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Revealing the Interaction Mechanism Stabilizing Crystalline Cellulose Iβ by Molecular Dynamics Simulations*

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Abstract

Revealing the interaction mechanism of cellulose Iβ 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 Iβ. 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 Iβ; Molecular Dynamics

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 Iα and Iβ [6-7]. Allomorph Iα is dominant in cell walls of some algae and bacteria, whereas Iβ preponderates in terrestrial plants such as cotton and ramie [8]. Cellulose Iβ is found more thermally stable than Iα [9]. Nishiyama and coworkers found the crystal form and analyzed the hydrogen bonding networks for native cellulose Iβ and Iα with X-ray crystallography and

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neutron diffraction [6-7]. Revealing the interaction mechanism of cellulose Iβ 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 Iβ 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 Iβ 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 Iβ and solubility of cellulose. This leads to most research on cellulose mainly focusing on the hydrogen-bonding interaction [10-12]. The interaction of cellulose Iβ 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 Iβ [14]. These results can elucidate the interaction mechanism of native crystalline cellulose Iβ, 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 Iβ. 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 β-cellobiose, α-maltose, and α-galabiose [16]. The results showed that the empirical force fields GLYCAM-06, GROMOS,

and MM3 are in accord with experiments [17]. They are also closely followed by MM4, CSFF, and OPLS-2005. Although GROMOS takes the explicit hydroxyl hydrogens into account, united atom is used to represent aliphatic groups. The Van der Waals forces and electrostatic interaction are not considered in this force field. This leads to the relatively large discrepancy in the predicted unit cell parameters compared to the crystallographic data. GLYCAM-06 is an all atom carbohydrate force field. It is consistent and transferable for modeling carbohydrates and glycoconjugates. The work of Spiwork indicated that this force field was remarkably correspond to quantum metadynamics studies for free energy surface calculation [18]. This indicates that the GLYCAM-06 is a pertinent force field to study the molecular interactions of cellulose. Amber software is introduced to simulate the different interactions of cellulose Iβ, and this force field is compatible with Amber. In light of these works, we deployed GLYCAM-06 force field to explore the residual problems regarding interaction of cellulose Iβ.

2 Simulation and Interaction Analysis Method

The initial structure of cellulose Iβ was generated from the coordinates reported by Nishiyama et al [6]. The parameters of unit cell were set according to X-ray crystallography and neutron diffraction [6]. To build the cellulose crystal model, a program cellulose-builder was used [19]. Molecular dynamics simulations were carried out at first and all simulations were performed with Amber 12. The interactions were analyzed by post-processing program MMPBSA.py of AmberTools 14. Details as below:

2.1 Molecular Dynamics Simulation

The initial structure of cellulose Iβ was built up according to cellulose elementary fibrils proposed by Ding and Himmel [13]. Cellulose Iβ was composed of 36 parallel chains, each chain was consisting of eight glucoses units (Fig. 1). Cellulose Iβ is a monoclinic P21 structure, while unit cell parameters originate from the results reported by Nishiyama et al [6]. They are set as $a = 7.784\mathring{A}$, $b = 8.201\mathring{A}$, $c = 10.38\mathring{A}$, $\alpha = \beta = 90°$, $\gamma = 96.5°$, and c is the chain direction. The initial atom coordinates of cellulose Iβ were automatically generated by a user-friendly program cellulose-builder [19]. No translational symmetry operations were done along direction b and c. No special action was set to endow crystallites with translational symmetry along the crystal direction. This meant that there was no further translational symmetry operation after initial model was built. In order to set periodic covalent bonding along crystal direction, a hydrogen atom (H) and a hydroxyl group (OH) were deleted to both ends for each chain. In this model, Crystallographic surfaces (100) and (010) were exposed.

The molecular dynamics simulations were performed at different temperatures 298 K, 350 K, 400 K, 450 K, 500 K and 550 K. The GLYCAM-06 was selected as most suitable force field in the simulation processing. In this force field, the 1–4 electrostatic and non-bonded interaction scaling factors were set to unity. This is vital to interaction calculation. All simulations were performed with explicit water TIP3P. A 12 Å buffer of water was placed around the cellulose Iβ in three directions. In this way, all atoms in the cellulose Iβ initial structure were no less than 12 Å from the brink of the periodic solvent box. The larger cut off value is, the less possibility the error is likely to emerge for the non-bonded force evaluation. With the threshold value increasing, the computation becomes more complex and spends more time in the simulations. Taken together

Fig. 1: The model of cellulose projected onto the ab base plane

these two factors, 12 Å is a reasonable trade-off for non-bonded force evaluation in all minimization and molecular dynamics simulations of this cellulose model. Here, non-bonded interactions were calculated with cutoff radii 12 Å.

The minimization procedure for solvated cellulose was integral and it was the best way to run a dual stage minimization. The first stage used position restraints on cellulose so that only the water was minimized. Then in the second stage, it turned to the whole system. The steepest descent minimization was performed 1000 steps firstly and then 1000 steps of conjugate gradient minimization. In the second stage, the steepest descent minimization was performed 2000 steps firstly and then 2000 steps of conjugate gradient minimization. The equilibration protocol allowed the whole system to heat up from 0 K to the target temperature. In order to avoid problems with wild fluctuations in the solute, the Langevin temperature equilibration scheme was used. Since the calculation of pressure was imprecise in the first few ps at low temperatures while using constant pressure periodic boundaries, we executed 1 ns of molecular dynamics at constant volume with weak restraints initially. The second stage of molecular dynamics was to run production dynamics at constant temperature and pressure (NPT) and get it closer to laboratory conditions. The motion balance was integrated with the time step of 2 fs. The bonds involving hydrogen atoms were kept rigid with the SHAKE algorithm. The Langevin dynamics were used to control the temperature corresponding to the canonical (constant T) ensemble. The pressure was controlled to be 1 bar through the Brendsen barostat. At each temperature, the procedure ran 100 ns and trajectory were saved every 10 ps.

The system was followed by the relatively stable temperature fluctuations about 298 K, 350 K, 400 K, 450 K, 500 K, 550 K during the 50-100 ns simulation. The total system energy can be decomposed to the total potential energy and the total kinetic energy. It was used to supervise the equilibration of system. Each total energy of different temperature equilibrates to approximate value during 50-100 ns (Fig. 2). This corresponds to a change as the total energy of the system converges.

2.2 Interaction Analysis Method

The topology files of cellulose Iβ and the simulation trajectory were used to calculate the interaction energy by program MMPBSA.py of AmberTools 14. This was a post-processing method with which representative snapshots from trajectory were used to calculate the interaction energy between two glucose residues. This procedure performed Molecular Mechanics and Generalized Born Surface Area (MM/GBSA) calculations. Pairwise energy decomposition with 1-4 electrostatic interaction increased electrostatic potential and 1-4 Van der Waals interaction increased Van der Waals potential terms. The Fig. 2 shows that the system can reach equilibrium within 50 ns for cellulose Iβ of target temperature, so the snapshots of last 50 ns from the simulation trajectories were extracted to calculate the interaction energy between glucose residue pairs.

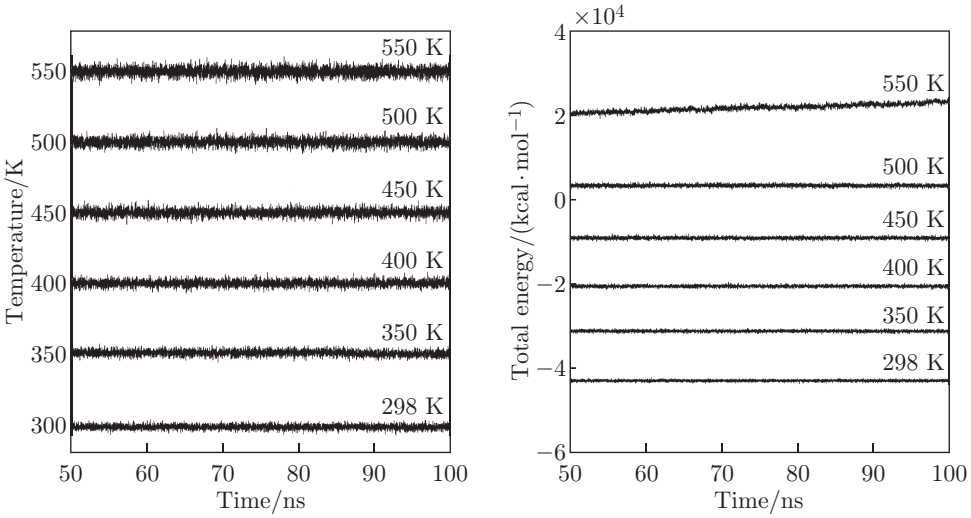

Fig. 2: The temperature functions and total energy equilibrates

The total interaction energy consists of four parts: internal (potential terms consisting of bond, angle and dihedral), van der Waals, electrostatic, solvation energy, according to the program MMPBSA.py and GLYCAM-06. Since the internal energy of each glucose is zero, it was not considered in the following discussion. The solvation energy is the sum of polar solvation and non-polar solvation. The Van der Waals, electrostatic and solvation interaction energy of each glucose residue i were reckoned by the formulas $E_i = \sum_j E_{ij}$ respectively, where E_{ij} represented the interaction energy of different type between glucose i and j respectively, j belonging to set A. The set A included the glucose residues belonging to the sheet or chain which we were interested in. The distribution of different interactions were described by the profile of $(E, P(E))$ respectively, where $P(E) = N(E)/N$, $N(E)$ was the number of residues belonging to the value of free energy equals to E, N was the total glucose residues number.

3 Results and Discussions

The intersheet hydrogen bonding is pretty weak and does not play the core role for stacking sheets. The previous work dissected the Van der Waals and electrostatic interactions of cellulose Iβ [14]. The results indicate that the Van der Waals is important to stacking sheets, and the electrostatic interaction should be paid attention as well. The intrasheet is stabilized by the hydrogen-bonding

and electrostatic interaction. In order to reveal the interaction mechanism further, the solvation energy, total energy and relation of them were analyzed besides Van der Waals and electrostatic in this work. Comparing to the work in TBIS [14], the mean energy of each residue was discussed and the correlations of these interaction to temperature were commented.

3.1 Average Interaction per Chain

Fig. 3 exhibits the average Van der Waals, electrostatic, solvation and total interaction energy per chain at different temperature. At 298 K, the Van der Waal, electrostatic, solvation and total interaction energy per chain are −43.91 kcal/mol, −26.24 kcal/mol −20.87 kcal/mol and −90 kcal/mol respectively. Their standard deviations are 2.72 kcal/mol, 1.83 kcal/mol, 1.37 kcal/mol and 5.68 kcal/mol respectively. The low standard deviation indicates that the energy of each chain tends to be very close to the mean. The result indicates that these interactions play unlike role in stabilizing cellulose respectively and there are huge gap within them. Results show that the Van der Waal energy per chain of different temperatures is higher than electrostatic and solvation energy. The sum of these interaction is substantial for cellulose. The values of Van der Waal and electrostatic energy are nearly consistent with the average nonbonded interaction energy (39.19 kcal/mol and 19.60 kcal/mol) determined by the earlier molecular dynamics simulation [1]. Attention should be paid for Van der Waal, electrostatic and solvation intermolecular energy especially when the stability of cellulose Iβ is mentioned. The Van der Waa and solvation energy recede when the temperature rises from 298 K to 400 K, meanwhile they dwindle as the temperature goes beyond 400 K. The electrostatic energy increases initially and then decreases. The one-way ANOVA (Table 1) manifests that the interaction energies upon temperatures have a significance impact with P value less than 0.05. This indicates that the effects and influences of these three interactions are different in thermal stability of cellulose. In order to analyze the correlations of different interaction energy between temperatures profoundly, the details were discussed in the following. The explanation focuses on the difference of the intermolecular energy distribution between intrachain, interchain and intersheet by the bar chart.

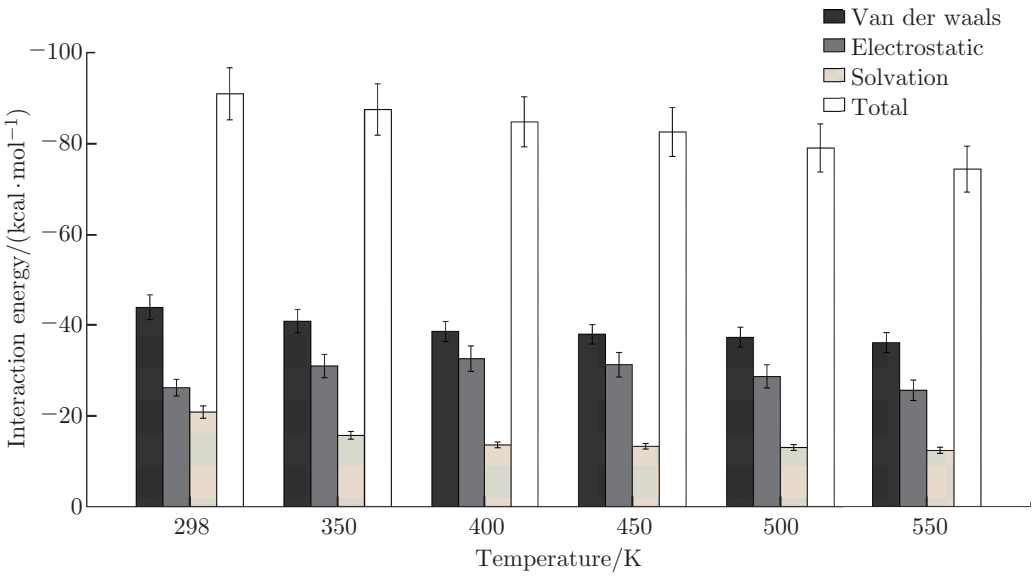

Fig. 3: The average interaction energy per chain of different types

Table 1: ANOVA between different temperatures

Interaction Type	F	P.
Van der Waal	3.221	0.008
Electrostatic	2.982	0.013
Solvation	31.458	0.000
Total	2.728	0.021

3.2 Interaction of Intrasheet and Intersheet

The Van der Waals, electrostatic and solvation interaction energy distributions of each glucose residue for the intrachain, interchain and intersheet of cellulose Iβ were illustrated in Fig. 4, Fig. 5 and Fig. 6 respectively. It could be feasible to discuss their absolute value merely for all interaction energies are negative. The Fig. 4 shows that the Van der Waals interaction of most glucose residues for intrachain lies in the range 0-2 kcal/mol at 298 K and a few in the range of 2-4 kcal/mol. The mean interaction is 1.0494 kcal/mol and the standard deviation 0.47475 kcal/mol (Table 2). This indicates that the contribution of Van der Waals to stability is little at room temperature. The probability of 2-4 kcal/mol increases slightly as the temperature rises to 450 K and then decreases (Fig. 4). The maximum mean interaction is 1.6842 kcal/mol and the standard deviation 0.46155 kcal/mol at 450 K (Table 2). These results reveal that the Van der Waals interaction in intrachain have minuscule devotion to the thermal stability of cellulose Iβ.

The electrostatic energy of 70.5% residues for intrachain lies in the range of 12-14 kcal/mol and 6-8 kcal/mol at 298 K (Fig. 4). The mean interaction is 7.6476 kcal/mol and the standard deviation 4.13536 kcal/mol (Table 2). The high standard deviation indicates that there is great deviation between the energy of part residues and the mean value. The electrostatic interaction

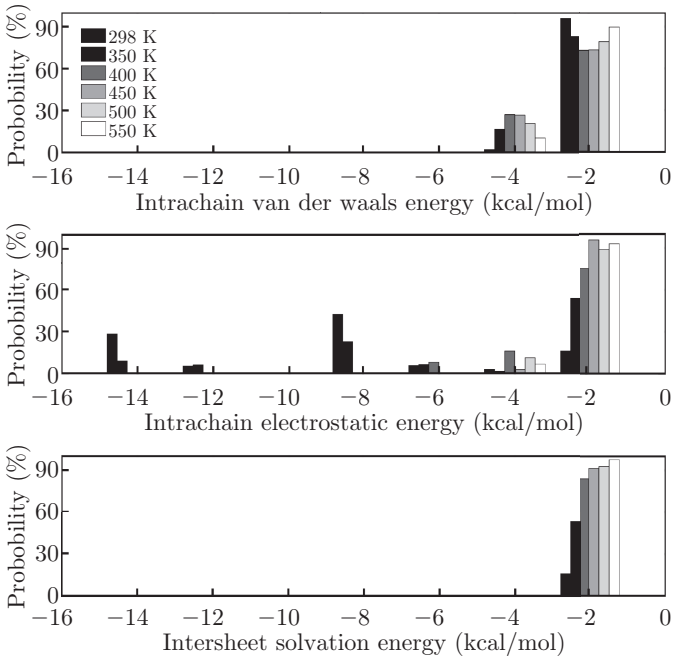

Fig. 4: The bar chart of intrachain interaction

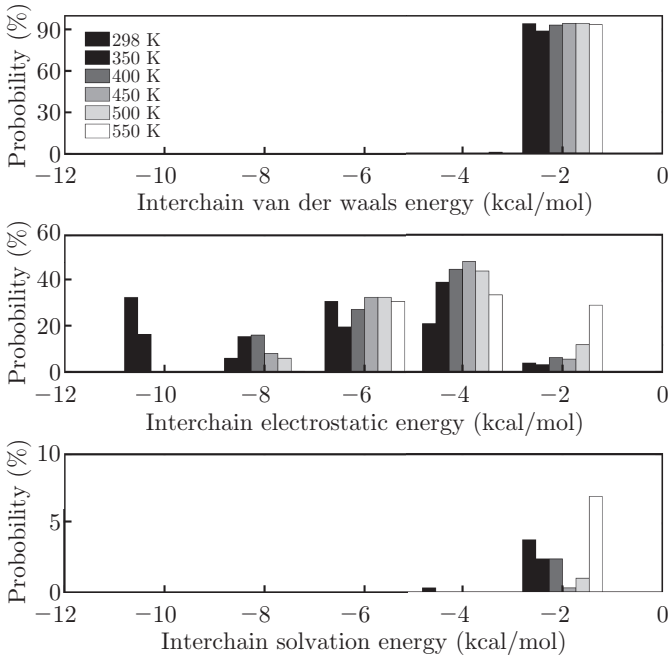

Fig. 5: The bar chart of interchain interaction

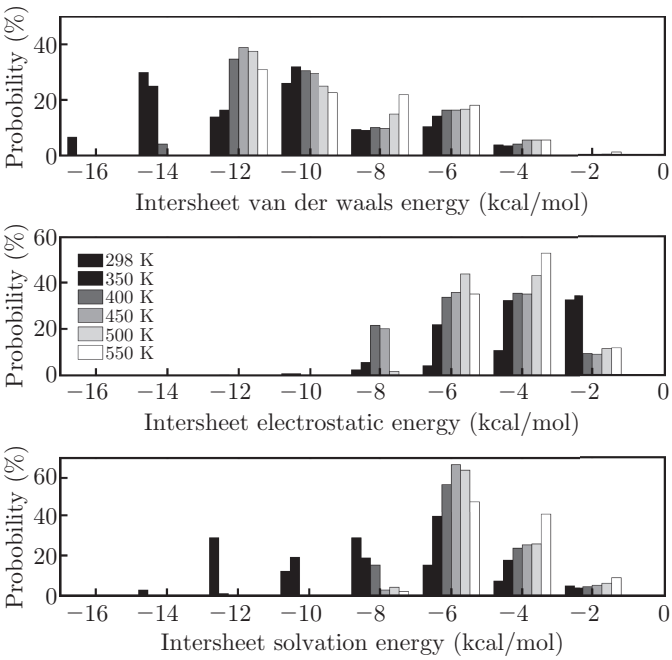

Fig. 6: The bar chart of intersheet interaction

of intrachain is sturdier than Van der Waals at room temperature. This indicates that the contribution of electrostatic to stability outweighs that of Van der Waals. The probability of high electrostatic energy of intrachain decreases to some degree at 350 K (Fig. 4) and the mean energy increases to 4.3360 kcal/mol. As temperature increases to 400 K, the probability of energy higher than 4 kcal/mol is remarkably low and the mean is 1.6565 kcal/mol. The mean electrostatic energy is far behind 1.3 kcal/mol when temperature is higher than 450 K (Fig. 4). This indicates that the bond length increases and the molecular chains get stretched at high temperature. When

Table 2: The mean intrachain interaction energy at different temperatures

Temperature (K)	Interaction	Intrachain (kcal/mol)	
		Mean	Std. Deviation
298	Van der Waals	−1.0494	0.47475
	Electrostatic	−7.6476	4.13536
	Solvation	−0.6412	0.29177
350	Van der Waals	−1.3850	0.56182
	Electrostatic	−4.3360	4.08952
	Solvation	−0.06733	0.21854
400	Van der Waals	−1.6512	0.46545
	Electrostatic	−1.6565	1.18055
	Solvation	−0.5776	0.24896
450	Van der Waals	−1.6842	0.46155
	Electrostatic	−1.1565	0.47151
	Solvation	−0.6107	0.21669
500	Van der Waals	−1.6372	0.43926
	Electrostatic	−1.2645	0.54509
	Solvation	−0.5742	0.21891
550	Van der Waals	−1.6071	0.41618
	Electrostatic	−1.1823	0.48274
	Solvation	−0.5615	0.22856

the temperature is below 400 K, the electrostatic interaction of intrachain has some contributes to the stability of cellulose. For high temperature, the electrostatic has teeny contribution to the thermal stability just as Van der Waals.

The solvation energy of all glucose residues for intrachain is less than 2 kcal/mol and the mean energy is underneath 1.0 kcal/mol (Table 2). There is no sensible difference between solvation and Van der Waals energy, both of them have little contribution to the stability of cellulose. For the temperature below 400 K, the electrostatic energy notably exceeds the other interactions. The intrachain interaction consists the hydrogen-bonding as the main force of the cellulose stabilizing [6]. The electrostatic play a mirror role in the stabilizing mechanism.

The Fig. 5 displays that the Van der Waals energy of all glucose residues for interchain are less than 2 kcal/mol at 298 K and the mean energy is 0.8455 kcal/mol (Table 3). The electrostatic energy of 68.8% residues for interchain assigns in the range of 4-10 kcal/mol at 298 K (Fig. 5). The mean energy is 5.8036 kcal/mol and the standard deviation 2.50227 kcal/mol (Table 3). Compared to the intrachain, the electrostatic interaction of interchain is feebler than that of intrachain at room temperature. The interchain solvation energy of few glucose residues is 2-4 kcal/mol and the mean is 1.0411 kcal/mol. It surpasses that of intrachain, but it has little contribution to the stability of cellulose still. These results indicate that the contribution of electrostatic to stability overtakes that of Van der Waals and solvation and is fainter than that of intrachain.

The Van der Waals and solvation interaction energy are almost unchanged for interchain with the temperature ascending (Fig. 5). The interchain Van der Waals and solvation interactions have

Table 3: The mean interchain interaction energy at different temperature

Temperature (K)	Interaction	Interchain (kcal/mol)	
		Mean	Std. Deviation
298	Van der Waals	−0.8455	0.35020
	Electrostatic	−5.8036	2.50227
	Solvation	−1.0411	0.52327
350	Van der Waals	−0.8171	0.37776
	Electrostatic	−4.8375	2.40031
	Solvation	−0.6527	0.25141
400	Van der Waals	−0.7539	0.35957
	Electrostatic	−3.9776	1.68702
	Solvation	−0.1883	0.05280
450	Van der Waals	−0.7737	0.34322
	Electrostatic	−3.6908	1.46717
	Solvation	−0.1036	0.08837
500	Van der Waals	−0.7862	0.32547
	Electrostatic	−3.4746	1.47775
	Solvation	−0.1647	0.04041
550	Van der Waals	−0.9519	0.38467
	Electrostatic	−2.9369	1.49500
	Solvation	−0.3048	0.13532

no effect to the thermal stability of cellulose Iβ. Comparing to 298 K, the interchain electrostatic energies of 8-10 kcal/mol and 4-6 kcal/mol descend to some extent at 350 K, but the probability of 4-8 kcal/mol rises (Fig. 5). This leads to that the mean energy barely diminish and the value is 4.8375 kcal/mol. According to the changes of distribution and mean energy, the interchain electrostatic energy decreases little with the temperature coming up (Fig. 5). This indicates that the molecular topology structure between chains has minuter shift than that of intrachain. The interchain electrostatic has some contributes to the stability of cellulose for both low and high temperatures. That is to say, the interchain electrostatic interaction has more contribution to the thermal stability than that of intrachain ones.

At 298 K, the intersheet electrostatic interaction energy of glucose residues are almost below 2kcal/mol and the mean is 1.9129 kcal/mol (Fig. 6). Van der Waals interaction energy of most glucose residues between sheets are mainly concentrated in 10-16 kcal/mol and the probability is 86.39% (Fig. 6). The mean is 10.1246 kcal/mol and the standard deviation is 3.13734 kcal/mol (Table 4). The bar chart and table 4 of intersheet solvation energy show that 72.57% are higher than 6 kcal/mol and the mean is 7.6697 kcal/mol. These results indicate that the intersheet Van der Waals and solvation energy are noteworthy binding forces for stacking sheets.

The mean intersheet Van der Waals interaction decreases somewhat with the temperature increasing, the Van der Waals energy of most glucose residues are above 8 kcal/mol (Fig. 6). This brings about the higher mean above 8 kcal/mol also. This indicates that the Van der Waals interaction is essential for the stacking sheets at different temperatures, and likewise plays a

Table 4: The mean intersheet interaction energy at different temperature

Temperature (K)	Interaction	Intersheet (kcal/mol)	
		Mean	Std. Deviation
298	Van der Waals	−10.1246	3.13734
	Electrostatic	−1.9129	1.96153
	Solvation	−7.6697	2.95429
350	Van der Waals	−9.4152	2.94850
	Electrostatic	−3.0418	1.88685
	Solvation	−5.6785	2.14862
400	Van der Waals	−8.8732	2.58155
	Electrostatic	−4.2742	1.72187
	Solvation	−4.6085	1.37386
450	Van der Waals	−8.6910	2.50404
	Electrostatic	−4.2403	1.62193
	Solvation	−4.4147	1.28157
500	Van der Waals	−8.5164	2.56619
	Electrostatic	−3.7804	1.41018
	Solvation	−4.2916	1.34769
550	Van der Waals	−8.0673	2.55371
	Electrostatic	−3.4968	1.19131
	Solvation	−3.8807	1.35012

main role to the thermal stability of cellulose Iβ. The intersheet solvation energy shrinks with the temperature increasing from 298 K to 400 K, while the electrostatic energy grows gradually. When the temperature rises to 400 K, the electrostatic and solvation energy of most glucose residues are below 6 kcal/mol (Fig. 6), but the means are 4.2742 kcal/mol and 4.6085 kcal/mol respectively. The previous molecular dynamics showed that the twisting of chains existed in cellulose [20]. The twisting was also found in this molecular dynamic simulation (Fig. 7). The twisting of chains related to the change of average distance between sheets on some level. This change resulted to the electrostatic energy increase. When the temperature raised from 450 K to 550 K, these interactions began to decline. At 550 K, means are higher than 3.4968 kcal/mol still. In spite of the electrostatic and solvation energy are remarkably less than Van der Waals, they exist and play a minor role to stacking sheets at high temperature. These results are consistent with the case of interaction energy per chain.

In order to clarify the interaction mechanism further, the total energy for intrasheet and intersheet was taken into consideration. For the intrachain and interchain, the total energy of most residues is above 4 kcal/mol (Fig. 8) and the means of this cases are 7.7787 kcal/mol and 4.5727 kcal/mol at 298 K, which are extraordinarily lower than that of the intersheet mean 18.2185 kcal/mol (Table 5). With the temperature arising, the total energy of most residues is below 6 kcal/mol and the means of them are about 4 kcal/mol also. According to previous researches, the intrachain hydrogen-bondings O3H3$\cdots$O5 and O2H2$\cdots$O6 dominate the intrachain, while the hydrogen-bonding between the O6 (donor) in one chain and O3 (acceptor) in the neighboring chain dominates the interchain [15, 20]. This indicates that hydrogen-bonding interaction dom-

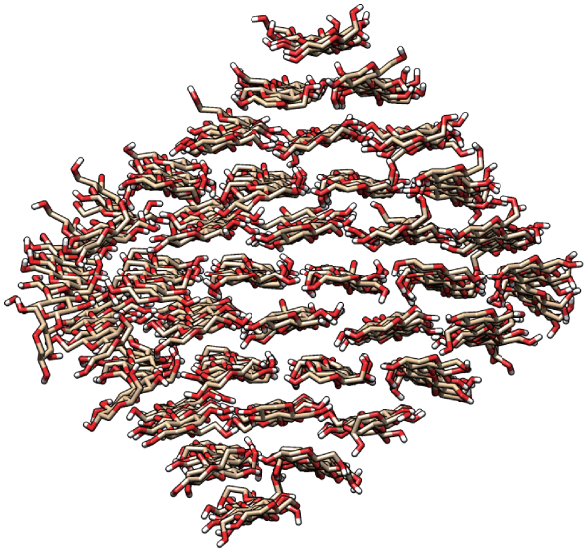

Fig. 7: The twisting of chains at 400 K

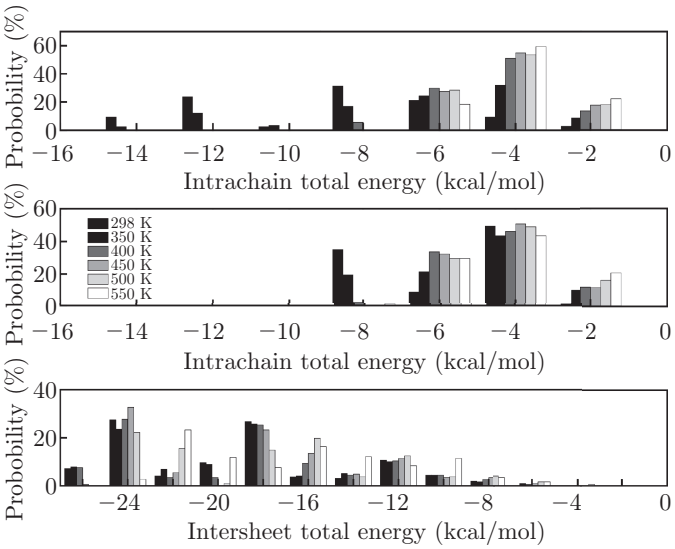

Fig. 8: The bar chart of total interaction

Table 5: The mean of total energy at different temperature

Temperature (K)	Intrachain (kcal/mol)		Interchain (kcal/mol)		Intersheet (kcal/mol)	
	Mean	Std. Deviation	Mean	Std. Deviation	Mean	Std. Deviation
298	−7.7787	3.22157	−4.5727	1.73431	−18.2185	4.95182
350	−5.5642	3.02633	−3.9559	1.75655	−17.9666	5.01097
400	−3.7657	1.22959	−3.4887	1.35734	−17.7558	5.19106
450	−3.3856	0.90217	−3.3378	1.22939	−17.3472	5.12604
500	−3.4344	0.92825	−3.2110	1.20575	−16.5892	5.08004
550	−3.3339	0.91612	−3.1652	1.29706	−15.4327	4.89897

inates the intrasheet, while the total of Van der Waals, electrostatic and solvation interaction is minor. In essence, the intersheet O-H$\cdots$O hydrogen-bonding interactions did not contribute to the cohesion of cellulose sheets. For the intersheet, the total energy of most residues is higher than 12 kcal/mol (Fig. 8) at various temperature, the minimum mean is 15.4327 kcal/mol (Table 5). This indicates that the total interaction of Van der Waals, electrostatic and solvation interaction superiors the intersheet interaction. The Van der Waals interaction accounts almost half of the total and it dominates the intersheet interaction. The sum of electrostatic and solvation energy are also deemed to play a part in stacking cellulose.

4 Conclusion

In summary, Van der Waals, electrostatic interaction and solvation interaction of cellulose Iβ were analyzed by molecular dynamics simulations with the GLYCAM06 force field. These interactions for each glucose residue were discussed combing with the interaction energy per chain and mean interaction energy. The results showed that the total energy of Van der Waals, electrostatic and solvation interaction were over 15 kcal/mol at various temperature. This indicates that these interactions should not be ignored, although they are often regarded negligible. The reason for the outcome is that the interaction energy of residues pairs is almost less than 0.1 kcal/mol. This leads to these interactions being overlooked in past works habitually. According to above discussion, the Van der Waals, electrostatic and solvation interaction of many glucose residues are fairly strong and they should not be ignored. The hydrogen-bonding dominates the intrasheet interaction, whereas the Van der Waals, electrostatic and solvation interaction are of significance for intersheet interaction. The findings support the previous work [14]. In intrachain and interchain, the thermal stability mechanism is different. These characters assist us to reveal the interaction mechanism of cellulose Iβ more clearly. The solvation interactions were discussed only in water, and no comparison to other solvents. In the next step, we are going to focus our attention on molecular interaction in different solvent environments.

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