LETTERS
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Fractionalization of interstitials in curved colloidal crystals

William T. M. Irvine[1]*, Mark J. Bowick[2]* and Paul M. Chaikin[3]*

Understanding the effect of curvature and topological frustration in crystals yields insights into the fragility of the ordered state. For instance, a one-dimensional crystal of identical charged particles can accommodate an extra particle (interstitial) if all the particle positions are readjusted, yet in a planar hexagonal crystal interstitials remain trapped between lattice sites and diffuse by hopping[1–3]. Using optical tweezers operated independently of three-dimensional imaging, we inserted interstitials in a lattice of similar colloidal particles sitting on flat or curved oil/glycerol interfaces, and imaged the ensuing dynamics. We find that, unlike in flat space, the curved crystals self-heal through a collective particle rearrangement that redistributes the increased density associated with the interstitial. This process can be interpreted in terms of the out-of-equilibrium interaction of topological defects with each other and with the underlying curvature. Our observations suggest the existence of particle fractionalization on curved surface crystals.

Much in the way that a sticker does not naturally fit on the surface of a car bumper, crystals must deform to fit on curved surfaces. Curvature changes the rules of geometry. The interior angles in a triangle, for example, no longer add to 180° and initially parallel lines can diverge or converge, leading to compression and stretching. This very general geometry-induced frustration applies to any phase that possesses orientational order in flat space, such as nematics, smectics and crystals.

A recent flurry of activity[9–12] has investigated how a crystal can undergo structural changes to relieve this frustration by introducing topological defects (Fig. 1a–d). In hexagonal crystals (Fig. 1e), two types of topological defects are found: disclinations (Fig. 1f,g), which correspond to a missing (inserted) 60° wedge of lattice and disrupt orientational order, and dislocations (Fig. 1h), which correspond to two extra rows of particles that terminate at the core of the defect and disrupt translational order. Clearly both are non-local in origin, and influence[3] and disrupt order in the crystal. On surfaces that are curved, however, topological defects can play a complementary role, relieving both compressive and shear stress[4–12,21]. For example, on a sphere, on which the sum of the interior angles in a triangle is increased from 180° by the Gaussian curvature, 5-fold coordinated disclinations can make up this angular excess (as seen on a soccer ball with its twelve pentagonal panels). When the lattice spacing is much less than the radius of curvature of the surface, the isotropic and shear stress created by curvature is relieved by groups of defects that organize into grain-boundary-like structures, characterized by the excess disclination charge, that freely terminate within the medium; examples of such structures, both neutral ('pleats'[9]) and charged ('scars'[6]), are shown in Fig. 1c,d.

Our experimental system consists of positively charged colloidal poly(methyl methacrylate) (PMMA) particles (~2 μm in diameter) coated in a layer of poly(hydroxy stearic acid) and suspended in oil (a cyclohexyl bromide/dodecane mixture). In the presence of an oil/glycerol interface, image charge effects drive the binding of the particles to the interface, where, without wetting, they form a monolayer (Fig. 2a). The repulsive screened Coulomb interactions cause them to self-organize into a crystalline lattice that conforms to the curved surface. By index matching the mixture of cyclohexyl bromide and dodecane to the glycerol we obtain a clean system that can be imaged fully using a confocal microscope (Fig. 2c). The system equilibrates into scarred and pleated structures[9].

To study the behaviour of interstitials we add a particle to this system using optical tweezers decoupled from the imaging (see Methods) and, by simultaneously imaging in three dimensions, we follow the out-of-equilibrium dynamics of the defects on the curved surface.

Interstitial defects have a local material origin, resulting from a single extra particle forced into an otherwise ordered crystalline array. When a particle that is identical to the other particles is added to the crystal, however, its identity becomes ambiguous; the crystal accommodates its presence by local re-adjustments that leave two signatures of the interstitial's presence. The first is a localized spike in the compressional strain (density) field that corresponds to the additional particle's mass; the second is a bound triplet or doublet of dislocations[18–20], as can be seen in Fig. 2b and Supplementary Movie S2. In flat space these dislocations remain bound, affecting neither translational nor orientational order.

Once added, an interstitial can move or diffuse by hopping between lattice inter-sites[13–15], with the dislocations remaining bound, preserving the local character of the interstitial. Note that the original particle need not diffuse with the interstitial defect, but rather may remain in the region it was added, as can be verified by tracking the added particle in this case.

The diffusive motion can be biased by stress fields[2]. We observe this in both flat and curved spaces: if the particle is added in close proximity to a grain boundary, the latter can absorb the interstitial with little change in structure while eliminating the stress energy associated with the interstitial. The interstitial hops towards the grain boundary and is absorbed. This is the case in flat or curved spaces alike—as can be seen in Fig. 2d,e and Supplementary Movies S3 and S4.

Adding particles to crystals bound to positively and negatively curved surfaces, however, we observe a further, strikingly different behaviour: the addition of a particle is followed by the fissioning of the normally bound dislocations into pairs, which travel, gliding along parallel Bragg planes in opposite directions, leaving the

[1]James Franck Institute, University of Chicago, 929 E 57th street, Chicago, Illinois 60637, USA, [2]Physics Department, Syracuse University, Syracuse, New York 13244-1130, USA, [3]Center for Soft Matter Research, New York University, 4 Washington Place, New York, New York 10003, USA.
*e-mail: wtmirvine@uchicago.edu; bowick@physics.syr.edu; chaikin@nyu.edu.

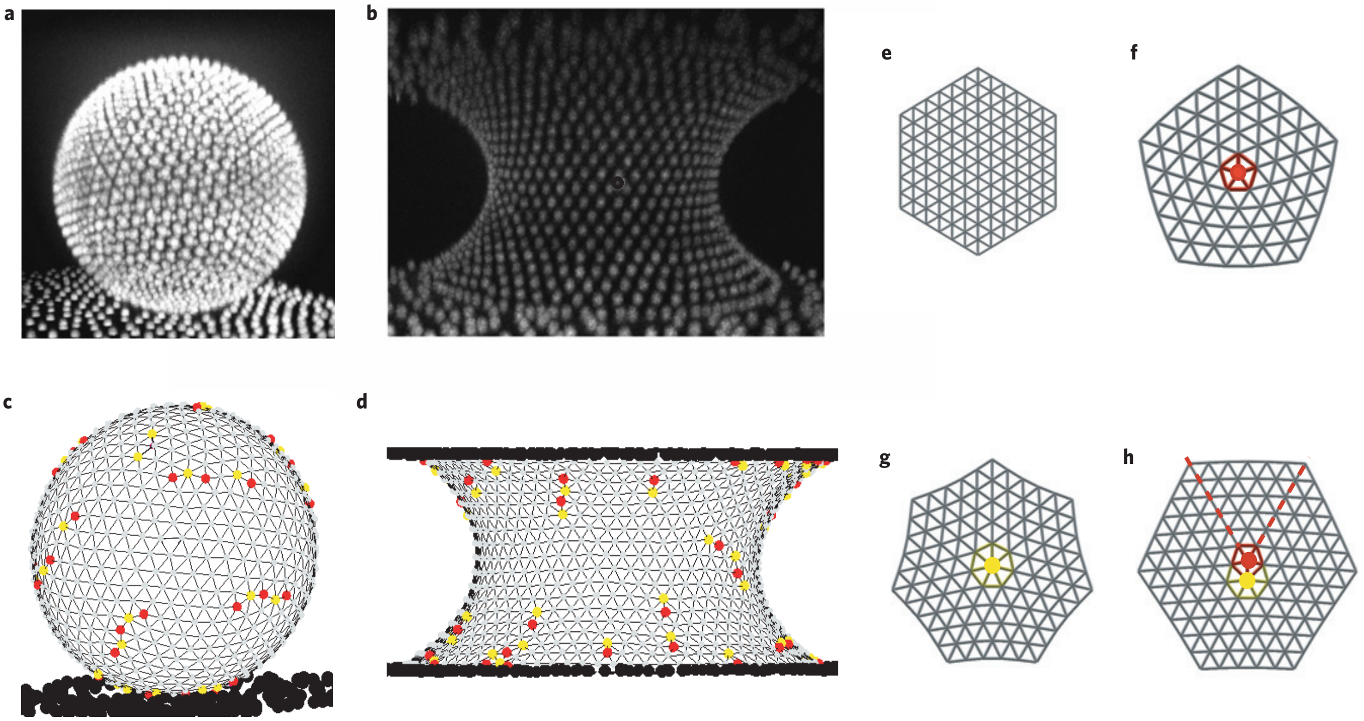

Figure 1 | Curved crystals and topological defects. a, A spherical crystal formed by self-assembled colloidal beads on a liquid droplet (diameter ∼60 μm). **b**, A negative-curvature crystal formed by the same colloidal beads on the surface of a capillary bridge (bridge diameter ∼45 μm). **c**, A Delaunay triangulation of a typical equilibrated configuration for the crystal in **a** with 5-coordinated particles shown in red and 7-coordinated particles shown in yellow; black dots depict particles not bound to the oil/water interface. **d**, A Delaunay triangulation of a typical equilibrated configuration for the crystal in **b**. **e**, A regular hexagonal lattice configuration. **f**, A 5-disclination in a planar crystal. **g**, A 7-disclination in a planar crystal. **h**, A dislocation in a planar crystal.

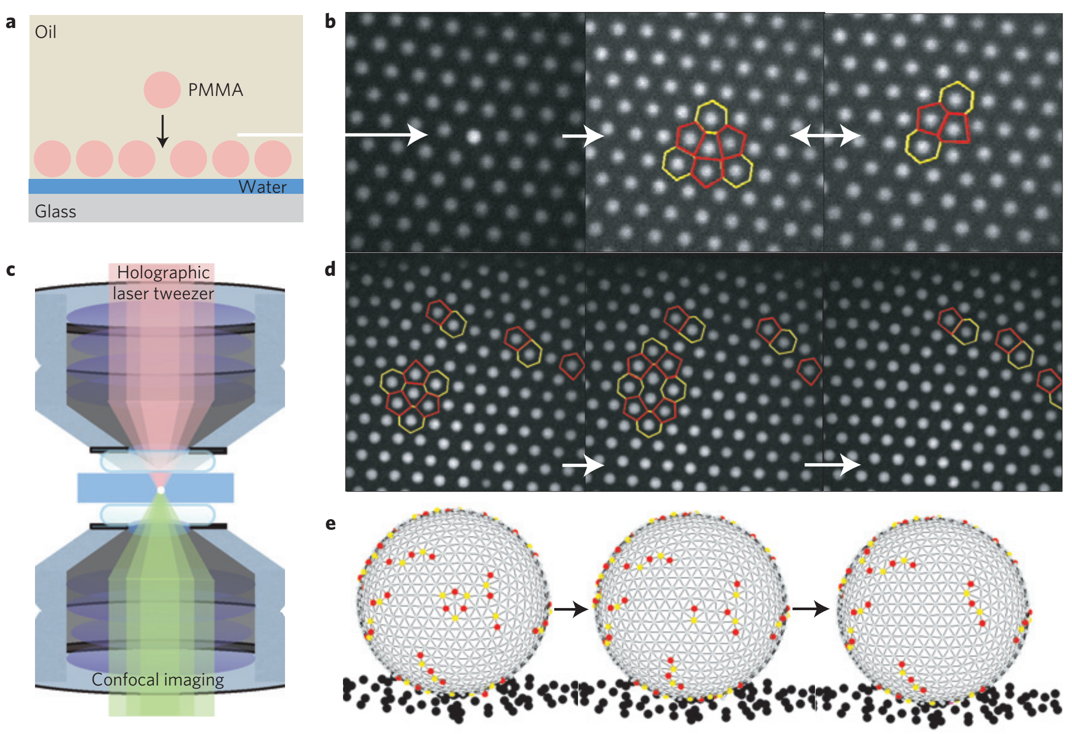

Figure 2 | Interstitials in flat space and interstitial absorption by grain boundaries. a, Inserting a particle to create a self-interstitial. **b**, An interstitial in flat space typically evolves into bound states of three or two dislocations with vanishing net Burgers' vector (lattice spacing ∼3 μm). The colour coding of defects is the same as in Fig. 1. **c**, Schematic of confocal imaging combined with laser tweezers. **d**, An interstitial in flat space close to a grain boundary is absorbed by the latter (see also Supplementary Movies). **e**, An interstitial created on a spherical crystal and subsequently absorbed by a grain boundary scar. Arrows show sequence of events.

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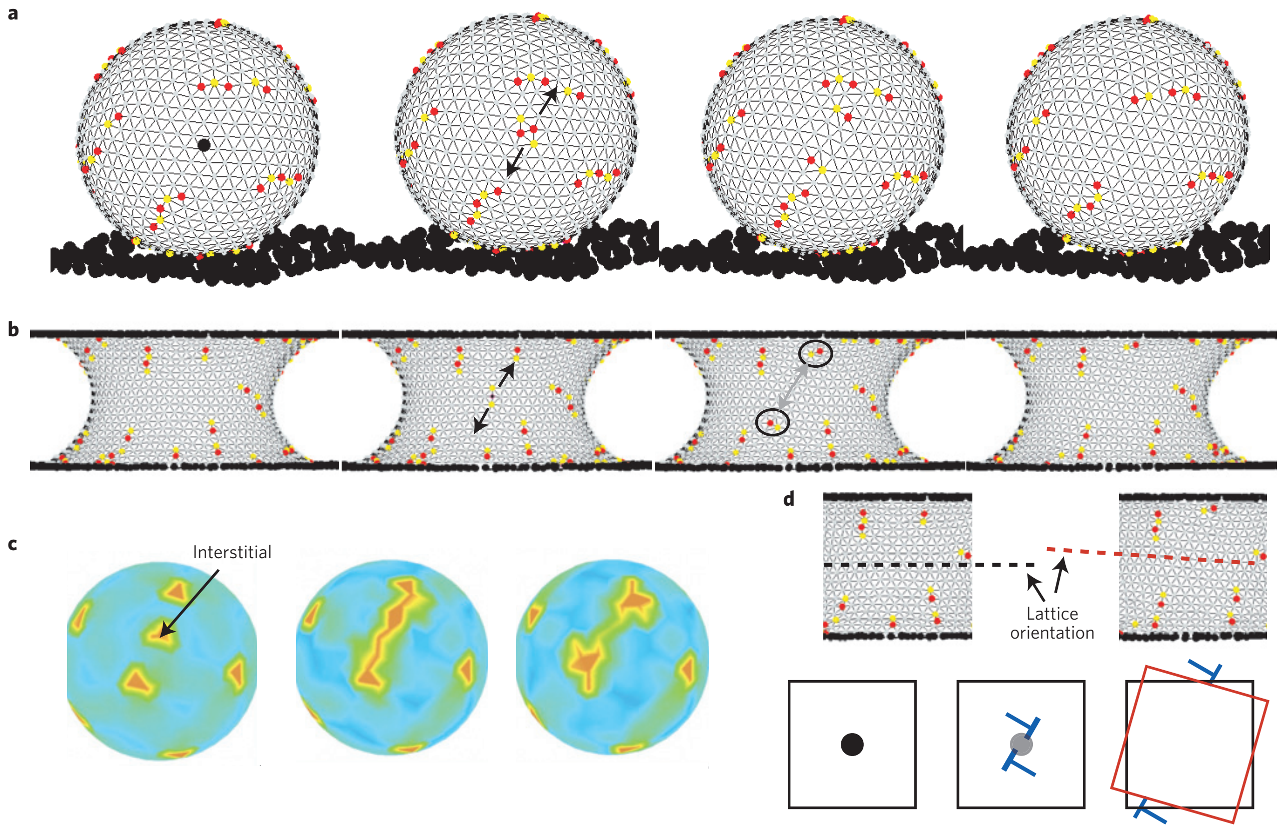

Figure 3 | Interstitial fractionalization. a, The insertion of an interstitial in a spherical crystal is followed by its fissioning into two dislocations which migrate, gliding along parallel Bragg planes in opposite directions, and are subsequently absorbed into existing grain boundary scars. **b**, Insertion of an interstitial (black-purple dot, representing an initially 4-fold coordinated defect, surrounded by two 7-fold coordinated defects) on a negatively curved capillary bridge followed by its fissioning into two dislocations—the upper dislocation is absorbed by an existing dislocation that rotates to absorb the Burgers' vector and the bottom dislocation is absorbed by an existing grain boundary scar. **c**, Plot of the compressional strain distribution that accompanies a fractionalization event as evaluated numerically on a sphere. **d**, The twisting of Bragg rows resulting from interstitial fractionalization as deduced from imaged configurations before and after fractionalization. The schematic illustrates the twisting of the crystalline patch (square) containing an interstitial as its constituent dislocations (blue nails) separate to globally distinct locations on the lattice. The colour of defects is the same as in Fig. 1.

crystal region in which the particle was added rotated (Fig. 3a for a spherical crystal and Fig. 3b,d for a negatively curved crystal; see also Supplementary Movies S6 and S7).

We find that this intriguing mechanism, predicted theoretically and numerically in the special case of un-equilibrated arrangements of disclinations on spheres[16,17], occurs generically in experiments on equilibrated spherical droplets and equilibrated negatively curved capillary bridges.

This non-local behaviour raises the question—where does the particle go? By partially bleaching the particles and subsequently adding an unbleached, and therefore brighter particle to the crystal (Fig. 1b), we verified that in both types of instability, the specific particle that was added remains in the region in which it was added, in agreement with the behaviour in flat space. However, in the case where the dislocations remain bound as they diffuse in flat space, or migrate towards a grain boundary as seen before, the density increase associated with the added particle remains localized and has a continuous trajectory to the grain boundary. In contrast, for the case in which the interstitial fractionalizes, the mass transport cannot be similarly localized—although the mass associated with an extra particle clearly leaves the region.

We investigated this transport through a numerical (Fig. 3c) and experimental (Supplementary Movie S3) investigation of the stress fields associated with a fractionalization event. Figure 3c shows how the compressive part of the stress field extends in the case of the sphere creating two branches, which join up to the scars, effectively delocalizing the increased density associated with the particle in the process.

Although fractionalization could also be achieved in planar crystals by applying a strong shear to a region enclosing an interstitial, and could in principle occur if a particle is added in the centre of a small grain, these represent very special conditions in flat space, whereas the conditions occur generically in curved space. As defects have localized cores with quantized angular charge, the angular frustration generated by curvature is more gradual, and some residual stress remains in the regions in between pleats or scars. It is this residual stress that drives the self-healing.

Just as topological defects find a new life on curved surfaces—going from order-disrupting to order-restoring excitations—interstitials that are normally localized stable point defects develop complementary non-local character. The spontaneous morphing of interstitials into sets of dislocations that glide through the lattice provides particle arrays access to configurations that might normally be difficult to reach without additional thermal noise or external perturbations. This allows new mechanisms for the equilibration of ordered phases on curved space, which could prove important for the practical realization of self-assembly schemes based on defects[22]. Our unique experimental combination of a versatile model system with full three-dimensional control and imaging further paves the way for studying non-equilibrium effects in ordered and disordered phases in arbitrarily curved interfaces.

Methods

The PMMA particles, synthesized following the methods of refs 23,24, are coated with a layer of poly(hydroxy stearic acid), which charges positively (∼100 charges per particle) in the oil[25]. The particles were suspended in a mixture of cyclohexyl bromide and dodecane (approx. 72% w/w), which was mixed before each experimental run to match the refractive index of glycerol as measured by an Abbe refractometer. This avoids lensing by the oil/glycerol interface, while allowing for a small index contrast between the particles and the oil phase for optical tweezing. The glycerol/oil interfaces were prepared by emulsification (in the case of spherical surfaces) and by deposition of glycerol droplets in contact with air in capillary channels that were subsequently filled by the particle suspension (in the case of capillary bridges) and sealed to avoid evaporation. The samples were imaged using a Yokogawa CSU-10 spinning disk confocal scanner. Optical tweezing independent of the confocal imaging was achieved by substituting the microscope condenser with a second microscope objective. A holographically shaped 1,064 nm trapping laser was then projected through the upper objective into the sample. Particle location was determined from the images using the Interactive Data Language routines of ref. 26, and triangulation and defect identification were done using custom codes written in Matlab.

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References

1. Chaikin, P. & Lubensky, T. *Principles of Condensed Matter Physics* (Cambridge Univ. Press, 1995).
2. Hirth, J. P. & Lothe, J. *Theory of Dislocations* (McGraw-Hill, 1968).
3. Nelson, D. R. *Defects and Geometry in Condensed Matter Physics* (Cambridge Univ. Press, 2002).
4. Nelson, D. R. & Peliti, L. Fluctuations in membranes with crystalline and hexatic order. *J. Phys.* **48,** 1085–1092 (1987).
5. Pèrez-Garrido, A., Dodgson, M. & Moore, M. Influence of dislocations in Thomsons problem. *Phys. Rev. B* **56,** 3640–3643 (1997).
6. Bowick, M. J., Nelson, D. R. & Travesset, A. Interacting topological defects on frozen topographies. *Phys. Rev. B* **62,** 8738–8751 (2000).
7. Vitelli, V., Lucks, J. B. & Nelson, D. R. Crystallography on curved surfaces. *Proc. Natl Acad. Sci. USA* **103,** 12323–12328 (2006).
8. Bausch, A. R. *et al.* Grain boundary scars and spherical crystallography. *Science* **299,** 1716–1718 (2003).
9. Irvine, W. T. M., Vitelli, V. & Chaikin, P. M. Pleats in crystals on curved surfaces. *Nature* **468,** 947–951 (2010).
10. Lipowsky, P., Bowick, M. J., Meinke, J. H., Nelson, D. R. & Bausch, A. R. Direct visualization of dislocation dynamics in grain-boundary scars. *Nature Mater.* **4,** 407–411 (2005).
11. Einert, T., Lipowsky, P., Schilling, J., Bowick, M. J. & Bausch, A. R. Grain boundary scars on spherical crystals. *Langmuir* **21,** 12076–12079 (2005).
12. Bowick, M. J., Giomi, L., Shin, H. & Thomas, C. K. Bubble-raft model for a paraboloidal crystal. *Phys. Rev. E* **77,** 021602 (2008).
13. Pertsinidis, A. & Ling, X. S. Diffusion of point defects in two-dimensional colloidal crystals. *Nature* **413,** 147–150 (2001).
14. Pertsinidis, A. & Ling, X. S. Equilibrium configurations and energetics of point defects in two-dimensional colloidal crystals. *Phys. Rev. Lett.* **87,** 098303 (2001).
15. Pertsinidis, A. & Ling, X. S. Video microscopy and micromechanics studies of one- and two-dimensional colloidal crystals. *New J. Phys.* **7,** 33 (2005).
16. Bowick, M. J., Shin, H. & Travesset, A. Dynamics and instabilities of defects in two-dimensional crystals on curved backgrounds. *Phys. Rev. E* **75,** 021404 (2007).
17. Bowick, M. J., Nelson, D. R. & Shin, H. Interstitial fractionalization and spherical crystallography. *Phys. Chem. Chem. Phys.* **9,** 6304–6312 (2007).
18. Fisher, D. S., Halperin, B. & Morf, R. Defects in the two-dimensional electron solid and implications for melting. *Phys. Rev. B* **20,** 4692–4712 (1979).
19. Cockayne, E. & Elser, V. Energetics of point defects in the two-dimensional Wigner crystal. *Phys. Rev. B* **43,** 623–629 (1991).
20. Jain, S. & Nelson, D. R. Statistical mechanics of vacancy and interstitial strings in hexagonal columnar crystals. *Phys. Rev. E* **61,** 1599–1615 (2000).
21. Bowick, M. J. & Giomi, L. Two-dimensional matter: Order, curvature and defects. *Adv. Phys.* **58,** 449–563 (2009).
22. DeVries, G. A. *et al.* Divalent metal nanoparticles. *Science* **315,** 358–361 (2007).
23. Bosma, G. *et al.* Preparation of monodisperse, fluorescent PMMA-Latex colloids by dispersion polymerization. *J. Colloid Interface Sci.* **245,** 292–300 (2002).
24. Antl, L. *et al.* The preparation of poly(methyl methacrylate) latices in non-aqueous media. *Colloids Surf.* **17,** 67–78 (1986).
25. Leunissen, M. E., van Blaaderen, A., Hollingsworth, A. D., Sullivan, M. T. & Chaikin, P. M. Electrostatics at the oil–water interface, stability, and order in emulsions and colloids. *Proc. Natl Acad. Sci. USA* **104,** 2585–2590 (2007).
26. Crocker, J. & Grier, D. G. Methods of digital video microscopy for colloidal studies. *J. Colloid Interface Sci.* **179,** 298–310 (1996).

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Author contributions

M.J.B., P.M.C. and W.T.M.I. designed the research. W.T.M.I. and P.M.C. designed the experimental system. W.T.M.I. developed the apparatus for simultaneous confocal imaging and optical tweezing, performed experiments, wrote analysis software and analyzed data. W.T.M.I., M.J.B. and P.M.C. wrote the manuscript.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to W.T.M.I., M.J.B. or P.M.C.

Competing financial interests

The authors declare no competing financial interests.