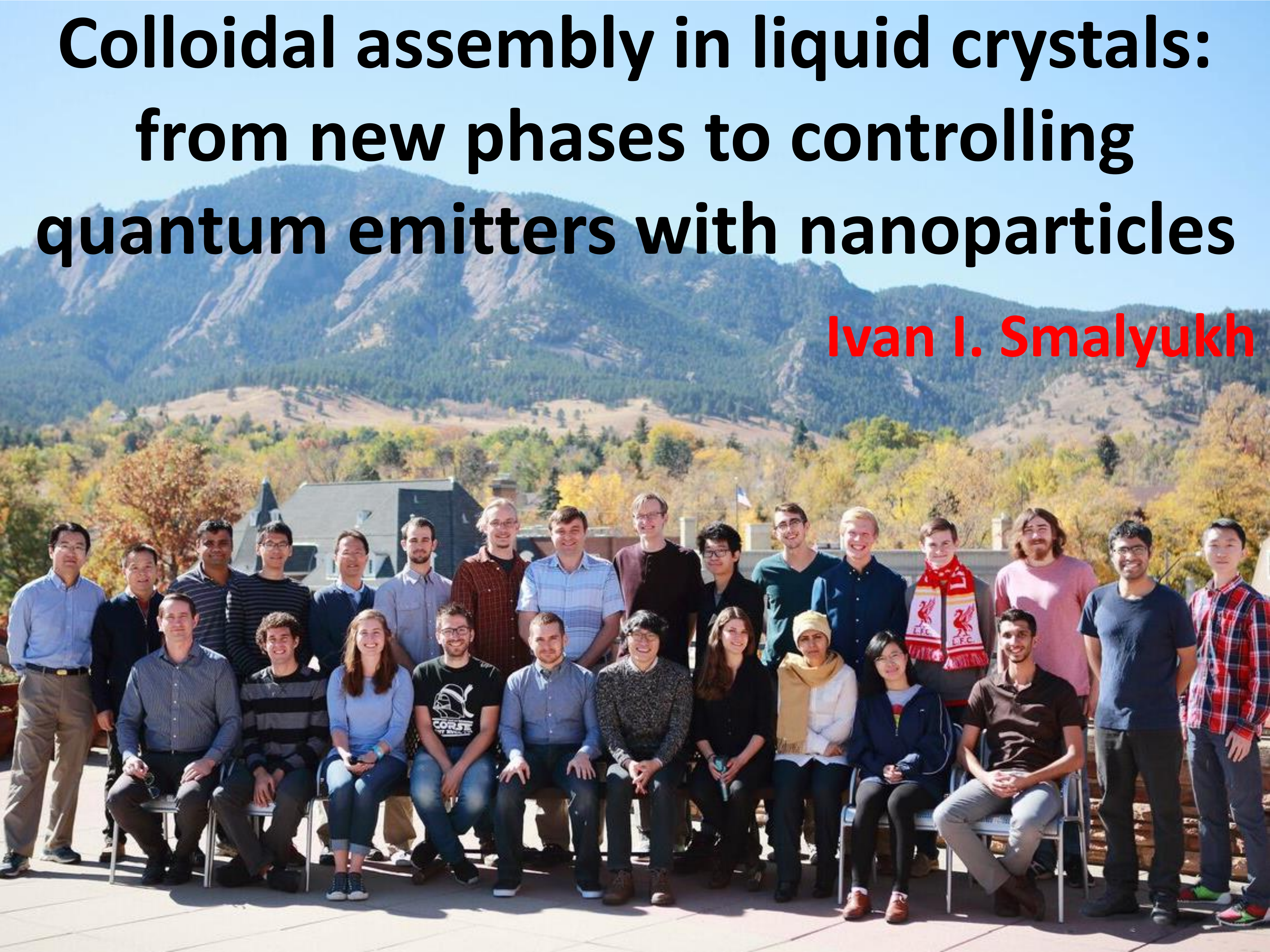
Colloidal assembly in liquid crystals: from new phases to controlling quantum emitters with nanoparticles



Ivan I. Smalyukh

From Einstein to new pre-designed materials

→1905 PhD: from Brownian motion to existence/size of atoms
→Colloidal atom/molecule paradigm & nanoparticle assembly
→Material from nanoparticles & property engineering
→Mimic and **exceed** what is known for natural systems

Albert Einstein
in 1904, age 25

→Buildings consume 40% of all generated energy
→20% of building energy wasted due to windows
→Super-insulation with transparent aerogels
→Fabricated from colloidal nanofibers

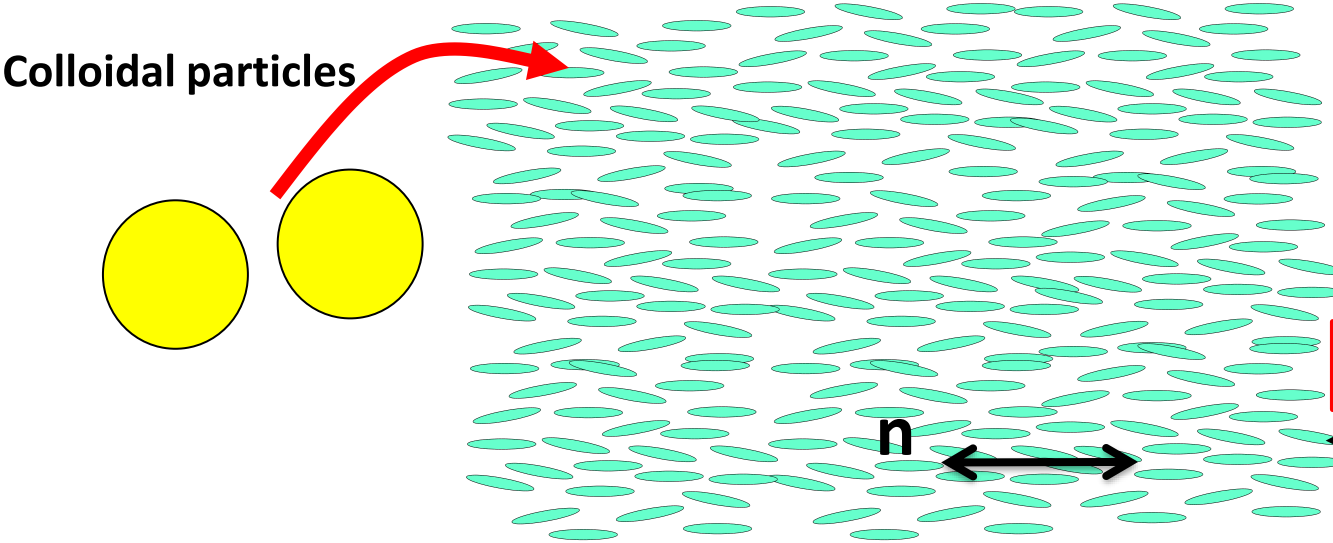
www.nature.com/naturexxxxxxx/Month 20XX Vol.XX No.X

nature energy

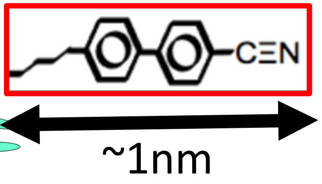
Image 03: Smalyukh

Abraham, Cherpak, Senyuk, Lee, Liu & Smalyukh. *Nature Energy* (2023)

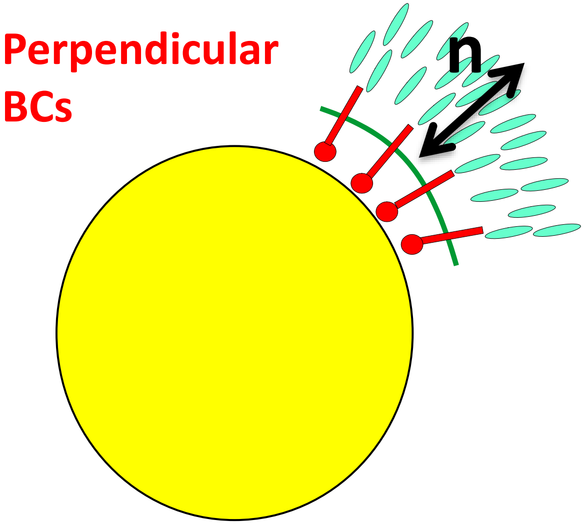
Colloidal particles in nematic liquid crystals

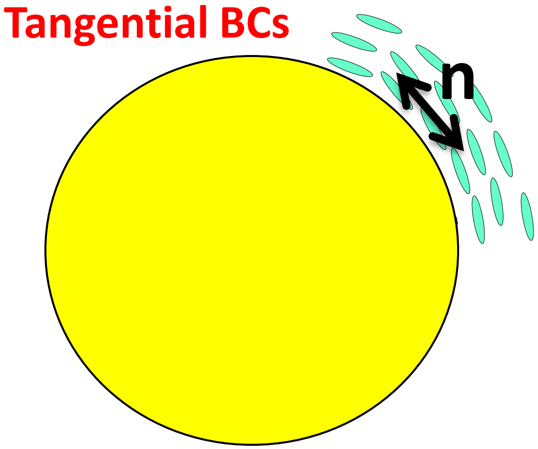


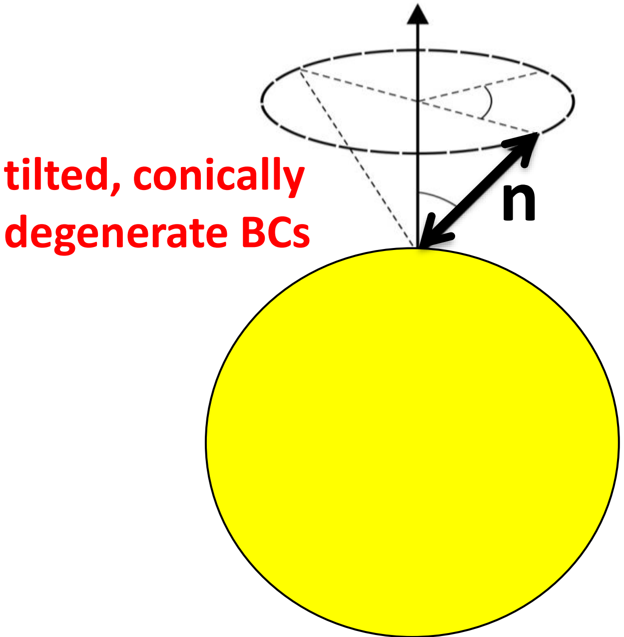
Liquid crystal:
→Flows like liquid
→Anisotropic



Define boundary conditions (BCs)


Perpendicular BCs

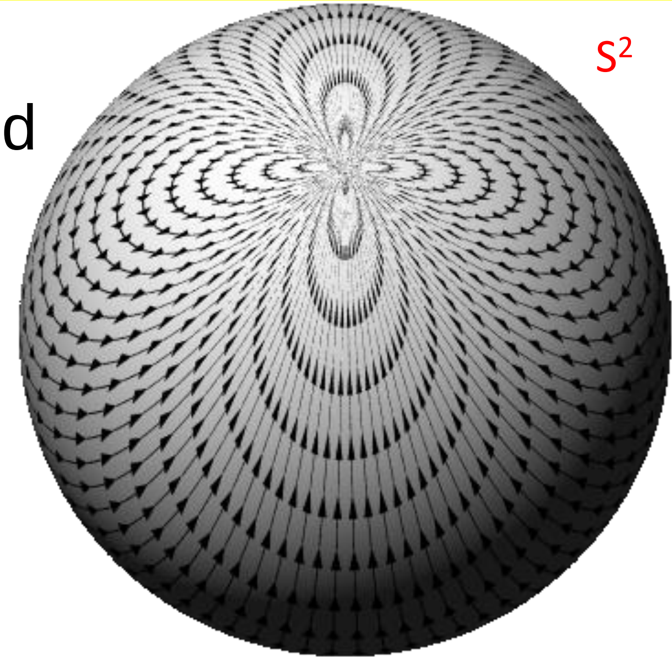

Tangential BCs


tilted, conically degenerate BCs

Interaction of topology of colloidal surfaces & nonpolar director fields?

Hairy Ball & Poincare-Hopf theorems

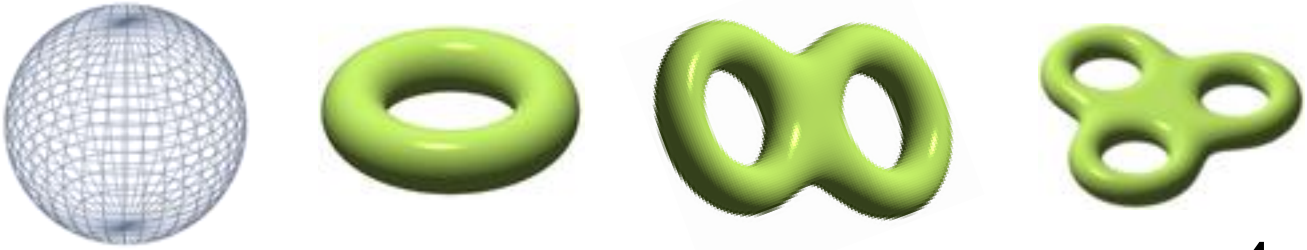
Hairy Ball Theorem: there is no nonvanishing continuous tangent vector field on even dimensional S^n-spheres (e.g. S^2)



Poincare-Hopf theorem: indices (winding numbers) of defects in the vector field add to the Euler characteristic: $c = 2 - 2g$

http://en.wikipedia.org

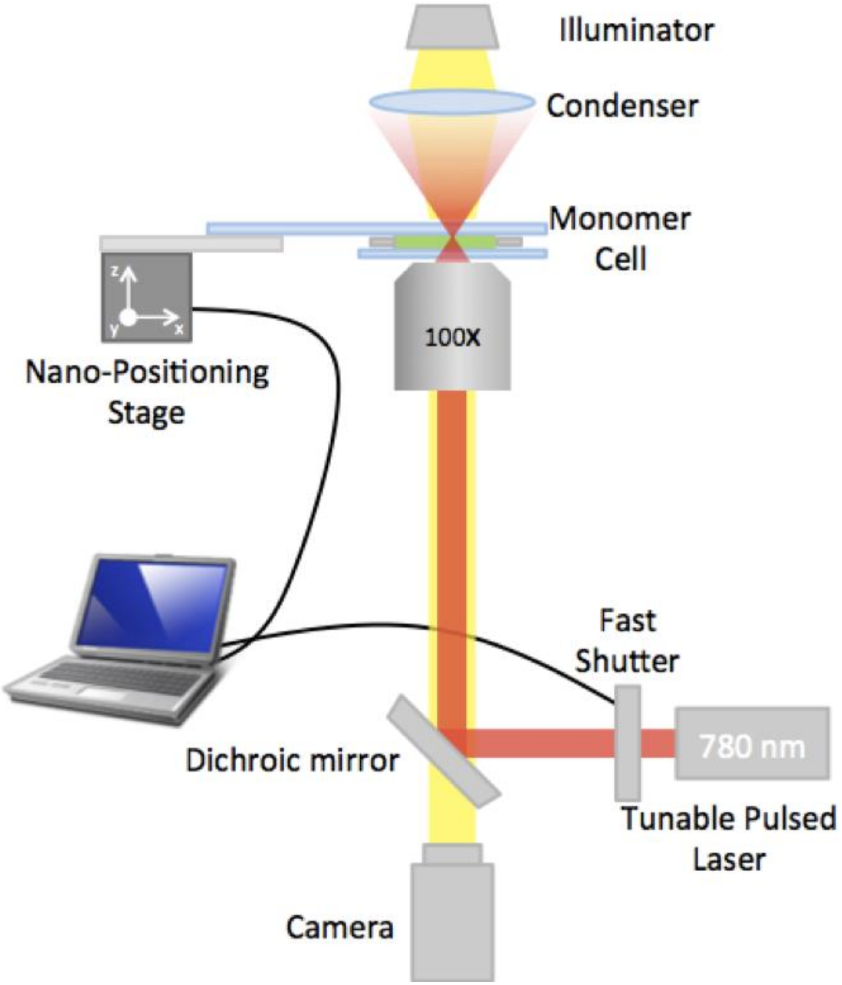
$g = 0$ $g = 1$ $g = 2$ $g = 3$

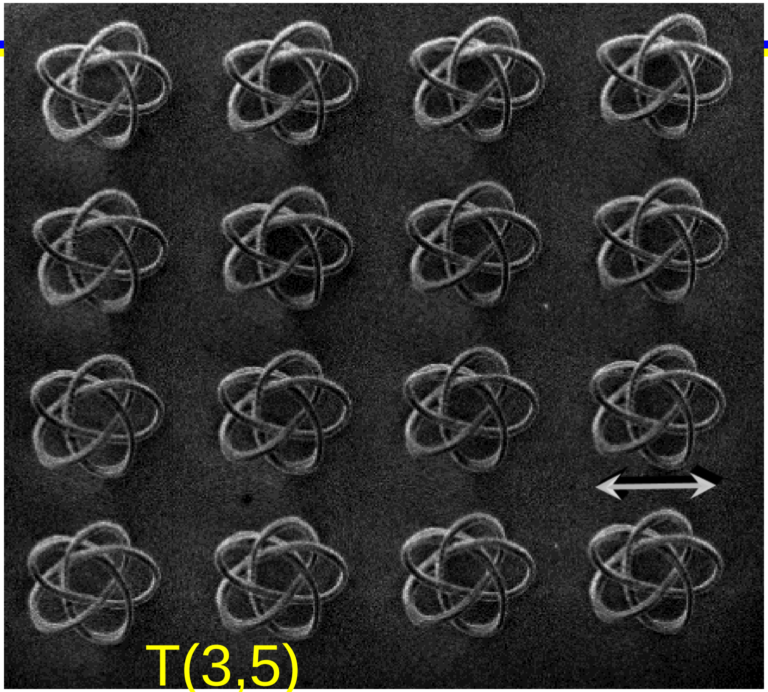


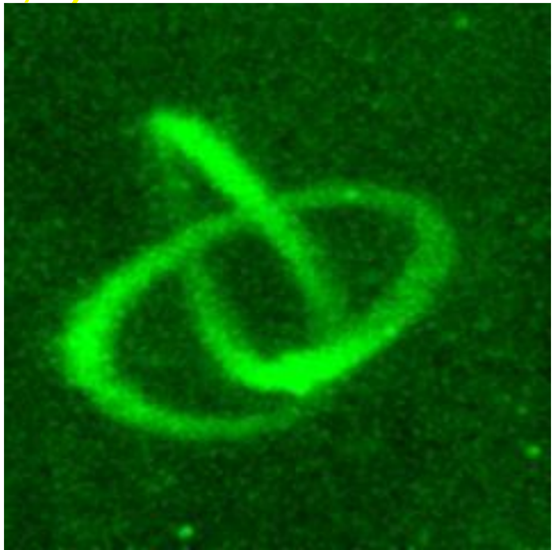
. . .

$c = 2$ $c = 0$ $c = -2$ $c = -4$

Colloidal particles fabricated by two-photon polymerization







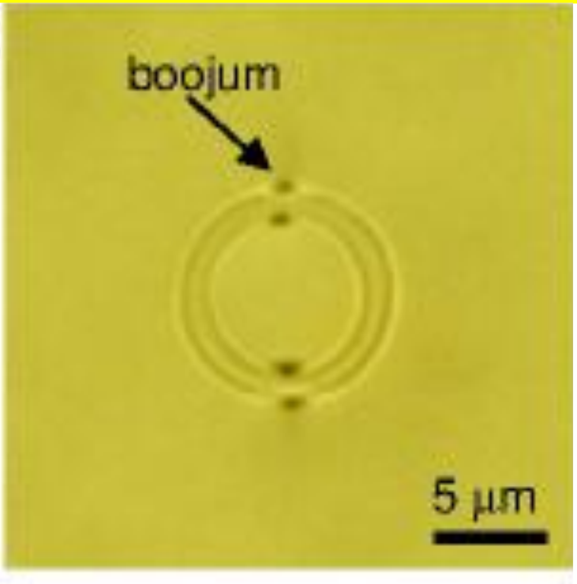
A. Martinez, T. Lee, I.I. Smalyukh, *Soft Matter* ***7****, 11154-11159*

B. Senyuk, I. I. Smalyukh. *Nature Comm* **6**, 7157

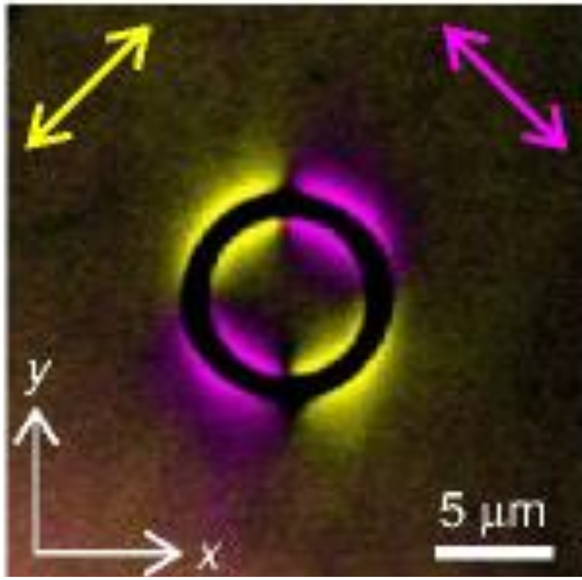
Surface boojums on colloidal rings

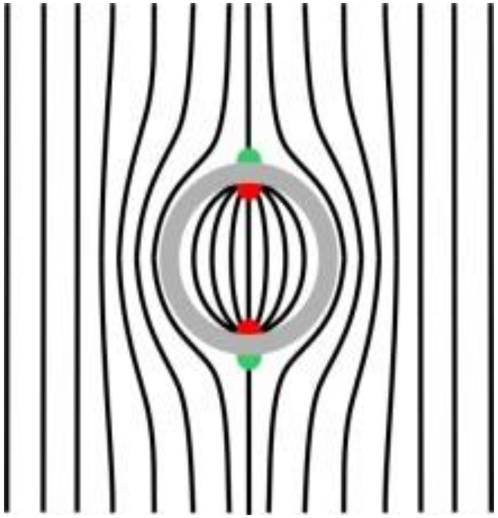
Optical microscopy

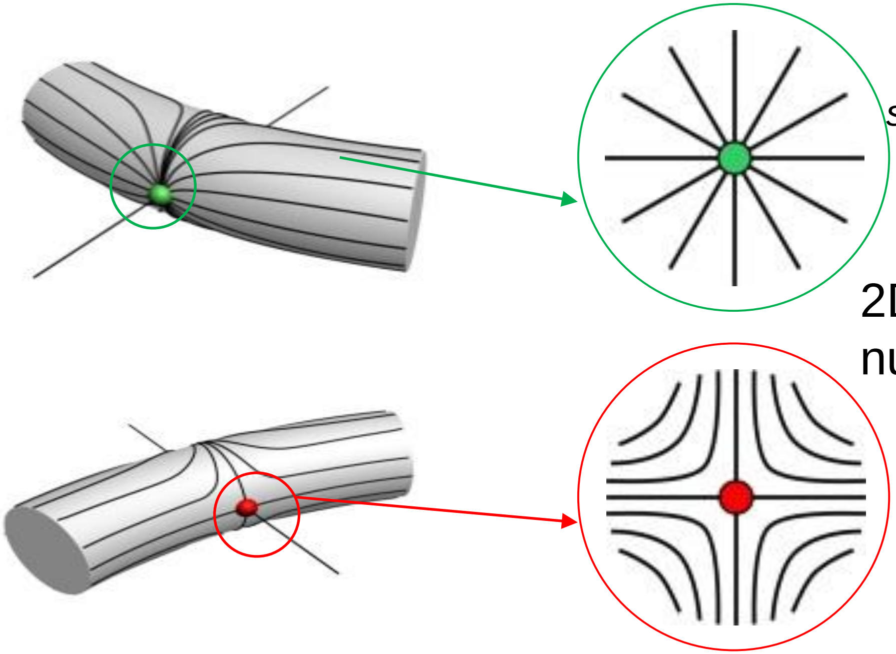
-2+2=0



Nonlinear optical imaging







s = +1

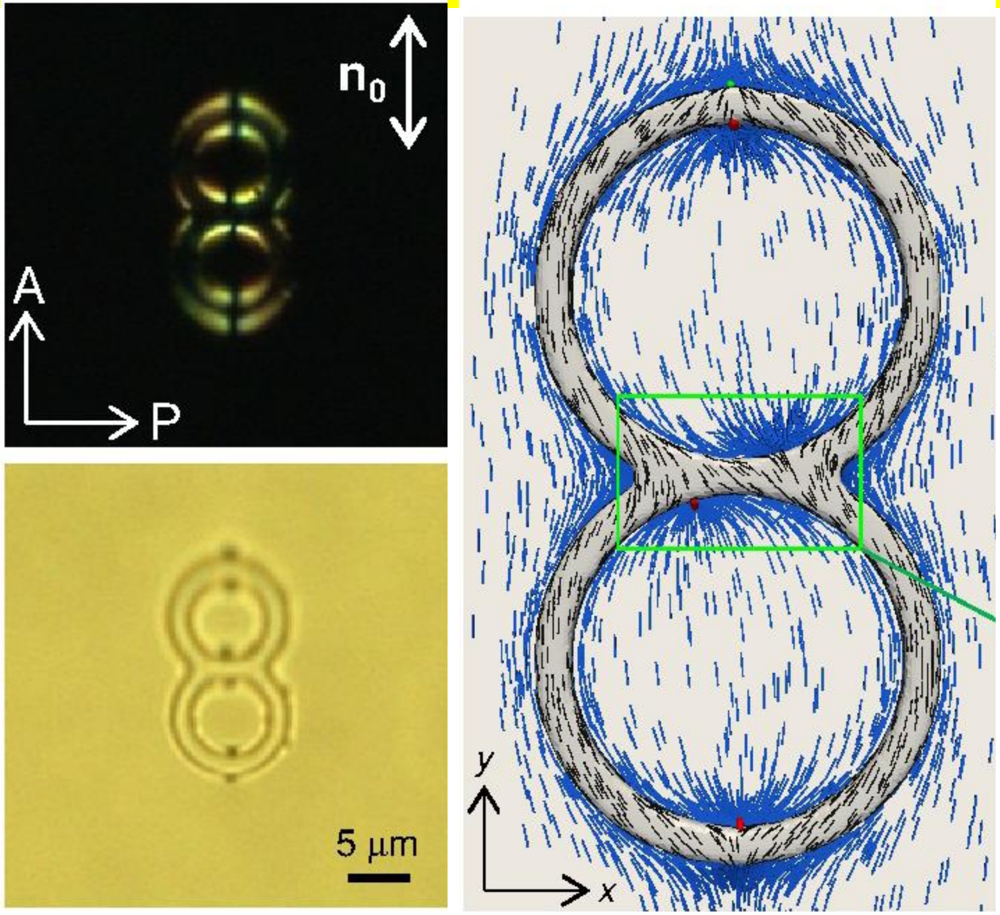
2D defect winding numbers

s = -1

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

Boojums on g=2 handlebodies

-6+4=-2

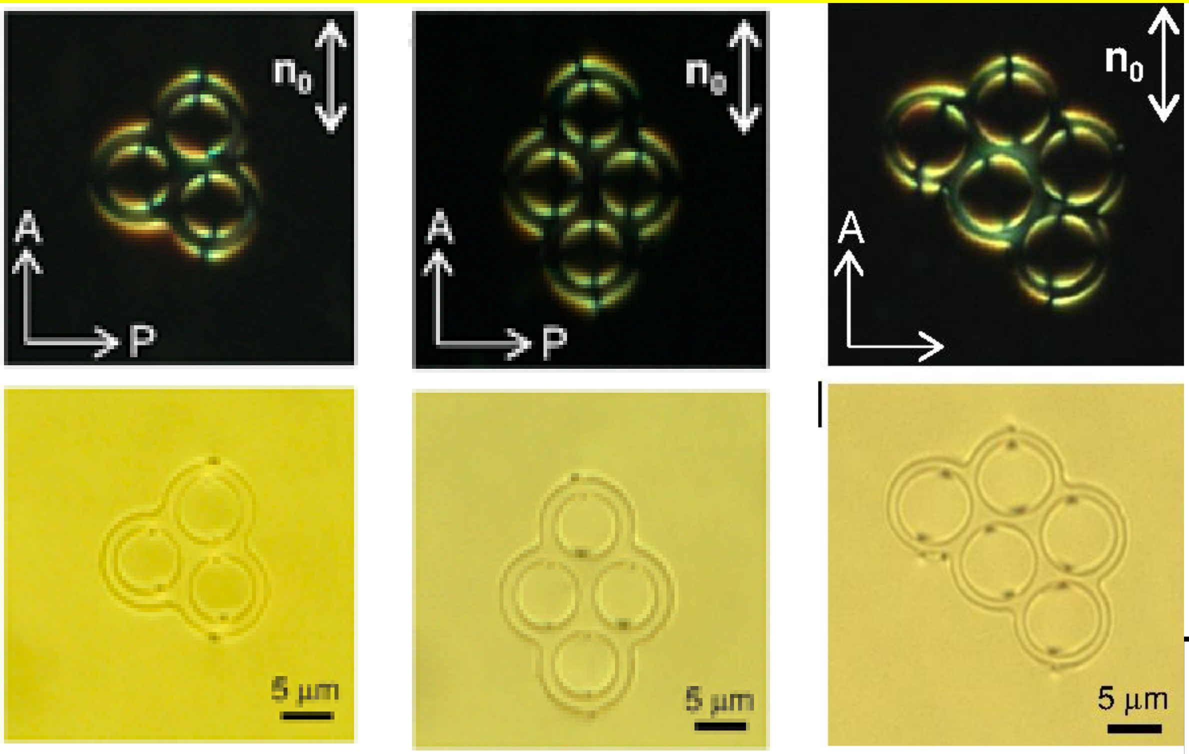


- **Satisfy predictions of topological theorems:**

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

- **…with extra self-compensating defects!**

Boojums on colloidal handlebodies



g=3,4,5 handlebodies

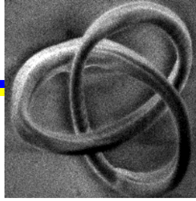
g	$c = \Sigma_i s_i$	Number of defects	
		s = +1	s = -1
1	0	2	2
		0	0
2	-2	2	4
		4	6
3	-4	2	6
		4	8
4	-6	2	8
		4	10
5	-8	2	10
		3	11

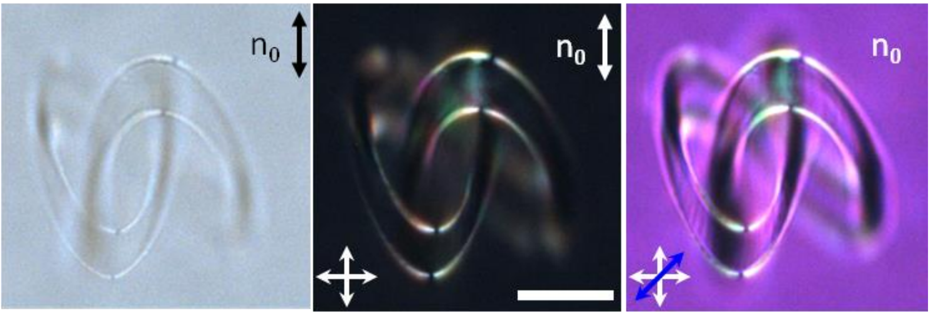
Theorems & charge conservation:

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

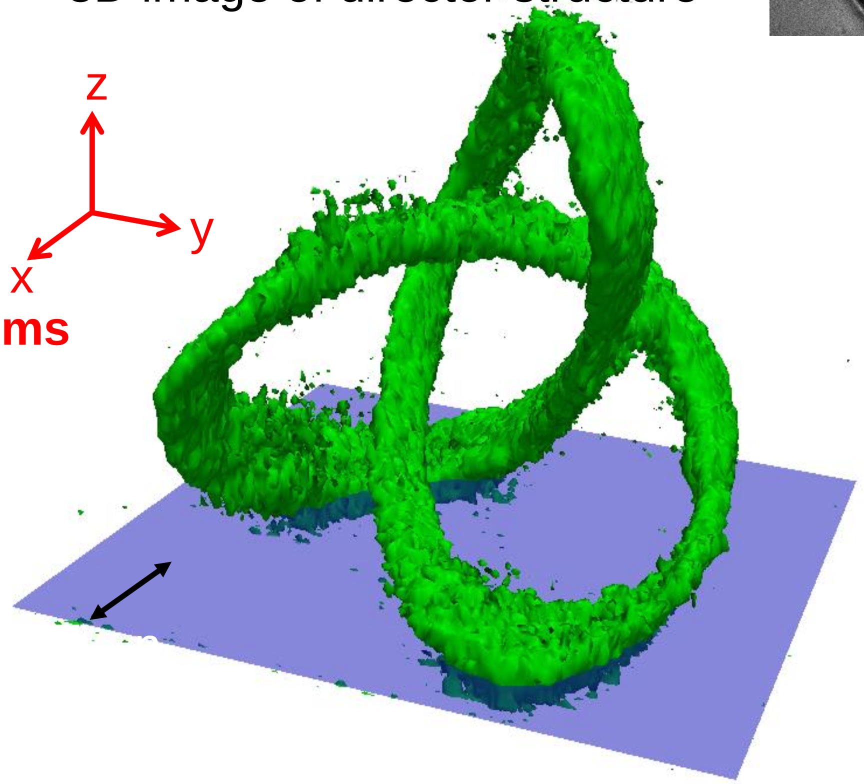
Frequency of observation of different states depends on free energy of elastic distortions

Trefoil Colloidal-knot-induced defects

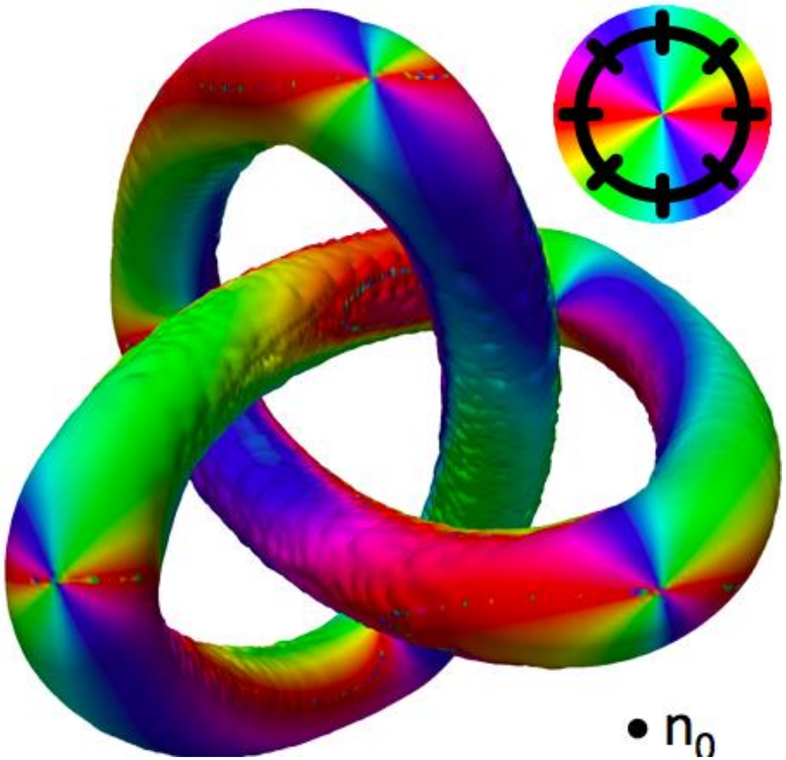




3D image of director structure



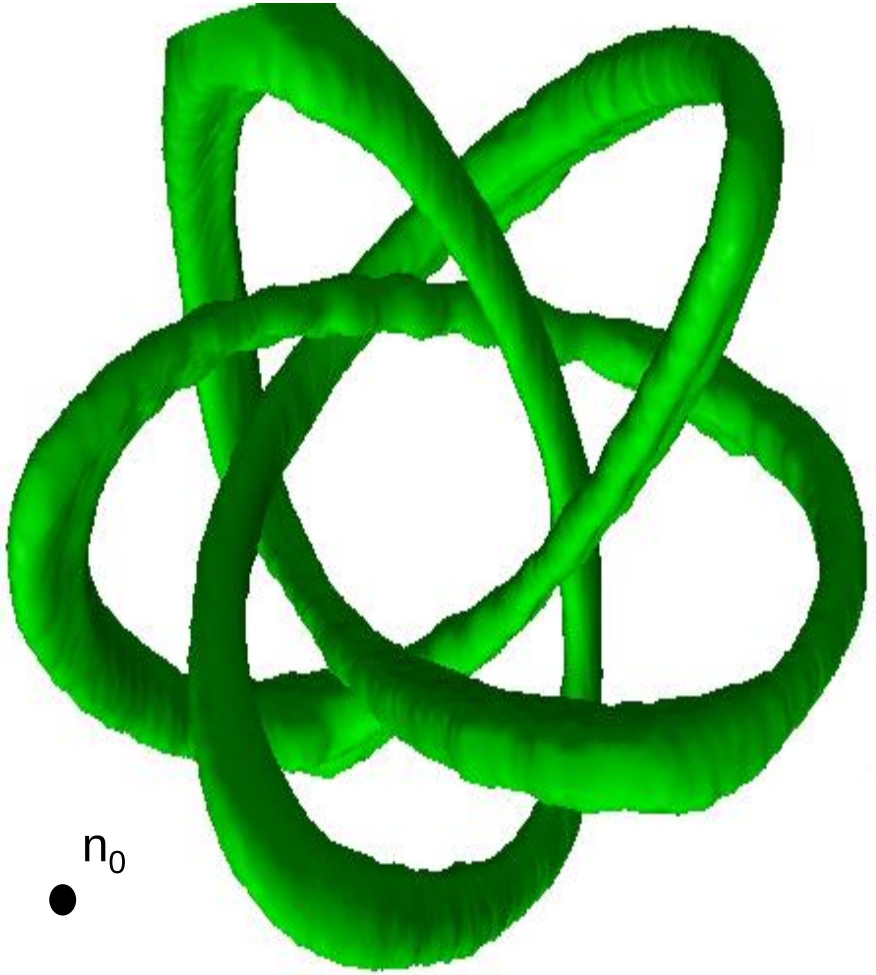
Knots induce 12 self-compensating boojums

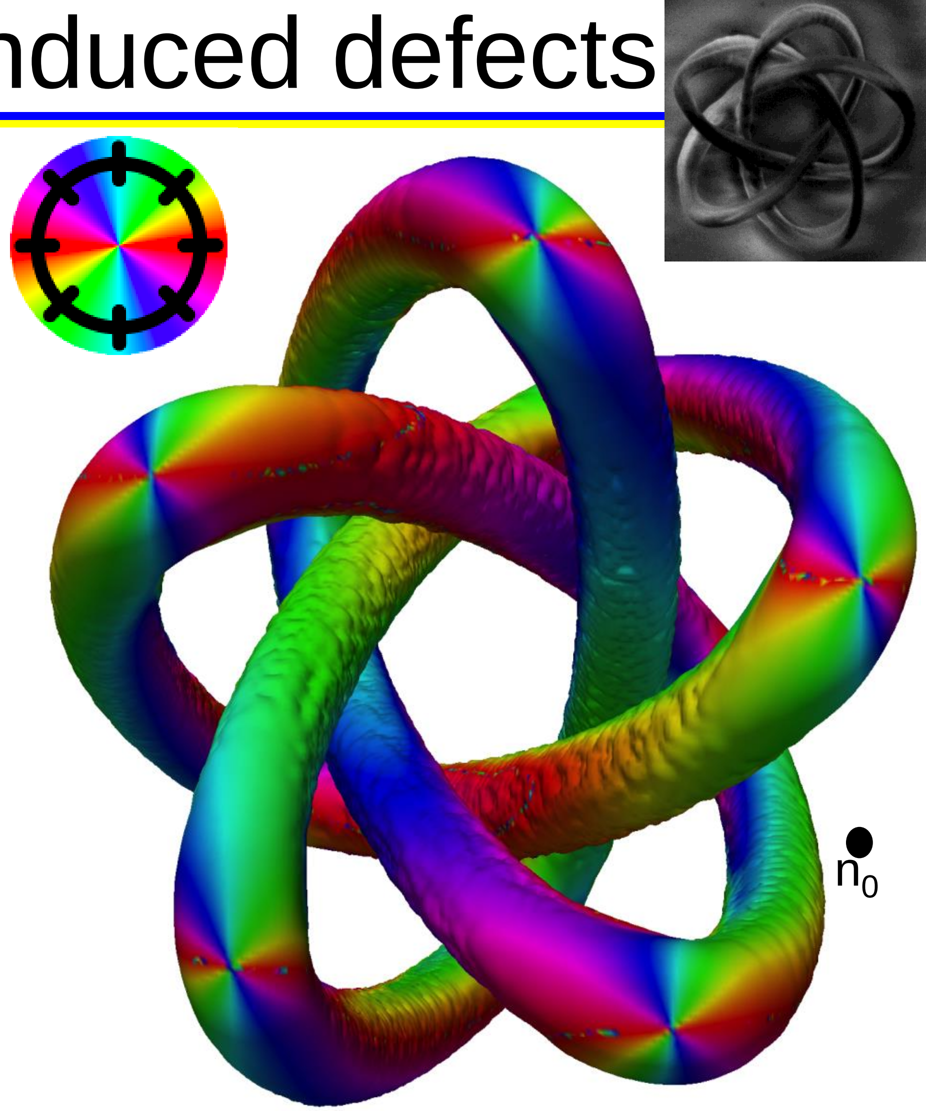


- →**6 *s*=1 & 6 *s*=-1 boojums compensate each other**
- → **consistent with /=0**
- →**T(p,q)=T(2,3)**
- →**The total number of boojums is 4q**

A. Martinez, M. Ravnik, B. Lucero & I.I. Smalyukh, *Nature Mater* 13, 258

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



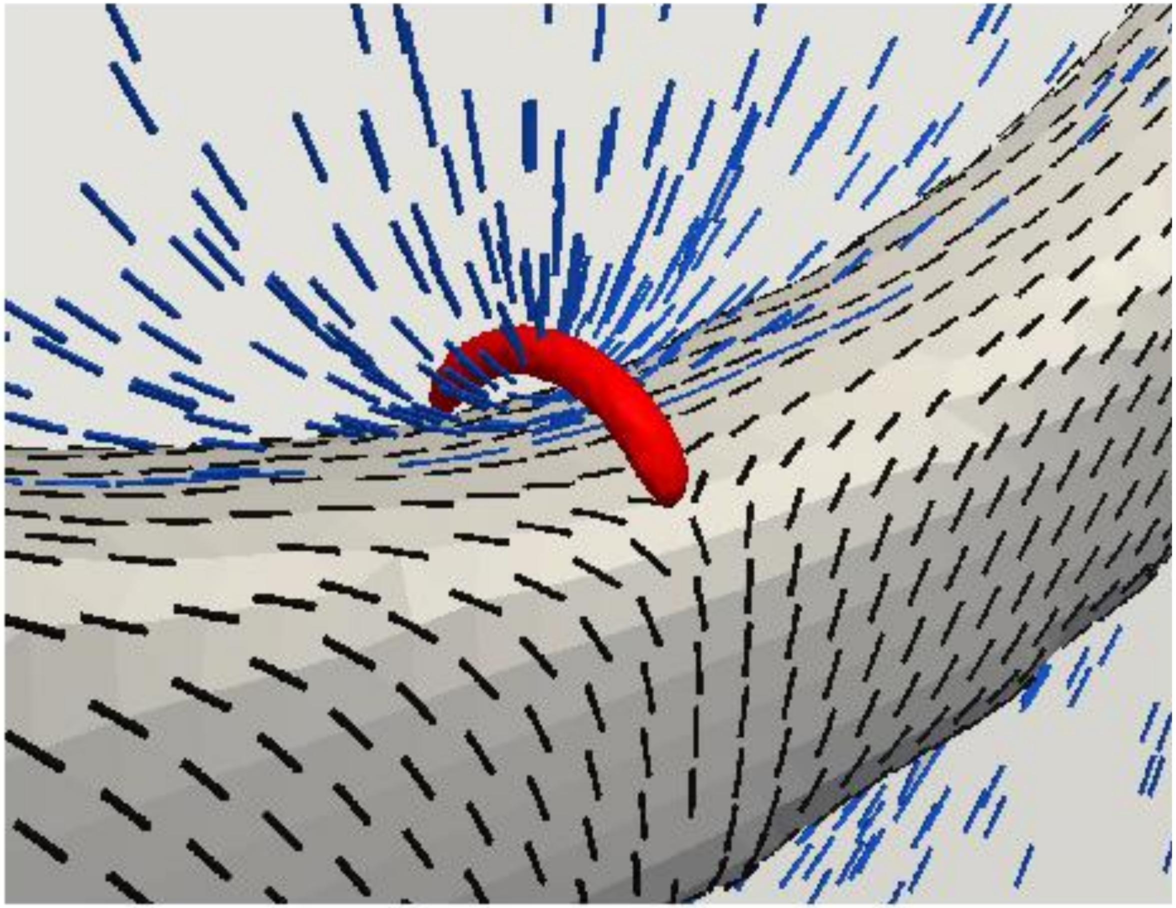


→**10 *s*=1 & 10 *s*=-1 boojums compensate each other**

→ **consistent with /=0**

→**The total number of boojums is 4q again**

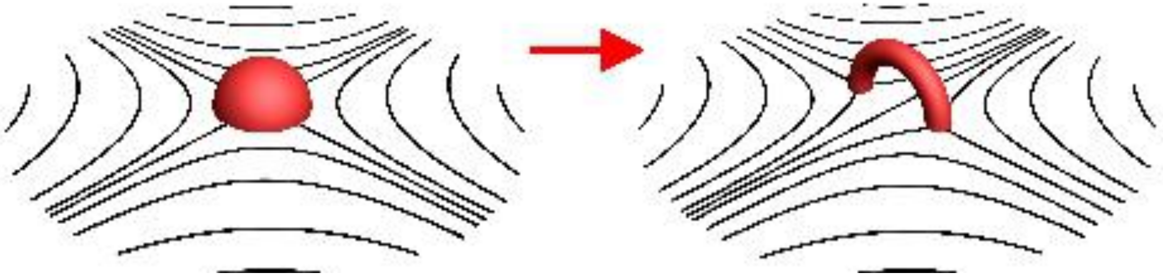
Boojums **form handles** on colloidal handlebodies

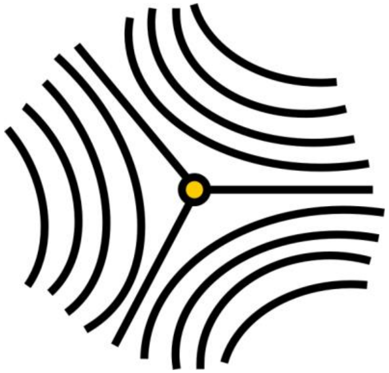


Elastic energy minimization & strong BCs promote boojum splitting into vortex semi-rings

handle-shaped boojums on colloidal handlebodies

Because of nonpolar nature of the field (would not emerge in vector fields)

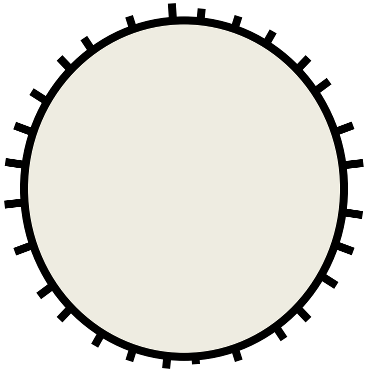




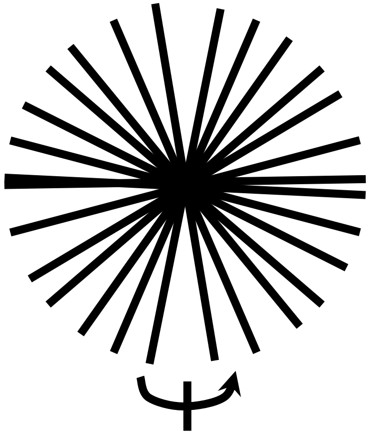
Q. Liu, B. Senyuk, M. Tasinkevych, and I. I. Smalyukh, Proc. Natl. Acad. Sci. U.S.A. **110**, 9231

Colloidal spheres & induced defects in 3D

Particle:



Equivalent to:

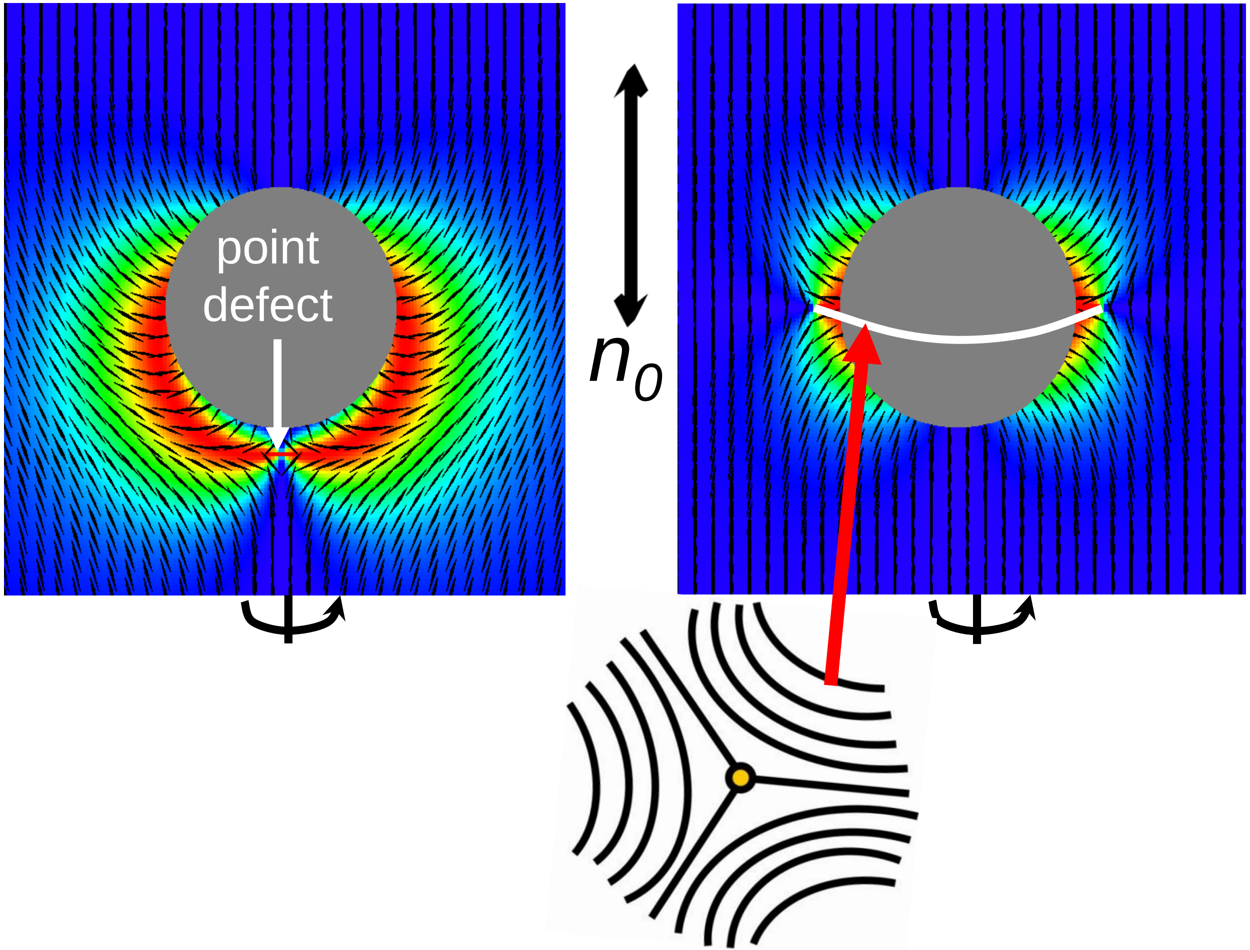


Topological charge due to particles is compensated by defects of opposite charge

Point defect

Disclination ring

s=-1/2 around bead



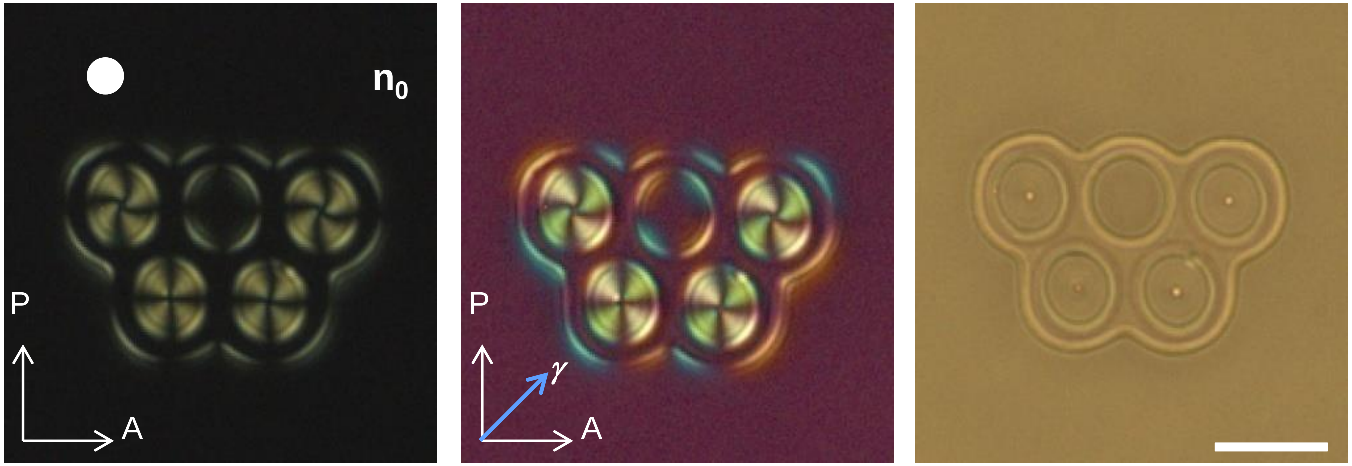
Theorems predict:

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

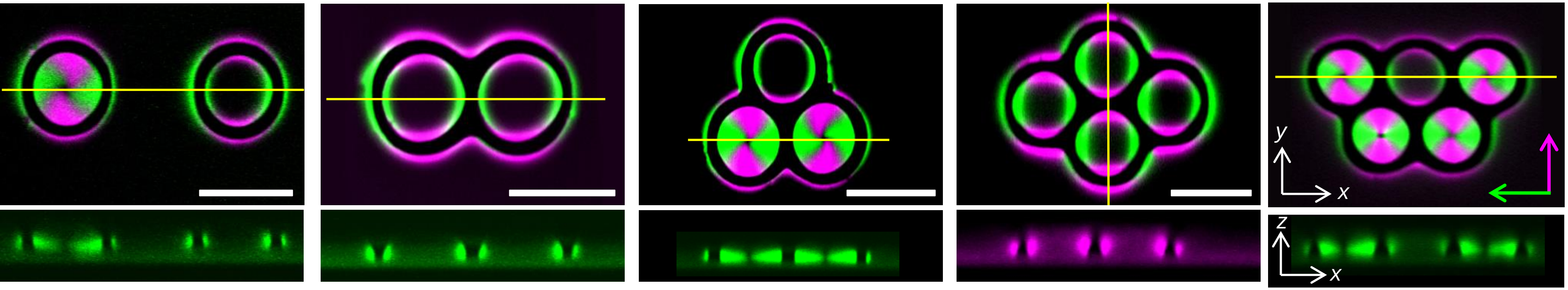
Effects of topology: handlebody colloids

Theorems predict:

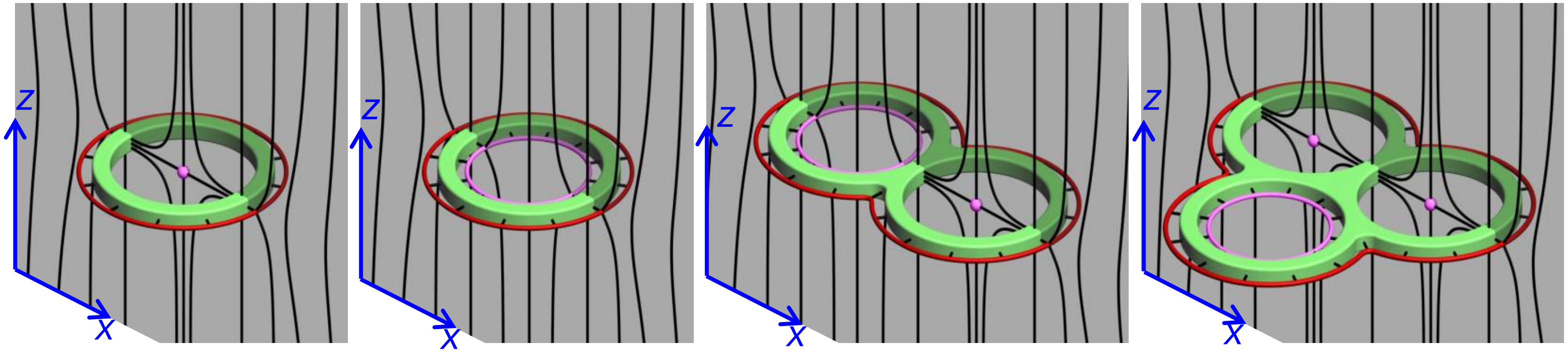
$$\sum_i m_i = \pm \chi / 2$$



3D imaging



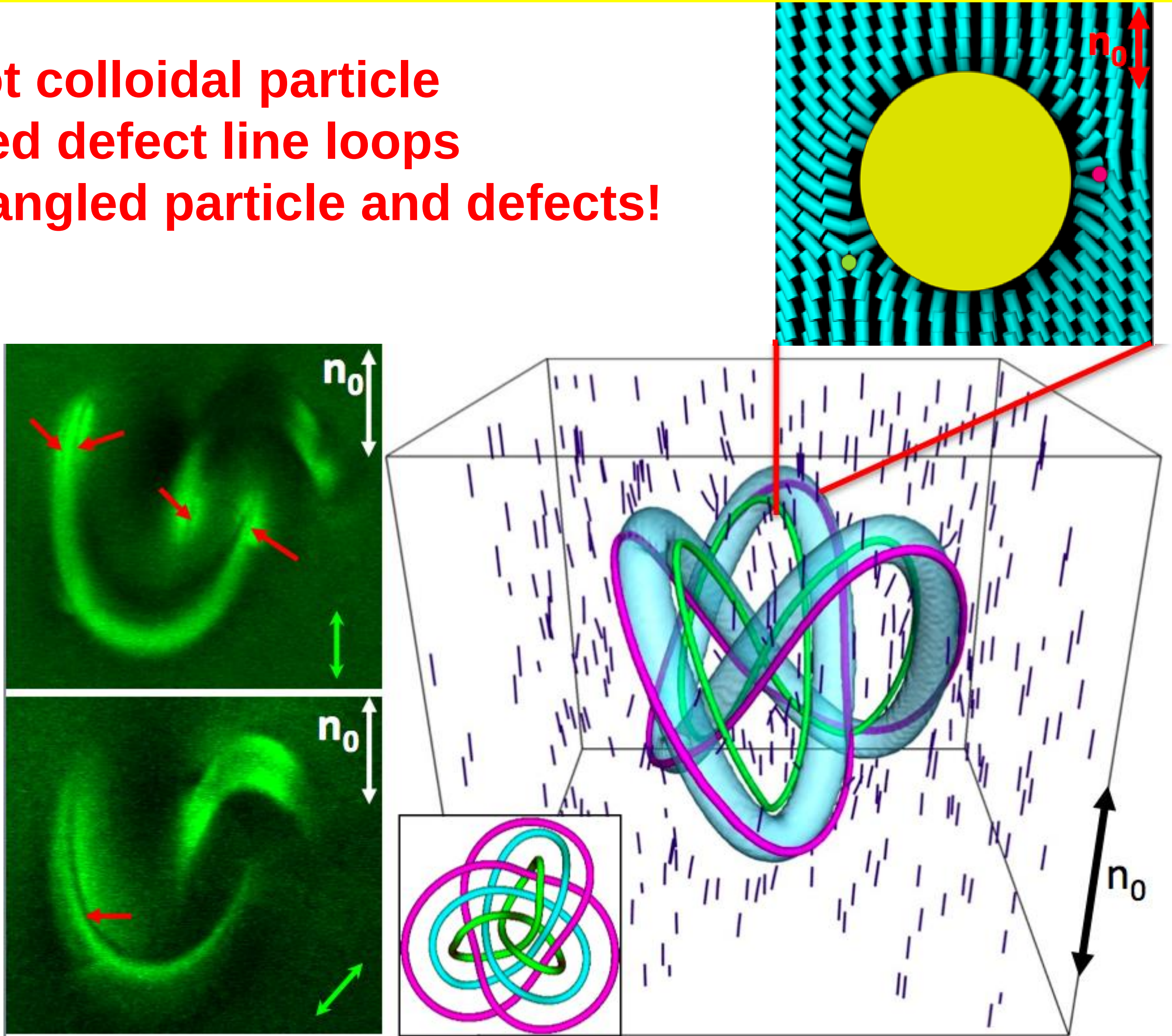
Reconstructed director structures and defects around colloidal hanlebodies



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

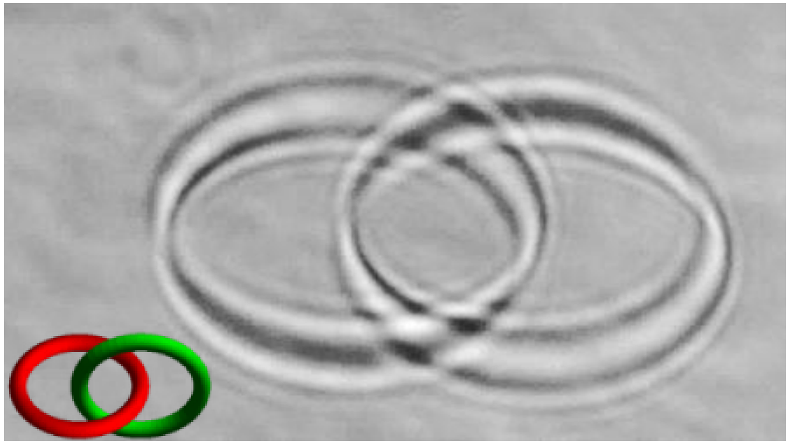
Mutually tangled particle knots & director field

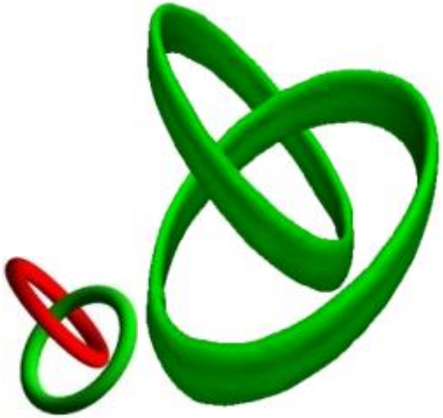
→Trefoil knot colloidal particle
→Two knotted defect line loops
→Mutually tangled particle and defects!



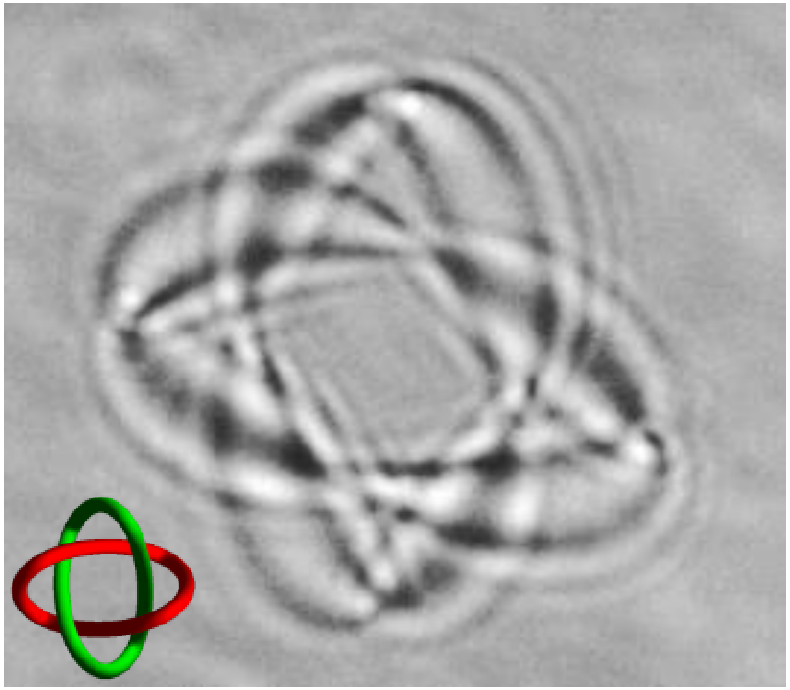
Multi-component particles: colloidal links

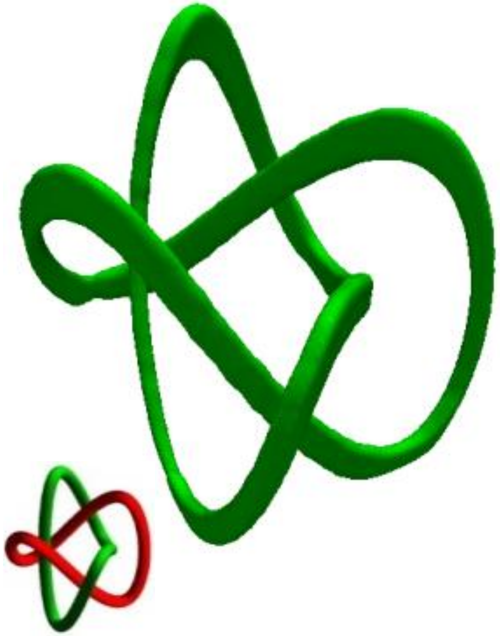
Hopf Links





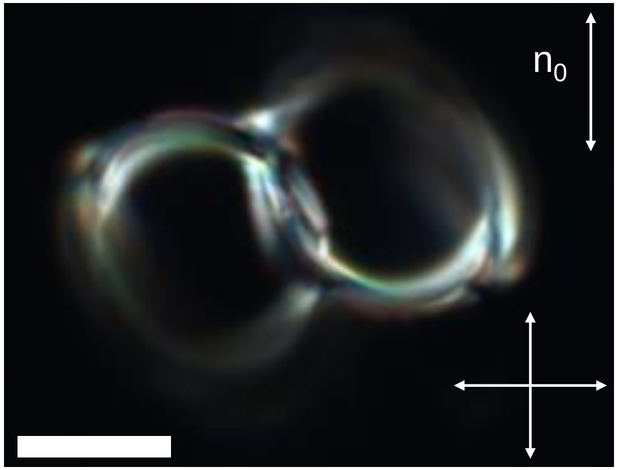
Solomon Links

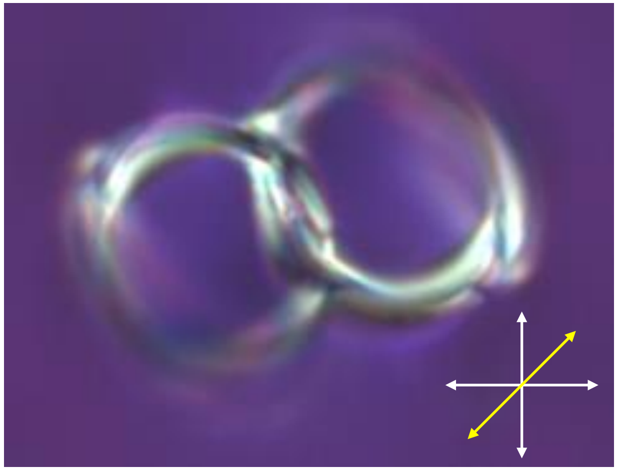


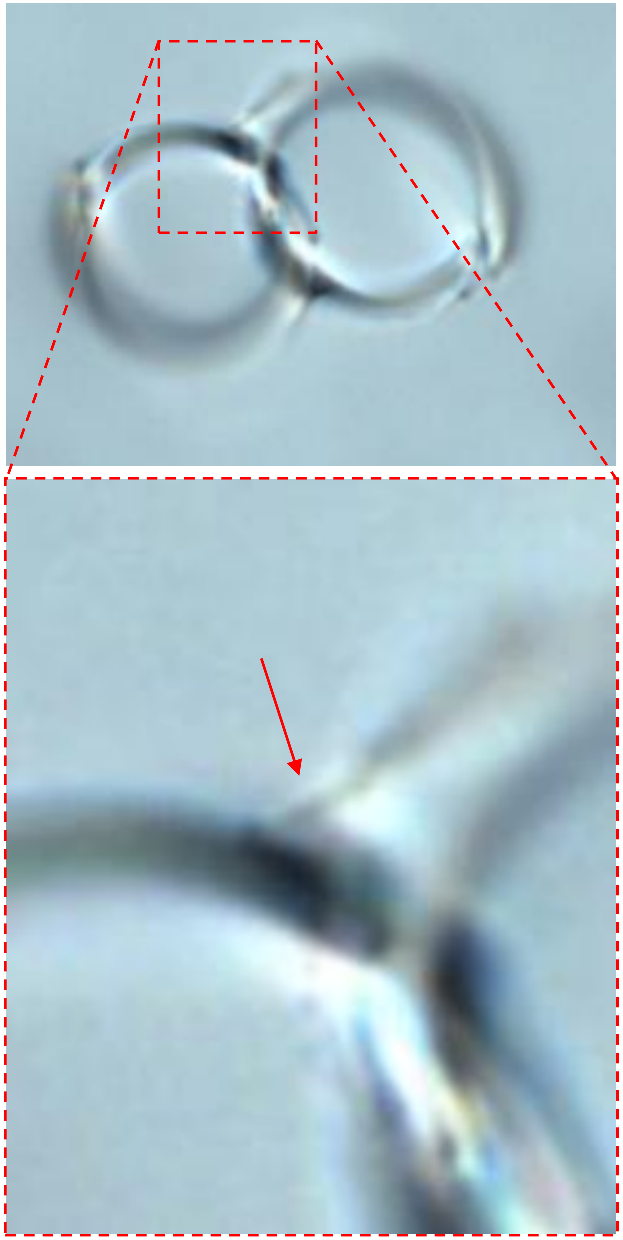


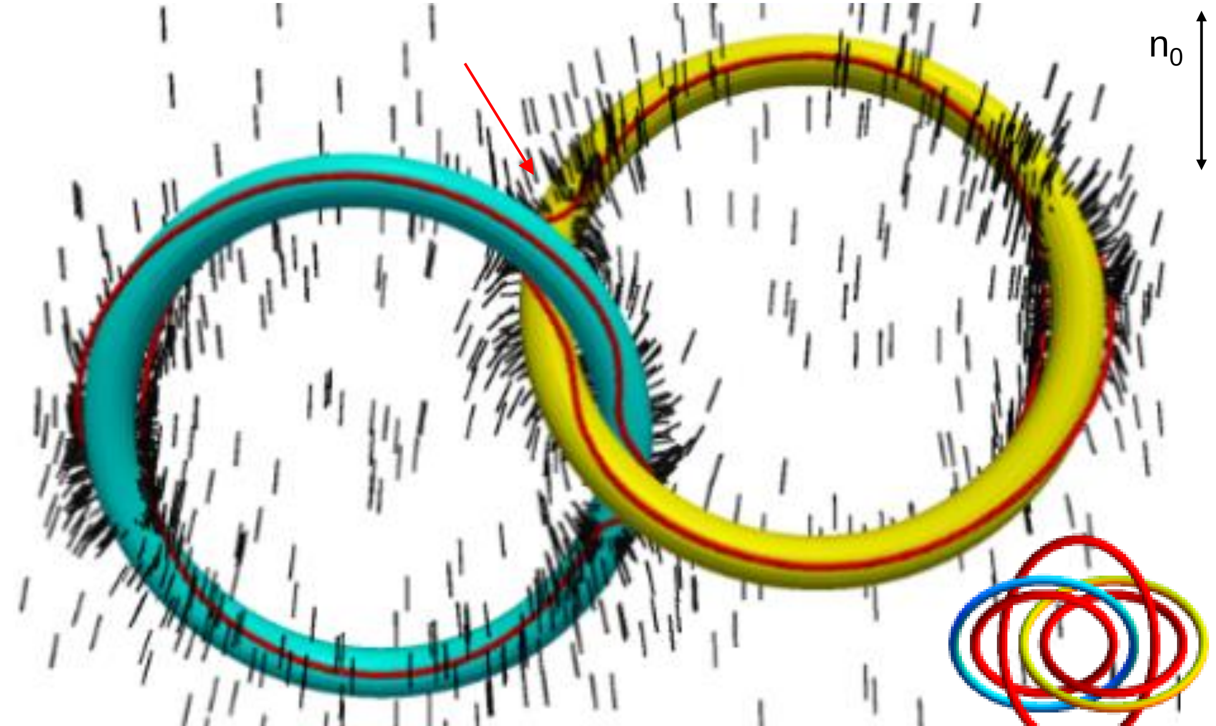
A. Martinez, L. Hermosillo, M. Tasinkevych, and I. I. Smalyukh. PROC. NATL. ACAD. SCI. U.S.A. 112, 4546-4551

Colloidal Hopf Links with perpendicular BCs



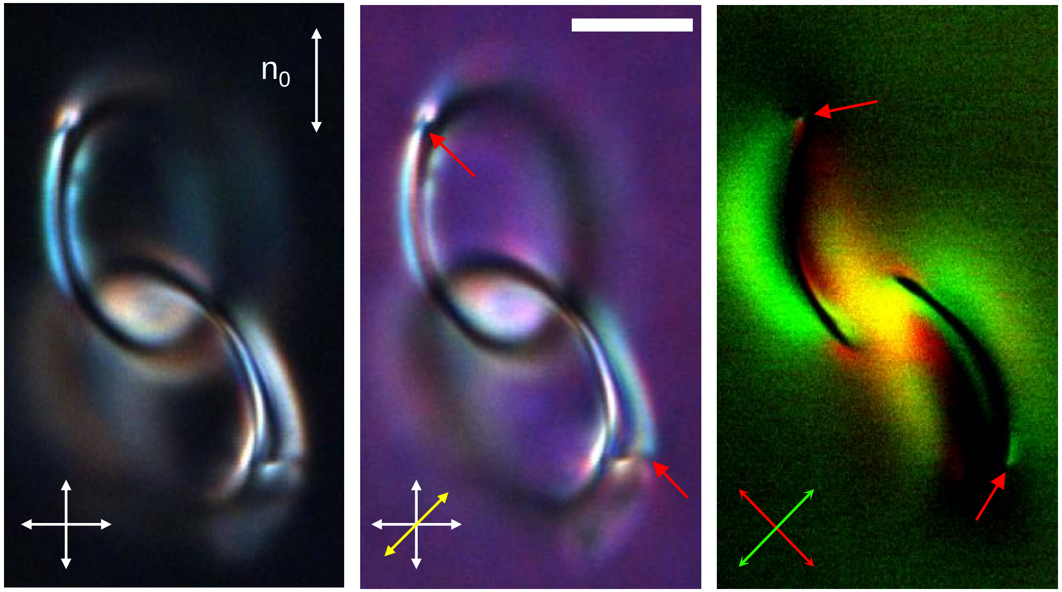


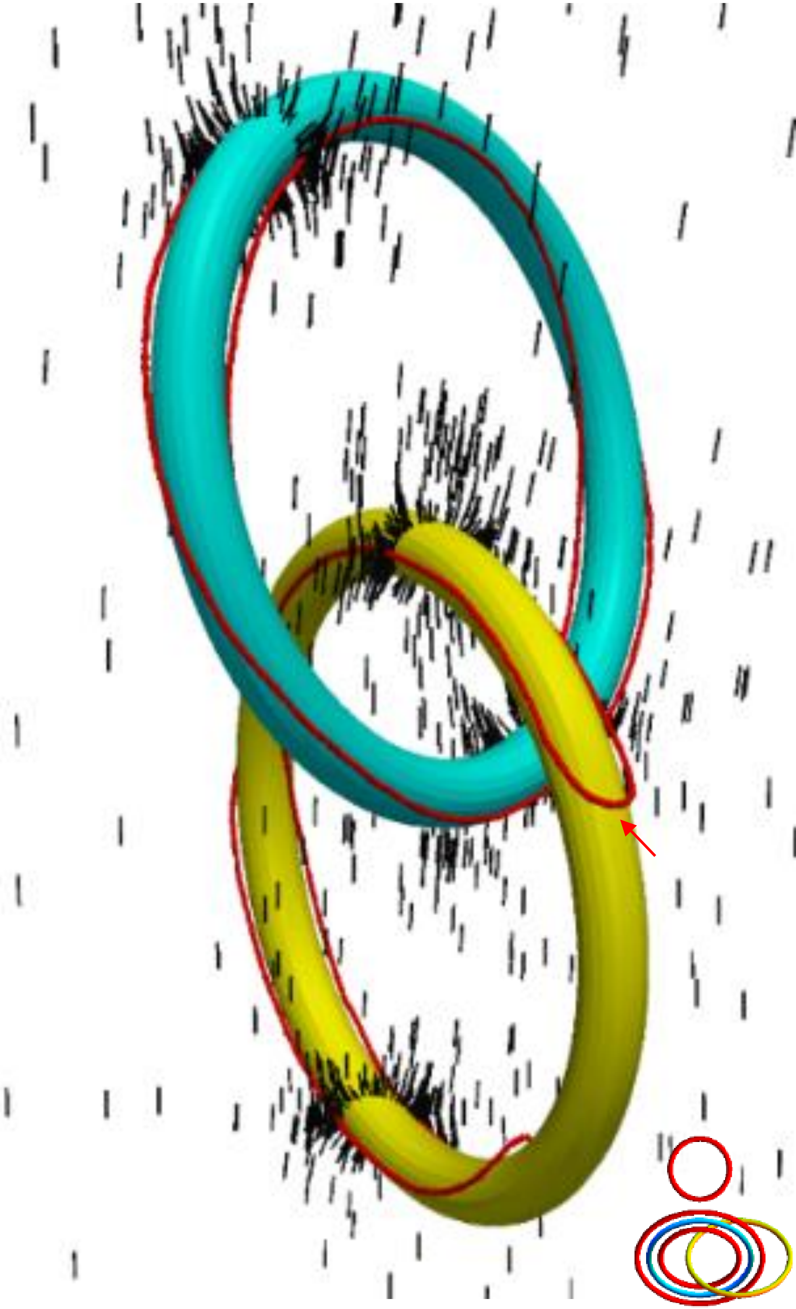




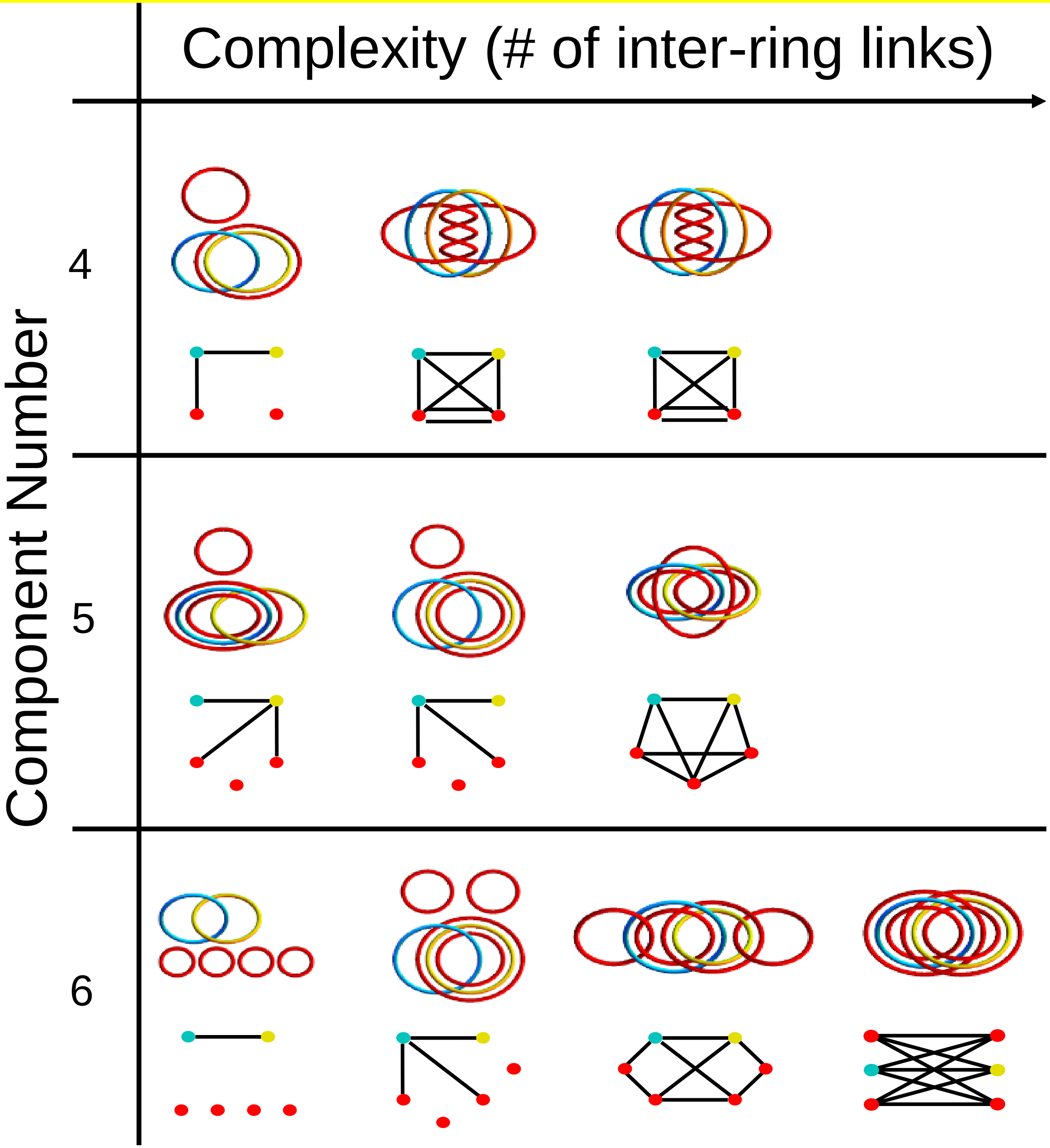
disclination “jumping” to the other particle

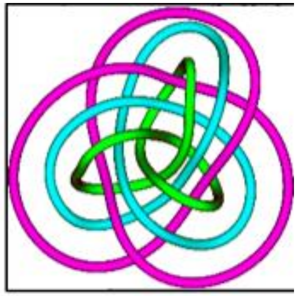
Metastable Hopf links with perpendicular BCs





Simplified graph diagrams & open questions



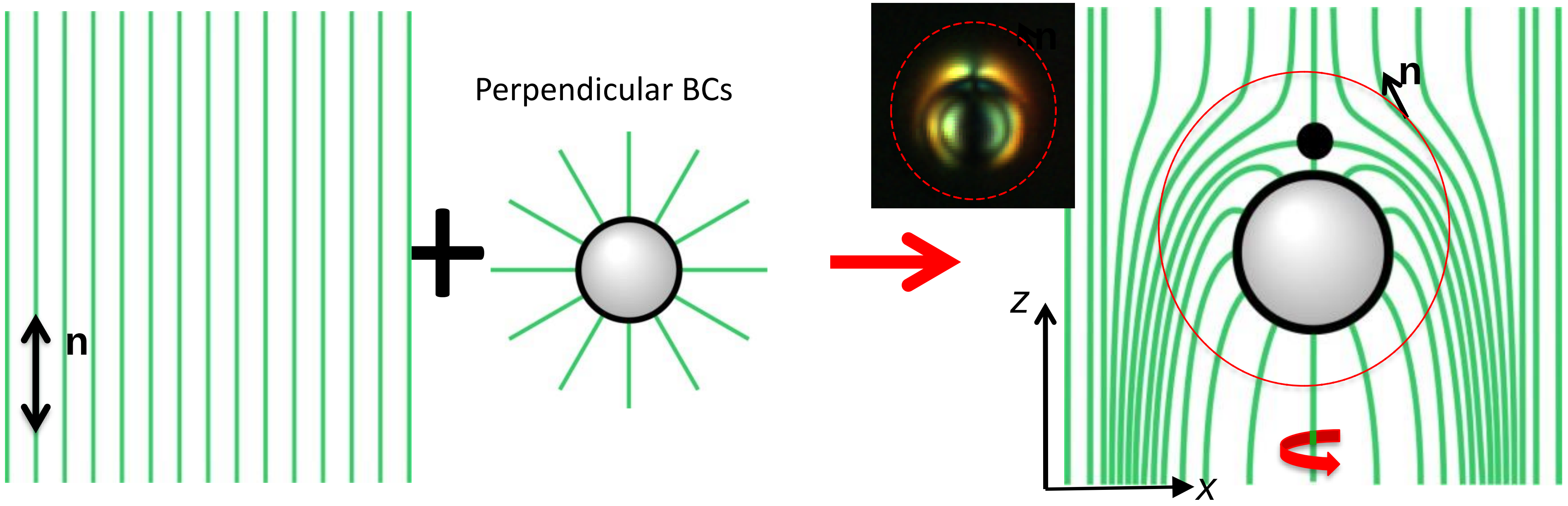


- colloidal Hopf links & knots induce 2 or more vortex rings
- Nonpolar nature - new topological interaction between fields & surfaces
- **NONE OF THIS** could not be realized in vector fields!
- **Open question: how to extend statements of Poincare-Hopf theorem to nonpolar fields interacting (inter-linking!) with surfaces?**

A. Martinez, L. Hermosillo, M. Tasinkevych and I. I. Smalyukh. PROC. NATL. ACAD. SCI. U.S.A. 112, 4546-4551

Colloidal interactions & new condensed matter phases?

Nematostatics & elastic multipoles: dipole



Elastic free energy of the LC (simplest):

$$F_{\text{bulk}} = \frac{K}{2}\int d\mathbf{r}\left\{(\operatorname{div}\mathbf{n})^2 + (\operatorname{rot}\mathbf{n})^2\right\}$$

Electrostatic analogy: 2^l-pole

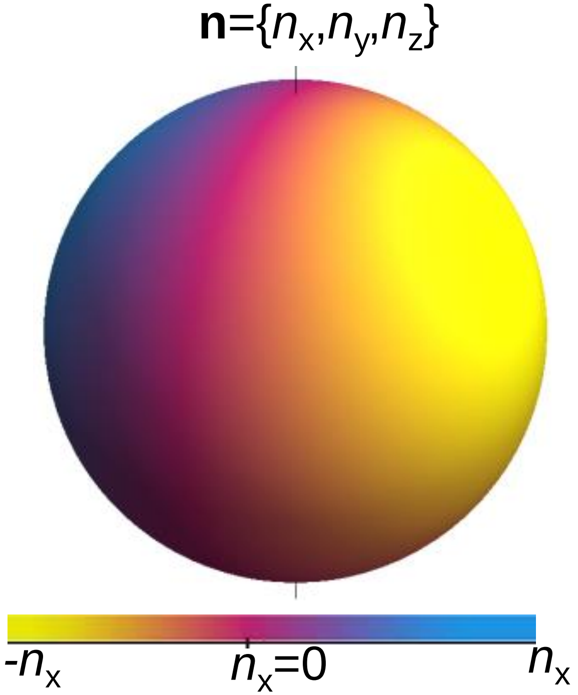
$$\boxed{\sigma_l^{\,m} \propto \cos(m\phi)\, P_l^{\,m}(\cos\theta)}$$

Dipole: $l = 1,\ m = 1$

→ **Minimization of free energy**

→**Laplace's equation for director**

→**Solutions expanded in multipoles** (2^l-poles)



Nematic colloidal monopoles... hexadecapoles…

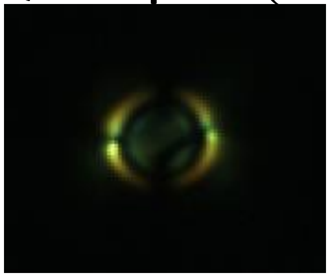
Elastic 2^l-poles

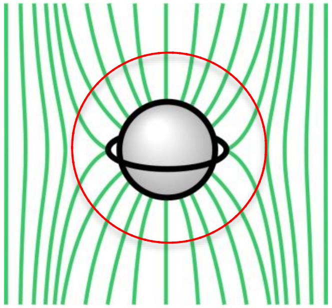
Monopoles (l=0):

$l = 0$

Y. Yuan, Q. Liu, B. Senyuk & I. I. Smalyukh. *Nature* ***570****, 214 (2019).*

Quadrupoles (l=2):

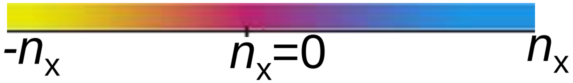




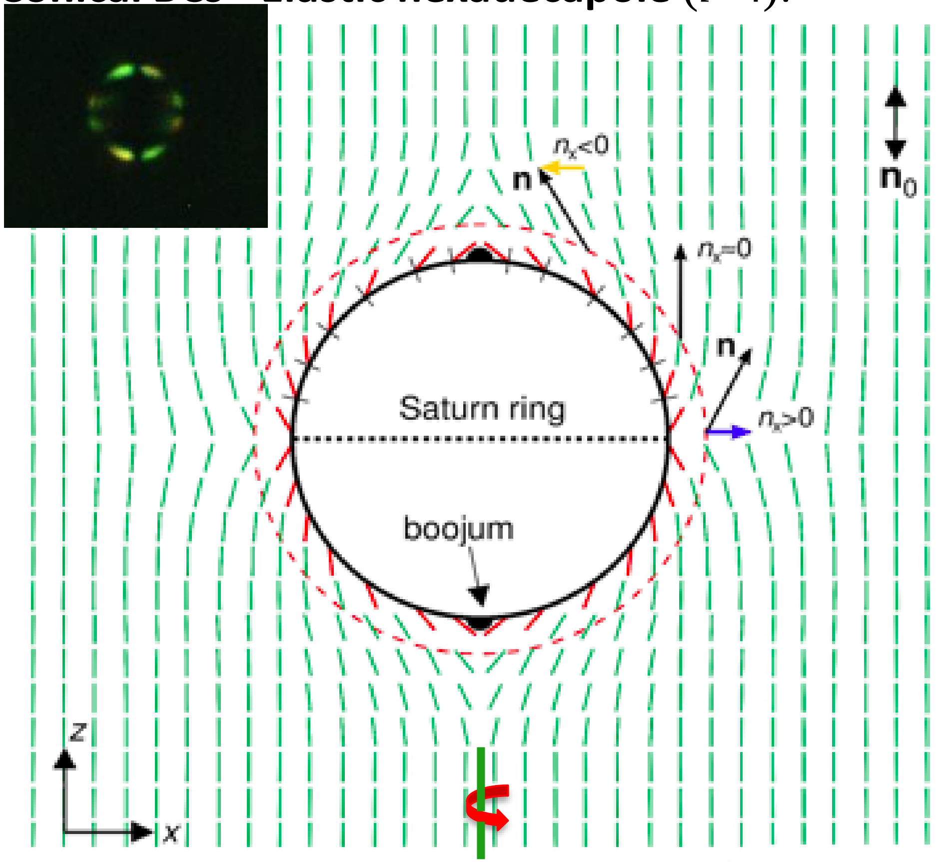
$l = 2,\ m = -1$

C. Lapointe, T. Mason I. I. Smalyukh *SCIENCE* **326**, 1083-1086 (2009)

$$\boxed{\sigma_l^m \propto \cos(m\phi)\, P_l^m(\cos\theta)}$$

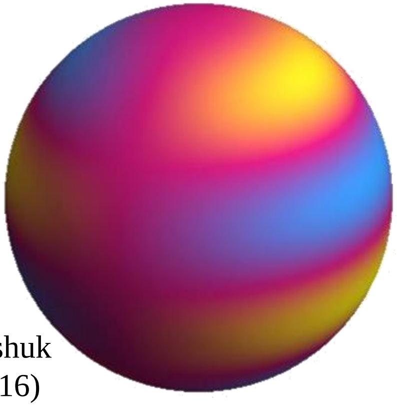


Conical BCs - Elastic hexadecapole (l=4):



$l = 4,\ m = 1$

$2^l = 16$ – **hexadecapole**

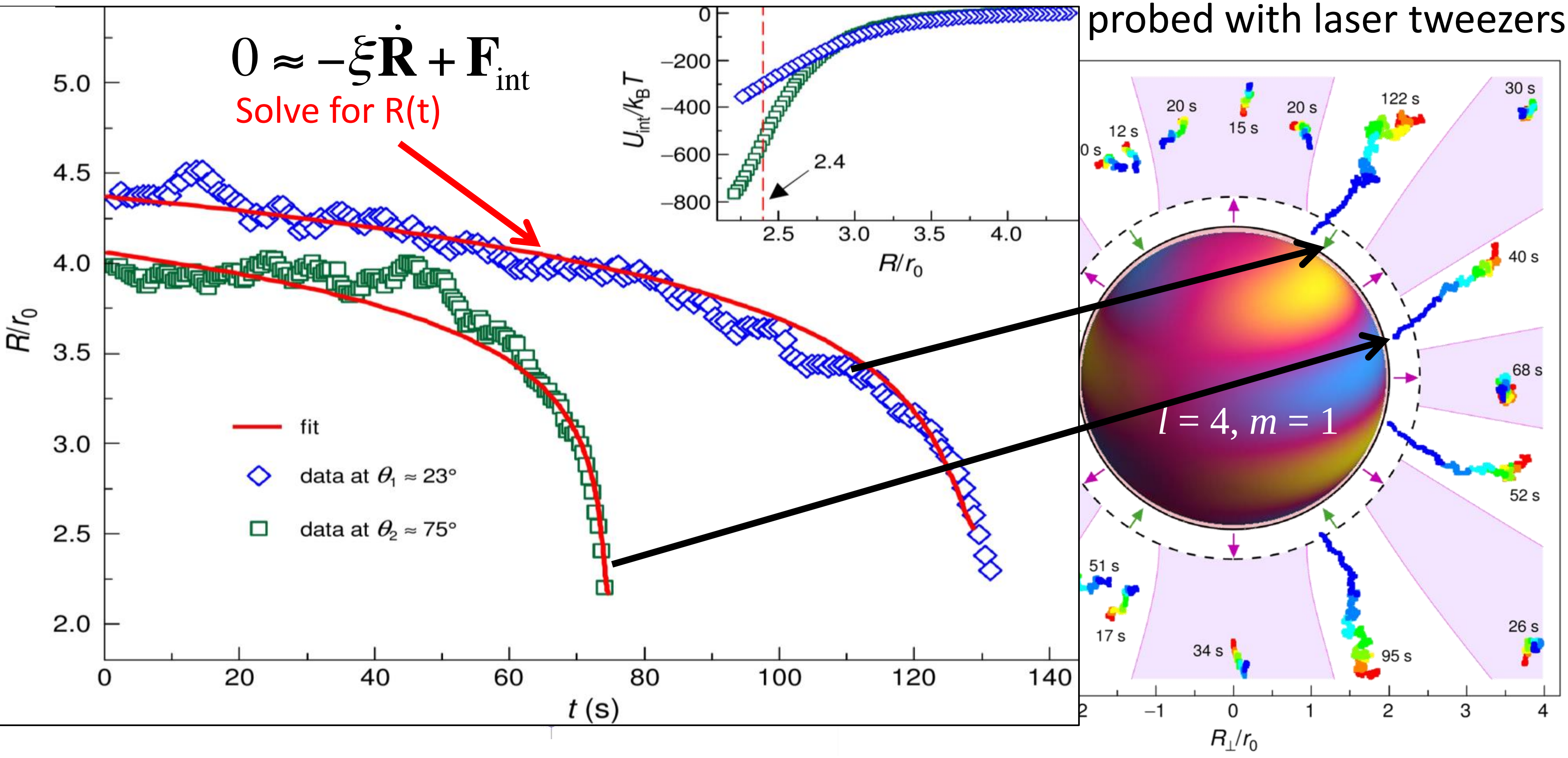


B. Senyuk, O. Puls, O. Tovkach, S. Chernyshuk I. I. Smalyukh. ***Nature Comm*** **7**, 10659 (2016)

Elastic pair interactions between hexadecapoles

- →**Analogy with electrostatics**
- →**Pair-interaction energy (leading order)** $U_{hexa} \propto P_8\left(\cos q\right) / R^9$
- →**8 sectors of attraction + 8 sectors of repulsion**

probed with laser tweezers



$$0 \approx -\xi \dot{\mathbf{R}} + \mathbf{F}_{\text{int}}$$

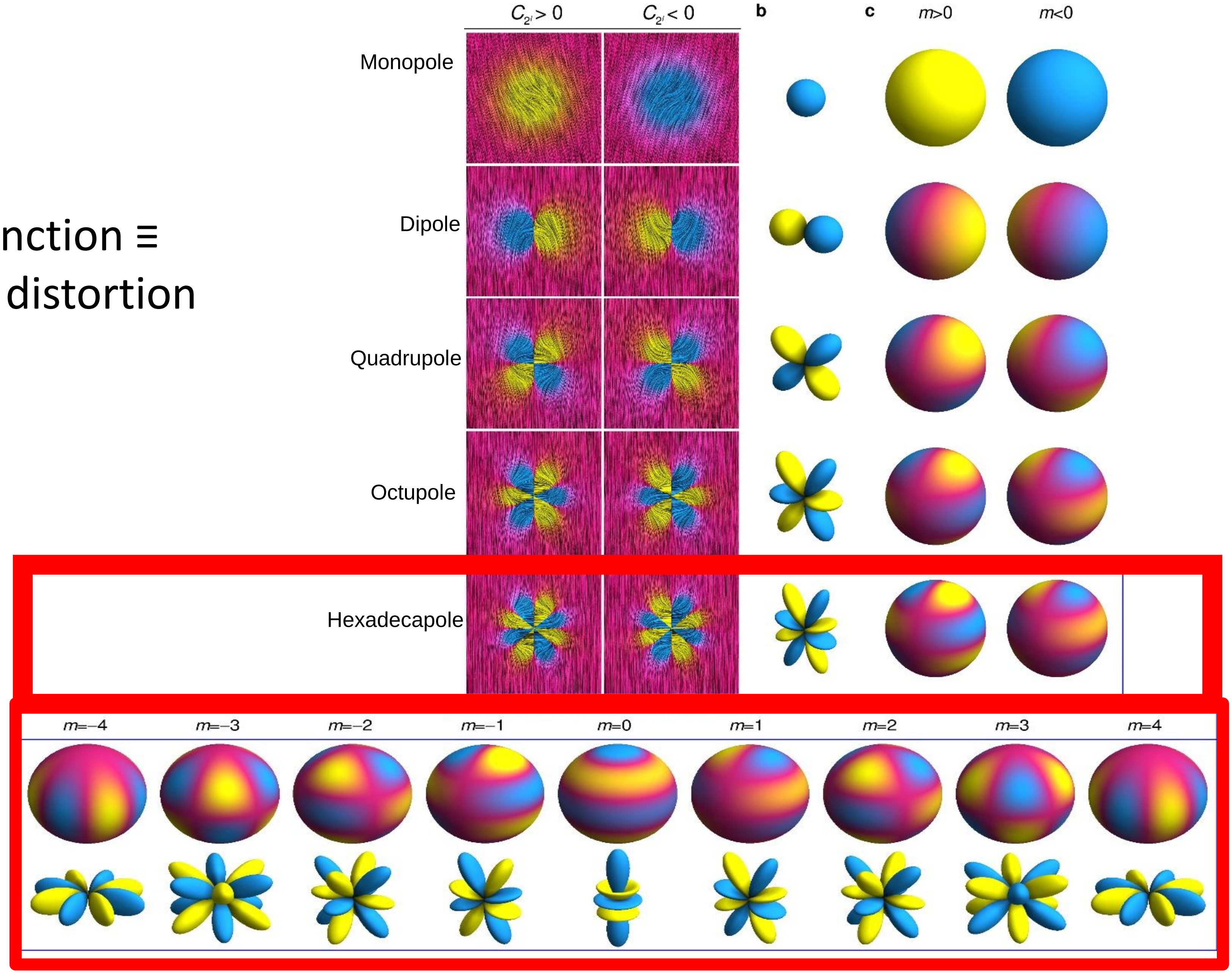
Solve for R(t)

B. Senyuk, O. Puls, O. Tovkach, S. Chernyshuk, I. I. Smalyukh. ***Nature Comm* 7**, 10659

Y. Zhou, B. Senyuk, R. Zhang, I. I Smalyukh and J.J. de Pablo. ***Nature Comm* 10**, 1000

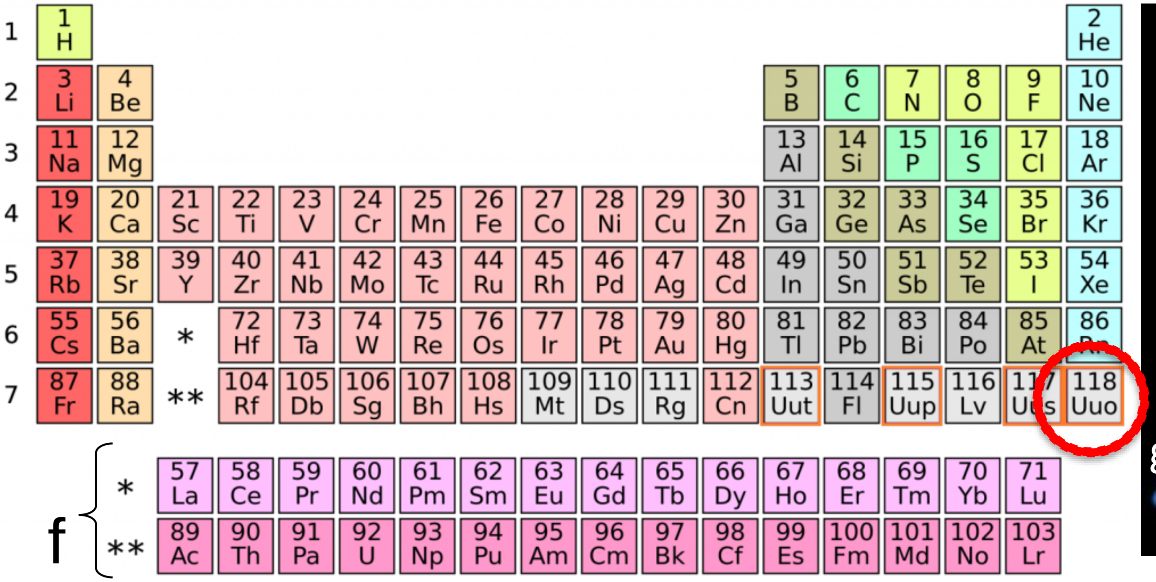
Nematic colloidal multipoles & electron shells

Wave function ≡ director distortion



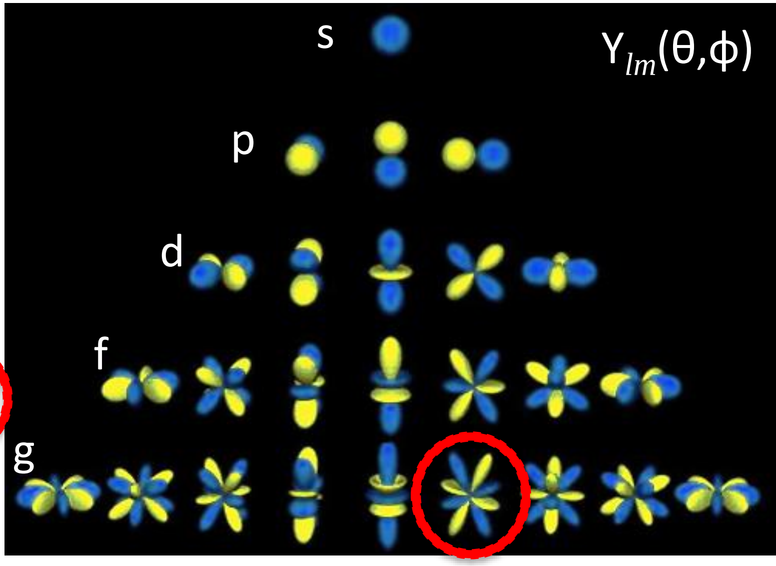
B. Senyuk, J. Aplinc, M. Ravnik, I. I. Smalyukh. ***Nature Comm* 10**, 1825 (2019).

Table of Elements & Diversity of Colloidal Atoms



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	*	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	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

f	*	57 La	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
	**	89 Ac	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

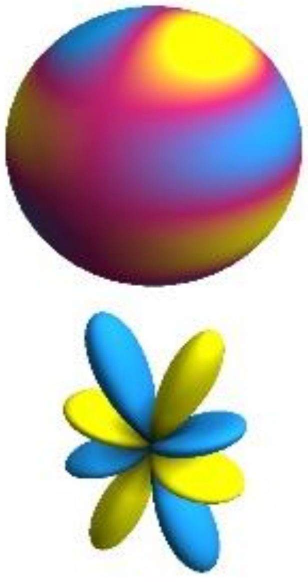


→Element #118 added in June 2016

→Elements with filled s,p,d,f-orbitals

→No atoms with filled g-orbitals discovered so far!

$l = 4$, $m = 1$



→Colloidal Hexadecapole has symmetry of atoms with g-orbitals starting from #121

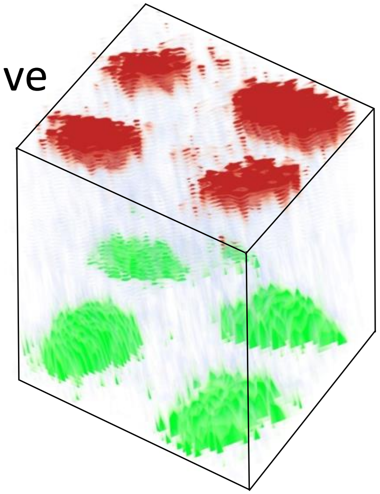
→"Colloidal" atom diversity exceeds that of atoms!

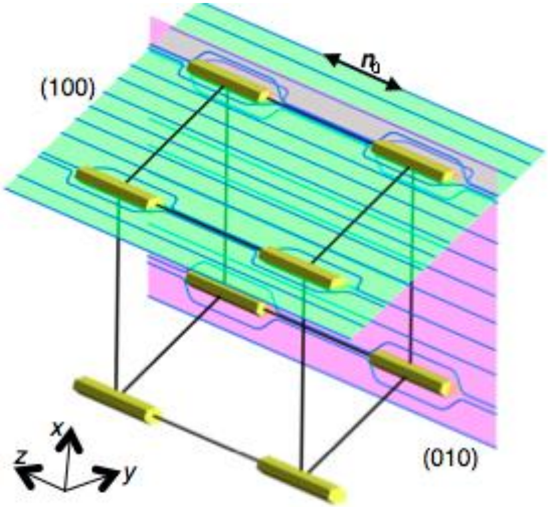
The same mathematical description with spherical harmonics $Y_{lm}(\theta,\phi)$

B. Senyuk, O. Puls, O. Tovkach, S. Chernyshuk, I. I. Smalyukh. ***Nature Comm* 7**, 10659

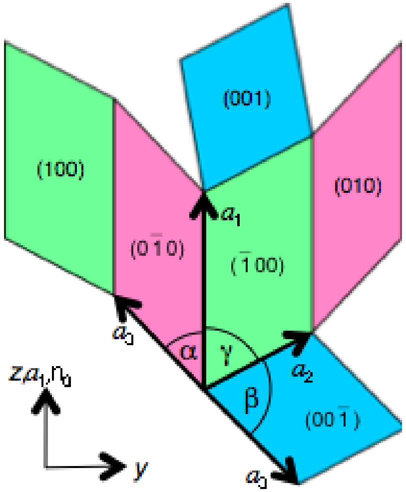
Crystallization of triclinic colloidal crystals

primitive cell





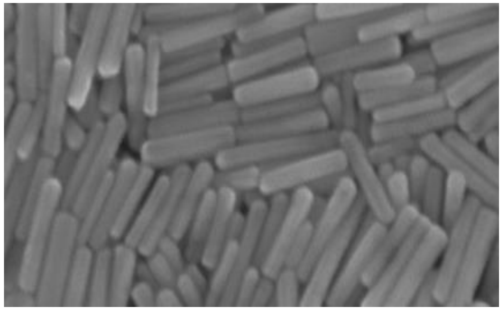
"paper" model

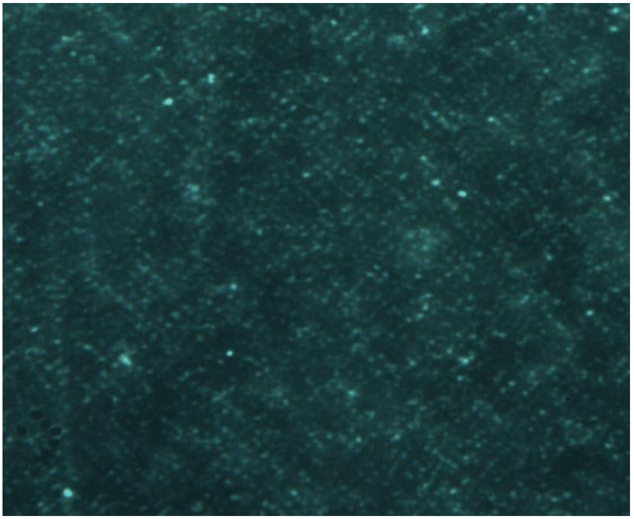


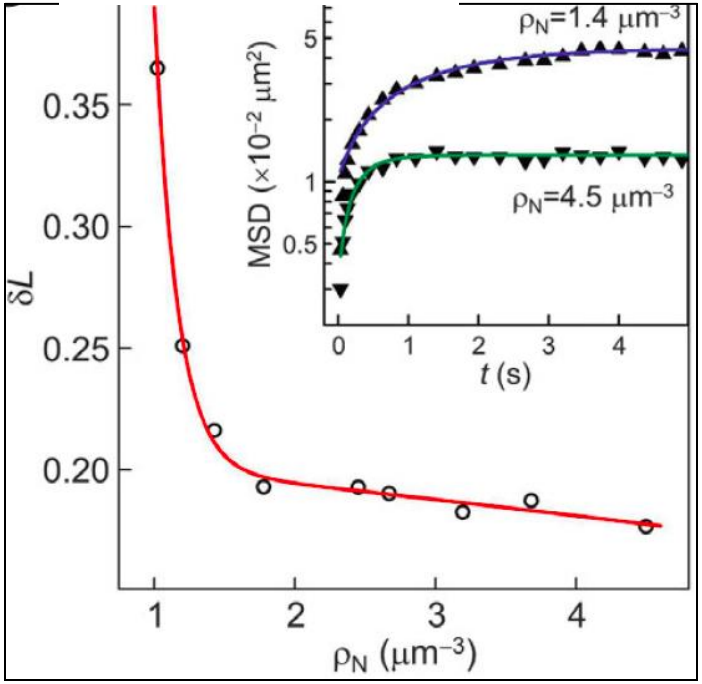
→Crystallization with increased concentration;

→Filling factor <<1%

→Lindemann parameter





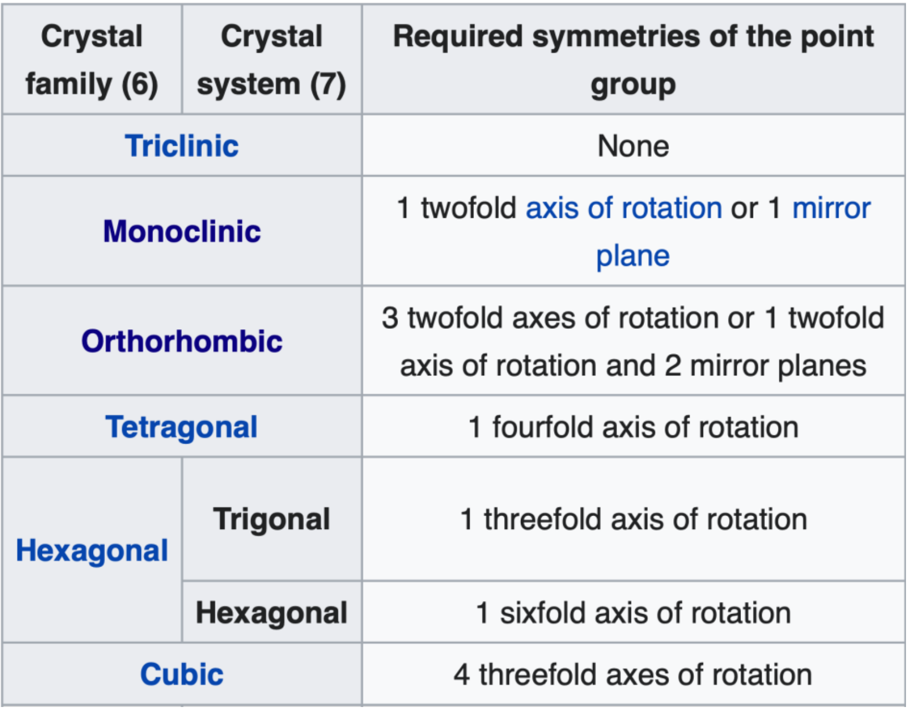


→All lattice parameters & angles different

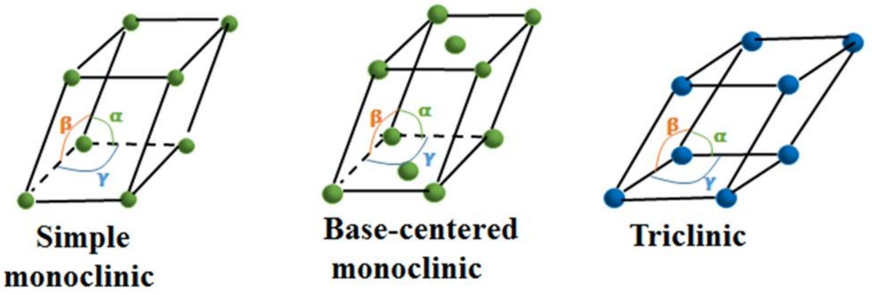
→Triclinic crystal of aligned 30 × 150 nm nanords

H. Mundoor, B. Senyuk & I. I. Smalyukh. *Science* **352**, 69-73

Soft matter analogs of 3D crystalline solids?



Crystal family (6)	Crystal system (7)	Required symmetries of the point group
Triclinic		None
Monoclinic		1 twofold axis of rotation or 1 mirror plane
Orthorhombic		3 twofold axes of rotation or 1 twofold axis of rotation and 2 mirror planes
Tetragonal		1 fourfold axis of rotation
Hexagonal	**Trigonal**	1 threefold axis of rotation
	Hexagonal	1 sixfold axis of rotation
Cubic		4 threefold axes of rotation

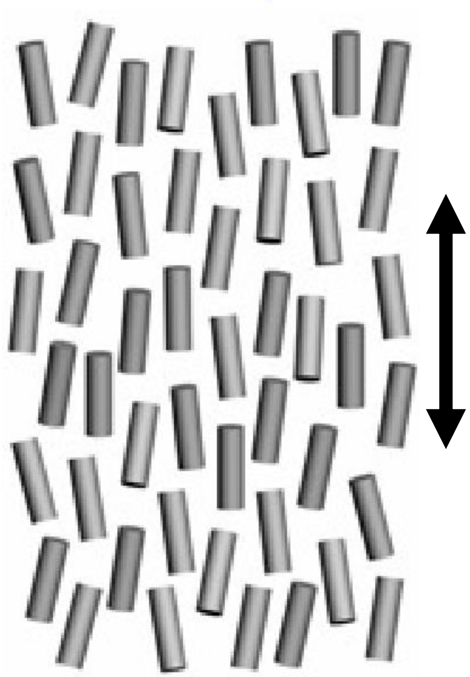


Simple monoclinic **Base-centered monoclinic** **Triclinic**

→Low-symmetry nematic fluid analogs?

Fundamental question: how order & fluidity coexist?

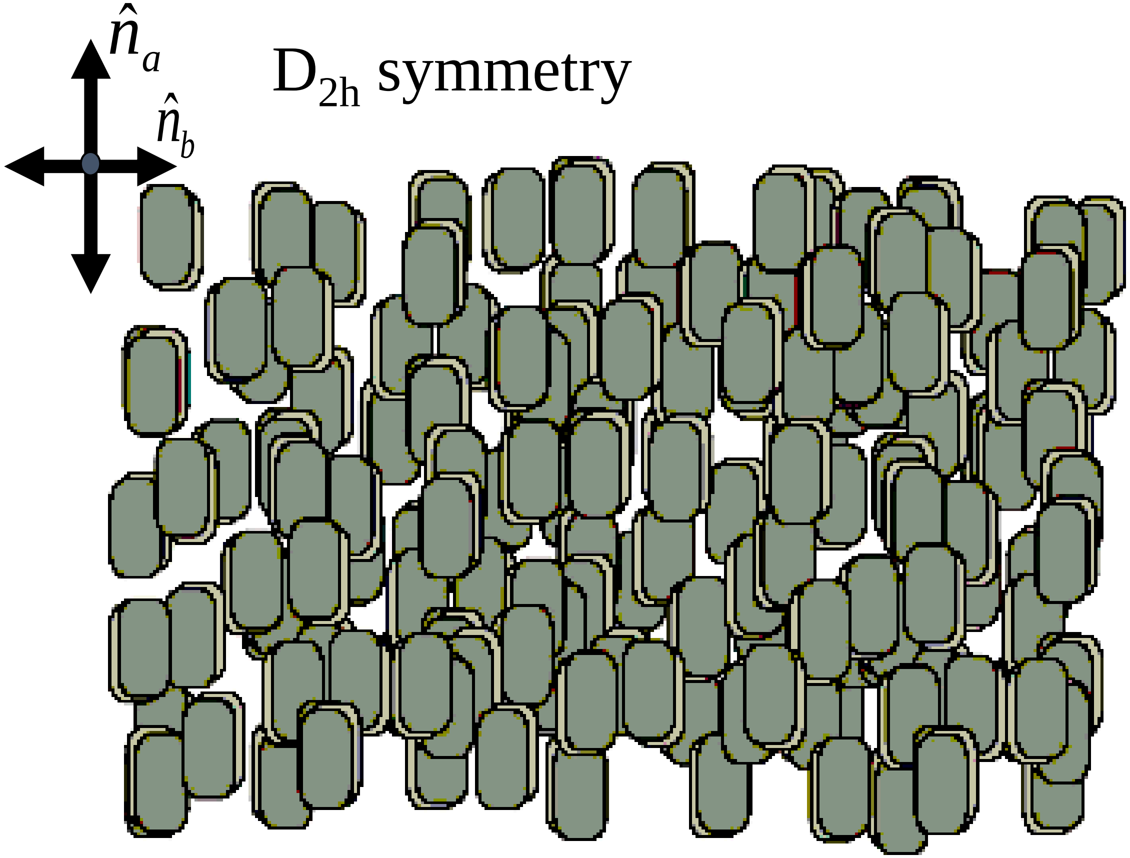
Uniaxial nematics



$D_{\infty h}$ symmetry

Biaxial nematic fluids

D_{2h} symmetry

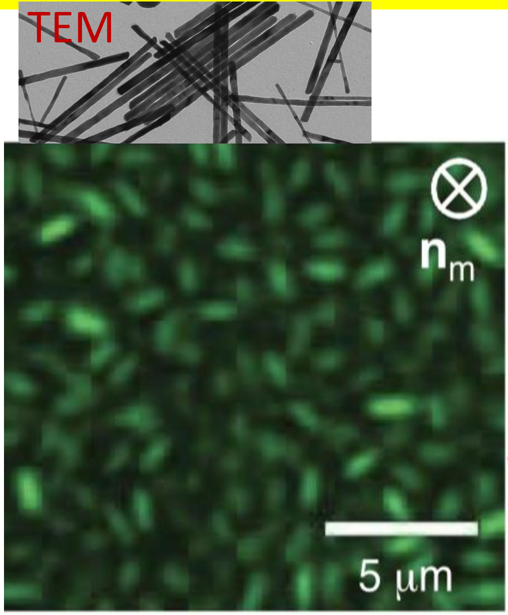


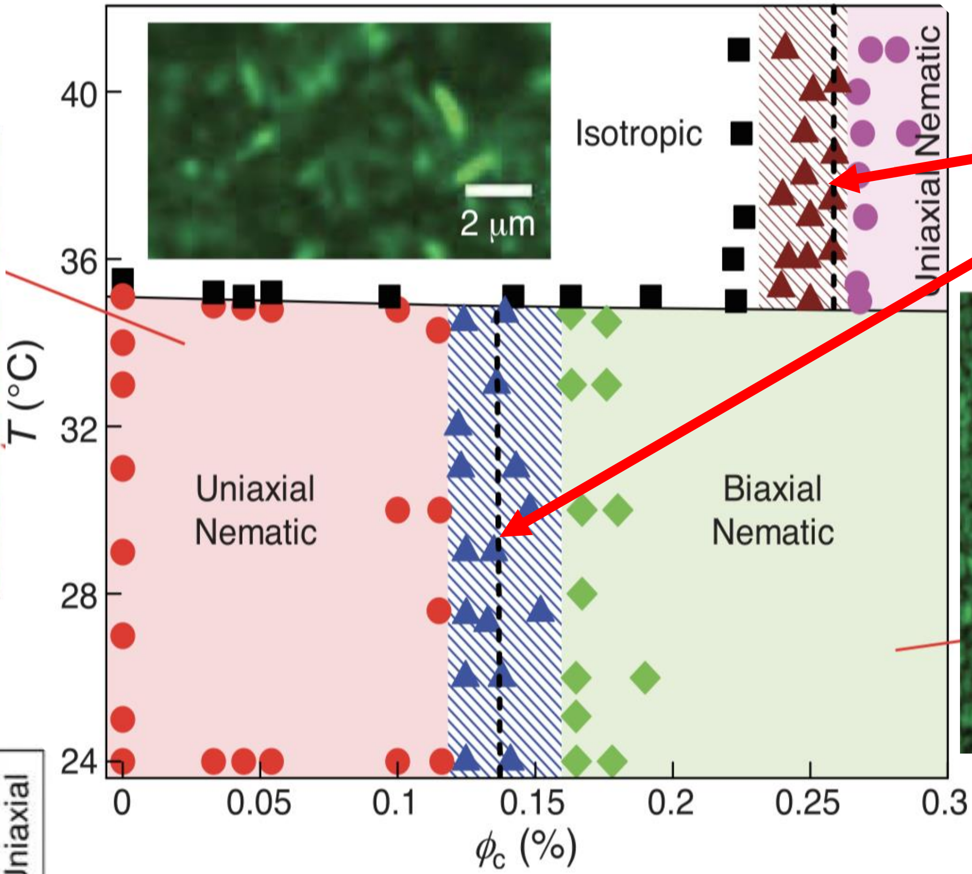
M.J. Freiser. PRL **24**,1041 (1970)

→Somewhat like ”Higgs Bosons” of Soft Matter

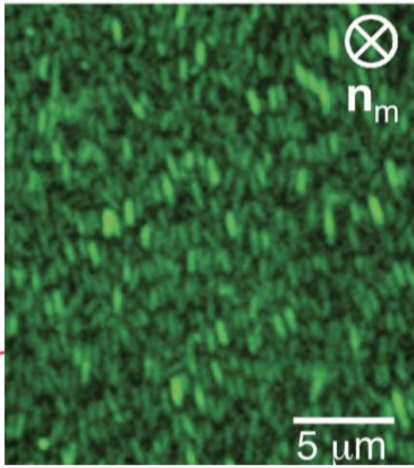
→50-year of search & studies in micellar, colloidal & molecular systems…

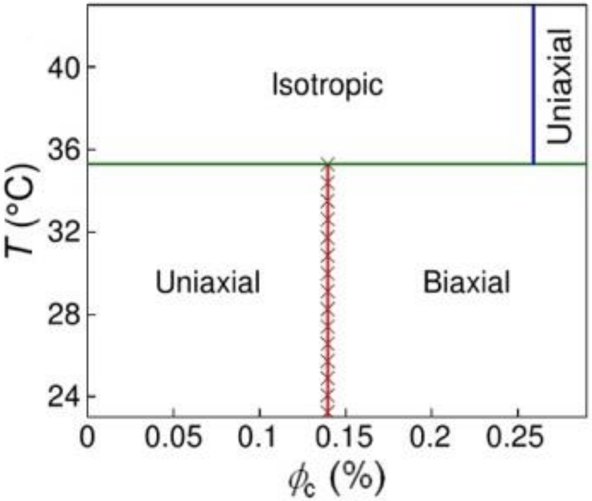
Molecular-colloidal orthorhombic biaxial nematic





$$\frac{\phi_{\mathrm{cIN}}}{\phi_{\mathrm{cUB}}} \approx 1.9$$



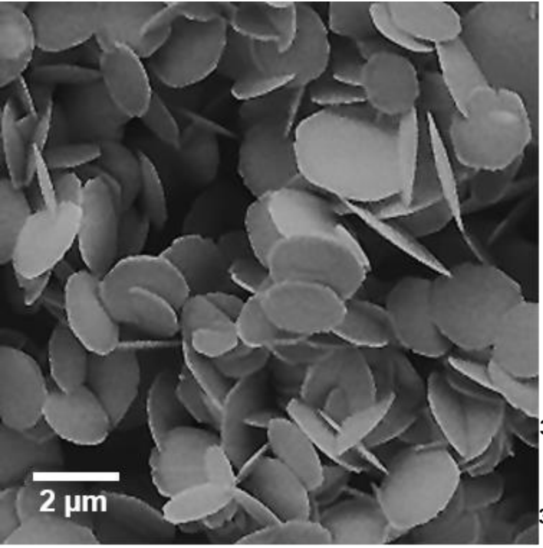


→Modified Onsager model
→In presence of LC-colloid interaction potential
→Reduced degrees of freedom of colloidal rods

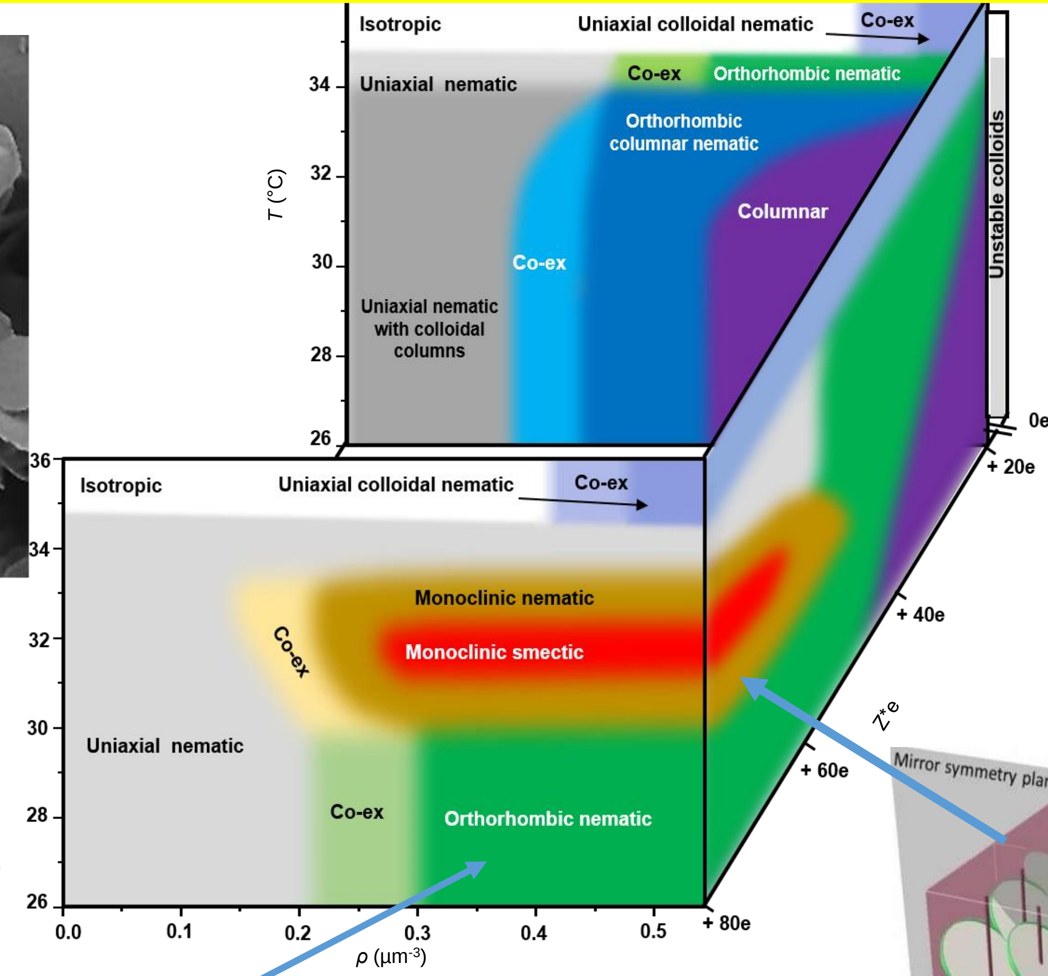
H. Mundoor, S. Park, B. Senyuk, H. Wensink & I.I. Smalyukh. *Science* **360**, 768-771 (2018)

Monoclinic LCs from discs in a nematic host

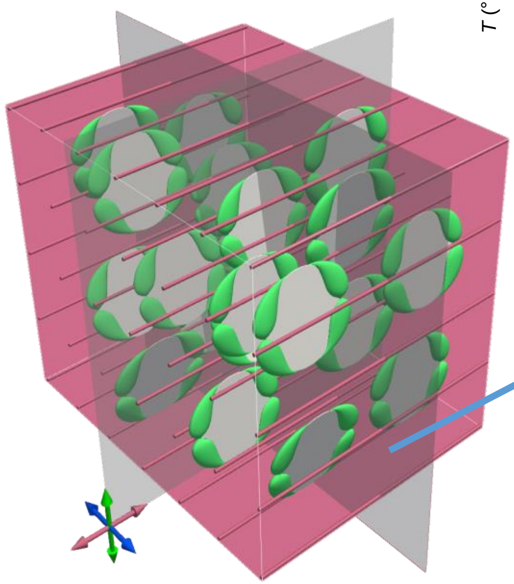
10nm-thick discs

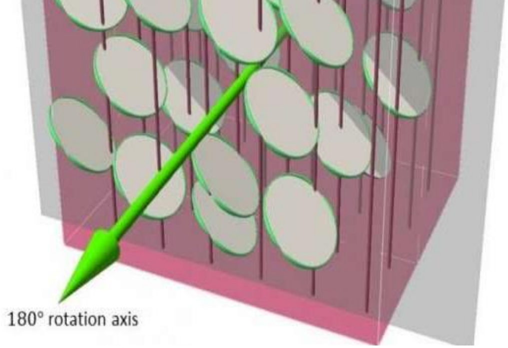


Mundoor, Wu, Wensink, Smalyukh.
Nature **590**, 268-274 (2021)



My conference talk in May at KITP



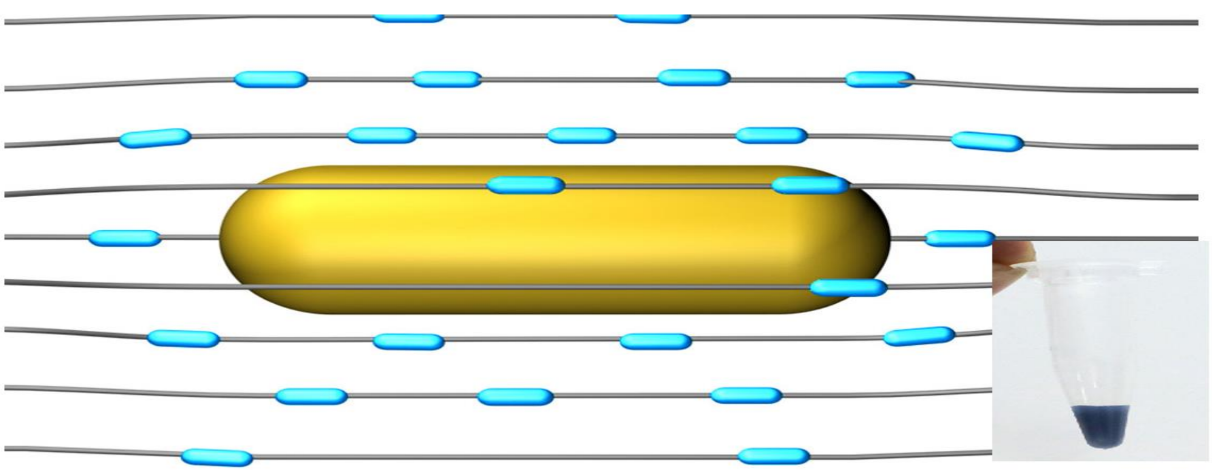


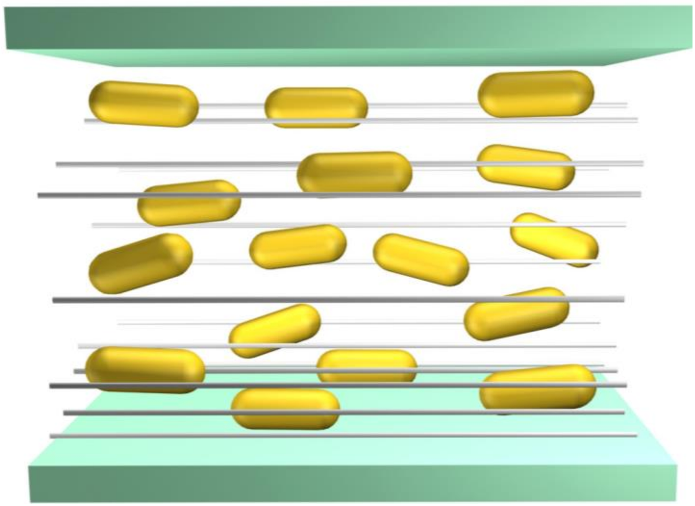
Open questions:

Can we achieve a triclinic nematic?
What other symmetries of nematic fluids & other LCs can be realized?

Nanoparticle-enabled emergent physical behavior?

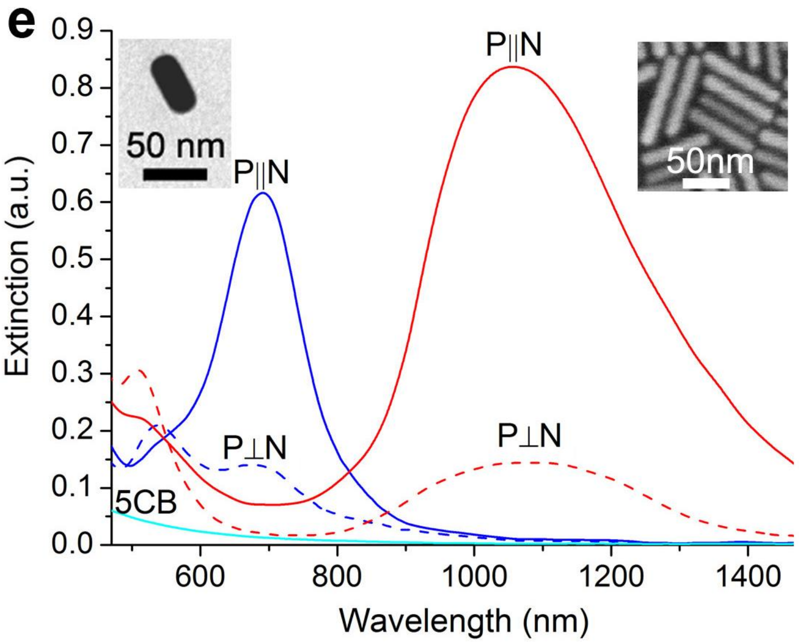
Gold nanorods (GNRs) aligned in a thermotropic LC (5CB...)

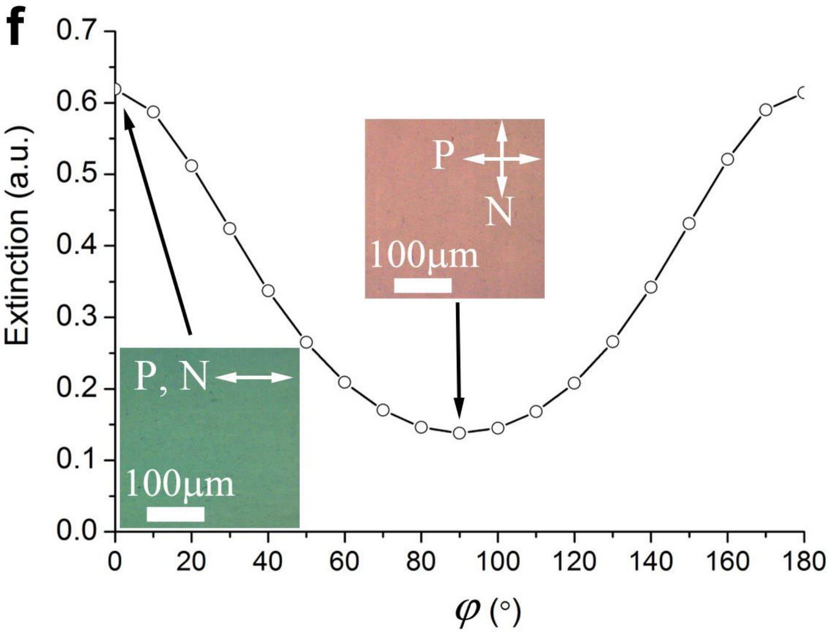




→Alignment yields strong polarization sensitivity;
→PEG-functionalized, ~1vol% in 5CB

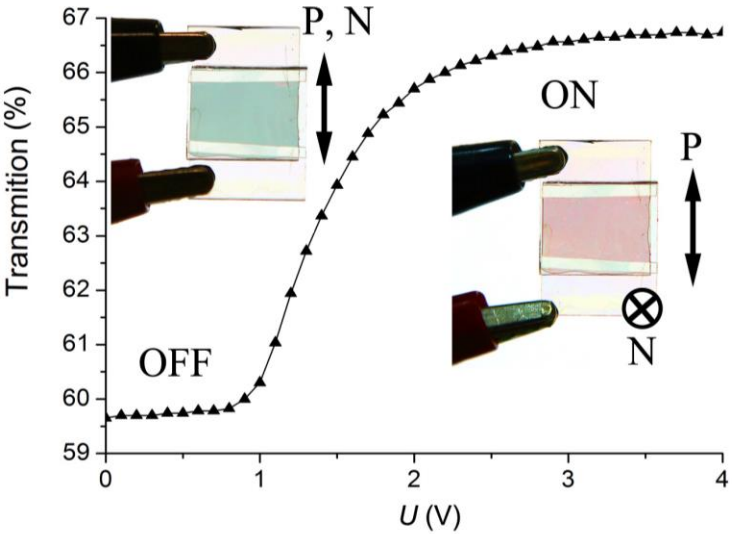
Q. Liu, Y. Yuan, and I. I. Smalyukh.
Nano Lett. 14, 4071–4077

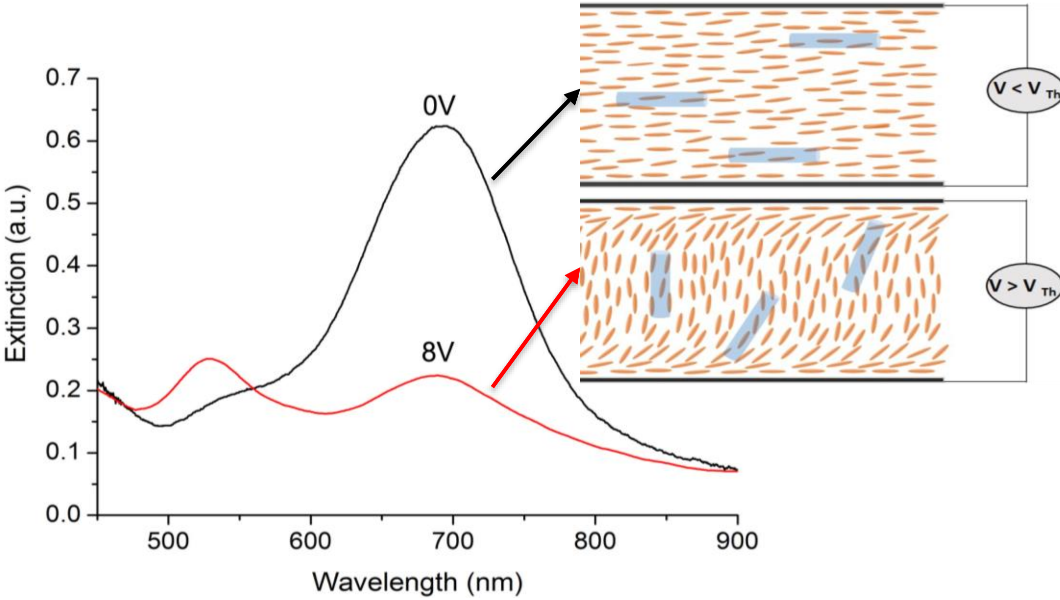




Plasmonic guest-host LCs: electric switching

→Can switch at ~1V

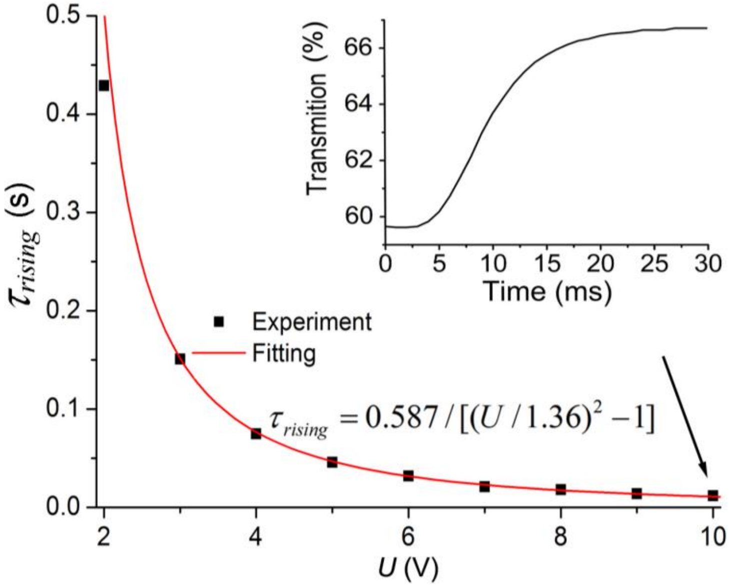


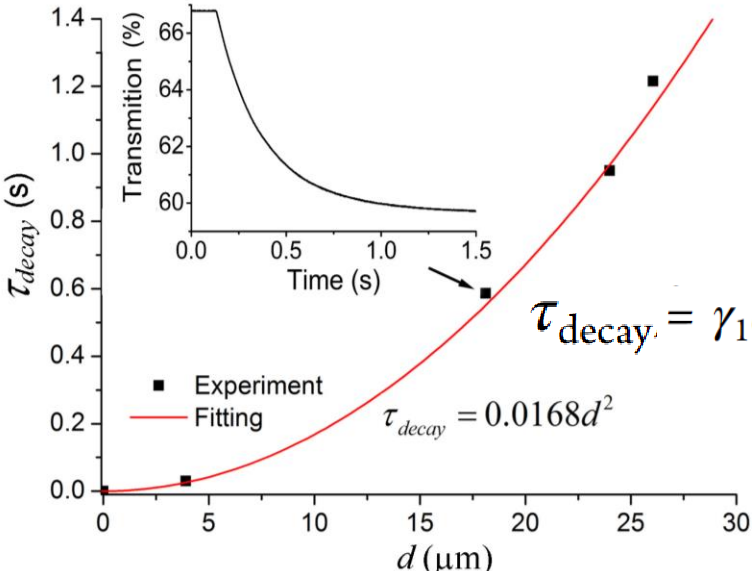


→GNRs follow the director

→Switching response times comparable to that of LCs

$$\tau_{\text{rising}} = \tau_{\text{decay}} / [(U/U_{\text{th}})^2 - 1]$$

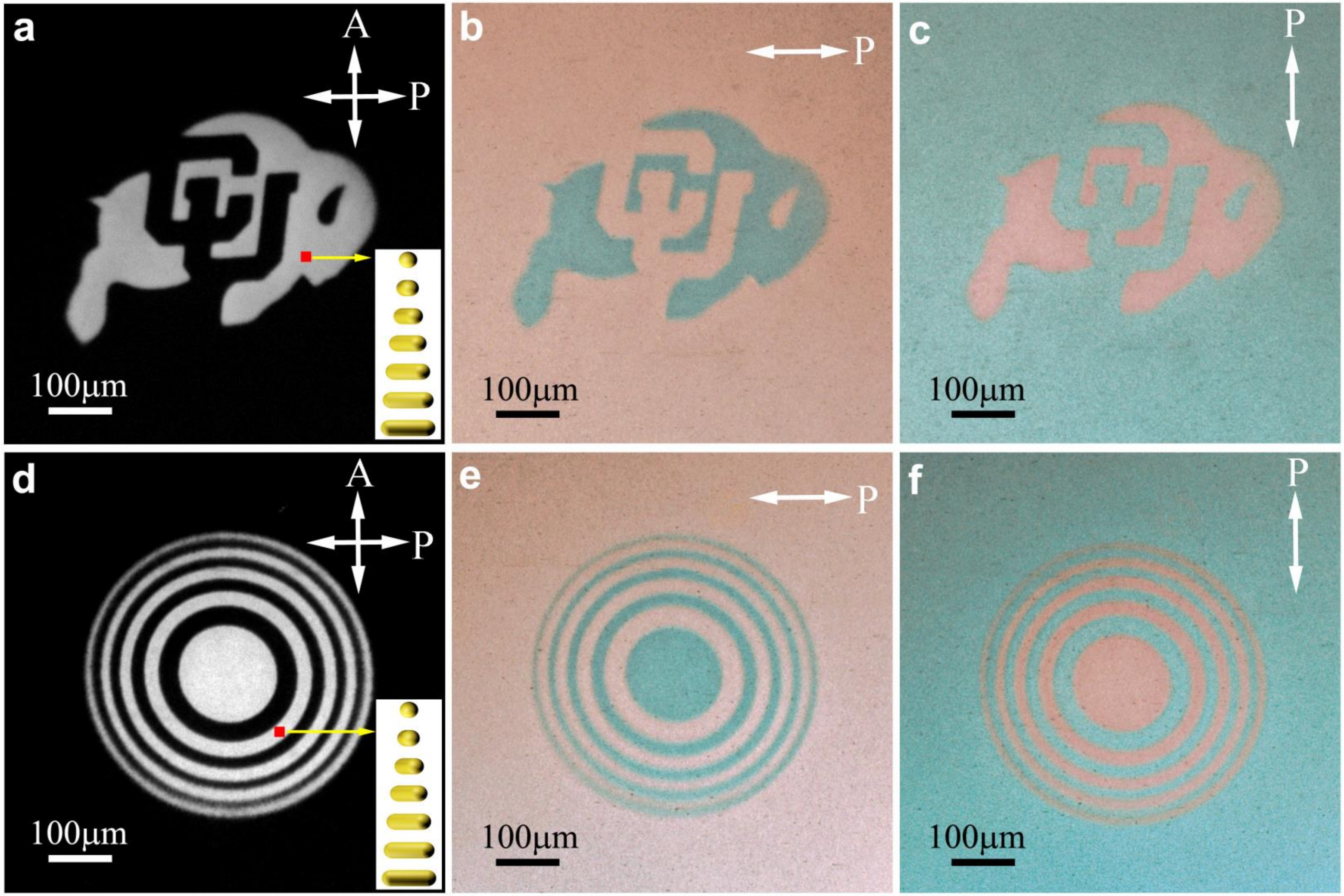




$$\tau_{\text{decay}} = \gamma_1 d^2 / (K_{11} \pi^2)$$

Alignment & dynamic control by photo-responsive layers

→CU – Colorado University;



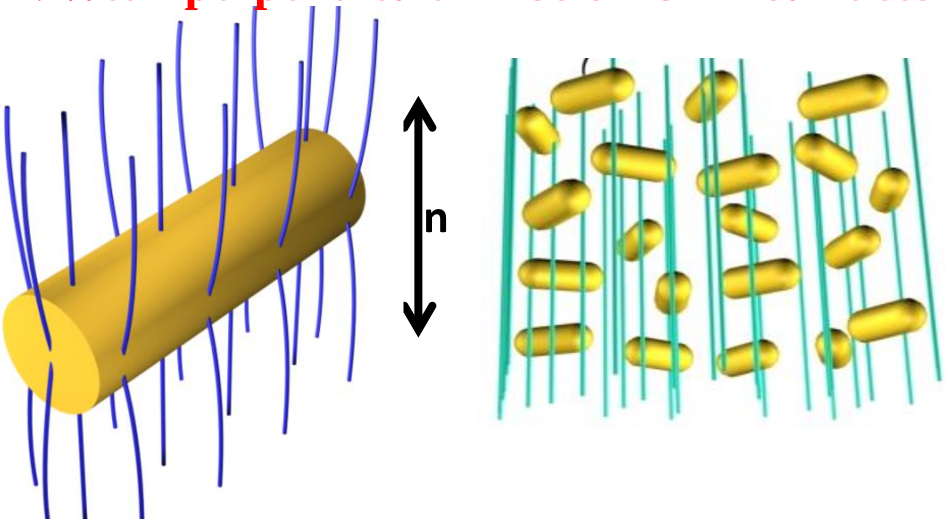
→Polarized illumination of PAAD-22 azobenzene alignment layer;

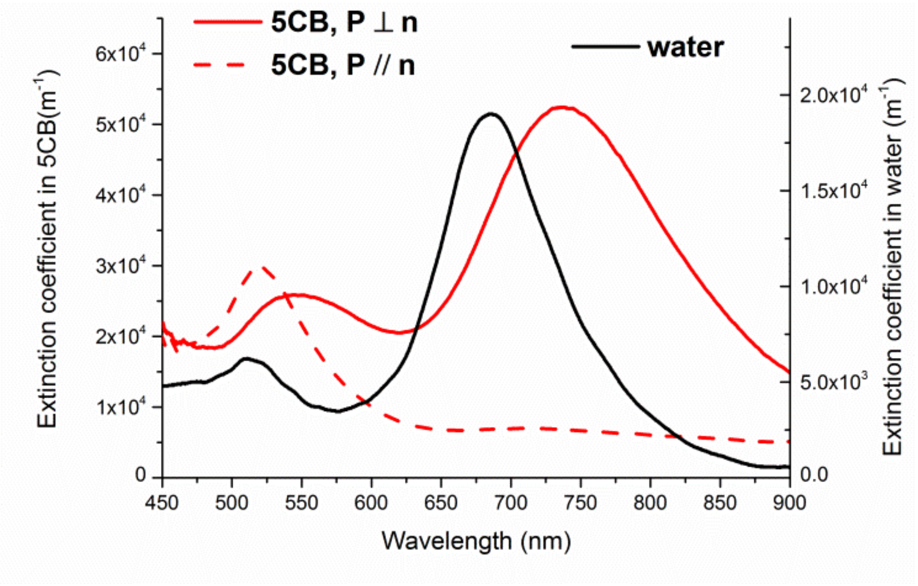
→Twisted domains/patterns in uniform nematic – transverse & longitudinal modes

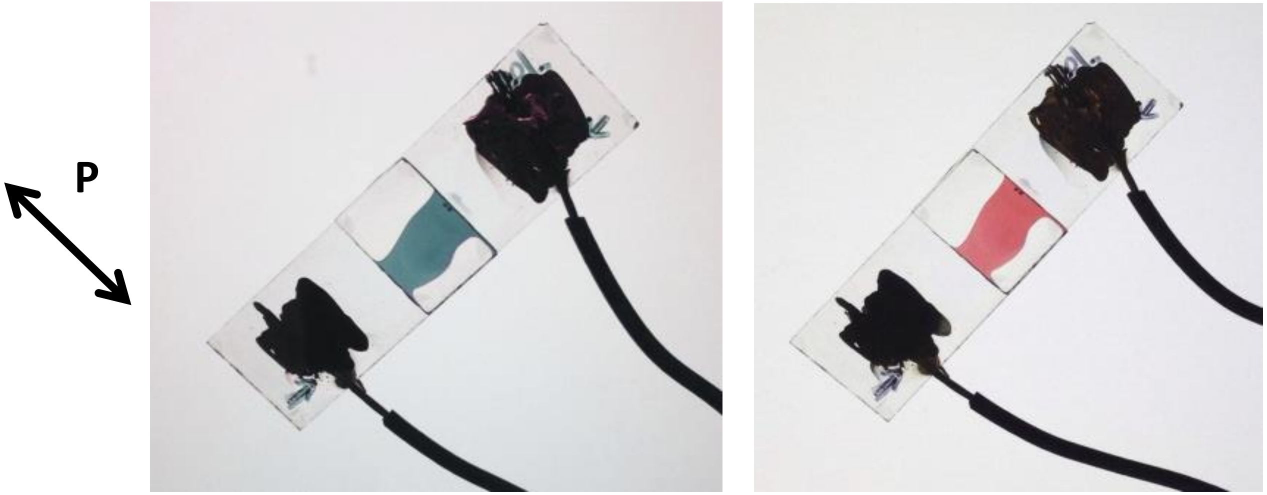
Q. Liu, Y. Yuan, and I. I. Smalyukh. Nano Lett. 14, 4071–4077.

Perpendicular boundary conditions & alignment of GNRs

→Weak perpendicular BCs on GNR surfaces





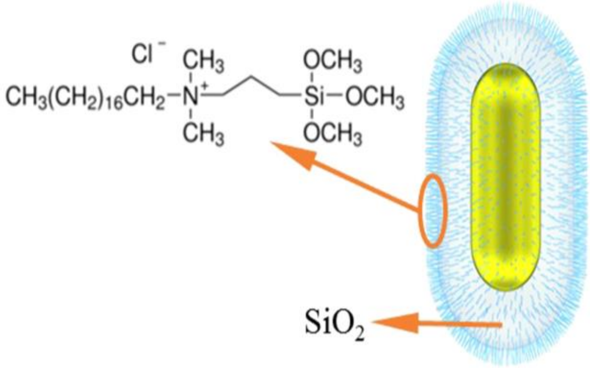


→Alignment & switching guided by LC

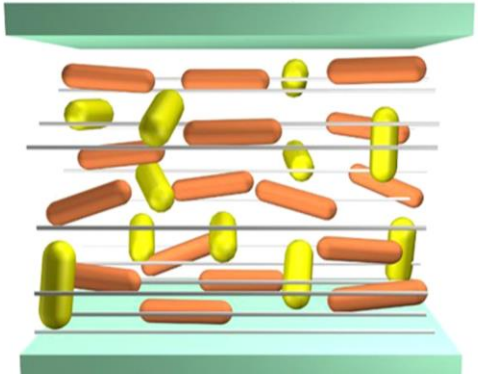
Y. Zhang, Q. Liu, H. Mundoor, Y. Yuan, I. I. Smalyukh. *ACS Nano* **9**, 3097-3108.

Switching of Orthogonally Aligned Plasmonic Nanorods

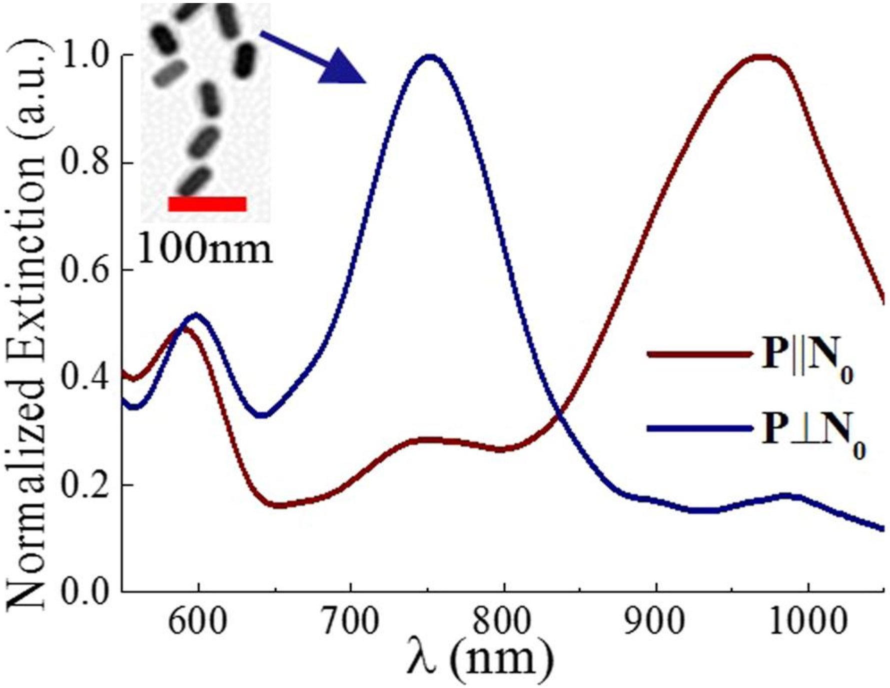
→DMOAP surfactant treatment

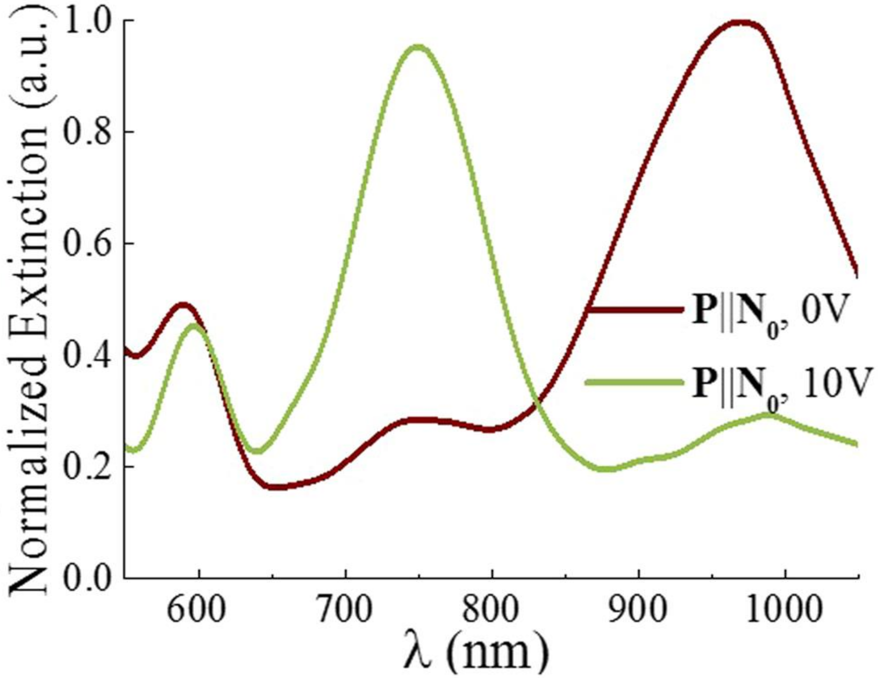


→Orthogonal ordered colloidal co-dispersion

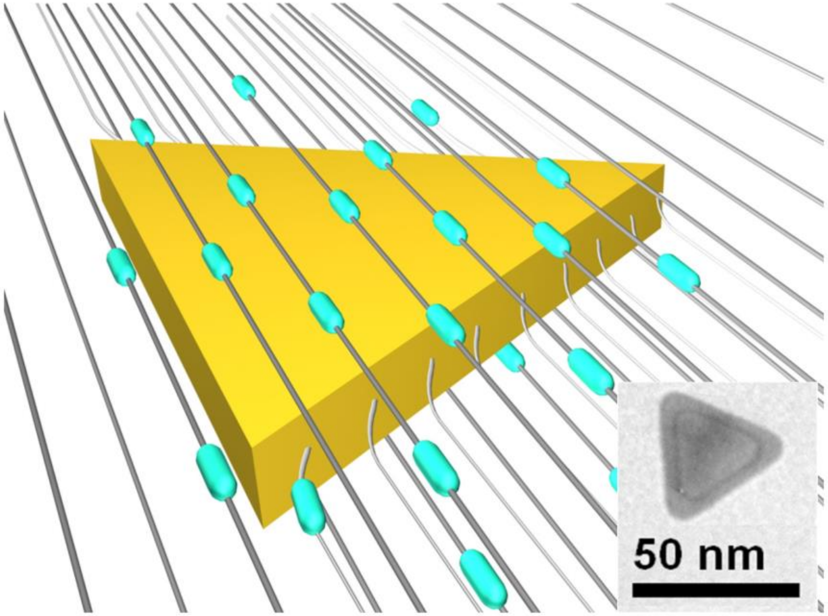


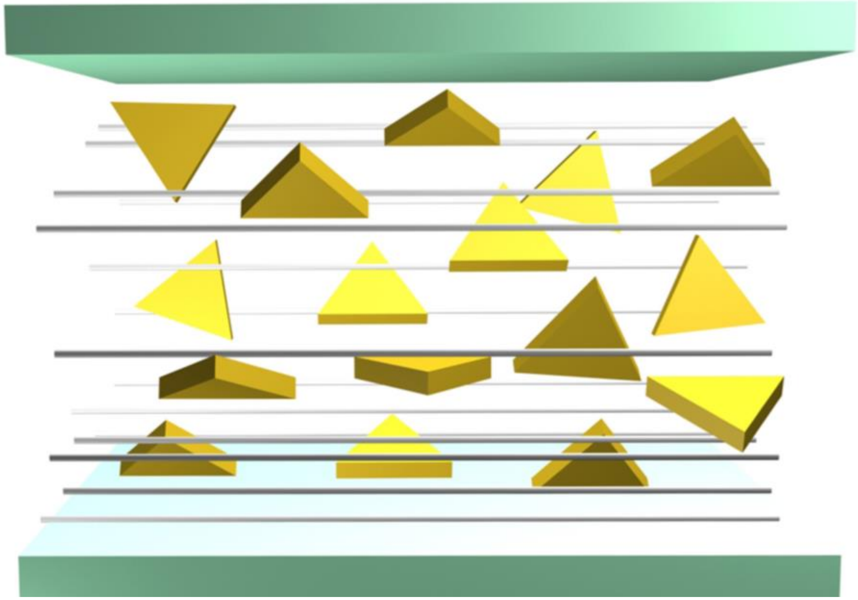
→Polarization dependence & electric switching of spectra



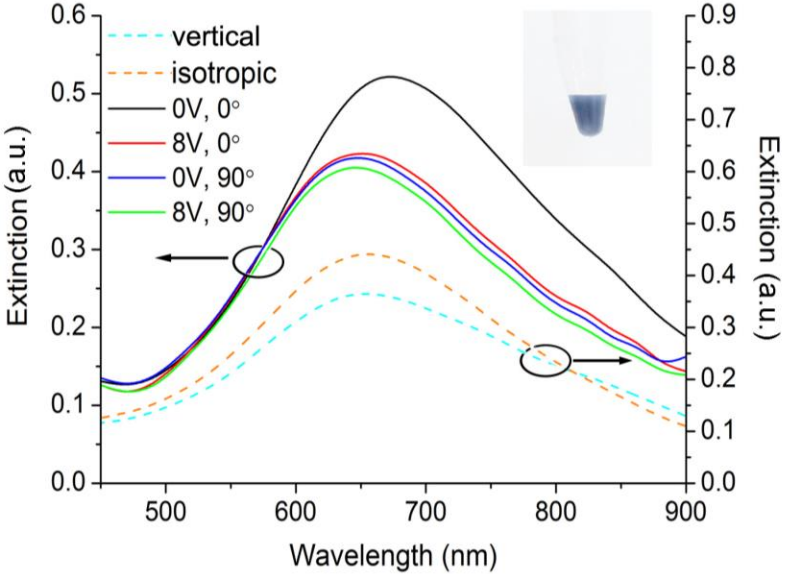


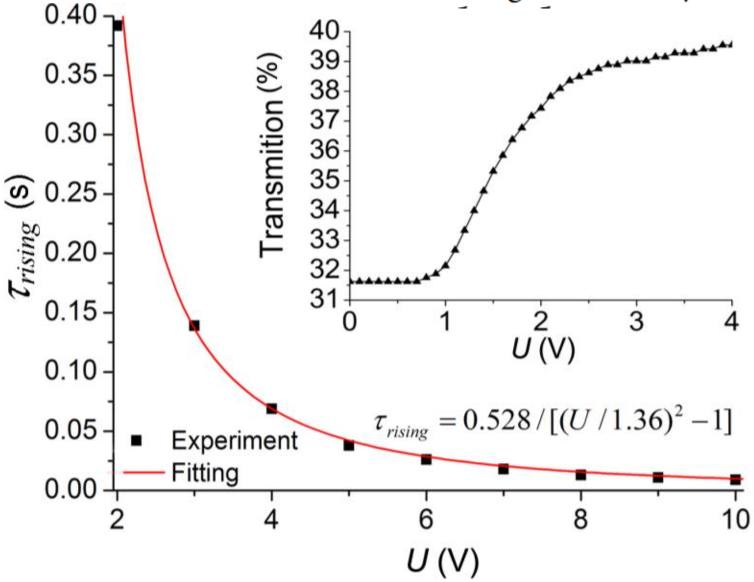
Alignment of polygonal (e.g., triangular) nanoplatelets



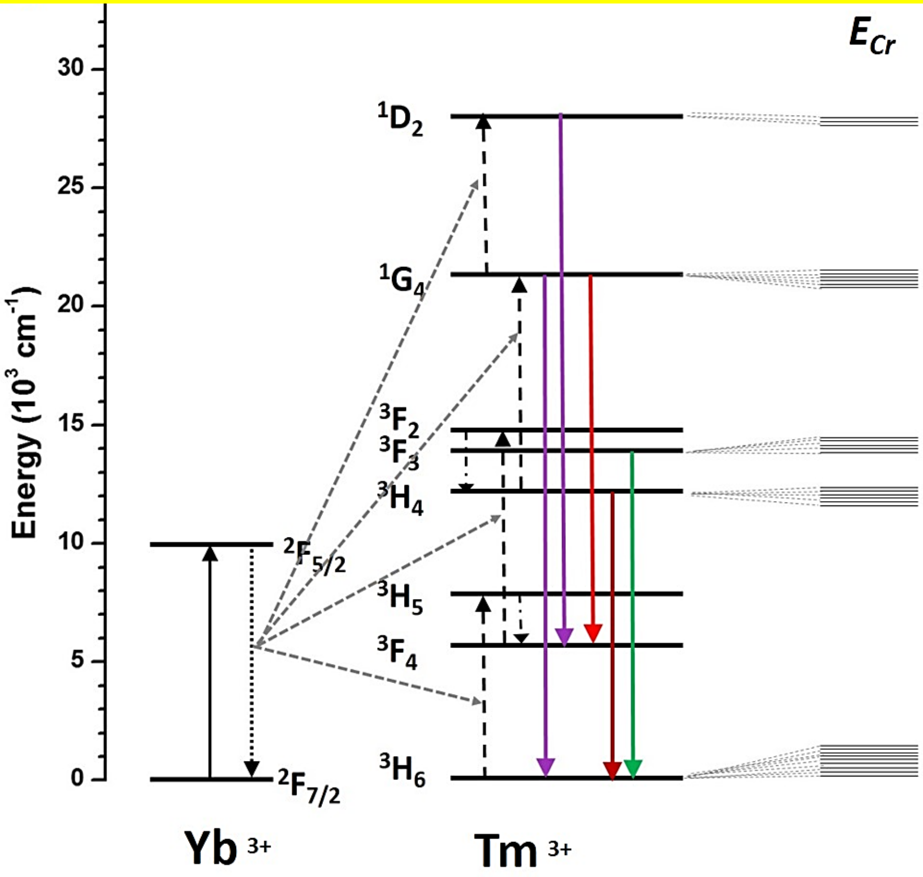


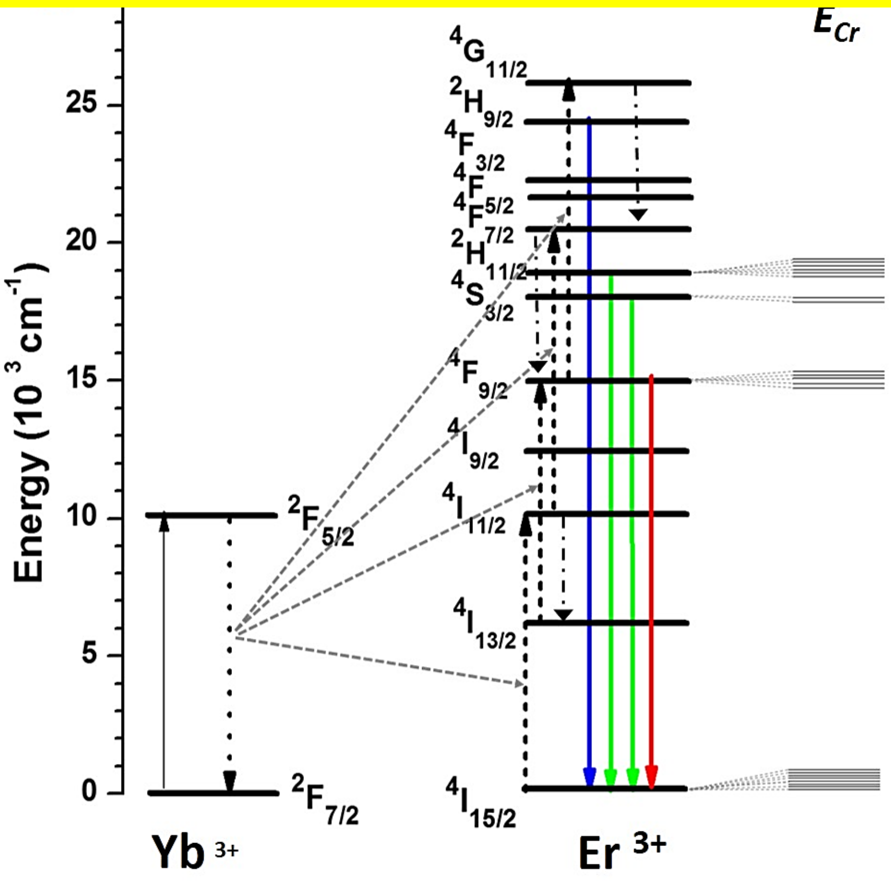
→Orientational ordering & electric response: $\tau_{\text{rising}} = \tau_{\text{decay}}/[(U/U_{\text{th}})^2 - 1]$



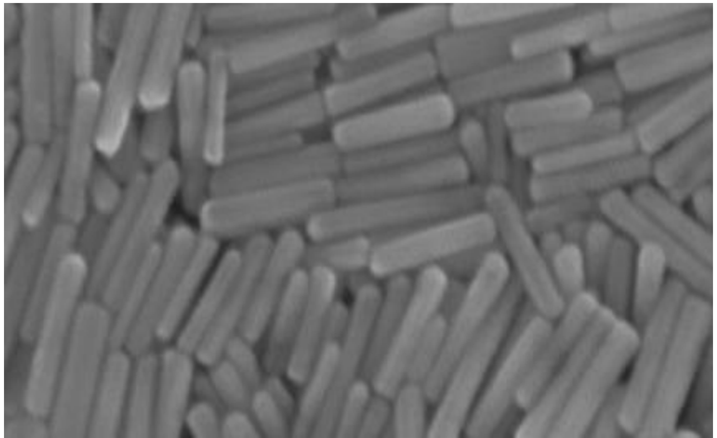


Upconversion semiconductor nanorods (infrared->visible)

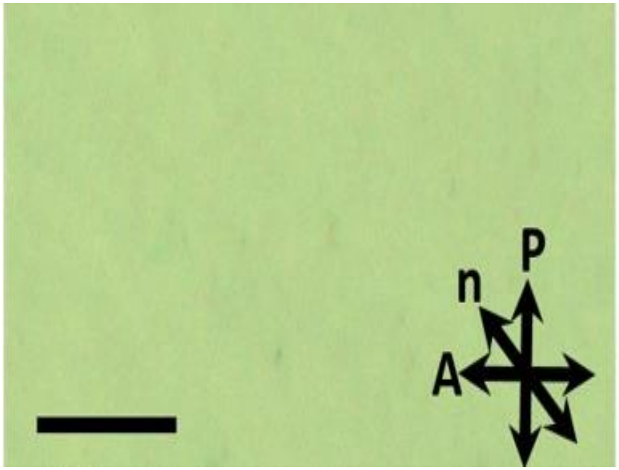


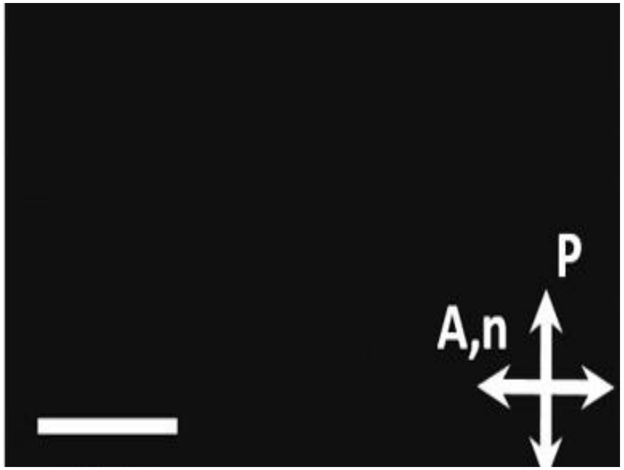


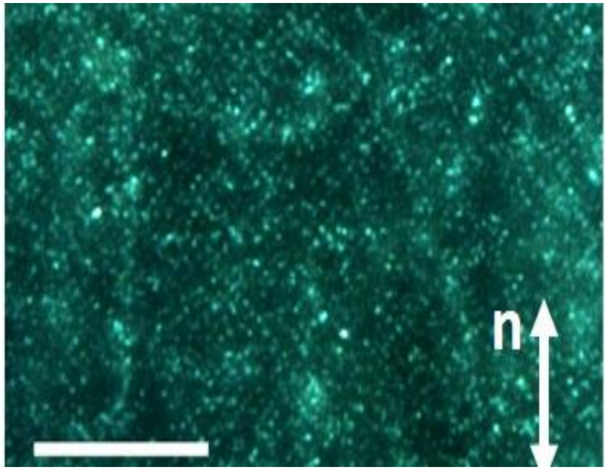
→Energy level diagram for the upconversion process
→ through energy transfer from Yb3+ Ions to Tm 3+ & Er3+ ions
→β-NaYF4 doped by 30%Gd3+, 18%Yb3+, 2%Tm3+



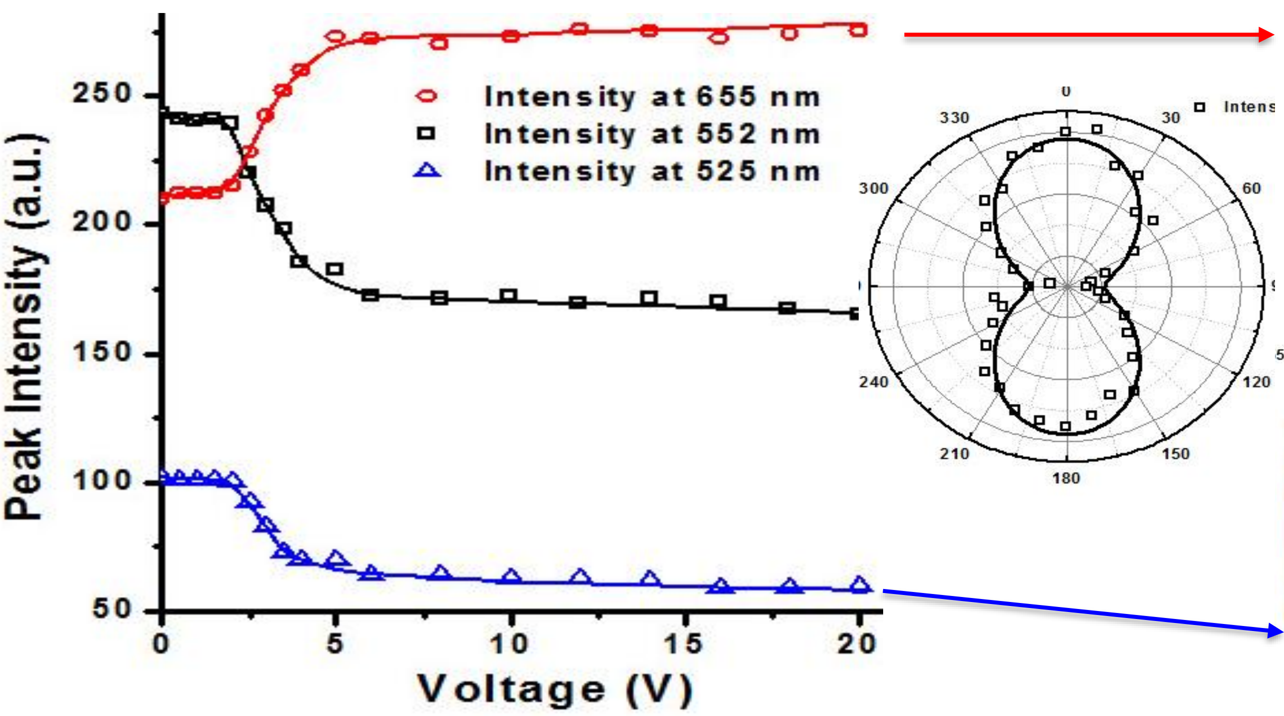
Upconversion nanorods dispersed in 5CB

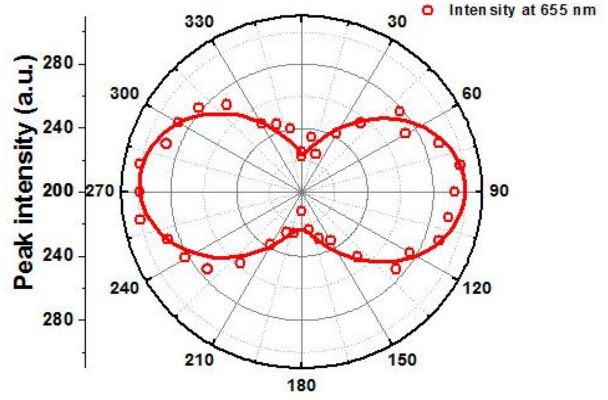


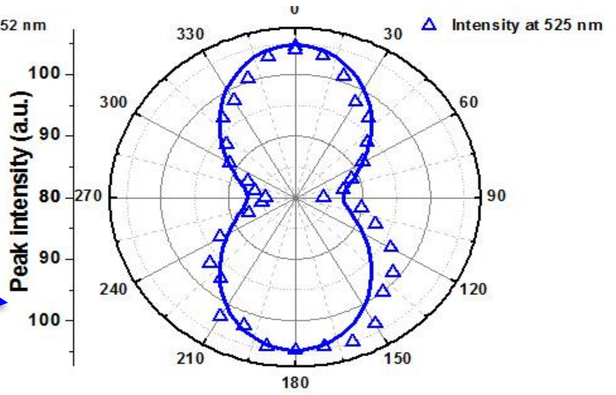




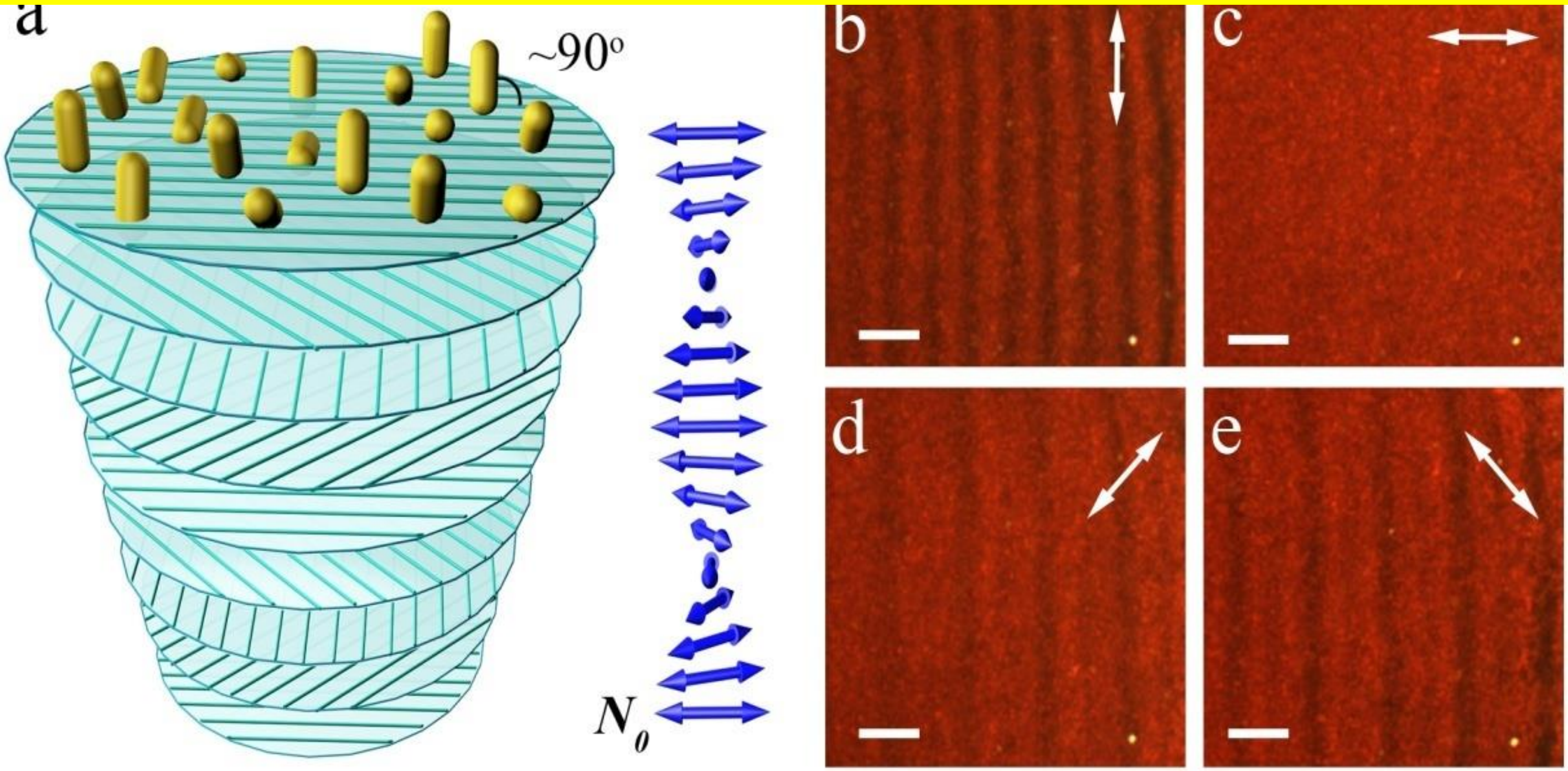
Electric switching & polarization dependencies



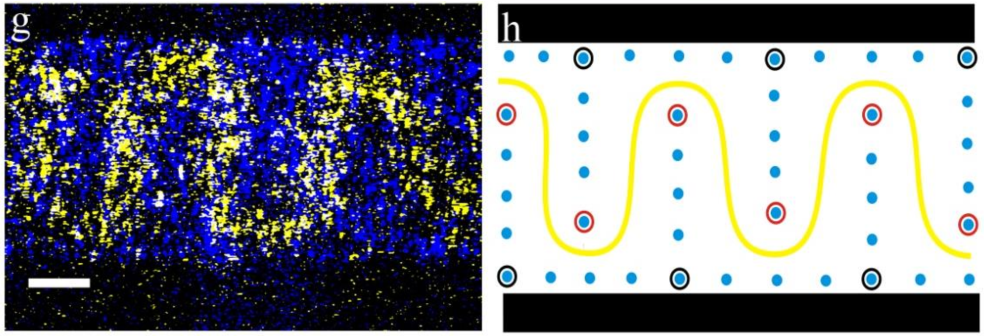




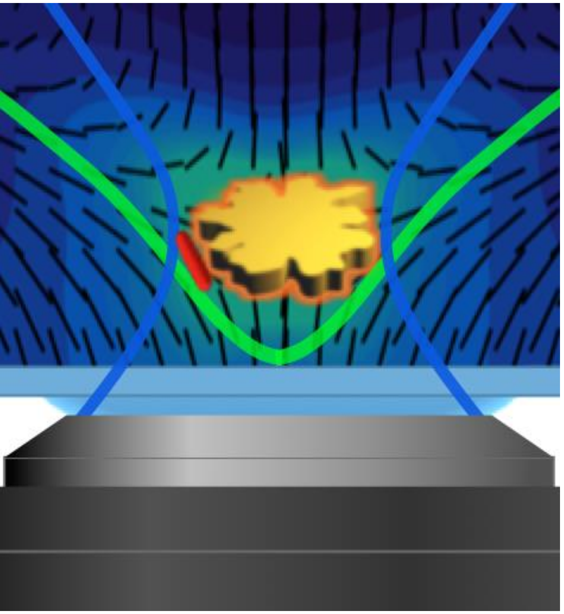
Chiral nematic assemblies with negative scalar orientational order parameter of GNRs in LC



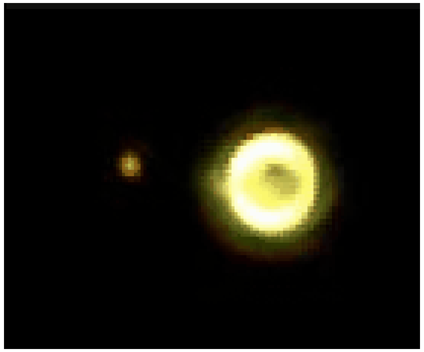
→By applying fields or mechanical stresses – further control patterns of nanorods through LC

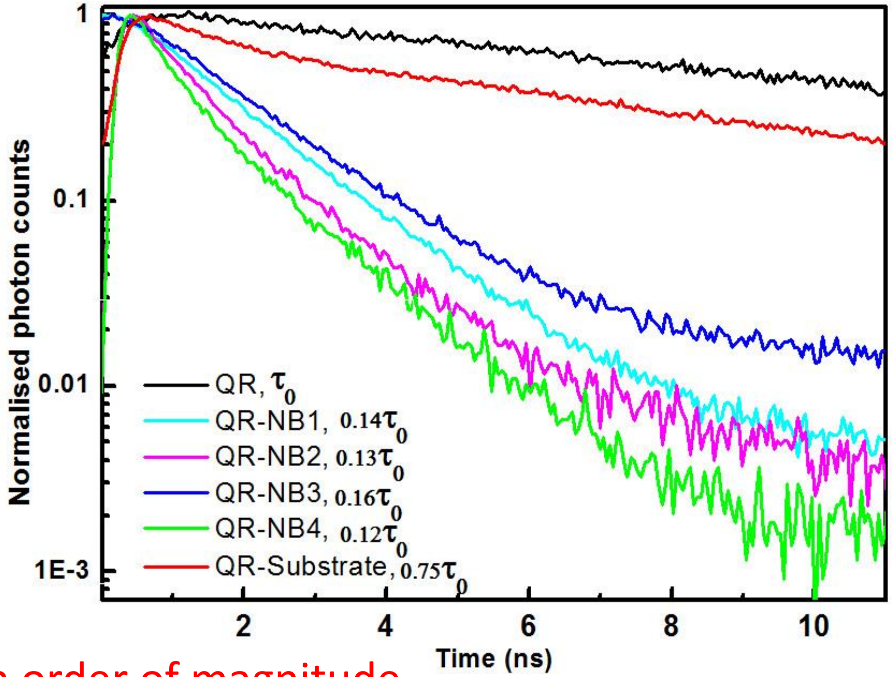


Topological point singularity as a nanolaboratory



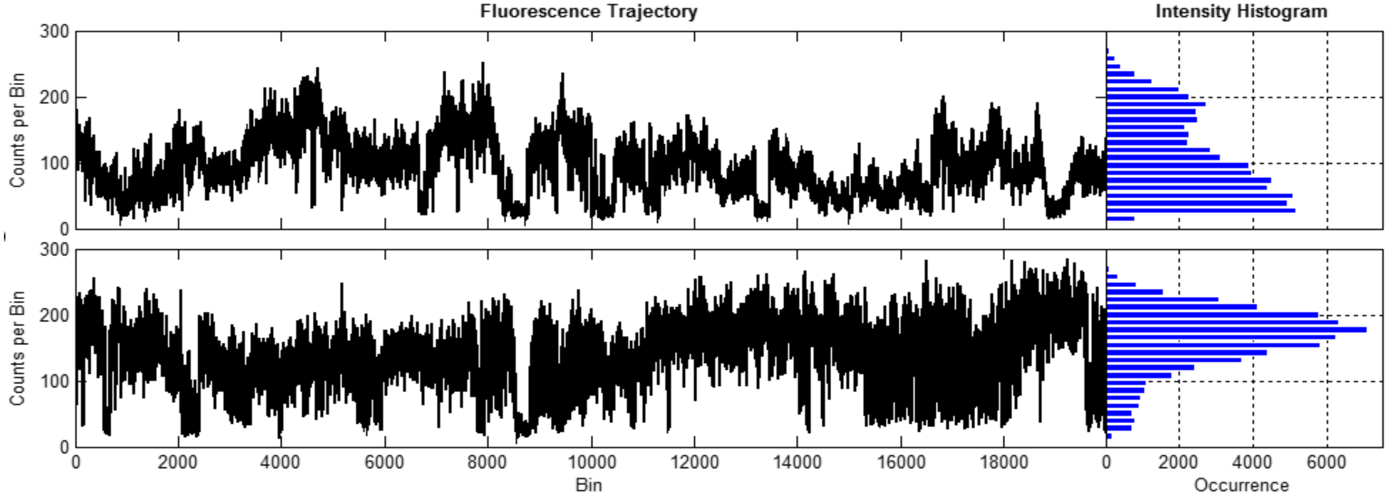
plasmonic NP +QD

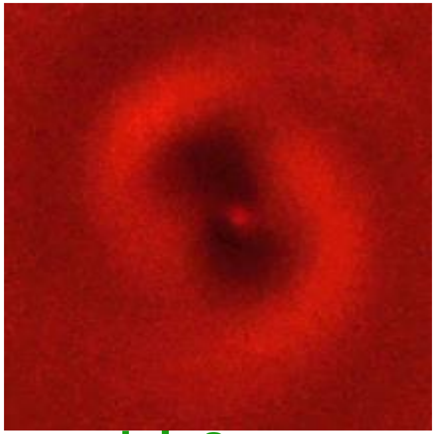




→ Plasmonic effects shorten lifetime by nearly an order of magnitude

→ Modify the quantum dot blinking statistics (increase the on time)



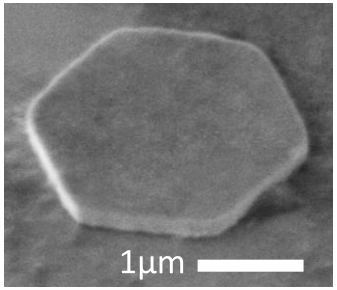


Open question: how to use such emergent effects to make metamaterials?

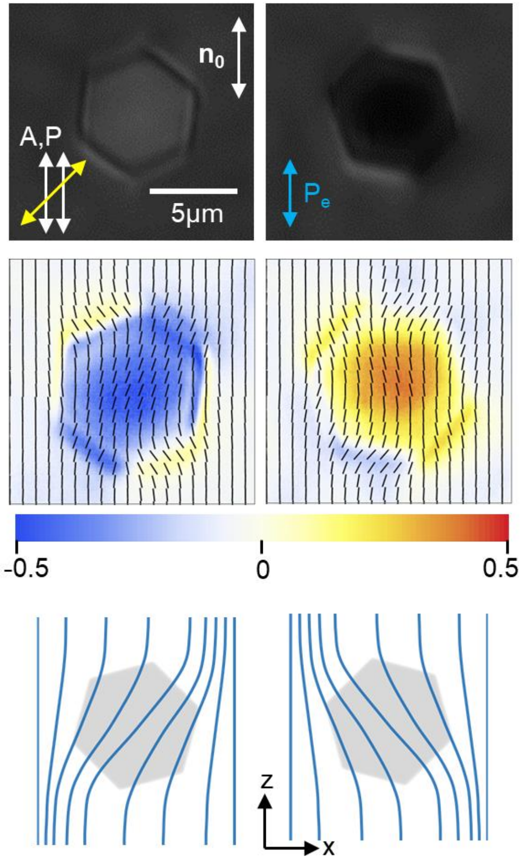
Self-assembled colloidal motors & machines?

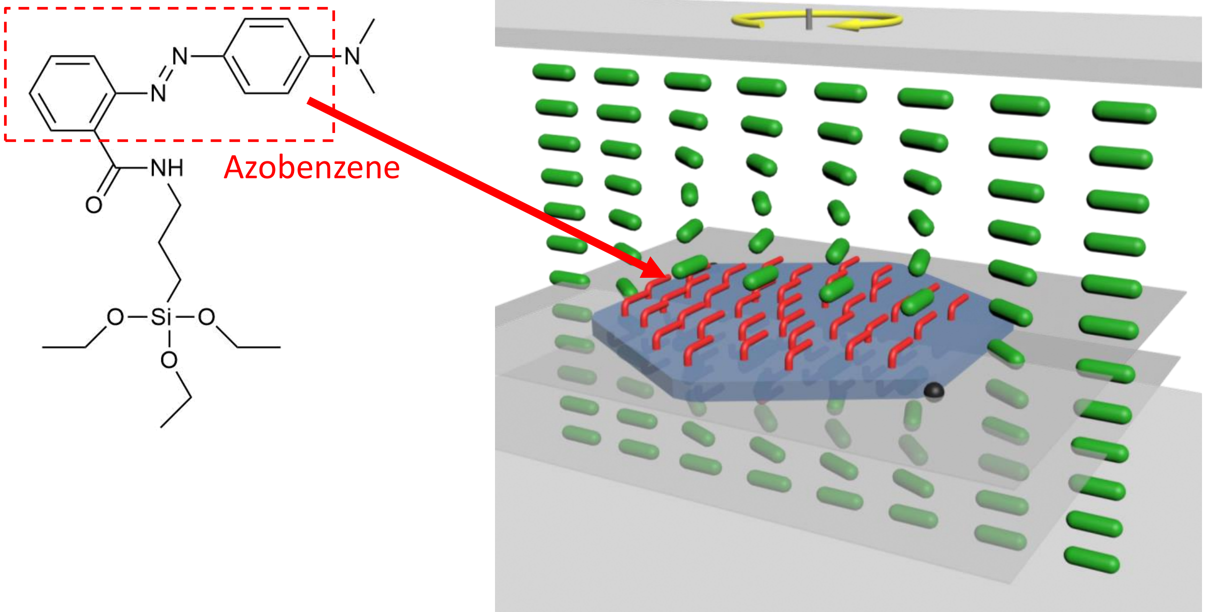
Develop elastic colloidal monopoles/hydrogen

→Silica platelets



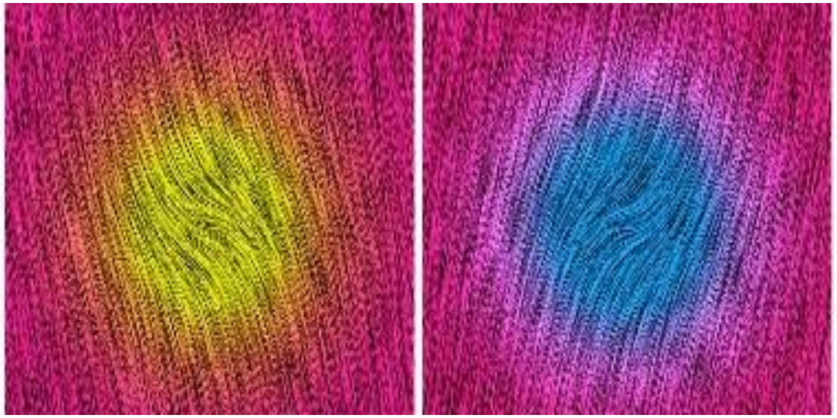
→POM & Polarimetry:





→Low intensity light (<1nW) torques platelets

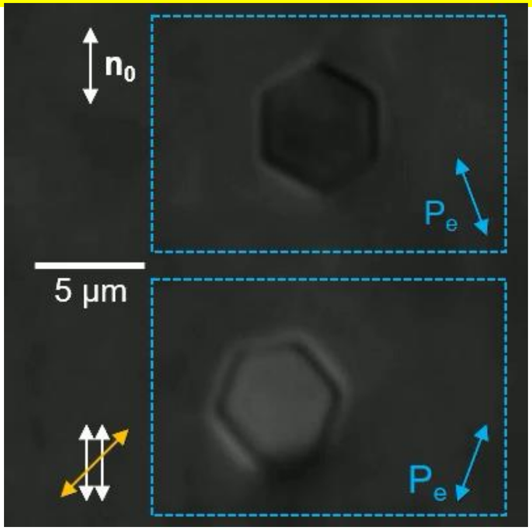
→Symmetry breaking creates elastic monopoles:

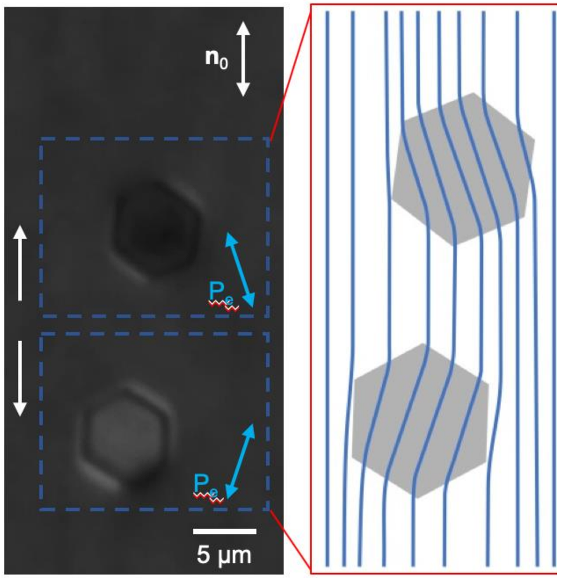


Optical switching of the elastic interactions

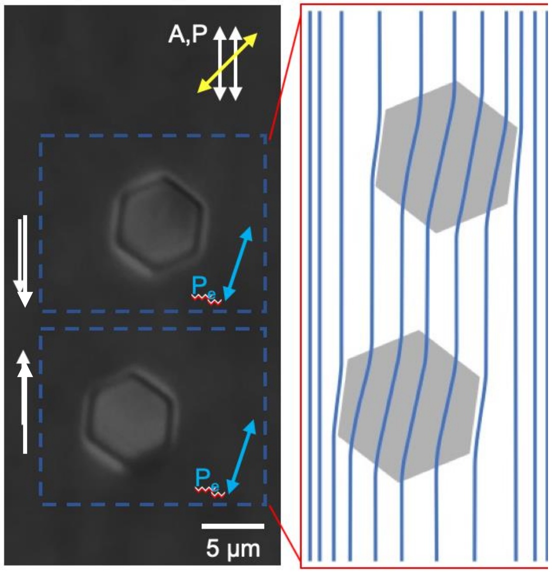
→ **Switch the elastic monopole sign with <1nW light**

→ **Interactions switch between attractive & repulsive**

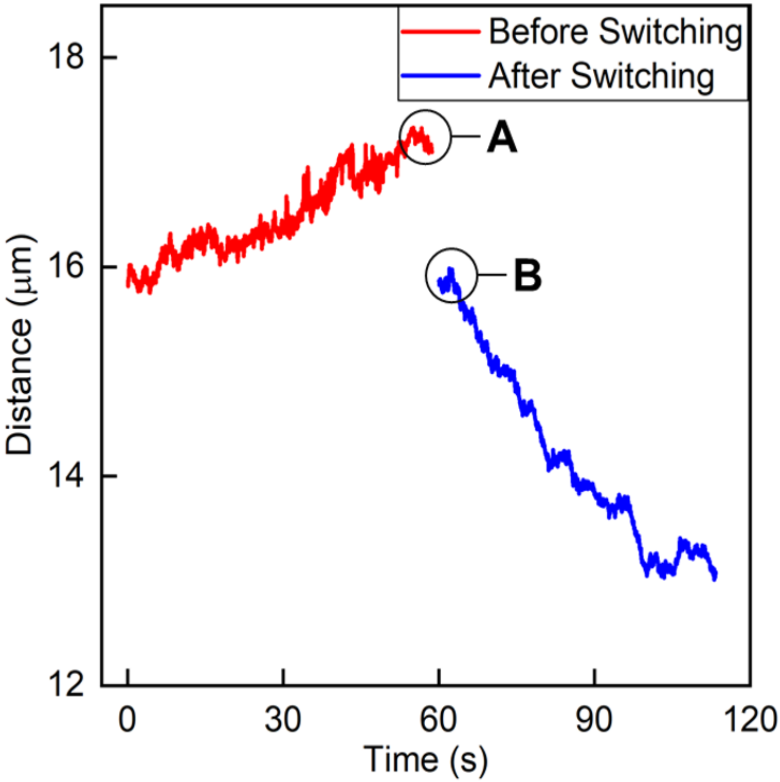




Before switching: repel



After switching: attract

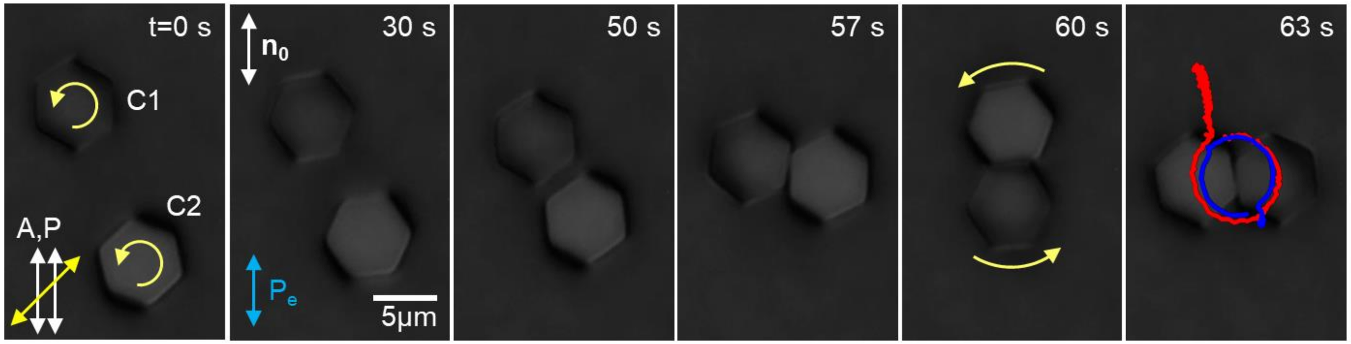


→ **Interactions minimize free energy of elastic distortions**

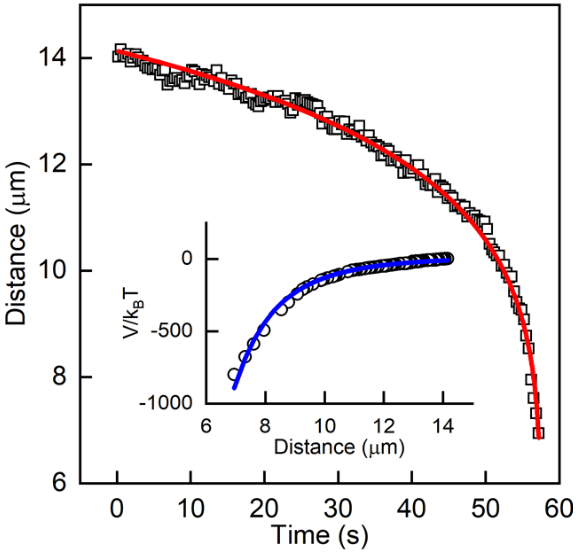
Out-of-equilibrium elastic self-assembly

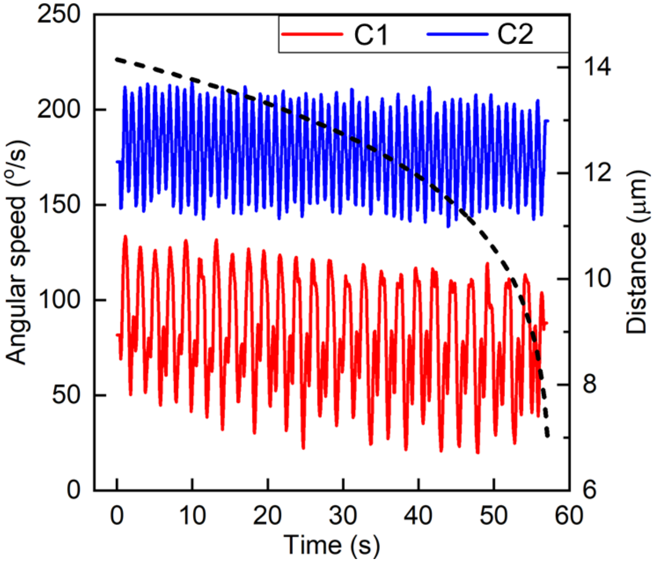
→ **Platelets attract while spinning in the same direction**

→ **The spinning rates are different**



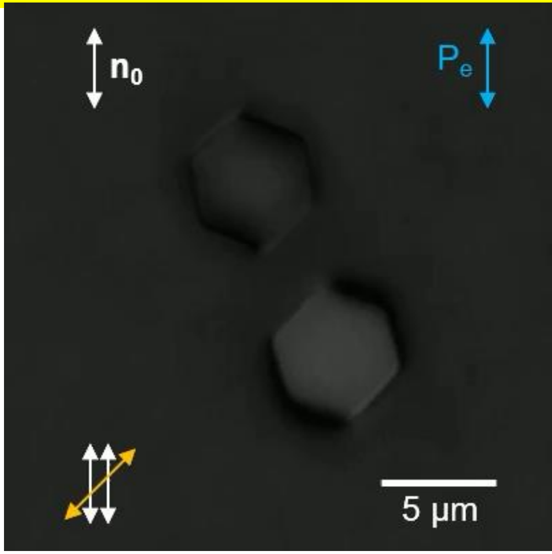
Fitting of $R(t) = (R_0^n - n\alpha_d t)^{1/n}$, n=7



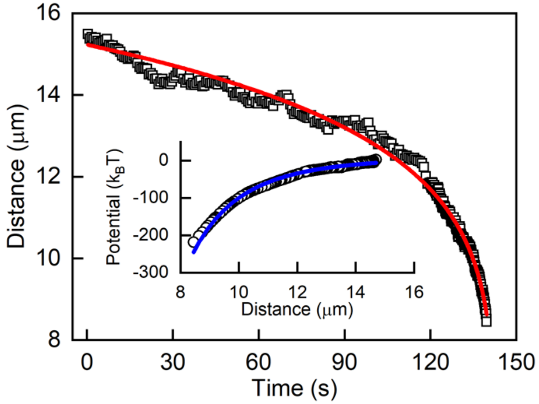


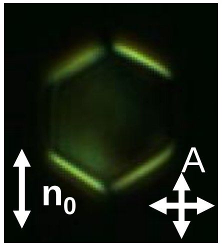
→ **Monopole signs periodically change at different rates**

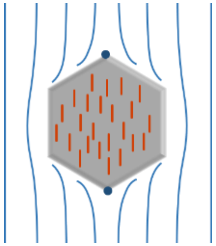
→ **As a result, monopole interactions average out**



→**Like quadrupole interaction in equilibrium**

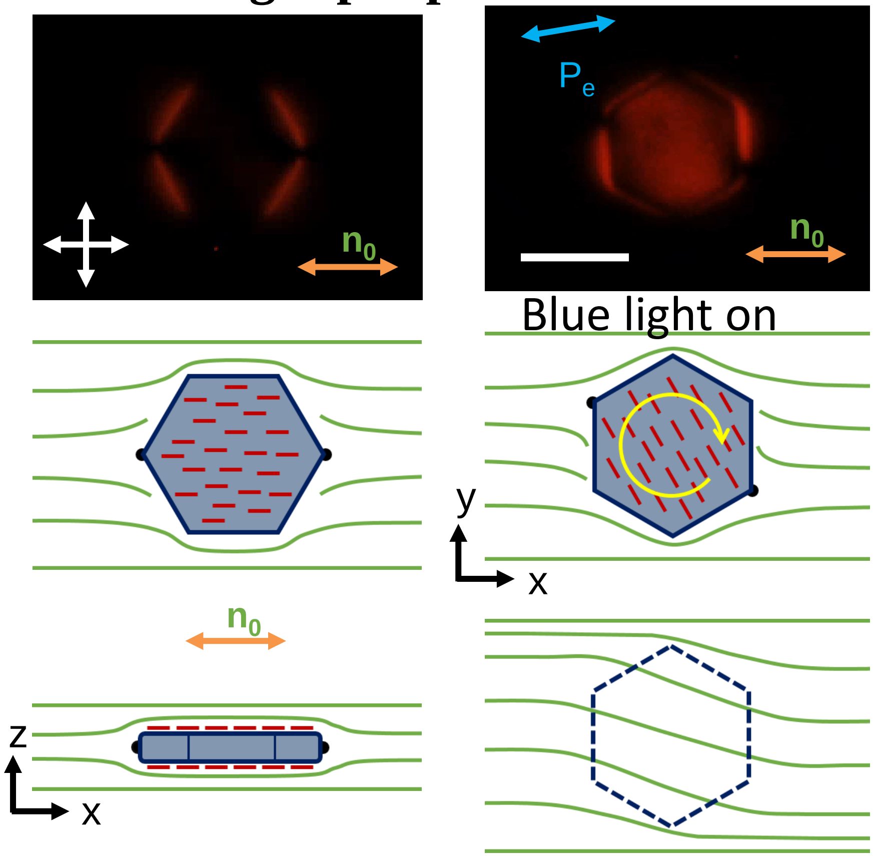


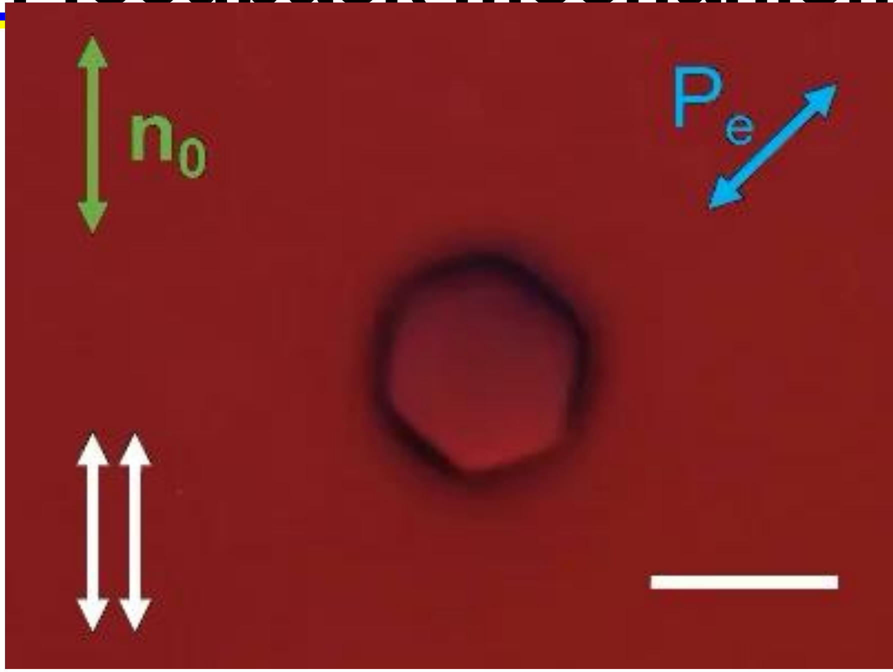


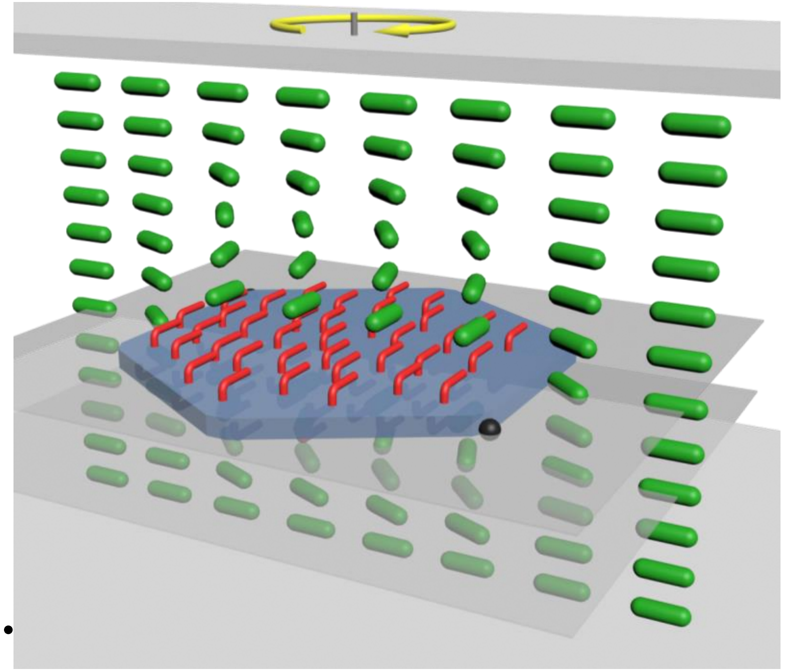


From monopole to motor: feedback mechanism

→ What if we go from <1nW to 2nW light per particle?







Spontaneous feedback mechanism:

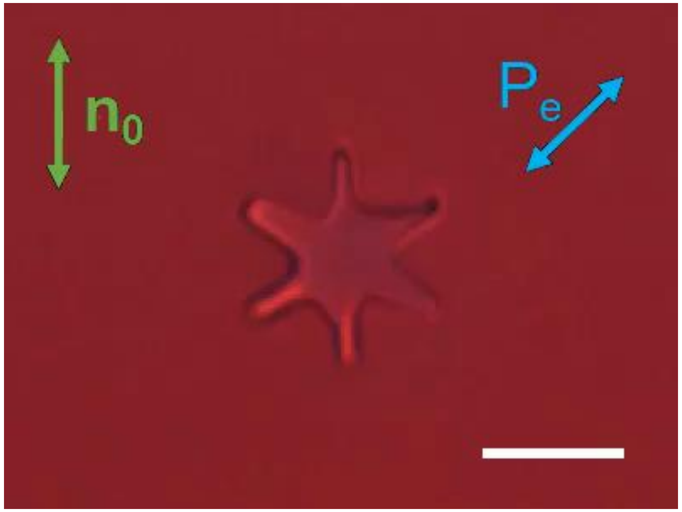
→ Light rotates platelet/dMR & distorts LC

→ LC changes polarization

→ Light rotates platelet more, distorts LC more…

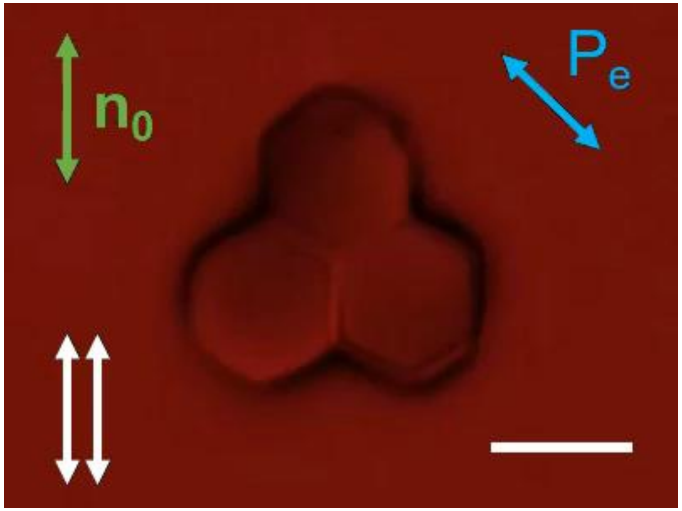
Colloidal shapes & self-assembled structures

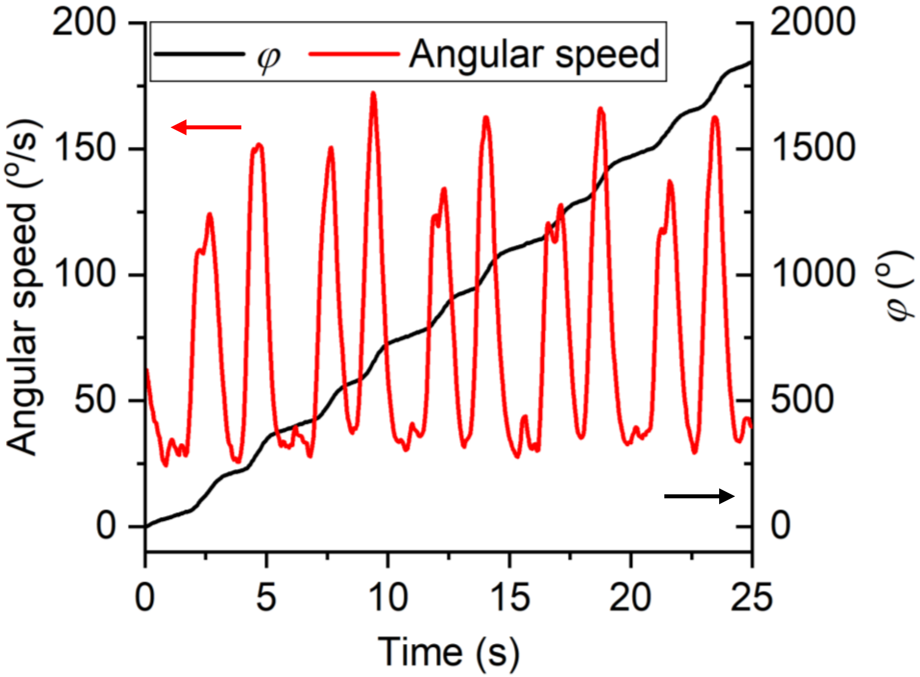
Cogwheel-like

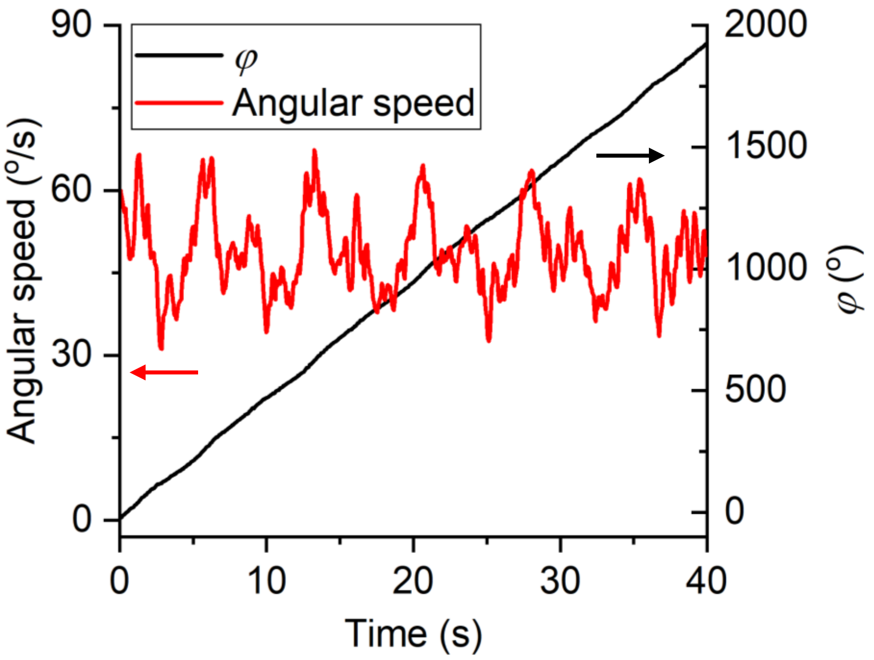


→Both showing periodic rotation

Self-assembly

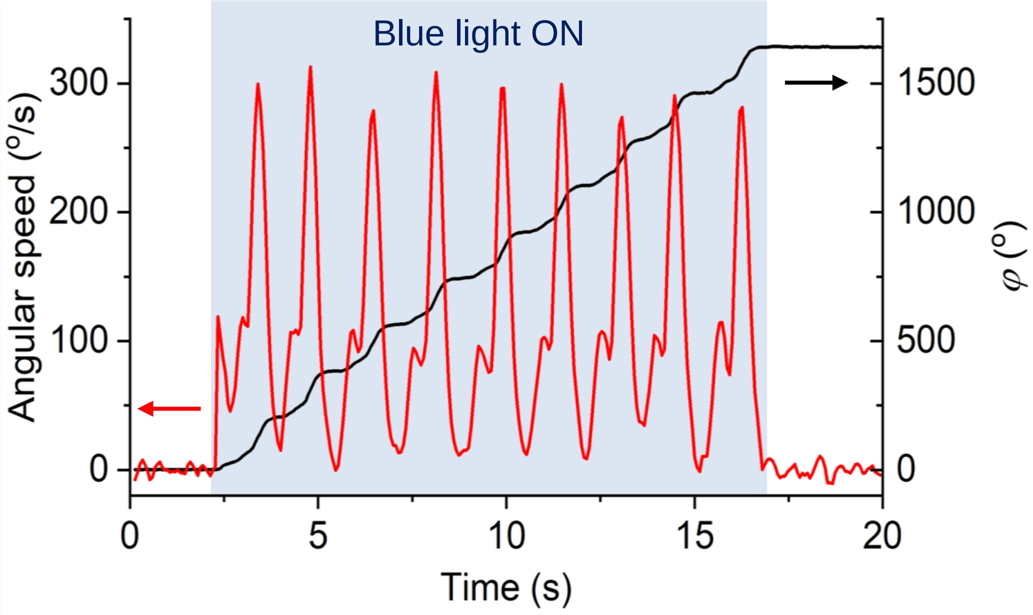


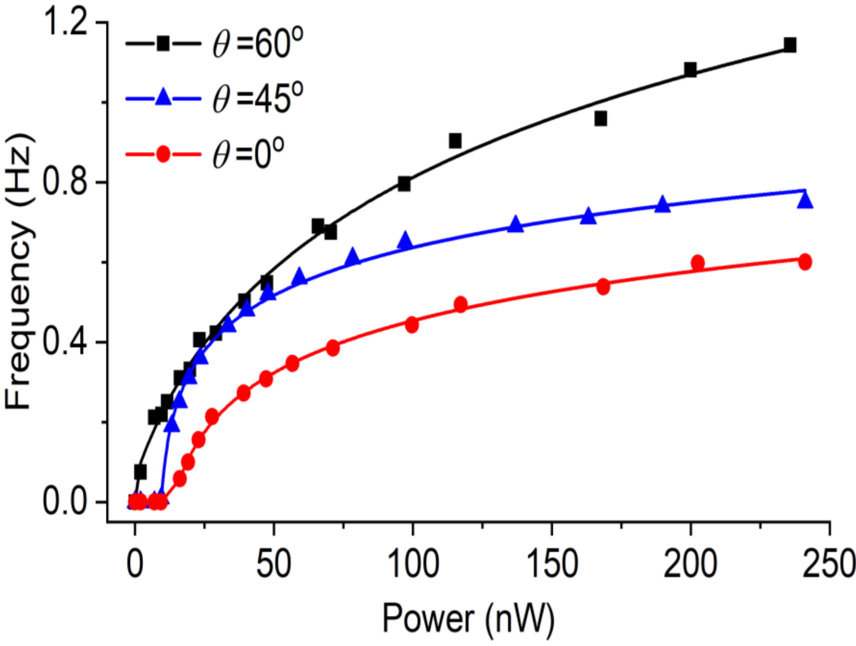




Light-driven motor: sensitivity & rotation rates

→ **Rotation when blue light is on**





Low Reynolds number system

$$W_m \approx \omega^2 (k_B T / D_\varphi + \gamma_{\mathbf{n}} d A_p)$$

Stokes drag

Director twist

→ **Rotation frequency vs intensity**

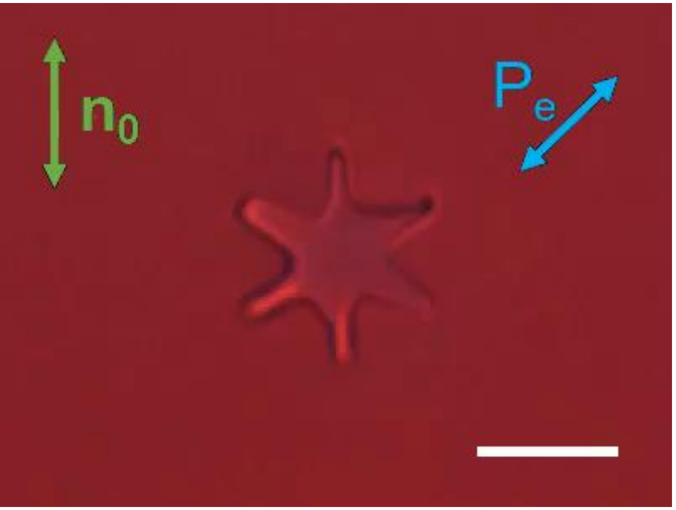
→ Frequency scales as ∝ $(W_o - W_{oth})^{1/2}$

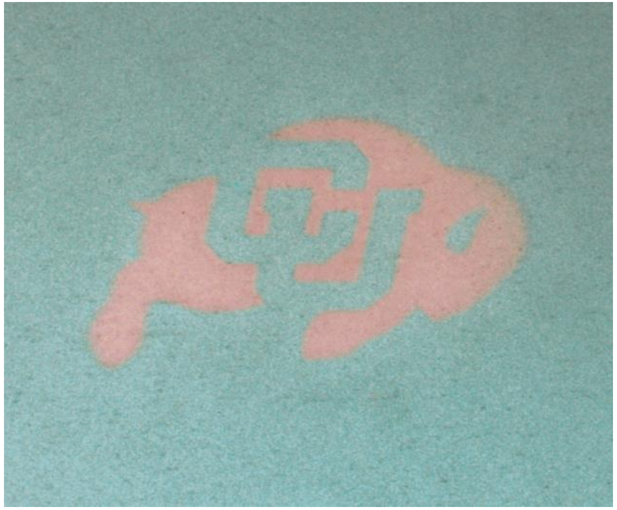
→ Threshold ~ a few nW per particle, rotates in ambient light!

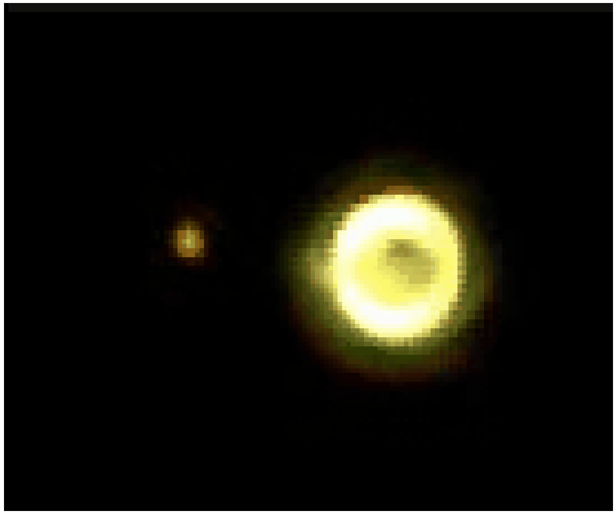
Open question: What kind of self-assembled machines & active matter systems can be made from spinning light-powered nano/micro-particles?

Conclusions & Deign Opportunities

→Colloids in LCs & inspirations for pure math
→Electrostatic analogy & diversity of quasi-atoms
→Self-assembled low-symmetry condensed matter phases
→Physical behavior from assembling solid nanoparticles in LCs
→Switchable colloidal interactions & light-powered motors







Thank you!

Thank you !!!