

Nano Crystalline Cellulose – Structural and Optical Properties by Molecular Dynamic Simulations

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ABSTRACT

Structural and optical properties of Nano Crystalline Cellulose (NCC) in liquid solutions were investigated by molecular dynamics simulation using empirical Coulombian interaction potential. The latter was modified by taking into account measurements of the density in the stable liquid at room temperature and atmospheric pressure.

Our calculations give a good description of the self-organization of NCC in liquid solution. On the other hand, the bond-angle distribution function between the different lattice planes allows us to predict the half period of this self-organization, and it compares quite well with the experimental measurements made by our research team. In the light of these experiments, our theoretical study indicates that (i) the chosen potential remain a realistic empirical model for the prediction of structural and optical properties of NCC and (ii) we can predict the wavelengths of iridescent colors of nematic films by the calculation of the bond-angle distribution function.

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

1 INTRODUCTION

How NCC rods interact with each other is one of the key issues that determine our ability to interpret experimental results for structural properties in liquid and solid phases and our ability to reproduce its optical behaviors. The long-accepted theories for answering this question have been challenged by results from recent experiments. Herein we show from molecular dynamic 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 solutions prepared and sonicated at different levels of energy. The role of sonication remains poorly understood but it was used, in our laboratory, to disperse the solution and to reveal the iridescent colors of the nematic films. In

this paper we try to predict, by the molecular dynamics method, the structure of this self-organization and the distances between different lattice planes

2 NCC BUILT MODEL

We use the Lennard-Jones 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 rod of NCC. According to our calculations, each rod of NCC 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 1. This model is in good agreement with microscopic observations of Kondo [3]. The distances between chains and guidelines are consistent with measurements made by Kondo [3].

Several microscopic measurements [4,5,6,7] confirm that the native nano crystalline cellulose is mainly formed from $150 \times 10 \times 5 \text{ nm}^3$ parallelepiped nano rods. That's way we took these dimensions to model our molecular dynamic calculations NCC rods.

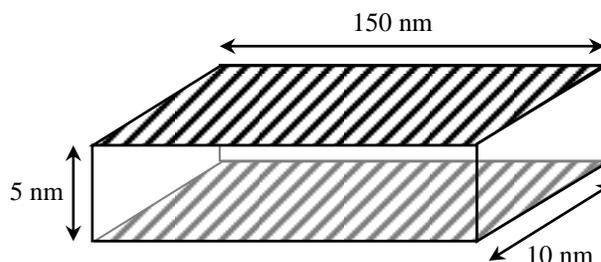


Figure 1: The modeled shape of NCC rod. The charged sides are the stripped.

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

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

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

2.1 Interaction potential

Molecular dynamics is one of the most powerful techniques, if not the only one, to study the structural properties of this kind of particles in the liquid state and to test directly the inter-particles interactions. To perform our molecular dynamic 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 for finding a particle at a distance r from another. The 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:

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

and the Percus-Yevick equation:

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

where $k_B T$ the thermal energy and ρ and T the system density and temperature respectively. We solve this equation system with Lado algorithm [8,9].

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

Taking the measurements of the density into account in the present work, we choose the parameters of our simulations to reproduce the experimental density of NCC in the solution $\rho = 6.19 \times 10^{-6}$ mol/l at temperature $T = 25^\circ\text{C}$. These data correspond to the experimental conditions at which the structural and optical properties of NCC in the stable liquid have been measured in our experiments. To do it, we carry out molecular dynamic simulations in the isobaric-isoenthalpic ensemble in order to obtain the thermodynamic state of interest. To fit and to test our model, we performed other calculations with two other densities, 3.69×10^{-6} mol/l and 7.46×10^{-6} mol/l at the same temperature. We made other experimental measurements under these conditions.

In order to calculate the structural properties of NCC in stable liquid, $N = 5324$ rods are set in a cubic box subject to the standard periodic boundary conditions. Such a large number of rods are used to minimize finite size effects. Verlet's algorithm [10] 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 great number of independent configurations.

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 at $T = 25^\circ\text{C}$ and $\rho = 3.69 \times 10^{-6}$ mol/l, we have chosen to investigate the situation in which the system is crunched stepwise by increasing the density. This procedure was adopted to simulate the drying operation whose aim was the creation of nematic films. The increase of density is obtained by reducing the size of the simulation box to get the final values $\rho = 6.19 \times 10^{-6}$ mol/l and $\rho = 7.46 \times 10^{-6}$ mol/l at $T = 25^\circ\text{C}$, which correspond to the experimental conditions investigated by our team.

3 PHYSICAL PROPERTIES

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

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

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 in Figure 2. As expected, the mean-square displacement has an asymptotic linear behavior for the states studied, which denote a Brownian motion until the completion of rods self-organization. After this, mean-square displacement becomes twisted and fluctuates slightly around the equilibrium position, which means that the rods do not move much more once self-organized. Each rod has two kinds of interactions, electrostatic 'direct' interactions described by the empirical Coulombian potential and hydrodynamic interactions modeled by a virtual continuum medium.

In Figure 3, we display the distance between anti-parallel lattice planes (planes 180° oriented between each other) obtained with our calculations in comparison with our recent experimental data. For the three densities, the measurement of this distance and the prediction of the self-organization half period are in very good agreement with the experiment, as the consequence of our fitting procedure.

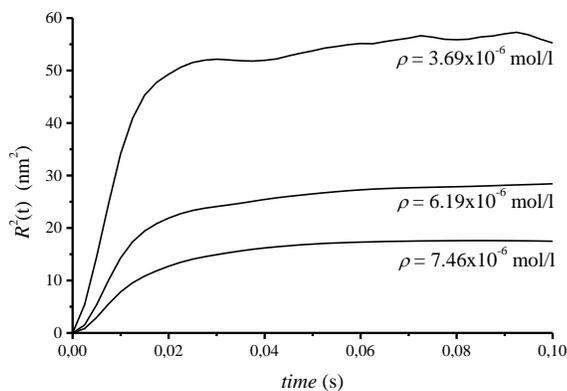


Figure 2: Mean square displacement as a function of time for three densities.

Other measurements were made on other NCC rods solutions previously sonicated at different energy levels. How sonication affects the NCC and their organization is not fully understood yet. But it appears that increasing the charge density of the NCC rods in molecular dynamic calculations could lead to a really good correlation between the model and experimental data.

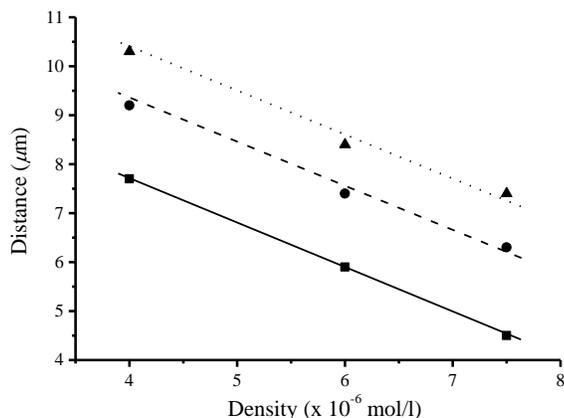


Figure 3: Distance between two anti-parallel lattice planes for three densities at 0 J sonication energy (circles), at about 500 J (squares) and at about 800 J (triangles). These experimental data are compared with our molecular dynamic calculations made with initial charge density (line) and made with increasing the charge density of the nano rods by 8 % (dashed line) and by 11 % (dotted line).

We now complete our analysis on the angular nature of the structural properties in considering the triplet correlation function $g_3(\theta, r_c)$. This latter measures the probability of finding neighbor, of a rod taken as the origin, with an angle θ between the two rods, provided that both the two rods are situated within a sphere of radius r_c . The

two considered rods, into r_c , are taken from two adjacent lattice planes. In Figure 4 we plot the bond-angle distribution function calculated between two anti-parallel lattices planes to obtain the half-period of the NCC self-organization in liquid phase. For both densities, our curves of $g_3(\theta, r_c)$ consist in a broad distribution with a single maximum containing a bump at around the mean angle between two successive lattice planes. Using this function we find the following angles between two adjacent lattice planes, 15.7° for 3.69×10^{-6} mol/l, 9.2° for 6.19×10^{-6} mol/l and 6.9° for 7.46×10^{-6} mol/l. This distribution demonstrates the tendency of the NCC rods to self organize in a helical shape [11,12].

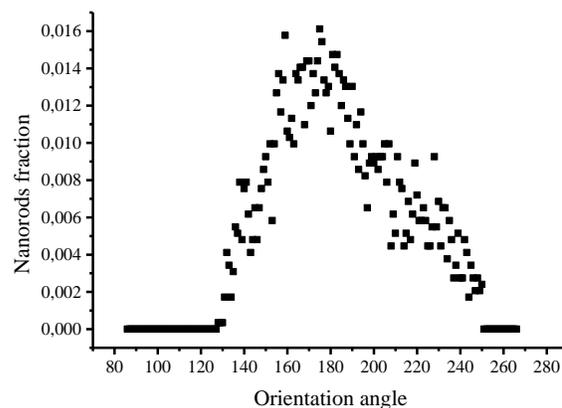


Figure 4: The bond-angle distribution function calculated between two anti-parallel lattices planes for 7.46×10^{-6} mol/l.

4 CONCLUDING REMARKS

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 and between rods with our recent experimental results. Therefore, it is suggested that as this bond-angle theoretical configuration is exactly known, this could now be used for the analysis of the optical properties of NCC. Studying the structure of NCC in suspension, we will be able to predict the wavelengths of iridescent colors of nematic films, which are observed in the experiments.

The authors would like to thank Valérie Vigne and Alice Vermeulin from the Quebec Institute of Graphic Communications for fruitful discussions during the course of this work.

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