Topological Colloids & Dispersed Liquid Crystals: From Theorems to Self-Assembly

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Collaborators

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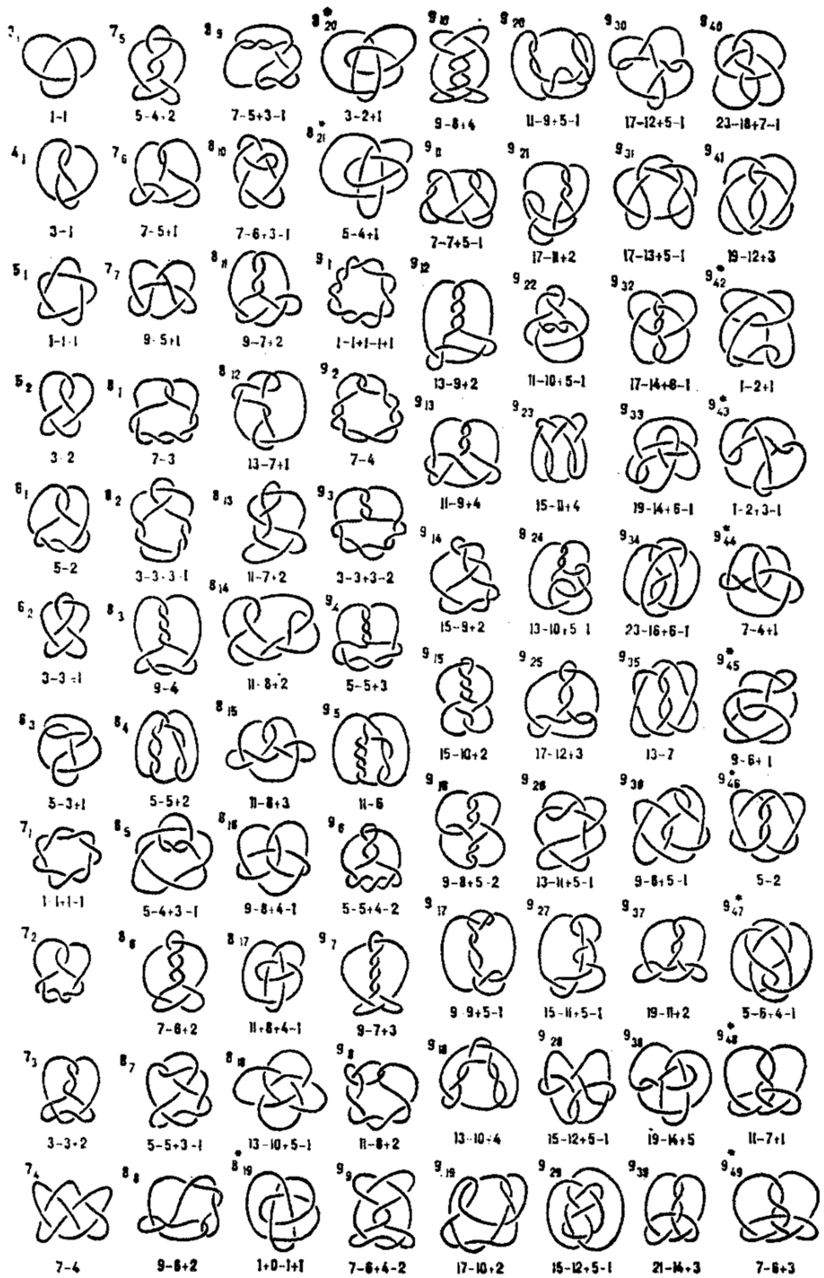
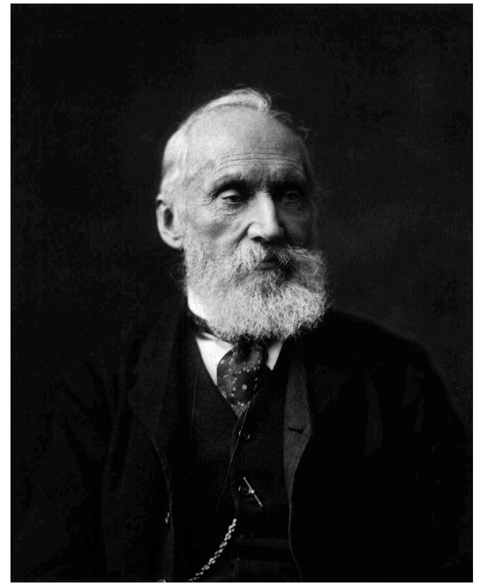
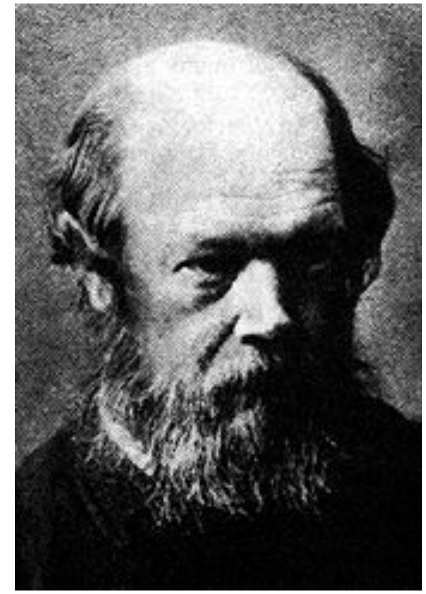
- S. Zumer & M. Ravnik, Ljubljana, Slovenia

Knot theory motivated by early models of atom





William Thomson,
Lord Kelvin



Peter Tait

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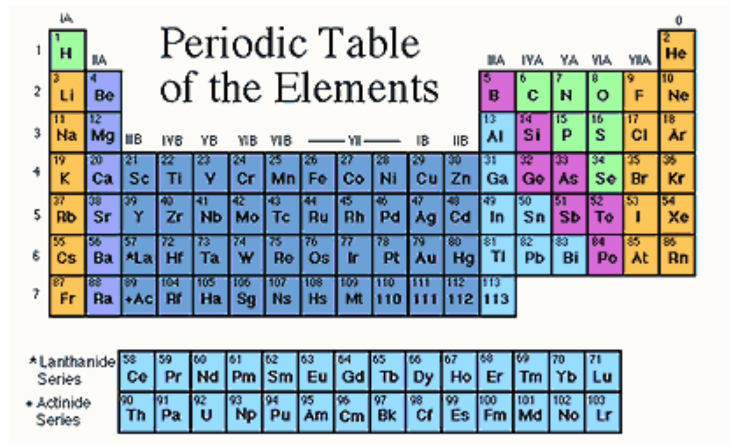


Periodic Table of the Elements

	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VII	VII	VII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 *La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 +Ac	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt	110 110	111 111	112 112	113 113					

* Lanthanide Series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
+ Actinide Series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

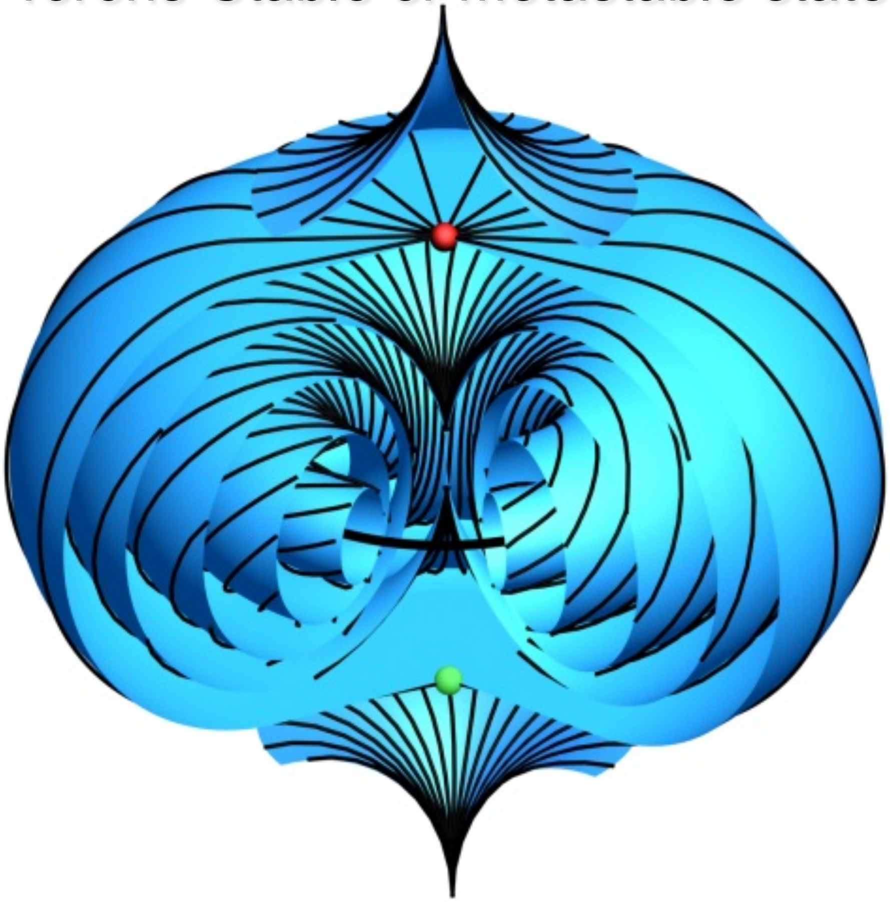
Mathematical Theory of Knots & Physics

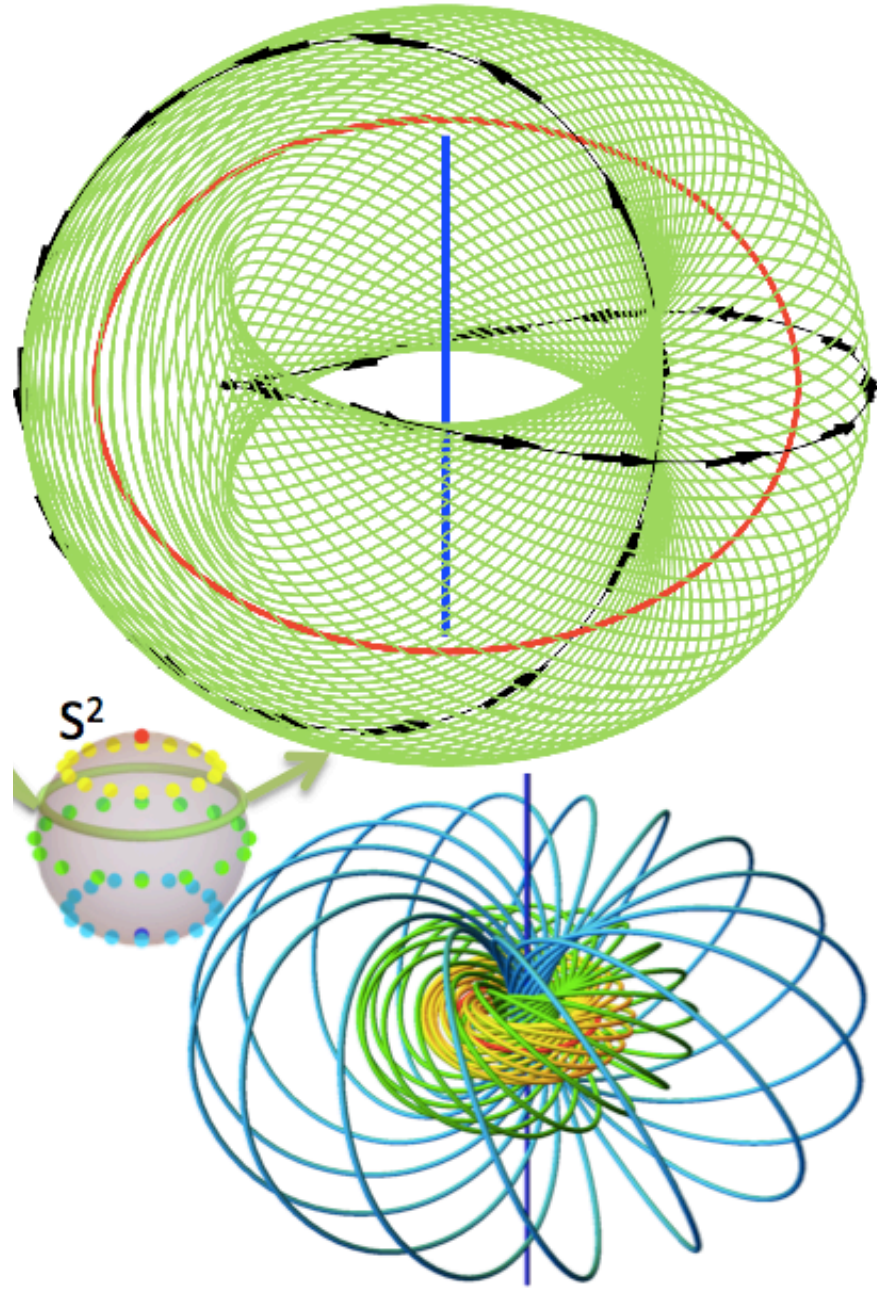
Edward Witten

- Applications of knot theory in physics;
- Insights into the knot theory from quantum physics & field theories;
- 1990 Fields medal (the only physicist to receive);
- Knotted fields: from elementary particles to cosmology

Knotting in nematic director “flow” lines

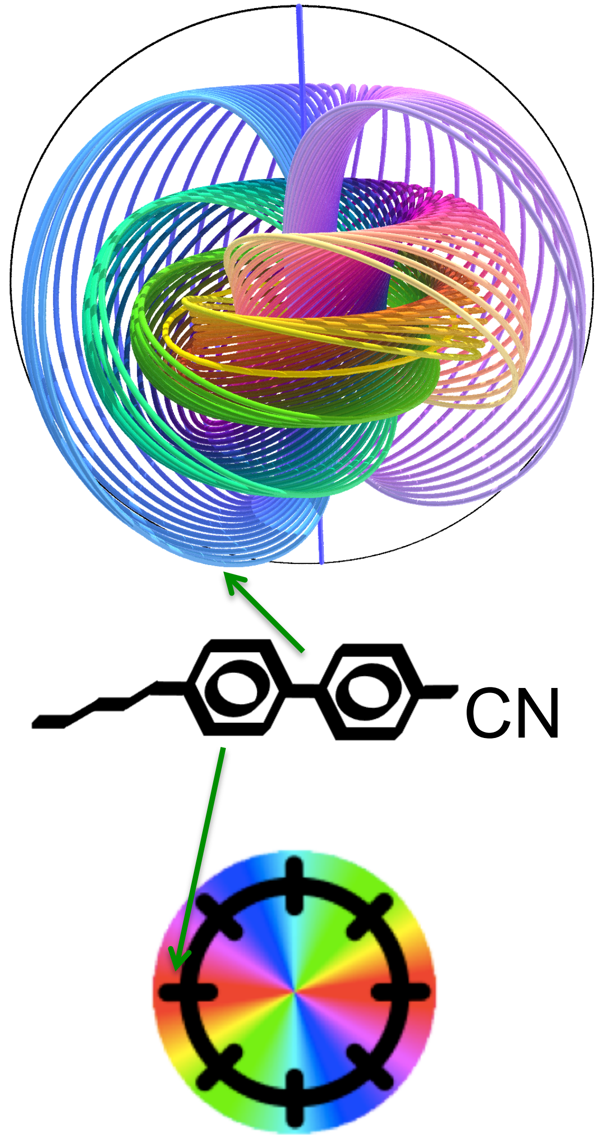
Torons-Stable or metastable states





- I. Smalyukh *et al. Nature Materials* **9**, 139-145 (2010)
- P. J. Ackerman, J. van de Lagemaat, and I. I. Smalyukh. *Nature Comm*. **6**, 6012 (2015)
- Q. Zhang, P. J. Ackerman, Q. Liu, & I. I. Smalyukh, *Phys Rev Lett* **115**, 097802 (2015)

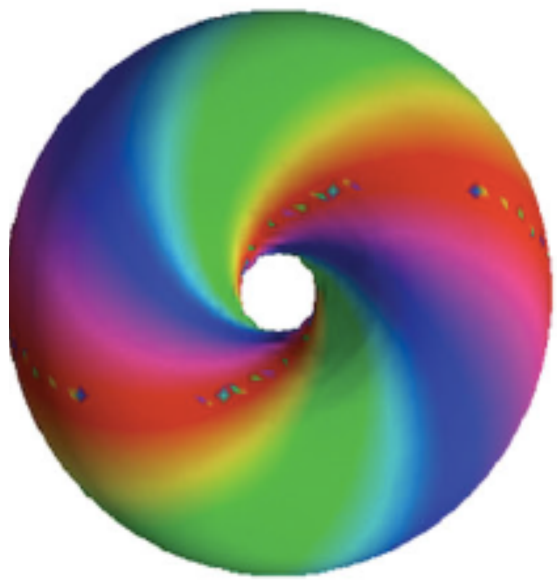
Links/knots for every possible orientation



Color-coded molecular orientation field

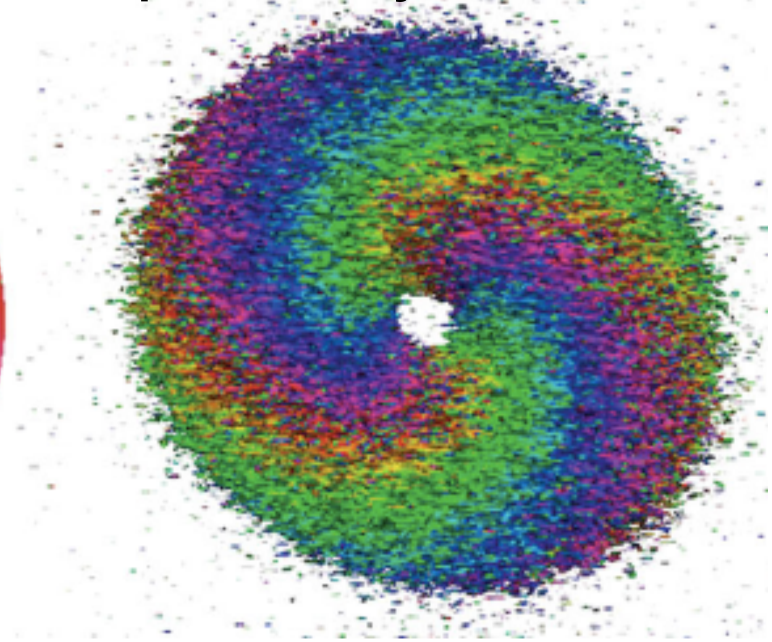
Pontryagin-Thom reconstruction:

computer-simulated



Hopf index H=1

experimentally reconstructed



$$\pi_3(\mathbb{R}P^2) = \mathbb{Z}$$

- Chirality, LC anisotropy, & confinement in chiral nematic LCs
- Derrick's theorem on stability of 3D solitons

B. Chen, P. Ackerman, G. Alexander, R. Kamien, & I. Smalyukh. *Phys. Rev. Lett.* **110**, 237801 (2013)

Topology and Soft Matter

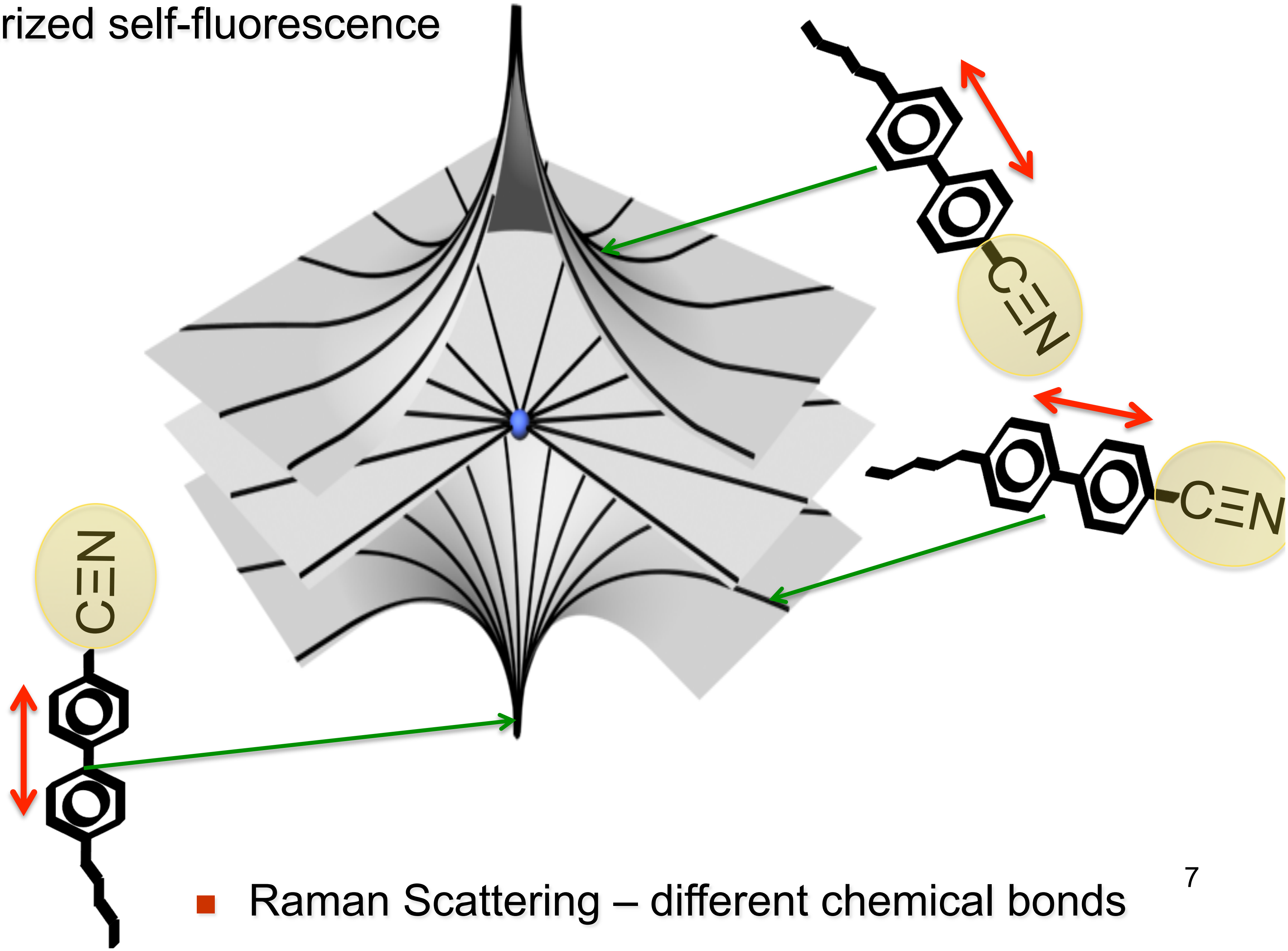
Approach: Experiments vs. LdG modeling

Intro: Imaging, manipulation, fabrication

- Interplay of topologies of surfaces, fields & defects
- topological colloids
- topologically nontrivial confinement of LC
- knotted defects
- Implications of non-polar nature of LC director
- Energy-minimizing subset of topologically allowed states

Label-free study of the director fields in 3D?

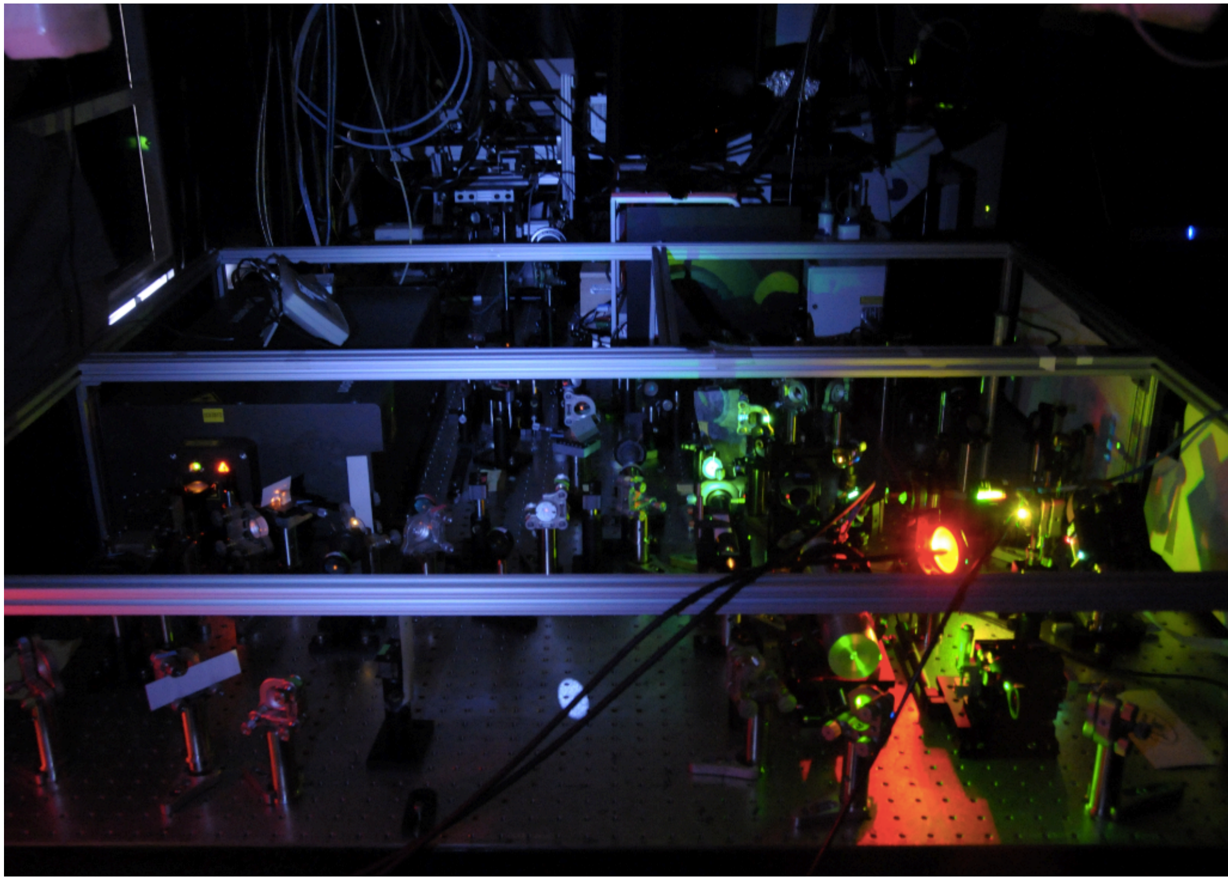
- Polarized self-fluorescence



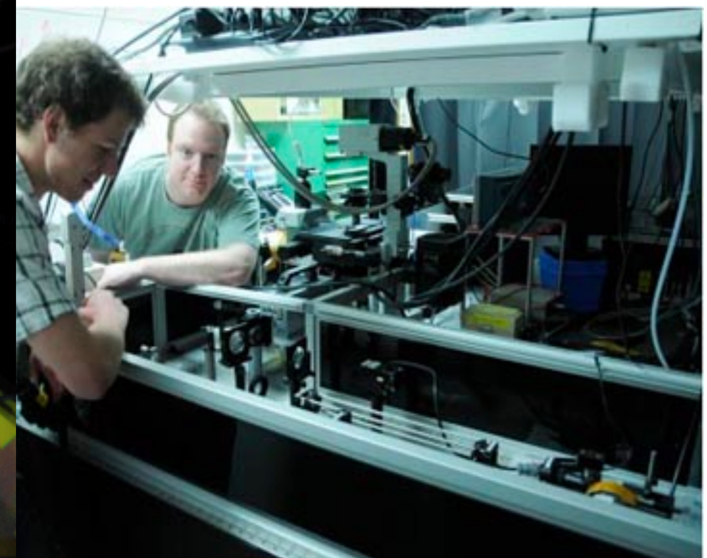
- Raman Scattering – different chemical bonds

Multimodal nonlinear optical imaging of LCs

→3D linear/nonlinear optical imaging



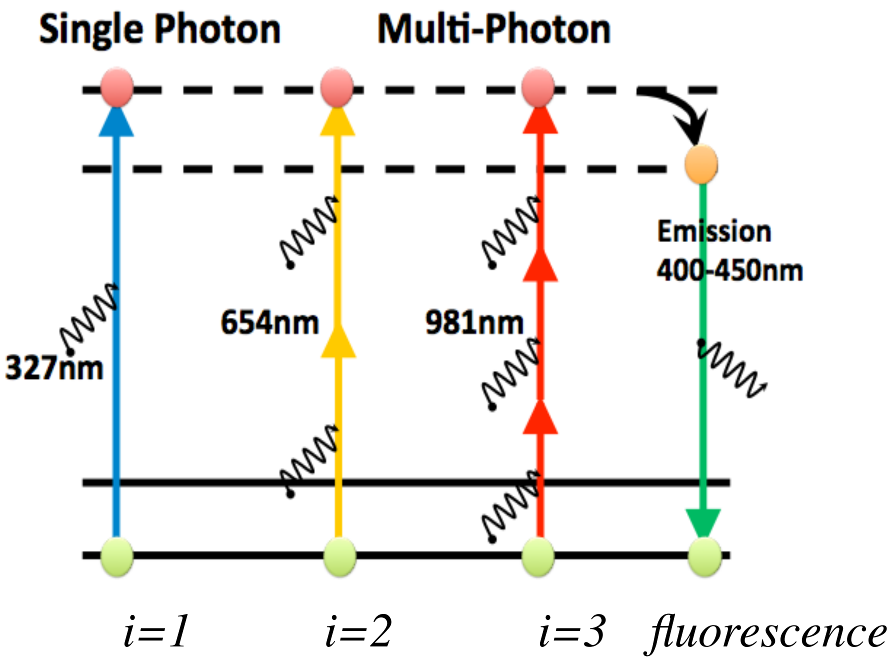
→3D optical manipulation

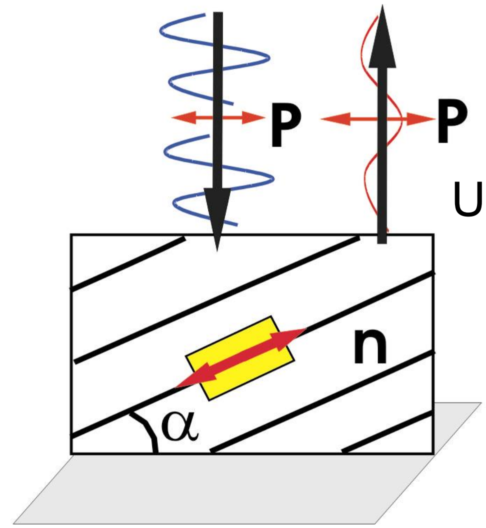


→**Broadband CARS-PM**
→**Broadband SRS-PM**
→**Multiphoton fluorescence**
→**Multiple harmonic generation**
→**Holographic Optical Tweezers**

→**Label-free chemically-specific orientationally-sensitive 3D imaging**
→**Simultaneous with non-contact optical manipulation in 3D**
→**Many imaging modalities with complementary capabilities**

Multiphoton self-fluorescence imaging: no dyes





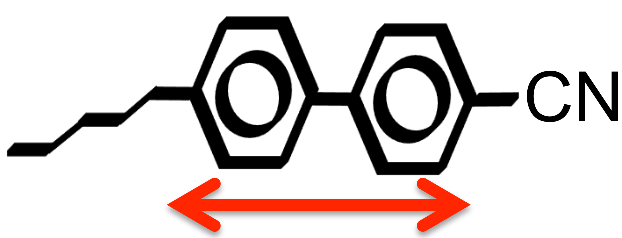
Unpolarized detection:

$$I_{em} \propto I_0 \cos^{2i} \alpha$$

Polarized detection:

$$I_{em} \propto I_0 \cos^{2(i+1)} \alpha$$

5CB



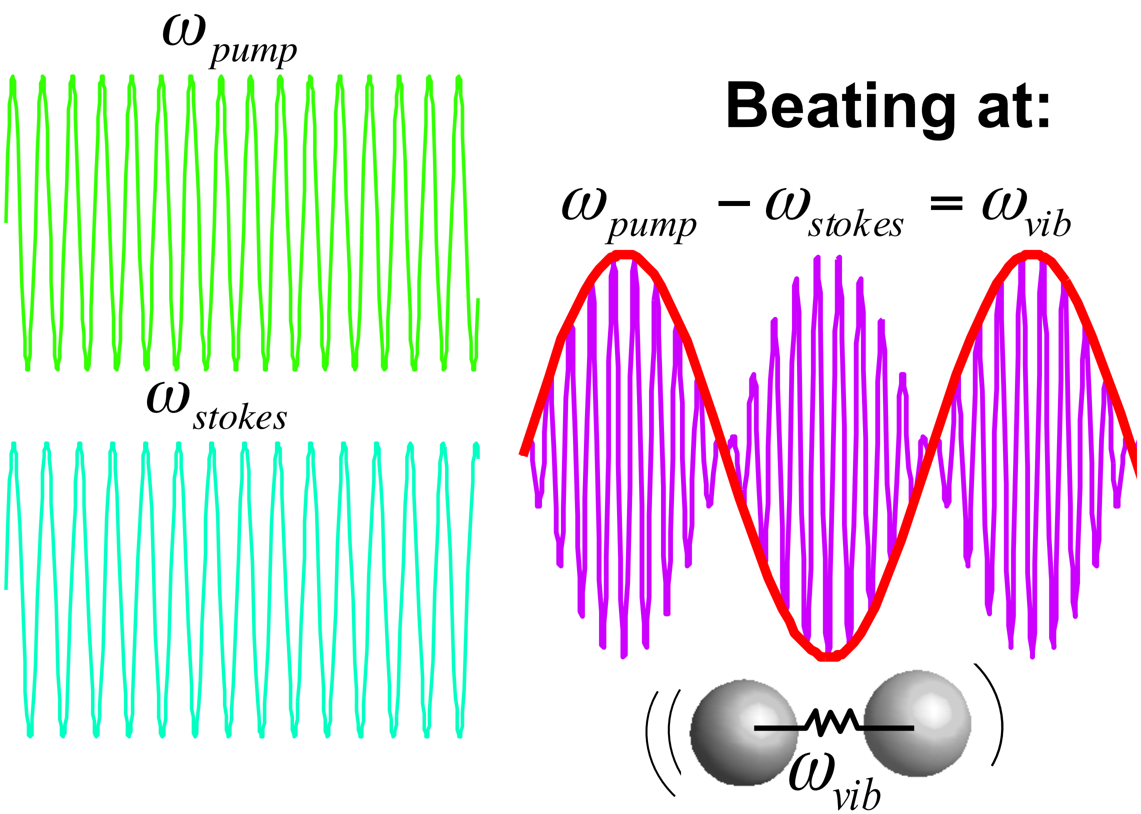
Absorption/emission transition dipole

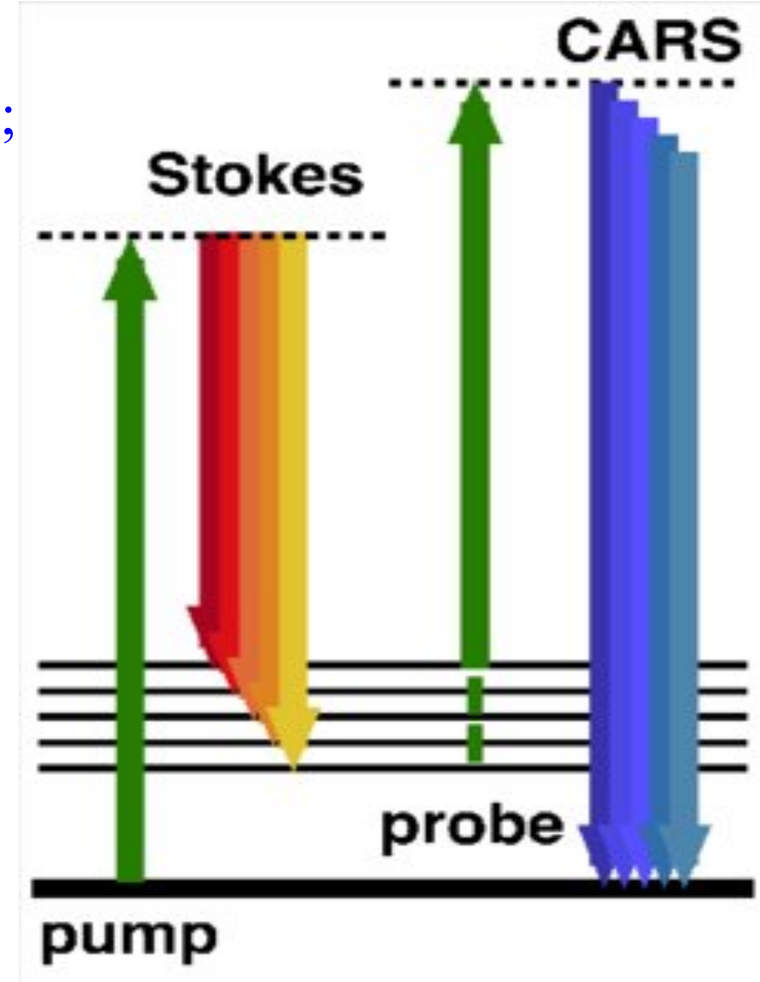
- **Strong orientational sensitivity!**
- **No dyes needed!!!**

T. Lee, R.P. Trivedi, & I.I. Smalyukh, *Opt. Lett.* 35, 3447-3449 (2010).

Coherent anti-Stokes Raman Scattering (CARS)

→ CARS uses two laser frequencies to interact resonantly with a specific molecular vibration;



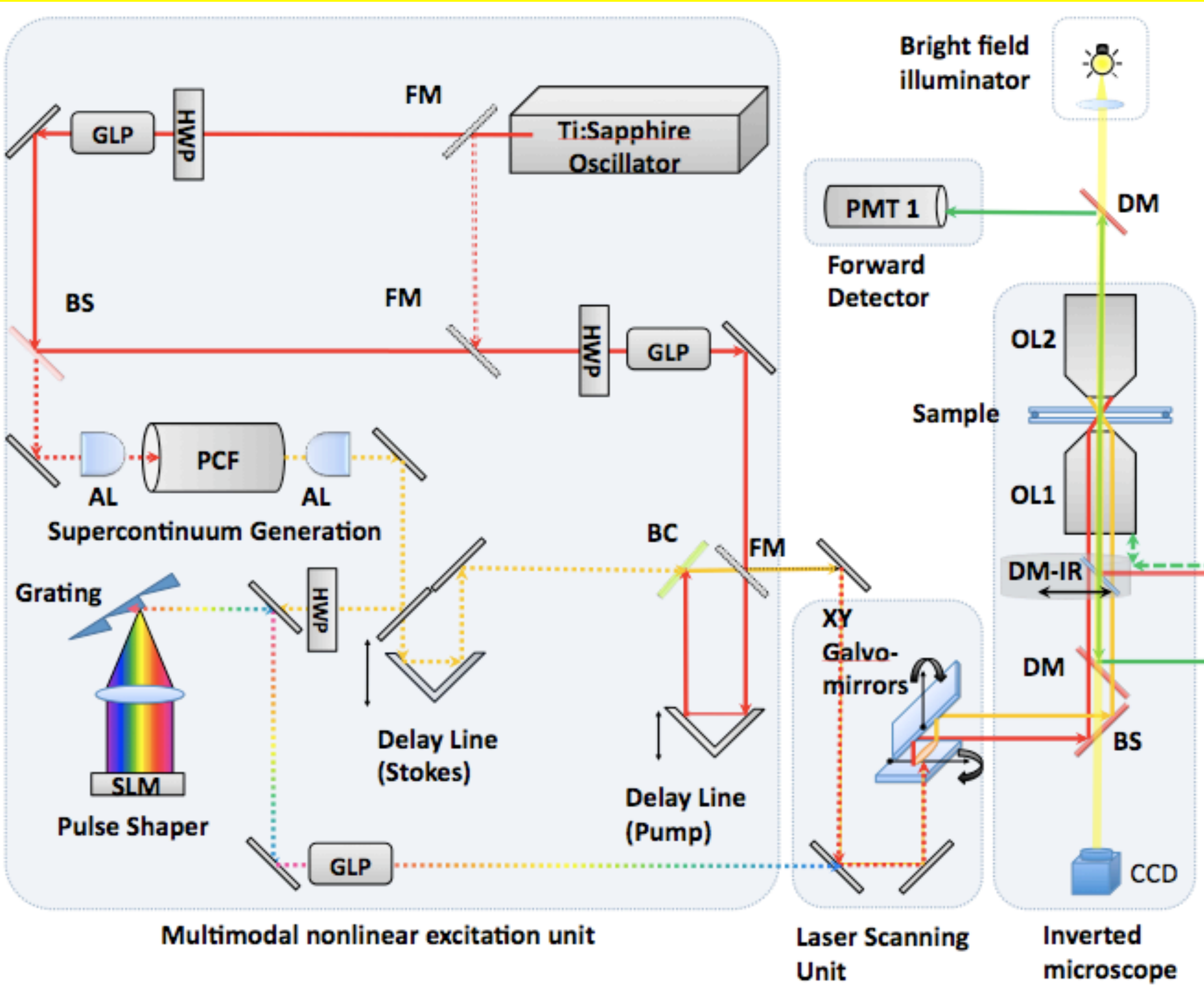


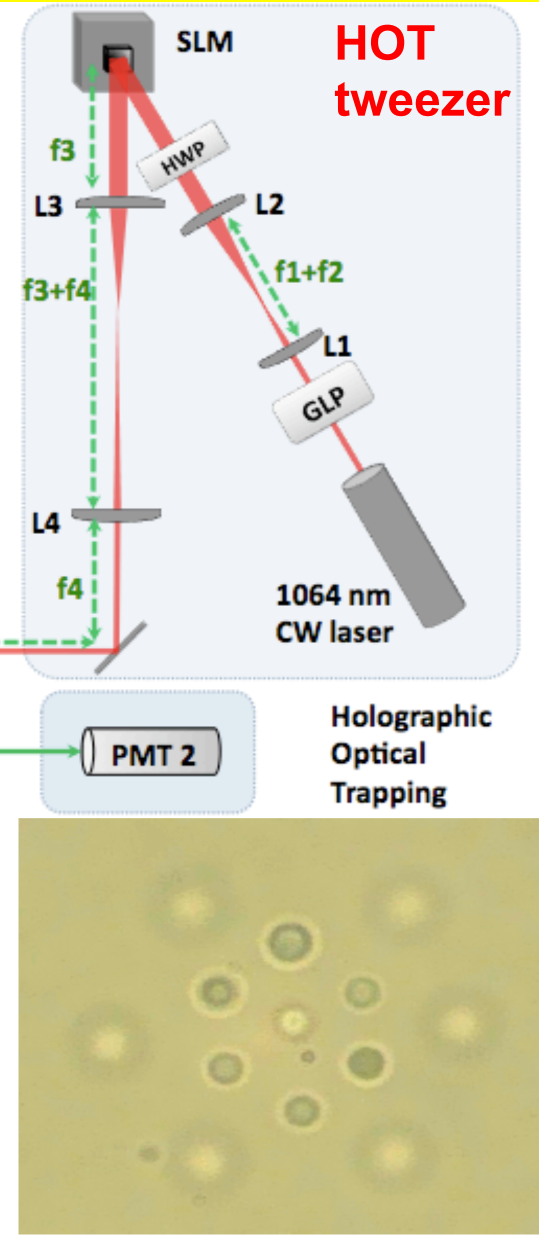
→ 3rd order nonlinear process

→ Beat frequency matches that of a Raman vibration -> signal at $\omega_{as}=2\,\omega_p - \omega_S$

→ Broadband Stokes excitation & CARS detection with Spectral shaping;

Integrated holographic optical tweezers & multimodal 3D imaging: setup schematic

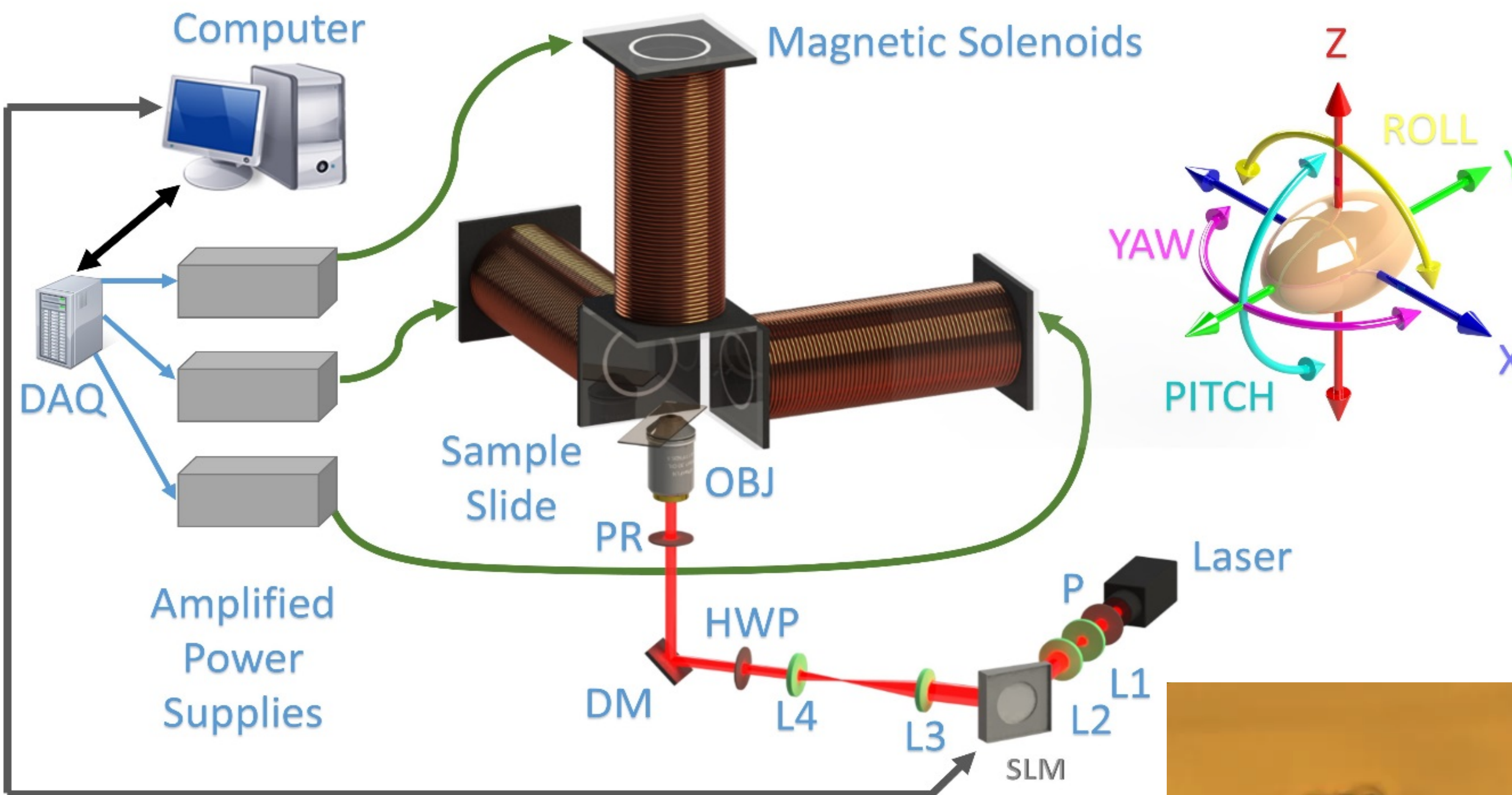


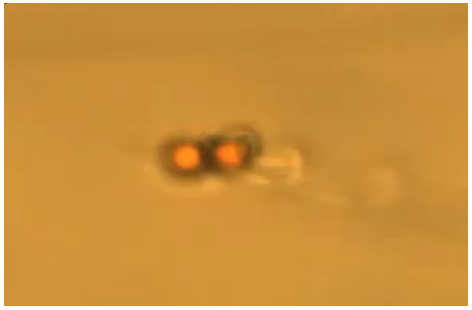


T. Lee, R. P. Trivedi & I. I. Smalyukh, *Opt. Lett.* 35, 3447 (2010);

R.P. Trivedi, T. Lee, K. Bertness, & I.I. Smalyukh, *Opt. Express* 18, 27658-27669 (2010).

Magnetic & optical holonomic control

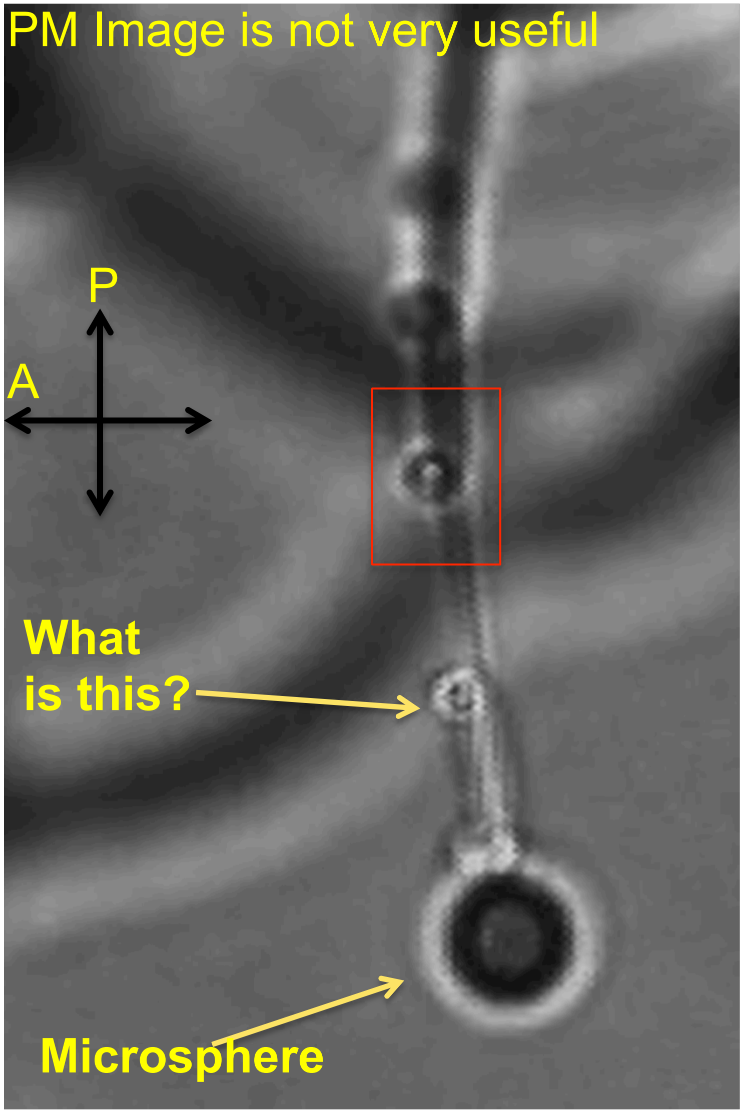




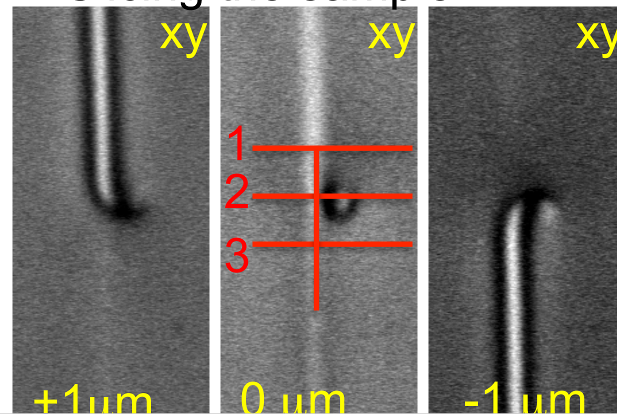
→Use colloidal objects with super-paramagnetic properties
→Control all degrees of freedom: rotational & translational

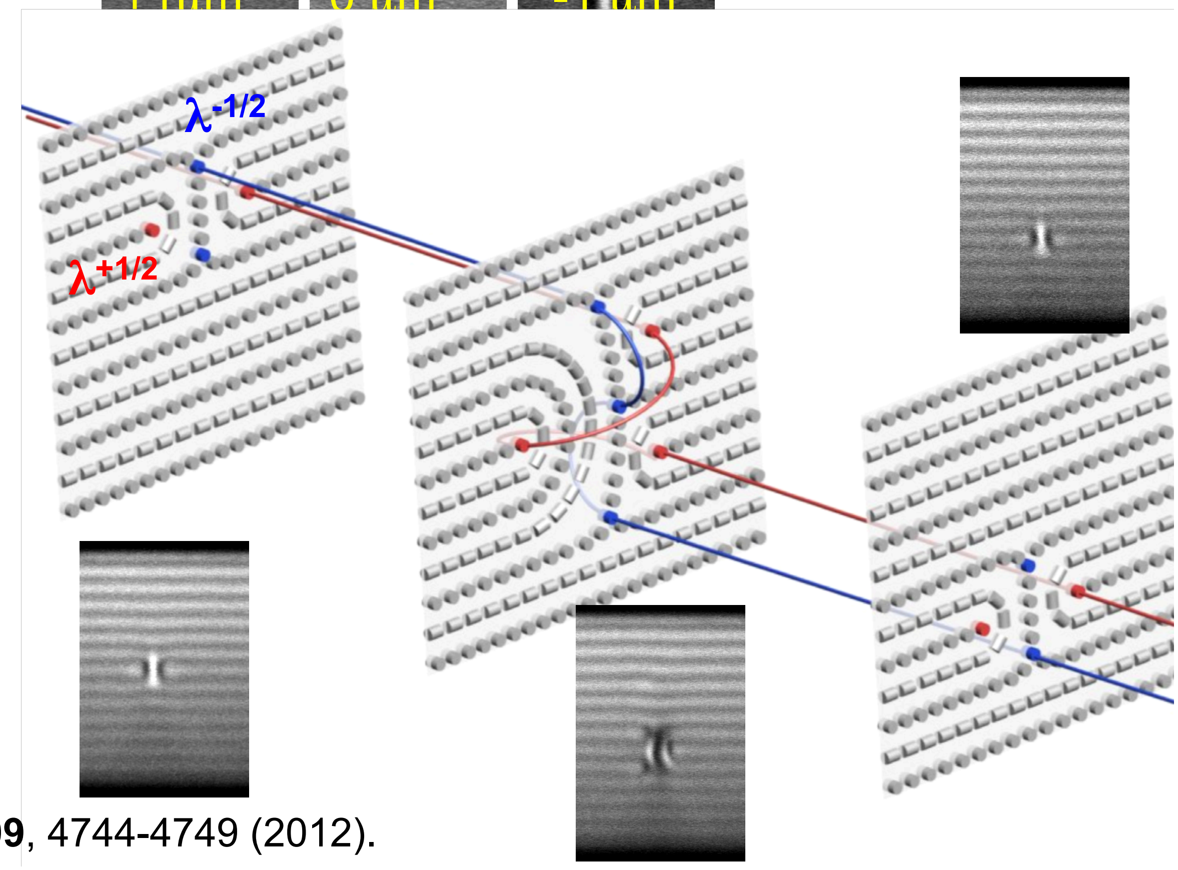
Simultaneous 3D "drawing" & imaging of defects

3D drawing of defects by a particle



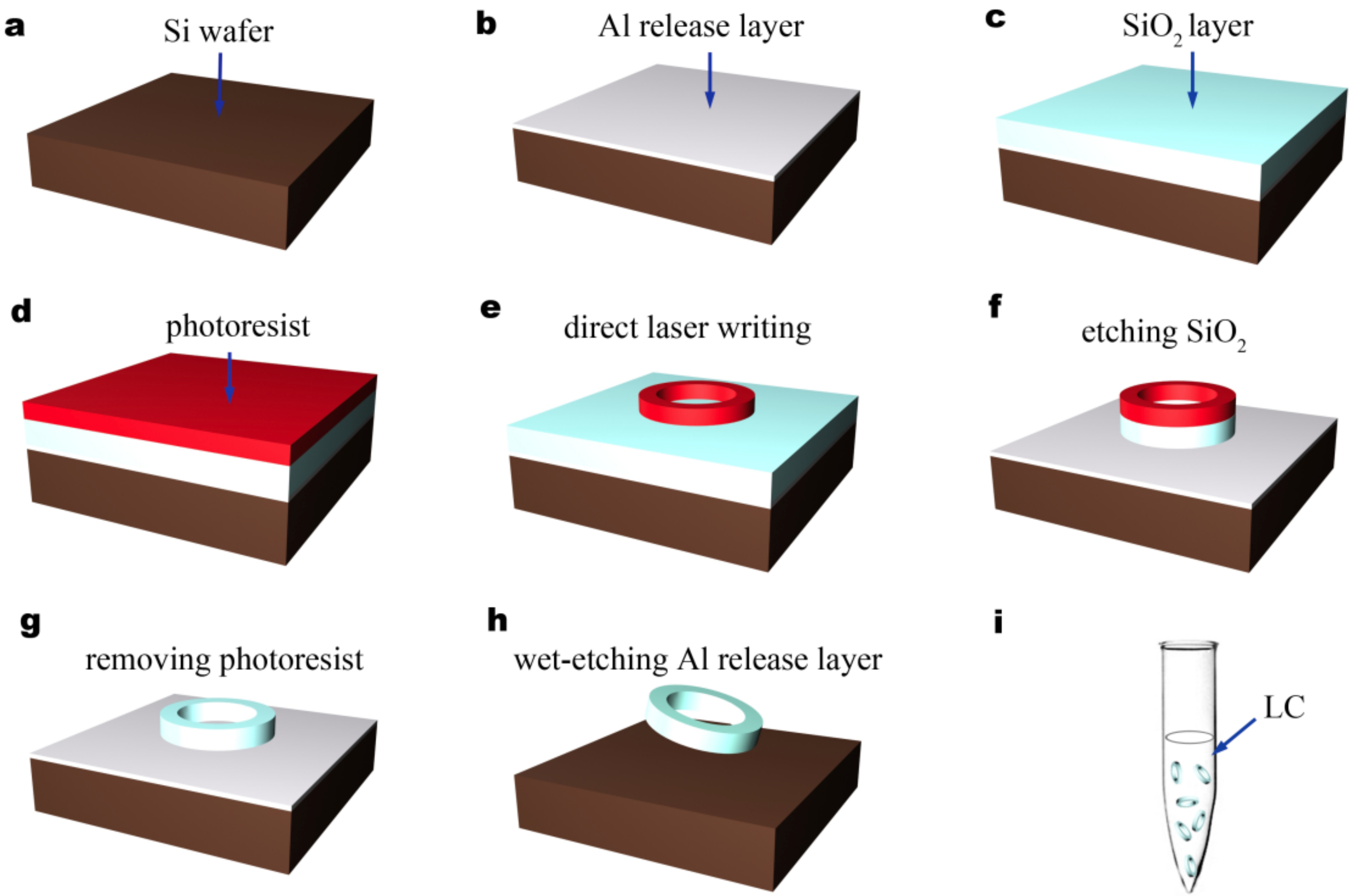
Slicing the sample





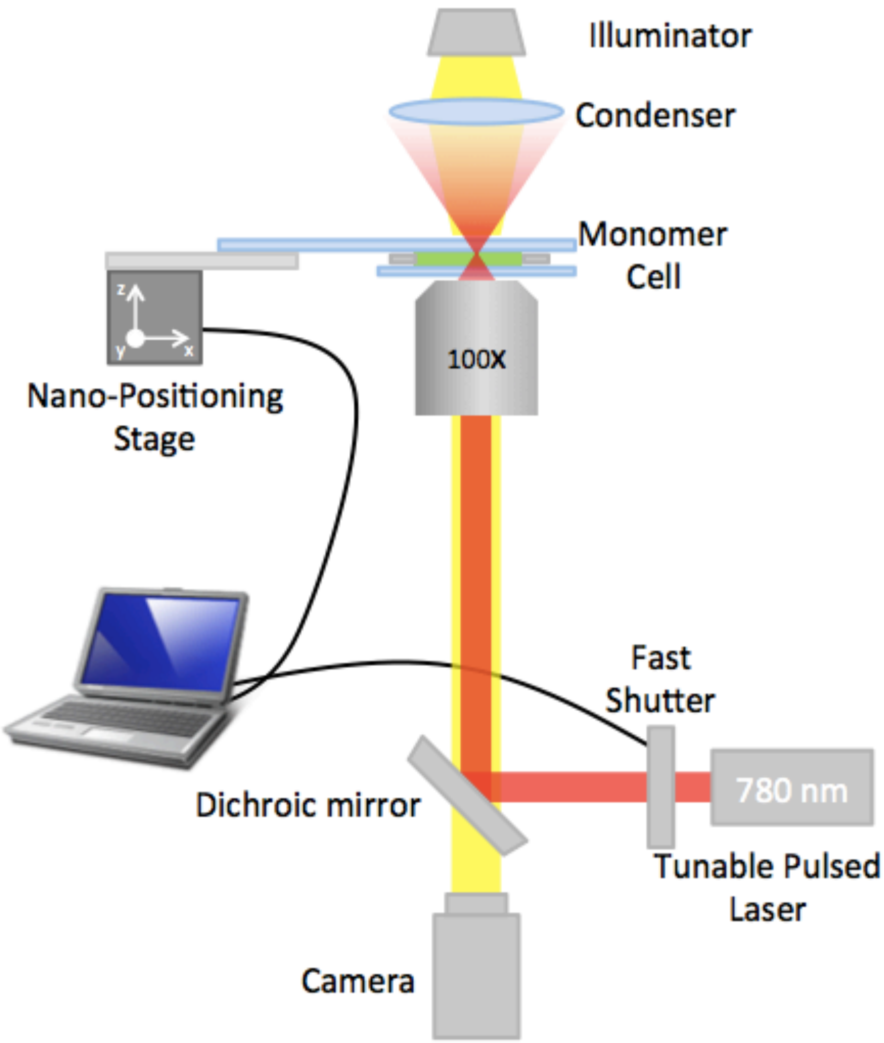
Trivedi, Senyuk, Lee, Smalyukh, PNAS **109**, 4744-4749 (2012).

Micro-fabrication of non-spherical colloids

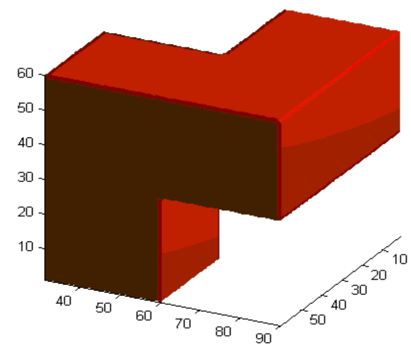


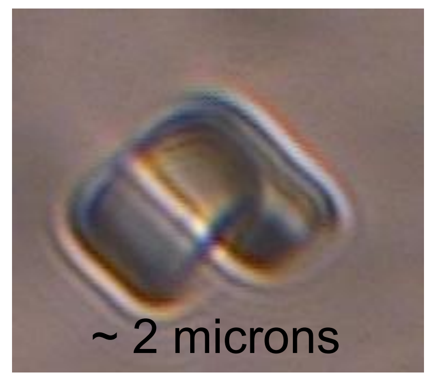
B. Senyuk, Q. Liu, S. He, R. Kamien, R. Kusner, T. Lubensky, & I.I. Smalyukh, Nature **493**, 200-205 (2013)

3D complex-shaped colloidal particles



- two-photon photopolymerization

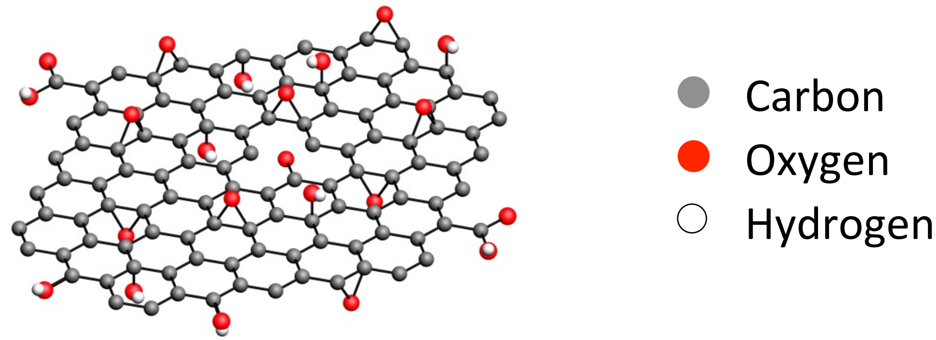




A. Martinez, T. Lee, T. Asavei, H. Rubinsztein-Dunlop, & I.I. Smalyukh, *Soft Matter* ***7****, 11154-11159 (2012).*

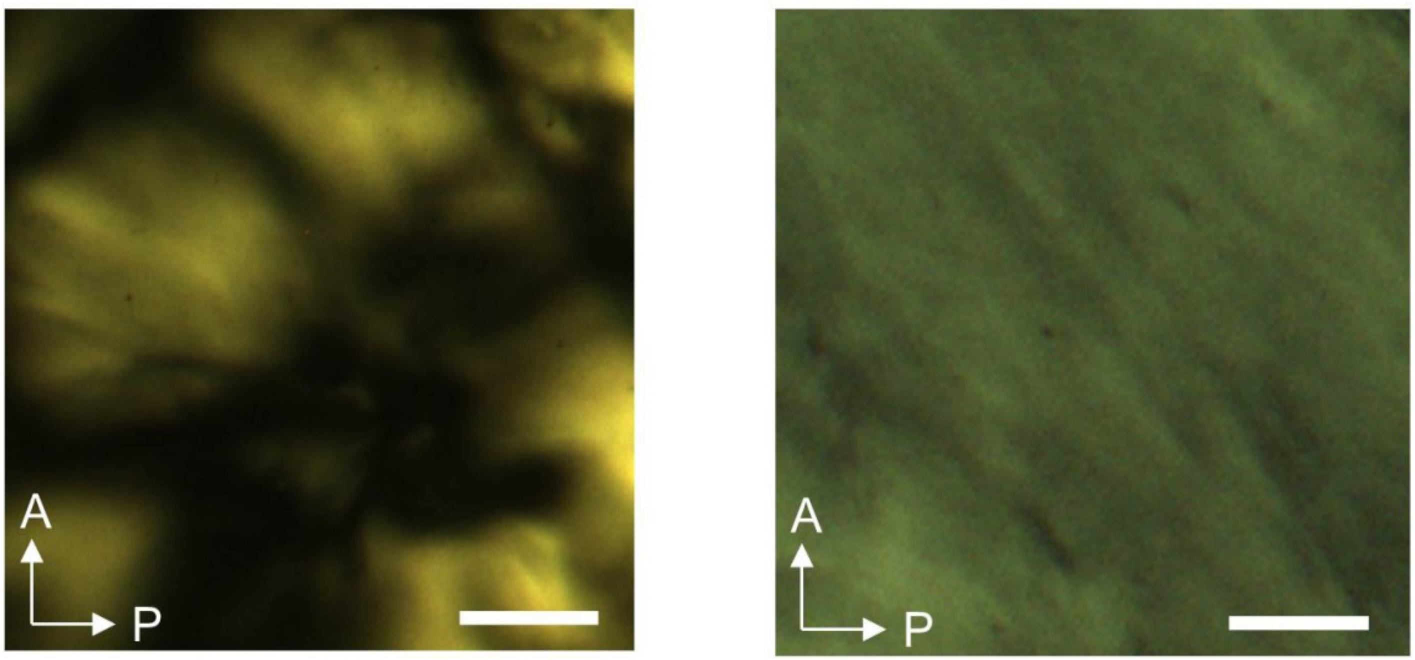
Aqueous Graphene Oxide Colloidal Liquid Crystals

Aqueous GO flakes – 0.3-0.5 vol%, lateral size ~ 0.4 μm on average



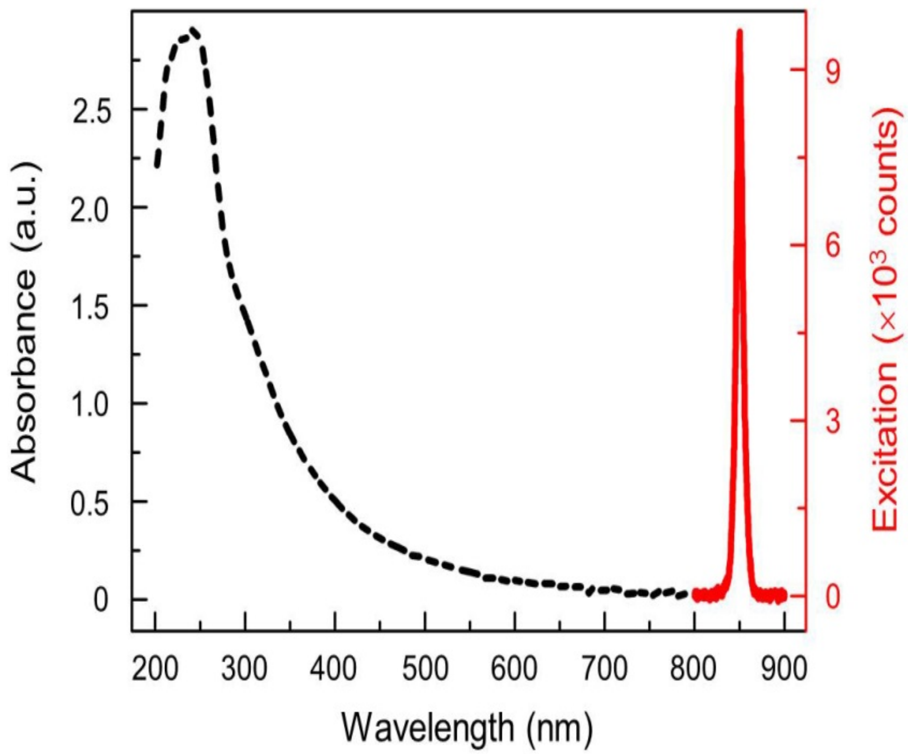
→Electrostatic stabilization due to the charged groups!

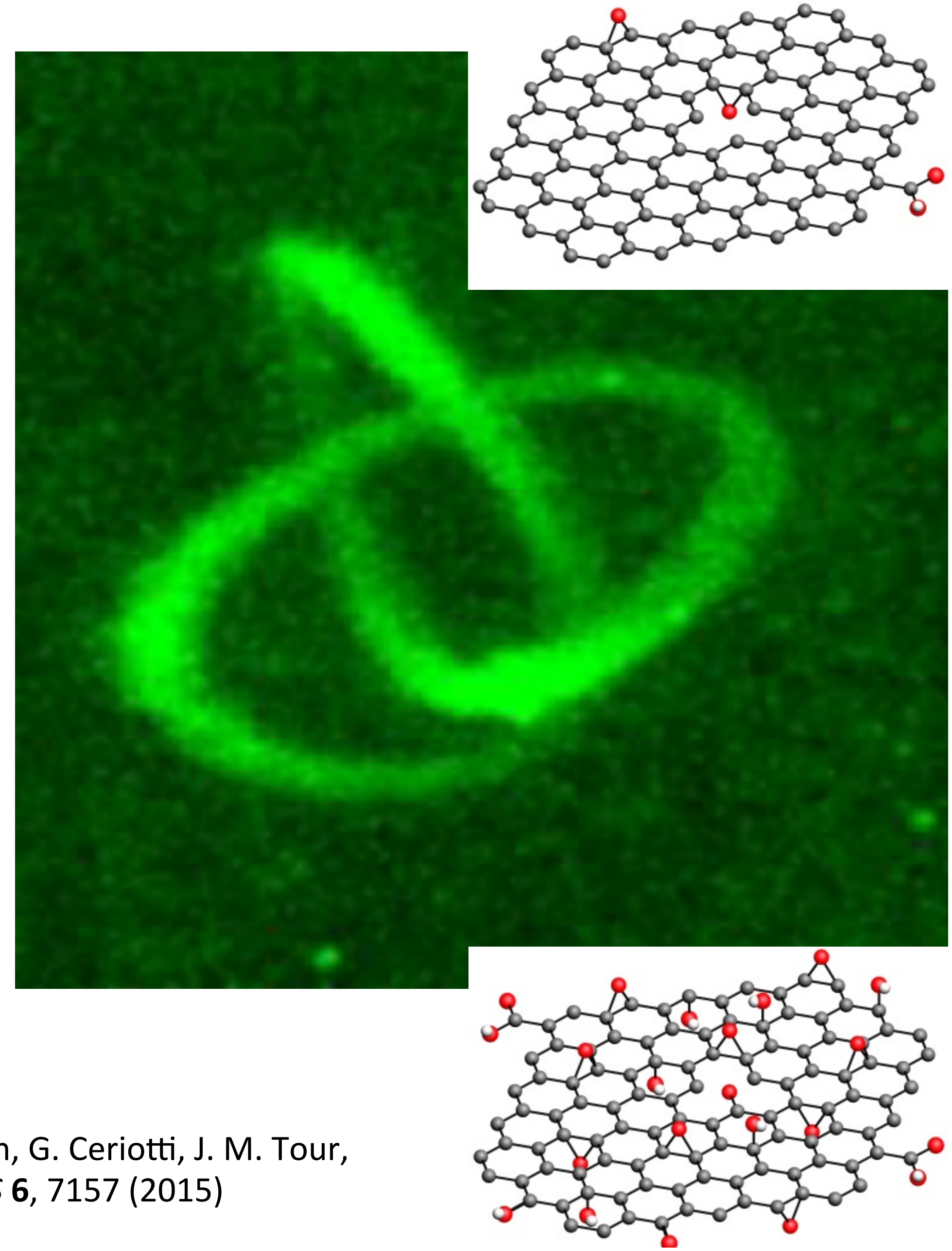
Textures of a GO nematic liquid crystal at concentration 0.7 wt. %



Defining complex-shaped colloidal microparticles

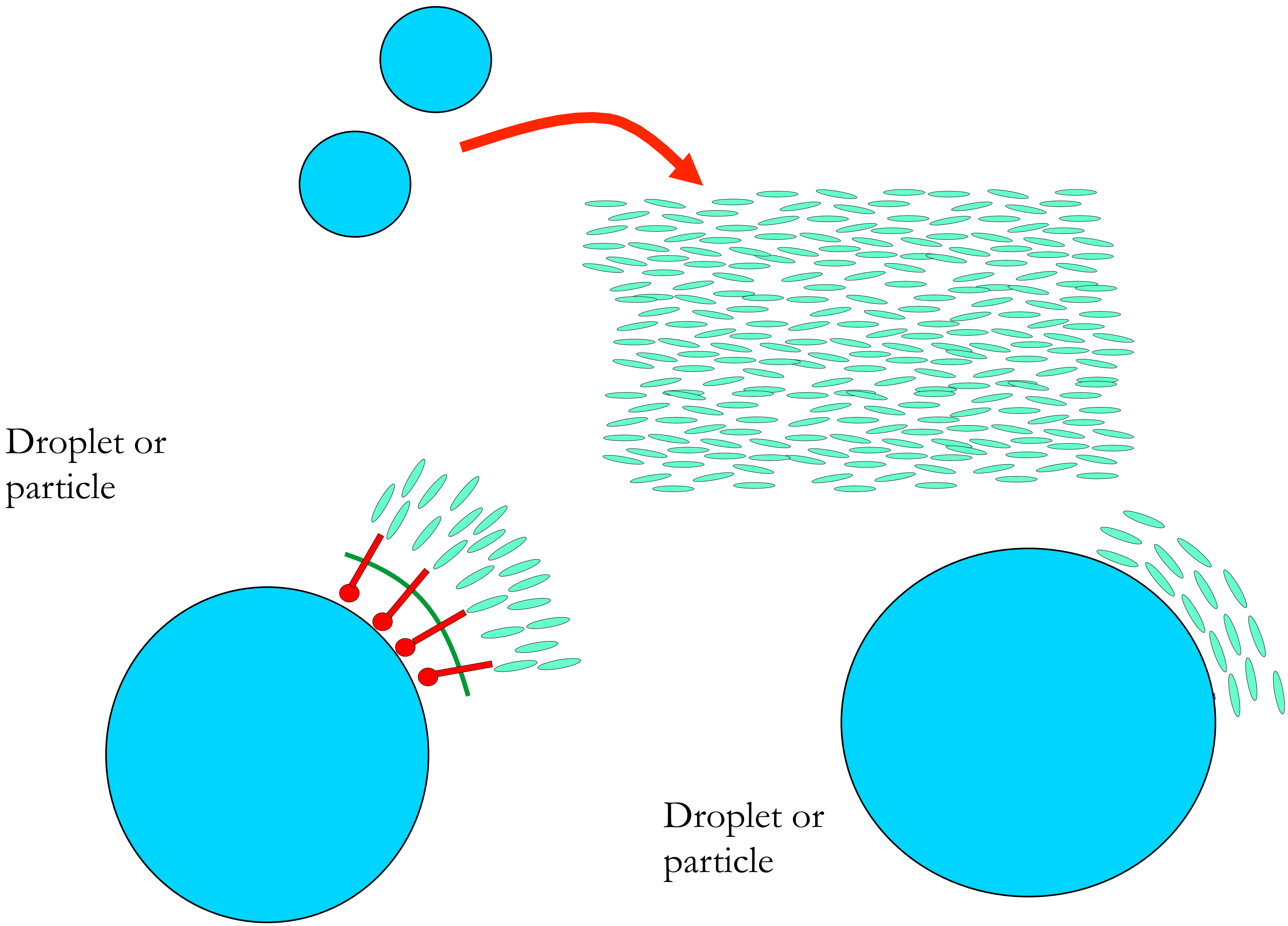
Optical properties of a GO nematic liquid crystal at concentration 0.7 wt. %





B. Senyuk, N. Behabtu, A. Martinez, T. Lee, D. E. Tsentalovich, G. Ceriotti, J. M. Tour, M. Pasquali, and I. I. Smalyukh. *NATURE COMMUNICATIONS* **6**, 7157 (2015)

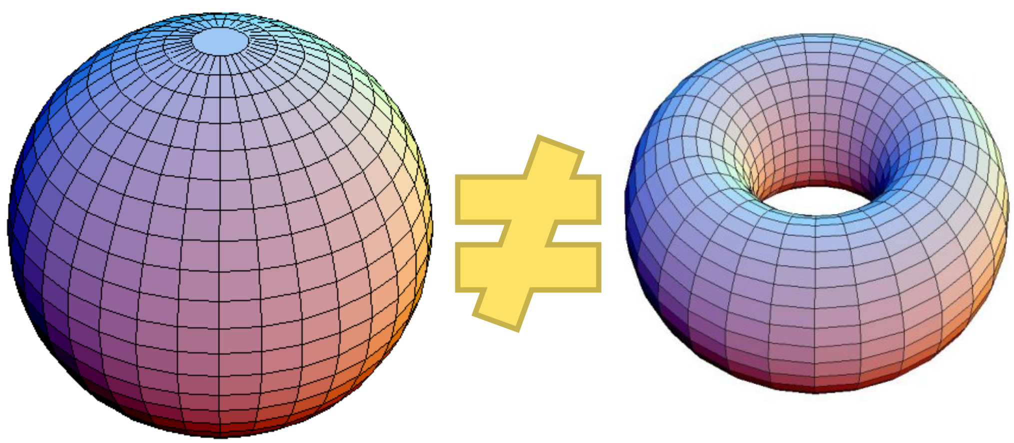
Inclusions/colloids in liquid crystals



Boundary conditions which drive the distortions

Topologically distinct colloidal surfaces?

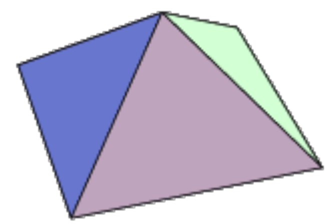
- Homeomorphic



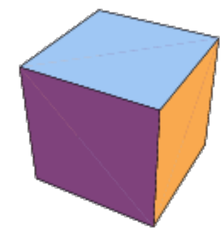
- Topologically distinct!

Topology of Surfaces: beyond spheres

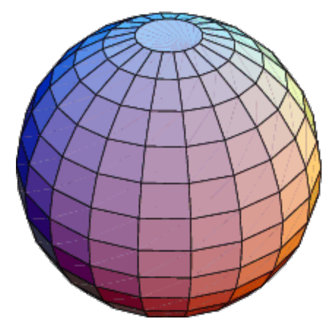
- Every surface can be assigned an Euler characteristic.
- For a geometry with F faces, V vertices, and E edges, the Euler characteristic is given by $\chi=V-E+F$.
- For an n-torus, the Euler characteristic is given by $\chi=2-2n$.



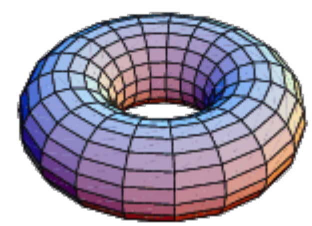
$\chi=2$



$\chi=2$



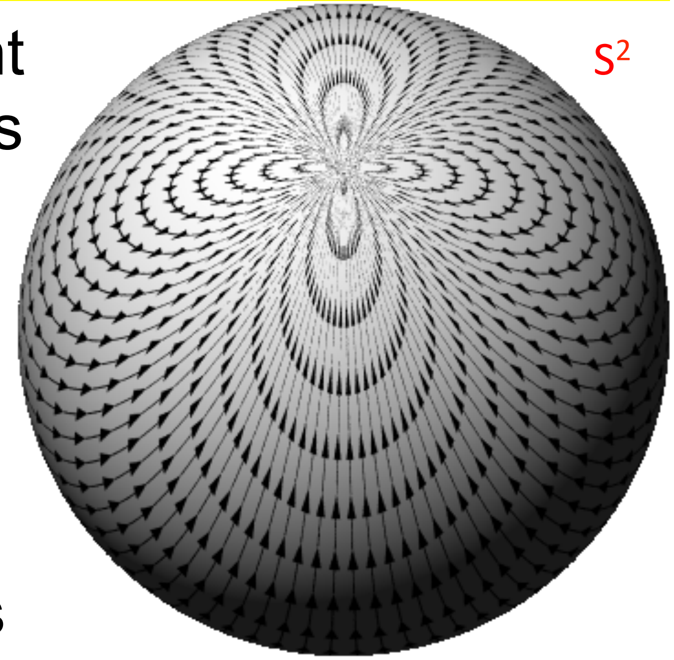
$\chi=2$



$\chi=0$

Hairy Ball & Poincare-Hopf theorems

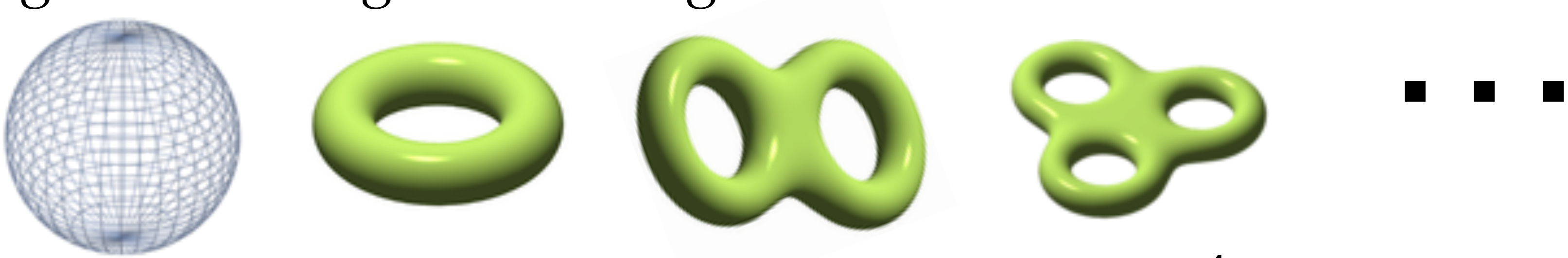
Hairy Ball Theorem: no continuous tangent vector field on even-dimensional S^n-spheres (e.g. S^2)



– discussed previously in relation to spherical droplets & particles

Poincare-Hopf theorem: winding numbers of defects in the vector field add to the Euler characteristic: $\chi = 2 - 2g$

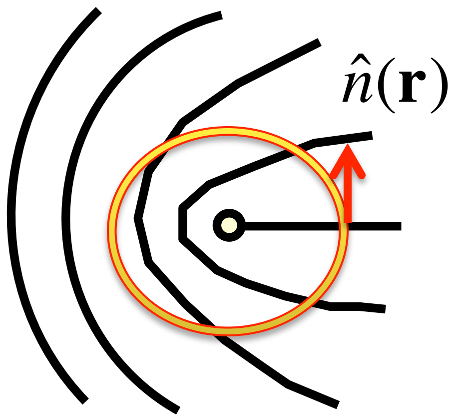
$g = 0$ $g = 1$ $g = 2$ $g = 3$



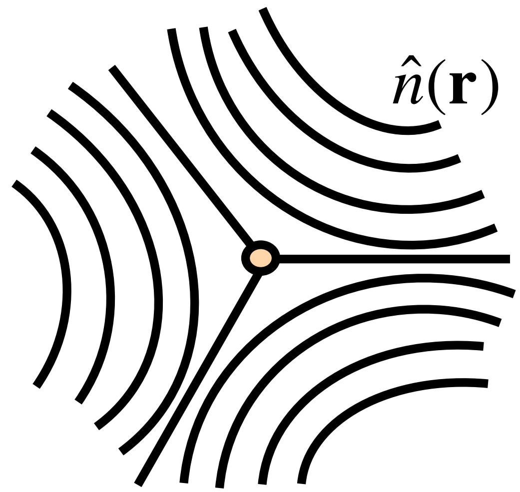
$\chi = 2$ $\chi = 0$ $\chi = -2$ $\chi = -4$

Defects in 2D: Winding Number

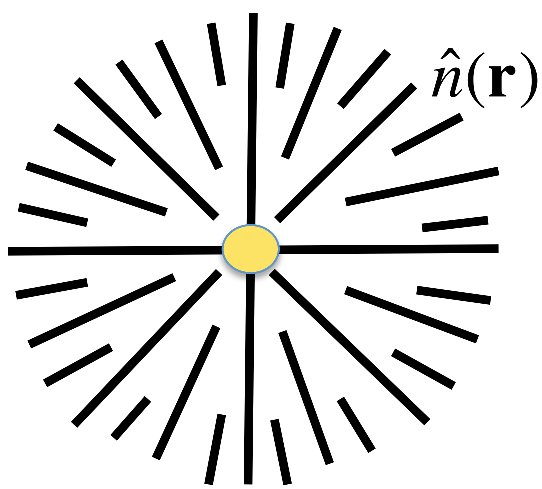
s=1/2



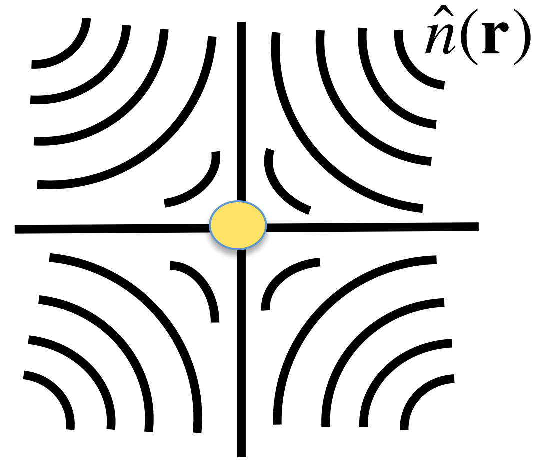
s=-1/2



s=+1



s=-1



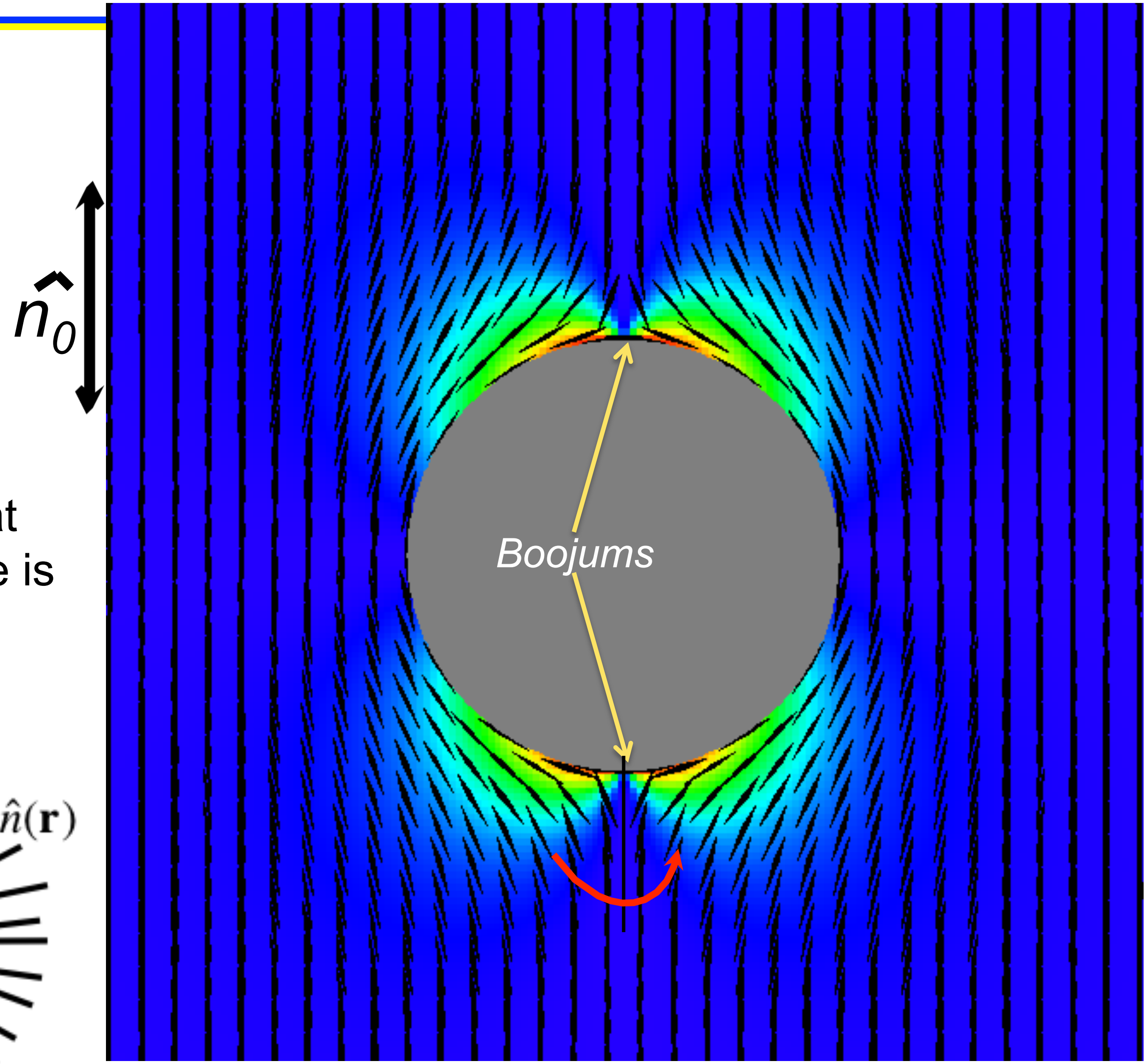
- Director rotates by $2\pi s$ on going around it (s is the winding number)
- Recall this is different in 3D (integer unstable...)

Topology-required surface defects - boojums

Spherical particle with

tangential surface BCs

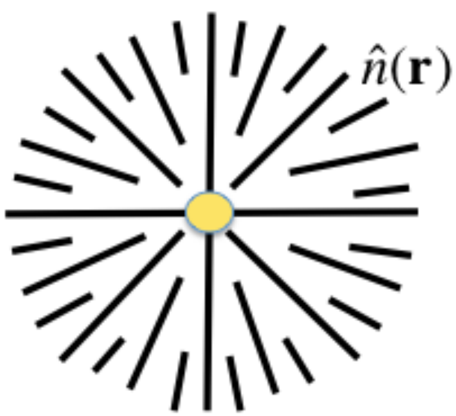
Two boojums at poles



Winding number of defects in the 2D field at the LC particle interface is

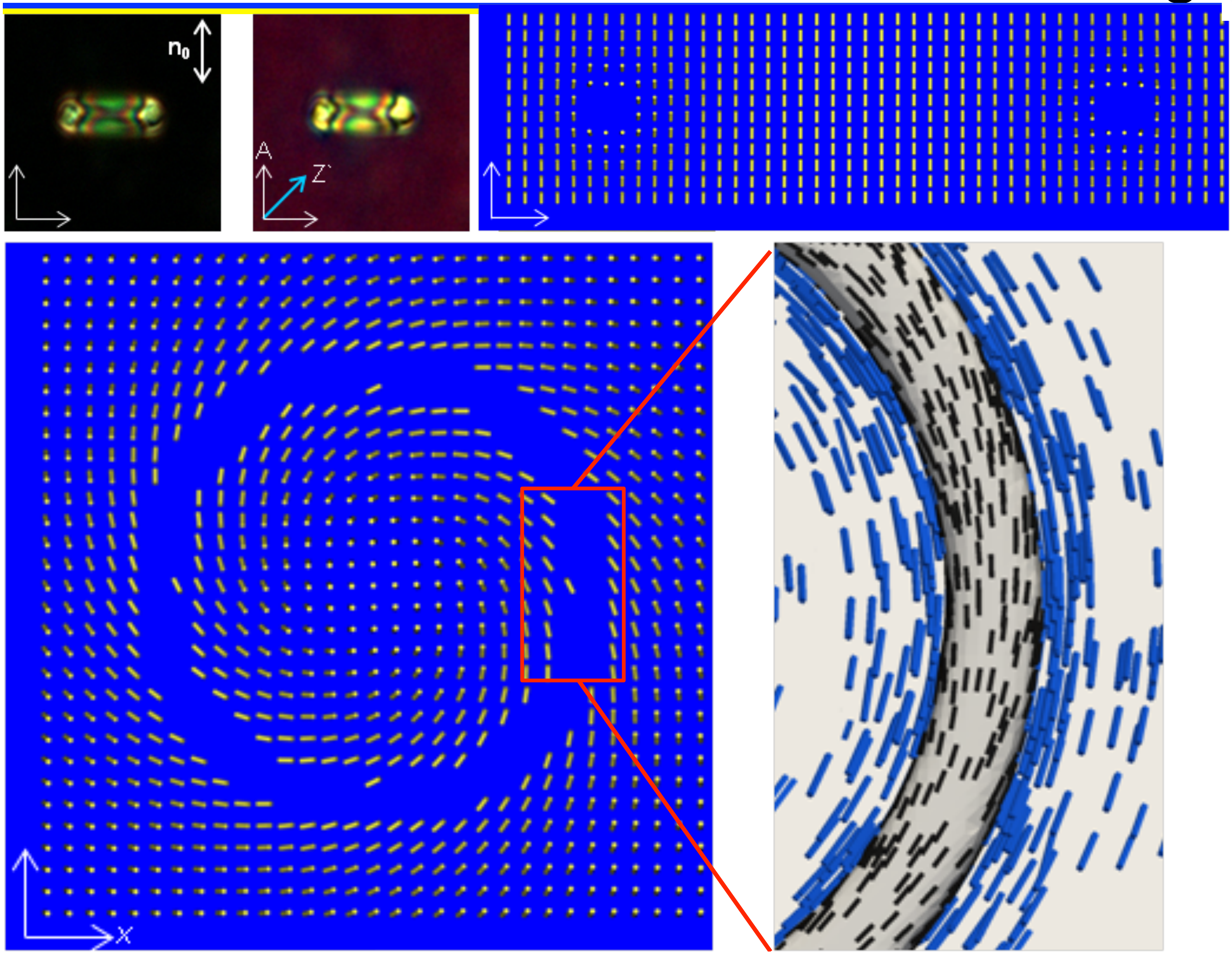
$$s = \chi = 2$$

s=+1



Proc. Natl. Acad. Sci. U.S.A. **103**, 18048 (2006)

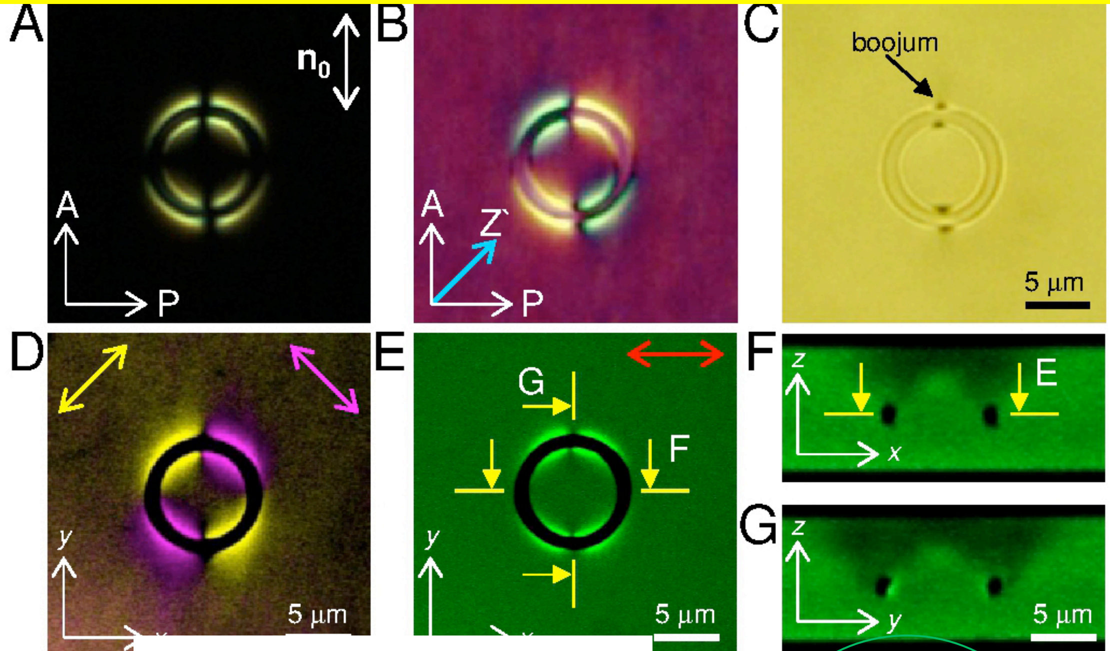
Defect-free structures around a ring

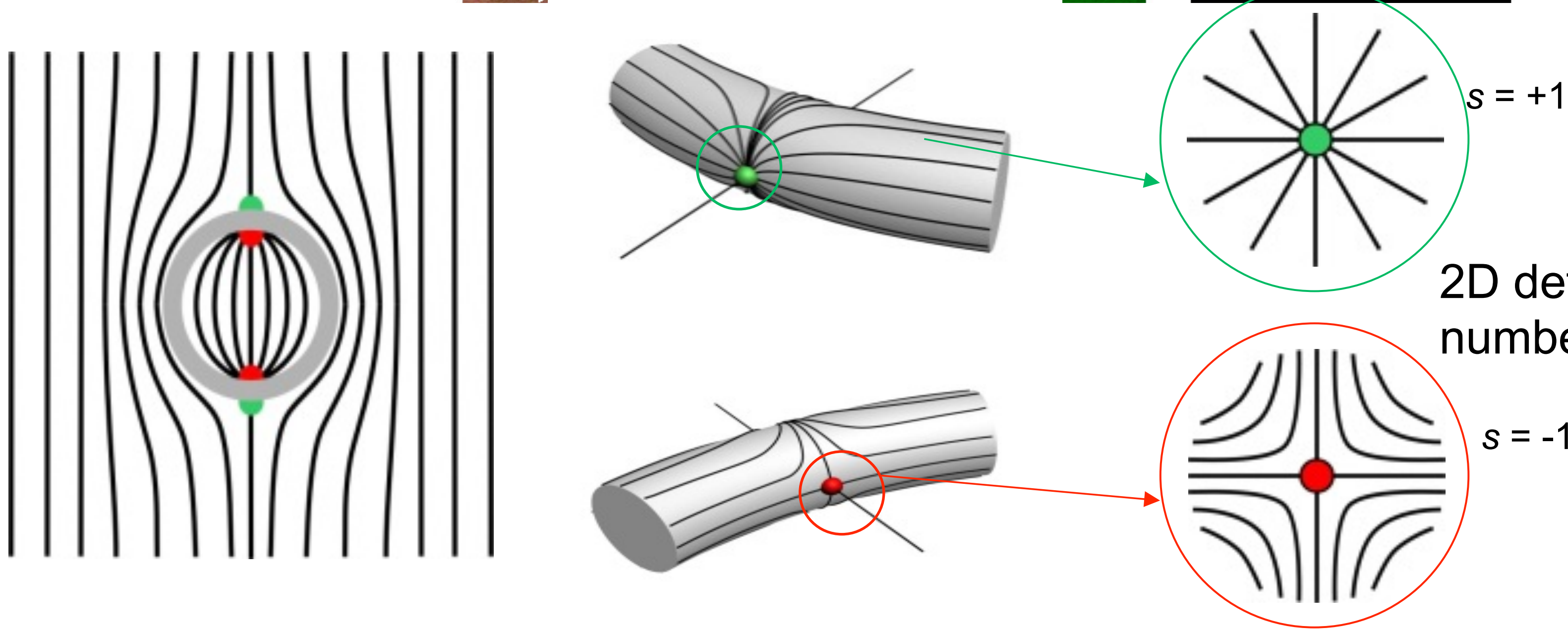


Boojums on colloidal rings

Polarizing optical microscopy

3D imaging



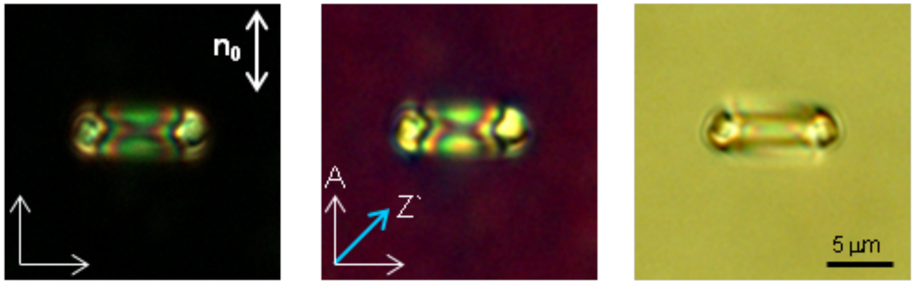


2D defect winding numbers

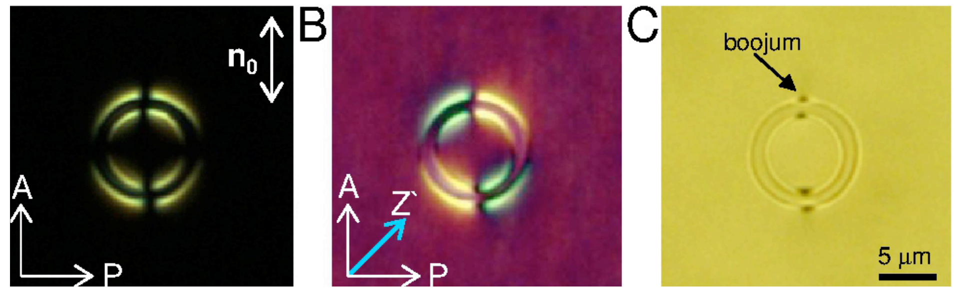
Liu, Senyuk, Tasinkevych, Smalyukh. *Proc. Natl. Acad. Sci. U.S.A.* **110**, 9231 (2013)

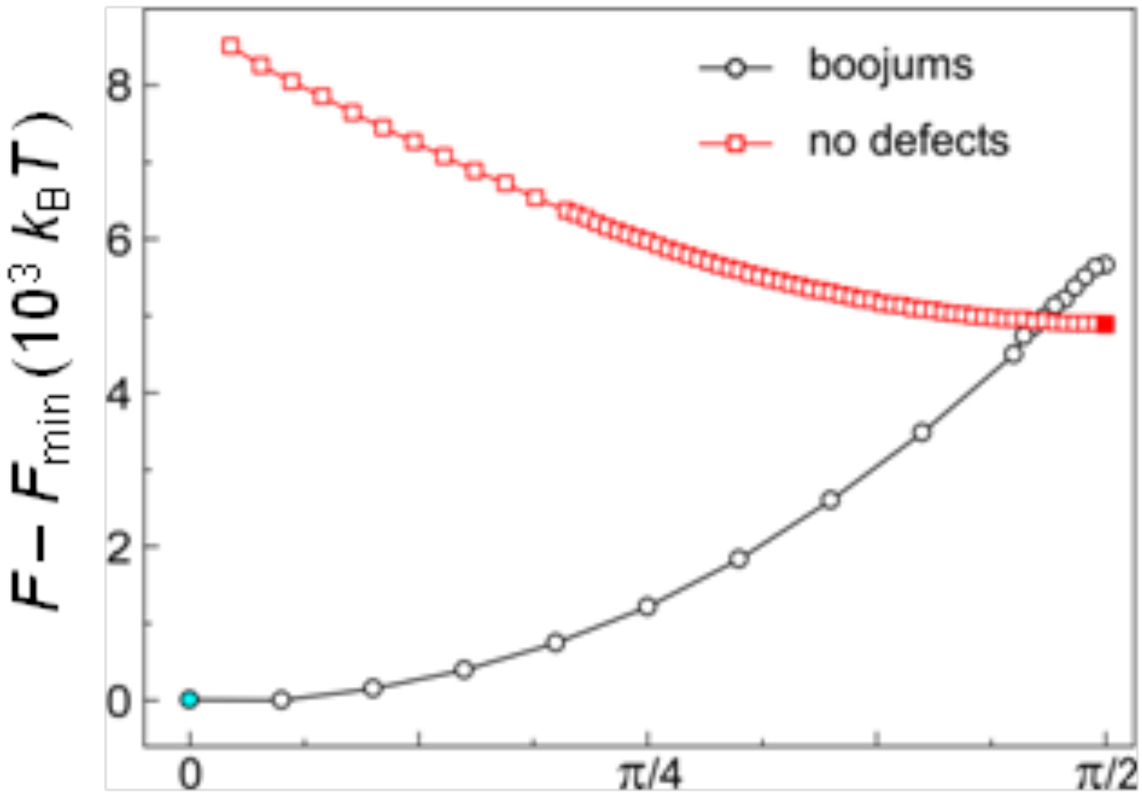
Structural stability

No defects



With boojums

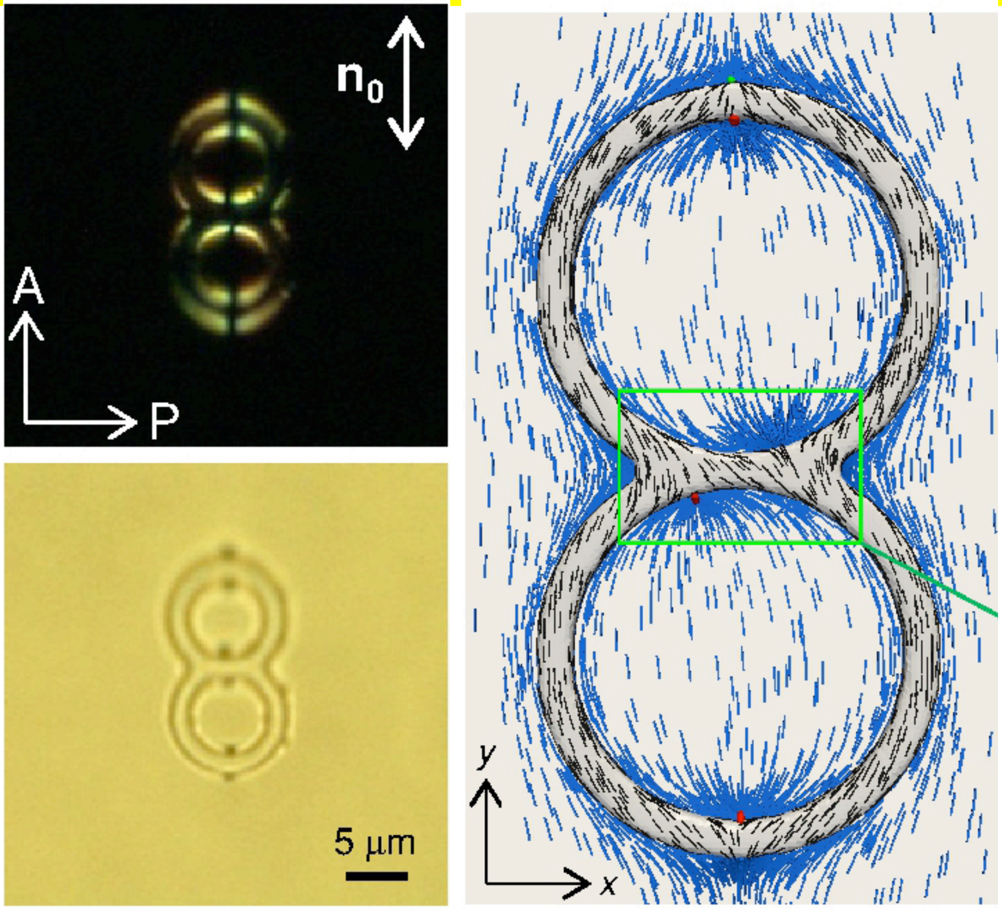




Energetic barrier - bistable

→Defects are not required but appear to reduce free energy!
→Still satisfy topological constraints (winding numbers add to zero)

Boojums on g=2 handlebodies

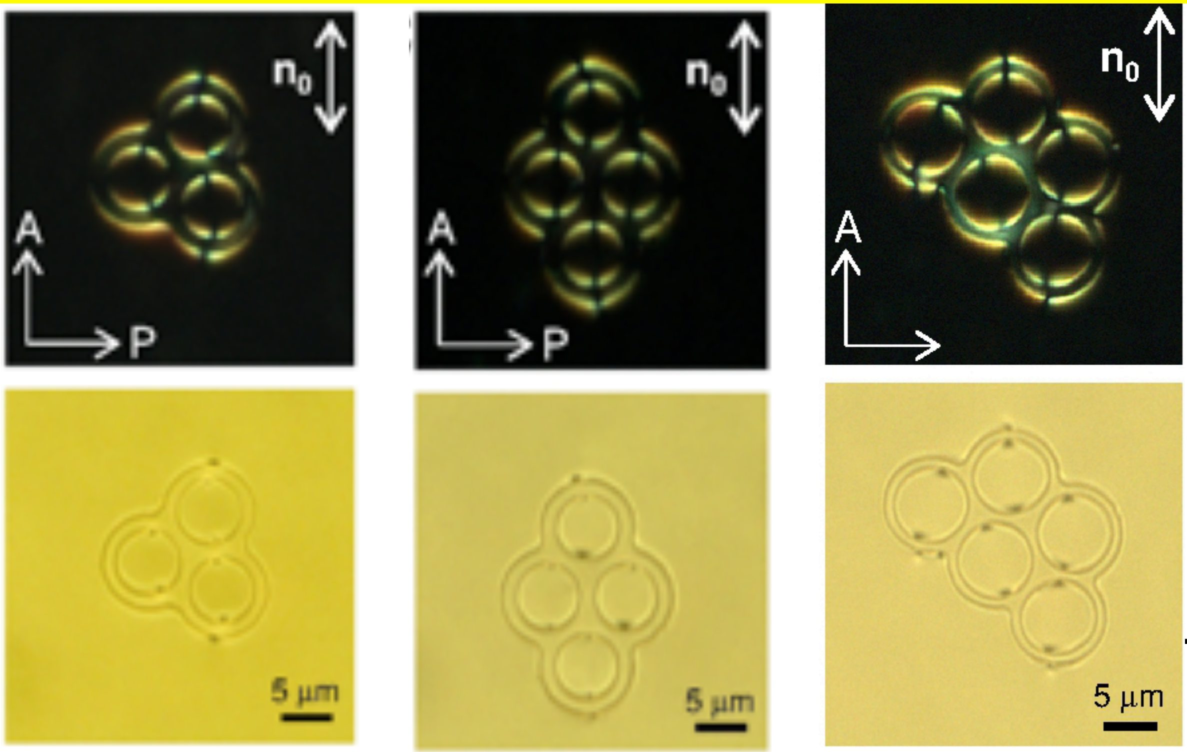


- **Different orientations, but the same net 2D winding numbers of boojums**
- **Satisfy predictions of topological theorems:**

$$\sum_i s_i = \chi = 2 - 2g$$

- **To induce boojums of net winding numbers *s* use a particle of right g**

Boojums on colloidal handlebodies



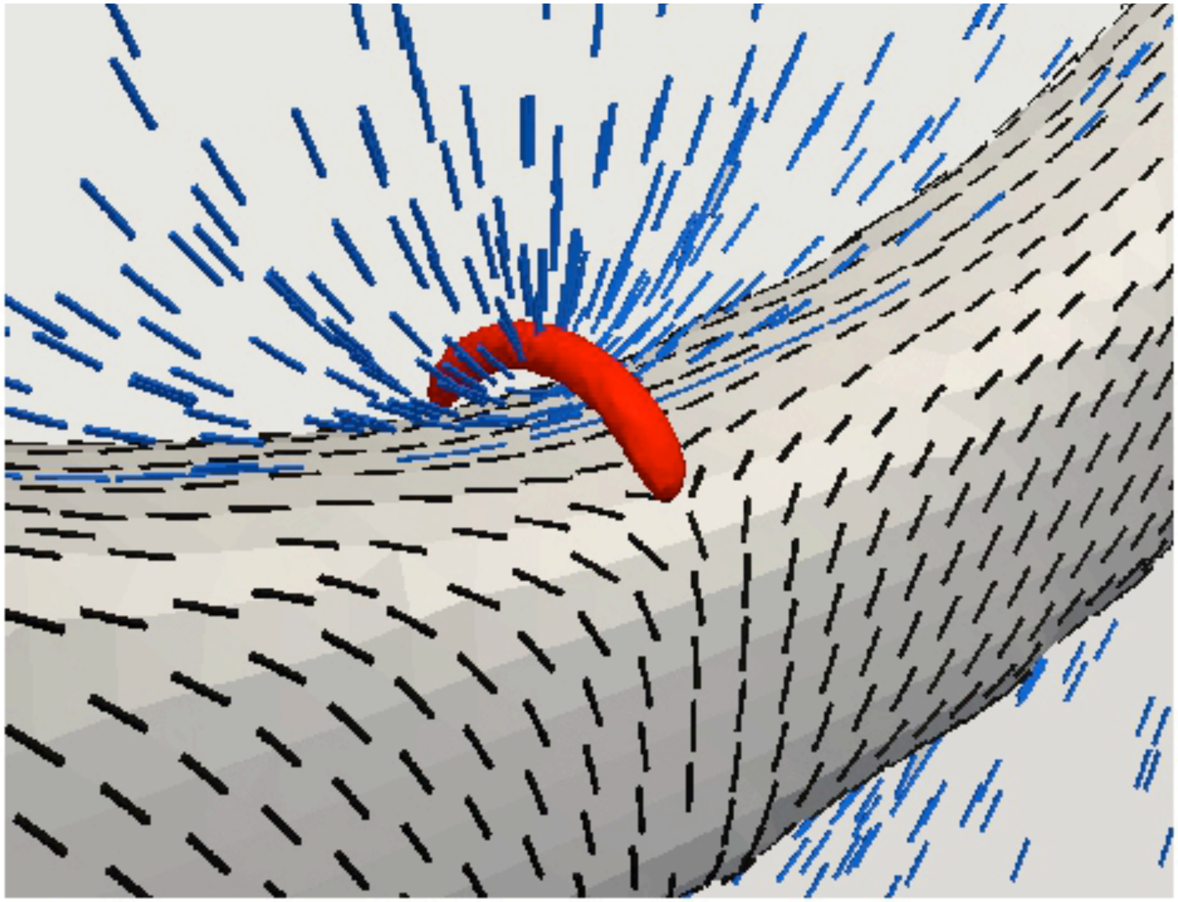
g=3,4,5 handlebodies

Theorems & charge conservation:

$$\sum_i s_i = \chi = 2 - 2g$$

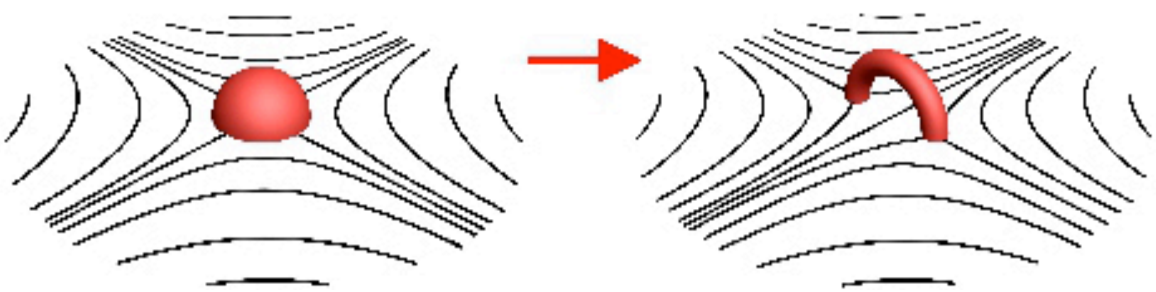
g	$\chi = \Sigma_i s_i$	Number of defects	
		$s = +1$	$s = -1$
1	0	2	2
		0	0
2	-2	2	4
		4	6
3	-4	2	6
		4	8
4	-6	2	8
		4	10
5	-8	2	10
		3	11

Boojums form handles on colloidal handlebodies



Strong tangential anchoring promotes boojum splitting into disclination semirings

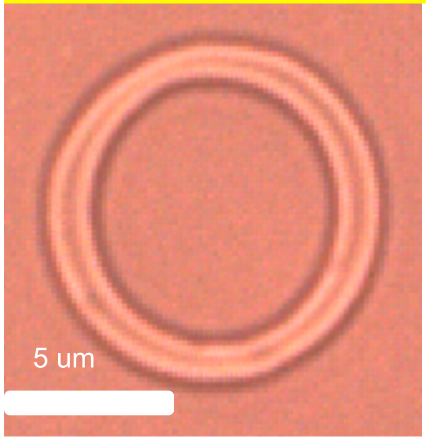
Splitting of boojum points to semi-rings increases g:
handle-shaped boojums on colloidal handlebodies

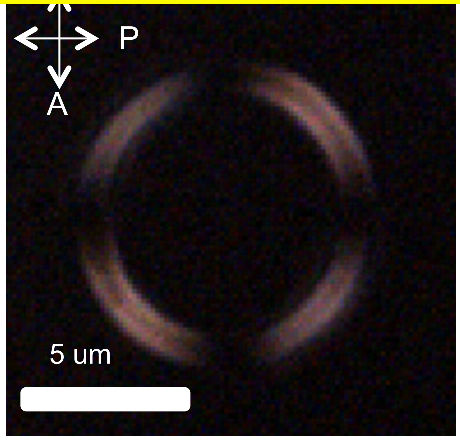


Q. Liu, B. Senyuk, M. Tasinkevych, and I. I. Smalyukh, Proc. Natl. Acad. Sci. U.S.A. **110**, 9231 (2013)

Drops of LCs with g>0?

Torus-shaped droplet confinement

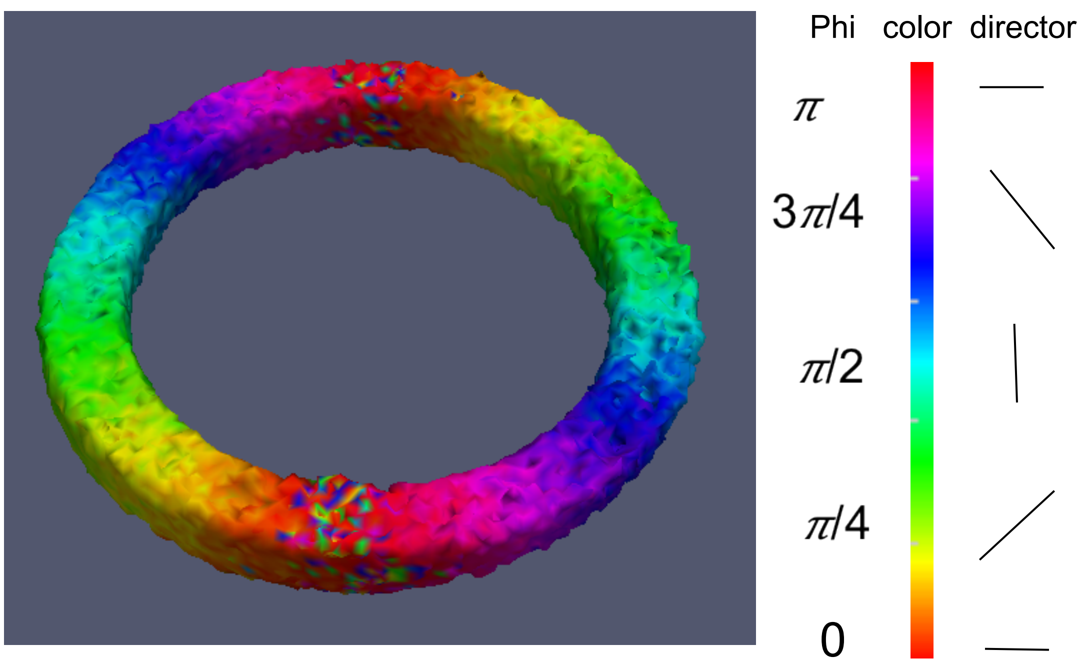


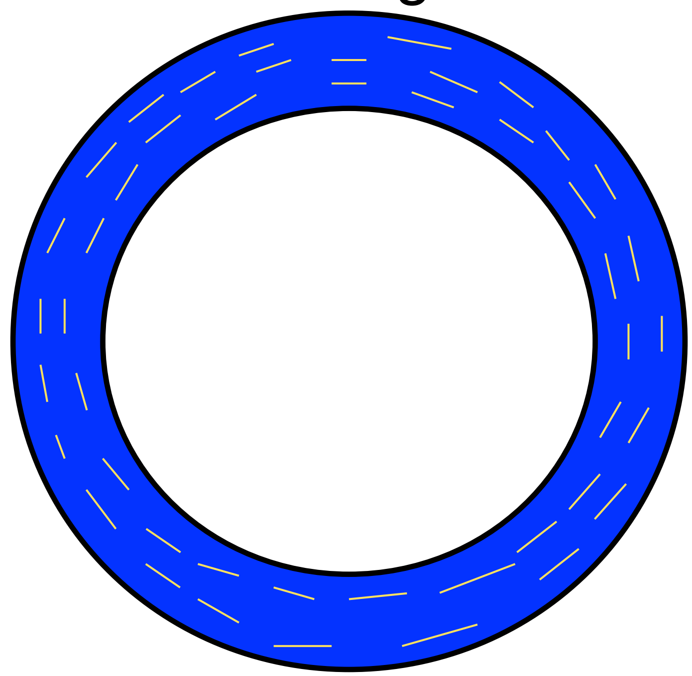


- No topological defects induced;

$$\sum_i s_i = \chi = 2 - 2g$$

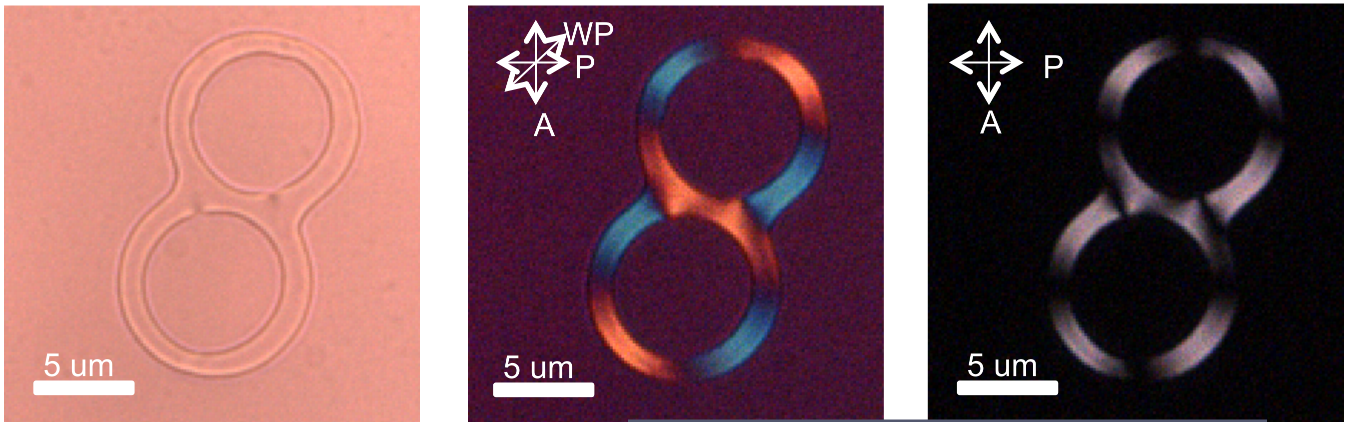
- Director field reconstructed from 3D 3PEF-PM images





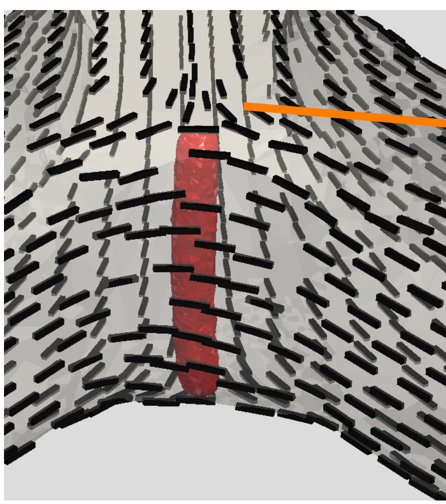
M. Campbell, M. Tasinkevych, I. Smalyukh. *Phys. Rev. Lett.* **112**, 197801 (2014).

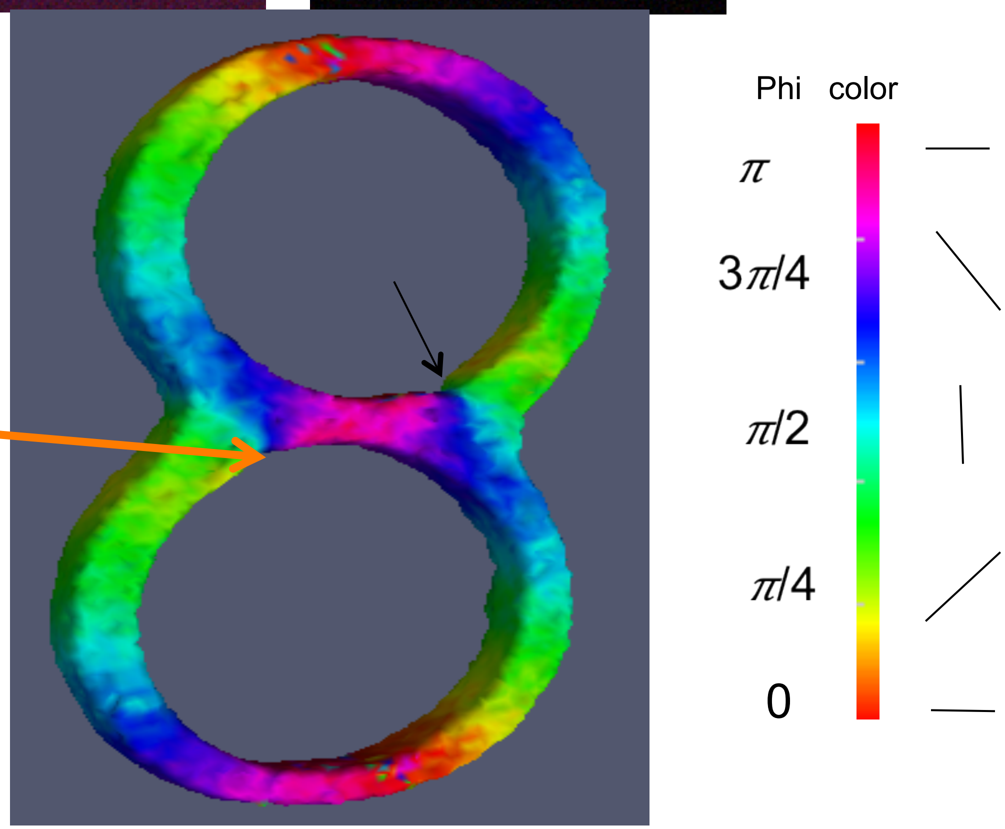
g=2 Torus



$$\sum_i s_i = \chi = 2 - 2g$$

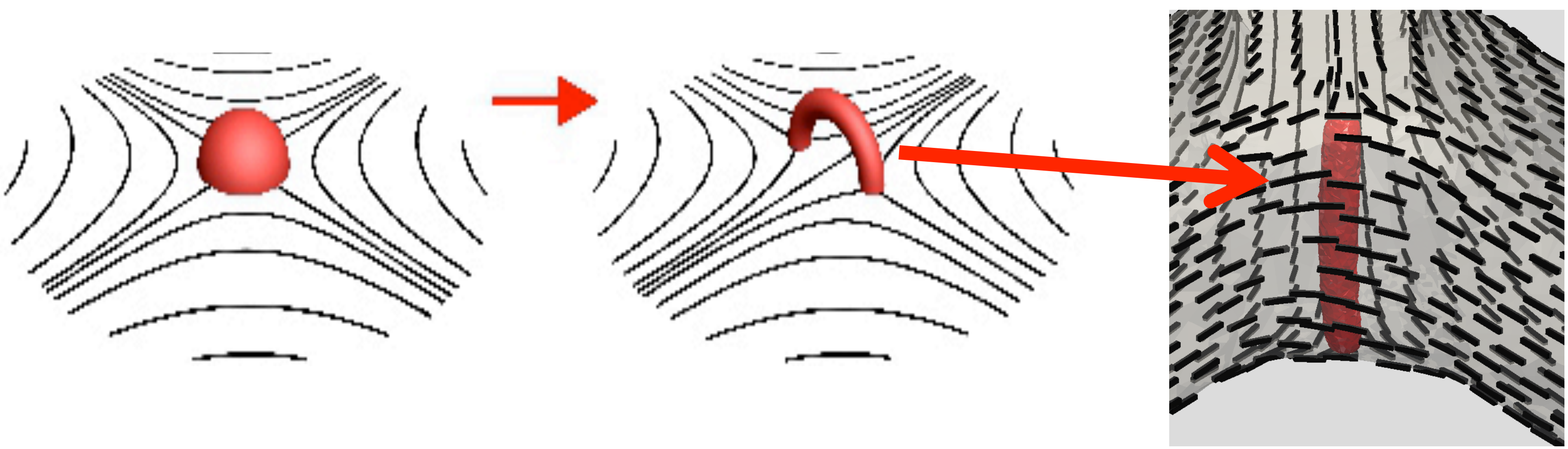
s=-1/2 disclination





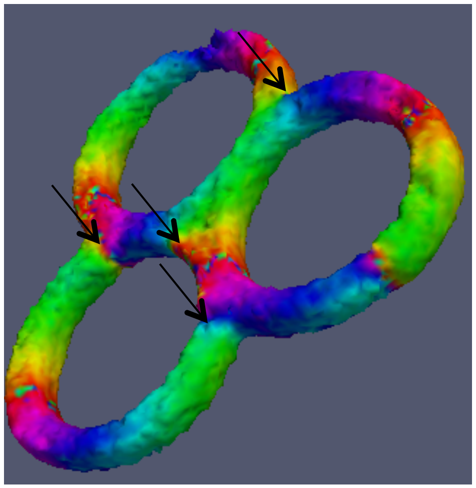
Defect Structure

- Rather than boojums, we observe line defects of winding number -1/2.
- These structures are topologically equivalent.
- The line defect is lower energy than the boojum in small drops.



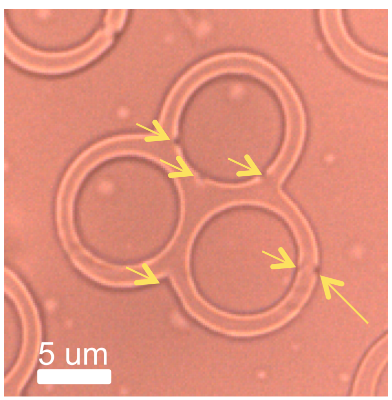
M. Campbell, M. Tasinkevych, I. Smalyukh. *Phys. Rev. Lett.* **112**, 197801 (2014).

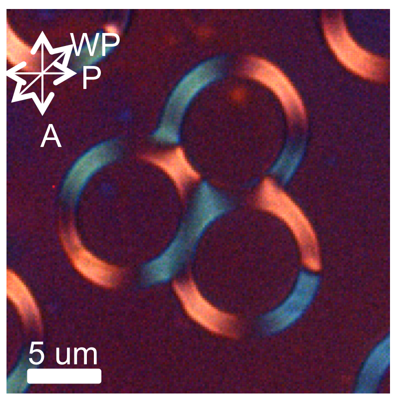
g=3 torus

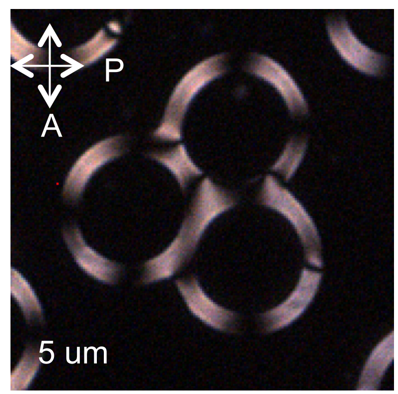


- The defects are -1/2 line defects spanning across the pore thickness
- They are located at the intersection of the three tori
- The strength at surfaces adds to satisfy topology

$$\sum_i s_i = \chi = 2 - 2g$$



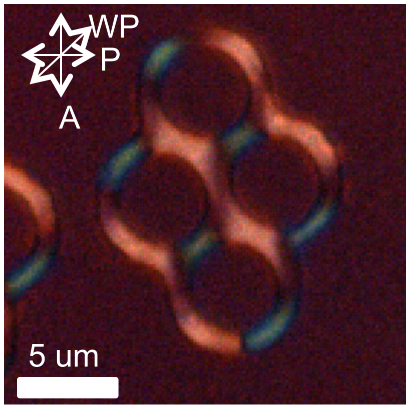


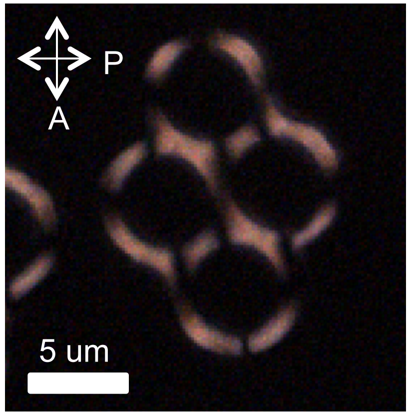


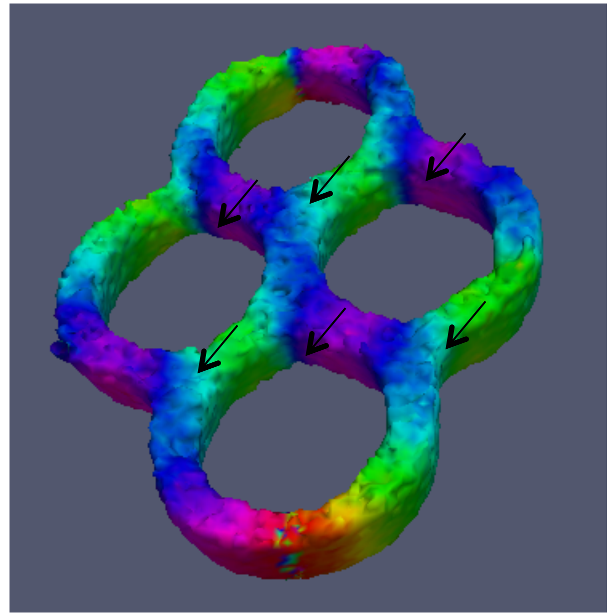
M. Campbell, M. Tasinkevych, I. Smalyukh. *Phys. Rev. Lett.* **112**, 197801 (2014).

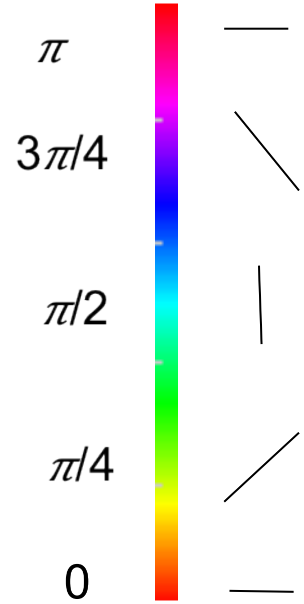
g=4 and g=5 tori

minimum 6 defects



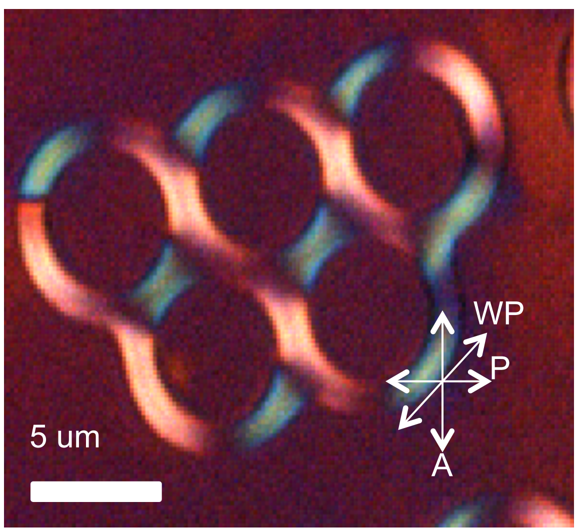


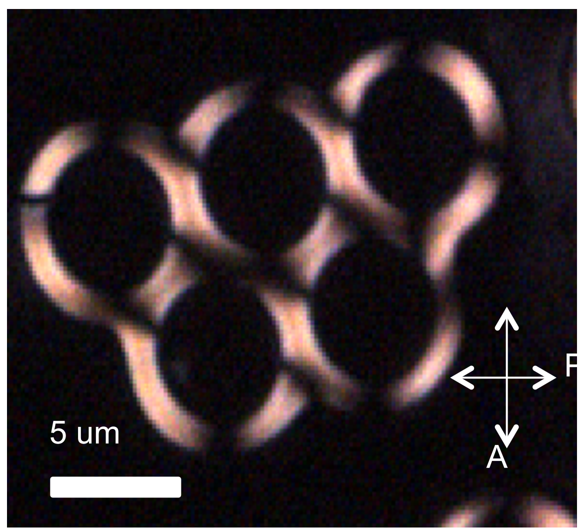


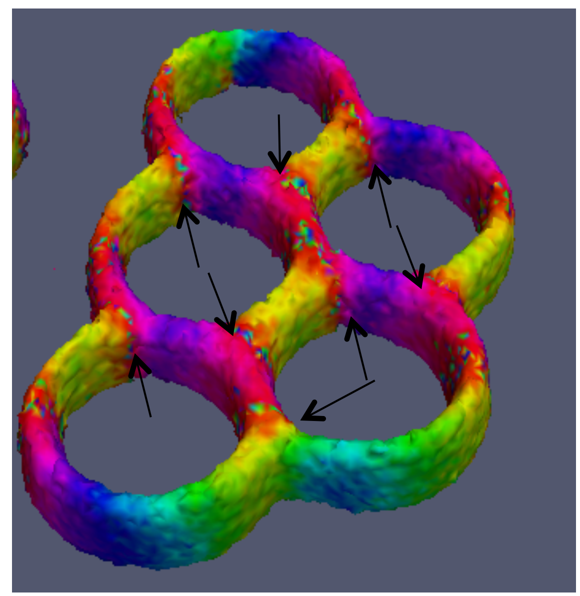


$$\sum_i s_i = \chi = 2 - 2g$$

minimum 8 defects

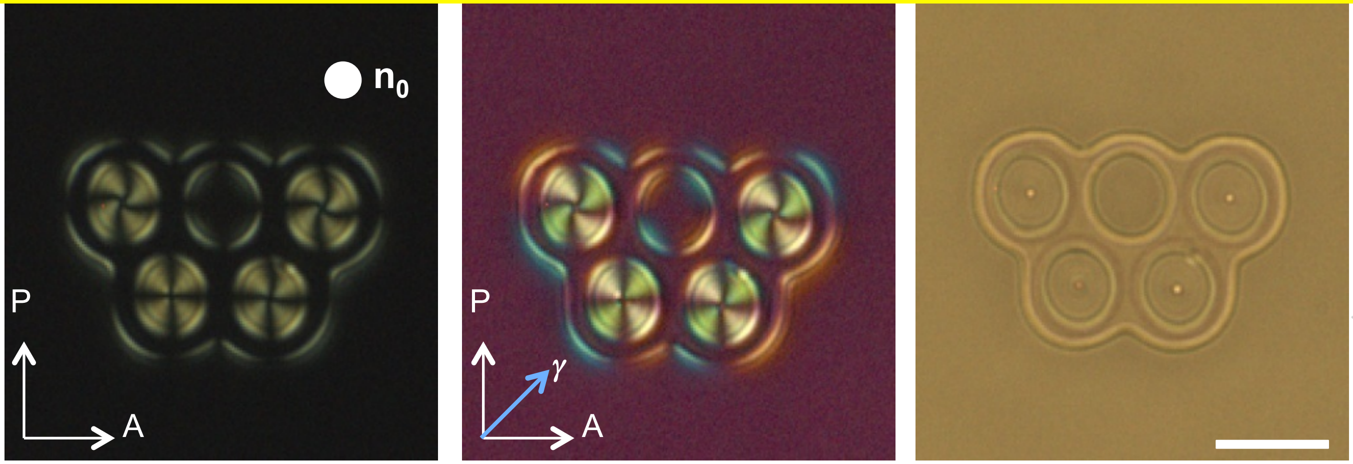




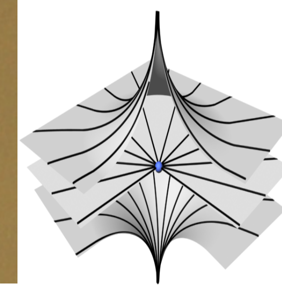


Handlebody-shaped colloids, perpendicular BCs

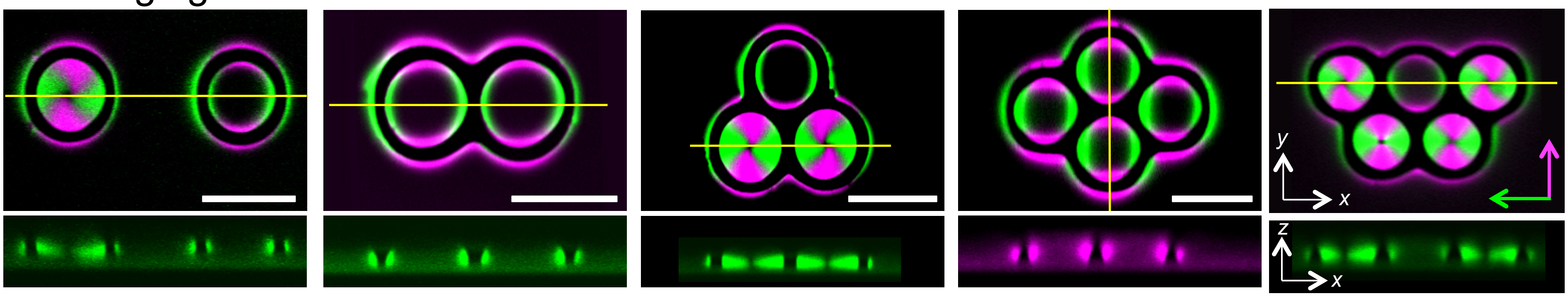
Polarizing optical m-py



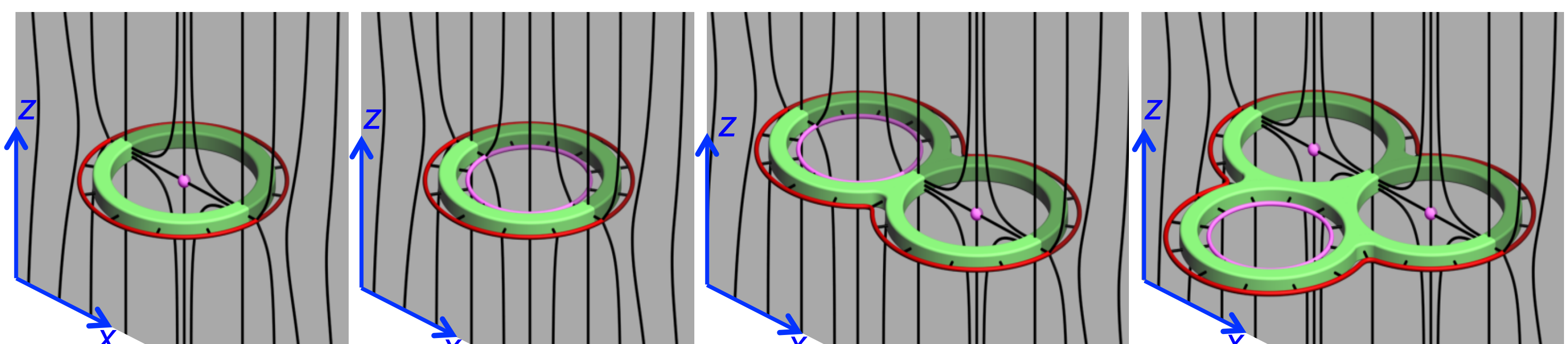
characterized by hedgehog charge like point defects



3D imaging



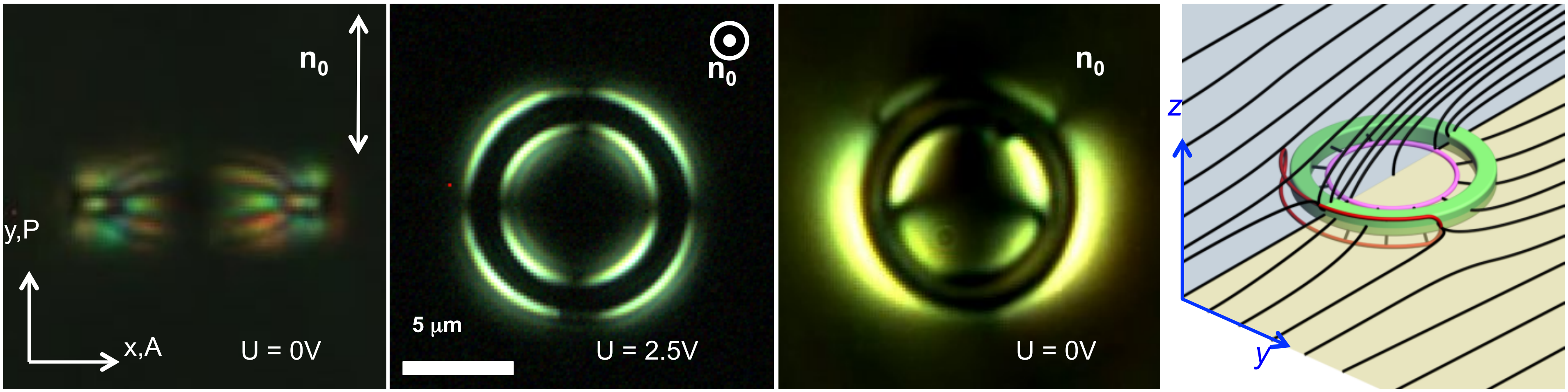
Reconstructed director structures and defects around colloidal hanlebodies

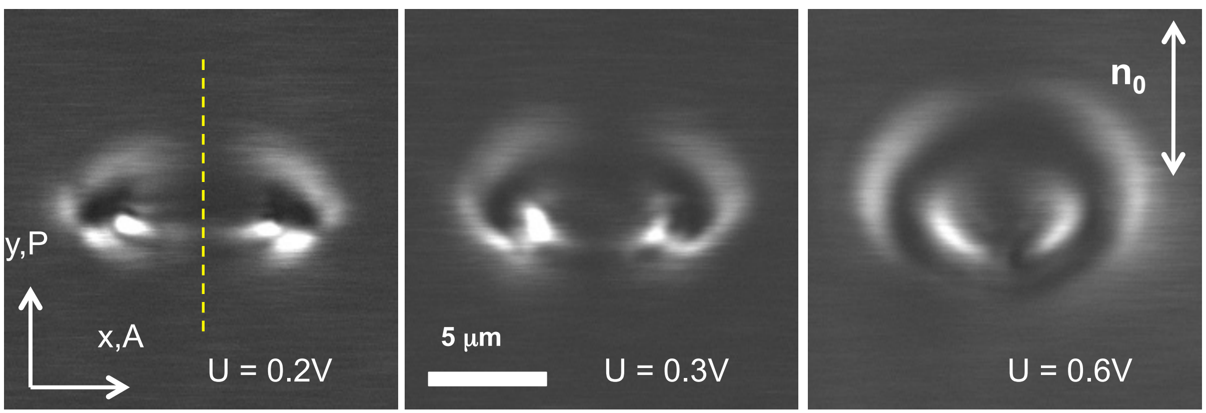


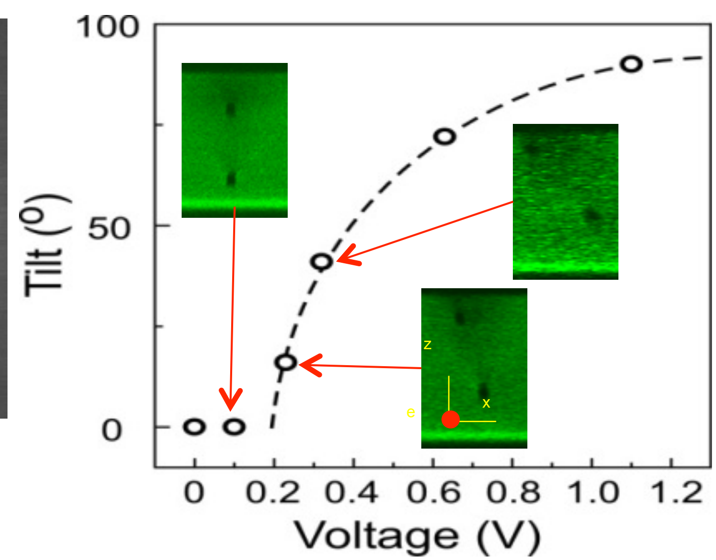
Senyuk, Liu, He, Kamien, Kusner, Lubensky, & Smalyukh, *Nature* **493**, 200-205 (2013)

Switching director & rotating colloidal tori

- **Transformation of defects in applied electric field;**
- **Bistable particle orientations & fields at no field;**



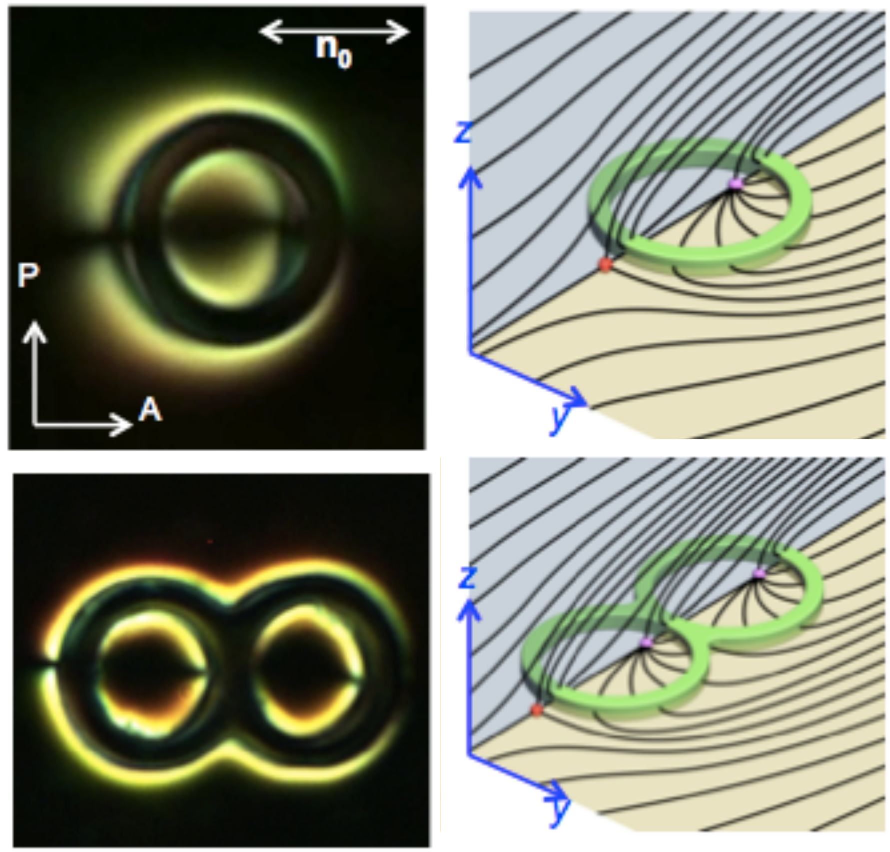




B. Senyuk, Q. Liu, S. He, R. Kamien, R. Kusner, T. Lubensky, & I.I. Smalyukh, " Nature **493**, 200-205 (2013)

Transforming LC defects around colloidal tori

Alignment parallel to the far-field director



Nature **493**, 200 (2013)

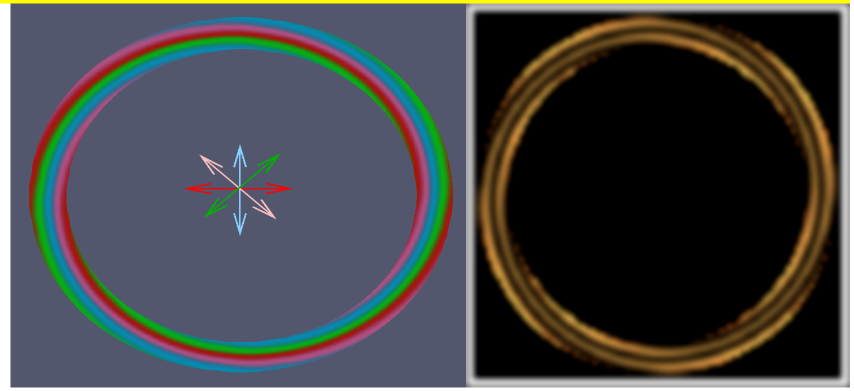
- **In all configurations bulk defects compensate the charge of particle;**
- **Satisfy predictions of the Poincare-Hopf index theorem:**

$$\sum_i m_i = \pm\chi/2 \qquad\qquad \chi = 2-2g$$

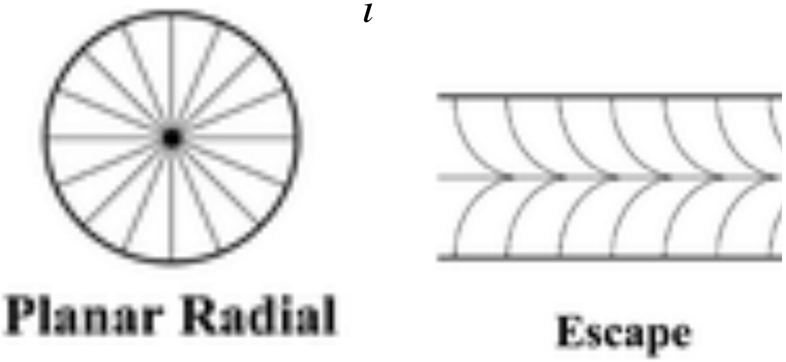
- **Induce net topological charge m (mod 2) by a particle of right g**

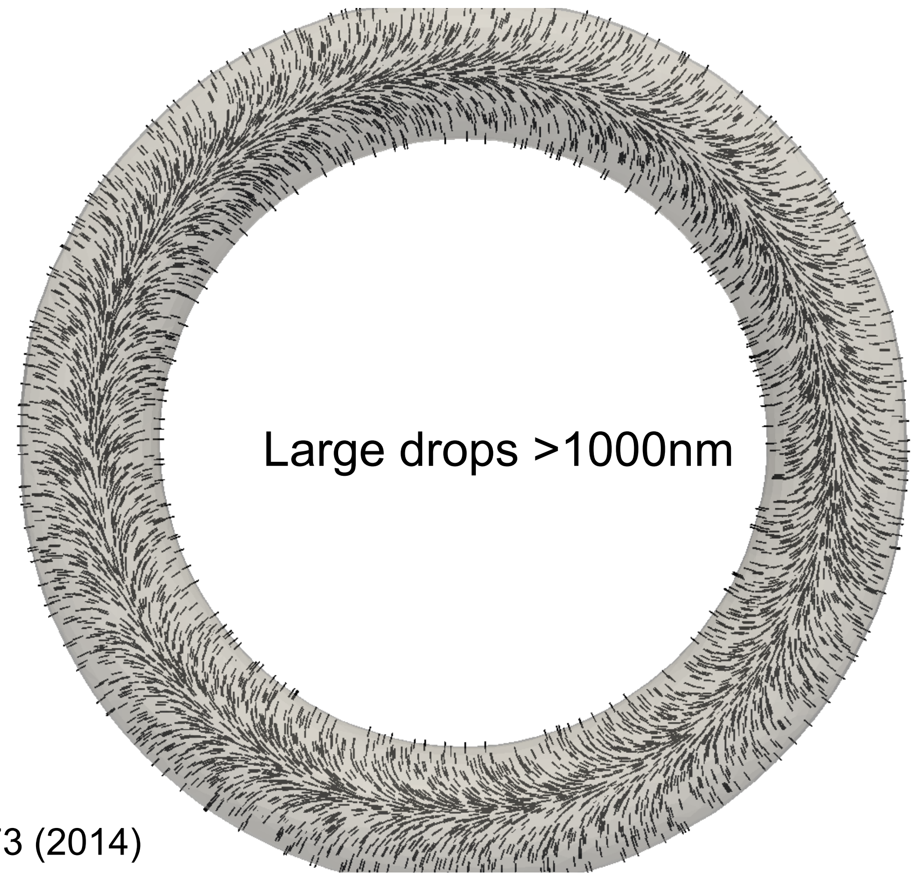
Perpendicular BCs: g=1 torus

- Escape in 3D dimension:
  - in cylindrical capillary;
  - under torus confinement;



$$\sum_i m_i = \pm \chi / 2$$





Tasinkevych, Campbell, Smalyukh, PNAS. **111**, 16268-16273 (2014)

g=1 confinement with knotted/linked defect lines

Small drops:

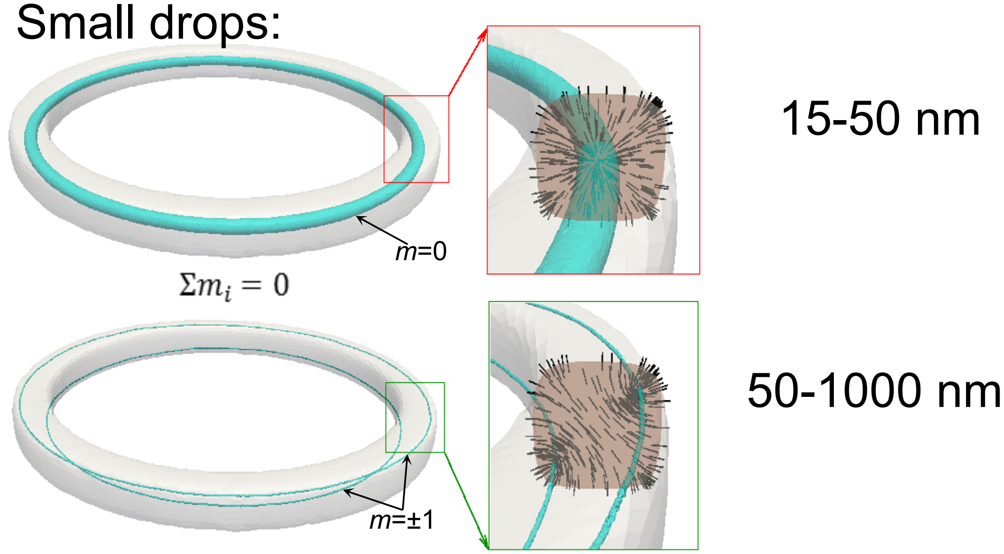
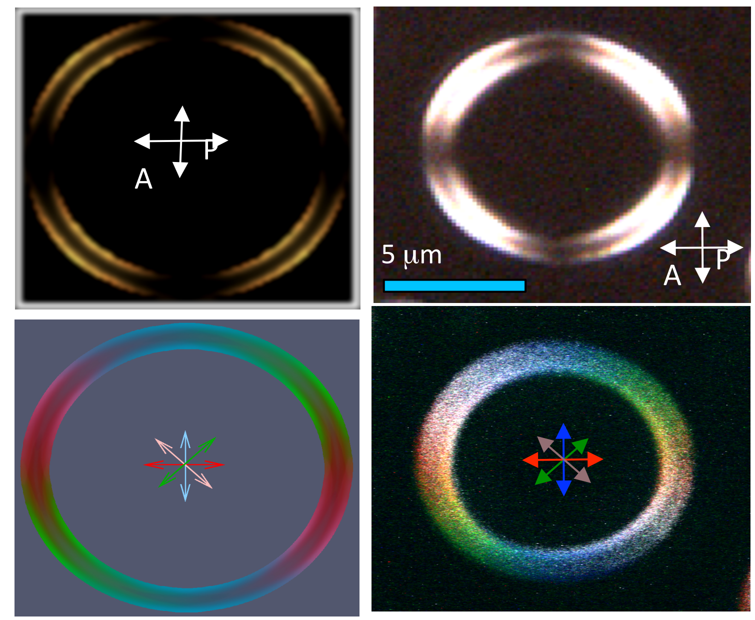
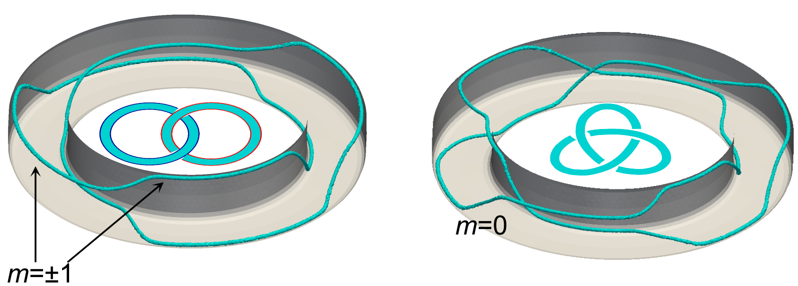


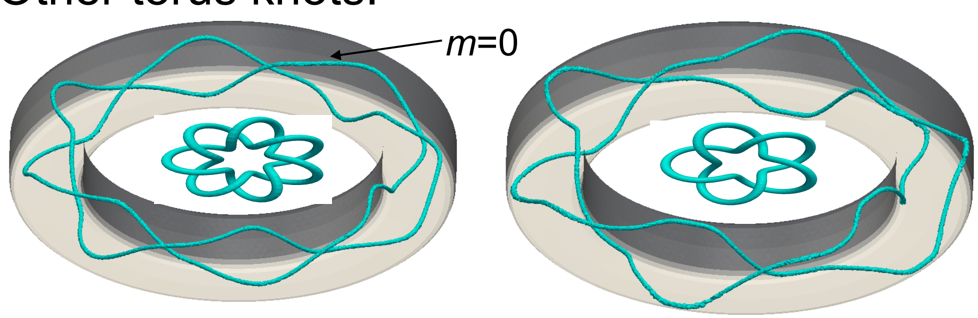
Image comparison:

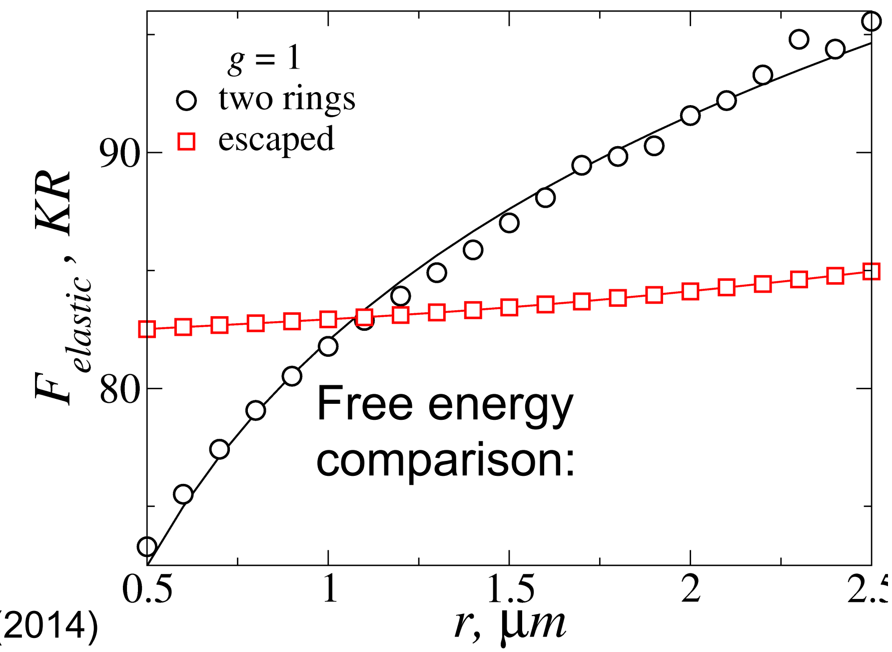


Links & trefoil knots:



Other torus knots:

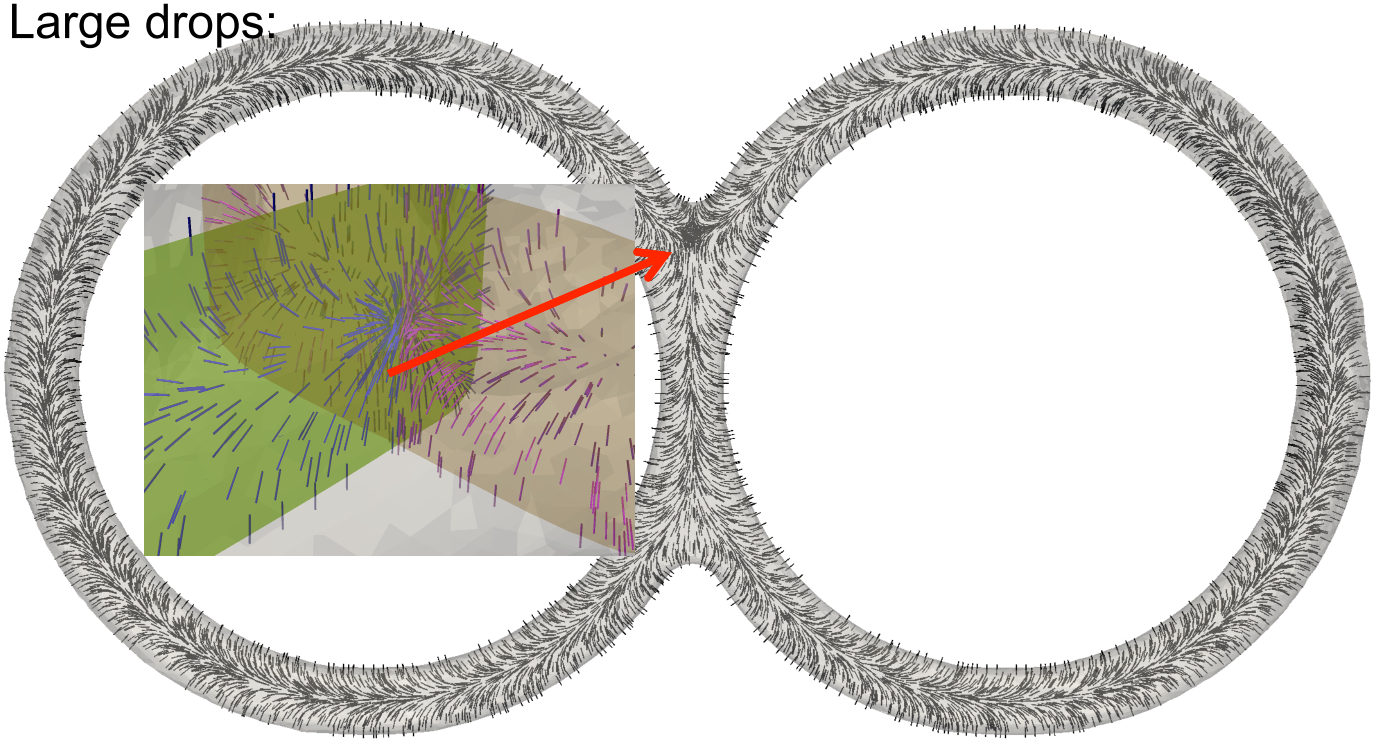


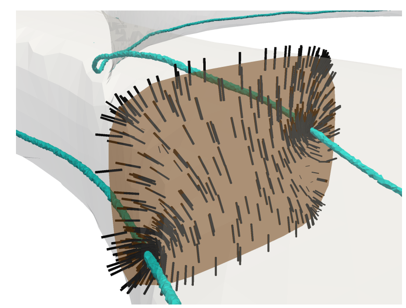


Tasinkevych, Campbell, Smalyukh, PNAS. **111**, 16268-16273 (2014)

Equilibrium structures in g=2 drops

Large drops:





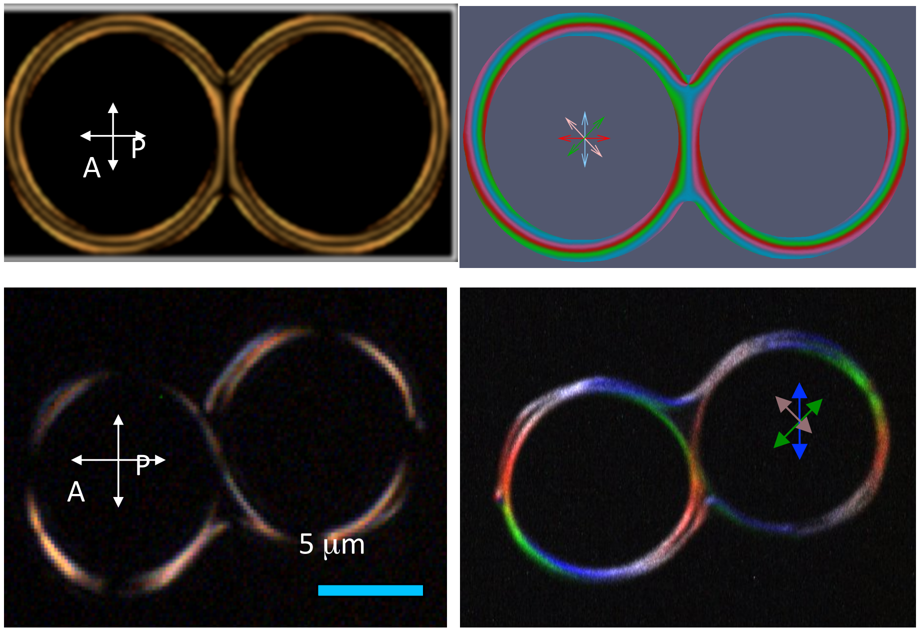
Small drops:

$$\sum_i m_i = \pm \chi / 2$$

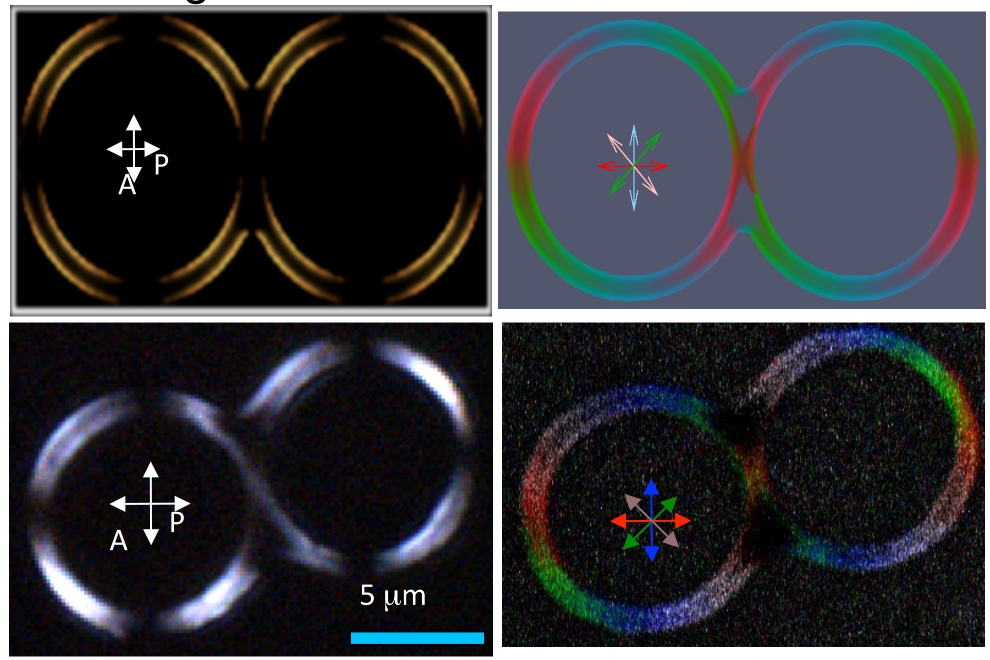
M. Tasinkevych, M. Campbell, I. Smalyukh, PNAS. 111, 16268-16273 (2014)

Imaging and Elastic Energy

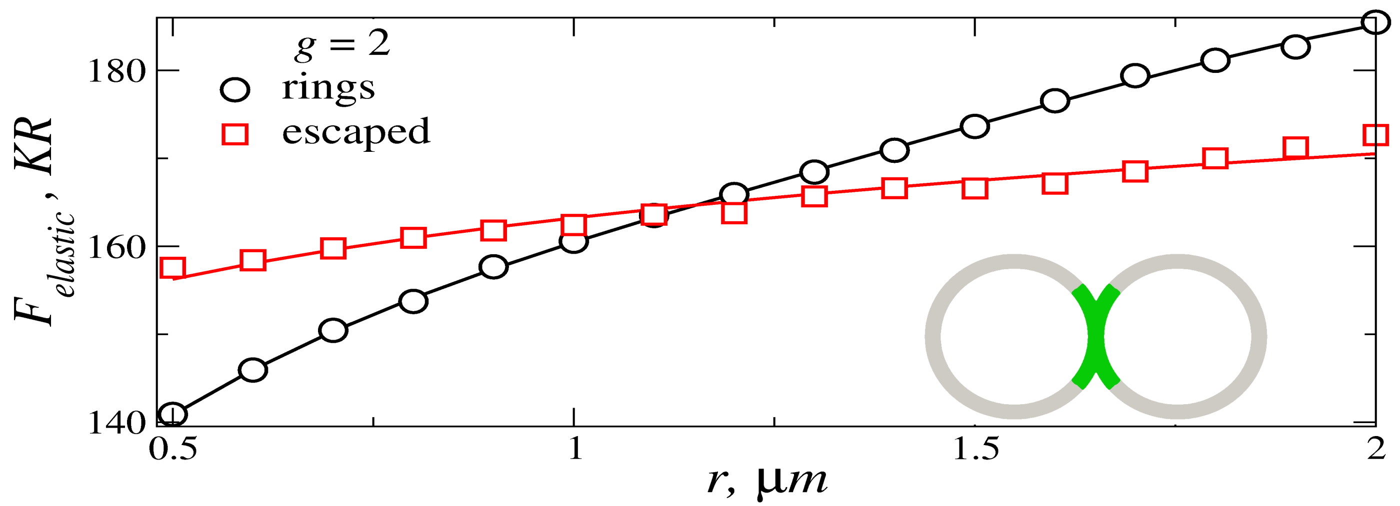
Escaped:



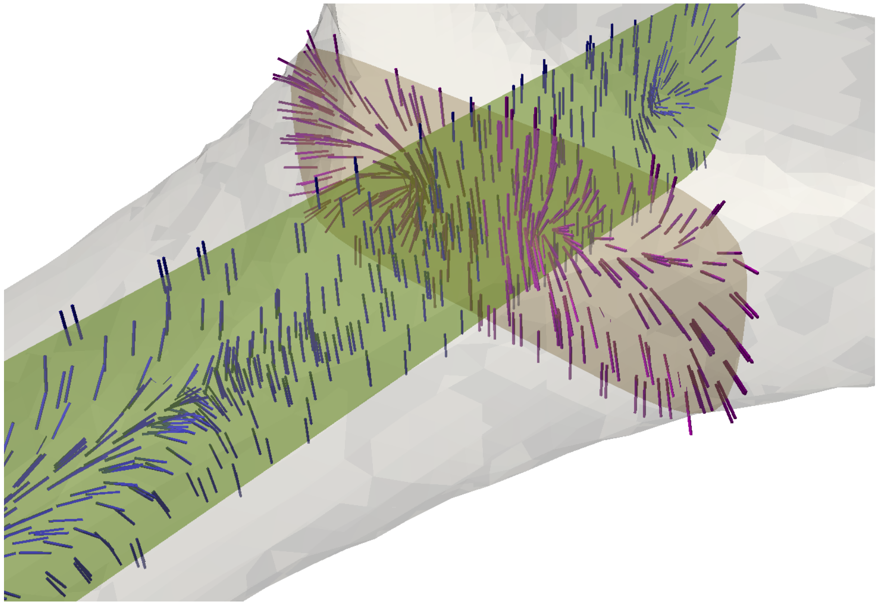
With singular defect lines:



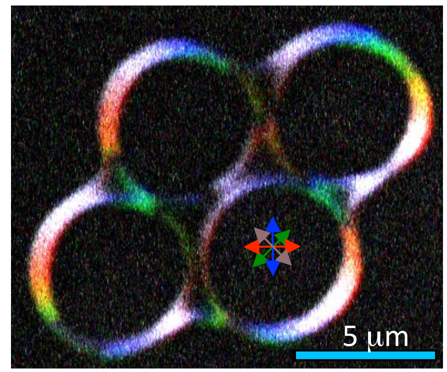
Free energy comparison:

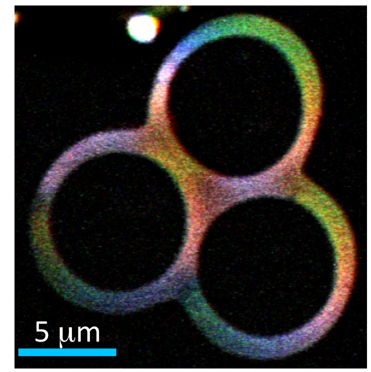


g=4,5 handlebody confinement with “escaped” director field

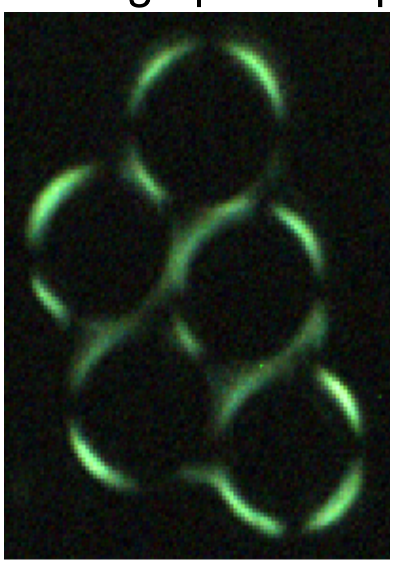


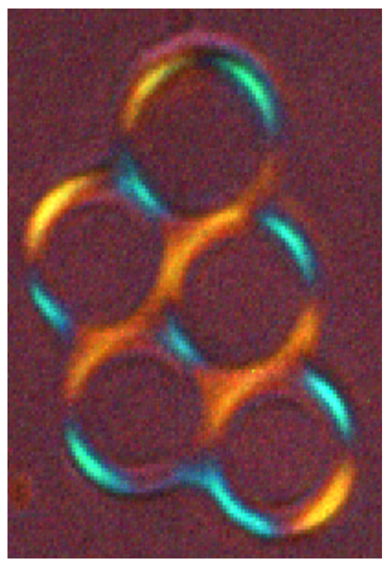
Nonlinear optical images:

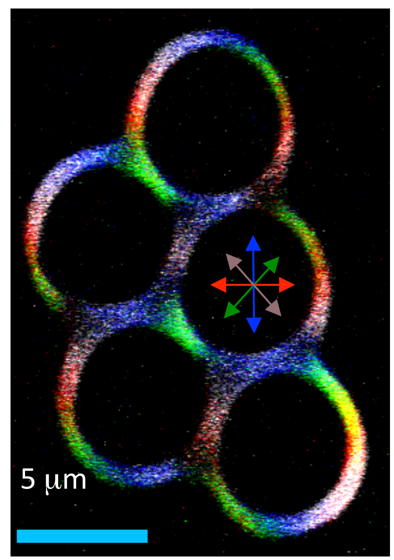




Polarizing optical m-py:

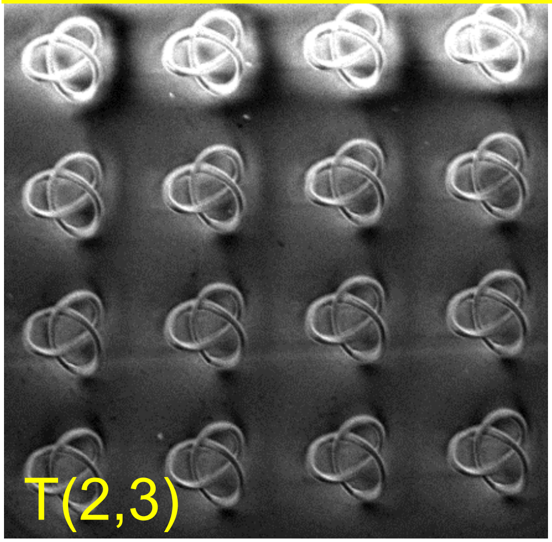


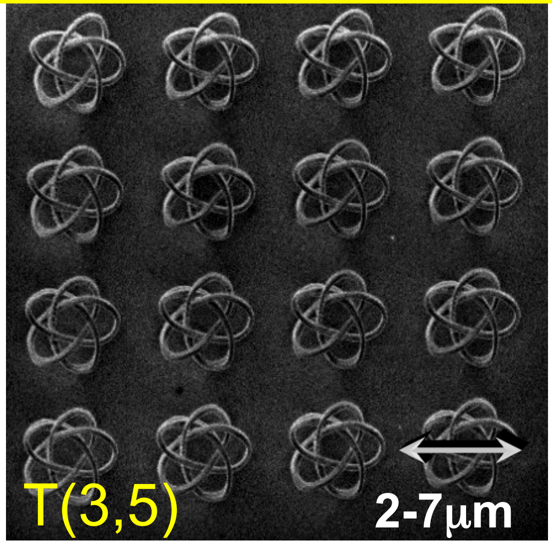


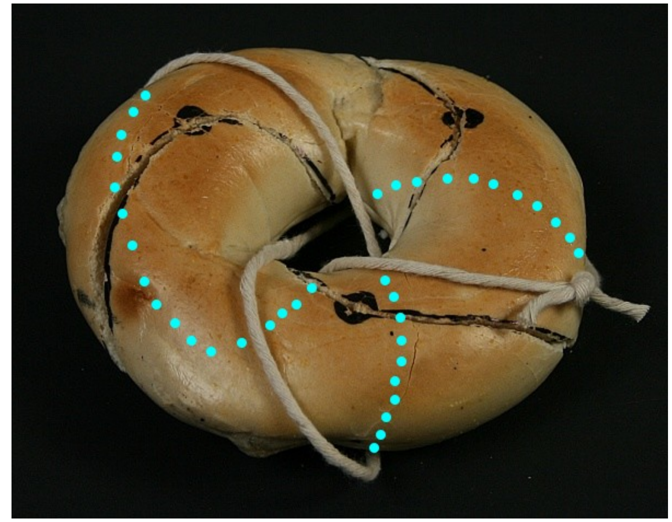


$$\sum_i m_i = \pm \chi / 2$$

Knot-shaped topological colloids (SEM)



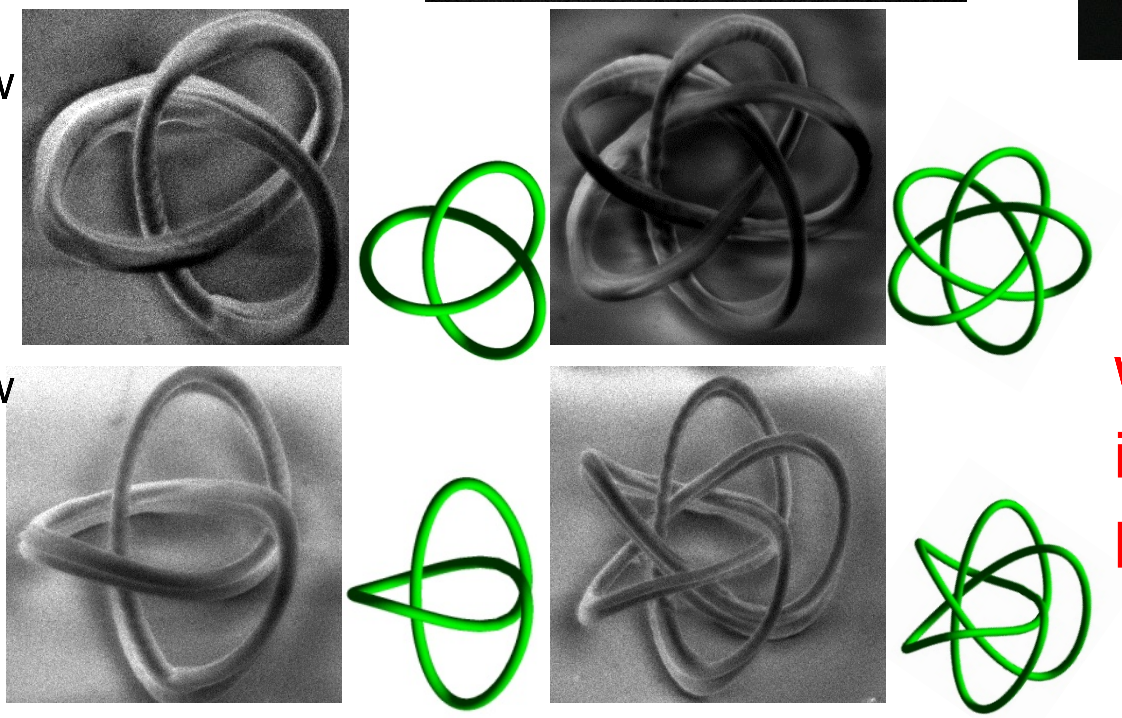




http://georgehart.com/bagel/knot.html

top view

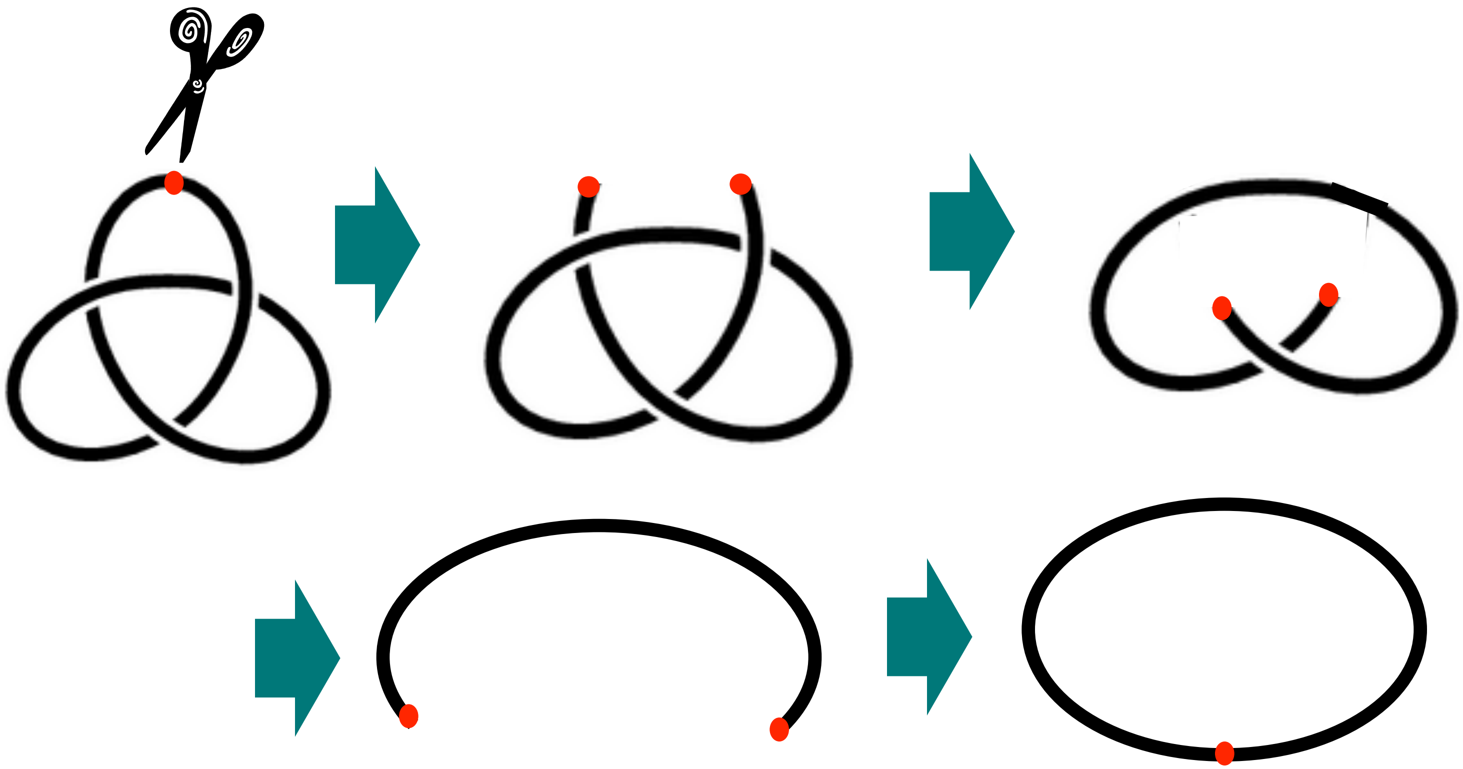
side view



What defects can be induced by knotted particles?

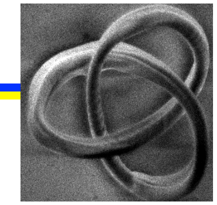
T(P,Q) knot winds Q times around a circle in interior of a torus & P times around its axis

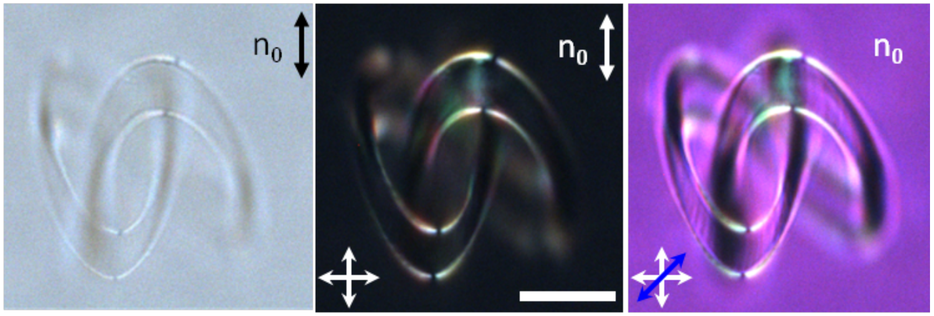
Euler characteristic of a torus knot



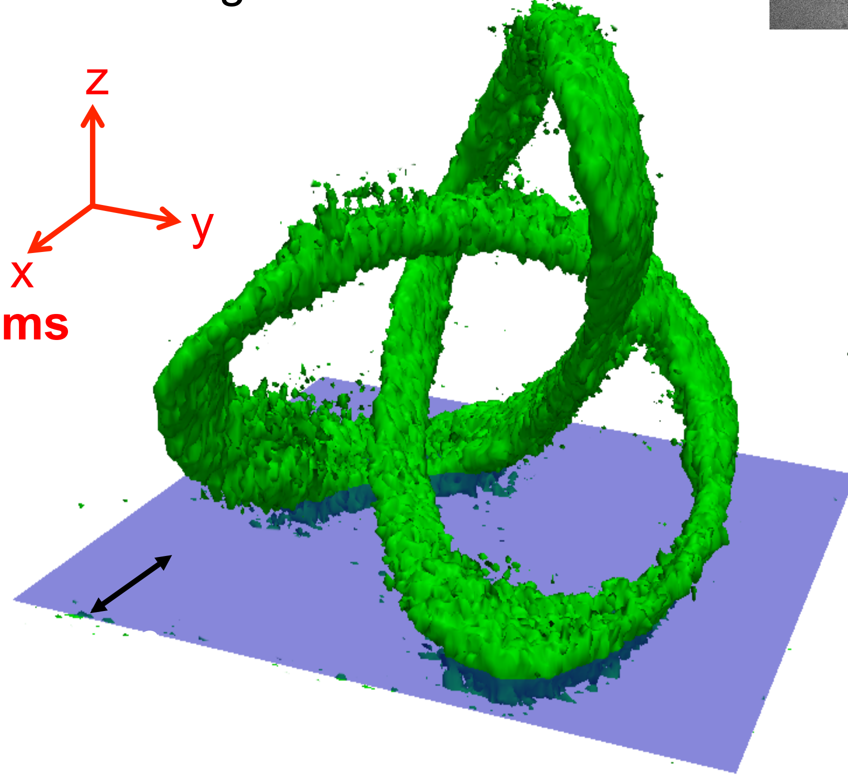
→Euler characteristic of torus knots is χ=0

Trefoil Colloidal-knot-induced defects

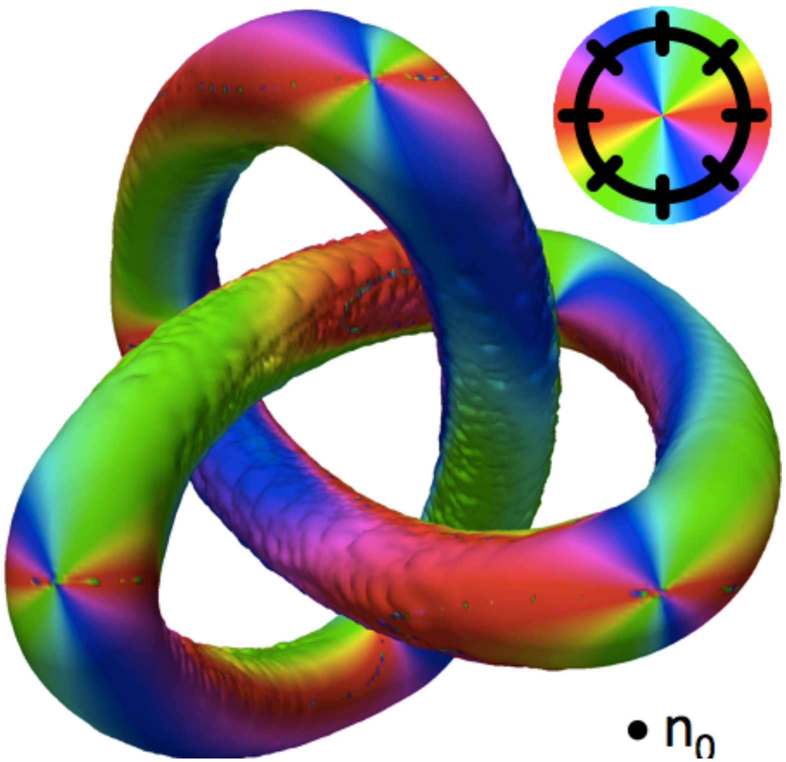




3D image of director structure



Knots induce 12 self-compensating boojums



→6 *s*=1 & 6 *s*=-1 boojums compensate each other

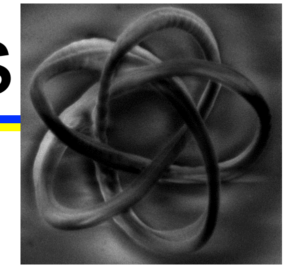
→ consistent with χ=0

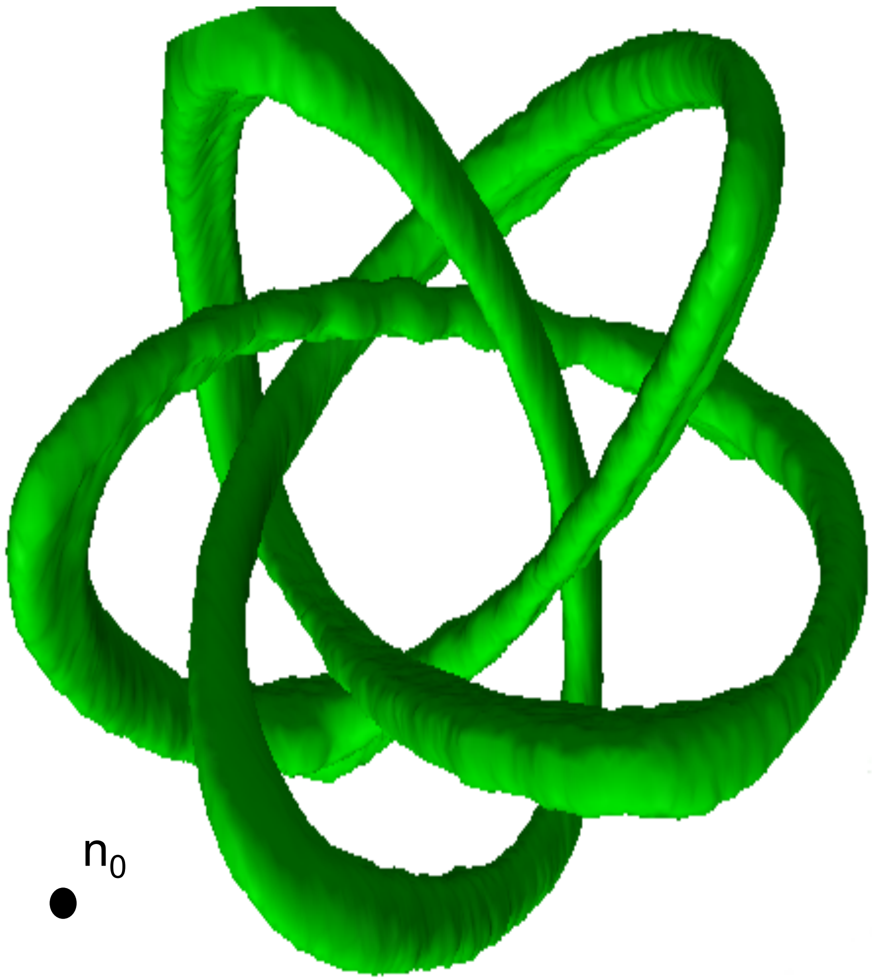
→T(p,q)=T(2,3)

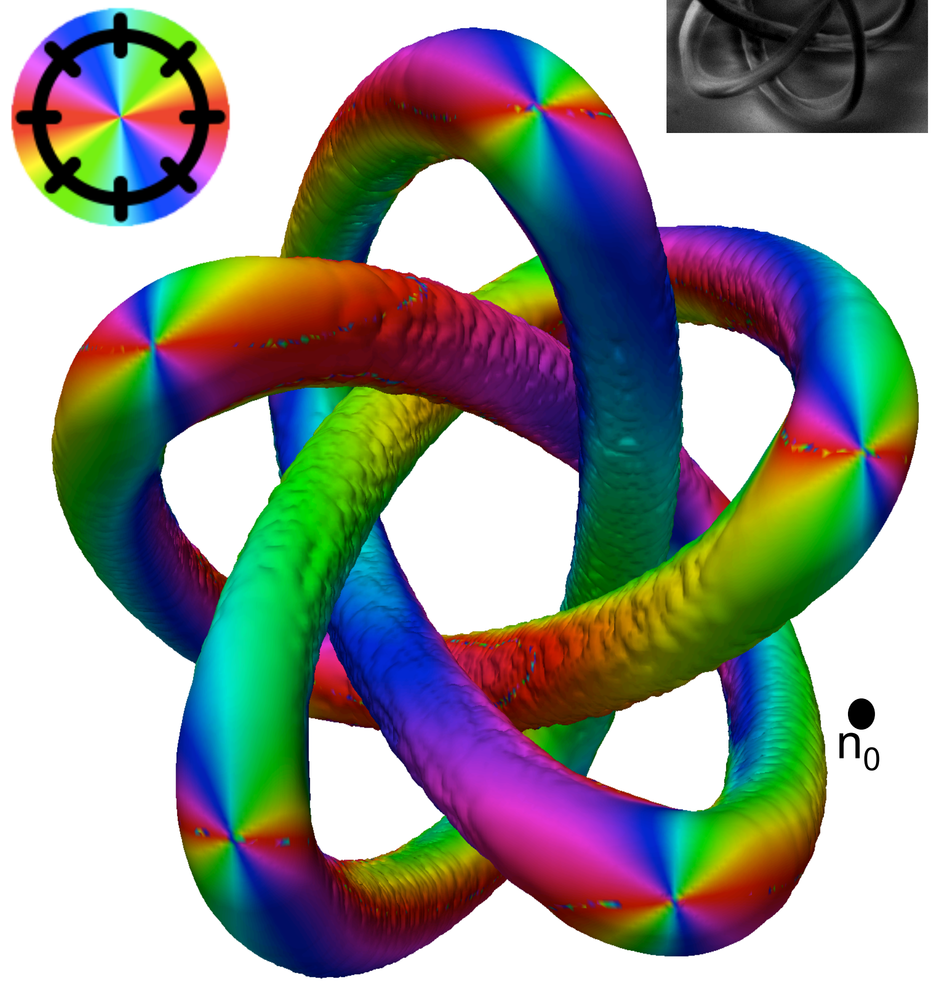
→The total number of boojums is 4q

A. Martinez, M. Ravnik, B. Lucero, R. Vishvanathan, S. Zumer, & I.I. Smalyukh, *Nature Mater* (2014)

T(3,5) colloidal-knot-induced defects







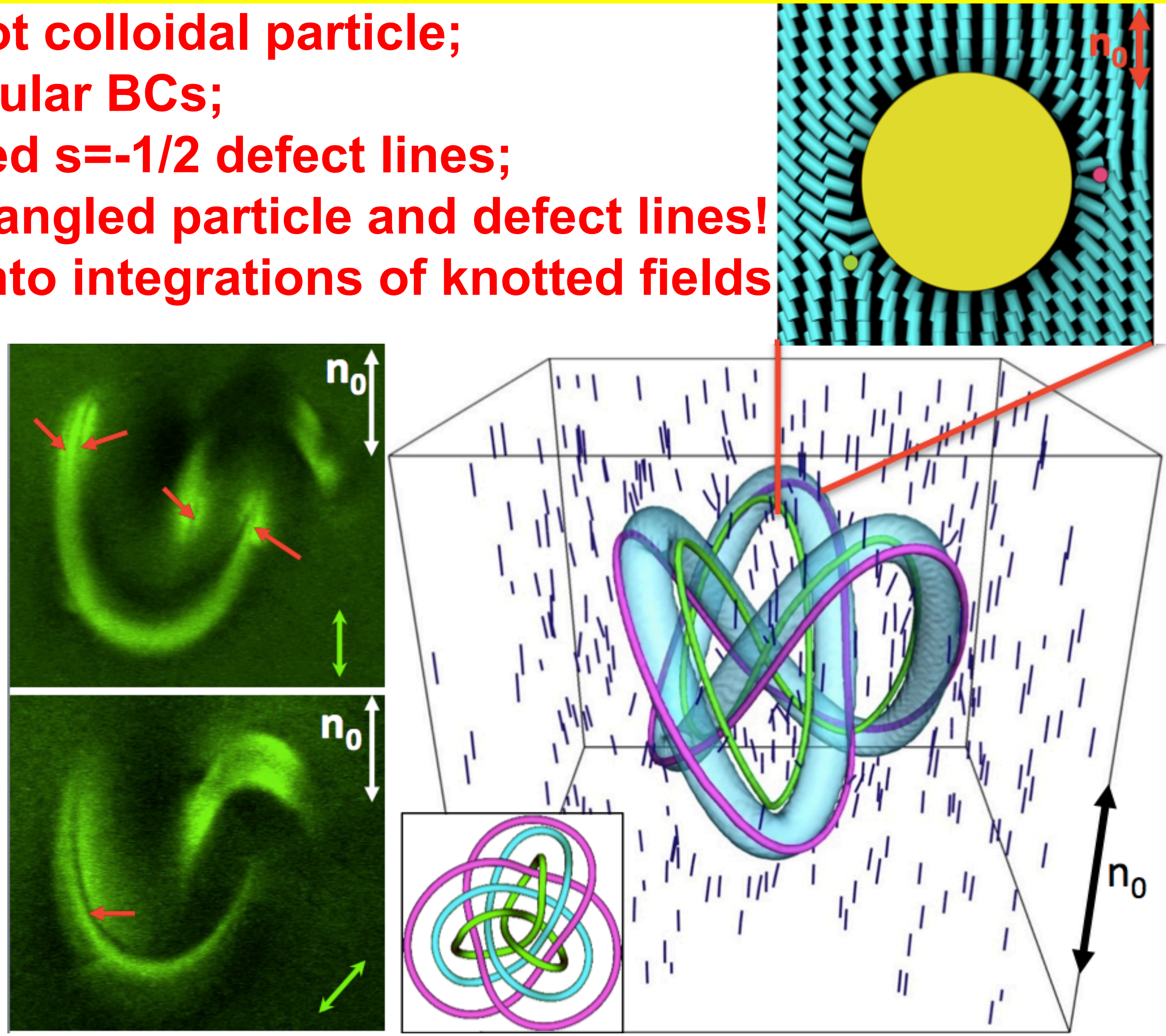
→10 *s*=1 & 10 *s*=-1 boojums compensate each other

→ consistent with χ=0

→The total number of boojums is 4q again

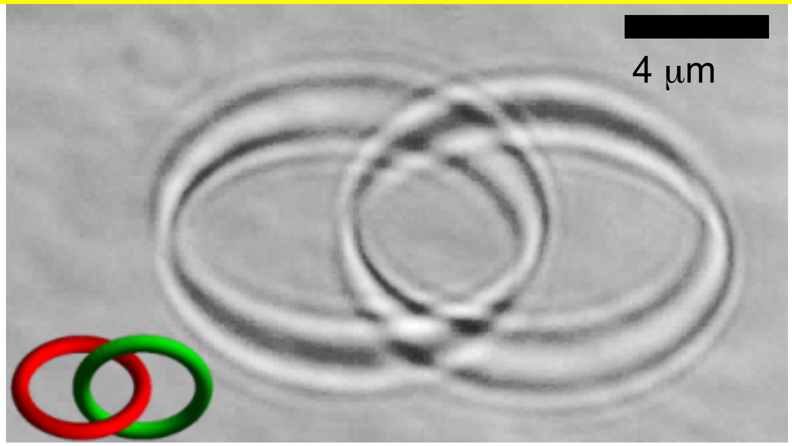
Mutually tangled particle knots & director field

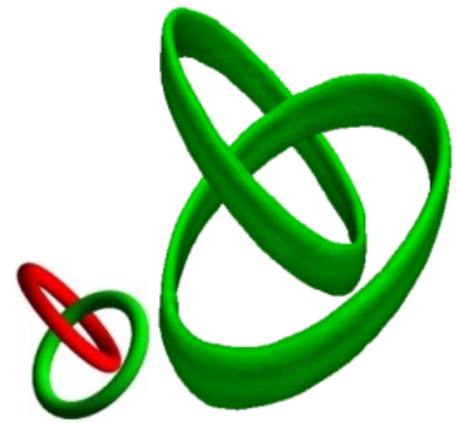
→Trefoil knot colloidal particle;
→perpendicular BCs;
→two knotted s=-1/2 defect lines;
→Mutually tangled particle and defect lines!
→Insights into integrations of knotted fields & surfaces



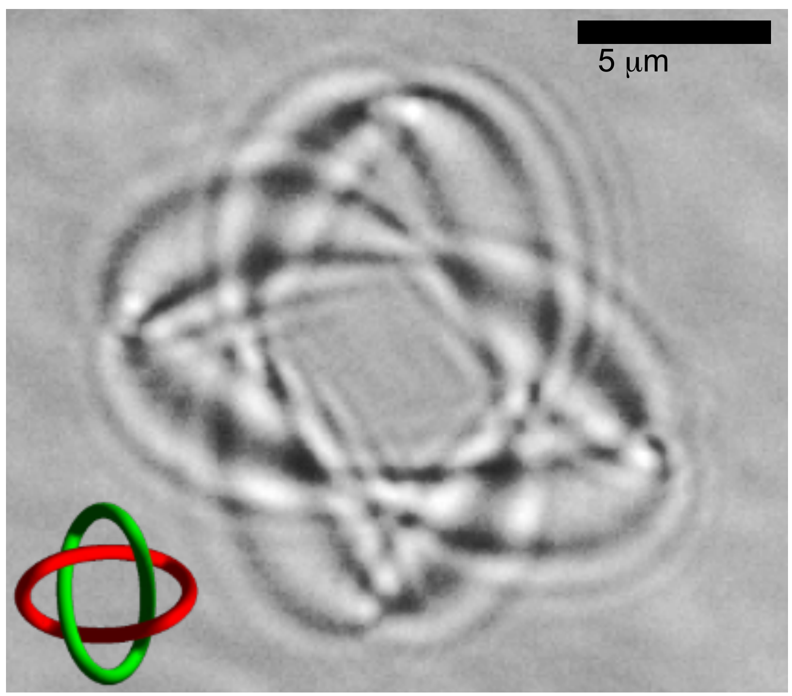
Multi-component particles lacking surface connectivity: colloidal links

Hopf Links





Solomon Links



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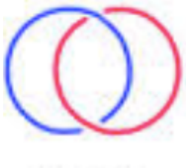
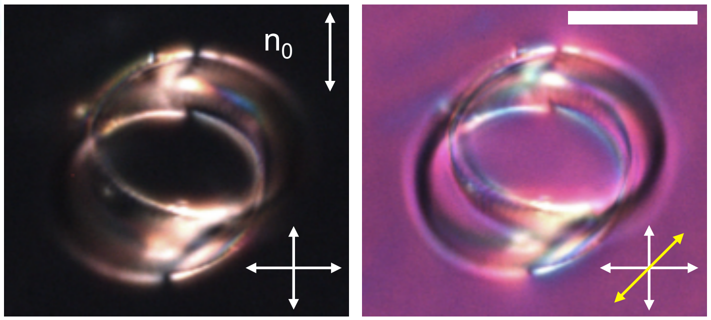
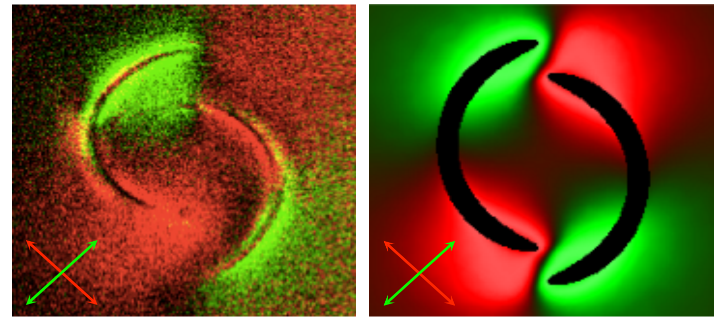
Colloidal Hopf Links with tangential BCs



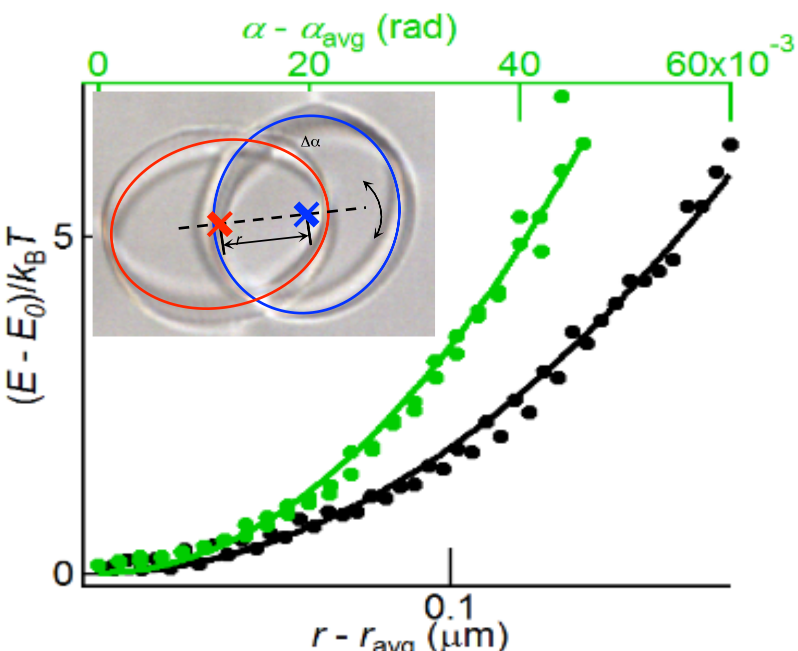
Polarizing optical microscopy

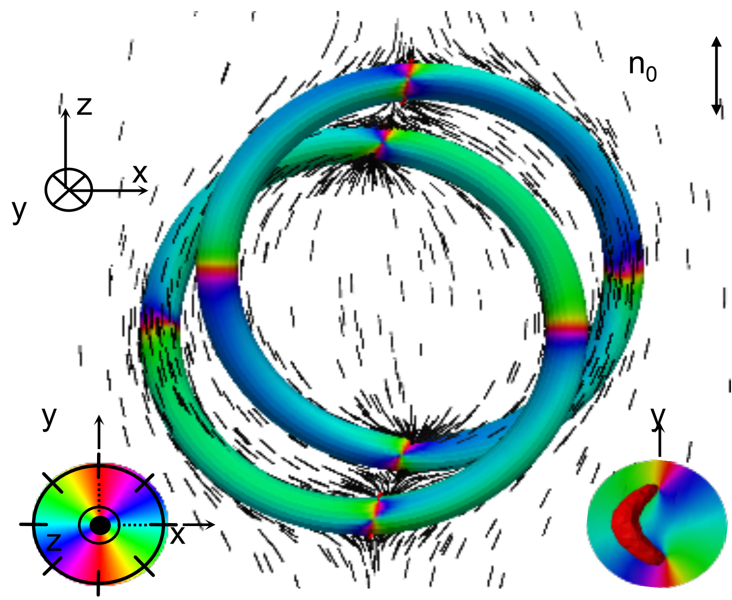


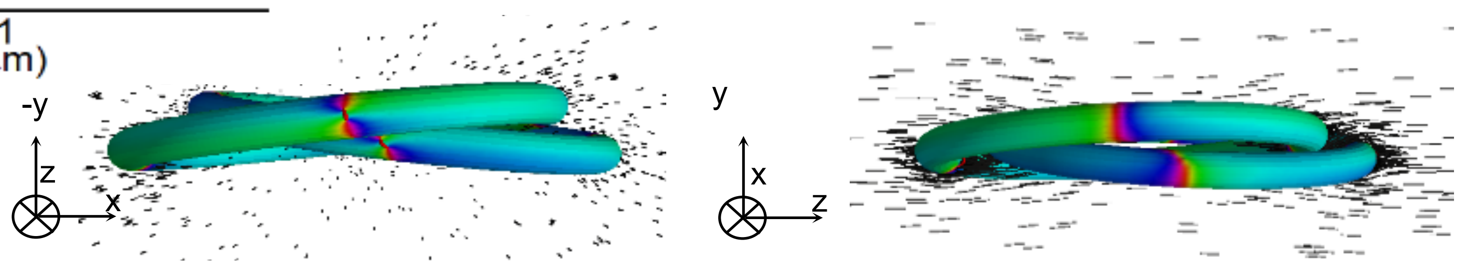
Nonlinear depth-resolved optical microscopy



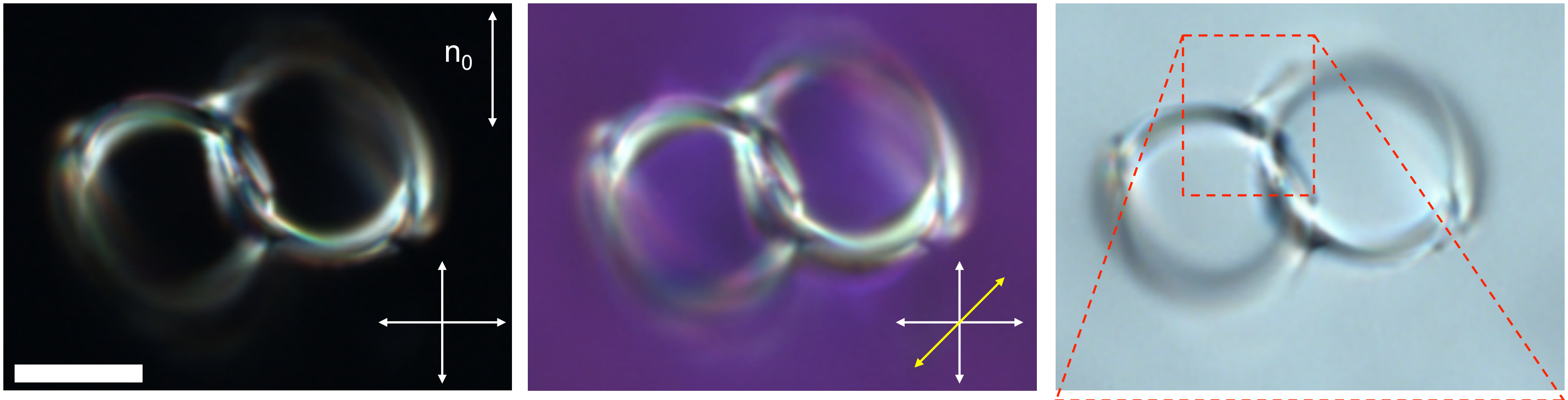
Rotational & translational elastic coupling:

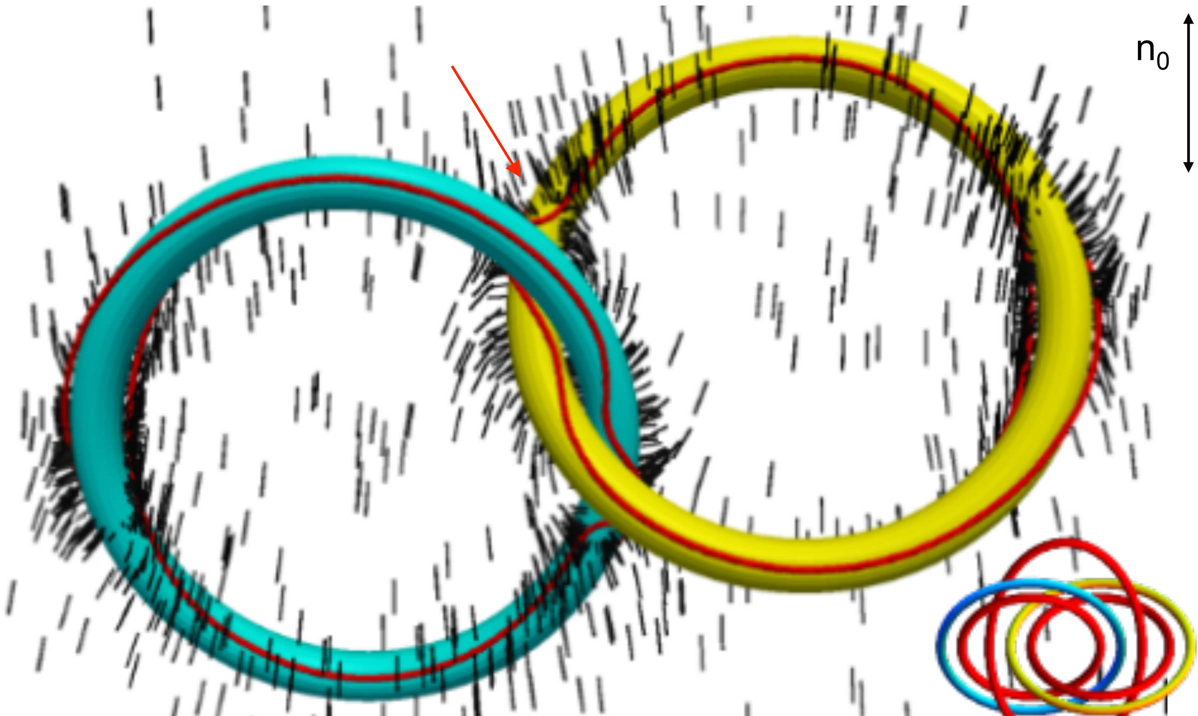


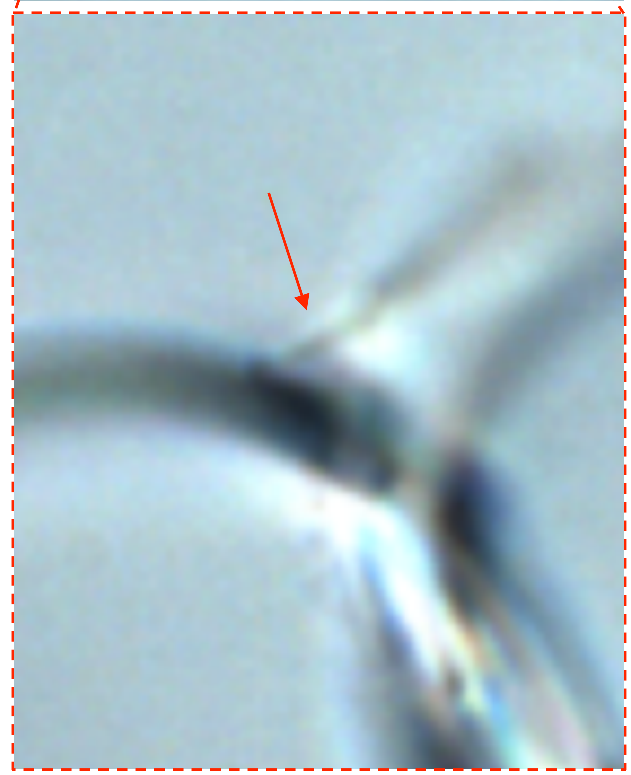




Colloidal Hopf Links with perpendicular BCs

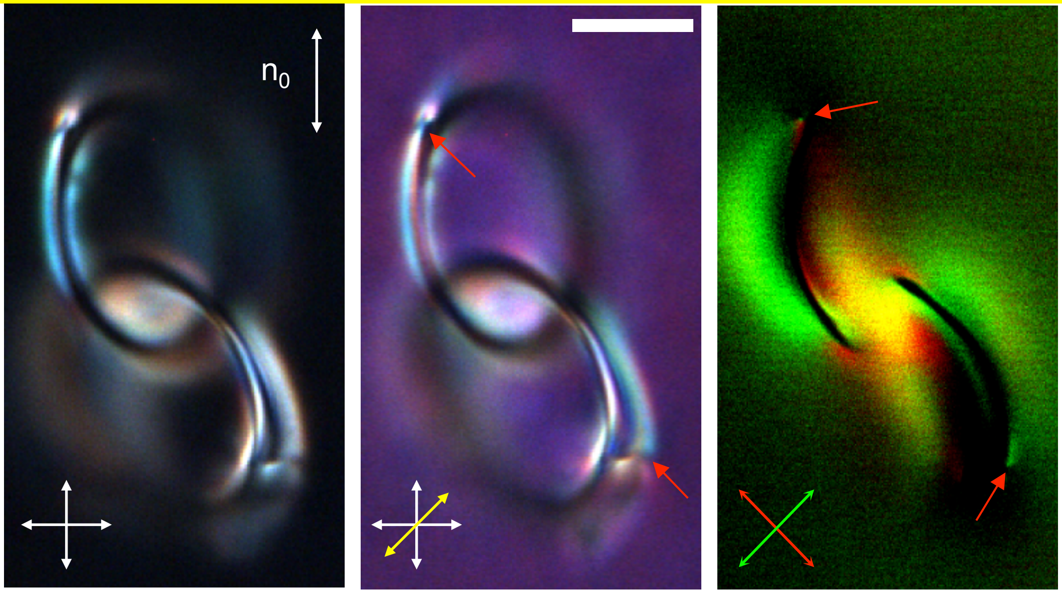




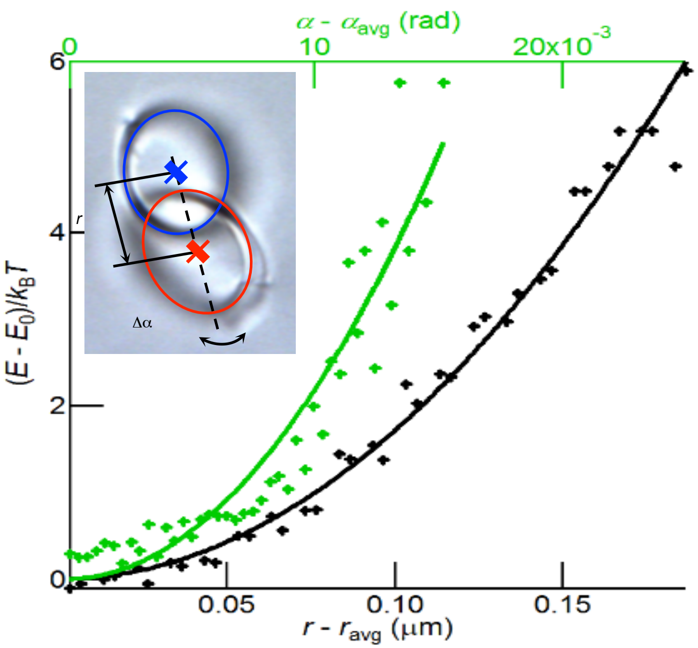


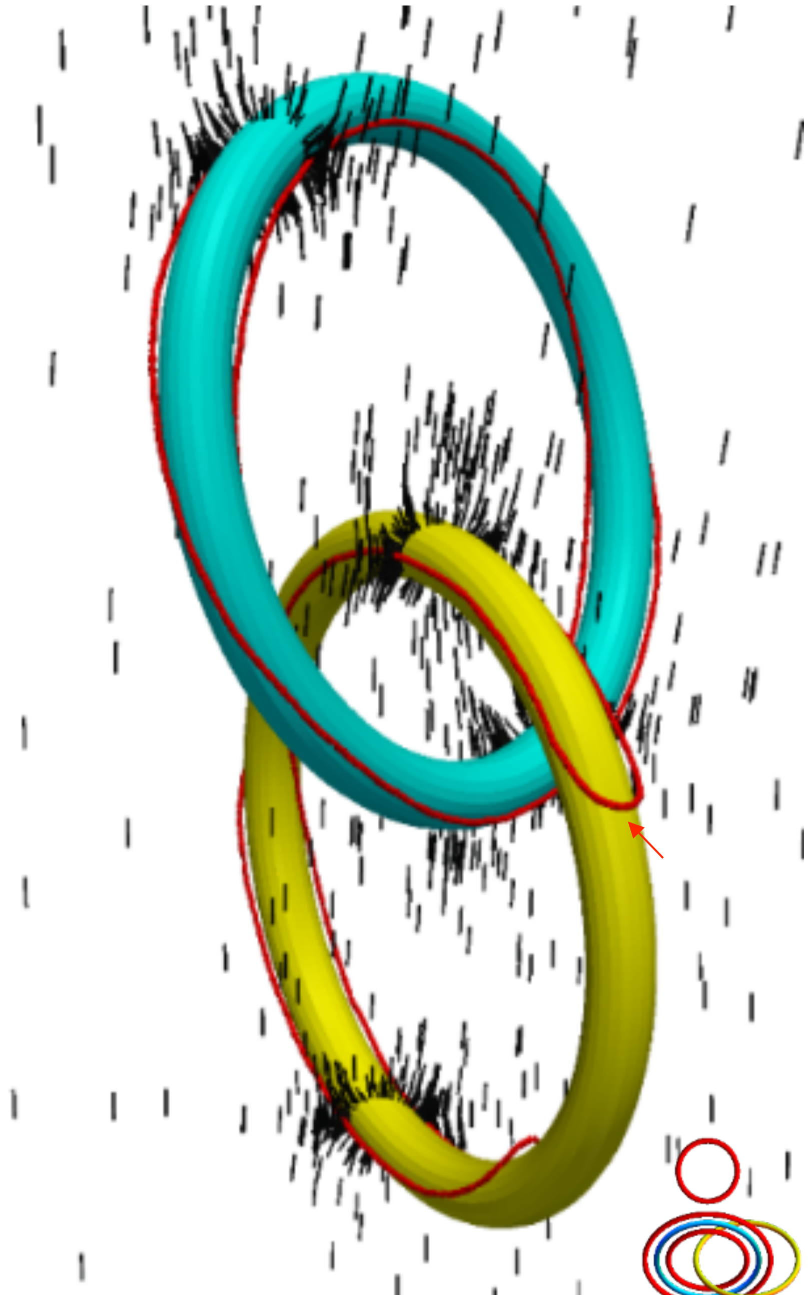
disclination “jumping” to the other particle

Metastable Hopf links with perpendicular BCs

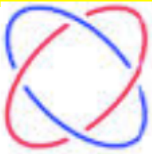


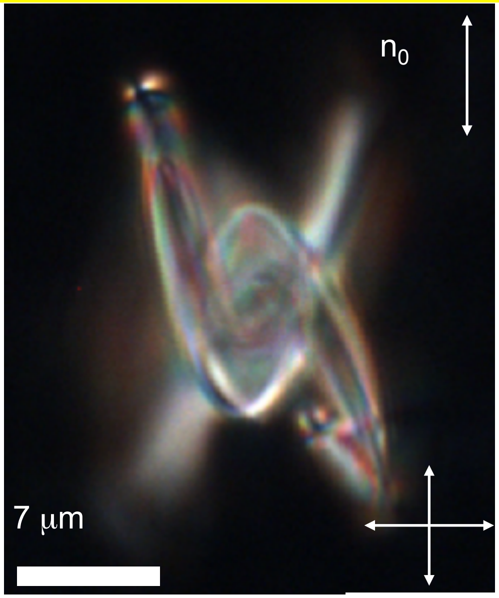
Rotational & translational elastic coupling:

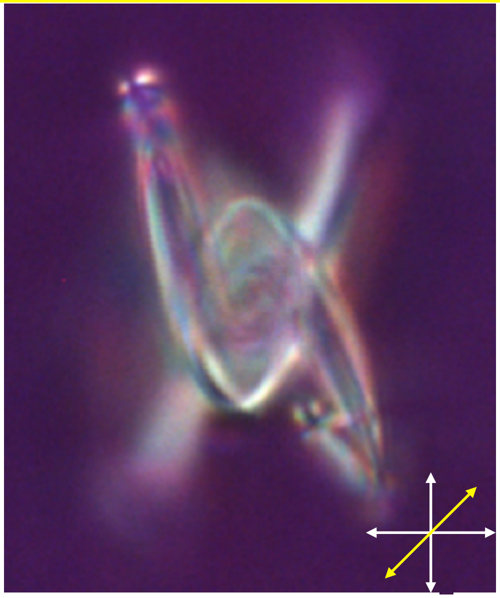


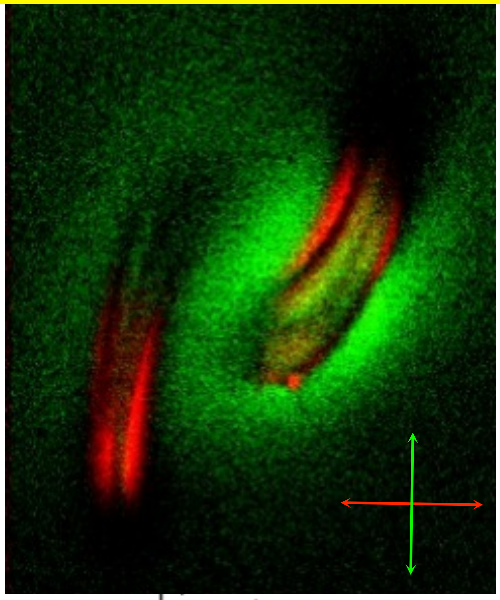


Colloidal Solomon links with homeotropic BCs

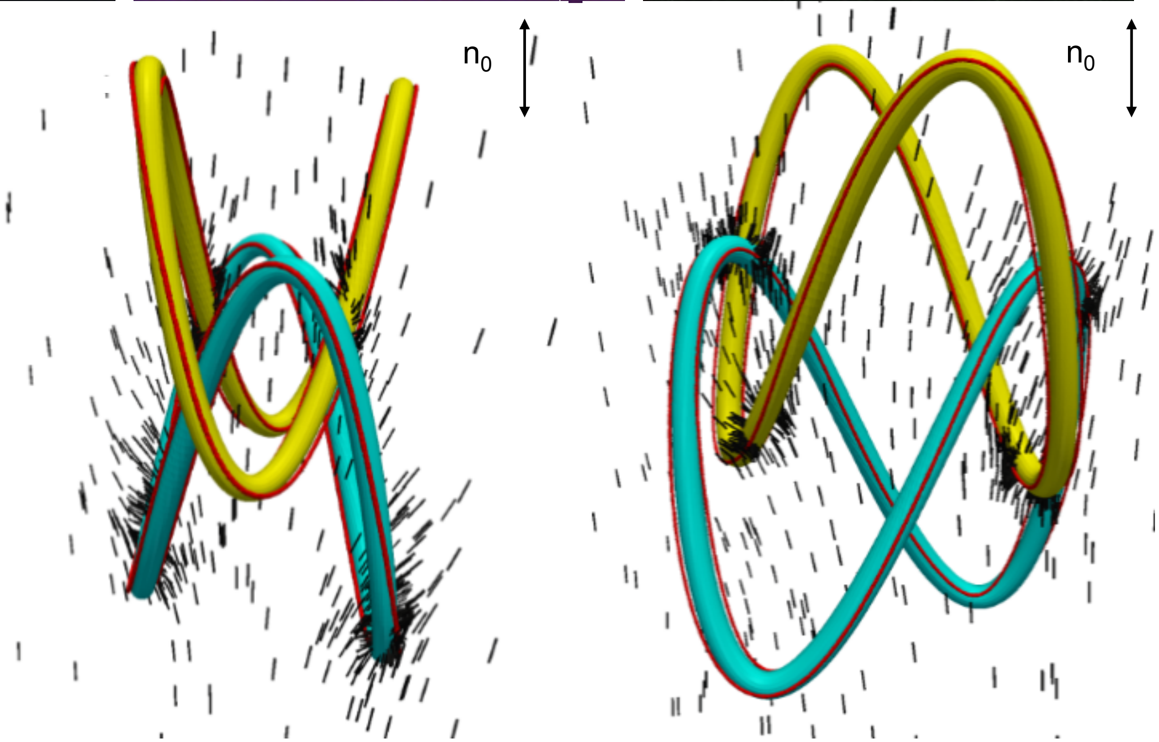




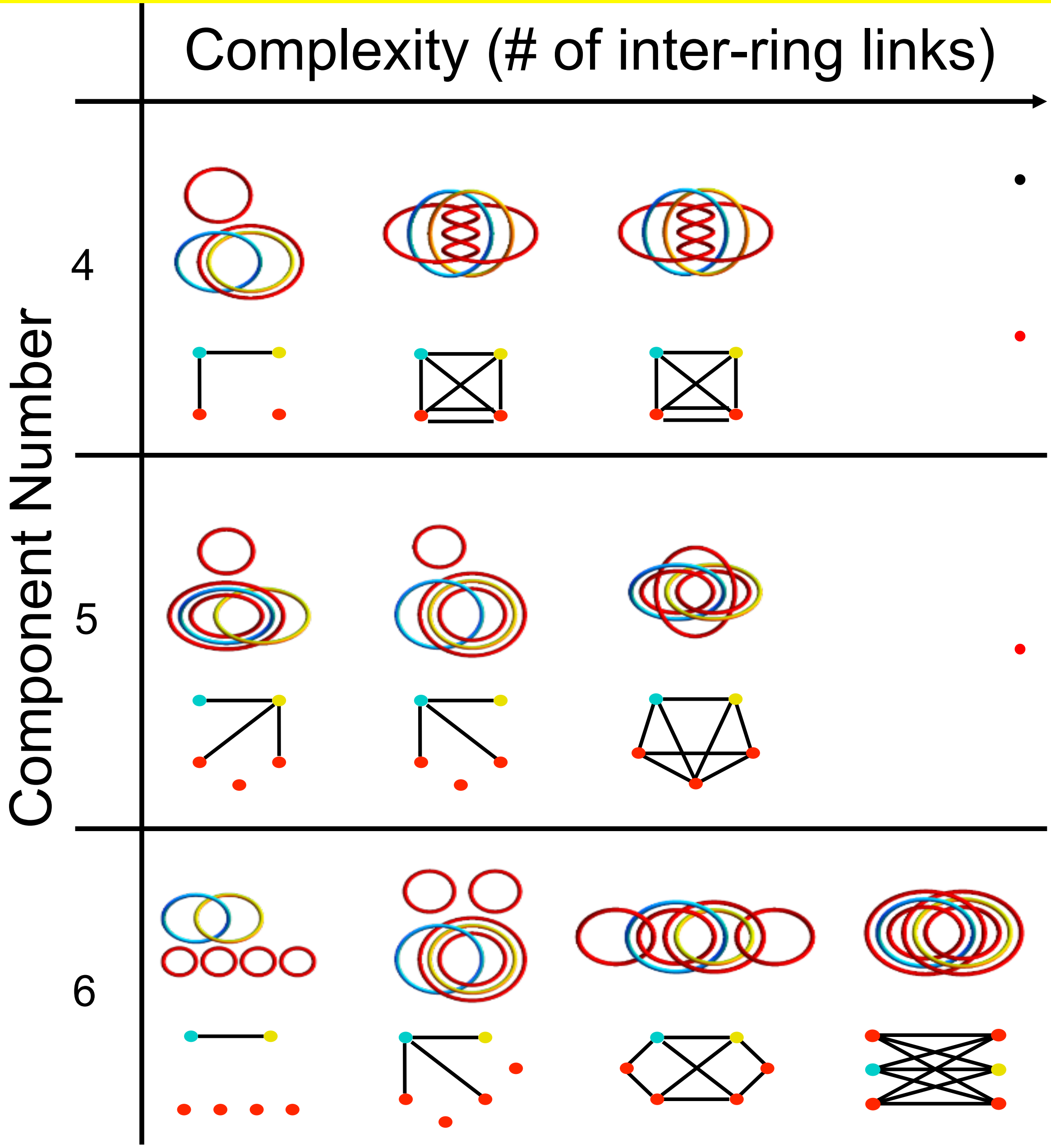




Half-integer line defects follow the particle's tubes



Summary: graph presentations of links



Homeotropic BCs:

- colloidal Hopf links accompanied by 2 or more defect rings
- Nonpolar nature provides many ways of satisfying topological constraints of topological interaction between fields, defects & surfaces
- Could not be realized in vector fields!

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Conclusions

→**Soft Matter provides an experimental toolkit of exploring topology;**

→**Interplay of line field and surface topologies – much more is left to be explored**

→**Topology – the basis for controlling self-assembly (can use defect linking as means of self-assembly!)**

→**Inter-linking of defect loops brings around defect structures distinct from classic results for vector fields!**

→**Probing topological interplay through the survey of local and global minimizers of states in LC colloids**

Thank you!