TOPOLOGICAL SOFT MATTER

S. ŽUMER

Univerza v Ljubljani & Institut Jožef Stefan,
in Center odličnosti NAMASTE, Ljubljana

Coworkers:
simulations
& theory:

S. ČOPAR
T. PORENTA
M. RAVNIK
D. SEČ

Experimental
collaborators:

I. MUŠEVIČ
M. ŠKARABOT
U. TKALEC
V.S.R. JAMPANI

Support of Slovenian Research Agency and Center of Excellence NAMASTE is acknowledged

SOFT MATTER

liquids, liquid crystals, polymers, elastomers, colloids, gels, foams, biomaterials...

molecular interactions ~ thermal energy (room temp.)

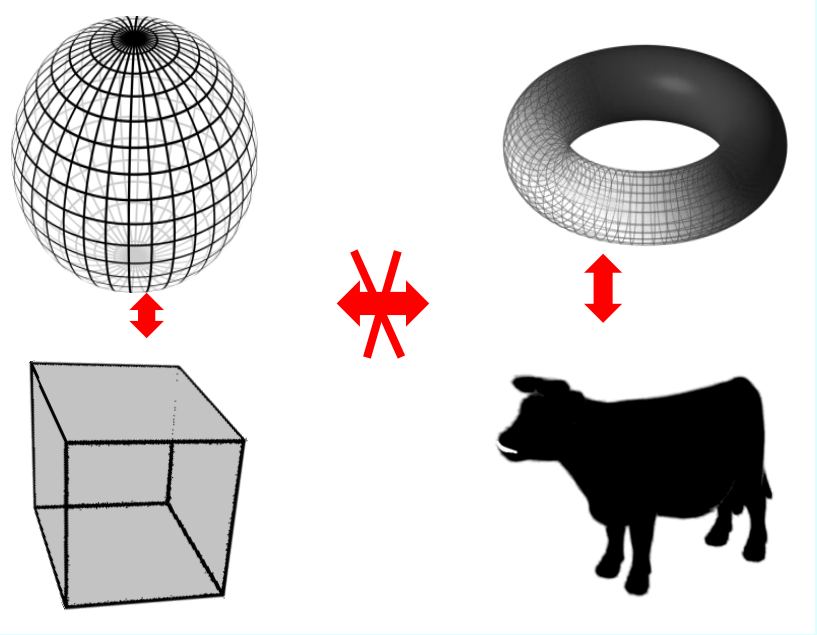
softness: large susceptibility to external stimuli & self-assembly
symmetry breaking transitions at room temperature

molecular shape asymmetry

long range orientational order, topological defects in director fields

TOPOLOGY →

study properties that are
preserved under continuous
deformations of objects



TOPOLOGICAL SOFT MATTER

liquid crystal blue phases, liquid crystal colloids & composites...

frustrated orientational ordering
(confinement, external fields, intrinsic chirality,...)

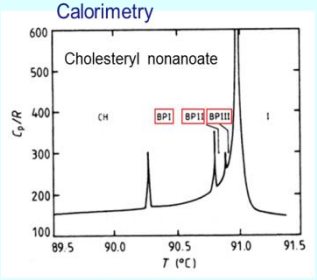
stable defects in the molecular-orientation order parameter
crucially determine properties like:
complex topology, superstructures, tunable physical properties...

APLICATIONS

photonics, plasmonics, sensorics, metamaterials, nanotechnology.....

Sir Charles Frank on blue phases in 1983

"They are totally useless, I think, except for one important intellectual use, that of providing tangible examples of topological oddities, and so helping to bring topology into the public domain of science, from being the private preserve of a few abstract mathematicians and particle theorists."

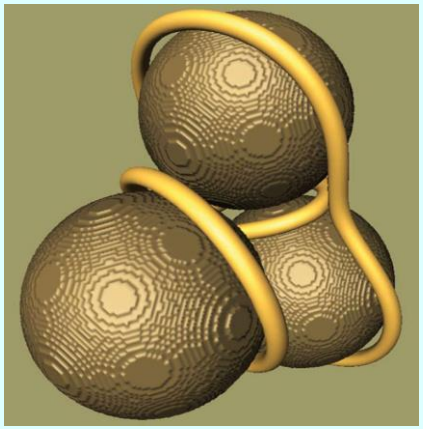


Thoen, Phys. Rev. A (1988)

Last 10 years: blue phases with stability range ~ 50K .
Polymer stabilized (Kikuchi et al., Nature Materials 2002).
Bimesogens: (Coles&Pivnenko, Nature 2005)

The interest in liquid crystal colloids is growing for 15 years (Poulin et al., Science 1997).

It was strongly stimulated by the discovery of disclination entangled colloidal microstructures (M. Ravnik, M. Škarabot, S. Žumer, U. Tkalec, I. Poberaj, D. Babič, N. Osterman, & I. Muševič, PRL 2007).



Ravnik & Žumer,
Soft Matter 2009

OUTLINE

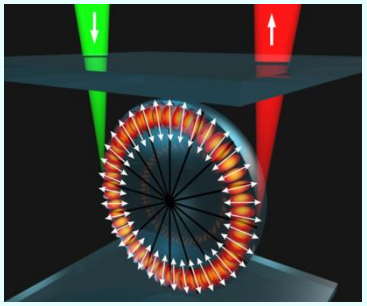
- Motivation:
- Phenomenological modeling of nematics and chiral nematics
- Nematic colloids:
  - Entanglement & nematic braids stabilized by geometry and chirality
  - Local rewiring of disclinations
  - Linking & knotting of disclinations
- Opal structures permeated by nematics
- Cholesteric droplets with knotted disclinations
- Conclusions

MOTIVATION

COMPLEXITY OF TOPOLOGICAL SOFT MATTER FOR PHOTONICS & OPTICS

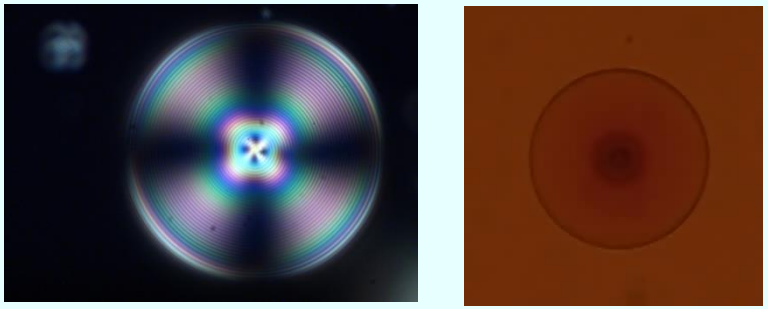
Confinement & chirality

WGM in nematic droplets



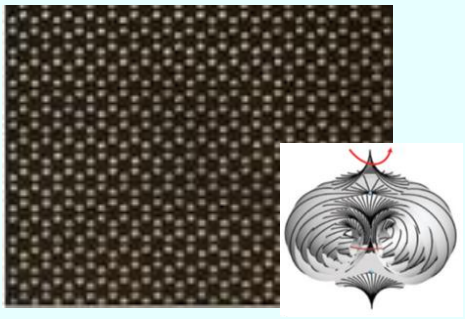
Humar et al. Nature Phot.2009

Cholesteric 3D micro-droplet laser



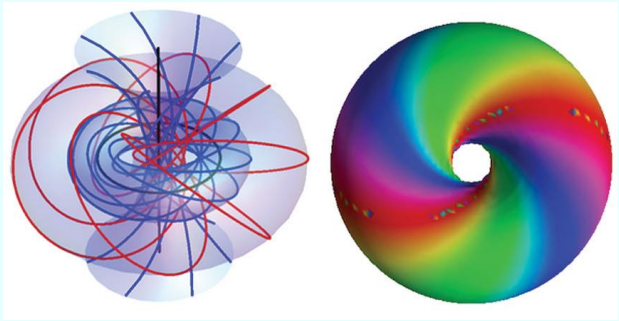
Humar & Musevic, Optics Exp. 2010

Array of torons



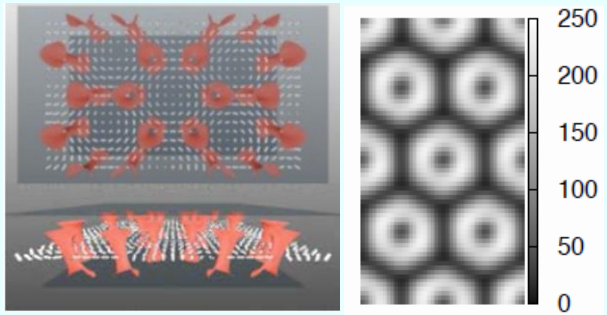
Smalyukh Nature Mat. 2011, Opt.Exp.2012

Nematic hopfion (Hopf fibration)



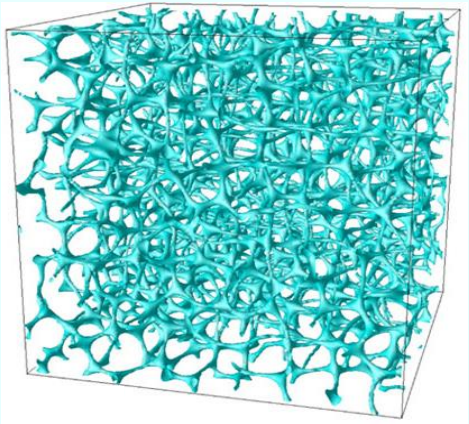
Chen et al. PRL 2013

Confined BPs: skyrmions & light scattering



Fukuda et al. Nature Comms 2011

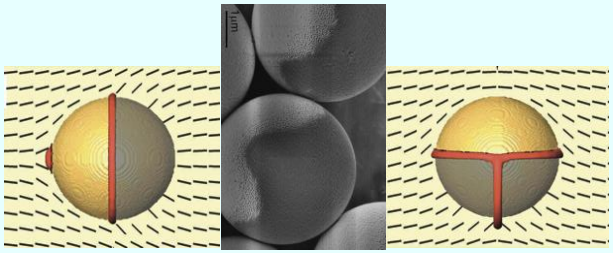
Blue Phase III



Henrich et al. PRL 2011

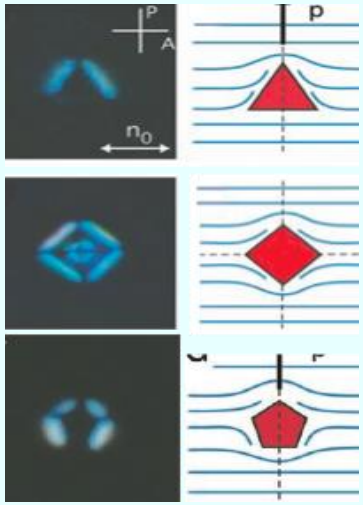
MOTIVATION

NONTRIVIAL COLLOIDAL PARTICLES: Some of the recent studies

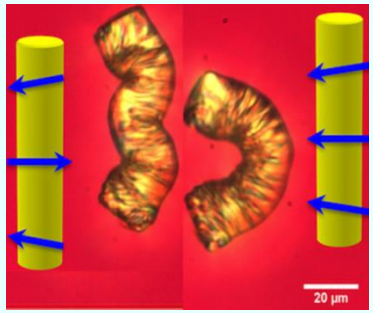


Janus particles
(Conradi et al, Soft Matter 2009)

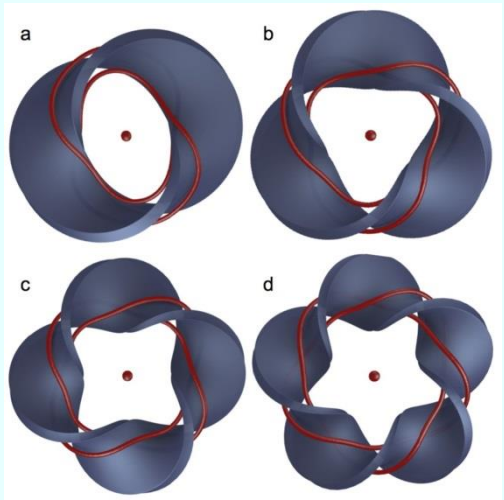
Smalyukh group:



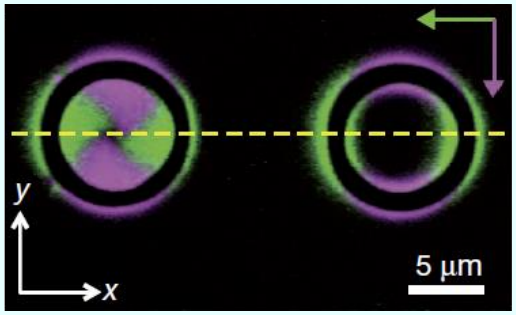
Colloidal platelets
Lapointe et al. Science 2009



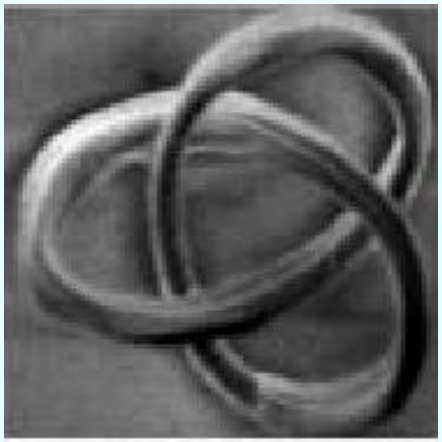
Shapeable particles
Sun et al. APL 2012



Moebius strip colloid
Alexander et al. PNAS 2013



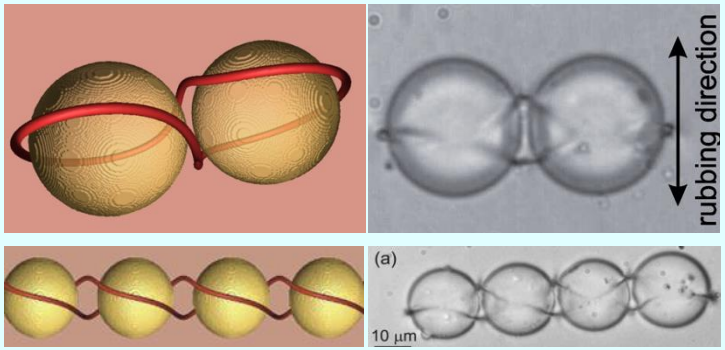
Toroidal particles
Senyuk et al. Nature 2013



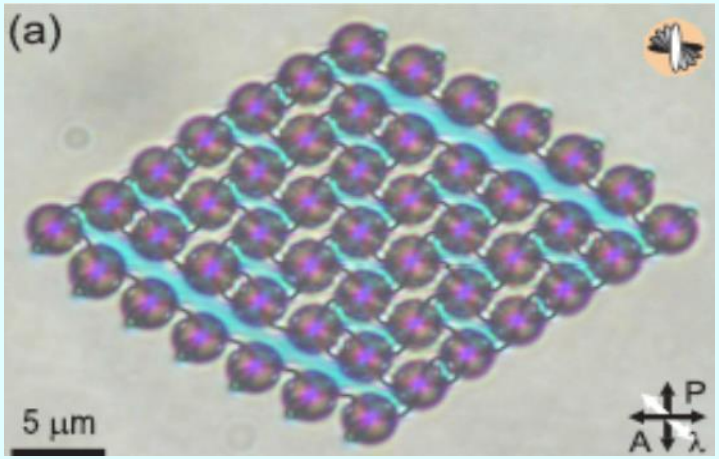
Knotted particles
Martinez et al.(including Ravnik & Žumer)
Nature Materials 2014

MOTIVATION

2D structures: disclination entanglement the clue to nematic braids

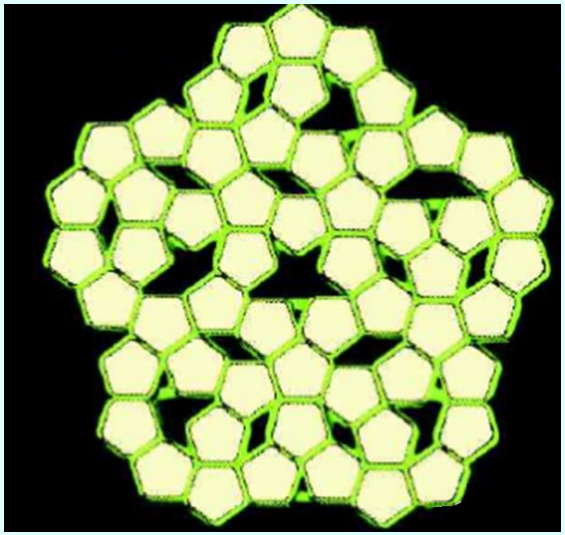


Entangled nematic colloidal particles
Ravnik et al. PRL 2007



Nematic braids with knots & links
Tkalec et al. Science 2011

2D structures: complex colloidal particles

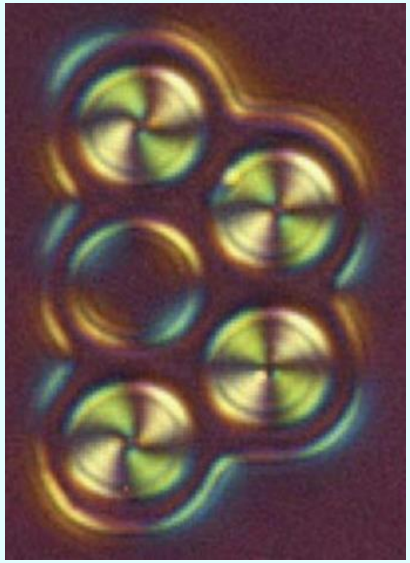


Faceted particles quasicrystalline tiling

Dontabhaktuni, Ravnik, Žumer PNAS 2014

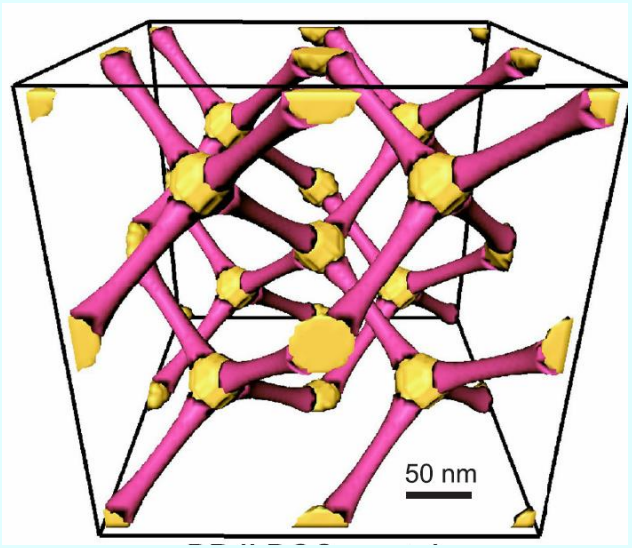
Colloidal handle-bodies in nematics

Senyuk et al, Nature 2013

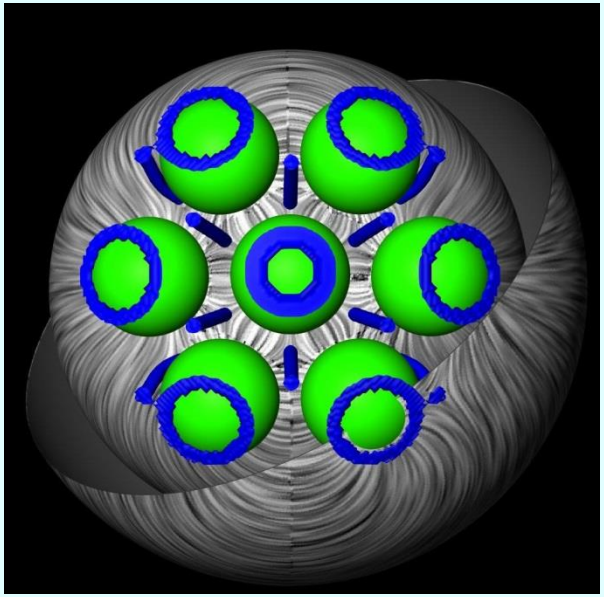


MOTIVATION

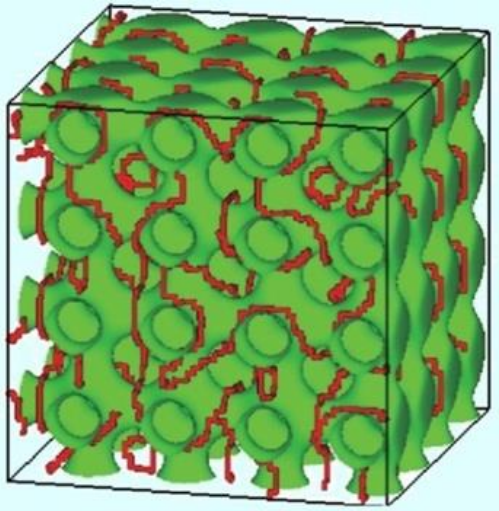
3D COLLOIDAL STRUCTURES



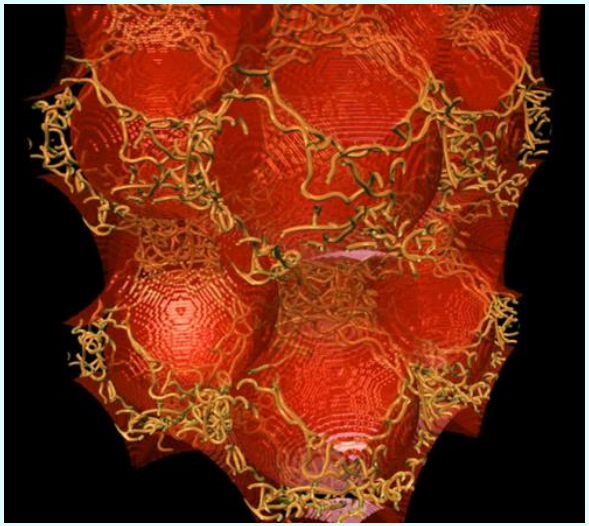
BP II colloidal crystal
Ravnik et al. PNAS 2011



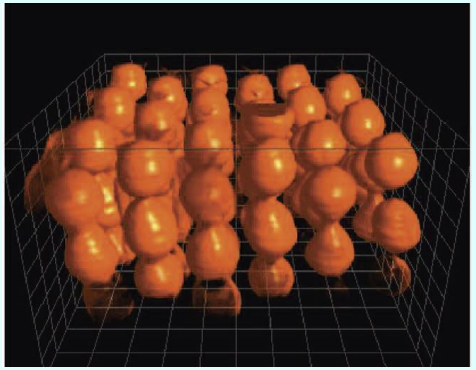
Nematic shell decorated by colloidal particles
Gharbi, Seč et al.,
Soft Matter 2013

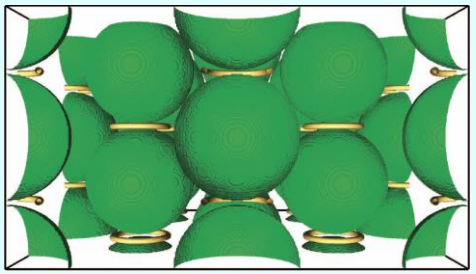


Araki et al. Nature Mat. 2011



3D cholesteric colloid structure
Čopar 2013





3D nematic dipolar colloid
Nych et al. Nature Comms 2012

OUTLINE

- Motivation:
- Phenomenological modeling of nematics and chiral nematics
- Nematic colloids:
  - Entanglement & nematic braids stabilized by geometry and chirality
  - Local rewiring of disclinations
  - Linking & knotting of disclinations
- Opal structures permeated by nematics
- Cholesteric droplets with knotted disclinations
- Blue phases & confinement induced exotic structures
- Conclusions

NEMATIC ORDER

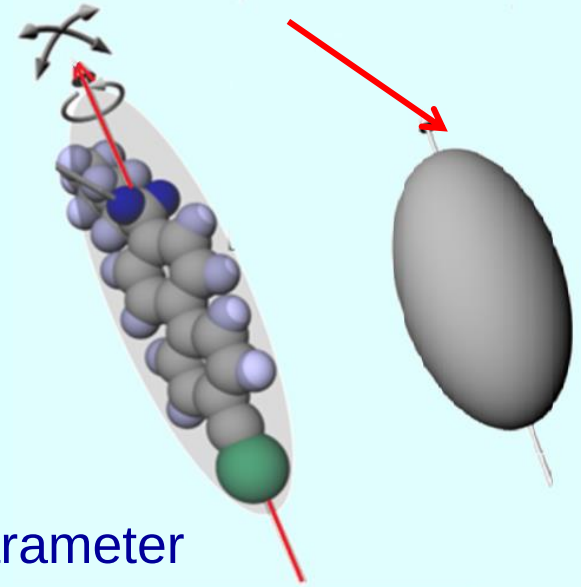
Scalar nematic order parameter

$$S = < P_2(\cos\vartheta) >$$

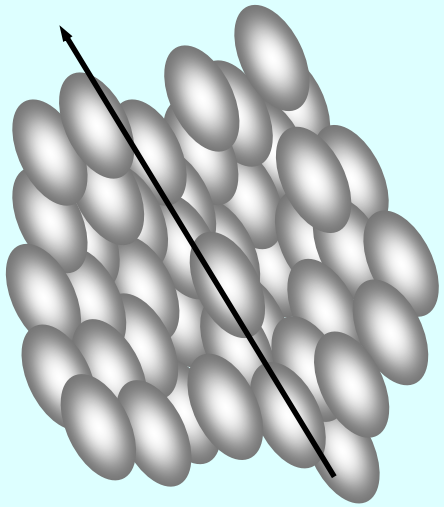
nematic phase

Director **n** to **–n** symmetry

Fluctuations



n



Tensorial order parameter

$$Q_{ij} = \frac{S}{2}(3n_i n_j - \delta_{ij}) + \frac{P}{2}(e_i^{(1)} e_j^{(1)} - e_i^{(2)} e_j^{(2)})$$

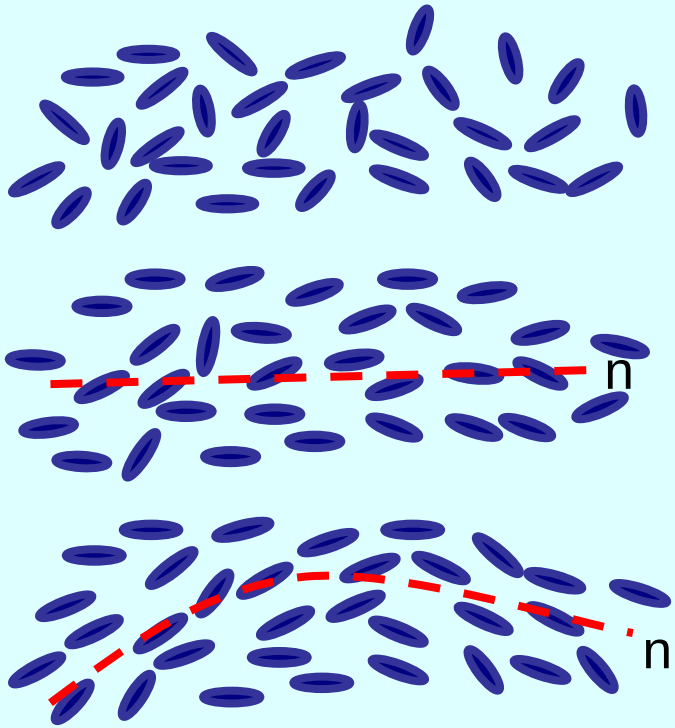
Eigen frame: $\boldsymbol{n}$, $\boldsymbol{e^{(1)}}$, $\boldsymbol{e^{(2)}}$

eigen values:

$$\underline{Q} = \begin{bmatrix} -(S+P)/2 & 0 & 0 \\ 0 & -(S-P)/2 & 0 \\ 0 & 0 & S \end{bmatrix}$$

DEFORMED NEMATIC

Isotropic phase $S = 0$ short range order variations



Nematic phase $S \neq 0$, ***n***

Soft materials easy to deform

Short range order variations of S & P

Long range director (***n***) variations

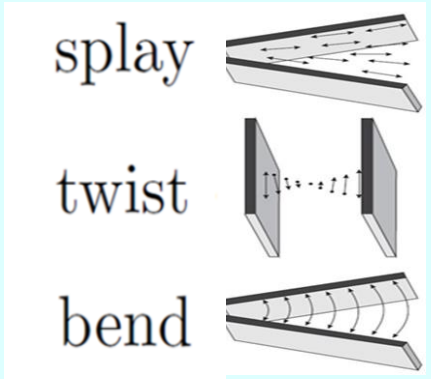
(elastic deformations)

Inducing & stabilizing deformed states:

Intrinsic chirality

Confinement: surface anchoring & geometry

External fields (electric, magnetic, optical)



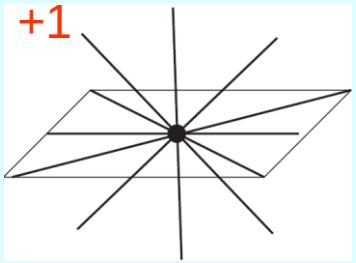
TOPOLOGICAL DEFECTS

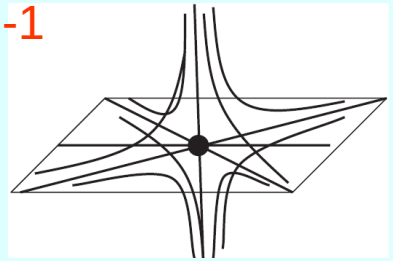
- discontinues director fields & variation in nematic order (2D&3D objects)
- defects are formed after fast cooling, or by other external perturbations,
- topological picture (symmetry of the order parameter - director field, equivalences, and conservation laws):

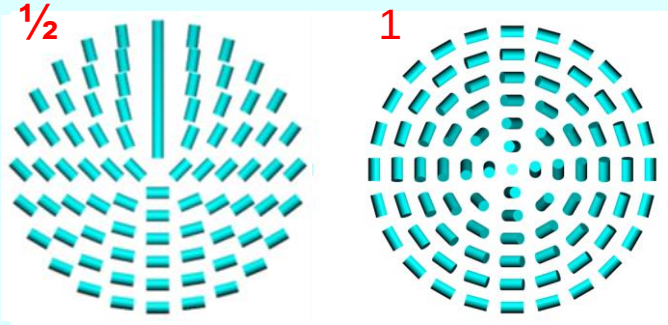
  - point defects:

    - topological charge

$$q = \frac{1}{2} \oint dS_i \epsilon_{ijk} \vec{n} \cdot (\partial_j \vec{n} \times \partial_k \vec{n})$$



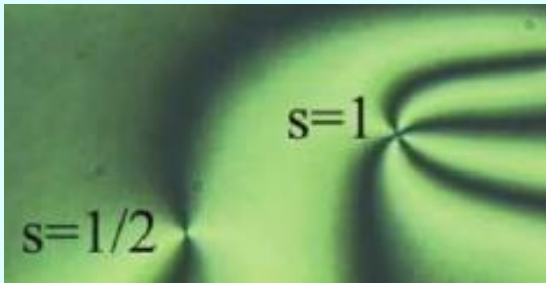




  - line defects (disclinations) :
    - winding number,
    - topological charge of a loop

- core structure:

biaxiality & decrease of order (tensorial fields)



LANDAU - DE GENNES FREE ENERGY

Landau - de Gennes free energy based on the tensorial nematic order parameter $Q_{ij} = \frac{S}{2}(3n_i n_j - \delta_{ij}) + \frac{P}{2}(e_i^{(1)} e_j^{(1)} - e_i^{(2)} e_j^{(2)})$ includes: phase term, bulk elastic (gradient) term that includes chiral segment, nematic surface anchoring, and dielectric coupling term:

$$
\begin{aligned}
F \;=\; & \int_{LC} \left(\frac{1}{2} A Q_{ij} Q_{ji} + \frac{1}{3} B Q_{ij} Q_{jk} Q_{ki} + \frac{1}{4} C (Q_{ij} Q_{ji})^2 \right) dV \\
& + \frac{1}{2} L \int_{LC} \left(\frac{\partial Q_{ij}}{\partial x_k} \frac{\partial Q_{ij}}{\partial x_k} + 4 q_0 \epsilon_{ikl} Q_{ij} \frac{\partial Q_{lj}}{\partial x_k} \right) dV \\
& + \frac{1}{2} W \int_{Conf.\ Surf.} (Q_{ij} - Q_{ij}^0)(Q_{ji} - Q_{ji}^0) dS_c
\end{aligned}
$$

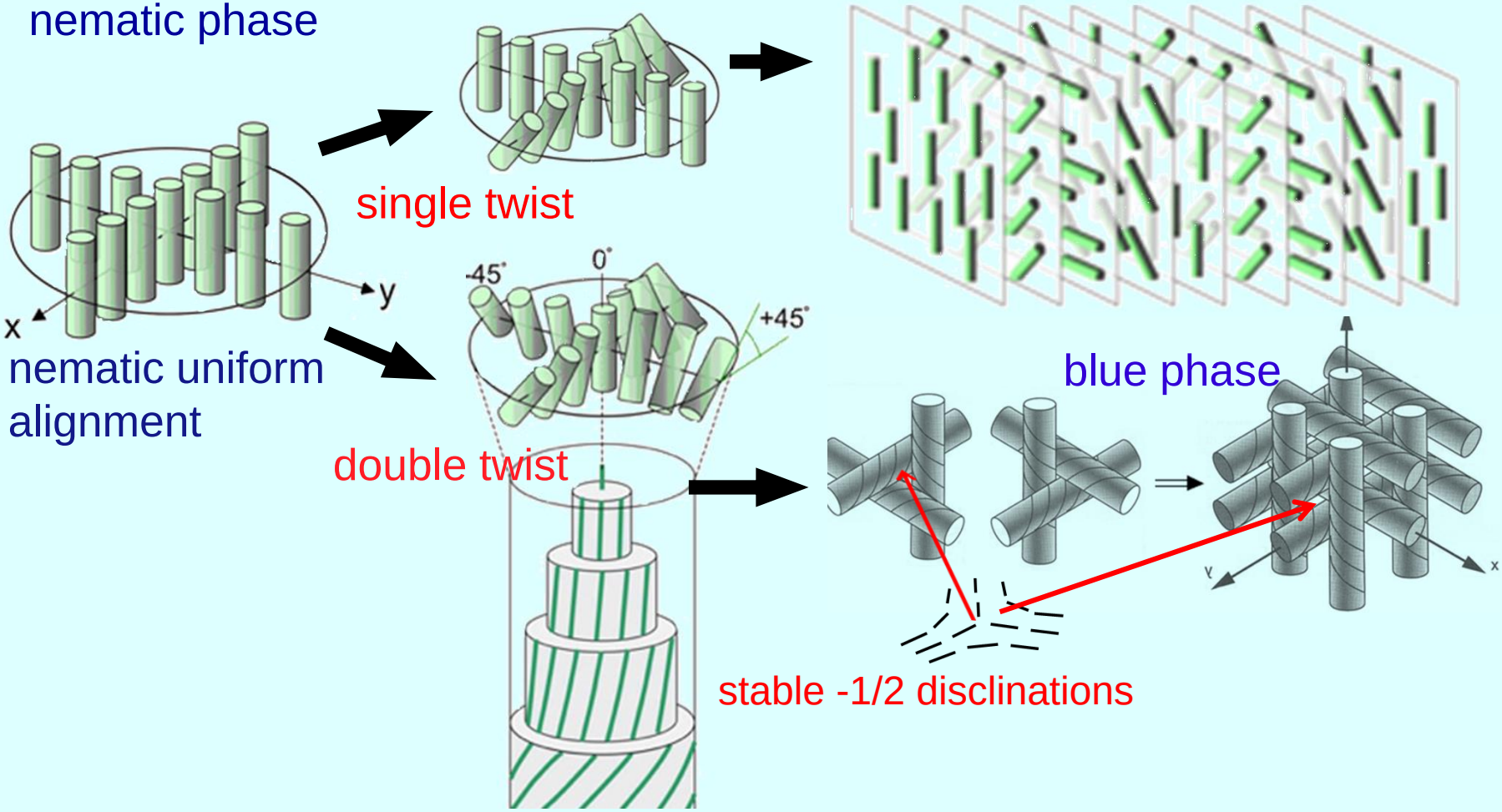
Minimization of free energy yields stable and metastable structures. Explicit Euler finite difference relaxation on cubic mesh typically covers $10^6 – 10^7$ mesh points. Limit on sample size that includes defects comes from ξ_N = 5 – 10 nm that requires around 10 nm lattice distance for the finer mesh and 100nm for the low resolution mesh. Usually 10^4 to 10^5 steps are needed.

ACHIRAL AND CHIRAL NEMATIC ORDERING

achiral molecules chiral molecules

nematic phase

cholesteric phase



Blue phases: fluidic 3D orientationally ordered cubic lattices with stable defects

http://kikuchi-lab, http://www.eng.cam.ac.uk

VISUALIZATION

Visualization of defect using tensorial order parameter:

- Director lines are not enough for defects where order is depressed.
- Surfaces of constant order parameter are useful for visualization of the disclination lines with singular cores.
- Surfaces of constant derivatives of order parameter stress specific deformations of the ordering field.

Example: -1/2 disclination:

$$S_{TW} = \left(\varepsilon_{ikl} Q_{ij} \frac{\partial Q_{lj}}{\partial x_k} - \frac{9}{4} S^2 q_0\right) \xi_N$$

$S_{TW} > 0.42$ $S_{TW} < -0.42$

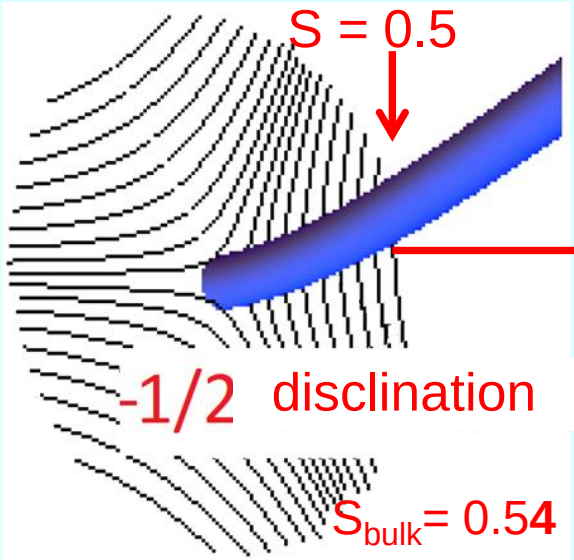
splay & bend

$$S_{SB} = \frac{\partial^2 Q_{ij}}{\partial x_i \partial x_j} \xi_N{}^2$$

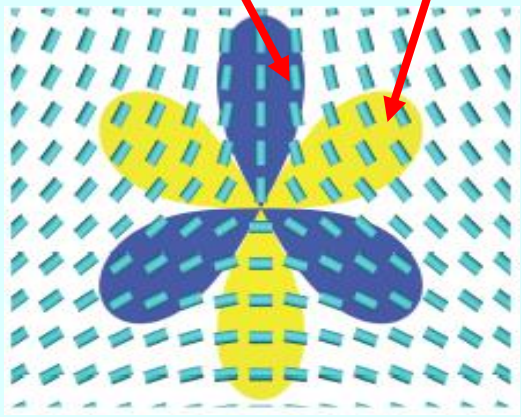
splay $S_{SP} > 0.02$ bend $S_{SP} < -0.02$

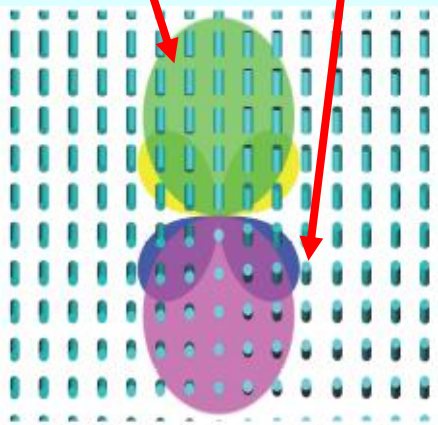
deviations of twist

iso-surface S = 0.5



3 fold ribbon





Čopar et al. LC 2013

OUTLINE

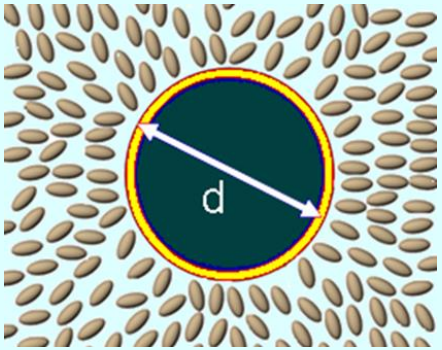
- Motivation:
- Phenomenological modeling of nematics and chiral nematics
- Nematic colloids:
  - Entanglement & nematic braids stabilized by geometry and chirality
  - Local rewiring of disclinations
  - Linking & knotting of disclinations
- Opal structures permeated by nematics
- Cholesteric droplets with knotted disclinations
- Conclusions

COLLOIDAL DISPERSIONS

Spherical particles in nematics

- Surfactants – interfacial coupling
  Anchoring (strong homeotropic)

- Confinement to a thin layer comparable to the particle diameter.

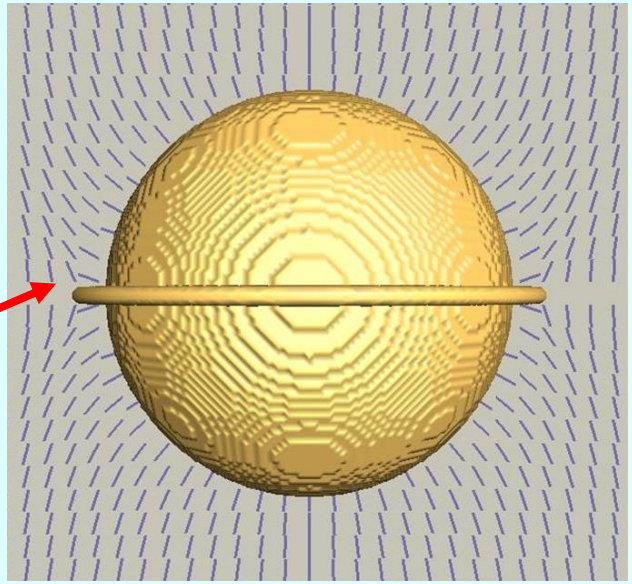


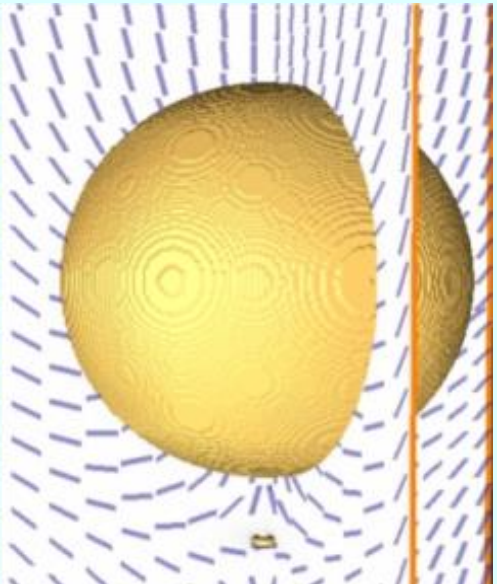
4μm particle with strong normal anchoring (both structures has comparable energy):

Saturn ring (quadrupolar) structure

with

-1/2 disclination loop iso - order plot 5% below bulk





Dipole structure

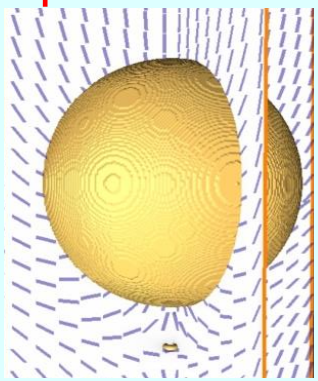
with small ring defect

PARTICLES IN HOMOGENOUS NEMATIC FIELD

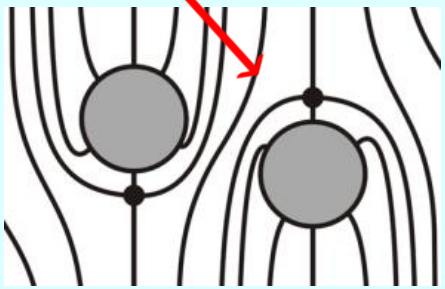
EFFECTIVE INTERACTIONS: CLUES TO ASSEMBLING

Nematic mediate effective particle – particle interaction as a result of the minimization of the total free energy – > “thermodynamic” forces.
Homogenous farfield: zero total topological charge

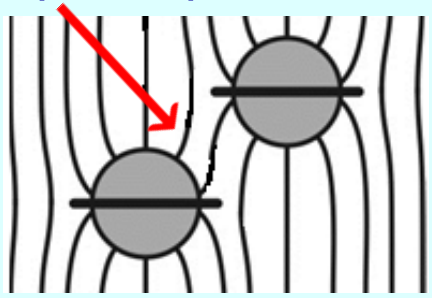
Interaction mechanism: Sharing of deformed areas associated to the defects & disclinations localized to colloidal particles. Distance dependent: power law & confinement induced screening

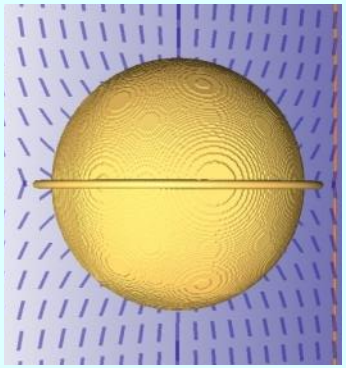


dipolar



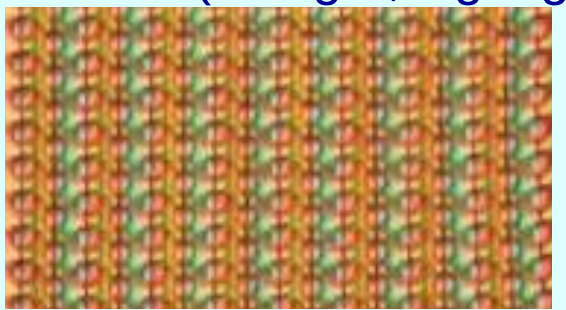
quadrupolar



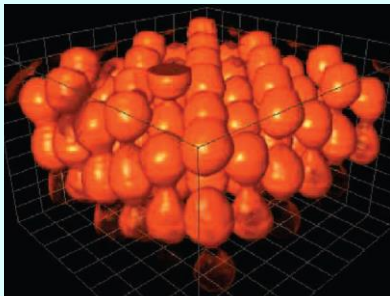


Dimers → 1D chains (straight, zigzag) → 2D lattices → 3D lattices

Musevic et al.
Science 2006

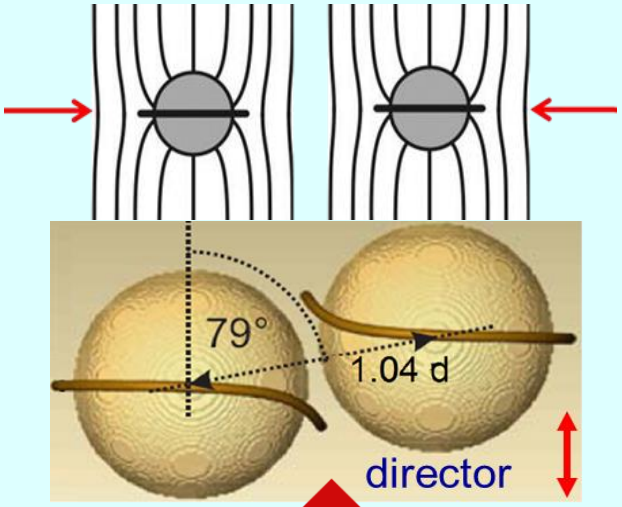


Nych et al.
Nature Comms 2012

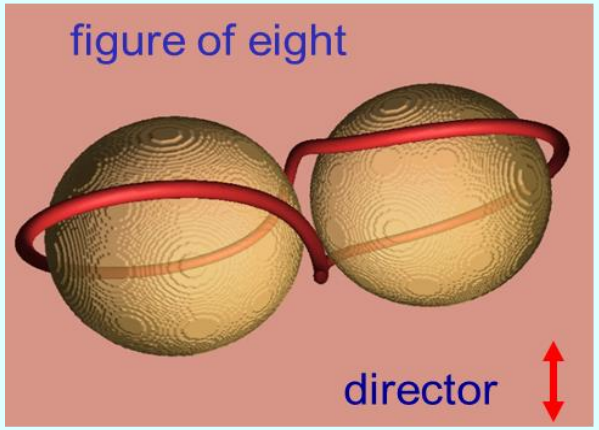


ENTANGLING OF PARTICLES BY DISCLINATIONS

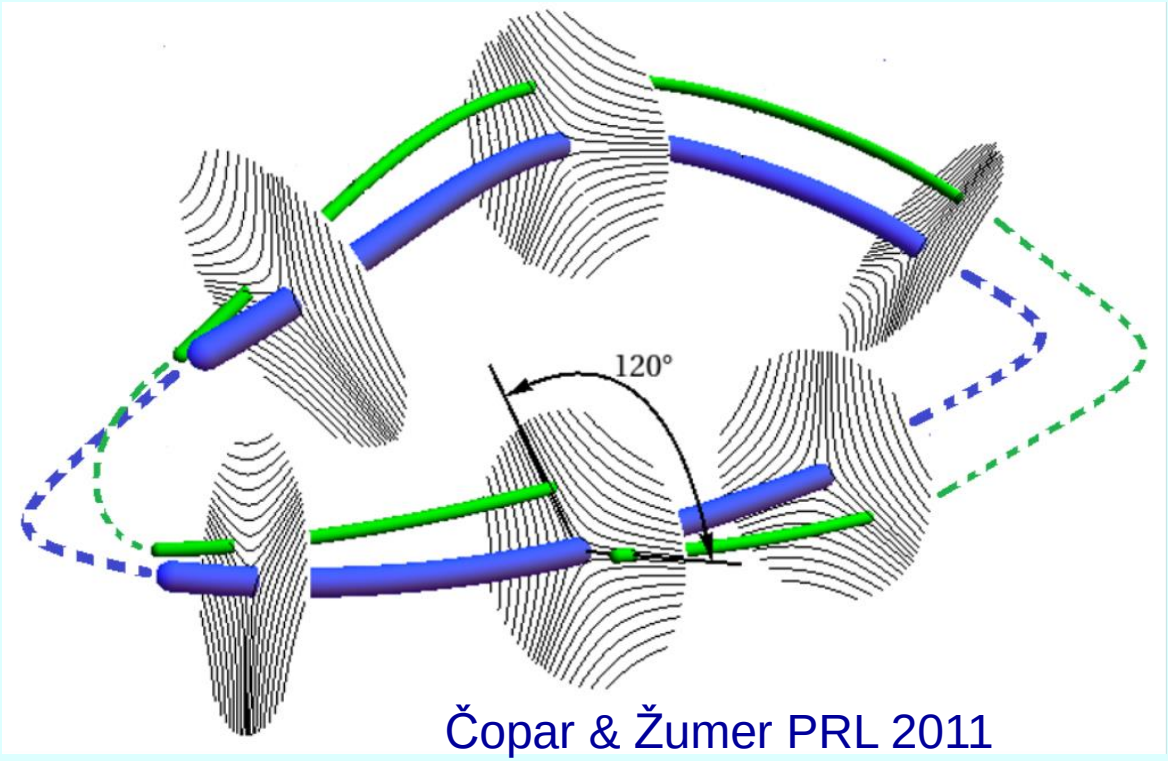
- Energy minimization: sharing of disclinations (entanglement): → string like interactions
- Topological constrains:
  - zero total topological charge is conserved
  - restructuring of defect loops must obey the ribbon structure of disclinations



Local laser heating
& thermal quench



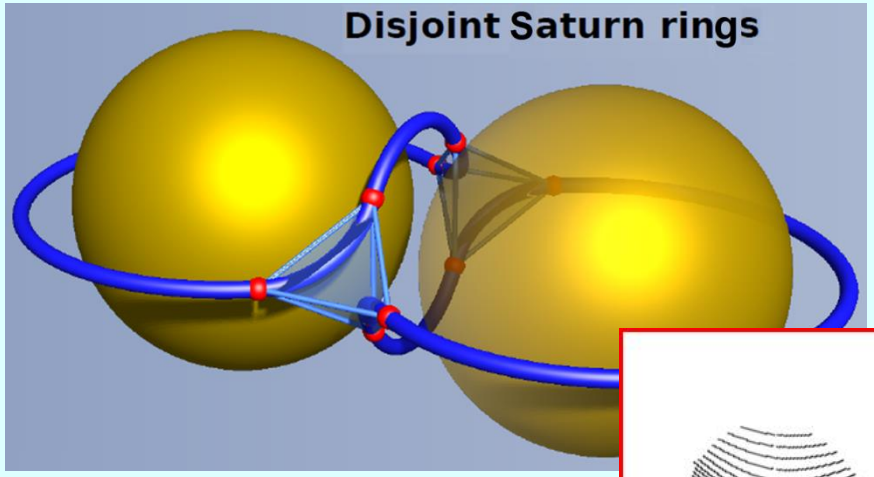
Ravnik et al. PRL 2007

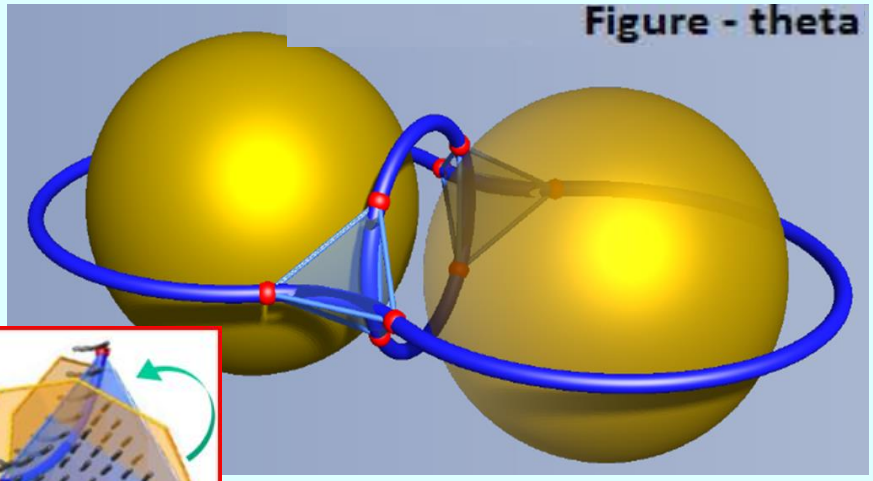


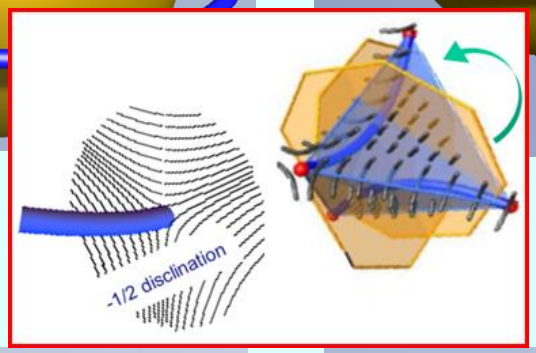
Čopar & Žumer PRL 2011

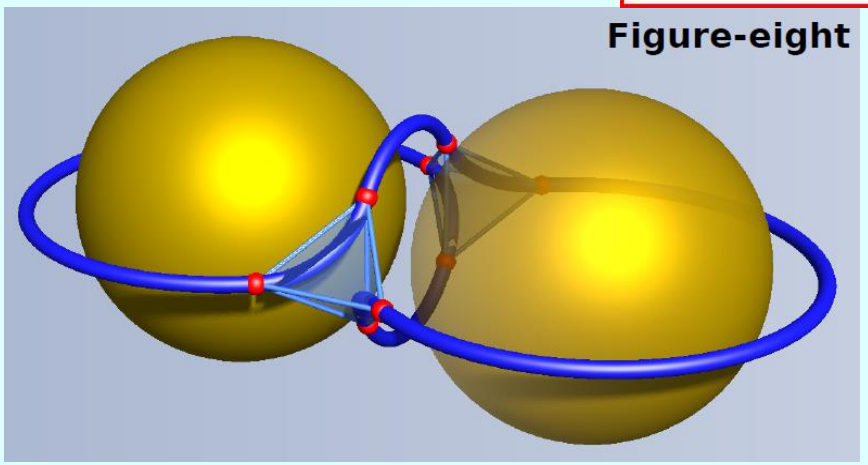
LOCAL RESTRUCTURING OF DIMERS

AT POINTS OF ORTHOGONAL DISCLINATION CROSSING









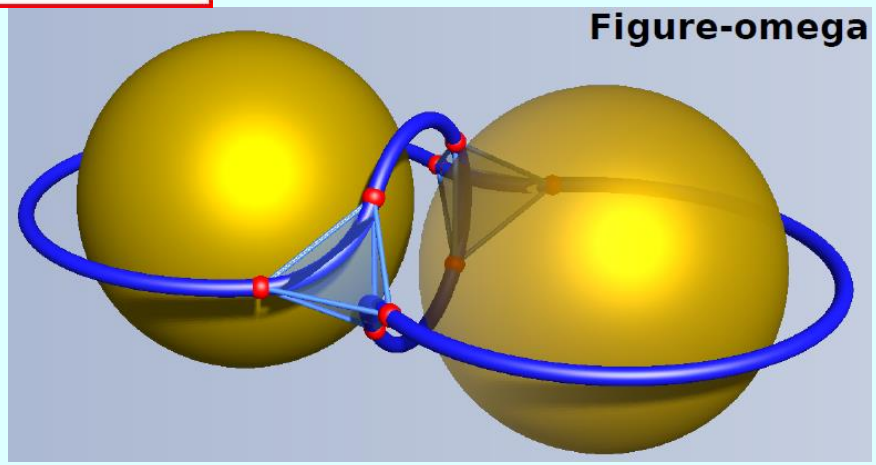
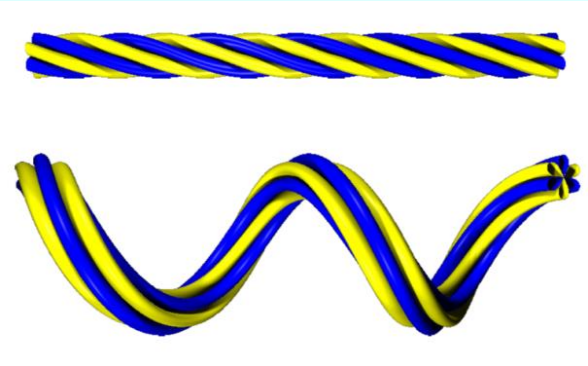


Figure of eight and figure of theta have left and right structures so that 6 different configurations are topologically possible.

Čopar & Žumer PRL 2011

SELF-LINKING NUMBER, WRITHE & TWIST

Topological invariant of a loop with a ribbon profile - self-linking number *SL* - is equal to the number of times the ribbon turns around its tangent before closing a loop.



Twist *Tw*: line integration of local twist along the loop.

Writhe *Wr* : 2D integral measuring how tangent at different segments of the loop is related. Zero for planar loops.

$$Sl = Wr + Tw$$

(Calugareanu theorem, 1959)

Writhe and twist are obtained via well know integrals along the closed loops.

Linked loops are characterized by the linking number Lk counting the number of times the loops pass through each other.

TOPOLOGICAL CHARGE: DISCLINATION NETWORKS

- *n* self-standing, linked, or knotted disclination loops
- *q* topological charge of the whole disclination network including *n* dislclination loops with constant -1/2 profile.

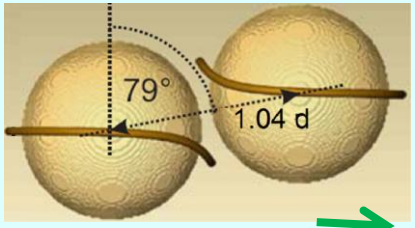
Combining self-linking numbers and linking numbers one finds the conservation law for the topological charge *q*. Unfortunately it provides only the conservation of the parity:

$$\frac{3}{2}\left(\sum_{i}^{n} Sl_i + 2\sum_{i>j}^{n} Lk_{ij}\right) + n = q \mod 2$$

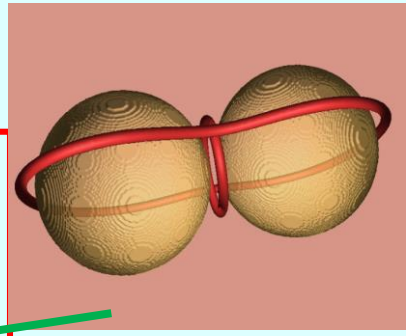
When the charge is prescribed by a confining geometry or by a homogenous nematic far-field we thus have a certain freedom on the number of loops, linking numbers, and self-linking numbers.

Čopar & Žumer, PRL 2011

CLASSIFICATION: NEMATIC COLLOIDAL DIMERS



For all our loops $Tw = 0$

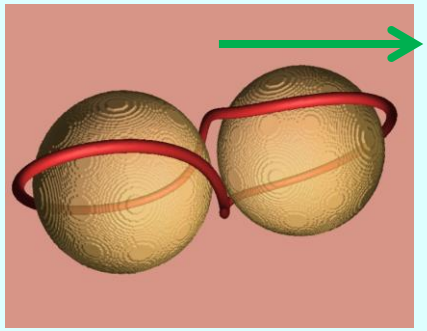


Disjoint Saturns $n = 2,\ Sl = Wr = 0$

Figure of theta $n = 2,\ Sl = Wr = 0$

Figure of eight $n = 1,\ Sl = Wr = \pm 2/3$

Figure of omega $n = 1,\ Sl = Wr = \pm 2/3$



$$Sl + n = 2 \text{ or } 0$$

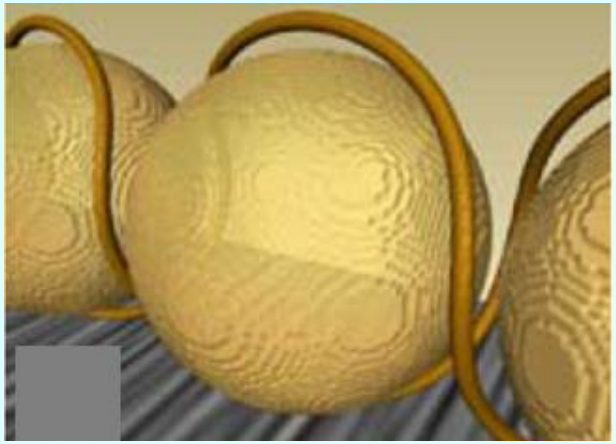
is within *mod 2* equivalent to -2
required by zero total charge condition

Structures differ in free energy. Left-right degeneracy is lost in twisted cells.

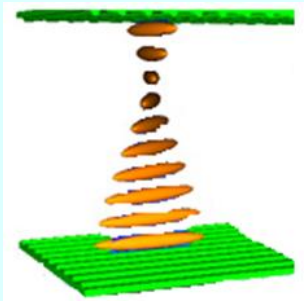
Čopar & Žumer PRL 2011 & supplement

STABILIZING NEMATIC BRAIDS

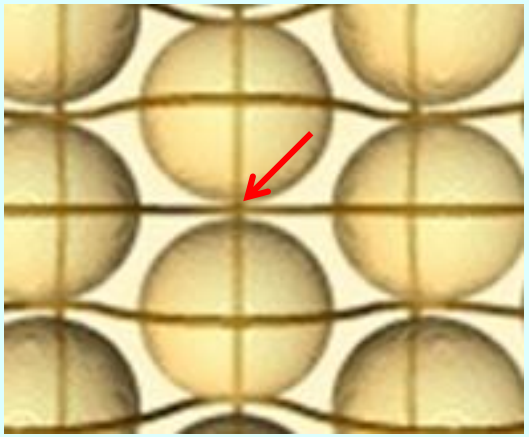
1D network in planar cell

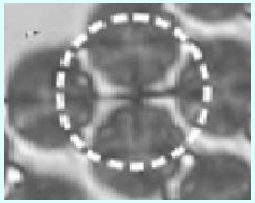


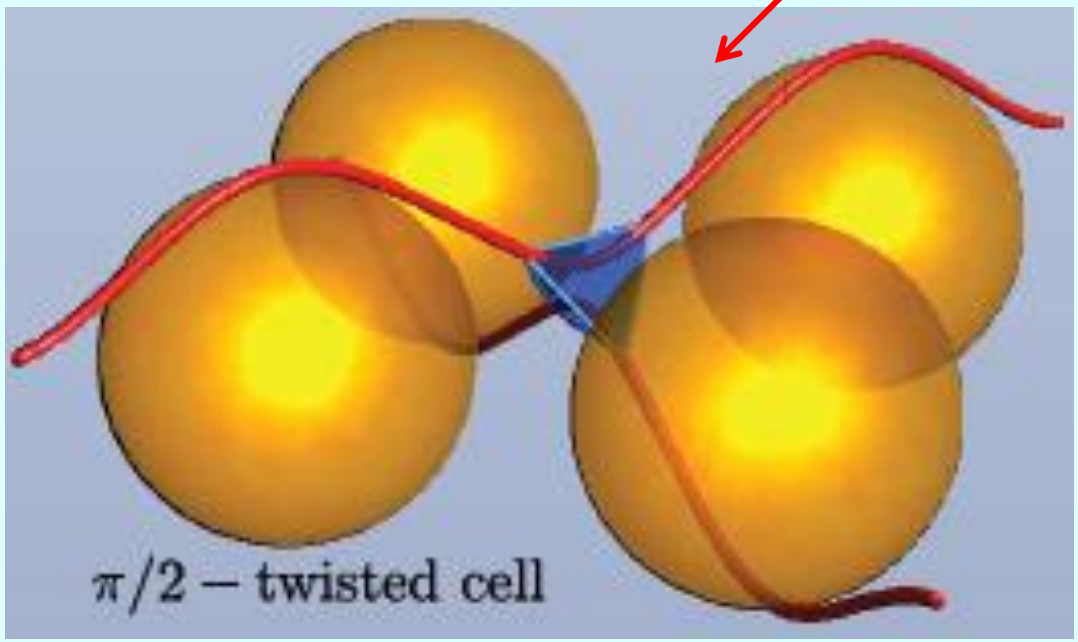
$\pi/2$ TWIST



2D network in twisted cell





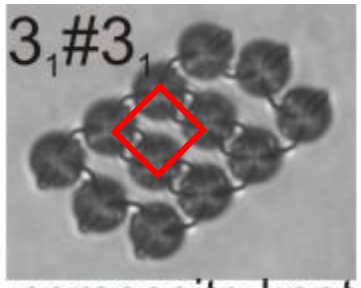


tetrahedral rewiring sites between four neighboring particles leads to possible knot and links

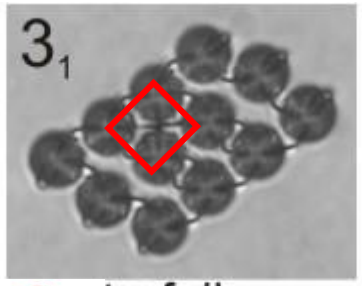
KNOTS AND LINKS – RECONFIGURABILITY

Particles tightly confined to $\pi/2$ twisted nematic cell

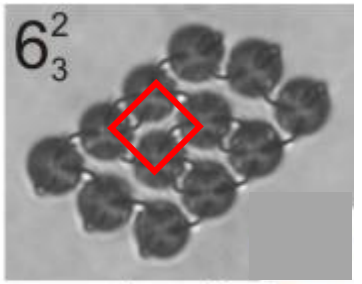
Reconfiguration by changing local tangles:



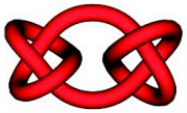
composite knot (granny knot)



trefoil



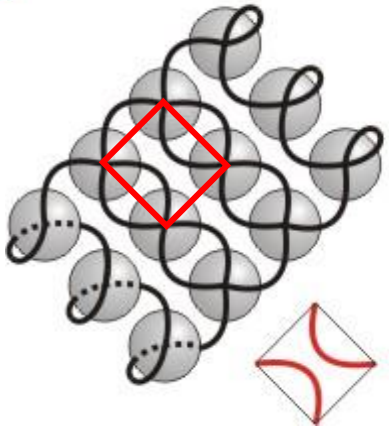
prime link

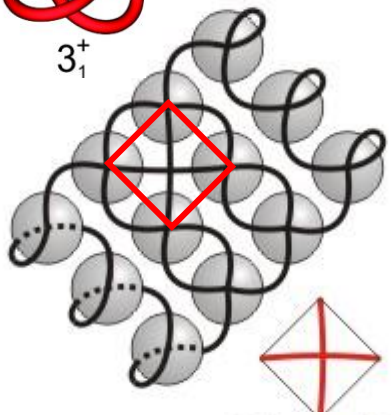


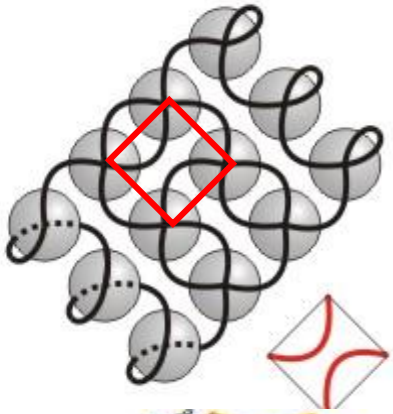
$3_1^-\#3_1^-$

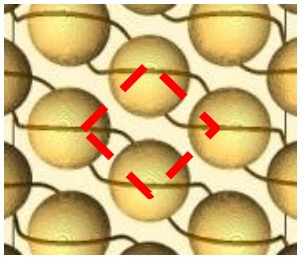
3_1^+

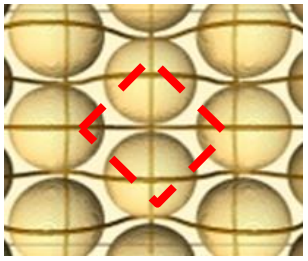
6_3^2

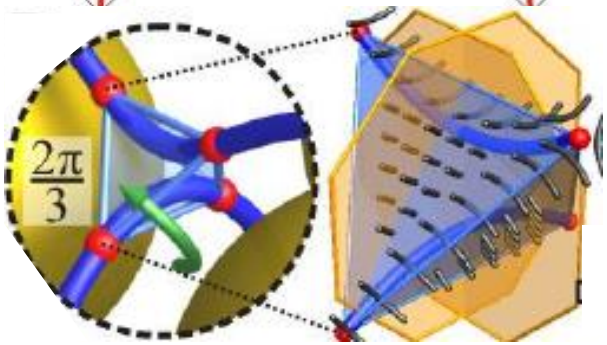








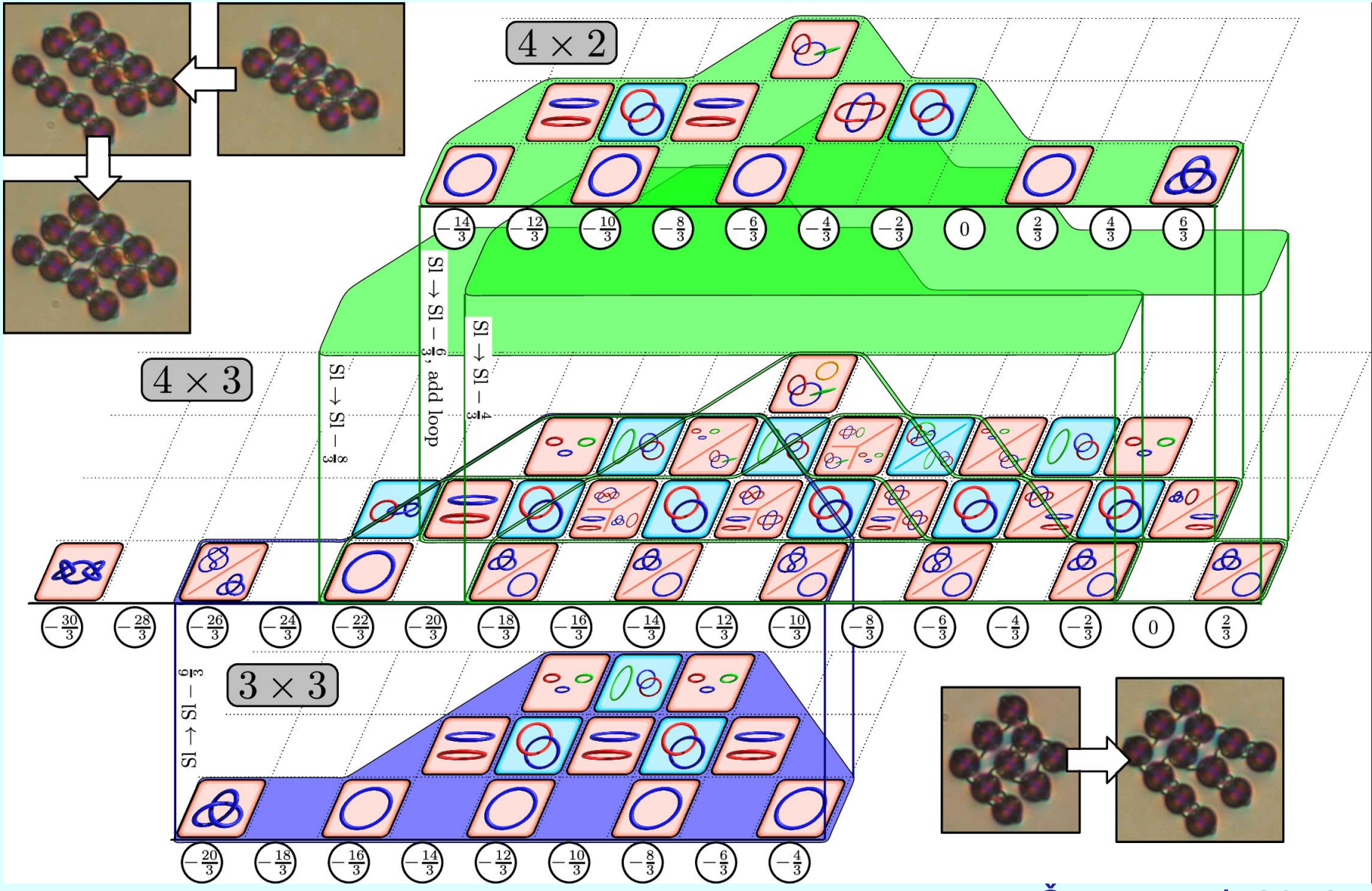




Tkalec et al. Science 2011

CLASIFICATION OF 2D BRAIDS

$\pi/2$ twisted nematic cell



Čopar et al. 2013

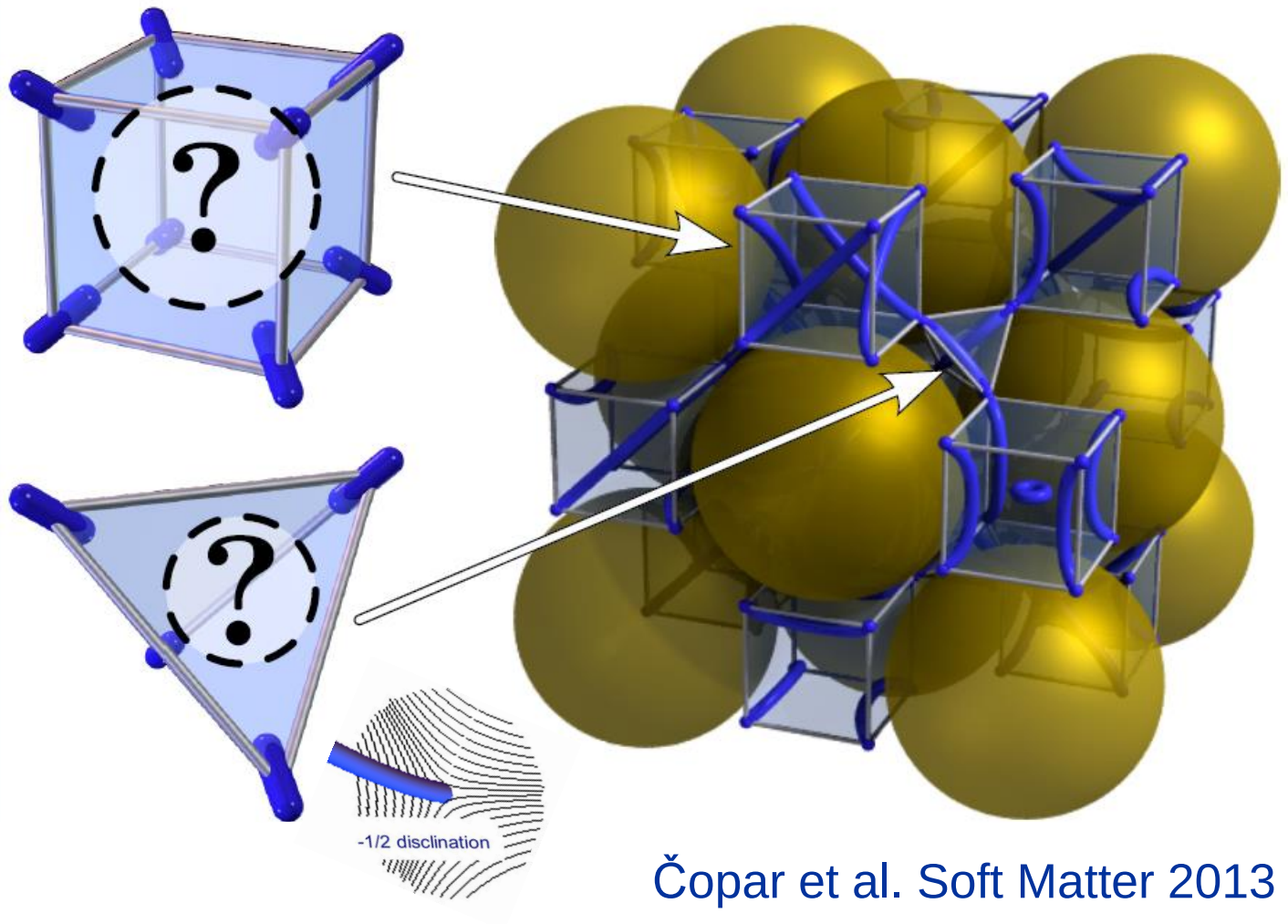
OUTLINE

- Motivation:
- Phenomenological modeling of nematics and chiral nematics
- Nematic colloids:
  - Entanglement & nematic braids stabilized by geometry and chirality
  - Local rewiring of disclinations
  - Linking & knotting of disclinations
- Opal structures permeated by nematics
- Cholesteric droplets with knotted disclinations
- Conclusions

OPAL STRUCTURE PERMEATED BY A NEMATIC

Face centered cubic lattice of tightly packed colloidal particles permeated by a nematic. The first experiment by Kang et al. PRL2001.

Strong confinement: Particle surfaces induce normal nematic anchoring.

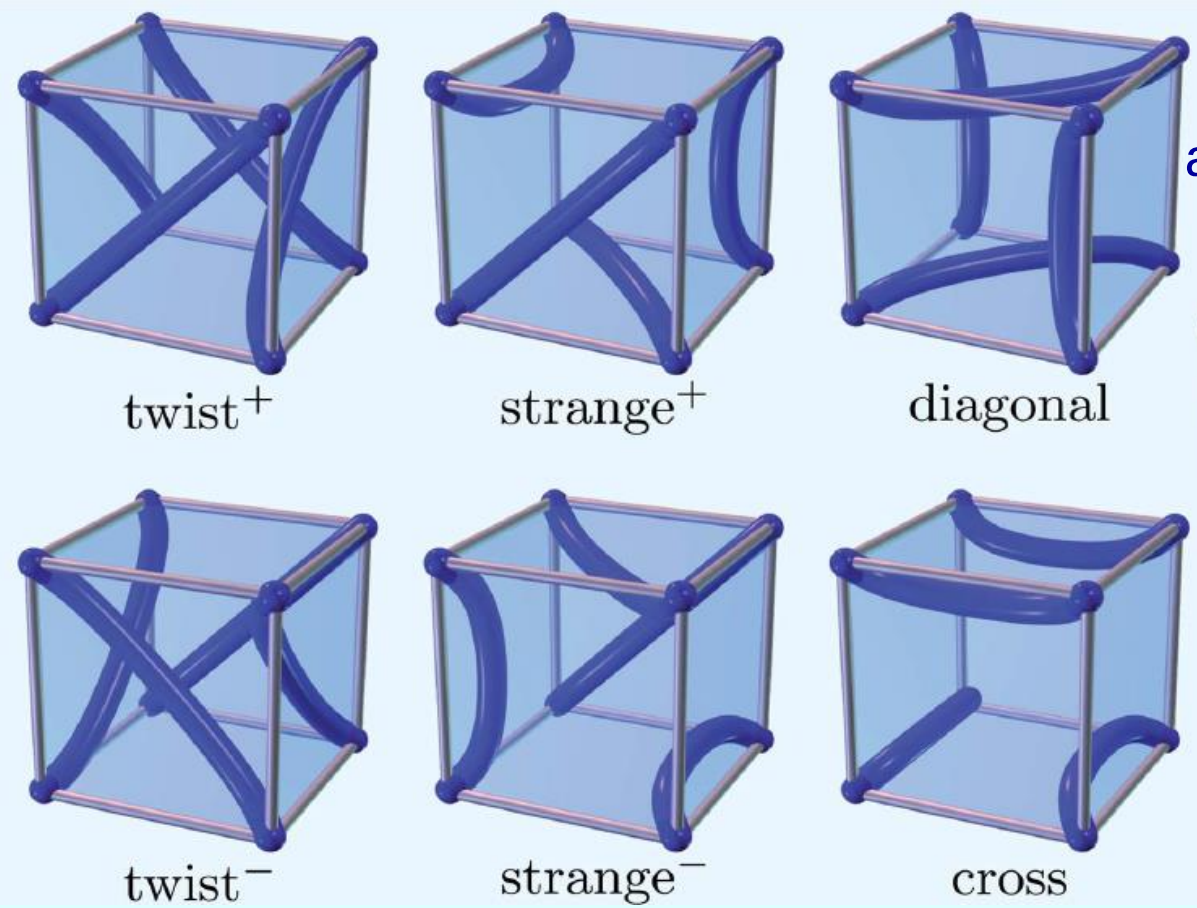


Čopar et al. Soft Matter 2013

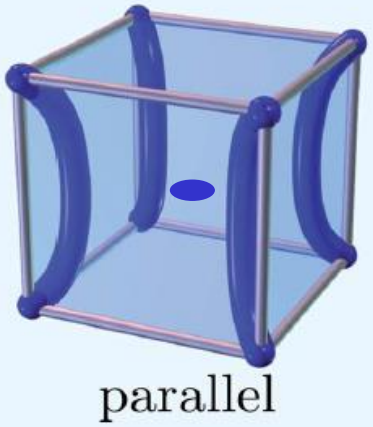
Decomposition of the space among particles to a network of touching voids of cubic and tetrahedral shapes.

-½ disclinations enter voids via vertices.

ALLOWED DISCLINATION ARRANGEMENTS IN VOIDS



7 states
after symmetry
allowed rotations
45 states



Less than 10% different free energy

3 states

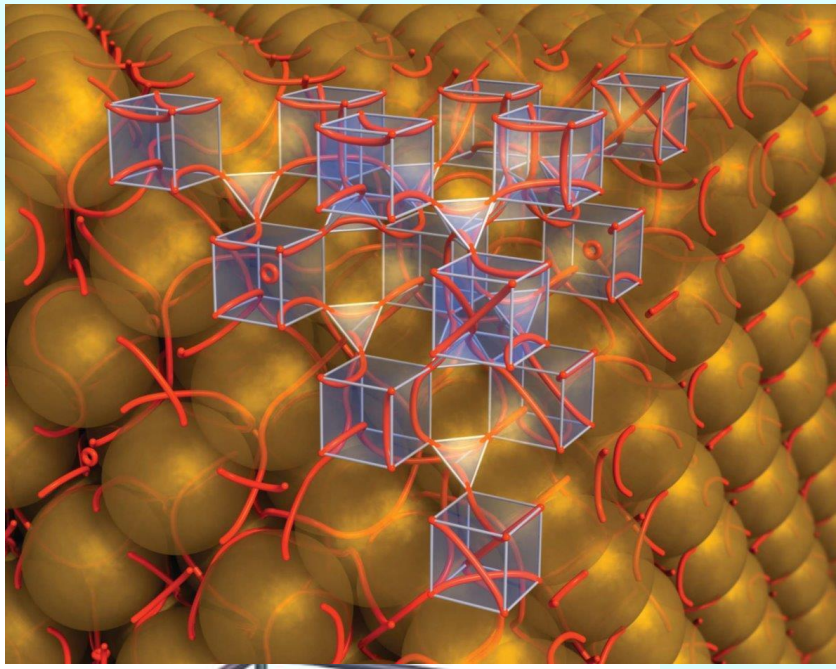
Using the allowed disclination setups in voids and allowing disclinations to continuously progress from among voids a topologically correct ansatz for the disclination network is obtained.

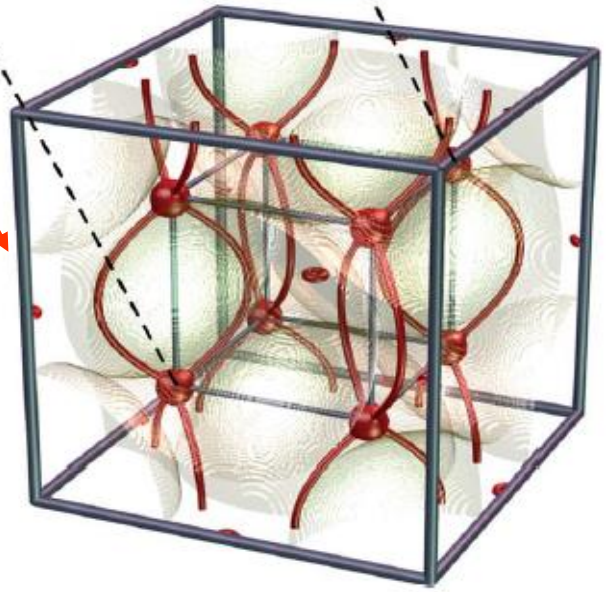
Čopar et al. Soft Matter 2013

RELAXATION: FROM ANSATZ TO EQUILIBRIUM

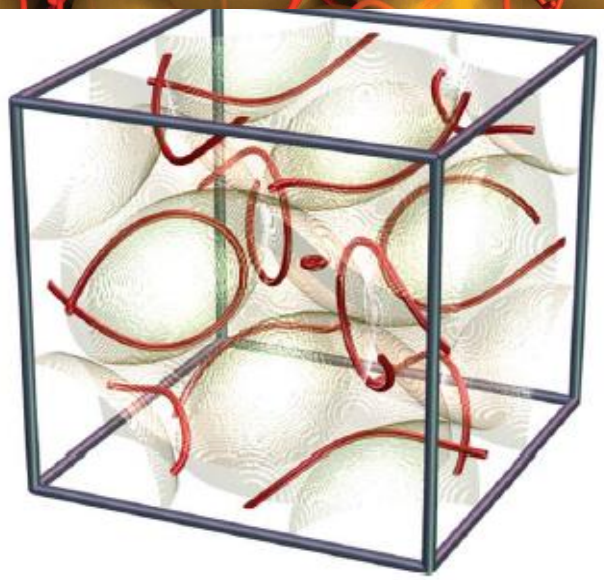
Unit cell has 4 cubic voids &
8 tetrahedral voids and thus
$45^4 x 3^8 \sim 2.7\ 10^{14}$ states

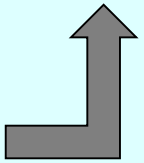
Can such a system be an optically addressable memory?





numerical relaxation





Čopar et al. Soft Matter 2013

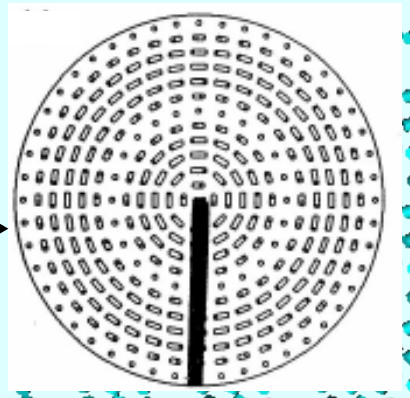
OUTLINE

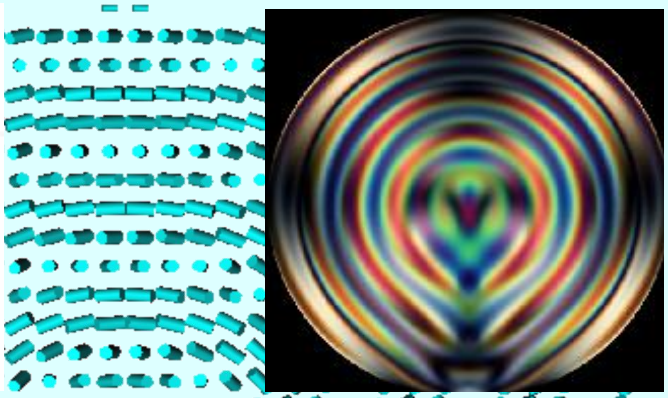
- Motivation:
- Phenomenological modeling of nematics and chiral nematics
- Nematic colloids:
  - Entanglement & nematic braids stabilized by geometry and chirality
  - Local rewiring of disclinations
  - Linking & knotting of disclinations
- Opal structures permeated by nematics
- Cholesteric droplets with knotted disclinations
- Conclusions

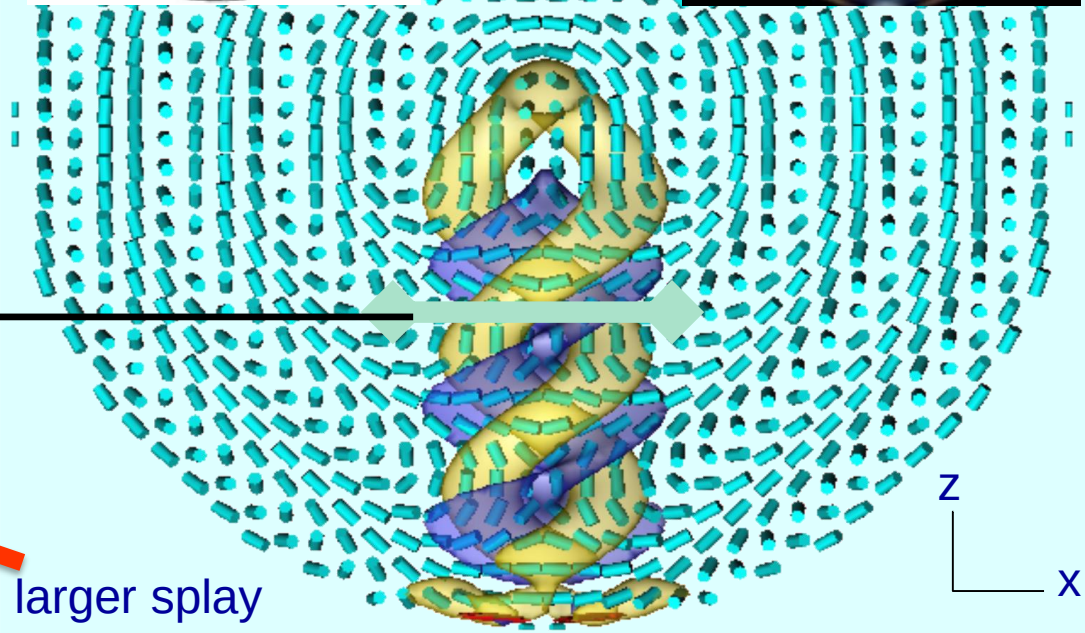
CHOLESTERIC DROPLETS: DEGENERATE PLANAR ANCHORING

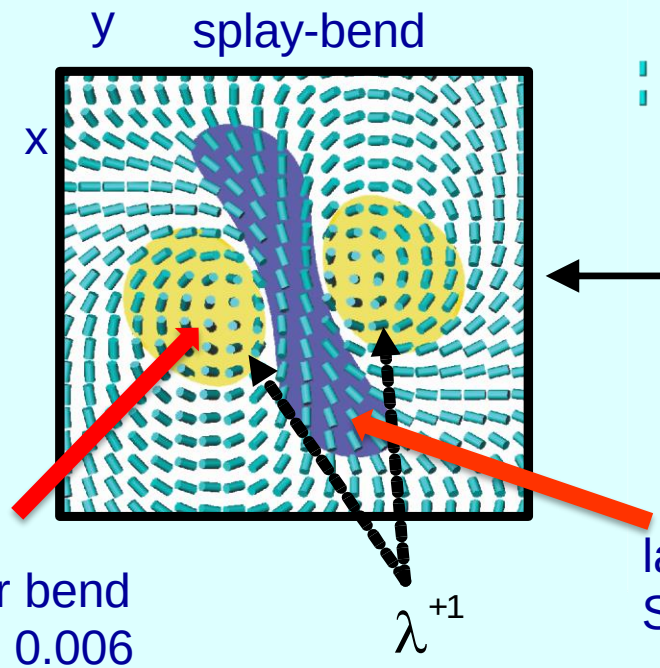
radial spherical structure

Two λ^{+1} disclinations form of a double helix instead of one +2 disclination within the Frank-Pryce model.









larger bend
$S_{SB} < 0.006$

larger splay
$S_{SB} > 0.006$

Seč et al., Soft Matter **8**, 11982 (2012)

CHOLESTERIC DROPLETS:

HOMEOTROPC ANCHORING

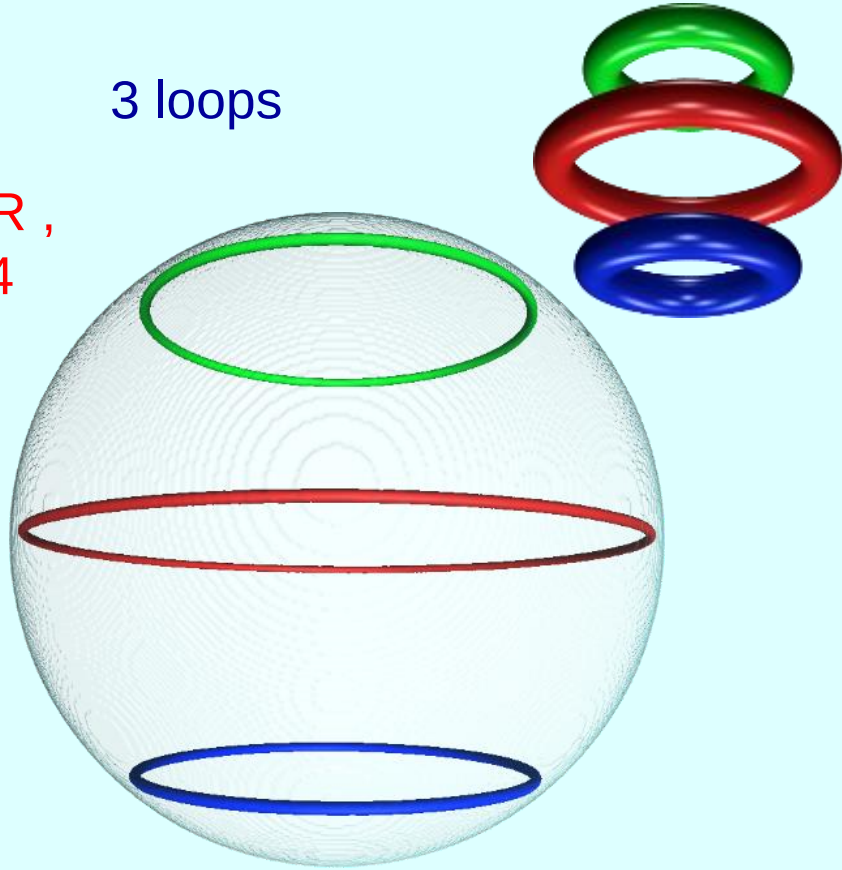
Some simple structures appearing after quench

$N = 4R/p_0$ number of π turns across the diameter

1 loop

$p_0 \sim R$,
$N = 4$

3 loops



more symmetric → lower free energy

Seč, Čopar, & Žumer, Nature Communications 2014

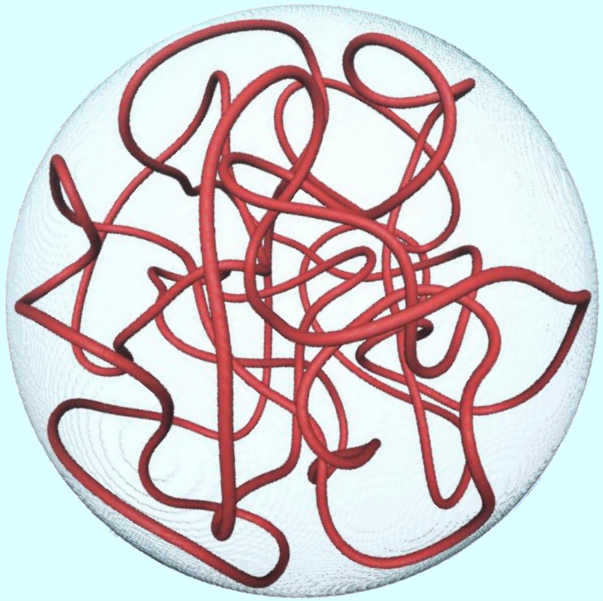
Homeotropic cholesteric droplet with a single disclination loop (Čopar 2013)

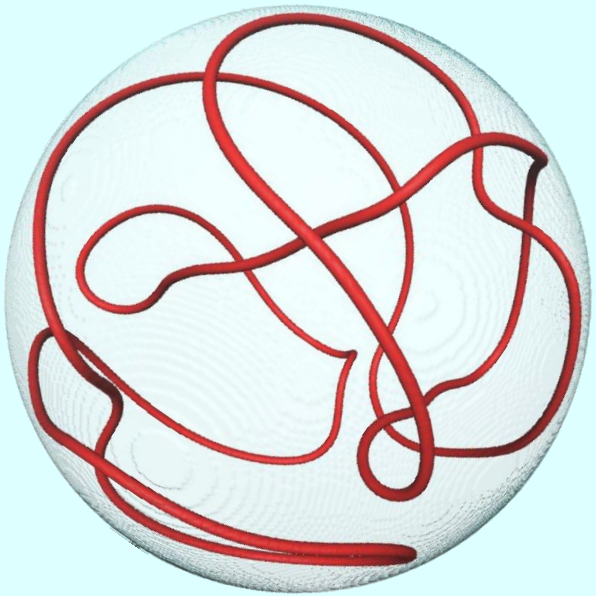
Seč, Čopar, & Žumer, Nature Communications 2014

CHOLESTERIC DROPLETS:
HOMEOTROPC ANCHORING

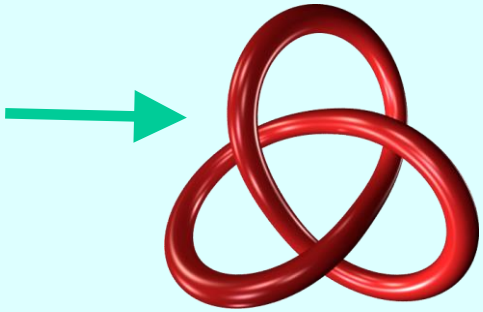
- Strong anchoring: disclinations do not touch surface.
- This restriction, allows only closed disclinations
- Pitch $p_0 \leq R \rightarrow$ knots & links

N = 5





numerical extraction via geometrical simplification

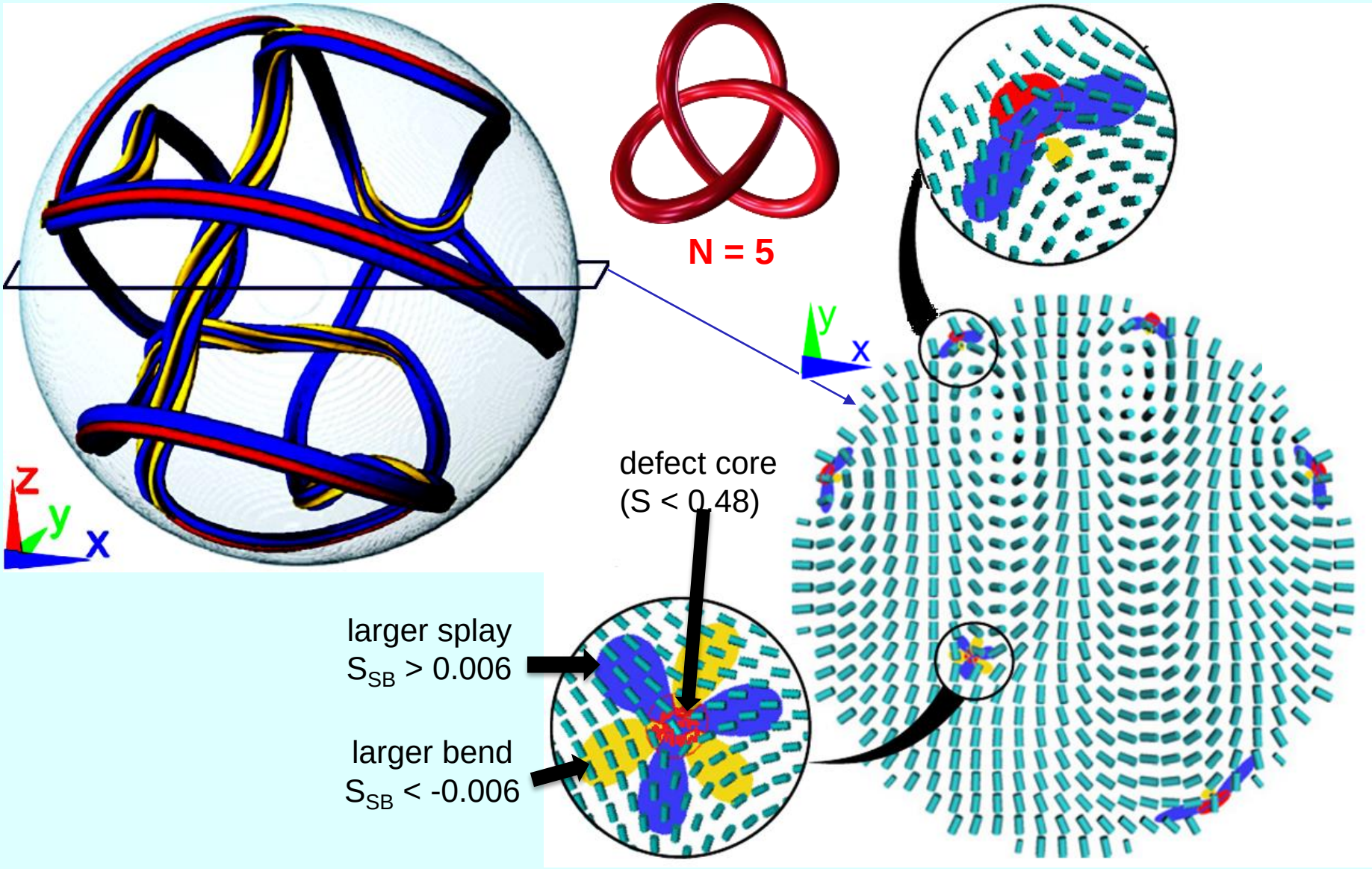


trefoil knot

thermal quench → time → equilibrium structure

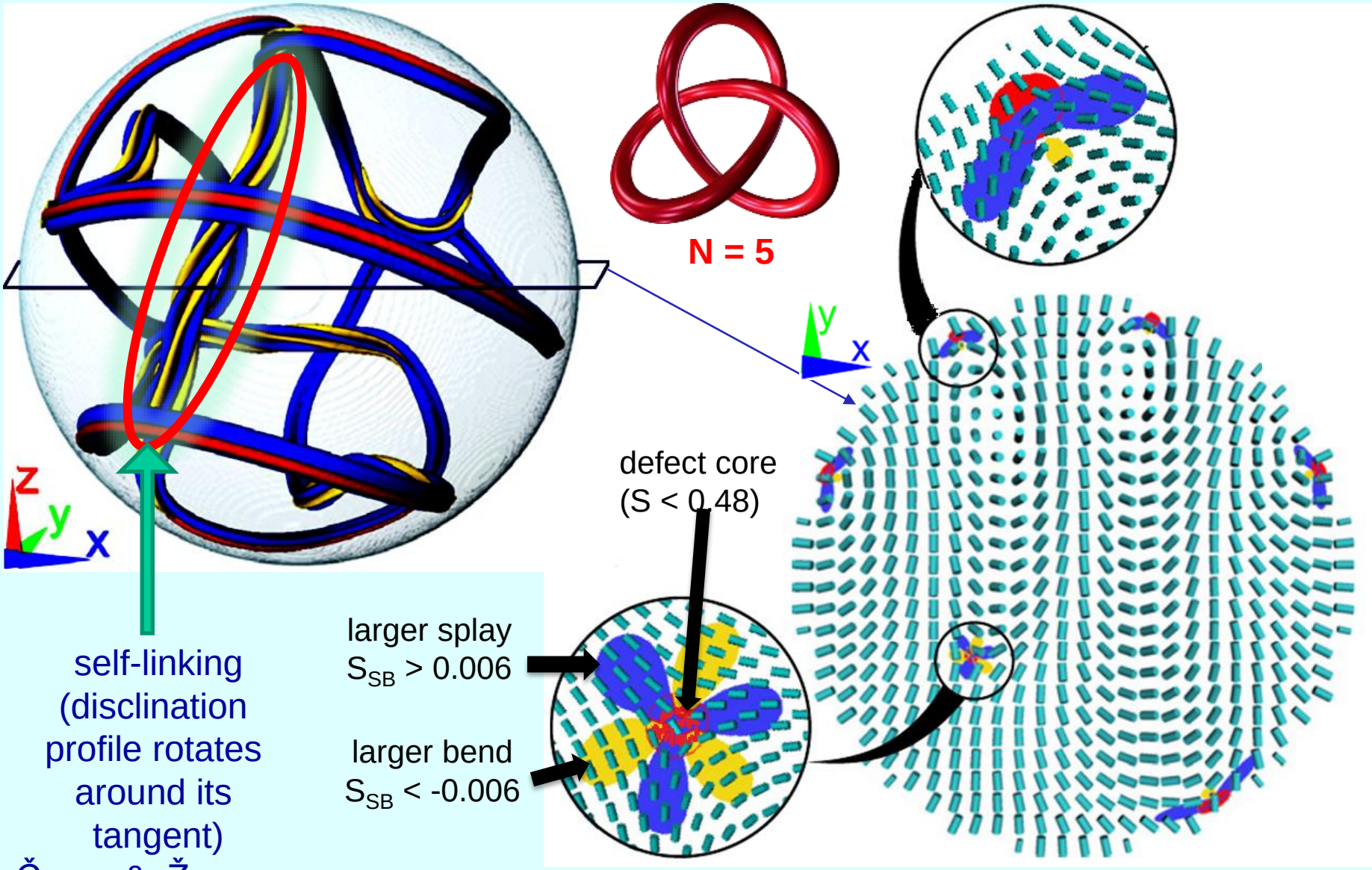
Seč, Čopar, & Žumer, Nature Communications 2014

CHOLESTERIC DROPLETS:
HOMEOTROPC ANCHORING



Seč, Čopar, & Žumer, Nature Communications 2014

CHOLESTERIC DROPLETS:
HOMEOTROPC ANCHORING



self-linking (disclination profile rotates around its tangent)
Čopar & Žumer, PRL 2011

Seč, Čopar, & Žumer, Nature Communications 2014

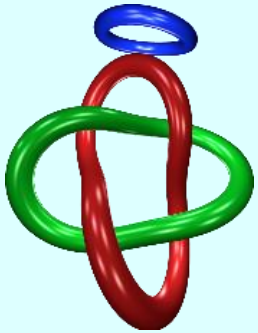
CHOLESTERIC DROPLETS:

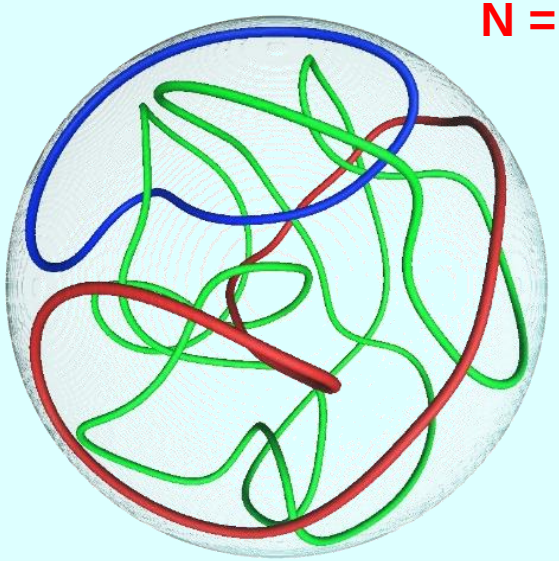
HOMEOTROPC ANCHORING

Some linked structures appearing after quench

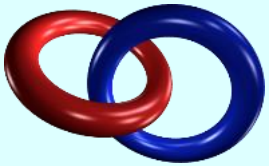
N = 5

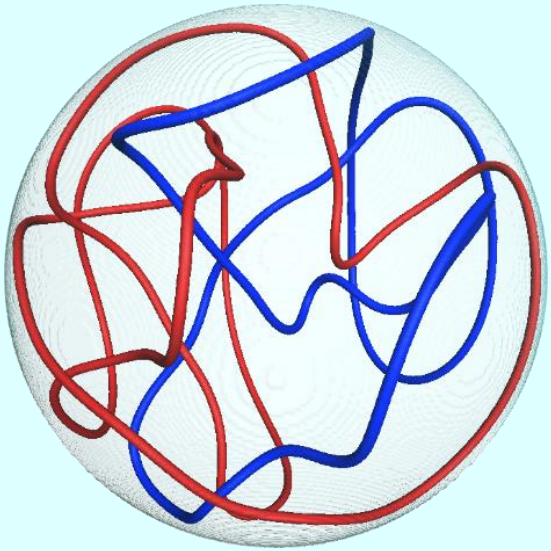
Solomon link



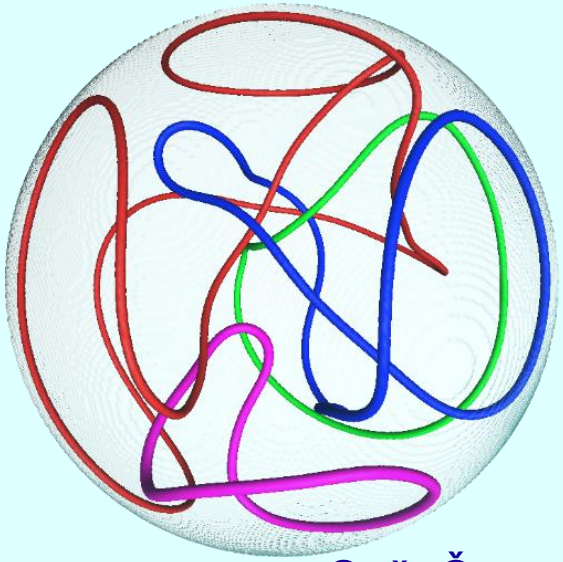


Hopf link

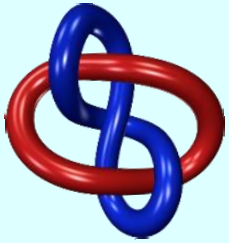


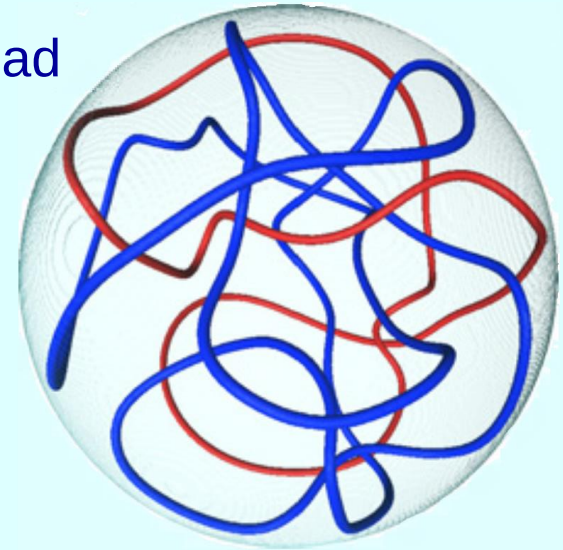


6^3_3 + 1 loop



Whitehead link

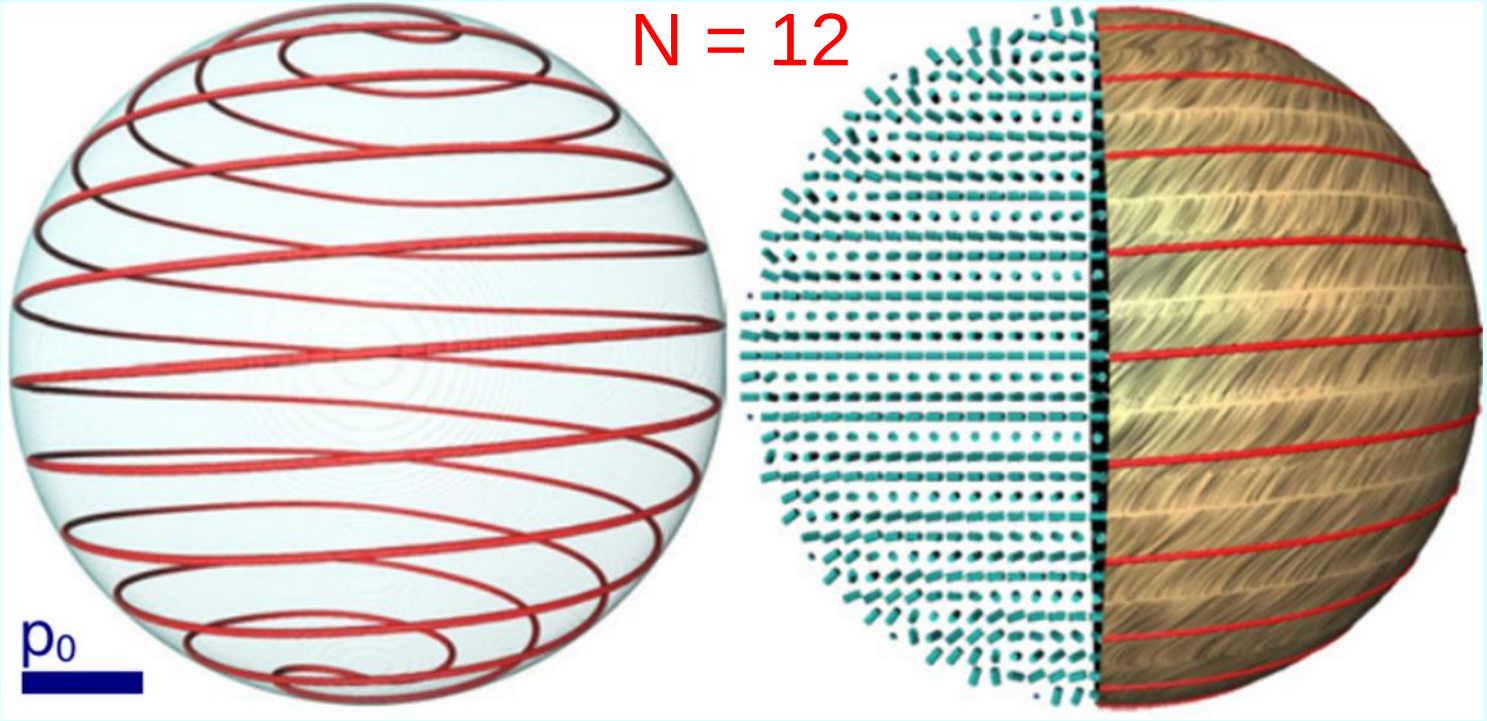




Seč, Čopar, & Žumer, Nature Communications 2014

CHOLESTERIC DROPLETS:
HOMEOTROPC ANCHORING & SHORT PITCH

stable configuration

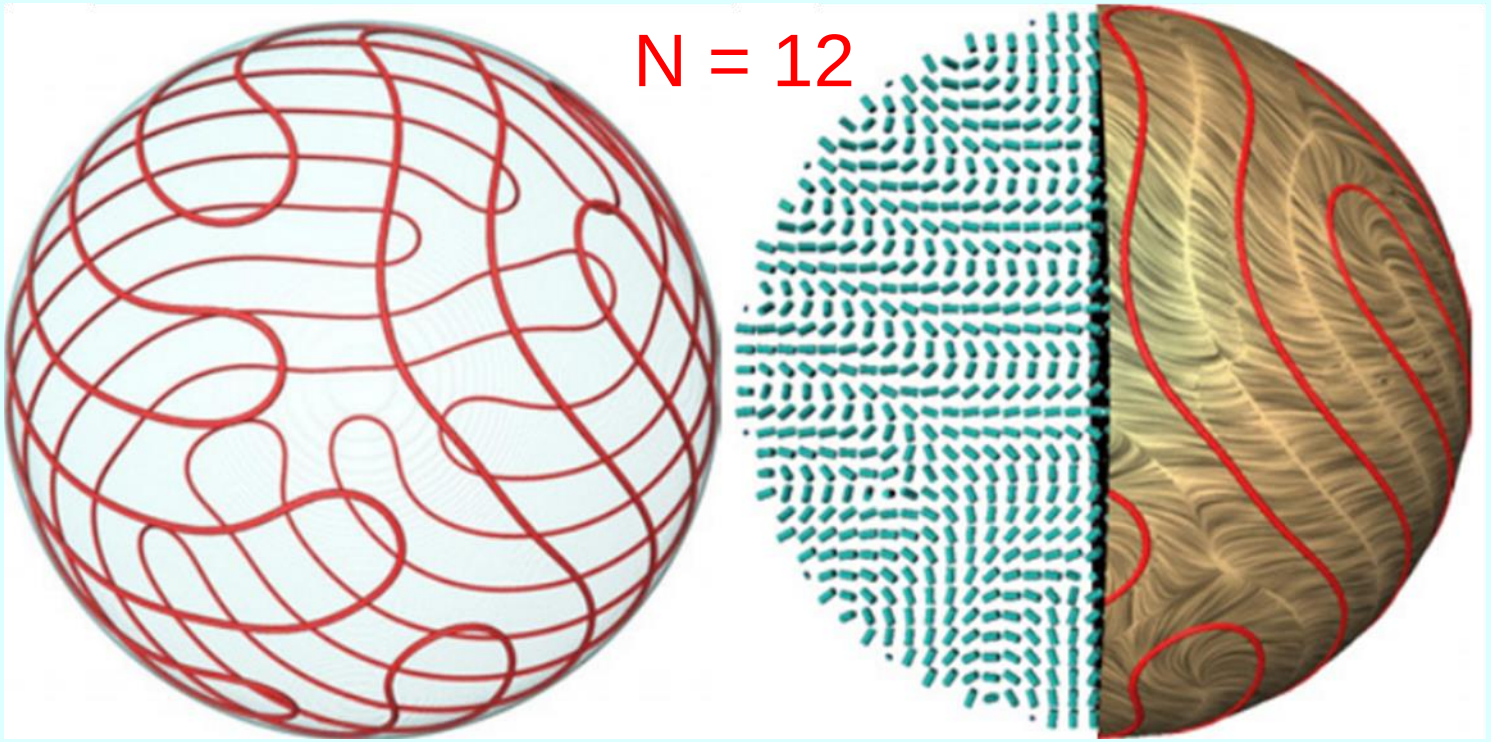


- uniformly layered cholesteric director field, quasi 2D structure
- constant spacing of disclinations
- smectic-like ordering of cholesteric layers

Seč, Čopar, & Žumer, Nature Communications 2014

CHOLESTERIC DROPLETS:
HOMEOTROPC ANCHORING & SHORT PITCH

metastable configuration



- smectic kinks
- obey topological rules for a smectic on a sphere

For the high-chirality limit (N>6) disclinations are expelled in a narrow boundary layer. For the weak-chirality limit (N<4) simple twisted structures appear. Only for the narrow intermediate range links and knots appear as (meta)stable structures.

Seč, Čopar, & Žumer, Nature Communications 2014

CONCLUSIONS

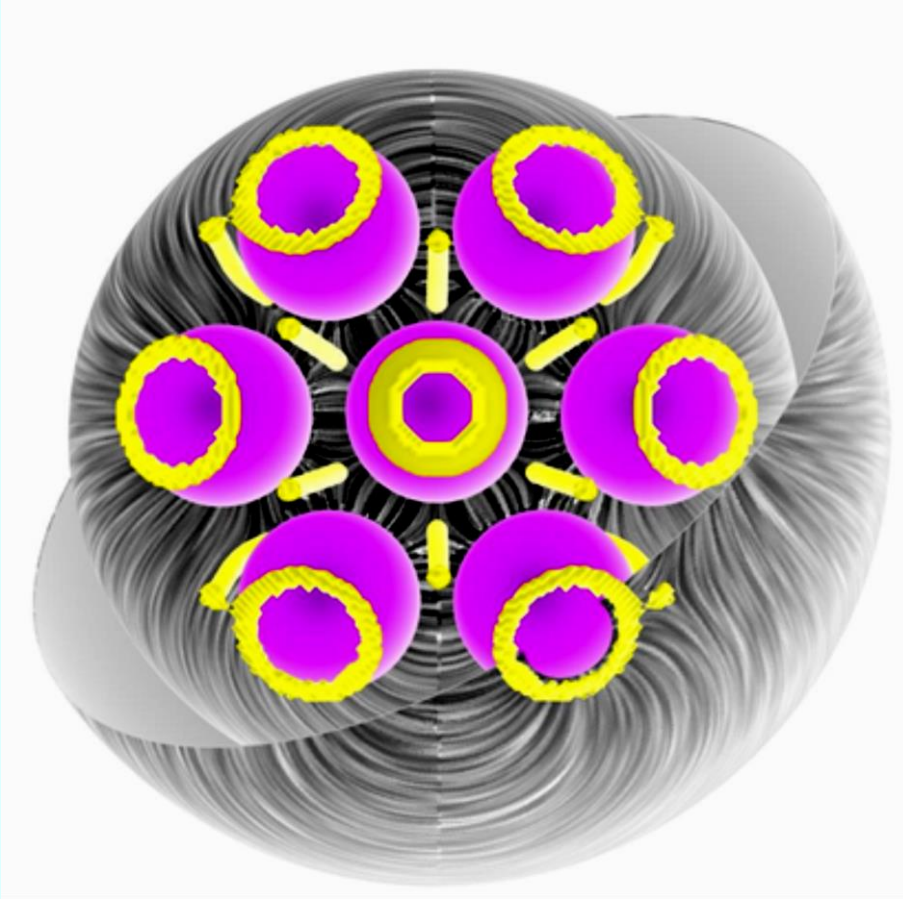
Topological soft matter is illustrated by selected examples:

- Topological description of nematics braids in colloidal systems where disclinations entangle particles based on a topological invariant of a nematic disclination loop was described. Nematic braids including knots and links are predominantly stabilized by geometry and anchoring of confining surfaces.
- 3D disclination networks in nematics permeating opal colloidal structures were topologically characterized and numerically simulated. The description of the orthogonal crossing of disclinations in a tetrahedral voids was extended to cubic voids.
- It was demonstrated that intermediate chirality together with the confinement lead to frustration of nematic fields and thus to formation of free standing knots. .

Topological soft matter is expected to have potential beyond a topological playground.

FURTHER RESEARCH
KNOTTED COLLOIDAL PARTICLES & DECORATED NEMATIC SHELLS

Ravnik & Žumer,
Collaboration with Boulder group,
Nature Material 2014



Seč & Žumer,
Collaboration with Montpelier group,
published in Soft Matter 2013

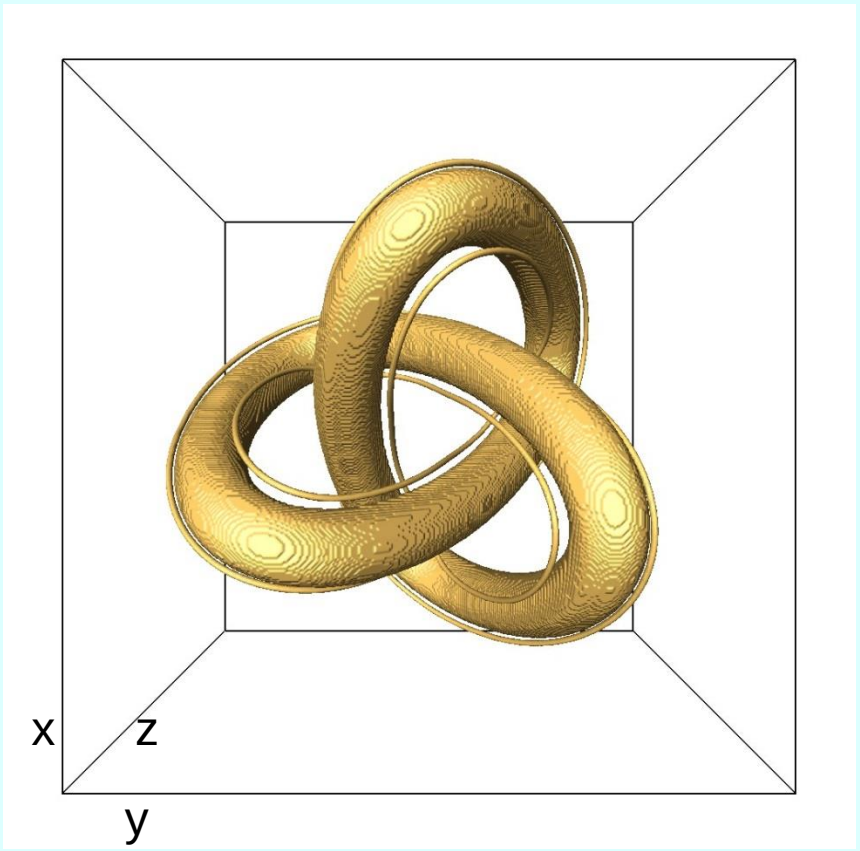
NONTRIVIAL PARTICLE

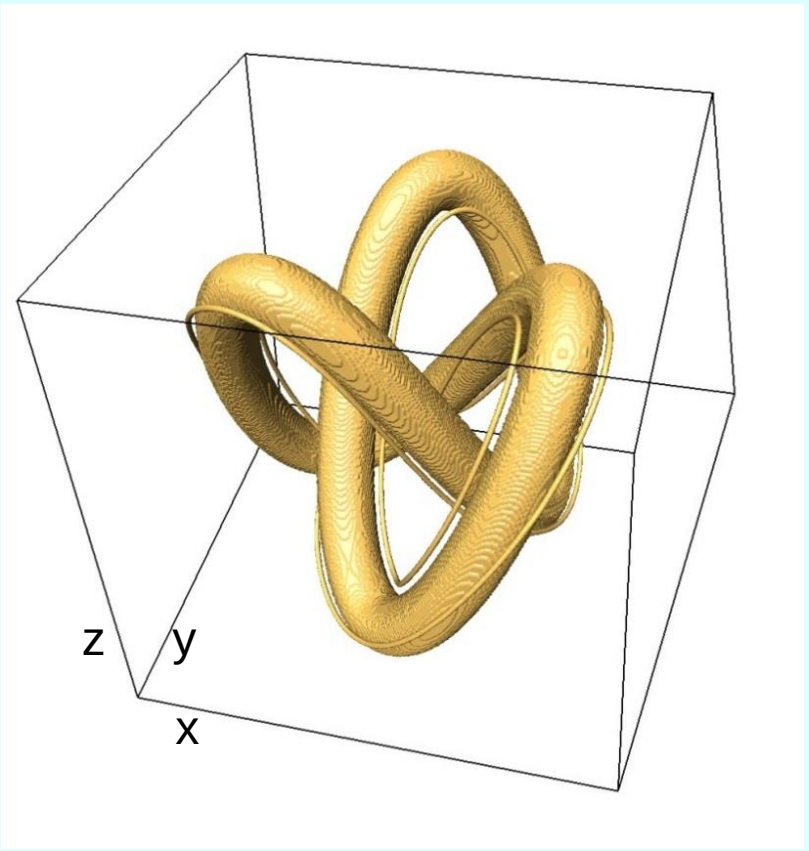
RESHAPEABLE PARTICLE IN A FORM OF A TREFOIL KNOT

with homeotropic surface anchoring in a homogenous nematic

Knots are stabilized by particle topology

2 knotted loops ⟶ 1loop & residual surface lines





director farfield along z-axis

Ravnik, Žumer 2013

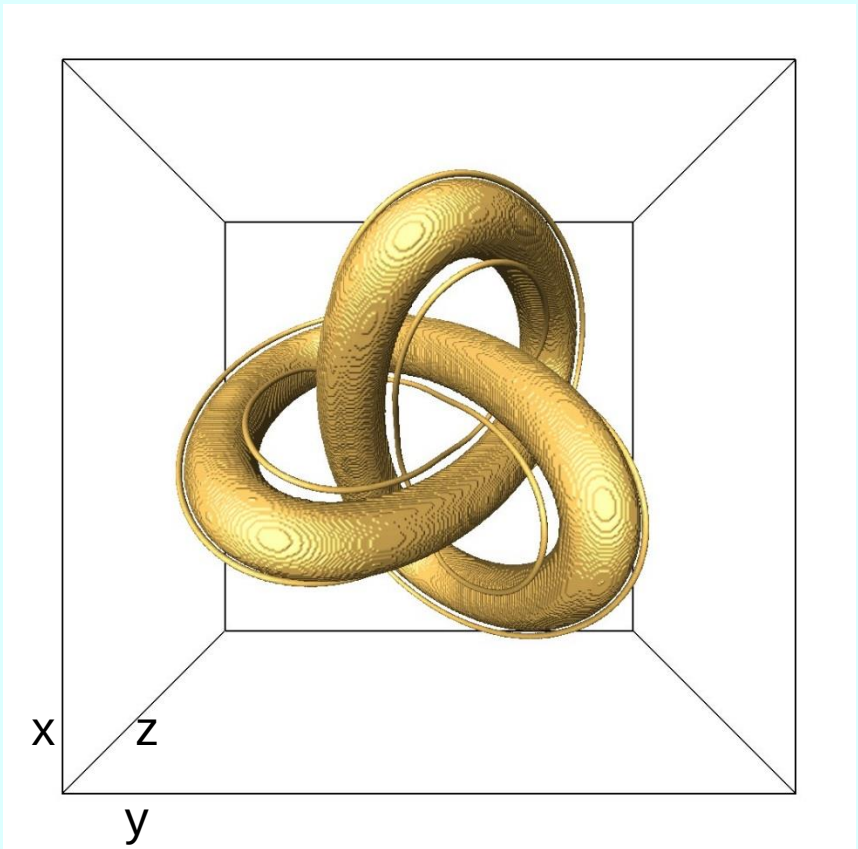
NONTRIVIAL PARTICLE

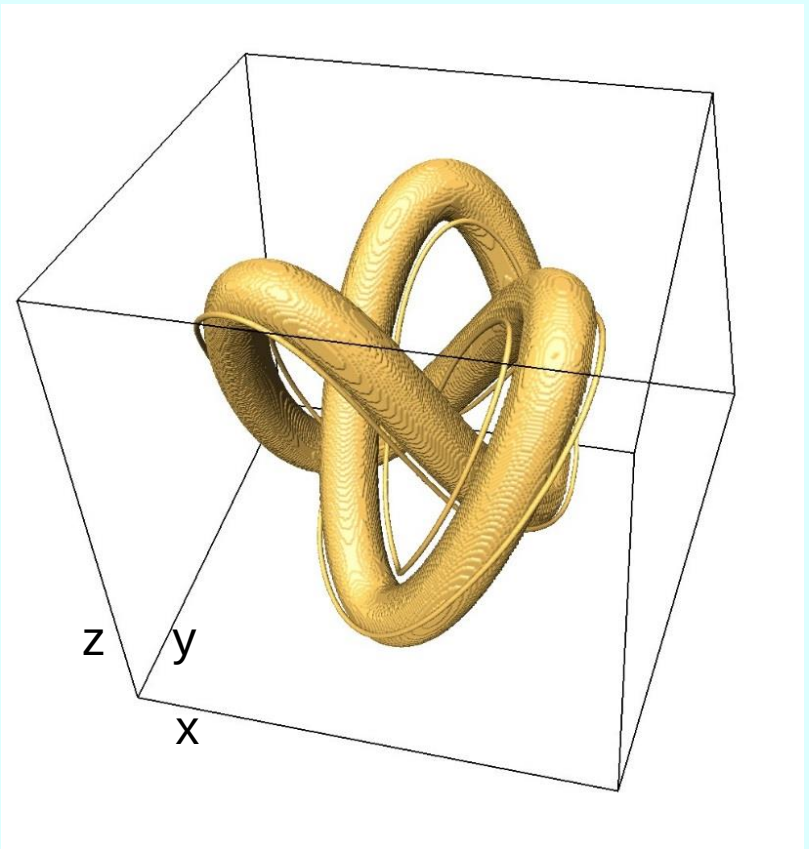
RESHAPEABLE PARTICLE IN A FORM OF A TREFOIL KNOT

with homeotropic surface anchoring in a homogenous nematic

Knots are stabilized by particle topology

2 knotted loops ⟶ 1loop & residual surface lines





director farfield along z-axis

Ravnik, Žumer 2013

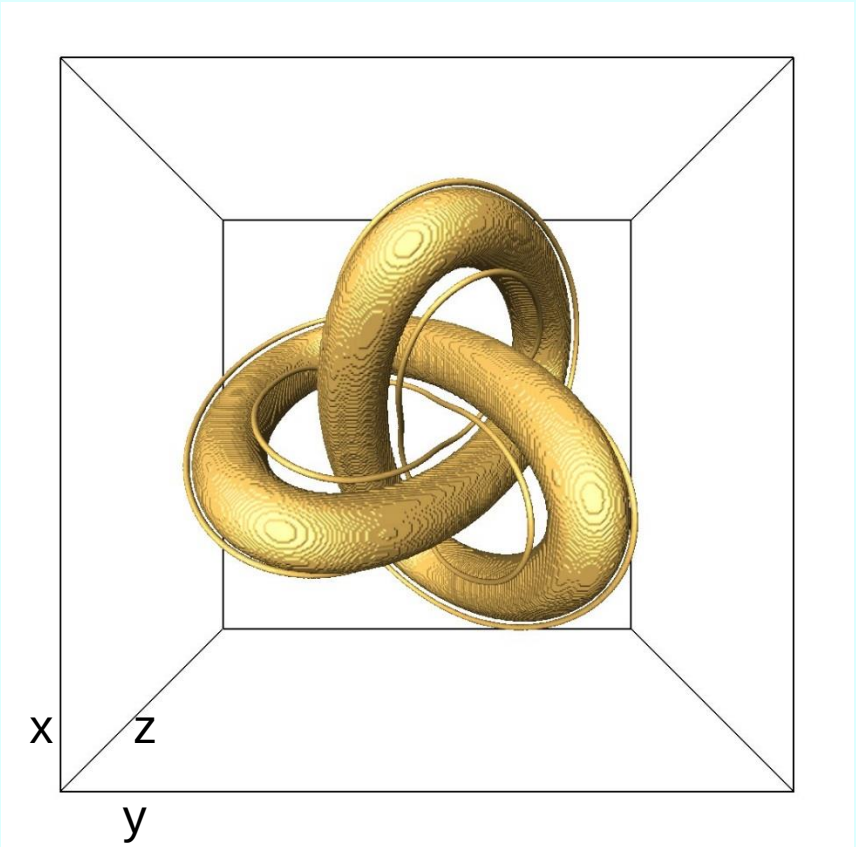
NONTRIVIAL PARTICLE

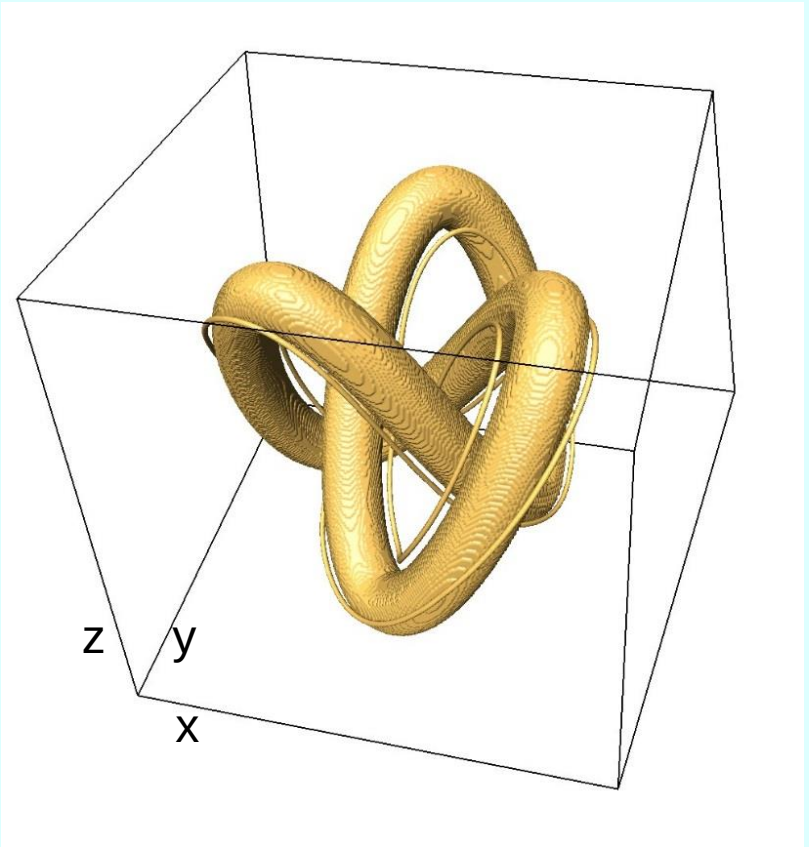
RESHAPEABLE PARTICLE IN A FORM OF A TREFOIL KNOT

with homeotropic surface anchoring in a homogenous nematic

Knots are stabilized by particle topology

2 knotted loops ⟶ 1loop & residual surface lines





director farfield along z-axis

Ravnik, Žumer 2013

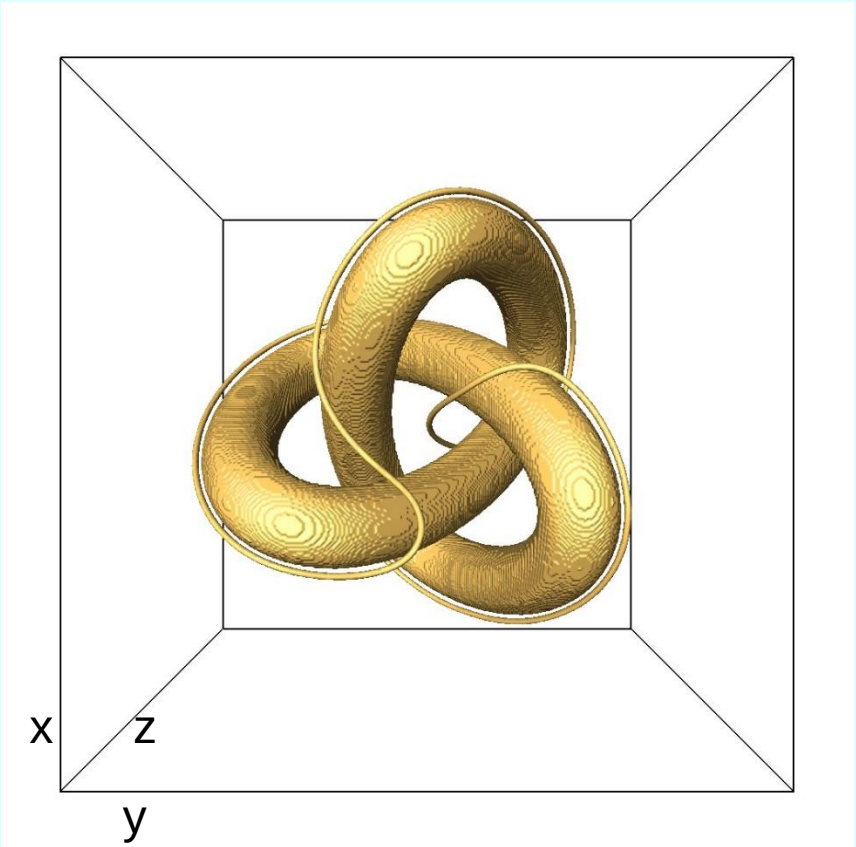
NONTRIVIAL PARTICLE

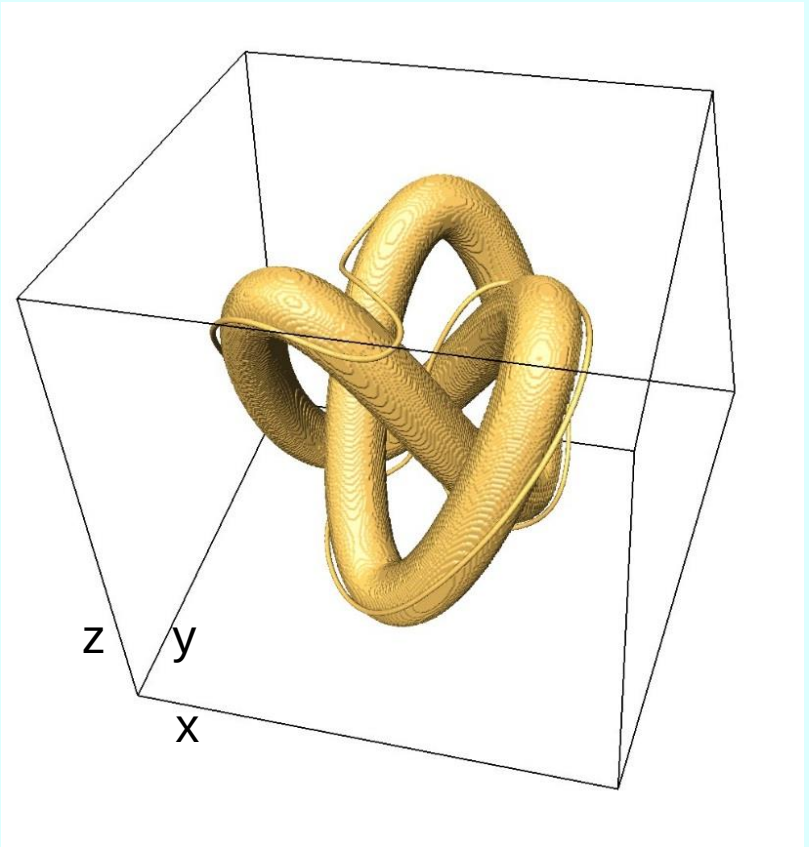
RESHAPEABLE PARTICLE IN A FORM OF A TREFOIL KNOT

with homeotropic surface anchoring in a homogenous nematic

Knots are stabilized by particle topology

2 knotted loops ⟶ 1loop & residual surface lines





director farfield along z-axis

Ravnik, Žumer 2013

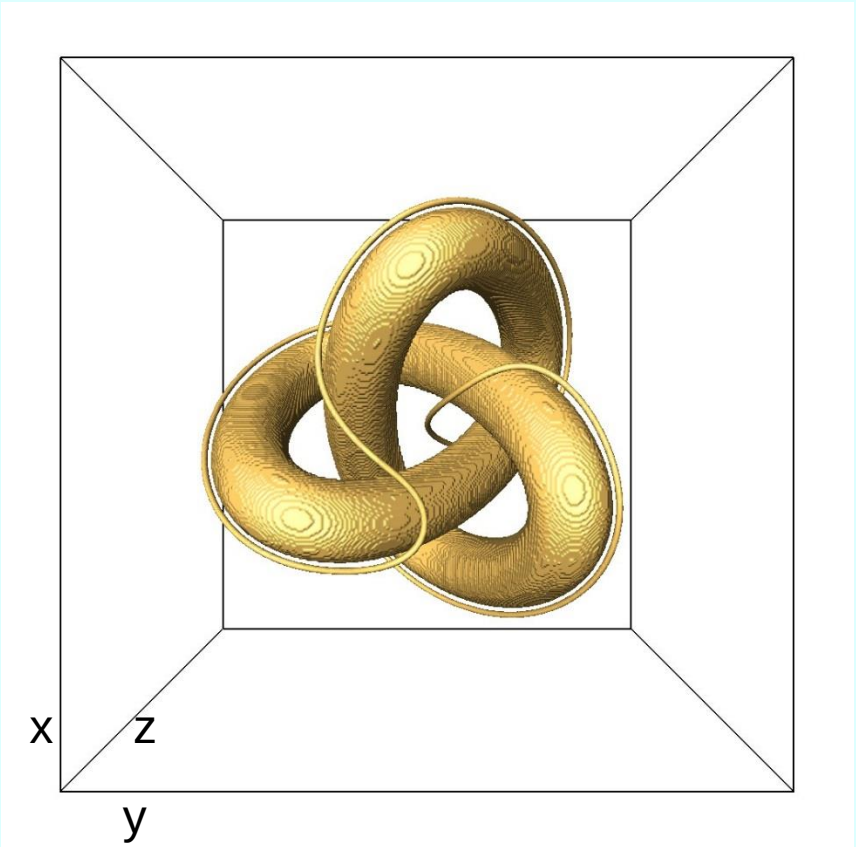
NONTRIVIAL PARTICLE

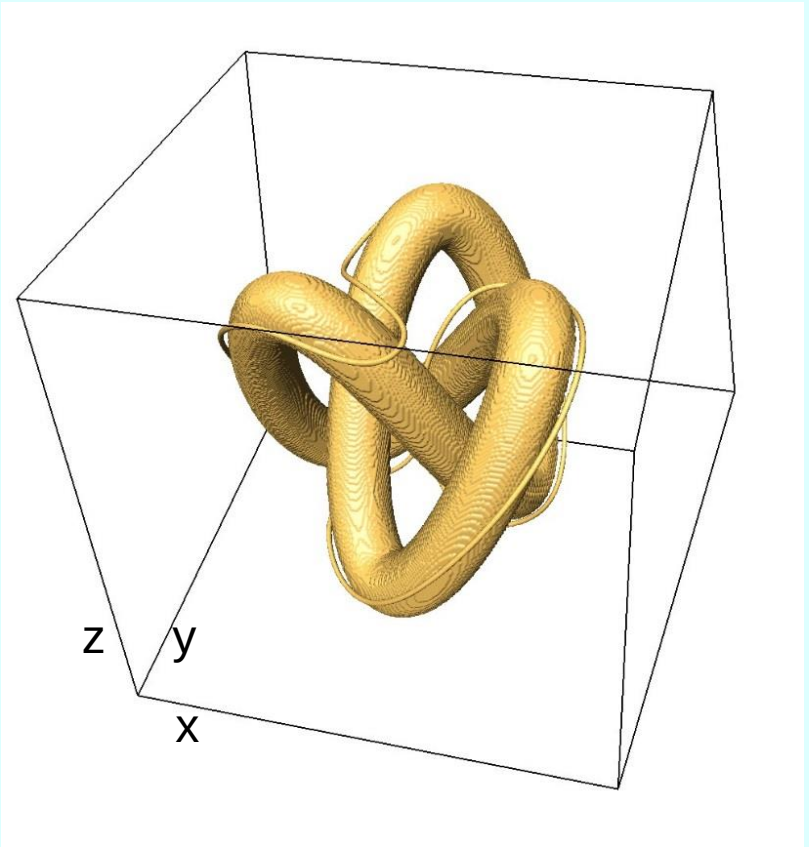
RESHAPEABLE PARTICLE IN A FORM OF A TREFOIL KNOT

with homeotropic surface anchoring in a homogenous nematic

Knots are stabilized by particle topology

2 knotted loops ⟶ 1loop & residual surface lines





director farfield along z-axis

Ravnik, Žumer 2013

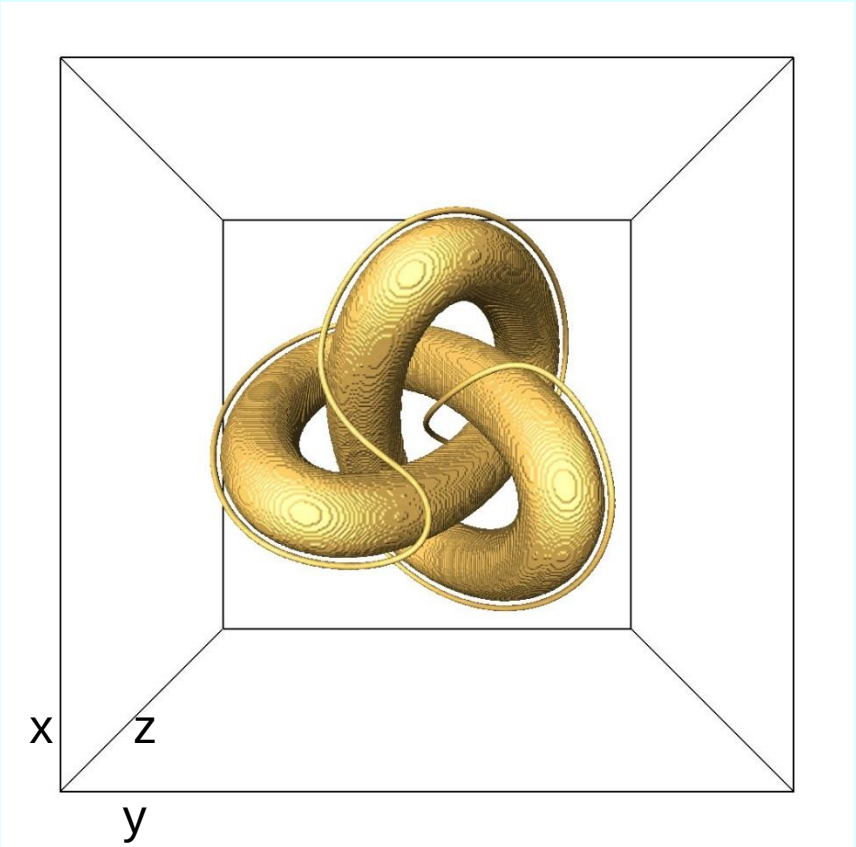
NONTRIVIAL PARTICLE

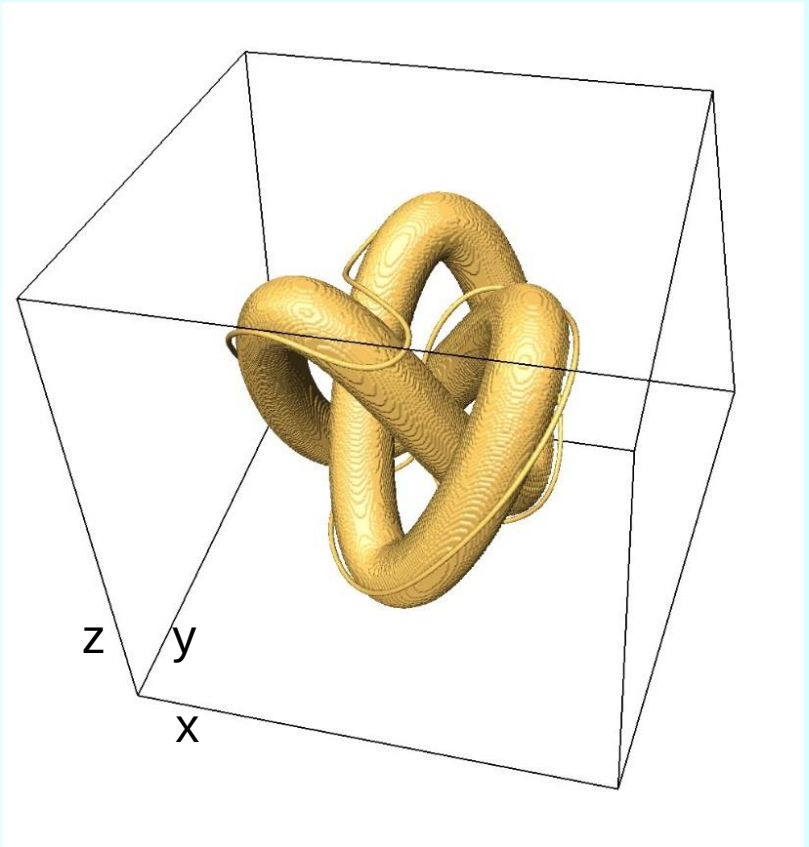
RESHAPEABLE PARTICLE IN A FORM OF A TREFOIL KNOT

with homeotropic surface anchoring in a homogenous nematic

Knots are stabilized by particle topology

2 knotted loops ⟶ 1loop & residual surface lines





director farfield along z-axis

Ravnik, Žumer 2013

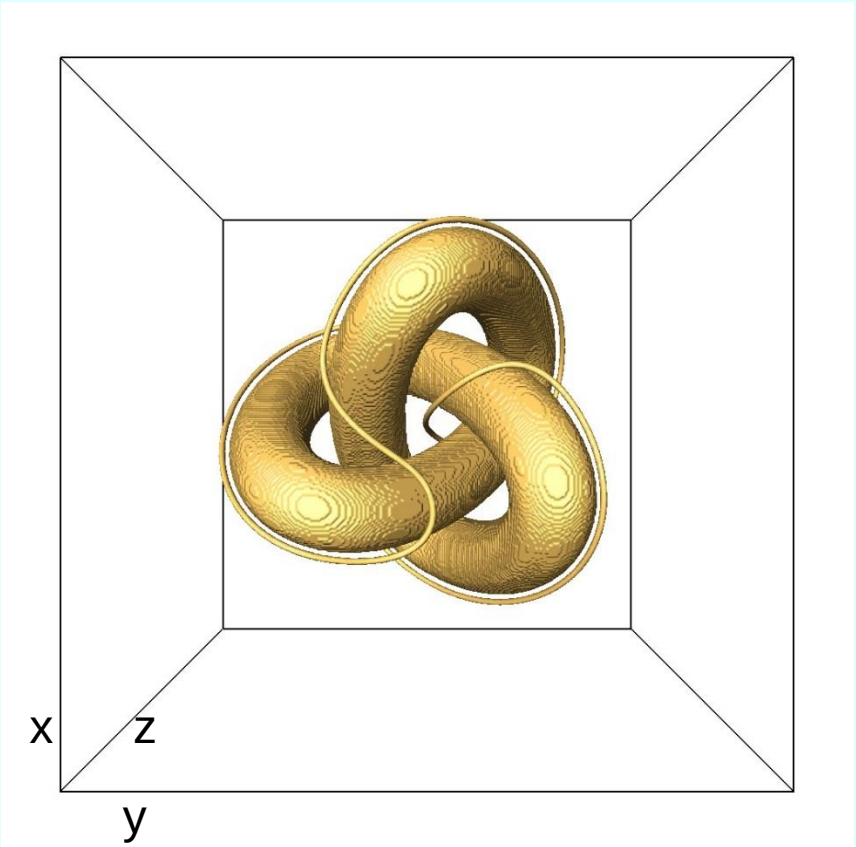
NONTRIVIAL PARTICLE

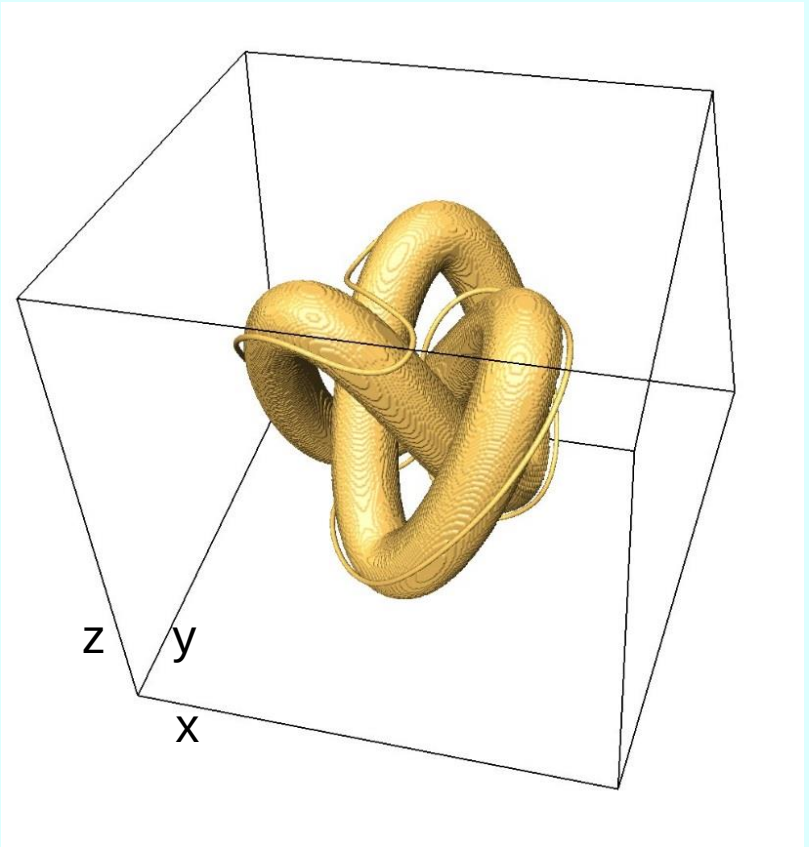
RESHAPEABLE PARTICLE IN A FORM OF A TREFOIL KNOT

with homeotropic surface anchoring in a homogenous nematic

Knots are stabilized by particle topology

2 knotted loops ⟶ 1loop & residual surface lines





director farfield along z-axis

Ravnik, Žumer 2013

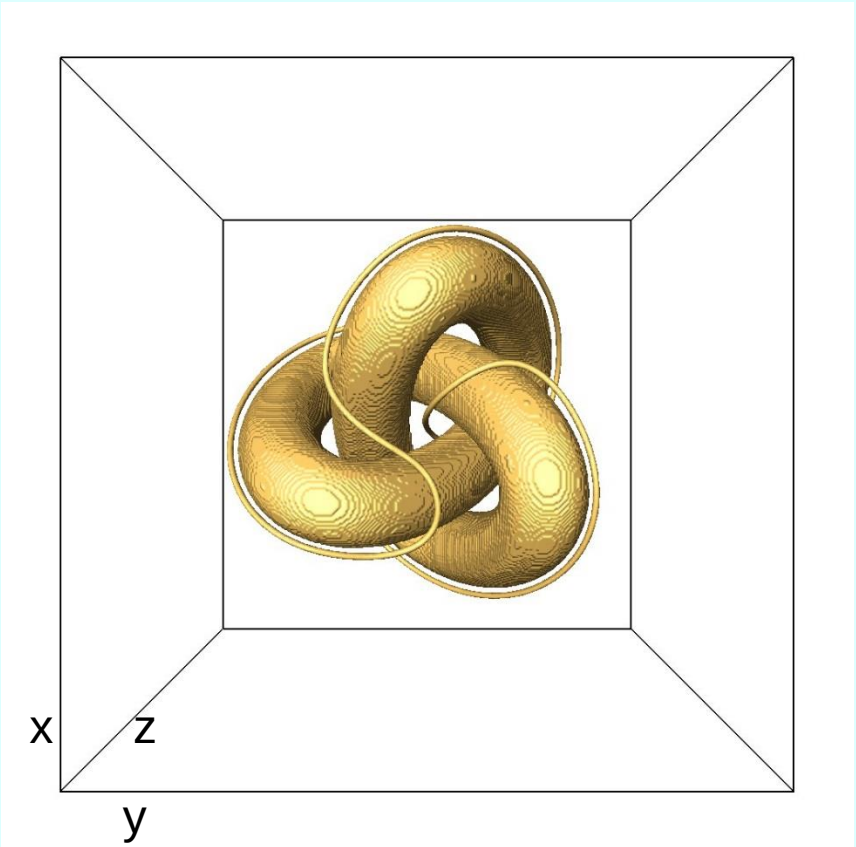
NONTRIVIAL PARTICLE

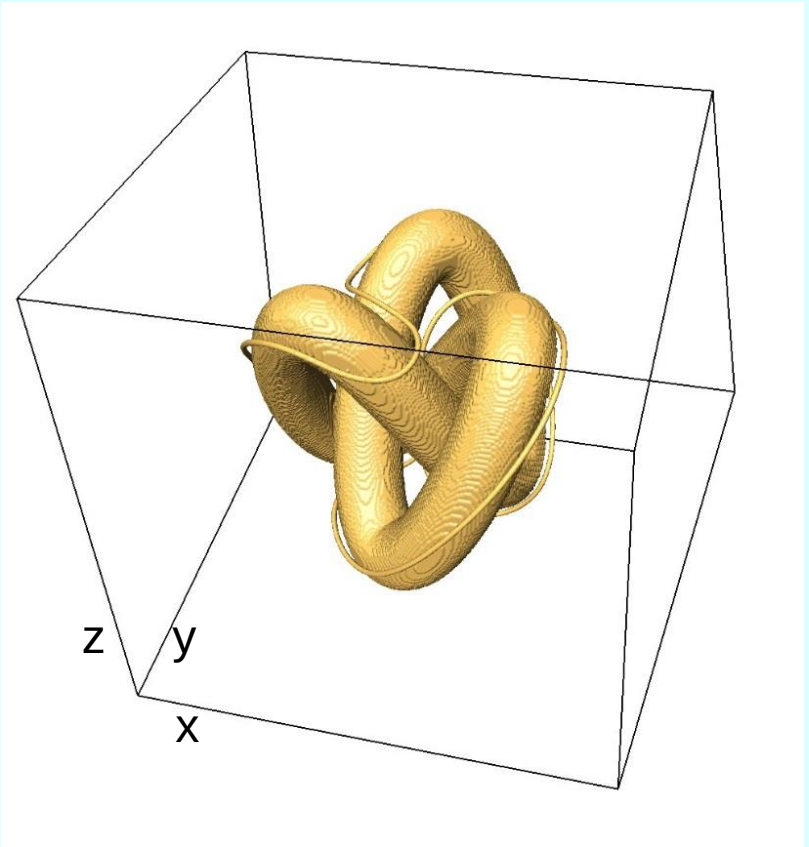
RESHAPEABLE PARTICLE IN A FORM OF A TREFOIL KNOT

with homeotropic surface anchoring in a homogenous nematic

Knots are stabilized by particle topology

2 knotted loops ⟶ 1loop & residual surface lines





director farfield along z-axis

Ravnik, Žumer 2013

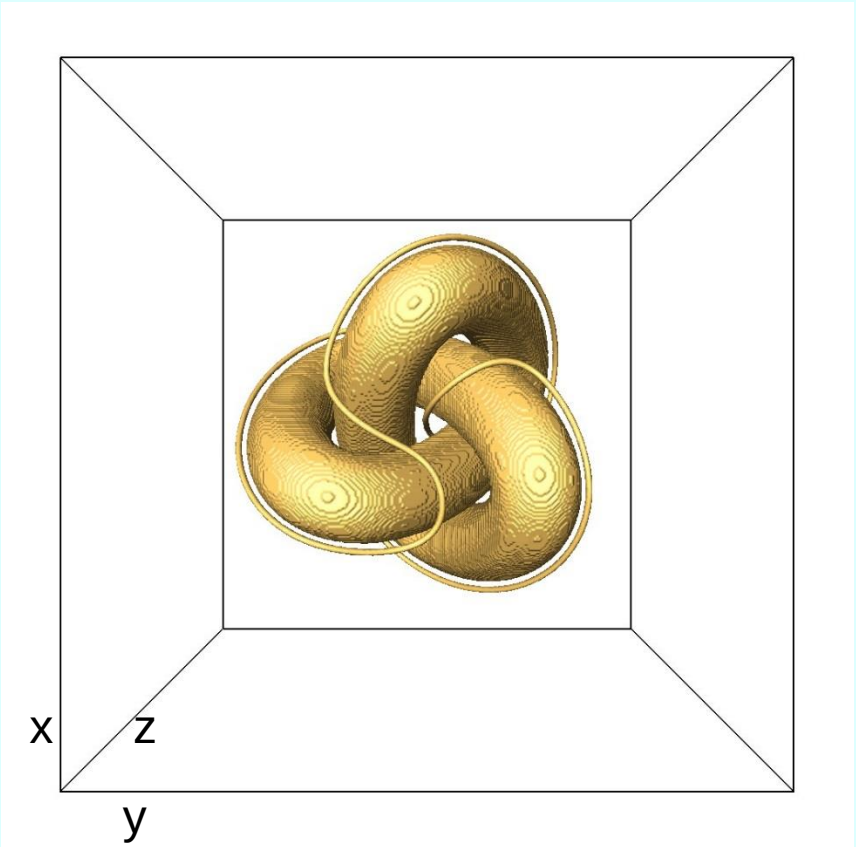
NONTRIVIAL PARTICLE

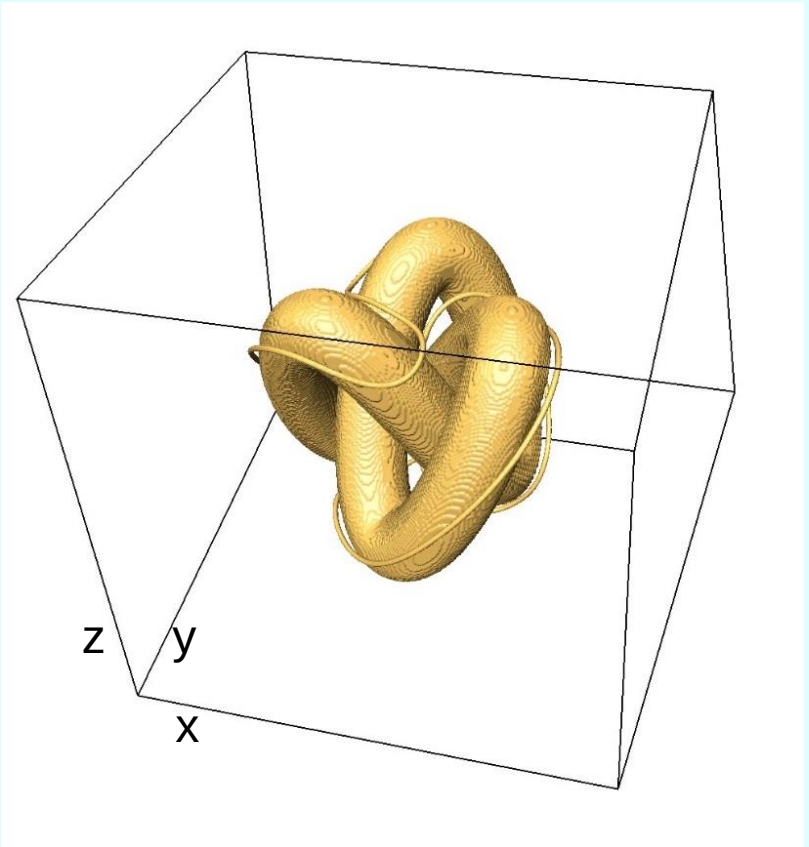
RESHAPEABLE PARTICLE IN A FORM OF A TREFOIL KNOT

with homeotropic surface anchoring in a homogenous nematic

Knots are stabilized by particle topology

2 knotted loops ⟶ 1loop & residual surface lines





director farfield along z-axis

Ravnik, Žumer 2013

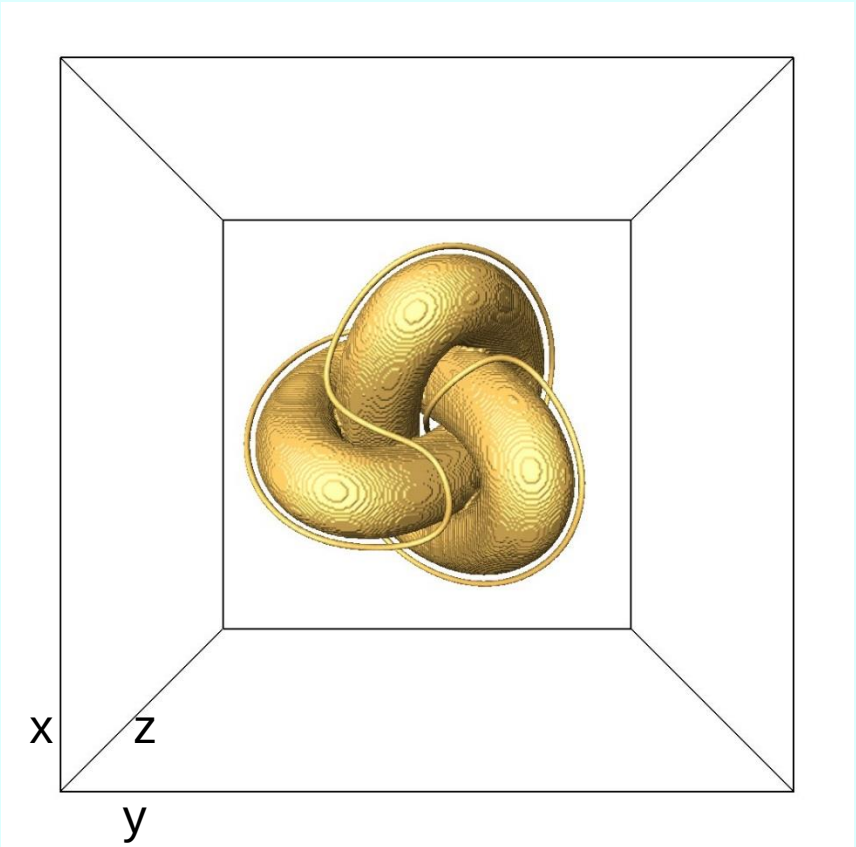
NONTRIVIAL PARTICLE

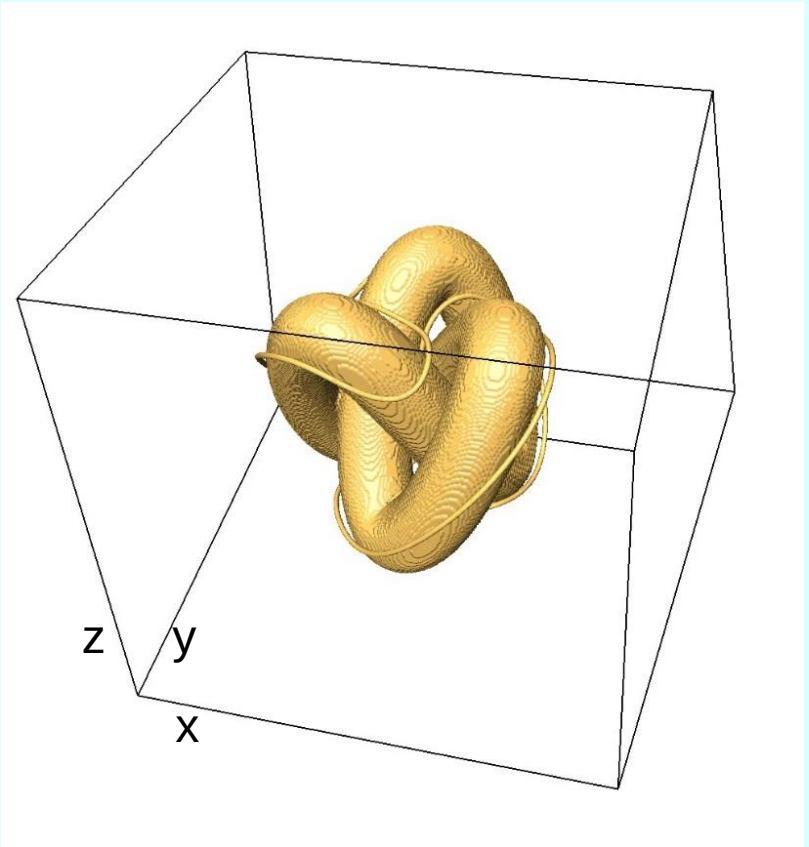
RESHAPEABLE PARTICLE IN A FORM OF A TREFOIL KNOT

with homeotropic surface anchoring in a homogenous nematic

Knots are stabilized by particle topology

2 knotted loops ⟶ 1loop & residual surface lines





director farfield along z-axis

Ravnik, Žumer 2013

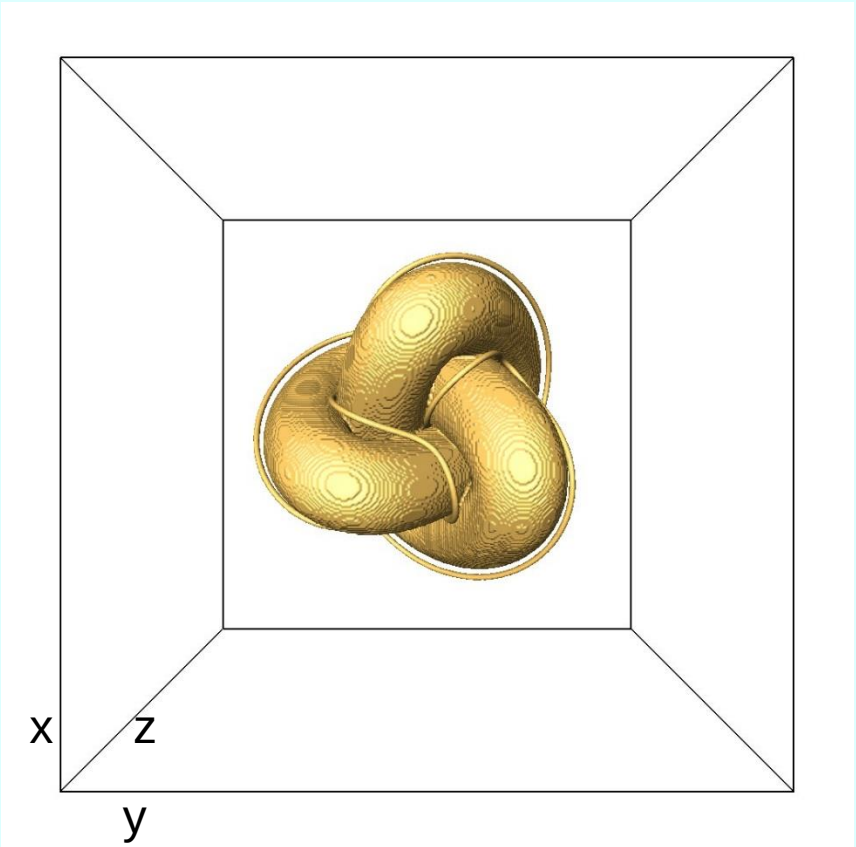
NONTRIVIAL PARTICLE

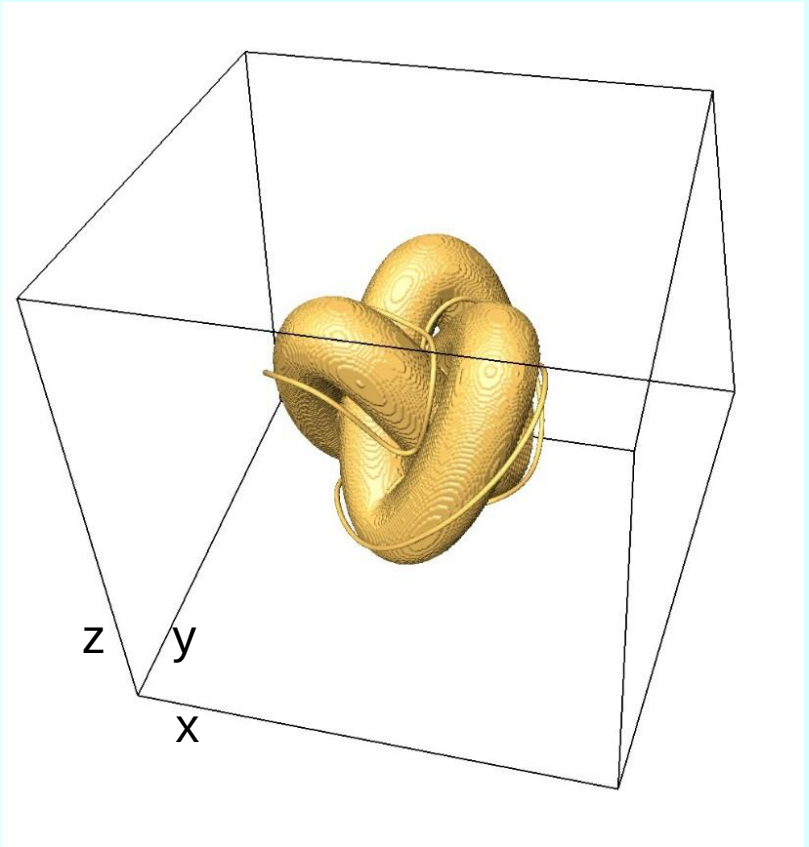
RESHAPEABLE PARTICLE IN A FORM OF A TREFOIL KNOT

with homeotropic surface anchoring in a homogenous nematic

Knots are stabilized by particle topology

2 knotted loops ⟶ 1loop & residual surface lines





director farfield along z-axis

Ravnik, Žumer 2013

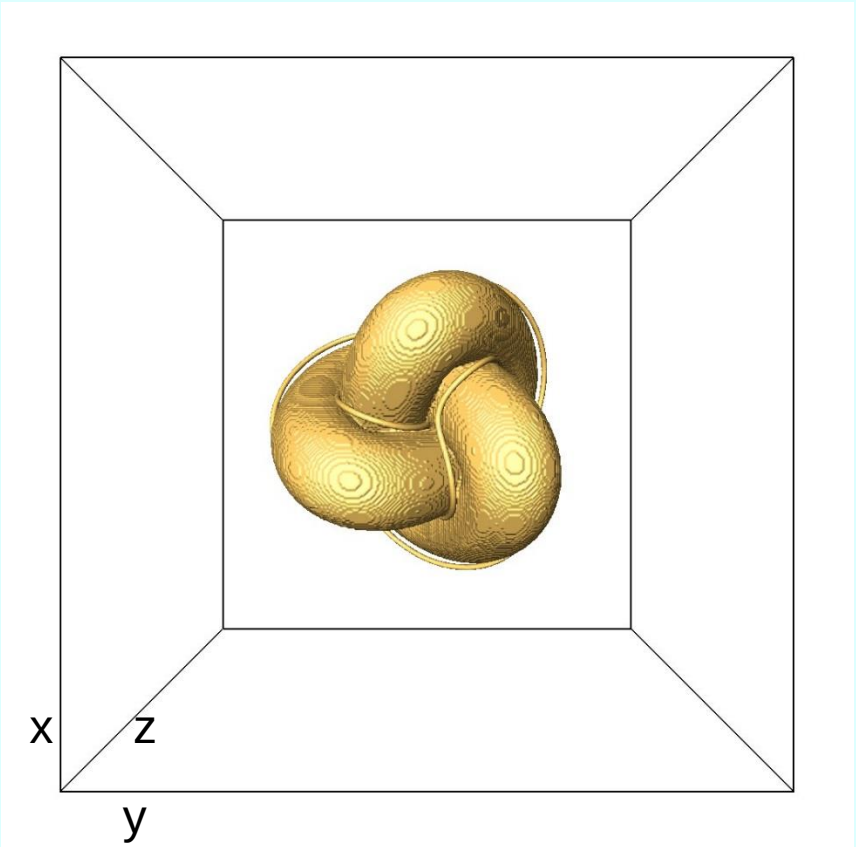
NONTRIVIAL PARTICLE

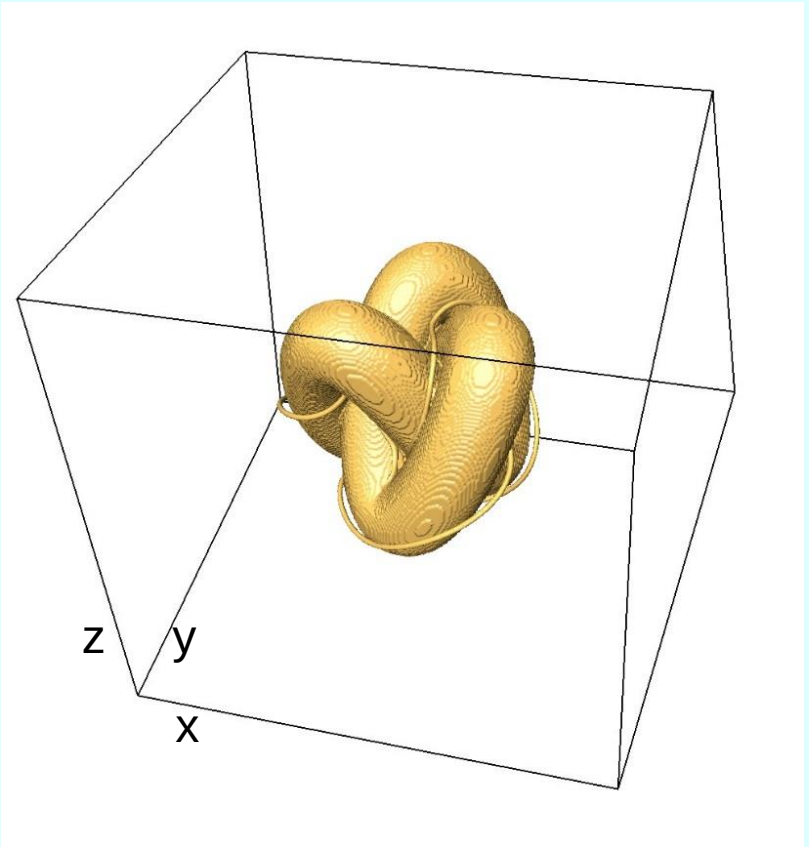
RESHAPEABLE PARTICLE IN A FORM OF A TREFOIL KNOT

with homeotropic surface anchoring in a homogenous nematic

Knots are stabilized by particle topology

2 knotted loops ⟶ 1loop & residual surface lines





director farfield along z-axis

Ravnik, Žumer 2013

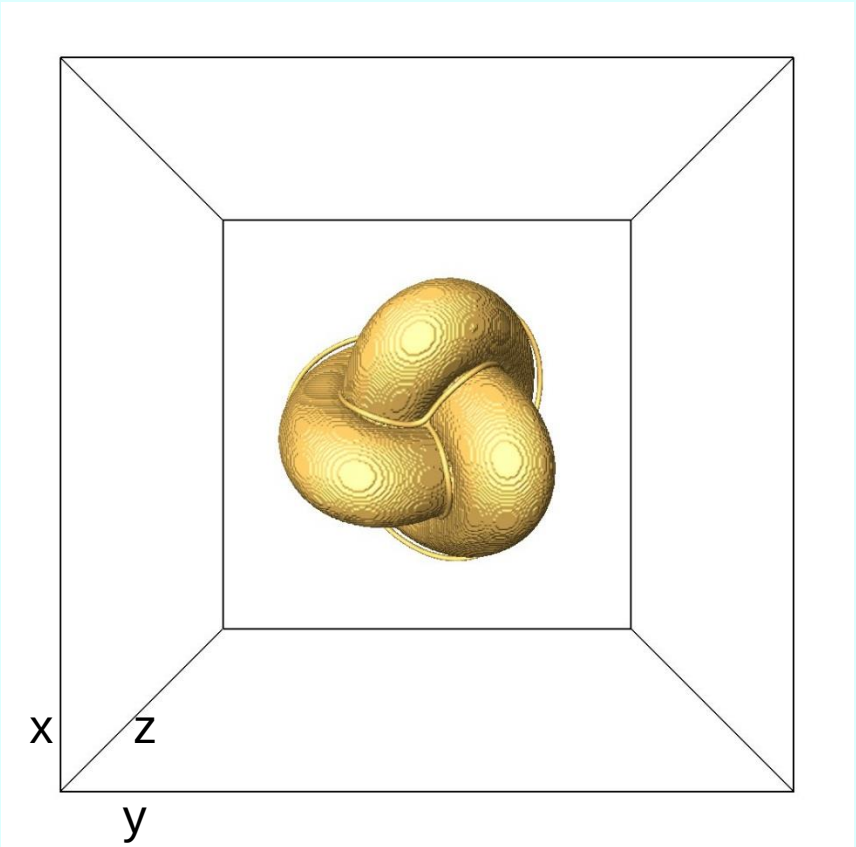
NONTRIVIAL PARTICLE

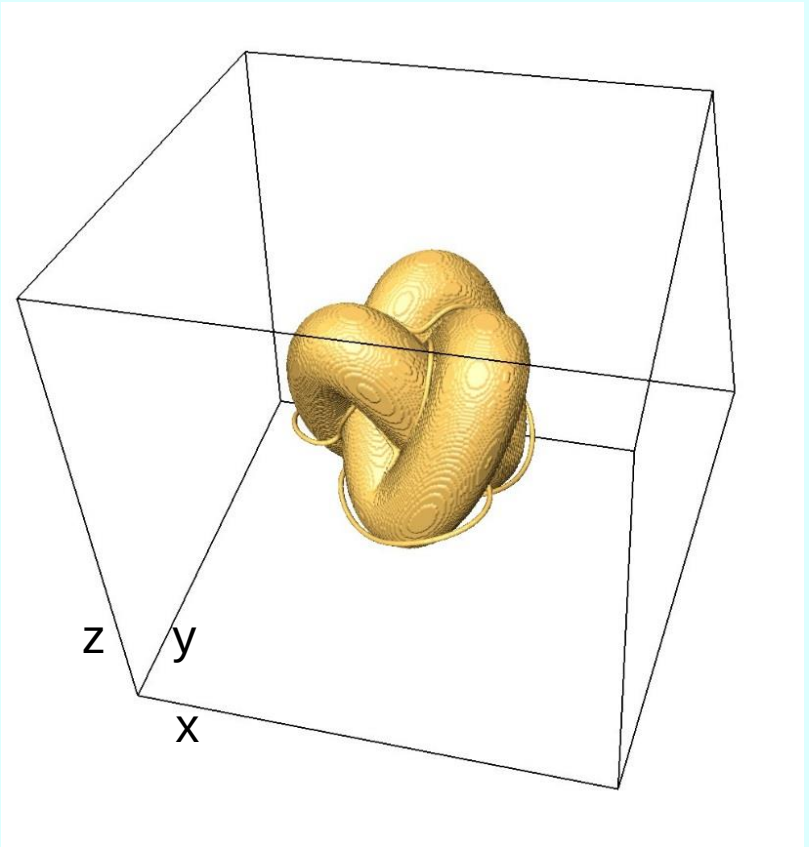
RESHAPEABLE PARTICLE IN A FORM OF A TREFOIL KNOT

with homeotropic surface anchoring in a homogenous nematic

Knots are stabilized by particle topology

2 knotted loops ⟶ 1loop & residual surface lines





director farfield along z-axis

Ravnik, Žumer 2013