Strong collective currents of gold nanoparticles in an optical vortex lattice

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Gold nanoparticles moving in aqueous solution under a optical vortex lattice are shown to present a complex collective optofluidic dynamics. Above a critical field intensity and concentration the system presents a spontaneous transition towards synchronised motion, driven by nonconservative optical forces, thermal fluctuations and hydrodynamic pairing. The system exhibits a rich assortment of collective dynamics such as strong unidirectional currents of nanoparticles at speeds of centimetres per second. This relatively simple optofluidic setup offers an alternative way to control mass and heat transport at the nanoscale, which has been so far elusive.

Efficient transport of nanoscale objects is a very active area of research where optofluidics is heavily involved [1]. Beyond Optical Tweezers [2], light forces induced by stochastic optical fields [3–5] can be used to to “activate” and control nanoparticle motion. Optically active micron-sized particles interacting in a time-varying fluctuating speckle light field can diffuse about three times faster than thermally, moving at microns per second [3, 4]. However, below microns, active control becomes elusive due to strong thermal fluctuations [6].

A clever setup has recently been tested [1] using plam-on-enhanced optical trapping to fix nanoantennas in microscopic arrangements. In conjunction with an oscillating electric field, photo-induced heating of these nanoantennas leads to microscopic natural convection of the surrounding liquid at velocities of tens of μm/s [1]. The driving mechanisms in these previous examples are either of stochastic origin (random speckle patterns) [3, 4] or deterministic (buoyancy) [1].

Instead, self-organized collective motion [7] is inspiring new designs of micron-size “artificial swarms” [6, 8, 9] following the ubiquitous examples nature offers (bacteria, ants, birds and more [7, 10]). Its universality is revealed by toy-models, such as the Vicsek model [7], based on extremely simple individual-activation and interaction rules. Hydrodynamics provides a powerful interaction kernel affecting, for example, the complex rotational dynamics of particles [11], often leading to swarming [7]. The “colloidal rollers” are a recent example outside optofluidics. They consist in micron-sized spheres in suspension which, activated by electric [9] or magnetic [8] fields, rotate near a surface and can self-organize into flocks with cluster-speeds of centimetres per second [8].

In this Letter we present a new class of optically controlled active media on time stationary optical curl-force fields [12–18] acting on a suspension of gold nanoparticles (NP). In accordance with self-organized critical phenomena, NPs spontaneously synchronize moving coherently in unidirectional currents at speeds of cm/s. We have numerically investigated these optofluidic dynamics by developing accurate Brownian hydrodynamics solvers which resolve the optical force from the incident light and the many-body forces induced by the light scattered by each NP. The proposed setup is relatively simple and we hope that the striking results presented here will foster experimental work on this subject.

We consider a suspension of N gold NPs of R = 50 nm radius in water at dilute volume fraction (φ = 4πR3N/(3V) ≈ 10−4) exposed to an optical field formed by the intersection of two perpendicular coherent laser beams [12, 13] pointing in the x and y directions (optic plane) polarized along z with a phase difference θ = π/2 rad (see Fig. 1). This primary field with wavelength λ and wavenumber k = 2π/λ equals E0(r) = 12|E0| (sin(kx) + eiθ sin(ky)) ẑ with |E0|2 = 2fn/(cε0) controlled by the intensity of the laser beam I and the refractive index of water n = √(ε (ε is the relative permittivity and c is the vacuum speed of light). The electrodynamical response of spherical nanoparticles, much smaller than the laser wavelength R ≪ λ, can be well described by their complex optical polarizability α = α′ + iα″ (see Suppmental Material, SM). The spatially modulated field Eexc will induce a dipole p(r) = ε00α Eexc(r) centered on the position of each particle r, and, consequently, a non-vanishing averaged Lorentz force with components F(r) = (ε0002)Re {α Eexc(r) ∇ E∗ exc(r)}r;r, the primary optical force arises from Eexc = E0,

\[ F^{(1)}(x, y) = 2\alpha n c \nabla \left( \sin^2(kx) + \sin^2(ky) \right) \]

\[ + 2\alpha n c \nabla \times \left[ 2\cos(kx)\cos(ky) \hat{e}_z \right]. \quad (1) \]

This nonconservative force field (1) forms a periodic
the NPs remain confined to a cubic box of side $L$. Isocontours of single-particle probability density and streamlines of the NP velocity field in a periodic domain, folded into each NP (brighter regions mean higher $|E|$). We show a fixed-$z$ cross section of the force field and the modulus of the total electric field $|E|$ including the incident beams and the light scattered by each NP (brighter regions mean higher $|E|$). In this setup, the NPs remain confined to a cubic box of side $L \approx 7.0 \lambda$. (b) Isolines of single-particle probability density and streamlines of the NP velocity field in a periodic domain, folded into the Bravais unit cell of the primary optic field $x \in [-\lambda/2, \lambda/2]$ (same for $y$) against phase-coordinates $\varphi_x = 2\pi(x/\lambda)$. The non-dimensional laser energy (see text) corresponds to $u = 1$ (below) $u = 2$ (above) the transition to coherent NP motion (volume fraction $\phi = 3.0 \times 10^{-3}$). Brighter regions correspond to denser domains. The unstable saddle nodes (SD) of the primary force field (Eq. 1) are indicated in the $u = 1$ panel. The dashed line for $u = 2$ illustrate a zig-zag path followed by NPs under coherent dynamics.

pattern of optical vortices [12], with a Bravais unit cell in $(x, y) \in [-\lambda/2, \lambda/2]$ (see Fig. 1(b)). Its non-conservative part $\nabla \times A(x, y) \hat{z}$, proportional to $\alpha''$ [19] embodies the so-called “curl forces” [13, 16–18]. It resembles a chequerboard, with alternating squares of positive and negative vorticity. Curl-forces neatly convert the laser energy into work [12, 16, 17] and $U \equiv 2I(n/c)\alpha'' = \epsilon_0|E_0|^2\alpha''$ (related to the energy per NP) is a convenient unit to compare with the thermal counterpart $k_B T$. The primary field has no stationary nodes where the NP can rest [15], but four unstable saddle nodes (SD) instead (see Fig. 1(b)). As a consequence, an isolated gold NP experiences giant normal diffusion [14] with a diffusion coefficient $D_{op} \sim \lambda^2/\tau_{op} = u D_{th}$ which is larger than the thermal value $D_{th}$ for $u \equiv U/k_B T > 1$. This non-dimensional laser energy $u$ can be increased up to $\sim 10^2$ before cavitation takes place [20, 21].

We investigate the collective behaviour of a suspension of gold NPs. Aside from the primary force in Eq. (1) and the thermal kicks, NPs interact optically through multiple scattering forces $F^{(2)}(\{r_i\})$, and also hydrodynamically, with a collective drag velocity $v^{(c)} = \sum_j \mu_{ij}(r_{ij}) \mathbf{F}_j$ arising from the mutual hydrodynamic mobility $\mu_{ij}$ dominated by the Oseen term $\mu_{ij} \sim 1/r_{ij}$. In order to isolate the effect of hydrodynamic interactions (HI) at fixed $\phi$, we first solved these dynamics under periodic boundary conditions (PBC), without taking into account multiple scattering. These dynamics were solved using the Fluctuating Immersed Boundary method (FIB), which is an immersed boundary method for Stokesian particles in fluctuating hydrodynamics [22] (see SM). We evaluate the (time-dependent) single particle diffusion defined as, $D(t) = \Delta^2(t)/\langle t \rangle$ where $\Delta^2 = \langle (\mathbf{r}_1(t_0 + t) - \mathbf{r}_1(t_0))^2 \rangle$ is the in-plane ($\parallel$) mean square displacement (MSD) of a tracer NP with position $\mathbf{r}_1 = \mathbf{r}_1 + z_1 \hat{z}$. At a fixed $\phi$, Fig. 2(a) shows a sudden transition from (enhanced) normal diffusion $D = D_{op}$ to superdiffusion $D(t) \sim t^\beta$, where the diffusion exponent jumps to the ballistic value $\beta = 1$ above the critical laser energy $u > u_c(\phi)$. In periodic boundaries, the superdiffusive regime corresponds to a large current of NPs occupying the whole box in the $z$ direction and flowing with vorticity in $\mathbf{d} = (\pm 1, \pm 1)$ direction. This 3D roll, illustrated in Fig. 2(c), would be qualitatively similar in an enclosure with walls.

The phase diagram of Fig. 2(d) draws the critical line $(u_{cr}, \phi_{cr})$ separating uncorrelated walkers from the synchronized flow of NPs. Beyond, at larger $u$ or $\phi$, an extremely rich collective dynamics unfolds (more details in SM). The critical line satisfies $\xi^* = (u_{cr} - u^*) (\phi_{cr} - \phi^*)$, where $u^*$ and $\phi^*$ are threshold values below which the transition does not occur. Under PBC we find $\xi^* = (1.55 \pm 0.05) \times 10^{-4}$ while $\phi^* = (1.5 \pm 0.1)$ and $u^* = 1.0$. Interestingly, coherent dynamics cannot ensue unless the energy per NP surpasses the thermal energy $U > U^* \approx k_B T$. Also remarkable, is the low threshold concentration $\phi^*$ involving an average separation of $3\lambda$ between NPs.

To investigate the effect of multiple scattering we calculate the many-body secondary optic forces $\mathbf{F}_2(\mathbf{r})$ (see SM) and plugged them into a Brownian solver implemented with the Rotne-Prager-Yamakawa mobility tensor for HI [23]. To fix $\phi$ we first considered a confined domain where a repulsive external potential impedes NPs from escaping out from a cubic box of side $L = 7\lambda$. This confined geometry mimics an experimentally feasible laser-trap [24]. In this case we analyzed
FIG. 2. (a) Effective diffusion coefficient of gold NPs $D(t) = \Delta z^2 / (4t)$ in periodic boundaries at $\phi = 2 \times 10^{-3}$, obtained from single-particle in-plane MSD $\Delta z^2(t)$ and scaled with the thermal value $D_{th} = k_b T / (6\pi \eta R)$. For $U/K_b T = u > u_{cr} \sim 1$ the dynamics become ballistic $D \sim t^3$ with $\beta = 1$. (c) The superdiffusion exponent $\beta$ against $\xi = [u - u_{cr}(\phi)][\phi - \phi_{cr}(u)]$ for periodic (star symbols) and confined setups. Results with and without hydrodynamic interactions (+HI and −HI) and/or secondary optical forces (+SF and −SF) are compared. (c) The coherent 3D roll of NPs recirculating in the periodic domain with a sinusoidal velocity profile in the $z$ direction. (d) Dynamic phase diagram showing the transition from enhanced normal diffusion ($D \sim u D_{th}$) to coherent dynamics $D \sim t^3$ at the (green) critical line $\xi^* = (u_{cr} - u^*)(\phi_{cr} - \phi^*)$ (see text for details).

...ary solution $\rho_0(r)$, illustrated in Fig.1(b) ($u = 1$). The instability is triggered by the collective current $\mathbf{v}^{(c)}$ arising from HI. As shown in 1(b), this current breaks one of the symmetries of the primary optical field (mirrored by $\rho_0(r)$) and creates an average mass flow across the system. The particles tend to follow each other along zig-zag paths which move along one of the four possible diagonal directions of the lattice $\mathbf{d} = (\pm 1, \pm 1)$. This is consistent with hydrodynamic pairing [26] which is known to happen if particles are forced to follow curved paths in a liquid. Note that the instability is degenerate in $\mathbf{d}$ and the NP current might jump from one diagonal to another, after many optical times $\tau_{op}$.

Although the dynamic transition stems chiefly from hydrodynamic interactions (HI) [see case −HI in Fig. 2(b)], secondary forces have a measurable effect in reducing the intensity of the collective current. Secondary forces may be viewed as a self-generated, spatio-temporal pattern induced by multiple scattering of light. This pattern disrupts the periodic stationary curl force field, thus reducing the coherence of the zig-zag paths followed by the NP’s under coherent motion [see Fig 3(c)]. The phase lag term $\exp[\mathbf{i} \mathbf{k} \cdot \mathbf{r}_{ij}]$ present in the optical Green function (see SM) creates undulating force patterns [5] which become quite complex, even for just two isolated NPs $\mathbf{F}^{(2)} = \mathbf{F}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ (see Fig.3). As illustrated in Fig. 3(a), two NPs in the same optic plane tend to repel each other. In a confined domain (see SM), this leads to the expansion of the NP’s ensemble volume. However, along $z$, the scatter produces marginally stable domains $[F_z = 0$ and $dF_z / dz < 0$, see Fig. 3(b)]. In suspension, this effect leads to transient layers of NPs separated by roughly $\Delta z \sim 2 \lambda$ (SM).

A nontrivial question is what happens if the confinement is removed. As a possible outcome, the extra pressure from secondary forces might destroy coherent motion by inducing a fast dispersion of NPs over the optic plane. We prepared experiments placing NPs in the confined domain, with $u$ and initial concentration $\phi(t = 0)$ above the transition line. Upon removing the confining potential, we immediately observe the formation of a jet of NPs moving at an impressive velocity (see video in SM). The trajectories of single NPs, the CoM displacement and velocity $v_{cm}(t)$ are shown in Fig. 4 for one of the cases considered. The jet moves along one of the diagonals $\mathbf{d}$ and its direction remains stable until dispersion (mostly along $\mathbf{d}$ direction) leads to $\phi(t) < \phi_{cr}(u)$ [see Fig. 4(b)]. Notably, the flock disperses much less in $z$ direction when secondary forces are added. As shown in SM, attractive secondary normal forces counter-balance the repulsive Oseen drag in $z$ direction. As shown in Fig. 4(c) and (d), the collective velocity scales like $v_{cm} \propto (\phi - \phi_{cr})^{1/3}$ which differs from that observed in the collective motion of microrollers $v_{cm} \sim (\phi - \phi_{cr})$ [8, 9]. A simple scaling argument unifies both results. In terms of the interparticle distance $r_{12}$, the leading term in the
mutual mobility generally scales like $\mu_{12} \sim 1/r_{12}^d$ while, in a $d$-dimensional system, $r_{12} \sim \phi^{-1/d}$. One thus expects the collective velocity $v_{cm} \sim \mu_{12} F_2$ to scale like $v_{cm} \sim \phi^{2/d} F$. Groups of microrollers move with $v_{cm} \sim \phi$ [8, 9] close to a wall, where $d = 2$ and $\alpha = 2$. In our setup $d = 3$ and the laser force $F \sim U/\lambda$ activates monopole (Oseen) couplings $\alpha = 1$, providing $v_{cm} \sim \phi^{1/3} U/\lambda$. To complete our scaling, we impose $v_{cm} = 0$ below the critical line, leading to $v_{cm} \propto (u - u_{cr})(\phi - \phi_{cr})^{1/3}$ which agrees quite well with results in periodic, unconfined and confined domains, as shown respectively in (Fig. 4(c), (d) and SM (confined case).

We have presented a collective dynamic transition of optically driven gold nanoparticles, which shares many generic features of (deterministic) micron-sized active colloidal flocks [8, 9]. By contrast, here, thermal forces are strong but also essential for the enhanced diffusion and the collective dynamics. Without fluctuations the
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[1] J. C. Ndukaife, A. V. Kildishev, A. G. A. Nanana, V. M. Shalaev, S. T. Wereley, and A. Boltasseva, Nature Nanotechnology 11, 53 (2016).
[2] P. H. Jones, O. M. Maragó, and G. Volpe, Optical Tweezers: Principles and Applications (Cambridge University Press, Cambridge, 2015).
[3] K. M. Douglass, S. Sukhov, and A. Dogariu, Nature Photonics 6, 834 (2012).
[4] G. Volpe, G. Volpe, and S. Gigan, Scientific Reports 4, 3936 (2014).
[5] G. Brügger, L. S. Froufe Pérez, F. Scheffold, and J. J. Sáenz, Nature Communications 6, 7460 (2015).
[6] C. Bechinger, R. Di Leonardo, H. Löwen, C. Reichhardt, G. Volpe, and G. Volpe, Reviews of Modern Physics 88, 045006 (2016).
[7] T. Vicsek and A. Zafeiris, Physics Reports 517, 71 (2012).
[8] M. Driscoll, B. Delmotte, M. Youssef, S. Scanna, A. Donev, and P. Chaikin, Nature Physics 13, 375 (2017).
[9] A. Bricard, J.-B. Caussin, N. Desreumaux, O. Dauchot, and D. Bartolo, Nature 503, 95 (2013).
[10] G. Theraulaz, E. Bonabeau, S. C. Nicolas, R. V. Solé, V. Fourcassié, S. Blanco, R. Fournier, J.-L. Joly, P. Fernández, A. Grimal, et al., PNAS 15, 9645 (2002), URL http://europepmc.org/articles/PMC124961.