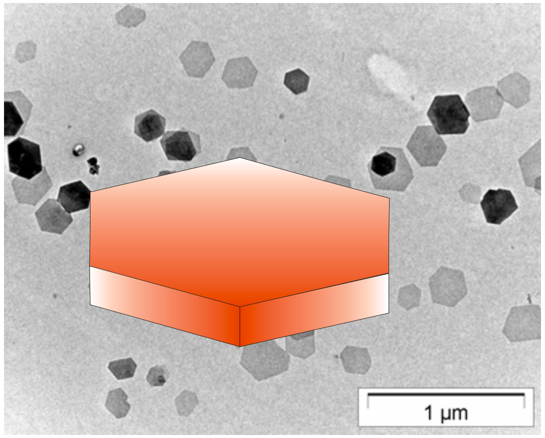
The Program

- Lecture 1: Phase transitions in atomic and molecular systems
- Lecture 2: Colloids as atoms
- Lecture 3: Hard spheres
- Lecture 4: Hard spheres + attraction
- Lecture 5: Rods
- Lecture 6: Platelets



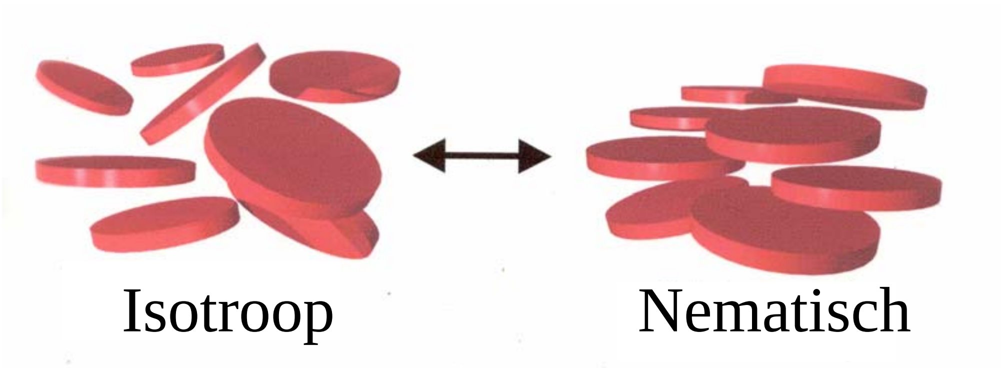
Lars Onsager (1903-1976)

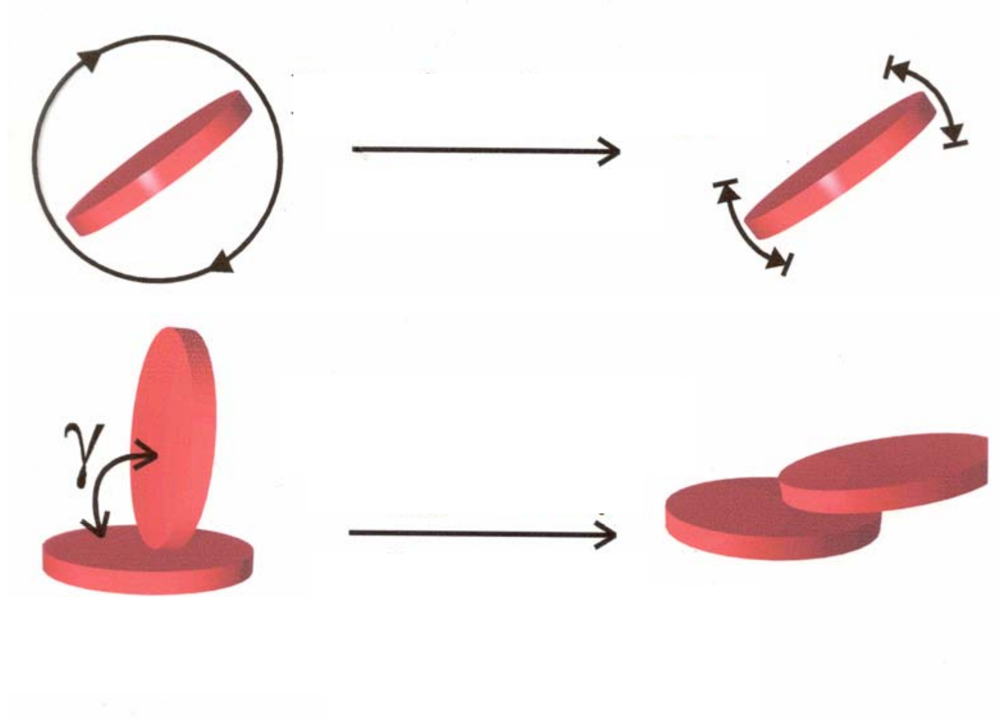
Nobelprijs Scheikunde 1968

1. **Anisotropic Solutions of Colloids.** LARS ONSAGER, *Yale University*.—The solutions of certain colloids comprised of highly asymmetrical particles—plates or rods—are known to form anisotropic phases at remarkably low concentrations. For tobacco mosaic virus (rods), isotropic solutions containing 2–3 percent virus are in equilibrium with anisotropic phases containing 3–4.5 percent, respectively, according to the amount of electrolyte present. This phenomenon can be explained as a result of repulsive forces by the observation that the mutual co-volume of two swarms of parallel rods (or plates) is roughly proportional to the sine of the angle between their orientation, and larger than the volume of the particles by a factor which is proportional to the asymmetry. The case of rods is particularly simple in that the virial coefficients of order higher than 2 in Mayer's expansion are small, and a quantitative theory is possible. The computed ratio of concentrations at equilibrium is 1.34. The predicted osmotic pressure of the anisotropic phase is nearly proportional to the concentration, in fact, slightly greater than $3cRT/V$.

Physical Review (1942)

I-N ook bij colloïdale plaatjes





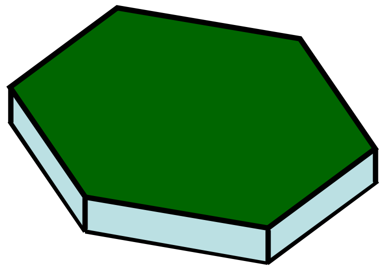
oriëntatie-entropie neemt af

vrij volume-entropie neemt toe

$Al\text{-}(OR)_3$ in acidic aqueous solution

85 ^{0}C, 3 days

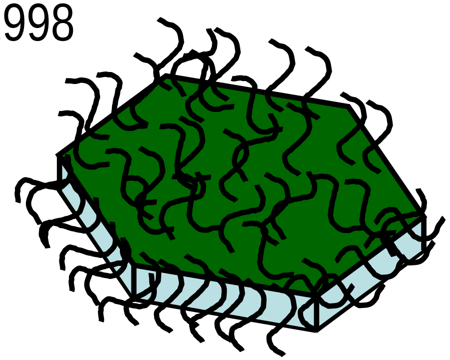
A.M. Wierenga, T.A.J. Lenstra,
A.P. Philipse, 1998

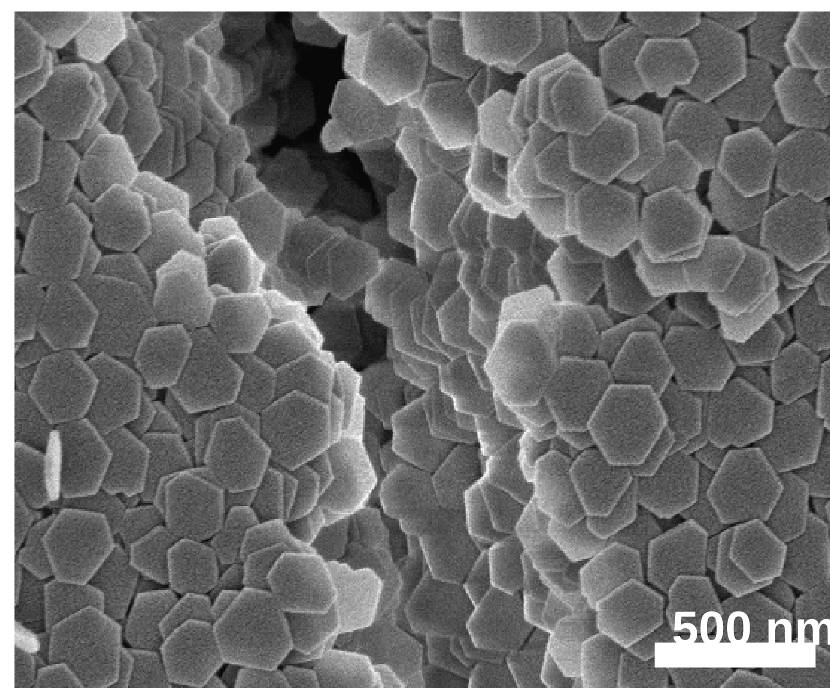


gibbsite, $Al(OH)_3$

Coating PIB

F.M vd Kooij, HNWL, 1998

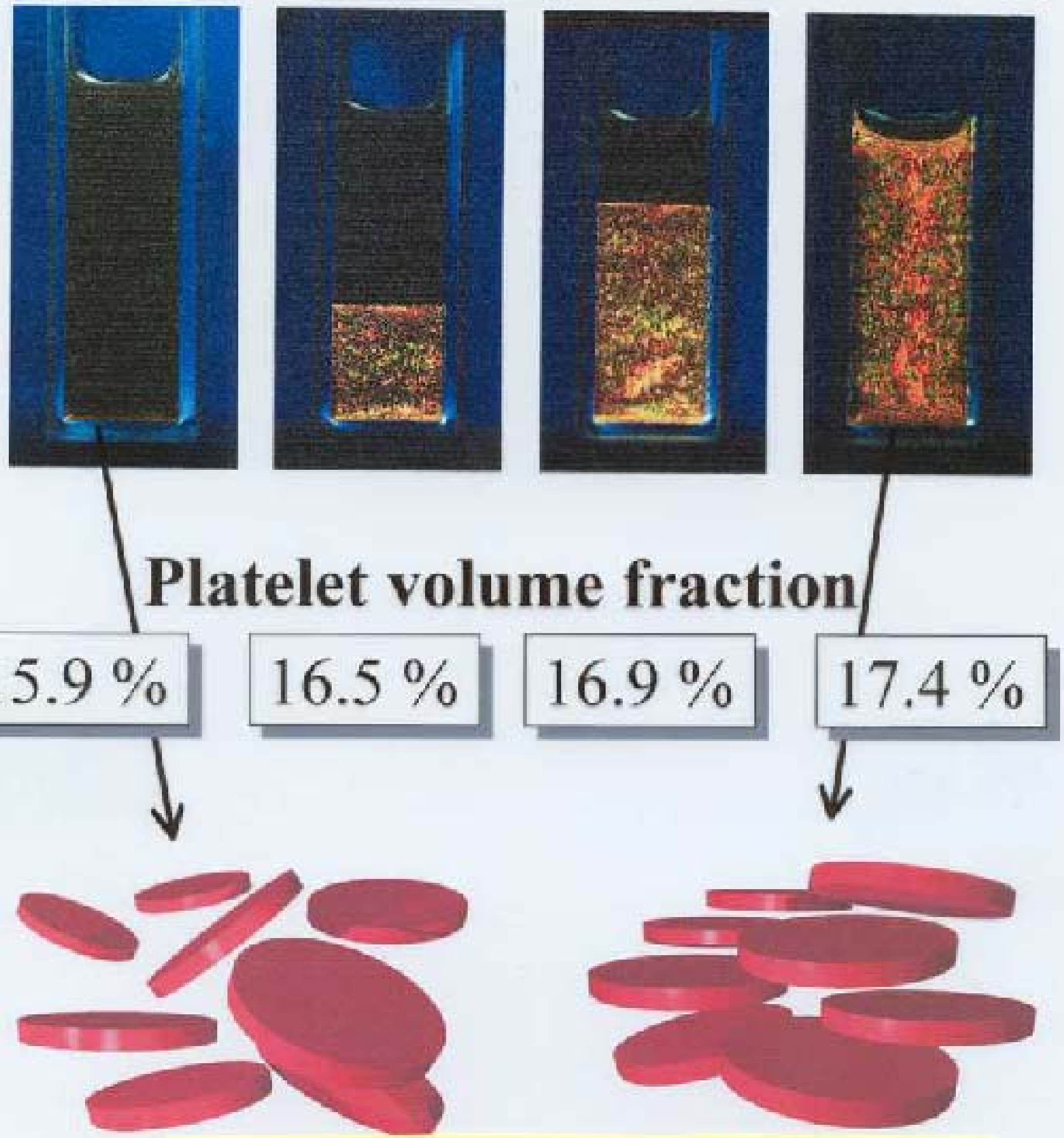




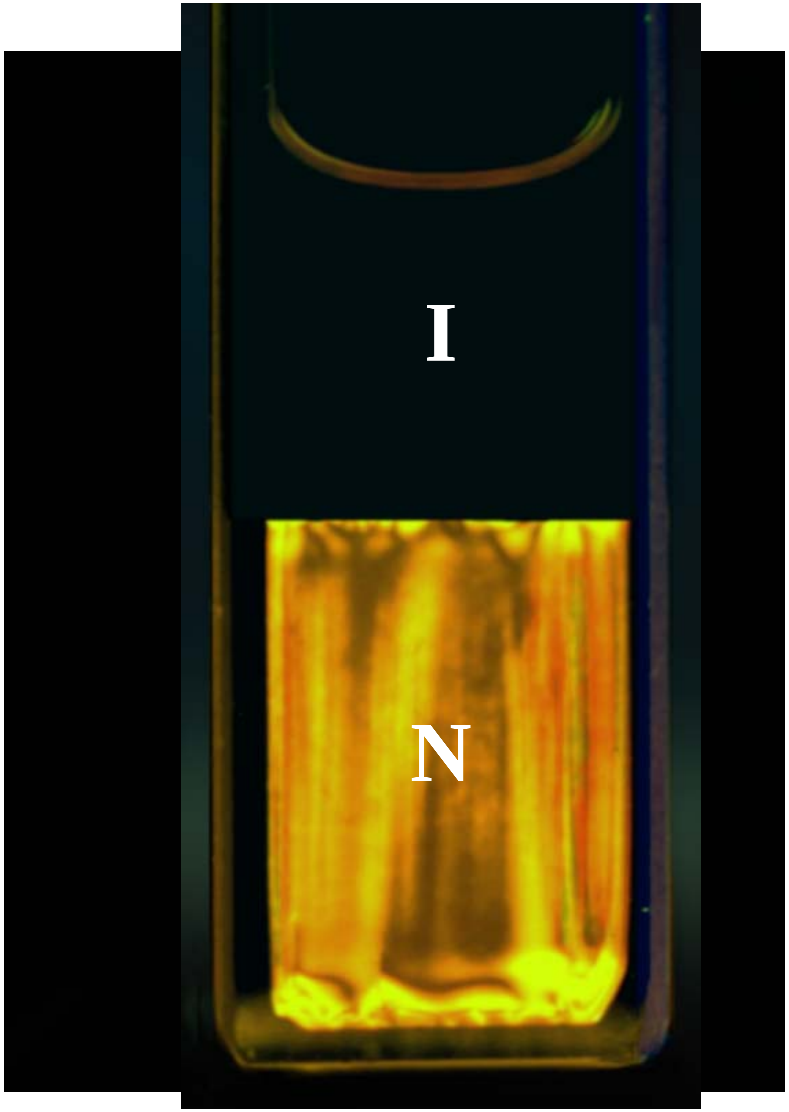
F.M. VAN DER KOOIJ + H NWL

J. Phys. Chem B 102 7829 (1998)

FORMATION OF NEMATIC LIQUID CRYSTALS IN SUSPENSIONS OF HARD COLLOIDAL PLATELETS

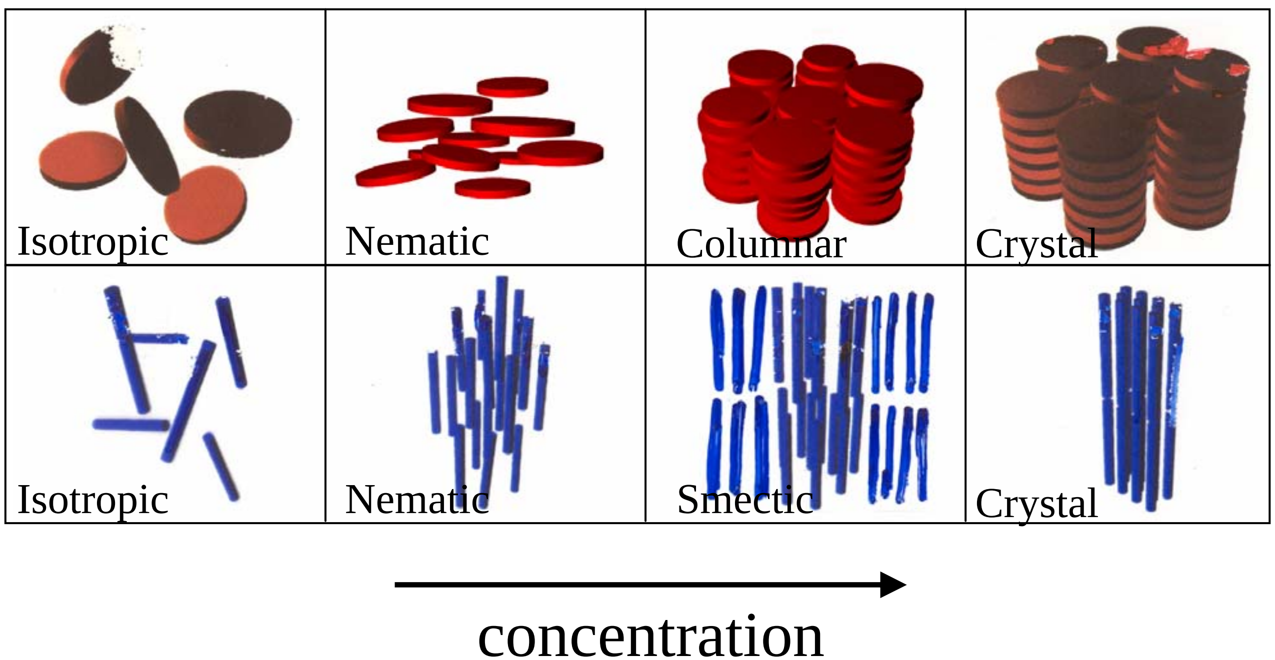


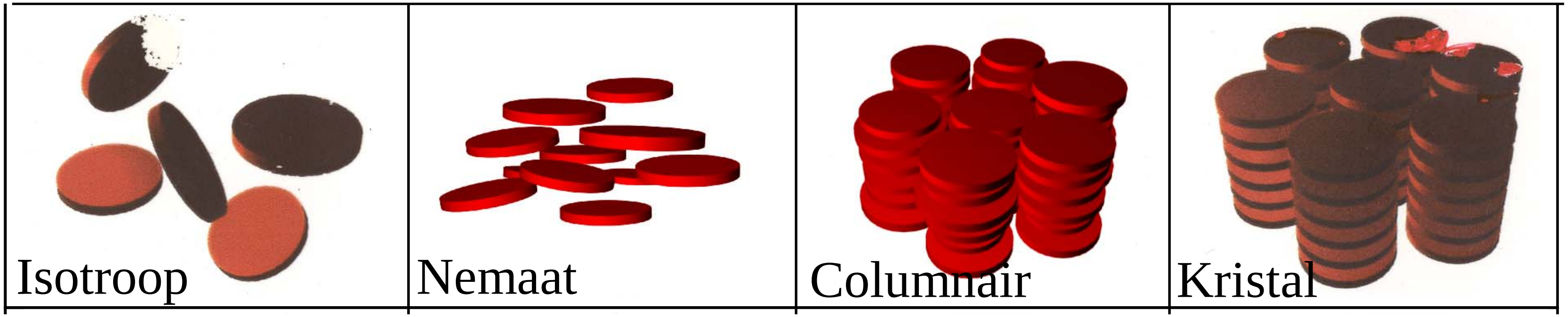
Isotroop-Nematisch fase-evenwicht



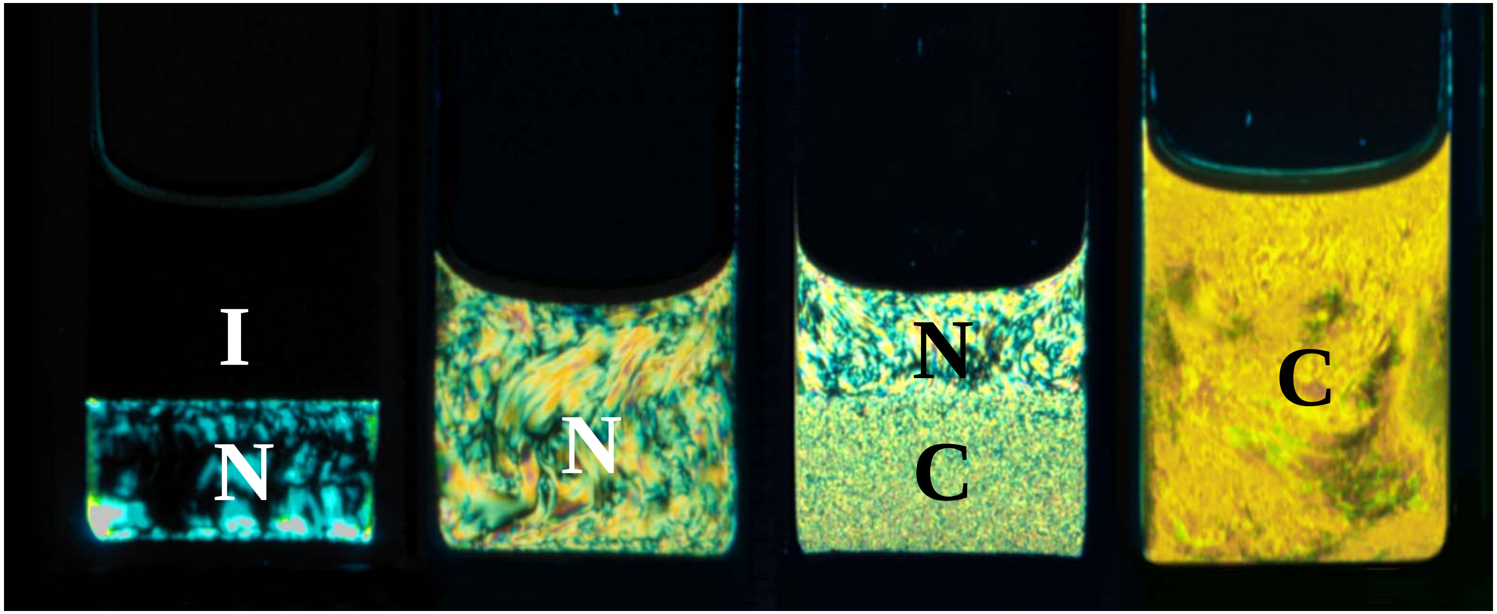
volumefractie = 18%

The phases for hard disks & rods





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

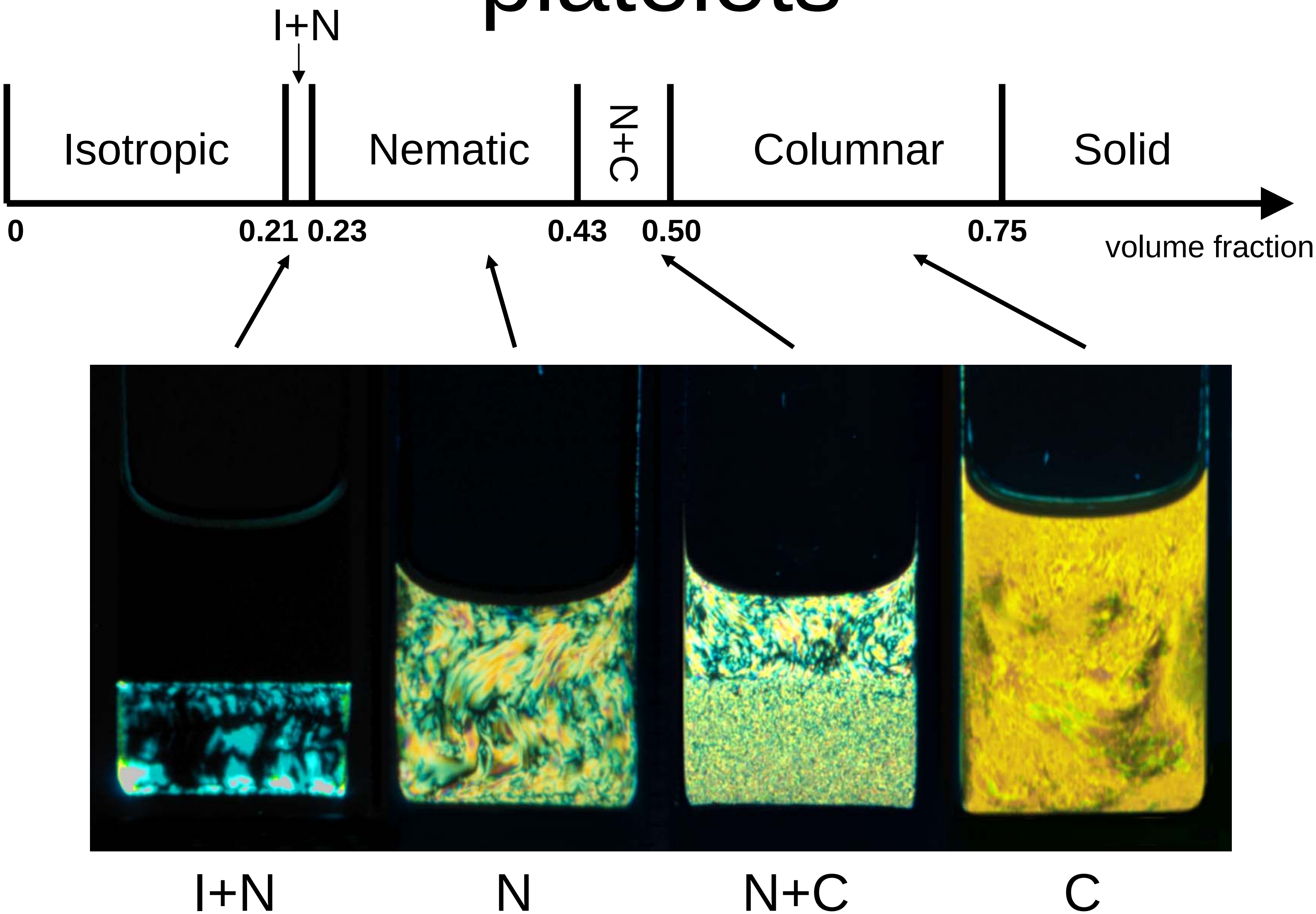


19% 28% 41% 47%

volumefractie

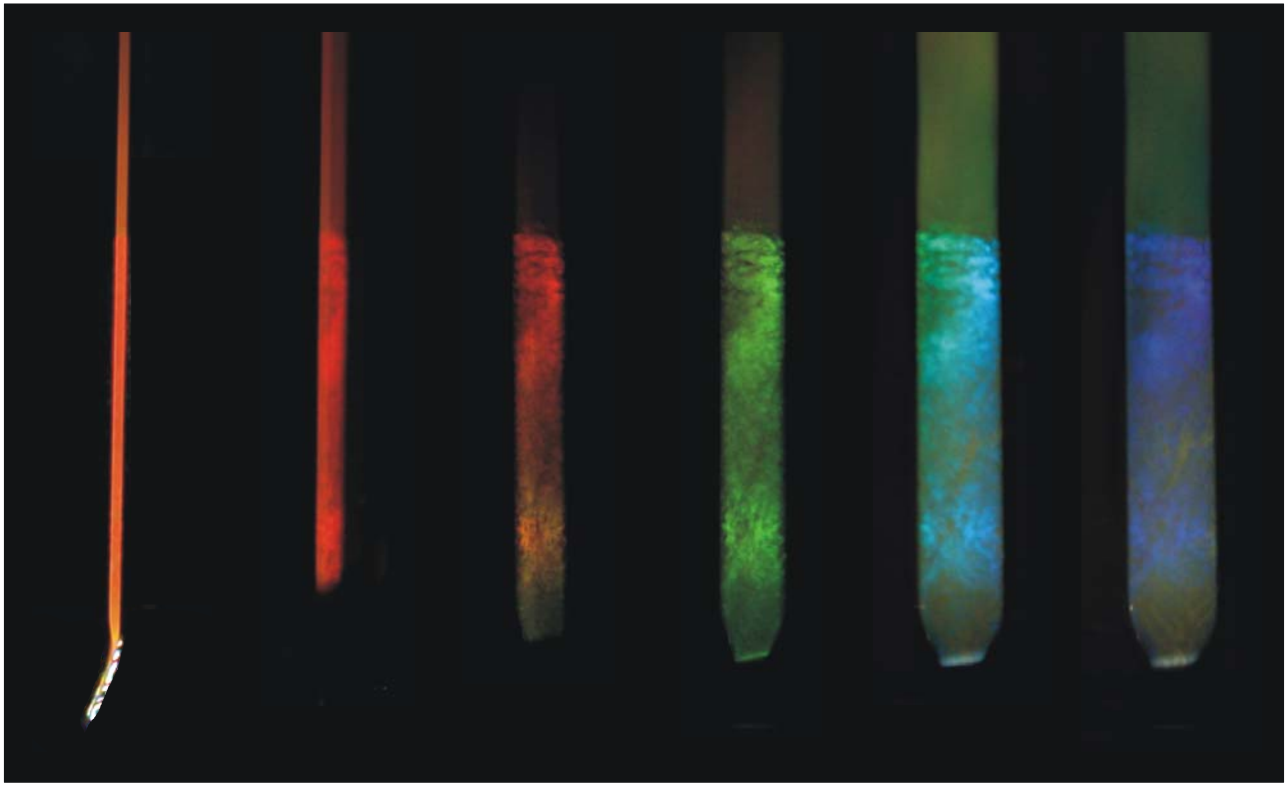
F.M. van der Kooij, K. Kassapidou, HNWL, *Nature* (2000)

Phase behaviour of the hard platelets



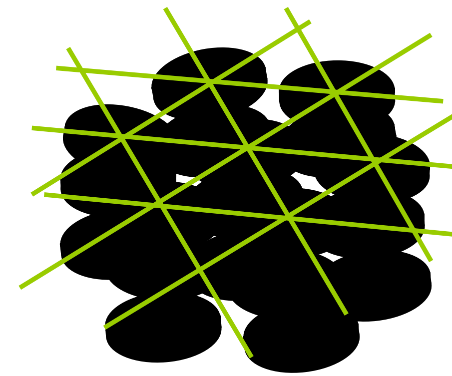
F.M. van der Kooij, Thesis, Utrecht University (2000)

The columnar phase



180° 160° 140° 120° 100° 90°

columns of platelets:



hexagonal lattice
with spacing *d*

Bragg condition:
$2\, n\, d \sin 2\theta = \lambda$

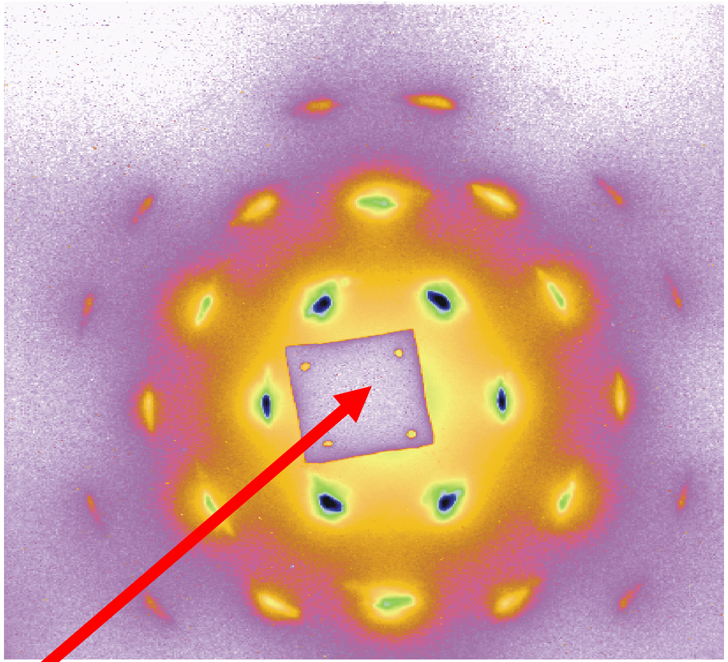
n = index of refraction ~ 1.5
2θ = Bragg-angle (measured)

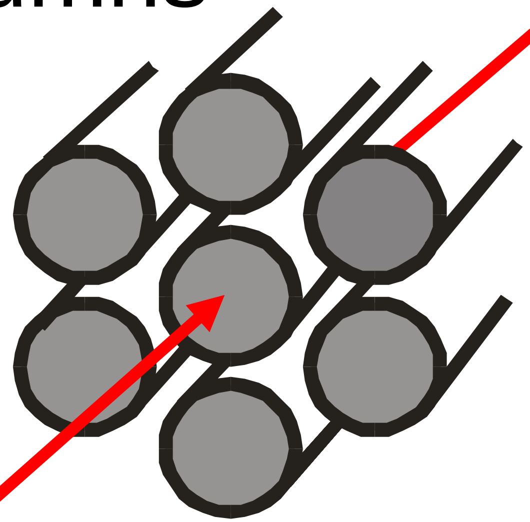
$d_{(100)} = 215$ nm

D. van der Beek, A.V. Petukhov, S.M. Oversteegen, G.J. Vroege, and H.N.W. Lekkerkerker, Eur. Phys. J. E (2005)

Columnar crystal:

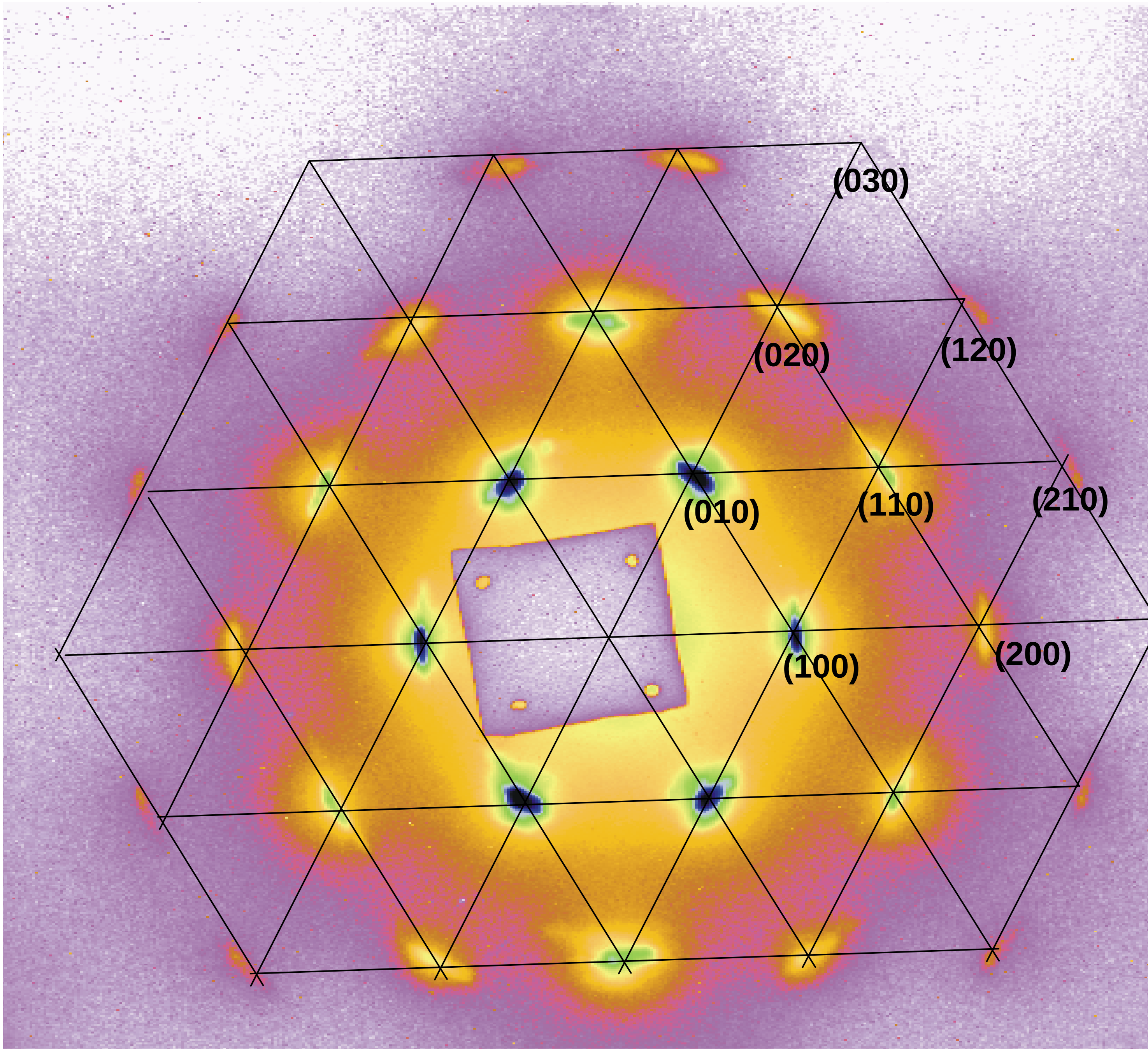
Hexagonal arrangement of columns





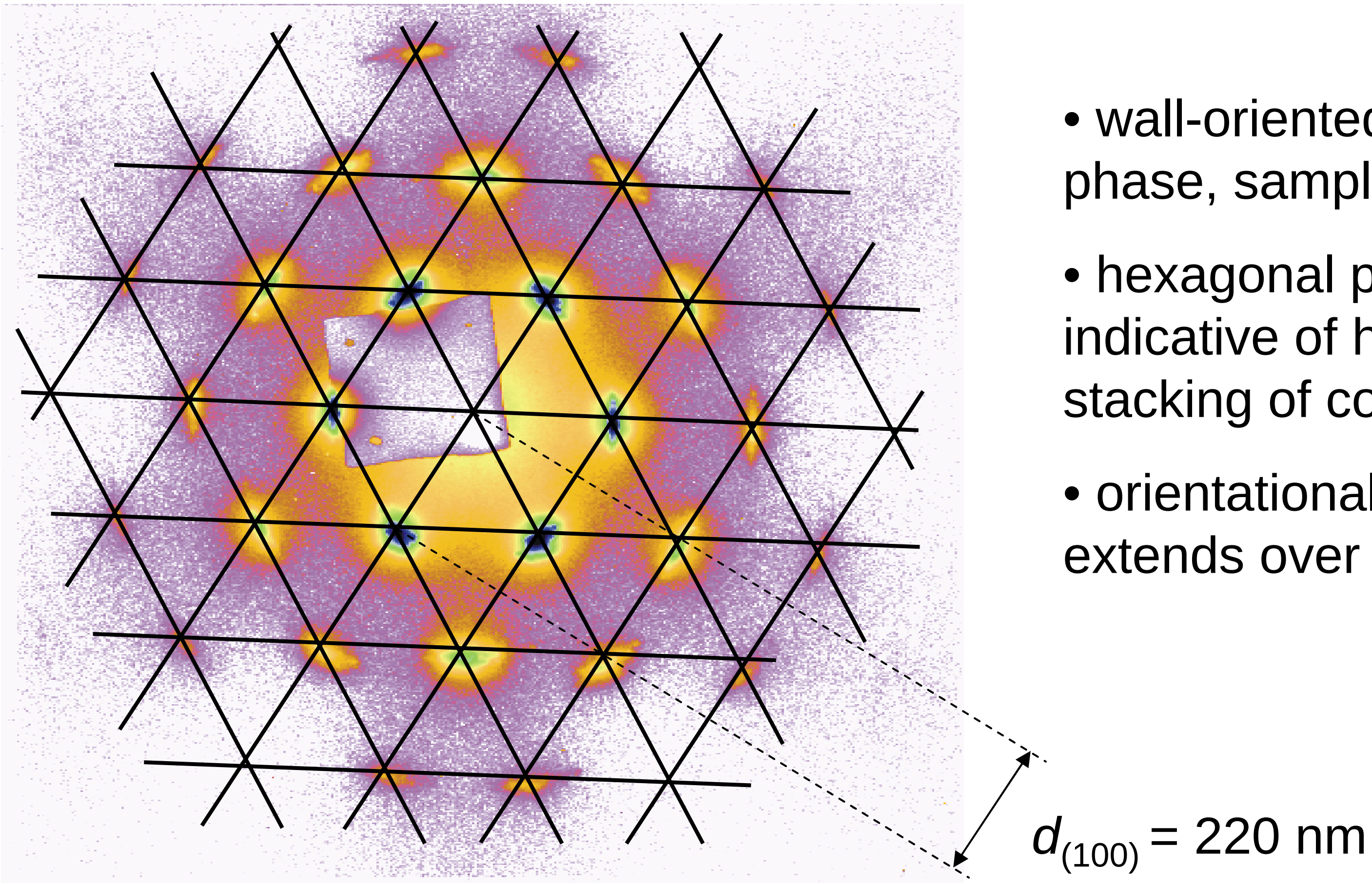
DUBBLE @ ESRF

**A.V. Petukhov, D. van der Beek,
S.M. Oversteegen, G.J. Vroege, HNWL**


(030)
(020)
(120)
(010)
(110)
(210)
(100)
(200)

SAXS on columnar phase

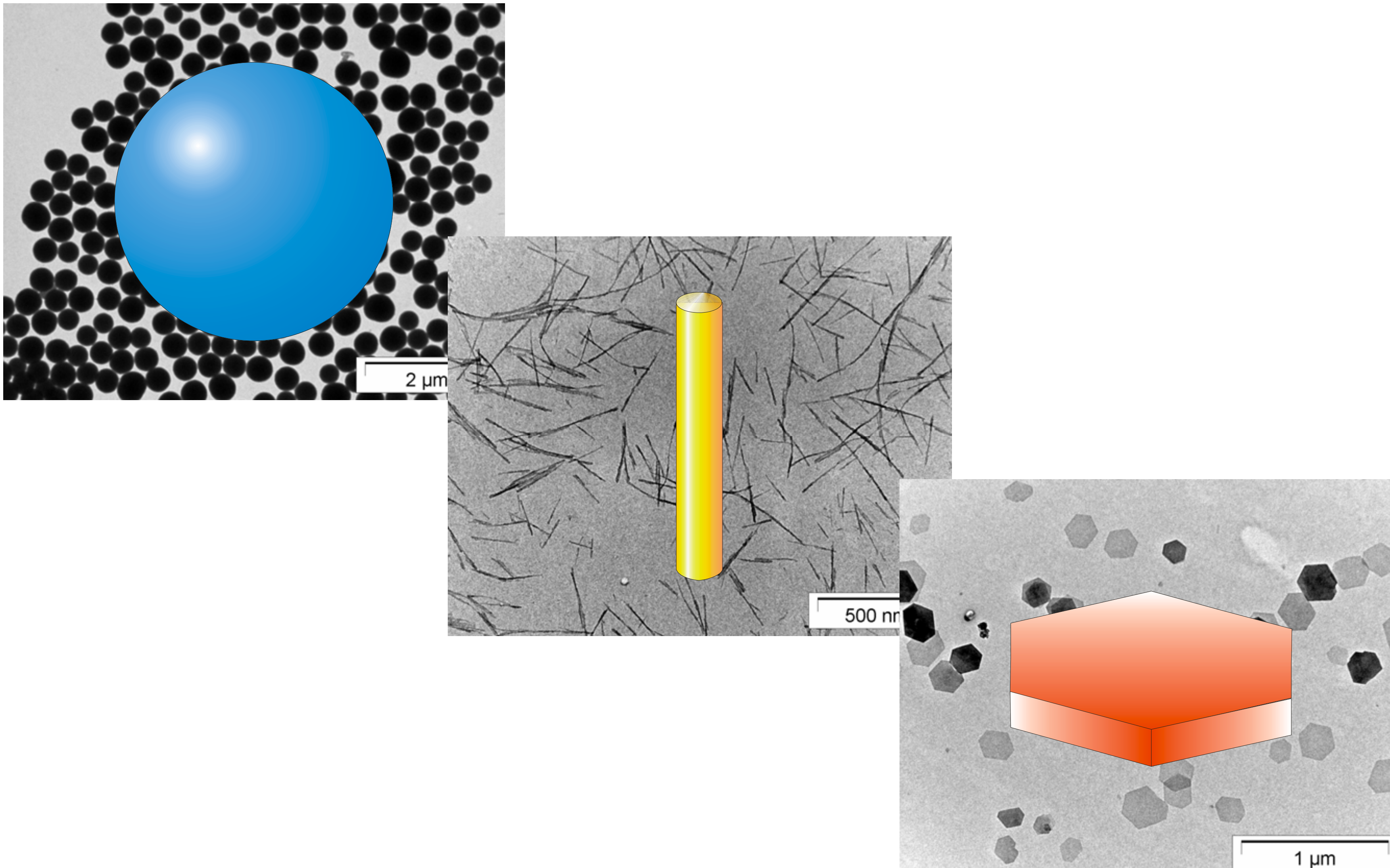
(SAXS = small-angle X-ray scattering)



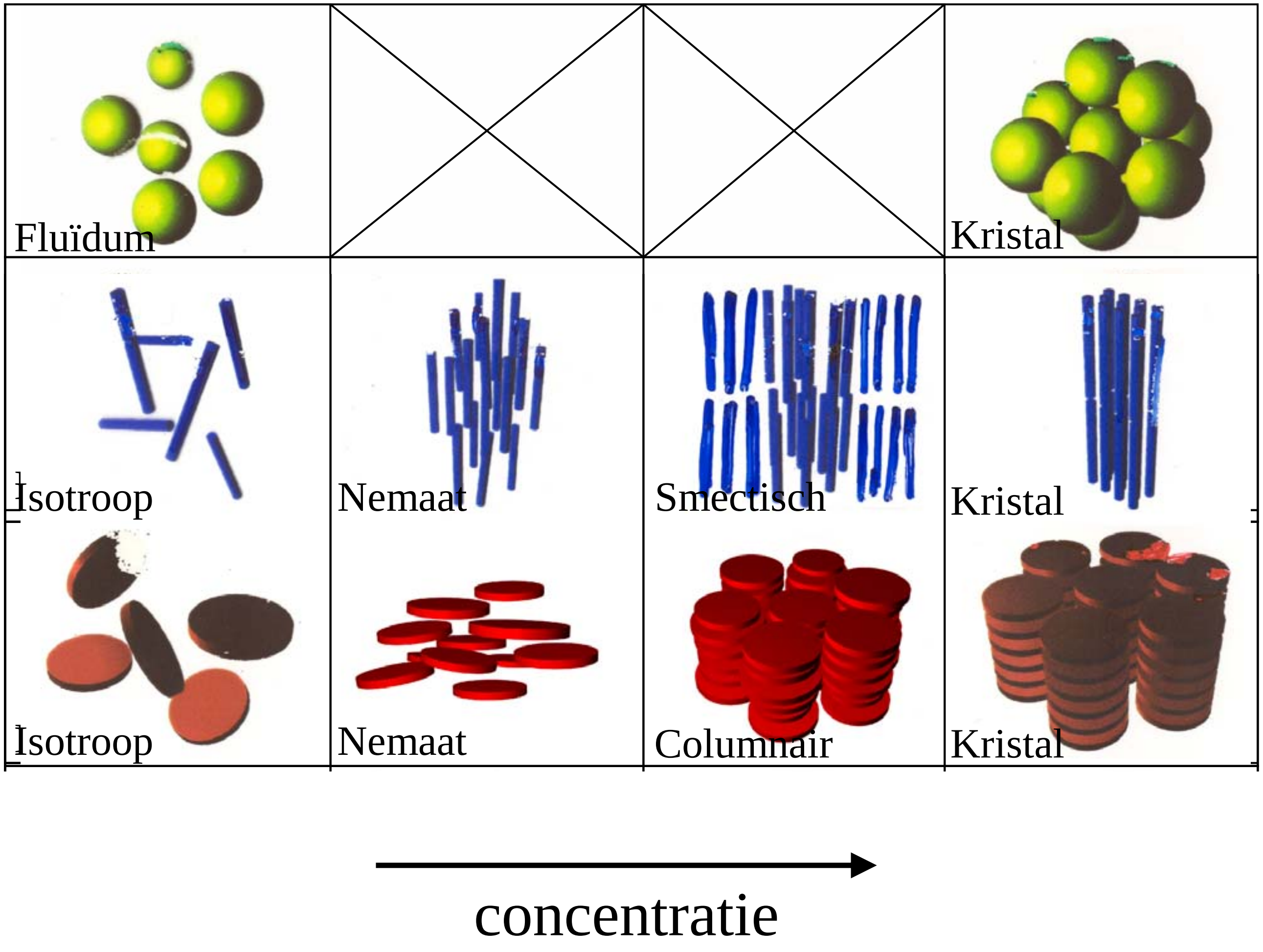
- wall-oriented columnar phase, sampled head-on
- hexagonal pattern indicative of hexagonal stacking of columns
- orientational order extends over *centimetres*!

A.V. Petukhov, D. van der Beek, R.P.A. Dullens, I.P. Dolbnya, G.J. Vroege, and H.N.W. Lekkerkerker, Phys. Rev. Lett. (2005)

Summary



Ordening in colloïdale suspensies



Alder en Wainwright (1957)

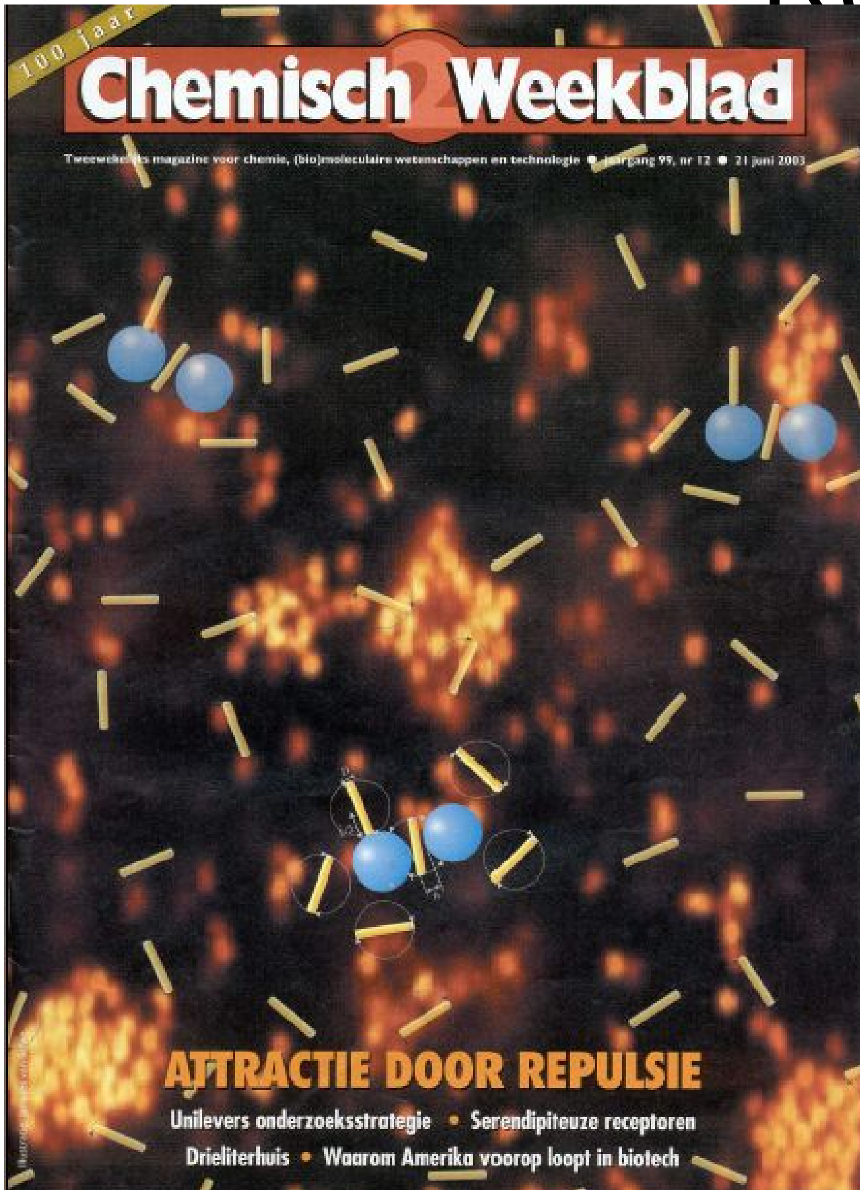
Frenkel, HNWL en Stroobants (1988)

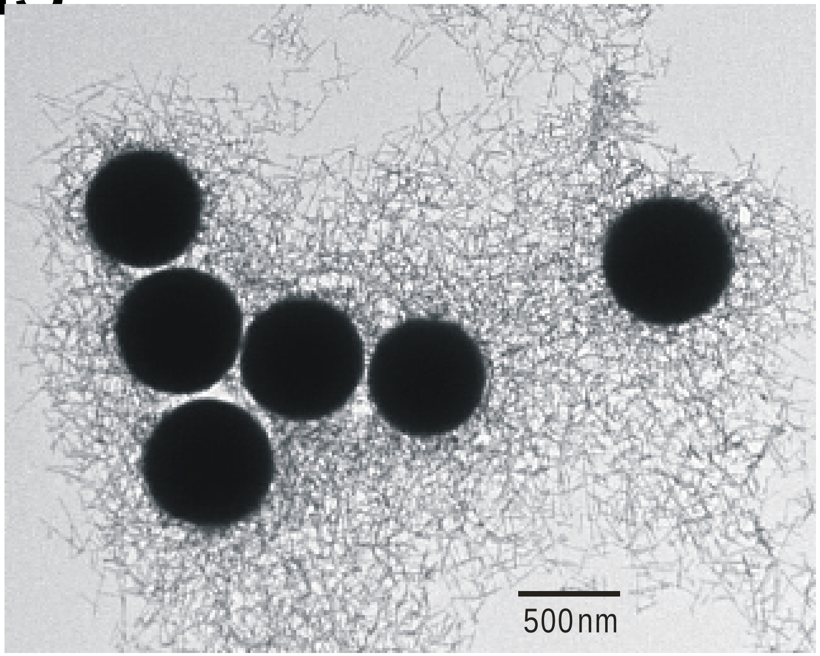
Veerman en Frenkel (1992)

Bauhaus 1926


3
linie
punkt
fläche

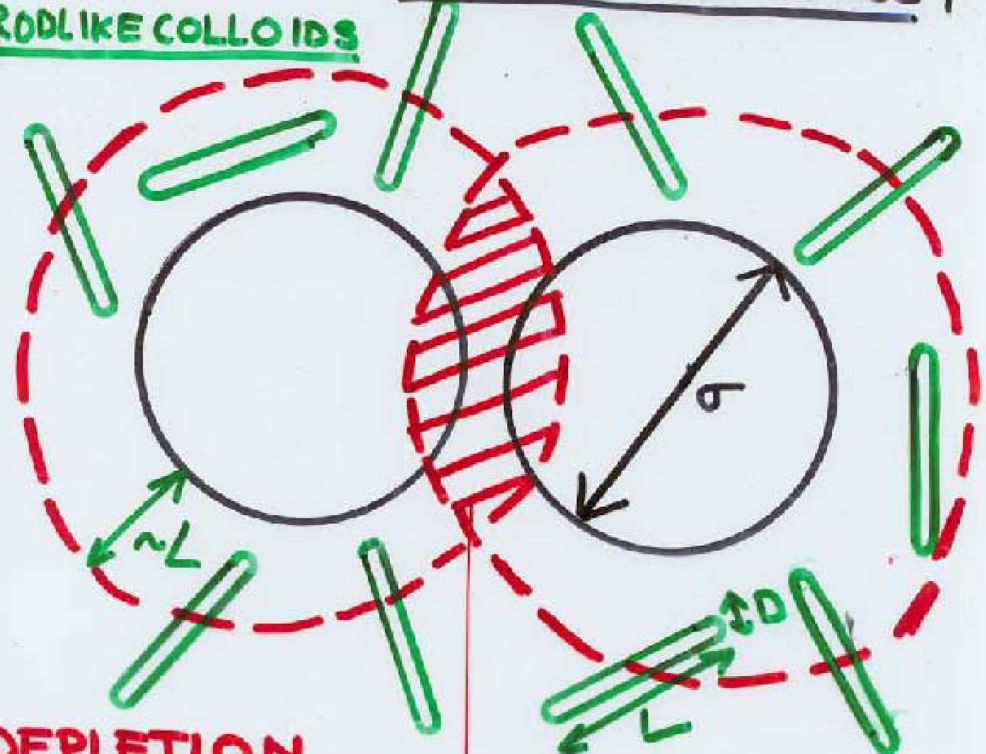
Mixed shaped colloids: Spheres and Rods





S.M. Oversteegen, G.H. Koederink,
J.G.E.J. Wijnhoven & HNWL
C2W, 21 juni 2003

MIXTURES OF SPHERICAL COLLOIDS + RODLIKE COLLOIDS



DEPLETION INTERACTION

$$W = -\left(\frac{N_{rod}}{V} kT\right)\left(\sigma L^2\right)$$

$$\sim -kT\left(\frac{\sigma}{D}\right)\left(\frac{L}{D}\right)\phi_{rod}$$

SHAPE MATTERS!

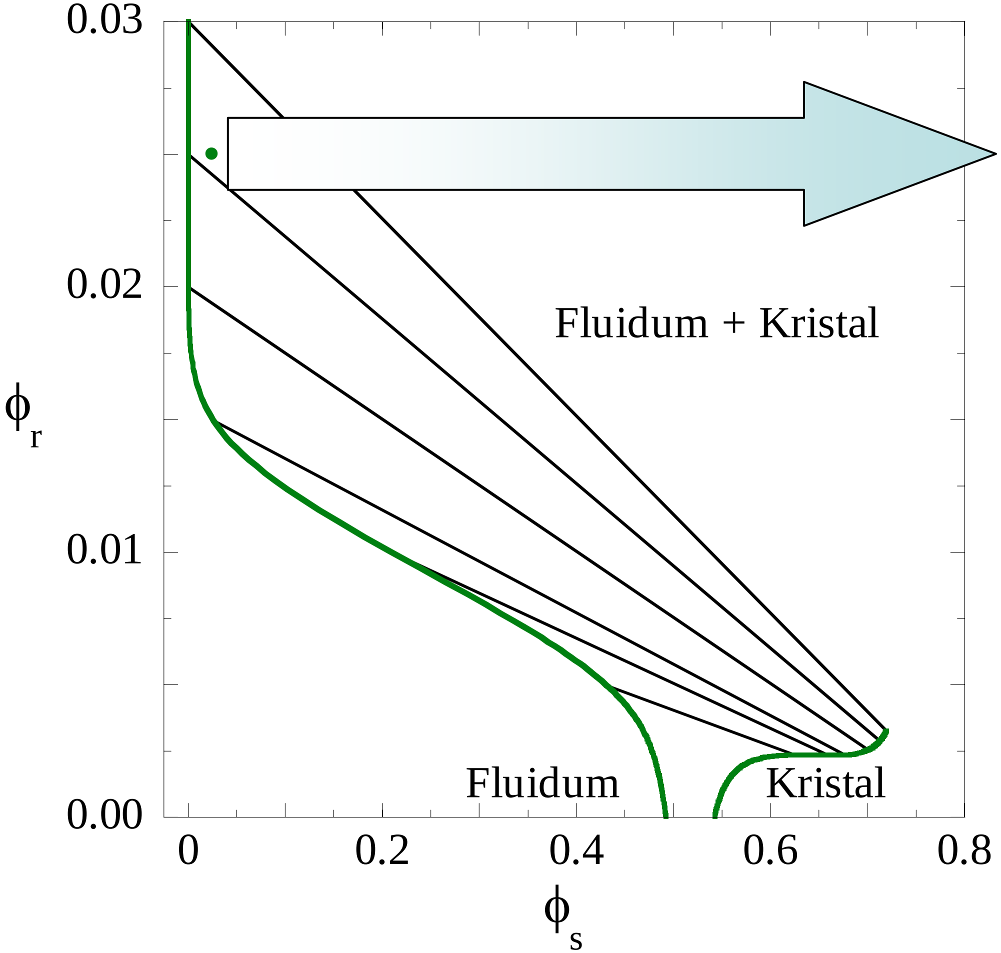
Example → $50 \times 20 = 1000$

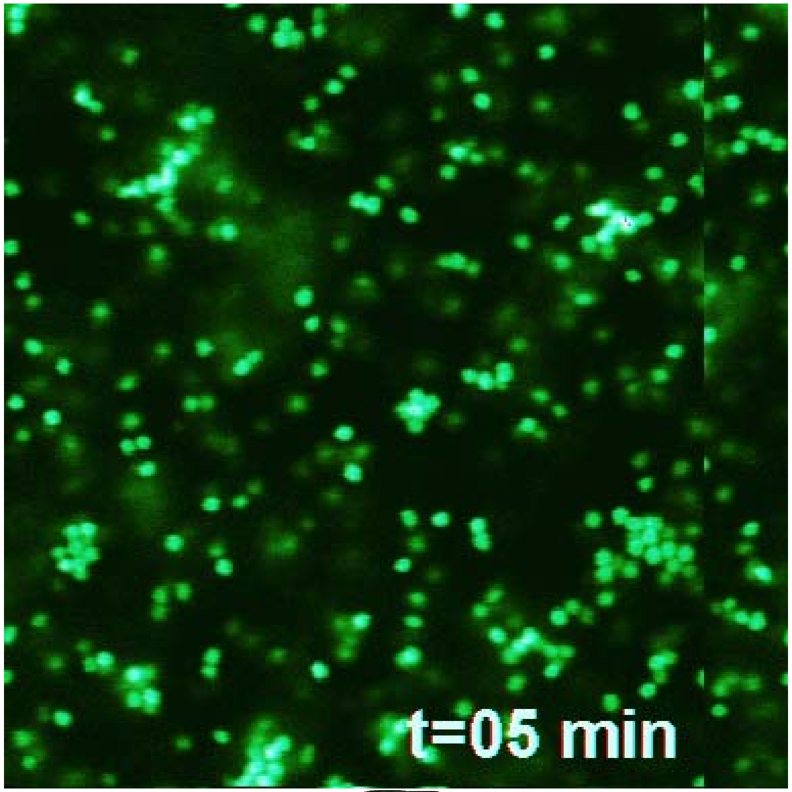
$\sigma = 500$ nm
$L = 200$ nm
$D = 10$ nm

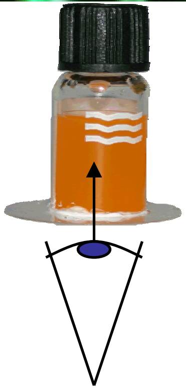
L. Auvray
J. Physique 42, 79 (1981)

Y. Mao M. Cates H N W L
PRL 75 4548 (1995)

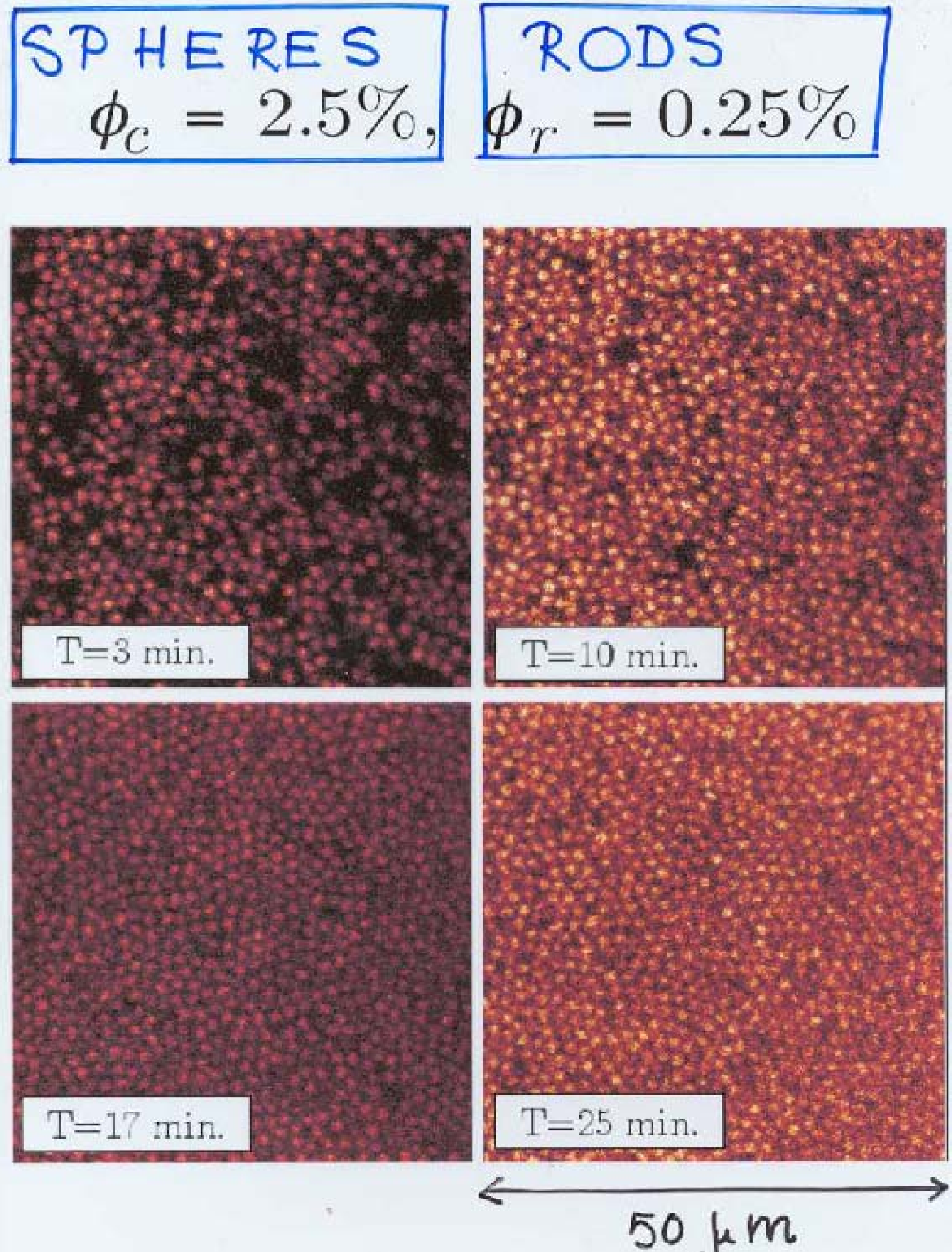
Staven en bollen: fasegedrag







Vliegenthart, Van Blaaderen, HNWL (1999);
Oversteegen, Wijnhoven, Vonk, HNWL (2003).

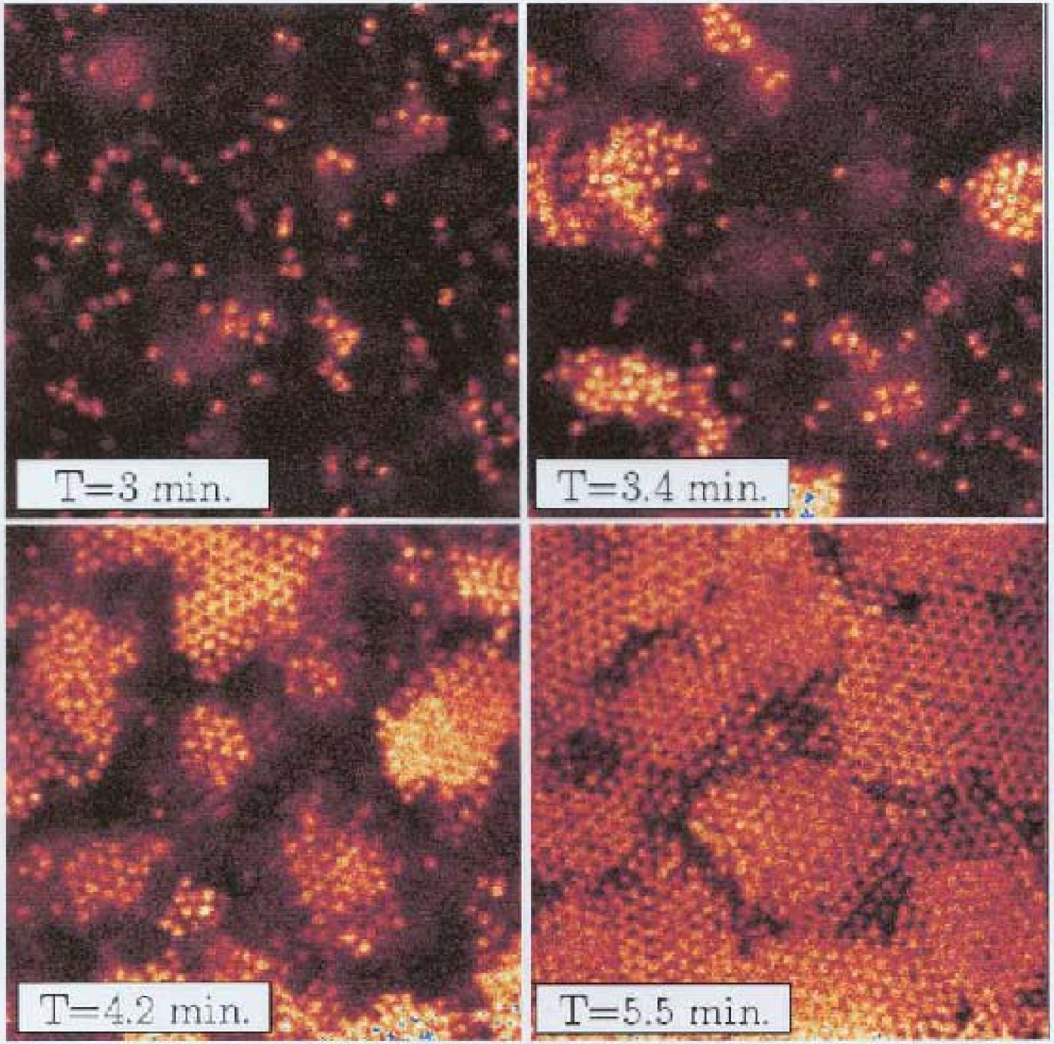

SPHERES
$\phi_c = 2.5\%$,
RODS
$\phi_r = 0.25\%$
T=3 min.
T=10 min.
T=17 min.
T=25 min.
50 μm

SPHERES

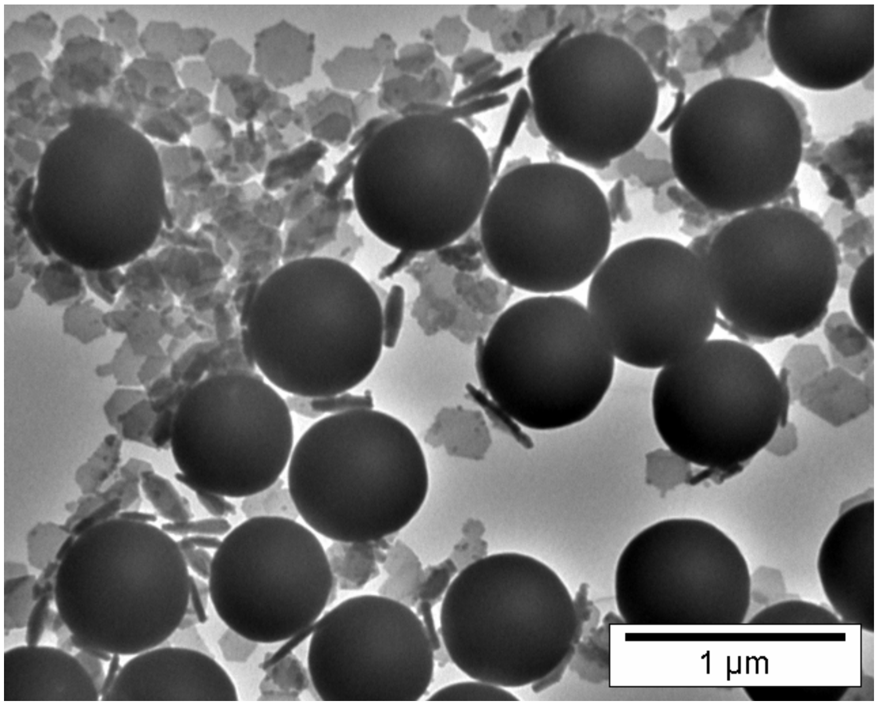
$\phi_c = 2.5\%$,

RODS

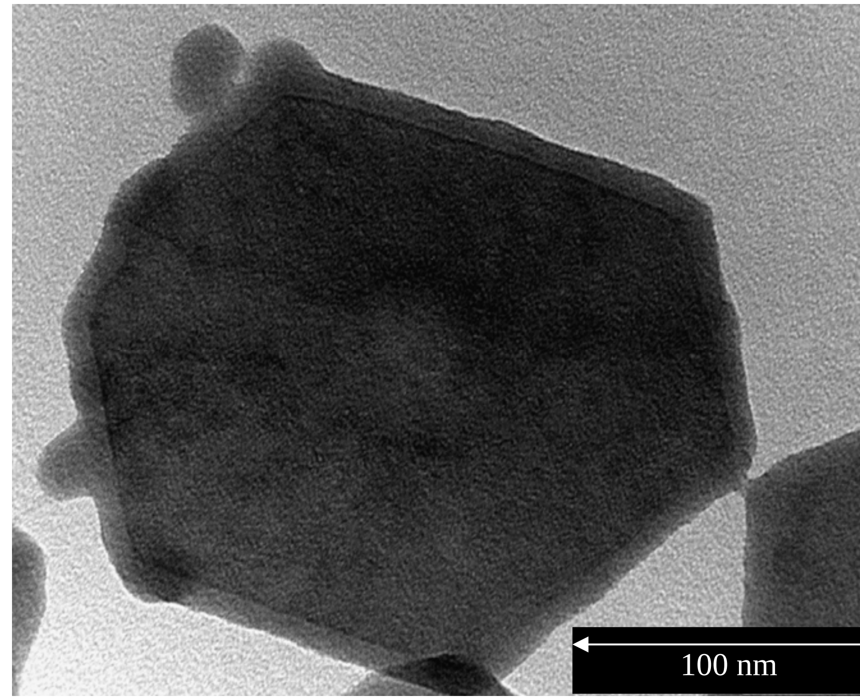
$\phi_r = 0.5\%$



Platelets and spheres

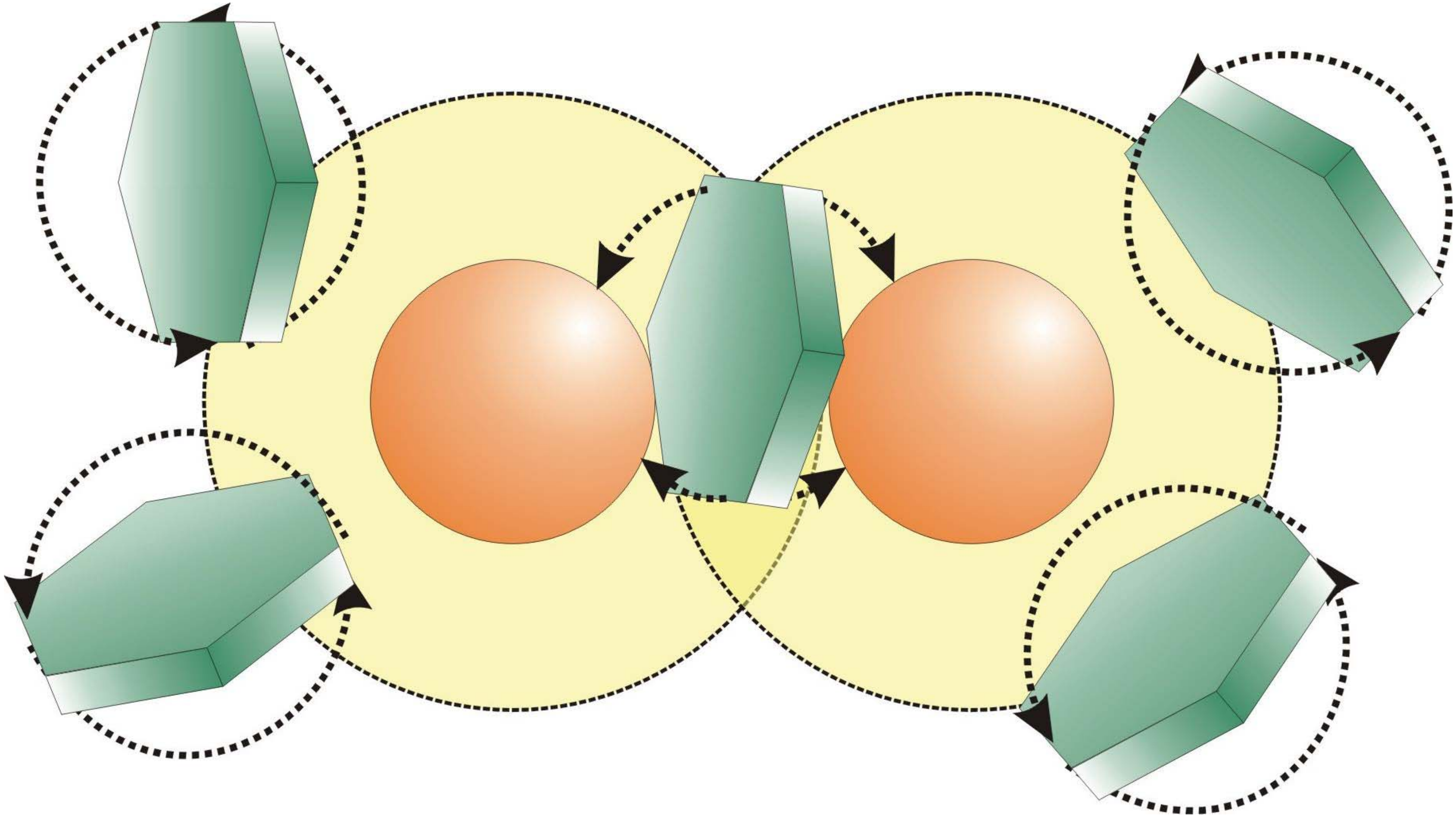


TEM of silica spheres
and silica coated gibbsite plates



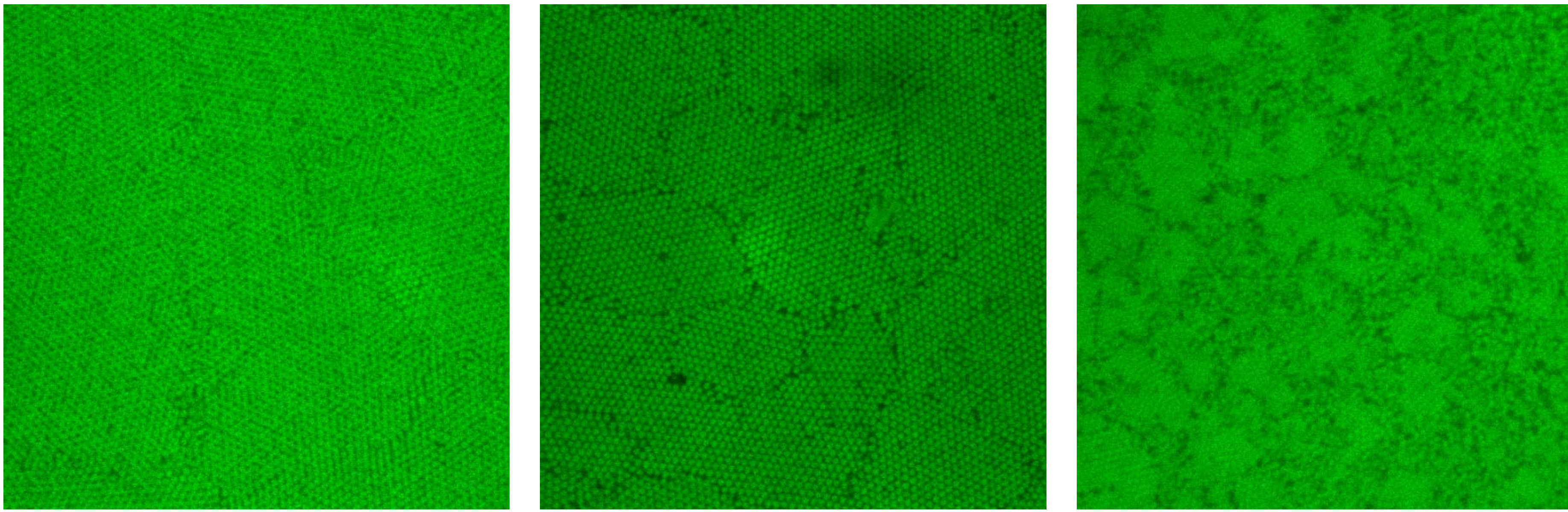
Wijnhoven, Chem. Mater. 2004

Depletion Interaction Induced by Gibbsite Particles



Oversteegen & HNWL, Phys. Rev. E, 2003; J. Chem. Phys., 2004

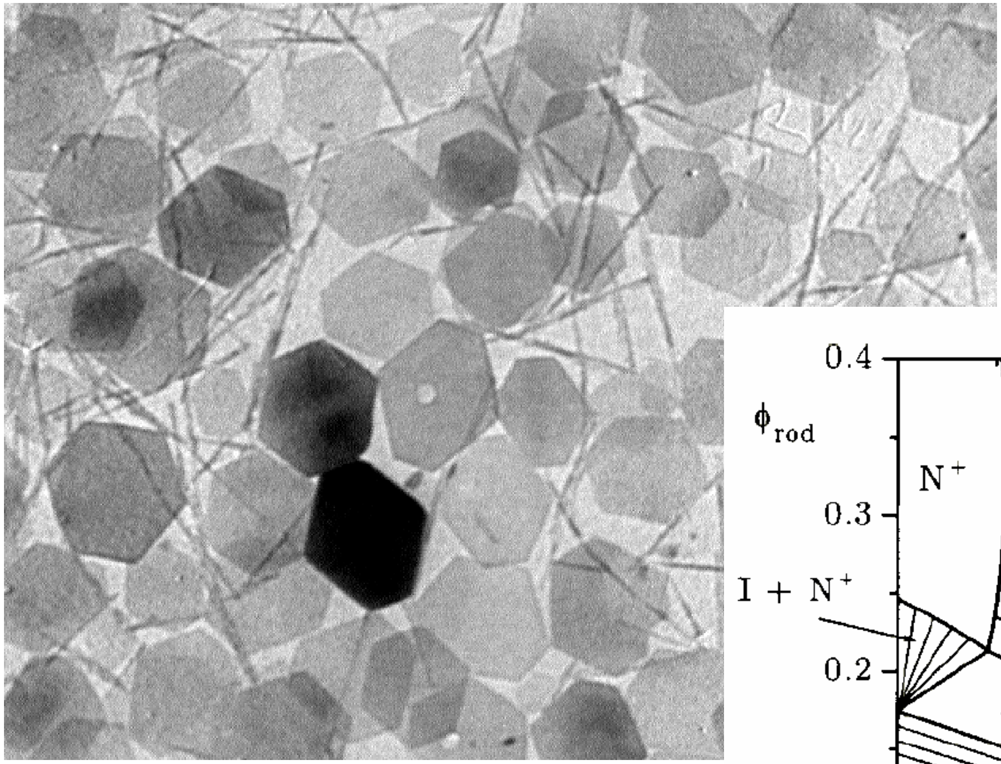
CSLM of fluorescent silica spheres and silica coated gibbsite plates

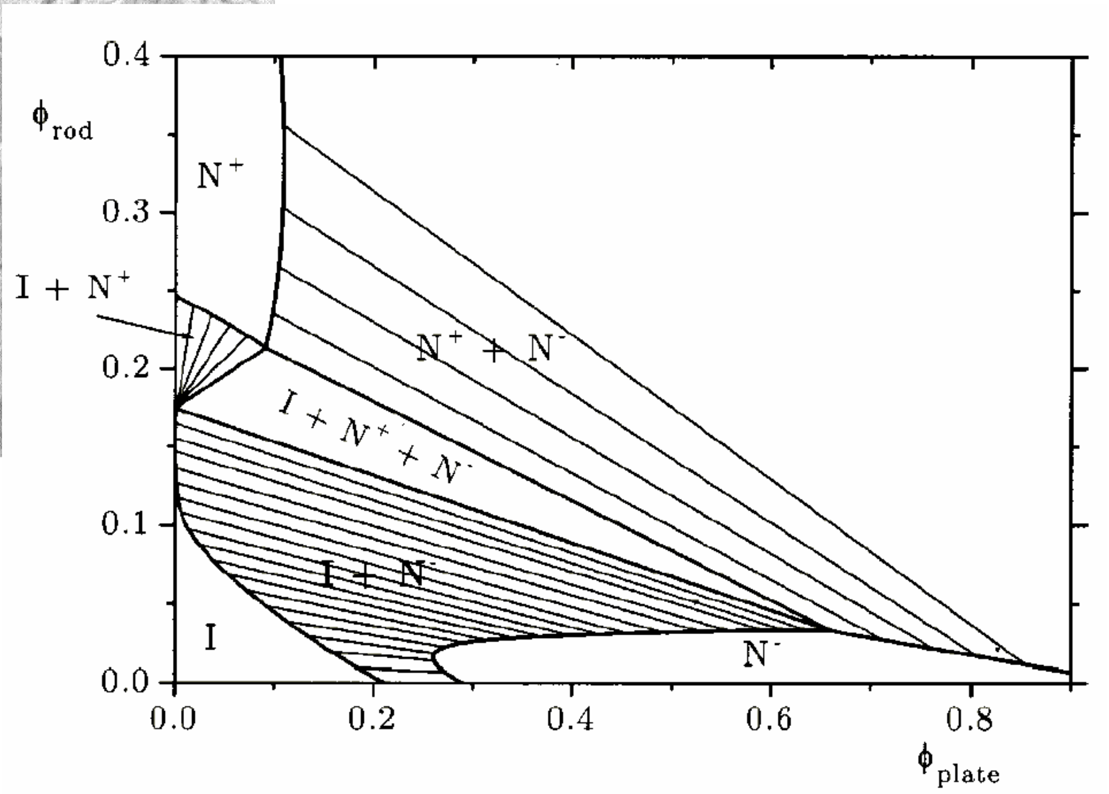


Increasing Gibbsite Concentration

Oversteegen, Vonk, Wijnhoven, HNWL, Phys. Rev. E, 2005

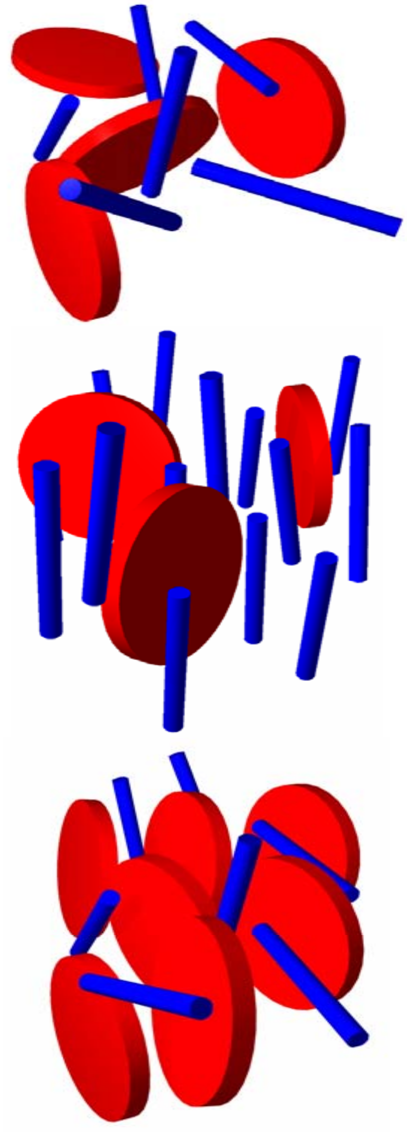
Staven en platen

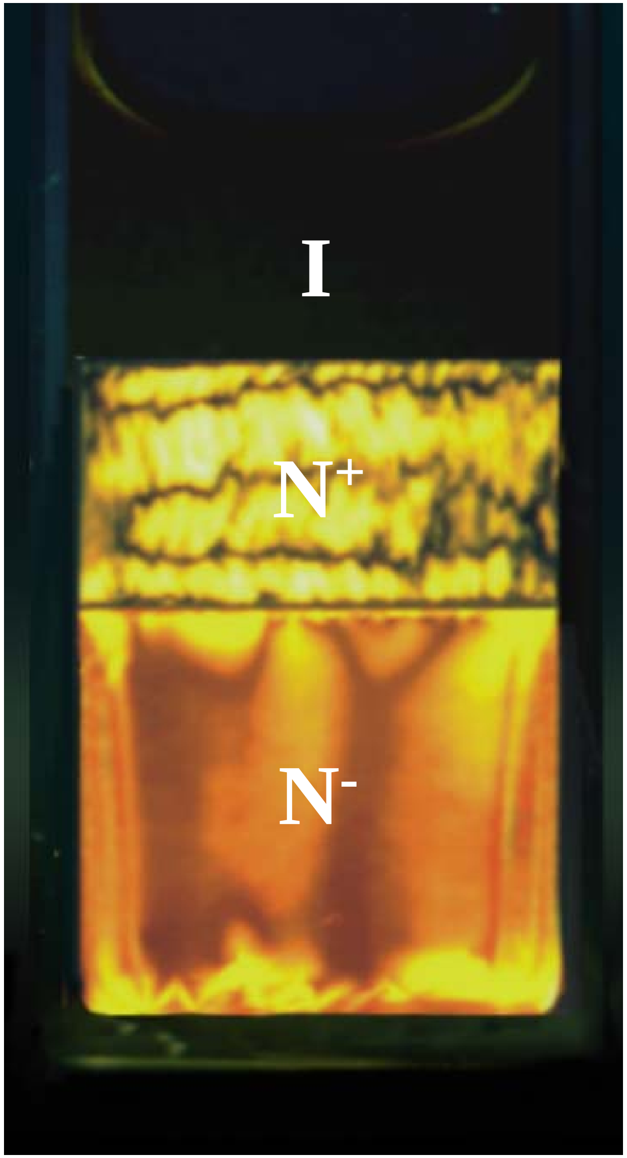


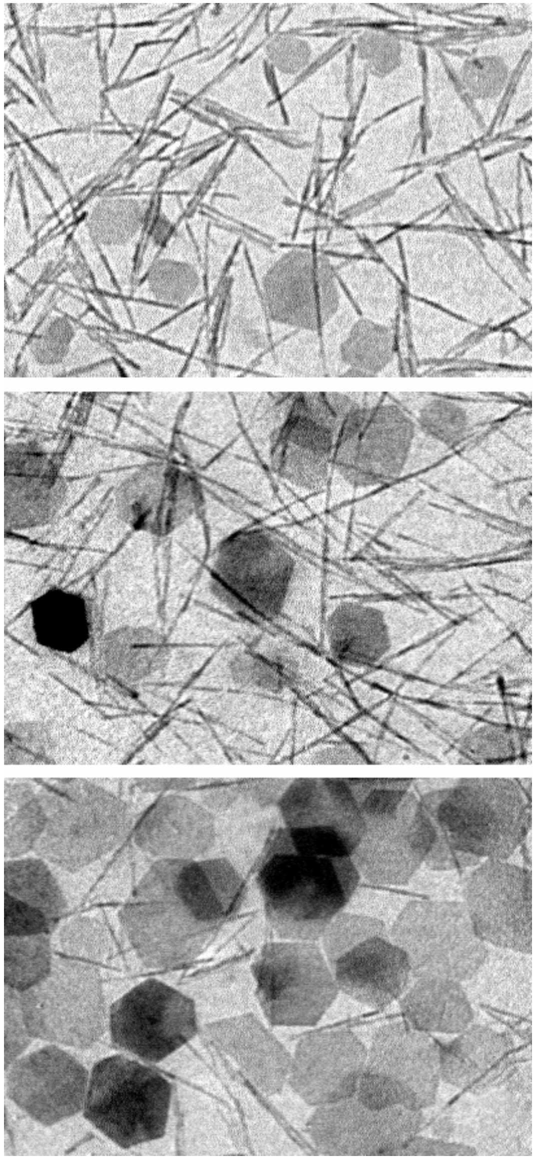


Wensink, Vroege, HNWL (2001).

Staven en platen: fasegedrag







Van der Kooij, HNWL (2000).

THE END