Nano cellulose crystallites: optical, photonic and electro-magnetic properties

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ABSTRACT

Nano cellulose crystallites (NCC) are nano tubes, about 200 nm long and 10 nm in diameter. This is a natural product, found in trees. With unmodified NCCs, optical properties like iridescence and polarization were found either in aqueous suspension or in a dry state. To better understand and exploit the optical properties of NCCs, a mathematical model to describe the nano-crystalline cellulose NCC is presented. We use a periodic potential and allow the electrons to interact with each other by a weak coulombian potential. Thus, our model of the NCC is a finite cylinder; r and L are respectively, its radius and length. The carbon atoms are on the surface of the cylinder. They are arranged periodically. The model represents correctly the NCCs and is therefore fit for exploitation in the field of wood-based nano devices.

Keywords: cellulose, crystallite, optics, photonic, magnetic

1 INTRODUCTION

The nano crystalline cellulose (NCC) is one of the structuring components of trees. This is a natural product that was long time ago been identified by the pulp and paper industry. The NCCs were found together with the long fibers, essential elements for the preparation of paper. Typically, during the paper process, the fine fibers were separated from the long ones, and were simply rejected in massive volumes. As a consequence, the NCCs remained byproducts for nearly a century, its inherent qualities remaining largely unused.

Due to the present strong nanotechnological dynamism, the properties of the NCCs were revisited, and examined under a fresh perspective. Indeed, NCCs are 2D crystals, rolled up in a tubular geometry, about 200 nm long and 5 nm in diameter. The geometrical and chemical similarity with CNT is interesting, both containing carbon atoms. NCCs present mechanical properties comparable to fiber glass. Combined with the thinness of the nano tubes, an unusual flexibility is obtained, one of the best. For the fabrication of nano devices, this mechanical characteristics make the NCCs good candidates for commercial applications.

The NCC inner and outer surfaces are also chemically active: grafting of other chemical groups is therefore possible, providing the NCCs various potential fields of applicaitons. NCCs could also be deposited to coat surfaces. The permeation of gases though a fibril coat can be tailored to any value. This has an immediate application in solar cells, fuel cell or else, packaging in food industries. Indeed, the new trend is green, and the NCCs are fit for this challenge for those reasons. Together, the material is good for making composite structures, foams, and stratified layers for a large variety of applications.

The mechanical properties of the NCCs were also simulated with success. The modelisation by computer of the nano crystalline cellulose mechanical properties provides an excellent tool for nano engineering the product is goods for consumers. In this work, another interesting aspect of the NCCs that was not extensively investigated is presented. The optical and photonic properties of the nano crystals are approached from the electro-magnetic point of view. Indeed, with the unmodified NCCs, optical properties like iridescence and polarization were found either in aqueous suspension or in a dry state. As a matter of fact, NCC's naturally tends to self align under specific physico-chemical conditions. The interaction of the visible electro-magnetic waves with the monocrystal tubes apparently generates some rotational in the polarization plane. Moreover, various materials can be introduced in the tube inner volume, the lumen, providing them with electro-magnetic properties suitable for various specific applications.

2 MATHEMATICAL MODEL

We introduce a mathematical model to describe the nano-crystalline cellulose NCC. We use a periodic potential and assume the electrons to interact with each other by a weak coulombian potential.

Then we analyze the effects of light on the NCC described by a simple one-dimensional model. This external perturbation is a classical time function electromagnetic field polarized in the direction of the NCC. It is processed using the theory of linear response. The disruption is seen as a small perturbation of the system.

The NCC is a crystalline structure cylindrically shaped. Its length is about 200 nm and its diameter is about 10 nm. Thus, our model of the NCC is a finite cylinder; r and L are respectively, its radius and length. The carbon atoms are on the surface of the cylinder. They are arranged periodically. Each atom has six electrons. We assume that only one electron can relocate and be seen as a "free" particle. The two heart electrons are localized around the nucleus. The other three electrons participate in the inter-atomic bonds. The NCC is modeled as N-electrons system on the surface of a cylinder. These electrons are subjected to a periodical potential. It is assumed that the atoms are immobile. We adopt the Born-Oppenheimer approximation. We neglect the interaction between electrons and phonons. We use the periodic boundary conditions for the Hamiltonian describing the system.

One point of the cylinder is located by $x \in \left[-\dfrac{L}{2}, \dfrac{L}{2} \right]$ along the axis cylinder and by $y \in \left[-\pi r, \pi r \right]$ following the circumference. We use a periodic potential in x and y.

We model the potential by the V_{at} function. a and b are, respectively, the longitudinal and the transversal periods of atoms. So, for each fixed x and y,

$$V_{at}(x+a, y) = V_{at}(x, y) = V_{at}(x, y+b) \qquad (1)$$

The rectangle $a \times b$ contains in most configurations over 4 atoms. L, N, a and b are linked because the length of the cylinder as well as the perimeter are multiples of an entire number of atoms. We assume that it has n atoms in the $a \times b$ rectangle area. We choose N pairs and we obtained:

$$\frac{L}{a} \times \frac{r}{b} \times n = N \qquad (2)$$

where n is the electrons number in $a \times b$.

We suppose the potential attractive. First, we suppose that we have a single electron on the cylinder where N ions are present. Its Hamiltonian is:

$$\mathbf{H}_1 = -\frac{\hbar}{2m_e}\frac{\partial^2}{\partial x^2} \otimes 1 + 1 \otimes -\frac{\hbar}{2m_e}\frac{\partial^2}{\partial y^2} + V_{at}(x, y) \qquad (3)$$

with m_e the electron mass.

V_{at} depends on the physical parameters ε, the cylinder permittivity and e, the electron load, so:

$$V_{at}(x, y) = \frac{e^2}{\varepsilon}\widetilde{V}_{at}(x, y) \qquad (4)$$

where $\widetilde{V}_{at}$ is a none dependent on physical constants function.

The same goes for the potential for interaction between electrons. We make the change of variables: $\widetilde{x} = x / a_0, \widetilde{y} = y / a_0$ where:

$$a_0 = \frac{\hbar^2 \varepsilon}{m_e e^2} \qquad (5)$$

Energy will be a multiple of the Rydberg constant of the material:

$$R_y = \frac{\hbar^2}{2m_e a_0} \qquad (6)$$

Thus the physical constants will not appear explicitly in the Hamiltonian.

We want to study some optical properties of the NCC which heavily depend of the interactions between the electrons. So we will introduce in the Hamiltonian a potential describing this coupling. We choose naturally a "periodical" Coulomb potential usually used when we work in a finite box, with periodic boundary conditions.

We note that (x, y), $x \in \mathbb{R}$, $y \in \left[-\pi r, \pi r \right]$, the coordinates of a point on the infinite cylinder. We introduce the distance d_{12} between two particles $(x_1; y_1)$ and $(x_2; y_2)$ on the surface of the cylinder:

$$d_{12} = d_{12}(x_1 - x_2, y_1 - y_2) \qquad (7)$$

$$d_{12} = \sqrt{(x_1 - x_2)^2 + 4r^2 \sin\frac{y_1 - y_2}{2r}} \qquad (8)$$

$\left| 2r \sin\dfrac{y_1 - y_2}{2r} \right|$ is the length of the rope connecting two points y_1 and y_2 on the circle of radius r.

The function

$$V_c^r(x,y) = \frac{\lambda}{\sqrt{x_2 + 4r^2 \sin^2 \dfrac{y}{2r}}} \quad (9)$$

for $\quad x \in \mathbb{R}, x \in [-\pi r, \pi r]$

with $\lambda > 0$. The expression above with $\lambda = 1$ is the Coulomb potential on the infinite cylinder.

We choose to treat the case of weak interactions between electrons. The parameter λ is then very small.

The Hamiltonian associated with the N electrons system is formally defined by

$$H_C = \sum_{j=1}^{N} \left(-\frac{1}{2}\frac{\partial^2}{\partial x_j^2} - \frac{1}{2}\frac{\partial^2}{\partial y_j^2} + V_{at}(x_j, y_j) \right)$$
$$+ \sum_{j \neq k=1}^{N} V_C^{r,L}(x_j - x_k, y_j - y_k) \quad (10)$$

The first simplification of the problem is that the radius of the NCCs is very small. This characteristic property of the NCCs led to the strengthening of interaction between electrons.

We established that the potential between electrons is:

$$v_L(x_1 - x_2) =$$

$$\frac{1}{(2\pi r)^2} \int_{-\pi r}^{\pi r} \int_{-\pi r}^{\pi r} V_C^{r,L}(x_1 - x_2, y_1 - y_2) dy_1 dy_2 \quad (11)$$

$$= \frac{1}{2\pi r} \int_{-\pi r}^{\pi r} V_C^{r,L}(x_1 - x_2, y) dy \quad (12)$$

And the atomic potential projected on the circle is:

$$v_{at}(x) = \frac{1}{2\pi r} \int_{-\pi r}^{\pi r} V_{at}(x, y) dy \quad (13)$$

$$= \frac{1}{2\pi} \int_{-\pi}^{\pi} V_{at}(x, ry) dy \quad (14)$$

3 PHYSICAL MODEL

After introducing a mathematical model for the NCCs, summarized in the Hamiltonian $\mathbf{H}_c$, we used one of the properties of the NCC, their small diameter, to reduce the problem to a one-dimension Hamiltonian $\mathbf{H}_0$. This better reflects the low dimensional nature of the nano objects, in the shape of hollow nano cylinders.

A low amplitude and frequency variable monochromatic light is passed through the NCCs. Part of this light is absorbed by the electrons and allows the system cylinder + N electrons moving in an excited state. The other part, not absorbed, travels through the cylinder and is measured. Thus we obtained the absorption spectrum, depending on the frequency of light.

We apply an electromagnetic field classic, time-dependent, modeling light. We want to know the linear answer of the system to this disturbance.

To model the incident monochromatic light, we introduce the electric field $E(t)$, $E_0 > 0$ is the field amplitude and $\omega > 0$ its frequency. The adiabatic lighting is controlled by the parameter $\eta > 0$:

$$E(t) = E_0 \cos(\omega t) \exp(\eta t) \quad (15)$$

The Space is one-dimensional, and we are on a circle. It is impossible to define the disruption caused by the light from the electric field as we do normally in the Coulomb gauge, because the potential partner is not periodic. We use a different gauge:

$$a(t) = \mathrm{Re}\left(\frac{\exp(i\omega t + \eta t)}{i\omega + \eta} \right)$$

$$= \frac{\eta \cos(\omega t) + \omega \sin(\omega t)}{\omega^2 + \eta^2} \exp(\eta t) \quad (16)$$

$$a'(t) = \frac{da(t)}{dt} = \mathrm{Re}(\exp(i\omega t + \eta t))$$

$$= \cos(\omega t) \exp(\eta t) \quad (17)$$

so: $\quad E(t) = E_0 a'(t) \quad (18)$

The N electrons system with the light disturbance is described by the Hamiltonian:

$$H(t) = \frac{1}{2} \sum_{j=1}^{N} \left\{ \left(\frac{1}{i} \frac{\partial}{\partial x_j} - a(t)E_0 \right)^2 + v_{at}(x_j) \right\}$$

$$+ \frac{1}{2} \sum_{j \neq k=1}^{N} v_L(x_j - x_k) = H_0 + W(t) \qquad (19)$$

$$W(t) = -a(t)E_0 \sum_{j=1}^{N} \frac{1}{i} \frac{\partial}{\partial x_j} + \frac{1}{2} Na^2(t)E_0^2 \qquad (20)$$

4 CONCLUSION

In this work, we study the linear response of the NCC to the light excitation. We use two approaches: numerical simulation using *ab initio* methods and the theory of perturbation to get the absorption spectrum of the NCC. Then we graft metal atoms on the cylindrical wall of the NCC to change the conduction properties of the NCC and measure its influence on the optical response.

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