Structure of Nano Crystalline Cellulose Established by Large-Scale Parallel Molecular Dynamic Simulations

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ABSTRACT

Structural and optical properties of Nano Crystalline Cellulose (NCC) in liquid dispersions and in solid films were investigated by large-scale parallel molecular dynamics (MD) simulation using empirical Coulombian interaction potentials. The latter was modified by taking into account density measurement in the stable liquid at room temperature and atmospheric pressure.

MD simulations were performed using several thousands of particles (from 500.000 to 4 millions) in a cubic box submitted to the standard periodic boundary conditions. To treat such a large number of particles, we use a parallel algorithm based on the spatial decomposition of the simulation box. The computational load is therefore distributed among several processors of a parallel machine.

Our calculations give a good description of the self-organization of NCC in liquid dispersion and in solid films and allowed us to question the NCC nematic structure theory and to propose an original structure for NCC self-organization. On the other hand, our model allows us to predict the distance between the different lattice planes, and it compares quite well with experimental measurements made by our research team. In the light of these experiments, our theoretical study indicates that (i) the chosen potentials remain a realistic empirical model for predicting the proposed structure of NCC, (ii) the iridescent colors' wavelengths of solid films are closely related to the distance between lattice planes, (iii) distance between lattice planes depends on the dispersion level of NCC suspension and (iv) MD simulations with such large numbers of particles allowed to model more realistic systems.

Keywords: nano crystalline cellulose, large-scale parallel molecular dynamic simulations, self-organization, optical and structural properties

1 INTRODUCTION

In this paper, we present investigations of interactions between NCC rods in liquid dispersion and then their organization in solid film. We try to reproduce experimental results for structural properties in liquid and solid phases to be able to interpret its optical behaviors. For this purpose, we simulate several thousands particles systems using parallel molecular dynamics. The long-accepted theories for answering this question have been challenged by results released by recent experiments. Herein we show from large-scale MD simulations the electrostatic interactions between charged NCC rods investigated on the basis of the Poisson-Boltzmann equation under the Debye-Hückel approximation [1,2]. The electrostatic free energy and interaction energy are obtained by the charging process.

We have made several measurements of distances between lattice planes of self-organized NCC rods in liquid dispersion prepared and sonicated to obtain a maximized dispersion level of NCC rods. In this work, we propose an original structure of the NCC rods self-organization and we try to predict, with molecular dynamics method, the proposed structure of this self-organization and distances between different lattice planes.

2 NCC BUILT MODEL

We use the Lennard-Jones (LJ) pair interaction potential to calculate minimum energy configurations between carbon atoms to build glucose chains. Then we pile up these chains of glucose to build a NCC rod.
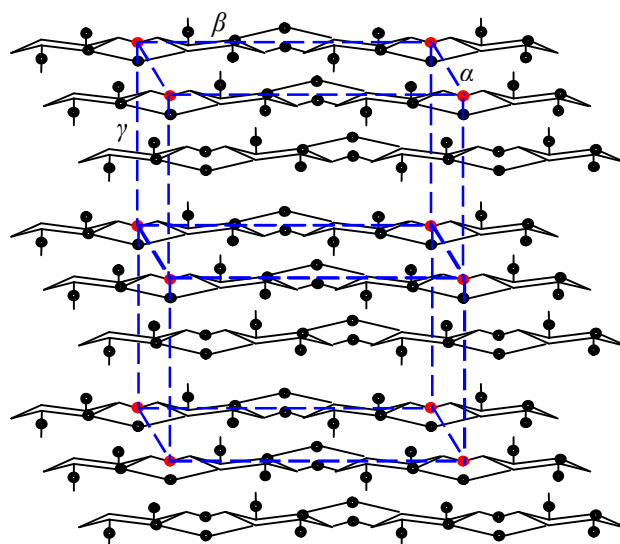

Figure 1: The plans of glucose chains overlapped in the LJ built NCC crystal.

Figure 1 shows the NCC crystalline structure built by molecular dynamics calculations using the LJ potential. Crystalline dimensions ($\alpha = 8,65$ Å, $\beta = 10,4$ Å and $\gamma = 7,45$ Å) obtained by our calculations are in good agreement with other experimental works and theoretical calculations [3,4,5,6].

According to our calculations, each NCC rod has a parallelepiped shape. Our model allows us to think that two opposite sides of the parallelepiped are negatively charged and the others are not as shown in Figure 2. This model is in good agreement with microscopic observations of Kondo [7]. Distances between chains and guidelines are consistent with measurements made by Kondo [7].

Several microscopic measurements [8,9,10,11] confirm that the native nano crystalline cellulose is mainly formed from $150 \times 10 \times 5$ nm^3 parallelepiped nano rods. We use these dimensions to model our molecular dynamic calculations of NCC rods.
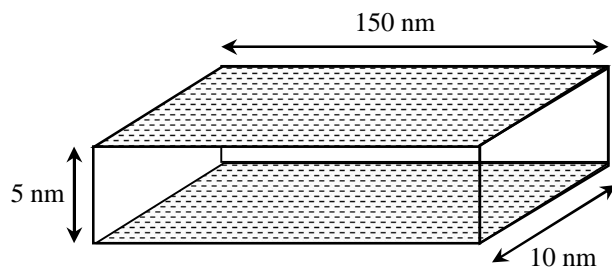

Figure 2: The modeled shape of NCC rod. Charged sides are the stripped ones.

The electric potential $u(r)$ established within the electrolyte solution enclosed by two planes can be depicted by the linearized Poisson-Boltzmann equation, which is valid as $Ze\ u(r) << k_BT$,

$$\frac{\partial^2 u(r)}{\partial x^2} + \frac{\partial^2 u(r)}{\partial y^2} = \frac{1}{\lambda_D^2} u(r), \qquad (1)$$

where λ_D is the Debye screening length, k_B the Boltzman constant and e the fundamental charge.

2.1 Interaction potential

Molecular dynamics simulation is one of the most powerful techniques, if not the only one, to study structural properties of this kind of particles in a liquid state and to test directly inter-particles interactions. To perform our molecular dynamics calculations we use an empirical repulsive Coulombian interaction potential. Mapping the particles positions by microscopy techniques, allows obtaining the radial distribution function $g(r)$, which measures the probability of finding a particle at a distance r from another. Determination of the radial distribution function $g(r)$ allows the calculation of the empirical interaction potential $u(r)$ that we used by the following equation system:

Ornstein-Zernike equation:

$$g(r) - 1 = c(r) + \rho \int c(r')[g(r - r') - 1] dr', \qquad (2)$$

and the Percus-Yevick equation:

$$c(r) = g(r)\left[1 - \exp\left(\frac{u(r)}{k_B T}\right)\right], \qquad (3)$$

where $k_B T$ is the thermal energy and ρ and T are respectively the system density and temperature. We solve this equation system with Lado algorithm [12,13].

This potential is strongly repulsive at short range and is able to correctly describe electrostatic interactions between NCC rods to reproduce their self-organization.

2.2 Molecular dynamics method

In order to determine properly the structure of NCC liquid dispersion, a sufficient spatial extension of the calculated functions is needed. Thus molecular dynamics (MD) simulations are performed using N = 500.000 to 4 millions NCC rods in a cubic box submitted to the standard periodic boundary conditions. To treat such a large number of particles subject to an empirical Coulombian interaction potential, we use a parallel algorithm based on the spatial decomposition of the simulation box. The computational load is therefore distributed among several processors of a parallel machine.

Such a large rod's number is used to minimize finite size effects. Verlet's algorithm [14] in the velocity form is used to produce a discrete phase-space trajectory in the micro-canonical ensemble (NVE) with a time step $\Delta t = 10^{-6}$s. For each state investigated, the system is equilibrated during 10^4 time steps before the production period of 10^6 time steps is achieved, essential to gather statistics over a large number of independent configurations.

Taking density measurements into account in the present work, we choose the parameters of our simulations to reproduce the experimental NCC density in the dispersion $\rho = 6.19 \times 10^{-6}$ mol/l at temperature $T = 25°C$. These data correspond to the experimental conditions at which structural and optical NCC properties in the stable liquid have been measured in our experiments. For this purpose, we carry out molecular dynamics simulations in the isobaric-isoenthalpic ensemble in order to obtain the thermodynamic state of interest. Stable states were produced by performing computer experiments from a very close thermodynamic equilibrium state where we put our system to reduce computing times. Beginning from the liquid state, we have chosen to investigate the situation in which the system is crunched stepwise by increasing the

density. This procedure is adopted to simulate the drying operation whose aim was the creation of solid films.

3 PHYSICAL PROPERTIES

If we build our system with perfectly identical NCC rods, witch an idealistic vision, they organize them-selves in the best known nematic structure widely described in the literature. We adopt a more realistic configuration with different sizes and charge distributions for the built NCC rods. We varied the token parameters (size and charge) in a range of 10%. We note that small groups of NCC rods agglomerate in microscopic ellipsoid bundles. Figure 3 shows the shape and dimensions of those bundles.
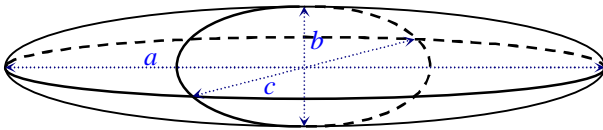

Figure 3: Bundle shape. According to our calculations, the mean values of the dimensions *a*, *b* and *c* are: $a = 2,16$ μm, $b = 0,17$ μm and $c = 1,05$ μm.

Our simulations, with large numbers of particles over long production periods allow large statistical samples. The structure obtained with those calculations is as described in Figure 4. Bundles are aligned next to each other in clusters of about twenty bundles wide and are stacked one above the other in different lattice planes.
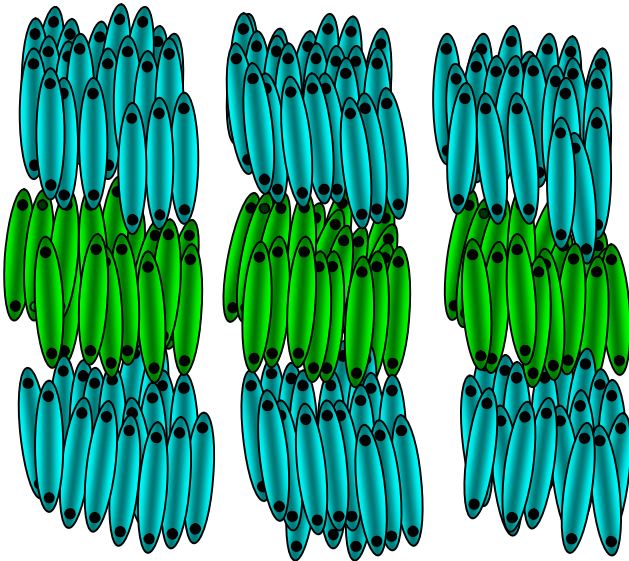

Figure 4: Lattice planes of self-organized bundles of NCC rods. Distances between lattice planes were calculated for different conditions.

Our experimental data are obtained on sonicated samples to obtain a maximized dispersion level. Then salt is added to stabilize the dispersion. To simulate those manipulations we modify the charge density of the NCC rods and the dispersion level of NCC suspension. In Figure 5, we display the distance between lattice planes obtained with our MD calculations in comparison with our recent experimental data. Measurement of this distance and prediction of the self-organization structure are in very good agreement with the experiment, as the consequence of our fitting procedure.
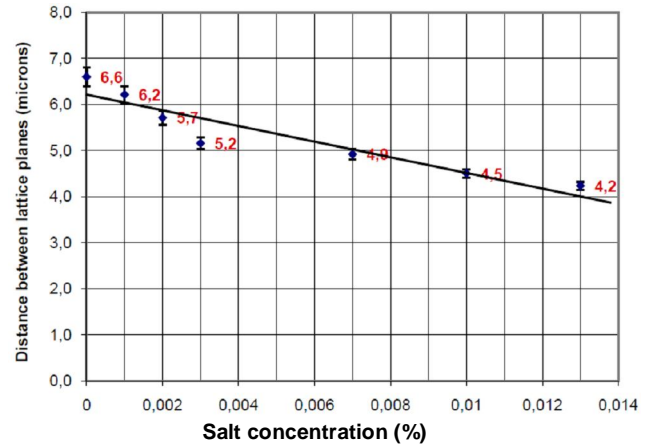

Figure 5: Experimental data of distance between lattice planes for several salt concentrations (points) compared with molecular dynamic calculations made with increasing charge density of the NCC rods (black line). We obtain the same results by varying the dispersion level of NCC suspension in our MD calculations.

Our measurements were made on NCC rods suspensions previously sonicated at different energy levels. We can now simulate the effects of sonication by varying the level of dispersion of NCC rods in the simulation box and by increasing the charge density of the NCC rods in molecular dynamic calculations. Thus we obtain a really good correlation between the model and experimental data.

To be sure that at equilibrium, NCC rods do not move much more and are in their specific arrangement; we check the mean-square displacement:

$$R^2(t) = \left\langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \right\rangle$$
$$= \left\langle \frac{1}{N} \sum_{i=1}^{N} |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \right\rangle \quad (4)$$

N being the total number of particles and $\mathbf{r}_i(t)$ the position vector of particle i at time t.

Mean-square displacement has been plotted against time for different densities and as expected, the mean-square

displacement has an asymptotic linear behavior for the studied states, which denotes a Brownian motion until the completion of bundles self-organization. After this, mean-square displacement becomes twisted and fluctuates slightly around the equilibrium position, which means that bundles do not move much more once self-organized. Each bundle has two kinds of interactions, electrostatic 'direct' interactions described by the empirical Coulombian potential and hydrodynamic interactions modeled by a virtual continuum medium.

4 CONCLUSIONS

The chosen empirical interaction potential used in this work gives us a good agreement for the structure of the NCC rods self-organization and the different distances between lattice planes with our recent experimental results. Therefore, it is suggested that as this theoretical structure is exactly known, this could now be used for the analysis of NCC optical properties. Studying the structure of NCC in dispersion, we will be able to predict the wavelengths of iridescent colors of solid films, which are observed in the experiments.

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