et al.* The authors showed that the generation of bubbles by local laser heating could be used to block or redirect a flow.<sup>185</sup> Finally, we would like to underline the existence of nanoporous membranes, modified with spiropyran (Fig. 4B) to provide a photosensitive permeability.<sup>199</sup> Such membranes might be integrated in a microfluidic device to control flow rates using light.

## 4.2. Photocontrol of multiphase flows

Many microfluidic applications involve multiphase flows. A typical example consists in generating and manipulating droplets flowing continuously in an immiscible liquid (*e.g.*, water-in-oil). These pL- to nL-sized microdroplets can be used as individual containers to perform reactions and/or analysis for biology and/or chemistry.<sup>3,4</sup> We review herein how light can be used to actuate and control microfluidic operations in multiphase flows. Table 3 shows an overview of the different strategies.

**4.2.1. Microfluidic control using laser-induced thermocapillary effect.** We showed that laser-induced heating generates a thermocapillary stress that repels a droplet when  $d\gamma/dT > 0$  (see section 3.3). This phenomenon was applied to control several microfluidic operations in water-in-oil flow focusing devices.<sup>11</sup> A laser applied at the front oil/water meniscus of the

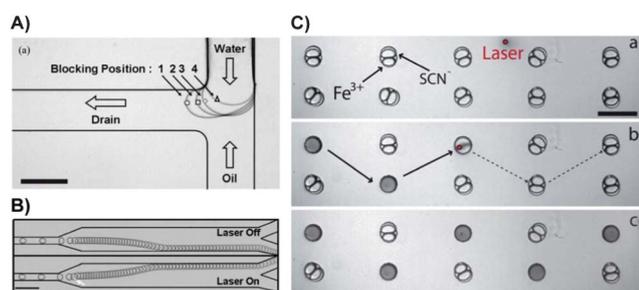


**Fig. 8** Optical valves and pumps. A) SEM picture of a disk-shaped pump inside a microchannel fabricated by two-photon polymerization. Adapted with permission from [Ref. 181]. Copyright 2007, American Institute of Physics. B) Superposition of microscopy images showing the laser actuation of the pump shown in A. The channel is filled with glycol ether ester and the disk rotates at 27 rpm. Each green spot indicates the position of a tracer particle taken every 2 s. Adapted with permission from [Ref. 181]. Copyright 2007, American Institute of Physics. C) A valve composed of a  $3 \mu\text{m}$  silica sphere linked to several  $0.64 \mu\text{m}$  silica spheres is actuated with time-shared optical tweezers. The white arrow indicates the direction of the flow ( $\sim 33 \text{pL min}^{-1}$ ). Tracer particles show that the flow is directed to the bottom channel when the valve is levelled up (frames 1–3) and then to the top channel when the valve is levelled down (frames 4–6). Adapted with permission from [Ref. 25].

droplet generating part could block the water phase for several seconds and thus constituted a transient valve (Fig. 9A).<sup>188–190</sup> When the laser was applied on a flowing droplet, it was possible to change its direction, to control droplet division<sup>188,189</sup> or to perform high-speed droplet sorting (Fig. 9B).<sup>192</sup> By using holographically generated light patterns, relatively complex droplet manipulations could be achieved.<sup>193</sup> A similar thermocapillary effect was used to selectively remove target droplets from traps.<sup>191</sup> Finally it was shown that a laser could induce the fusion of two droplets in contact,<sup>189</sup> a phenomenon that was attributed to the evacuation of surfactants<sup>190</sup> together with the oil film between the droplets. Interestingly, this was applied for selective laser-induced fusion of droplet pairs immobilized in traps (Fig. 9C).<sup>191</sup> All these operations make up a rather complete optical toolbox, which offers the advantages of being simple, easy to implement, and versatile. However, as already mentioned, it requires local heating, which can be a limitation especially in biology-oriented applications. Moreover, the operations usually work for relatively low flow rates, *i.e.*, when thermocapillary forces (up to a few hundreds of 100 nN in classical geometries<sup>200</sup>) can compete with other capillary and hydrodynamic forces.

**4.2.2. Flow shift by light-induced hydrodynamic effect.** We have mainly considered the use of a light-induced heating to create an interfacial tension gradient resulting in a force. This approach is interesting because it can work with a moderate increase in temperature ( $\sim 10$  K). By using a higher elevation of temperature, it is also possible to change viscosity in a way that is sufficient to create significant hydrodynamic changes. For instance, Lou *et al.* recently showed that local laser heating on one side of a liquid flowing into another could locally decrease viscosity and induce a significant shift of the central liquid.<sup>201</sup> However, direct applications of this phenomenon remain to be demonstrated.

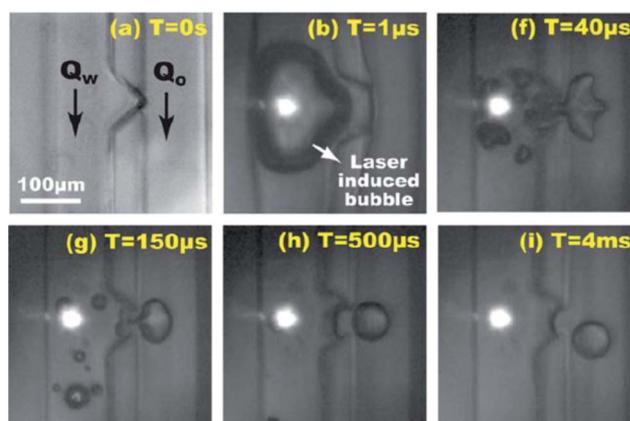
**4.2.3. High-speed droplet generation by laser-induced cavitation.** All of the methods described previously can be implemented on



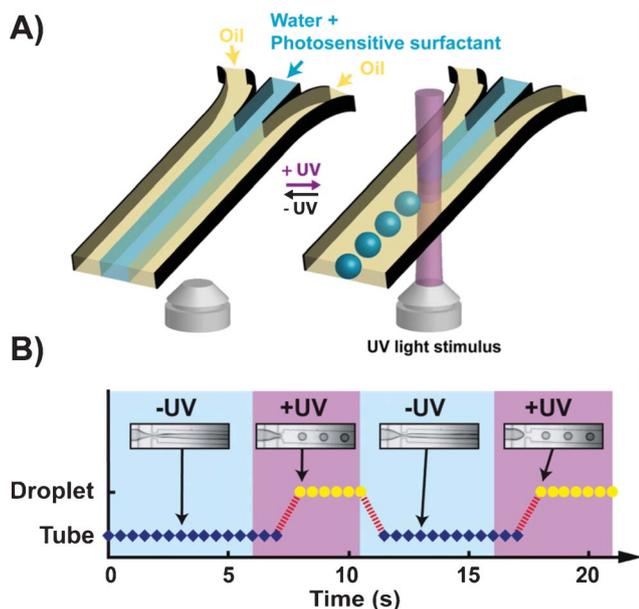
**Fig. 9** Microfluidic control using laser-induced thermocapillary effect. A) A focused laser is blocking the water interface for several seconds at the different positions indicated by arrows in a T-junction with a constant applied oil flow rate ( $0.05 \mu\text{L min}^{-1}$ ) and a constant applied water pressure ( $2.3 \cdot 10^3$  Pa). Scale bar is  $100 \mu\text{m}$ . Adapted from [Ref. 189]. B) Superposition of images taken every 10 ms showing the direction switching of water droplets ( $0.1 \mu\text{L min}^{-1}$ ) in an oil flow ( $10 \mu\text{L min}^{-1}$ ) when a 111 mW laser is focused at the point indicated by the white arrow. Scale bar is  $400 \mu\text{m}$ . Adapted with permission from [Ref. 192]. Copyright 2008, American Institute of Physics. C) A laser selectively induces the fusion of pairs of trapped droplets containing KSCN and  $\text{FeCl}_3$ , which results in the formation of a red, strongly absorbing solution. Scale bar is  $400 \mu\text{m}$ . Adapted from [Ref. 191].

already formed droplets. In the two coming paragraphs, we show how droplet generation can be controlled by light. A first strategy was proposed recently by Park *et al.*<sup>195</sup> By focusing an intense laser pulse on a water phase, they induced a cavitation bubble whose expansion induced the formation of a water droplet in a nearby channel containing oil (Fig. 10). By controlling the position of the laser pulse, they could generate a nearly monodisperse population of water droplets with controllable volumes in the range 1–100 pL. This is a truly high-throughput approach with a frequency of droplet generation up to 10 kHz. This approach thus offers excellent performance for on-demand droplet generation controlled by light. A first limitation is the generation of the droplets, which is based on a cavitation mechanism that can be harmful for species being encapsulated (*e.g.*, living cells, DNA or proteins). A second limitation is the absence of spatial selectivity since the droplets can only be generated at the junction between the water phase and the oil phase.

**4.2.4. Reversible and spatially resolved photocontrol of droplet generation using an isothermal light-induced dewetting effect.** We recently proposed a strategy, which allowed us to control, with both spatial and temporal resolution, the high-speed generation of pL-sized droplets in an isothermal way.<sup>196</sup> Our method consisted of adding the photosensitive surfactant AzoTAB (Fig. 5A) to the water phase of a standard water-in-oil flow focusing microfluidic device (Fig. 11A). Interestingly, the wettability of the microfluidic substrate by the water phase depends on the isomerization state (*cis* or *trans*) of AzoTAB: low wettability in the presence of *cis*-AzoTAB (*i.e.*, when UV is applied) and high wettability in the presence of *trans*-AzoTAB (*i.e.*, when UV illumination stops). In this way, we showed that many cycles of reversible and rapid switches between continuous laminar flows ( $-UV$ , wetting situation) and stable droplet regimes ( $+UV$ , non wetting situation) could be achieved (Fig. 11B). In the droplet generation regime, the droplets are nearly monodisperse and are generated at a frequency of up to 1 kHz. Interestingly, by applying the UV light stimulus through a photomask, we were able for the first time to dynamically



**Fig. 10** Droplet generation by laser-induced cavitation. Phosphate-buffered saline water solution ( $12 \text{ mL h}^{-1}$ , left) and corn oil ( $0.2 \text{ mL h}^{-1}$ , right) flow in channels connected through a nozzle-like orifice. Application of a  $100 \mu\text{J}$  laser pulse creates a cavitation bubble followed by the ejection of a  $137 \text{ pL}$  droplet of the water solution into the oil flow. Adapted from [Ref. 195].



**Fig. 11** Photoreversible droplet generation by UV-induced dewetting. A) A water solution containing a photosensitive surfactant is flowing into a water-in-oil flow focusing device. Without UV, the water phase is wetting the microfluidic substrate and form a stable “tube” regime. Application of UV induces a dewetting transition and the water phase enters a stable droplet generating regime. Adapted from [Ref. 196]. B) Observation of successive stable “tube” (blue diamonds) and “droplet” (yellow disks) regimes by continuous alternation of dark (–UV, light blue background) and illumination at 365 nm (+UV, purple background). Water phase (10 mM AzoTAB) and oil phase (oleic acid) flow at  $3 \mu\text{L min}^{-1}$  and  $2 \mu\text{L min}^{-1}$ , respectively, in a  $100 \mu\text{m}$  wide channel. Adapted from [Ref. 196].

control the position of the droplet generation. This method, which is based on a photochemical light-induced dewetting effect, offers several advantages. First, it is isothermal because the change of wetting properties is due to photochemical properties and not to a local increase in temperature. Second, it can be easily implemented in many kinds of microdevices. Moreover, it does not require a specific optical set-up and a standard illumination source (LED) can be used to actuate the droplet generation. Finally, it offers spatio-temporal photocontrol over droplet generation. The main limitation is the necessity to use a photosensitive surfactant.

**4.2.5. Optically induced dielectrophoresis.** Dielectrophoresis, *i.e.*, the force applied on dielectric particles in nonuniform fields, is a major separation method in microfluidic systems.<sup>202</sup> It is therefore an important target for light-controllable microfluidic operations. In a breakthrough paper, Chiou *et al.* showed in 2005 that the projection of a light pattern on a photoconductive layer allowed massively parallel manipulation of single cells and microparticles through the photocontrol of dielectrophoretic forces.<sup>167</sup> In this case, the light pattern was used to create a network of “virtual electrodes”, which could be reconfigured at will without any wiring problems. This principle was later applied to separate oil-in-water droplets according to their size in a microfluidic device.<sup>194</sup>

## 5. Perspectives

### 5.1. Digital optofluidics

Digital microfluidics, the high-throughput manipulation of discrete pL- to  $\mu\text{m}$ -sized droplets as individual containers or reactors, is a particularly successful part of microfluidics and has already provided a large variety of applications in chemistry and biology.<sup>3,4,152,154–157</sup> We showed that several principles and techniques are now available to efficiently manipulate discrete droplets with light (Table 1). Each method has its own advantages and drawbacks but, interestingly, a large spectrum of applications seems to be reachable by choosing the most adequate method for each target application. Therefore, we are probably ready to enter the era of digital optofluidics where light will be the main actuator of discrete droplet manipulation. Massively parallel photomanipulation is now possible by using light patterns and projected images,<sup>167,162</sup> which is a great advantage over standard actuation methods relying on highly complex arrays of pumps, valves, or electrodes. Digital optofluidics shall arguably enable a very large number of applications across chemistry and biology, while reducing the cost and improving efficiency, performance, and versatility of the devices compared to standard digital microfluidic schemes.

### 5.2. All-optical fluidic chips

The concept of an all-optical fluidic chip, where light could serve as both sensor and actuator in the same device, was initially proposed by Glückstadt.<sup>203</sup> With all the light-controllable microfluidic operations that we have mentioned in this review, with additional possibilities such as sensing,<sup>204</sup> particle sorting,<sup>205</sup> or optical beam control,<sup>206</sup> and with the capacity of light source integration,<sup>184</sup> the concept of Glückstadt is more than ever a realizable target. Compared to standard microfluidic devices that need to be physically connected to complex external electric, hydraulic or pneumatic devices, such all optical fluidic chips will offer improved flexibility, robustness, and portability.

### 5.3. Light-reconfigurable devices

Most microfluidic systems work well for a given application. But because they rely on the integration of several actuators such as electrodes, pumps or valves, they are usually highly specific to a given set of operations and applications. With the absence of immobilized actuation element inside the device, a great advantage of controlling microfluidic operations using light is the possibility to reconfigure the device at will to adapt and optimize it for each new application. Some examples have already been reported, especially the reconfiguration of some optofluidic systems using an external light stimulation.<sup>207</sup> This can be easily extended to light-driven microfluidic operations. We can now imagine using standard, robust, and low-cost microfluidic devices, in which all desired microfluidic operations (*e.g.*, injection, pumping, mixing, sorting) will be controlled by light stimulation according to a protocol that will be decided by the user for its target application. Interestingly, reconfigurability will allow the user to i) optimize his/her device for the best performance and ii) reuse the device for new applications.

## 5.4. Time for applications

Clearly, most of the light-driven microfluidic operations reviewed here emphasized the actuation aspect, *i.e.*, how light could be used to drive and control fluids at a micro-scale. Most of applications have been demonstrated as proof-of-concepts only. Now that researchers have a complete set of tools to control microfluidics by light, it seems to be time to demonstrate real applications in chemistry and biology that cannot be done by using standard approaches. Moreover, the development of stand-alone, user-friendly and highly flexible optofluidic platforms could be of interest for a wide community of researchers working in various fields including chemistry, biology, physics, and drug discovery.

## 6. Conclusions

We showed that a complete toolbox is now available to control microfluidic systems by light. Several strategies exist and can be selected according to a desired performance and target applications. Light-driven microfluidic systems will offer new platforms with unprecedented flexibility, robustness, and parallelization capabilities. They will have a great impact in academic laboratories, where they will allow new discoveries in natural and physical sciences, as well as in industry where they will allow large-scale development of standardized devices that can be fully controlled through optical stimulation.

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