Adsorption Mechanism of Cellulose Hydrogel by Computational Simulation

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Abstract

In this chapter, different adsorption mechanisms of cellulose hydrogel will be investigated. For this aim, computational simulation will be used. On an atomistic scale, cellulose hydrogel has different hydrogen bond properties. The OH groups can only act as hydrogen bond acceptors, but due to the negative charge density, there are still more water molecules assembled around adsorbents. Besides intermolecular hydrogen bonding, it has some hydrophobic properties. It means that some hydrophobic materials can be adsorbed on the surface of cellulose hydrogel at specific conditions. Most force fields for this simulation are empirical and consist of a summation of bonded forces associated with chemical bonds, bond angles, and bond dihedrals and nonbonded forces associated with van der Waals forces and electrostatic charge. Empirical potentials represent quantum mechanical effects in a limited way through ad hoc functional approximations.

Keywords
Cellulose · Hydrogel · Adsorption · Computational simulation

1 Introduction

1.1 Computer Simulations of Cellulose

In the past, coordinates from electron diffraction were widely used as starting configurations for computer simulations of cellulose derivative. But one always has to bear in mind the problems connected with the interpretation of raw data. For example, it is very difficult to determine the chain alignment in cellulose crystals [1]. Meanwhile, in the case of native cellulose derivative, the parallel orientation is established, but this question is left unsolved for regenerated cellulose. Cellulose derivative If consists of parallel sheets of hydrogen-bonded chains. This was confirmed by several simulation studies [2].

Previous simulation of various systems, including glucose, cellobiose, and carbohydrates, has been undertaken. Some authors simulated crystal-like cellulose, but under unrealistic conditions, like mini-crystals with only monosaccharide residues and with vacuum boundary conditions. Aablo and French calculated the energies for various packings of cellotetraose molecules [3]. Intra-chain hydrogen bonding occurs between different intrasheet bonding in adjacent planes (a prime indicating a second glucose ring). The conformational space of cellobiose and higher oligomers under vacuum conditions with respect to glucosidic torsions was explored by Hardy using molecular mechanics, both for charged and uncharged models. In the uncharged case, the minima are in agreement with

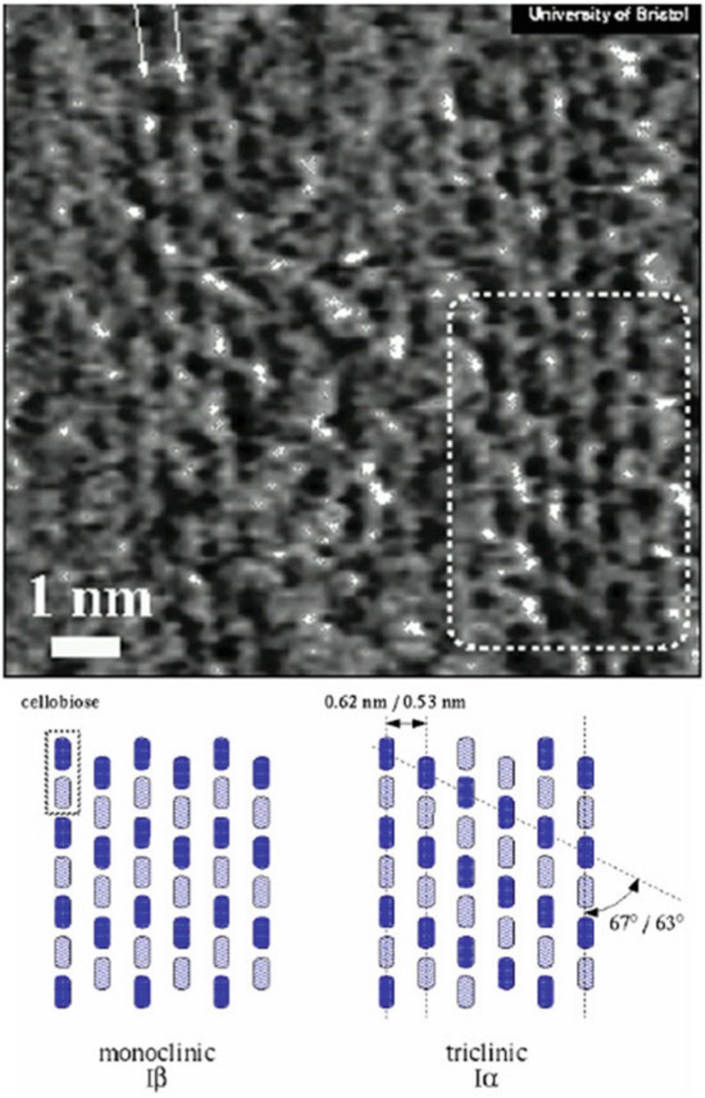

Fig. 1 A software zoom of an AFM image of microcrystalline valonia surface. The arrows point along the cellulose chain direction; the dotted box highlights an area with spots in the length of the cellobiose repeating interval. Bottom: The schematic diagram below shows the expected AFM pattern for monoclinic and triclinic surfaces of cellulose I. Each rectangle represents a single glucose unit [3]

experimental crystal structures of cellobiose and cellulose. However, in the charged model, the appearance of hydrogen bonding distorts this conformation, thereby leading to a new structure [3] (Fig. 1).

1.2 Crystalline Systems and Surfaces

All simulations known from literature deal with the non-orthorhombic unit cells by using monoclinic/triclinic periodic boxes, as implemented in molecular dynamics simulation packages like AMBER or GROMOS. Prework used the cellulose I crystal structure of Blackwell and Gardner, which is now considered to be wrong [4]. Other simulations suffer from a restriction to small systems or from the chosen force field, which does not allow full atomistic details. Recently Heiner performed united-atom simulations of If and If cellulose with the GROMOS force field starting from X-ray diffraction data of Sugiyama. The monoclinic system was built from an ff array of unit cells, the triclinic system from an ff array. Both runs extend over 1000 ns of simulation time. The experimentally observed energy difference between them was confirmed. Most surprising is the small tilt angle observed between glucose ring planes in crystal planes of the monoclinic phase. Alternating chains were termed even and odd; the different tilt angle with respect to the surface was attributed to better interplane hydrogen bonding. More details about the hydrogen bonding pattern were determined using radial distribution functions and energy calculations [2]. The only existing simulation of an cellulose surface was performed by Heiner. In the first paper, the crystal face and, in the second paper, both of them and surfaces were exposed to water. Only the topmost cellulose layers are structurally affected by hydration. The cellulose properties of the interface layers (which are in contact with the solvent) differ only slightly from that of the crystal's bulk. The odd/even duplicity is absent in the interface layers toward water for If and If cellulose, and there are changes in the hydrogen bond patterns, due to completion of cellulose-cellulose bonds with cellulose-water hydrogen bonds. The cellulose-water interface for both the monoclinic and triclinic crystals was classic [5]. From a comparison of the surface-water pair distributions, the monoclinic and the triclinic surfaces are found to be more hydrophobic than the monoclinic and triclinic surfaces. This becomes evident from the first hydration peak, which is repelled from the surface and more unpronounced. In their second paper, the authors focus on similarities and differences between different cellulose surfaces. They found the monoclinic and triclinic surfaces to be very similar. Likewise, the monoclinic surface is similar to the triclinic surface [6]. The latter surfaces are denser and more hydrophilic than the former two. As for f, the odd/even differences disappear on the cellulose-water interface [1] (Fig. 2).

1.3 Carboxymethyl Cellulose

Cellulose is further substituted to cellulose esters and ethers, by either reaction with acid anhydrides or halogen-carboxylate, respectively. An example for cellulose ether is carboxymethyl cellulose (CMC), which is gained by basic conversion of cellulose slurry with sodium chloroacetate or chloroacetic acid [7]. CMC is mass-produced, because of its versatile properties. It is used as thickener, former, or protective colloid. Consumer care products take advantage of its nontoxicity, and it is employed particular for foodstuff and as soil redeposition inhibitor [8]. CMC has a high affinity

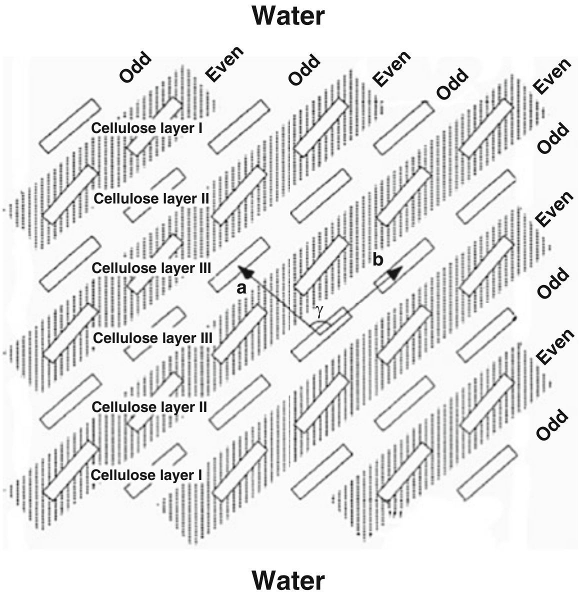

Fig. 2 Schematic picture of the simulation cell of Heiner, taken from. The sketch shows a monoclinic cellulose crystal, the 110 surfaces (top and bottom) exposed to water. Alternate even and odd 200 crystal planes are shaded white and gray. Glucose rings of even 200 planes are tilted with respect to the 200 planes and glucose rings of even planes [1]

to cellulose, and it is therefore a good coating for textiles. CMC coatings improve paper properties, like ink and surface gloss. Crude commercial-grade CMC is produced for detergents, for oil-drilling, or for the paper industry. Product properties of CMC are mostly determined by the degree of substitution (DS) and the substituent distribution within one anhydroglucose unit (AGU) and along the CMC chain. The degree of substitution ranges from zero (no substitution) to three (all three hydroxy groups of a glucose unit substituted). In the case of heterogeneous cellulose derivatization, statistical substitution patterns and polydisperse CMC are produced. The chemical characterization of CMC is almost restricted to the average degree of substitution, which is measured by titrimetric methods or chromatography where the persistence length of CMC is found by size exclusion chromatography to be 20 nm [9]. Owing to this, only little information is available on the interplay between the CMC structure (substitution pattern, degree of substitution) and its macroscopic properties. The actual substitution pattern of industrial cellulose derivatives can be rationalized by both kinetic and energetic arguments if cellulose is produced as alkaline slurry. Hydroxyl groups can only be carboxy-methylated if the bulk cellulose is swollen and hydroxyl sites are free from hydrogen bonding and accessible to the solvent and substituting agent. The carboxy methylation reaction takes place at the solvent-cellulose phase boundary [10]. From this, the dynamics of swelling and hydrogen bond cleavage are responsible for the degree of substitution and the substitution pattern. The glucosidic linkage of CMC was hydrolytically cleaved, and on this way, information on the distribution along the backbone was lost. The same results can be found by high-pressure liquid chromatography, which allows separating and identifying differently substituted units. There are eight different substituted monomer units possible. CMC polyelectrolyte properties are only understood from a technical point of view. There is a good experience how to tailor a CMC through the production procedure to a certain property, like a high viscosity. The underlying molecular chemistry is still beyond our knowledge. The missing link between microscopic structure and macroscopic properties can be established by molecular dynamics simulations [11].

1.4 Nanocellulose

The various forms of nanomaterials that can be produced from cellulose are often collectively referred to as cellulosic nanomaterials or nanocellulose [12]. For example, the extraction of cellulose nanofibrils (CNFs) and cellulose nanocrystals (CNCs) from plants, bacteria, and some animals (e.g., tunicates) is leading to a wide array of worldwide research to use these nanomaterials in product applications [13, 14]. Examples include using CNFs as reinforcing agents in composites due to their high strength properties, relative low cost, and availability or CNCs due to their incredibly high strength (Fig. 3), renewability, lightweight, high surface area, and unique photonic characteristics [15]. As you will see when reading this book, research and development is currently taking place worldwide within academia, industry, and government agencies to study, characterize,

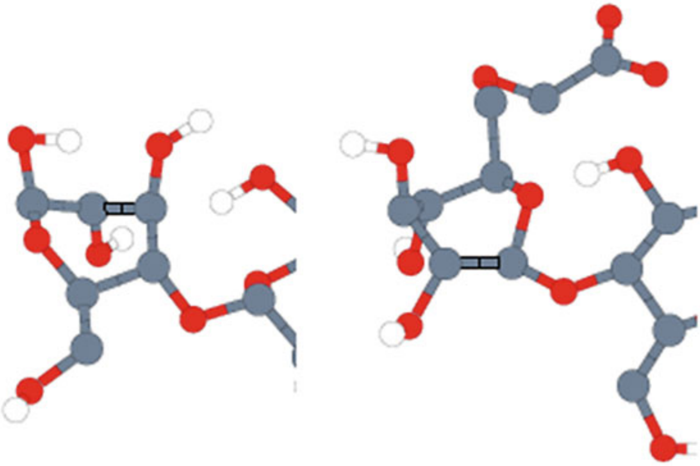

Fig. 3 Two terminal anhydroglucose units during the initial phase of a CMC I equilibration. The 4C1 conformation is lost and the OH oxygens take an axial position. Both rings are twisted neither in a proper chair nor boat form

and use these highly complex cellulosic nanomaterials. Nanocellulose in its various forms contains unique structures and self-assembly features that we can exploit to develop new nano-enabled green products. A specific example is the use of cellulosic nanomaterials in lightweight, high-performance composites. Such nanocellulose-enabled composites could eventually replace carbon fiber mats and strands by weaving cellulose-derived nanomaterials and fiber into mats. This could lead to replacement of the nonrenewable and fossil-based materials currently used to make automotive parts such as dashboards, seats, floor mats, and even body panels or frames. The world may not be ready yet to step back into a wooden airplane, but the day will come when aircraft will have wings and fuselage components containing lightweight, high-performance nanocellulose-enabled composites. Fiberglass is a common composite with which most people have experienced. It is used to manufacture diverse products including tool handles, sporting goods, bike frames, boats, and even the bodies of some sports cars. Fiberglass cannot be made transparent and is a heavy material for a composite. Replacing fiberglass mat with nanocellulose-containing mat could lead to new lighter-weight materials and the eventual replacement of nonrenewable products with sustainable and renewable cellulosic materials [14].

1.5 Polyelectrolytes

Polyelectrolytes play an important role in industrial chemistry. The fields of application range from tailor-made thickeners to paper finishing or ore preparation. Polysaccharide derivatives represent one interesting class of polyelectrolyte. In particular, cellulose products are important compounds [16]. For our simulation study, carboxymethyl cellulose (CMC) is chosen as an example for a polyelectrolyte derived from a natural polymer [17]. Aqueous CMC solutions exhibit valuable properties, like a wide range of viscosity, nontoxicity, and biodegradability. Particularly for the high-purity consumer-product market (cosmetics, food stuffs), CMC is used. However, pricing becomes more important in bulk applications (clay and ore treatment, oil-drilling). Hence, it is desirable to replace some of the high-cost high-selective chemicals with low-cost equivalents, like polypeptide, which is the prototype of medical synthetic polyelectrolytes. Polypeptide is the other polymer studied in this work. Most published works on aqueous CMC and polypeptide solutions were done experimentally using chromatography, C nuclear magnetic resonance, and rheological techniques [18]. Theoretical approaches are scarce. We are aware of only one paper, which treats CMC by the wormlike chain theory. This electrostatic theory successfully rationalizes some of the global properties of CMC, but as a rather generic approach, it does not allow for detailed predictions on an atomistic time and length scale. Similar restrictions apply also to Monte Carlo simulations of polyelectrolyte chains in a cell model, where the solvent is treated as a dielectric continuum. Especially local interactions such as hydrogen bonds (hydrogen bridges) are neglected in theories and non-atomistic simulations. With two or three hydrogen bond donor groups per repeat unit and even more acceptor sites (including charged COOH groups), this type of interaction is likely to be very important for the behavior of CMC in water. Experimental techniques, on the other hand, suffer from different problems: NMR provides averaged local properties. Rheology derives and verifies scaling laws, but different polyelectrolytes lose their chemical identity and show the generic behavior of excluded volume chains. Atomistic molecular dynamics (MD) simulations cannot overcome all these problems, but they can provide some more detailed information [19].

Polypeptide is important for industrial applications because of good water solubility and as a (strong) model polyelectrolyte in science. Polypeptide is known for only weak adsorption to cellulose but binds with hydrophilic glass (SiO_2) surfaces. At high concentration, polypeptide forms networks, cross-linked by hydrogen bonds and entanglements. The water structure around the polyelectrolyte was investigated by Tsukida et al. using Raman spectroscopy. They found a high perturbation of water-water hydrogen bonds at a degree of neutralization below 10 and concluded that a certain amount of carboxylic groups enhances water-hydrogen bonds in the polymer vicinity. There is a minimal disruption of hydrogen bonds near a degree of neutralization. Even at higher ionization, polypeptide is assumed not to be fully stretched. The local conformation of polypeptide is assumed not to be dependent on ionization or salt concentration. Like in the case of CMC, no experimental method has been applied, which goes beyond a macroscopic view of PP. Methods applied to polypeptide are rheology, viscometry, light scattering, and calorimetric methods. The only simulation work was done by Ullner et al. This is a Monte Carlo study of one polypeptide chain in solution. But even though counterions are accounted for explicitly, the simulation is done in the generic cell model for polyelectrolytes [20]. However, there is some agreement that polypeptide behaves like a flexible coil in a “good solvent” instead of having rodlike structure. One aim of this thesis is to understand better the structural and dynamic aspects of the hydration of CMC and polypeptide and to compare the two polymers. To this end, we investigate both the chain properties and the interaction of chains with their immediate solvent environment. Atomistic simulation is confined to the study of small system sizes. However, in combination with coarse-graining methods, even some mesoscopic properties may be explored. Thus, a second goal of this study was to produce atomistic structural information, from which coarse-grained models of, e.g., polypeptide and the cellulose surface can be generated. The coarse-grained models can be used to study the adsorption of polyelectrolytes on cellulose beyond the size and time limitations of atomistic molecular dynamics [21].

2 Materials and Methods

Computer simulations came into fashion among scientists, as fast hardware became affordable. Early computer simulations were done on the MANIAC computer in Los Alamos by Metropolis and Rosenbluth. From this milestone in scientific computing, character and size of simulated systems changed. In the first years, there was research to develop, validate, and try new methods, even with simple systems like hard spheres, where often a theoretical solution was already present. With the Lennard-Jones potential, it was possible to compare the outcome of simulations with experimental results. There was a need for a new method to simulate not only static properties (ensemble averages) but extend simulation to explore dynamical (transport) properties as well. Molecular dynamics (MD) is the new technique. If a given system follows Newton's equation of motion and we know one state of the system, then we can calculate every state of the system (both in the future and in the past). Classical particles are moved by integration of the system's equation of motion in time. By means of this, a molecular dynamics simulation is very simple; after initialization, the simulation cycles through successive molecular dynamics steps. For each step, the force is calculated, particle velocities plus positions are updated, and finally, properties of interest are sampled.

This was first done for hard spheres by Alder and Wrainwright and later by Rahman for Lennard-Jones particles. Later, the method was extended to molecular systems (by the introduction of bonds) and different algorithms devoted to handle different ensembles and conditions like nonequilibrium molecular dynamics. In particular, the Lennard-Jones potential has proven useful, and it is the most common model for nonbonded interactions.

The work of Rahman was pioneering, because it showed the benefits of molecular dynamics simulation over theoretical approaches, which often fail to describe. Moreover, MD is valuable also for nonideal, multiparticle systems. One recent example to show the versatility of the method is the dissipative particle dynamics method. Even if it is still based on the simple molecular dynamics scheme, it can be used for mesoscopic simulations through a modified equation of motion. The second route to handle large systems is to use more elaborated programs on multiprocessor computers. This enlarges the number of simulated particle from about on a workstation to several million particles on a supercomputer. To mention but a few trends in atomistic molecular dynamics, these are the calculation of free energy-related properties; the application to larger molecular systems, like polymers or biopolymers; the programming of user-friendly simulation programs to allow for easy standard calculations; and the development of new and better force fields. The last item development of force fields is very crucial. Although there exist a variety of different force fields, none of them describes all faces of a system completely. In consequence, there are many force fields available, and it is not always clear in advance, which one will give the best results to our questions. In other words, there is nothing like unique natural force fields for a given molecular or system: Even approaches with a high number of terms do not necessarily give good results [22]. The general layout is almost the same for all common force fields. They divide interactions into nonbonded (Lennard-Jones dispersion repulsion interaction, Coulomb electrostatic interaction) and bonded (bonds, angles, torsions, etc.) [23]. Some force fields employ special terms to treat hydrogen bonds or similar phenomena, but this is not very common, as a good description may be obtained by other terms as well.

2.1 Force Fields

While the kinetic part of the Hamiltonian uses only particle masses as parameters, the potential energy part is dealt with by a force field. The force field is the major choice or input of a simulation. It gives an expression for the potential energy as a function of particle coordinates (r). This expression consists out of different terms, which are usually chosen intuitively to mimic the nature of molecules. The splitting of the potential energy into a sum of bonds, angle, and other terms is arbitrary and only rejects a human understanding of chemistry. The second approach to a force field is the pragmatic, technical one, where terms are not even meant to have a special physical meaning but originate from some technical issue or procedure. To name but a few technical force field contributions, there are position restraint terms to keep atomic sites fixed in space or bond constraints to keep the distance between atoms constant. Nevertheless, the use of force fields instead of true electronic interactions has proven useful in lots of simulations from simple Lennard-Jones systems to much more complex molecular systems.

2.2 Nonbonded Interaction

The separation of a force field into distinct mathematical terms in molecular simulation is justified usually by computational convenience or reasons of transferability. There is no question that all interaction would have to be calculated by quantum mechanical methods. Unfortunately, this way is by far too time-consuming, even if fast semiempirical methods are employed. For systems with more than several thousand or even hundreds of thousands of atoms, it is inevitable to use a force field with pairwise additive terms. All electronic degrees of freedom are ignored, and every atom is taken as the position of its nucleus. Methods which rely on this statement are commonly summarized under the term molecular mechanics. Energy functions are called “effective potentials,” as they try to incorporate many-body effects into a site-site potential. They do not resemble the potential as it would be correct for two interaction sites in vacuum but are representative for say two argon atoms in liquid argon. On one hand, this is an important breakthrough, as we do not bother about the explicit calculation of many-body terms, but on the other hand, this may reduce transferability of a parameter set, as there is an influence of the environment onto a single site’s force field parameters. This leads to a rough categorization into force fields for inorganic (crystal) and for organic (soft) matter and for solutions, the latter one with a special emphasis on water as solvent. Some force fields are very biased toward aqueous solutions of (bio) organic compounds like DNA or carbohydrates. To achieve transferability, which is often considered a key property of force fields, the energy function is divided into several contributions. To name but a few, there is a bond term, often modeled by a spring, or a bond angle modeled by a harmonic angle potential. Nonbonded interactions are divided into electrostatic and dispersion/ repulsion (induced dipole, Pauli repulsion) contributions:

One example is the dispersion energy, which is often expressed as a (computationally cheap) Lennard-Jones potential, but some approaches use the Buckingham form, which models Pauli repulsion using an exponential function. Knowing the potential between two sites is only the first steps toward calculating the energy of a N-body system and all forces. Instead of using an order N double loop over all site-site combinations ij, the most efficient way is the use of a cut of rc together with a neighbor list to speed up the simulation by a factor of order N. This is a point where physical and technical issues meet and compete. From a physical point of view, one wants to take the cutoff as large as possible, but with limited computer resources, one should take it as short as possible.

2.3 Bonding Interaction

Bonding interactions are somehow better to understand, because their concept is rather intuitive. Usually they define some minimum energy state in terms of an equilibrium angle or bond distance. Deviations from this value impose an energetic penalty. The only exception are bond lengths, which if treated by a harmonic spring would require very tiny time steps and are thus not feasible. The bond vibrations of large molecules are of no interest. Therefore the harmonic bond potential is replaced with a rigid constrained bond, which on the one hand introduces additional calculations into the molecular dynamics simulation but on the other hand allows increasing the integrator's time step ft by one order of magnitude.

2.4 Constraint Dynamics

The SHAKE procedure of Ryckaert, Ciccotti, and Berendsen is one of the most explained and cited paper in molecular dynamics. The SHAKE method allows us to consider atomic connectivity without using harmonic bonds. Valence bonds vibrate at high frequency and impose a small integration time step to a simulation. SHAKE now alleviates this shortcoming by fixing (constraining) the distance r between two sites to a parameter value. This equality is usually written down in the form of a holonomic constraint.

First the unconstrained motion of all atoms is calculated and after the equation of motion is expanded by the introduction of a constraining force (as a Lagrange multiplier). The resulting equations of motions are now solved in an iterative fashion until all constraints k in the equation are within some tolerance. Our simulation packages use a special SHAKE algorithm, which performs well on vector machines like the Cray T or NEC SX.

2.5 Other Force Field Terms

Besides the nonbonded Lennard-Jones and Coulomb interaction and the constrained bonds, there are several other force field terms. They are computationally cheap and more generic as, for example, the nonbonded potential parameters. Examples include bond angles and bond torsions.

2.6 Periodic Boundary Conditions

Periodic boundary conditions are the way to generate pseudo-infinite systems, thus simulations which do not suffer from boundary or edge effects. Periodic boundaries are achieved by putting a grid of copies around the central simulation box. The algorithm ensures that no interatomic distance in one direction is larger than one box length (this holds strictly only for orthorhombic boxes). To calculate the force on a site in the central box, neighbors from the central and surrounding boxes are used, if they are within the cutoff distance. If one atom travels out of the central box, it reenters at the opposite side of the box. The internal coordinate format does not store these folded but unfolded coordinates, so that the folding is applied in the force loop. To avoid self-interaction, the box has to be larger than two times the cutoff.

3 Results and Discussion

3.1 Interactions and Force Fields

The actual parameterization of the GROMOS force field for carbohydrates has evolved since 2000 and was mainly tested on cyclodextrin, as well as on other sugars. Kroon-Batenburg, Bouma, and Kroon made use of the GROMOS parameter set for simulations of cellulose in solution and compiled an overview of different parameter sets in conjuncture with Ewald sums by Kouwijzer et al. One application of the GROMOS force field to crystalline cellulose was reported by Heiner, Teleman, and coworkers. Their simulations covered both the crystalline phase of cellulose and the interface with water. The successful simulations and the compatibility of the GROMOS force field terms in particular the treatment of electrostatics without an Ewald sum were decisive factors to choose the GROMOS force field. A second point is our interest in multicomponent, heterogeneous systems, with both a cellulose surface, a solvent, and a polyelectrolyte solute molecule. Our force field of choice should be able to give a good description for every component, not only of the sugar. So the use of a building block based and thus force field is sensible. However, there are plenty alternatives for carbohydrate force fields. Besides generic ones, like AMBER, CHARMM, and the OPLS, parameter sets, some authors developed special approaches for carbohydrates. Most of these expert models have some special application in mind, like the exploration of anomeric equilibrium of sugar rings. An overview is given by French and in various articles published in a special issue Carbohydrate Modeling of the *Journal of Molecular Structure*. A recent approach was done by Neyertz et al. to develop a cellulose all-atom potential model from various origins (mainly from other sugar parameters and quantum chemistry). Despite the mixed sources, the Neyertz approach reproduces unit cell parameters, thermodynamic stability, and moduli in close agreement with experiment. Tests or applications for this force field in solution are not known yet. The authors develop the force field with PEO-cellulose interface simulations in mind. In contrast to the Neyertz model, the GROMOS approach is a so-called united-atom force field. Aliphatic oxygens are not modeled by an explicit interaction site. Only polar/OH hydrogens are explicitly treated. Aliphatic hydrogen atoms are accounted for by a change of the parameters for the parent carbons, which grow in size (+%) compared to all-atom force field (like AMBER) and get a higher minimal energy (+%). For organic materials, this has proven feasible if the stereochemistry at chiral centers is preserved using additional terms in the parameterization. The GROMOS force field tackles this by harmonic dihedral angles, which fixes four atoms in a given tetrahedral geometry. The major benefit is the reduced amount of computer time. However, for our cellulose-water systems, the savings are less pronounced. Even if the united-atom model removes one third of all atoms for a glucose ring (aliphatic hydrogens), there is still the large amount of polar hydrogen sites left.

Torsions in the GROMOS force field are considered by (a) the torsion potential and (b) modified interactions. United atoms separated by exactly three bonds interact through a reduced Lennard-Jones potential. For atoms other than united atoms, the interaction is not modified. The sum of both terms results in a physical torsional potential. There is usually only one torsional term for each bond i-j-k-l, but this rule is changed for sugar rings, where additional torsions guarantee for the correct ring puckering. All interactions are dealt with by some force field term (bonds, angles); all atom pairs with a topological distance greater than four bonds interact by unmodified nonbonded interactions. We make use of an effective model potential. This is because the parameter set is chosen to incorporate many-body effects by the physicochemical environment. For example, charges are taken to reproduce average polarization effects by the solvent. Because of this, we avoid mixing of different force fields and used SPC-water (simple point charge) throughout, where parameters harmonize well with the GROMOS cellulose force field. Furthermore, it is a rigid model, and it has the minimal number of sites, which makes it computationally efficient. The CMC and polypeptide force field terms were taken to be compatible with the cellulose parameters. Because of this, CMC and polypeptide are modeled with the GROMOS force field as well. The CMC parameterization is based on cellulose, with extra parameters for the CH–COOH group. The CH parameters were taken from an aliphatic sub-chain in the GROMOS force field, and the carboxylic group is an generic parameter set which is used for all kinds of carboxylic acids in the GROMOS handbook.

3.2 Computational Details: Polyelectrolyte in Dilute Solution

For the polyelectrolyte simulations in dilute solution (CMC and polypeptide with counterions but without a surface), a single oligomer was solvated in about (see below for exact numbers) water molecules. The water configuration has been prepared from a cubic centered lattice by an equilibration run of 1000 ps until density converged. The initial polyelectrolytes' configurations were generated from a Z-matrix for a linear molecule. The sodium counterions were placed into the simulation box at random but not closer than 5 nm to any atoms of the solute. All coordinate sets were joined together, and overlap was removed by either f removing water molecules, closer than 9 nm to any of the solute atoms, or f pushing overlapping water molecules away from the solute: All water molecules in the vicinity of the solute are moved away from the polyelectrolyte along a solute water vector r, defend for every water molecule. The displacement vector starts at the polyelectrolyte site, which is closest to the water oxygen and ends at this oxygen. The length of the vector is scaled by an exponential decay function (jrj = c); c was chosen by trial and error to be nm. Water molecules far apart from the solute are hardly displaced at all (Figs. 4 and 5).

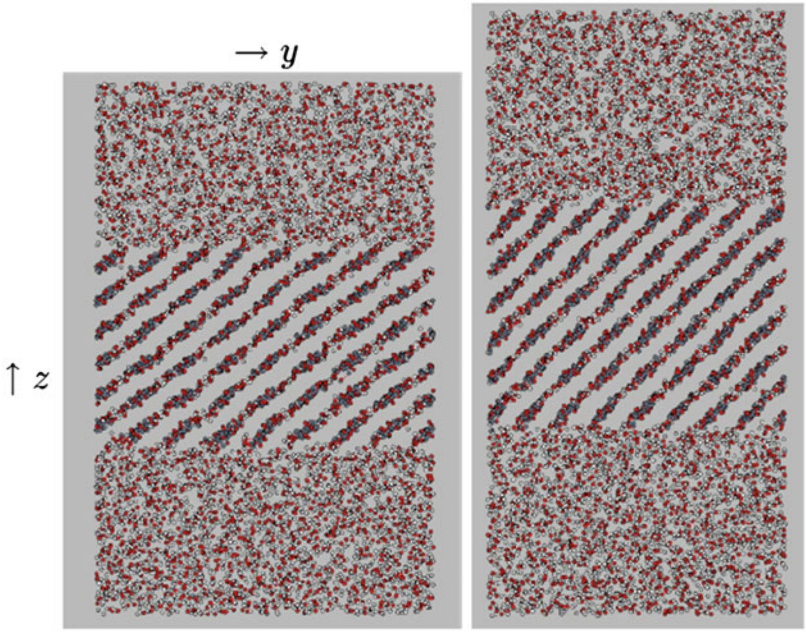

Fig. 4 Pictures of surface-water simulations after equilibration of about 400 ps. Left: 110-cellulose (wide), Right: 1–10-cellulose (narrow). The cellulose chains run into the drawing plane (x-direction)

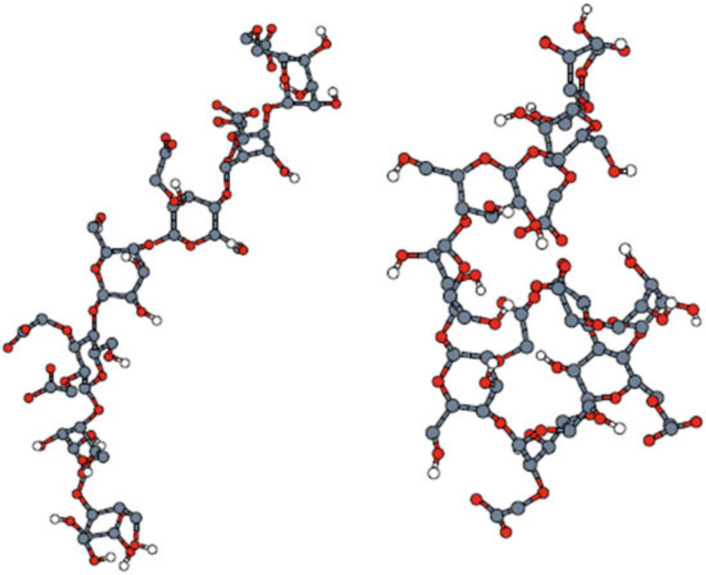

Fig. 5 Snapshots of CMC I (left at 2:0 ns simulation time) and CMC IIa (right at 3 ns)

3.3 Computational Details: Cellulose Surfaces

We examined two different cellulose-water systems: The first one with an interface between the monoclinic surface and water and the second one with the monoclinic surface exposed to water. The simulation setup is almost identical with that used by Heiner. A slab of six cellulose layers has two interfaces toward water. The z-axis of the periodic box is parallel to the normal of the respective surface. The cellulose crystal's c-axis (chain direction) runs along the Cartesian x-axis. Eight cellulose chains of each three cellobiose units are staggered with a shift of c = along the periodic box's y-axis. However, the simulation of the monoclinic cellulose surface employing an orthorhombic simulation box leads to some distortions of the molecular coordinates. The deviations from the native monoclinic structure are minor and were neglected. The exact procedure, to change the unit cell's geometry, is described. In the angle, from a small change of the monoclinic cell, we arrive at a unit cell which packs into an orthorhombic lattice.

3.4 Computational Details: Aqueous Polyelectrolyte-Cellulose Systems

The third kind of systems examined was the combination of the two systems above: A cellulose-water interface simulation with CMC or polypeptide oligomers dissolved in the aqueous phase. As the oligomers of CMC and polypeptide described above are too large to fit into a reasonable sized cellulose-water simulation box, we used smaller oligomers: For CMC the first molecules, CMC I was cut into two pieces, a trimer and a tetramer with molecular weights.

With two polymers and two different surfaces, we have four possible solute-surface combinations. The polymers are irregularly placed into the dense water system, by shifting water molecules away from the solute atoms radically as described on page 14. By this procedure, we obtain suitable starting coordinates without overlapping atoms. The cellulose sites are fixed in space using position restraints, and the system is quenched into a low energy stat, and equilibration is started afterward without position restraints. All simulation parameters (temperature, time step, weak coupling, etc.) are as for the cellulose-water system. Cellulose and water coordinates are taken from the respective cellulose-water simulations. an overview over all four solute-surface simulations.

The carboxymethyl side groups are strong H acceptors, because of their flexibility from the carbohydrate backbone and because of their negative charge. The globular CMC conformation is both stable through a multinanosecond simulation and builds dynamically from a stretched starting geometry. On a local scale, the globular conformation undergoes less hydrogen bonding with the solvent, as more intramolecular H-bonds are present and some H-donor and acceptor sites are buried inside the globule and are not accessible to water. This is also visible in the CMC-water radial distribution functions, where the globule state has a more distorted and irregular hydration shell. The polypeptide oligomer in aqueous solution is stretched and is readily solvated by water molecules. Because polypeptide has a high charge density on COOH groups, the mass of salvation water exceeds the polymer's own mass by a factor. The hydrogen bonding for CMC is more complex. There is inter- and intramolecular hydrogen bonding, latter one can be subdivided into inter- and intraglucose-ring bonding. For the collapsed, globule CMC molecules, all kinds of H-bonds are found in a significantly amount. Most remarkable are H-bonds spanning six or seven glucose rings, thus closing the CMC chain to a ring [24].

There are only few counterions close to the CMC strand (about Na^+-ions/AGU). The PP sodium radial distribution function is better defended due to the higher number of counterions. There are about sodium ions under the first peak of the PP-Na^+-rdf. The difference between CMC and polypeptide is understood, as the main interaction of sodium takes place with the carboxylic side groups of the polymers, which favors PP [23]. Counterions play a role during the (dynamic) collapse of the second CMC molecule. Simultaneous with the collapse, the number of sodium ions close to the backbone raises. The increased concentration of positive charges screens the repulsion of COOH groups and initiates the collapse. Two crystal planes of the monoclinic cellulose crystal were simulated for several nanoseconds with an interface to water. Both surfaces are representative for other surfaces like the triclinic ones. The surface has a wider interchain spacing than the surface. Both surfaces are stable against water and they are not penetrated by the solvent. This is due to the mainly hydrophobic and lipophilic character of both surfaces. This property has been accessed either through water densities on the surface [25].

4 Conclusion

Even though poly(acrylate) and (carboxymethyl) cellulose both are water-soluble polyelectrolytes, their behavior in water and toward water differs markedly. This is due to the different charge densities as well as to the different types and qualities of hydrogen bonds that either form with water. In PP, there is one strong hydrogen bond with the deprotonated carboxylate acting as an acceptor. In CMC, the smaller density of carboxylates is only partly offset by the possibility of alcoholic OH groups participating both as donors and as acceptors in hydrogen bonds. Hydrogen bonds to the ether oxygens are irrelevant. Taken per molecular weight of the polymer, it seems safe to say that polypeptide forms at least twice as many hydrogen bonds to water as CMC and that they are of larger binding energy (charge-dipole, rather than dipole-dipole). Based on this argument, the salvation of polypeptide in water should be more exothermic than that of CMC. Unfortunately, no measurements appear to be available for comparison. The comparison of the two CMC oligomers shows that the particular carboxymethylation pattern has an immense influence on the local structure in solution. The two assume entirely different conformations: CMC I is stretched and flexible, whereas CMC II favors a rigid cyclic conformation. We are therefore left to conclude that industrial CMC with its statistical substitution of OH groups behaves locally very diversely. As a consequence of its globular structure, CMC II shows more intramolecular hydrogen bonds than CMC I, fewer hydrogen bonds to water, slower hydrogen bond dynamics, and more contacts with the counterions. Aqueous polyelectrolyte solutions of carboxymethyl cellulose (CMC) and poly(acrylate) (PP) have been investigated. With respect to the size and CH-COOH distribution pattern, two aqueous solutions of different CMC oligomers (one heptamer and octamer) result in two chain structures: We observe one stretched structure, which is for a polyanion is rationalized by repulsion of negative charges, and a globule-like, collapsed structure. The compact structure is held together by intramolecular hydrogen bonds, which bridge multiple anhydroglucose units and often involve COOH groups.

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