Crystallization of interfacially tethered colloids in an emergent optofluidic potential

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The interplay between laser light, trapped particles, and fluid flow can produce counterintuitive effects in optical tweezing. Here we uncover an attractive, long-ranged, non-equilibrium force field centered on an optically trapped particle near a water-oil interface, produced by local heating and mediated by global fluid flow. This causes surrounding untrapped colloids, tethered to the interface but allowed to diffuse freely along it, to crystallize around the force center. In this configuration, the non-equilibrium force is the gradient of a potential, of strength proportional to the local heating, which, surprisingly, allows for an effective equilibrium description. Our results open unexplored routes to optofluidic manipulation and assembly of colloidal particles.

Since their introduction [1], optical tweezers have revolutionised the manipulation of matter at the nano- to micro-meter scale [2–6]. Tweezers have found extensive use in the trapping and assembly of micron-sized colloidal particles [7–9] and yielded novel forms of colloidal matter that are held together by optical forces [10–16]. While these forces have been thoroughly understood in terms of the transfer of momentum from radiation to particles, much less studied are the effects of heating, due to the transfer of energy from radiation to the surrounding fluid medium. Such effects can be unexpectedly subtle, as for example in the vicinity of fluid-fluid interfaces, where local heating, by altering the interfacial tension, can set both fluids into motion [17, 18]. While trapping and heating are caused by the interaction of light with, respectively, the particles and the medium, it is natural to ask what new effects might arise from the combined interaction of light, particles, and the medium.

Two recent experiments touch on this question. In the first, a light-controlled thermoelectric field is generated in the medium, which contains a mixture of surfactant, ions, and micellar depletants, to assemble colloidal particles into a variety of two-dimensional aggregates. In the second [19], the differential heating of trapped Janus particles is used to sustain a thermo-osmotic flow which entrains untrapped particles into clusters. These suggest the possibility of harnessing the interaction of laser light with simple solvents (like water or oil) and simple colloids (like polystyrene particles) for manipulation and assembly.

In this Letter, we show that the optical trapping of a thermophoretic colloidal particle near a water-oil interface sets up a long-ranged, non-equilibrium force field whose effect on untrapped particles, that are tethered to the interface but otherwise free to diffuse along it, is to cause them to crystallise around the force center. The sign, magnitude, and distance-dependence of this force cannot be accounted for by standard colloidal interactions or entrainment in surface-tension driven Marangoni flows. Using theory and simulation, we show that the force is mediated by hydrodynamic flow produced by stalled thermophoresis of the optically trapped colloid, whose effect on the fluid, to a very good approximation, is that of a hydrodynamic monopole. For motion parallel to the interface, the force is the gradient of a potential and the particle dynamics admits an effective equilibrium description. Brownian dynamics simulations in this emergent potential, whose strength is determined by the local heating, is in excellent agreement with experiments. The emergent potential is of much longer range than the optical trapping potential, couples to the size of the particle and not its dielectric properties, and manifests itself in simple solvents such as water or oil. These desirable features open unexplored routes to the optofluidic manipulation and assembly of colloidal particles on multiple spatial scales [20]. We now describe our experimental results, theoretical analyses, and numerical simulations.

Experimental setup: Our setup is shown schematically in the inner panel of Fig. (1). We prepare oil droplets of radius between 20µm and 30µm and coat them with a surfactant-polymer layer, following [21]. Single-stranded (ss)DNA chains denoted by A, attach to this layer and densely cover it. Polystyrene particles (PS) of radius a = 0.53µm, functionalised by complementary A′ ssDNA strands, are then grafted on to the coated interface. The DNA coating of the particles prevents them from aggregating. Compared to colloids straddling the interface, grafting eliminates capillary forces, light-wave reflections and long-ranged electrostatic dipolar interactions from the asymmetry of charge distributions on interfacially wetted colloids [22, 23]. The surfactant-polymer coating sterically stabilises the interface from deforming and maintains the grafted colloids approximately 50 nm away from it. The colloids thus diffuse freely on the interface, which appears almost flat on the particle scale. A grafted colloid is optically trapped by focussing the laser beam above the interface on the water side. A fraction of the colloids remain ungrafted and diffuse freely in the bulk. They serve as tracers, providing information on bulk fluid flow. Further details of the system and the calibration of the trap, using both standard and Bayesian methods, are provided in the SI [24].
Figure 1. Schematic of experiment and bright field microscopy of particle dynamics. The inner two panels show the water-oil interface coated with the surfactant sodium dodecyl sulphate (SDS) and the block copolymer polylysine-polyethylene glycole (biotin-PLL-PEG). The biotynilated PEG ends are functionalized with biotynilated A DNA via streptavidin and polystyrene (PS) particles are grafted on to this layer. The keys at the bottom mark each component. The particles diffuse freely on the interface when the laser is off (left panel); a single particle is optically trapped when the laser is turned on (right panel). The outer panels show the dynamics of crystallization of untrapped colloids around the optically trapped colloid (red circle) when the laser is turned on (red harpoons). The crystallite melts when the laser is turned off (blue harpoons). The motion of the particles circled green provides clear evidence of a long-ranged attraction to the center. See SI movie.

Reversible crystallization: The outer panels of Fig. (1) show our principal experimental result. Each frame shows the position of the colloids at the times indicated at its top left. The attached harpoons are blue (red) when the laser is off (on) and point to frames at future times. The optically trapped colloid is shown in red. The first two frames show free diffusion when the laser is off. When the laser is turned on in the third frame, diffusion is immediately replaced by directed motion towards the trapped particle with speeds of up to $50 \mu m/s$. This leads to rapid crystallization which is essentially complete within a few seconds, as shown in the frame at 6.2s. Thermal fluctuations cause small displacements in the core of the crystallite but large ones at the edges where particle rearrangements take place, as shown in the frames between 6.2s and 20.3s. The crystallite begins to melt as soon as the laser is turned off and a freely diffusing state is recovered within a few seconds. This cycle of freezing and melting in response to turning the laser on and off is rapid, robust and reproducible.

Optofluidic mechanism: What force underlies this phenomenon? By examining the motion of the colloids as the laser is turned on, it is clear that the force has a range of at least $5 \mu m$ and a magnitude of the order of pN, directed radially inwards to the trapped particle. The origin of the force in the entrainment of colloids by Marangoni flow can be immediately ruled out, as such a flow must point outwards from the hot region surrounding the laser focus. In the absence of other plausible mechanisms, we are led to postulate the following: the colloid nearest to the laser focus is optically trapped and local heating induces a thermal gradient in the surrounding fluid, decaying with distance from the focus. This drives a thermo-osmotic flow confined to a thin boundary layer around the colloid surface [25]. The conservation of momentum leads to thermophoretic motion of the colloid from the hotter region near the trap center to the cooler region near the interface (as the Soret coefficient is positive [26]). This compresses the DNA tethers and motion stalls when the thermophoretic force is balanced by the
tether reaction. Since the colloid remains in a thermal gradient, the thermo-osmotic flow continues unabated on its surface, but produces no particle motion. This leads to a monopolar hydrodynamic counterflow in the fluid, with the monopole pointing normal to the interface and into the water phase. The long-ranged and attractive character of the flow entrains untrapped, tethered particles and draws them towards the focus. The tethers prevent particles from being convected away normal to the interface. Thus constrained, the particles aggregate into crystallites under the action of the optofluidic force with local crystalline order being enhanced by short-ranged forces, including those due to optical binding (see below).

To make the above hypothesis quantitative and testable, we solve the equations of mass, momentum and energy conservation in the fluid with appropriate boundary conditions at the colloid surfaces and the oil-water interface (detailed in [24]). The geometry is shown schematically in Fig. 2(a). We use the boundary integral representation for the momentum (Stokes) and energy (Laplace) equations to impose boundary conditions at the colloid surfaces and use appropriate Green’s functions to satisfy the boundary conditions at the oil-water interface [27]. The integral equations are solved in a basis of irreducible tensorial harmonics to yield the temperature field \( T \) and fluid flow velocity \( v \) in an externally imposed temperature field \( T^\infty \) (representing laser heating). These are shown in Fig. 2(b) for a single trapped colloid. From these we obtain the thermophoretic force \( \mathbf{F}_T \) on the trapped colloid and the optofluidic force \( \mathbf{F}_H \) with which free colloids are attracted to the trapped colloid as,

\[
\mathbf{F}_T = -\frac{\mu_T}{\mu_\perp} \nabla T^\infty |_{1}, \quad \mathbf{F}_H = \frac{\mu_T}{\mu_\perp \mu_\parallel} \mathbf{G}^w \cdot \nabla T^\infty |_{1}. \tag{1}
\]

In the above, \( \mu_T \) is the thermophoretic mobility, \( \mu_\perp \) and \( \mu_\parallel \) are, respectively, the mobility perpendicular and parallel to the interface, \( \mathbf{G}^w \) is a Green’s function of the Stokes equation for a no-shear plane interface and \( |_{1} \) indicates evaluation at the center of the trapped colloid [24]. The optofluidic force, through its dependence on \( \mathbf{G}^w \), varies monotonically as the inverse square of the distance \( r \) from the trapped colloid. As particle motion is overdamped, the velocity scales as \( v \sim r^{-2} \), and hence displacements scale with time intervals as \( r^3(0) - r^3(t) \sim t \).

We test this from the experimentally measured positions to find excellent agreement, shown in the inset of Fig. 2(c).

**Optofluidic potential:** For motion at a constant height, the nonequilibrium optofluidic force \( \mathbf{F}_H = \mathbf{F}_H \dot{r} \) admits a potential

\[
\Phi(r) = -\frac{\mu_T}{4\pi\eta\mu_\perp\mu_\parallel} \left[ \frac{1}{\lambda + \lambda r^w} \frac{h}{1 + \lambda r^w} + \frac{2\lambda}{1 + \lambda r^w} h^3 \right] \partial_r T^\infty. \tag{2}
\]

Here \( r^* = \sqrt{r^2 + h^2} \), \( h \) is the height of the colloid from the interface and \( \lambda = \eta_w/\eta_o \) is the ratio of the viscosities of water and oil. Then, the in-plane coordinate \( \mathbf{R}_i = (X_i, Y_i) \) of an untrapped colloid \( (i = 2, 3, \ldots N) \) obeys the overdamped Langevin equation

\[
d\mathbf{R}_i = -\mu_\parallel \nabla_i (U + \Phi) \, dt + \sqrt{2k_B T \mu_\parallel} \, d\xi_i \tag{3}
\]

where \( U \) is a potential containing the sum of all short-ranged colloid-tether and colloid-colloid interactions, \( \Phi \) is the optofluidic potential evaluated at the location of the particle, and \( d\xi_i \) is a zero-mean Gaussian random variable with variance \( \langle d\xi_i, d\xi_j \rangle = \delta_{ij} \mathbf{I} dt \). The stationary distribution of the particle positions is Gibbsian, \( P \sim \exp[-(U + \Phi)/k_B T] \), even though the dynamics is out of equilibrium. At an air-water interface, where \( \lambda = 0 \), the optofluidic potential has a Coulomb form \( \Phi \sim 1/r^w \). The opposite limit of \( \lambda \to \infty \), corresponding to a no-slip wall, gives an optofluidic potential \( \Phi \sim 1/r^3 \).
latter form, with different prefactors, has been found in previous studies on charged [28], thermophoretic [29, 30], and active colloids [27, 31, 32].

The strength of the potential $\Phi$ when compared with the thermal energy $k_B T$ determines the onset of crystalline order. Denoting it by

$$\Phi_0 = \frac{1}{4\pi \eta \mu_{||} (1 + \lambda)} \cdot \frac{\mu_T}{\mu_\perp} \cdot \partial_z T^\infty \quad (4)$$

and using parameters $\mu_T = 10 \mu m^2 s^{-1} K^{-1}$, $\lambda = 30$, and $\eta_w = 8.9 \times 10^{-4} \text{Pas}$, we get $\Phi_0 \sim 100 k_B T$ when $\partial_z T^\infty = 15 K\mu m^{-1}$. Here we have used the experimentally measured positions in Fig. 2(c) to estimate the $\partial_z T^\infty$ from other known parameters. The strength is proportional to the thermal gradient and leads, curiously, to freezing by heating and melting by cooling. We show this explicitly in Fig. 3(a) by direct numerical simulations of Eq. (3) as a function of the strength of the optofluidic potential.

**Short-range forces:** The DNA tether exerts a short-range force on the particles and prevents them from being convected away from the interface. This is confirmed in Fig. 3(b) where an untethered particle appears and then disappears from the focal plane, consistent with the flow pattern shown in Fig. 2(b). Once the long-ranged optofluidic interaction draws particles into the center of force, the short-ranged optical binding force enhances crystalline order. The optical binding force is obtained from a numerical solution of the Maxwell equations in the Mie approximation (detailed in [24]). It is smaller in magnitude and shorter in range than the optofluidic force but, being oscillatory and anisotropic (see Fig. 2(d)), couples to both positional and bond order of the colloidal crystal. Its effect can be inferred indirectly from the rapid annealing of a defect (yellow circle) produced by the collision of a tethered particle with the crystallite, as shown in Fig. 3(c). We have not studied this coupling in detail and leave it to future work.

**Conclusion:** Our experiments show how a novel non-equilibrium optofluidic force can be used to transport particles towards (or away) from an optically trapped “seed” particle. Theoretical analysis shows that this non-equilibrium force derives from a potential, whose strength is proportional to the temperature gradient at the location of the seed. Untracted particles couple to this potential regardless of their material properties, enabling the optofluidic manipulation of particles that cannot, otherwise, be optically trapped. Both the location of the potential and its strength can be modulated by the laser and its sign can be altered by changing the ratio of thermal conductivities of the liquids. We foresee this to lead to novel mechanisms of switchable and addressable transport in microfluidics.

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\[ \text{Figure 3. (a) Competing Brownian motion and optofluidic potential determine the extent of crystallization: full crystallization is obtained if the strength of the potential } \Phi_0/k_B T > 10, \text{ while there is only a local crystallization around the center of the potential for lower strength, and finally, Brownian motion precludes any aggregation if } \Phi_0/k_B T < 1. \text{ The particles are coloured by their coordination number. (b) An untethered particle (yellow circle) being convected away from the interface by the optofluidic flow of Fig. 2(b). (c) Short-range forces promote the rapid annealing of a defect (yellow circle) produced by a particle colliding with the crystal (yellow circle) in the first frame. The scale bar is 10\mu m.} \]

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