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1 **Drying-induced bending deformation of cellulose nanocrystals studied by**  
2 **molecular dynamics simulations**

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8

9 **ABSTRACT**

10 Drying cellulosic materials from their water-swollen state can collapse their ultrastructure  
11 and alter their macroscopic material properties such as mechanical strength and water-  
12 retention ability. However, at the single-crystal or molecular level, little is known about the  
13 deformation of cellulose upon drying. We thus investigate herein the drying-induced  
14 deformation of a cellulose crystal by using an atomistic molecular dynamics simulation that  
15 considers a hydrated system composed of two short cellulose crystals, a lower one fixed to a  
16 flat substrate and an upper one free to deform. To mimic vacuum drying, the water is  
17 gradually removed from the system. As the drying proceeds, the upper cellulose crystal  
18 bends and forms a tight contact with the lower cellulose crystal. This result underlines the  
19 importance of lateral deformation of cellulose crystals in the collapse of the cellulose  
20 ultrastructure and provides insights into the molecular mechanisms responsible for  
21 modifying the properties of cellulose materials.

22

23 **Keywords:** cellulose; drying; lateral deformation; molecular dynamics

## 24 INTRODUCTION

25 Cellulose is extracted and processed in the aqueous condition in many industrial  
26 processes, from chemical pulping to fiber and textile production to nanocellulose  
27 production. As a result, producing cellulosic materials often requires drying or water  
28 removal. Drying cellulosic materials modifies its physical properties; for instance, in the  
29 process of paper manufacturing, pulp fibers stiffen and shrink laterally upon drying (Minor,  
30 1994; Giacomozzi and Joutsimo, 2017). In addition, once dried, the pulp does not fully  
31 recover to the original state upon rewetting, and repeated drying and wetting produces a  
32 more rigid and brittle material. This phenomenon, called “hornification,” poses a challenge  
33 to paper recycling because hornified fibers do not reswell to their initial hydrated state  
34 when resuspended in water, which weakens recycled paper. Such degradation of the  
35 material properties upon conventional drying (air, oven, contact, etc.) occurs not only with  
36 pulp fibers but also with different cellulosic materials such as hydrogels and nanocellulose  
37 materials (Peng et al., 2012; Rämänen et al., 2012). Retaining the fine structure of cellulosic  
38 materials and minimizing the impact of drying often requires more gentle and costly drying  
39 methods such as freeze-drying or critical-point drying (Jin et al., 2004; Heath and  
40 Thielemans, 2010; Hoepfner et al., 2008; Beaumont et al., 2017). Conversely, simple air  
41 drying also produces some exceptional material properties in cellulosic materials. For  
42 example, a cast film of cellulose nanofiber dried from an aqueous suspension forms an  
43 exceptionally high barrier against oxygen gas (Fukuzumi et al., 2009), which means that this  
44 simple drying method packs the cellulose nanofibers tightly enough to prevent gas  
45 molecules from permeating through the film.

46 These drying-induced modifications in the mechanical properties are due to  
47 microscopic, irreversible structural changes within cellulosic materials and at various length

48 scales (Hult et al., 2003; Newman, 2004; Oksanen et al., 1997). Given that, compared with  
49 the rigidity of cellulose the surface tension of water is very significant at the nanometric  
50 scale, the capillary force can collapse the ultrastructures such as micropores and nanofiber  
51 networks, as has been observed by using various analytical techniques (e.g., microscopy,  
52 nitrogen adsorption, solid-state NMR spectroscopy, differential scanning calorimetry)  
53 (Häggkvist et al., 1998; Lovikka et al., 2016; Park et al., 2006). Although this interpretation of  
54 the drying effect is well accepted, what remains unclear is how cellulose deforms at the  
55 single-crystal and molecular levels in these collapsed structures. Recent reports based on  
56 transmission electron microscopy and scanning probe microscopy testify to the increasing  
57 interest in the nanoscale deformation of cellulose crystals (Mattos et al., 2019; Ogawa,  
58 2019; Smith et al., 2019). Unfortunately, limitations in characterization methods (e.g.,  
59 spatial resolution) and the intrinsic heterogeneity of cellulose morphology hinder the  
60 understanding of such deformations on a molecular level. More detailed molecular-level  
61 descriptions are thus needed to fully understand the deformation mechanism of cellulose  
62 crystals and how it affects material properties.

63 We recently demonstrated that, for cellulose crystals, force-field-based atomistic  
64 simulations provide structural insights into various deformation modes such as shear and  
65 bending deformations (Chen et al., 2016; 2018; Molnár et al., 2018). These computational  
66 studies indicate that crystalline cellulose is highly pliant in its lateral plane, contrary to the  
67 general assumption that crystalline cellulose forms rigid rods. In the present study, we use  
68 atomistic molecular dynamics (MD) to simulate a simplified system to determine the  
69 deformation of cellulose crystals upon drying. The results indicate that crystalline cellulose  
70 undergoes a bending deformation upon gradual removal of water from a hydrated system  
71 composed of two short cellulose crystals.

72

## 73 **COMPUTATIONAL METHODS**

### 74 **Simulation setup**

75 All simulations were done with GROMACS (Abraham et al., 2015) using the GROMOS  
76 56Acarbo force field (Hansen and Huenenberger, 2011), including the optimized Lennard-  
77 Jones repulsive parameter for the united CH1 atom type (Chen et al., 2014). This optimized  
78 GROMOS force field has already been used to investigate the lateral deformation of  
79 cellulose crystals in vacuum, which is similar to the simulation presented herein (Chen et al.,  
80 2016; Molnár et al., 2018). Although not designed specifically to model such a solid-vacuum  
81 interface, the deformation of cellulose crystals given by the force field is quantitatively  
82 consistent with the results of finite-element analysis and qualitatively consistent with  
83 transmission electron microscopy observations of kinked cellulose crystals (Chen et al.,  
84 2016). Thus, we believe that it can reproduce the deformation of cellulose crystals induced  
85 by dehydration.

86 MD simulations were done in the *NVT* ensemble with a 2 fs integration time step. The  
87 stochastic velocity-scaling algorithm of Bussi et al. (2007) was used to maintain the  
88 temperature at 300 K, and O-H bonds were constrained by using the LINCS algorithm (Hess  
89 et al., 1997). The long-range electrostatic interactions and Lennard-Jones interactions were  
90 both calculated by using the cutoff method with a cutoff distance of 0.9 nm. The analyses  
91 were done by using GROMACS and in-house scripts. The MD structures were visualized by  
92 using PyMOL (PyMOL ver. 2.1.0).

93

### 94 **Model construction**

95 The cellulose microfibril model of the major native allomorph I $\beta$  was built from crystal  
96 structures (Nishiyama et al., 2002) by considering the dominant hydrogen-bond network,  
97 pattern A. The crystal had dimensions of approximately 3.5 nm  $\times$  3.5 nm  $\times$  20 nm and  
98 consisted of 36 chains (6  $\times$  6), each 40 residues long, exposing the (1 1 0) and (1  $\bar{1}$  0)  
99 surfaces. Note that the crystal width is similar to that of higher plant cellulose microfibrils  
100 ( $\approx$ 3 nm), whereas the crystals are much shorter than natural cellulose microfibrils.

101 This crystal model was duplicated and two crystals were positioned parallel to each  
102 other, separated by 1.8 nm, in a small simulation box (4.5  $\times$  9.5  $\times$  22 nm<sup>3</sup>), as shown in Fig.  
103 1a. The system was then solvated with simple-point-charge water (Berendsen et al., 1981),  
104 and the energy was minimized by using the steepest descent method followed by the  
105 conjugate gradient method, with the convergence criterion being a maximum force of  
106 10 kJ mol<sup>-1</sup> nm<sup>-1</sup>. The positions of the selected atoms were then constrained as shown in Fig.  
107 1b to maintain the separation between the central sections of the crystals, and this position  
108 constraint was retained in the following MD simulations. The system was then stepwise  
109 heated in the *NPT* ensemble from 0 to 300 K in 20 ns. The pressure was regulated by using a  
110 Berendsen barostat with a relaxation time of 2.0 ps (Berendsen et al., 1984).

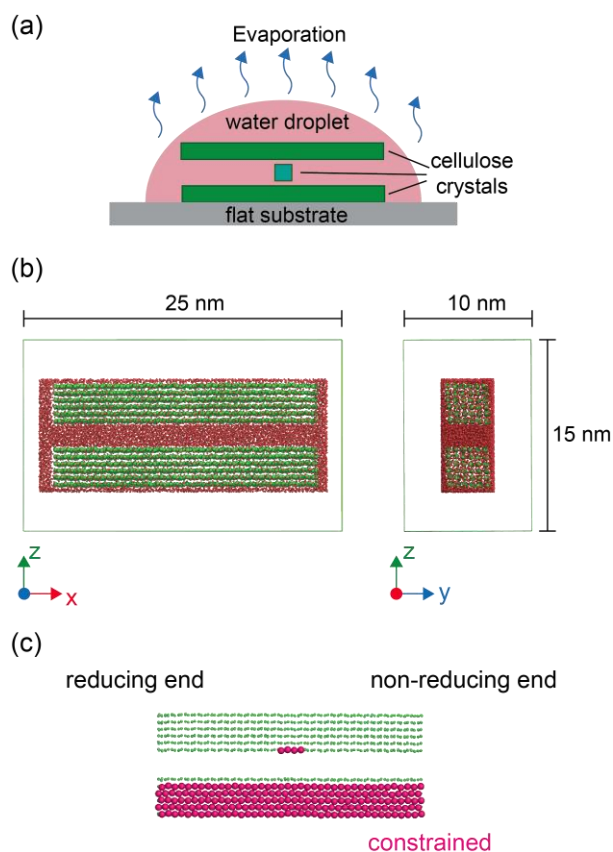
111

## 112 **General strategy for modeling the drying process**

113 To demonstrate the drying-induced deformation of cellulose, we studied the simple  
114 model shown in Figure 1. As illustrated in Fig. 1a, we considered a geometry where an upper  
115 cellulose crystal is positioned parallel to and above another crystal laid on a flat substrate,  
116 and a crystal is sandwiched crossways between the two parallel crystals to maintain a  
117 constant separation between them. We used this crossed-fibril geometry to mimic the  
118 random orientation of cellulose crystals in a film drop-casted from aqueous suspensions

119 (Fukuzumi et al., 2009). In the model studied, all atomic positions in the bottom crystal were  
120 constrained except those at the upper surface that faced the upper crystal. The third crystal  
121 was treated implicitly to reduce the system size. The inter-crystal spacing was maintained by  
122 constraining the atomic positions of four residues at the center of each molecular chain on  
123 the bottom layer of the upper crystal. The side surfaces of the cellulose crystals were  
124 hydrophilic (1  $\bar{1}$  0) and (1 1 0), and the surfaces facing the opposing crystal were both  
125 (1 1 0) surfaces.

126 Water evaporation was modeled by stepwise removal of water molecules in the gas  
127 phase. First, the hydrated system was heated to 300 K, and then the volume of the  
128 simulation box was expanded fourfold (10  $\times$  15  $\times$  25 nm) to generate vacuum space. The MD  
129 simulation was then executed at a constant volume at 300 K but was stopped every 100 ps  
130 to remove isolated water molecules ("isolated" water molecules were defined as those with  
131 no neighbor molecule within 1 nm). Upon restarting the simulation, the atomic velocities  
132 from the previous MD trajectory were retained, so the system temperature remained  
133 essentially constant at 300 K.



134

135 **Figure 1.** Model used to simulate drying of cellulose crystals: (a) Schematic drawing showing

136 geometry of simulation. (b) Initial dimensions of simulation box containing two crystals and

137 water molecules. For clarity, only the C1 atoms of cellulose (green) and the oxygen atoms of

138 water (red) appear in these snapshots. (c) Constraints on atomic positions within cellulose

139 crystals. The positions of the magenta glucose residues were constrained in the x, y, and z

140 directions. For simplicity, only C1 atoms (green) are shown for each residue, but the

141 constraints were applied to all atoms in the residues. The left and right extremities of the

142 upper (lower) surface of the lower (upper) cellulose crystal are called the reducing and non-

143 reducing ends, respectively. The cellulose crystals are maintained in this orientation in all

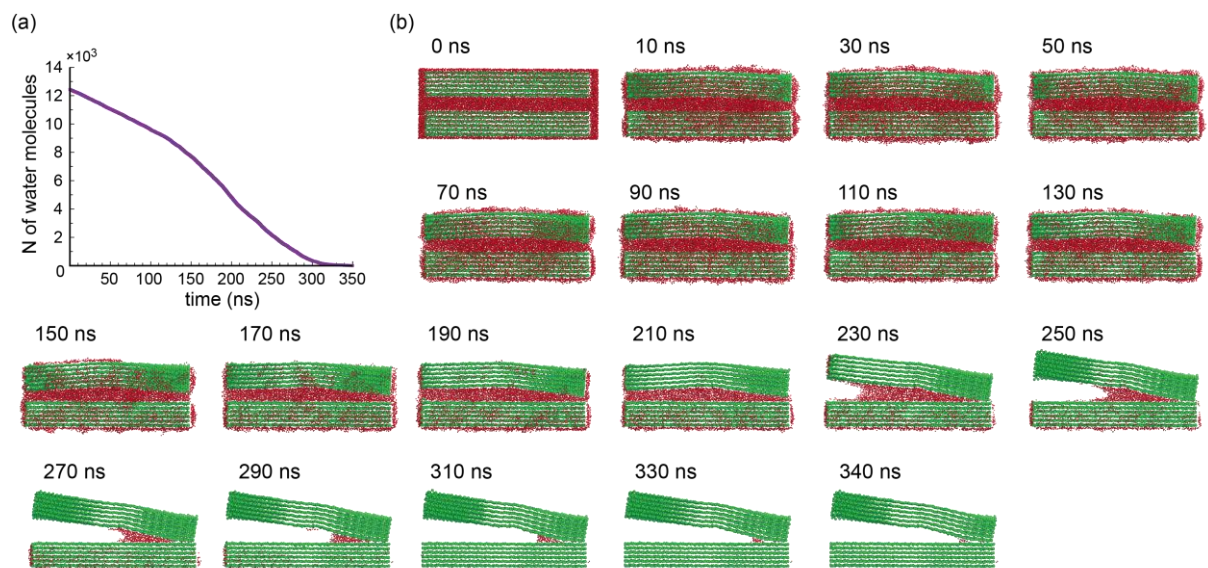
144 figures presented herein.

145

146 **RESULTS AND DISCUSSION**

147 Figure 2 summarizes the general features of the drying process. As shown in Fig. 2a, the  
 148 number of water molecules decreases monotonically in time, indicating that the strategy  
 149 adopted is suitable for simulating the gradual removal of water on the nanometer scale.  
 150 Almost all water molecules are removed after 340 ns (32 and 8 water molecules remain at  
 151 340 and 350 ns, respectively). Figure 2b shows snapshots of the simulated system during  
 152 the drying process and reveals a bending deformation of the upper cellulose crystal and the  
 153 heterogeneous removal of water.

154



155

156 **Figure 2.** Result of drying simulation: (a) Number of water molecules as a function of time.

157 (b) Snapshots of simulated cellulose-crystal system during drying.

158

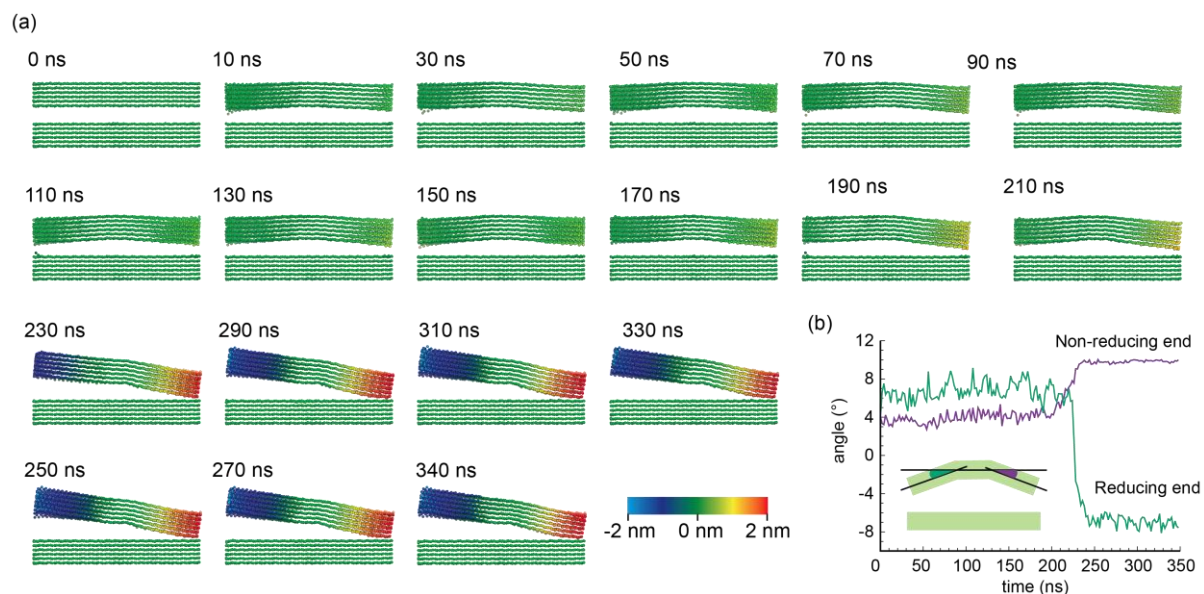
### 159 Deformation of cellulose crystal

160 At 10 ns, the upper cellulose crystal deforms from its initial linear form into a  
 161 continuous curve (Fig. 3a). This deformation occurs immediately upon starting the  
 162 simulation as can be seen in the bending angle evolution in Fig. 3b. The curved morphology  
 163 is imposed by the water droplet to minimize the area of the liquid surface. This result

164 indicates that the surface tension of water suffices to cause a lateral deformation of very  
165 short cellulose crystals. At this point, the upper cellulose crystal becomes convex with  
166 respect to the lower cellulose crystal and roughly symmetric with respect to the center of  
167 the crystal (Fig. 3b).

168       The curved morphology persists until about 150 ns, at which point most water  
169 molecules have been removed from the upper and side faces of the upper crystal. After  
170 170 ns the crystal becomes asymmetrically bent about its center. The lower crystal surface  
171 at the non-reducing end (right-hand end) approaches to within significantly less than 0.9 nm  
172 of the upper surface of the bottom crystal, which is the cutoff distance for non-bonding  
173 interactions in this simulation. At 220 ns (Fig. 3), the edge of the non-reducing end of the  
174 upper crystal makes contact with the bottom crystal. The bending angle of the upper crystal  
175 increases from 4° in the initial curved state (i.e., at 10 ns) to 10°. The reducing end of the  
176 upper crystal has moved upward, away from the bottom crystal. This displacement of the  
177 reducing end is initiated by the rupture of the continuous water layer that previously forced  
178 the curved morphology of the upper crystal. As the drying proceeds further, the crystal-  
179 contact area expands and produces surface-to-surface contact (Figs. 3a and 4b). After 240  
180 ns, this contact area remains constant because the bending angle for the non-reducing end  
181 remains constant once the contact area is well established. In contrast, the bending angle of  
182 the free reducing end fluctuates (Fig. 3b). The non-reducing end of the upper crystal forms a  
183 concave curvature. As detailed below, the water molecules between the two crystals are  
184 expelled from the contact area.

185



186

187 **Figure 3.** (a) Deformation of upper cellulose crystal in drying simulation. The color code

188 indicates the atomic displacement in the z direction (vertical direction in the figure). (b)

189 Bending angle plotted as a function of time during drying for upper cellulose crystal at

190 reducing end (green) and non-reducing end (purple). The bending angles are the angles

191 between the tangent to the central section and the tangents to the ends of the crystal, as

192 schematized in the inset.

193

### 194 **Water removal**

195 Immediately after the simulation box expands fourfold in volume, the surface tension of

196 water causes the water molecules to form an elongated droplet surrounding the two

197 cellulose crystals (Fig. 2). The water molecules gradually evaporate from the outer side of

198 the droplet, whereas the number of water molecules trapped between the cellulose crystals

199 remains roughly constant. As mentioned above, most of the water molecules around the

200 crystals have evaporated after 170 ns, leaving only a monolayer of water molecules directly

201 adsorbed on the cellulose-crystal surfaces. As seen in Fig. 2a, the evaporation rate increases

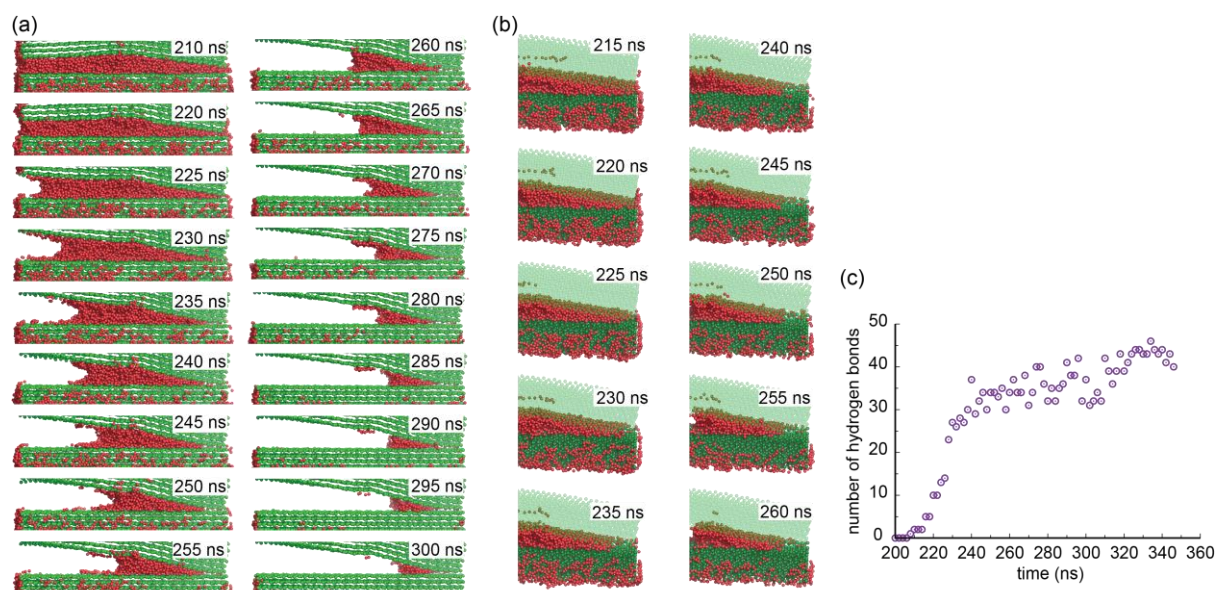
202 at this stage. Such evaporative behavior is evocative of a type-II isotherm, implying that a

203 strong interaction exists between the cellulose-crystal surface and the water. The position  
204 constraints that lead to a temperature of 0 K for the constrained part of the crystal means  
205 that water adsorbed on the bottom crystal evaporates much more slowly than water  
206 adsorbed on the upper crystal.

207       Once the contact between the cellulose crystals occurs at 220 ns, a water meniscus  
208 forms on the reducing end where the two crystals are widely separated (Fig. 4a). The  
209 meniscus is concave, which is indicative of strong adhesion between water and the  
210 cellulose-crystal surfaces. As the drying proceeds further, the water molecules evaporated  
211 from the reducing end (i.e., the left side where the crystals are separated), and the  
212 meniscus surface gradually moves toward the non-reducing end where the cellulose crystals  
213 are in contact. The water molecules are retained in this opening until the end of the drying  
214 process, as indicated by the few molecules still apparent at 340 ns in Fig. 3.

215       Conversely, the water molecules near the contact area between the two crystals are  
216 expelled independently of the drying within the open space between the reducing ends of  
217 the cellulose crystals. Figure 4b shows a series of close-up snapshots of the contact area. As  
218 mentioned above, the crystals make contact after about 210 ns, at which point only the  
219 edge of the upper crystal touches the upper surface of the bottom crystal. In the following  
220 20 ns, the water molecules move away from this contact line, inducing direct contact  
221 between the two cellulose-crystal surfaces. This direct contact leads to the formation of  
222 hydrogen bonds between the two cellulose-crystal surfaces, as shown in Fig. 4c. From 210  
223 to 240 ns, the number of hydrogen bonds rapidly increases as water is removed from the  
224 contact area; beyond 240 ns, this number increases slowly, indicating a further extension of  
225 the contact area. These hydrogen bonds likely contribute to further stabilizing the contact  
226 between the two cellulose crystals.

227 Water is removed from the contact area much faster than in the adjacent open space  
 228 between the two cellulose crystals, despite the two surfaces in the contact being hydrophilic.  
 229 Previous atomistic MD simulations of similar duration indicate that water molecules are  
 230 often incorporated into aggregates of cellulose crystals in the aqueous condition (Chen et al.,  
 231 2019; Paajanen et al., 2019). The asymmetric geometry at the drying front induces  
 232 compressive stress at the extremity where the crystals touch each other, which would also  
 233 contribute to squeezing out water rather than evaporative drying. This removal of water  
 234 molecules from between the cellulose crystals and the subsequent tight adhesion of the  
 235 cellulose surfaces is presumably the main factor on the nanometric scale that causes the  
 236 collapse of the cellulose structure upon drying.



237  
 238 **Figure 4.** (a) Formation of water meniscus between two cellulose crystals. (b) Removal of  
 239 water from the contact area between the two crystals. The upper crystal is translucent to  
 240 reveal the water molecules between the crystals. (c) Number of hydrogen bonds between  
 241 the two cellulose-crystal surfaces as a function of time.

242

243 **CONCLUSIONS**

244 By using atomistic MD simulations of a simplified cellulose-crystal system in water,  
245 we show that drying may cause a significant bending deformation of a cellulose crystal and  
246 a tight adhesion between cellulose-crystal surfaces, even without external forces. The  
247 simulation shows that the crystal bending occurs not only because of the adhesion between  
248 cellulose crystals but also because of the surface tension of the surrounding water. The  
249 formation of a concave water meniscus in the opening between the two crystals is indicative  
250 of strong interactions between cellulose and water, and the water molecules are quickly  
251 excluded from the contact area between the two crystals. Such preferential drying between  
252 two crystals leads to adhesion between the cellulose surfaces.

253 The deformation of the upper cellulose crystal constitutes a complex phenomenon  
254 induced by the interplay between the cellulose crystals and water molecules, and the details  
255 of the simulated deformation may depend not only on the force-field parameters but also  
256 on the simulation conditions. Thus, the evolution of the deformation should be compared  
257 and verified with experimental observations such as atomic force microscopy images of  
258 deformed cellulose crystals. Such a comparison should allow a more complete  
259 understanding of the nanoscale structural modifications that are at the origin of the  
260 property changes of cellulosic materials.

261

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265 University Grenoble Alpes.

266

## 267 **References**

268 Abraham MJ, Murtola T, Shulz R, Páll S, Smith JC, Hess B, Lindahl E (2015) GROMACS: high  
269 performance molecular simulations through multi-level parallelism from laptops to  
270 supercomputers. *SoftwareX* 1-2:19-25

271 Beaumont M, König J, Opietnik M, Potthast A, Rosenau T (2017) Drying of a cellulose II gel:  
272 effect of physical modification and redispersibility in water. *Cellulose* 24:1199-1209

273 Berendsen HJC, Postma JPM, van Gunsteren WF, Hermans J (1981) Interaction models for  
274 water in relation to protein hydration. In *Intermolecular Forces*; Pullman, B., Ed.;  
275 Springer: Dordrecht, pp 331-342.

276 Berendsen HJC, Postma JPM, van Gunsteren WF, DiNola A, Haak JR (1984) Molecular  
277 dynamics with coupling to an external bath. *J Chem Phys* 81:3684-3690.

278 Bussi G, Donadio D, Parrinello M (2007) Canonical sampling through velocity rescaling. *J*  
279 *Chem Phys* 126:014101/1-014101/7

280 Chen P, Nishiyama Y, Mazeau K (2014) Atomic partial charges and one Lennard-Jones  
281 parameter crucial to model cellulose allomorphs. *Cellulose* 21:2207-2217

282 Chen P, Ogawa Y, Nishiyama Y, Ismail AE, Mazeau K (2016) Linear, non-linear and plastic  
283 bending deformation of cellulose nanocrystals. *Phys Chem Chem Phys* 18: 19880-  
284 19887

285 Chen P, Ogawa Y, Nishiyama Y, Ismail AE, Mazeau K (2018) I $\alpha$  to I $\beta$  mechano-conversion and  
286 amorphization in native cellulose simulated by crystal bending. *Cellulose* 25:4345-  
287 4355

288 Chen P, Terrenzi C, Furó I, Berglund LA, Wohler J (2019) Quantifying localized  
289 macromolecular dynamics within hydrated cellulose fibril aggregates. *Macromolecules*  
290 52: 7278-7288

291 Fukuzumi H, Saito T, Iwata T, Kumamoto Y, Isogai A (2009) Transparent and high gas barrier  
292 films of cellulose nanofibers prepared by TEMPO mediated oxidation.  
293 *Biomacromolecules* 10:162-165

294 Giacomozzi DE, Joutsimo O (2017) Drying temperature and hornification of industrial never-  
295 dried *Pinus radiata* Pulps. 2. Voith Sulzer Refining. *BioResources* 12:1532-1547

296 Häggkvist M, Li TQ, Ödberg, L (1998) Effects of drying and pressing on the pore structure in  
297 the cellulose fibre wall studied by  $^1\text{H}$  and  $^2\text{H}$  NMR relaxation. *Cellulose* 5:33-49

298 Hansen HS, Huenenberger PH (2011) A re-optimized GROMOS force field for hexopyranose-  
299 based carbohydrates accounting for the relative free energies of ring conformers,  
300 anomers, epimers, hydroxymethyl rotamers, and glycosidic linkage conformers. *J*  
301 *Comput Chem* 32:998-1032

302 Heath L, Thielemans W (2010) Cellulose nanowhisker aerogels. *Green Chem* 12:1448-1453

303 Hess B, Bekker H, Berendsen HJC, Fraaije JGEM (1997) LINCS: a linear constraint solver for  
304 molecular simulations. *J Comput Chem* 18:1463-1472

305 Hoepfner S, Ratka L, Milow B (2008) Synthesis and characterization of nanofibrillar cellulose  
306 aerogels. *Cellulose* 15:121-129

307 Hult EL, Larsson PT, Iversen T (2001) Cellulose fibril aggregation - an inherent property of  
308 kraft pulps. *Polymer* 42: 3309-3314

309 Jin H, Nishiyama Y, Wada M, Kuga S (2004) Nanofibrillar cellulose aerogels. *Colloids Surf A*  
310 240:63-67

311 Lovikka VA, Khanjani P, Väisänen S, Vuorinen T, Maloney TC (2016). Porosity of wood pulp  
312 fibers in the wet and highly open dry state. *Microporous Mesoporous Mater* 234:326-  
313 335.

314 Mattos BD, Tardy BL, Rojas OJ (2019) Accounting for substrate interactions in the  
315 measurement of the dimensions of cellulose nanofibrils. *Biomacromolecules* 20:2657-  
316 2665

317 Minor JL (1994) Hornification – Its origin and meaning. *Progress in paper recycling* 3:93-95

318 Molnár G, Rodney D, Martoia F, Dumont PJJ, Nishiyama Y, Mazeau K, Orgéas L (2018)  
319 Cellulose crystals plastify by localized shear. *Proc Natl Acad Sci U.S.A.* 115:7260-7265

320 Newman RH (2004) Carbon-13 NMR evidence for cocrystallization of cellulose as a  
321 mechanism for hornification of bleached kraft pulp. *Cellulose* 11: 45-52

322 Nishiyama Y, Langan P, Chanzy H (2002) Crystal structure and hydrogen-bonding system in  
323 cellulose I $\beta$  from synchrotron X-ray and neutron fiber diffraction. *J Am Chem Soc*  
324 124:9074-9082

325 Ogawa, Y (2019) Electron microdiffraction reveals the nanoscale twist geometry of cellulose  
326 nanocrystals. *Nanoscale* 11:21767-21774

327 Oksanen T, Buchert J, Viikari L (1997) The role of hemicelluloses in the hornification of  
328 bleached kraft pulps. *Holzforschung* 51:355-360

329 Paajanen A, Ceccherini S, Maloney T, Ketoja JA (2019) Chirality and bound water in the  
330 hierarchical cellulose structure. *Cellulose* 26:5877-5892

331 Park S, Venditti RA, Jameel H, Pawlak JJ (2006) Changes in pore size distribution during the  
332 drying of cellulose fibers as measured by differential scanning calorimetry. *Carbohydr*  
333 *Polym* 66:97-103.

334 Peng Y, Gardner DJ, Han Y (2012) Drying cellulose nanofibrils: in search of a suitable  
335 method. *Cellulose* 19:91-102

336 PyMOL, The PyMOL Molecular Graphics System, Version 2.1.0 Schrödinger, LCC.

337 Rämänen P, Penttilä P, Svedström K, Maunu SL, Serimaa R (2012) The effect of drying  
338 method on the properties and nanoscale structure of cellulose whiskers. Cellulose  
339 19:901-912

340 Smitåh KB, Tisserant J-N, Assenza S, Arcari M, Nyström G, Mezzenga R (2019) Confinement-  
341 induced ordering and self-folding of cellulose nanofibrils. Adv Sci 6:1801540.  
342 DOI:10.1002/adv.201801540