Cellulose I & II structures & molecular interactions

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Cellulose I & II structures & molecular interactions

- Cellulose I is an enzymatically *directed* structure (cellulose synthase complexes in cell membrane)
- Cellulose I (all-parallel chains) is not the lowest free energy organization of the β(1→4) glucan chains

- Cellulose II (regenerated or mercerised) represents lower free energy organizations (anti-parallel chains)
- End-product depends on regeneration path (change of parameter with time, e.g. pH, temp., mechanical forces)

Molecular interactions

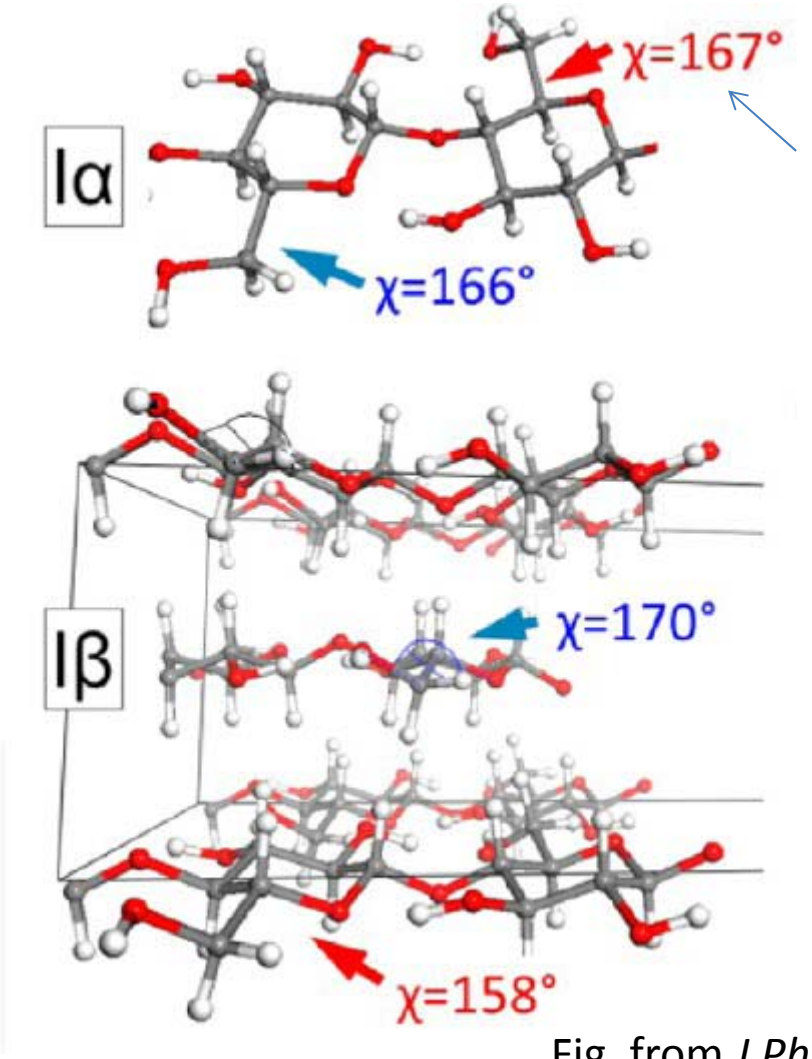
- Strongest: Covalent interactions (define bonding, steric interactions, e.g. tg/gt/gg of hydroxymethyl groups, etc., reflected in high frequency (IR/Raman) vibrations)
- Medium - weak: Hydrogen bonding (-COH · · · -COH, -COH · · · O_{ring}, affects relative conformer energetics, reflected in *shifts* of high frequencies, e.g. νOH, δOH), hydrophobic interactions
- Weak: Dispersion / van der Walls (-CH · · O/C, relative conformer energetics)

Currently accepted structures are based on X-ray & neutron diffraction

Seminal works

- A Revised Structure and Hydrogen-Bonding System in Cellulose II from a Neutron Fiber Diffraction Analysis, P. Langan, Y. Nishiyama, and H. Chanzy, *J. Am. Chem. Soc.* 1999, *121,* 9940-9946.
- X-ray Structure of Mercerized Cellulose II at 1 Å Resolution, P. Langan, Y. Nishiyama, and H. Chanzy, *Biomacromolecules* 2001, 2, *410-416.*
- Crystal Structure and Hydrogen-Bonding System in Cellulose Iβ from Synchrotron X-ray and Neutron Fiber Diffraction, Y. Nishiyama, P. Langan, and Henri Chanzy, *J. Am. Chem. Soc.* 2002, 124, 9074-9082
- Crystal Structure and Hydrogen Bonding System in Cellulose Iα from Synchrotron X-ray and Neutron Fiber Diffraction, Y. Nishiyama, J. Sugiyama, H. Chanzy, and P. Langan,|*J. Am. Chem. Soc.* 2003, 125, 14300-14306

Cellulose I: C6O6OH torsional conformation



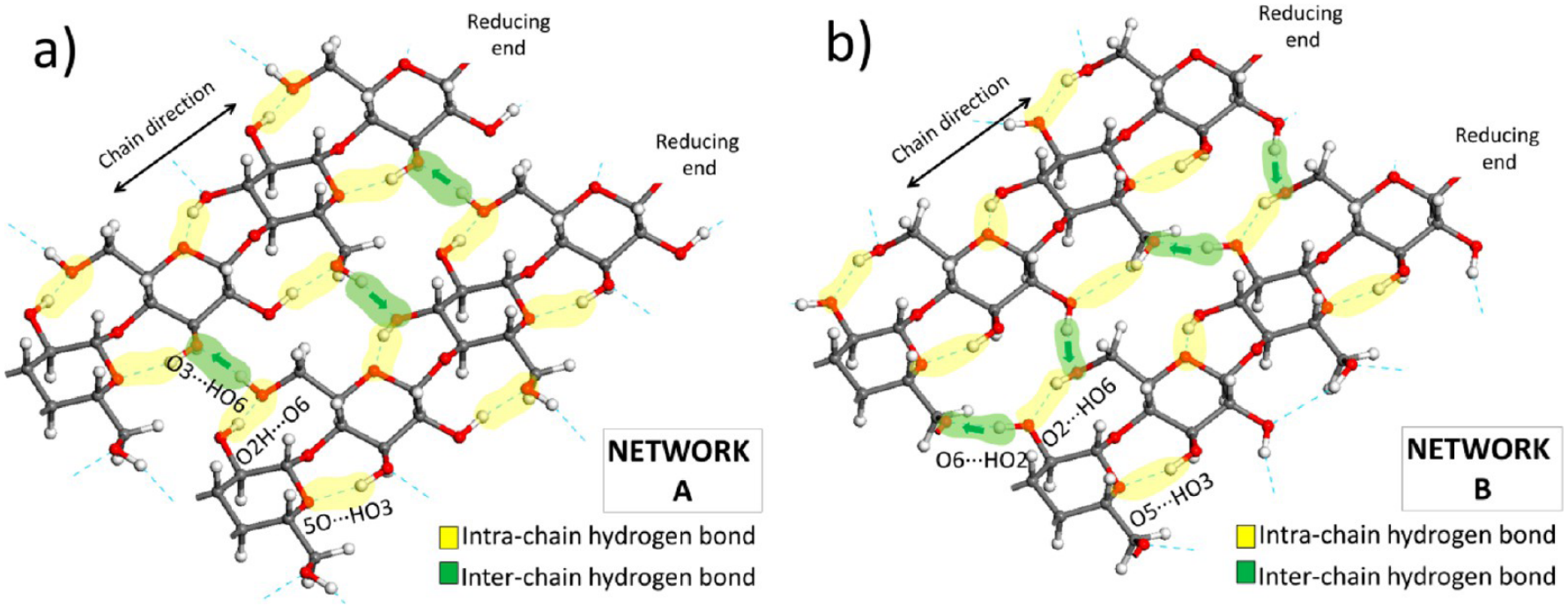
ca. *tg*

χ(O5-C5-C6-O6)

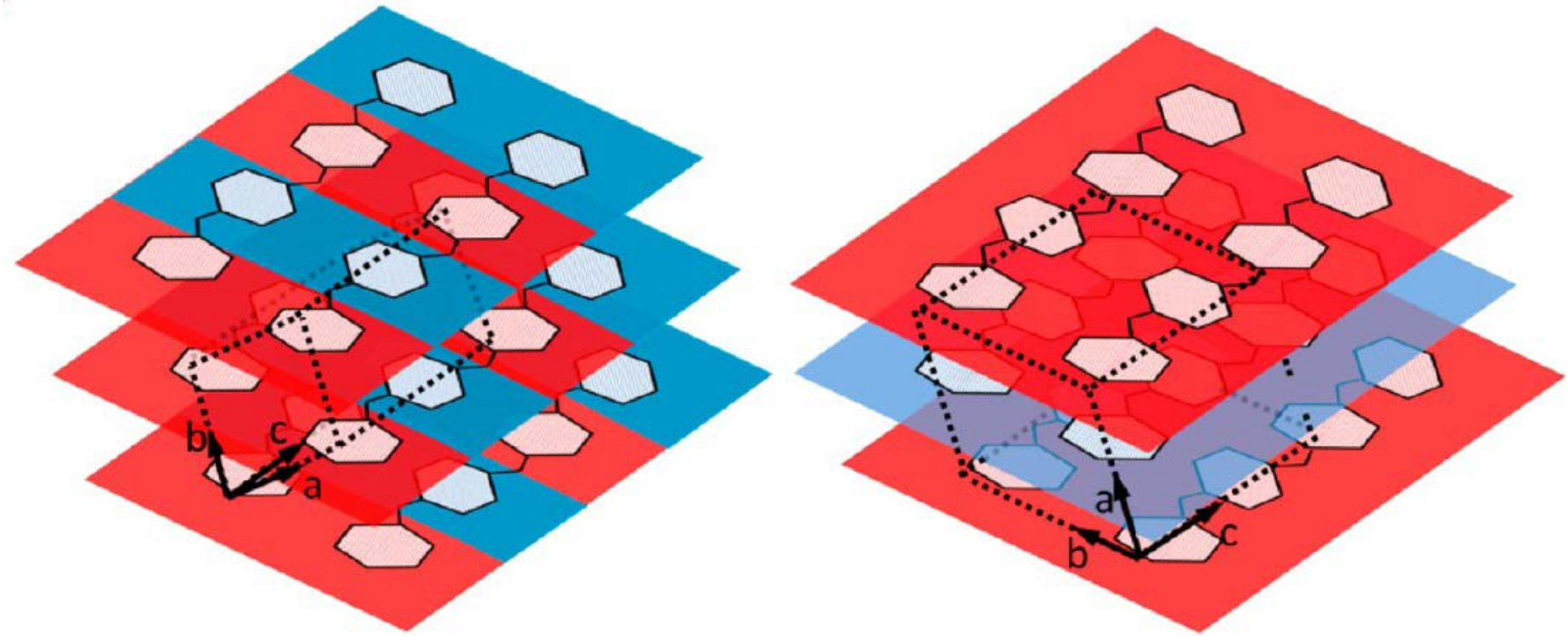
can also be
χ(C4-C5-C6-O6)

Fig. from *J Phys Chem B* 2013, **117**, 6681

Cellulose I H-bond networks are *all intra-sheet*

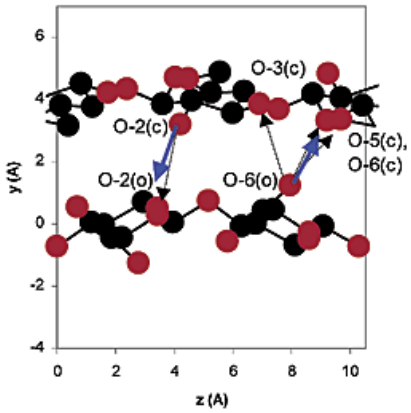


Sheets ”stack up” by weaker interactions (& hydrophobic interactions during biosynthesis)



Iα Iβ

Cellulose II – H-bonding

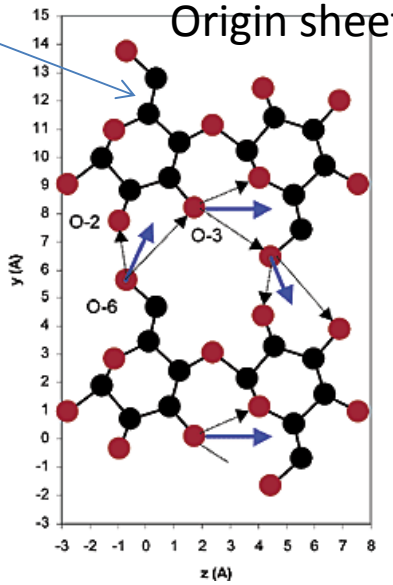


Inter-sheet
H-bonds

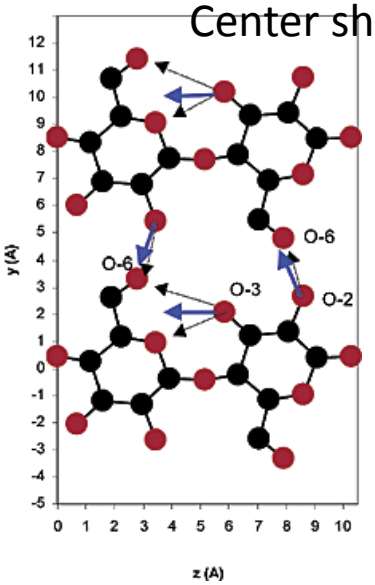
(from Biomacrom. 2003, 4, 1589)

gt conformation
(origin: some *tg*)

Origin sheet



Center sheet



Cellulose I & II order *vs* disorder

- Lack of well-defined (high-probability) torsional conformations (multiple low free energy states, role of mutually excluding H-bond networks)
- Lack of (or reduced) inter-chain interactions (”loose” detached chains, surface-situated chains)
- ”Geometrical” effect (infinite crystal modelling of a finite crystal) = ”artificial disorder”?

Cellulose I & II order *vs* disorder

For cellulose II materials:

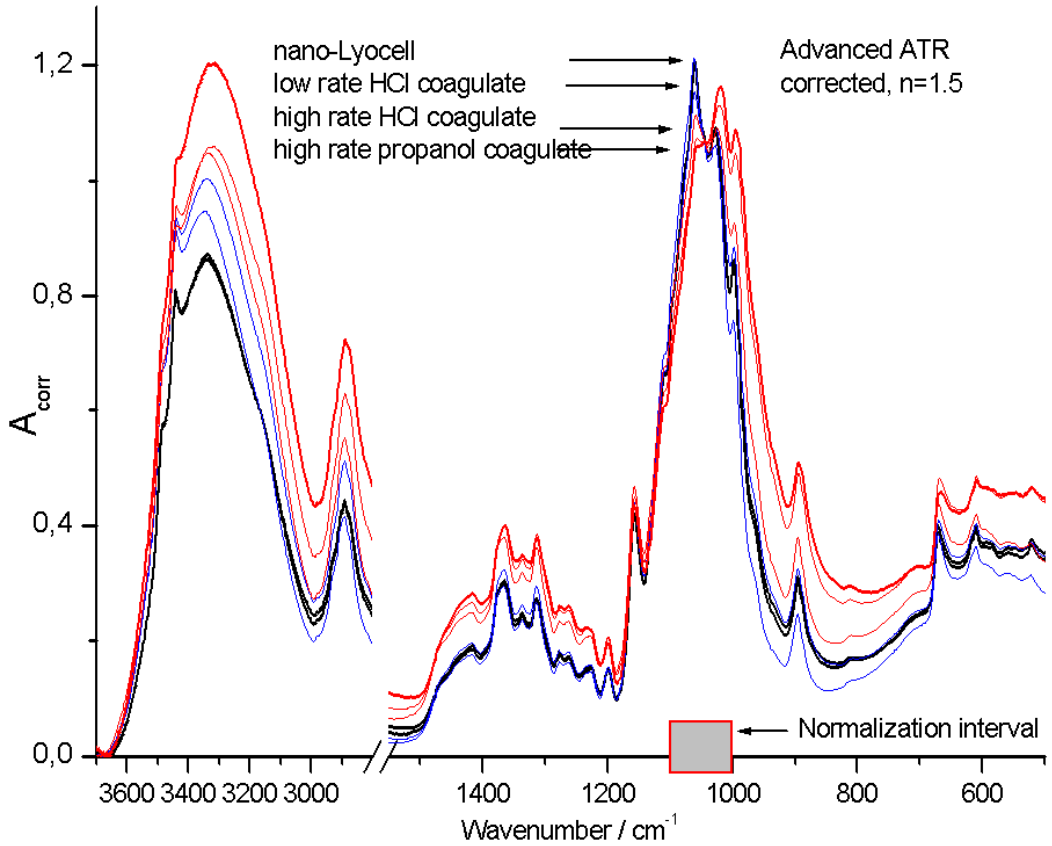
Is it possible to *control* physico-chemical disorder resulting from a regeneration process ?

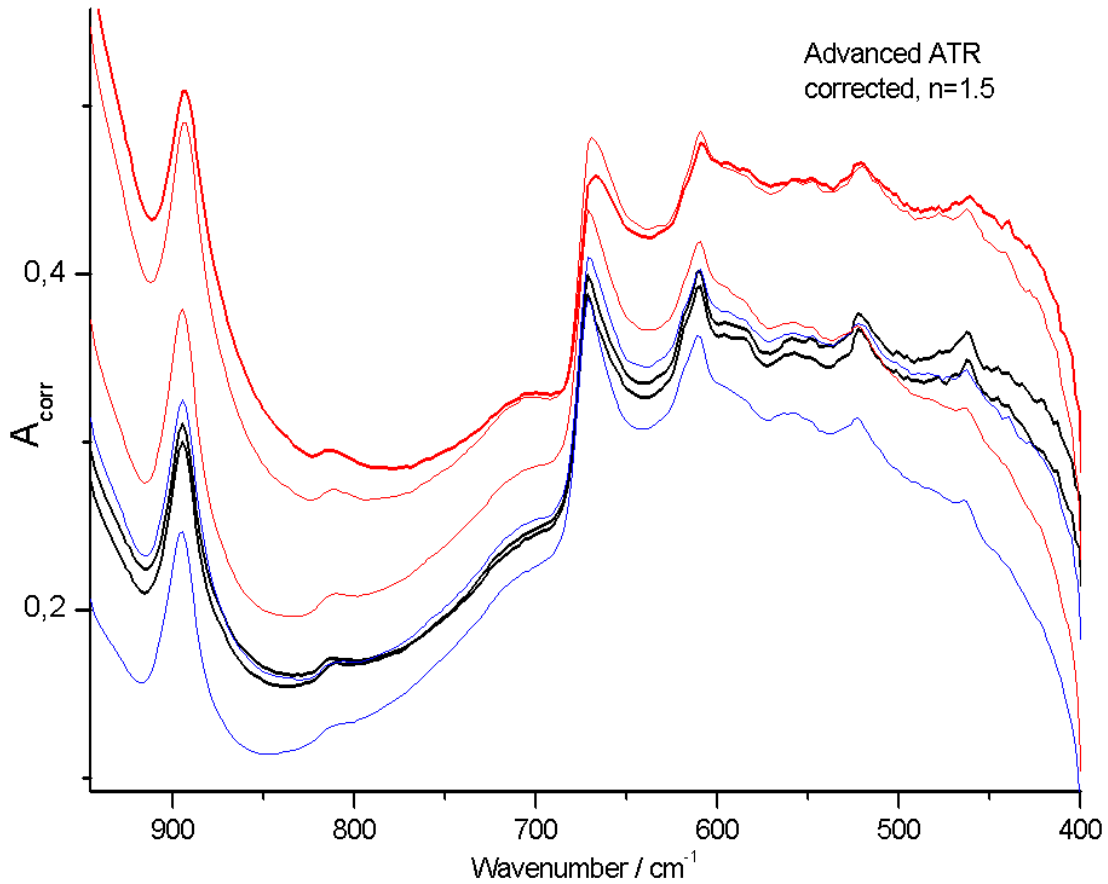
Can we monitor degrees of disorder through spectroscopy (IR/Raman/NMR), and learn about its nature & causes?

Coagulation procedure

- Lyocell (wet) dissolved to 1% dry weight in 7:12:81 NaOH:Urea:H_2O
- Coagulation/Precipitation solution: HCl
- Ca. 10 mL HCl solution added via syringe pump to 5 mL 1% cellulose solution (*end*-pH always pH ≈ 0.7)
- Addition at constant rate from 0.07h to 70h
- Coagulated cellulose ”lump” rinsed by

  0.1% HCl → di-Water (x 5, each ca. 20h)
- Final freeze drying


nano-Lyocell
low rate HCl coagulate
high rate HCl coagulate
high rate propanol coagulate
Advanced ATR
corrected, n=1.5
Normalization interval
A corr
1,2
0,8
0,4
0,0
3600 3400 3200 3000
1400
1200
1000
800
600
Wavenumber / cm-1


Advanced ATR
corrected, n=1.5
0,4
0,2
A corr
900
800
700
600
500
400
Wavenumber / cm-1

Observations

- Significant band intensity changes, especially νCO (glycosidic linkage, ring C-O, hydroxyl C-O)
- Hydroxyl modes also affected (e.g. νOH, δOH)
- Changes of the ca. 900 cm-1 mode (is it a superposition of a narrow & a broad component?)

Causes

- Qualitatively different from mechanical stress induced changes (typically position shifts with strain)
- Deviation from crystalline arrangement allows more optimal H-bonding (vOH readshift+intensity increase)?
- Same deviation perturbes conformer distribution of hydroxymethyl group, and –OH's?
- Each conformer (distribution) couples differently with cellulose chain vibrational modes (gly linkage)?

Future directions

- SEM (sample morphology)
- X-ray
- IR, Raman & NMR (C13)

- Suggestions/advice are welcome!