Investigation of Nitrocellulose using X-ray Diffraction

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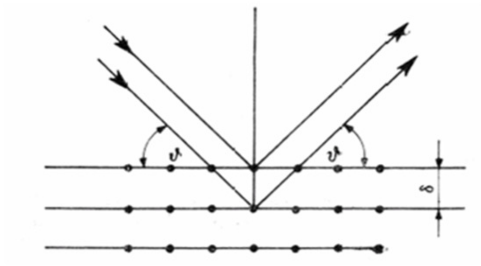
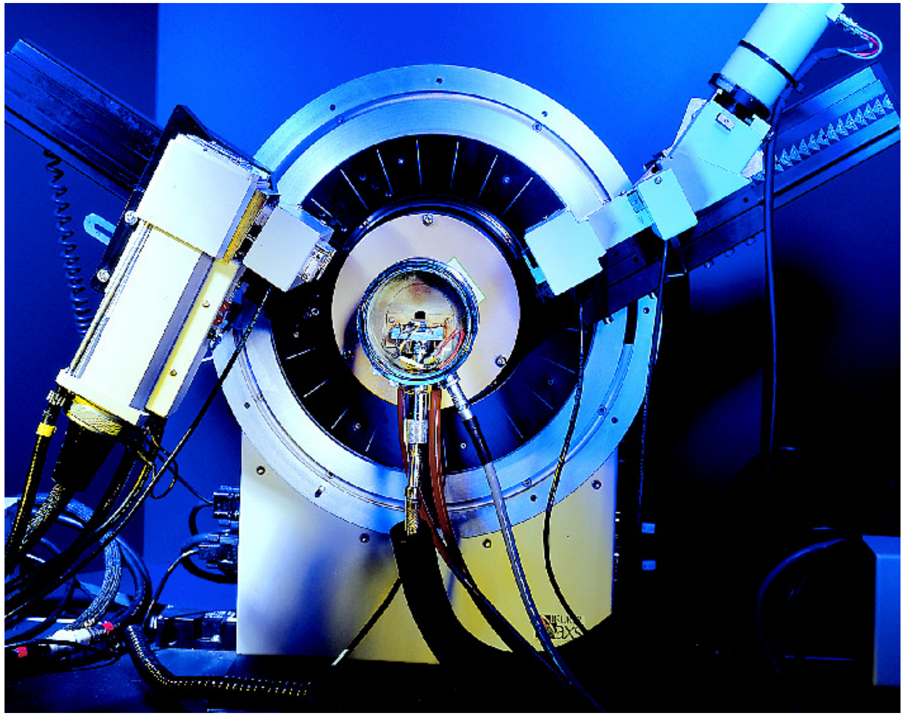
Inhalt

- Principles of X-ray diffraction
- Amorphous and partial crystalline structures
- Application to Nitrocellulose
  - Diffraction patterns
  - Degree of Crystallinity
- Further approaches to the microstructure
  - Cellulose/NC structure (literature)
  - Domain size by XRD
  - Molecular simulation
  - PDF: New evaluation techniques for XRD
- Summary

X-ray Diffraction @ Fraunhofer ICT



$$d_{hkl} \sin\theta = \frac{n\lambda}{2}$$



- Non destructive method
- For periodic structures, crystals
- Application to crystalline explosives since ~30 years
  -> AN, ADN, RDX, HMX, FOX-7, FOX-12, CL-20
  -> Phase transitions/Stabilization
  -> Quality assessment
  (Degree of crystallinity, lattice defects,
- Application to amorphous and partial amorphous energetic materials since 2007
  -> nano-EM, PBX, LED, E-Binder, NC

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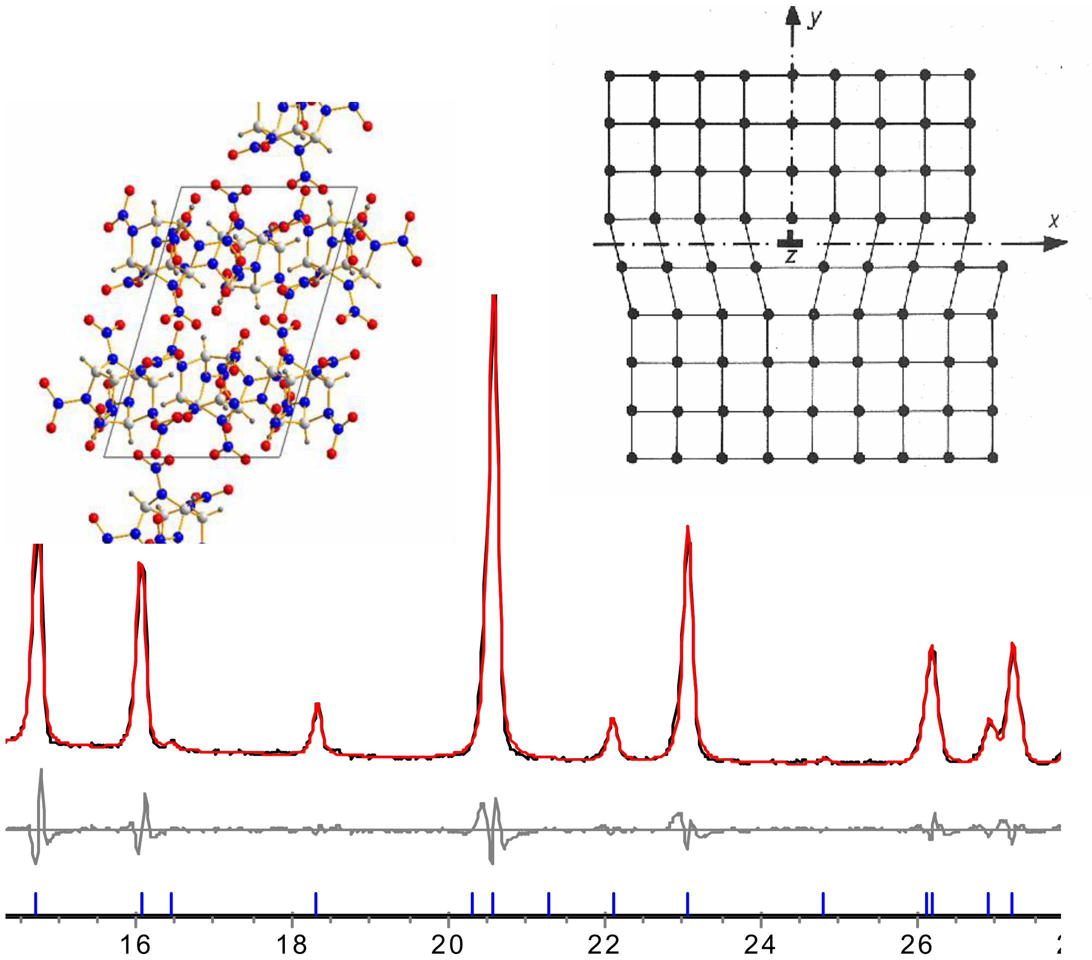
Principles X-ray Diffraction



$$y_i(calc) = s \sum_K p_K L_K \left| F_K \right|^2 G(\Delta\theta_{iK}) P_K + y_{ib}(calc)$$

Information of diffraction patterns / Rietveld Analysis

- Peak position
  - -> Lattice parameter
    Space group
  - -> Crystal density
  - -> Residual strain
- Profile
  - -> Crystallite size
  - -> Microstrain, defects
- Intensity
  - -> Composition
  - -> degr. of crystallinity
  - -> atom coordinates
- Background……

s = Scale factor; L = Lorenz factor; F = Structure factor;
P = Preferred orientation function; p = multiplicity; G = Profile function;
y = Background; K ~ (hkl)

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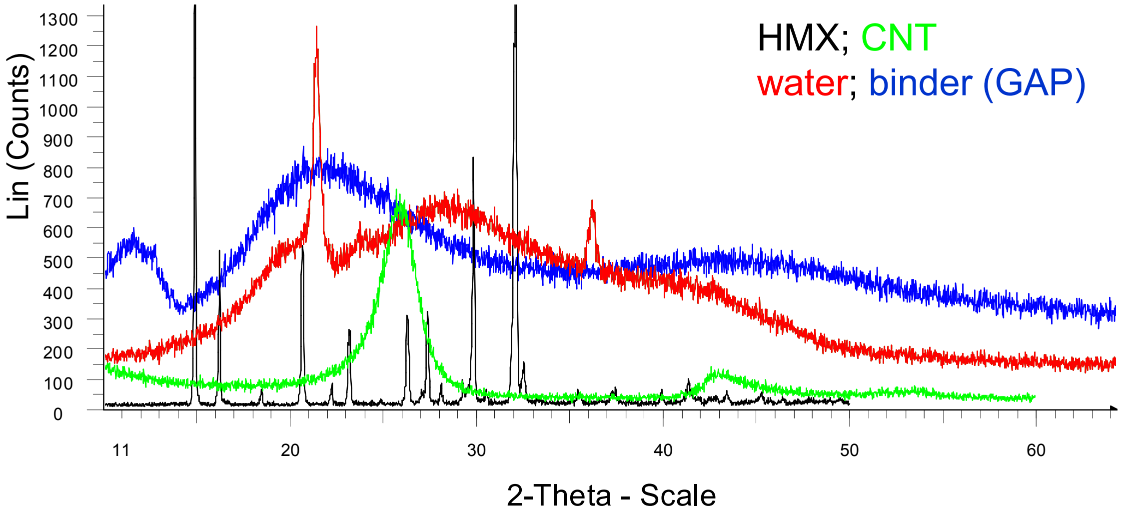
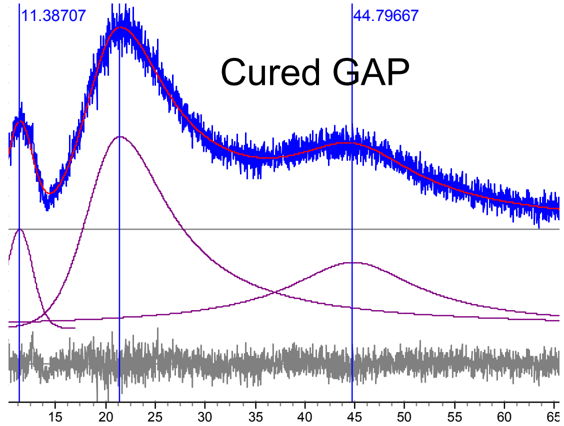
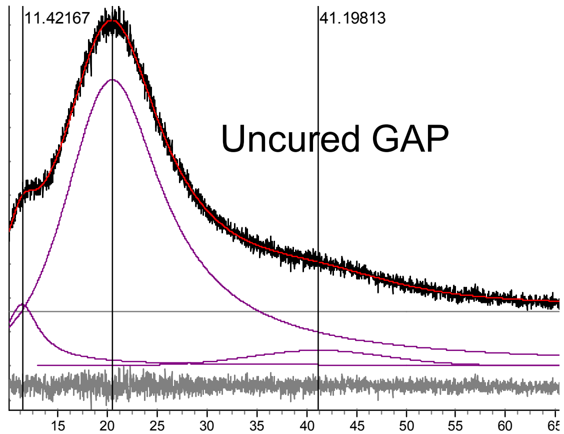
Amorphous energetic materials and XRD







- Broadened Halos instead of peaks, but…
- still characteristic diffraction patterns even for water
- longer measuring times required

Herrmann, M. et al., Proc. of the 14th NTREM, Pardubice, Czech Republic, April 13–15, **2011**, pp 681-686

Nitrocellulose

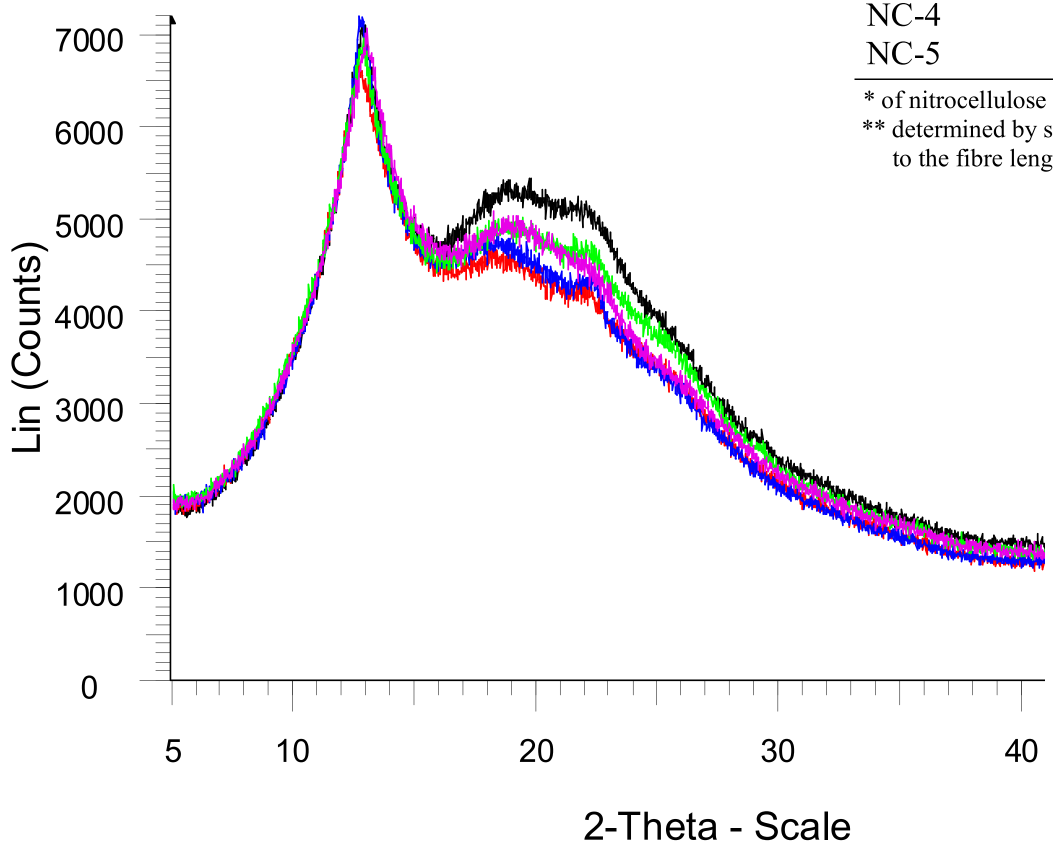


Table 1: Specification of nitrocellulose samples.

Sample	wetted by	Viscosity* [cP]	Fineness** [ml]	Degree of Nitration [%]
NC-1	alcohol	32.0	72.0	12.56
NC-2	water	14.1	83.0	12.56
NC-3	alcohol	35.0	70.0	12.56
NC-4	water	--	--	11.60
NC-5	water	70	67.0	12.56

* of nitrocellulose in ethyl alcohol and acetone;
** determined by sedimentation test, where the settling volume of nitrocellulose correlates to the fibre lenghts.

- 5 NC samples
- Characteristic patterns
- Spike + halo superposed by weak peaks
- Different run of the curves

Herrmann, M. et al.; Proc. 42nd Int Annu Conf of ICT, **2011**, 53.1-7

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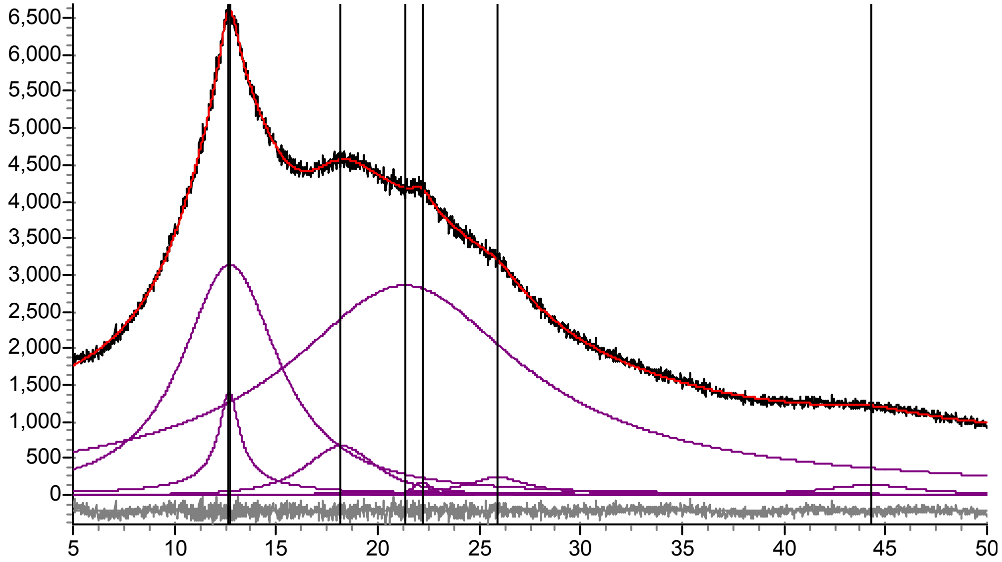
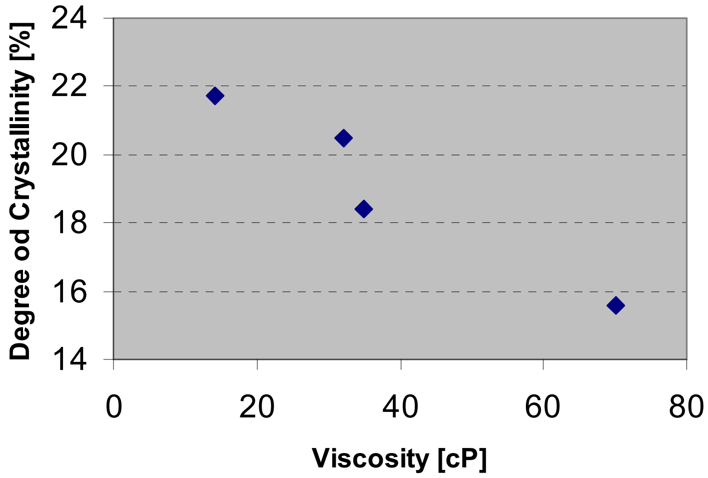
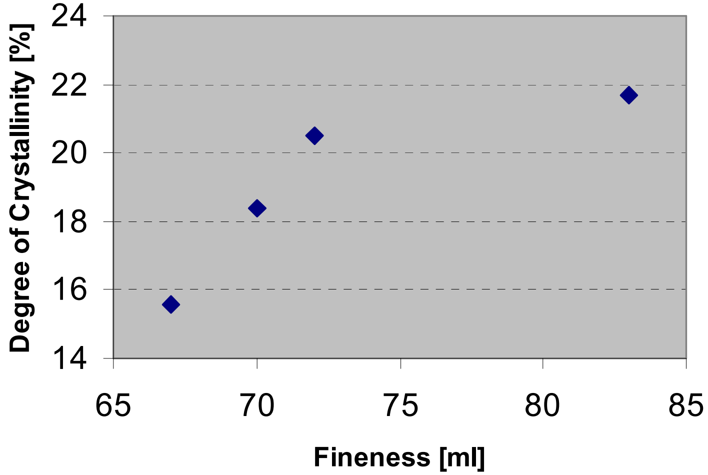
Decomposition of NC-patterns







Degr. of crystallinity [%]

$A_{cryst}/(A_{cryst} + A_{amorph})*100$

- Viscosity und Fineness correlated to degree of crystallinity…..
- but the degree of nitration didn't.

Herrmann, M. et al.; Proc. 42nd Int Annu Conf of ICT, **2011**, 53.1-7

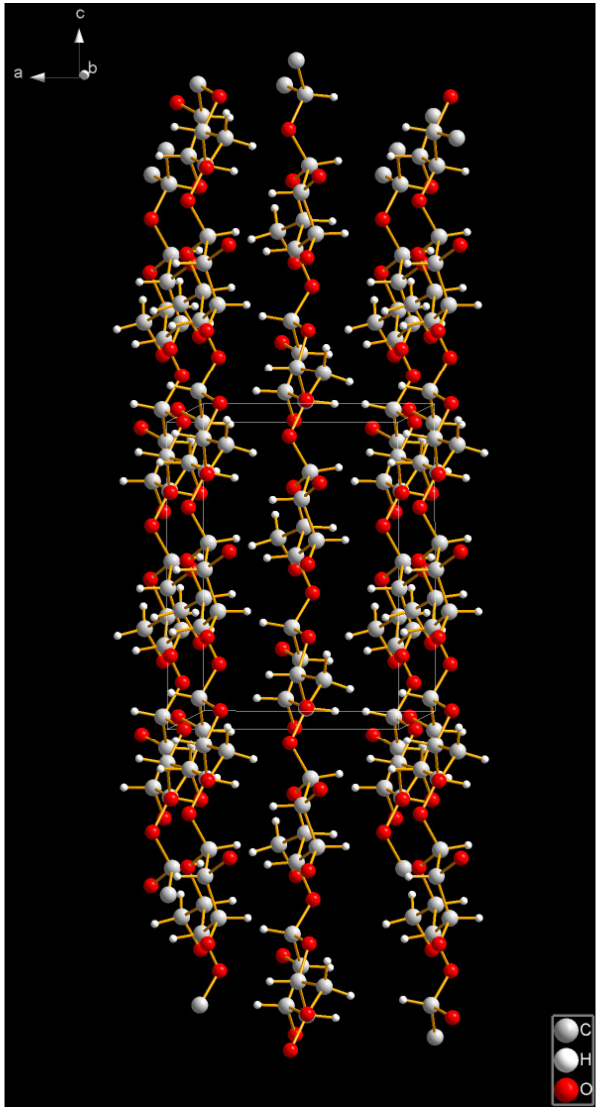
How to get more information on the micro structure of NC and refine evaluation techniques?

- Literature review on crystal structures
- Advanced detector (silicon strip detector)
- Molecular simulation
- Further samples

No crystal structure data of NC found… but of native Cellulose (I)

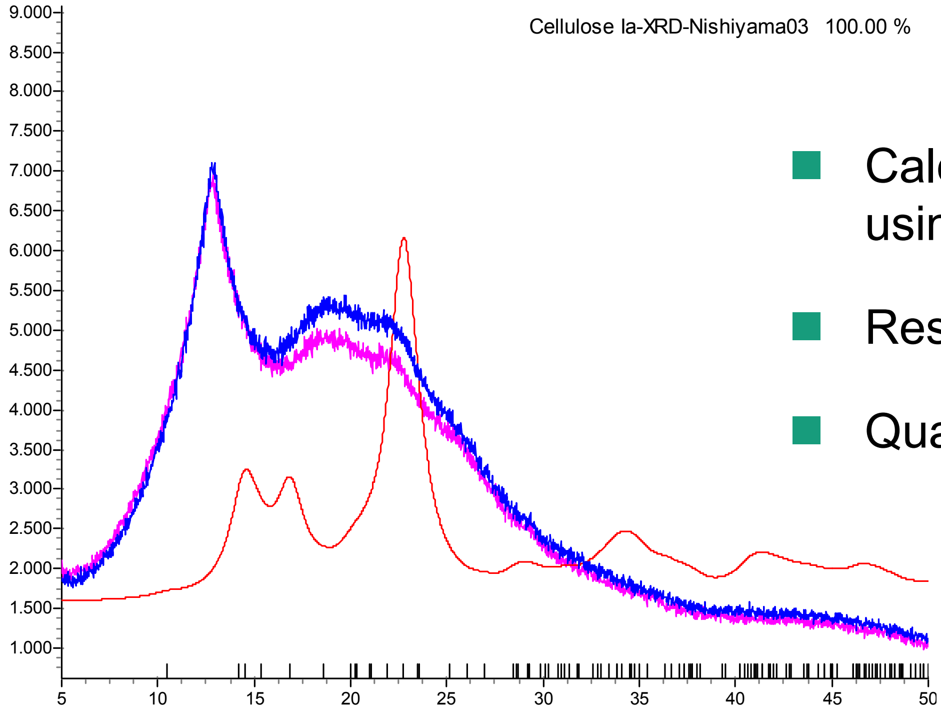
- C is built up of crystalline microfibrils consisting of parallel, hydrogen-bonded molecules.
- Two crystalline phases I_α and I_β , both can be found not only within the same cellulose sample, but also along a given microfibril.

  I_α-rich: cell wall of some algae and in bacterial cellulose
  I_β-rich: cotton, wood and ramie fibers
- Crystal structures solved by X-ray and Neutron Diffraction



Crystal Data: Y. Nishivama et al., *J. Am. Chem. Soc.*, **2002**, *124* (31), pp 9074-9082
Displayed using DIAMOND Crystal and Molecular Structure Visualization, Version 3.2f

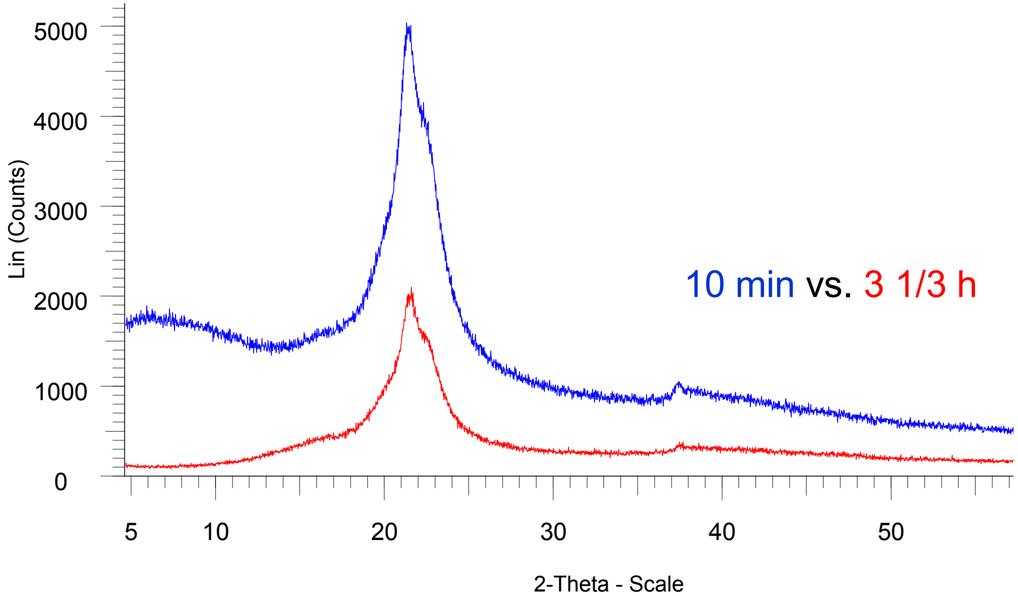
Comparison measured NC with calculated Cellulose patterns



- Calculated pattern of Cellulose I_α using Rietveld-Analysis
- Residual C-I_α in NC?
- Quantification possible

Advanced experimental setup

- LynxEYE silicon strip detector (Bruker AXS)
- Intensity gain 200x compared to scintillation counter
- ….and high resolution!



Example: crystalline polymer

- scarves peaks and halos out of the underground
- but increased underground at small angles

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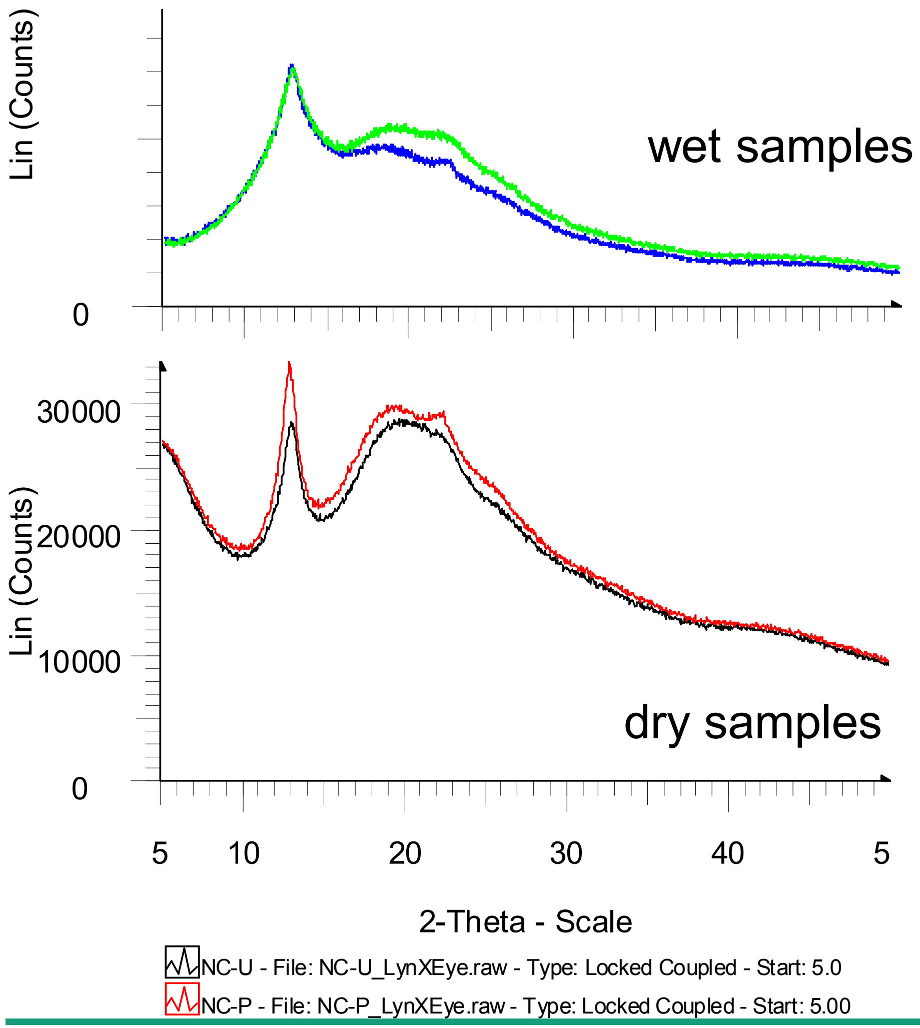
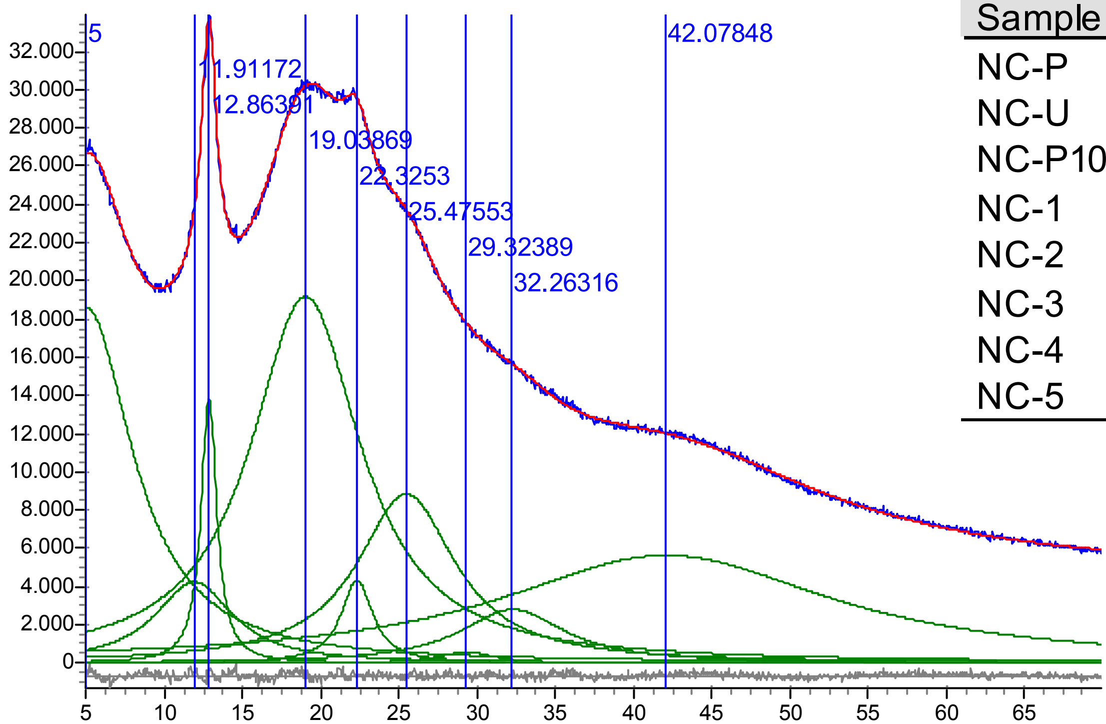
Further NC-Qualities



- Dry Samples
  NC-U, NC-P, NC-P10
- Much narrower crystalline peaks and halos compared to wet samples (NC1 – NC5)

Decomposition and Size-Analyse

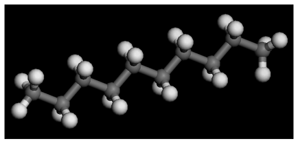


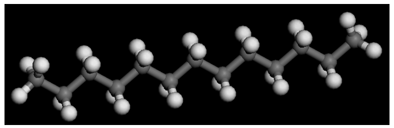
Cry Size L	[nm]		
Sample	Spike	Halo	Peak
NC-P	7.4	1.1	5.0
NC-U	6.3	0.9	4.7
NC-P10	7.5	1.0	3.7
NC-1	3.5	0.5	5.6
NC-2	5.4	0.4	4.7
NC-3	3.5	0.4	3.9
NC-4	3.6	0.4	2.4
NC-5	3.3	0.5	3.1

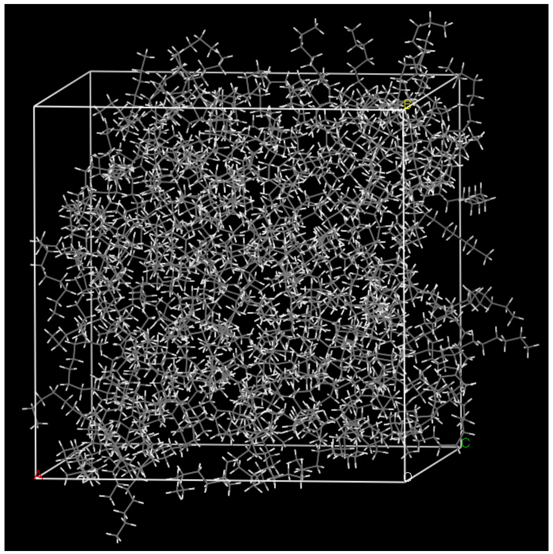
- larger “crystalline domains” in dry samples 6,3 -7,5 nm compared to nm 3,3 - 5,4 nm for wet samples

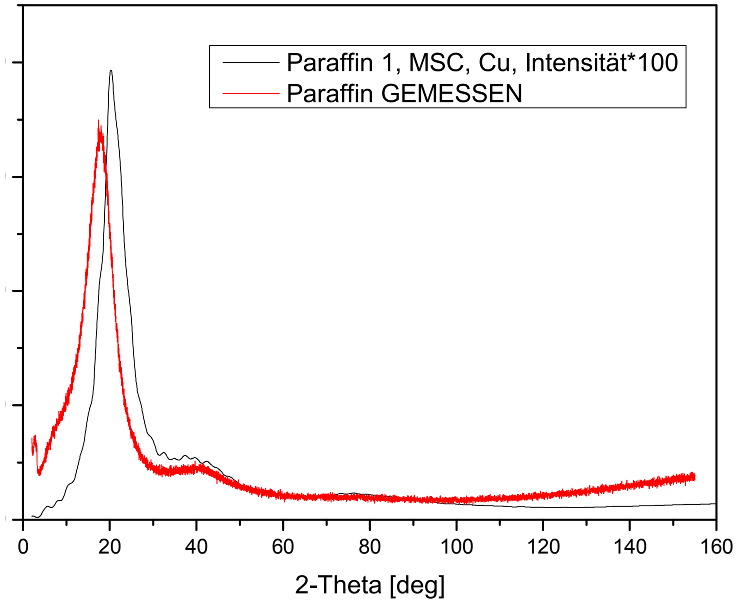
Approach: Molecular Simulation (example)

- Material Studio; Amorphous Cell / COMPASS
- Construction of cubic super cell (36,7 Å) with
  160 Paraffin molecules, C10 – C16; density 0,88 g/cm^3 (5840 atoms)
- Comparison of calculated and measured XRD-patterns









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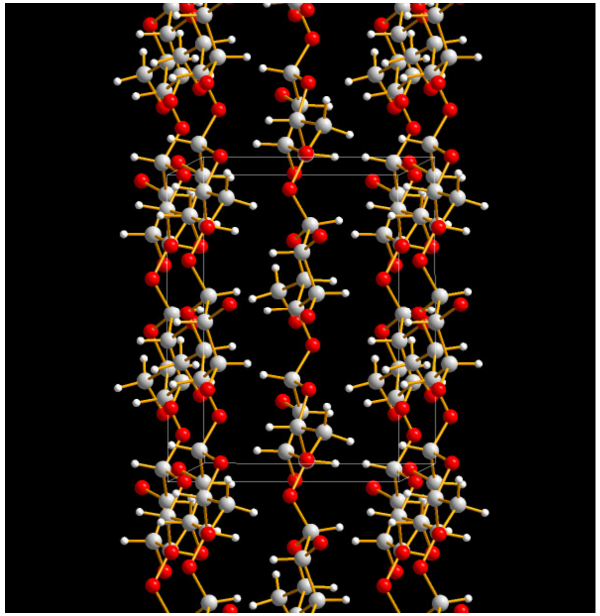
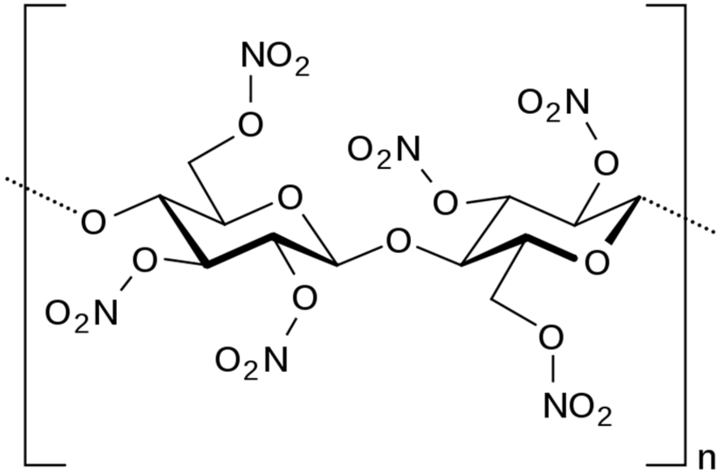
Simulation of Nitrocellulose

- Starting from Cellulose structure and stepwise nitration
- Super cell of NC molecules
- Combining with atomic pair distribution function PDF -> Structure refinement of models

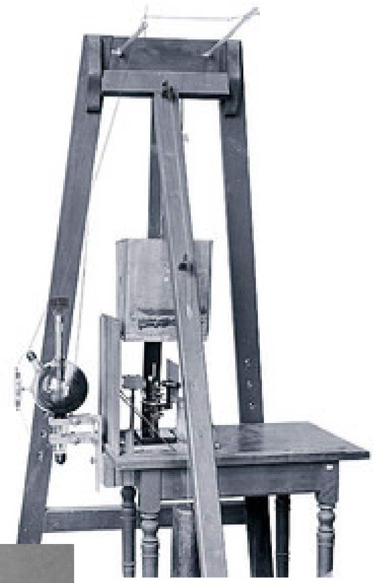




Lessons learned

- XRD provides structure related information of amorphous materials and particularly of NC
- Characteristic patterns and DoC from peak/halo intensities
- Broadening: Crystallite size relates e.g. to wetness
- Wanted: More structural input
- Combining with atomic pair distribution function PDF
  -> Structure refinement of models

100 Years X-ray Diffraction



1895 Wilhelm Conrad Röntgen discovered X-rays

1901 Wilhelm Conrad Röntgen won the first Nobel prize in physics

1912 Max von Laue discovered the diffraction of X-rays by crystals

1914 Max von Laue won the Nobel prize in physics

Questions?

Max von Laue