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# Revealing the Interaction Mechanism Stabilizing Crystalline Cellulose I$\beta$ by Molecular Dynamics Simulations[⋆]

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## Abstract

Revealing the interaction mechanism of cellulose I$\beta$ can help us to understand dissolution and modification mechanisms of cellulose fiber. In this paper, molecular dynamics simulation was used to analyze different interaction of cellulose I$\beta$. We found that the total interaction of Van der Waals, electrostatic and solvation energy per chain are $-90.93$ kcal/mol at 298 K. In order to get insight into the interaction mechanism, the energy distribution of each residue and mean interaction were analyzed. The interaction were divided into the intrachain, interchain and intersheet. The results show that Van der Waals interaction is important to stacking cellulose sheets, while the sum of electrostatic and solvation energy is also play a major role in intersheet interaction. Electrostatic energy plays a role certainly in the intrasheet interaction, and the thermal stability mechanism of intrachain is different to interchain.

*Keywords*: Van der Waals Interaction; Electrostatic Interaction; Cellulose I$\beta$; Molecular Dynamics

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# 1 Introduction

Cellulose is a ubiquitous renewable resource on the earth. It is widely used in industry sectors such as textile material, food processing, medical materials, paper and so on. Much effort has focused on investigation of natural crystalline cellulose and synthetic crystalline cellulose during the past few years [1-5]. As for cellulose crystal structures, it has been known that it has several different conformations from I to IV. There are two distinct allomorphs of native crystalline cellulose I named I$\alpha$ and I$\beta$ [6-7]. Allomorph I$\alpha$ is dominant in cell walls of some algae and bacteria, whereas I$\beta$ preponderates in terrestrial plants such as cotton and ramie [8]. Cellulose I$\beta$ is found more thermally stable than I$\alpha$ [9]. Nishiyama and coworkers found the crystal form and analyzed the hydrogen bonding networks for native cellulose I$\beta$ and I$\alpha$ with X-ray crystallography and

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neutron diffraction [6-7]. Revealing the interaction mechanism of cellulose I$\beta$ enables us to know which energy is the main factor for stabilization of cellulose fiber such as cotton and ramie fibers. It is pivotal in native cellulose degradation and modification. In order to get more information about the stabilization mechanism, different interaction was discussed in this paper.

Cellulose I$\beta$ has been found to have a monoclinic $P2_1$ structure with two cellobiose chains in each unit cell, while $a = 7.784\mathring{A}$, $b = 8.201\mathring{A}$, $c = 10.38\mathring{A}$, $\alpha = \beta = 90°$, $\gamma = 96.5°$, and $c$ is the chain direction [6]. Crystalline cellulose I$\beta$ are formed by stacking cellulose sheets, which linear chains are packed in a specific crystal form. It is well known that the hydrogen-bonding interaction is the main binding force for maintenance of the molecular crystals. Each sheet is stabilized by the interchain hydrogen-bonding (O6H6$\cdots$O3$'$) between the O6H6 (donor) in one chain and O3 (acceptor) in the neighboring chain. Each chain is stabilized by intrachain hydrogen-bonding O3H3$\cdots$O5 and O2H2$\cdots$O6 [2,6]. That is to say, the hydrogen-bonding is significant for stabilizing crystalline cellulose I$\beta$ and solubility of cellulose. This leads to most research on cellulose mainly focusing on the hydrogen-bonding interaction [10-12]. The interaction of cellulose I$\beta$ can be split up into intrasheet and intersheet, the former can be further divided into intrachain and interchain. The hydrogen-bonding stabilize each sheet, but it is very weak for stacking sheets. In fact, cellulose is very stable. This suggests that other interactions should be considered besides the hydrogen-bonding. The work of Heiner showed that the binding forces between the sheets were thought to be mainly of Van der Waals forces and weak intersheet C-H$\cdots$O hydrogen-bonding [1, 13]. Though the hydrogen-bonding is the main binding forces for intrasheet, it is not for stacking sheets in normal temperature. Our previous work suggested that the Van der Waals forces should be taken into consideration when revealing stability mechanism of cellulose I$\beta$ [14]. These results can elucidate the interaction mechanism of native crystalline cellulose I$\beta$, but there remains a number of important questions concerning the peculiar stabilization mechanism of cellulose. Besides Van der Waals and hydrogen-bonding interaction, whether there are other interactions that takes effect to the stability of cellulose and how about the magnitude. At different temperatures, what is the discrepancy between the different interaction mechanisms to the stability of cellulose? These questions are closely related to the stable mechanism and thermodynamic stability of cellulose I$\beta$. In order to unravel these questions, the details of different interaction and the correlation with total interaction will be discussed in this paper.

Molecular dynamics simulation is an effective computer modeling technology and is valid tool to study material. Not only can we get the trajectories of atoms, but also microscopic details can be observed. It is a powerful complement to theoretical and experimental researches. It has been broadly used in materials science, bio-physical, and drug design. Molecular dynamics simulation has been identified as an excellent tool to understand the structure and interactions of crystalline cellulose in molecular level. Molecular dynamics simulation has been used to understand the hydrogen-bonding interactions of cellulose in some researches [1-2, 4-5]. The simulation results are in good accordance with experimental results. These works were not accounting for Van der Waals forces and other interactions. The interactions between cellulose sheets are not referred to within those references. In this paper, molecular dynamic simulations were used to investigate the interaction mechanism.

The force field is of great importance to the progression of molecular dynamics simulation. Several force fields have been used in simulations of cellulose, such as GROMOS [1], and GLYCAM06 [15]. In the work of Stortz and his co-worker, eighteen empirical force fields are compared with experiments and the semi-empirical quantum methods for studying $\beta$-cellobiose, $\alpha$-maltose, and $\alpha$-galabiose [16]. The results showed that the empirical force fields GLYCAM-06, GROMOS,