Molecular Dynamics of cellulose crystal surfaces with ChemShell

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Abstract

We report the modelling of cellulose Iα and Iβ crystals and surfaces to reproduce properties of artificial cellulose coatings. Starting from x-ray structures we optimized the bulk structure using the GLYCAM06 force field and ChemShell in a sequence of short molecular dynamics and geometry optimizations runs. With these bulk structures we constructed slabs to model the respective surfaces and optimized the surfaces in the same way. Distinctive structural features were found such as the alteration of interlayer distances of the Iβ crystal on the surface and the increase of the number of hydrogen bonds in the outermost cellulose layer.

Keywords: cellulose, molecular dynamics, ChemShell, GLYCAM06

1. Introduction

Cellulose is the main component of plant cell walls and thereby the most abundant organic material on earth. Its complex structure is still not fully understood. Unravelling the structure and the adsorption and solvation properties would help to stimulate technological applications, such as new nanostructured functionalized tissue based on cellulose. The development of such materials is the topic of the EU project SURFUNCELL. In this project more than 13 partner groups work on efficient coating of cellulose films and modification of those via adsorption of e.g. soluble cellulose derivatives, inorganic nanostructures (nanoplatelets, nanoparticles). From a technological point of view this functionalization by adsorption is preferred over direct surface modification in chemical reactions, but needs detailed knowledge of the surface structure to optimize the adhesive interactions in the surface-adsorbate interface.

The bulk structure of native cellulose is composed of two different polymorphs, the triclinic Iα structure and the more stable monoclinic Iβ crystallite, as well as amorphous parts [1]. The two polymorphs also differ in the number of cellobiose units contained in the unit cells. Whereas the Iα [2] phase and the Iβ [3] phase have many times been the subject of structural studies, the structure of amorphous cellulose still remains unclear. Experimental findings identify amorphous parts of cellulose as regions of less density and higher mobility [4]. These regions will be also on the surface and, thus, accessible to the solvent and to adsorbates. It is expected that thin films of cellulose are mainly amorphous. Mazeau et al. described amorphous cellulose as an ensemble of unperturbed randomly oriented chains [5]. But due to the technological process of surface grafting, it is most likely an arrangement of small crystallites connected by less dense, irregular regions with higher hydration.

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In this contribution we report first steps in modelling complex cellulose surfaces and their adsorption behaviour. We investigated perfect crystal systems and model surfaces as they are partly found in experimental surfaces. Thereby the structures are equilibrated and optimized and surface reorganization against vacuum, as well as the software setup and the applicability of the method are evaluated.

2. Methodology

We use the GLYCAM naming convention for atoms and torsion angles as depicted in Fig.1. The Iα [2] and Iβ [3] crystal structures were taken out of recent x-ray diffraction studies. The supercells were created with the extend command of ChemShell [6]. They contained 5x5x4 (a=53.5 Å, b=34.6 Å, c=23.8 Å, α=80.4°, β=118.1°, γ=114.87°), respectively 2x5x5 (a=16.0 Å, b=42.2 Å, c=53.4 Å, α=β=90°, γ=96.6°) unit cells, both with 4200 atoms (Fig.2). These dimensions were selected so that each cell contained 4 layers. The Iα system can be seen as built up by 4 layers of tilted cellulose chains, the Iβ, respectively, as built up by layers of planar ones.

All calculations were performed with the ChemShell code [6, 7], which is a shell program that provides interfaces to a large number of quantum mechanical codes, including TURBOMOLE, NWChem, GAMESS-UK, and molecular mechanics codes like DL_POLY, CHARMM and GROMOS which do the time consuming energy evaluations while ChemShell is concerned with data handling and optimization, but also with molecular dynamics (MD) [8] using a built-in version of DL_POLY [9]. With the interface offered by this program, force fields like CHARMM, AMBER and UFF and their derivatives can be used.

We tested different force fields (CHARM36, CSFF, GLYCAM06) on small carbohydrates and cellulose crystals, and decided to take the AMBER type force field GLYCAM06 [10]. Not only did we find good agreement of bonds lengths, angles and torsional angles of small oligosaccharides compared to DFT, it also exceeded other force fields in a recent comparison of carbohydrate force fields [11]. Furthermore, GLYCAM06 offers convenient usage in combination with the DL_POLY interface and the topology builder leap, distributed via AmberTools 1.2 [12]. It also includes parameters for amino groups, carboxy groups, sulfates etc. which will be used in conjunction with adsorption studies of water soluble cellulose derivatives on these surfaces. For the input generation and visualisation of output data of ChemShell with VMD 1.8.6 package [13], a few small routines had to be written, e.g. for converting the data structure of Chemshell optimizations or dynamics trajectories into standard coordinates.

The optimization procedure is based on the sequence used by Mazeau et al. [5]. For the bulk optimization of the experimental x-ray structure the sequence was: geometry optimization, 20 ps NVT MD at 600 K, geometry optimization, 40 ps NPT MD at 450 K, geometry optimization, 20 ps NVT MD at 300 K, geometry optimization.

We also investigated the Iα [0,1,0] and the Iβ [1,0,0] surfaces as models for a hydrophilic and a hydrophobic surface, respectively. These systems seemed to be a good starting point for modelling the surfaces found in conjunction with artificial cellulose coatings. The slabs modelling the respective surfaces were built from the optimized bulk

Figure 1: GLYCAM06 naming convention of atoms and torsional angles within a β-glukopyranose residue of cellulose.
structures. They consist of four layers, the atoms of the bottom layer were kept frozen during the optimization. The vacuum was simulated by increasing the b parameter for Iα and the a parameter for Iβ by 20 Å. The surfaces were optimized with the sequence: geometry optimization, 20 ps of NVT MD at 600 K, geometry optimization, 20 ps NVT MD at 300 K, geometry optimization.

3. Results

During the optimization of both experimental crystal structures (Fig.2) the volume of the elementary cell expanded by 9%, accompanied by structural changes of the interchain distances. We observe a decrease of the interlayer and an increase of the interchain distances.

Hydrogen bonding patterns of the investigated structures are in good agreement with similar studies [14]. Intrachain bonds were mainly between OH3 and O5 as well as OH6 and O2 atoms for both species. Hydrogen bonds between two chains were mainly found between OH3 and O6 and OH2 and O6 atoms. Between two layers strong hydrogen bonds were found between the OH6 and O4 atoms. An interesting difference between the two species is the number of these interlayer bonds, which is about 3 times higher in the Iβ cell than in the Iα allomorph. This is in agreement with an observed thermal inverconversion between the two species and a postulated higher stability of Iβ cellulose [15].

Optimization of the slabs yielded the structures in Fig.3 and Fig.4. For the Iα we found the same interlayer distance with the same number of interlayer hydrogen bonds as in the bulk. The chains on the surface show very diverse conformations with respect to the torsion angles (χ2, χ3, χ6) of the hydroxy groups. At the surface several hydroxy groups reorient so that new hydrogen bonds between the layers are formed. On the surface we find about twice as much interlayer hydrogen bonds in the optimized slab (12-14 hydrogen bonds with cutoff 2 Å) compared to the number in the corresponding layer of the optimized bulk structure (4-6 hydrogen bonds per layer). Due to this effect the distance between the surface chains is reduced (Fig.3).

In the Iβ slab the interlayer distance is changed significantly with respect to the bulk. This was shown by averaging over 10 equivalent distances between two glycosidic oxygen atoms on top of each other for each layer. We did this in the bulk structure and the slab. The results are shown in Table 1. Whereas in the bulk structure the average interlayer distance is constant, considering the deviations, we found an increased distance between the first two layers and contraction in the second and the third layer spacing. The vacuum takes away bonding pressure of the first layer and thereby allows relaxation, whereas the next interlayer distance is contracted. The fact that the third spacing is again larger allows the assumption that this behaviour will converge towards the bulk interlayer distances within a few additional layers. However these changes in the distance appear without changing significantly the number of interlayer hydrogen bonds.

In the surface layer, the number of the interchain hydrogen bonds (44 with cutoff 2 Å increased by about 30% compared to the corresponding layer in the optimized bulk model (34 hydrogen bonds in one layer). This again can be interpreted as rearrangements of the surface layer to decrease strains and high energy conformations of the bulk structure exposed to vacuum.
Figure 3: Cut through the chains of the slab of \( \alpha \) cellulose model after optimization. The top represents the surface. Hydrogen bonds are represented as dashed lines.

Figure 4: Cut through the chains of the slab of \( \beta \) cellulose model after optimization. The top represents the surface. Hydrogen bonds are represented as dashed lines.
Table 1: Averaged distances and standard deviations between glycosidic oxygen atoms of chains lying upon another in the I\(\beta\) models. Distances were averaged over 10 oxygen pairs for each layer. Layer spacings are numbered from the surface down. There is no fourth spacing in the slab. All values given in Å.

| # of layer spacing | I\(\beta\) bulk model distance & dev. | I\(\beta\) surface model distance & dev. |
|--------------------|----------------------------------------|-----------------------------------------|
| 1                  | 4.516 & 0.230                          | 4.657 & 0.475                           |
| 2                  | 4.474 & 0.221                          | 4.361 & 0.229                           |
| 3                  | 4.497 & 0.286                          | 4.386 & 0.253                           |
| 4                  | 4.506 & 0.276                          | - & -                                  |

4. Summary and Outlook

The described calculations are in good agreement with similar studies performed in this field [14, 16] concerning the hydrogen bond patterns and crystal structures. Whereas many previous publications report adsorption and solvation of cellulose crystal surfaces, the rearrangement of surfaces solely against vacuum has never been addressed before. The rearrangements show that this specific surface of the I\(\alpha\) crystal exposes a large amount of hydroxyl groups in an irregular fashion and must thereby be more hydrophilic than the chosen I\(\beta\) surface, which exposes the hydrogens bonded directly to the carbon atoms of the glucose ring. These attributes have also been observed in recent wetting simulations of cellulose surfaces [17].

To our knowledge this is the first application of ChemShell in combination with GLYCAM for the simulation on carbohydrates. The package has a high potential in this field, but is also in need of further development to ensure easy applicability to these systems, especially concerning topology recognition with periodic boundary conditions. In the further modelling process of this system the next steps will be the transition to less dense amorphous phases, which hold a strong fraction of the structures observed in cellulose coatings. This could be achieved by stepwise replacing some cellulose chains with water. A model comprised of small crystallites connected by less dense and less ordered regions, containing water and, possibly, ions is the aim in this project and could help shed light on the adsorption processes on these complex composite films.

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