Liquid Crystal Phase Transitions in Suspensions of Mineral Colloids:New Life fromOld Roots

Henk Lekkerkerker

28 March 2012

Menu

- Tuesday 1 May 1990:A visit with serious consequences
- Clay and Liquid Crystals:The disappointment
- Gibbsite :Less is more
- Clay 2.0Liquid Crystals :New hope
- Some final comments

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Van 't Hoff Laboratorium voor
Fysische en Colloidchemie
Universiteit Utrecht

ONDERZOEKSJAAR COLLEGE FYSISCHE EN COLLOIDCHEMIE

Onderdeel: Wisselwerkingen tussen colloidale deeltjes

Prof. H.N.W. Lekkerkerker

$$C = \frac{\alpha^A(\mu^B)^2 + \alpha^B(\mu^A)^2}{(4\pi\varepsilon_0)^2} \qquad \text{inductie-effect} \qquad (2.28)$$

$$C = \frac{3}{2}\frac{E^A E^B}{E^A + E^B}\cdot\frac{\alpha^A\alpha^B}{(4\pi\varepsilon_0)^2} \qquad \text{dispersie interactie} \qquad (2.29)$$

Met behulp van deze formules kan men de verschillende bijdragen aan de lange afstandsinteractie berekenen. Zonder preciese berekeningen uit te voeren kunnen we toch al wel een schatting maken van de grootte orde van de verschillende bijdragen uitgaande van de volgende grootte ordes voor dipool moment, polariseerbaarheid en excitatie-energie.

$$|\mu| \sim 0.1\, e\sigma$$

$$\frac{\alpha}{4\pi\varepsilon_0} \sim 0.1\, \sigma^3$$

$$E \sim 0.1 \frac{e^2}{4\pi\varepsilon_0 a_0}$$

waar σ de diameter van het atoom of molecuul is ($\sigma \approx 3\text{x}10^{-10}$ m), $a_0 = \frac{\varepsilon_0 h^2}{\pi m e^2} = 0.53\text{x}10^{-10}$ is de Bohr-straal (constante van Planck: $h = 6.62\text{x}10^{-34}$ Js; massa van het elektron: $m = 0.91\text{x}10^{-30}$ kg) en $\frac{e^2}{4\pi\varepsilon_0} = 2.3\text{x}10^{-28}$ Jm. Gebruik makend van deze uitdrukkingen vinden we

$$C_{oriëntatie} \sim \frac{(0.1)^4\sigma^4}{kT}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \sim 10^{-77}\ \text{Jm}^6$$

$$C_{inductie} \sim (0.1)^3\, \sigma^5 \frac{e^2}{4\pi\varepsilon_0} \sim 10^{-78}\ \text{Jm}^6$$

$$C_{dispersie} \sim (0.1)^3 \frac{\sigma^6}{a_0}\frac{e^2}{4\pi\varepsilon_0} \sim 10^{-77}\ \text{Jm}^6$$

waar we gebruikt hebben $kT = 4\ 10^{-21}$ J, bij $T = 298$ K.
Dit betekent dat, zoals London (1936) liet zien dat de steeds aanwezige dispersie interactie in het algemeen de belangrijkste bijdrage levert aan de interactie energie. We illustreren dit aan de hand van de volgende tabel die we ontlenen aan Maitland et al. (1981) p. 21.

Tabel 1

Molecule	$10^{30}\mu$/C m	$10^{30}\alpha(4\pi\varepsilon_0)^{-1}$/m^3	$-$Coefficient of $r^{-6}/10^{-79}$ J m^6: Electrostatic	Induction	Dispersion
Ar	0	1·63	0	0	50
Xe	0	4·0	0	0	209
CO	0·4	1·95	0·003	0·06	97
HCl	3·4	2·63	17	6	150
NH_3	4·7	2·26	64	9	133
H_2O	6·13	1·48	184	10	61

Referenties

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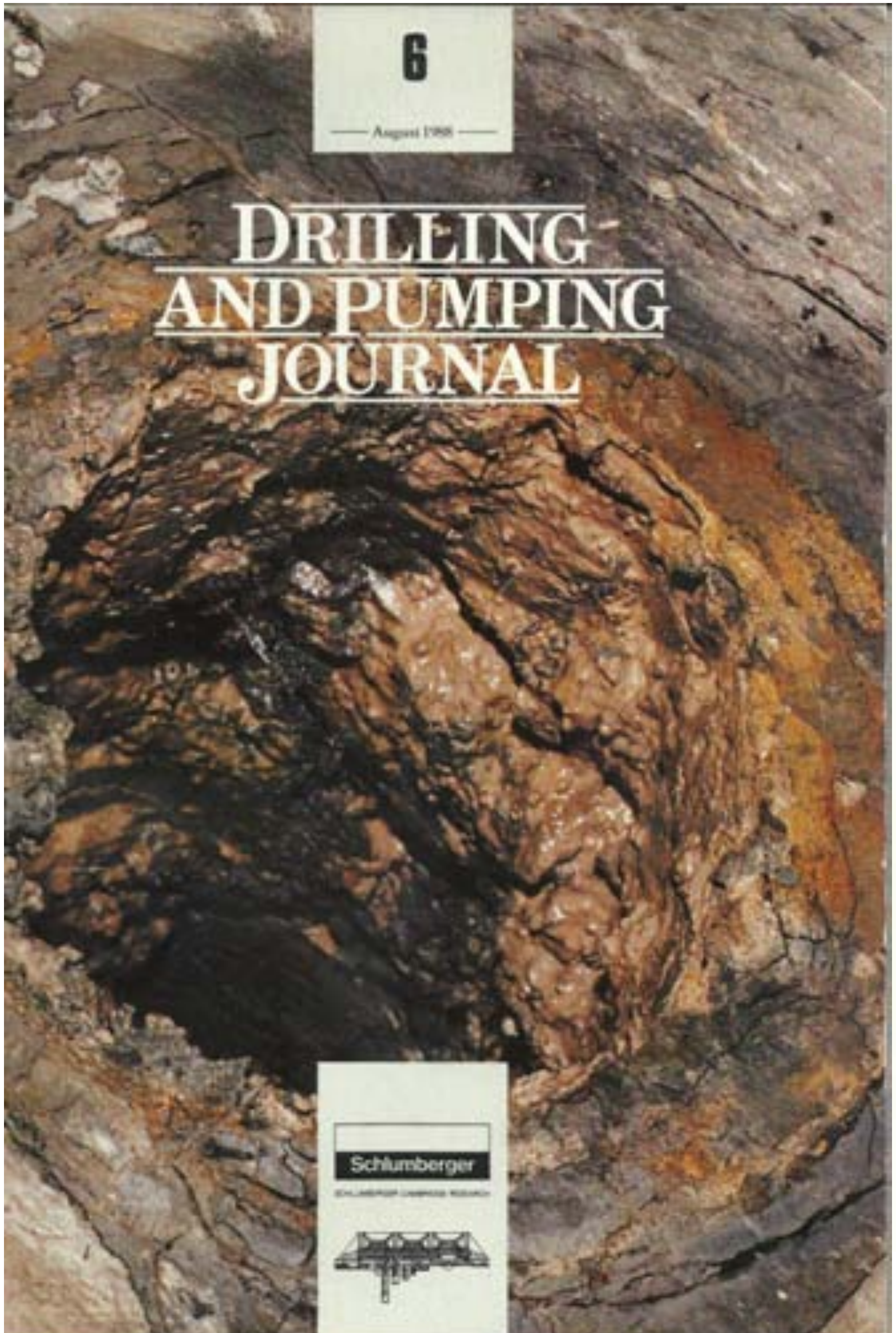


DRILLING FLUID PHYSICS

EDMUND FORDHAM
GEOFFREY MAITLAND
GERRY MEETEN
JOHN SHERWOOD

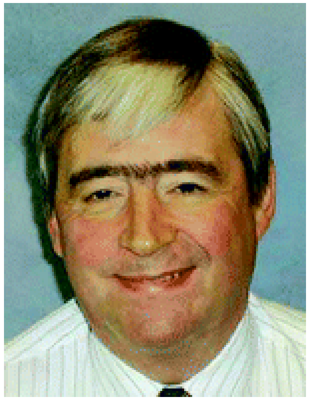
SCHLUMBERGER CAMBRIDGE RESEARCH

GEOFFREY MAITLAND IS HEAD OF THE ROCK AND FLUID PHYSICS DEPARTMENT AT SCR. HE IS A GRADUATE OF OXFORD UNIVERSITY, WHERE HE OBTAINED HIS DPhil IN PHYSICAL CHEMISTRY. GEOFF WAS A SENIOR LECTURER IN CHEMICAL ENGINEERING AT IMPERIAL COLLEGE, UNIVERSITY OF LONDON, FROM 1974 UNTIL HE JOINED SCHLUMBERGER CAMBRIDGE RESEARCH IN 1986.

INTRODUCTION

The drilling, completion and treatment operations for oil and gas wells all use a range of specialised fluids, which are usually multicomponent dispersions and/or polymeric solutions. Each of these complex fluids is required to fulfil many roles, including pressure control in the wellbore, transport of material to or from specific downhole locations and protection of the formation against any harmful modification by the fluid itself. Because of this multifunctional nature, the design of the ideal fluid for any particular job becomes a complex optimisation exercise. It requires a specification in terms of *fluid function* to be converted to one involving a *fluid recipe*. The key links in this process are the physical properties of the fluid.

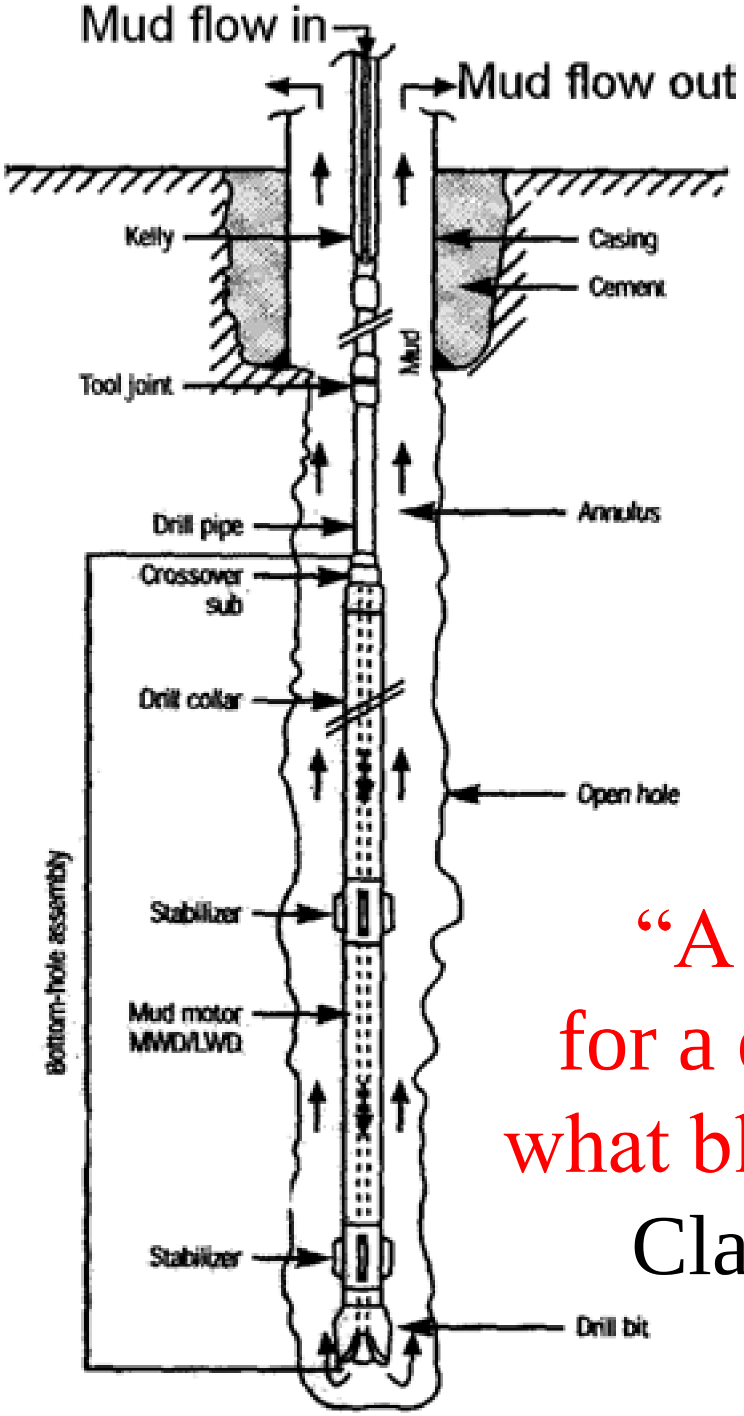
From **Fluid Function** to **Fluid Recipe** to ......



SCHLUMBERGER CAMBRIDGE RESEARCH

Dr.Geoffrey Maitland

FLUID STYLIST



A succesful drilling fluid must

Carry the drilled cuttings to the surface

Suspend the drilled cuttings when the circulation is stopped

Form a thin filtercake ("mudcake") which seals the formations penetrated by the bit

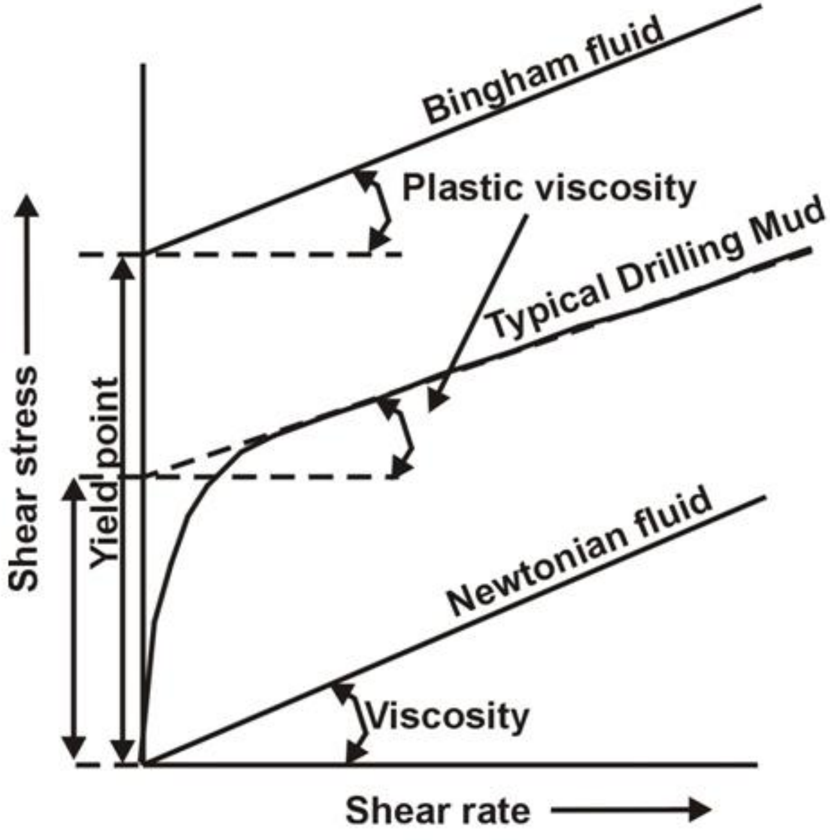
"A drilling mud is for a drilling operation what blood is to the body"

Claude Vercaemer

Schlumberger

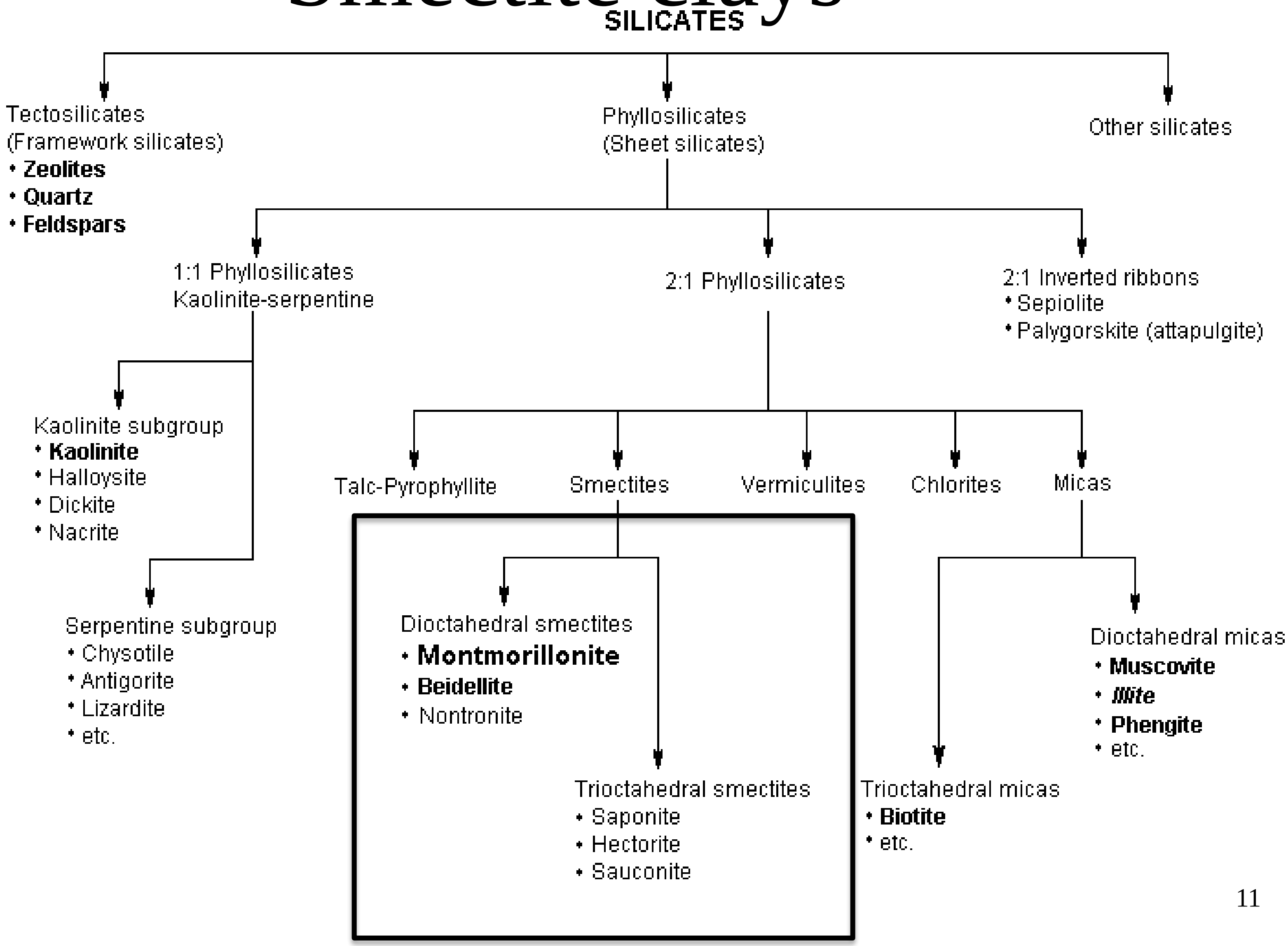
Desired properties
Drilling fluid

- Low plastic viscosity
- High yield point

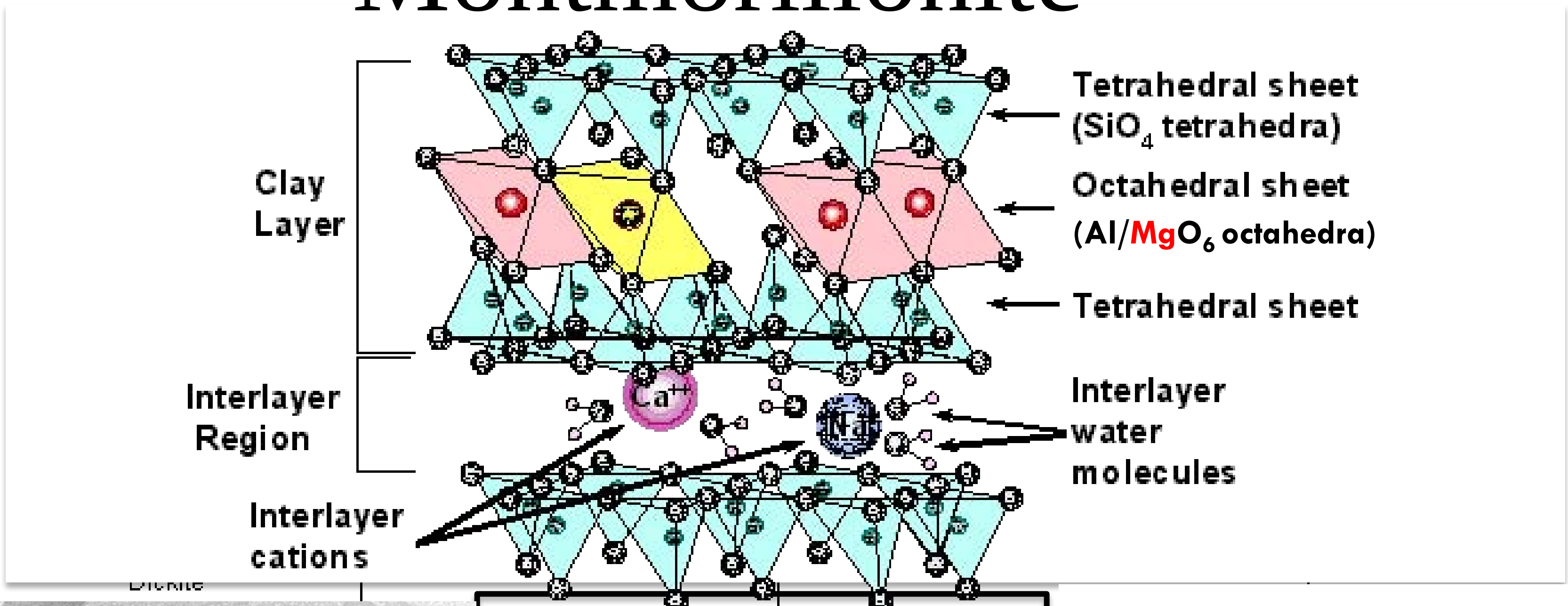


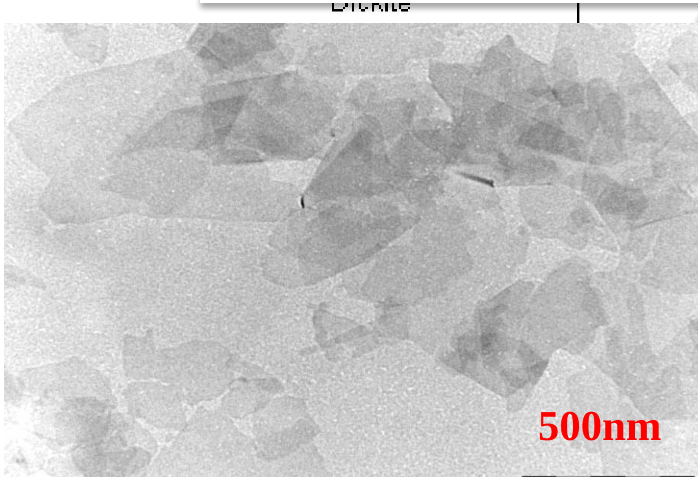
Clays gel

Smectite clays



Montmorillonite





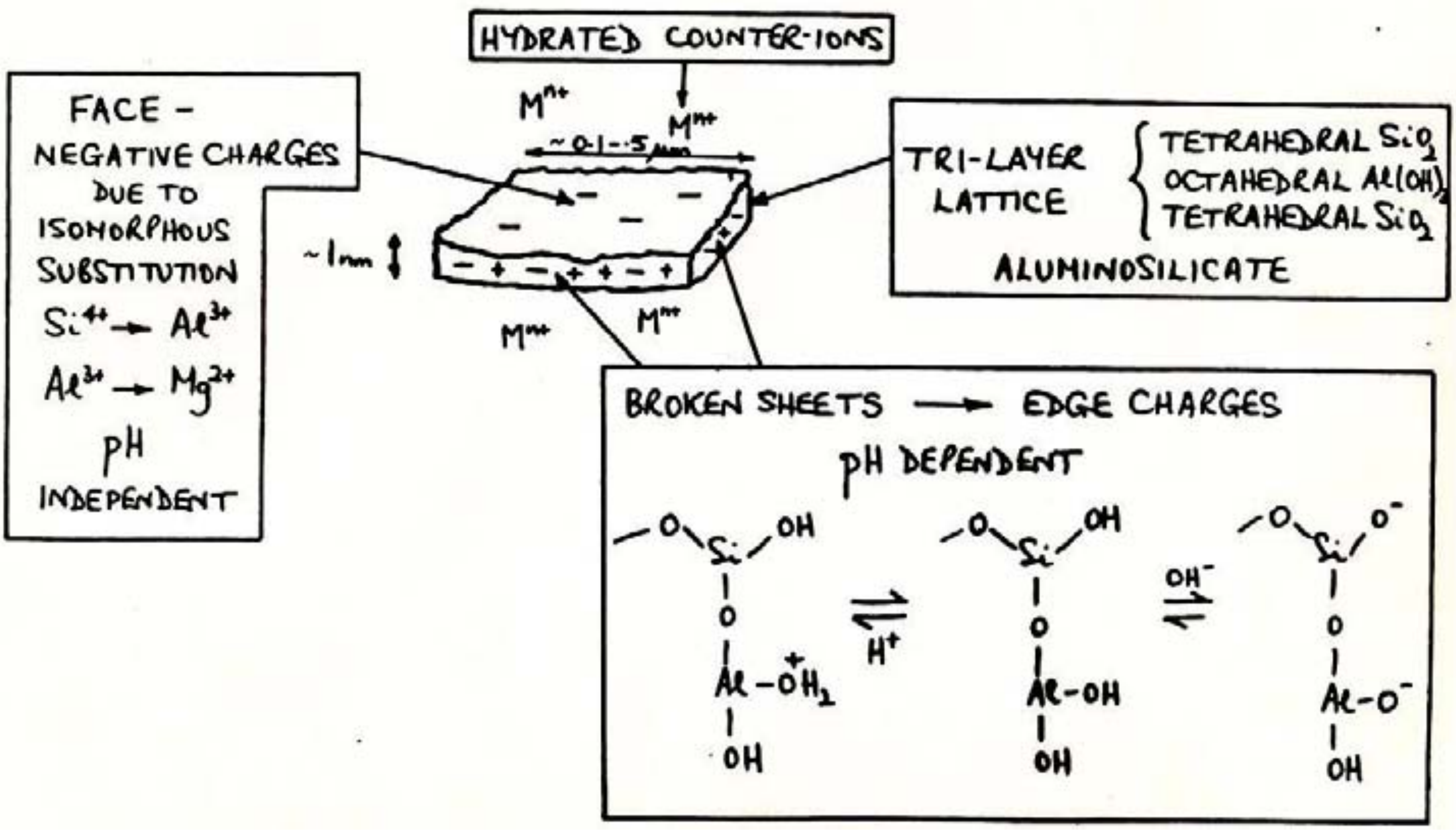
Dioctahedral smectites

- **Montmorillonite**
- **Beidellite**
- Nontronite

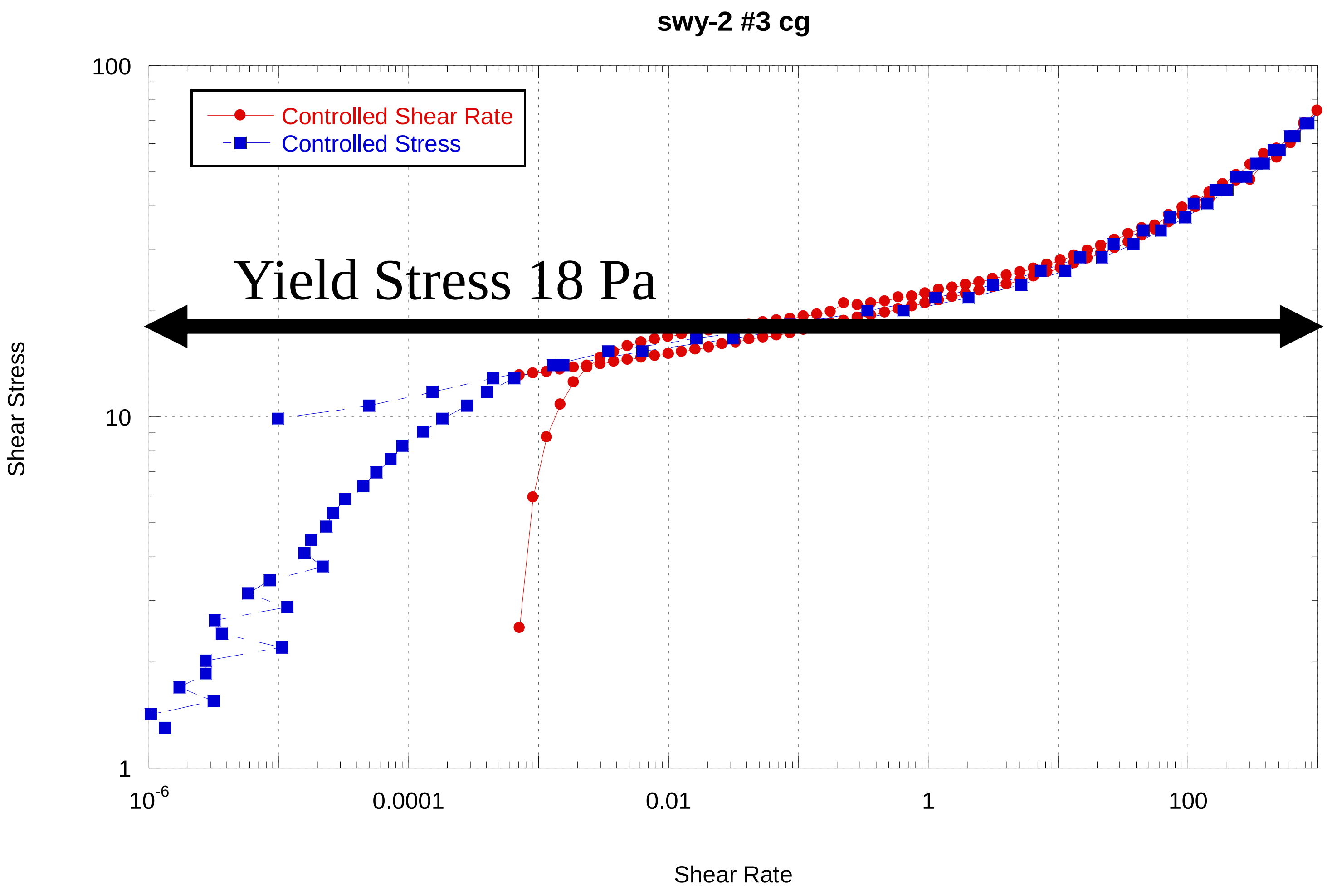
Trioctahedral smectites

- Saponite
- Hectorite
- Sauconite

Montmorillonite Clay Platelets – Bentonite(Geoff Maitland)



SWy-2 3.2% Viscometry (Louise Bailey)



I will not attempt to mediate between those who support and those who oppose the existence of a ***True Yield Stress*** *(see Judges 5:5)*

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Colloidal Liquid Crystals :A very brief history

Colloidal Liquid Crystals :A very brief history

1925
V2O5

Über freiwillige Strukturbildung in Solen.

(Eine neue Art anisotrop flüssiger Medien.)

Von H. Zocher.

(Ernst Werner) Hans Zocher

(27.04.1893 Bad Liebenstein/Thüringen - 16.10.1969 Rio de Janeiro)

Kolloidwissenschaftler, Taktosole

Pionier der Flüssigkristalldisplays (LCD)

(Nebst der Vorschrift zur Herstellung eines V_2O_5-Taktosols)

Colloidal Liquid Crystals :A very brief history

1925
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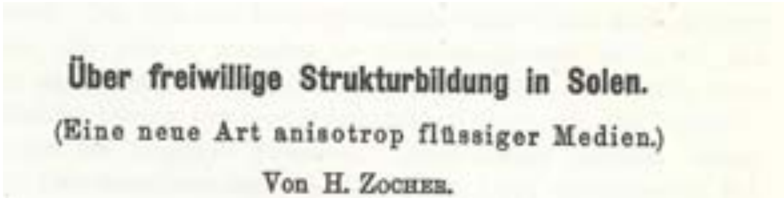
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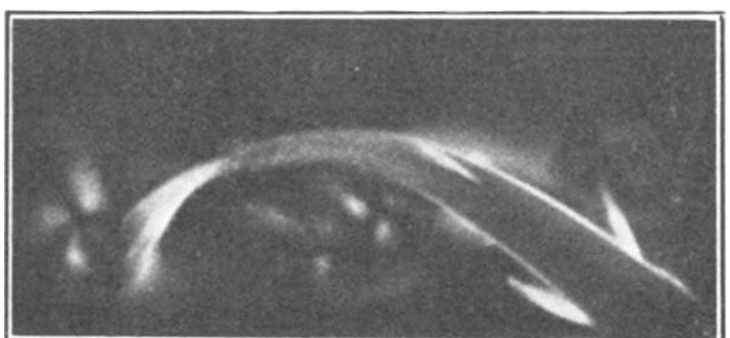
Pionier der Flüssigkristalldisplays (LCD)
(Nebst der Vorschrift zur Herstellung eines V_2O_5-Taktosols)

1936
TMV



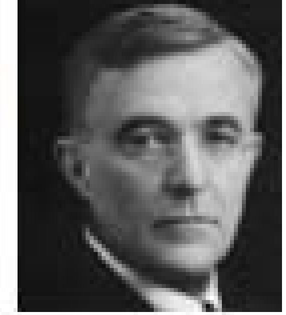
Wake of goldfish in TMV solution
Bawden *et al* Nature 138 (1936) 1051

18. Dorothy Hodgkin looks on as Sage demonstrates Tobacco Mosaic Virus gel to Irving Langmuir at the British Association Meeting, Nottingham 1937

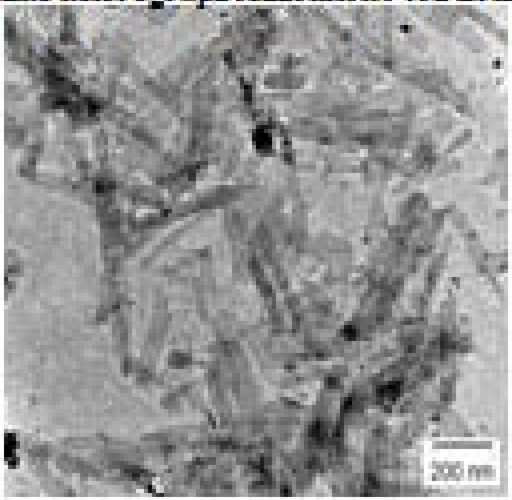
1938
Hectorite

Role of certain forces in colloids

Irving Langmuir , J.Chem.Phys.(1938)

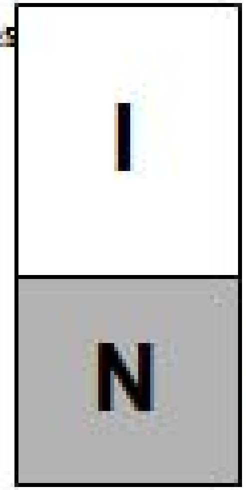


TEM Micrograph Annemieke ten Brinke



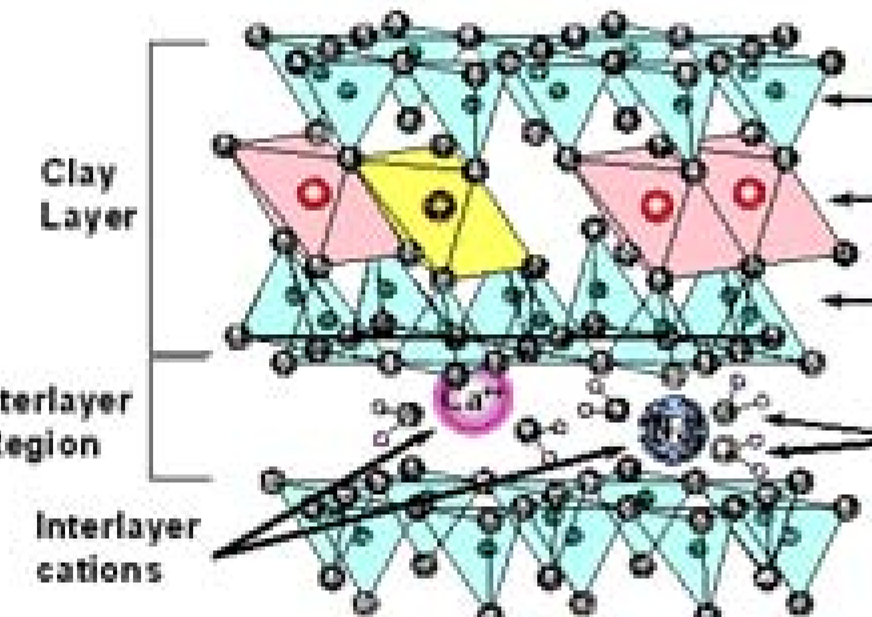
Lath-like particles
L=288 nm
W=43 nm
T=6nm(AFM)

Hectorite



I-N phase transition in Hectorite

phase separated between 2.0 and 2.2 wt% into Isotropic and Nematic



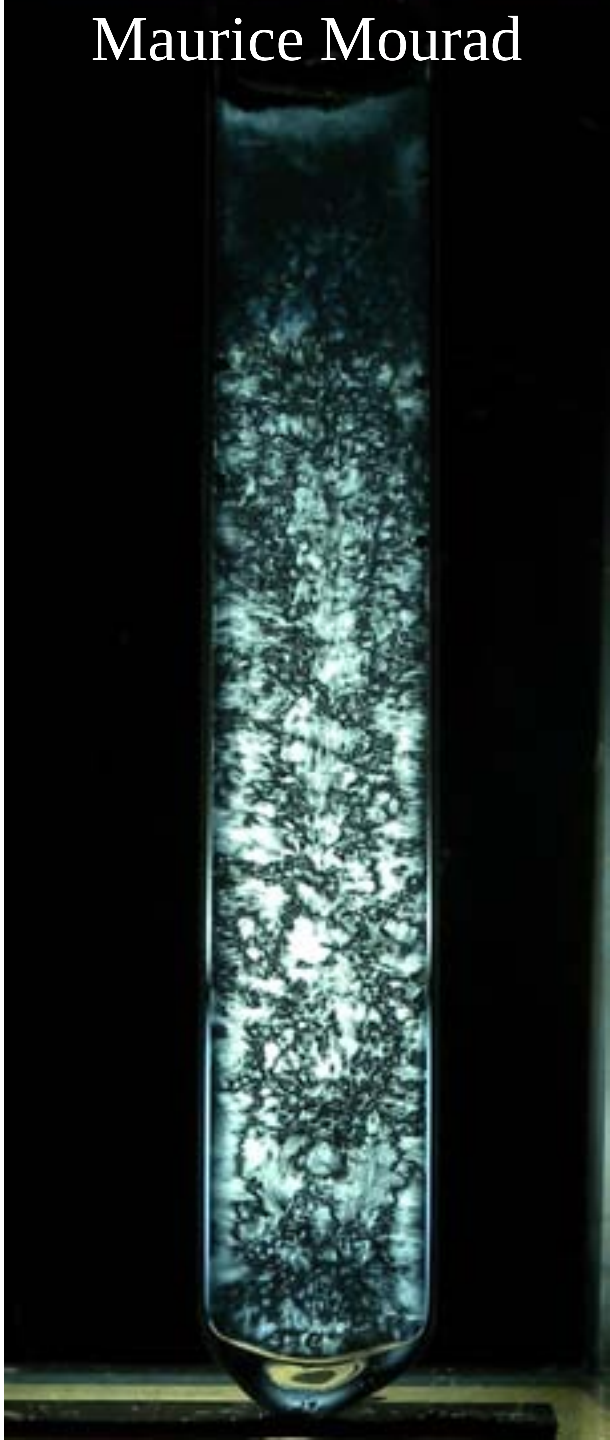
$(Si_{7.73}Al_{0.10})(Mg_{5.46}Li_{0.66})O_{20}(OH)_4Na_{0.94}$

Role of certain forces in colloids

Irving Langmuir , J.Chem.Phys. (1938)

- "It has often been thought that the property of separation into two phases one of which is isotropic and the other permanently birefringent, is characteristic only of sols having rod-like particles. *The optical properties of the hectorite sols, however, prove that the particles are flat plates or disks"*

- Experiment by Langmuir could not be repeated
- Birefringent Gel but no I-N phase separation!



Montmorillonite: Same Story

Birefringent Gel but No I- N Phase Separation

Bentonite suspension (4.3wt%) between cross polarizers

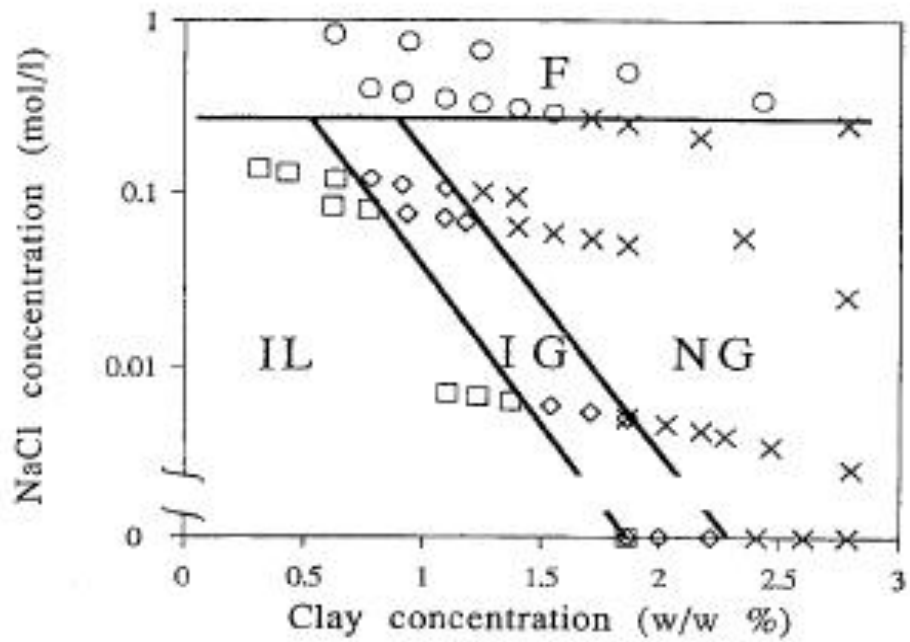


Figure 5. Phase diagram of the bentonite suspensions versus clay and NaCl concentrations. (○, F) Flocculated samples; (□, IL) isotropic liquid samples; (◇, IG) isotropic gel samples; (×, NG) nematic gels.

Gabriel, Sanchez, Davidson 1996

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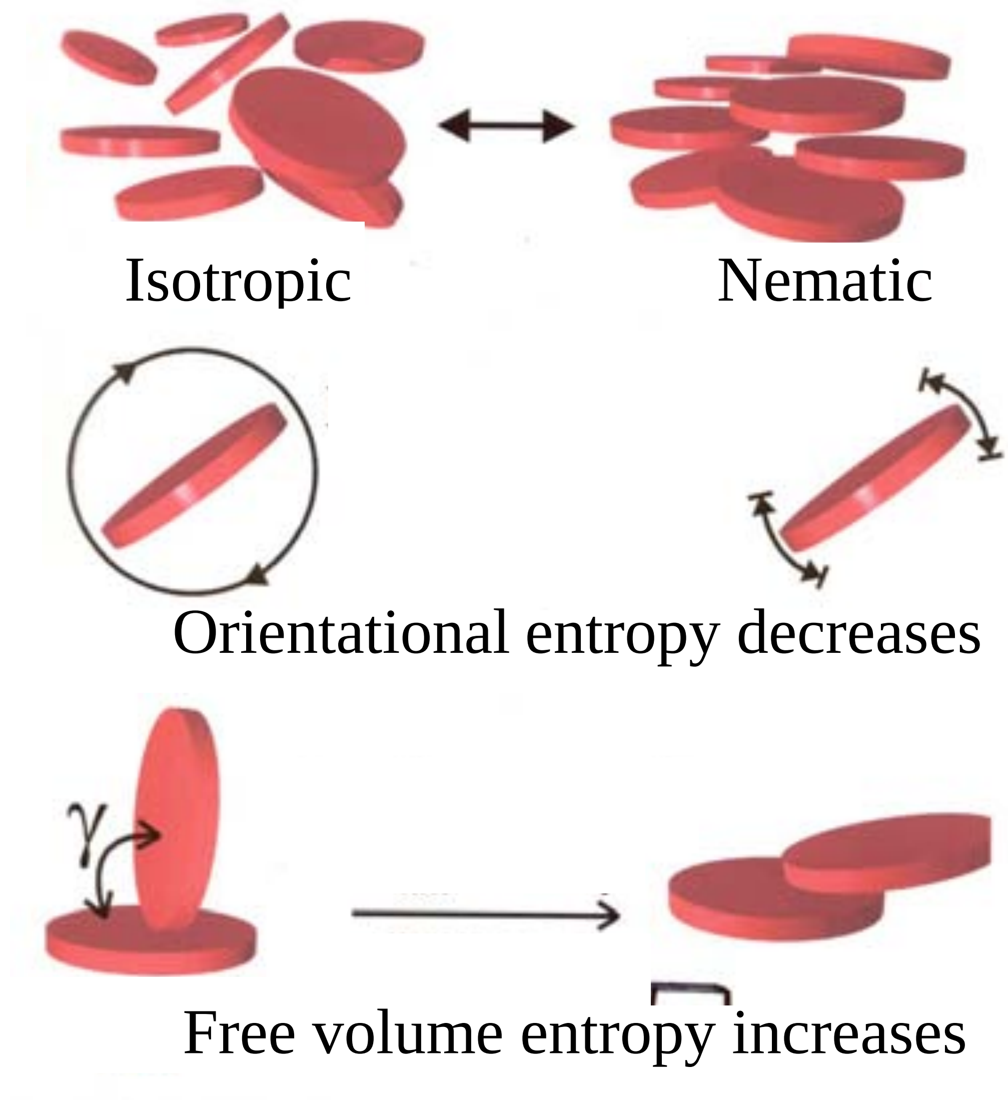
Disk Shape Drives I-N Transition

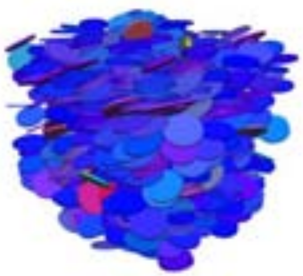


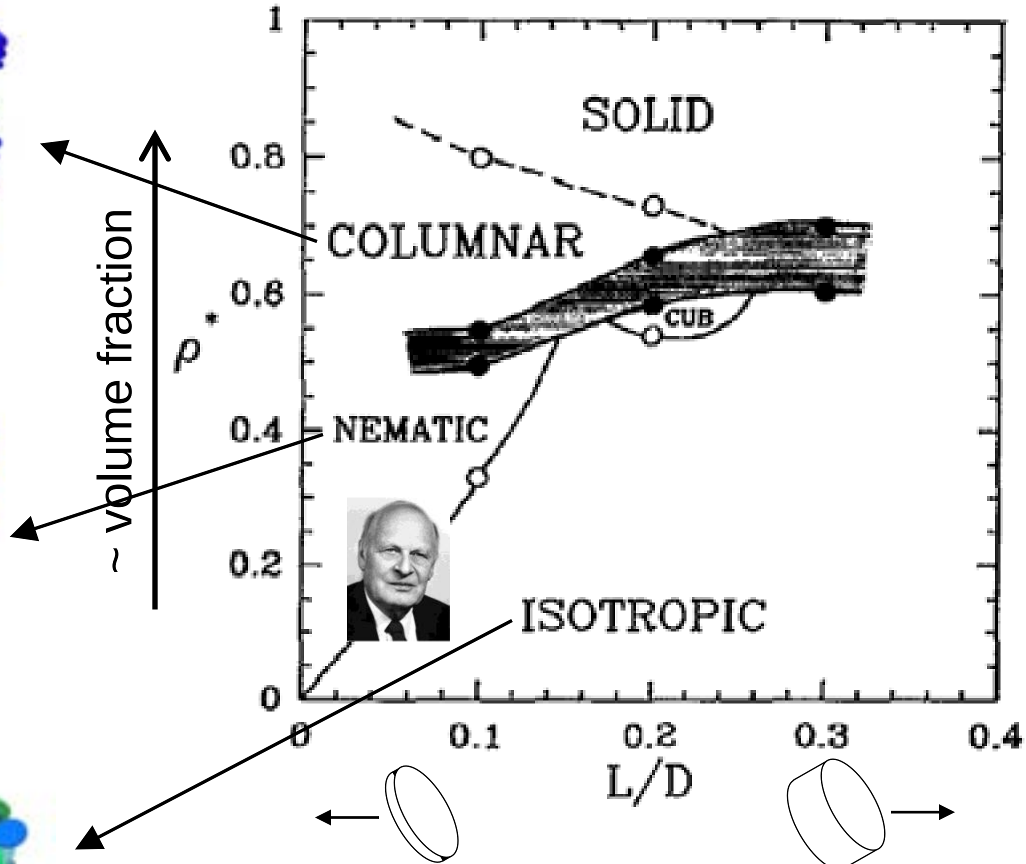
Lars Onsager,

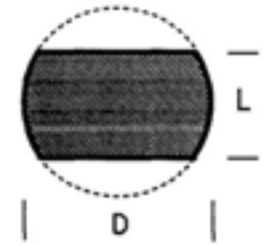
Phys.Rev.62,558(1942)

Phase diagram hard disks

from Monte Carlo simulation



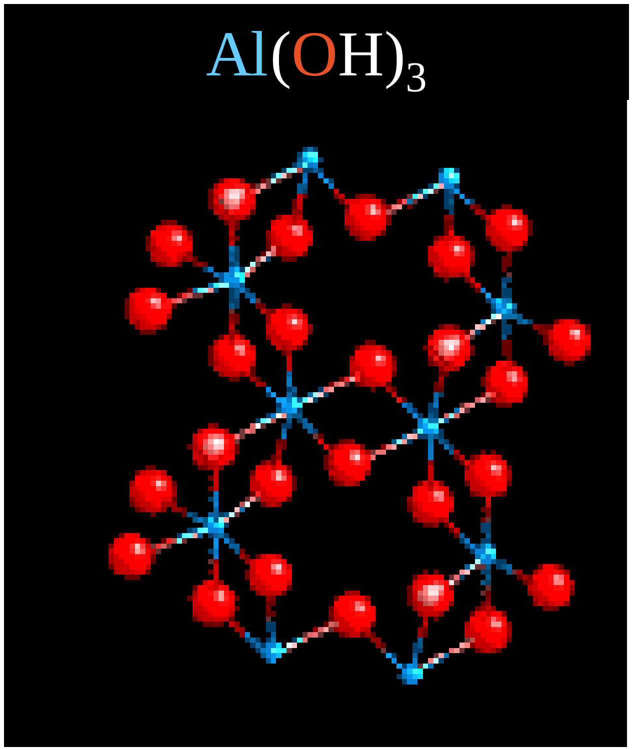


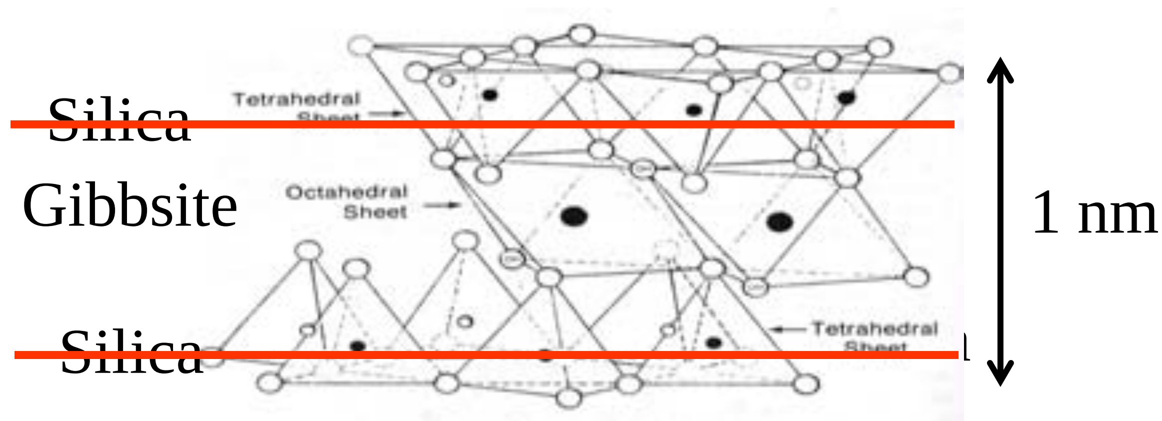


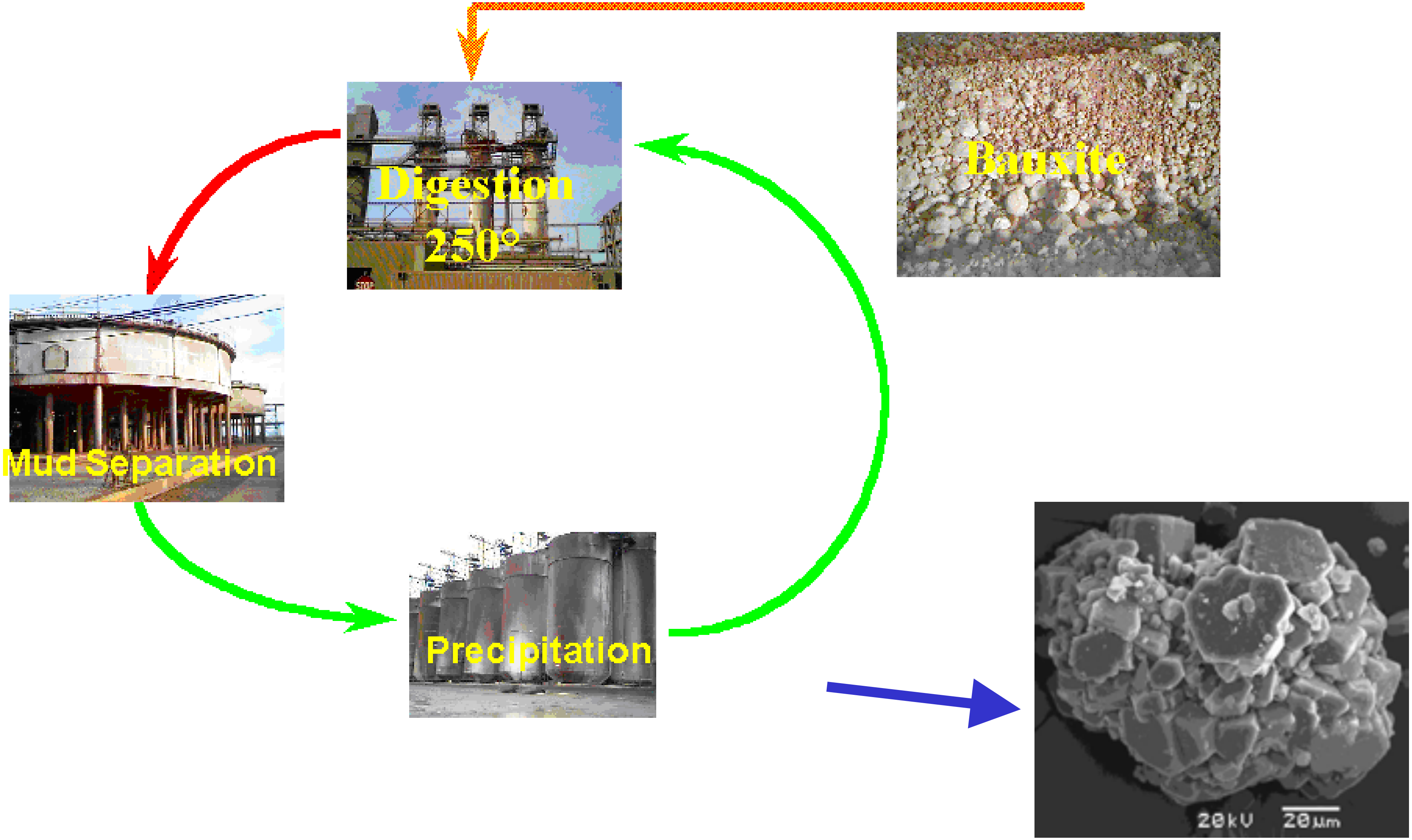
cut sphere

$$\rho^* = \frac{\phi}{\phi_{CP}}$$

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


$Al(OH)_3$


Silica
Tetrahedral
Gibbsite
Octahedral Sheet
Silica
Tetrahedral
1 nm



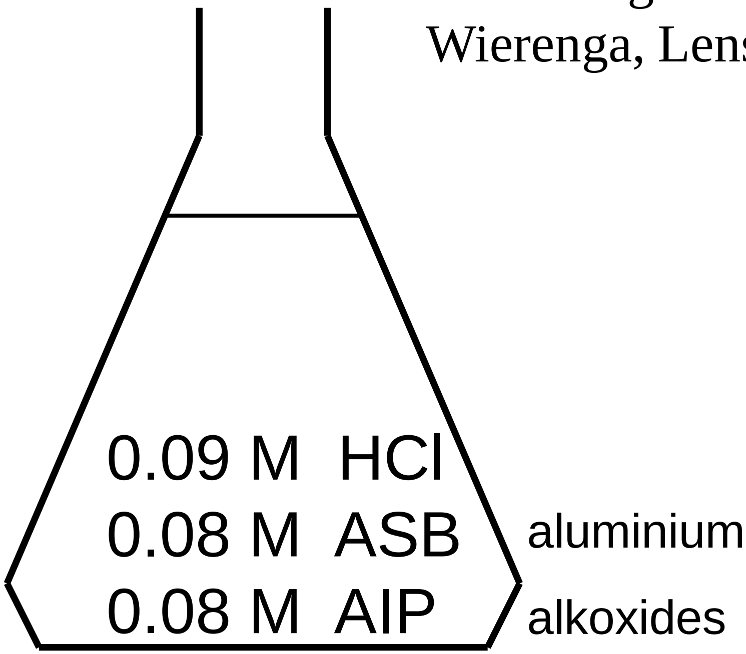
Gibbsite Production

50,000,000 tons/year!

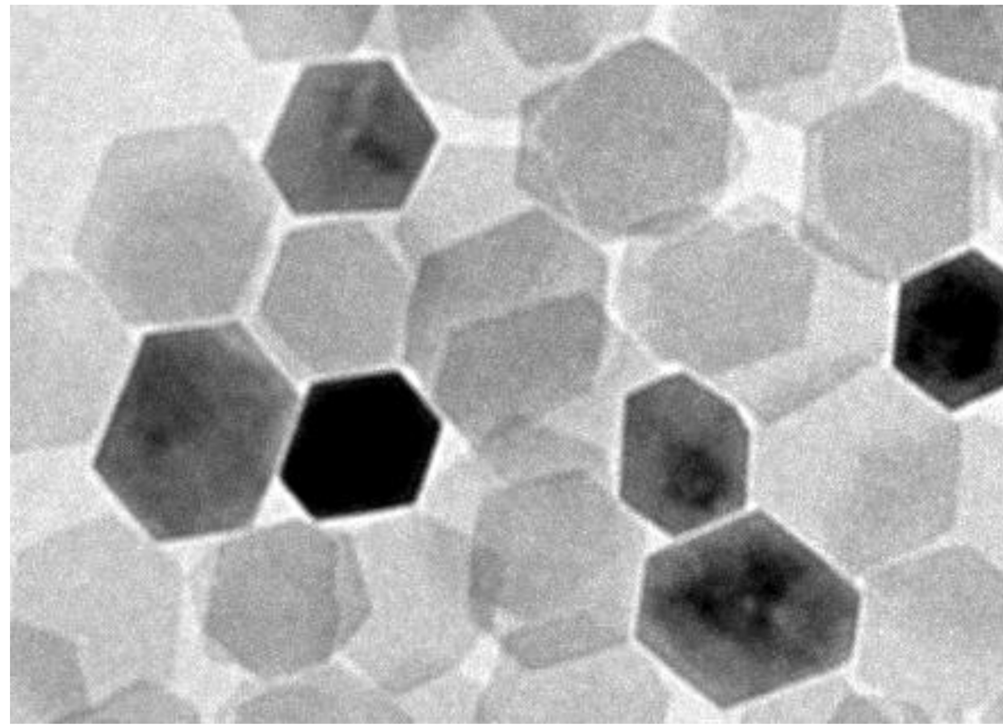
Gibbsite crystals
1 – 100 µm

Van’t Hoff Colloidal Gibbsite

Buining et al. J. Am. Ceram. Soc. 1991
Wierenga, Lenstra, Philipse Coll. Surf. 1998



- **10 days of stirring**
- **3 days at 85°C**
- **10 days of dialysis**



diameter: tunable from 100-500 nm
thickness: 10-50 nm
polydispersity 10-20%
0.0005 tons/year

Praise from the Press for Van't Hoff Gibbsite

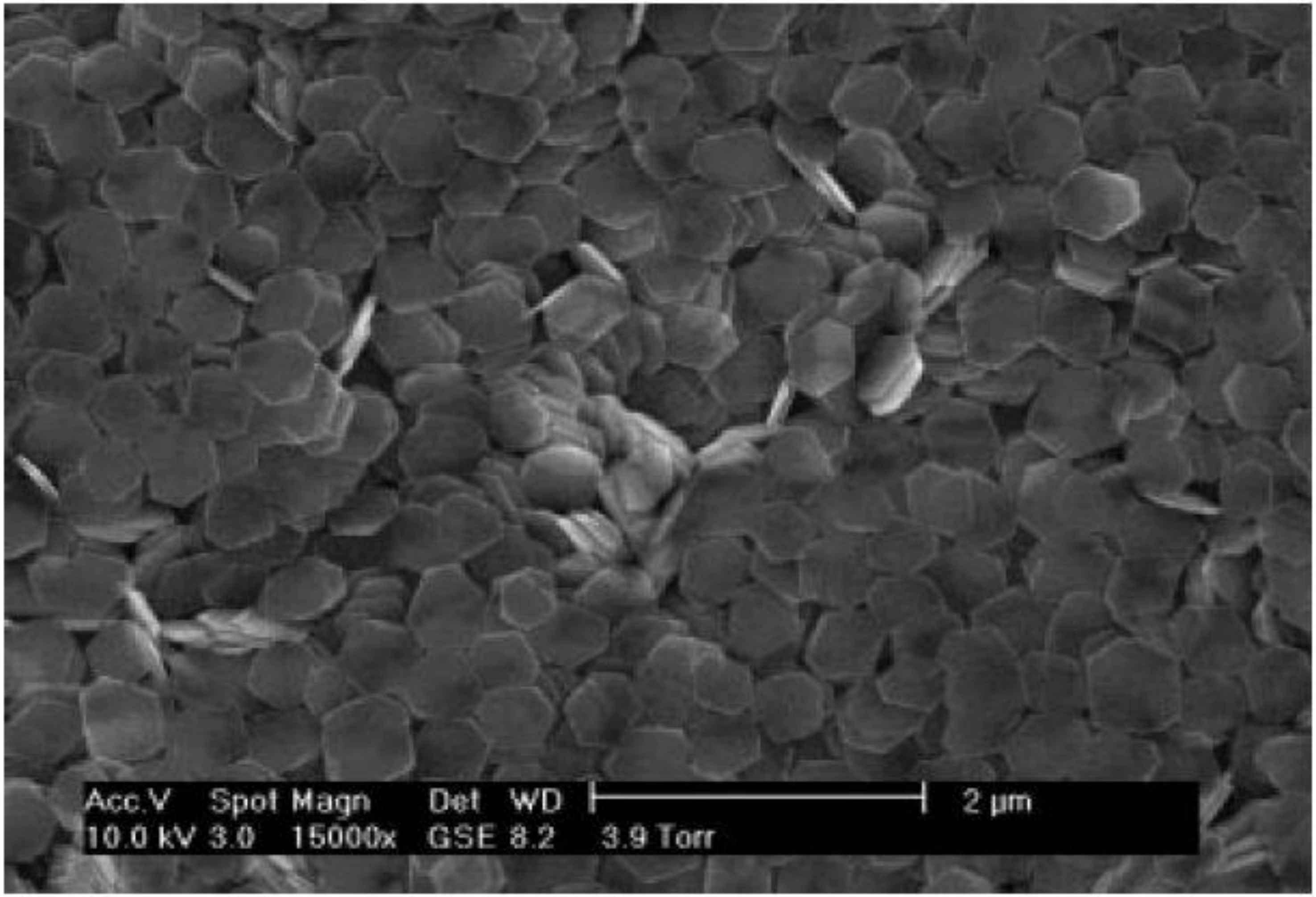
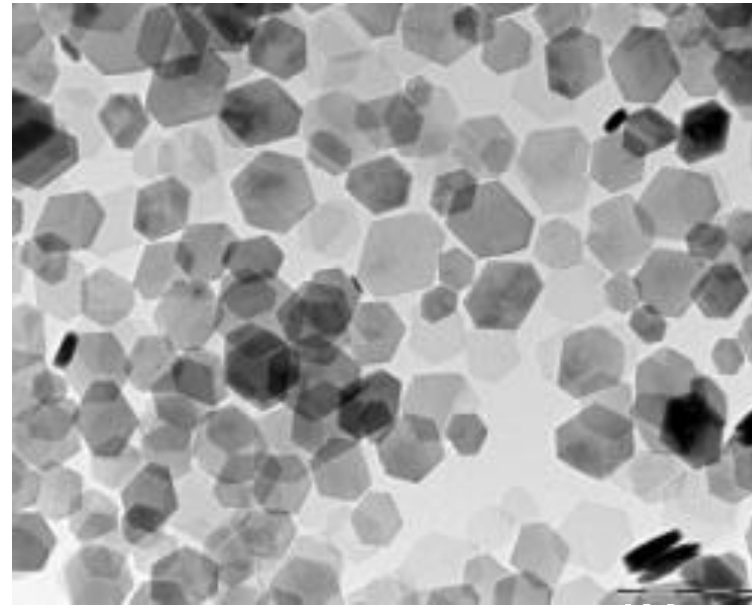
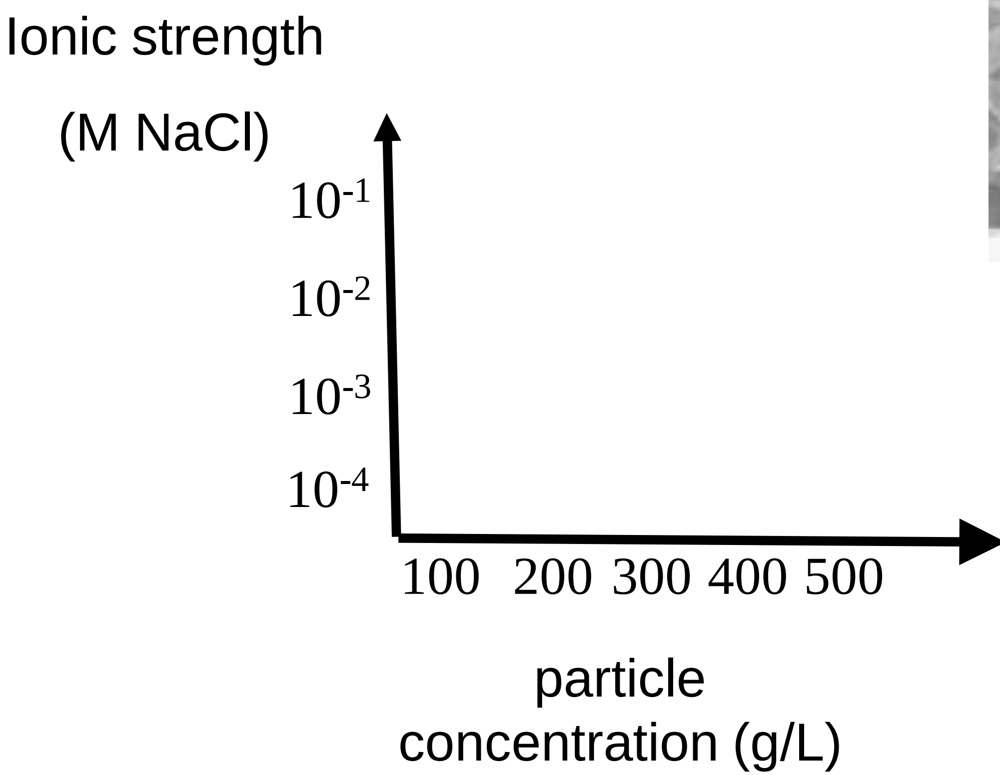


Fig 2. Gibbsite sample imaged after *in situ* drying in the ESEM. The larger, thicker individual plates are easily resolved making this an ideal candidate for further ESEM study.

Heather Houghton&Athene Donald 2008

Gibbsite suspensions

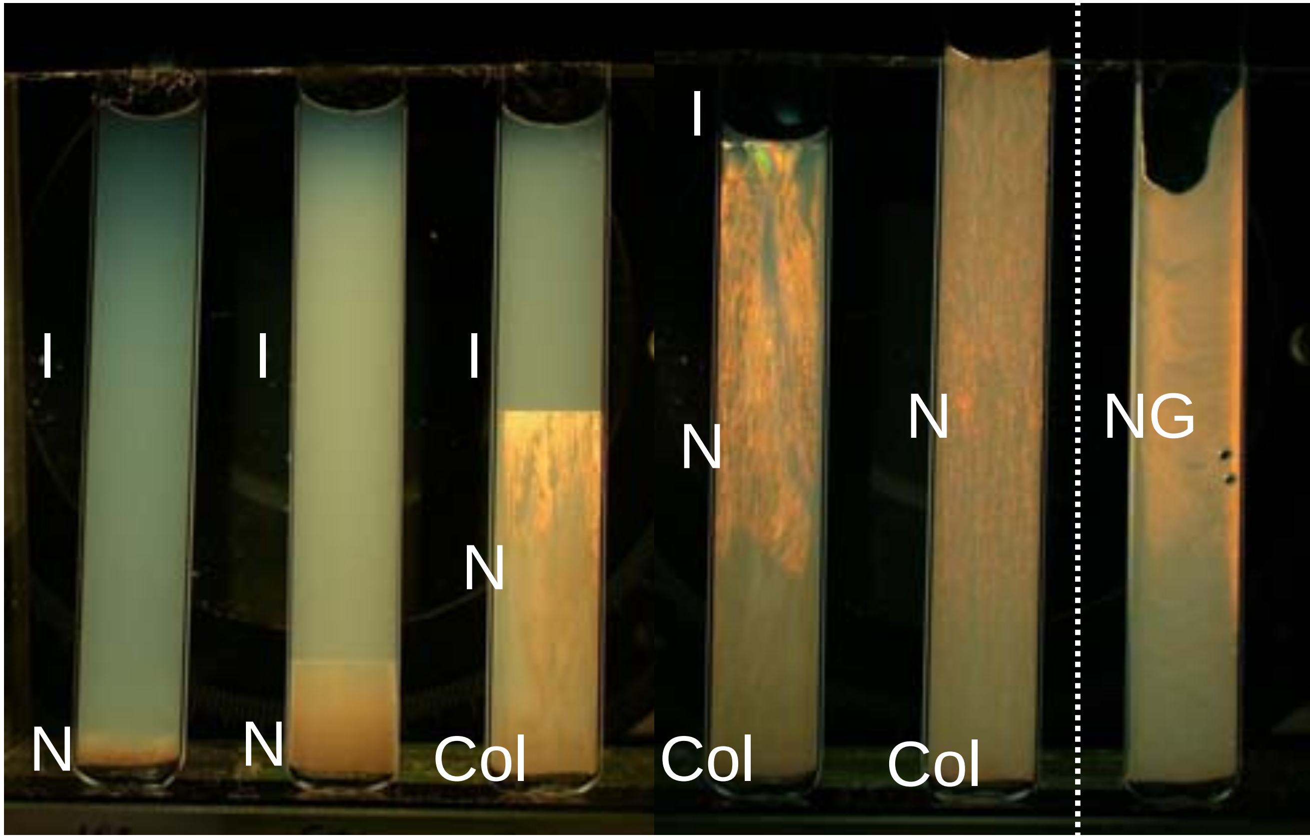


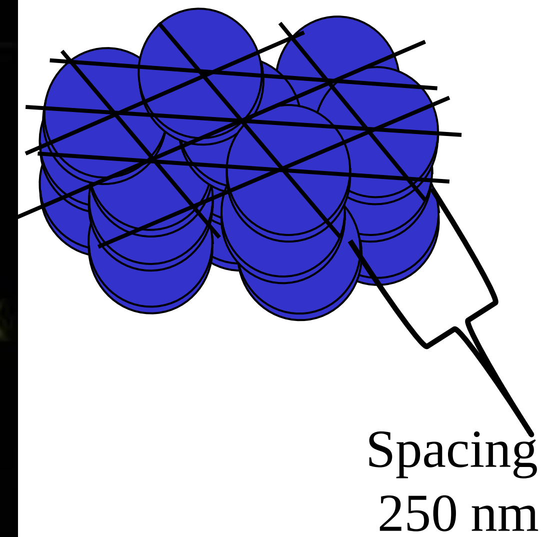


-D. van der Beek and H.N.W. Lekkerkerker, Langmuir 20 (2004) 8582-8586
-J.E.G.J. Wijnhoven, D.D. van 't Zand, D. van der Beek and H.N.W. Lekkerkerker,
Langmuir 21 (2005) 10422-10427
-M. C. D. Mourad, J. E. G. J. Wijnhoven, D. D. Van 't Zand, D. van der Beek and H. N. W. Lekkerkerker,
Phil. Trans. R. Soc. A 364 (2006) 2807-2816

2 Months after Homogenization

10^{-4} M NaCl



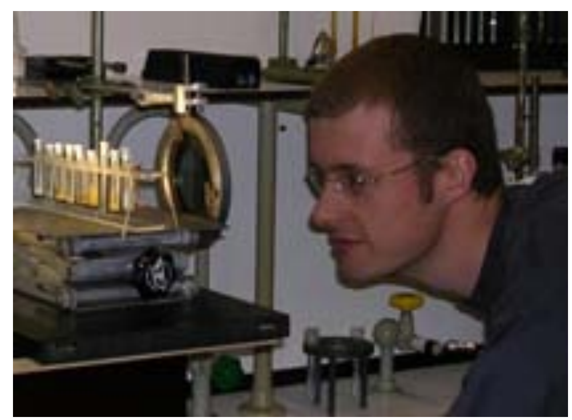


100 200 250 300 350 400 g/L

I = Isotropic N = Nematic Col = Columnar NG = Nematic Gel

Crossed Polarizers

hexagonal lattice with spacing *d* ~ 250 nm gives rise to Bragg reflections in the visible light



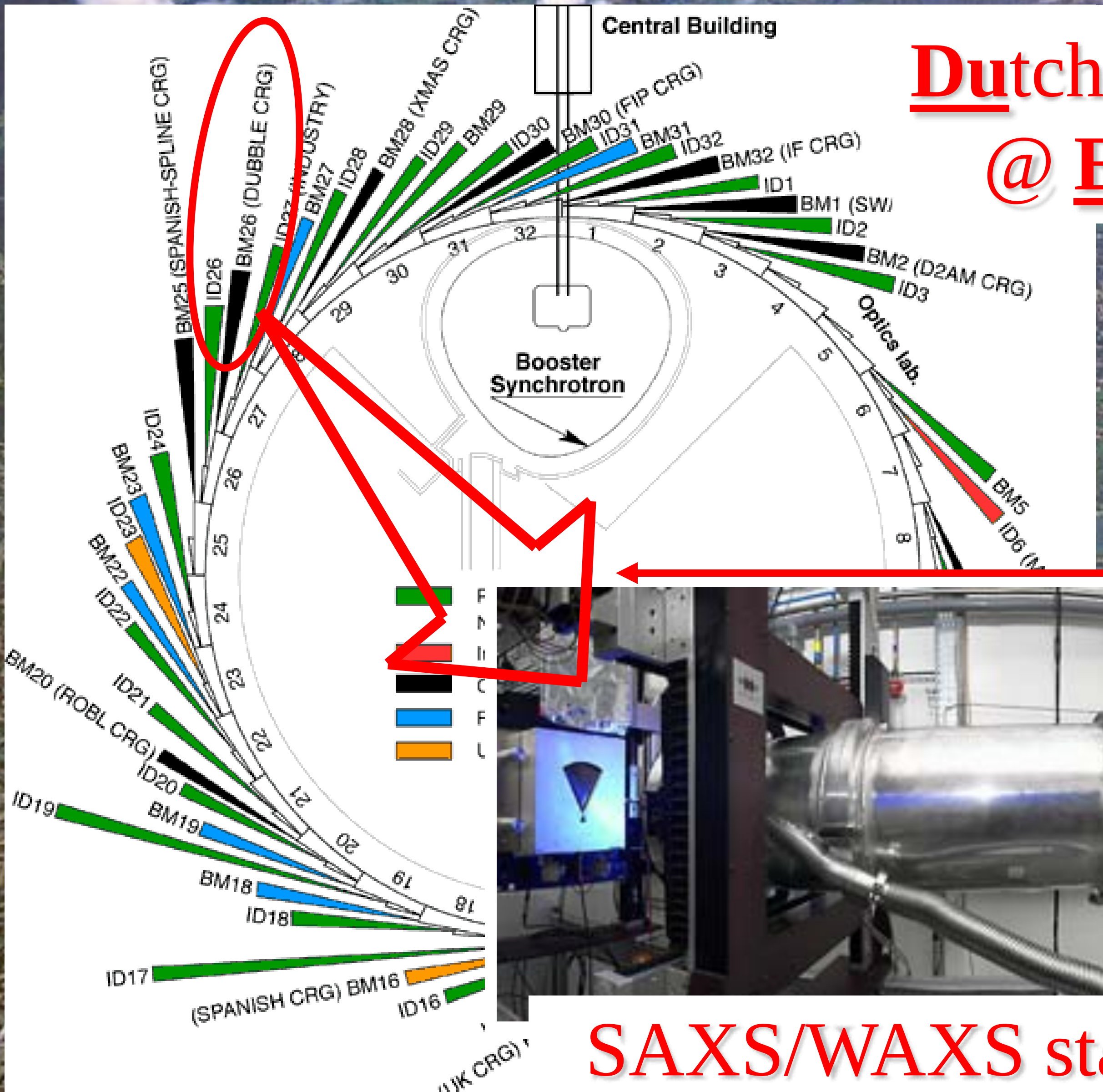
D. van der Beek & HNWL, *Langmuir* (2004)

….to big science

270 m!

European Synchrotron Radiation Facility, Grenoble

European **S**ynchrotron **R**adiation **F**acility (ESRF)

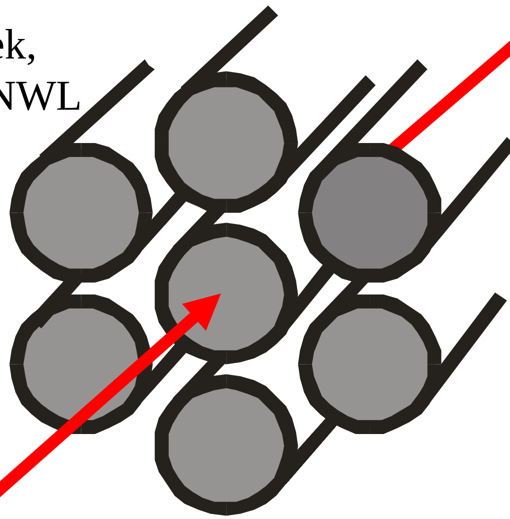


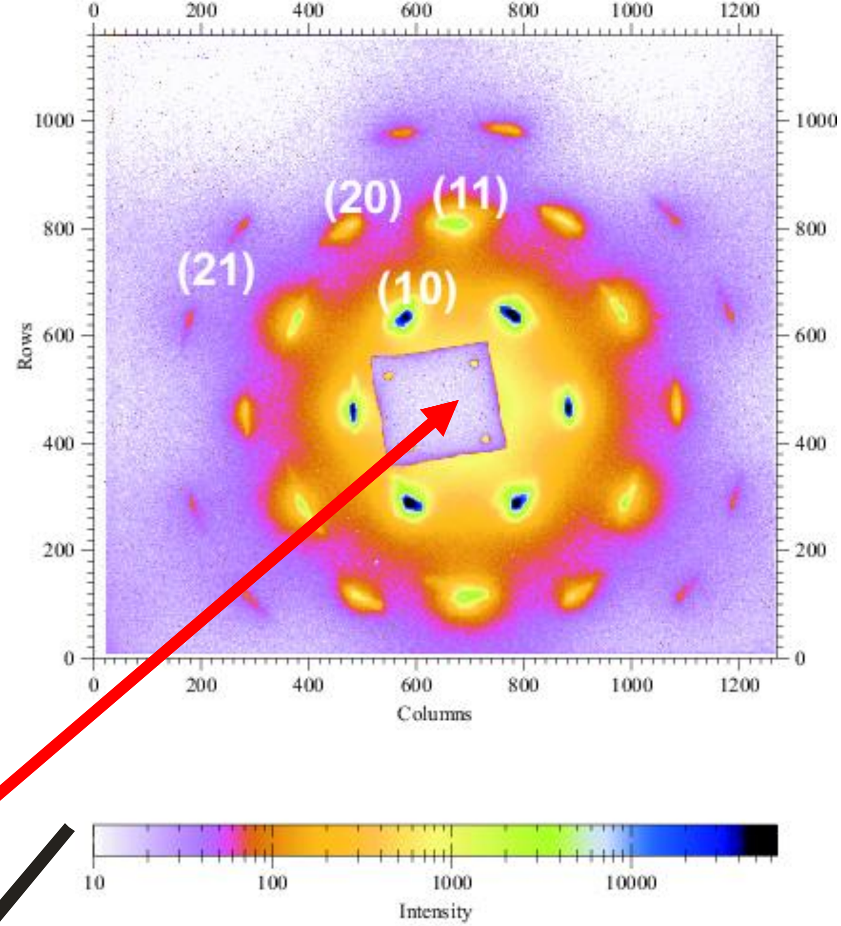
Dutch-**B**elgian **B**eam**L**ine @ **E**SRF (DUBBLE)

SAXS/WAXS station of DUBBLE

Columnar crystal: Hexagonal arrangement of columns

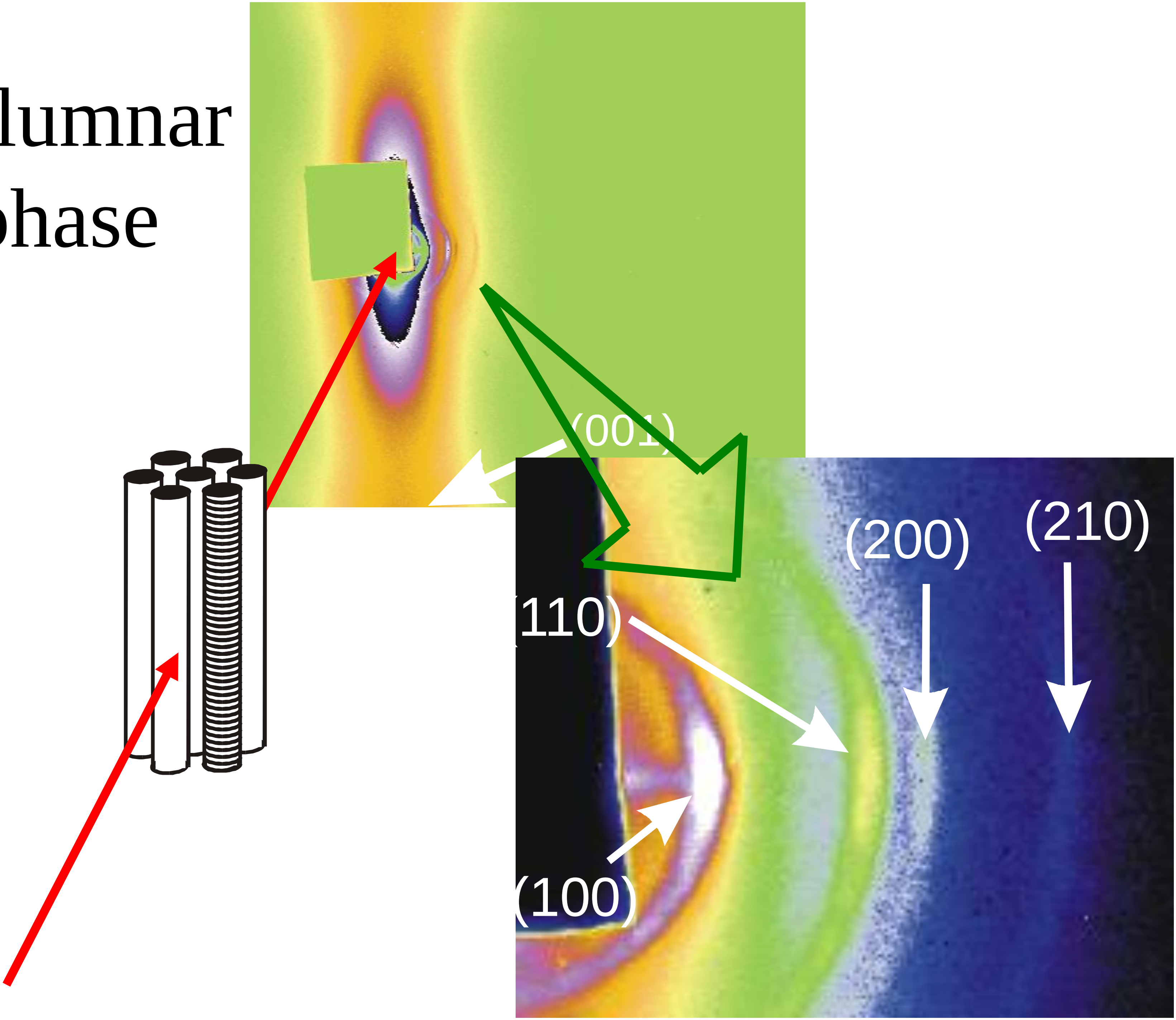
Petukhov, van der Beek, Oversteegen, Vroege, HNWL





DUBBLE @ ESRF

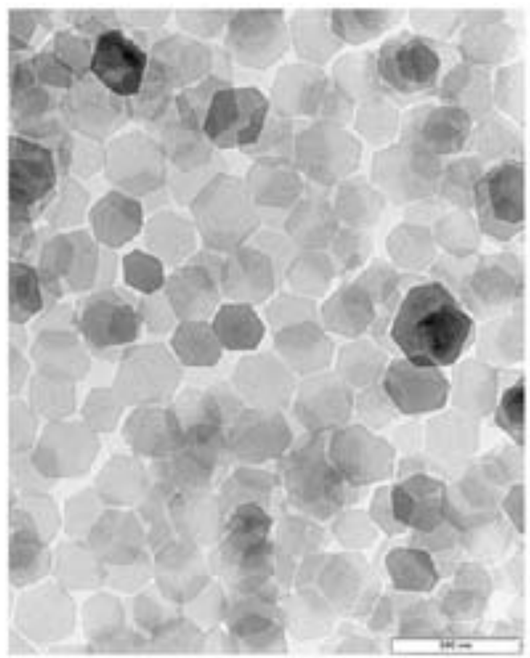
Columnar phase

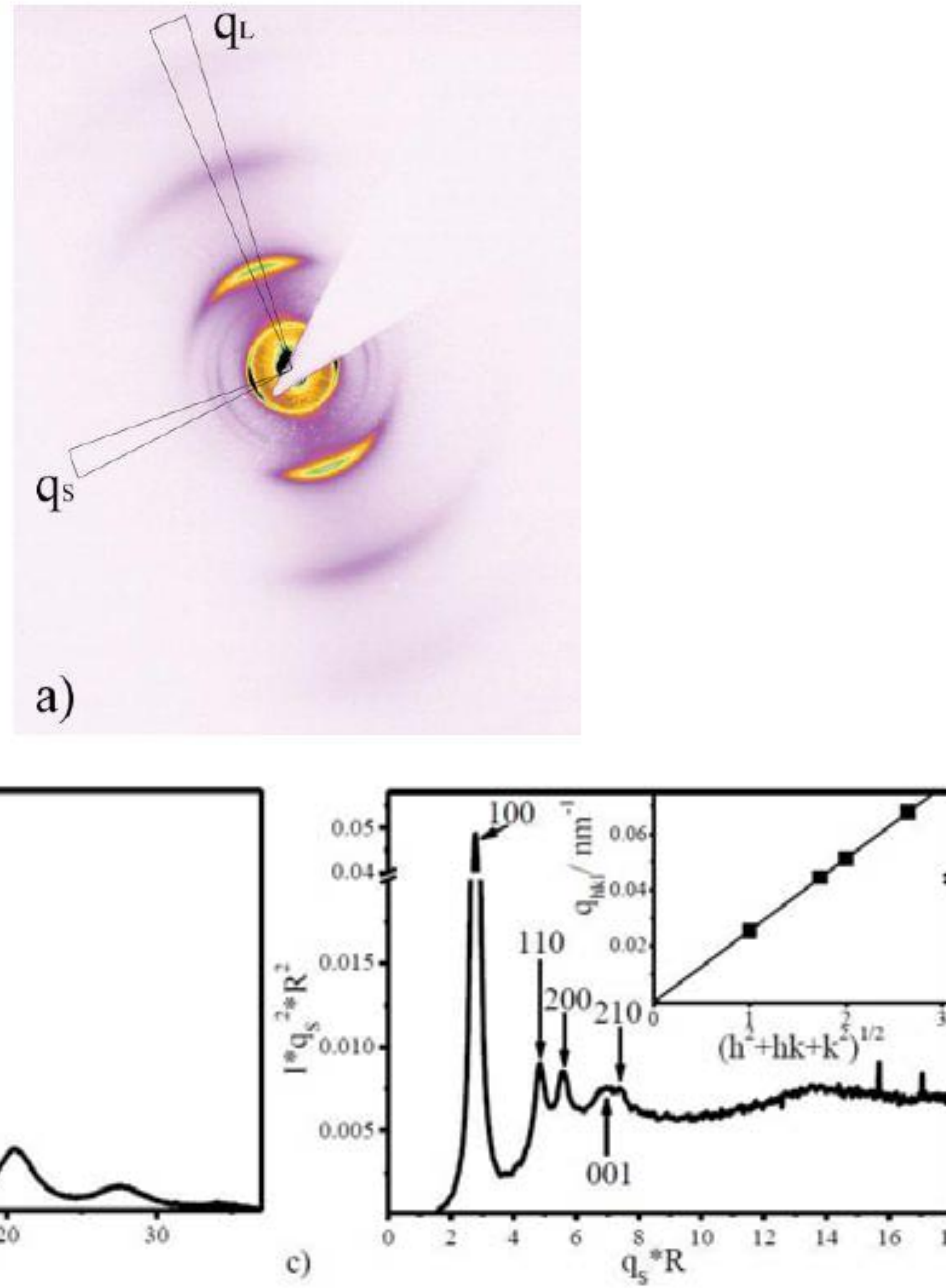


Latest News (JACS 2012)
Dzina Kleshchanok from Utrecht discovers the elusive colloidal Smectic B phase in a suspension of Gibbsite in DMSO

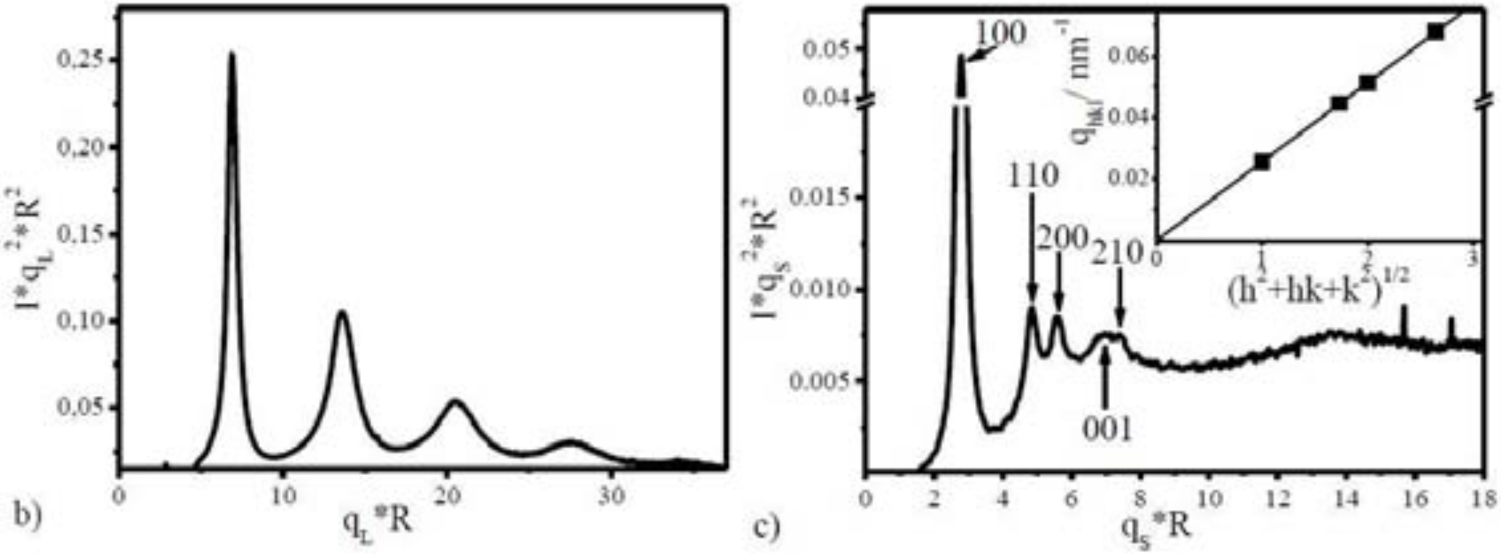
Table 1. Characteristic sizes of gibbsite platelets as determined from TEM and AFM.

	$\langle D \rangle$/ nm	σ_D/ nm	PDI_D/ %	$\langle L \rangle$/ nm	σ_L/ nm	PDI_L/ %
Gibbsite	218.4	34.5	15.8	7.9	2.0	24.8

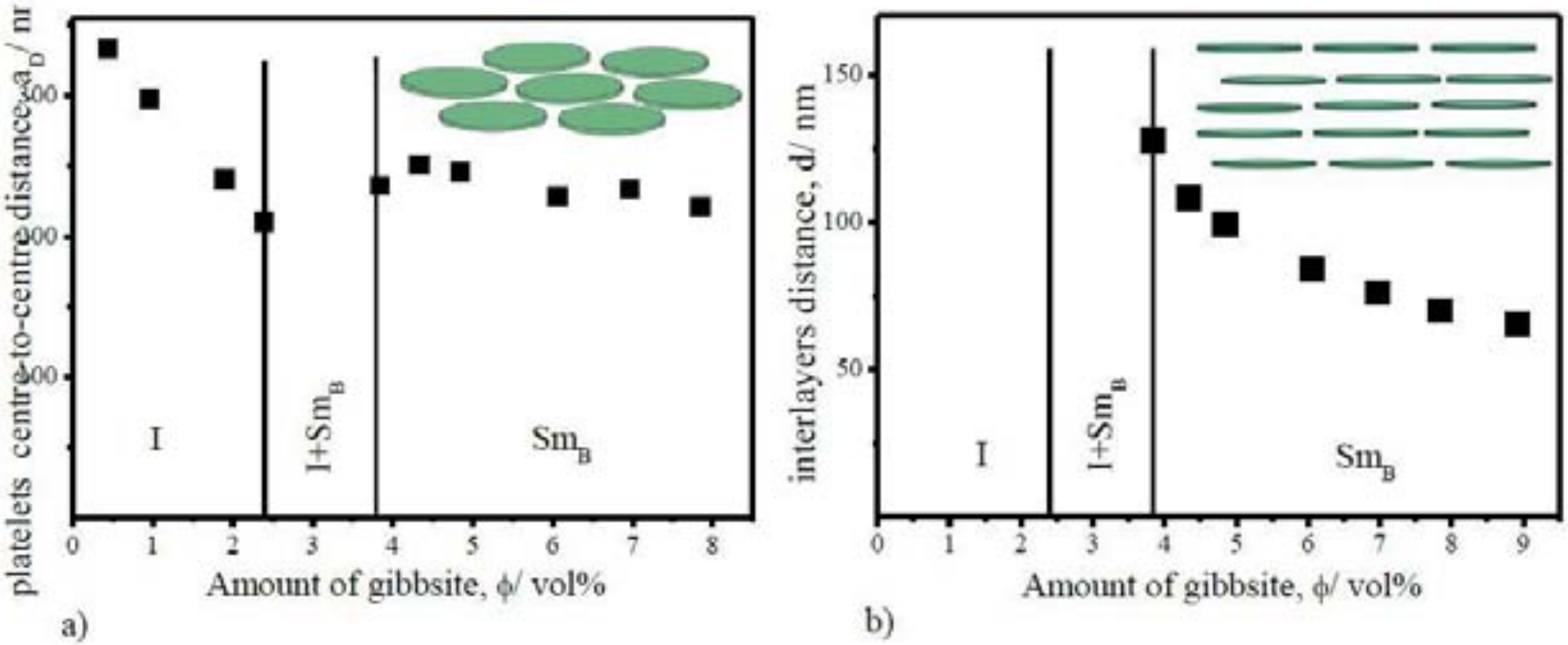




q L
q S
a)
0,25
0,20
0,15
0,10
0,05
I*q L 2*R 2
0
10
20
30
b)
q L *R
0.05
0.04
0.015
0.010
0.005
I*q S 2*R 2
100
110
200
210
001
q hkl / nm -1
0.06
0.04
0.02
(h 2+hk+k 2) 1/2
0
2
4
6
8
10
12
14
16
18
c)
q S *R



b)
$I*q_L^2*R^2$
q_L*R
0,25
0,20
0,15
0,10
0,05
0
10
20
30
c)
$I*q_S^2*R^2$
q_S*R
0.05
0.04
0.015
0.010
0.005
0
2
4
6
8
10
12
14
16
18
100
110
200
210
001
q_{hkl} / nm^{-1}
$(h^2+hk+k^2)^{1/2}$
0.06
0.04
0.02
0
1
2
3

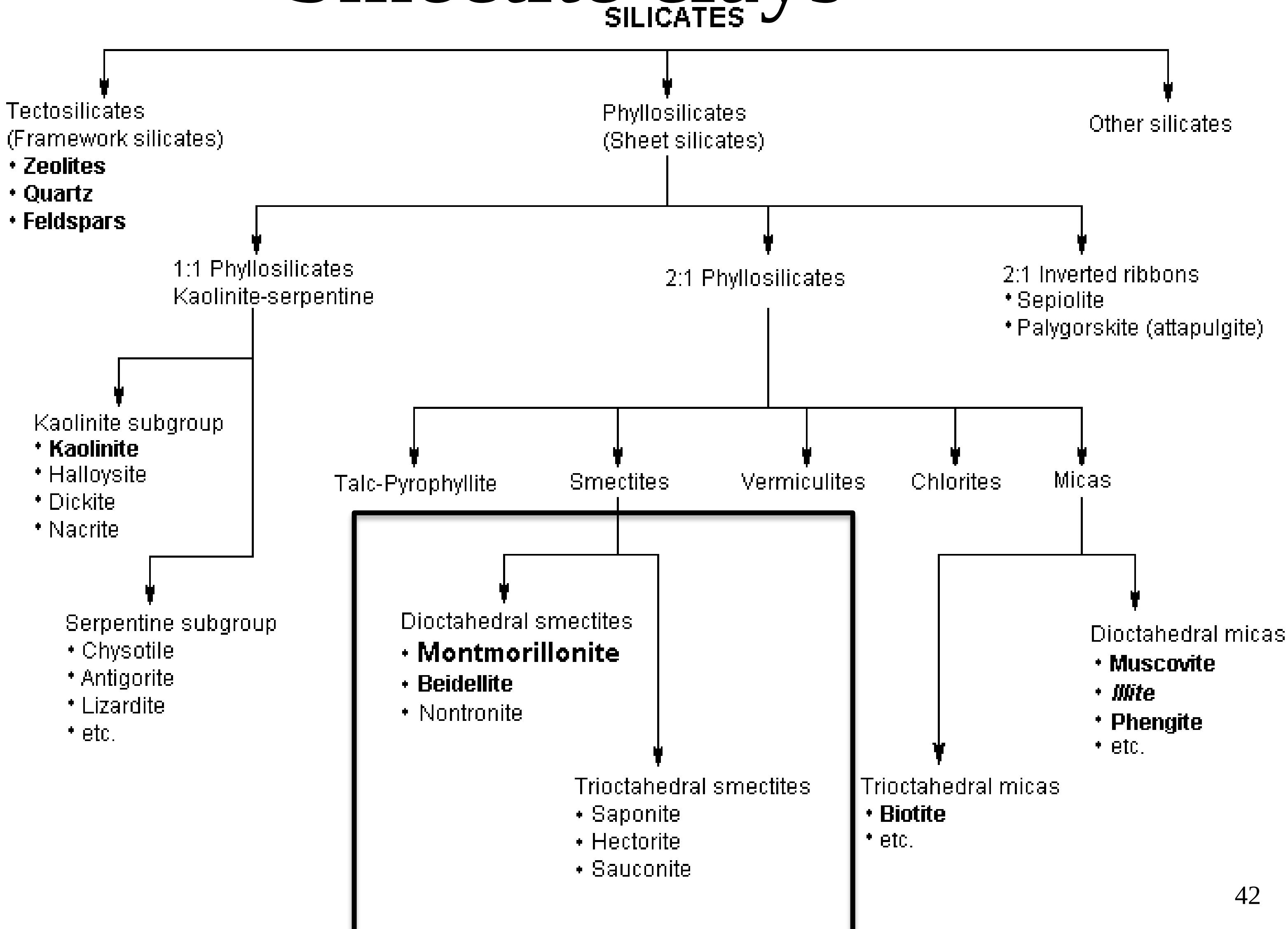


a)
platelets centre-to-centre distance, a_D / nm
Amount of gibbsite, φ/ vol%
0
1
2
3
4
5
6
7
8
I
I+Sm_B
Sm_B
b)
interlayers distance, d/ nm
Amount of gibbsite, φ/ vol%
150
100
50
0
1
2
3
4
5
6
7
8
9
I
I+Sm_B
Sm_B

Menu

- Tuesday 1 May 1990:A visit with serious consequences
- Clay and Liquid Crystals:The disappointment
- Gibbsite :Less is more
- **Clay 2.0 Liquid Crystals :New hope**
- Some final comments

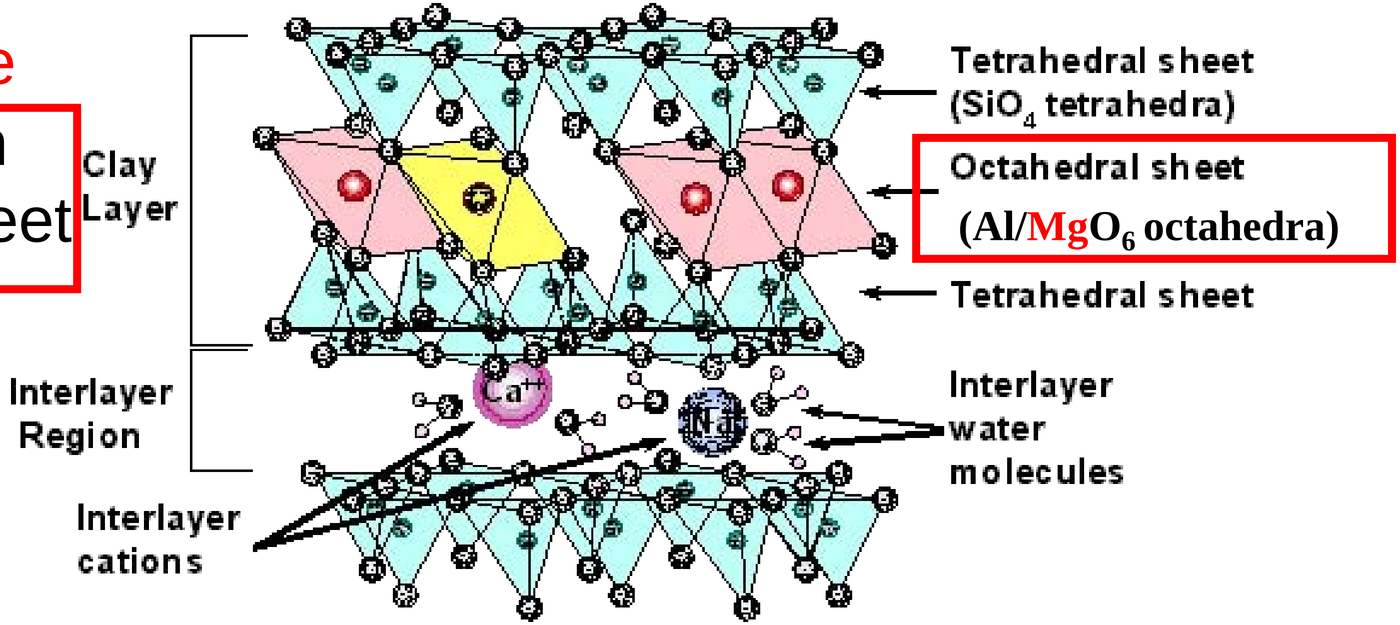
Smectite clays



What is the difference between Montmorillonite and Beidellite?

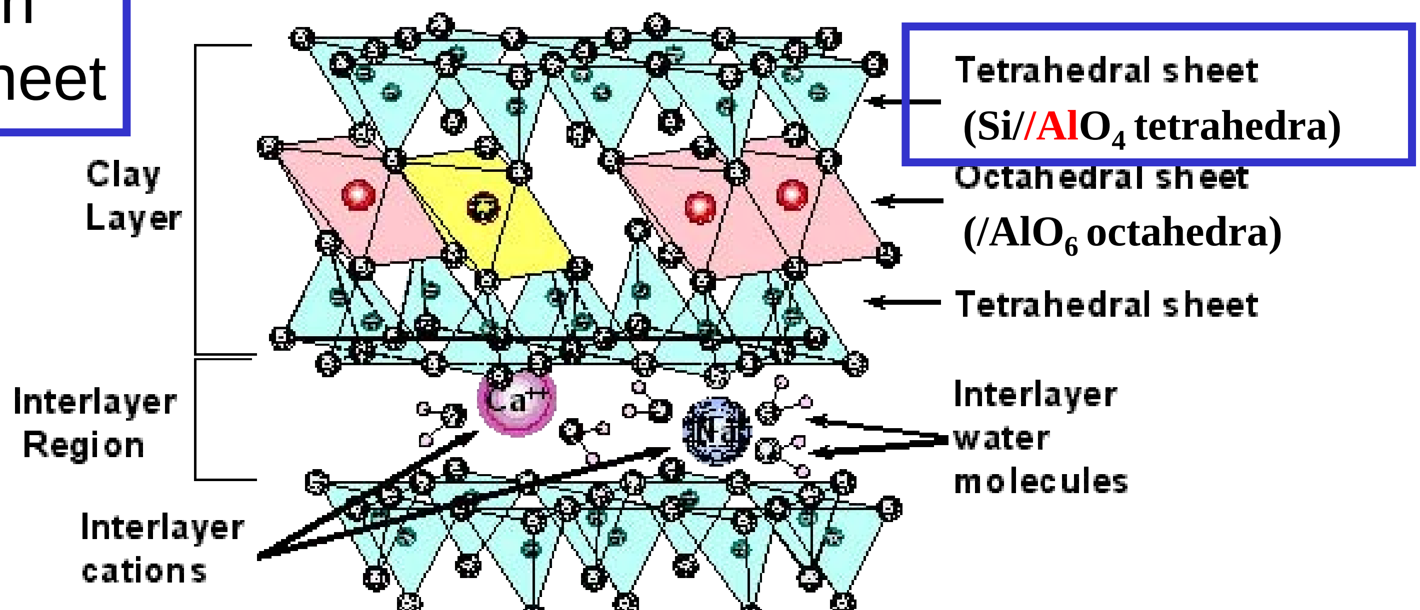
Montmorillonite

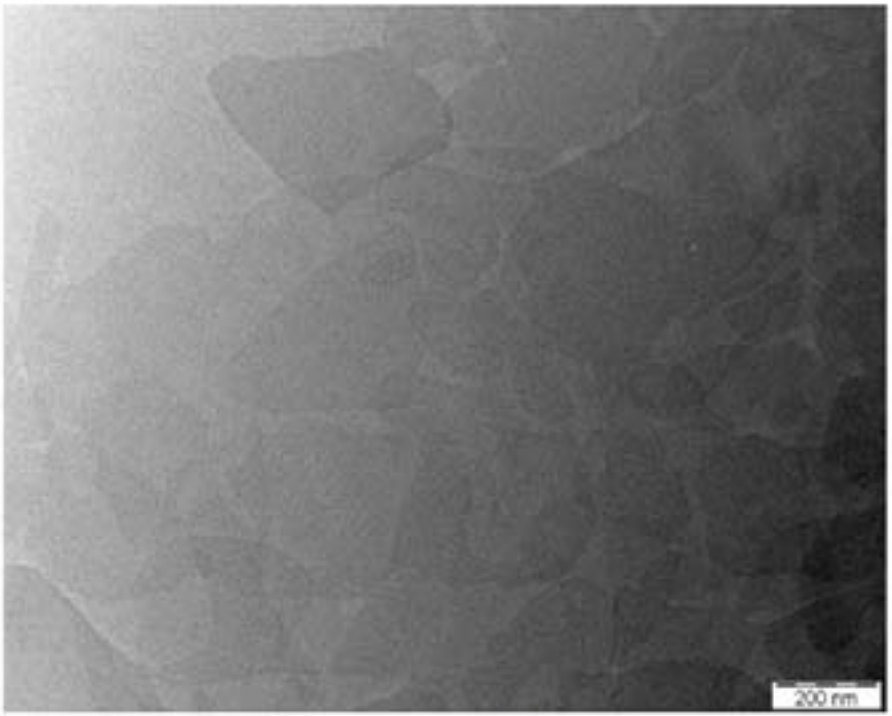
Substitutions in Octahedral Sheet



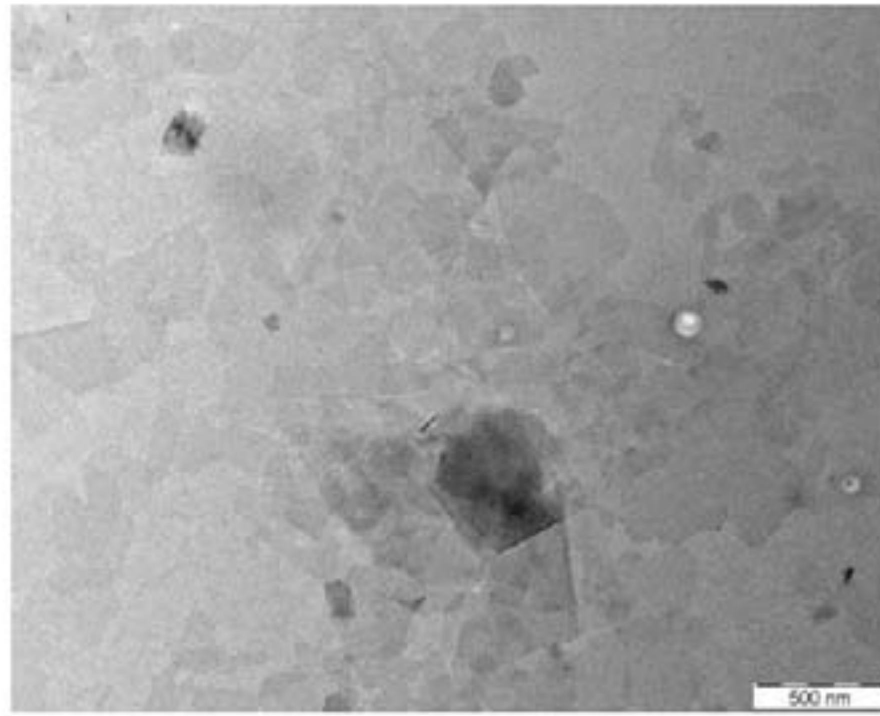
Beidellite

Substitutions in Tetrahedral Sheet





(a) TEM-micrograph of Beidellite (size c)

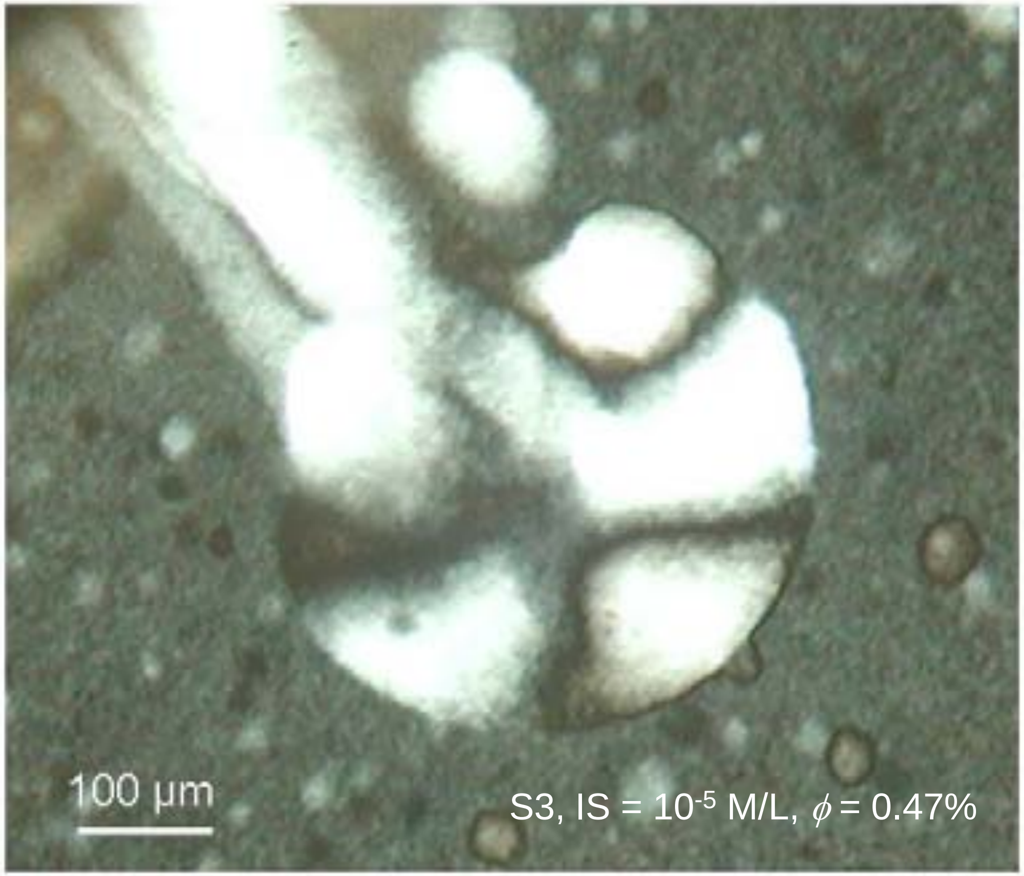


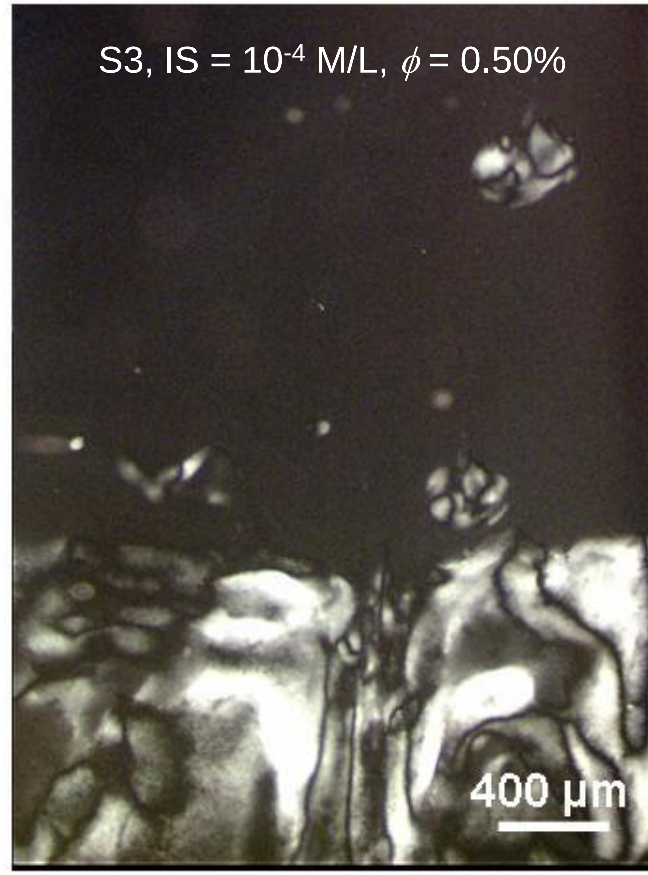
(b) TEM-micrograph of Montmorillonite

Figure 3.2: TEM micrographs of Montmorillonite and Beidellite

Mesophases in beidellite suspensions

- **Microscopical observations**

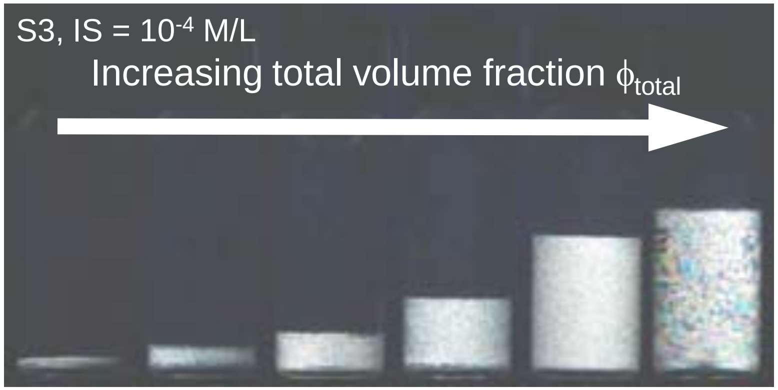


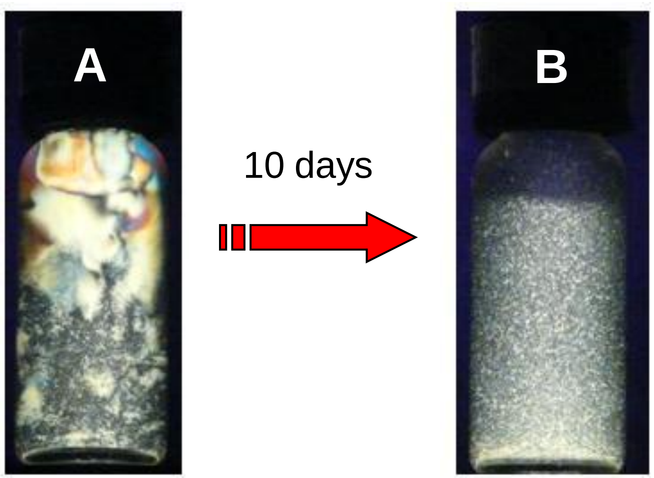


Tactoids nucleation following by phase separation process

Mesophases in beidellite suspensions

- **Macroscopical observations**



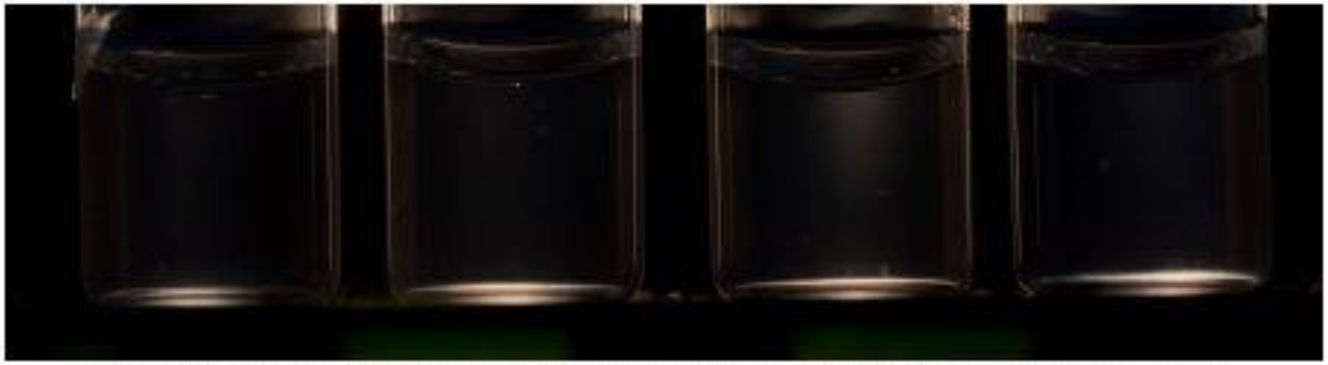


S3, IS = 10^{-5} M/L, ϕ = 0.47%

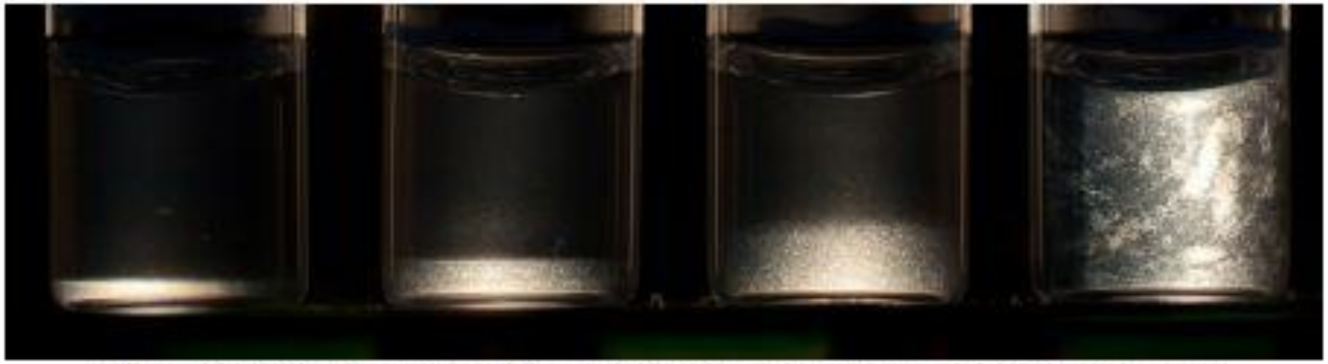
- formation of nematic droplets

- increase of ϕ_N with ϕ_{total}

⇨ **First I/N phase transition**



(a) Volume fractions of Beidellite are a) $\phi_{clay} = 0.33\%$; b) $\phi_{clay} = 0.35\%$; c) $\phi_{clay} = 0.37\%$; and d) $\phi_s = 0.39\%$



(b) Volume fractions of Beidellite are a) $\phi_{clay} = 0.41\%$; b) $\phi_{clay} = 0.42\%$; c) $\phi_{clay} = 0.44\%$; and d) $\phi_s = 0.46\%$.

(c) Volume fractions of Beidellite are a) $\phi_{clay} = 0.47\%$; b) $\phi_{clay} = 0.48\%$; c) $\phi_{clay} = 0.50\%$; and d) $\phi_s = 0.51\%$

Figure 6.3: Beidellite (size c) suspensions one month after preparation, observed between crossed polarisers

Jasper Landman Bachelor thesis UU 2011

Menu

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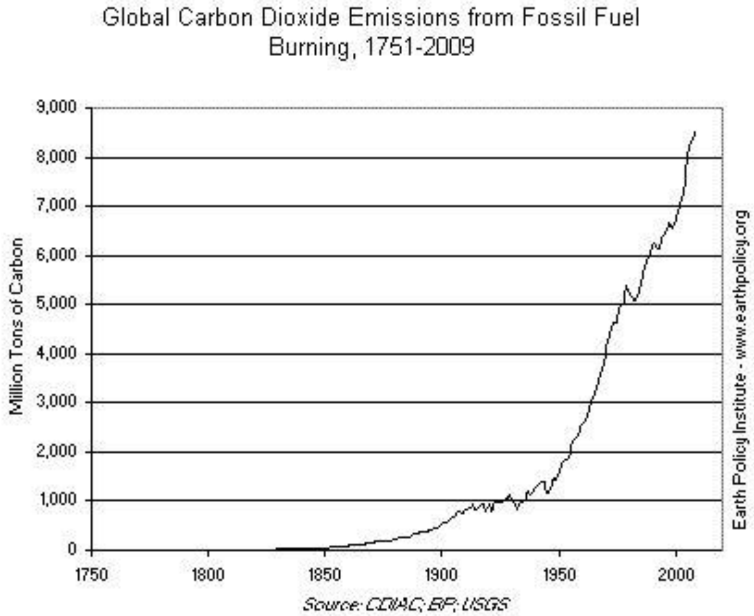
1 Clays mysterious and sometimes beautiful

2 Much more to be discovered !
Progress will be slow because
clays are nasty and will only reveal
their secrets to those who take them serious

Professor **Geoff Maitland** was cited for his distinguished research measuring and simulating polymeric fluid flows, in recognition of the benefits that this has brought to the oilfield and general drilling industry. He joined Imperial in September 2005 after 20 years working with Schlumberger in the oil and gas sector.

As Professor of Energy Engineering, he is looking at ways to mitigate the environmental impact of fossil fuels and manage the transition to alternative energies. He is also looking at ways to exploit unconventional sources of hydrocarbons and to recover existing hydrocarbons more efficiently.


Global Carbon Dioxide Emissions from Fossil Fuel Burning, 1751-2009
9,000
8,000
7,000
6,000
5,000
4,000
3,000
2,000
1,000
0
Million Tons of Carbon
1750
1800
1850
1900
1950
2000
Source: CDIAC; BP; USGS
Earth Policy Institute - www.earthpolicy.org


proof of
global warming
1720
1900
1950
1970
1980
1990
2006

2006 2012 2022 2032 2042 2062 2112

Thank you for your attention