Univerza v Ljubljani
Fakulteta za matematiko in fiziko

Energetics of entangled nematic colloids

<u>M. Ravnik</u>, U. Tkalec, S. Copar, S. Zumer, I. Musevic

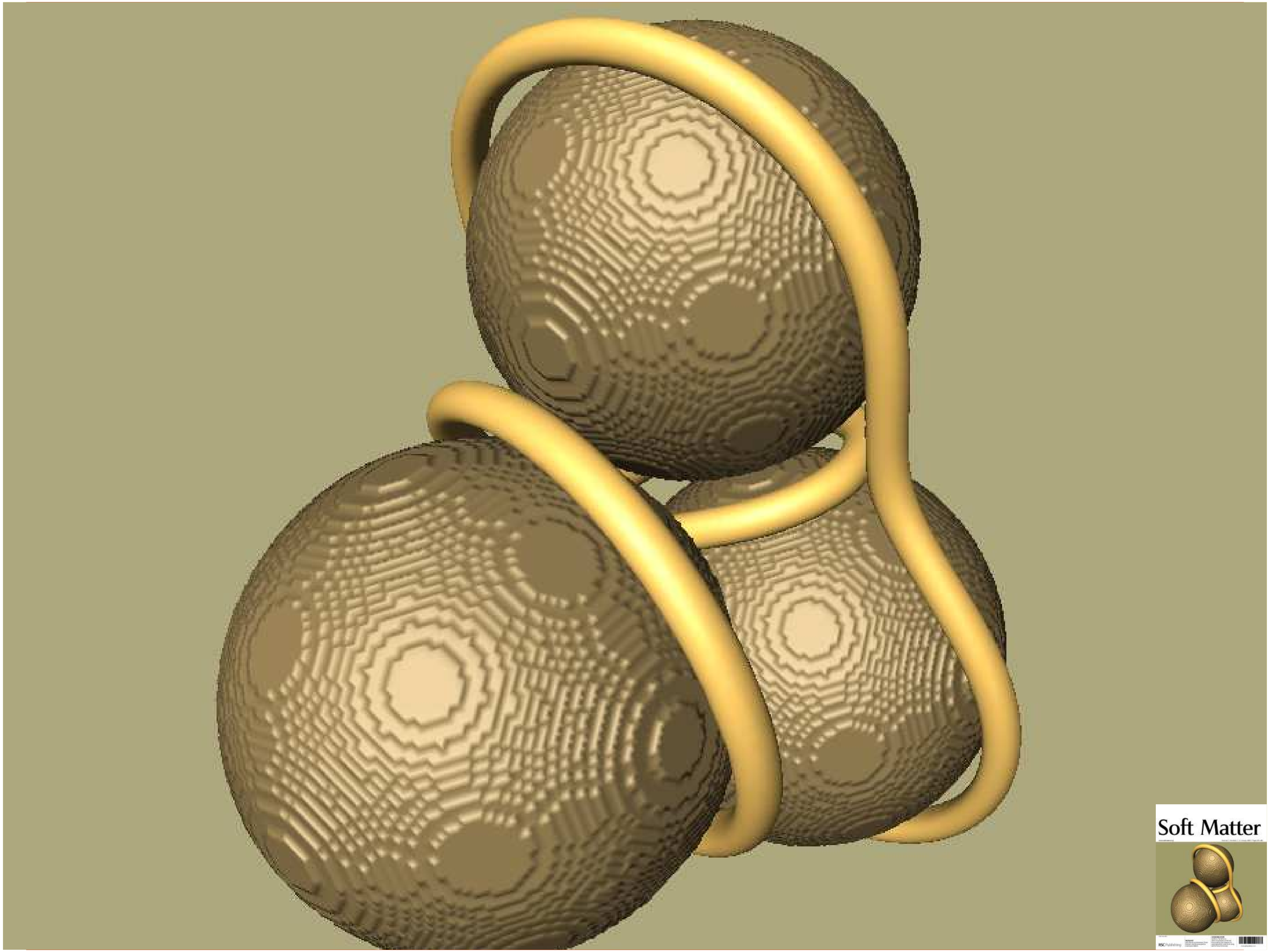
Faculty of Mathematics and Physics, University of Ljubljana, Ljubljana, Slovenia

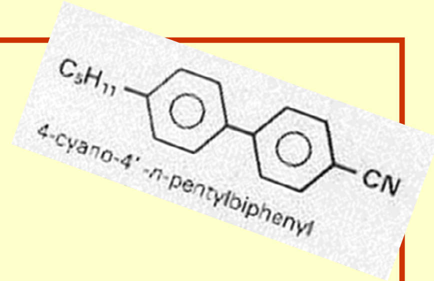
Josef Stefan Institute, Ljubljana, Slovenia

CO NAMASTE

Support of the EC under the Marie Curie project FREEFLUID is acknowledged. The contents reflect only the author's views and not the views of the EC.

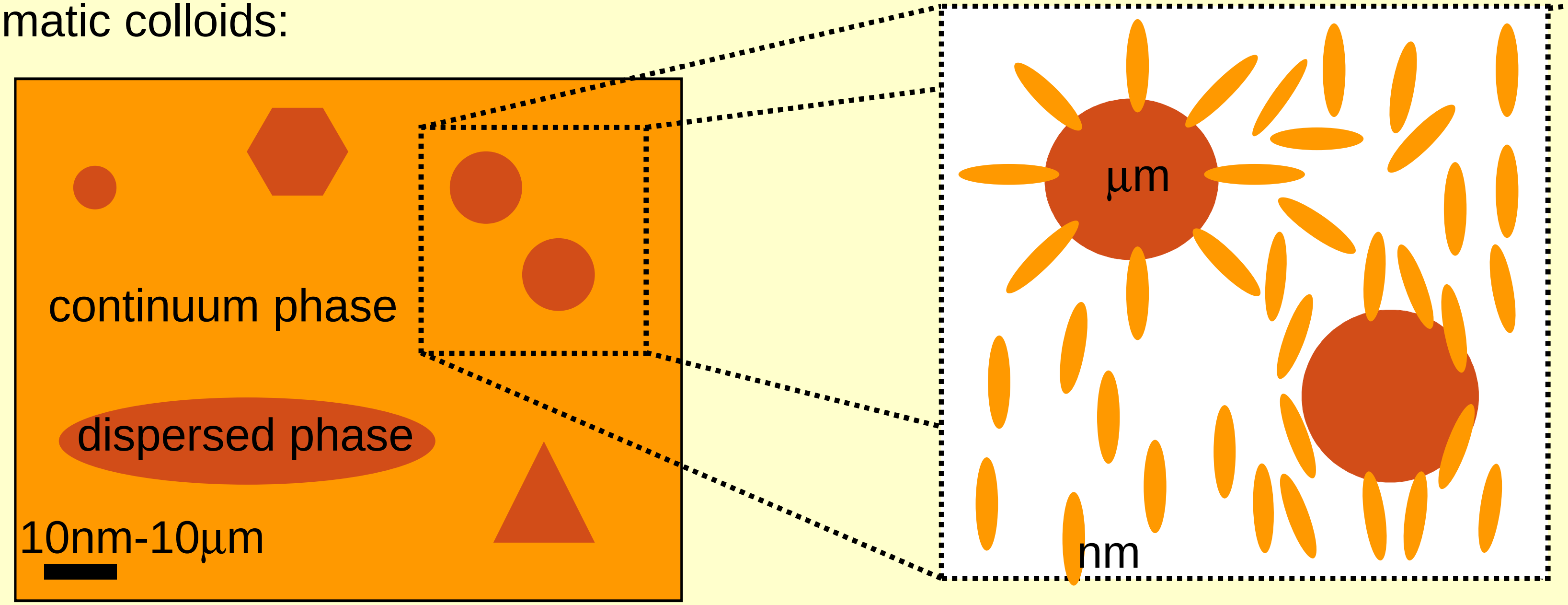
See also talks by Zumer and Musevic

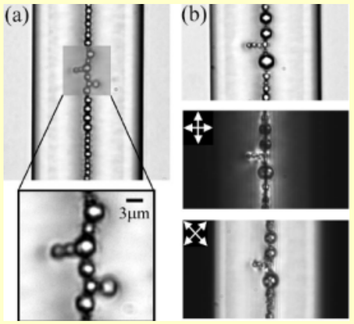

Soft Matter



Introduction

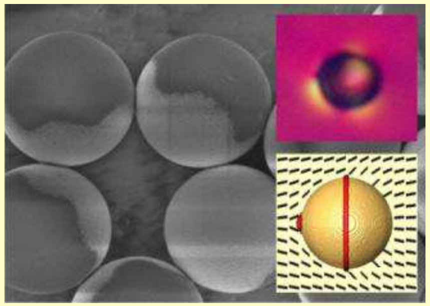
Nematic colloids:





PDMS polymer droplets, Kossyrev et al, PRL 2006

Micro-rods, Tkalec et al, Soft Matter 2008

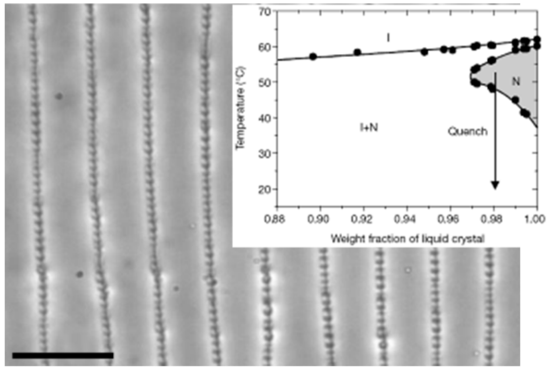


Janus nematic colloids, Conradi et al, Soft Matter 2009

Motivation – optical structures & advanced materials

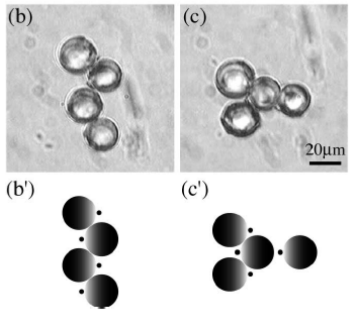
(i) Self assembly of optical structures:

Collodial chains:



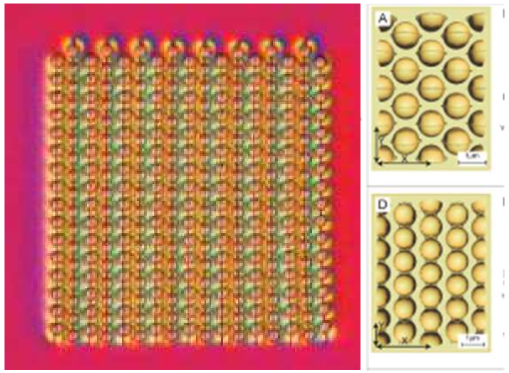
J.-C. Loudet, et al, Nature 407, 611(2000)

Collodial clusters:



M. Yada, et al, PRL 92, 185501(2004)

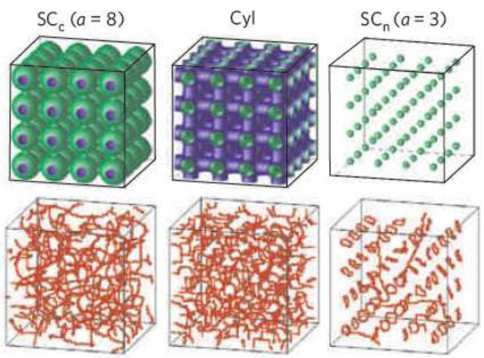
2D colloidal crystals:



I. Musevic, et al, Science 313, 954 (2006)

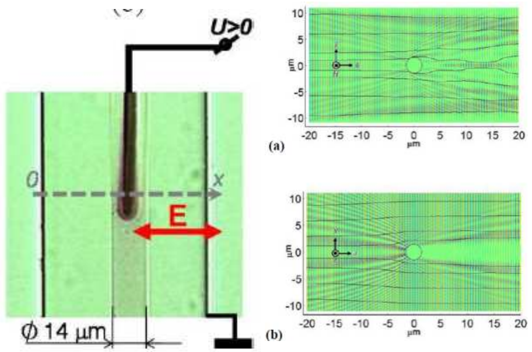
(ii) Advanced material characteristics:

Memory & topological frustration:



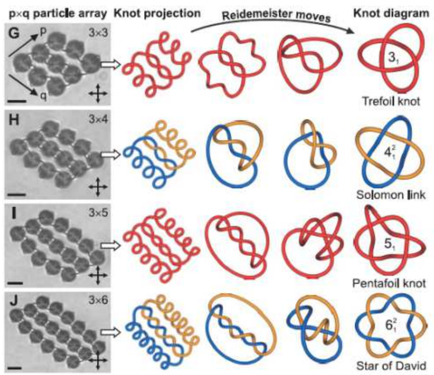
T. Araki, et al, Nat. Mater. 10, 303 (2011)

Tunable transformation optics:



A. B. Golovin, et al, Materials 4, 390 (2011)

Colloidal knots:

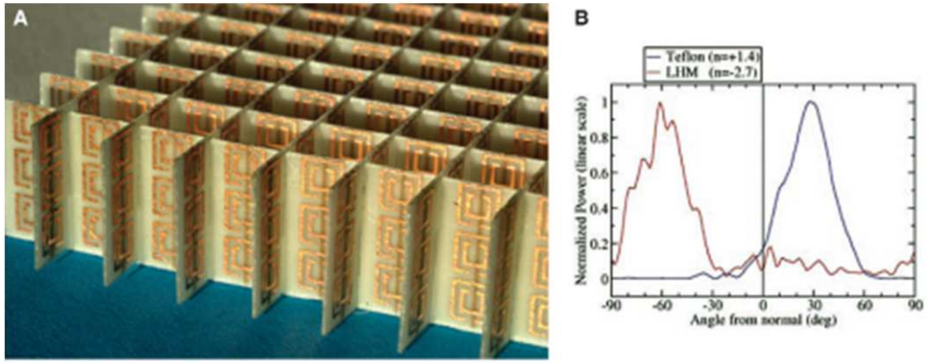


U. Tkalec, et al, Science 333, 62 (2011)

Motivation - photonics

Basic interest in liquid crystal colloids is for their application in optics:

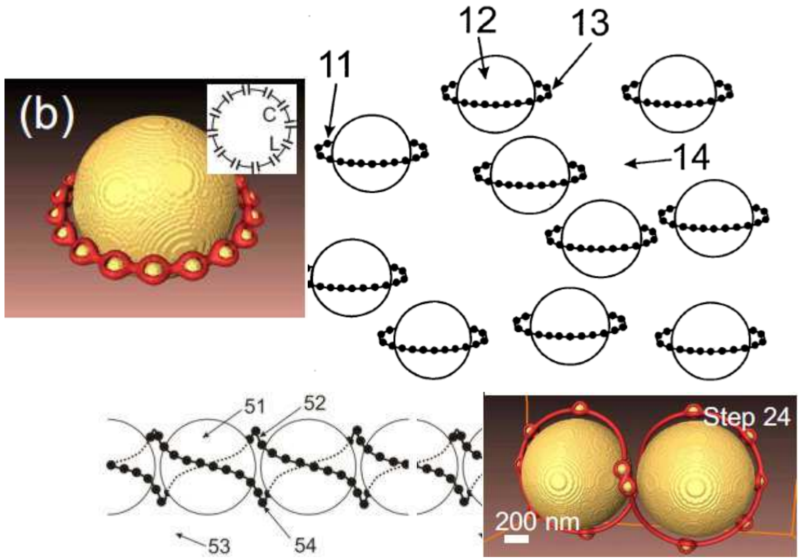
Metamaterials and negative refraction (V. G. Veselago, *Sov. Phys. Usp.* **10**, 509 (1968))

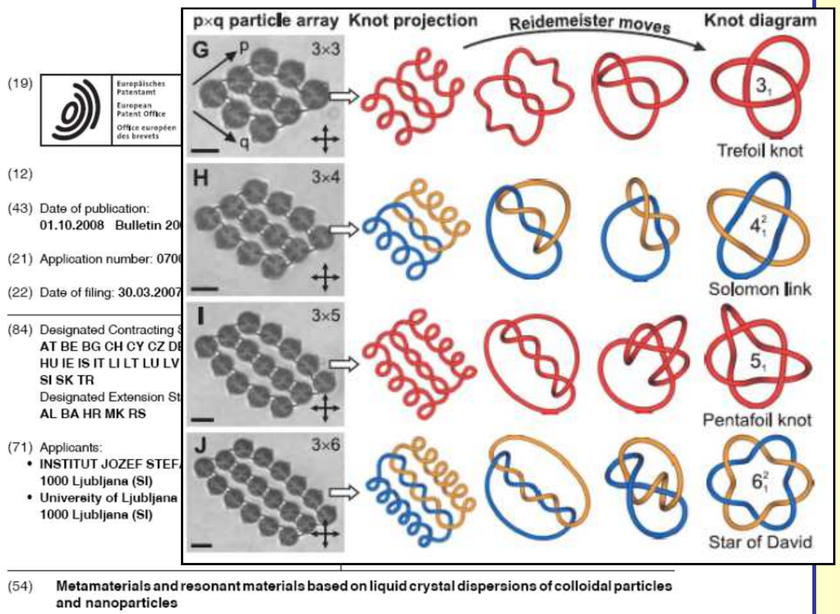


D. Smith, et al, Science 305, 788 (2004)

Fig. 3. (**A**) A negative index metamaterial formed by SRRs and wires deposited on opposite sides lithographically on standard circuit board. The height of the structure is 1 cm. (**B**) The power detected as a function of angle in a Snell's law experiment performed on a Teflon sample (blue curve) and a negative index sample (red curve).

Hierarchical LC colloids as metamaterials





Patent EU 1975656 B1 2011, PRE 08

Outline

@ how to generate defect loops in nematics

@ nematic continuum theory and numerical modelling

@ entangled nematic colloids and their energetics:
1D, 2D, and 3D structures

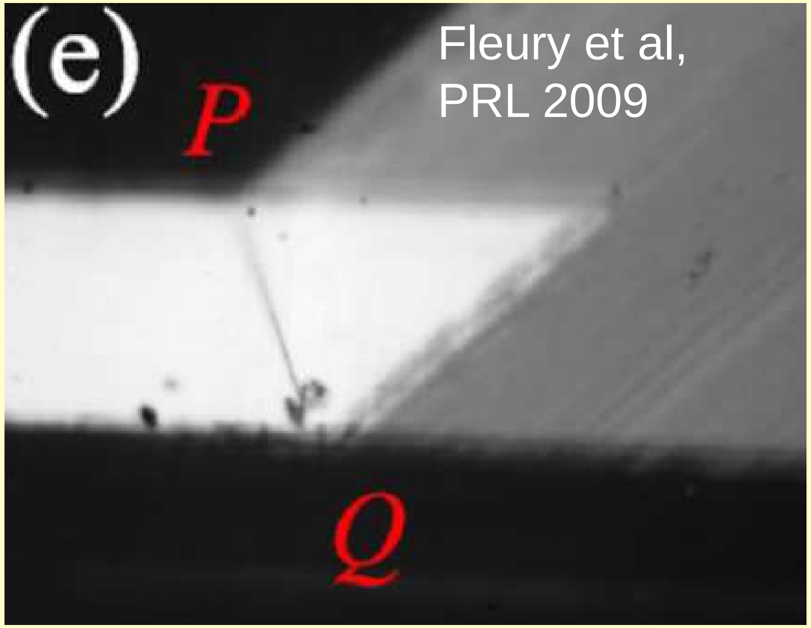
@ energetic stabilisation of topological structures by global twist

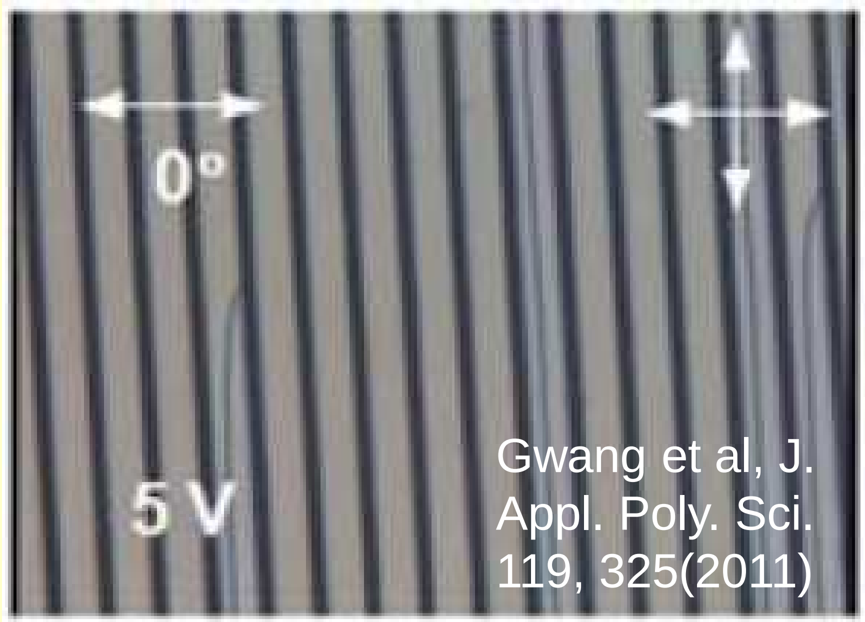
@ assembly of knots and links of defect loops

@ blue phases: more complex crossings and caging by defects

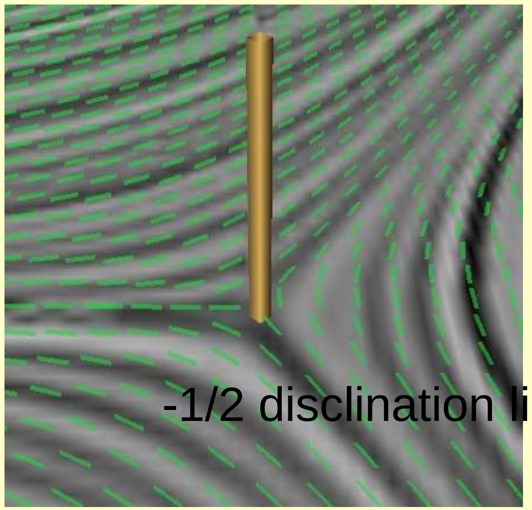
@ analogy of chiral liquid crystals and chiral ferromagnets

Defects in nematic LC

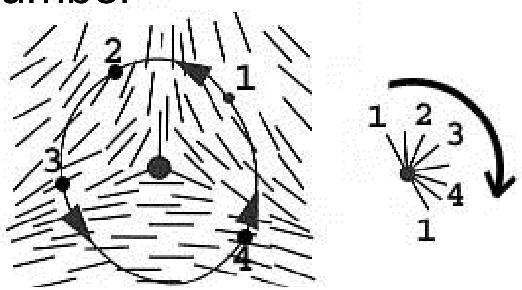




In nematic colloids:



Winding number

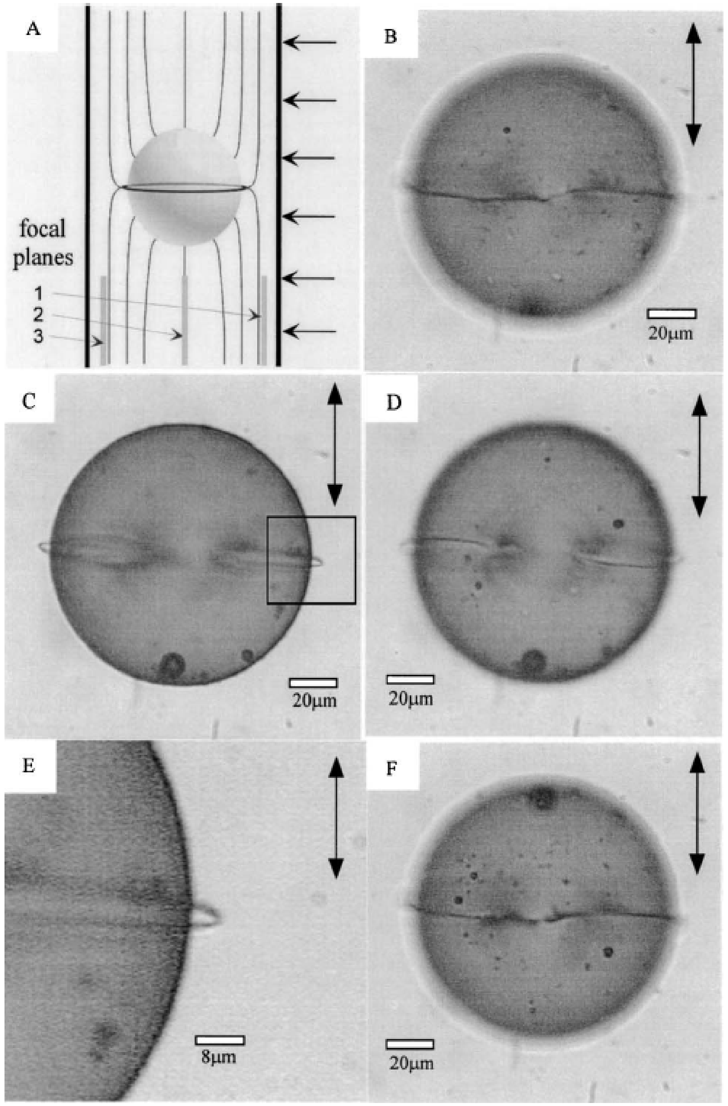


$$\oint \mathrm{d}\phi = 2\pi k$$

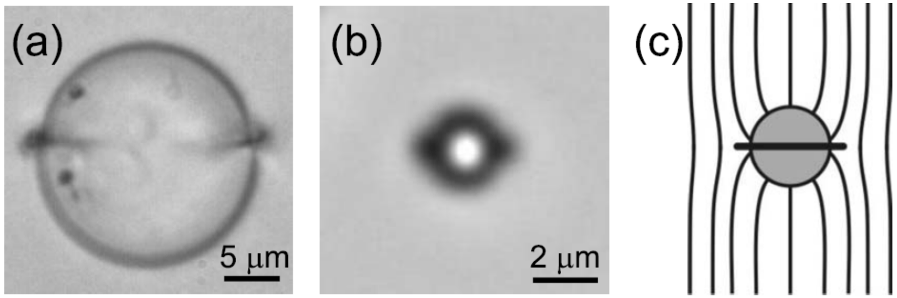
k=-1/2

Defect loops in nematic colloids

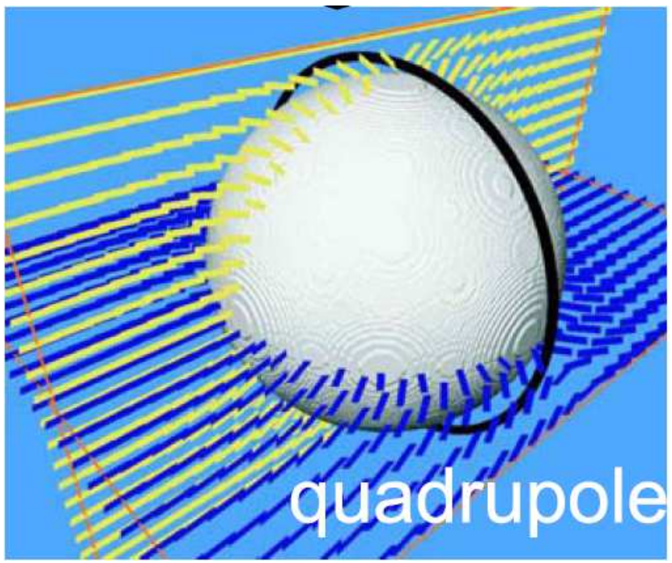
Defect loops form naturally in nematic colloids with HOMEOTROPIC anchoring:



Gu&Abbott, PRL 2000



Musevic & Zumer group, Science 2006, PRE 2007, 2008, PRL 2008



Elastic quadrupole, Saturn ring

Temperature I-N quench

Experimentally:

laser tweezers locally heat the nematic into the isotropic phase;

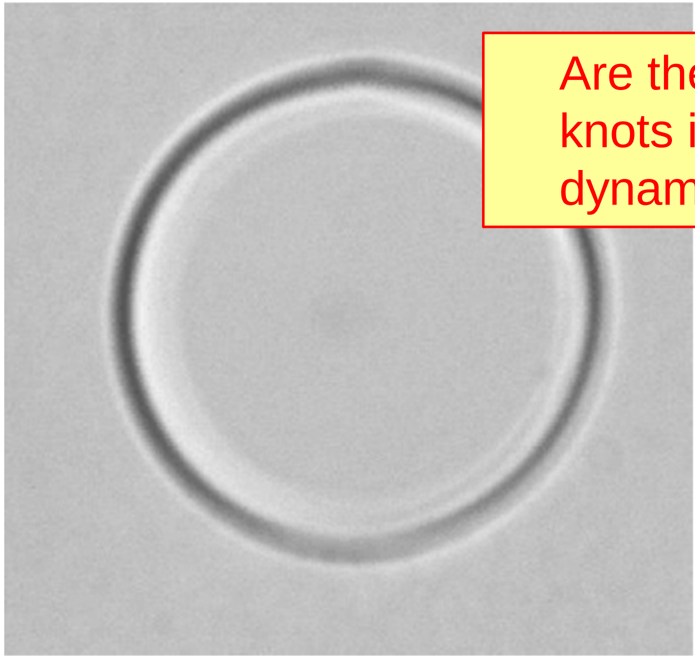
switch-off the laser beam

Numerical modelling:

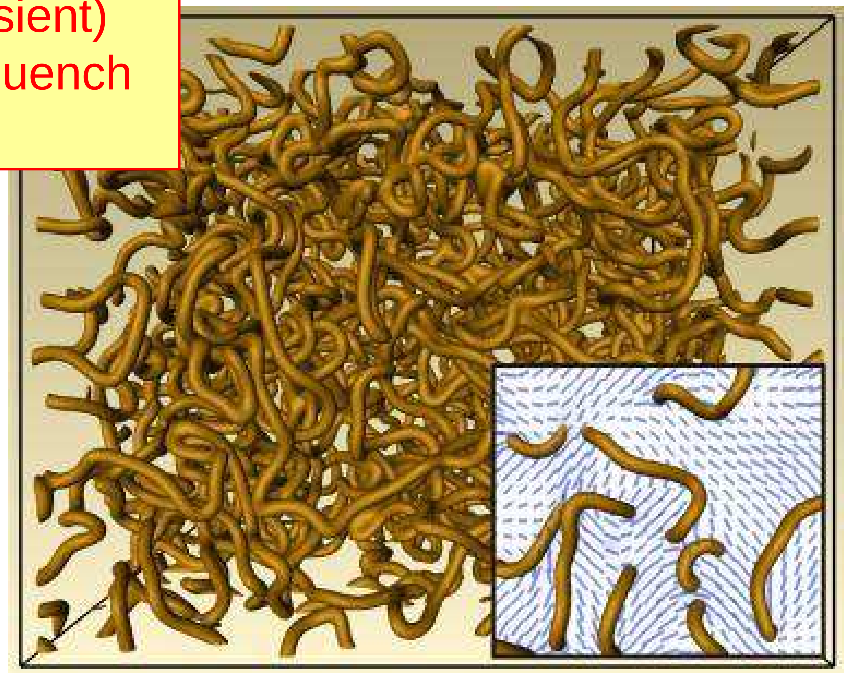
- random initial condition
- relaxation algorithm

$$\Gamma \frac{\mathrm{dQ_{ij}}}{\mathrm{dt}} = h_{ij}^{\cdots}$$

Are there (transient) knots in such quench dynamics?



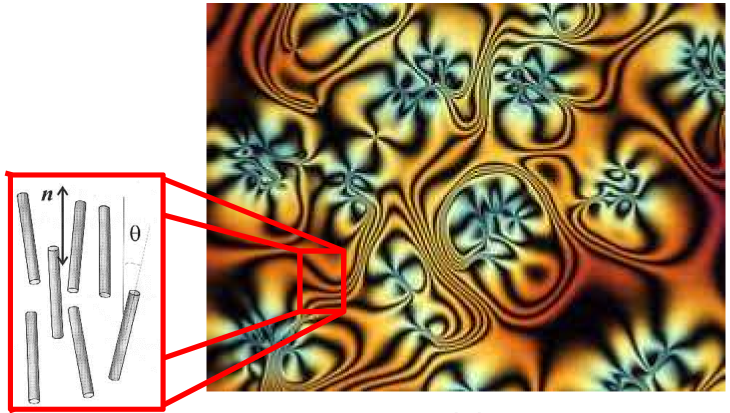
Courtesy M. Skarabot; real time ~0.1s



Mesoscopic theory of nematic fluids

Order parameter tensor:

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



By O. Lavrentovich, LCI, Kent, USA

Velocity field and density:

u_i , ρ

Q, u and ρ are spatial fields that characterise LC molecules.

I. Equilibrium physics of nematic fluids Landau – de Gennes phenomenological free energy

$$\begin{aligned} F = &+ \frac{1}{2}L\int_{LC}\left(\frac{\partial Q_{ij}}{\partial x_k}\right)\left(\frac{\partial Q_{ij}}{\partial x_k}\right)dV && \leftarrow \textit{elasticity} \\ &+ \int_{LC}\left(\frac{1}{2}AQ_{ij}Q_{ji} + \frac{1}{3}BQ_{ij}Q_{jk}Q_{ki} + \frac{1}{4}C(Q_{ij}Q_{ji})^2\right)dV && \leftarrow \textit{order} \\ &+ \frac{1}{2}W\int_{Surf.Col.}(Q_{ij}-Q_{ij}^0)(Q_{ji}-Q_{ji}^0)dS \quad . && \leftarrow \textit{surface} \end{aligned}$$

Additional coupling terms for external fields, flexoelectricity,chirality...

Ravnik & Zumer, Liq. Cryst. (2009), Handbook of LCs (2012)

Mesoscopic theory of nematic fluids

II. Dynamics of liquid crystals

Orientation:

molecular field

$$(\partial_t + \vec{u} \cdot \nabla)\mathbf{Q} - \mathbf{S}(\mathbf{W}, \mathbf{Q}) = \Gamma \mathbf{H}$$

Material derivative

LC alignment in flow

Flow:

Flow aligning:

Flow tumbling:

$$\rho(\partial_t + u_\beta \partial_\beta) u_\alpha$$

$$= \partial_\beta(\Pi_{\alpha\beta}) + \eta \partial_\beta(\partial_\alpha u_\beta + \partial_\beta u_\alpha + (1 - 3\partial_\rho P_0)\partial_\gamma u_\gamma \delta_{\alpha\beta})$$

Stress tensor

viscosity

possible compressibility

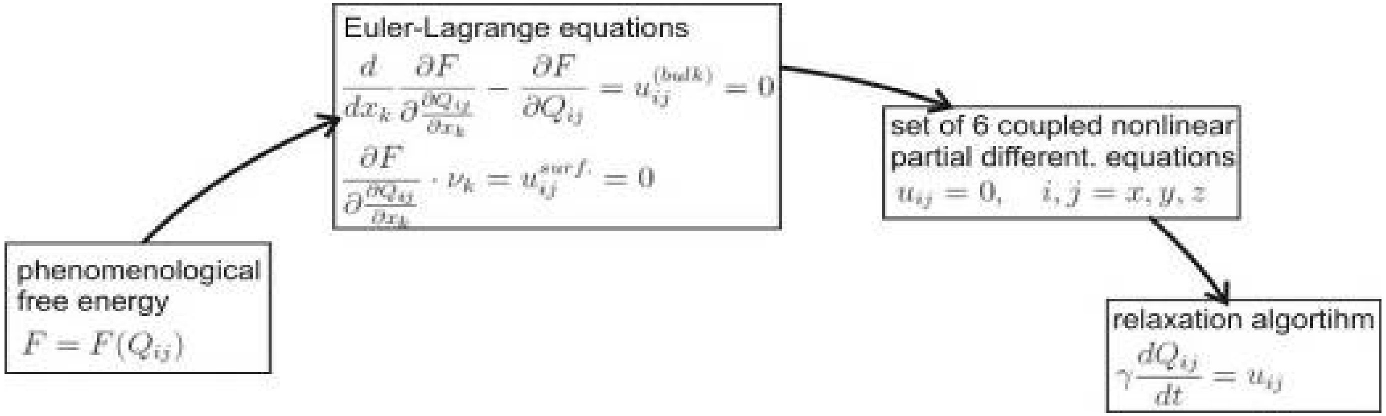
Generalized Navier – Stokes equation

$$\begin{aligned}
\Pi_{\alpha\beta} &= -P_0\delta_{\alpha\beta} + 2\xi\left(Q_{\alpha\beta} + \frac{1}{3}\delta_{\alpha\beta}\right)Q_{\gamma\varepsilon}H_{\gamma\varepsilon} \\
&\quad - \xi H_{\alpha\gamma}\left(Q_{\gamma\beta} + \frac{1}{3}\delta_{\gamma\beta}\right) - \xi\left(Q_{\alpha\gamma} + \frac{1}{3}\delta_{\alpha\gamma}\right)H_{\gamma\beta} \\
&\quad - \partial_\alpha Q_{\gamma\nu}\frac{\delta\mathcal{F}}{\delta\partial_\beta Q_{\gamma\nu}} + Q_{\alpha\gamma}H_{\gamma\beta} - H_{\alpha\gamma}Q_{\gamma\beta}.
\end{aligned}$$

Denniston et al, Phil. Trans 362, 1745 (2004)

Numerical modelling

A) Equilibrium - Finite difference explicit relaxation algorithm



B) Dynamics - Hybrid Lattice Boltzmann algorithm (developed with J.M. Yeomans, Oxford):

I. Finite differences for Q dynamics:

$$Q_{ij}^{t+\Delta t} = Q_{ij}^{t} + \frac{\Delta t}{\Gamma} h_{ij}^{\ldots,t}$$

II. Lattice Boltzmann method for material flow *u and density* ρ :

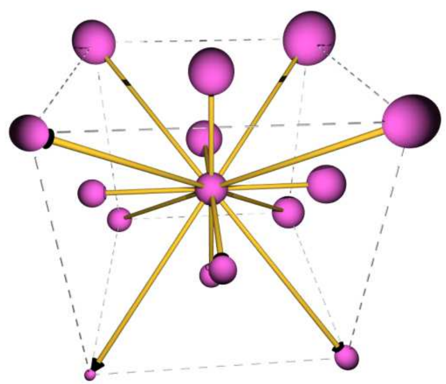
Distribution functions f_i:

$$\rho = \sum_i f_i, \qquad \rho u_\alpha = \sum_i f_i e_{i\alpha},$$

Streaming and collision

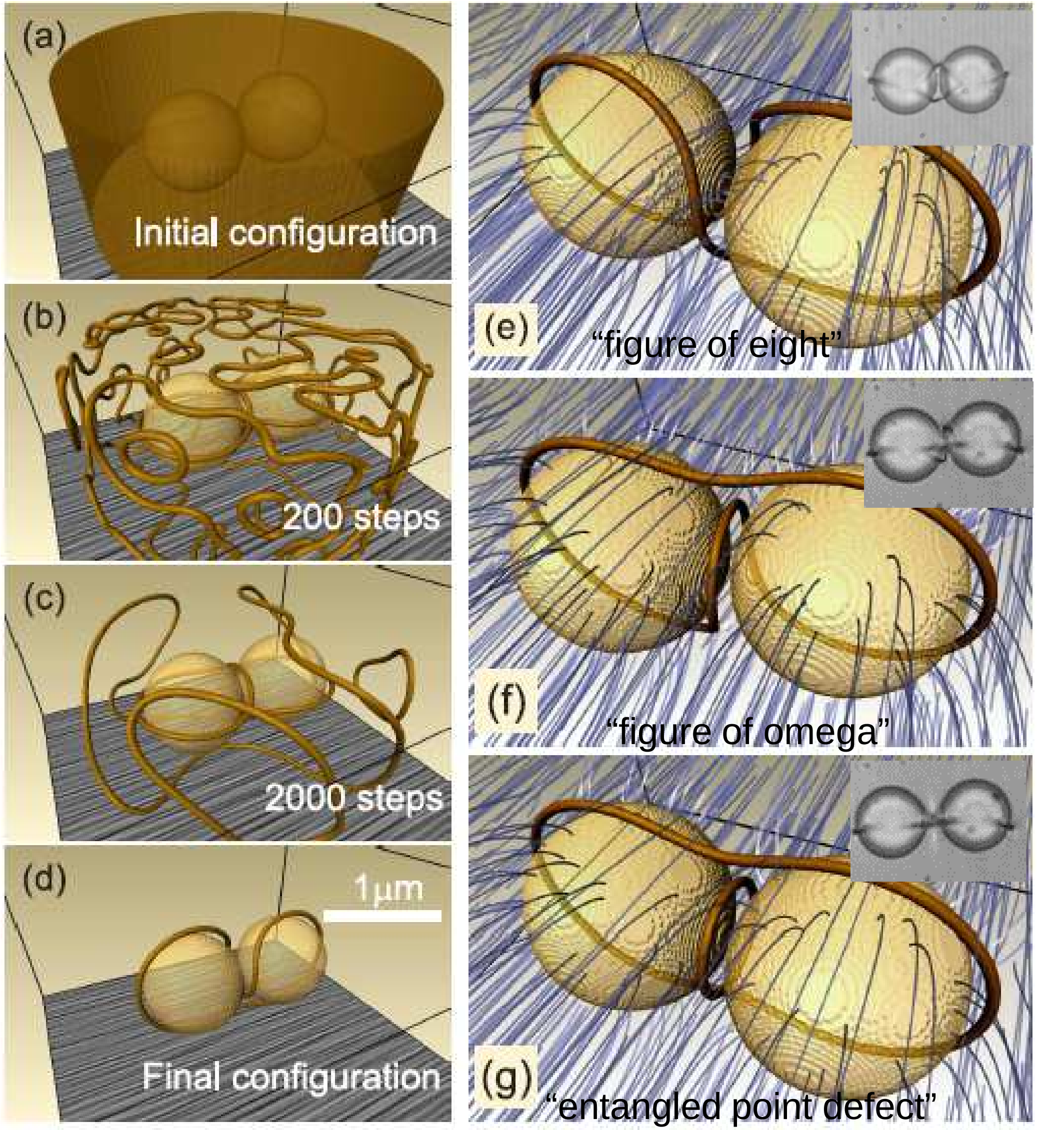
$$f_i(\boldsymbol{x} + \boldsymbol{e}_i \Delta t, t + \Delta t) - f_i(\boldsymbol{x}, t) = -\frac{1}{\tau_f}(f_i(\boldsymbol{x}, t) - f_i^{\mathrm{eq}}(\boldsymbol{x}, t, \{f_i\})) + p_i(\boldsymbol{x}, t, \{f_i\}$$

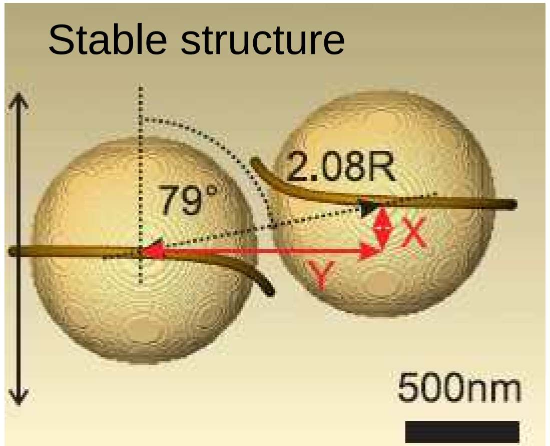
D3Q15 scheme



1D Entangled structures – complex conformations of defect loops

Local I – N temperature quench – now in the region of colloidal particles:





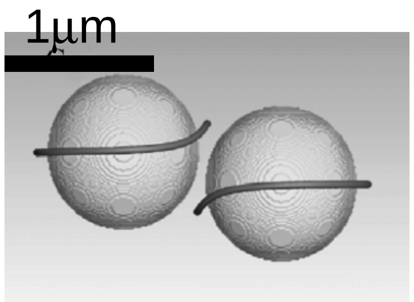
BUT the structures are energetically metastable!

Ravnik et al, PRL 2007, Soft Matter 2009

Ravnik et al, PRL 2007, Soft Matter 2009

1D Entangled structures –free energies and energy barriers

I. Equilibrium free energies:



2 Saturn rings

$F_{SR} = 1.451 \cdot 10^{-15}$ J

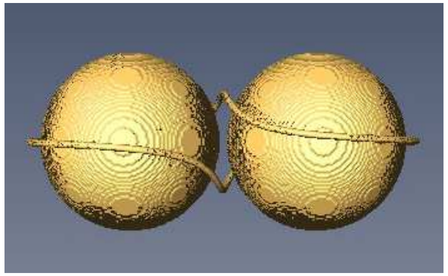


figure of eight

$F_{fig8} = 1.456 \cdot 10^{-15}$ J
$= 1.003\ F_{SR}$
$F_{fig8} - F_{SR} \sim 1050kT$

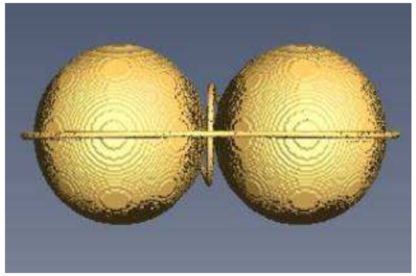
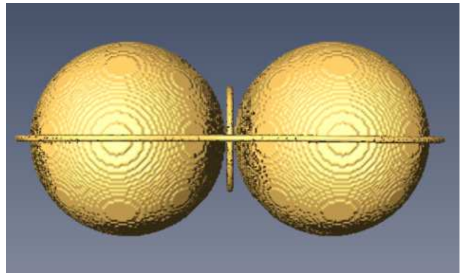


figure of omega

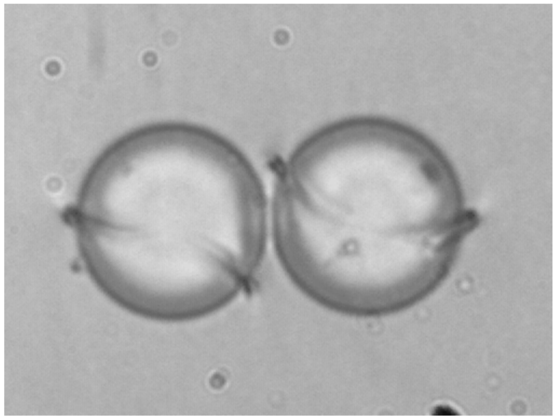
$F_{fig\Omega} = 1.464 \cdot 10^{-15}$ J
$= 1.009\ F_{SR}$
$F_{fig\Omega} - F_{SR} \sim 3150kT$

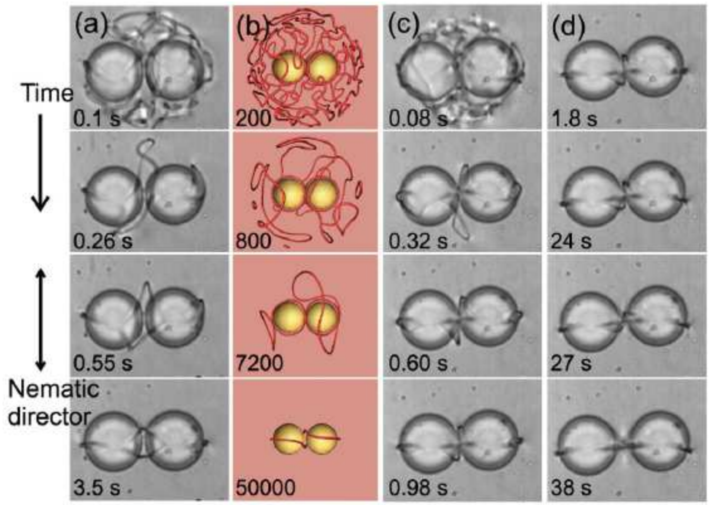


entangled point defect

$F_{ePD} = 1.475 \cdot 10^{-15}$ J
$= 1.017\ F_{SR}$
$F_{ePD} - F_{SR} \sim 5950kT$

Exp. occur: 52% 36% 13% 3%

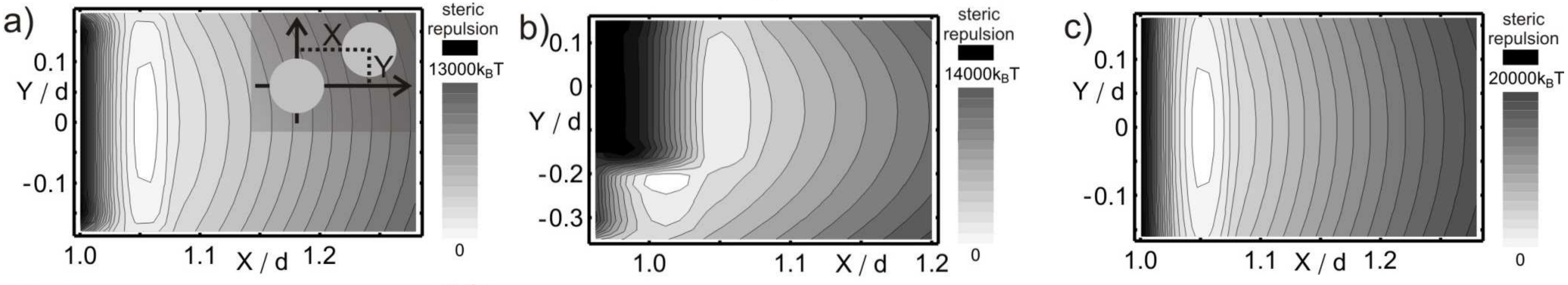




Ravnik et al, PRL 2007, Soft Matter 2009

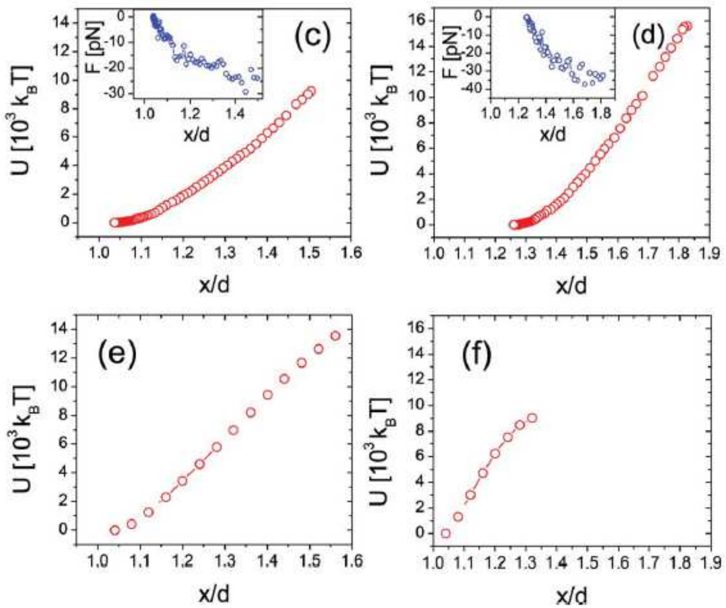
1D Entangled structures –free energies and energy barriers

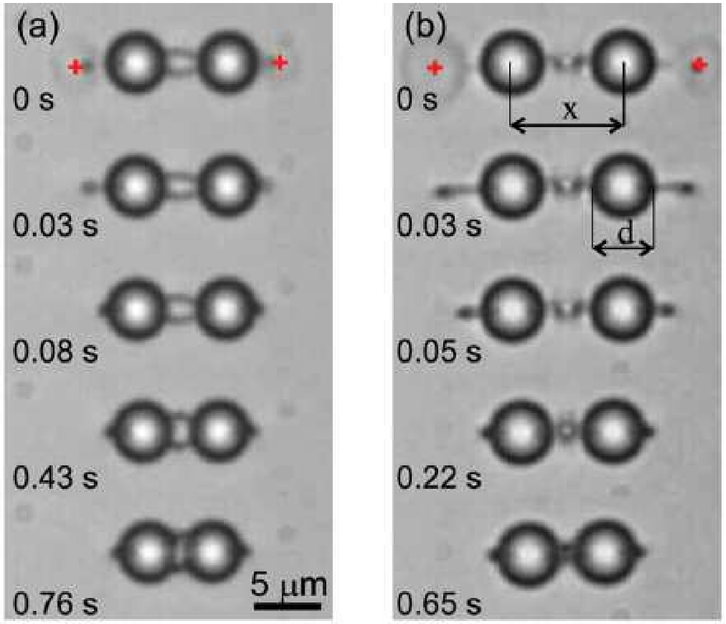
II. Energy barriers between the states:



Strongly anisotropic energy barriers; minimum heights of >1000 kT

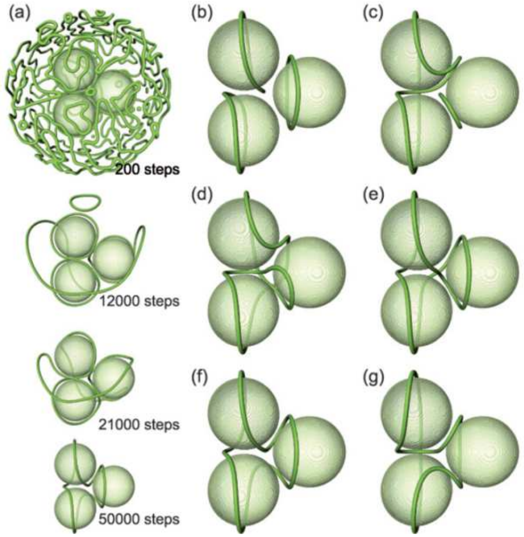
Comparison with experiments:

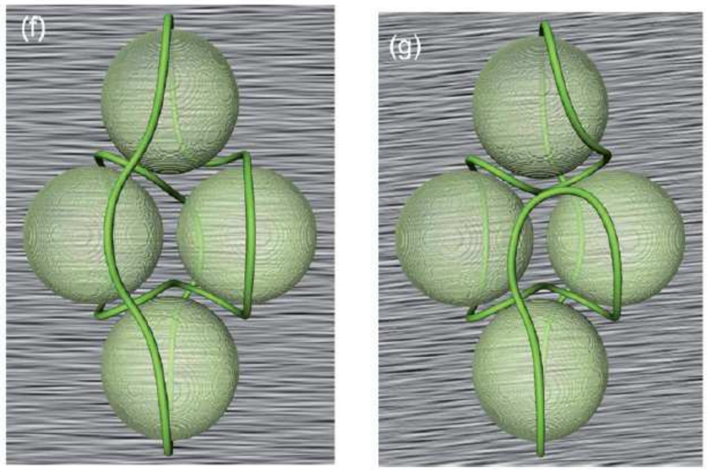




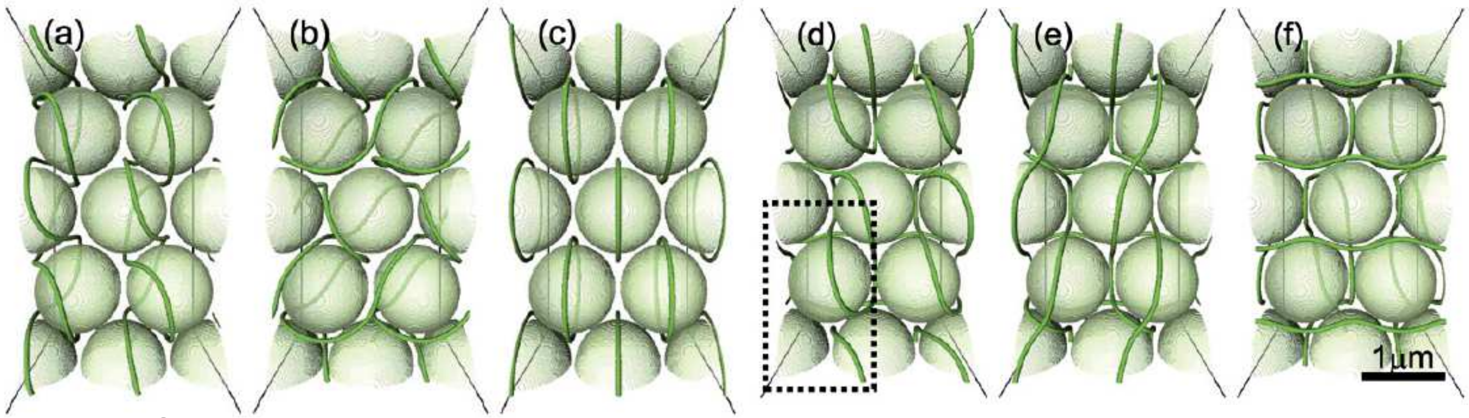
2D entangled structures – conformations of defects in 2D uniform nematic

Clusters:





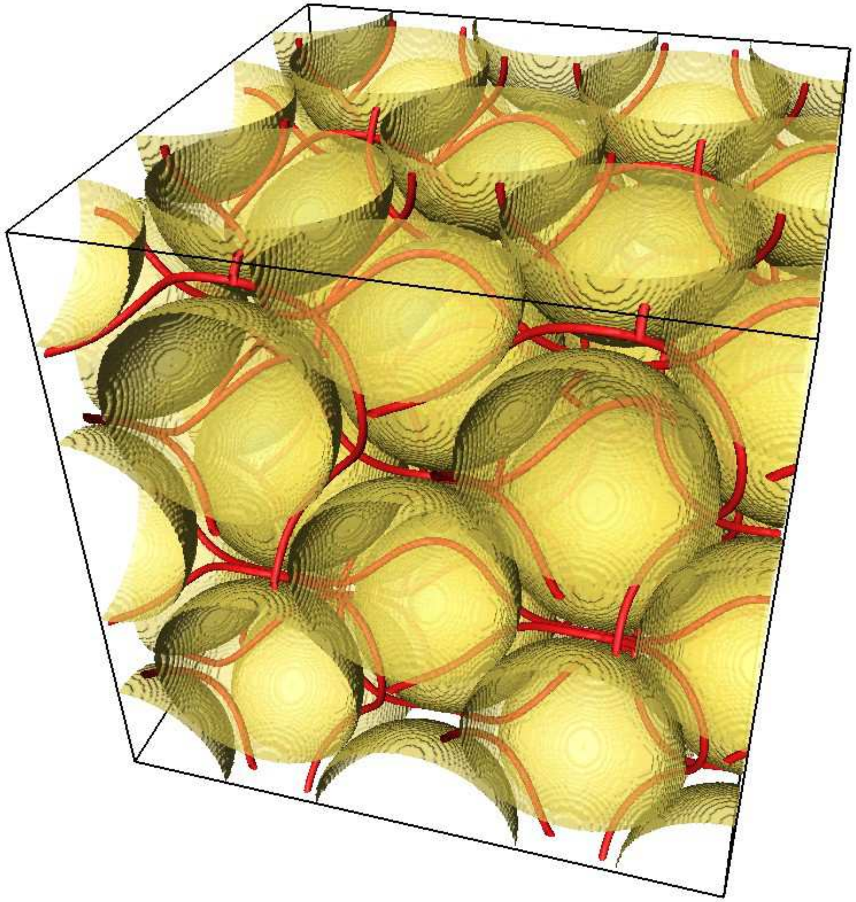
2D Colloidal crystals:

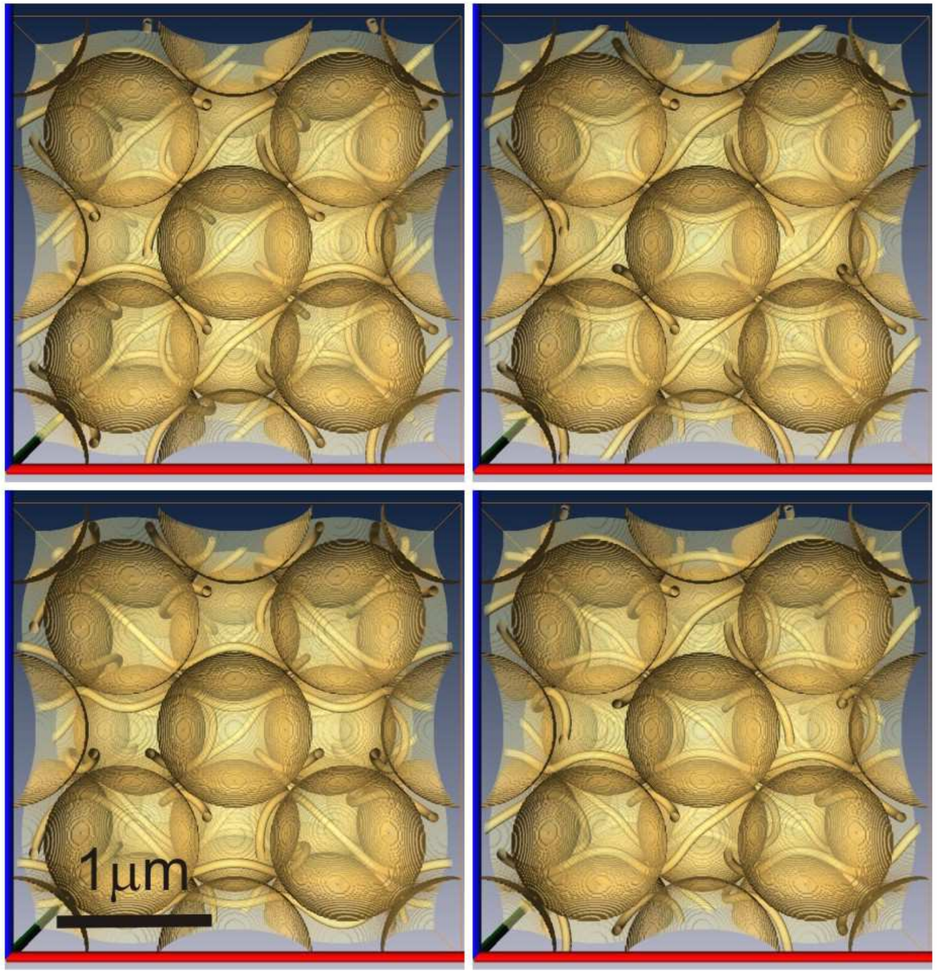


Free energies [fJ/UC]:	1.542	1.610	1.526	1.601	1.608	1.608

3D entangled colloids - defect motifs spanning in 3D uniform nematic

FCC nematic colloidal opals:



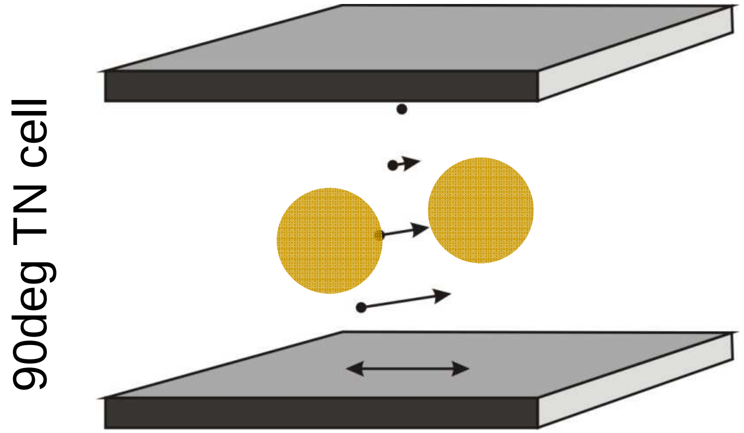


Also, in 3D structures (tetrahedral) rewiring sites emerge, their number depending on the colloidal lattice

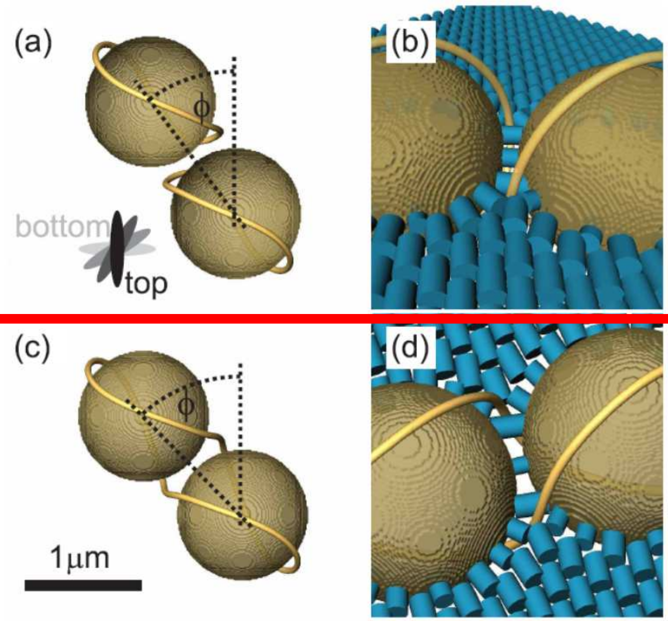
1D Entangled structures – reversing the (meta)stability by twist

Changing the far-field condition reverses stability and metastability of the entangled and non-entangled structures.

Geometry:



Entangled configuration is energetically the most favourable:



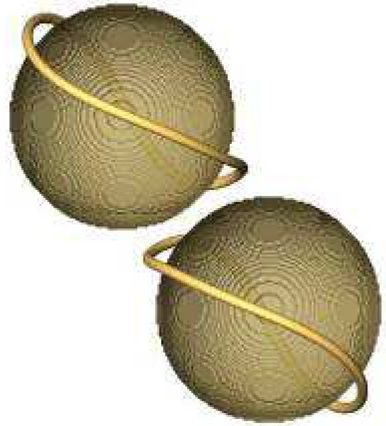
Free. En. (Saturn rings) = 1.975×10^{-15} J

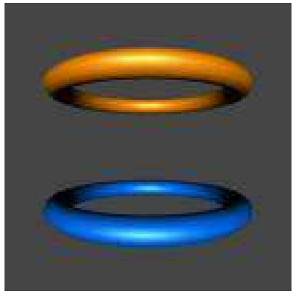
Free. En. (Figure-of-eight) = 1.926×10^{-15} J

Stable structure with minimum free energy

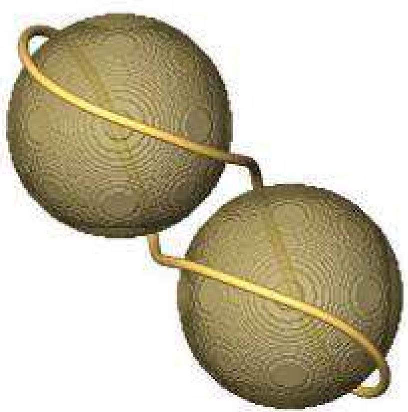
1D Entangled structures – Hopf link

Defect loops can have various conformations:





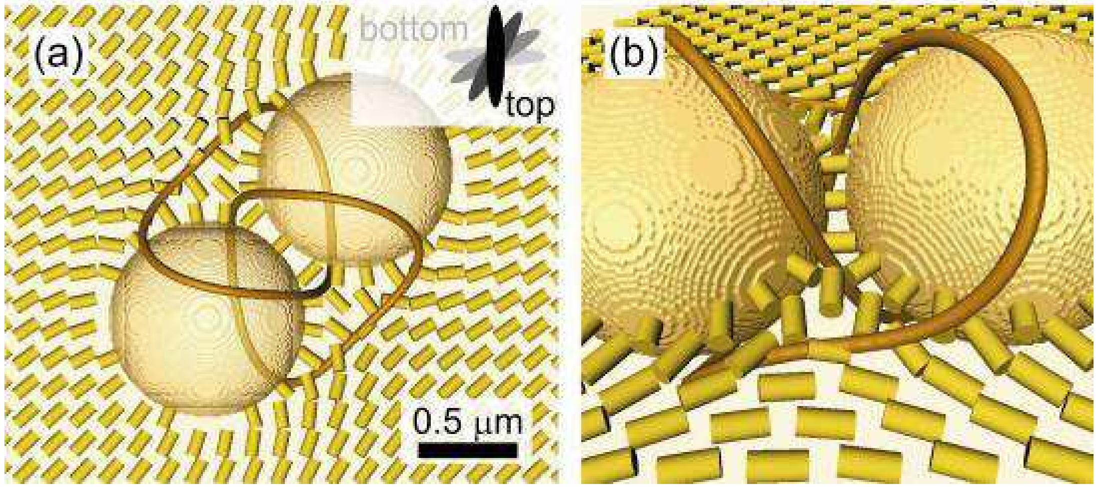
Unlink

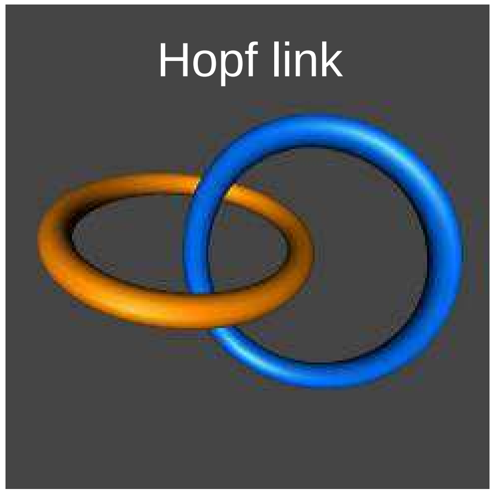


Unknot

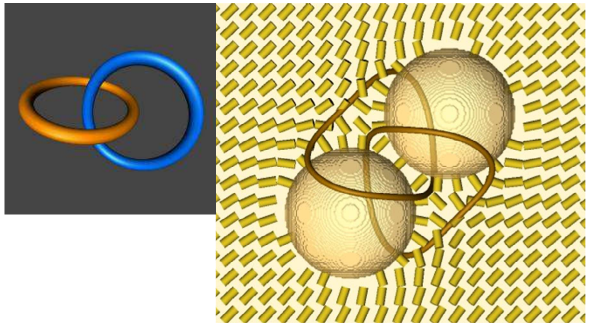
2 Saturn ring defects

Figure of eight

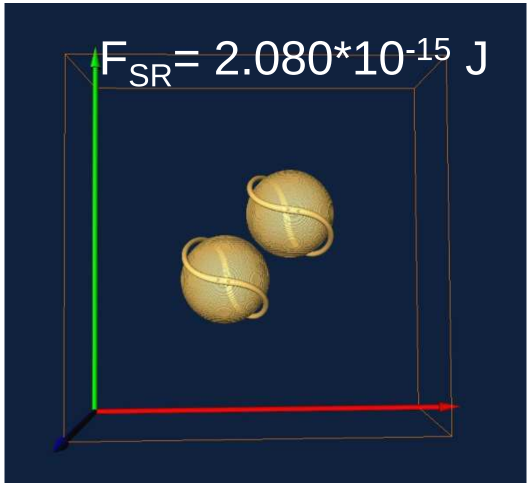


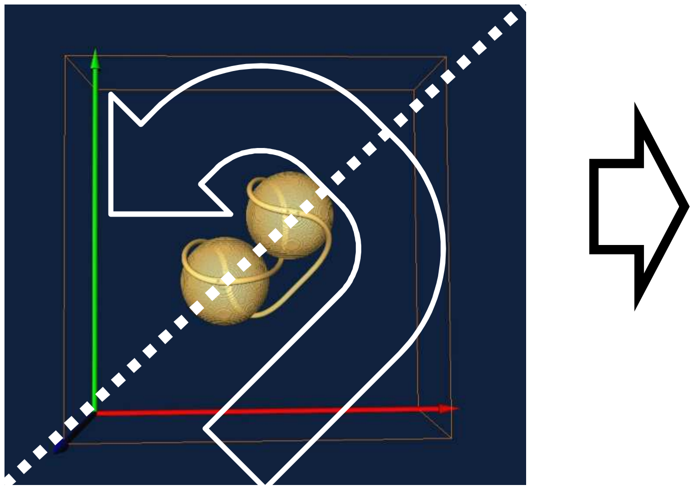


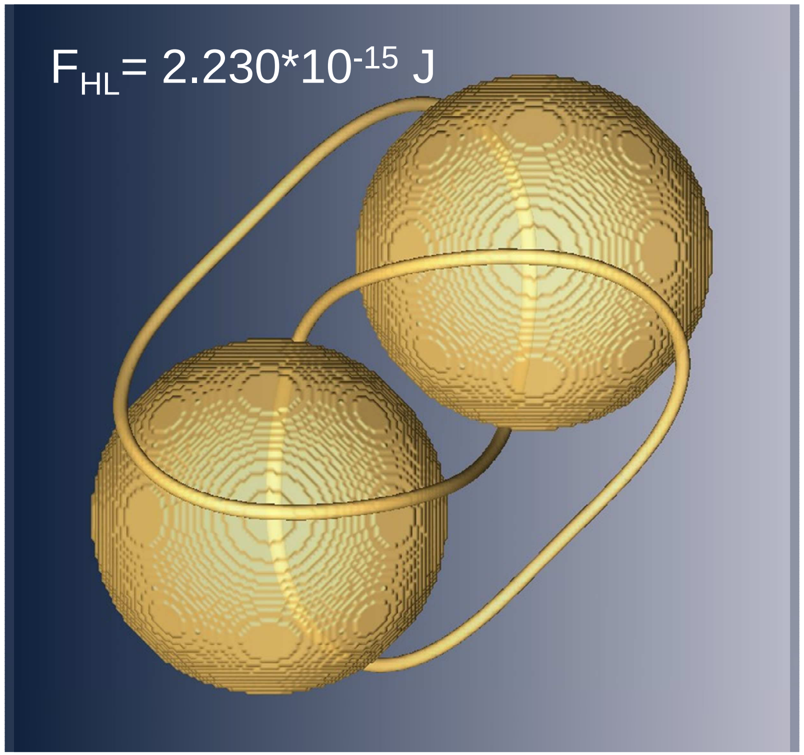
1D Entangled structures – Hopf link 2



How to access metastable knotted configurations:







Spontaneously formed colloidal structures– defect braids

Experiments: ~4.7μm homeotropic silica particles in ~6μm thick 90°TN cell.

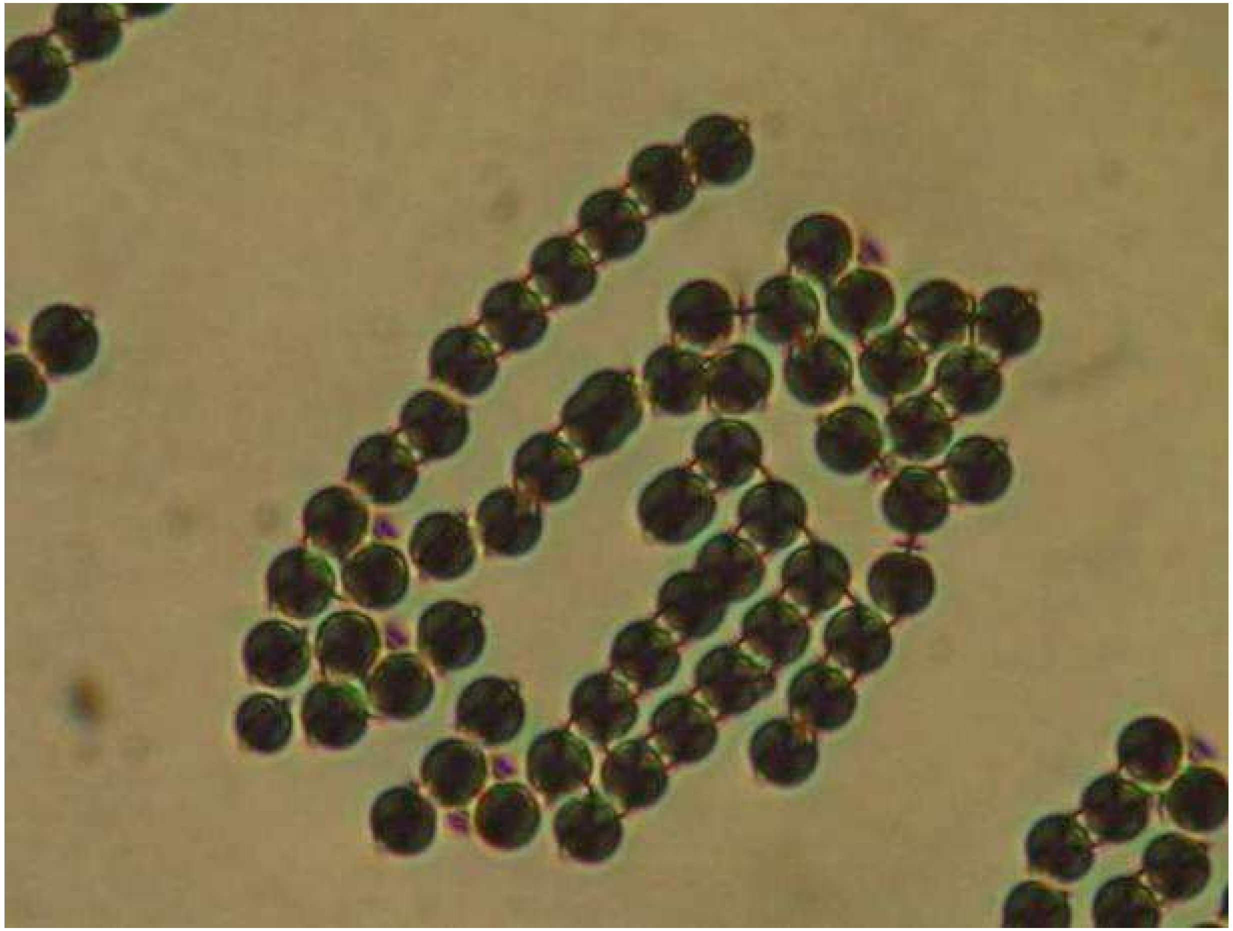
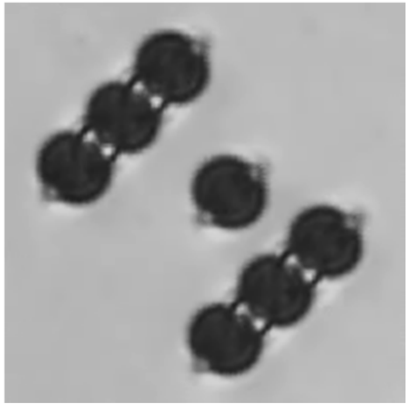


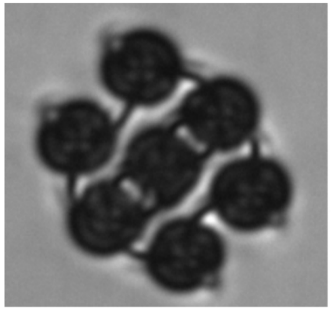
Image courtesy of U. Tkalec

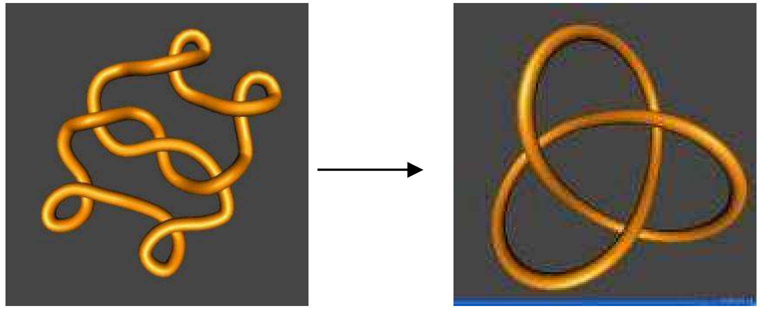
Structures assembled within capillary filling of the nematic cell

Knots and links – trefoil

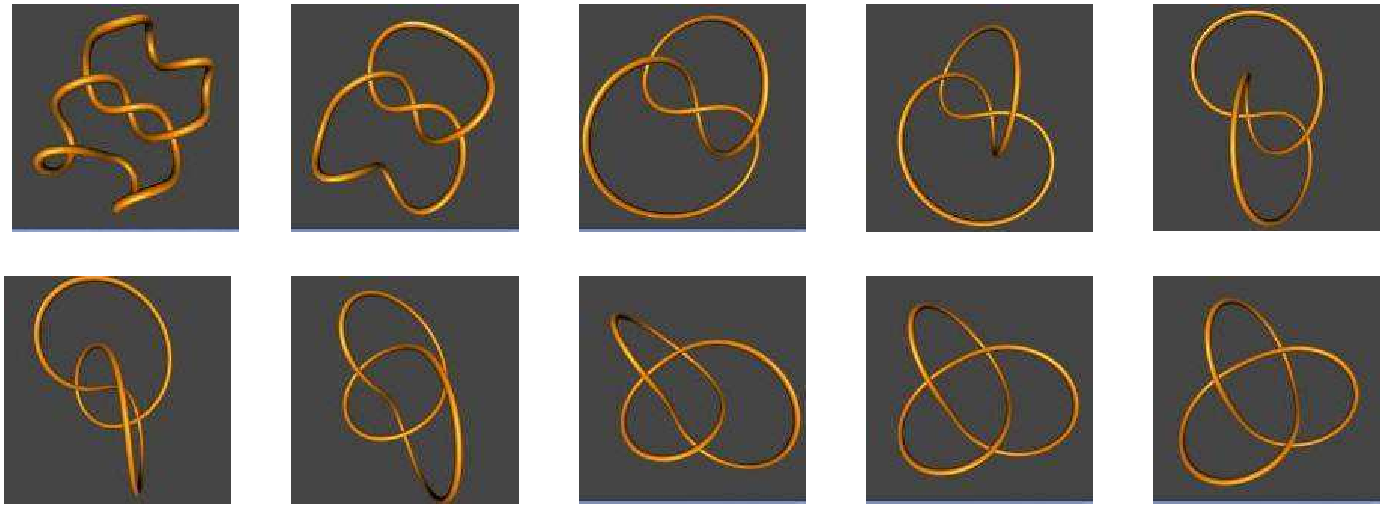
Complex inital conformation of the discliantion loop is equivalent (isotopic) to the trefoil knot:





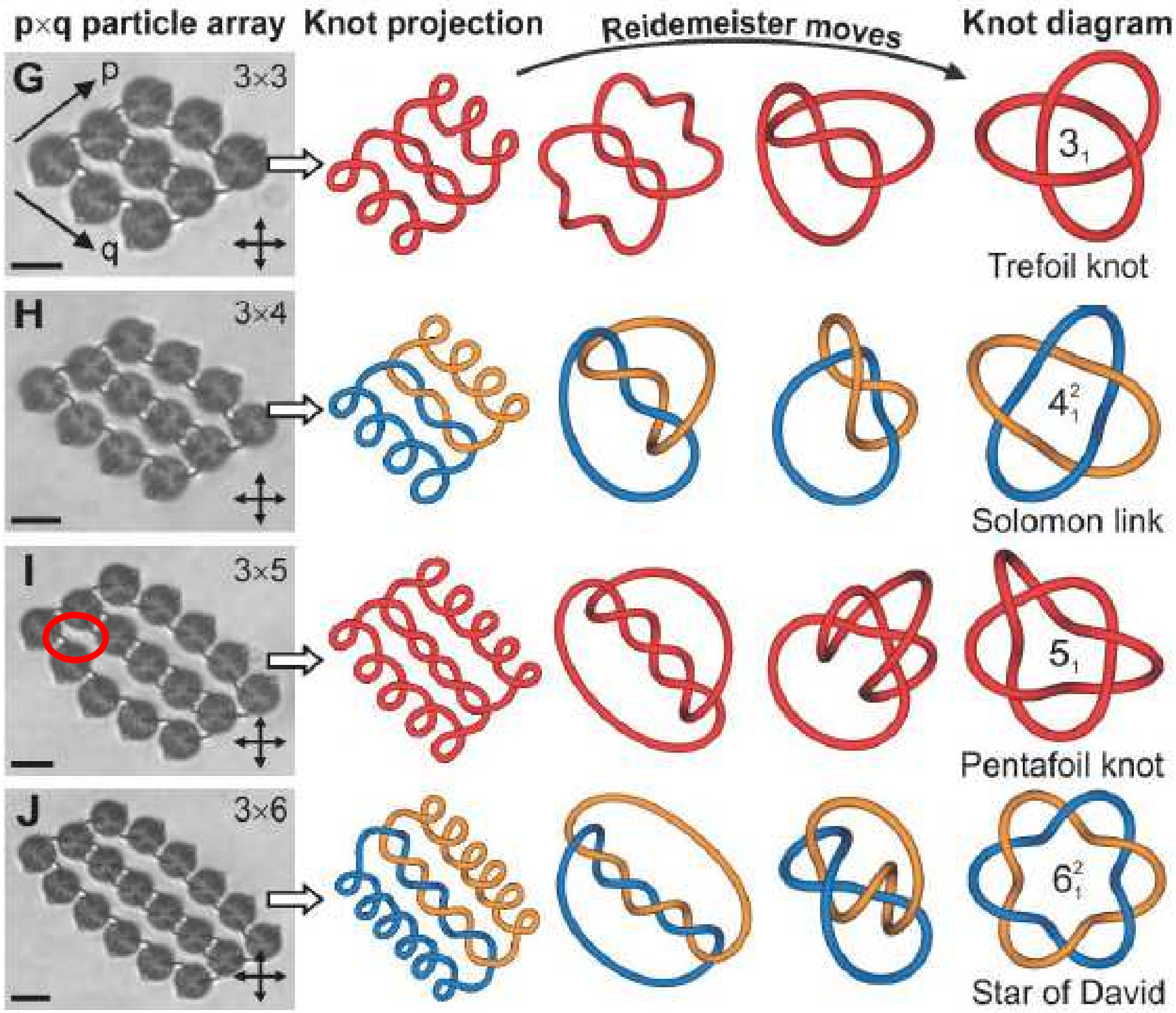


Continuous transformation of the disclination loop (Reidemeister moves):



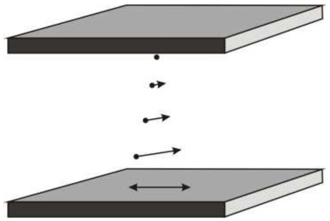
Torus knots and links

Full series of torus knots and links can be assembled

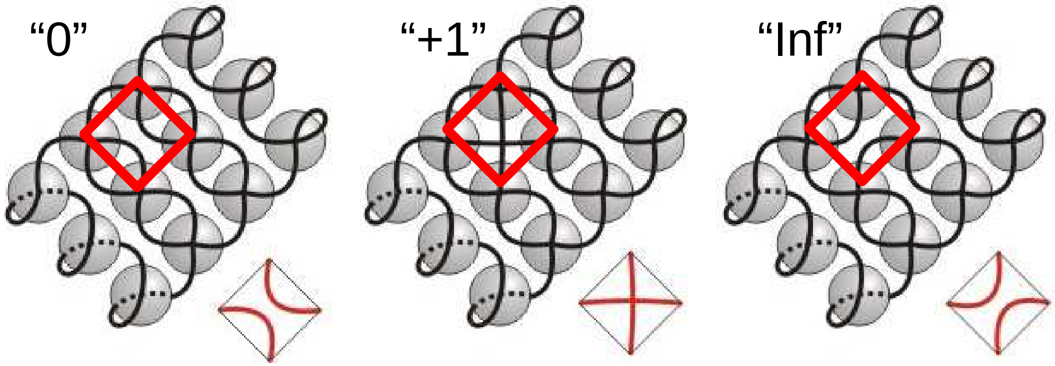


Classification after: V. V. Prasolov, A. B. Sossinsky: Knots, links, braids and 3-manifolds : an introduction to the new invariants in low-dimensional topology (1997)

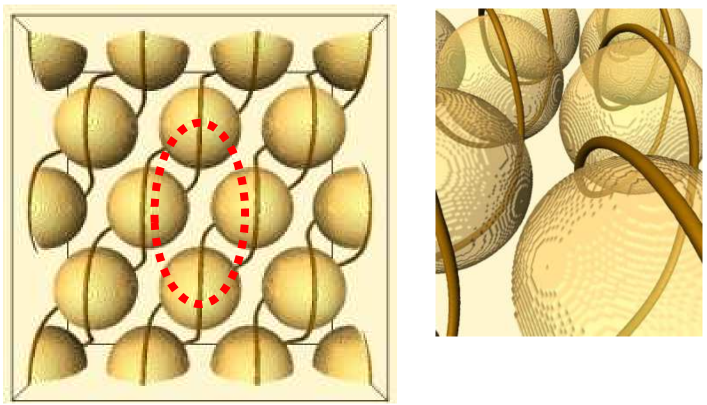
2D entangled structures – structures of tangles



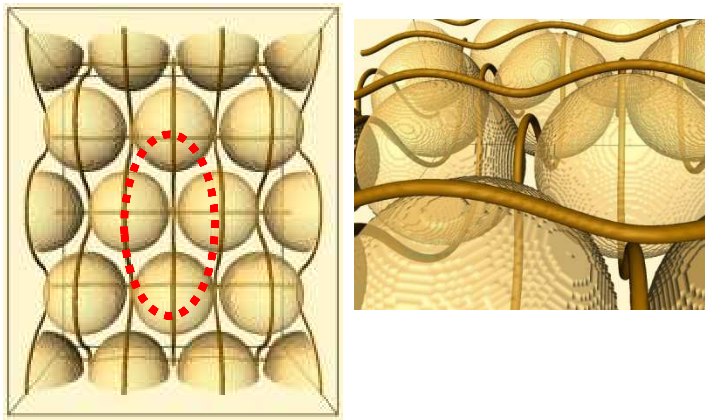
Nematic profile in tangles:



Numerically modelled tangles:



0 and Inf tangle



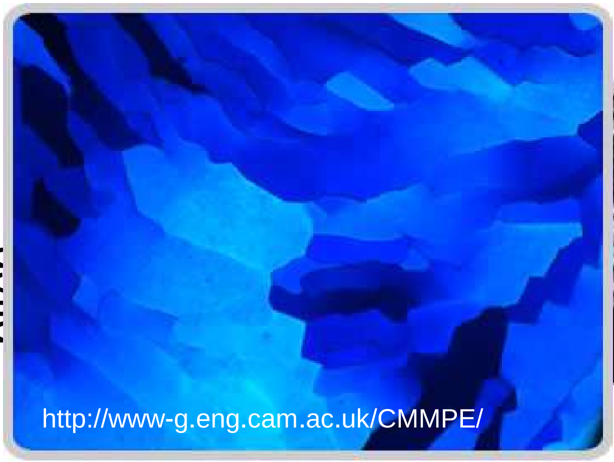
+1 tangle

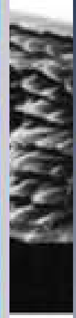
Numerically “assembling” the tangle regions gives full knotted nematic fields.

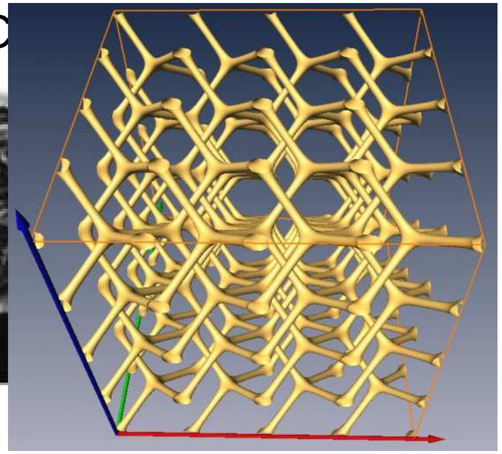
Liquid crystal blue phases – beyond simple crossings 1/3

Liquid crystals with chiral molecules twist spontaneously:

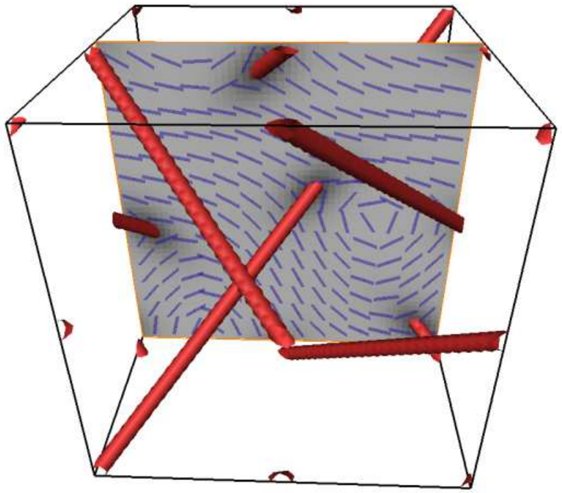
blue phases:



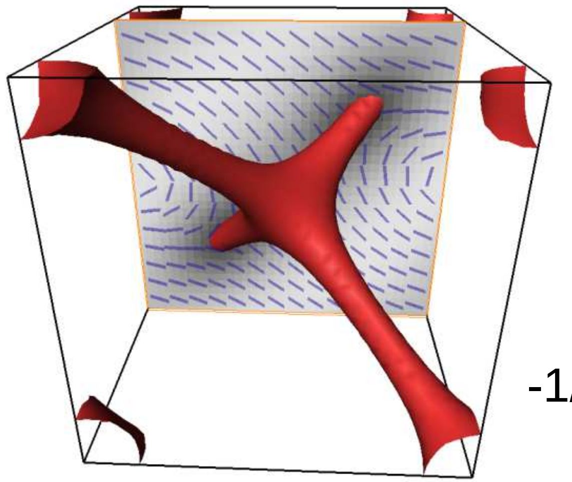




Unit cell of BP I



Unit cell of BP II



Blue phases are natural progenitors of topological defect lines

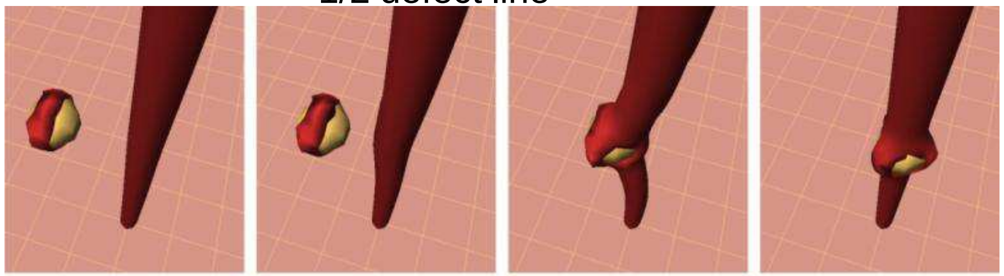
-1/2 disclination lines

Farad. Discuss. 2010, PNAS 2011

Liquid crystal blue phases – beyond simple crossings 2/3

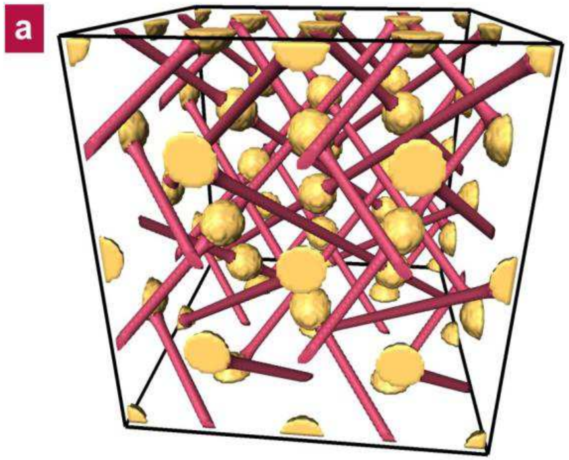
EFFECTIVE "SPLITTING": Colloidal particles CAN split the singular core of the topological defect line.

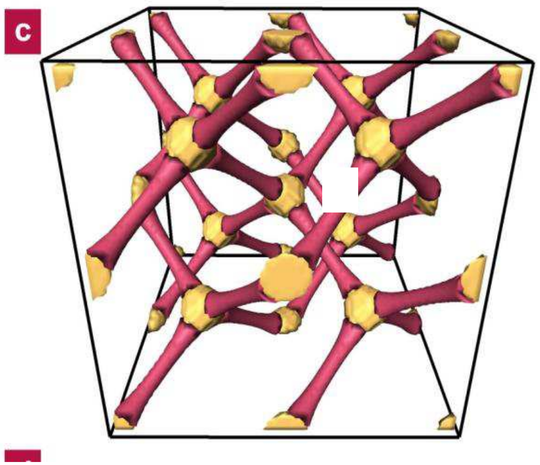
-1/2 defect line



Homeotropic 40nm particle

EFFECTIVE CUTTING: Colloidal particles can effectively cut the core of the topological defect line.



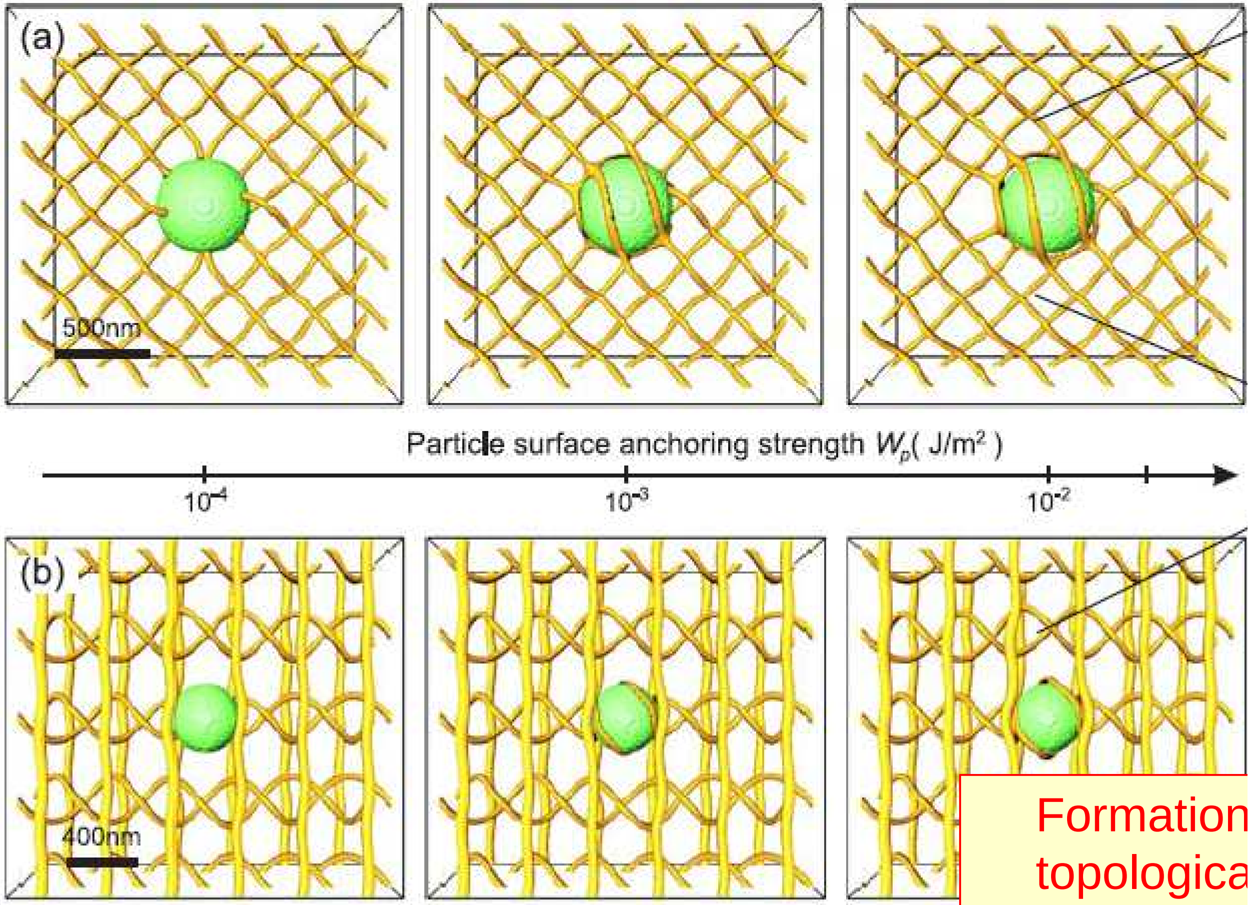


Splitting and cutting regime can be tuned by surface interactions

Ravnik et al, Soft Matter 2011

Liquid crystal blue phases – beyond simple crossings 3/3

Confinement of larger particles produces cages of topological defects:

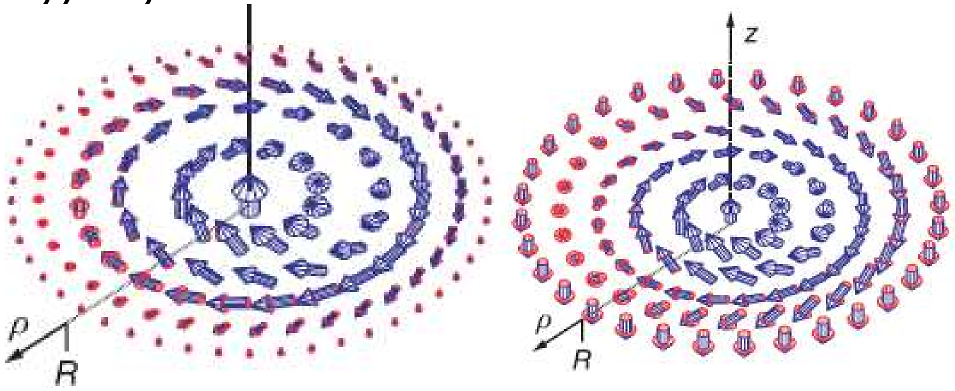


Formation
topologica
“cages”

Interesting topology and rheology.

Analogy: liquid crystals and chiral ferromagnets

Complex topological structures in the magnetisation field of chiral ferromagnets – the (baby) skyrmions:

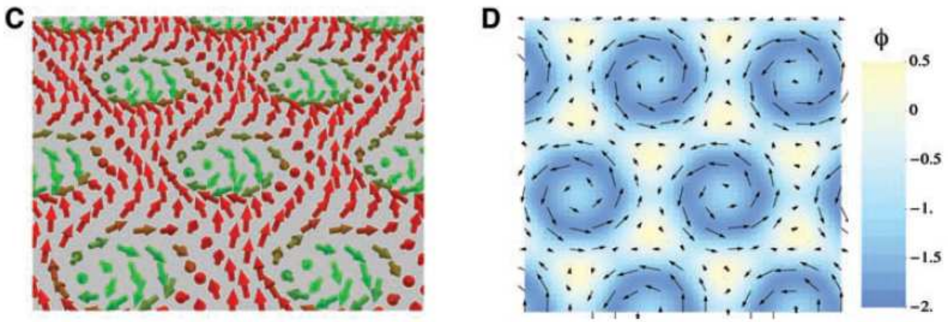


Magnetisation:

$$\mathbf{m} = m\mathbf{N}$$

Skyrmion Lattice in a Chiral Magnet

S. Mühlbauer,[1,2] B. Binz,[3] F. Jonietz,[1] C. Pfleiderer,[1*] A. Rosch,[3] A. Neubauer,[1] R. Georgii,[1,2] P. Böni[1]

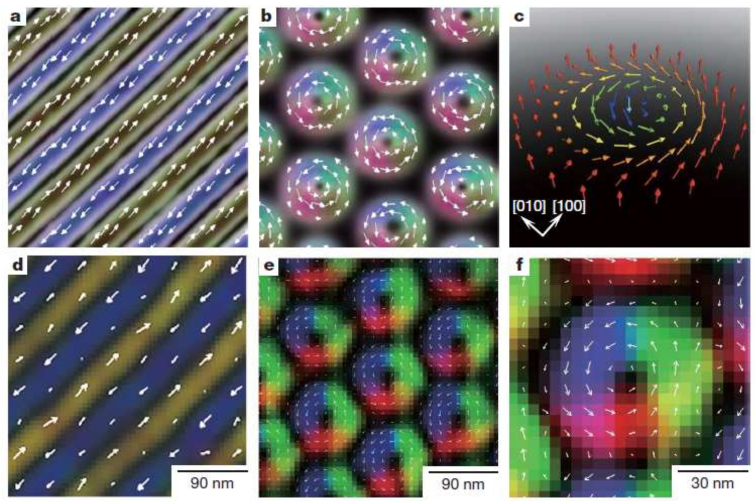


chiral itinerant-electron magnet MnSi

www.sciencemag.org SCIENCE VOL 323 13 FEBRUARY 2009

Real-space observation of a two-dimensional skyrmion crystal

X. Z. Yu[1,2], Y. Onose[2,3], N. Kanazawa[3], J. H. Park[4], J. H. Han[4], Y. Matsui[1], N. Nagaosa[3,5] & Y. Tokura[2,3,5]



Topological spin textures in the helical magnet $Fe_{0.5}Co_{0.5}Si$.

NATURE| Vol 465 |17 June 2010

Analogy liquid crystals and chiral ferromagnets

Free energy of chiral ferromagnets:

$$\boxed{\mathbf{m} = m\mathbf{N}}$$

$$f^M = Am^2(\nabla \mathbf{N})^2 + A\eta(\nabla m)^2 + rm^2 + bm^4 + Dm^2\mathbf{N}\cdot(\nabla\times\mathbf{N})$$

Freee energy of chiral nematic liquid crystal:

$$\boxed{Q_{ij} = S(3n_i n_j - \delta_{ij})/2}$$

$$\begin{aligned} F &= \int_{LC}\left[\frac{A_0(1-\gamma/3)}{2}Q_{ij}Q_{ij} - \frac{A_0\gamma}{3}Q_{ij}Q_{jk}Q_{ki} + \frac{A_0\gamma}{4}\left(Q_{ij}Q_{ij}\right)^2\right]\mathrm{d}V \\ &+ \frac{L}{2}\int_{LC}\left[(\epsilon_{ikl}\frac{\partial Q_{lj}}{\partial x_k} + 2q_0 Q_{ij})^2 + (\frac{\partial Q_{ij}}{\partial x_i})^2\right]\mathrm{d}V \end{aligned}$$

$$f^{LC} = \frac{9}{4}LS^2(\nabla\mathbf{n})^2 + \frac{3}{4}L(\nabla S)^2 + \frac{3}{4}aS^2 + \frac{1}{4}cS^3 + \frac{9}{16}dS^4 + \frac{9}{2}q_0 LS^2\mathbf{n}\cdot(\nabla\times\mathbf{n})$$

Mapping of parameters: $A \leftrightarrow 9L/4,\ \eta \leftrightarrow 1/3,\ r \leftrightarrow 3a/4,\ 0 \leftrightarrow c/4,\ b \leftrightarrow 9c/16$

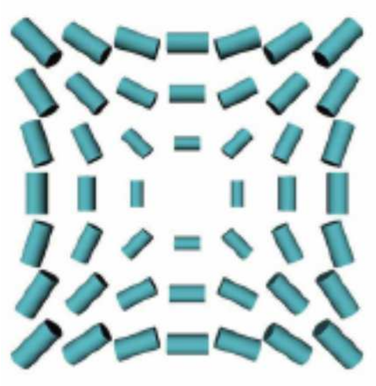
IMPORTANT: magnetisation **m** is vector field, whereas LC director **n** is vector with **n** to –**n** symmetry

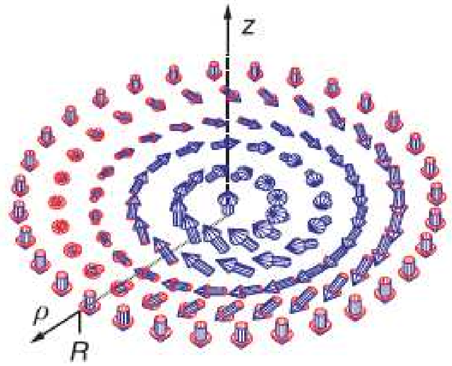
Analogy liquid crystals and chiral ferromagnets

PRL 09

Nematic escaped singular loops – bubble gum defects

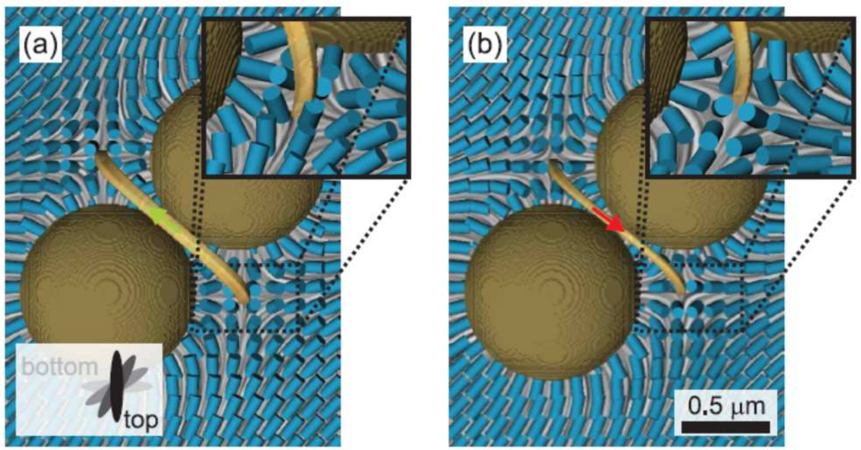
Hyperbolic -1 defect line

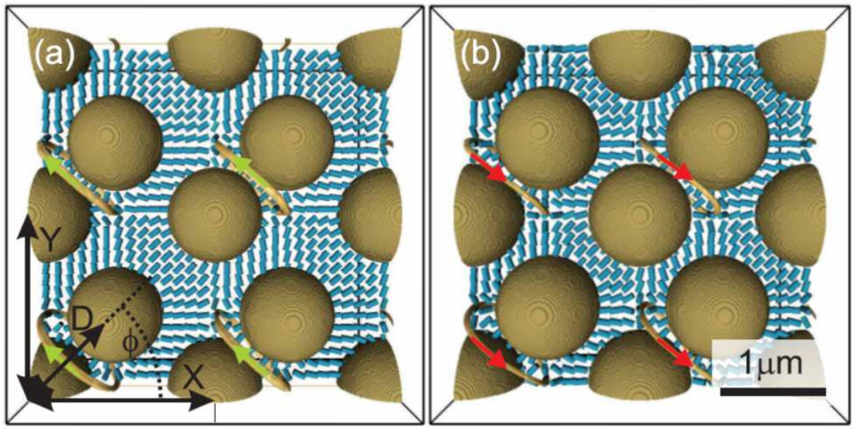




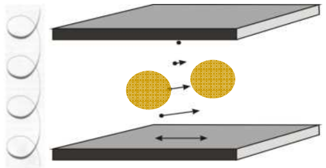
Escape into the 3rd dimension

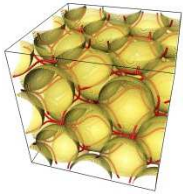
Particle dimers and 2D crystals: <u>loops of escaped -1 defect lines</u>

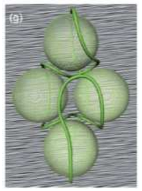


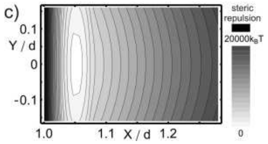


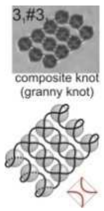
Conclusions

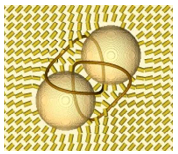


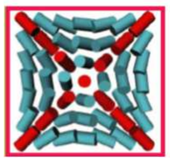


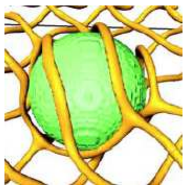












- Temperature quench is an efficient mechanism for generation of topological defect loops
- Nematic colloids can stabilise various defect loop conformations; within 1D, 2D and 3D particle structures
- Typical free energy differences between (meta)stable structures are ~1%; yet corresponding to ~1000kT.
- Energy barriers between states are strongly anisotropic and much higher than 100-1000kT.
- Twisted “environment” gives energetic stabilisation of structures with further complexity:

  assembly of arbitrary knots and links

Two possibly interesting systems that could give complex topology: liquid crystal blue phases, skyrmion structures.