Tearing apart cellulose nanofibers: the formation of unitary cellulose polymers

Gustavo H. Silvestre¹, Lidiane O. Pinto², Juliana S. Bernardes²,³, Roberto H. Miwa¹, and Adalberto Fazzio²,³

¹Instituto de Física, Universidade Federal de Uberlândia, C.P. 593, 38400-902, Uberlândia, MG, Brazil
²Brazilian Nanotechnology National Laboratory (LNNano), Brazilian Center for Research in Energy and Materials (CNPEM), Campinas, SP, 13083-970, Brazil and
³Center for Natural and Human Sciences, Federal University of ABC, Santo André, São Paulo 09210-580, Brazil

(Dated: October 30, 2020)

The atomic scale understanding of cellulose disassembly processes is an important issue in designing nanostructures using cellulose-based materials. In this work, we present a joint of experimental and theoretical study addressing the disassembly of cellulose nanofibrils. Through TEMPO-mediated oxidation processes, combined with atomic force microscopy results, we find the formation of nanofibers with diameters corresponding to a single cellulose polymer chain. Further first-principles calculations have been done to provide a total energy picture of interchain and intersheet interactions in pristine and oxidized cellulose nanofibrils. In the former, by using a number of different van der Waals approaches, we found the intersheet interaction stronger than the interchain one. In the oxidized systems, we have considered the formation of (charged) carboxylate groups along the sides of elementary fibrils. By mapping the total charge density, we show a net charge concentration on the carboxylate groups, supporting the emergence of repulsive electrostatic interactions between the cellulose fibers. Indeed, our total energy results show that the weakening of the binding strength between the fibrils is proportional net charge density of the carboxylate group. Moreover, by comparing interchain and intersheet binding energies, we found that most of the disassembly processes should take place by breaking the interchain O–H⋯O hydrogen bond interactions.

I. INTRODUCTION

Cellulose, the most abundant plant material resource, is a homopolymer with linear chains of glucopyranose rings linked through β-(1,4)-glycosidic bonds, which interact with other macromolecules as lignin and hemicellulose, within the plant cell walls. The search for more eco-friendly and energy-efficient technologies has accentuated the interest of using biomass to develop fuels, chemicals, and materials. Lately, nanoscale particles (cellulose nanofibers CNF and cellulose nanocrystals CNC) extracted from cellulose fibers by refinement have attracted attention as a next-generation material due to their outstanding mechanical properties.

The resistance of plant biomass to breakdown and to fractionate into its molecular constituents is denominated recalcitrance. The biopolymers assemble in the cell wall, forming a robust microstructure hardy to physical, chemical, and enzymatic processes. Partially crystalline cellulose fibers are significant contributors to recalcitrance. Thus, an understanding, at the electronic and atomic level, of the noncovalent interactions that bind the cellulose chains is vital in designing effective refinement processes. The combination of synchrotron X-ray and neutron diffraction of cellulose Iβ, the mostly found allomorph of cellulose in higher plants, allowed to determine the most accurate position of all atoms in the unit cell, including the hydrogens. The crystalline structure consists of two parallel chains presenting slightly different conformations and organized into packed sheets (Fig. 1). Both H-bondings within a single layer of cellulose (interchain interactions) and stacking interactions (intersheet interactions), mainly originated from vDW forces, contribute to stabilizing the cellulose crystal structure. However, the literature diverges on which interaction is the key player in cellulose recalcitrance.

Due to the compact and rigid structure of cellulose, size-reduction is very energy-intensive and demands harsh conditions. To extract nanofibers (CNFs), high-energy mechanical disintegration methods as refining, grinding, and homogenization are often used. Chemical and enzymatic treatments, before mechanical action, are promising strategies to reduce the recalcitrance of cellulose. An established type of chemical pretreatment consists of adding carboxylate groups (COO−) on the surface of cellulose through TEMPO-(2,2,6,6-tetramethylpiperidine-1-oxyl radical) mediated oxidation. This surface modification is particularly interesting since it displays position-selective catalytic oxidation under moderate aqueous conditions. Electrostatic repulsion and osmotic effects acting between anionically-charged surfaces lead to the formation of individualized nanofibers after the mechanical process. In a recent work, we observed that accomplishing TEMPO-mediated oxidation under a high concentration of NaClO, cellulose nanofibers from sugarcane bagasse were obtained without a mechanical defibrillation step. Besides, a significant number of nanofibers with diameters smaller than that corresponding to an elementary fibril (< 3.5 nm) were imaged by atomic force microscopy (AFM), suggesting that besides promoting the disassembling of the fiber bundles into individual elementary nanofibers, the chemical oxidation also affects the intersheet and interchain interactions.

In this work, we performed a joint of experimental and theoretical investigation of cellulose disassembly upon oxidation, and the rule played by the carboxylate groups on
FIG. 1. Structural model of monoclinic cellulose Iβ. Solid lines show a perspective view of the periodic unit cell.

II. MATERIALS AND METHODS

A. Experimental section

1. Cellulose Nanofibers Preparation

CNFs were isolated by a procedure described elsewhere [16]. Briefly, the cellulose pulp extracted from sugarcane bagasse was surface-carboxylated by TEMPO oxidation reaction using two volumes of a 12% (w/v) NaClO solution (78.0 or 156.0 mL per gram of cellulose). The average charge density was determined by three conductometric titration measurements, as previously described [17]. Oxidized samples from sugarcane bagasse (SC) were identified as SC-25 and SC-50, according to the concentration of NaClO used in the reaction (25 or 50 mmol/g substrate).

2. Morphology characterization

The morphology of oxidized CNFs was observed by atomic force microscopy (Park NX10) under ambient conditions and using the tapping mode. The cantilever from Nanoworld had a spring constant of 42 Nm⁻¹ and nominal resonance frequency of 75 kHz. Prior AFM analyses, a droplet of aqueous diluted CNF suspension (10 μL, 5 mg/L) was deposited onto cleaved mica substrate (TED PELLA) and dried by natural evaporation at room temperature. The length and height of CNFs were measured via Gwyddion 2.54 software by counting about 100 independent nanofibers.

B. Computational details

The calculations were performed by using the Density Functional Theory (DFT), as implemented in the computational codes Quantum ESPRESSO (QE) software [18], and Vienna ab initio software package (VASP) [19, 20]. The exchange-correlation term was described within the generalized gradient approximation as proposed by Perdew, Burke and Ernzerhof (GGA-PBE) [21]. The periodic boundary conditions were satisfied using the super-cell approach with a vacuum region in the direction perpendicular to the cellulose sheet of at least 12 Å to avoid image interactions. The Kohn-Sham (KS) orbitals were expanded in a plane wave basis set with an energy cutoff of 48 Ry (650 eV). We have verified the convergence of our results by increasing the energy cutoff up to 60 Ry (816 eV). The electron-ion interactions were solved using the Projector Augmented Wave (PAW) method [22], and the 2D Brillouin Zone (BZ) is sampled according to the Monkhorst–Pack method [23], using a gamma-centered 3x3x1 mesh for the cellulosic sheets and chains, and 3x3x3 for the cellulose crystalline phase. To determine the equilibrium configurations, the atomic positions and the lattice vectors were fully relaxed, considering a convergence criteria of 25 meVÅ⁻¹ for the atomic forces on each atom, and pressure smaller than 0.5 Kbar.

In order to perform a thorough study of the role played by the van der Waals (vdW) forces in the structural stability of the cellulose nanofibers, we have taken into account a set of vdW interactions by using the following approaches, viz.: (i) vdW density functional (vdW-DF) [24-27] implemented in the QE and VASP codes, (ii) parameterized vdW-D2 [28] implemented in the QE code, (iii) vdW-DF2 [29], and (iv) vdW-optB86b [30, 31] both implemented in the VASP code.
III. RESULTS AND DISCUSSIONS

A. Experimental results

1. Overview of the cellulose nanofibers

The oxidized CNFs were isolated from sugarcane bagasse pulp through TEMPO-mediated oxidation using high oxidant content, 25 and 50 mmol/g. This reaction converts C6 primary hydroxyls groups from cellulose to carboxylates (COO$^-$) Na$^+$, yielding gravimetrically normalized values of 1.10 and 1.40 mmol of COO$^-$ per gram of cellulose, respectively, which correspond to ca 25% of substitution. Electrostatic repulsion between charged cellulose microfibrils ($\zeta$-potentials ca $-65$ mV in water) together with osmotic effects promoted the disassembling of completely individualized CNF dispersed in water without the need for high-energy mechanical treatments, as can be visualized in Fig. 2(a). The nanofibers present average lengths in the range of 243-370 nm and an average width of 4 nm, which may correspond to elementary fibril diameter, according to Ding and Himmel’s model for maize biomass [32].

Further, height histograms of AFM images show a significant number of nanoelements with widths of less than the elementary fibril diameter [Fig. 2(b)]. This result suggests that in addition to disassembling the bundles, the oxidation may also weaken the noncovalent interchain and intersheet interactions within the elementary fibril, leading to the release of nanofibers with widths that correspond about to single (0.44 nm) and double (0.88 nm) cellulose polymer chains [33], as indicated by the arrows in Fig. 2(c). The width distribution may be an outcome of non-uniform distribution of charges along the fibers, as pointed out by Paajevan et al. [34].

B. Theoretical modeling

Here, we have performed a set of first-principles simulations in order to provide further theoretical support to the experimental results discussed above. We start our investigation with the pristine system, focusing on the role played by the hydrogen bonds and vdW forces in the strength of intersheet and interchain interactions. Next, we have considered the oxidized system, addressing the energetic stability of the CNFs upon the presence of charged carboxylate groups.

1. Pristine NC

In Fig. 1 we present the structural model of the monoclinic $I_\beta$ phase, where the periodic structure can be described by two misaligned molecular chains per unit-cell. The cellulotic sheets are composed of linear chains parallel to the a direction, where the lateral interchain interaction (b direction) are mostly ruled by O-H...O hydrogen bonds (HBs); while vdW interaction brings the main contribution to the structural stability to the sheet stacking along the normal direction (c). The strength of the intersheet (IS) and interchain (IC) interactions were quantified by the calculation of the IS and IC binding energies ($E_{b_{IS}}$ and $E_{b_{IC}}$, respectively),

\[ E_{b_{IS}} = E_{\text{bulk}} - E_{\text{sheet}} \]
\[ E_{b_{IC}} = E_{\text{sheet}} - E_{\text{chain}} \]

$E_{\text{bulk}}$, $E_{\text{sheet}}$, and $E_{\text{chain}}$ are the total energies of crystalline cellulose nanofibers, free-standing cellulotic sheet, and free-standing single molecular chain. The binding energy of the cellulose nanofibers ($E_{b_{\text{CNF}}}$) can be written as:

\[ E_{b_{\text{CNF}}} = E_{b_{IC}} + E_{b_{IS}} \]

By using the vdW-DF approach [24-27], we found $E_{b_{\text{CNF}}} = -2.027$ eV/unit-chain (unit-chain corresponds to two glucose rings) [35]. Our total energy results are summarized in Table I, where we have also considered the semi-empirical vdW-D2 [28] approach.
approach, to describe the long-range dispersive interactions. In Table II, we present a set of key information regarding the equilibrium geometry of the I_β crystalline cellulose, where we find a good agreement with the experimental measurements performed by Nishiyama et al. [9].

Focusing on the IS and IC binding energies, there is a lack of consensus regarding the energetic balance between IS and IC interactions, where we may find different results obtained through different calculation approaches. For instance, Qian et al. [10] found IC interaction stronger than the IS interaction; while in Ref. [36] the authors obtained nearly the same contribution for both interactions. Meanwhile, even upon the inclusion of vdW correction [28], Li et al. [12] obtained 0.8 and 1.1 eV/unit-chain, for IS and IC interactions, respectively. In contrast, based on molecular dynamic (MD) simulations, Gross and Chu [11, 67] pointed out that the IS iteration is larger than IC interaction. Our total energy results support these latter findings. We found that the IS interaction is stronger than the IC one by almost twice, \( E_{\text{IS}}^b / E_{\text{IC}}^b \approx 2 \) (vdW-DF results). By using the vdW-D2 approach, the strength of the IS (IC) interaction reduces (increases), however keeping \( E_{\text{IS}}^b \) larger than \( E_{\text{IC}}^b \) with \( E_{\text{IS}}^b / E_{\text{IC}}^b \approx 1.3 \). To check the accuracy of our results, we have calculated the binding energies using other non-local self-consistent vdW approaches. These results are summarized in Table III.

As pointed out by Gross and Chu, vdW interaction rules the IS interaction, while it presents a minor contribution to the IC one. In order to provide a quantitative picture of the role played by the dispersive forces to the structural stability of the I_β CNFs, we calculate \( E_{\text{IS}}^b \) and \( E_{\text{IC}}^b \), by turning-off the vdW contribution, but keeping the equilibrium geometry obtained by the vdW-DF calculation. Here, we found that the strength of the IS interaction reduces from \(-1.351\) to \(-0.127\) eV/unit-chain, while for the IC interactions change by less than 0.1 eV, \( E_{\text{IC}}^b = -0.676 \rightarrow -0.569 \) eV/unit-chain. Thus, revealing that vdW forces present (i) a dominant role on the energetic stability between the cellulolic sheets (about 90 % of the IS interactions), and (ii) a minor contribution to the IC interactions (\( \sim16\% \)). These findings [(i) and (ii)] will be helpful to provide an energetic picture for the disintegration of oxidized CNFs as discussed below.

## 2. Oxidized CNFs

The energy cost to disintegrate the cellulose fibers reduces upon the formation of charged carboxylate groups (COO\(^-\)) [28]. Indeed, previous experimental works have shown the disintegration of cellulose into nanofibers with diameters of 3-5 nm mediated by (TEMPO) oxidation processes [39, 40]. In parallel, MD simulations have been done addressing the effect of the presence of carboxylate groups, bonded to the CNF surfaces, on the inter-fibril interaction [34]. Here, we have used a recently proposed low energy cost pathway [41] to produce cellulose nanofibers with widths of single and double cellulose polymer chains, as depicted in Fig. 2.

Given such a scenario, and the present experimental findings, it is expected that the formation of carboxylate groups should take place not only on the surface of the elementary fibrils, but also at the inner sites of the CNFs [indicated by dashed lines in Fig. 2(d)], weakening the intersheet and interchain interactions.

The calculation procedure of the IS and IC binding energy, as a function of the charging state of the carboxylate group, is schematically shown in Figs. 3(a) and (b). Here, the binding energy \( (E^b) \) corresponding to the IS [IC] interaction was obtained by comparing the total energies of two free-standing cellulose sheets [chains] interacting to each other (final configuration), as shown in Fig. 3(a1) [3(b1)], and the ones far from each other (initial configuration), Fig. 3(a2) [3(b2)], for a given charging state \( (q) \) [31].

\[
E_{\text{IS/IC}}^b(q) = E_{\text{final}}(q) - E_{\text{initial}}(q).
\]

For each configuration (initial/final), the atomic positions were fully relaxed, and the total energies were obtained, including the vdW interactions within the vdW-DF approach [24, 27]. Within our supercell approach, we have considered the presence of carboxylate groups...
FIG. 3. Schematic representation of the IS (a) and IC (b) binding energy calculations. (a1)-(b1)/(a2)-(b2) Final/Initial configuration of two free standing cellulosic sheets (a) and chains (b). (c) Structural models of pristine (non-oxidized) NC chain (c1), and oxidized chains with linear concentration of carboxylate groups of $[\text{COO}^-] = 25\%$ (c2), $50\%$ (c3), and $100\%$ (c4). The carboxylate groups are within rectangles.

with different concentrations ($[\text{COO}^-]$), as shown in Figs.3(c1)-(c4). The localization of the net charge ($q$) was determined by using the Löwdin orbital population [32], where we found that most of charging lies on the carboxylate groups. In Figs.4(a) and (b), we present the increase of the net charge density along a cellulose chain with $[\text{COO}^-]$ of $50\%$ when the charging state increases from $q=0.25 \rightarrow 0.50 \, e$ and $q=0.50 \rightarrow 1.00 \, e$. To check the adequacy of our calculation approach, instead of charging our supercell, we have considered the presence of sodium ions nearby the carboxylate group [34]. In this case, we found a net charging of about $0.5 \, e$ per $[\text{COO}^-]$ unit.

Our results of binding energies for the IS and IC interactions as a function of charging state, presented in Figs.5(a) and (b), reveal that the weakening of the IS and IC interactions, compared with the ones of pristine systems (dashed lines in Fig.5), is proportional to the charging and the concentration of carboxylate groups. Indeed, the net (negative) charge localization in the carboxylate group, as shown in Fig.4, suggests that the repulsive electrostatic forces between the NC sheets/chains rule the weakening of the IS and IC interactions [38]. Further binding energy comparison [Fig.5(c)] shows that, in general, the IC interactions are more sensitive to the oxidation than the IS interactions. For instance, for $[\text{COO}^-]=50\%$ and charging of $q = 0.5e$ the IC binding energy reduces by $0.25 \, \text{eV/unit-chain}$, $E_{\text{IC}}^q = -0.48 \rightarrow -0.23 \, \text{eV/unit-chain}$, whereas for the IS interaction we found $E_{\text{IS}}^q$ reduces by $0.09 \, \text{eV/unit-chain}$, $-0.60 \rightarrow -0.51 \, \text{eV/unit-chain}$. These results not only support the present experimental findings (summarized in Fig.2) but also allow us to infer that the CNF disassembly should take place (preferentially) through a disruption of the interchain interactions [indicated by red dashed lines in Fig.2(d)].

As we have discussed above, in the pristine systems,
the IS binding energy is mostly dictated by vdW forces, while the hydrogen-like C–H···O bonds bring a minor contribution. In contrast, the IC binding strength is mostly ruled by O–H···O hydrogen bonds, followed by a minor contribution from vdW forces. Since, in the oxidized systems, $E_{\text{IC}}^b$ presents greater reduction compared with $E_{\text{IS}}^b$ [Fig. 5(c)], here we can infer that the weakening O–H···O and C–H···O bonds play the main role in the disassembly process of CNFs. In order to provide further support to such a statement, we calculate $E_{\text{IC/IS}}^b(q)$, for [COO$^-$]=50%, with no vdW contribution to the total energies. Our results for the IS and IC binding energies [indicated by empty squares in Figs. 5(a) and (b)] reveal a significant reduction of the former. For instance, for $q = 0.5e$, $E_{\text{IS}}^b(q)$ reduces from $-0.511$ to $-0.016$ eV/unit-chain, whereas the strength of the IC interaction reduces by about 0.08 eV/unit-chain, $E_{\text{IC}}^b(q) = -0.230 \rightarrow -0.151$ eV/unit-chain. In other words, the higher reduction of $E_{\text{IS}}^b$ compared with that of $E_{\text{IC}}^b$ is a consequence of the predominance of van der Waals forces in the intersheet interactions.

IV. SUMMARY AND CONCLUSIONS

We have performed an experimental and theoretical combined investigation of cellulose disassembly mediated oxidation processes. Based on a low energy cost pathway, single and double cellulose polymers chains have been synthesized from oxidized cellulose nano fibers (CNFs). Such a disruption of CNFs was attributed to the formation of carboxylate groups embedded within oxidized fibrils, weakening the noncovalent interchain (IC) and intersheet (IS) interactions. First-principles DFT calculations revealed that, indeed, the IC and IS binding energies [$E_{\text{IC/IS}}^b(q)$] reduce in the oxidized CNFs. We find that such a reduction of $E_{\text{IC/IS}}^b(q)$ is proportional to the charging state ($q$), indicating an electrostatic repulsion between the (charged) cellulose fibrils. Finally, comparing the IS and IC binding energies, we found that the disassembly processes of the oxidized CNFs should take place mostly through a disruption of the interchain interactions, giving rise to (predominantly) fibers and cellulose chains, instead of sheets, as a final structure.

ACKNOWLEDGMENTS

The authors acknowledge financial support from the Brazilian agencies CNPq, FAPEMIG, and FAPESP (grant 16/04514-7 and 17/02317-2), and the LNCC (SCAFMat2), CENAPAD-SP for computer time.

[1] N. G. Taylor, New Phytologist 178, 239 (2008).
[2] E. J. Mellerowicz and T. A. Gorshkova, Journal of experimental botany 63, 551 (2012).
[3] M. E. Himmel, S.-Y. Ding, D. K. Johnson, W. S. Adney, M. R. Nimlos, J. W. Brady, and T. D. Foust, science 315, 804 (2007).
[4] H. Jørgensen, J. B. Kristensen, and C. Felby, Biofuels, Bioproducts and Biorefining 1, 119 (2007).
[5] D. Klemm, F. Kramer, S. Moritz, T. Lindström, M. Ankerfors, D. Gray, and A. Dorris, Angewandte Chemie International Edition 50, 5438 (2011).
[6] Y. Habibi, L. A. Lucia, and O. J. Rojas, Chemical reviews 110, 3479 (2010).
[7] X. Zhao, L. Zhang, and D. Liu, Biofuels, Bioproducts and Biorefining 6, 465 (2012).
[8] A. Zoghlami and G. Paës, Frontiers in Chemistry 7, 874 (2019).
[9] Y. Nishiyama, P. Langan, and H. Chanzy, Journal of the American Chemical Society 124, 9074 (2002).
[10] X. Qian, S.-Y. Ding, M. R. Nimlos, D. K. Johnson, and M. E. Himmel, Macromolecules 38, 10580 (2005).
[11] A. S. Gross and J.-W. Chu, The Journal of Physical Chemistry B 114, 13333 (2010).
[12] Y. Li, M. Lin, and J. W. Davenport, The Journal of Physical Chemistry C 115, 11533 (2011).
[13] A. Devarajan, S. Markutsya, M. H. Lamm, X. Cheng, J. C. Smith, J. Y. Baluyut, Y. Kholod, M. S. Gordon, and T. L. Windus, The Journal of Physical Chemistry B 117, 10430 (2013).
[14] T. Saito, S. Kimura, Y. Nishiyama, and A. Isogai, Biomacromolecules 8, 2485 (2007).
[15] M. Pääkkö, M. Ankerfors, H. Kosonen, A. Nykänen, S. Ahola, M. Österberg, J. Ruokolainen, J. Laine, P. T. Larsson, O. Ikkala, et al., Biomacromolecules 8, 1934 (2007).
[16] L. O. Pinto, J. S. Bernardes, and C. A. Rezende, Carbohydrate polymers 218, 145 (2019).
[17] N. Lin, C. Bruzzese, and A. Dufresne, ACS applied materials & interfaces 4, 4948 (2012).
[18] P. Giannozzi et al., J. Phys.: Condens. Matter 21, 395502 (2009).
[19] G. Kresse and J. Furthmüller, Comput. Mater. Sci. 6, 15 (1996).
[20] G. Kresse and J. Furthmuller, Phys. Rev. B 54, 11169 (1996).
[21] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[22] P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).
[23] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
[24] T. Thonhauser, S. Zuluaga, C. Arter, K. Berland, E. Schröder, and P. Hyldgaard, Physical review letters 115, 136402 (2015).
[25] T. Thonhauser, V. R. Cooper, S. Li, A. Puzder, P. Hyldgaard, and D. C. Langreth, Phys. Rev. B 76, 125112 (2007).
[26] K. Berland, V. R. Cooper, K. Lee, E. Schröder, T. Thonhauser, P. Hyldgaard, and B. I. Lundqvist, Reports on Progress in Physics 78, 066501 (2015).
[27] D. Langreth, B. I. Lundqvist, S. D. Chakarova-Käck, V. Cooper, M. Dion, P. Hyldgaard, A. Kelkkanen, J. Kleis, L. Kong, S. Li, et al., Journal of Physics: Condensed Matter 21, 084203 (2009).
[28] S. Grimme, J. Comput. Chem. 27, 1787 (2006).
[29] I. Hamada, Physical Review B 89, 121103 (2014).
[30] J. Klimeš, D. R. Bowler, and A. Michaelides, Journal of Physics: Condensed Matter 22, 022201 (2009).
[31] J. Klimeš, D. R. Bowler, and A. Michaelides, Physical Review B 83, 195131 (2011).
[32] S.-Y. Ding and M. E. Himmel, Journal of agricultural and food chemistry 54, 597 (2006).
[33] I. Usov, G. Nyström, J. Adamicik, S. Handschin, C. Schütz, A. Fall, L. Bergström, and R. Mezzenga, Nature communications 6, 1 (2015).
[34] A. Paajanen, Y. Sonavane, D. Ignasiak, J. A. Ketoja, T. Maloney, and S. Paavilainen, Cellulose 23, 3449 (2016).
[35] Increasing the energy cutoff to 60 Ry we obtained $E_{IS}^b = -1.321$ eV/unit-chain and $E_{IC}^b = -0.665$ eV/unit-chain, resulting in a binding energy of $-1.986$ eV/unit-chain.
[36] R. Parthasarathi, G. Bellesia, S. Chundawat, B. Dale, P. Langan, and S. Gnanakaran, The Journal of Physical Chemistry A 115, 14191 (2011).
[37] A. S. Gross, A. T. Bell, and J.-W. Chu, The Journal of Physical Chemistry B 115, 13433 (2011).
[38] A. Tejado, M. N. Alam, M. Antal, H. Yang, and T. G. van de Ven, Cellulose 19, 831 (2012).
[39] T. Saito and A. Isogai, Biomacromolecules 5, 1983 (2004).
[40] T. Saito, Y. Nishiyama, J.-L. Putaux, M. Vignon, and A. Isogai, Biomacromolecules 7, 1687 (2006).
[41] We check the convergence of our results with respect to the size of the supercell, since in the charged systems a jellium background of opposite charge has been inserted in order to work with neutral supercells. Here, we found that by increasing the vacuum region from 24 to 40 Å our results of $E^b(q)$ change by ∼4%.
[42] P. Löwdin, Phys. Rev. 97, 1474 (1955).