I α to I β mechano-conversion and amorphization in native cellulose simulated by crystal bending

Pan Chen · Yu Ogawa · Yoshiharu Nishiyama · Ahmed E. Ismail · Karim Mazeau

Received: 4 September 2017 / Accepted: 17 May 2018 / Published online: 5 June 2018
© The Author(s) 2018

Abstract The bending of rod-like native cellulose crystals with degree of polymerization 40 and 160 using molecular dynamics simulations resulted in a deformation-induced local amorphization at the kinking point and allomorphic interconversion between cellulose I α and I β in the unbent segments. The transformation mechanism involves a longitudinal chain slippage of the hydrogen-bonded sheets by the length of one anhydroglucose residue (~ 0.5 nm), which alters the chain stacking from the monotonic

(I α) form to the alternating I β one or vice versa. This mechanical deformation converts the I α form progressively to the I β form, as has been experimentally observed for ultrasonication of microfibrils. I β is also able to partially convert to I α -like organization but this conversion is only transitory. The qualitative agreement between the behavior of ultrasonicated microfibrils and *in silico* observed I $\alpha \rightarrow$ I β conversion suggests that shear deformation and chain slippage under bending deformation is a general process when cellulose fibrils experience lateral mechanical stress.

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s10570-018-1860-x>) contains supplementary material, which is available to authorized users.

P. Chen (✉)
State Key Laboratory of Pulp and Paper Engineering,
South China University of Technology,
510640 Guangzhou, China
e-mail: panchen@kth.se

P. Chen
Wallenberg Wood Science Center, KTH Royal Institute of
Technology, 56-58 Teknikringen, SE-10044 Stockholm,
Sweden

Y. Ogawa · Y. Nishiyama · K. Mazeau (✉)
Univ. Grenoble Alpes, CNRS, CERMAV,
BP53, 38000 Grenoble Cedex 9, France

A. E. Ismail
Department of Chemical and Biomedical Engineering,
West Virginia University, Morgantown, WV 26505, USA

Keywords Bending · Chain slippage · Kink · Molecular dynamics simulation · Allomorphic conversion

Introduction

In recent years, cellulose nanofibers (CNF) and nanocrystals (CNC) have received increased interest in materials science (Habibi et al. 2010; Grishkewich et al. 2017). These cellulose nanomaterials are obtained by disintegrating cellulosic fibers in the plant cell wall through chemical or mechanochemical treatments. These materials may experience various stress conditions in industrial processes and in use that may alter the inner structure of the cellulose nanocrystals through dislocations (Hidayat et al. 2012) and allomorphic transitions. Understanding the mechanical response of crystalline cellulose to various external

forces is important for fundamental understanding and for development of more effective processing.

Processing cellulose by ultrasound is a scalable process currently used in many laboratories. It is often observed that sonicated cellulose fibrils have a tortuous morphology, showing numerous kinks and can be accompanied by an allomorphic transformation (Briois et al. 2013) from the triclinic cellulose I α to the monoclinic I β form.

We recently carried out molecular modeling to mimic a 3-point bending test of cellulose I β crystals (Chen et al. 2016). Upon bending, the crystal developed a sharp kink identical to that observed experimentally for processed celluloses (Kekaelaeninen et al. 2012; Wang et al. 2012; Zeng et al. 2012; Martoia et al. 2016). We found shear deformations are very important when the bending load is applied on the hydrophobic face, for which the bending rigidity is also the lowest.

In this study, we applied this bending protocol to produce kinks in molecular models of pure I α and pure I β cellulose crystals on their hydrophobic face. We followed the evolution of the internal atomic structure to investigate the molecular details of allomorphic transition and morphological changes. Results obtained on short crystals (about 20 nm in length) of I α and I β will be shown first, followed by results obtained on a long crystal (about 80 nm in length) of I α .

Computational methods

Model construction

The cellulose microfibril models of I α and I β were built from crystal structures (Nishiyama et al. 2002, 2003) refined from X-ray and neutron diffraction data. The dominant hydrogen bond network, pattern A, was considered. The constructed models consisted of 40 chains (5×8) of 40 residues each, exposing the 100 and 010 surfaces for I β and the 110 and $1\bar{1}0$ surfaces for I α , as shown in Fig. 1. The two models have approximately square cross sections with similar dimensions of $\sim 3.12 \text{ nm} \times \sim 4 \text{ nm} \times \sim 21 \text{ nm}$. To estimate if the size of the crystals affects the results, we have also considered a long crystal initially in the I α organization. Except for the length of

the chains, which have degree of polymerization 160 to produce a crystal of 80 nm in length, this crystal is identical to the one already described.

Each crystal model was energy minimized (EM) and then equilibrated by molecular dynamics (MD). EM was performed using the steepest descent method followed by the conjugated gradient method, with the convergence criterion being a maximum force of $10 \text{ kJ mol}^{-1} \text{ nm}^{-1}$. In the dynamics process, the temperature was slowly increased from 0 to 300 K over 6 ns, followed by a 94 ns equilibration period.

Bending

The bending was carried out as described in a previous paper (Chen et al. 2016). Briefly, the equilibrated crystals were rotated to align their long axes with the z -axis and their respective hydrophobic surfaces (the 110 surface for I α and the 100 surface for I β) parallel to the yz plane, as shown in Fig. 1. They were then bent normal to their hydrophobic surface by displacing bridge oxygen atoms at the center of the top surface to a fixed x coordinate. Constraints were also applied on the glycosidic oxygen atoms at the two ends of the bottom layers of cellulose chains, with the x coordinate constrained at the reducing end and the x and z coordinates constrained at the non-reducing end. The crystal was bent by gradually moving the x coordinate of the constrained atoms at the center of the microfibril. A stepwise displacement of -0.015 nm was applied, followed by either 1 or 3 ns of MD simulation, which was enough for the energy to converge (Chen et al. 2016).

Simulation setups

All simulations have been performed with GRO-MACS version 4.6 for cellulose chains with degree of polymerization 40 and version 2016.3 for the fibril with degree of polymerization 160 (Hess et al. 2008). The cellulose fibril was modelled using the GROMOS 56A_{carbo} force field, which is a mostly explicit-atom force field, although carbons bonded to a single hydrogen atom are replaced by a CH1 united atom (Hansen and Huenenberger 2011) whose Lennard–Jones parameters have been subsequently optimized (Chen et al. 2014). MD simulations were performed in the *NVT* ensemble using a 2 fs integration time step. The stochastic velocity-rescaling algorithm of Bussi

Fig. 1 Snapshots of cellulose I α and I β crystals kinked at their hydrophobic surface for various bending deflections. Top: typical crystal model showing the nomenclature of the crystallographic planes. The three black lines passing through the crystal cross-section (one at the bottom of each of the two extremities and one on top at the center) indicate the location of the constrained atoms. Glucose residues of pairs of consecutive chains of the inner 010 (I β) plane or the 1 $\bar{1}$ 0 (I α) plane highlighted in red were selected to estimate the chain slippage during bending. Bottom: snapshots of the kinked crystals; labels *a* to *h* correspond to bending deflections where chain slippage occurred. Atoms of some residues are colored and displayed as spheres to facilitate visualization of the monoclinic and triclinic characters of the internal organization within the two linear segments

et al. (2007) was used to control the temperature at 300 K. Bonds involving explicit hydrogen atoms were constrained using the LINCS algorithm (Hess et al. 1997). Electrostatic and Lennard–Jones interactions were both truncated with a cut-off radius of 1.2 nm; no long-range electrostatic or Lennard–Jones interactions were computed.

Analysis

To quantify the mutual sliding of adjacent chains, we defined the “chain slippage,” D_{slip} , as:

$$D_{\text{slip}} = \sqrt{D^2 - \frac{a^2 + b^2}{4}}$$

where D (nm) is the distance between the centers of gravity of two anhydroglucose units belonging to two consecutive chains in the bending direction (see Fig. 1), and $a = 0.78$ nm and $b = 0.80$ nm are the respective unit cell dimensions. We obtained a rough estimate of the free energy by calculating the torsional entropy contribution from the dihedral angle distribution (Chen et al. 2012).

In addition, powder diffraction profiles were calculated using the Debyer software package (Wojdyr 2011), which is based on the Debye scattering equation (Debyer 1915) and has been used previously (Nishiyama et al. 2012).

$$I(Q) = \sum_i \sum_j f_i f_j \frac{\sin(Qr_{ij})}{Qr_{ij}}$$

where Q is the scattering vector, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between atoms i and j , $I(Q)$ is the scattering intensity, and f_i and f_j are the scattering factors of atoms i and j . A wavelength of 1.5418 Å, corresponding to the wavelength of CuKα, is used.

Results

Local structures: amorphous kinks surrounded by crystalline straight segments

Figure 1 gives snapshots of the atomistic models of the two cellulose crystals, showing increasingly “kinked” deformations. Figures 2 and 3 report, respectively, the conformational states of the hydroxymethyl groups (Fig. 2) and the pyran rings (Fig. 3) as a function of deflection and of their position along the cellulose crystal. These two parameters are used to probe the local state of organization in the kinked crystals. The hydroxymethyl group explores exclusively the *tg* orientation ($\omega = 180^\circ$) in the core of the

perfect Iα and Iβ crystals (Nishiyama et al. 2002, 2003), whereas it explores the *gg* and *gt* orientations (ω at $\pm 60^\circ$) at the crystal surface or within the less organized zones (amorphous or paracrystalline) (Mazeau and Heux 2003). Similarly, pyran rings are in the most stable 4C_1 chair conformation in the unstressed crystals and departures from this form clearly indicate that the structure becomes amorphous (Mazeau and Heux 2003). Analysis of the kinked structures shows two populations of the polar angle, θ , of the puckering parameters (Cremer and Pople 1975). The dominant population is centered around $\theta = 15^\circ$, which is representative of the 4C_1 classical conformation of the pyran, while the minor population is centered at $\theta = 75^\circ$, indicating that some pyran rings adopt the boat and skew-boat conformations.

Figures 2 and 3 show that the linear segments remain highly organized for the entire range of studied deflections. The hydroxymethyl groups keep the initial *tg* conformation (Fig. 2) and the pyran rings adopt exclusively the 4C_1 conformation (Fig. 3). The regular organization of the linear portions of the crystals can be visualized in the snapshots shown in Fig. 1. Near the loading point, however, the structure becomes disorganized. The appearance of the *gg* and *gt*

Fig. 2 Conformational states explored by the hydroxymethyl groups as a function of deflection (horizontal axes) and location along the length of the crystals (vertical axes). Glucose residues are numbered from 1 to 40, starting from the non-reducing end of the crystals. Left: distribution of the *gg* (a: Iα, b: Iβ), *tg* (c: Iα, d: Iβ) and *gt* (e: Iα, f: Iβ) conformations for the Iα (a, c, e) and Iβ (b, d, f) crystals. Right: orientation of the O6 atom in a glucose residue in (from top to bottom) the *gg*, *tg* and *gt* conformations respectively. The fractions are indicated by the colors at the right of the plots

Fig. 3 Distribution of the 4C_1 chair conformation of the $I\alpha$ (a) and $I\beta$ (b) crystals explored by the pyran rings as a function of deflection (horizontal axes) and location along the length of

the crystals (vertical axes). Glucose residues are numbered from 1 to 40, starting from the non-reducing end of the crystals. The fractions are indicated by the colors at the right of the plots

conformers of the hydroxymethyl groups, together with the appearance of the unconventional forms of the pyran rings accompanying the kinking, is perceptible for deflections beyond 2–3 nm. The disorganized portion of the micro-fibril propagates progressively and symmetrically on both sides of the kink as deflection increases.

Figure 4 shows the predicted wide-angle X-ray powder diffractograms for $I\alpha$ (Fig. 4a) and $I\beta$ (Fig. 4b), respectively, at various deflections. The diffracted intensities decrease by increasing deflection, indicating an overall decrease in crystallinity induced by kinking. This feature is consistent with the previous observations about the distribution of the conformation of the hydroxymethyl groups and the pyran ring puckering.

Diffractograms predicted for $I\alpha$ and $I\beta$ at various levels of deflection are superimposed in Fig. 4c. As expected, at small deflections, the most intense diffraction peak of $I\beta$ (200) appears at a larger $2 - \theta$ value than that for $I\alpha$ (110). In contrast, the two diffractograms predicted from the strongly kinked $I\alpha$ and $I\beta$ become almost identical, indicating that the straight domains of the two kinked crystals undergo ultrastructural reorganizations and converge to a similar structure.

Discontinuities in the potential energy curves

Figure 5 shows how, taking the torsional entropy into account, the potential energy and free energy of the $I\alpha$ and $I\beta$ crystals vary with deflection. In the initial state, the total energy of the $I\alpha$ crystal is about 4.6 kJ/(mol

cellobiose) larger than that of $I\beta$, due to the increase in nonbonded interactions (16.6 kJ/mol cellobiose) that overcompensates for the stabilization of bonded interactions (−12 kJ/mol cellobiose). That $I\beta$ is more stable than $I\alpha$ agrees with previous modeling simulations, where differences of 8–10 kJ/(mol cellobiose) using empirical force-fields (Neyertz et al. 2000; Mazeau and Heux 2003) and of 1 kJ/(mol cellobiose) from DFT calculations (Bucko et al. 2011; Li et al. 2011) have been reported.

The energy-deflection curves show several discontinuities where small increases in deflection are accompanied by energy drops of up to 1.5 kJ/(mol cellobiose). Such energy drops are specific to bending at the hydrophobic surfaces of native cellulose crystals, as they are not observed in the other directions (Chen et al. 2016). For deflections larger than 5 nm, the energy of the kinked $I\alpha$ microfibril is lower than that of its initial equilibrated crystal, suggesting that the structural rearrangements for this allomorph are favorable, and probably irreversible, despite the presence of a significant amount of amorphous phase that has a higher energy than the crystals (Mazeau and Heux 2003). In contrast, no such behavior is observed for the $I\beta$ form, where the energies of the kinked $I\beta$ crystal are always higher than that of the initial straight form.

Torsional entropy compensation

The potential energy increase due to bending is accompanied by larger torsional freedom in the kinked region, resulting in a much smaller net increase in free

Fig. 4 Simulated wide-angle X-ray powder diffraction: kinked models of I α (a) and I β (b) and superimposed diffractograms of the I α and I β models at various deflections (c)

energy, between 2 and 4 kJ/(mol cellobiose) less than the potential energy for cellulose I α and I β , respectively (Fig. 5). Thus, under ambient conditions, cellulose chains should kink more easily than what the potential energy increase or the theoretical bending rigidity would imply.

Chain slippage at the origin of the energy drops

Figure 6 shows the variation of the chain slippage distances (D_{slip}) with deflection. In the straight segments, all of the chains within a sheet behaved similarly. Thus D_{slip} represents the longitudinal organization of consecutive sheets within the crystalline parts. D_{slip} fluctuates around a constant value, meaning that the supramolecular organizations are globally maintained in the linear segments of the microfibril during kinking. D_{slip} also shows occasional jumps at

the deflections where energy drops, indicating that the event is associated by longitudinal slip of the hydrogen-bonded sheets. The magnitude of the displacements is remarkably constant, ± 0.5 nm, which corresponds to the length of a glucosyl residue. In cellulose I α and I β , the hydrogen bonded sheets are staggered by about 0.25 nm. The main structural difference between the two allomorphs is the direction of the stagger, which is unidirectional in I α but alternating in I β . Mutual sliding of 0.5 nm thus corresponds to local I $\alpha \longleftrightarrow$ I β allomorphic transitions. The sliding of the hydrogen-bonded sheets can be visualized by inspecting the snapshots of the kinked microfibril models. Atoms of selected glucosyl units in the linear segments are represented by spheres in Fig. 1 to facilitate visualization of the loci of the allomorphic transitions. Figure 1b, c shows snapshots of the I α and I β microfibrils before and after the first

Fig. 5 Variation of the energies of $I\alpha$ and $I\beta$ as a function of bending deflection. **a** Total potential energies of the $I\alpha$ (red) and $I\beta$ (blue) crystals. Labels a–h refer to snapshots shown in Fig. 1. **b** and **c** variation with bending deflection of the potential energy (grey), torsion entropy TAS (green) and free energy (blue) of the $I\beta$ (**b**) and $I\alpha$ (**c**) crystals. All energies reported in **b** and **c** are relative to the initial uninked crystals

energy drop, while Fig. 1c, e, g give snapshots after each energy drop for the kinked $I\alpha$ and $I\beta$ microfibrils.

The initial organization of the cellulose chains in the crystal influences the number and location of the allomorphic transitions (Figs. 1, 6). For the $I\alpha$ system, the first transition takes place at a deflection of 1.8 nm, where D_{slip} between layers 3 and 4 on the reducing end side varies suddenly by + 0.5 nm (Fig. 5). Just after the transition (Fig. 1c), the reducing side of the microfibril is composed of two triclinic blocks separated by a monoclinic interface between layers 3 and 4. This structural event is repeated at each energy drop and, after each new sliding event, the total amount of the monoclinic form increases. This accumulation of the $I\beta$ -like form can be observed in Fig. 1g where the microfibril is strongly bent after three energy drops corresponding to six sliding events, and the vast majority of the crystal is in $I\beta$ -like organization, except for the amorphous kink. Note that, at this bending level, the non-reducing end side of the microfibril (to the right of the kink in Fig. 1e, g) is also affected by the structural reorganization.

Interestingly, the 5 kJ/(mol cellobiose) energy drop between tags f and g is due to three concerted sliding events on the non-reducing end side of the microfibril (Fig. 6). Finally, under extreme bending, at a deflection of 7.5 nm (Fig. 1g right), the organization is mainly $I\beta$ -like on both sides of the kink, showing that the allomorphic transformation is almost complete. This progressive transformation from triclinic form to a monoclinic form leads to the stabilization of the kinked state after being displaced 5 nm compared to its initial form (Fig. 5).

Similar relaxations by sliding exists for the $I\beta$ form, with the energy drops accompanying ~ 0.5 nm longitudinal displacements of the sheets (Fig. 5) resulting in local $I\beta \rightarrow I\alpha$ allomorphic transitions (Fig. 1c, e, g). The first transition occurs at a deflection of 2.5 nm between layers 4 and 5 on the non-reducing (right) end of the fibril, which, at tag c, is organized in two monoclinic blocks separated by a triclinic-like interface between layers 4 and 5). However, layers 4 and 5 in the $I\beta$ system undergo several successive transitions on the non-reducing side, converting the

Fig. 6 Variation of the chain slippage distance (D_{slip}) between adjacent hydrogen-bonded sheets as a function of bending deflection for $I\beta$ (left) and $I\alpha$ (right). Blue: reducing end, red: non-reducing end. Traces are displaced vertically by 1 nm for visibility. Layers are numbered from 1 (the layer opposite the loaded layer) to 8 (the loaded layer)

interface into $I\alpha$ at 2.5 nm of deflection, before reverting to $I\beta$ at 3.5 nm and transforming again into $I\alpha$ at 6.5 nm. This suggests that the $I\beta$ to $I\alpha$ -like conversion in $I\beta$ is transitory; after each new sliding event, the organization within the microfibril alternates between pure $I\beta$ and a $I\alpha/I\beta$ mixture. It is only for extreme curvatures greater than approximately 6 nm of deflection, that a significant portion of the non-reducing side of the microfibril transforms into $I\alpha$.

We note that the reducing end side of the microfibril is unaffected by bending and keeps its initial monoclinic organization. This asymmetry of the deformation with respect to the reducing end might come from the ratchet-like morphology of cellulose chains, which results in asymmetric shear compliance.

Effect of the crystal length

To keep the computational demands of our simulations reasonable, we first opted to study relatively short crystal segments to study the effect of bending on

the local structural transformation in vacuum. Experimentally, the allomorphic transition and creation of kinks by sonication is observed on long microfibrils but not on short fragments of crystals, and in aqueous media (Briois et al. 2013).

To address the question of size effects, we have repeated the kinking protocol on a 80 nm long $I\alpha$ crystal, corresponding to a degree of polymerization of 160. A load applied at the center of the crystal perpendicular to the hydrogen bonded layers produces a kink similar to that observed in the short crystals. Visual inspection of the model at large deflections also reveals two distinct coexisting organizational states, as the structure is clearly disorganized at the kinking point but remains highly organized on both sides of the kink. Figure 7 displays the evolution of the slippage distances as a function of deflection. Similar to that observed for the short crystals, the long crystal undergoes 0.5 nm relative displacements of the hydrogen-bonded layers, which indicates local allomorphic conversion. Among the seven pairs of adjacent layers, four such transitions are observed in

Fig. 7 Variation of the chain slippage distance (D_{slip}) between adjacent hydrogen-bonded sheets as a function of bending deflection for the long model of $I\alpha$. Layers are numbered from 1 (the layer opposite the loaded layer) to 8 (the loaded layer)

the deflection range 15–30 nm. However, the sliding of the layers in the short crystal appears at smaller kink angles compared to the long crystal, suggesting that sliding is easier in the short model. For example, the first transition takes place at a kink angle of 11.5° for the 20 nm model, whereas it appears only at 19.5° for the 80 nm model.

Overall, the evolution with kinking of the morphology, the local internal organization (amorphous or crystalline) as well as the allomorphic transitions are independent of size effects. This concordance of structural behavior between the short and long model suggests that the molecular mechanism of response to a lateral force by phase transition is general.

Discussion

Experimentally sonicated microfibrils showed numerous kinks when observed in TEM, with a 20% decrease in crystallinity and an increase in *gg* and *gt* conformers of the hydroxymethyl groups as estimated by solid-state CP-MAS NMR spectroscopy (Briois et al. 2013). Our models qualitatively agree with these experimental observations. The simulation also suggests that crystallinity degrades only at the kinking point and the linear segments remain crystalline.

We also reported that cellulose microfibrils from *Glaucocystis*, mostly in $I\alpha$, partly transformed into $I\beta$ by ultrasonication (Briois et al. 2013). Kinking the $I\alpha$ microfibril model agree with this observation. It has been recently measured that the maximum of the

distribution of the kink angle is 60° (Usov et al. 2015), which corresponds to a deflection of 5 nm in our model. To reach this level of deflection, the $I\alpha$ crystal model underwent two transitions on the reducing end and three on the non-reducing end (Figs. 1, 6), leading to an accumulation of the maximal possible amount of $I\beta$.

In contrast, the cellulose microfibrils from tunicate, dominated by the $I\beta$ phase, remain unchanged when they are sonicated. Our models show that the reducing end of $I\beta$ can undergo some transitions to $I\alpha$ during kinking, but at the observed kink angle of 60° the two straight segments surrounding the kink are entirely monoclinic ($I\beta$), corroborating that transitory $I\beta \rightarrow I\alpha$ conversions are undetected.

Thermal treatment transforms $I\alpha$ into $I\beta$ (Horii et al. 1987; Yamamoto et al. 1989; Debzi et al. 1991; Yamamoto and Horii 1993). The high thermal expansion perpendicular to the pyranose plane upon heating measured by in situ X-ray diffraction suggests the thermally induced phase transition is also due to mutual sliding at these hydrophobic interfaces.

Conclusions

We have performed molecular dynamics simulations of cellulose crystals of length 20 nm and 80 nm to study their behavior under bending deformations. Comparable to experimental observations, when bent on the hydrophobic plane, cellulose crystals tend to create kink zones with loss of crystalline order. while

the two linear segments on each side of the kink remain crystalline. The creation of kinks is accompanied by translations of the hydrogen-bonded sheets of the crystalline segments, corresponding to partial allomorphic transitions. The $I\alpha \rightarrow I\beta$ conversions accumulate with increasing bending deflection, while $I\beta \rightarrow I\alpha$ conversions are only transitory.

Acknowledgments This work was supported by the Wallenberg Wood Science Center (WWSC) funded by the Knut and Alice Wallenberg Foundation. This work was performed as part of the Cluster of Excellence “Tailor-Made Fuels from Biomass”, which is funded by the Excellence Initiative by the German federal and state government to promote science and research at German universities. We acknowledge the computational resource from the Centre d’Expérimentation et de Calcul Intensif (CECIC).

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

- Briois B, Saito T, Petrier C, Putaux J.-L., Nishiyama Y, Heux L, Molina-Boisseau S (2013) $I\alpha \rightarrow I\beta$ transition of cellulose under ultrasonic radiation. *Cellulose* 20:597–603
- Bucko T, Tunega D, Angyan JG, Hafner J (2011) Ab initio study of structure and interconversion of native cellulose phases. *J Phys Chem A* 115:10097–10105
- Bussi G, Donadio D, Parrinello M (2007) Canonical sampling through velocity rescaling. *J Chem Phys* 126:014101/1–014101/7
- Chen P, Nishiyama Y, Mazeau K (2012) Torsional entropy at the origin of the reversible temperature-induced phase transition of cellulose. *Macromolecules* 45:362–368
- Chen P, Nishiyama Y, Mazeau K (2014) Atomic partial charges and one Lennard–Jones parameter crucial to model cellulose allomorphs. *Cellulose* 21:2207–2217
- Chen P, Ogawa Y, Nishiyama Y, Ismail AE, Mazeau K (2016) Linear, non-linear and plastic bending deformation of cellulose nanocrystals. *Phys Chem Chem Phys* 18:19880–19887
- Cremer D, Pople JA (1975) General definition of ring puckering coordinates. *J Am Chem Soc* 97(6):1354–1358
- Debye P (1915) *Zerstreuung von Röntgenstrahlen*. *Ann Phys (Berlin)* 46:809–823
- Debzi EM, Chanzy H, Sugiyama J, Tekely P, Excoffier G (1991) The $I\alpha \rightarrow I\beta$ transformation of highly crystalline cellulose by annealing in various mediums. *Macromolecules* 24:6816–6822
- Grishkewich N, Mohammed N, Tang J, Tam KC (2017) Recent advances in the application of cellulose nanocrystals. *Curr Opin Colloid Interface Sci* 29:32–45
- Habibi Y, Lucia LA, Rojas OJ (2010) Cellulose nanocrystals: chemistry, self-assembly, and applications. *Chem Rev* 110:3479–3500
- Hansen HS, Huenenberger PH (2011) A re-optimized GRO-MOS force field for hexopyranose-based carbohydrates accounting for the relative free energies of ring conformers, anomers, epimers, hydroxymethyl rotamers, and glycosidic linkage conformers. *J Comput Chem* 32:998–1032
- Hess B, Bekker H, Berendsen HJC, Fraaije JGEM (1997) LINCS: a linear constraint solver for molecular simulations. *J Comput Chem* 18:1463–1472
- Hess B, Kutzner C, van der Spoel D, Lindahl E (2008) GRO-MACS 4: algorithms for highly efficient, load-balanced, and scalable molecular simulation. *J Chem Theory Comput* 4:435–447
- Hidayat BJ, Felby C, Johansen KS, Thygesen LG (2012) Cellulose is not just cellulose: a review of dislocations as reactive sites in the enzymatic hydrolysis of cellulose microfibrils. *Cellulose* 19:1481–1493
- Horii F, Yamamoto H, Kitamaru R, Tanahashi M, Higuchi T (1987) Transformation of native cellulose crystals induced by saturated steam at high temperatures. *Macromolecules* 20:2946–2949
- Kekaelaeninen K, Illikainen M, Niinimäki J (2012) Morphological changes in never-dried kraft fibers under mechanical shearing. *Cellulose* 19:879–889
- Li Y, Lin M, Davenport JW (2011) Ab initio studies of cellulose I: crystal structure, intermolecular forces, and interactions with water. *J Phys Chem C* 115:11533–11539
- Martoia F, Dumont PJJ, Orgeas L, Belgacem MN, Putaux JL (2016) On the origins of the elasticity of cellulose nanocomposites and nanopapers: a micromechanical approach. *RSC Adv* 6:47258–47271
- Mazeau K, Heux L (2003) Molecular dynamics simulations of bulk native crystalline and amorphous structures of cellulose. *J Phys Chem B* 107:2394–2403
- Neyertz S, Pizzi A, Merlin A, Maigret B, Brown D, Deglise X (2000) A new all-atom force field for crystalline cellulose I. *J Appl Polym Sci* 78:1939–1946
- Nishiyama Y, Langan P, Chanzy H (2002) Crystal structure and hydrogen-bonding system in cellulose $I\beta$ from synchrotron X-ray and neutron fiber diffraction. *J Am Chem Soc* 124:9074–9082
- Nishiyama Y, Sugiyama J, Chanzy H, Langan P (2003) Crystal structure and hydrogen bonding system in cellulose $I\alpha$ from synchrotron X-ray and neutron fiber diffraction. *J Am Chem Soc* 125:14300–14306
- Nishiyama Y, Johnson GP, French AD (2012) Diffraction from nonperiodic models of cellulose crystals. *Cellulose* 19:319–336
- Usov I, Nystrom G, Adamcik J, Handschin S, Mezzenga R, Schutz C, Fall A, Bergstrom L (2015) Understanding nanocellulose chirality and structure-properties relationship at the single fibril level. *Nat Commun* 6:7564
- Wang QQ, Zhu JY, Gleisner R, Kuster TA, Baxa U, McNeil SE (2012) Morphological development of cellulose fibrils of a bleached eucalyptus pulp by mechanical fibrillation. *Cellulose* 19:1631–1643

- Wojdyr M (2011) Debyer, 9 Jan 2017 version. <http://debyer.readthedocs.io> and <http://code.google.com/p/debyer/wiki/debyer>. Accessed 1 May 2018
- Yamamoto H, Horii F (1993) CPMAS carbon-13 NMR analysis of the crystal transformation induced for Valonia cellulose by annealing at high temperatures. *Macromolecules* 26:1313–1317
- Yamamoto H, Horii F, Odani H (1989) Structural changes of native cellulose crystals induced by annealing in aqueous alkaline and acidic solutions at high temperatures. *Macromolecules* 22:4130–4132
- Zeng X, Retulainen E, Heinemann S, Fu S (2012) Fiber deformations induced by different mechanical treatments and their effect on zero-span strength. *Nord Pulp Pap Res J* 27:335–342