Colloidal Liquid Crystals

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Orsay

Before renovation …

After renovation …

LPS
ORSAY

UNIVERSITÉ PARIS SUD
Comprendre le monde, construire l'avenir®

Colloids, colloidal suspensions, and liquid crystals

Colloids:
- objects that have at least one dimension in the 1 – 100 nm range
- would nowadays often be called « nanoparticles »

Colloidal suspensions (or dispersions):
- in a solvent at some concentration (or weight fraction, or volume fraction)
- stable colloid when interparticle attractions are weak enough to avoid particle aggregation
- important parameter: gravitational length $l_g = k_B T / gV\Delta\rho$
- brownian system if l_g is not too small compared to sample height

Liquid-crystalline colloidal suspensions:
- made of anisotropic nanoparticles (rods, wires, plates, sheets, ribbons …)
- beyond some concentration threshold
- usual nematic, smectic, columnar … liquid-crystalline phases
- but with length and time scales several orders of magnitude larger than those of usual small LC molecules

Hans Zocher (1925): the pioneer of colloidal liquid crystals

Hans Zocher

Über freiwillige Strukturbildung in Solen.

(Eine neue Art anisotrop flüssiger Medien.)

Von H. Zocher.

Mit 3 Figuren im Text und 4 Tafeln.

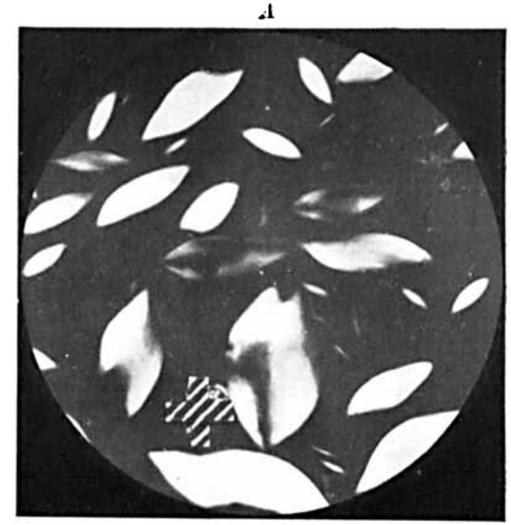
Eines der interessantesten Probleme der Kolloidlehre ist das von der Reichweite der Kräfte, die von Phasengrenzen ausgehen (1). Diese Kräfte sind zweierlei Natur. Erstens handelt es sich um molekulare Wirkungen, die man meistens als chemischer Natur, als Wirkung von Valenzkräften anzusehen geneigt ist. Äußerungen

i.e. A liquid crystal !

Tactoids in V_2O_5 suspensions:

A

P



A

Fig. 5.

H.Zocher, Zeit. Anorg. Allg. Chem. ***147****, 91 (1925)*

« Tactoids »: droplets of N phase in I phase

COLLOIDAL PARTICLES AND MACROMOLECULES 179

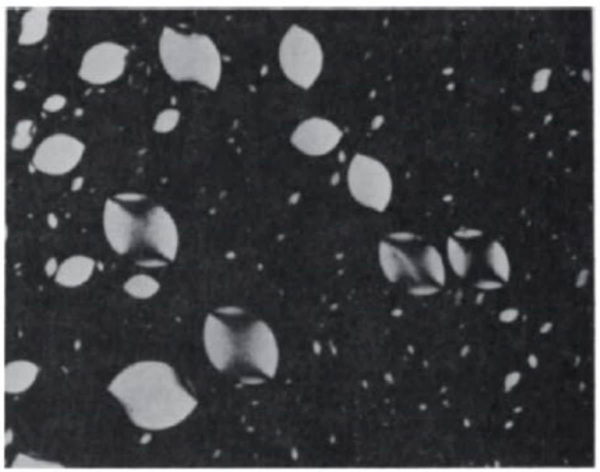


Fig. 15. Nematic tactoids of V_2O_5 observed in a polarizing microscope (crossed nicols).[24]

180 W. HELLER

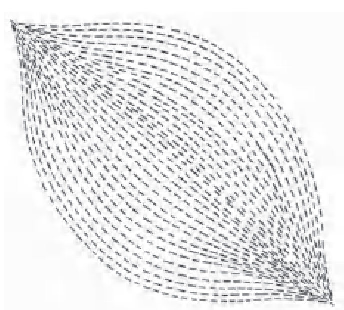
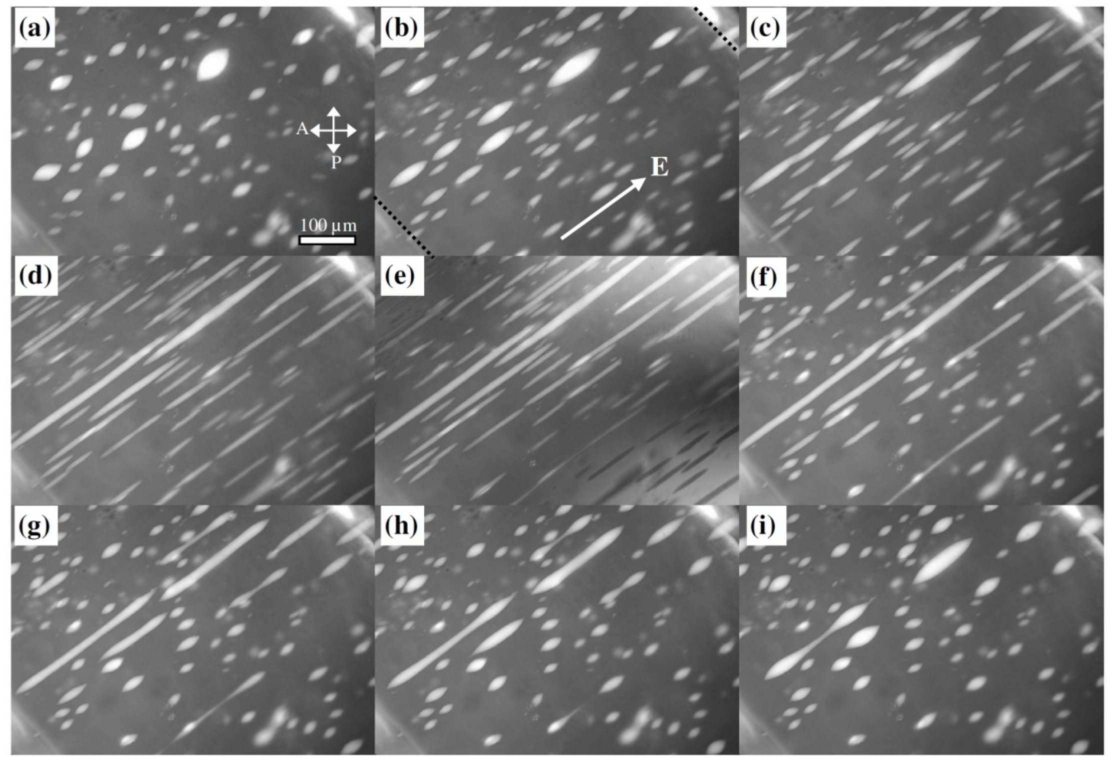


Fig. 16. Orientation of V_2O_5 crystals within a nematic factoid (schematic cross section containing axis of symmetry).

(W.Heller, in Polymer Colloids II, E. Fitch Ed., Plenum Press, NY, p 195 (1980))



Electric field effects on tactoids of chitin suspensions

*L.Metselaar et al, Phys. Rev. E, **96**, 022706 (2017)*

Irving Langmuir and montmorillonite clays (1938)

Irving Langmuir

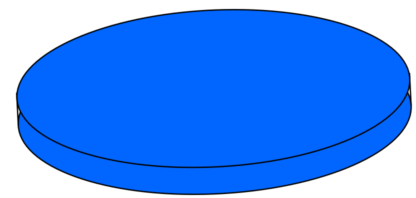
DECEMBER, 1938 JOURNAL OF CHEMICAL PHYSICS VOLUME 6

The Role of Attractive and Repulsive Forces in the Formation of Tactoids, Thixotropic Gels, Protein Crystals and Coacervates

IRVING LANGMUIR
General Electric Company, Schenectady, New York

(Received October 20, 1938)

percent. The sol containing 2 percent after several hundred hours become isotropic in its upper half, while the lower half remained permanently birefringent, showing a fine mosaic structure of crystal grains having optic axes inclined about 45° to the axis of the tube. With the tube containing the sol of 2.2 percent a sharply defined isotropic portion of about 6 cm depth separated out at the top of the tube. The lower part consisted of the fine grained crystal mosaic. The sols of still higher concentrations appeared to be permanently crystalline throughout. It was only in the concentration range of 2.0 to 2.2 percent that two distinct phases separated after long standing.

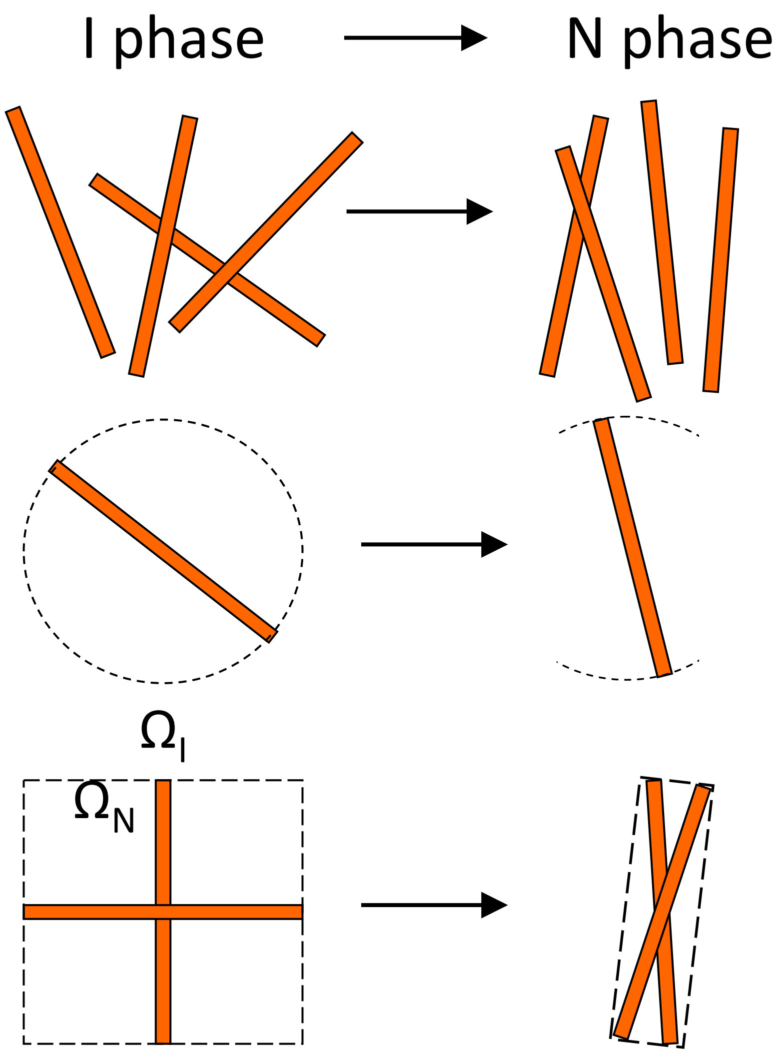


<D> = 300 nm

t = 0.65 nm

[11] This determination of the temperature coefficient of τ was made about four months after the solutions were sealed into the glass tubes. There had been a gradual change in the properties of the sols during this time, probably due to traces of substances taken up from the glass. During this time the value of τ for the tube containing 1.4 percent increased from 3 to about 100 seconds and similar increases were found with the other tubes. The property of giving two phases after long standing, which was originally observed with the 2.0 and 2.2 percent sols, was also gradually lost. These properties of bentonite solutions are extremely sensitive to traces of salts and other substances.

Lars Onsager and his model of the isotropic – nematic transition



Lars Onsager

Loss in **rotational** entropy:

$\Delta S_{or} = k_B \ln \Omega_N / \Omega_I \sim k_B$

Gain in **free volume** entropy:

$\Delta S_{vol} \sim k_B \rho L^2 D$

$\Delta S_{or} + \Delta S_{vol} = 0 \quad \rightarrow \quad \rho^* \sim 1 / L^2 D$

L.Onsager, Ann N.Y. Acad. Sci., ***51****, 627 (1949)*

Lars Onsager and his model (2)

Assumptions:
- rod-like particles
- only hard-core interactions
- very large aspect ratio $L/D \rightarrow \infty$

Conclusions:
- 1st order phase transition (with phase coexistence)
- volume fractions at coexistence: $\phi_I = 3.3\ D/L$ and $\phi_N = 4.2\ D/L$
- athermal system; no influence of temperature

Corrections and developments:
- for lower L/D
- for electrostatic repulsions
- for flexibility
- for plate-like particles

Extensively checked by numerical simulations

DNA and viruses

Proc. Natl. Acad. Sci. USA
Vol. 83, pp. 342–346, January 1986
Biophysics

Liquid crystalline phases in concentrated aqueous solutions of Na^+ DNA

RANDOLPH L. RILL

Department of Chemistry and Institute of Molecular Biophysics, The Florida State University, Tallahassee, FL 32306

Communicated by Michael Kasha, August 28, 1985

However, X-ray scattering studies (1950's) by Rosalind Franklin were probably made in the LC phase !... See also V. Luzzati.

For a nice review paper, see:
F.Livolant and A.Leforestier
Prog. Pol. Sci., ***21***, *1115 (1996)*

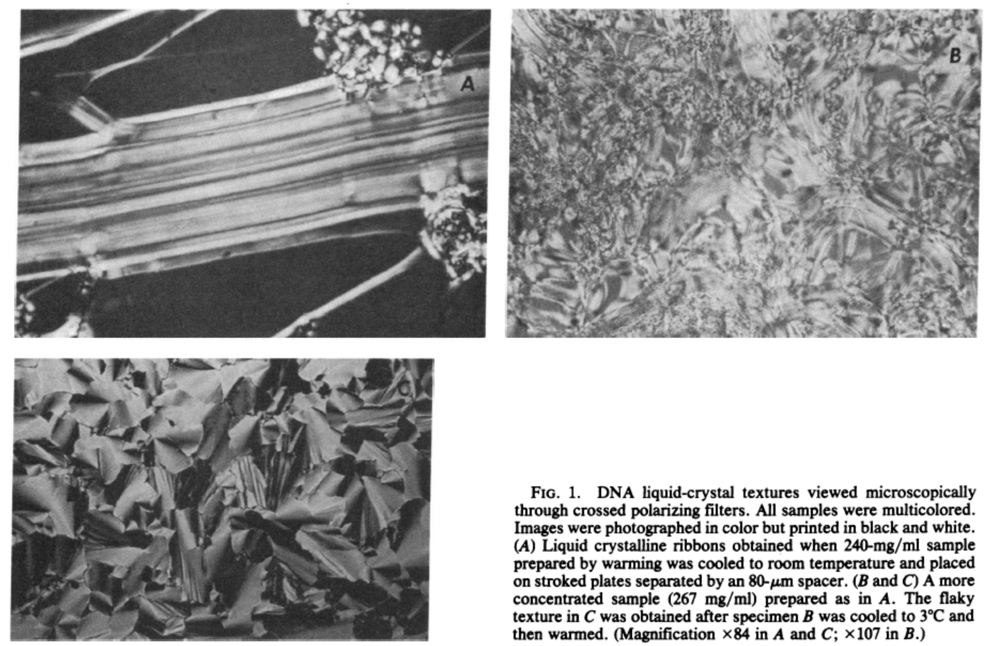
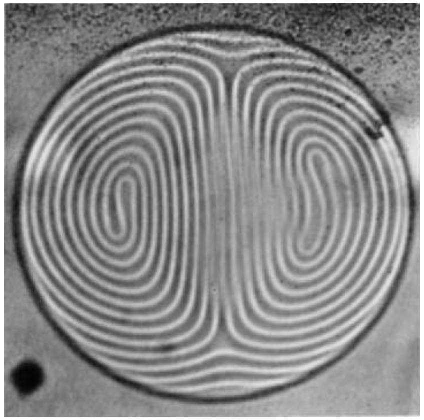


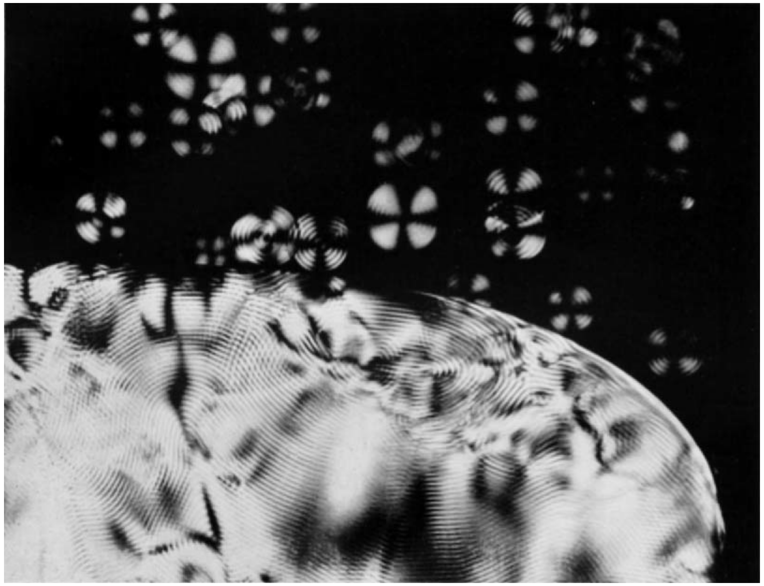
FIG. 1. DNA liquid-crystal textures viewed microscopically through crossed polarizing filters. All samples were multicolored. Images were photographed in color but printed in black and white. (*A*) Liquid crystalline ribbons obtained when 240-mg/ml sample prepared by warming was cooled to room temperature and placed on stroked plates separated by an 80-μm spacer. (*B* and *C*) A more concentrated sample (267 mg/ml) prepared as in *A*. The flaky texture in *C* was obtained after specimen *B* was cooled to 3°C and then warmed. (Magnification ×84 in *A* and *C*; ×107 in *B*.)

For the story of viruses, attend Eric Grelet's talk on Thursday !!!

Polypeptides and proteins

PBLG (poly-g-benzyl-L-glutamate):
Conmar Robinson
Transactions Faraday Society
***52**, 571 (1956)*



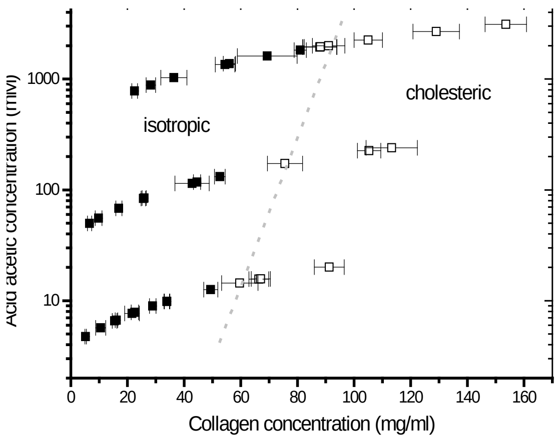


Collagen: *Y Bouligand et al, Tissue and Cell (1972)* ***4**, 189*

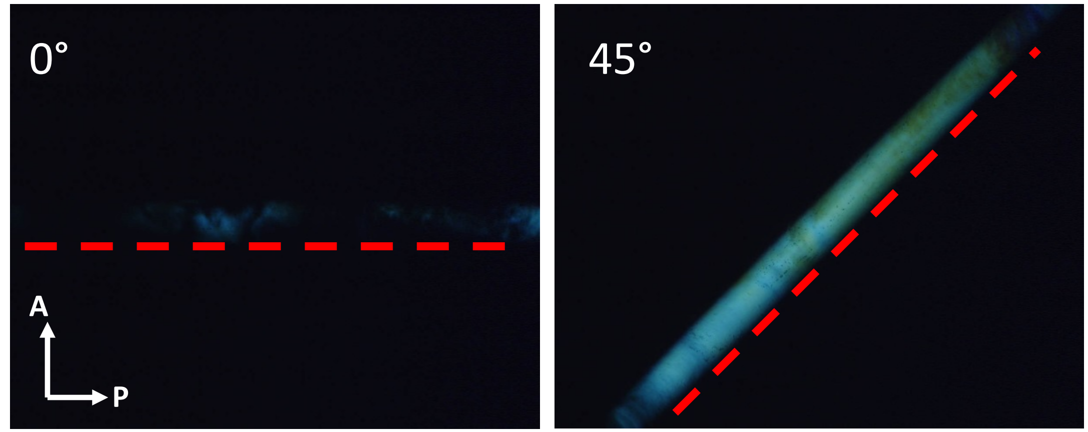
Actin: difficult system because gelation blurs the onset of LC ordering

Suspensions of collagen triple helices

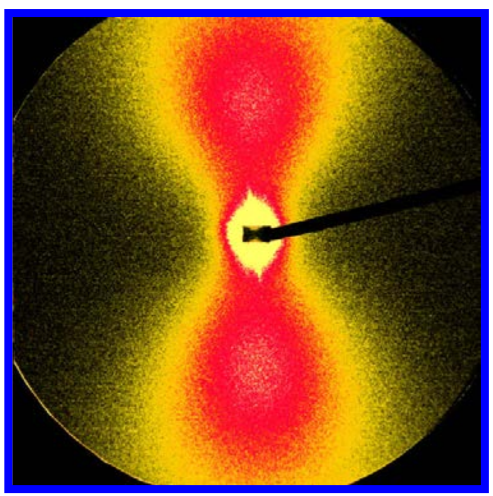
(Thèse F.Gobeaux; cf G.Mosser, E.Belamie)



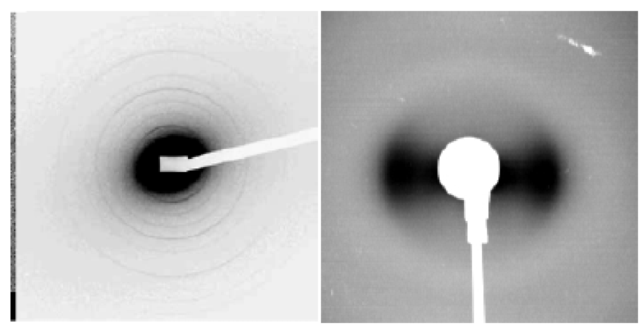
1st order I/N transition



Birefringent sample aligned in a capillary



SAXS pattern



Samples fibrillated through pH raise, to produce biomaterials

Frédéric Gobeaux

*F.Gobeaux et al, Langmuir, **23**, 6411 (2007); J. Mol. Biol. **376**, 1509 (2008)*

Cellulose and chitin

Cellulose: J.F.Revol, R.H.Marchessault, D.G.Gray , L.Heux …
Cf Bruno Frka-Petesic’s and Axel Foulques’ talks today

See:
- *R.H.Marchessault et al, Nature, **184**, 632 (1959)*
- *J.F.Revol et al, Int. J. Biol. Macromol., **14**, 170 (1992)*

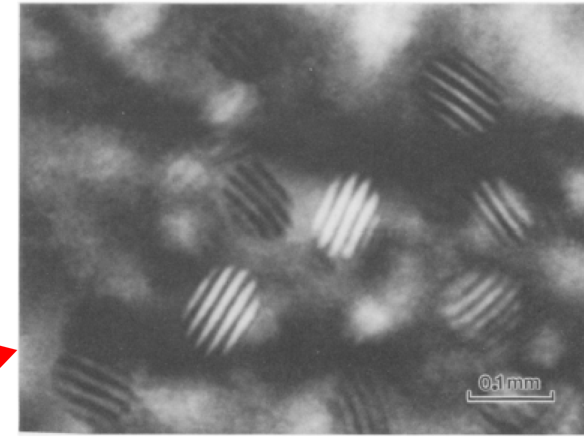
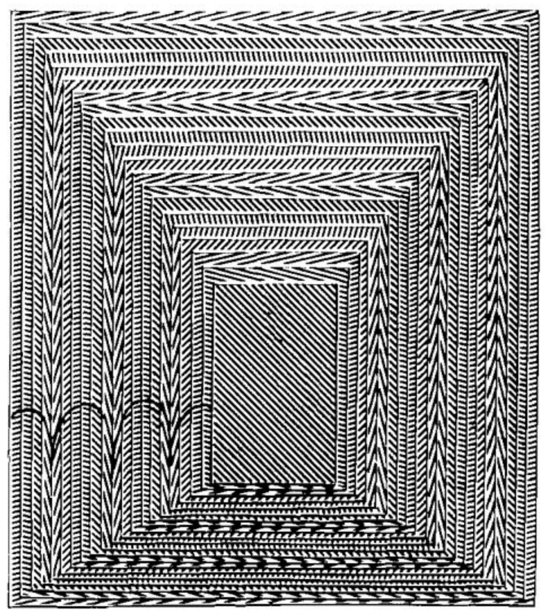


Figure 1 Optical micrograph (crossed polars) of an aqueous suspension of cellulose crystallites ($3 \pm 0.1\%$ by weight) a few minutes after sonication or shearing. Tactoïds exhibiting birefringent bands ($\sim 15\ \mu m$ spacing in this case) are visible

Bouligand’s arches in cholesteric structures
*Y. Bouligand et al, Tissue and Cell, **4**, 189 (1972)*
Géométrie du vivant : dessins d'Yves Bouligand (Paris, Hermann, 2018)



Yves Bouligand

Chitin: E.Belamie’s papers

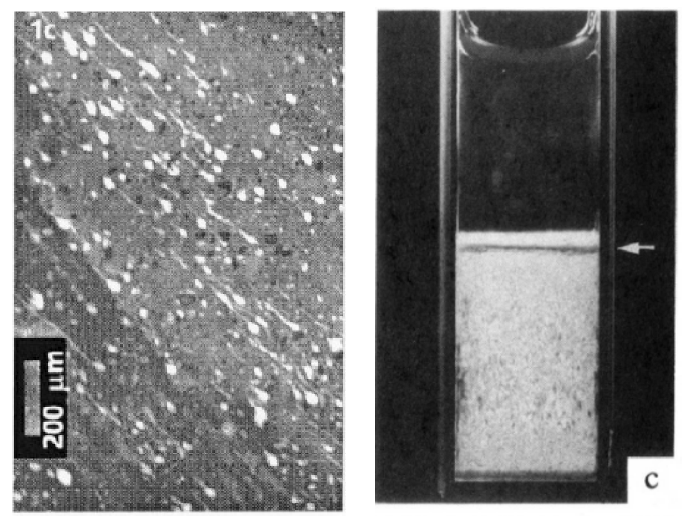
Listen also to M.Mitov’s talk today

Henk Lekkerkerker and the Vant'Hoff laboratory in Utrecht, Netherlands

Henk Lekkerkerker (on the right)

Theorist of colloidal LCs
Cf *Vroege and Lekkerkerker*
Rep. Progr. Phys. ***55****, 1241 (1992)*

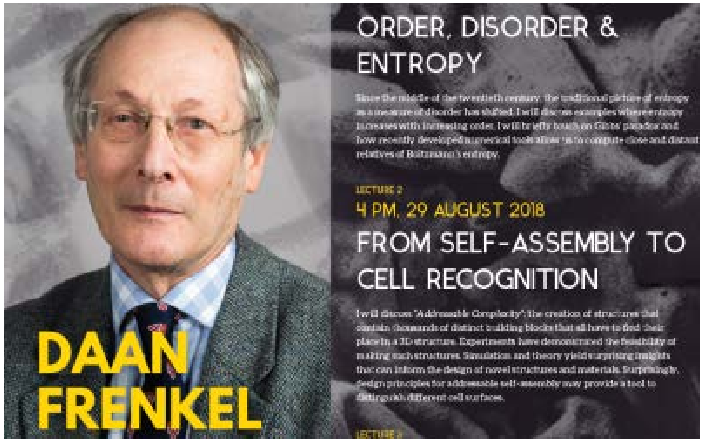
Also developed two experimental LC systems: boehmite nanorods and gibbsite nanodisks for comparison with theories

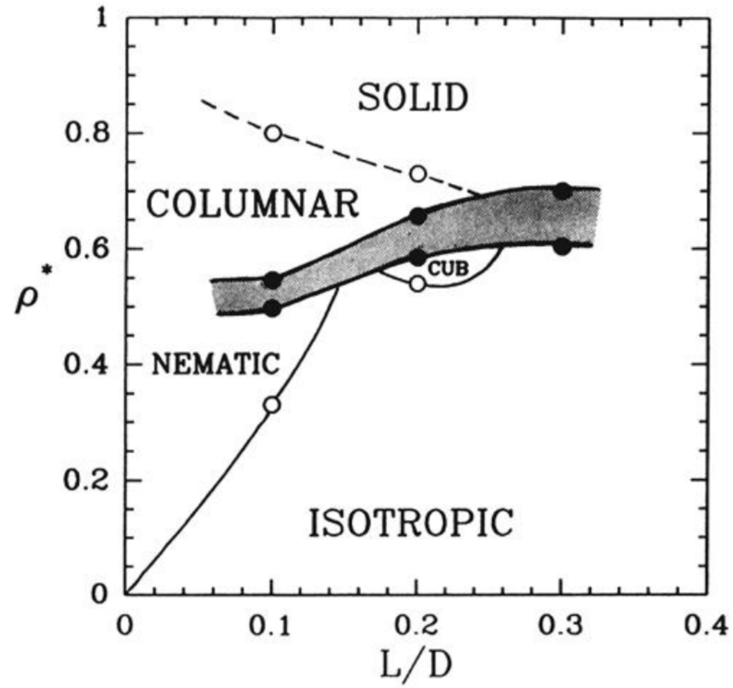


I/N transition in nanorod suspensions

M.P.B. van Bruggen, J. Phys. Cond. Matt., ***8****, 9451 (1996);*
P.A.Buining, J. Phys. Chem., ***97****, 11510 (1993)*

Computer simulations: Daan Frenkel





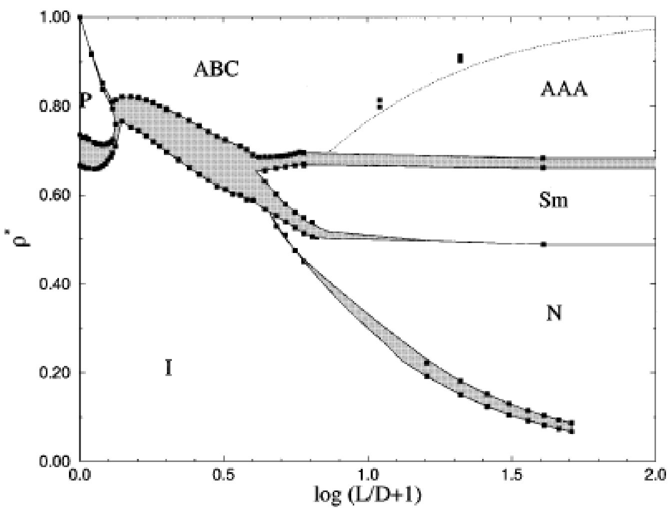


FIG. 2. Summary of the phase diagram of hard spherocylinders with L/D between 0 and 100. In order to give equal emphasis to all parts of the phase diagram, we have plotted ρ^* as a function of $\log(L/D+1)$. The dashed line is a crude estimate for the first order AAA-ABC transition as given in Eq. (52).

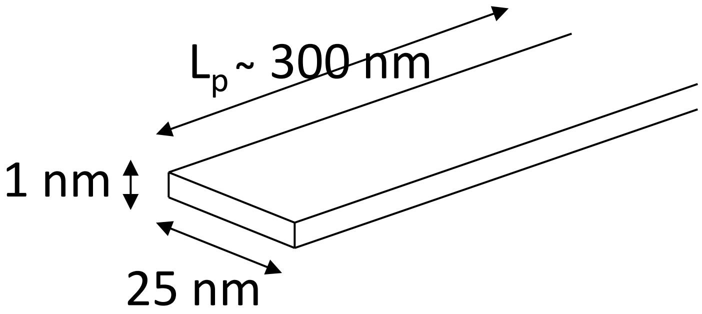
For disks:

J.A.C.Veerman and D.Frenkel, Phys. Rev. A, ***45****, 5632 (1992)*

For rods:

P.Bolhuis and D.Frenkel, J. Chem. Phys. ***106****, 666 (1997)*

Aqueous suspensions of V_2O_5 ribbons



Xerogel
TEM

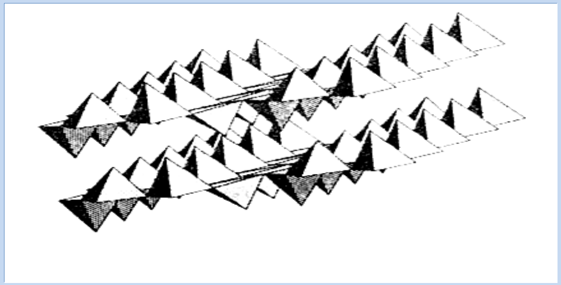
Mineral ribbons:

- dispersed in water
- semi-flexible:

$L_p \approx 0.3$ µm, $L_c \approx$ a few µm

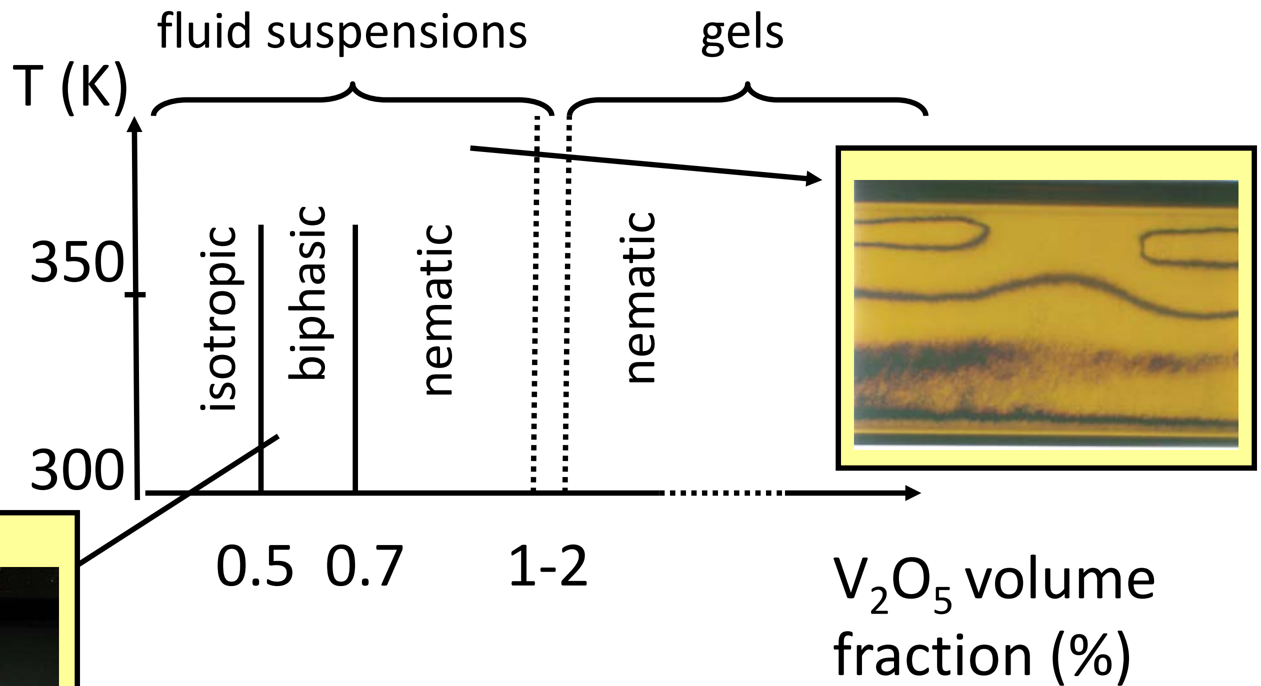
- and charged:

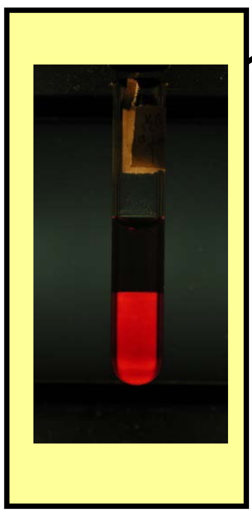
$V\text{-}0\text{-}H \rightarrow V\text{-}O^- + H^+$



Olivier
Pelletier

Phase diagram of the V_2O_5/H_2Osystem





• The fluid nematic phase has all the features usually associated with nematic order. For instance, it can be aligned in magnetic and electric fields (Frederiks transitions).

• The isotropic/nematic phase transition is consistent with the predictions of the Onsager model.

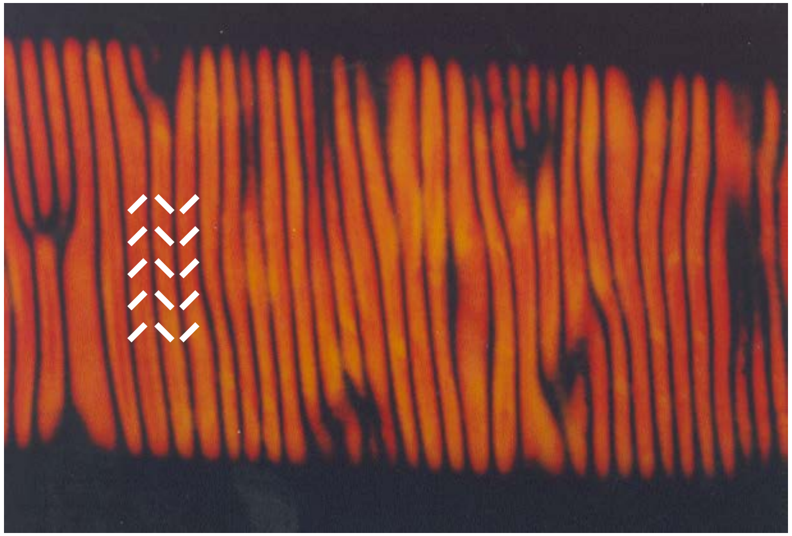
*P.Davidson et al, J. de Physique II, **5**, 1577 (1995)*

*S.Lamarque-Forget, Adv. Mat. **12**, 1267 (2000)*

Transient hydrodynamic instabilities

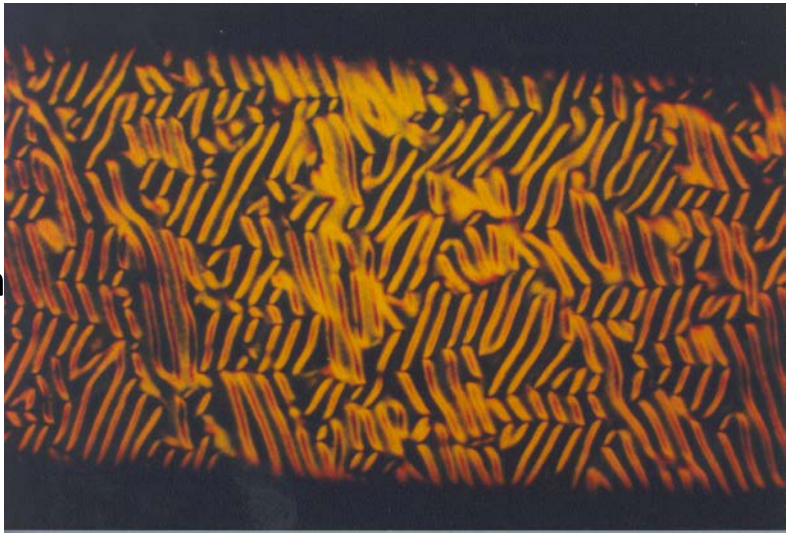
Reorientation of the liquid crystal upon a sudden change of the magnetic field direction

Magnetic field first applied in the horizontal direction



1 mm

Final magnetic field vertical



Final magnetic field perpendicular to the figure

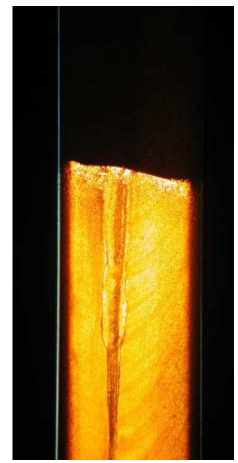
X.Commeinhes et al, Adv. Mat., ***9****, 900 (1997).*

(Just like suspensions of TMV …, cf *S.Fraden et al, J. de Phys. (1985)*)

Aqueous suspensions of goethite (α-FeOOH) nanorods

(B.Lemaire's PhD thesis)


Nematic threaded textures



Isotropic phase
5.5%

Nematic phase
8.5%

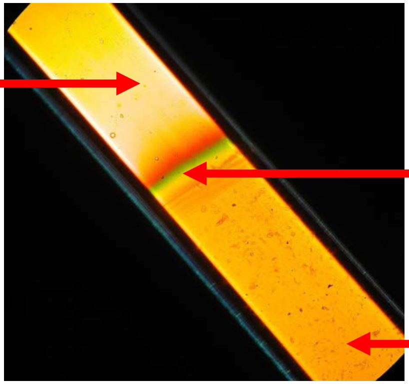
Phase coexistence
Thermodynamic equilibrium,
1^{st} order transition

Bruno Lemaire

Goethite suspensions are very easily aligned by a magnetic field

B = 200 mT

The isotropic phase turns birefringent



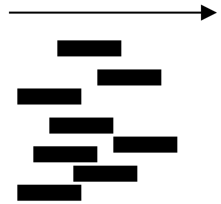
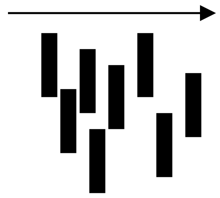
interface

Aligned nematic

Nematic phase: very low Frederiks threshold

20 mT for a thickness of 20 µm (25 times smaller than for usual molecular liquid crystals)

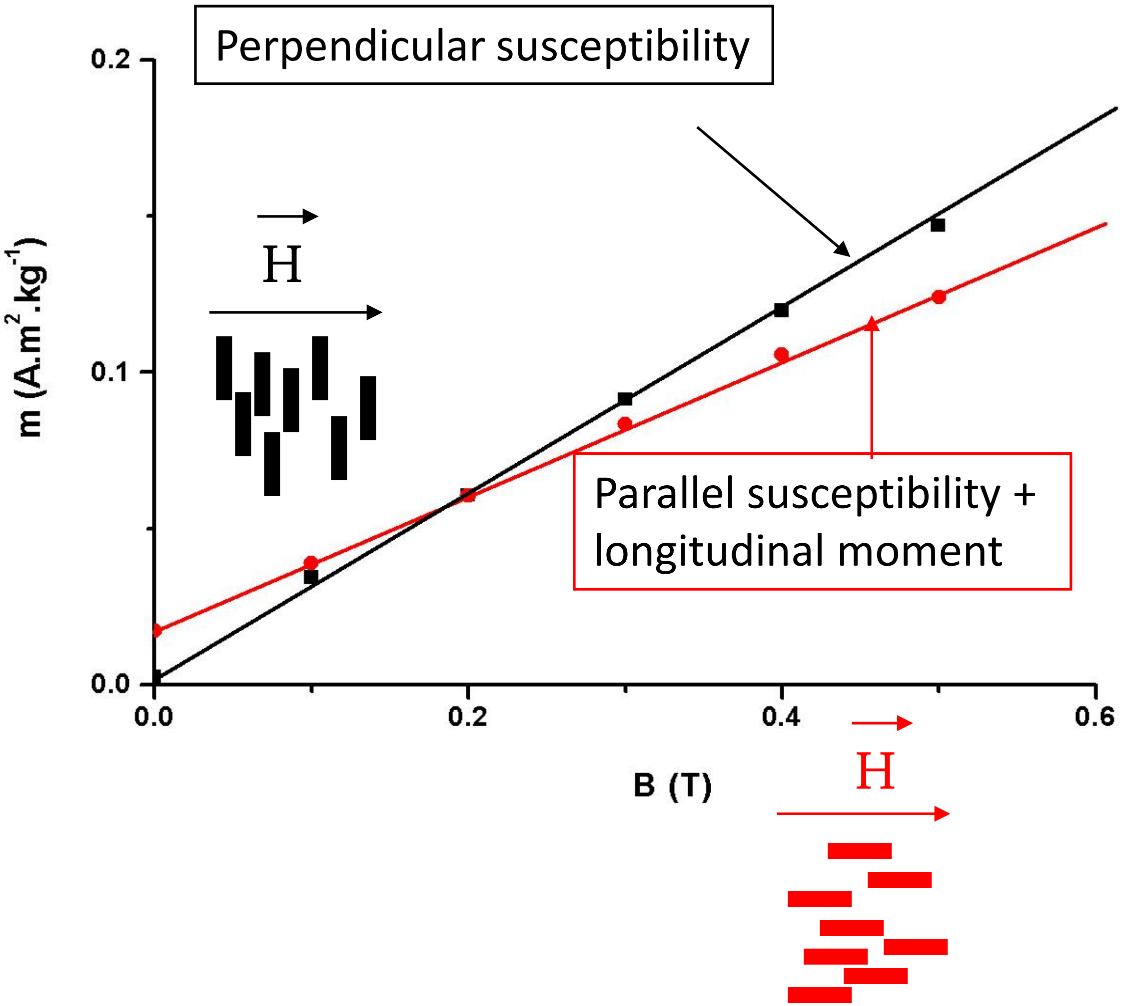
The nanorods reorient at a field of 250 mT

Before reorientation	After reorientation
Weak field	Strong field
	
30 mT	600 mT
$S = 0.9$	$S > 0.9$

SAXS patterns of the nematic phase under field

B.Lemaire et al, Phys. Rev. Lett., ***88****, 125507 (2002)*

Magnetic properties: remanent longitudinal moment and anisotropy of magnetic susceptibility



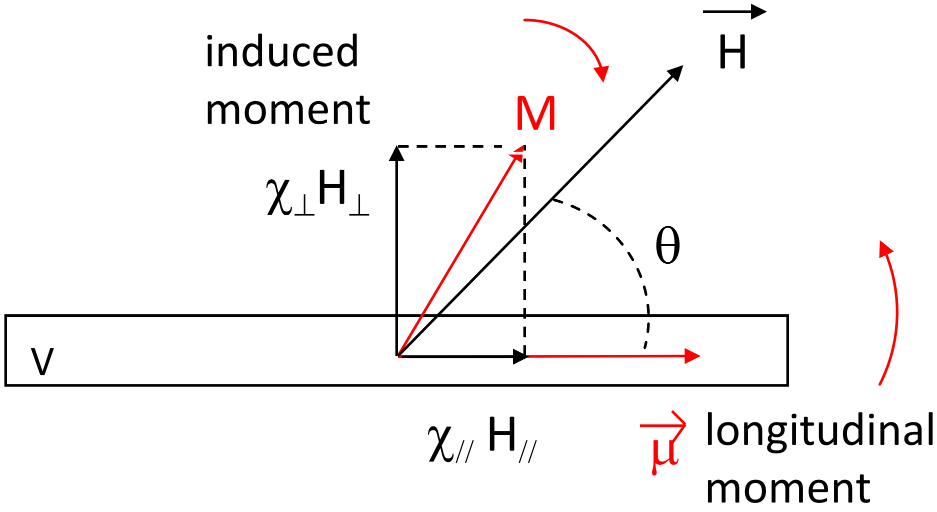
- Remanent longitudinal moment $\mu \sim 2.10^{-4}\ \mu_B$/Fe , i.e. 1000 μ_B per particle (Fe spin: 5 μ_B)

Possible origins of the longitudinal moment:
- crystalline defects
- non-compensated surface spins (L.Néel)

- Anisotropy of magnetic susceptibility:

$\chi_{//} - \chi_{\perp} = -4.10^{-4} < 0$

Nanorod reorientation



Reorientation threshold:
When the induced and remanent moments are equal;
-> 200 mT from SQUID measurements.

Hyp. : Non-interacting particles (dilute suspension)

$$\boxed{E_{magn}(\theta) = -\mu B\cos(\theta) - \frac{V(\chi_{//} - \chi_\perp)\, B^2 \cos^2(\theta)}{2\,\mu_0}}$$

*B.Lemaire et al, Eur. Phys. J. E, **13**, 291 (2004)*

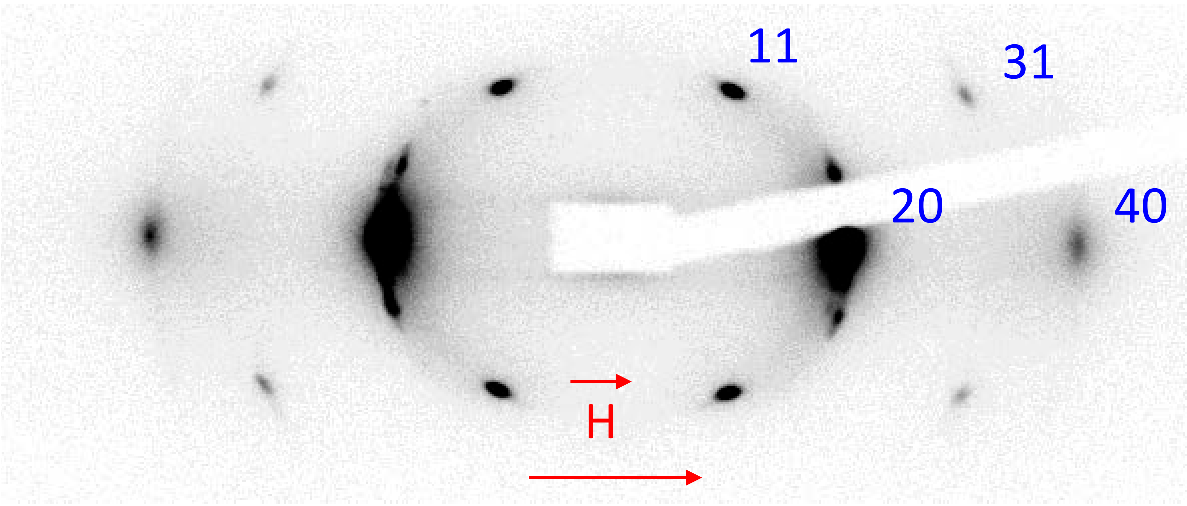
The remanent longitudinal moment favors the parallel orientation and is dominant at small field.

The induced moment favors the perpendicular orientation and is dominant at strong field.

In the Onsager model: *H.H.Wensink, Phys. Rev. E, **72**, 031708 (2005)*

Columnar phase induced by the magnetic field

Nematic phase submitted to a 1.5 T magnetic field

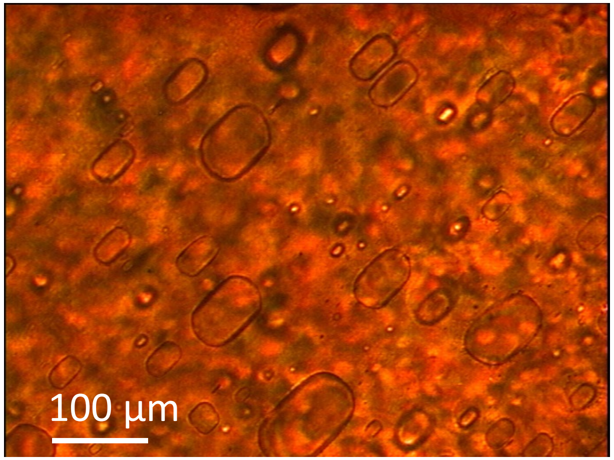


- Reproducible production of monodomains

- Threshold field B ~ 700 mT.

- 2-d centered rectangular cell, space group c2mm.

Why ???!!!

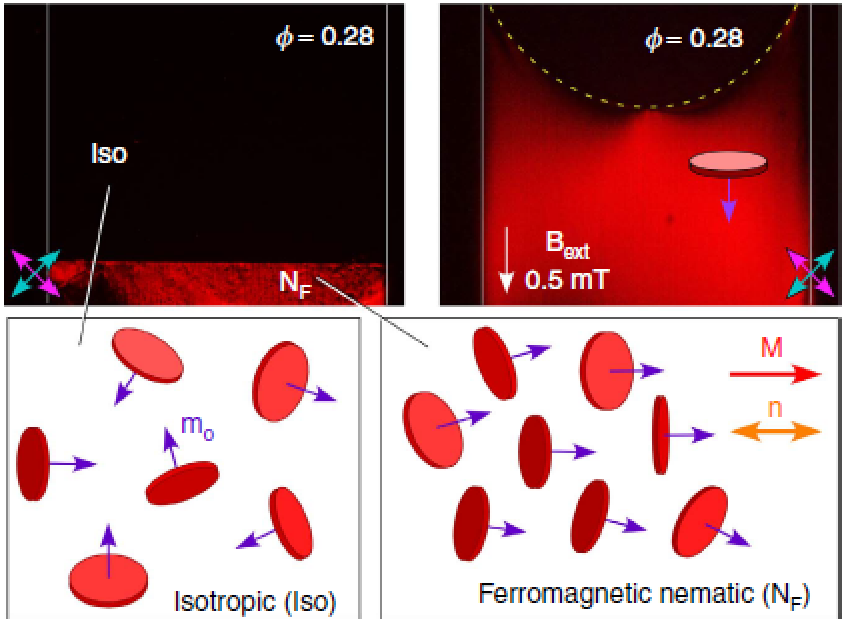


Columnar domains after 8 h under ~ 1T

B.J.Lemaire et al, Phys. Rev. Lett., ***93****, 267801 (2004)*

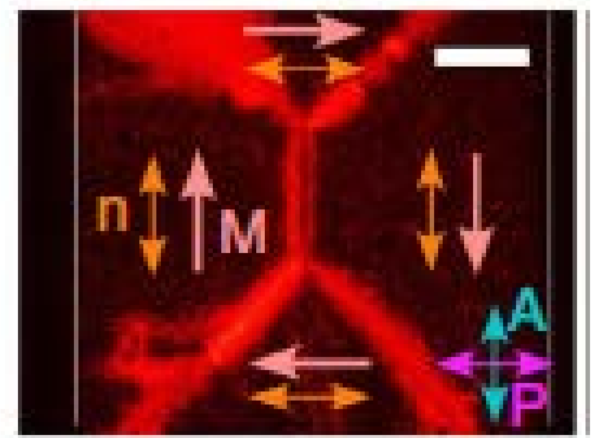
Ljubliana's ferrites: a ferromagnetic nematic ?

Suspensions of surfactant-stabilized baryum hexaferrite nanoplatelets in butanol (D = 48 nm, t = 7 nm, ϕ = 0.28)

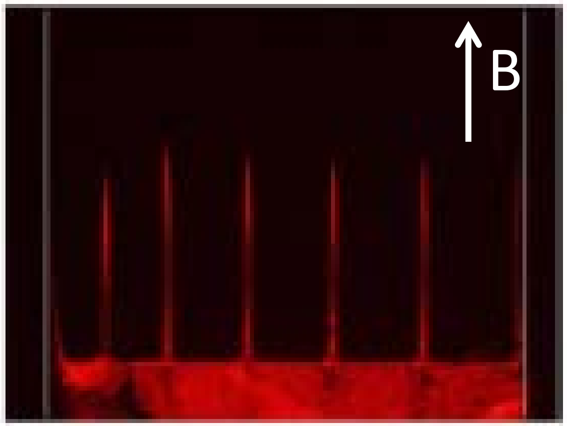


Extremely low Frederiks threshold (a few mT)!!!

M.Shuai et al, Nat. Comm., 7, 10314 (2016).

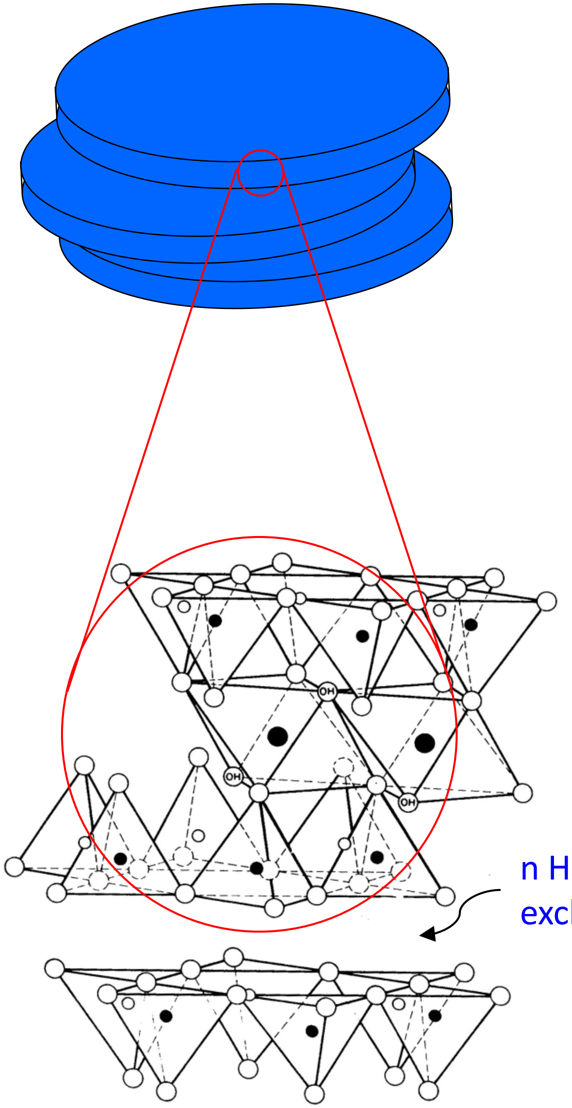


Magnetic domain configuration



I/N interface destabilization in a magnetic field

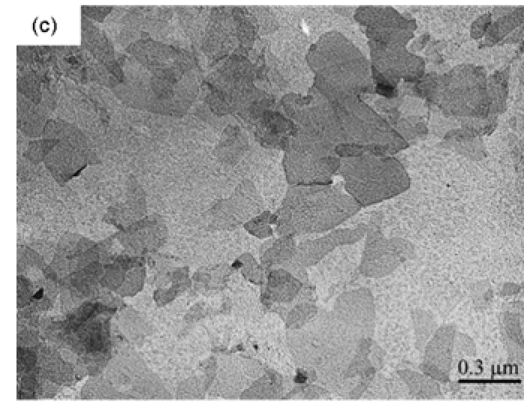
Beidellite: a natural clay



$\langle D \rangle \approx 300$ nm

$t \approx 0.65$ nm

Very large aspect ratio
$D/t \approx 450$!



Laurent Michot
(The Lord of the Clays)

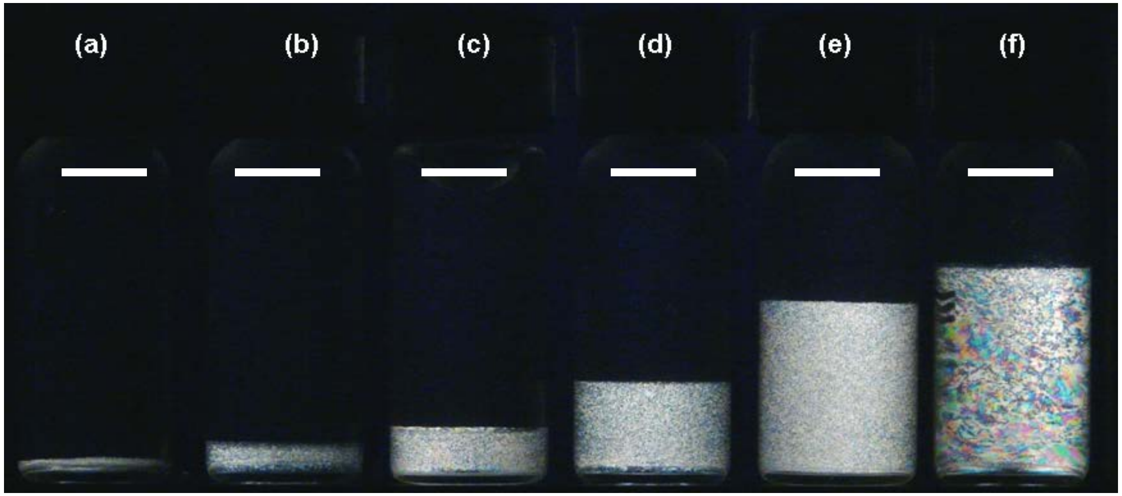
n H_2O layers and exchangeable cation

- ○ Oxygen
- (OH) Hydroxyl groups
- ● Aluminum, iron, magnesium
- ○● Silicon, aluminum, iron

SBId-1 : $(Si_{7.26}Al_{0.74})(Al_{3.74}Fe^{3+}_{0.2}Mg_{0.14})O_{20}(OH)_4Na_{0.66}$ *(Post et al., Clays and clay min., 1997)*

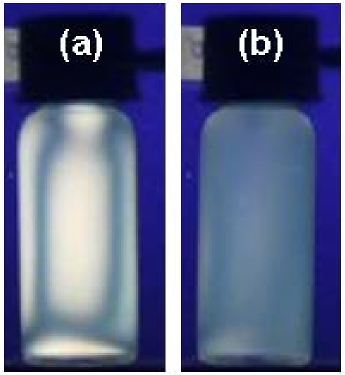
Observation of aqueous suspensions in polarized light

(E.Paineau's PhD thesis)



Aqueous suspensions of beidellite (D ~ 200 nm, IS = 10^{-4} M) observed between crossed polarisers. (a) ϕ = 0.40%; (b) ϕ = 0.42%; (c) ϕ = 0.44%; (d) ϕ = 0.46%; (e) ϕ = 0.48%; (f) ϕ = 0.50%.

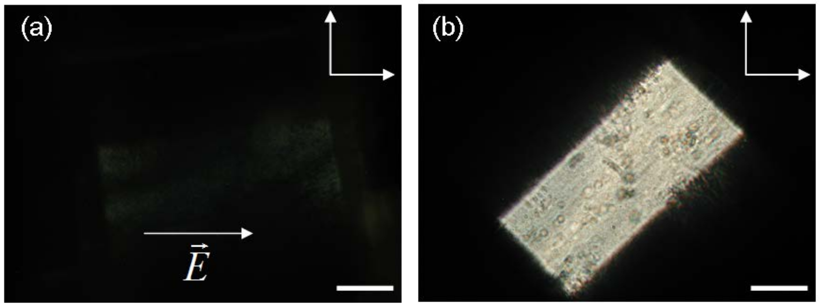
Erwan Paineau



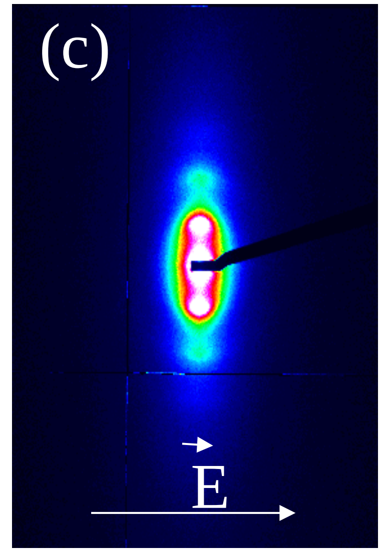
Aqueous suspension of beidellite (D ~ 300 nm, IS = 10^{-3} M, ϕ = 0.43 %) showing (a) flow birefringence and (b) relaxation after flow.

*L.J.Michot et al, Proc. Nat. Acad. Sci. USA, **103**, 16101 (2006)*
*E.Paineau et al, J. Phys. Chem. B, **113**, 15858 (2009)*
*E.Paineau et al, Liq. Cryst. Rev., **1**, 110 (2013)*

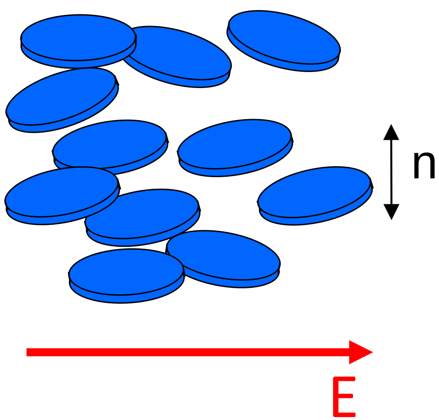
Electric-field alignment of the nematic phase



500 µm



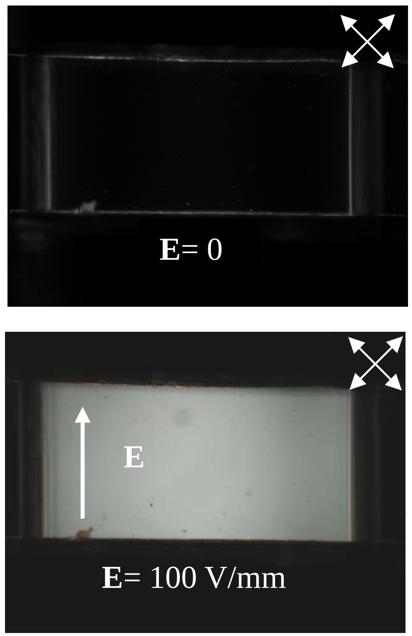
Ivan Dozov

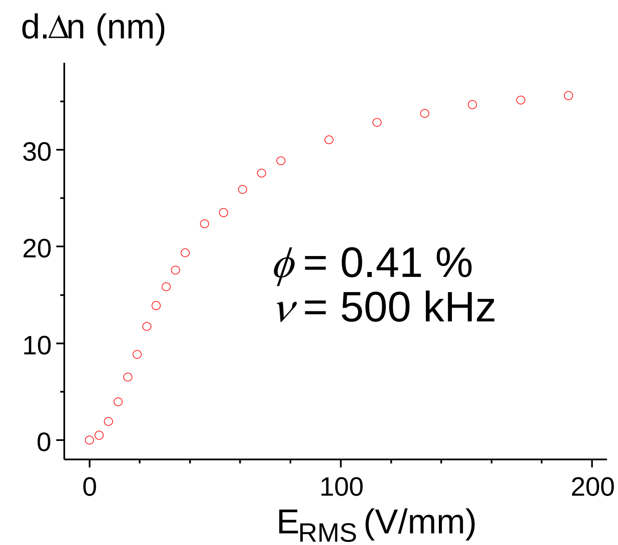


$$\Delta\varepsilon = \varepsilon_{//} - \varepsilon_{\perp} < 0$$

Optical textures and SAXS pattern of fluid nematic samples of beidellite suspensions in a 1mm cylindrical glass capillary aligned in a 4×10^4 V/m, f = 500 kHz field. (a,b) D ~ 300 nm, IS = 10^{-5} M, ϕ = 0.61%; (c) D ~200 nm, ϕ = 0.52% ,10^{-4} M.

Electric-field effects in the isotropic phase

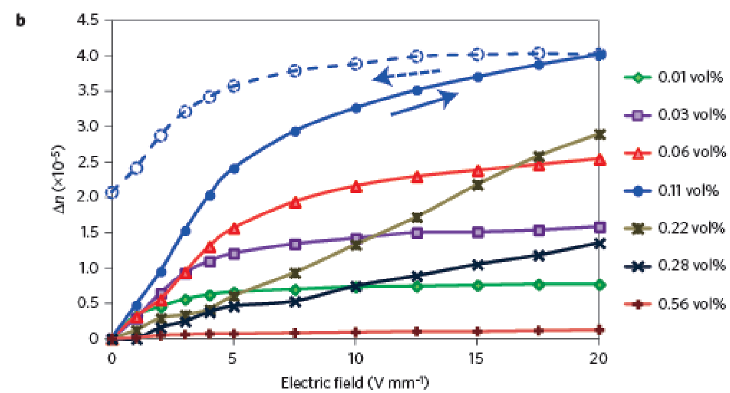




Very strong particle field-induced orientation in the isotropic phase !

Isotropic phase: faster response and no texture issues …

*I.Dozov et al, J.Phys. Chem. B, **115**, 7751 (2011)*



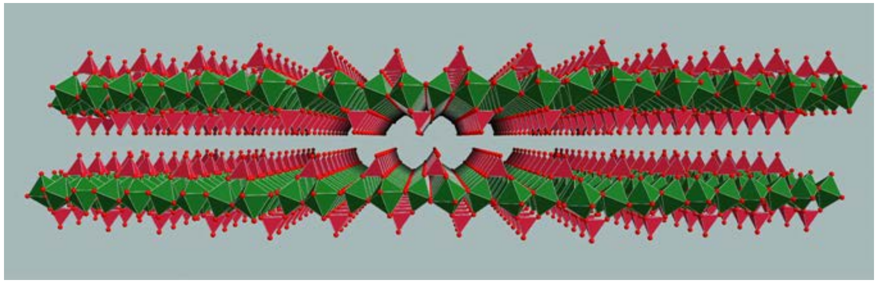
Graphene oxide

*T.Z.Shen et al, Nat. Mat., **13**, 394 (2014)*

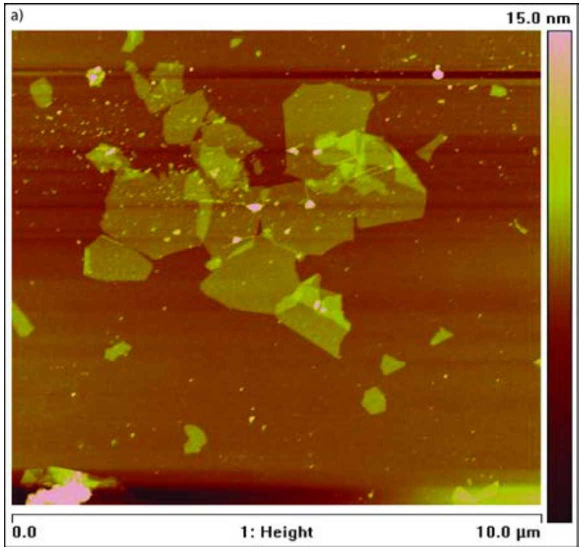
About colloidal LCs of carbon-based materials, see also:

*C.Zakri et al, Phil. Trans. Roy. Soc. A, **371**, 20120499 (2013)*

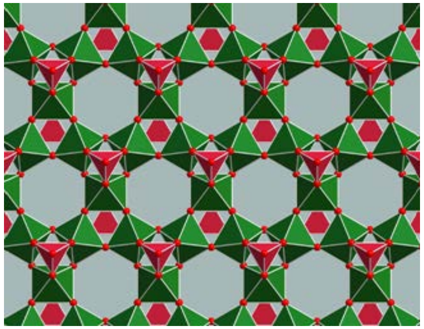
$H_3Sb_3P_2O_{14}$ nanosheets



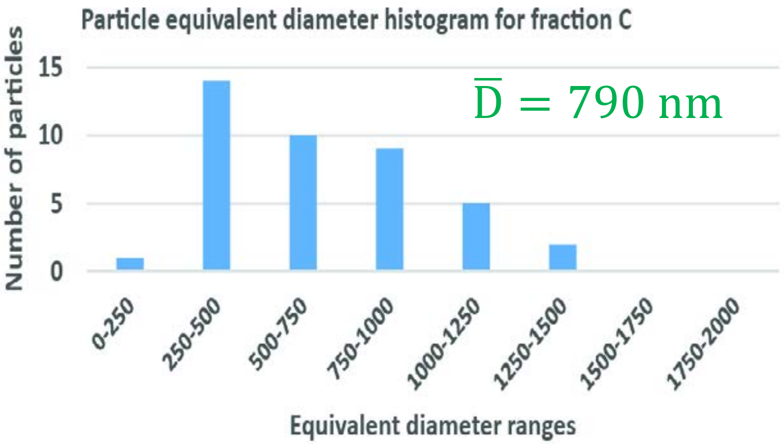
Side-view of two $H_3Sb_3P_2O_{14}$ nanosheets



AFM image of the nanosheets



Top view of a nanosheet



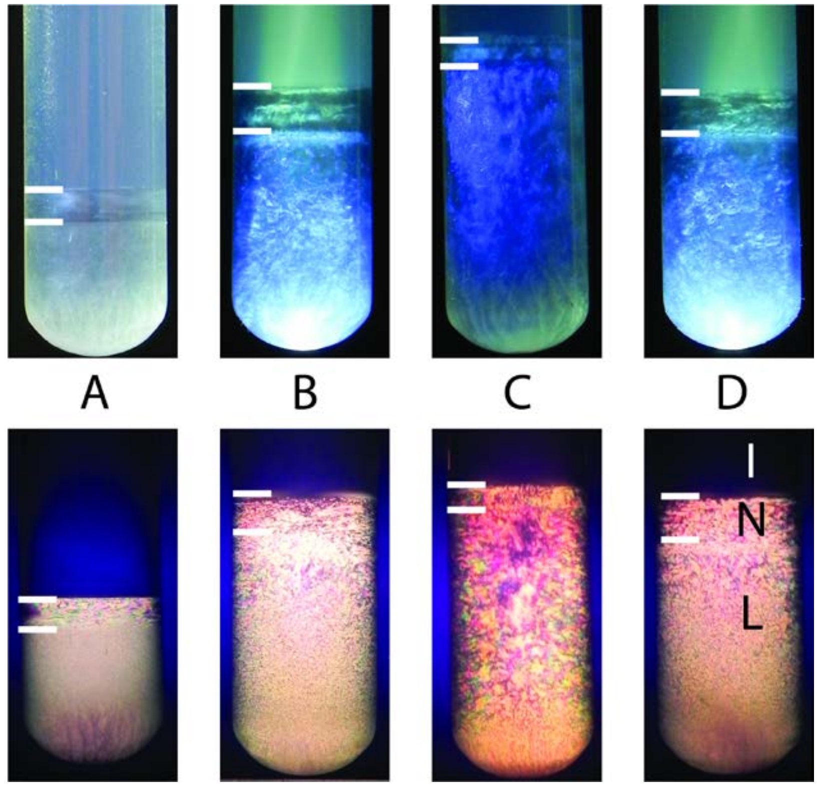
Typical particle diameter distribution histogram.

J.C. Gabriel

Observation of suspensions in test-tubes

Natural light:
3 distinct phases …

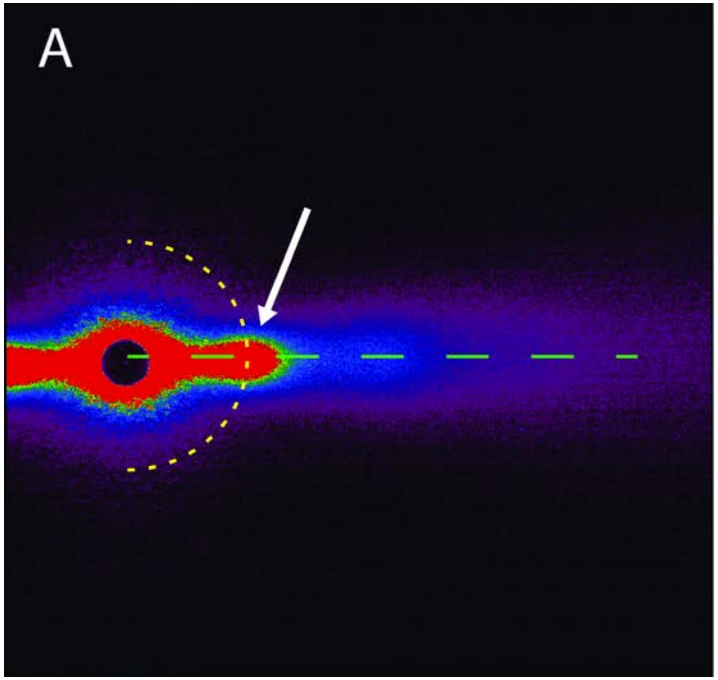
Polarized light:
… 2 of them birefringent



$\overline{\mathrm{D}} = 44\ \mathrm{nm}$	$\overline{\mathrm{D}} = 660\ \mathrm{nm}$	$\overline{\mathrm{D}} = 790\ \mathrm{nm}$	$\overline{\mathrm{D}} = 960\ \mathrm{nm}$
1.01 wt%	0.59 wt%	0.79 wt%	0.57 wt%

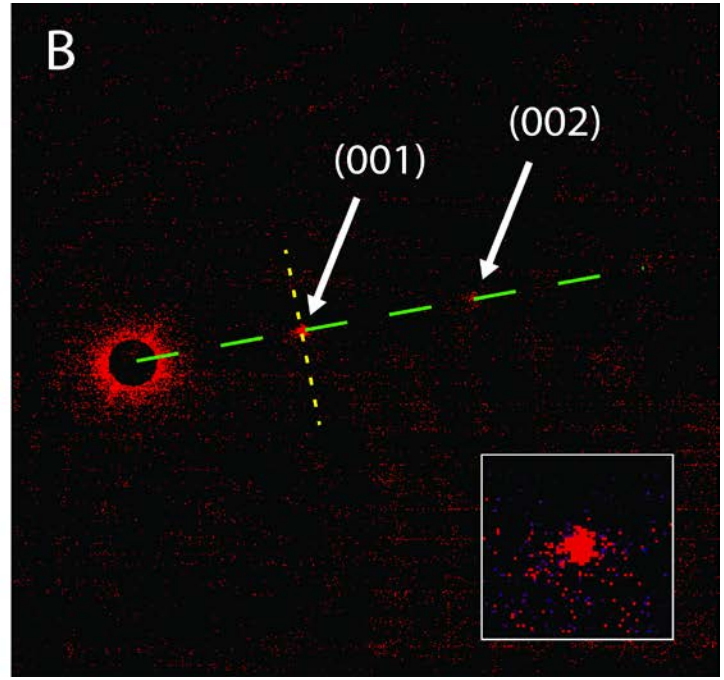
I: isotropic
N: nematic
L: lamellar

High-resolution SAXS patterns



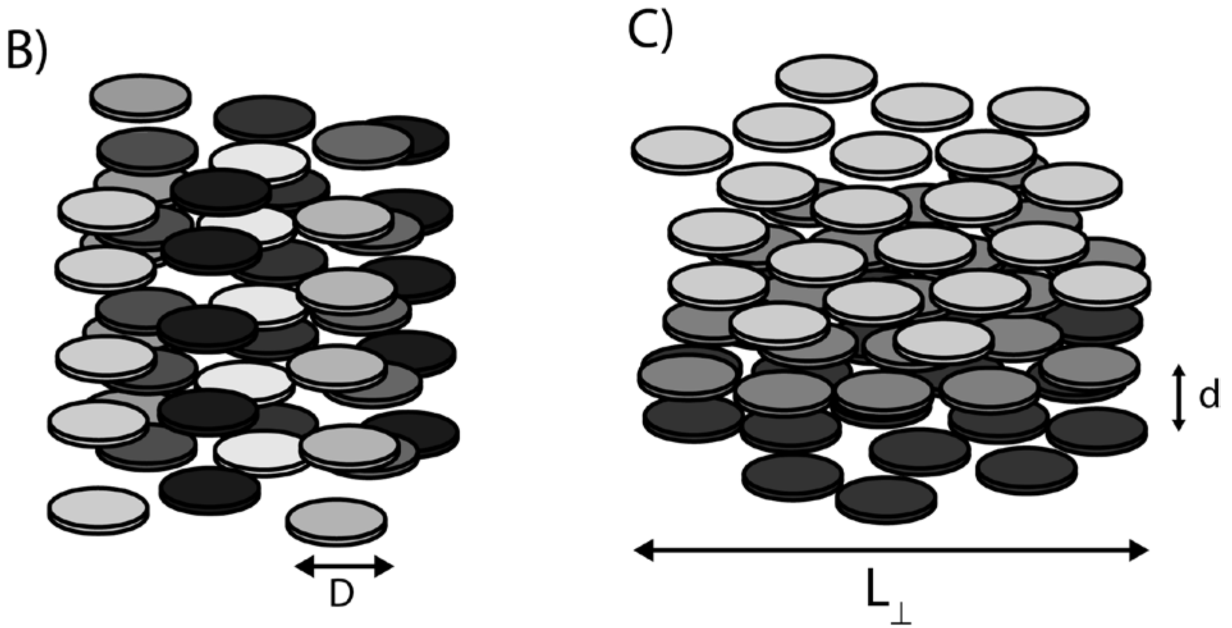
Nematic phase
($\overline{\mathrm{D}} = 660$ nm, 0.18 wt %)
Diffuse spots:
stacking short-range order
$\rightarrow$ "columnar" nematic

Nematic order parameter:
S = 0.93 ± 0.05



Lamellar phase
($\overline{\mathrm{D}} = 790$ nm, 0.24 wt %)
Sharp reflections:
layered structure

« Columnar » nematic and lamellar phases



"Columnar"
nematic

Lamellar (smectic)
phase

Lamellar order extends over a domain size $L_{\perp}$ = 20 µm

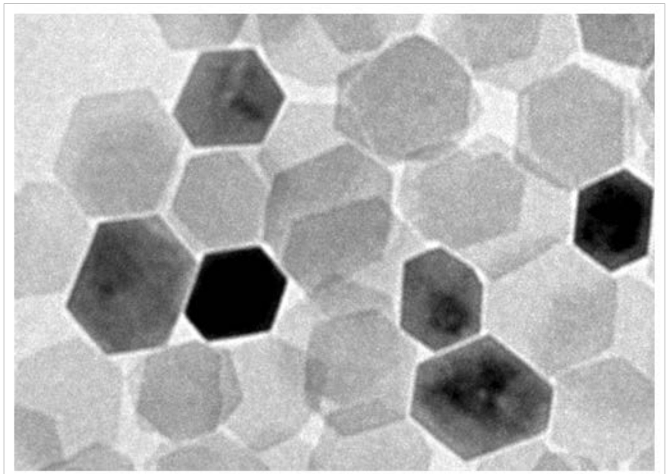
≈ 600 nanosheets build up a smectic layer

Why ???!!!

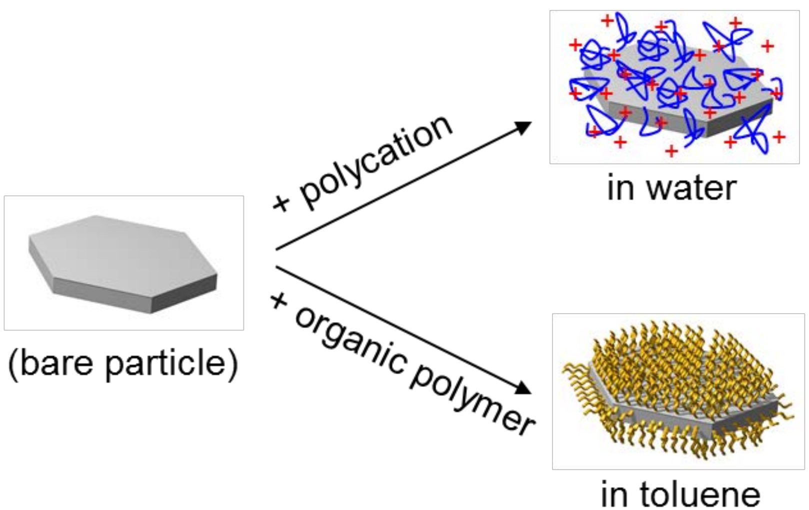
*P.Davidson et al, PNAS, **115**, 6662 (2018)*

Gibbsite (H.Lekkerkerker and the Utrecht group)

hexagonal $Al(OH)_3$ crystals:

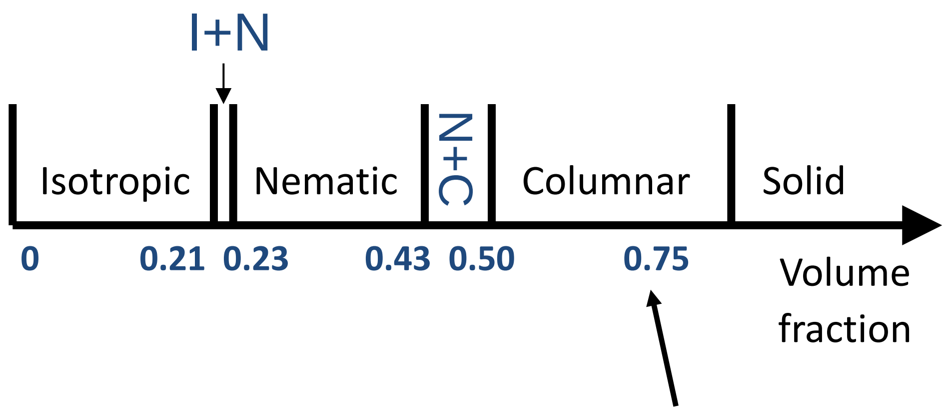


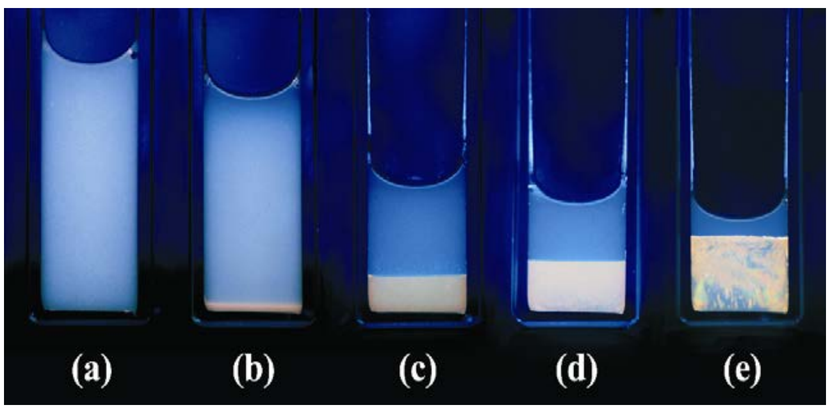
diameter: tunable from 100-300 nm
thickness: 10-20 nm



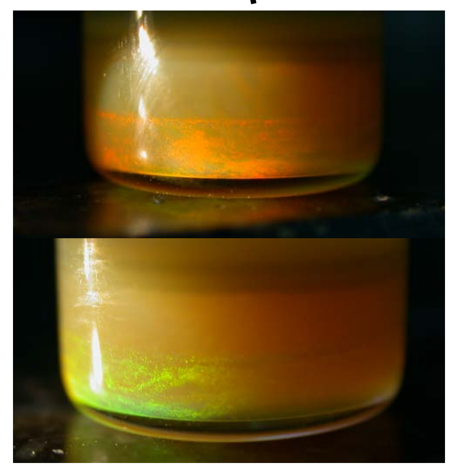
David
Van der Beek

Suspensions of synthetic gibbsite nanodiscs





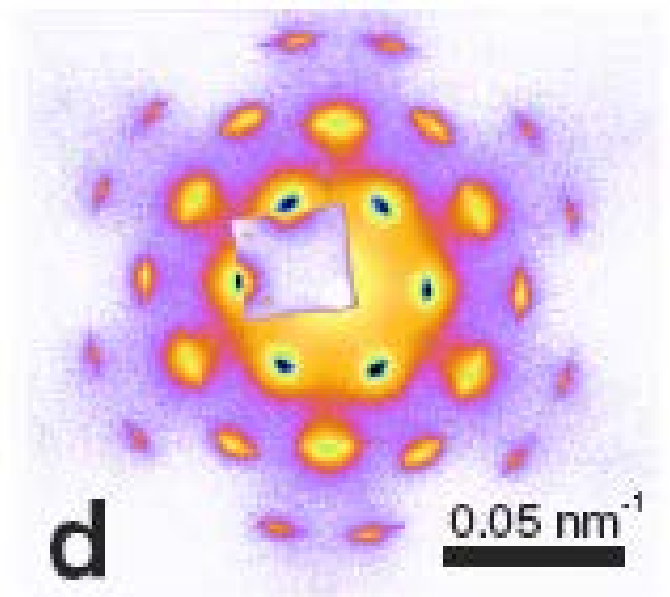
Increase of the proportion of nematic phase in the biphasic domain as the overall volume fraction increases.



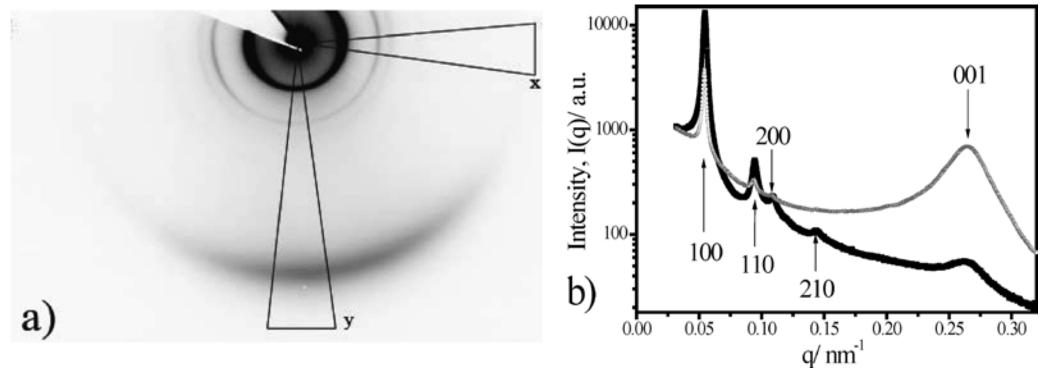
Periodic hexagonal structure showing Bragg reflections of visible light (period of a few hundred nm)

*D. van der Beek et al, J. Chem. Phys., **121**, 5423 (2004)*

X-ray scattering from the columnar phase



X-ray beam parallel
to C_6 axis

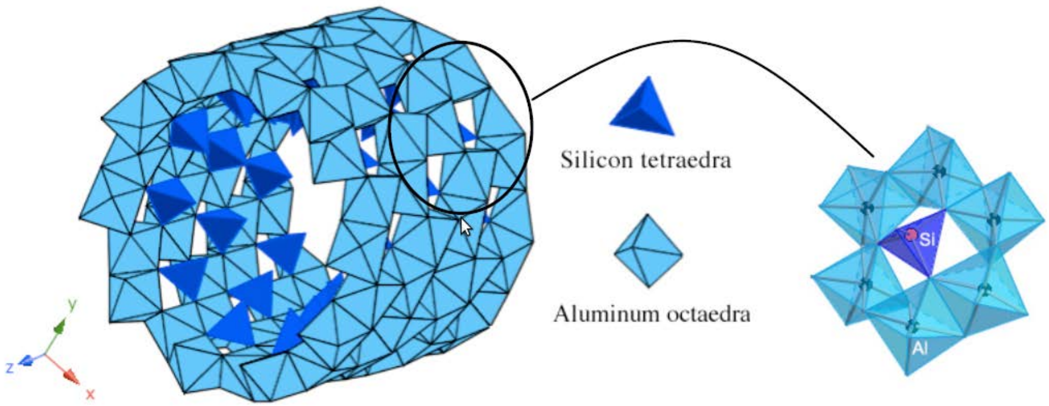


X-ray beam perpendicular
to C_6 axis

Columnar phase

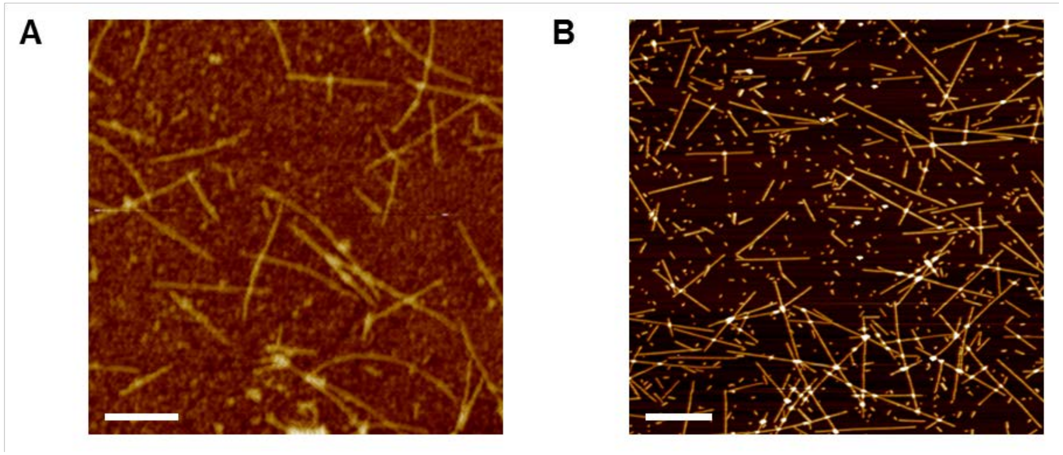
*F.M. van der Kooij et al, Nature, **406**, 868 (2000)*
*D. Van der Beek et al, Eur. Phys. J. E, **16**, 253 (2005)*
*A.V.Petukhov et al, Phys. Rev. Lett., **95**, 077801 (2005)*
*D.Kleshchanok et al, Langmuir, **26**, 13614 (2010)*

Imogolite: aluminosilicate nanotubes



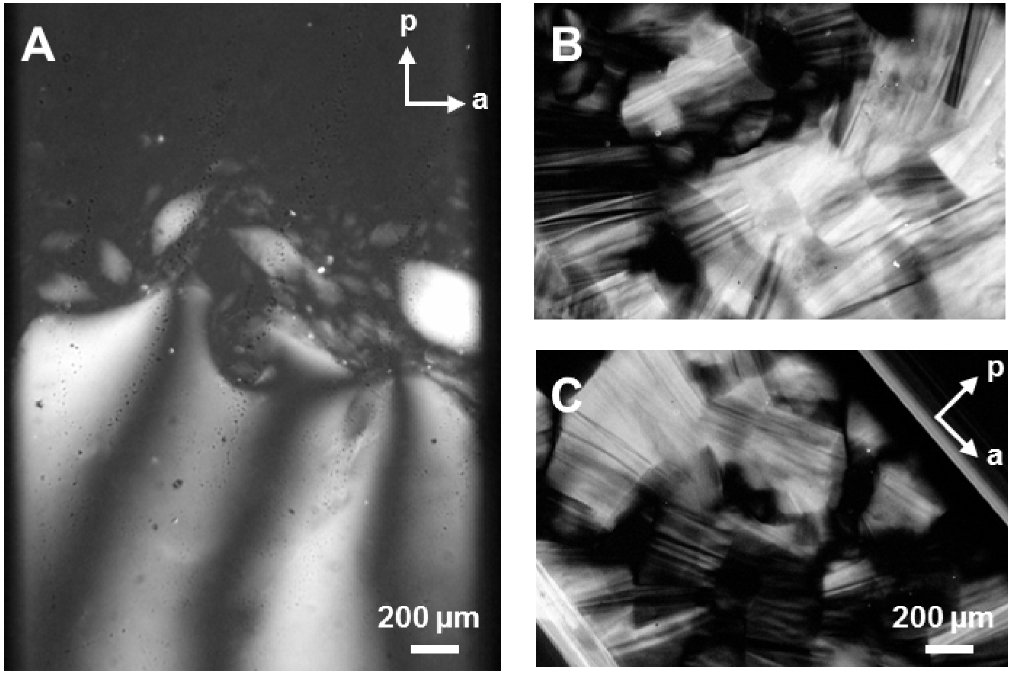
*C. Levard et al, JACS, **130**, 5862 (2008)*

More or less like carbon nanotubes but very hydrophilic !



(A) SW Si-INT and (B) DW Ge-INT. Scale bar: 500 nm.

Two mesophases in aqueous suspensions of INT ?!



Polarized-light microscopy of SW Si-INT suspensions.

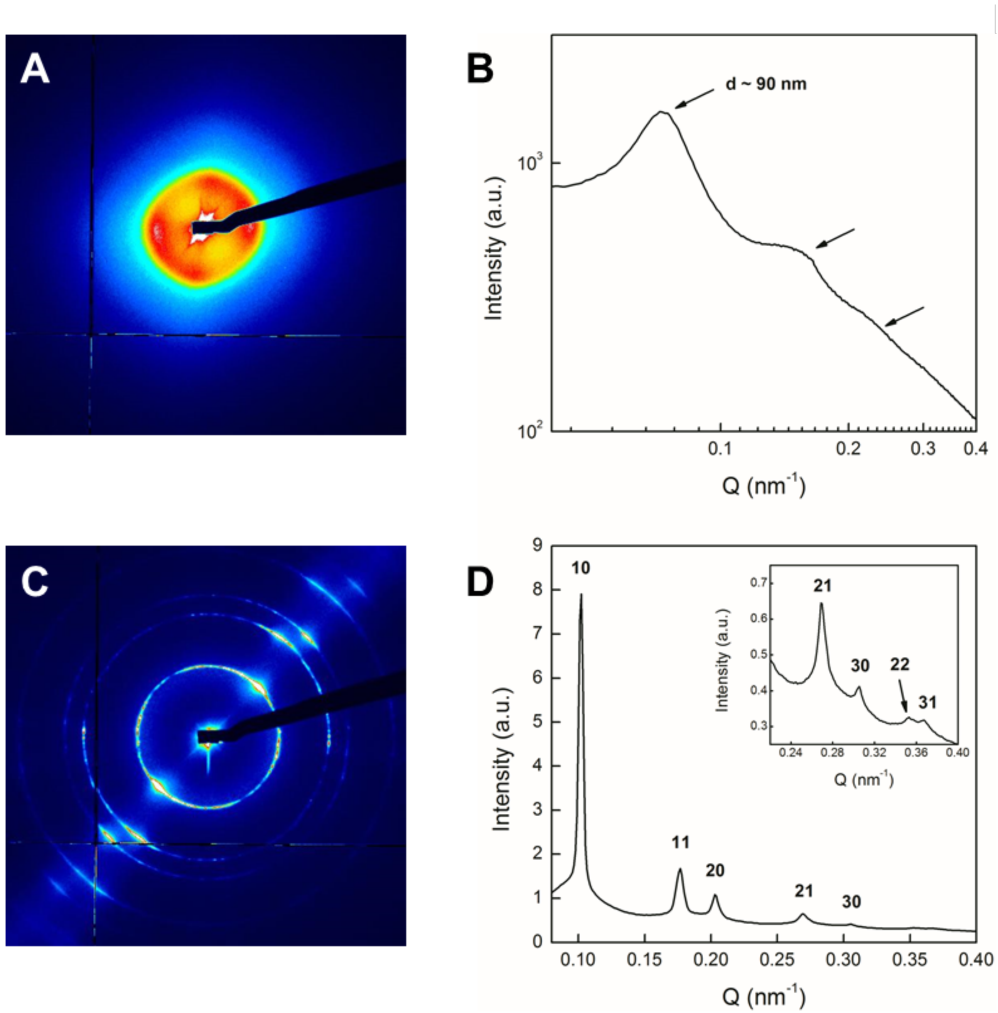
(A) Isotropic/Nematic phase coexistence, known long ago: *K.Kajiwara et al, Makromol. Chem.* ***187****, 2883 (1986)* (ϕ = 0.07%)
(B,C) additional mesophase ? (ϕ = 0.31%).

Aqueous suspensions of stiff electrically-charged objects
Nature of second mesophase is ambiguous: lamellar or columnar ?

SAXS from unoriented samples of DW Ge-INT

(Swing beamline at SOLEIL synchrotron, France)

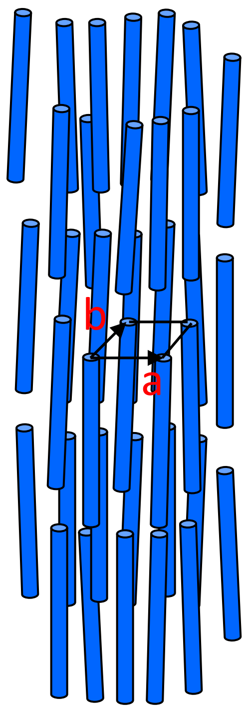
SAXS patterns | I(Q)



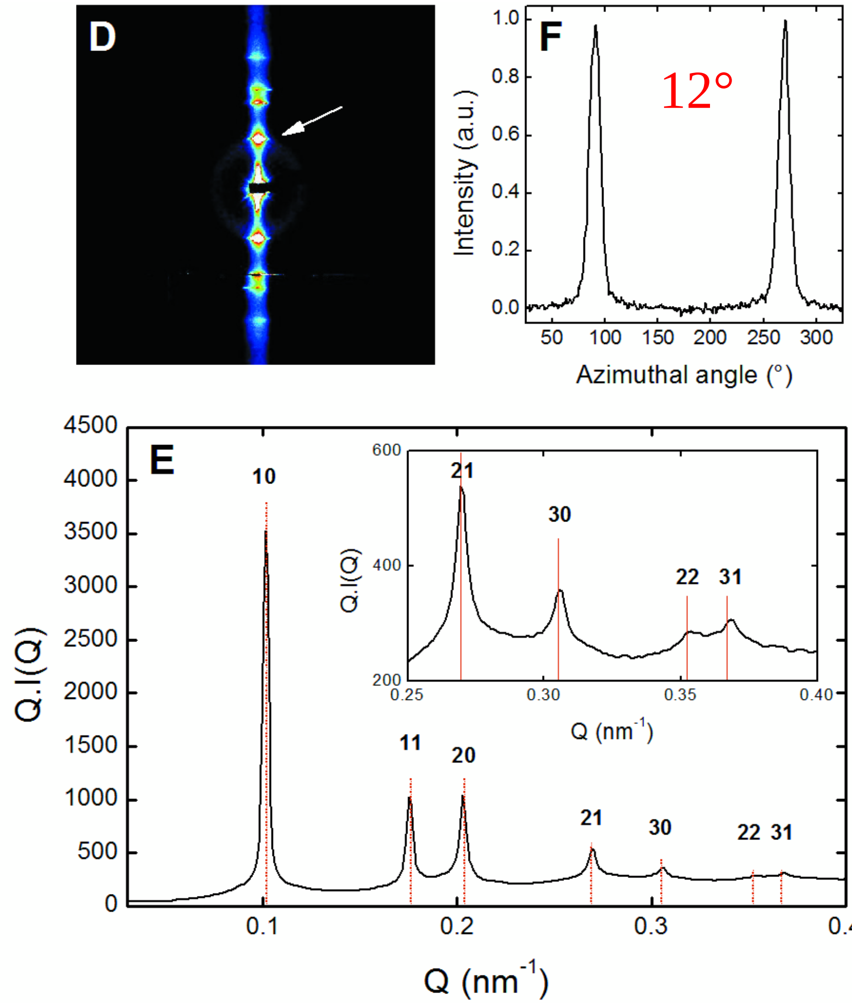
Nematic (ϕ = 0.12%) — Diffuse rings

Columnar (ϕ = 0.22%) — Diffraction lines

Mesophase alignment in an a.c. electric field



columnar
phase

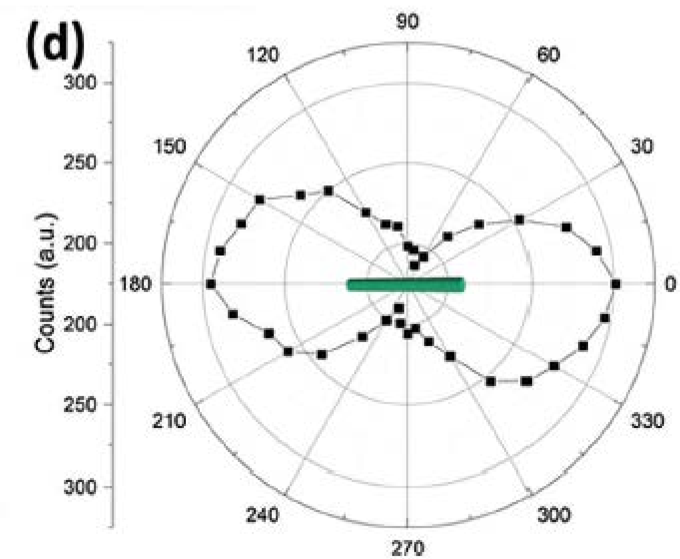


Very dilute columnar phase !

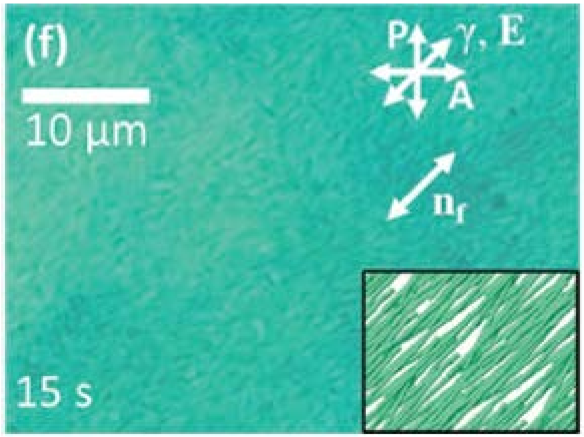
Columnar (ϕ = 0.22 %) DW Ge-INT suspensions submitted to E = 100 V/mm at 500 kHz.

E.Paineau et al, Nat. Comm., ***7****, 10271 (2016)*

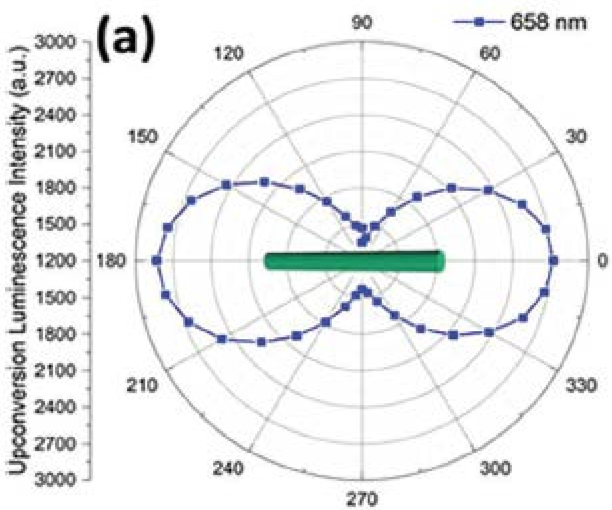
$NaYF_4$: Yb/Er nanorod aqueous suspensions: a luminescent nematic (coll. I.Smalyukh, S.Park)



Up-conversion luminescence indicatrix of a single nanorod



Electric-field alignment of the nematic phase



Up-conversion luminescence indicatrix of the nematic phase

Sungoh Park

S.Park et al, Adv. Opt. Mat., ***7****, 190041 (2019).*

Conclusions - Perspectives

Colloidal liquid crystals belong to an old but still lively sub-field of LC science
- They are useful to test key concepts in LC physics, with little influence of molecular details, and larger length and time scales
- They are also important in engineering, biology, and composite materials

See the next talks …

Open questions are still numerous and are often related to colloid science:

- Electrostatic interactions of charged objects in aqueous suspensions
- Van der Waals attractions can be important for mineral (or metallic) objects
- Influence of polydispersity on smectic and columnar phases
- Influence of particle flexibility, in particular for sheets
- Mixtures of particles (spheres, coils, rods, plates …)
- Macroscopic expression of chirality
- Active systems ?