Colloidal crystals studied with SAXS

Condensed matter physics of elephants

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Schedule

Part I

- Introduction to nanoelephants
- Instrumentation
- Example 1: Hard spheres

Part II

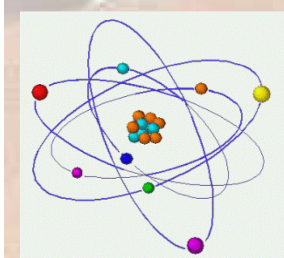
- Example 2: Rusted nanonails
- Conclusion

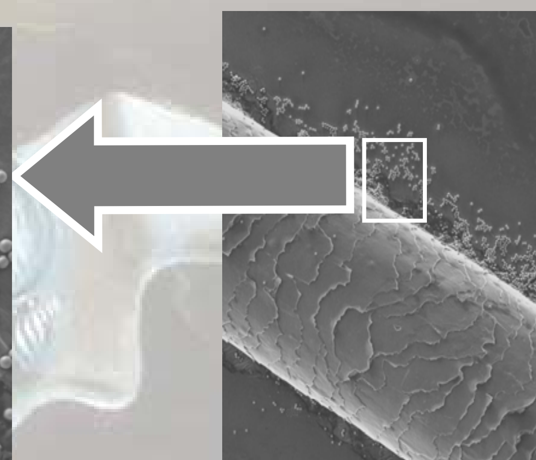
What is colloid?

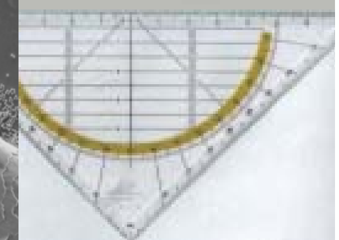
International Union of Pure and Applied Chemistry

"The term colloidal refers to a state of subdivision, implying that the molecules or polymolecular particles dispersed in a medium have at least in one direction a dimension roughly between 1 nm and 1 µm."

COLLOIDS







1 Å | 1 nm | 10 nm | 100 nm | 1 µm | 10 µm | 100 µm | 1 mm

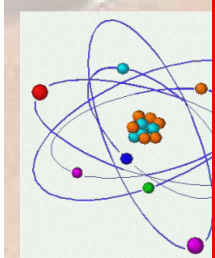
Micro-world

Brownian movers

Macro-world

What is colloid?

“The ... e
mole ... t
least ... ”



Hieronymus Bosch

1 Å | 1 nm | 10 nm | 100 nm | 1 μm | 10 μm | 100 μm | 1 mm

Micro-world

Brownian movers

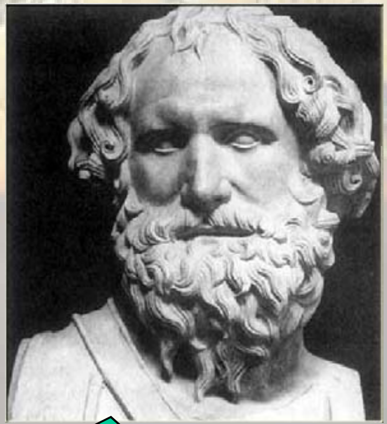
Macro-world

Why < 1 μm?

Or Newton versus Boltzmann

$$\Delta E = m^* g \, \Delta h$$

$$= \Delta\rho V \, g \, \Delta h$$

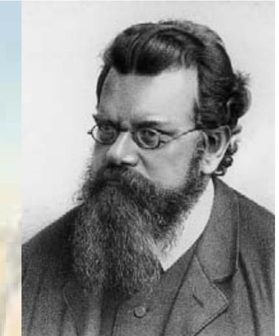


Δh

Thermal energy $k_B T$

$\approx 4\times10^{-21}\ J$ @ $T = 300$ K

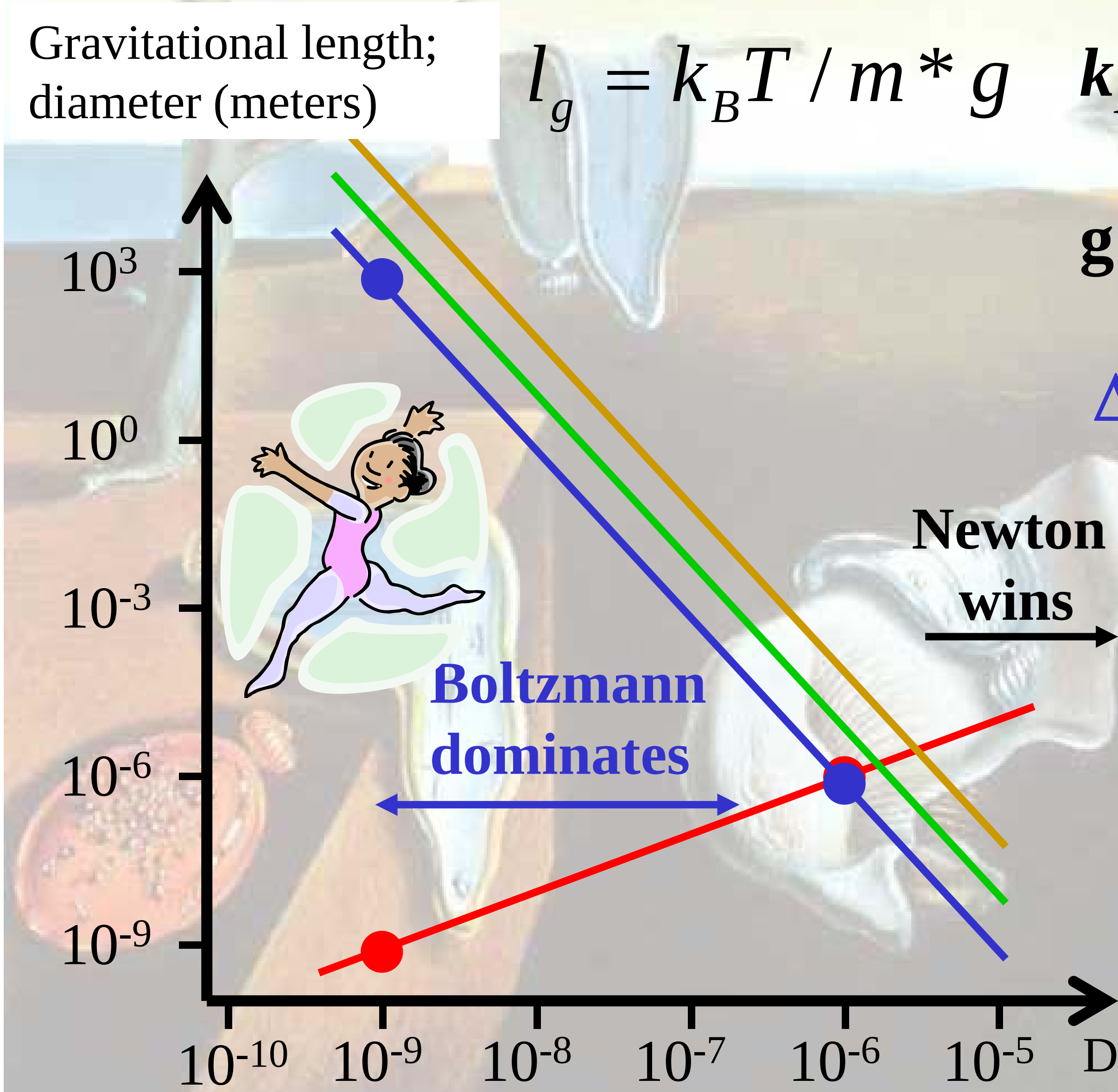
Let us see



$$l_g = k_B T / m^* g$$

$k_B T \approx 4\times10^{-21}$ *J* [@ *T* = 300 K]

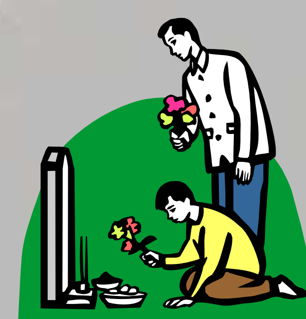
g = 10 m/s^2



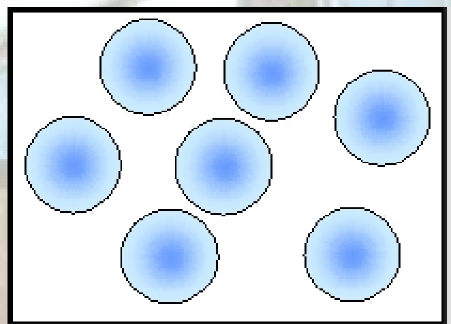
$\Delta\rho$ = 1 g/cm^3

$\Delta\rho$ = 0.1 g/cm^3

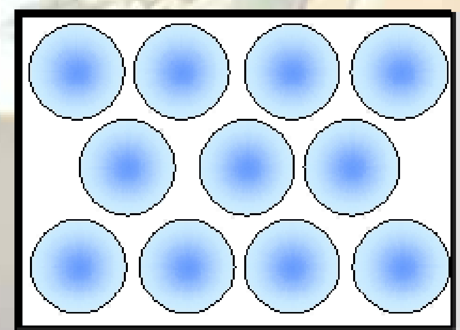
$\Delta\rho$ = 0.01 g/cm^3



Colloid self-assembly: Entropy-induced order



fluid

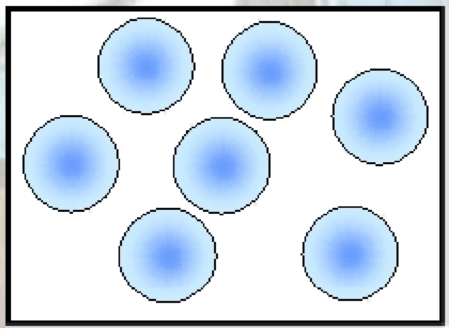


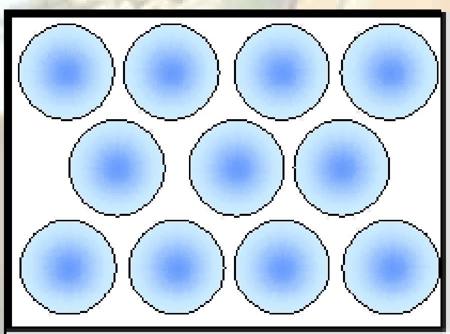
crystal

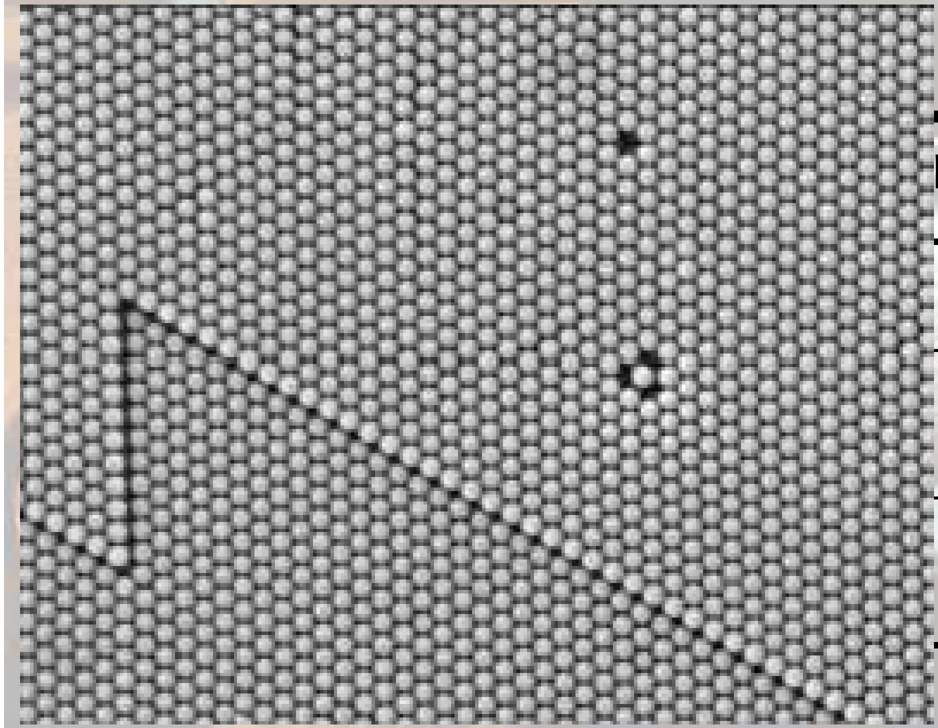
concentration →

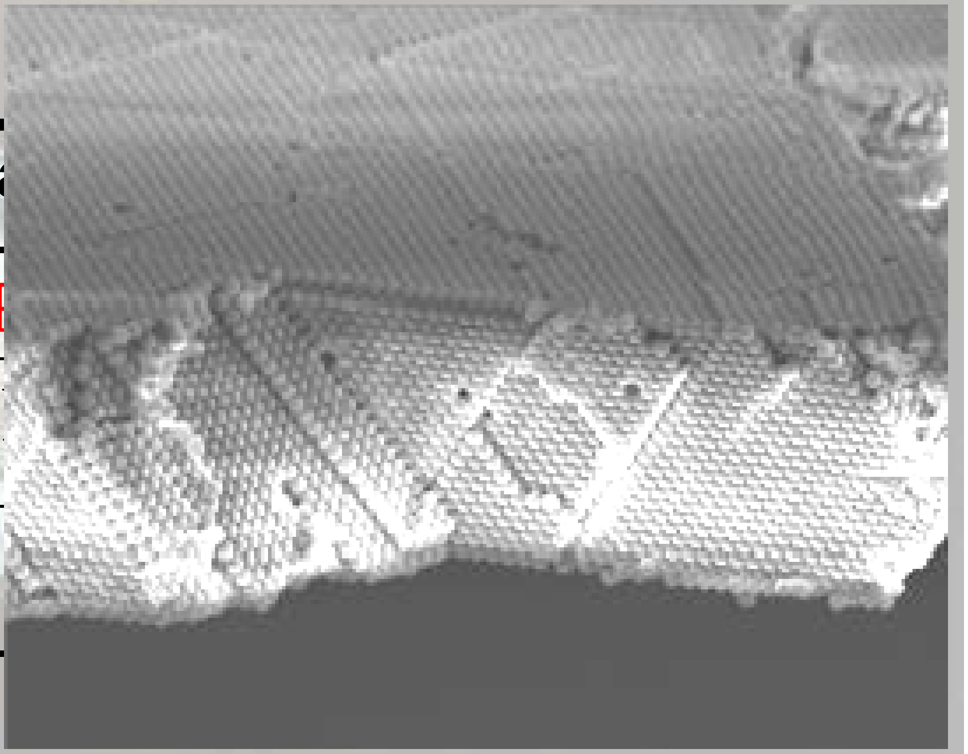
Entropy	Fluid	Crystal
Configurational (macroscopic)	high	low
Excluded volume (microscopic)	low	high

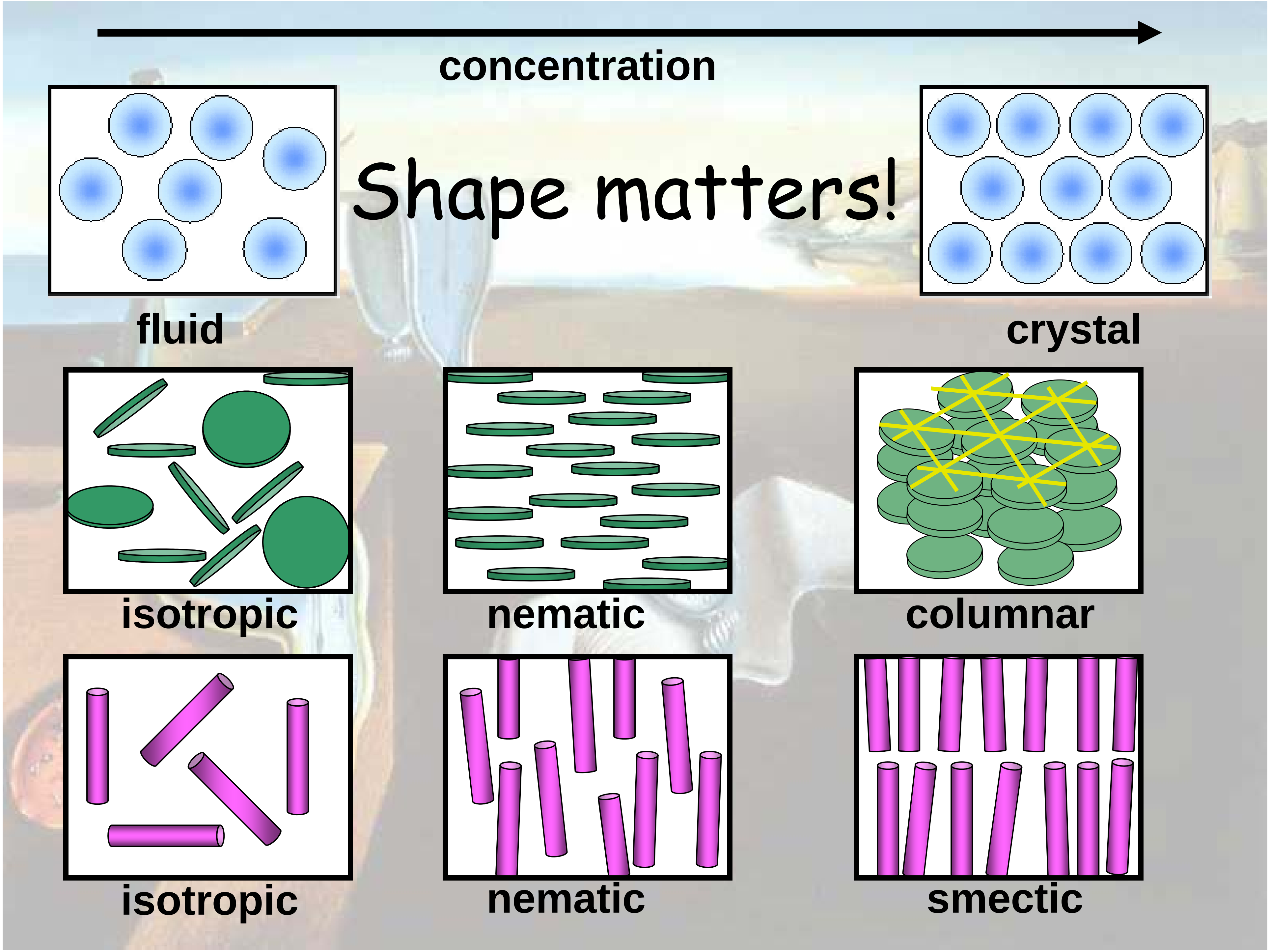
Colloid self-assembly: Entropy-induced order





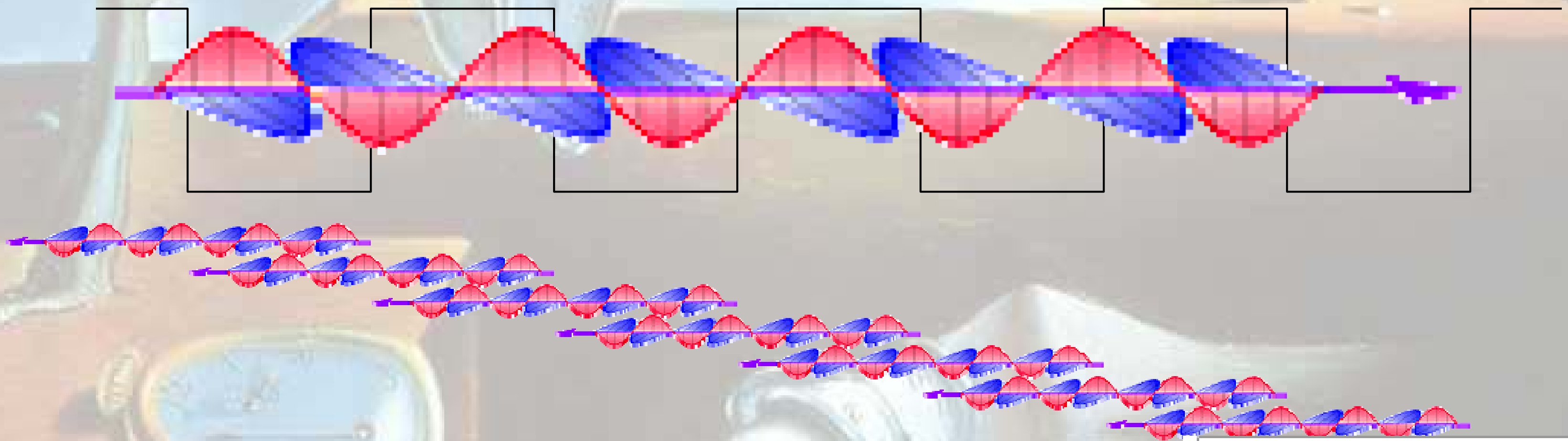





concentration
Shape matters!
fluid
crystal
isotropic
nematic
columnar
isotropic
nematic
smectic

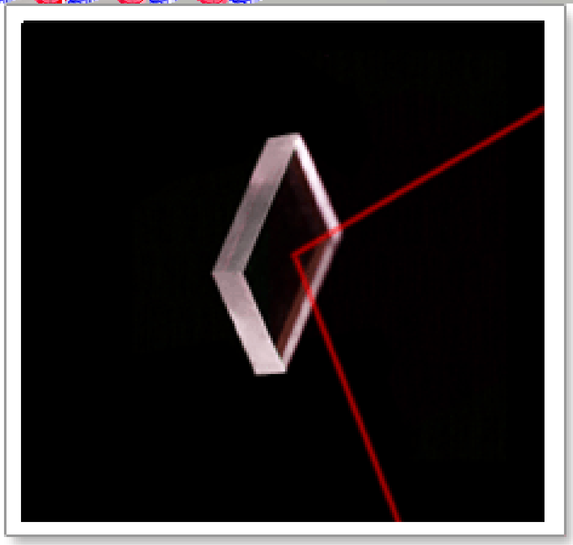
Why is it useful: Photonics

Material with periodic modulation of optical properties on the scale comparable to the wavelength of light (hundreds of nm).



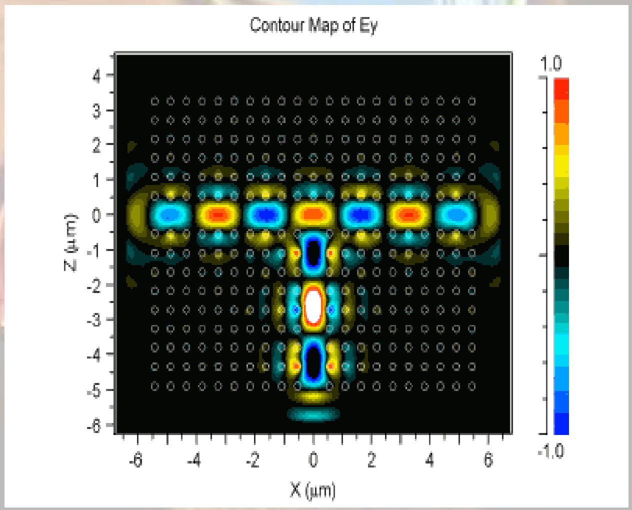
Resonant light scattering will cause photonic band gaps: light with certain wavelength will not be able to propagate through.

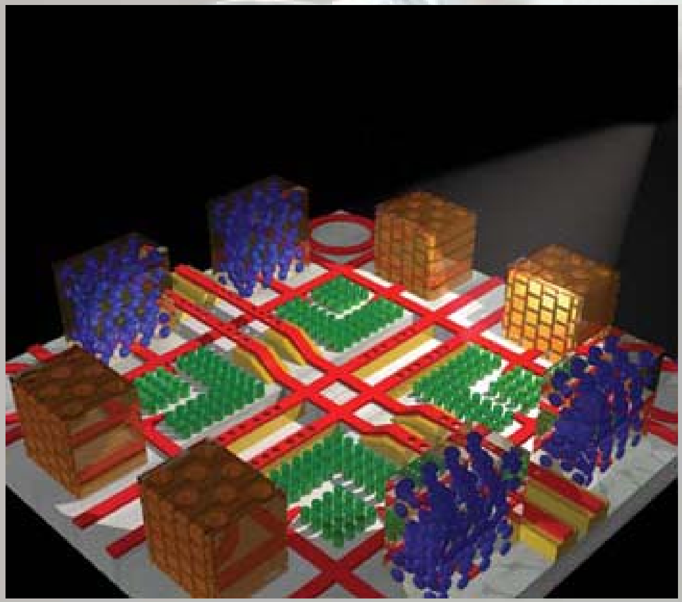
Example of 1D photonic nanomaterial: Dielectric multilayer laser mirrors

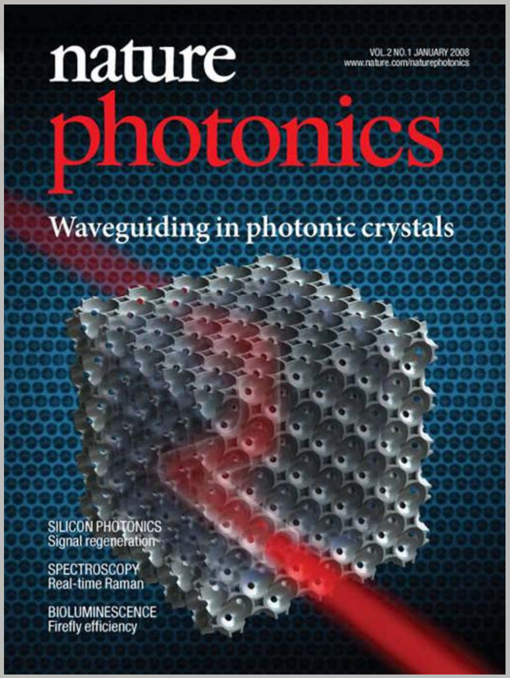


Going from 1D to 3D:

- Creating full band gap
  Photonic crystal = Semiconductor for light
- Fine control of light propagation
  & emission
- Optical circuits

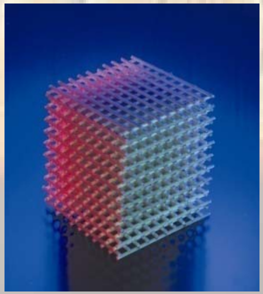


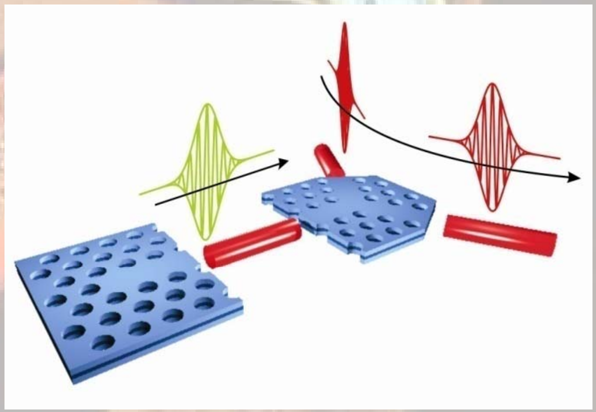


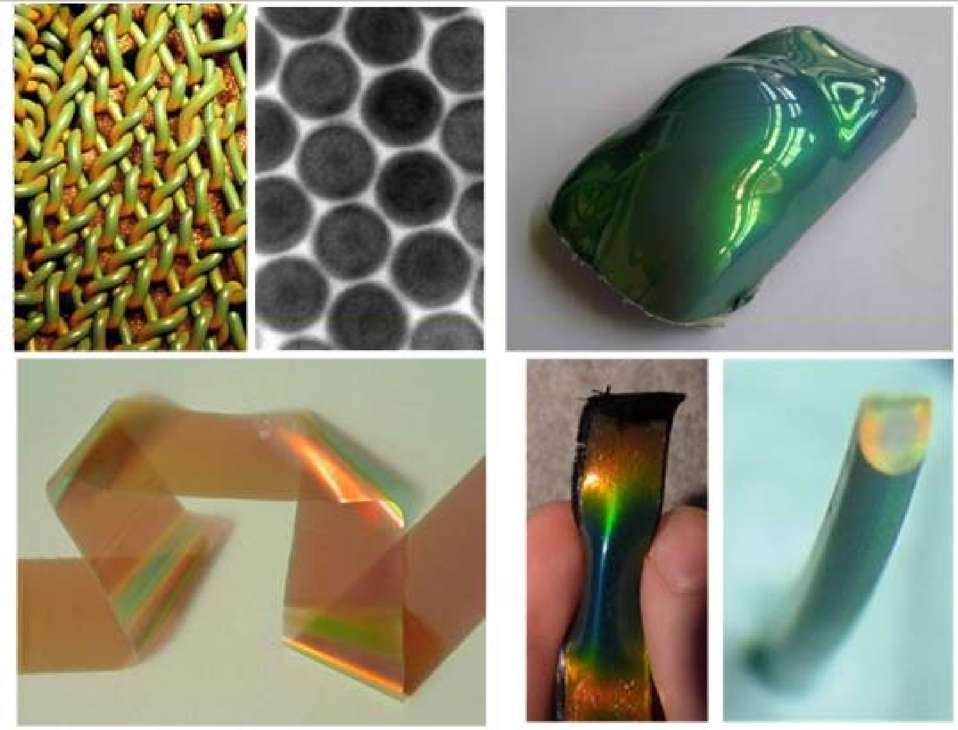


Applications

- Optical communications
- Optical computing
- Visualisation/display technology
- Light Harvesting (solar cells)
- Sensors
- Microlasers, ...

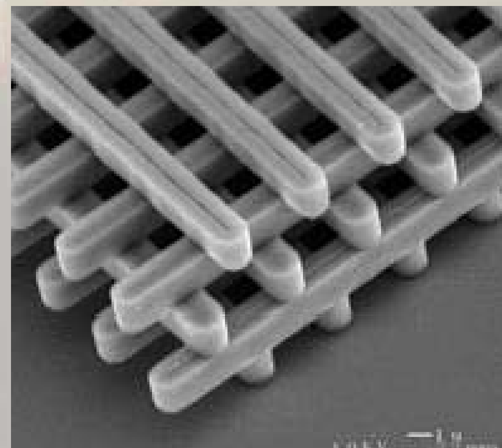


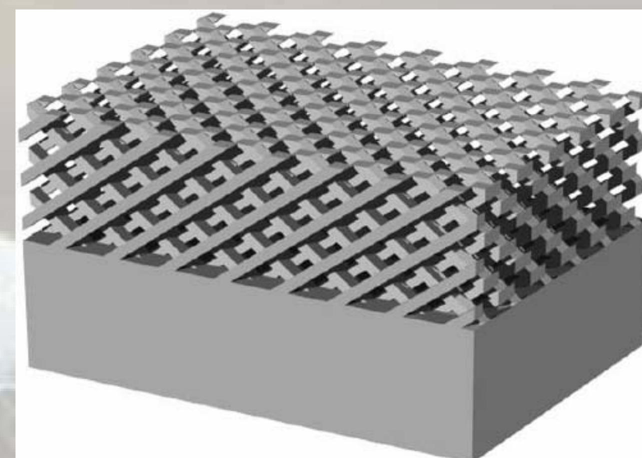




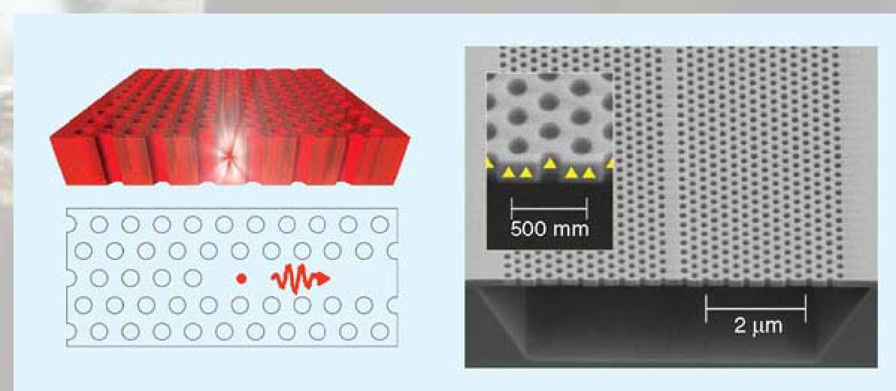
How can one synthesize photonic nanomaterials: Lythography techniques

- Electron Lythography
- Focused Ion Beam
- Optical Lythography
- ...

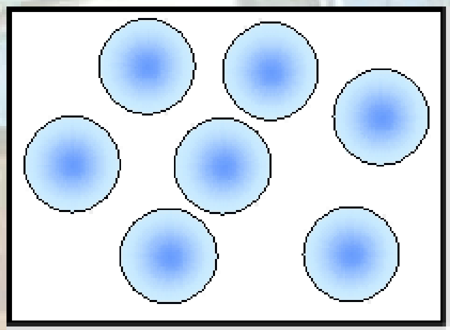




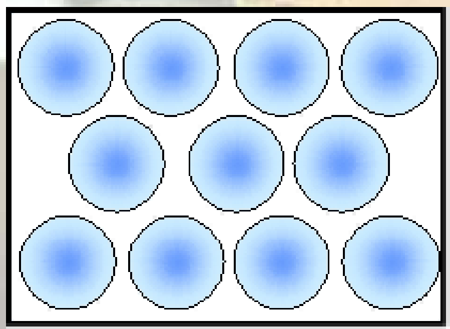
Beautiful design possibilities
BUT
- difficult in 3D
- Scale-up problems
- Too involved and too expensive



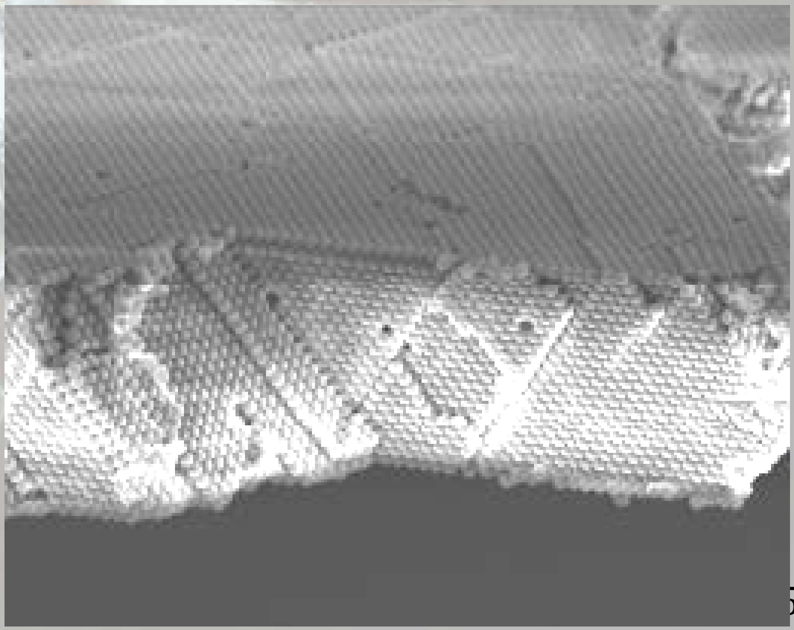
Alternative approach:
use colloidal self-assembly



fluid

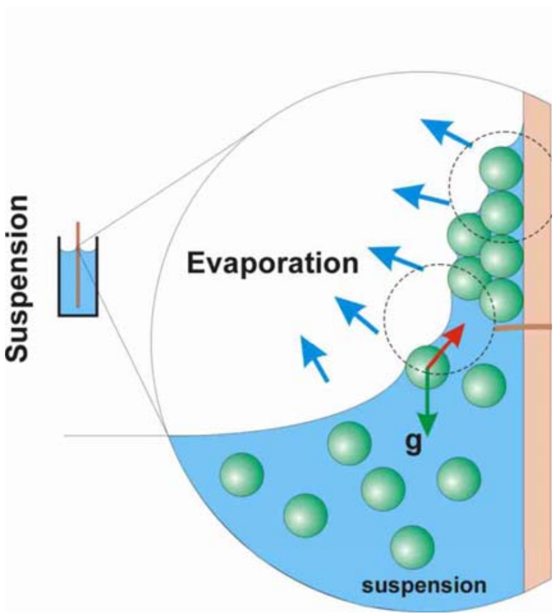


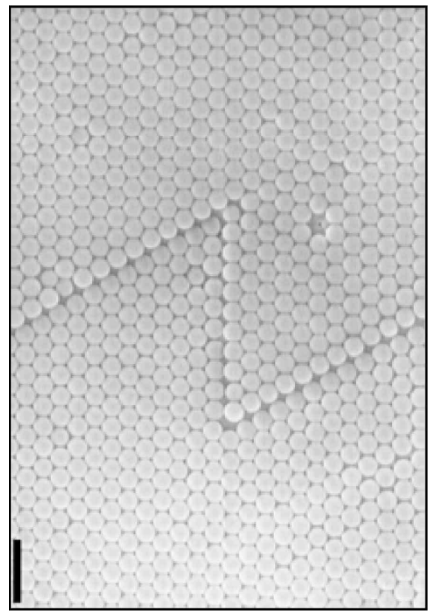
crystal

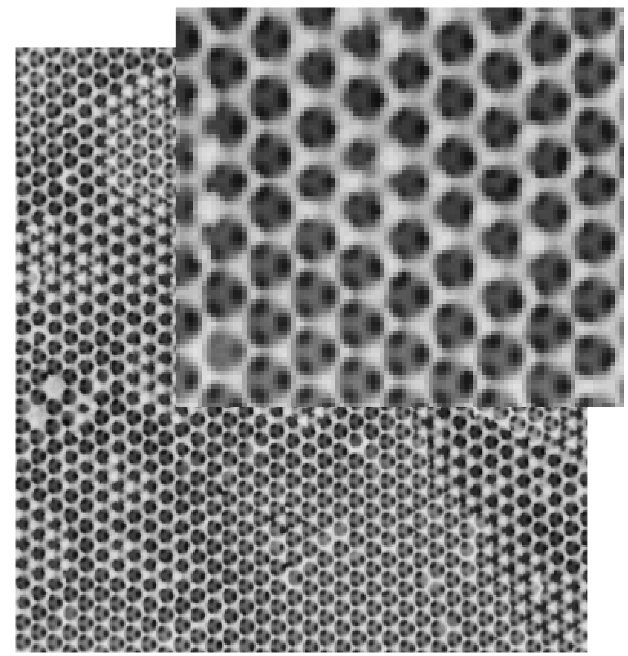


- Three-dimensional
- Easy tuneable
- Can be scaled up
- Inexpensive

photonic materials







Colloid self-assembly by convective & capillary forces

Filling the voids with another material and removing the spheres

high contrast (no optical techniques applicable)

Schedule

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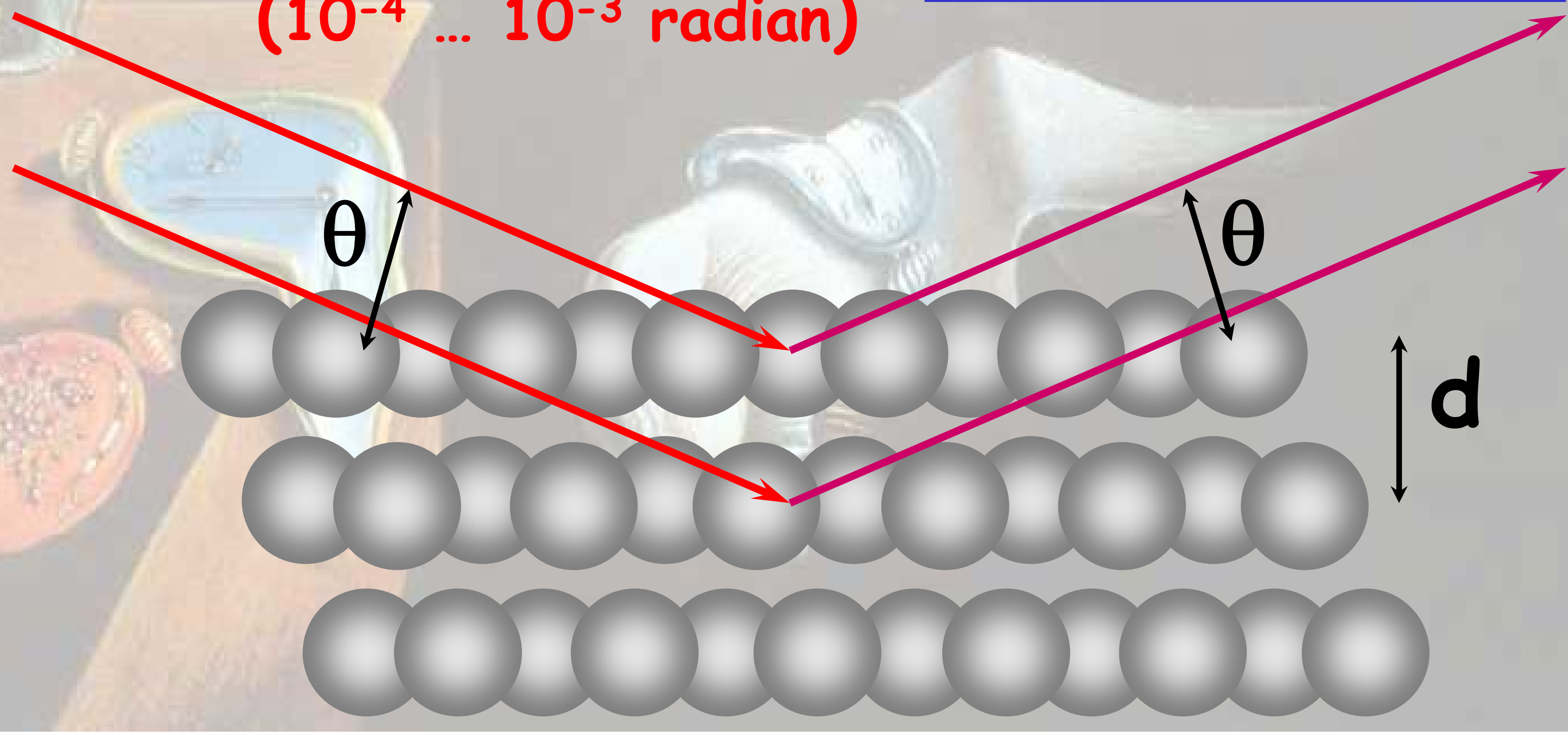
Theory: Bragg's law

Ordinary (atomic) crystals: d~λ
=> large diffraction angle 2θ

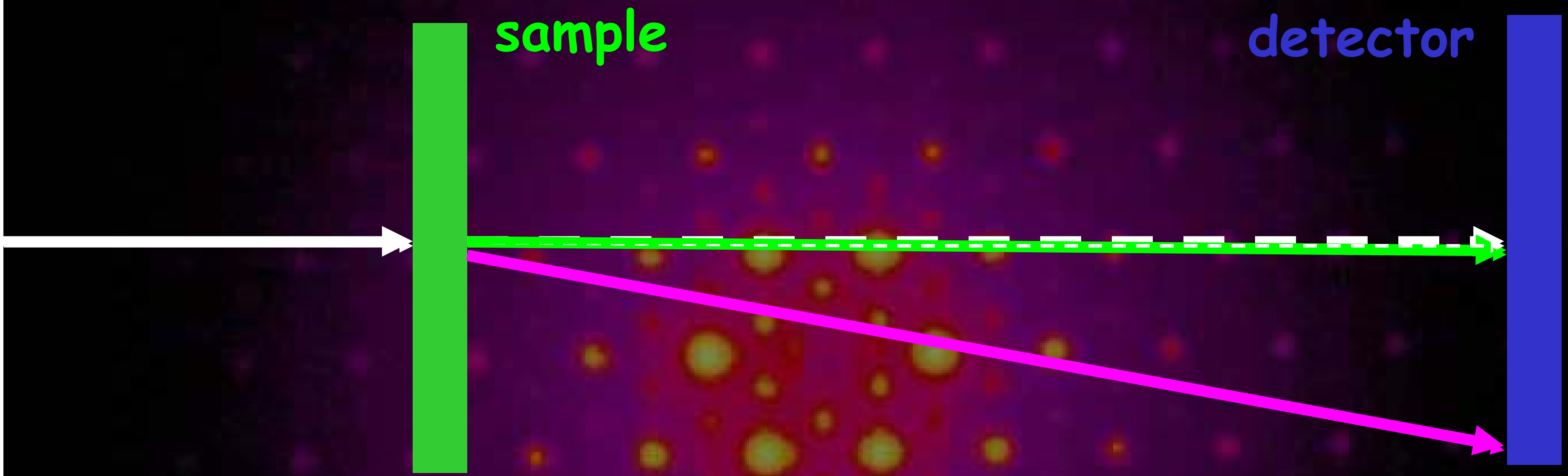
X-rays: λ~ 1 A

$\sin\theta = n\lambda/2d$; $n=1,2,...$

Colloidal crystals: d>>λ
=> small diffraction angle 2θ
(10^{-4} … 10^{-3} radian)

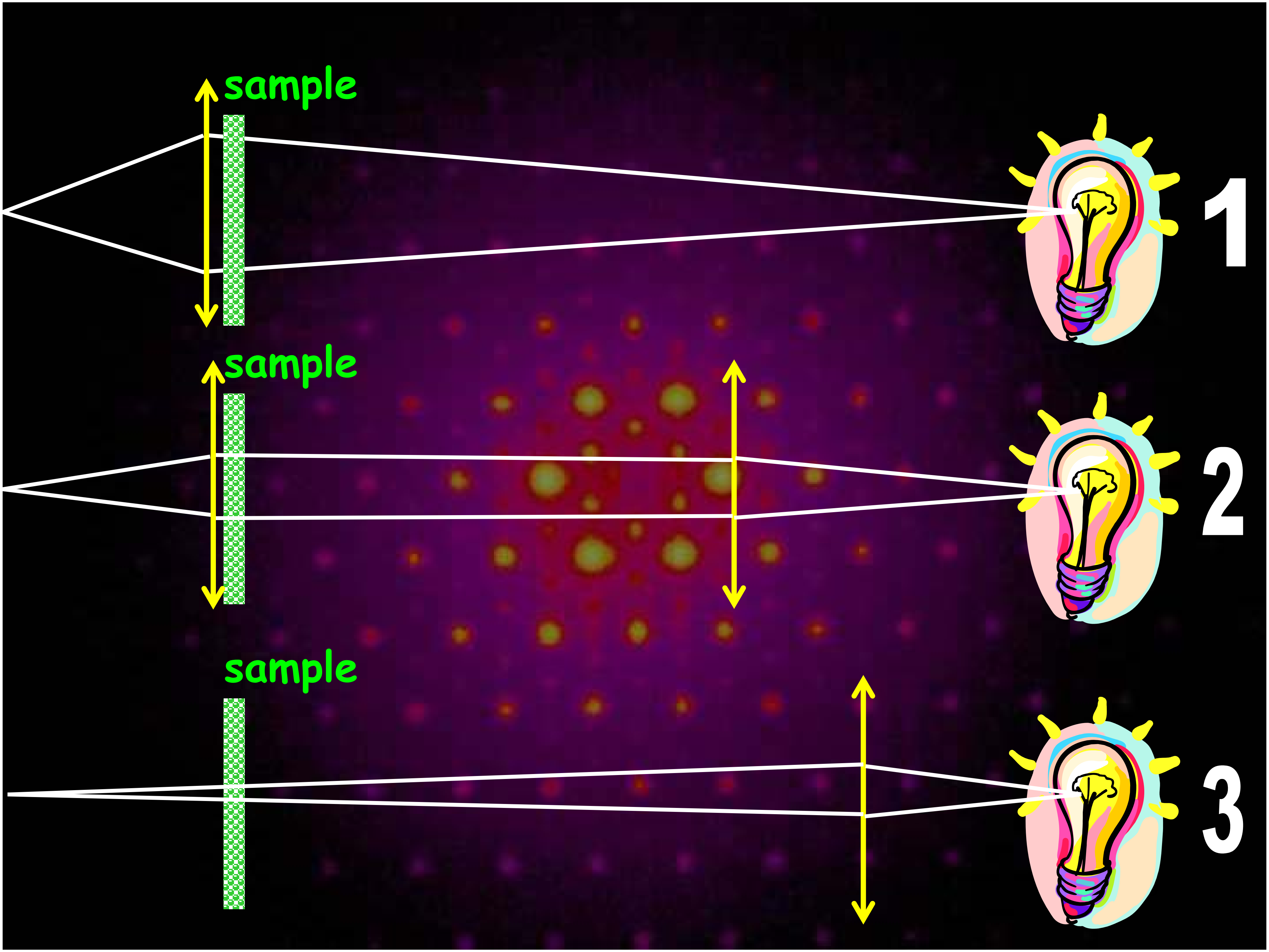


Scattering experiment

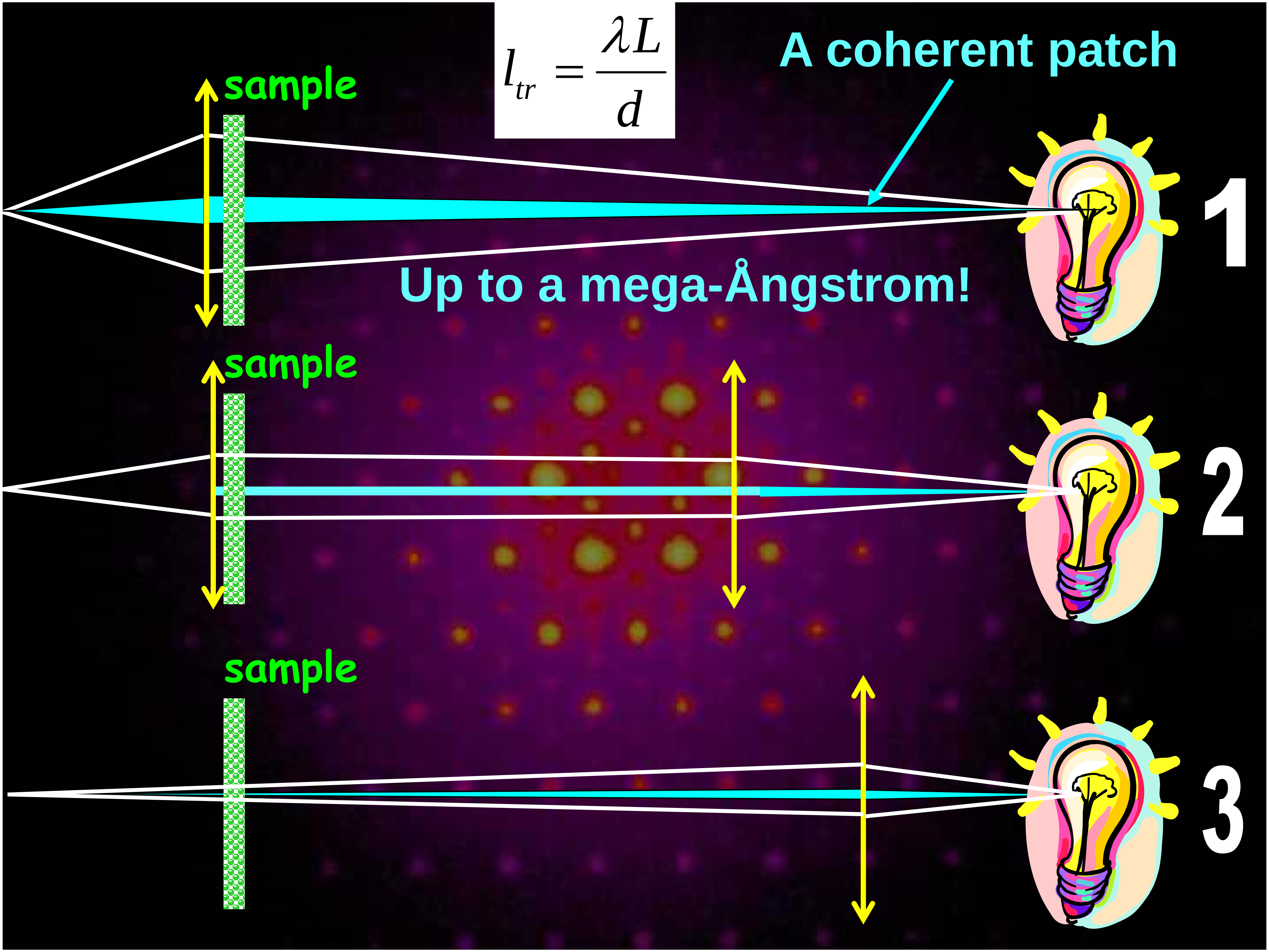


Extreme angular resolution is needed
How do we get it?

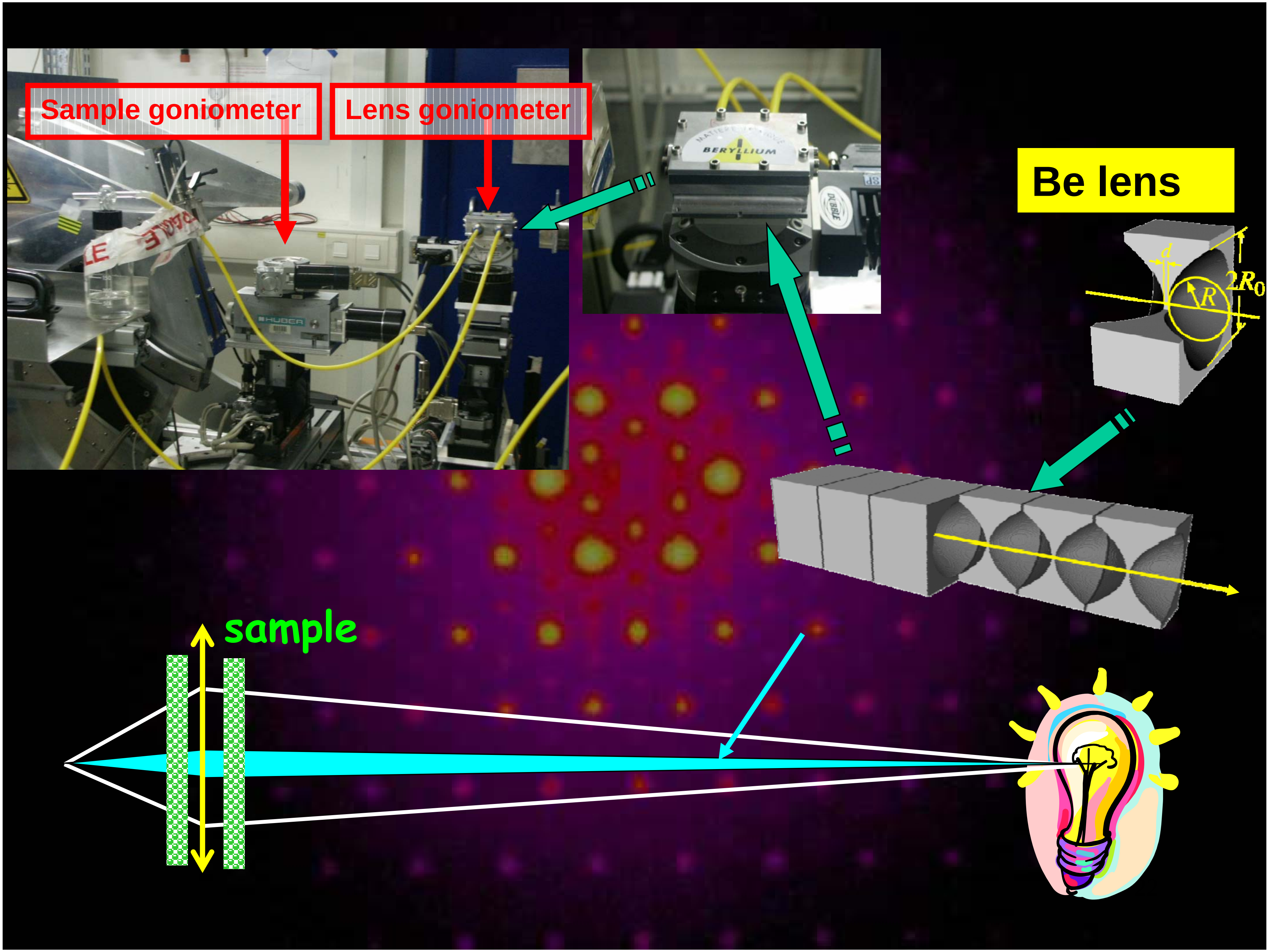
- **parallel beam?**
- **pencil beam?**



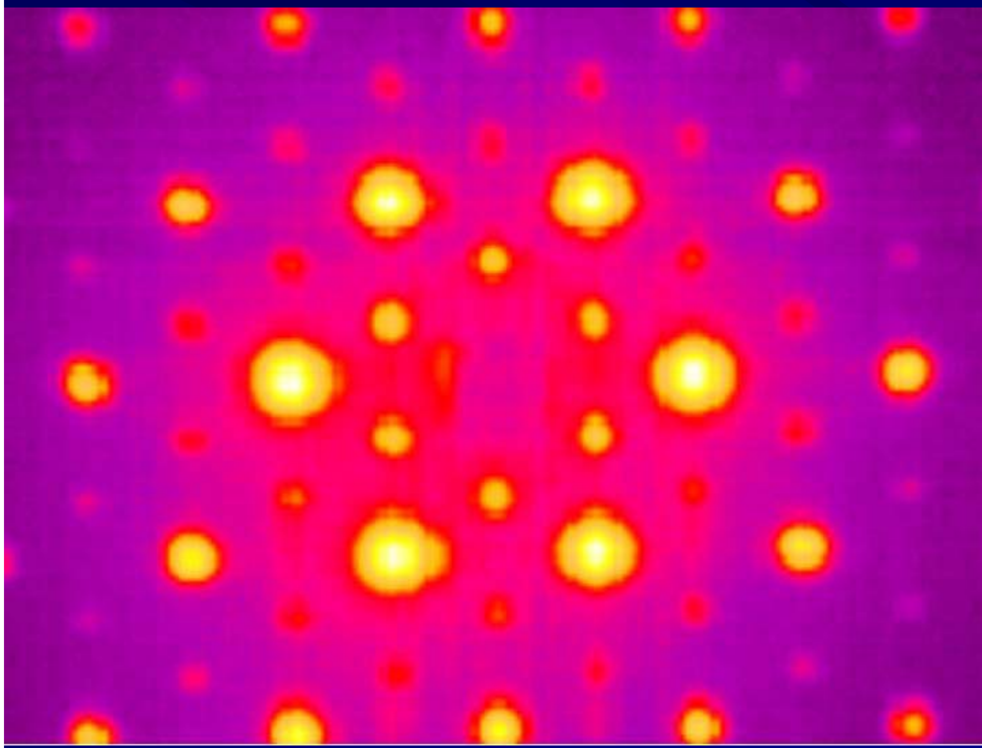
sample
sample
sample
1
2
3

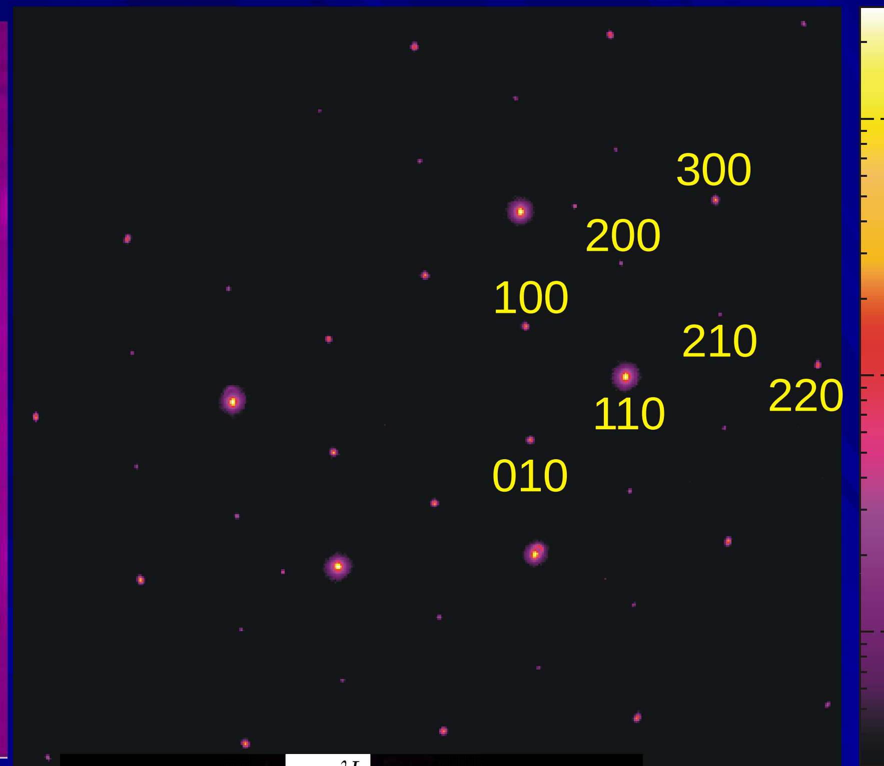


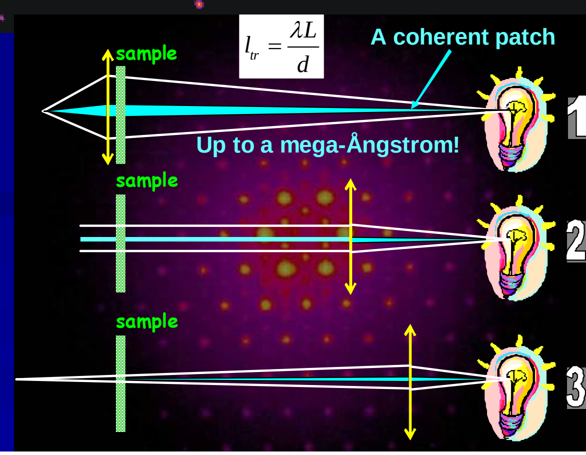
$$l_{tr} = \frac{\lambda L}{d}$$
A coherent patch
sample
sample
sample
Up to a mega-Ångstrom!
1
2
3


Sample goniometer
Lens goniometer
Be lens
d
2R0
R
sample

Microradian diffraction

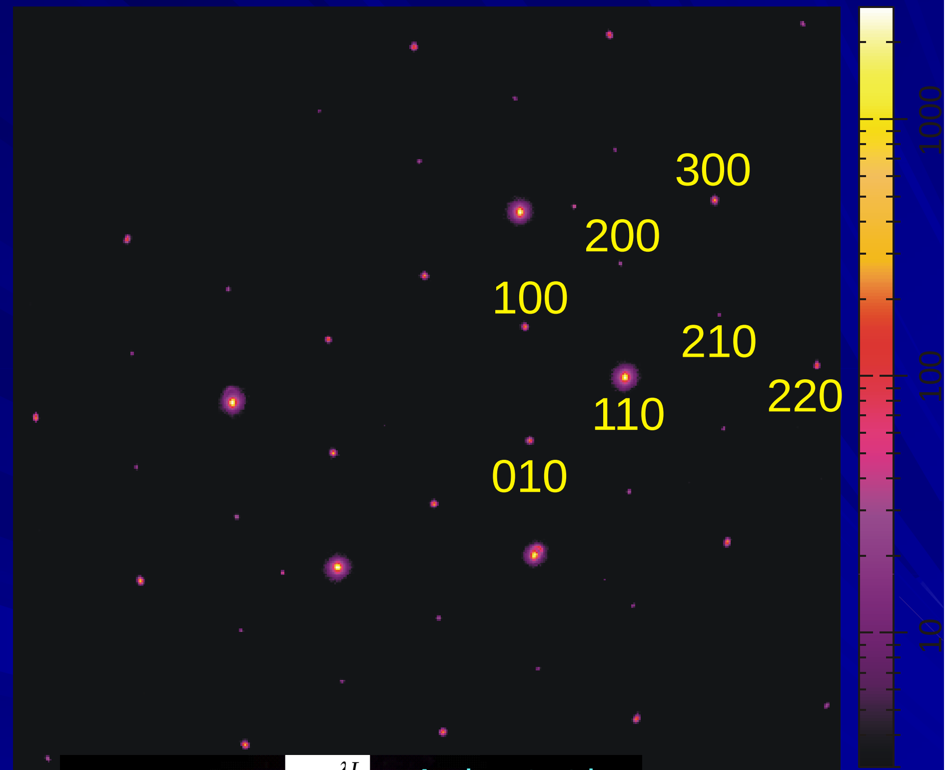


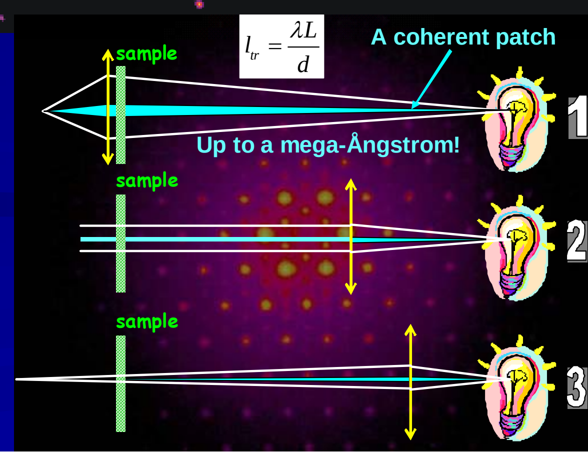




Microradian diffraction

- Colloids = elephants => microradian XRD
- Peak positions: Crystal structure
- Peak width: Long-range order
- Peak tails: fluctuations





Schedule

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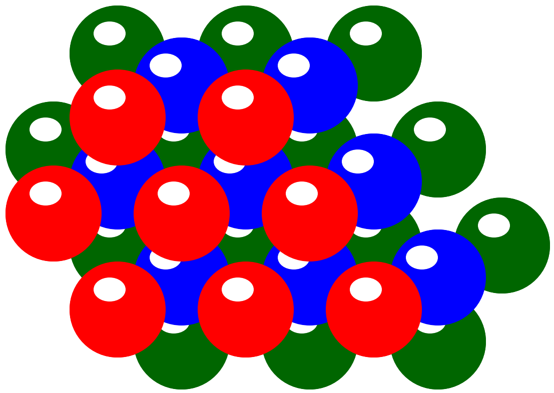
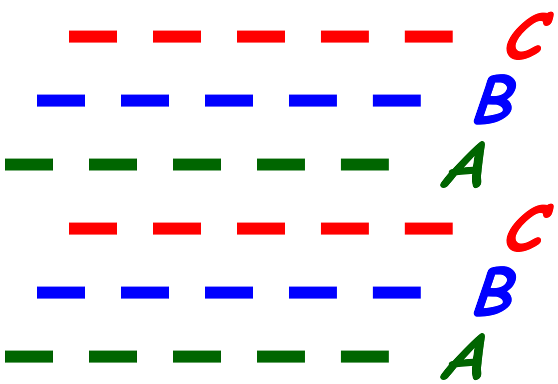
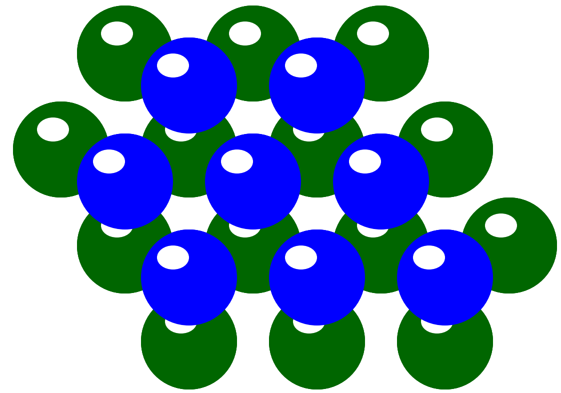
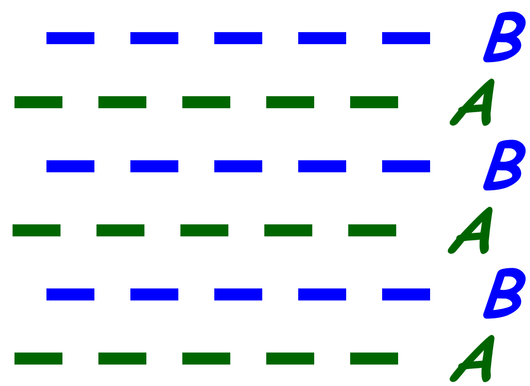
Example 1: Hard balls



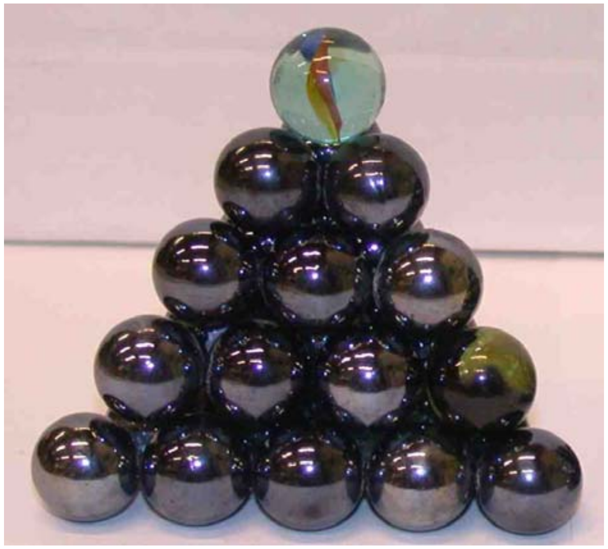


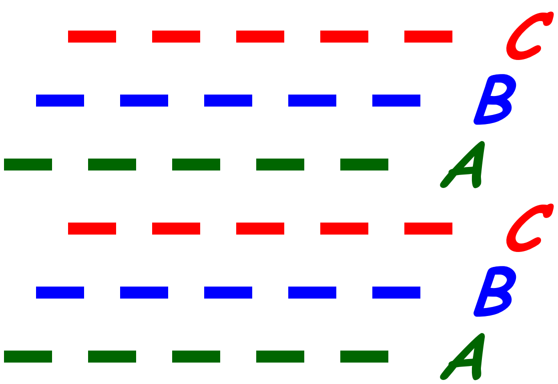
Face-centred cubic (fcc)



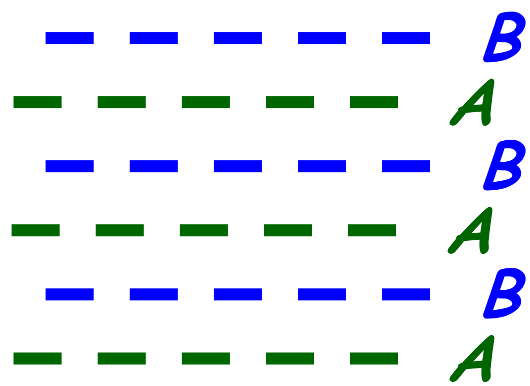


Hexagonal close packed (hcp)

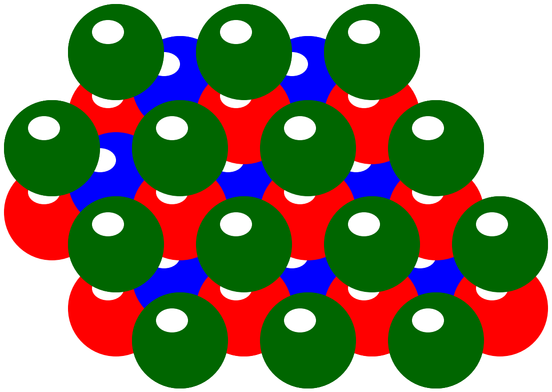


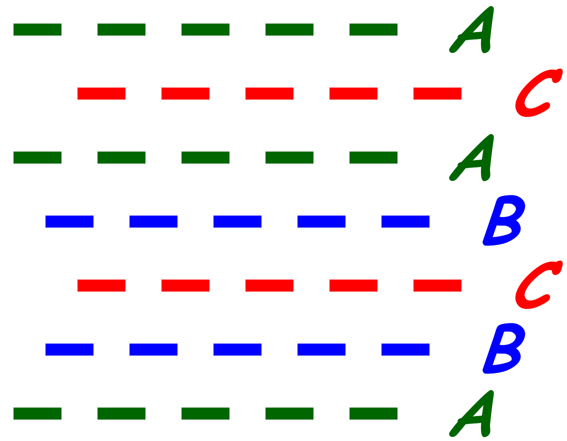


Face-centred cubic (fcc)



Hexagonal close packed (hcp)



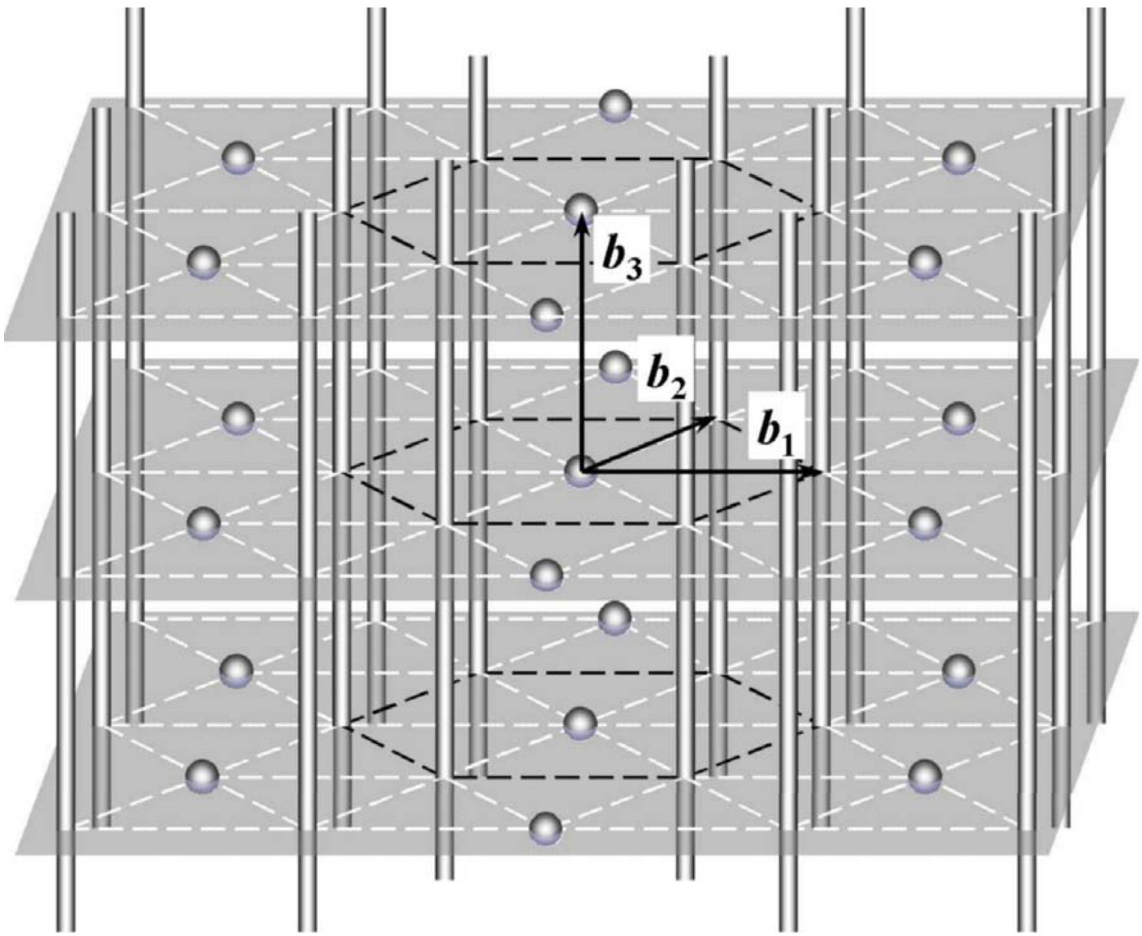


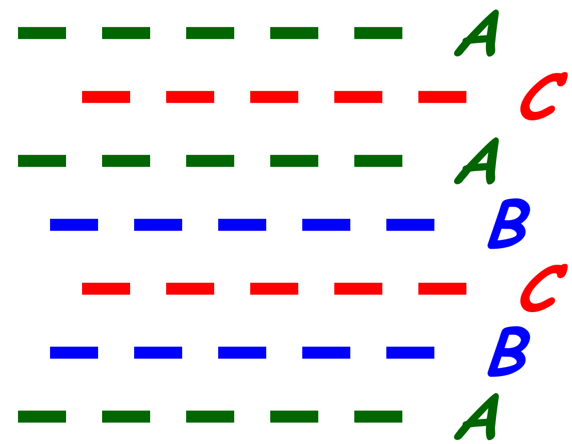
Random hexagonal close packed (rhcp)

All three (fcc, hcp & rhcp) have the same packing ratio

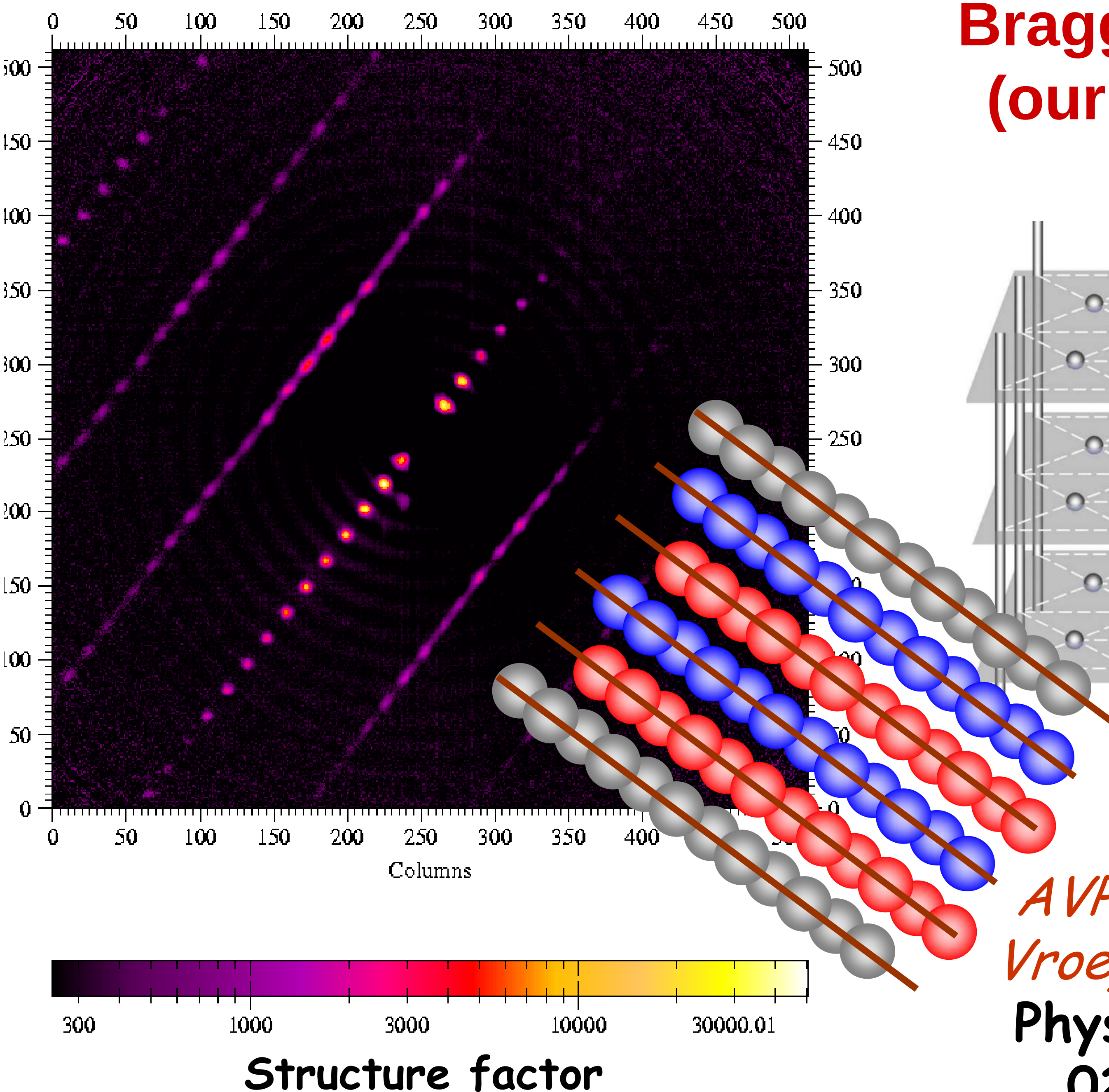
rhcp seen in the reciprocal space

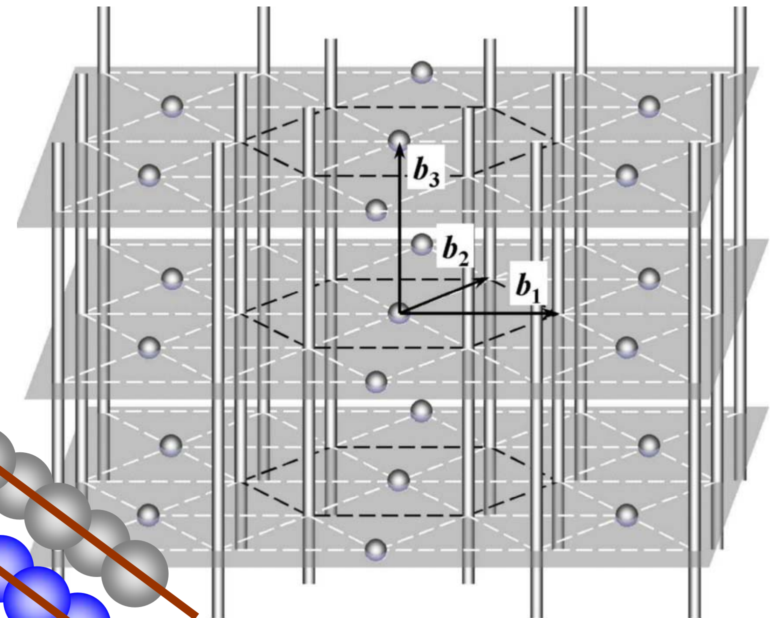
Truly periodic crystal – sharp Bragg spots
No interlayer periodicity => Braag rods
Yet, some reflections stay sharp (only 3 lateral positions)





Bragg rods are real!
(our earlier result)

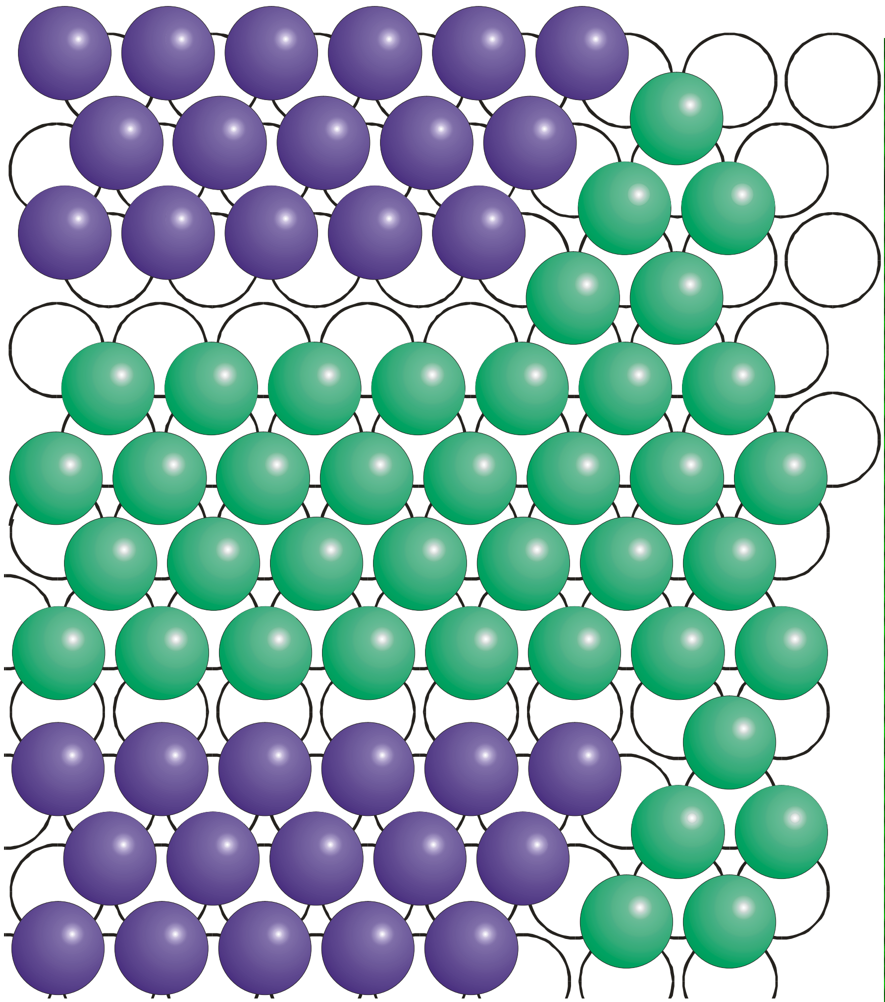


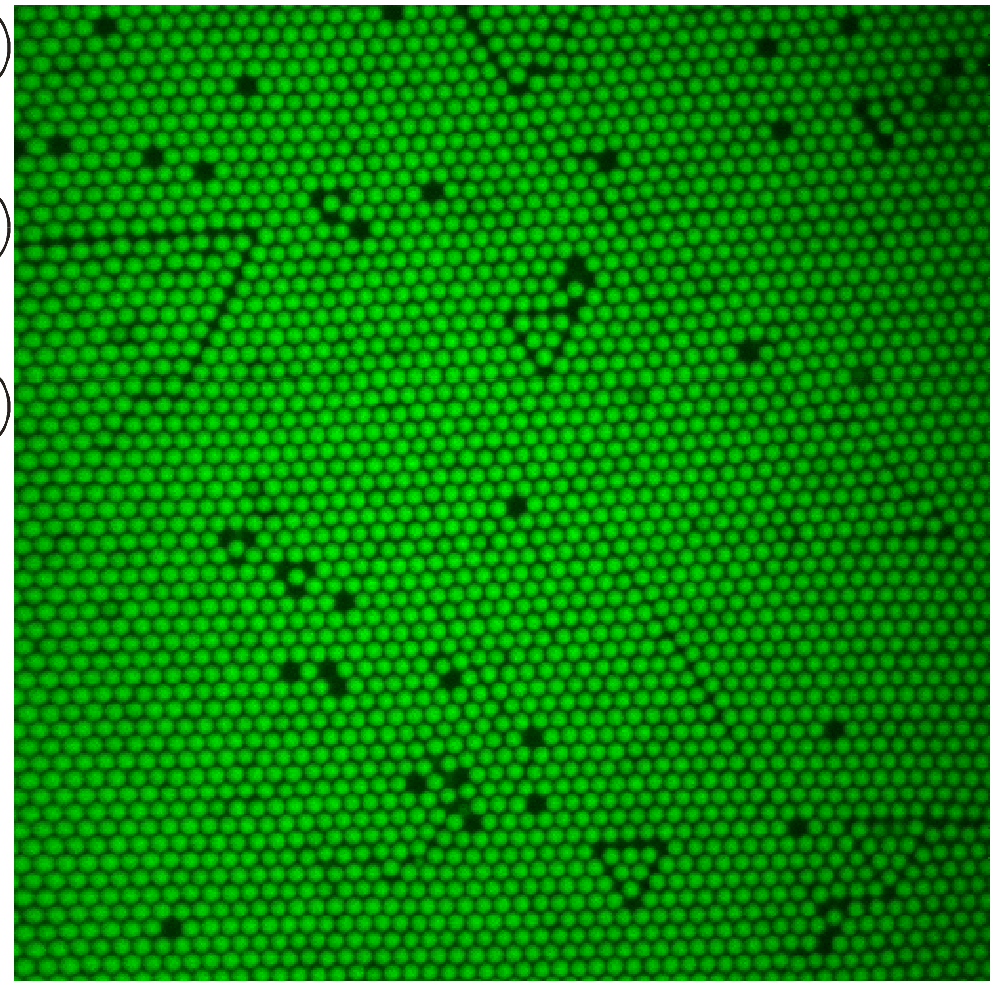


AVP, Dolbnya, Aarts, Vroege, Lekkerkerker, **Phys.Rev.Lett., 90, 028304 (2003).**

Earlier: in-plane stacking disorder

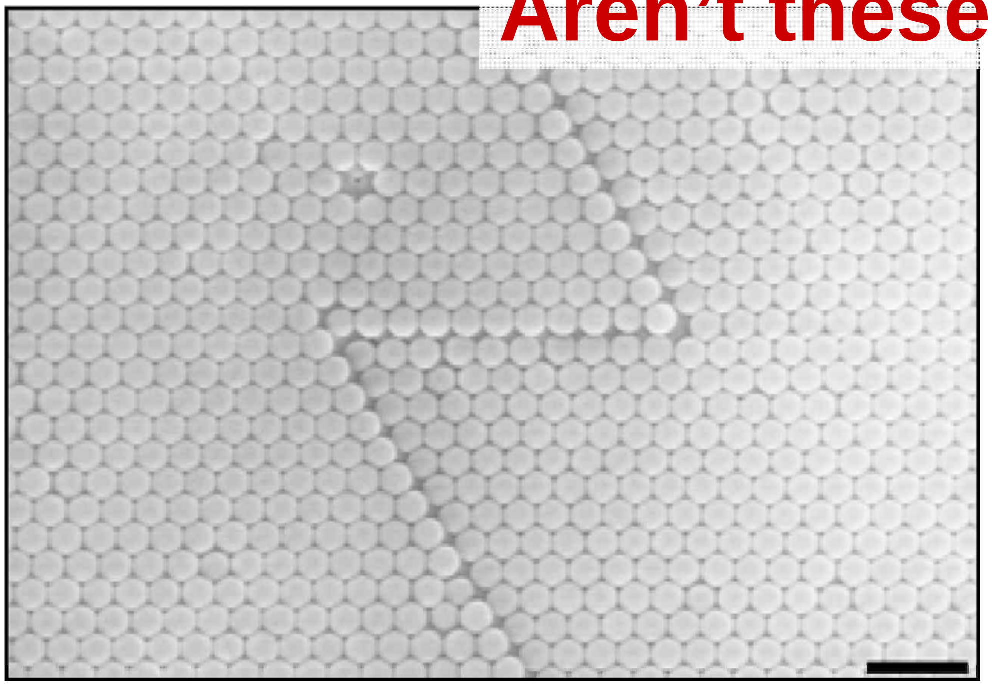
- J.M. Meijer, V.W.A. de Villeneueve, AVP, Langmuir, 23, 3554 (2007)
- V.W.A. de Villeneueve, P.S. Miedema, J.M. Meijer, AVP, EPL, 79, 56001 (2007)
- P.S Miedema, V.W.A. de Villeneueve, AVP, PRE, 77, 010401 (2008)

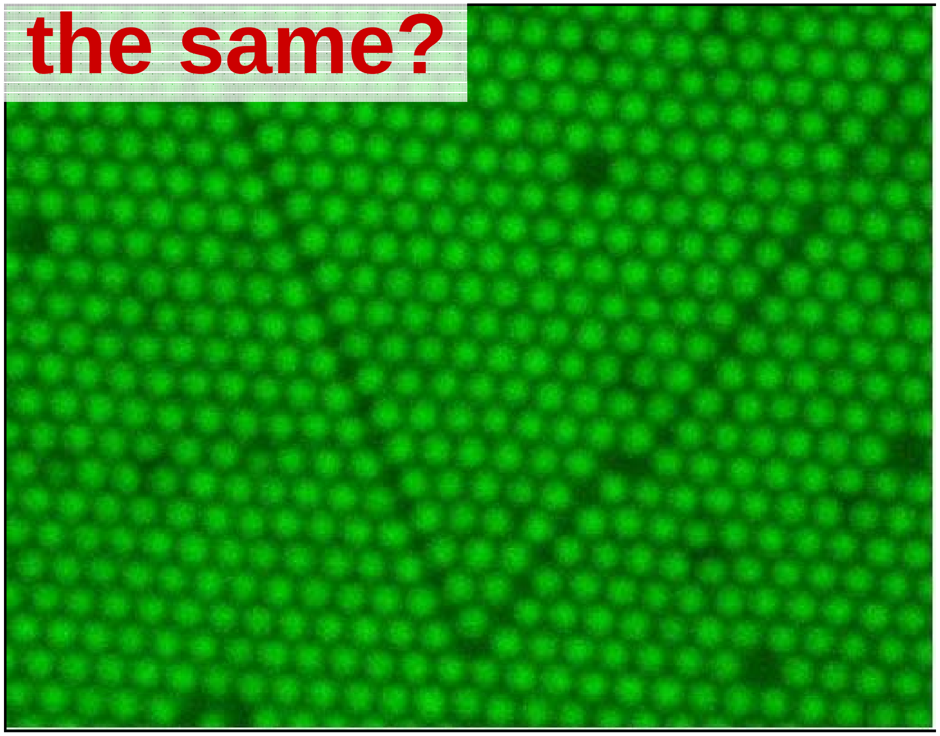




The idea of the experiment

Aren’t these the same?

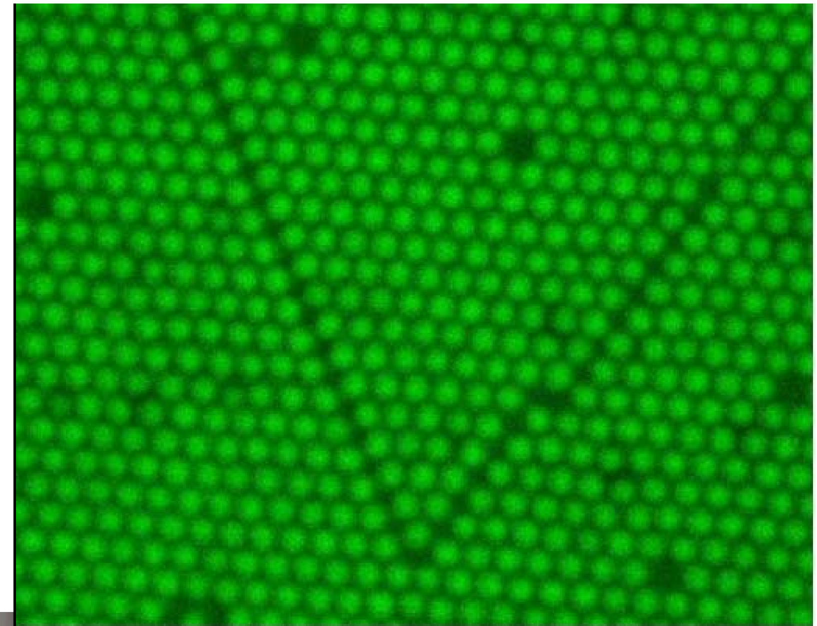


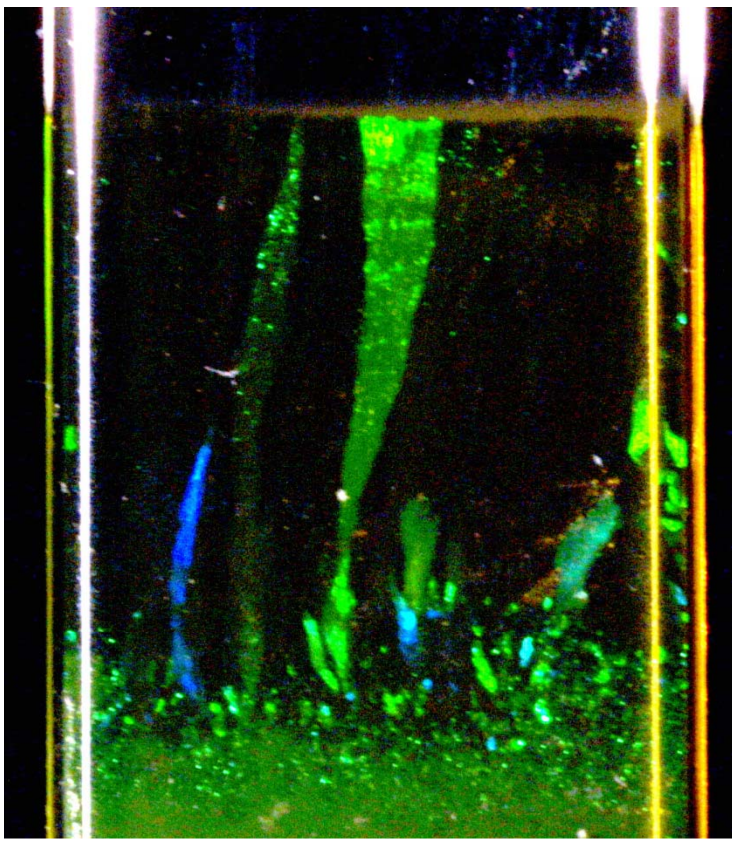


Alexander Sinitskii et al.
SEM of vertical deposition crystals
Mendeleev Comm., 2007

Volkert de Villeneuve et al.
Confocal microscopy of sedimentary crystals,
Langmuir & EPL, 2007

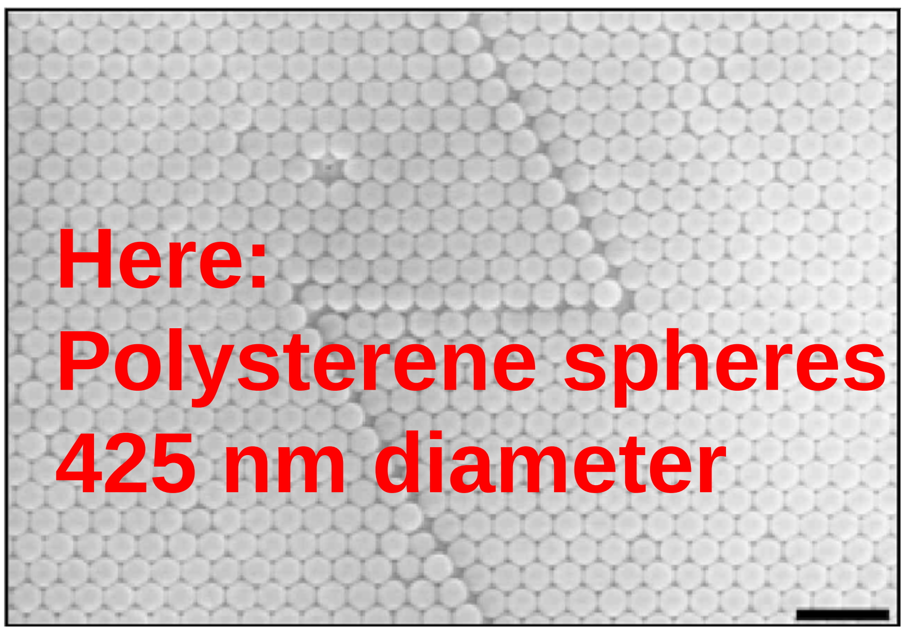
Sedimentary crystals

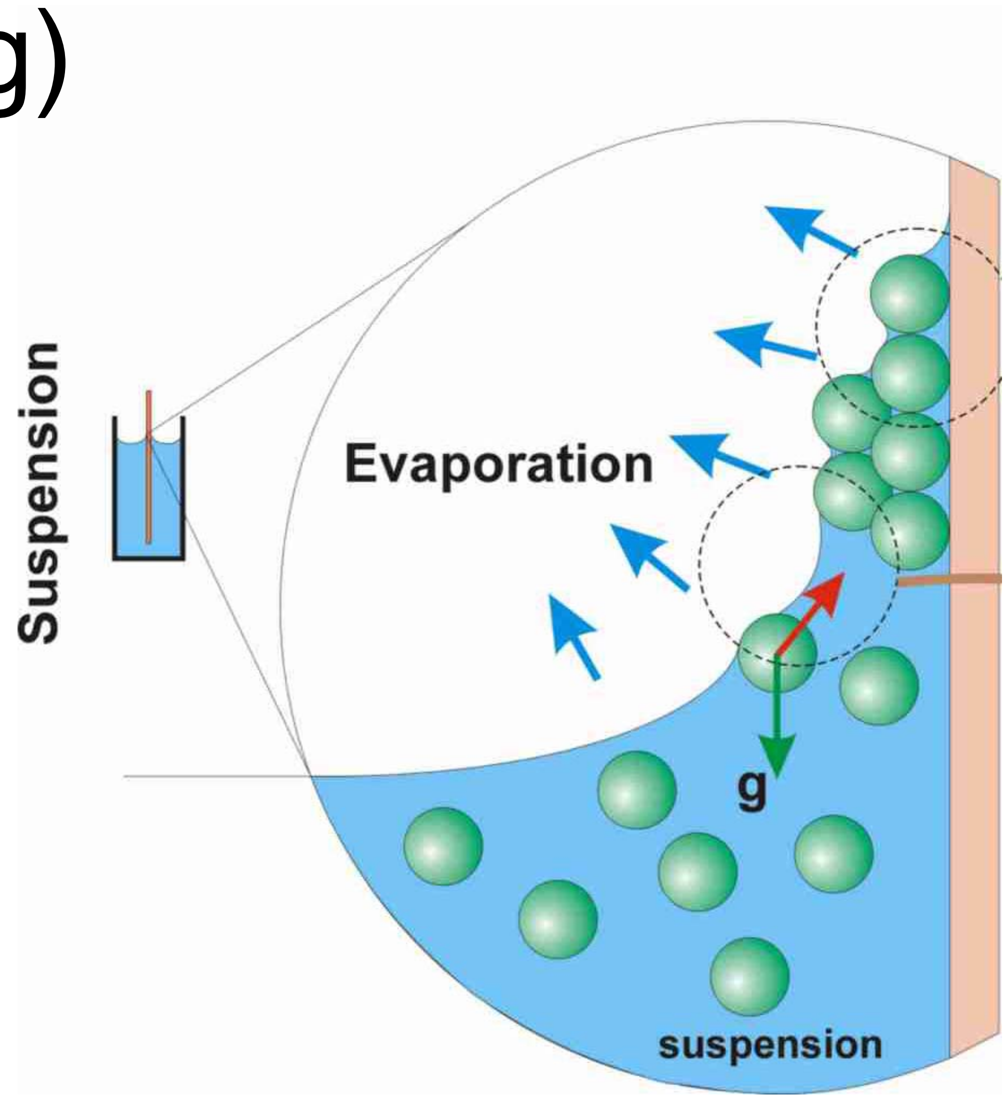




Vertical deposition crystals (controlled drying)

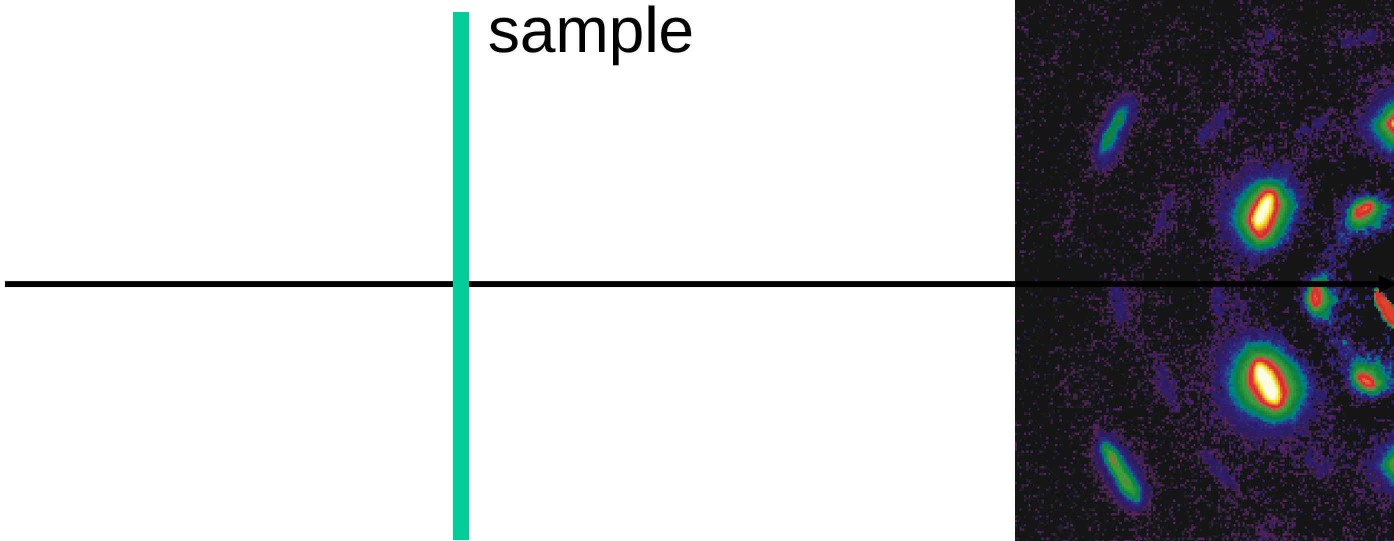
Popular technique to fabricate inverted photonic crystals

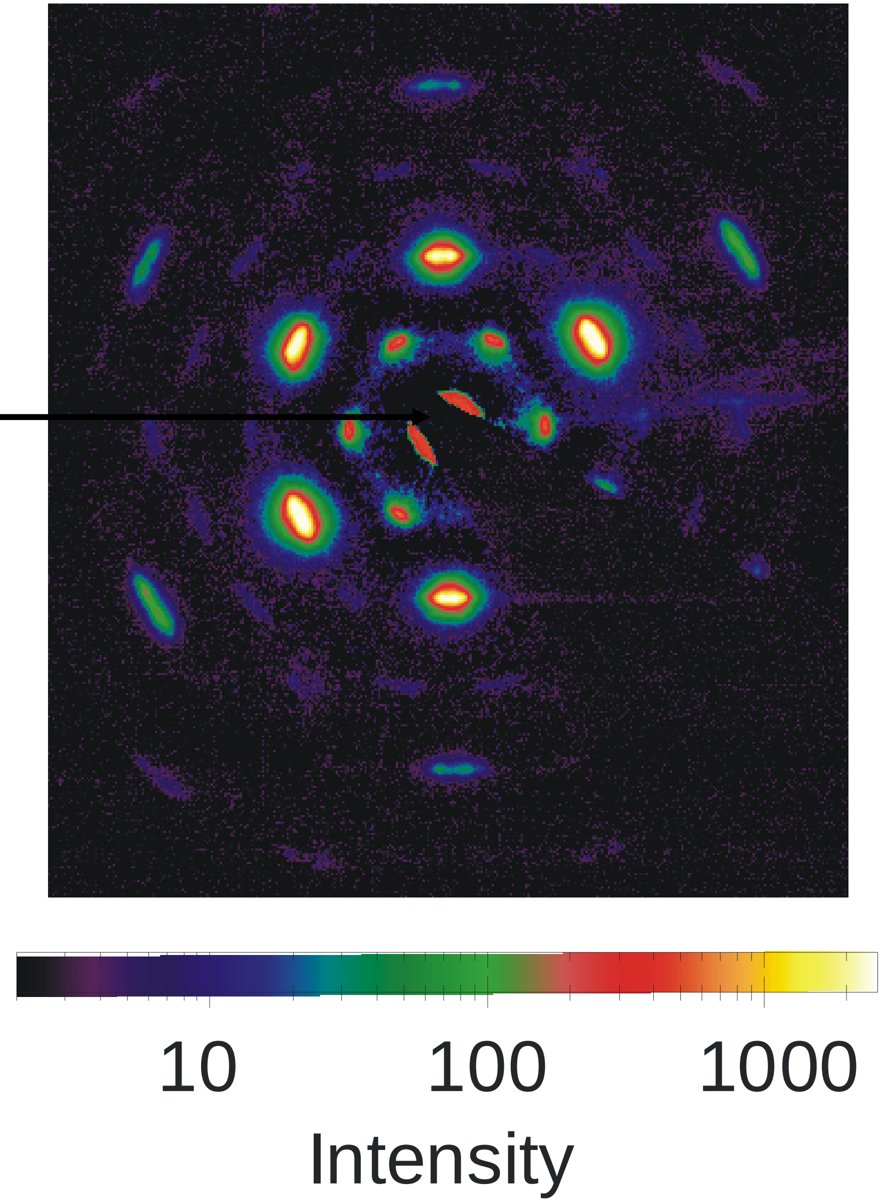


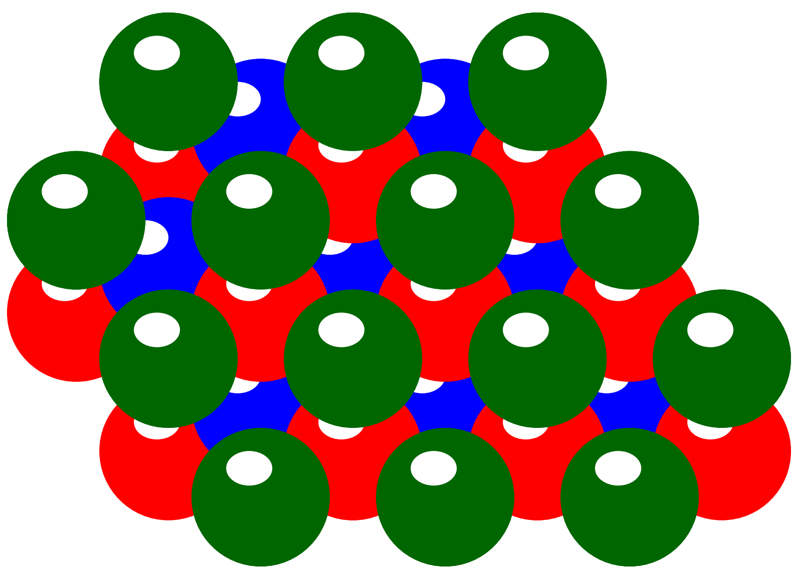


Picture courtesy K. Velikov

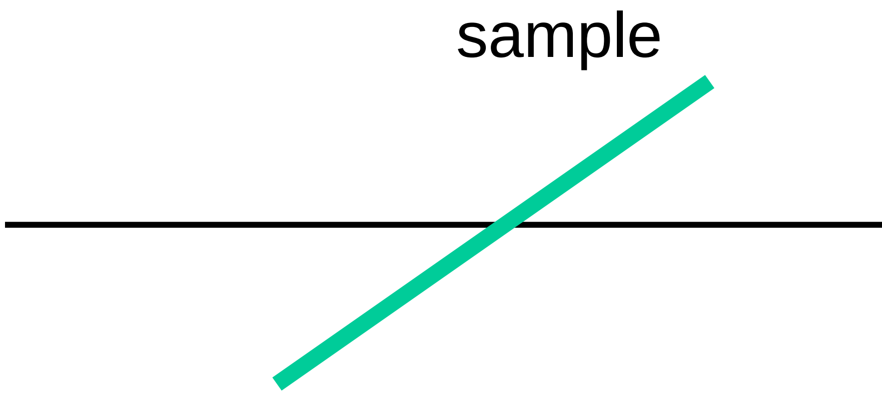
Pattern #1

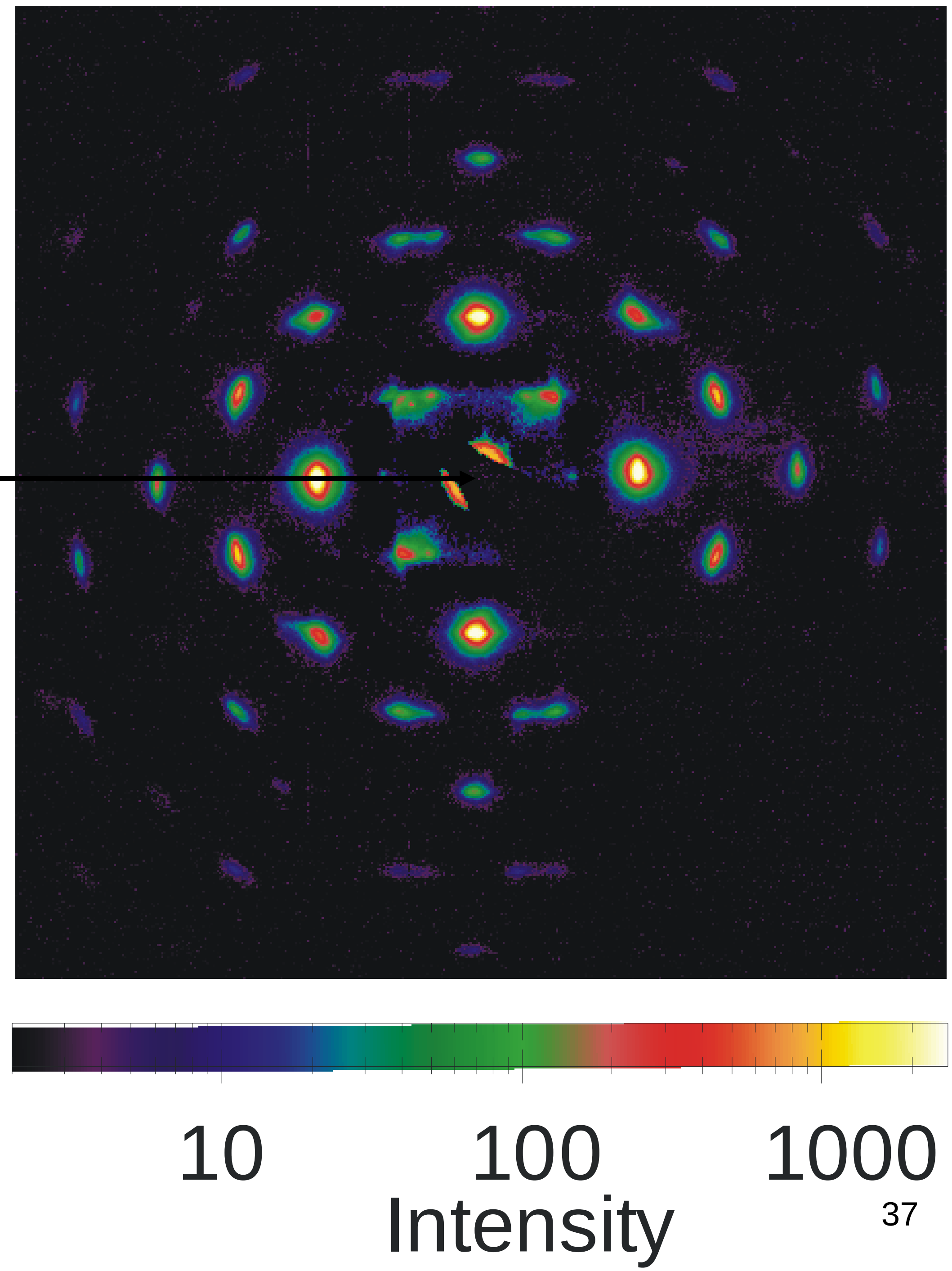




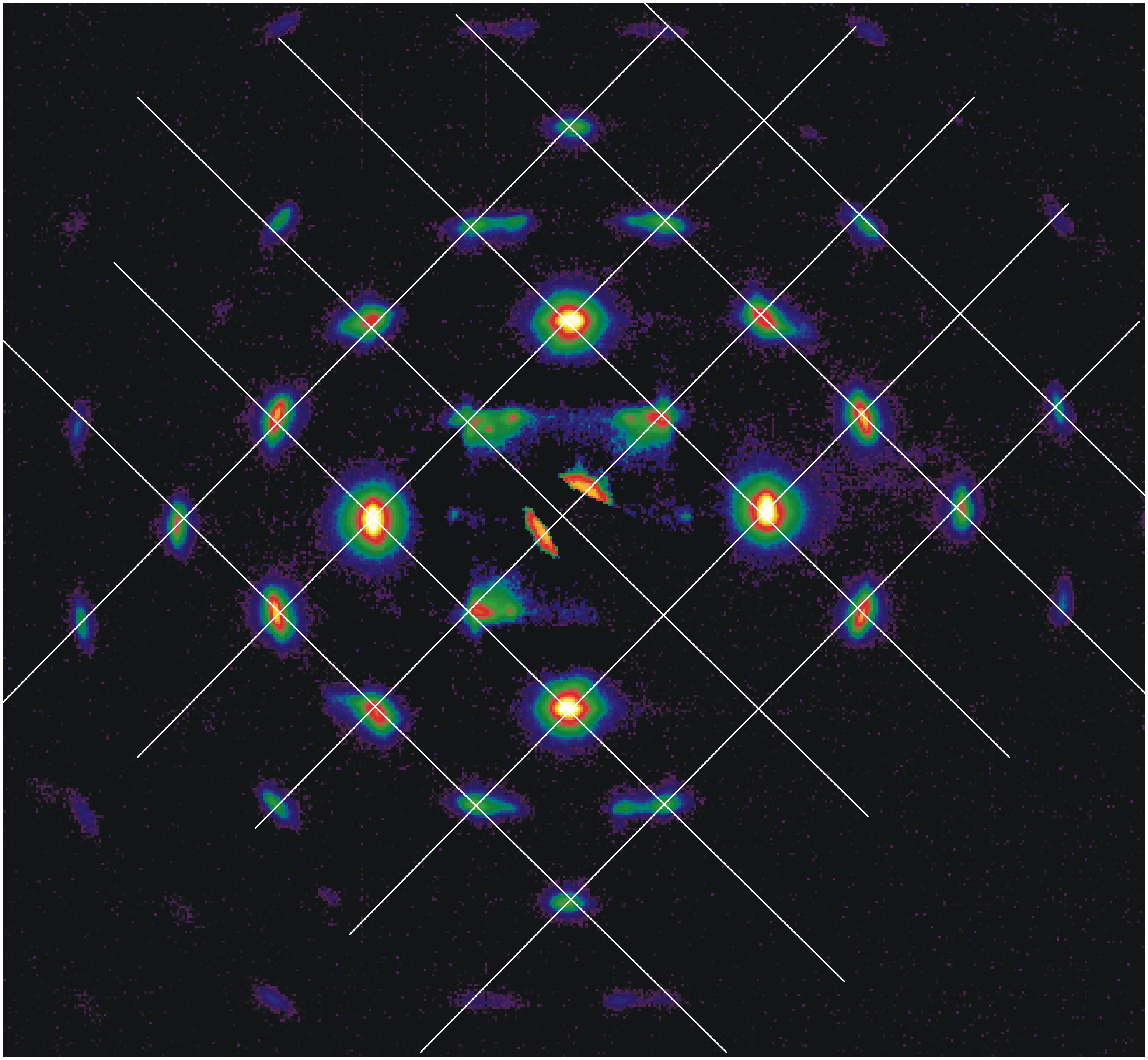


Pattern #2



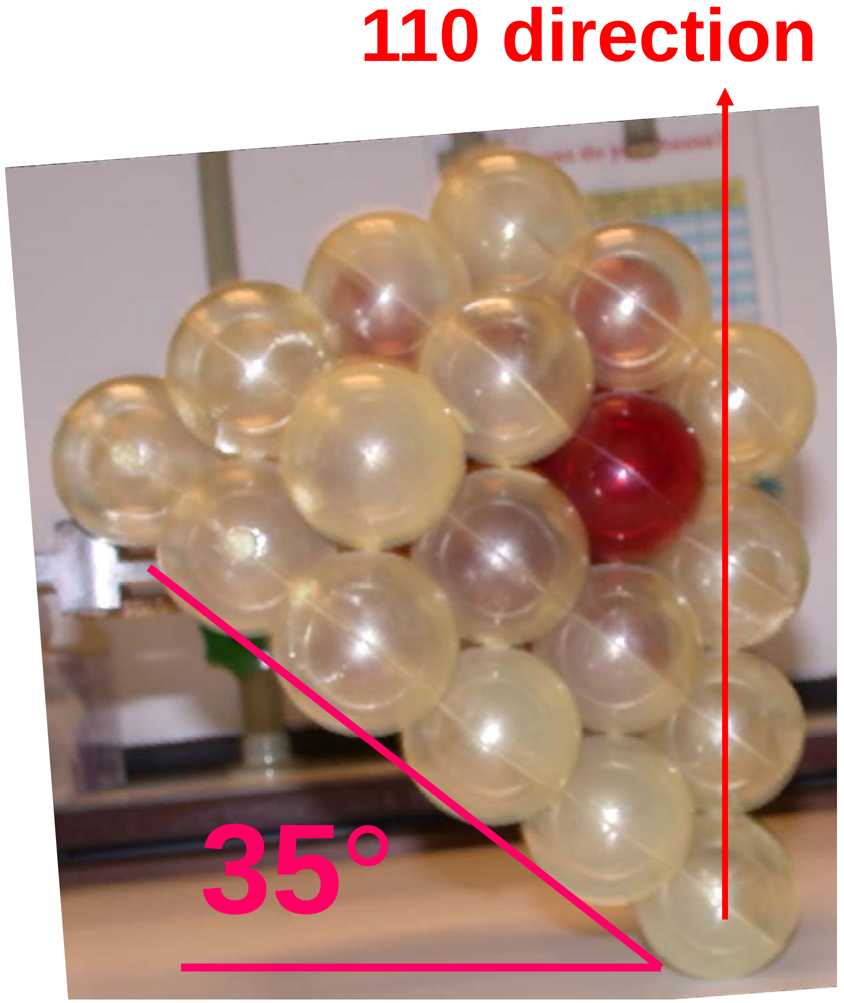


Sample turned
by 55 degrees

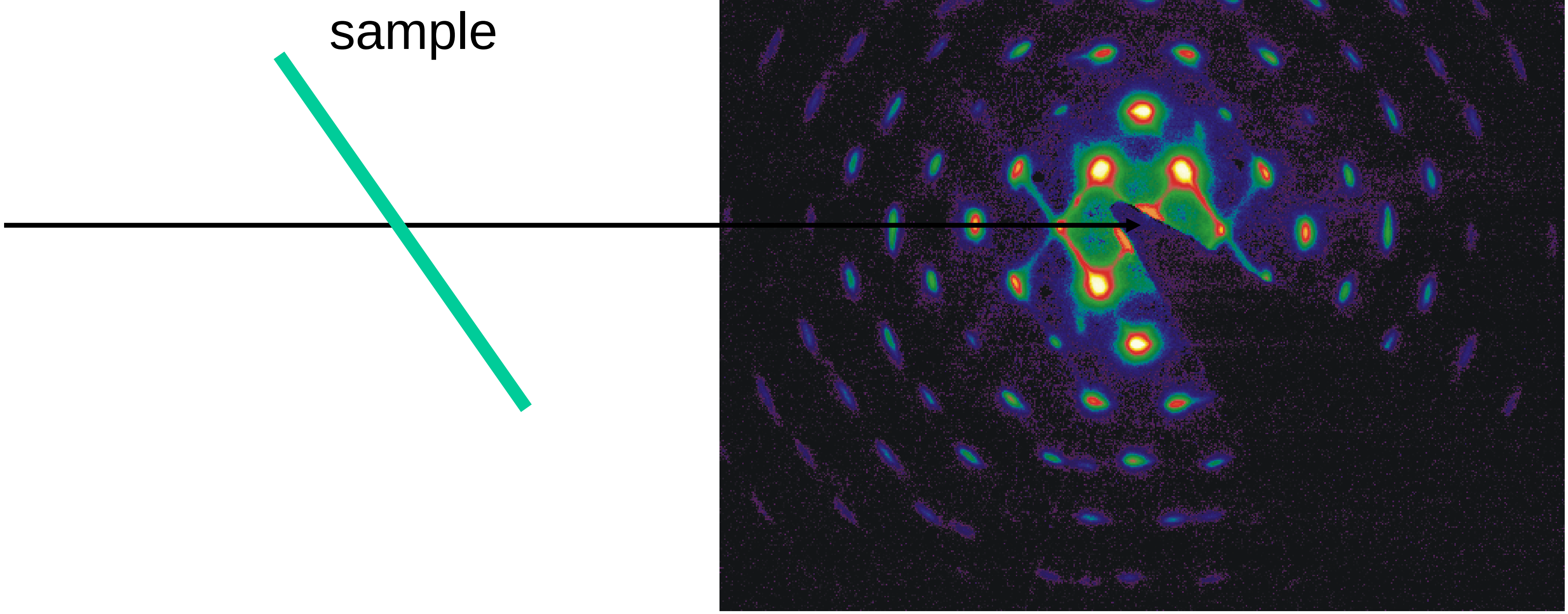


Can we look along the 110 direction?

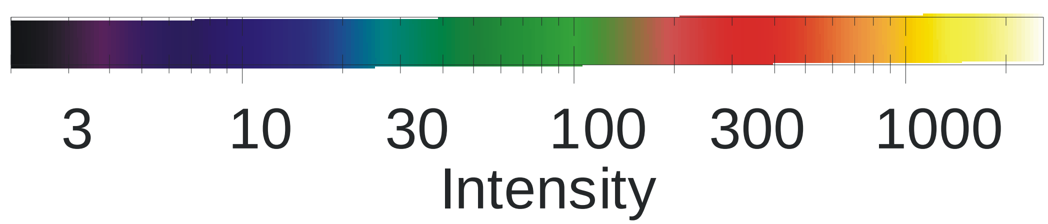
Sample is to be turned by 35 degrees



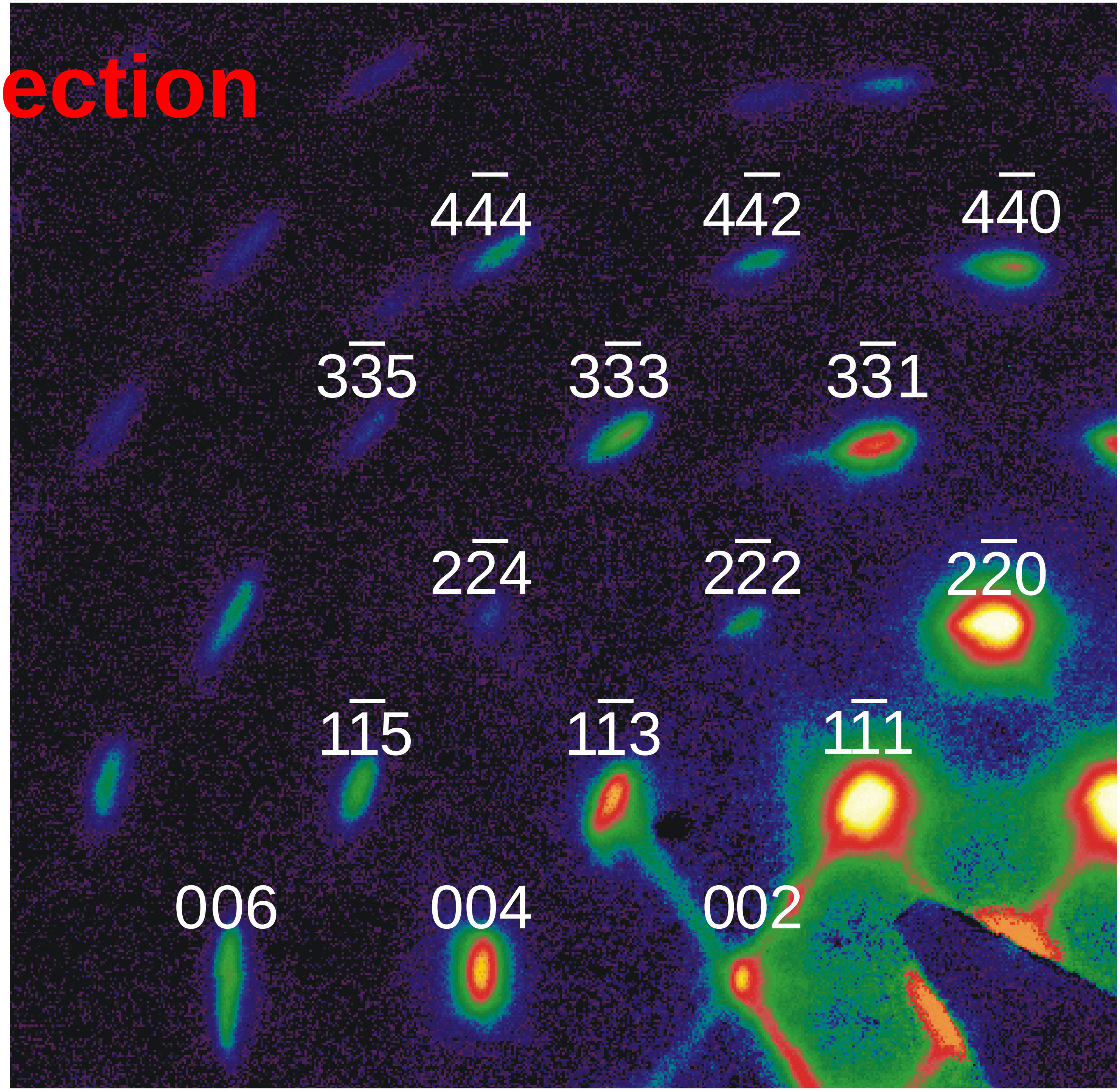
Pattern #3



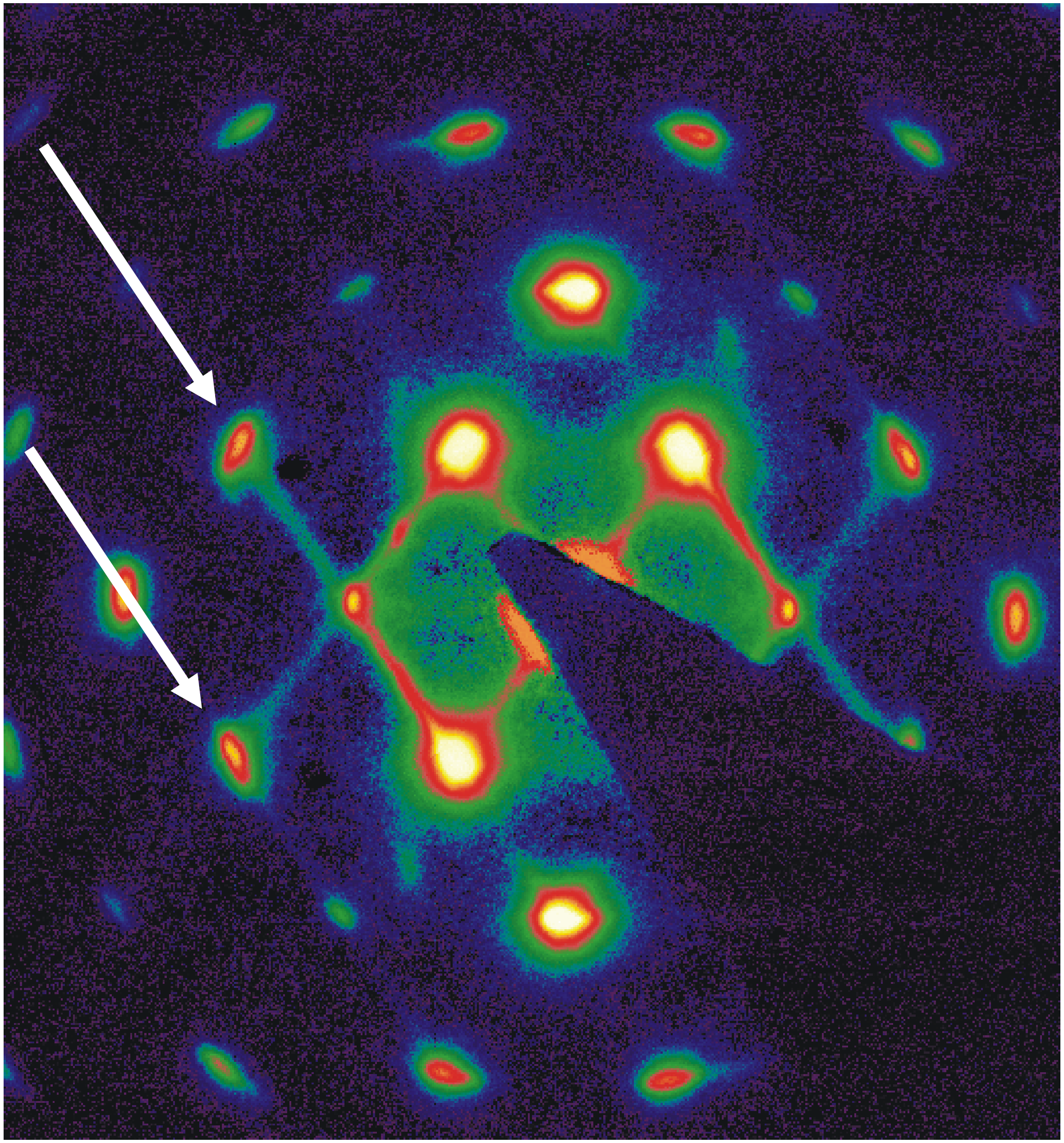
Sample is turned by 35 degrees



110 direction



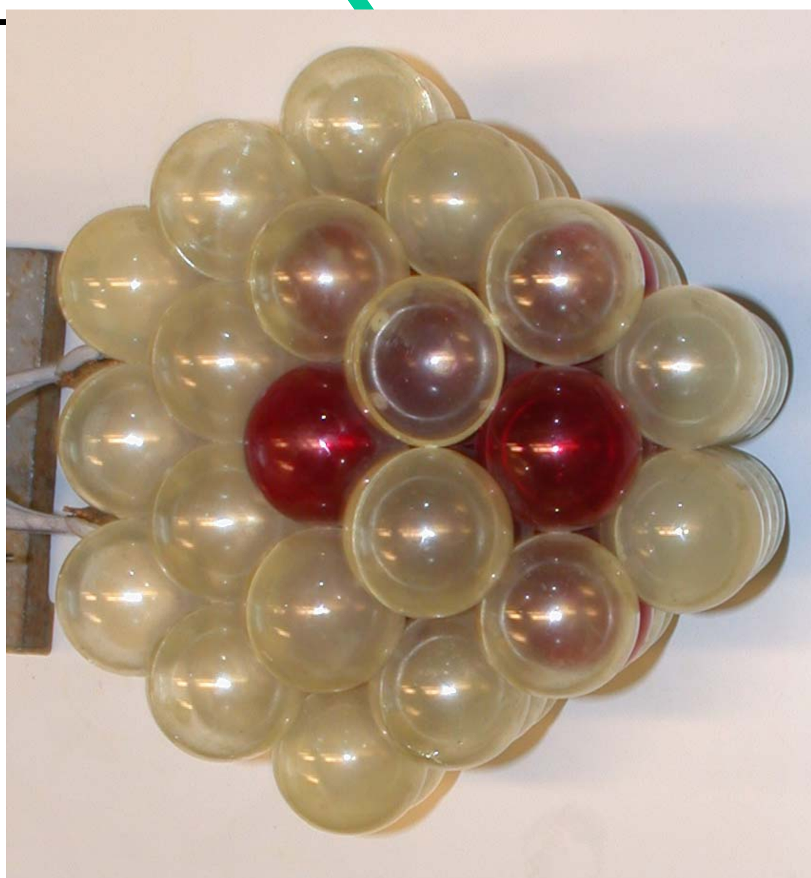
What are the lines?

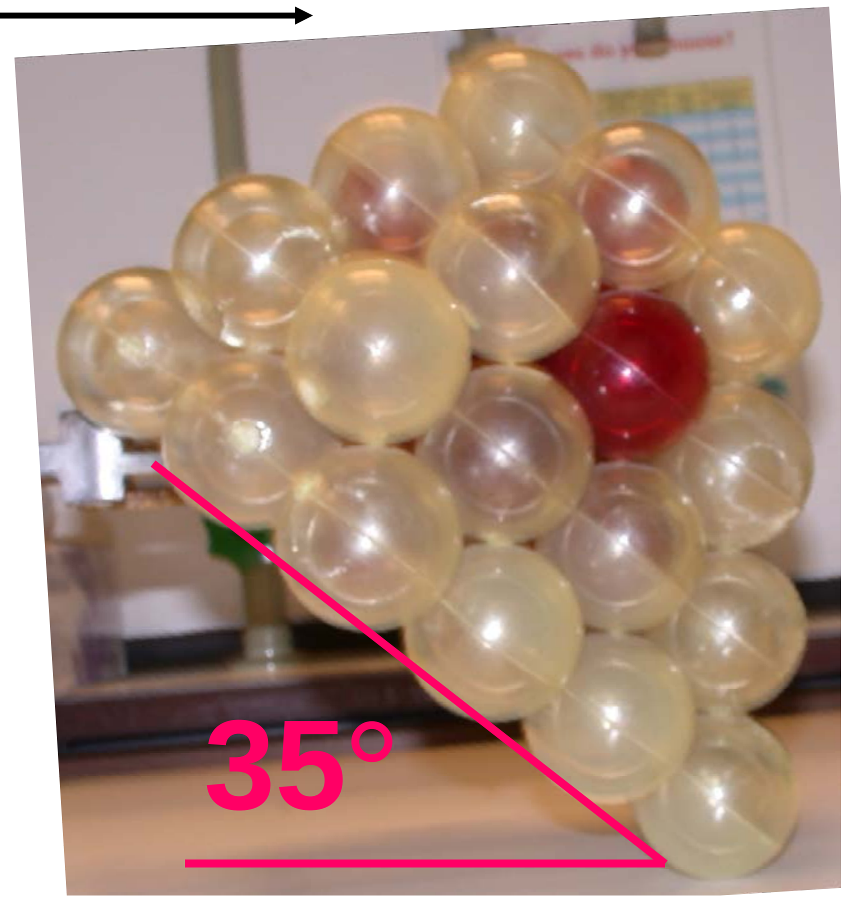


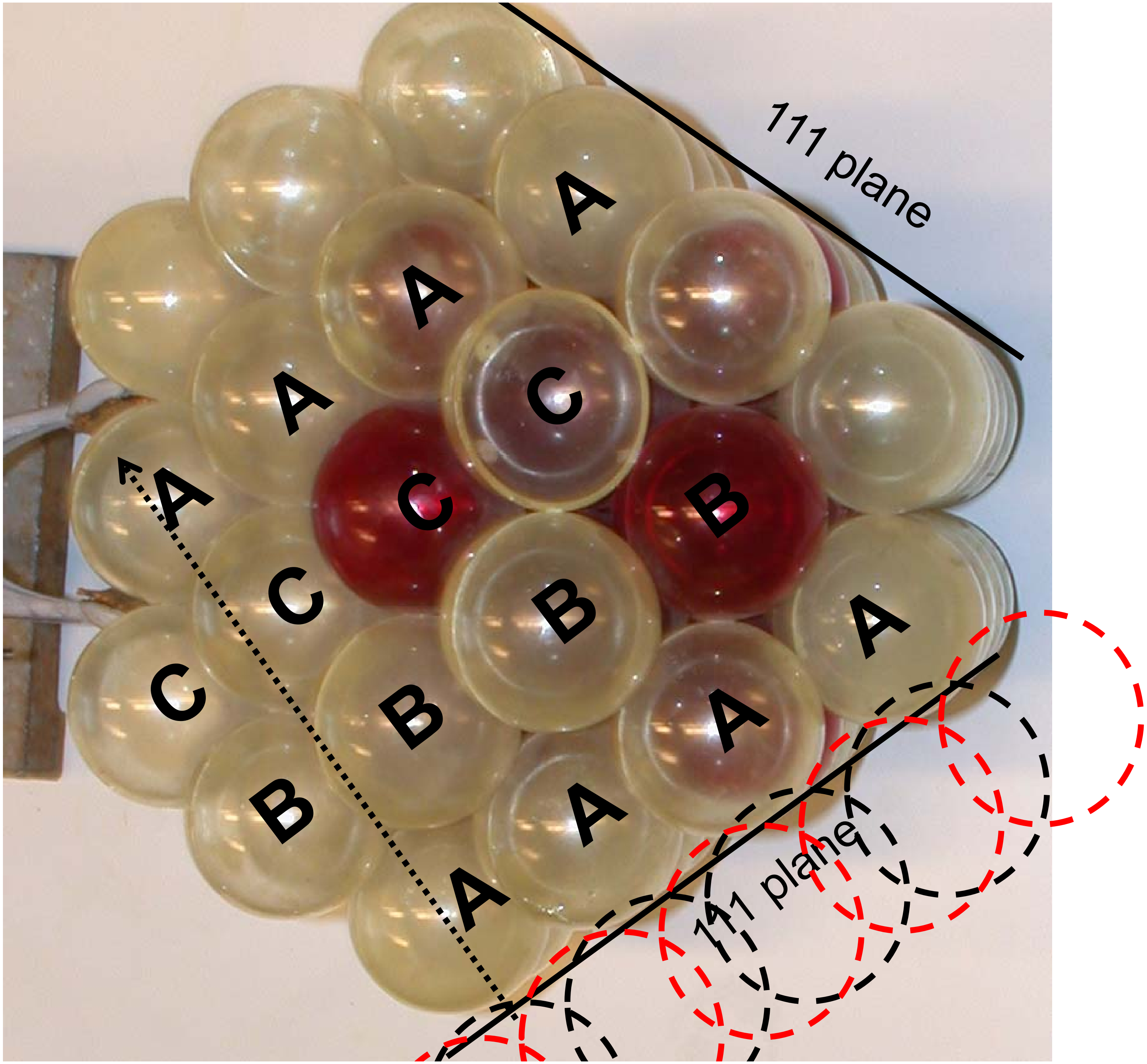
Pattern #3

Sample is turned by 35 degrees

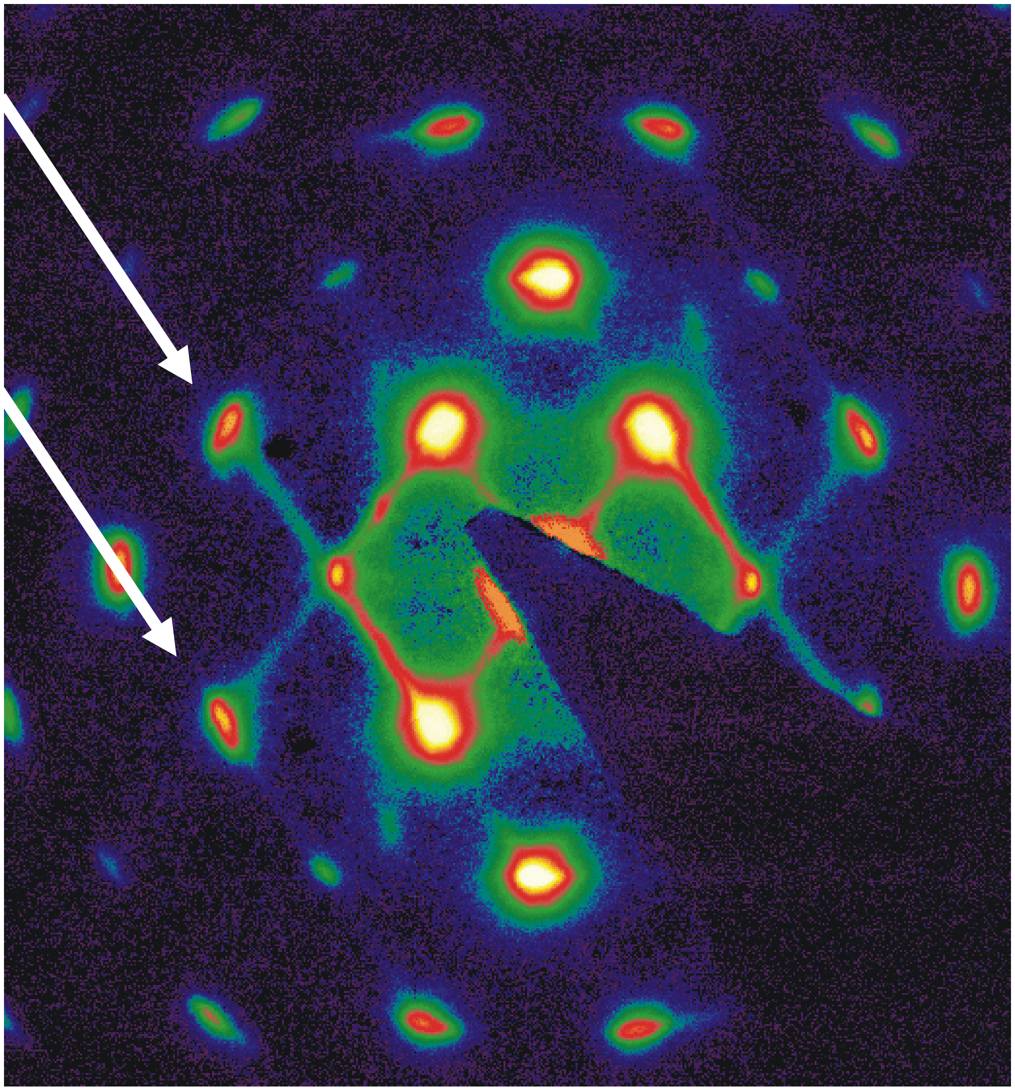
sample

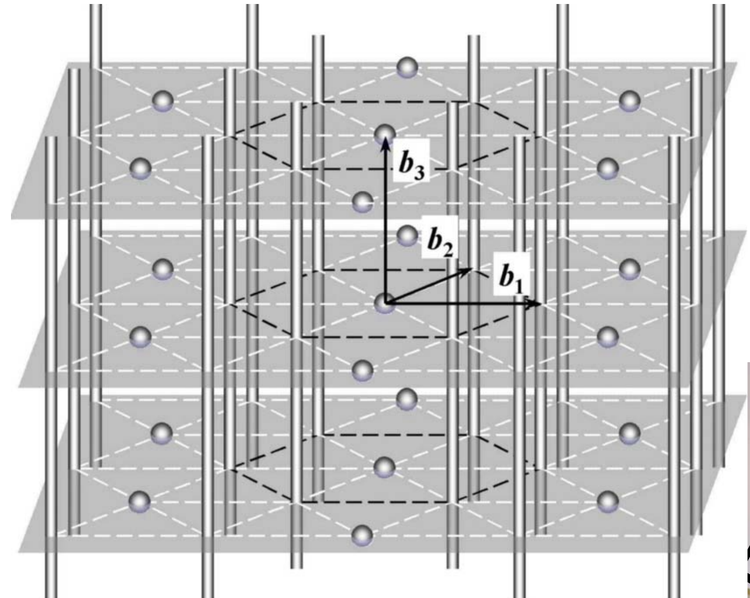


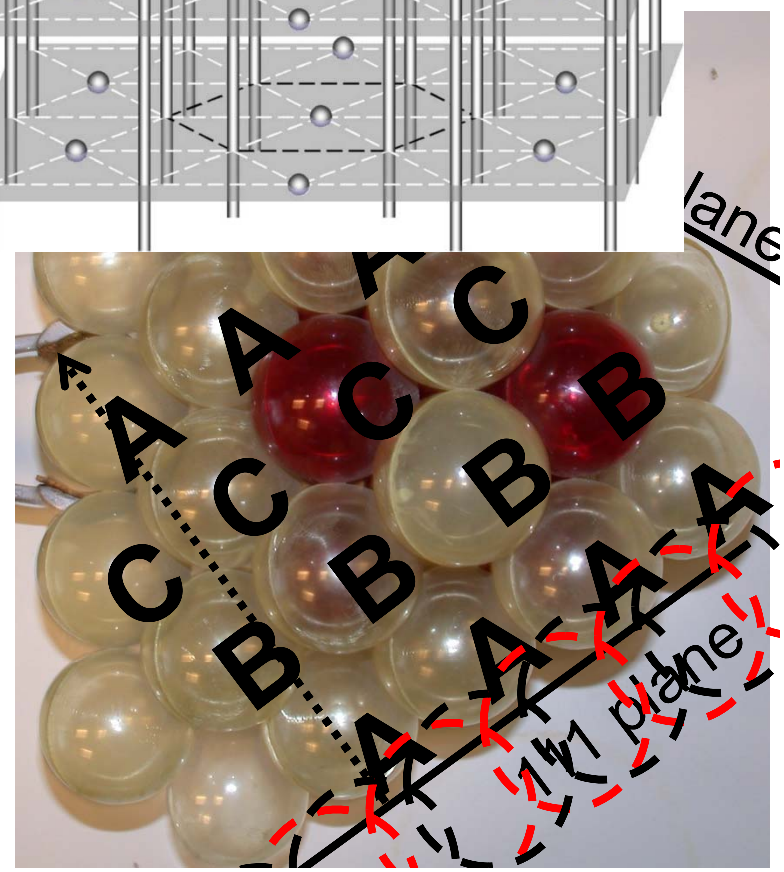



111 plane
A
A
C
A
A
C
B
A
C
B
A
C
B
A
B
A
A
111 plane

- Stacking disorder can be clearly seen in this projection!
- These are the Bragg rods!

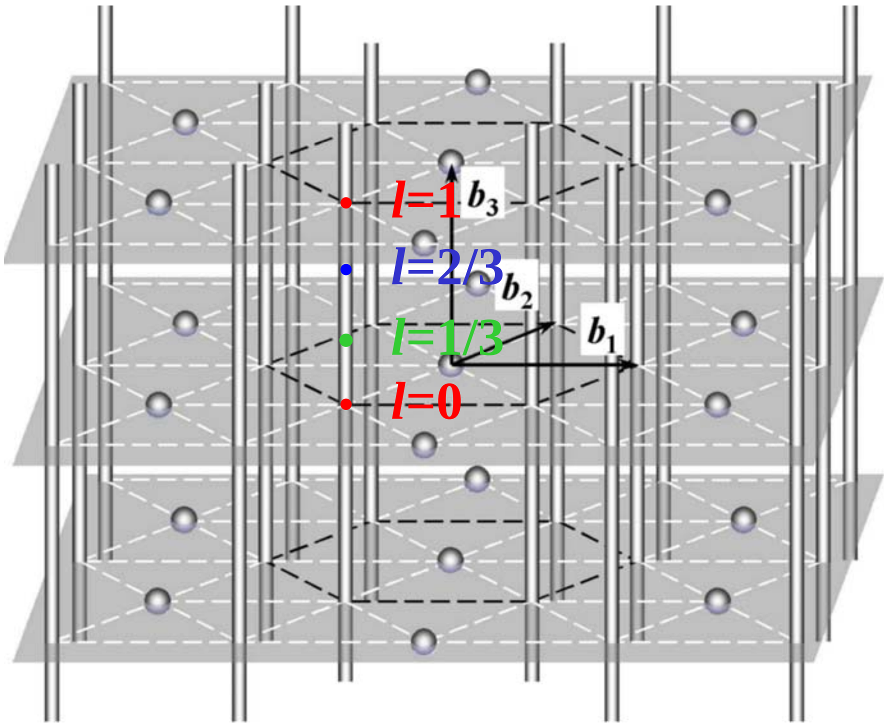


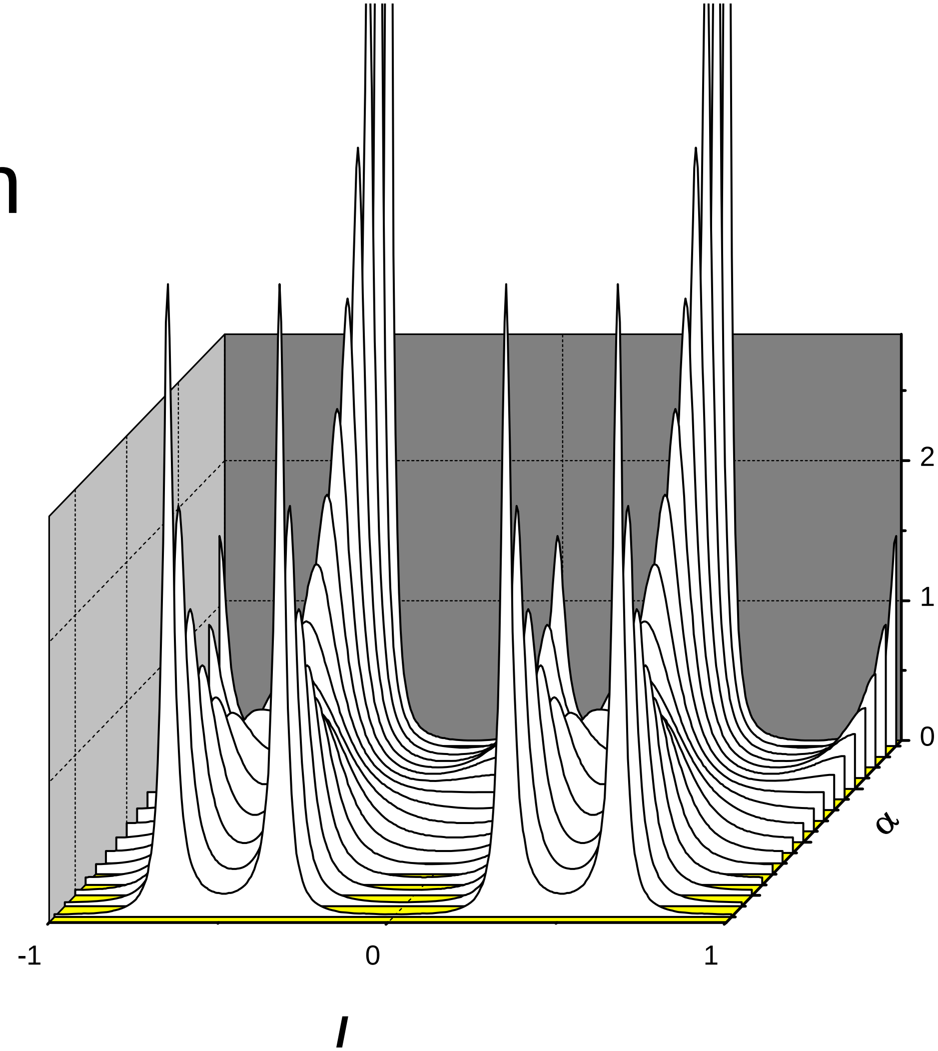




Wilson's theory:

Structure factor variation along Bragg rods

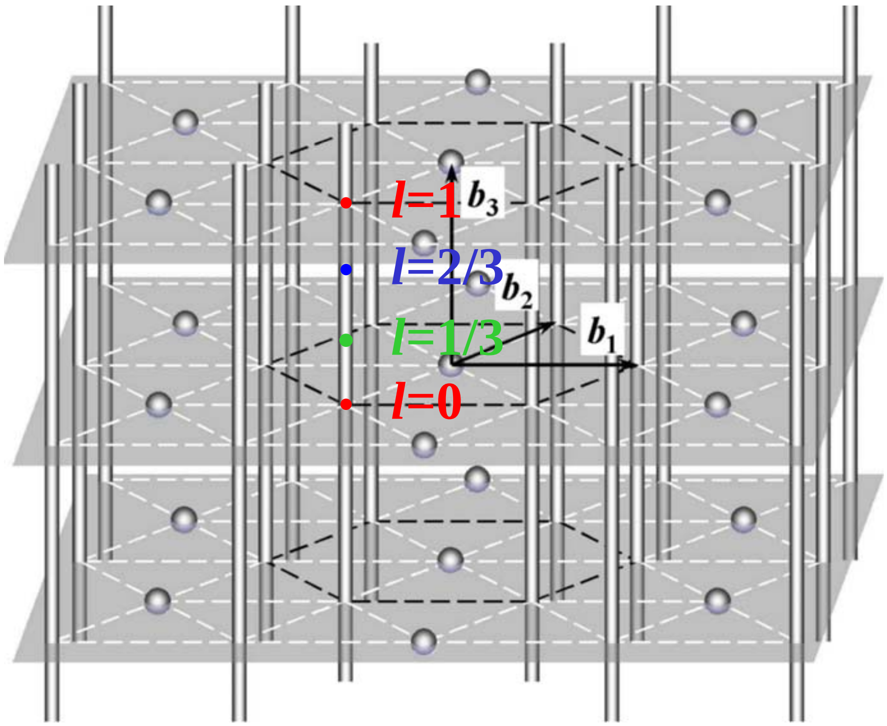


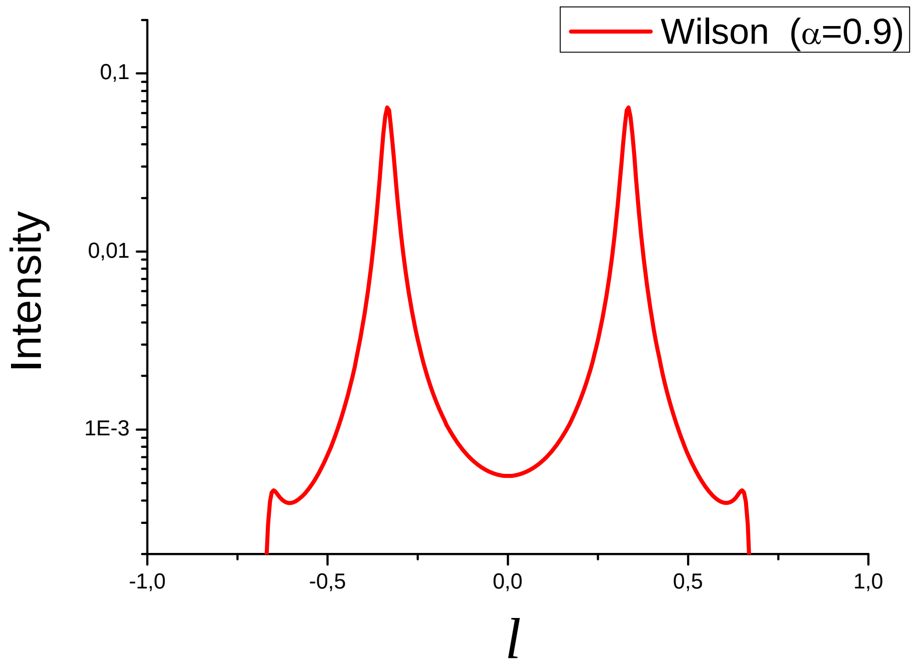


Is this what we see?

Wilson's theory:

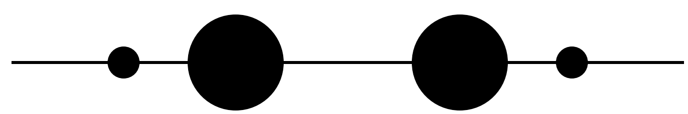
Structure factor variatic along Bragg rods



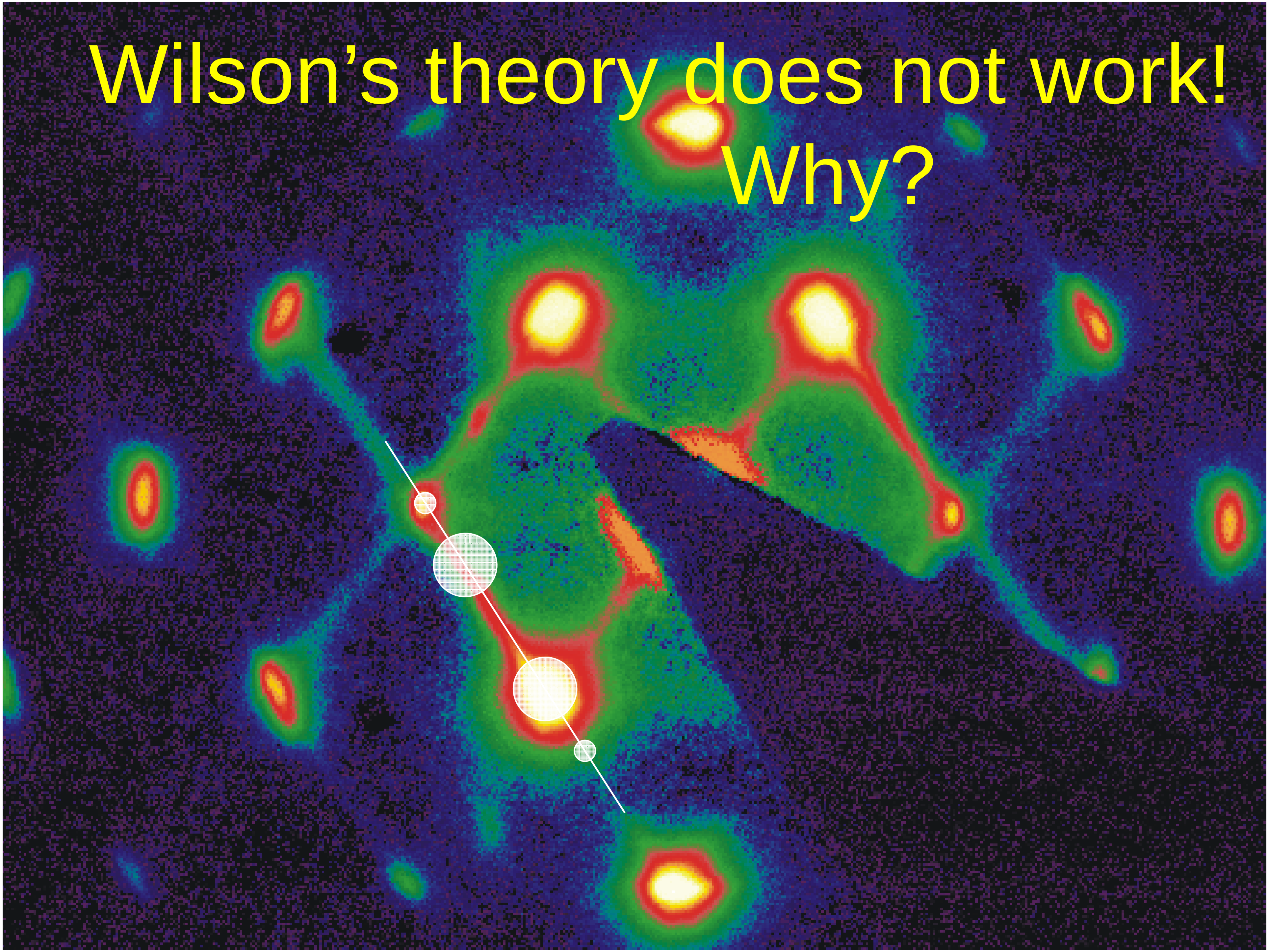


-1

Times the form factor:

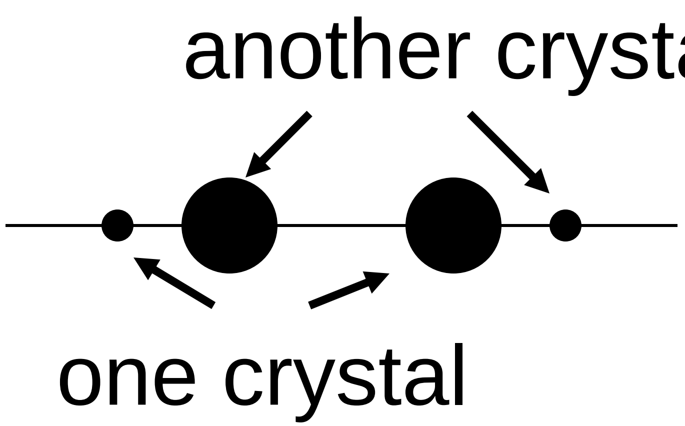


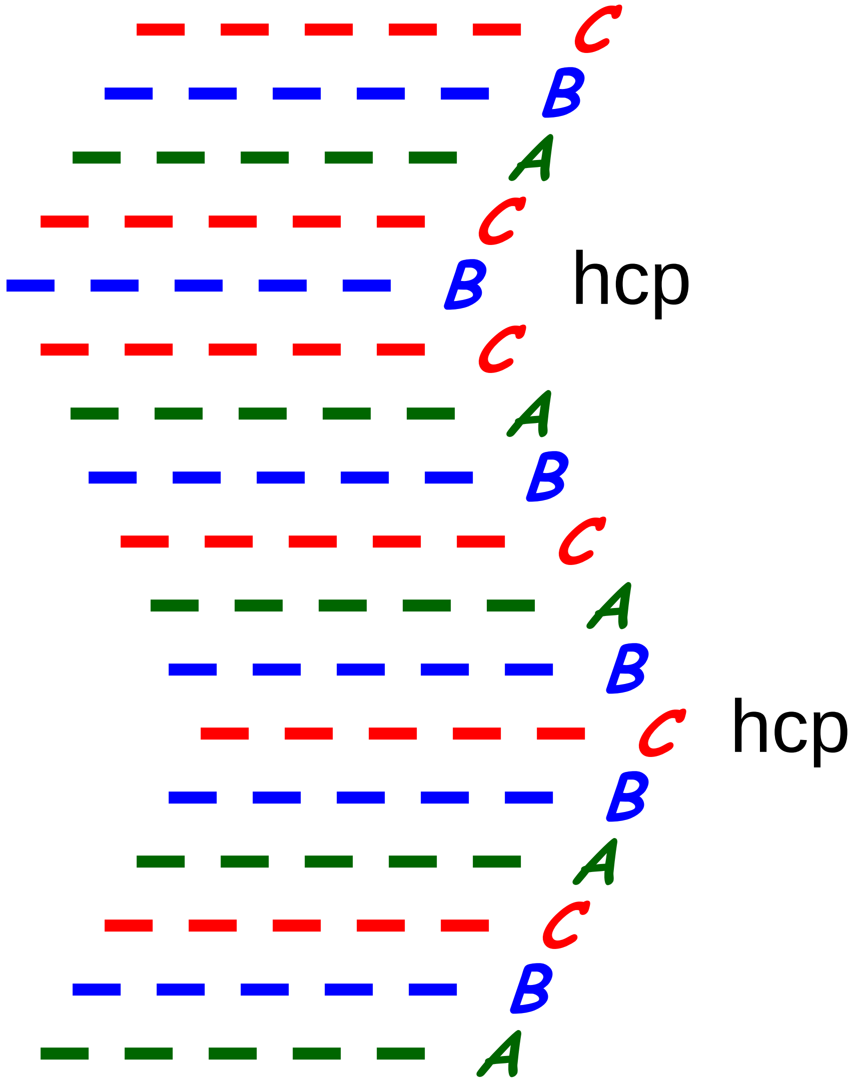
Is this what we see?


Wilson’s theory does not work!
Why?

Wilson's theory:

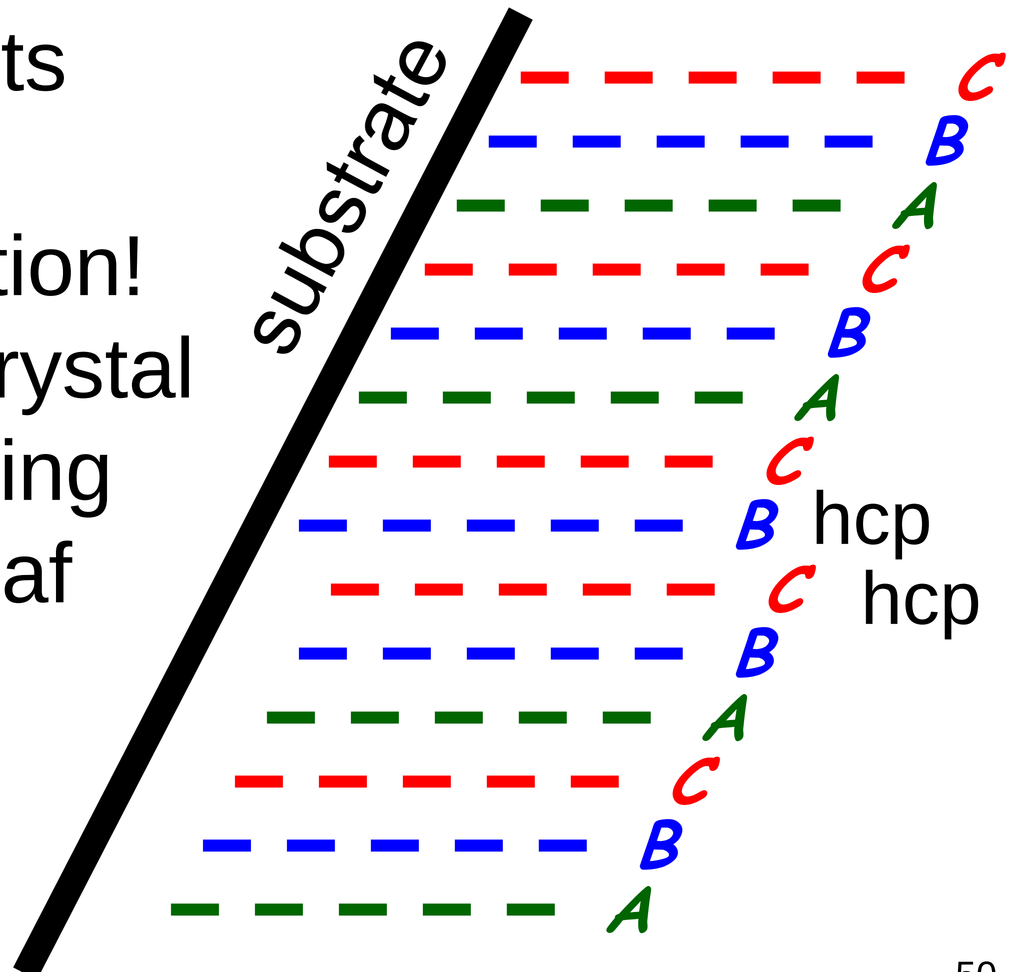
- Stacking fault changes stacking direction
- One gets not one but two (twin) crystals with …ABCABC… and …ACBACB… stacking

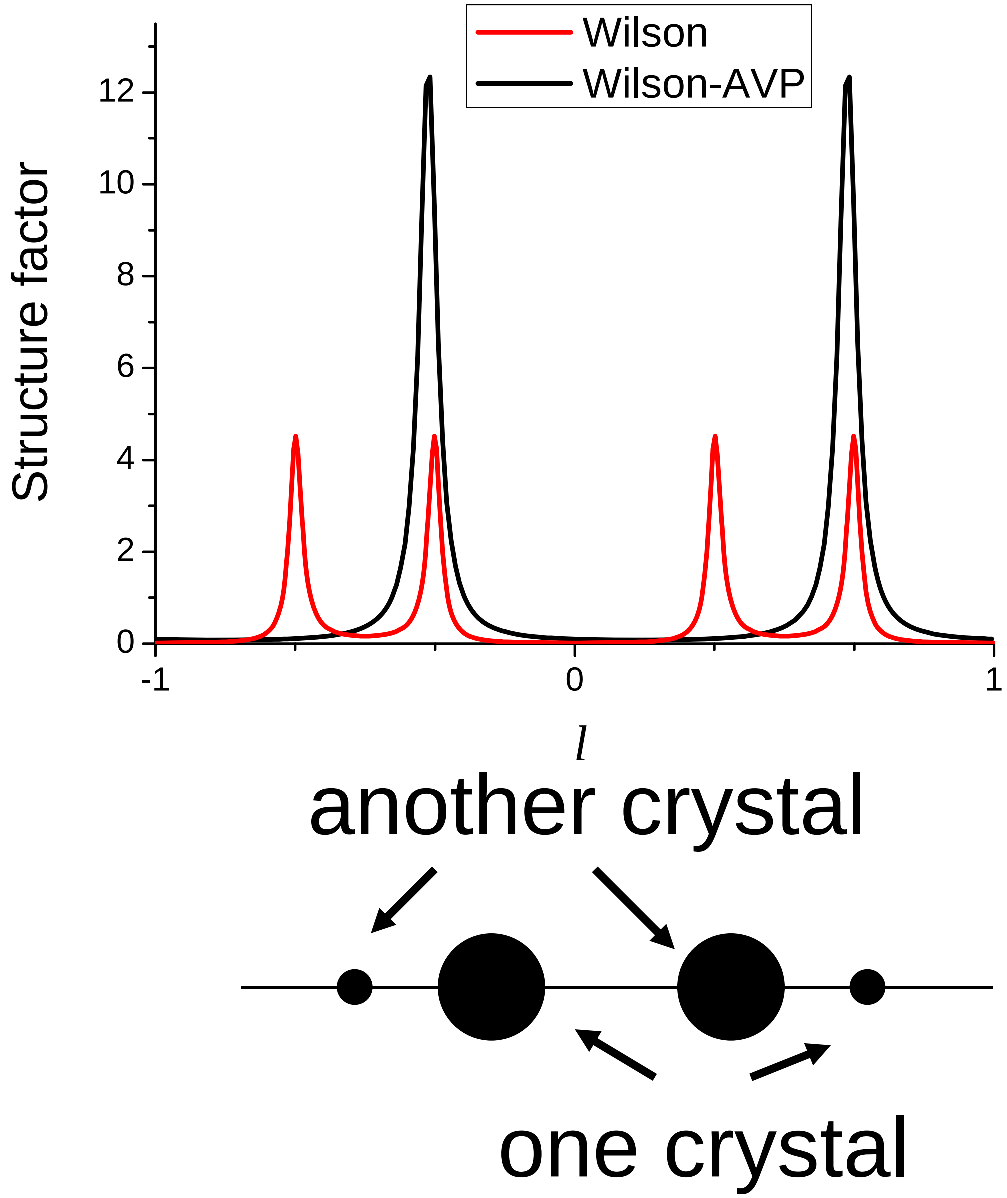




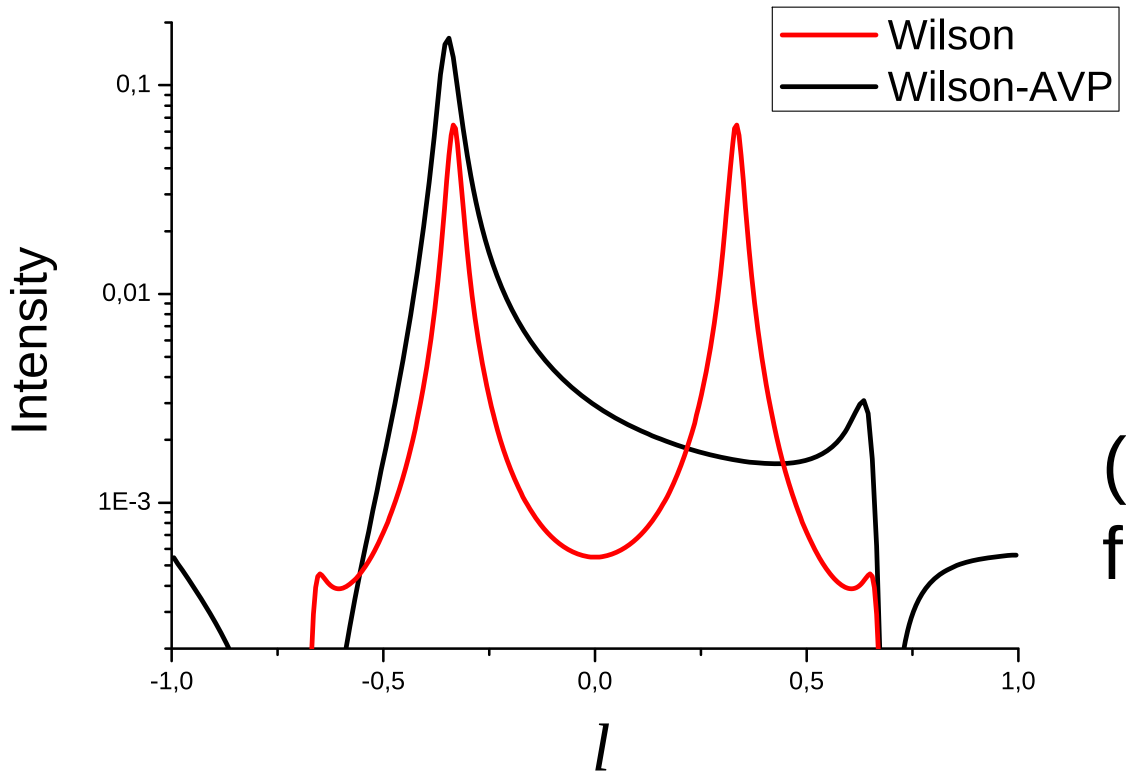
How should we modify Wilson's theory?

- Double stacking faults do not change the stacking direction!
- One gets only one crystal with a unique stacking
- Het is logisch achteraf te zien (Dirk Aarts)

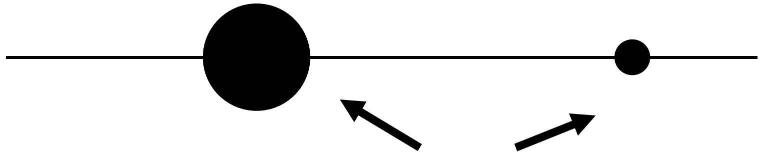




Paterson, M. S. J. Appl. Phys. 1952, 23(8), 805–811.



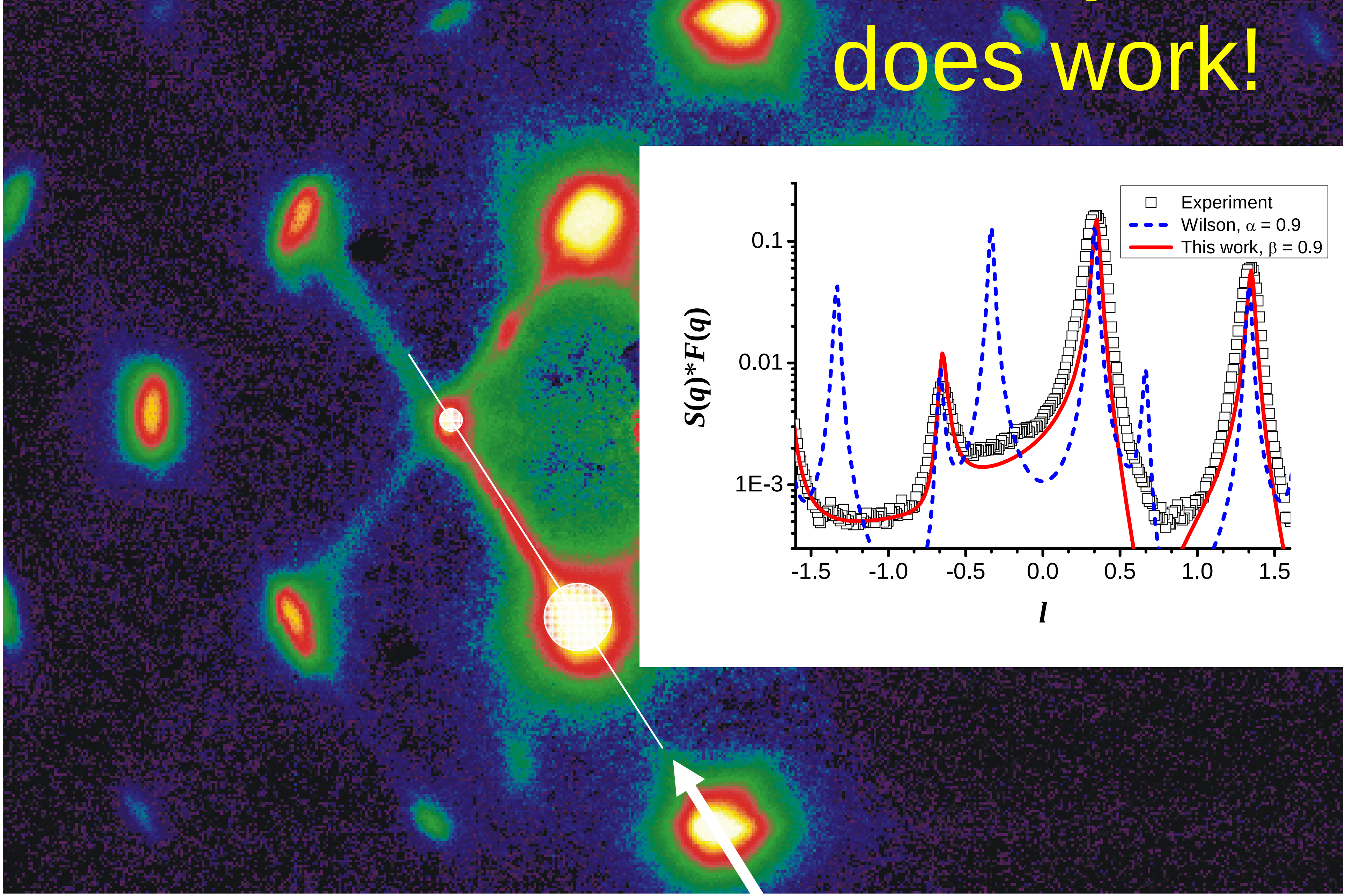
(times the form factor)

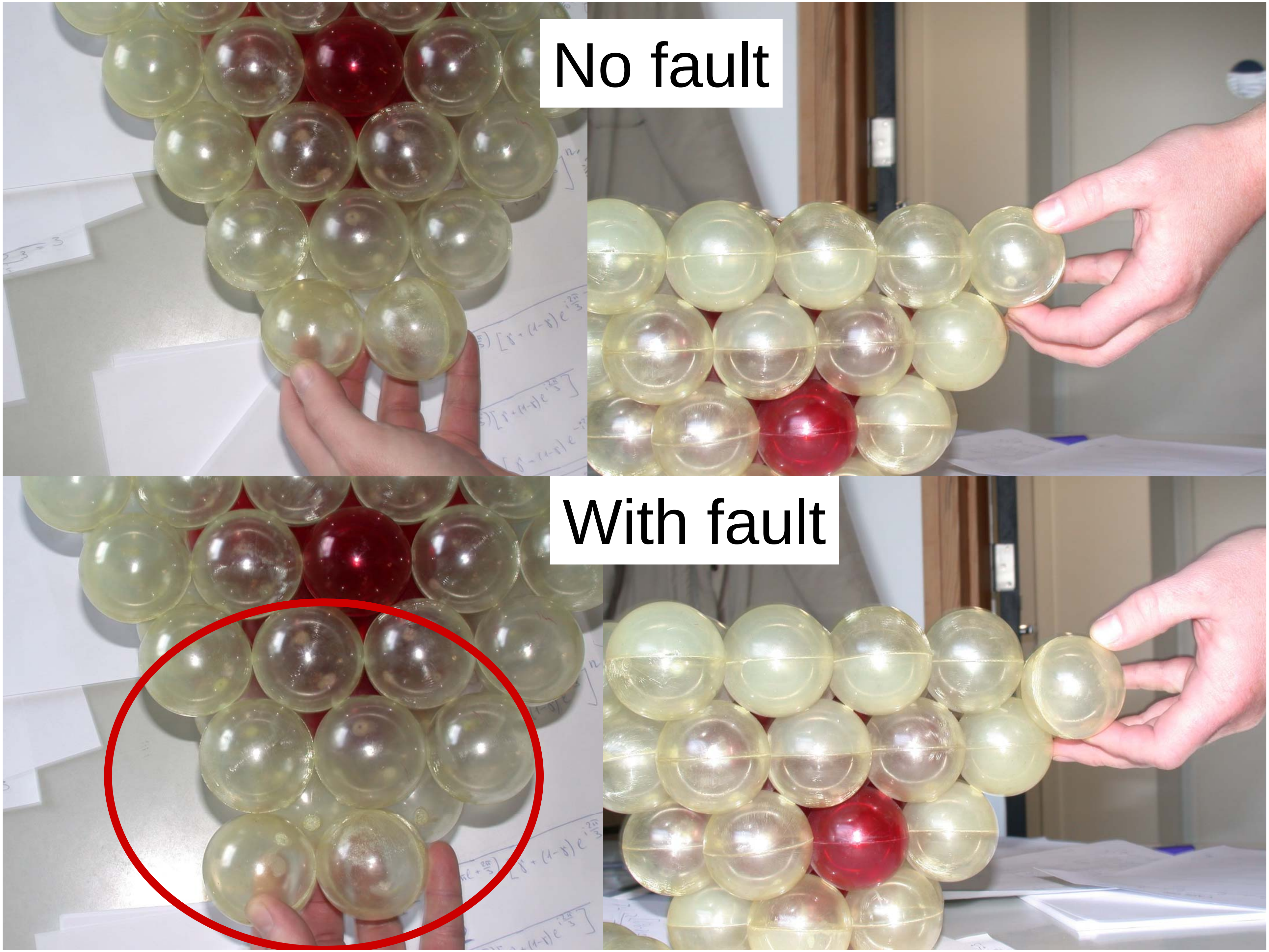


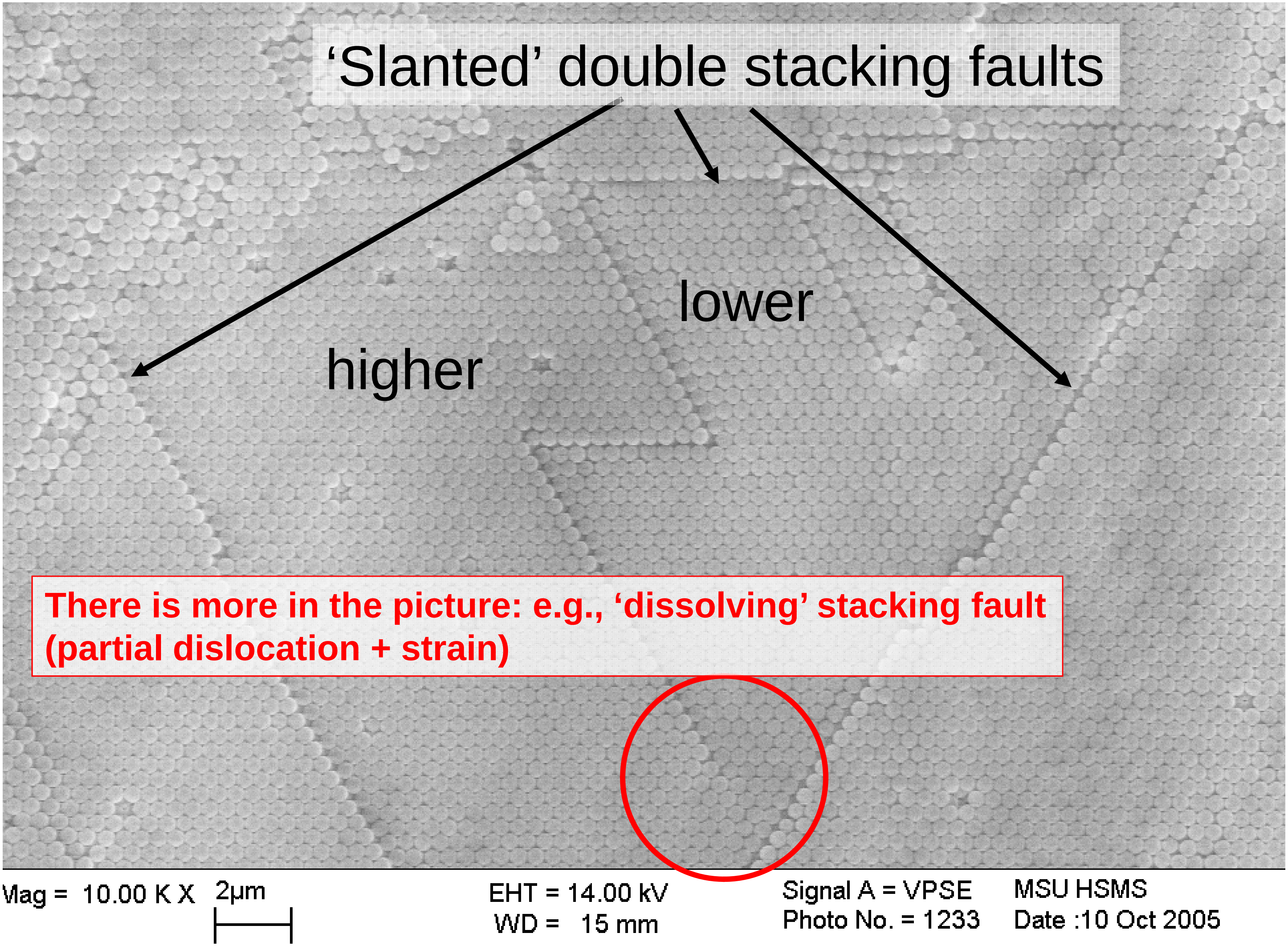
one crystal

Paterson, M. S. J. Appl. Phys. 1952, 23(8), 805–811.

Modified Wilson's theory does work!



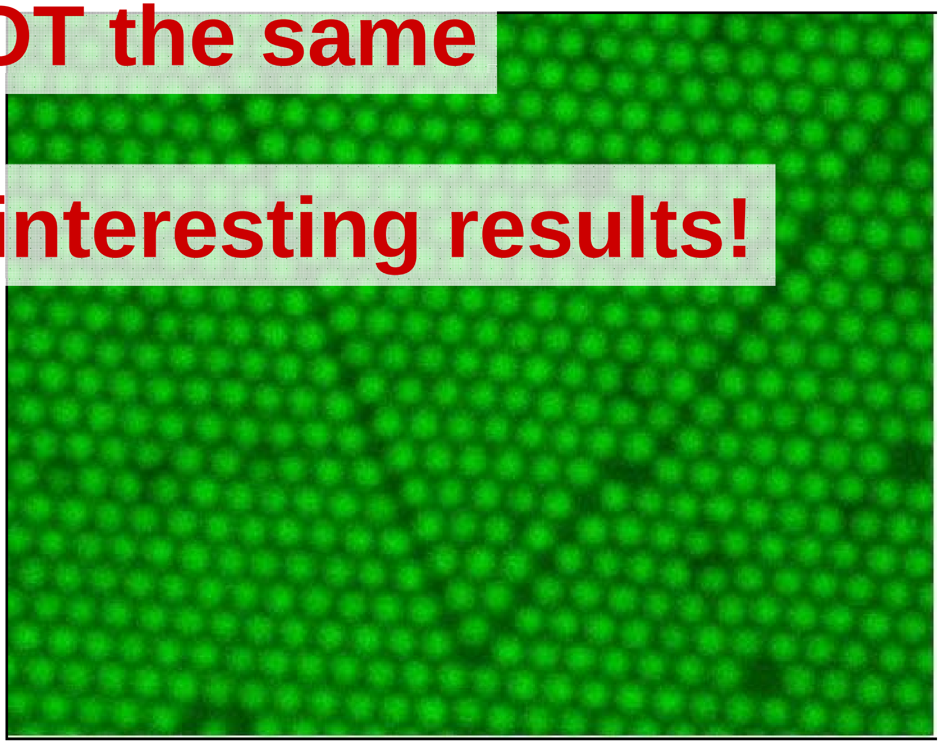

No fault
With fault


‘Slanted’ double stacking faults
lower
higher
There is more in the picture: e.g., ‘dissolving’ stacking fault
(partial dislocation + strain)
Mag = 10.00 K X
2µm
EHT = 14.00 kV
WD = 15 mm
Signal A = VPSE
Photo No. = 1233
MSU HSMS
Date :10 Oct 2005

The wrong idea of the experiment

These are NOT the same

Yet, we find lots of interesting results!



Alexander Sinitskii et al.
SEM of vertical deposition crystals
Mendeleev Comm., 2007

Volkert de Villeneuve et al.
Confocal microscopy of sedimentary crystals,
Langmuir & EPL, 2007

Conclusions

- X-ray diffraction from ‘nano-elephants’ is doable
  - period: > 1 micron
  - long-range order: > 10 micron
- New type of defects in colloidal crystals are found and characterized

Schedule

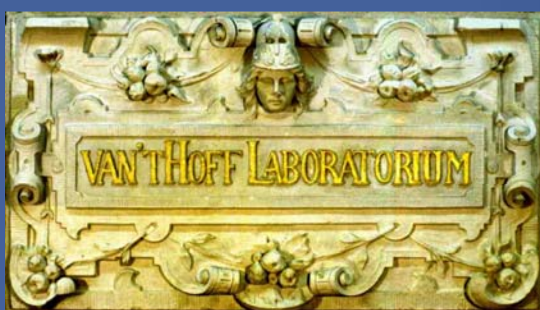
- Introduction to nanoelephants
- Instrumentation
- Example 1: Hard spheres
- Example 2: Rusted nanonails
- Conclusion

Самоорганизация ржавых наногвоздиков

(жидко-кристалличаские фазы коллоидных частиц гётита)

Andrei Petukhov

Van ’t Hoff laboratory for physical and colloid chemistry
Utrecht University, The Netherlands



DUBBLE

Universiteit Utrecht

ESRF

Colloidal Goethite

Горные вершины
Спят во тьме ночной;
Тихие долины
Полны свежей мглой;
Не пылит дорога,
Не дрожат листы...
Подожди немного,
Отдохнешь и ты.

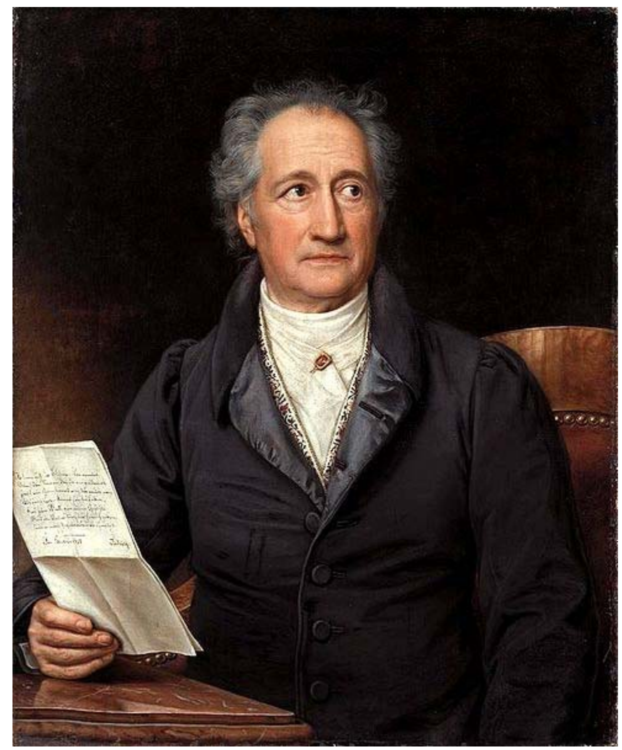
Лермонтов

Мирно высятся горы.
В полусон
Каждый листик средь бора
На краю косогора
Погружен.
Птичек замерли хоры.
Погоди: будет скоро
И тебе угомон.

Пастернак

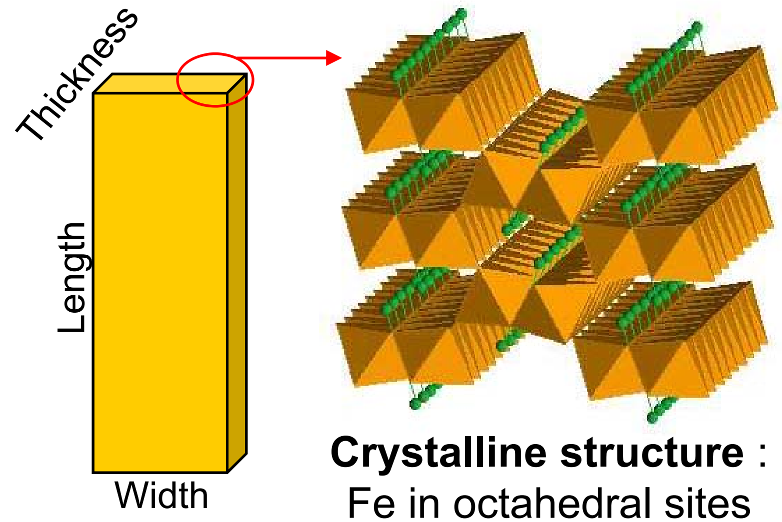
Uber allen Gipfeln
ist Ruh',
in allen Wipfeln
spurest du
kaum einen Hauch.
Die Vogelein schweigen im Walde.
Warte nur, balde
ruhest du auch.

Johann Wolfgang von Goethe

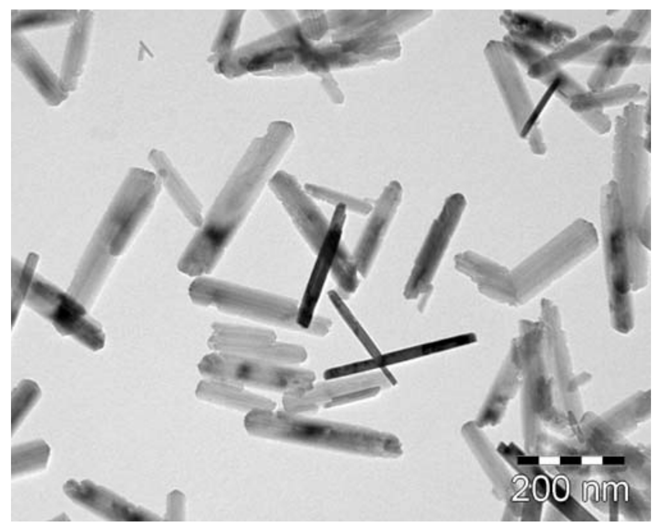


Goethite

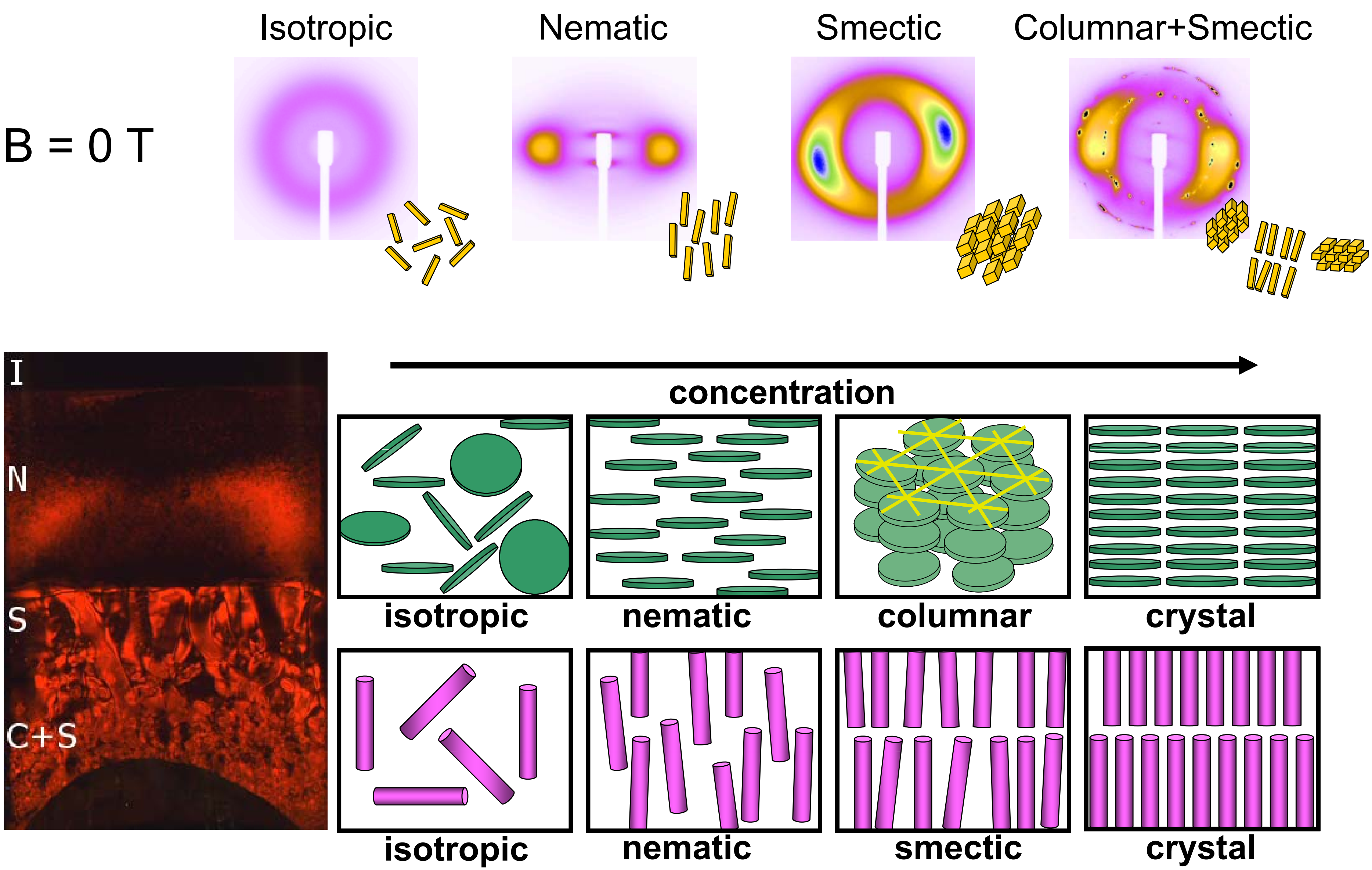
- α-FeOOH
- Preferred direction of crystal growth → boardlike particles
- Majorana 1902 / Cotton, Mouton 1907
- B.J. Lemaire / P. Davidson 2002-2005



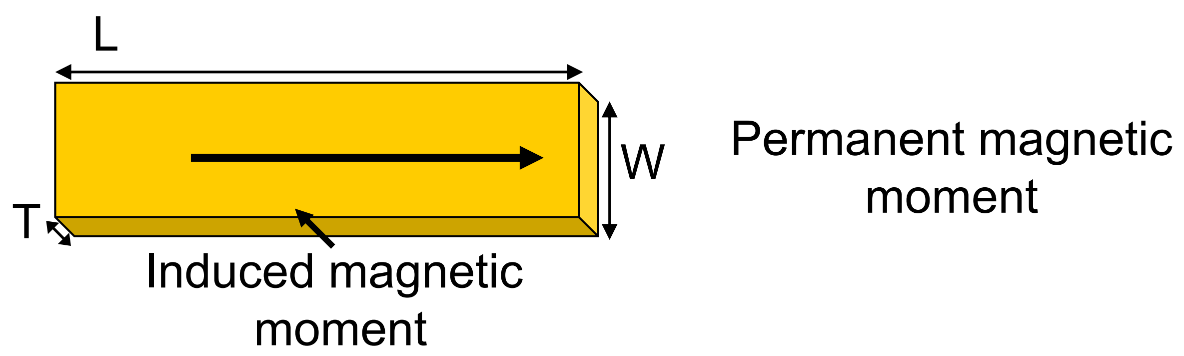
Crystalline structure : Fe in octahedral sites

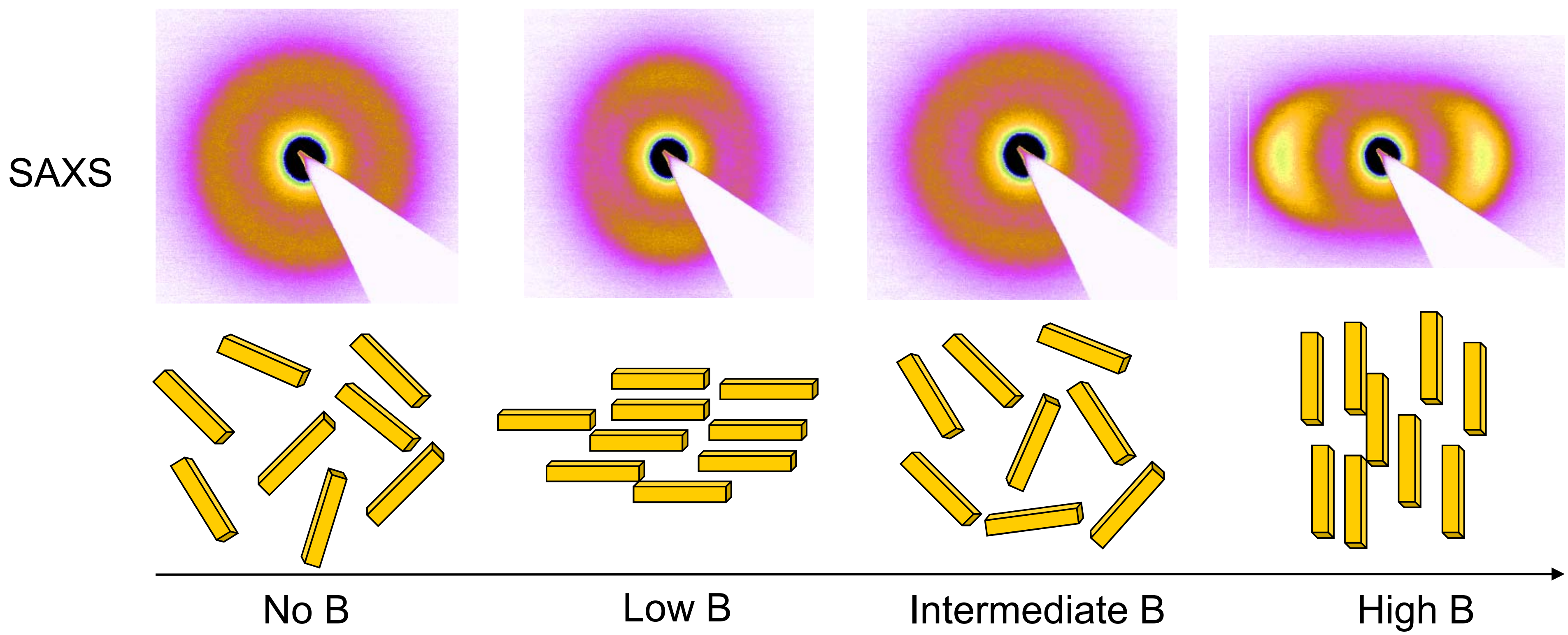


Self-organisation of colloidal goethite

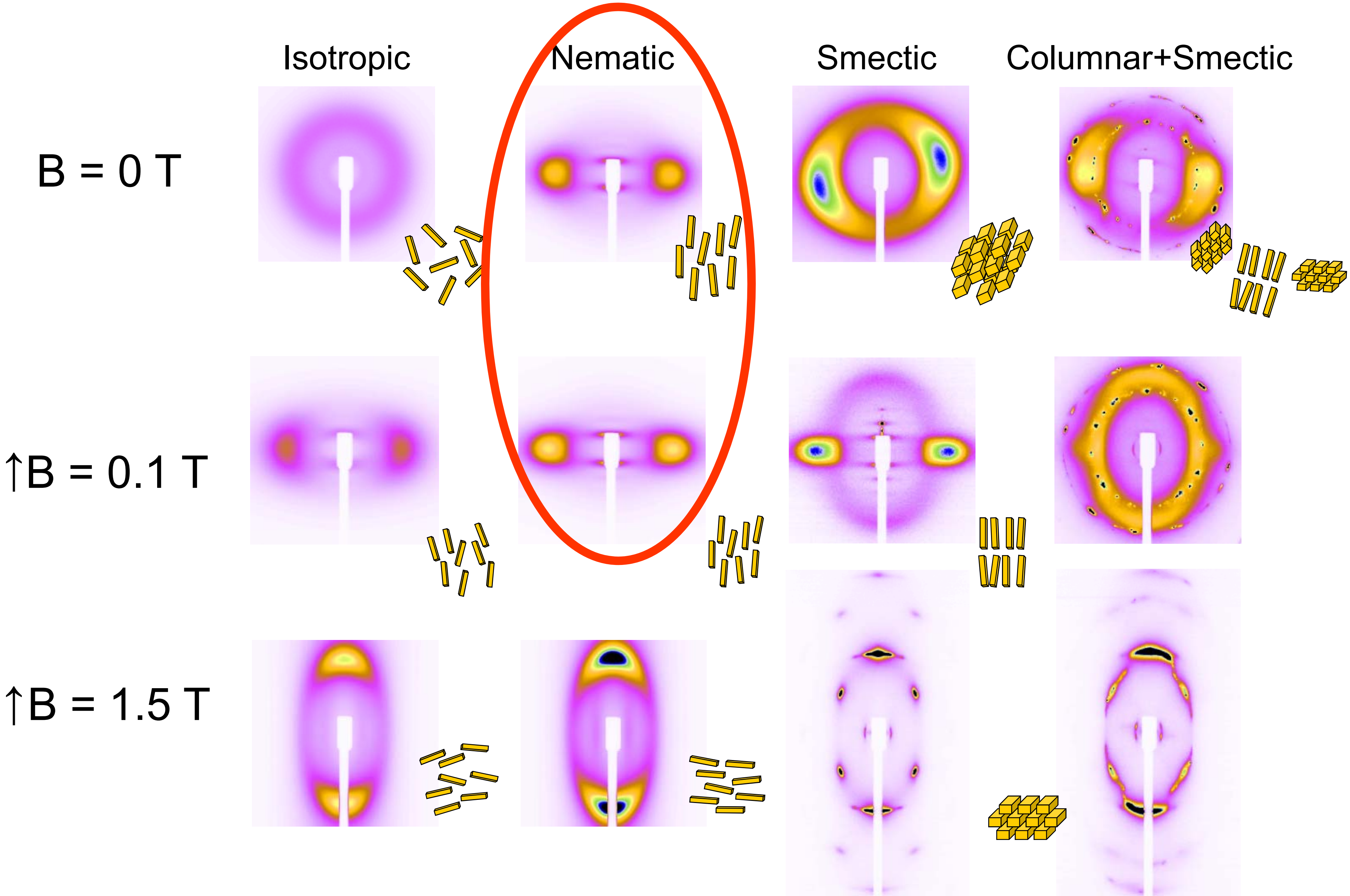


Magnetic properties





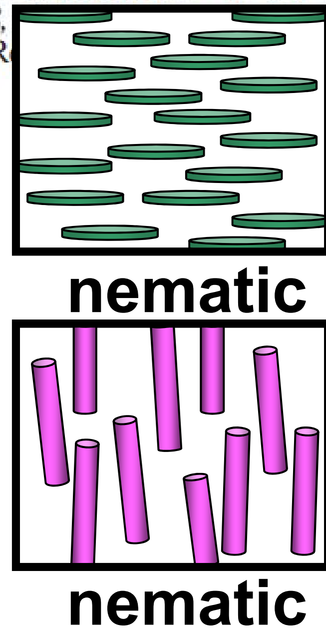
Influence of an external magnetic field

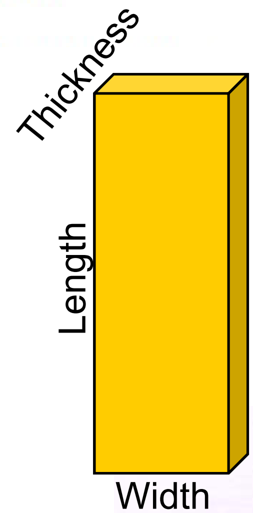


PHYSICAL REVIEW LETTERS

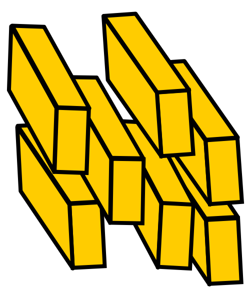
Experimental Realization of Biaxial Liquid Crystal Phases in Colloidal Dispersions of Boardlike Particles

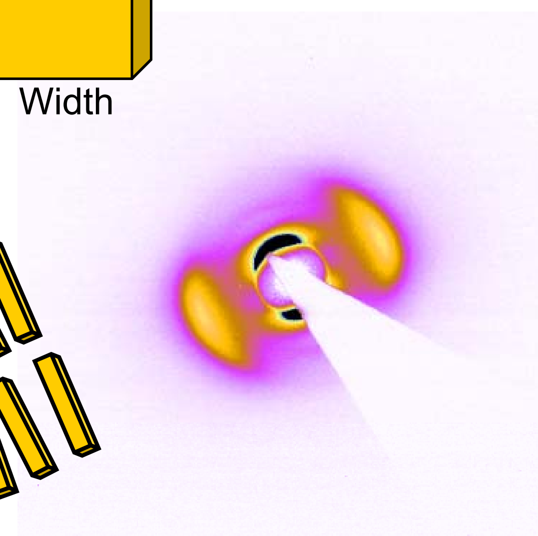
E. van den Pol, A. V. Petukhov, D. M. E. Thies-Weesie, D. V. Byelov, and G. J. Vroege*
Van 't Hoff Laboratory for Physical and Colloid Chemistry, Debye Institute for Nanomaterials Science, Utrecht University, Padualaan 8, *Netherlands*
(R)



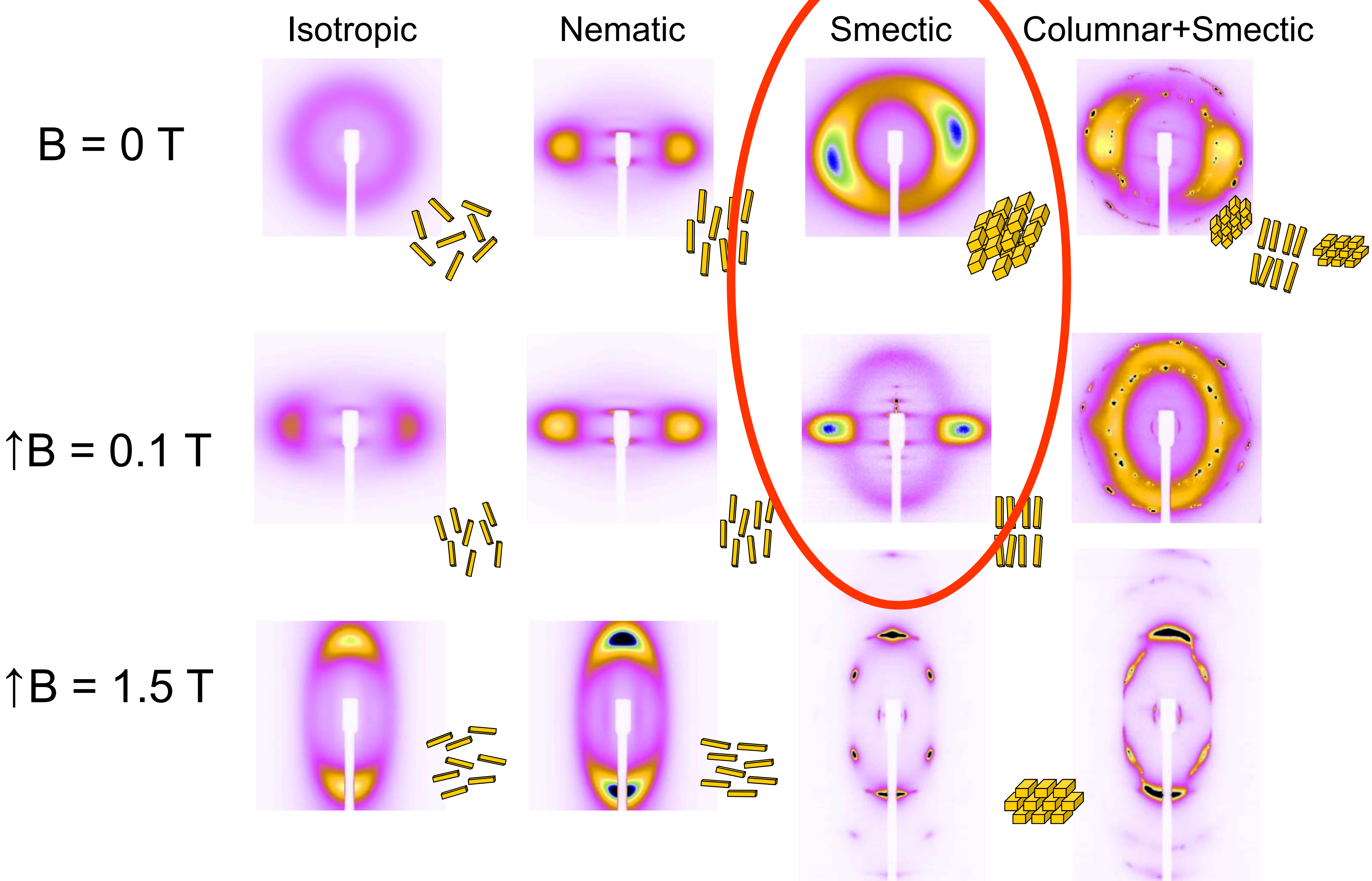


L/W ≈ W/T

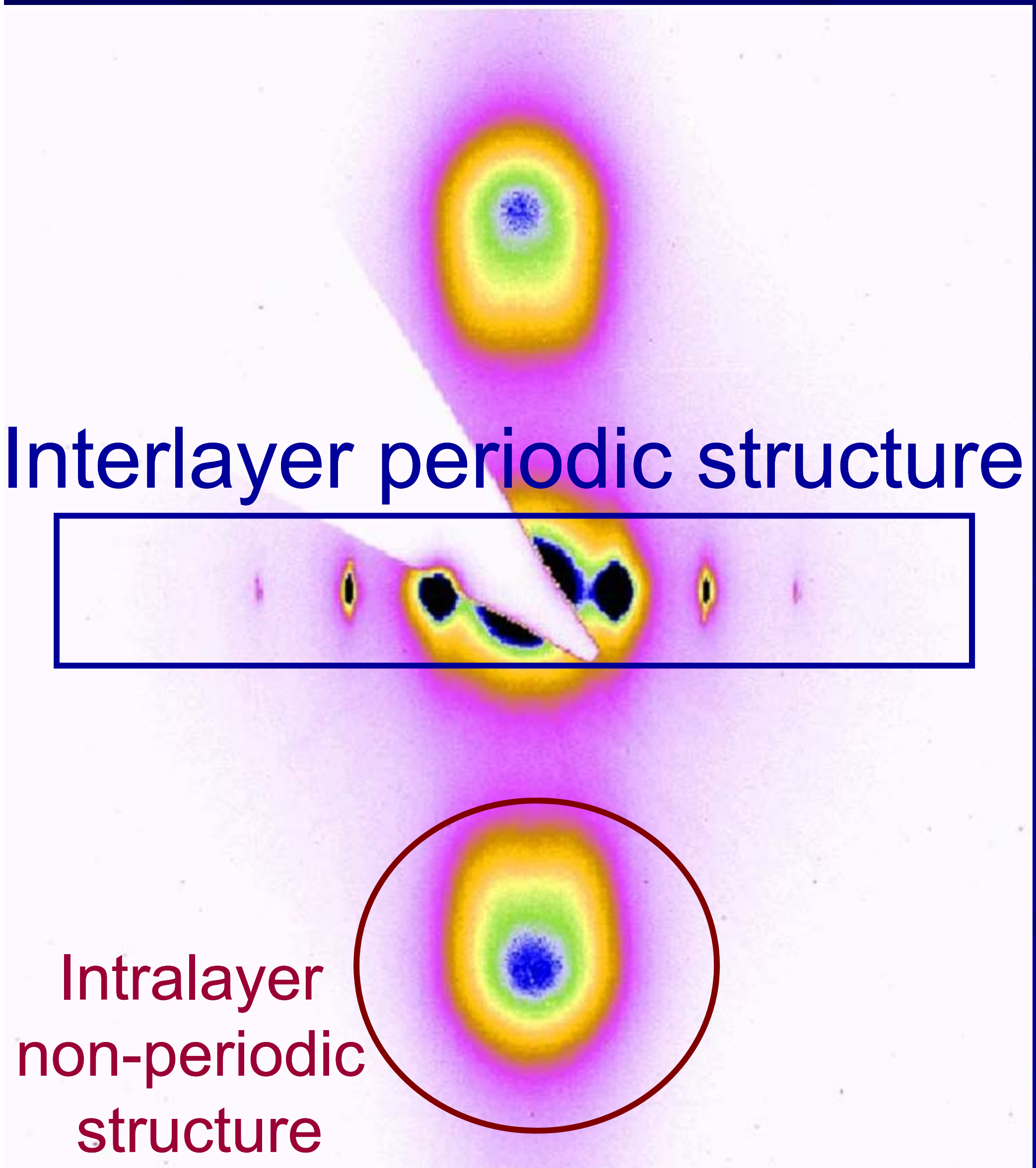




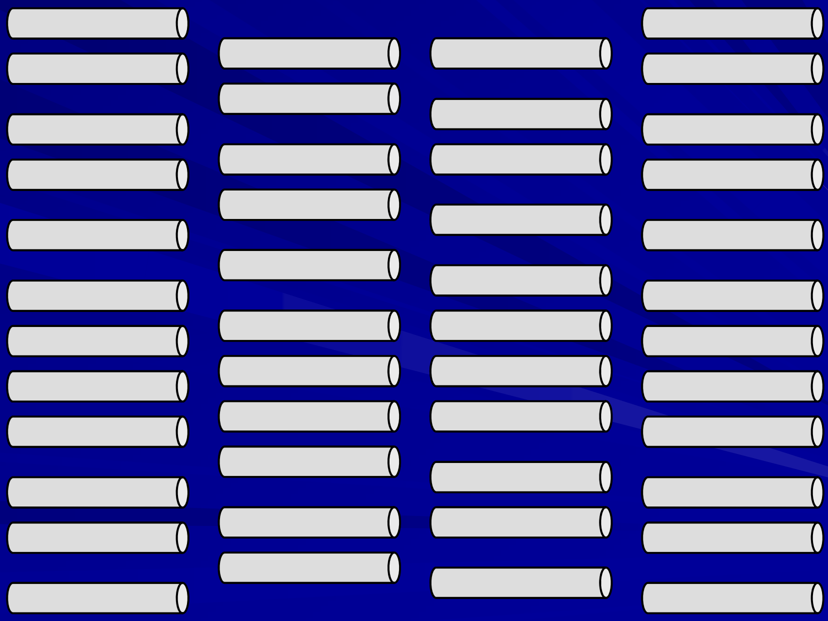
Influence of an external magnetic field



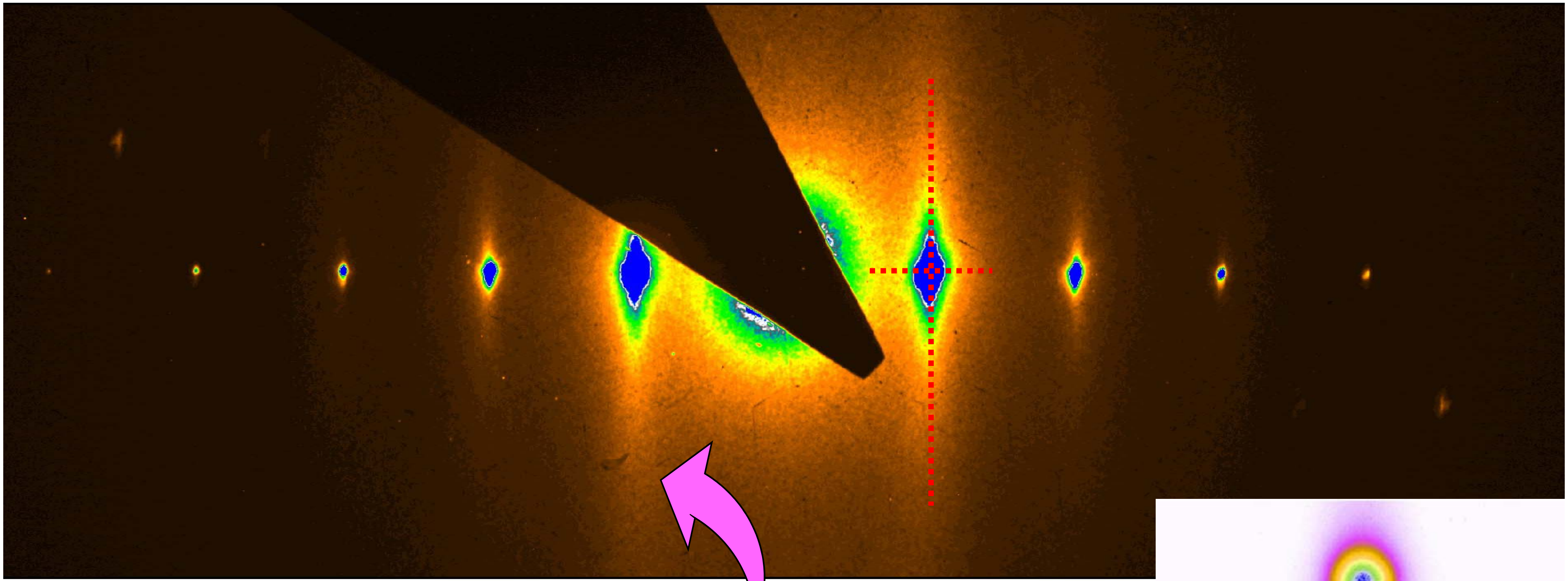
Smectic goethite: µrad XRD

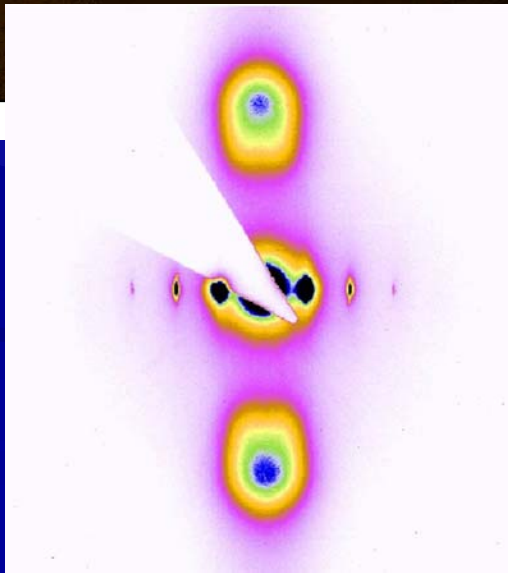


Sample aligned in magnetic field



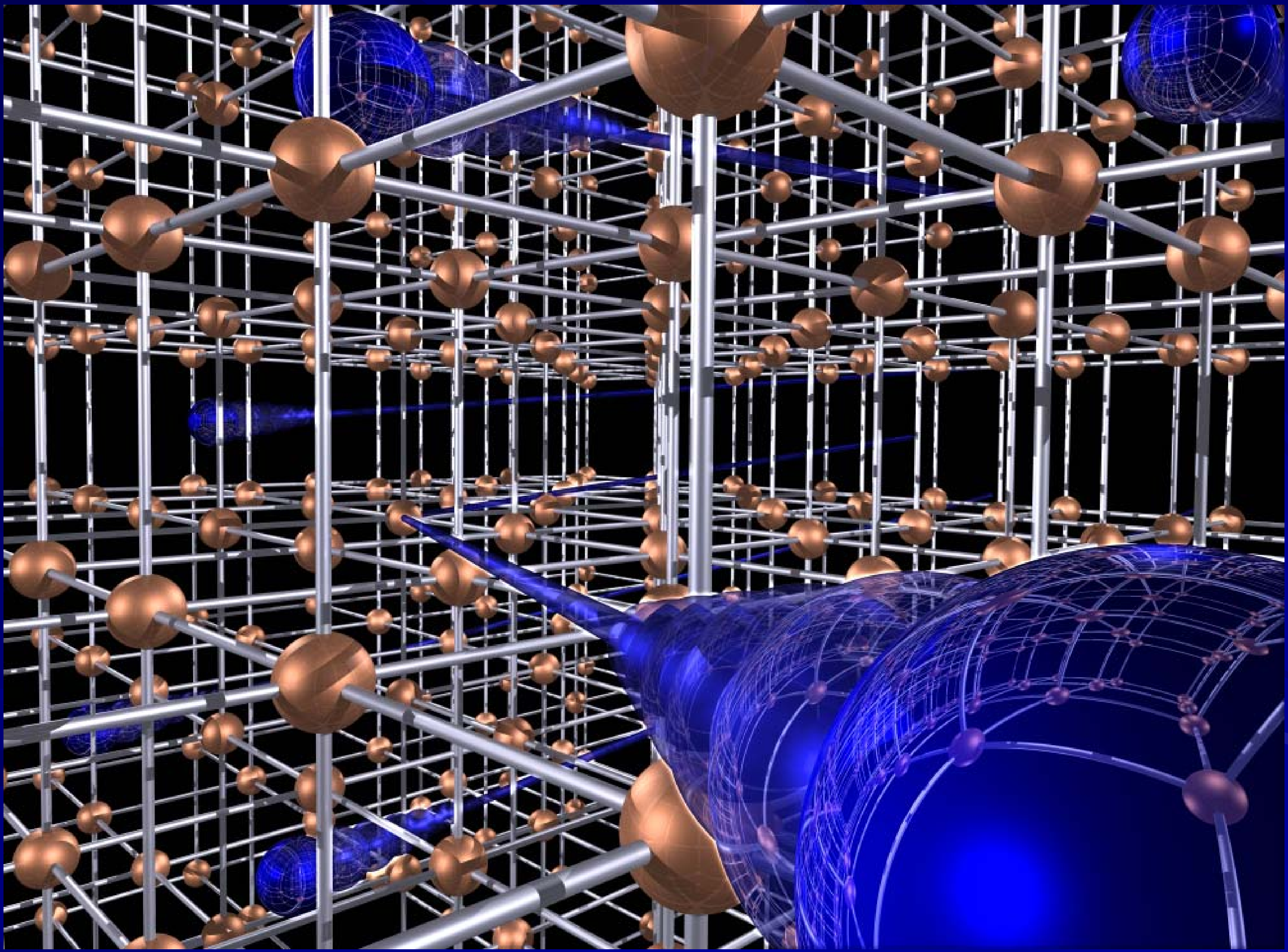
Closer look:





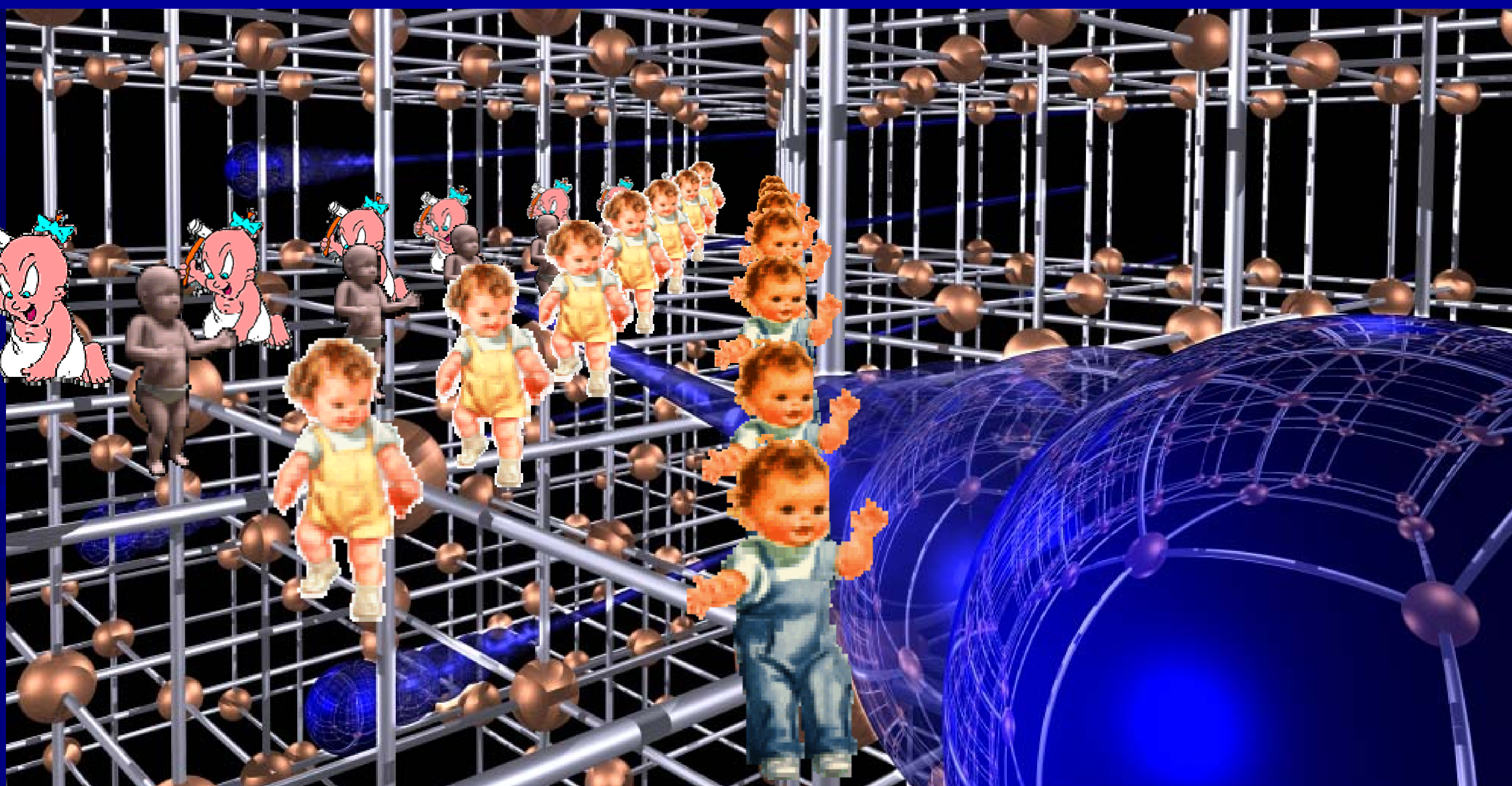
Diffuse scattering ‘streaks’

Long-range order



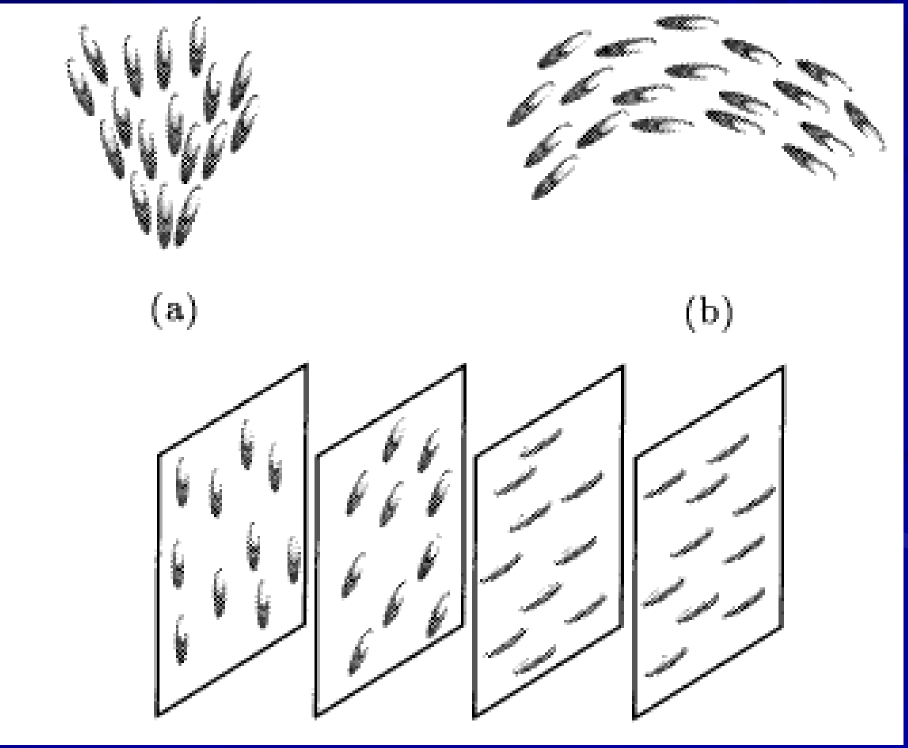
3D: Robust Order

few ($\sim q^2 dq$) long-wavelength modes in 3D
more ($\sim q^{D-1} dq$) in low-dimentional systems
(Landau-Peierls instability)



Nematic elasticity

$$F_n = \frac{1}{2}\int d^d x \{K_1(\nabla \cdot \mathbf{n})^2 + K_2[\mathbf{n}\cdot(\nabla \times \mathbf{n})]^2 + K_3[\mathbf{n}\times(\nabla \times \mathbf{n})]^2\}$$

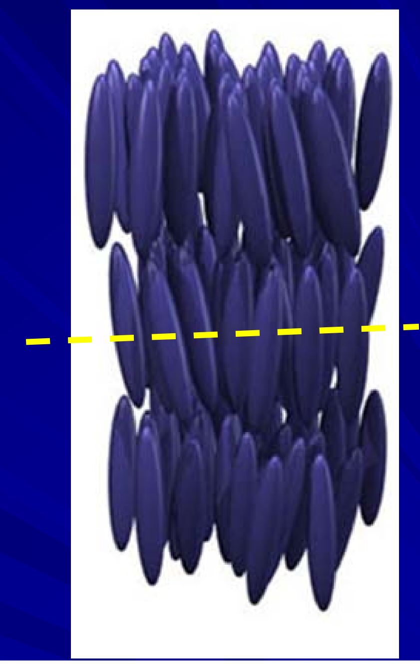


Splay, twist & bend

Coupling between smectic coordinates and nematic elasticity

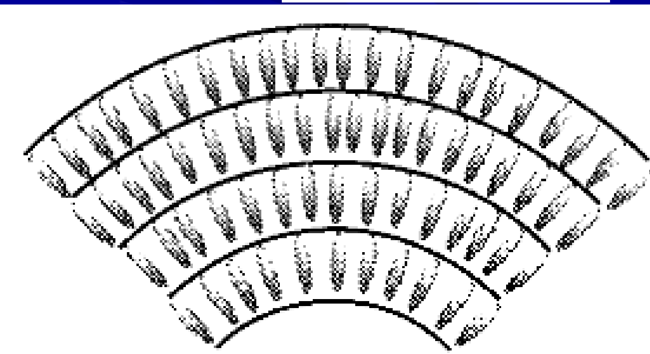
$$\delta n = -\nabla_{\perp} u$$

u: in-layer coordinate



First derivative: rotation

Second derivative: splay



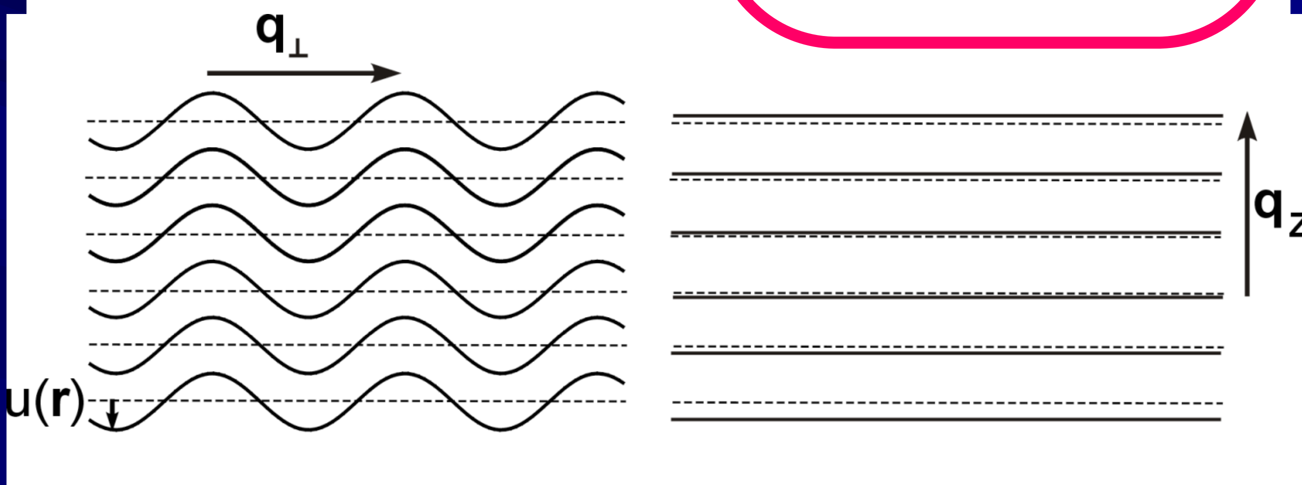
(b)

Smectic liquid crystals:
Landau-De Gennes free energy

$$F_B = \frac{1}{2}\int d^3r\left\{B\left(\frac{\partial u(\mathbf{r})}{\partial z}\right)^2 + K\left[\frac{\partial^2 u(\mathbf{r})}{\partial x^2} + \frac{\partial^2 u(\mathbf{r})}{\partial y^2}\right]^2\right\}$$

$\propto q^4$

Ultrasoft at low q



Undulation   Compression

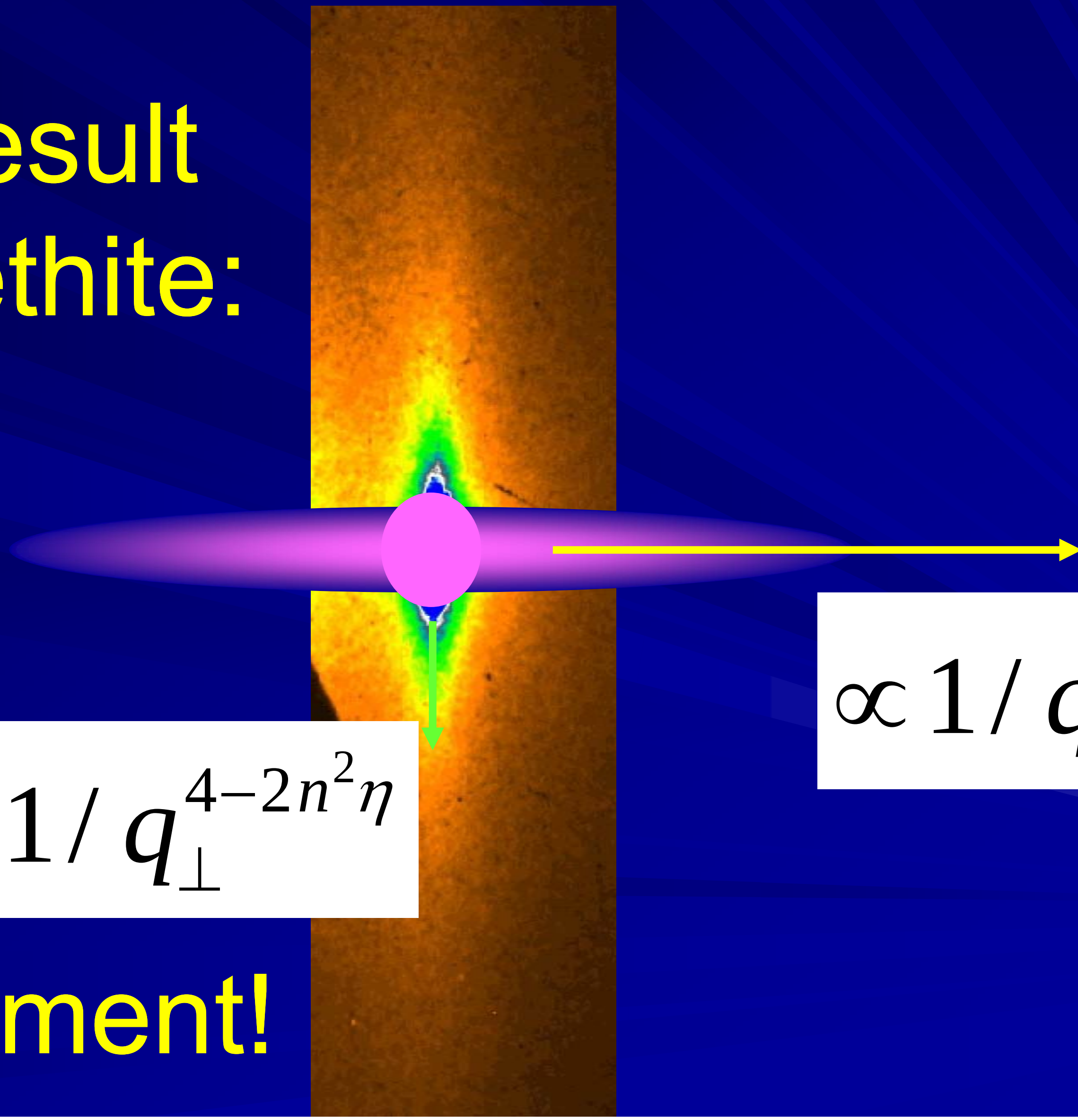
$$\langle u^2(\mathbf{r})\rangle = \frac{k_B T}{8\pi\sqrt{KB}}\ln\left(\frac{L}{d}\right)$$

Fluctuations destroy layer ordering for large L

Landau – Peierls instability

Effect of Peierls-Landau instability on reflections:

Our result for goethite:

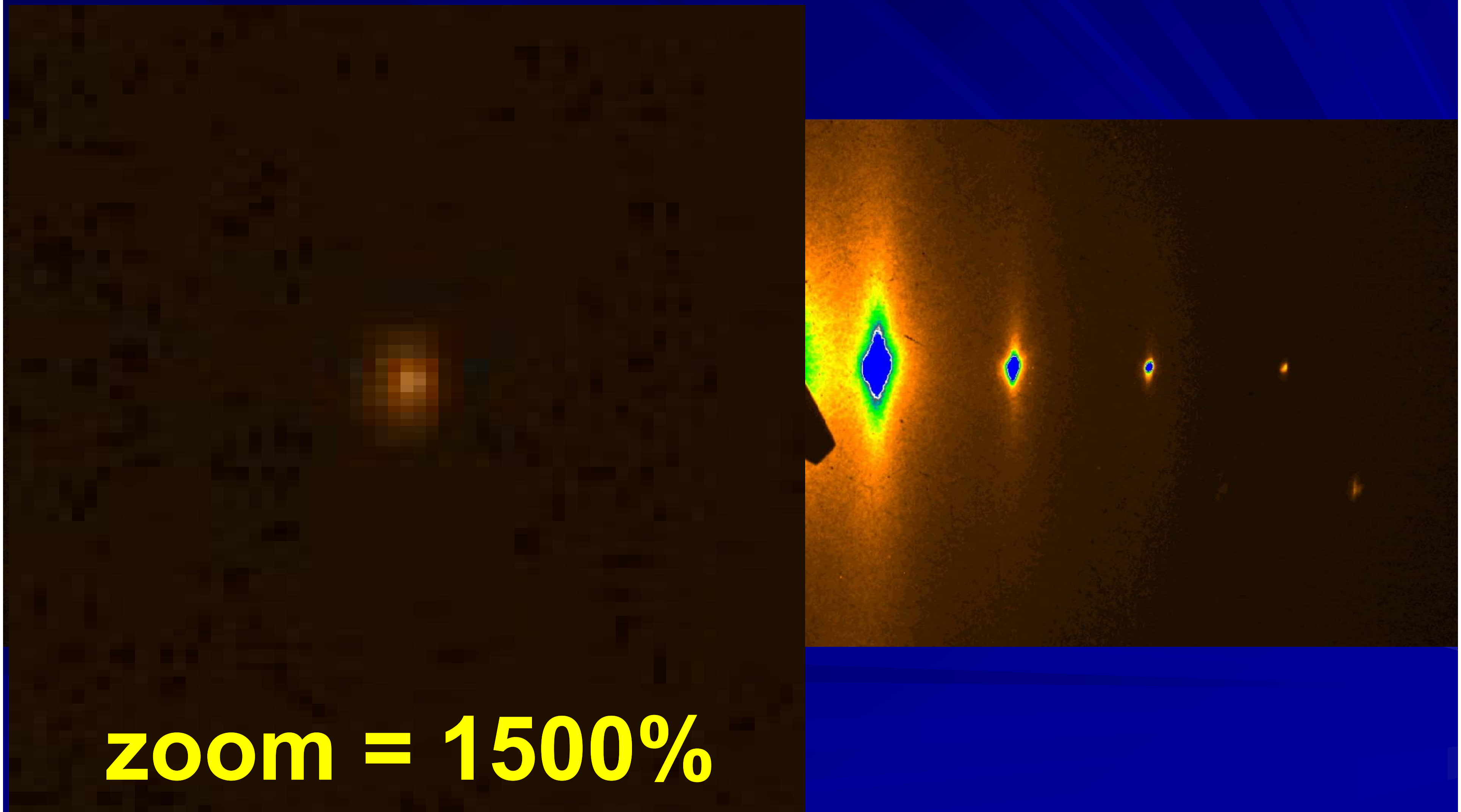


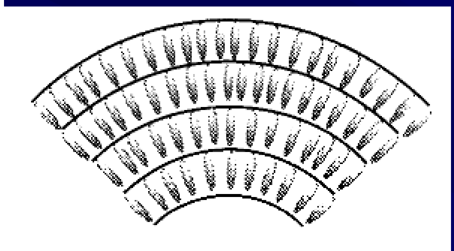
$$\propto 1/q_{\perp}^{2-n^2\eta}$$

$$\propto 1/q_{\perp}^{4-2n^2\eta}$$

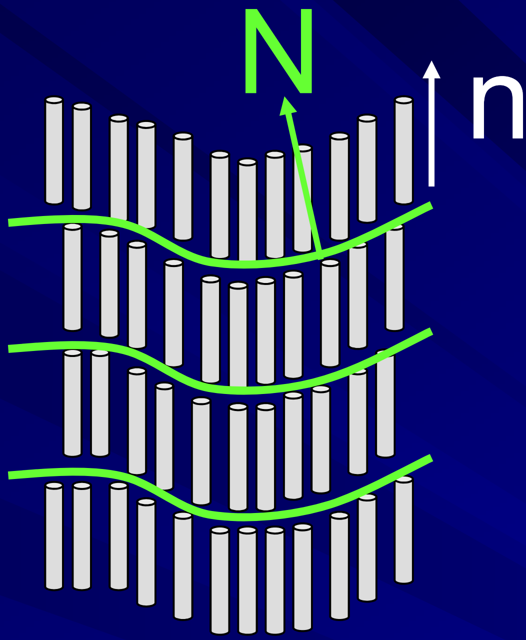
No agreement!

No sign of Landau-Peierls instability





(b)



Principles of
condensed matter physics

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If the layers and the molecules are rotated rigidly together, there is no free energy cost. There will, however, be an energy cost if the molecules are rotated away ...ferred local orientation normal to the layers. Thus, there should

$\propto q^2$ => 'Normal' elastic mode at low q?

To ... deviations from the uniform layered state, an energy proportional to $(\delta\mathbf{N}-\delta\mathbf{n})^2 = (\nabla_\perp u + \delta\mathbf{n})^2$ satisfies these requirements. The free energy for the smectic phase should, therefore, be

$$F_{\text{el}} = \frac{1}{2}\int d^3x[B(\nabla_\parallel u)^2 + D(\nabla_\perp u + \delta\mathbf{n})^2] + \frac{1}{2}\int d^3x[K_1(\nabla\cdot\mathbf{n})^2 + K_2\big(\mathbf{n}\cdot(\nabla\times\mathbf{n})\big)^2 + K_3\big(\mathbf{n}\times(\nabla\times\mathbf{n})\big)^2]. \quad (6.3.11)$$

$$F_{\mathrm{el}} = \frac{1}{2}\int d^3x[B(\nabla_{\parallel}u)^2 + D(\boldsymbol{\nabla}_{\perp}u + \delta\mathbf{n})^2] \tag{6.3.11}$$
$$+\frac{1}{2}\int d^3x[K_1(\boldsymbol{\nabla}\cdot\mathbf{n})^2 + K_2(\mathbf{n}\cdot(\boldsymbol{\nabla}\times\mathbf{n}))^2 + K_3(\mathbf{n}\times(\boldsymbol{\nabla}\times\mathbf{n}))^2].$$

D and K define a new scale:

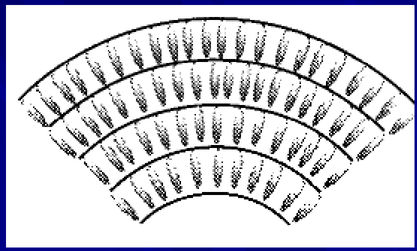
$$q_c = \sqrt{D / K_1}$$

For $q \ll q_c$ splay (K_1) undulations are the softest.

For $q \gg q_c$ another type undulations should be of importance:
n ≈ Const; n and N are decoupled.

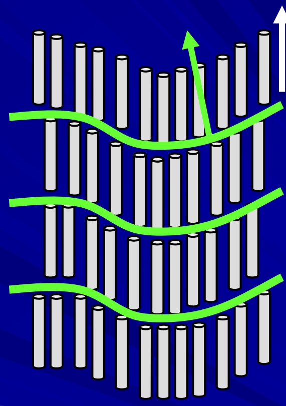
Our model:

Long wavelength:



$$F = \tfrac{1}{2} B (q_{||} u)^2 + \tfrac{1}{2} K (q_{\perp})^4 u^2$$

Short wavelength:



$$F = \tfrac{1}{2} B (q_{||} u)^2 + \tfrac{1}{2} D (q_{\perp} u)^2$$

Leads to diffuse 'halo':

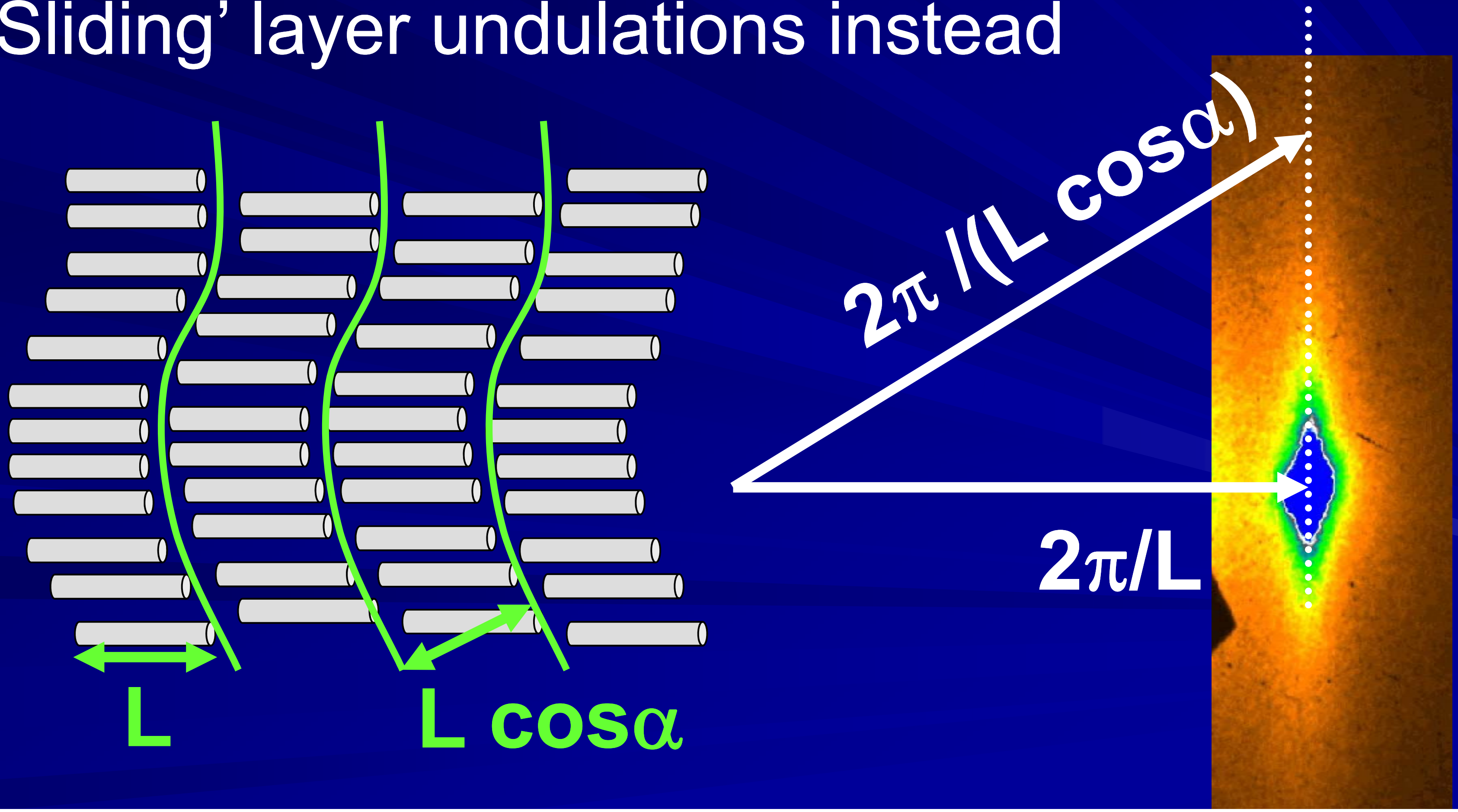
$$I(q) = I_0 / (B q_{||}^2 + D q_{\perp}^2)$$

Just like in ordinary crystals but (highly) anisotropic

Short wavelength undulations:

n=Const (e.g., due to high splay energy)

'Sliding' layer undulations instead



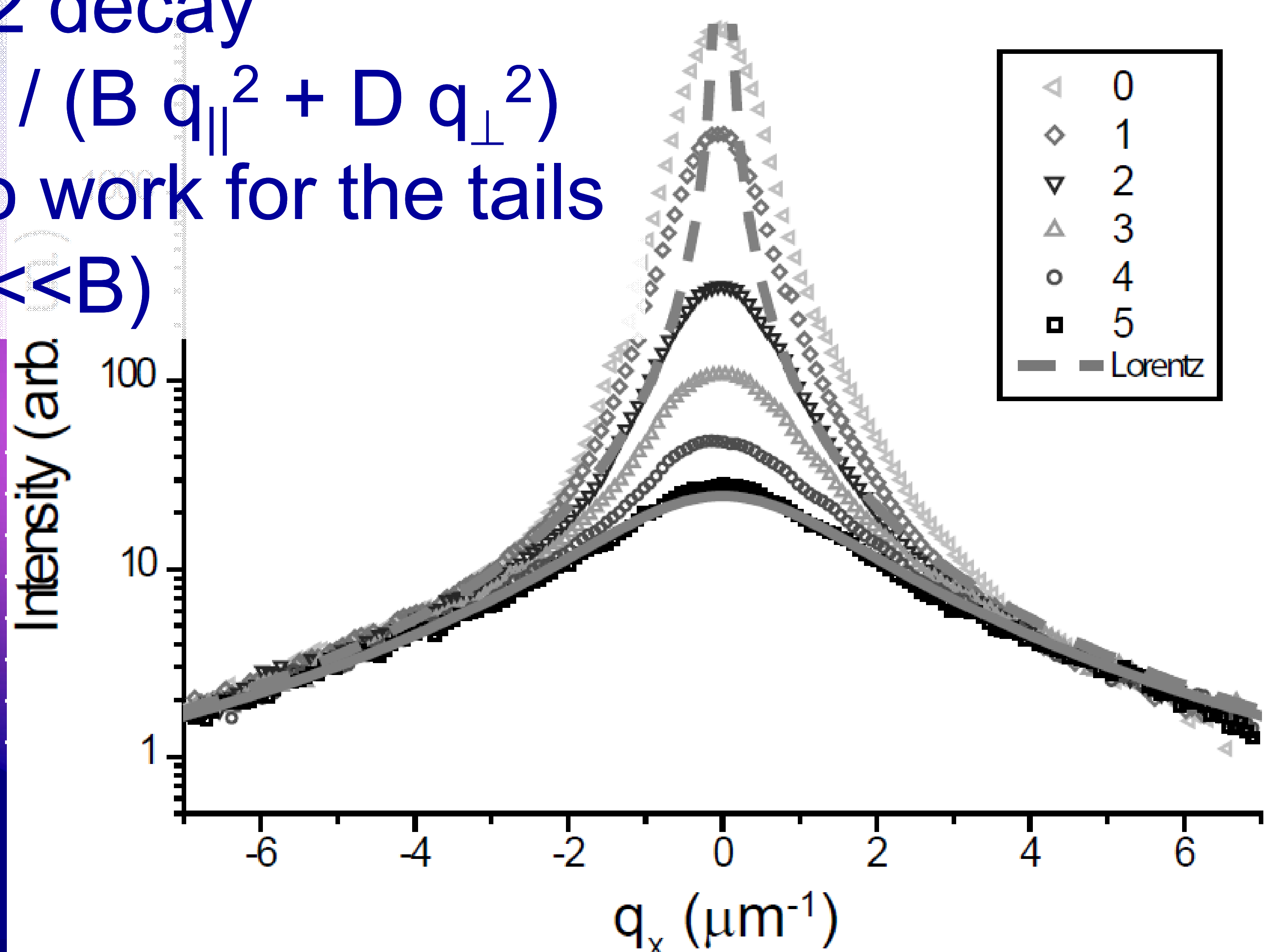
More exp. data: going 3D

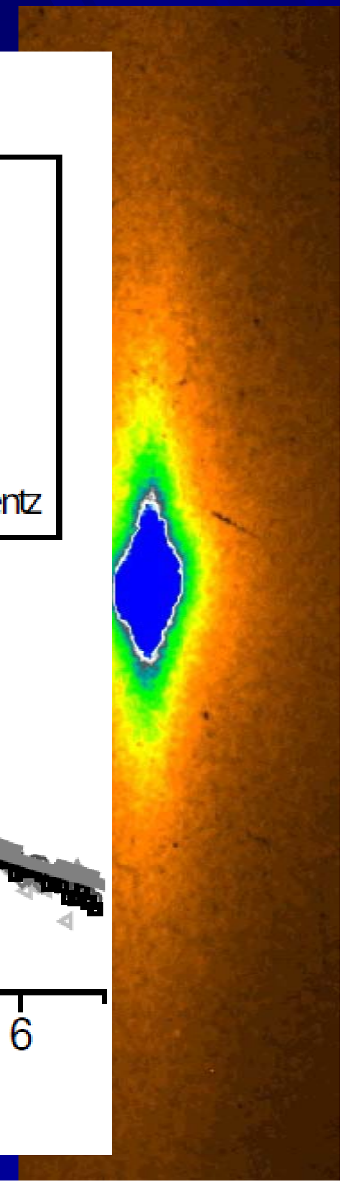
Power 2 decay

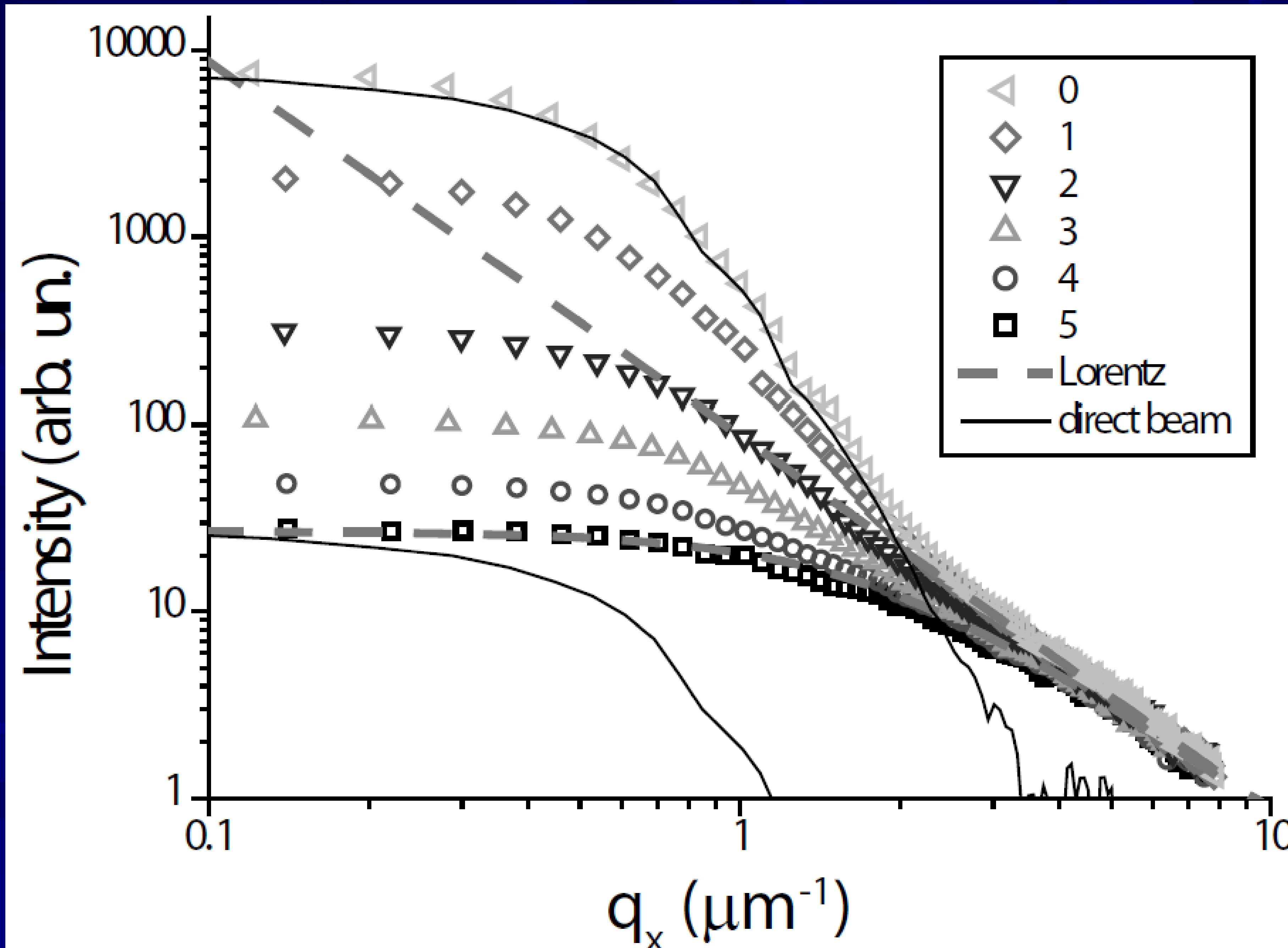
$I(q) = I_0 / (B\, q_{||}^2 + D\, q_{\perp}^2)$

seem to work for the tails

(with D<<B)







10000
1000
100
10
1
Intensity (arb. un.)
0.1
1
10
q_x (μm^{-1})
0
1
2
3
4
5
Lorentz
direct beam

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Undulation Properties of the Lamellar Phase of a Diblock Copolymer: SAXS Experiments

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Are there more examples?

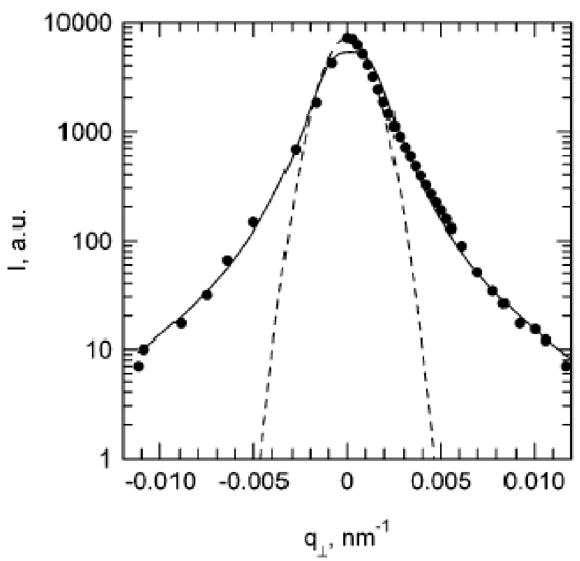
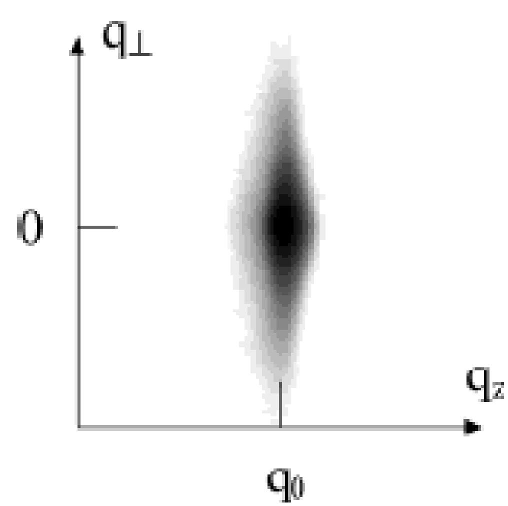


Figure 7. Scan of the Bragg spot in the $q_\perp$ direction. The dashed line corresponds to a Gaussian fit; the line shape is much better described by a Lorentzian law (full line).



raction spot of the first-order Bragg peak
: 30 °C. The intensity is represented on a
ə.

Conclusions: smectic

- Undulation fluctuations:
  - splay
  - slide
- The slide undulations do not lead to Landay-Peierls instability
- Demonstrated in goethite
- Similar story in block co-polymers? [Stepanek et al]
- Indications of similar fluctuations in columnar discotic

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DUBBLE

Universiteit Utrecht

ESRF

The conclusions

- Colloids: lot of fun
- Microradian x-ray diffraction: Mind the coherence
- Fine structural details on
  - structure
  - disorder
  - fluctuations