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# Orienting cellulose nanocrystal functionalities tunes the wettability of water-cast films

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## Abstract

Cellulose nanocrystal (CNC)-based materials display apparently erratic wetting behaviors with contact angle (CA) variations as large as 30° from sample to sample. This work hypothesizes that it is the orientation of CNC amphiphilic functionalities at the interface with air that causes the variability in CA. By exploiting relationships with Hansen solubility parameters theory, a set of surface tension parameters is proposed for both the polar and the non-polar surfaces of cellulose I<sub>β</sub> nanocrystals. These coefficients elucidate the wettability of CNC materials by establishing a correlation between the wetting properties of the air/sample interface and its chemical composition in terms of non-polar moieties. Advancing/receding CA experiments suggest that while spin-coating CNC suspensions yields purely polar films, oven-casting them produces amphiphilic surfaces. We proposed a mechanism where the state of dispersion (individual or agglomerated) in which CNCs reach the air/water interface during casting is

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3 the determining factor: while individual nanocrystals find it more stable to orient their  
4 non-polar surfaces toward the interface, the aspect ratio of CNC agglomerates favors an  
5 orientation of their polar surfaces. This represents the first compelling evidence of CNC  
6 orientation at an interface and can be applied to Pickering emulsions, nanocomposites,  
7 and to the production of CNC materials with tuned wettability.  
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## 15 Introduction

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18 Cellulose nanocrystals (CNCs) are biosourced rod-like nanoparticles whose high aspect ratio  
19 and mechanical properties may find applications in multiphase and interfacial systems such  
20 as nanocomposites, Pickering emulsions, and membranes.<sup>1-4</sup> This potential is favored by the  
21 amphiphilic nature of cellulose I<sub>β</sub> allomorph, whose surfaces display alternating polar and  
22 non-polar regions around their circumferences: this means that a simple rotation around  
23 their axis may change the nature of the functionalities exposed by these nanocrystals.<sup>2,5</sup>  
24 Polar surfaces are hydroxyl rich and usually negatively charged due to the presence of sulfate  
25 half-ester groups introduced during the sulfuric acid hydrolysis production step (the most  
26 common approach for large-scale production). Non-polar surfaces display C-H bonds and  
27 are described as being thinner than their polar counterparts.<sup>6,7</sup>  
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38 Investigating the orientation and the adhesion of CNCs at various interfaces is crucial  
39 to predict the stabilizing effect they may bring to multiphase systems. As a measure of a  
40 material's cohesive interactions, surface tension,  $\gamma$ , is the main predictor for the work of  
41 adhesion between a substrate and its environment. Attempts to estimate CNC surface ten-  
42 sion were essentially conducted through contact angle measurements,<sup>8-10</sup> but also through  
43 gas chromatography<sup>11</sup> and computer simulations.<sup>12</sup> Experimental approaches carried over  
44 large quantities of material usually yield surface tensions values that average the behavior  
45 of CNCs and cannot distinguish polar from non-polar surfaces. While computer simulations  
46 may overcome this problem, their results cannot be verified experimentally and surface ten-  
47 sions tend to be suspiciously high, with up to 155 mN m<sup>-1</sup> being reported.<sup>12</sup> This is to be  
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3 compared with  $\sim 20$  to  $50 \text{ mN m}^{-1}$  for commodity polymers.<sup>13</sup> Overestimation may arise from  
4 the hypotheses that must be formulated for the simulations to converge. Mazeau and Rivet<sup>14</sup>  
5 had, for instance, to hypothesize that CNC surfaces are flat and  $\sim 10 \text{ nm}$ -wide (nearly twice  
6 the diameter of a nanocrystal) in order to study their wetting behavior.  
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11 Here, we propose an alternate approach that combines modeling, to discriminate between  
12 the amphiphilic surfaces of the nanocrystals, with experimental validation. The model, which  
13 does not require any computer simulations, relies on two recent empirical investigations: the  
14 first determined the Hansen solubility parameters (HSP) of CNC polar and non-polar sur-  
15 faces;<sup>6</sup> the other established the first correlations between Hansen solubility and surface  
16 tension parameters for solids.<sup>15</sup> The method provides estimates for the surface tension pa-  
17 rameters of CNC surfaces that rely on empirical evidences only.  
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25 Experimental validation requires the production of macroscopic surfaces with a controlled  
26 orientation of the nanocrystals. There, our approach relies on the wetting behavior of CNC  
27 thin films: the water contact angle was measured to be as low as  $\sim 10^\circ$  on films prepared  
28 from spin-coated suspensions<sup>8</sup> and as high as  $\sim 45^\circ$  on films prepared by compressing CNC  
29 pellets.<sup>9</sup> Oven-cast films have intermediate water contact angle values.<sup>8,9</sup> The influence of the  
30 casting protocol, when discussed, is sometimes attributed to differences in surface roughness  
31 between the films.<sup>9</sup> This interpretation does not, however, hold up to scrutiny: ranking the  
32 films by roughness, spin-coated films are expected to be the smoothest, then oven-cast films,  
33 and finally those prepared from the compression of pellets. Based on Wenzel's equation for  
34 hydrophilic materials in the homogeneous wetting regime,<sup>6,16</sup> spin-coated films should hence  
35 have the highest water contact angle –the opposite is observed. Dankovich and Gray<sup>8</sup> noted  
36 that thicker CNC films (obtained through oven-casting) resulted in higher water contact angle  
37 values than thinner films (obtained through spin-coating). Their argumentation revolved  
38 around the thickness of the films and their potential for swelling.<sup>17</sup> While significant swelling  
39 of CNC films has indeed been reported with polar liquids,<sup>17</sup> this does not explain why large  
40 variations are also observed with a non-polar liquid such as diiodomethane.  
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Instead, our interpretation is that the variations observed in contact angles values capture a reorientation of the amphiphilic moieties of CNC particles at the air/sample interface as a function of the casting protocol. A similar argument is formulated to justify the stability provided by CNC particles at the interface of oil/water Pickering emulsions.<sup>7,18,19</sup> There, CNCs are thought to orient their non-polar surfaces toward the oil and their polar surfaces toward water. If such a mechanism is possible in micro-emulsions, it should also occur at the air/water interface of aqueous CNC suspensions and be reflected by the wettability of the films cast from these suspensions. Bertsch et al.<sup>20,21</sup> indeed demonstrated that a significant CNC adsorption at the air/water interface into a loose monolayer may occur over time for colloidal CNCs. Salt addition is critical for the formation of a dense viscoelastic layer in dilute conditions, but this requirement decreases with CNC concentration: a viscoelastic layer is observed from 25 mM of NaCl at 0.3 wt% of CNCs, and from 20 mM of NaCl at 0.5 wt% of CNCs.<sup>20,21</sup> At higher concentrations (starting in this work from 3 wt%) and upon drying, it is likely that this process will be observed even in the absence of added salt. What is left to determine is which surfaces these nanoparticles adsorb from at the interface. Our hypothesis is thus that the casting protocol has the potential to influence the migration and the orientation of CNC particles at the interface with air. This interface may then be investigated with liquids, whose wetting behaviors reflect the composition of the sample surface down to the molecular-scale.

Hence, this work first produces estimates for the surface tension parameters of CNC amphiphilic surfaces. These coefficients are used to predict how modeled surfaces, with various ratios of non-polar over polar functionalities, would behave upon wetting. The predictions are then compared with experimental results obtained on thin films that were either oven-cast or spin-coated. This yields an estimation of the surface fractions in non-polar moieties on both kinds of films. Using two probe liquids, ethylene glycol (EG) and diiodomethane (DIM), it is possible to validate our approach. These liquids were selected in order to minimize kinetic effects such as swelling (water was found unsuitable to yield high quality contact

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3 angle data on CNC materials). Our approach establishes that CNCs should be considered as  
4 amphiphilic particles that can orient their functionalities at air/sample interfaces and that  
5 this orientation process can influence macroscale properties such as surface wettability. A  
6 speculative mechanism is proposed to describe the influence of the casting protocol on the  
7 composition of the interface. It may apply to the production of CNC materials with tuned  
8 wetting behaviors. Finally, by providing the first experimentally-validated estimates for the  
9 surface tension parameters of CNC polar and non-polar surfaces, this work opens the field  
10 to quantitative predictions of CNC behavior in suspensions and multiphase systems such  
11 as Pickering emulsions and polymer blends. Note that a nomenclature of the symbols and  
12 abbreviations employed throughout this work is provided in Table SI.1.

## 23 24 25 **Experimental Section**

### 26 27 28 **Cellulose nanocrystals**

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31 Cellulose nanocrystals were provided by Celluforce (Montreal, QC, Canada) as a spray-dried  
32 powder. They were produced through the sulfuric acid hydrolysis of a bleached softwood  
33 kraft pulp followed by neutralization with sodium hydroxide. Since morphology has been  
34 reported to play a major role in the behavior of CNC particles at interfaces,<sup>5</sup> a detailed  
35 structural characterization of the particles is performed in supplementary information (SI).  
36 It includes transmission electron microscopy (TEM), elemental analysis, Zeta-potential, and  
37 X-ray-diffraction (XRD). Fig. 1.a is a TEM image of the rod-like nanocrystals that shows a  
38 mix of individual and agglomerated particles. It was obtained by drying a dilute suspension  
39 of nanocrystals over a TEM grid. Nanocrystals are  $\sim 7\text{-}8$  nm wide and  $\sim 105\text{-}120$  nm long  
40 based on these analyses (see details and protocols in SI). Fig. 1.b are atomic force microscopy  
41 (AFM) height images of CNCs that were either spin-coated (left) or oven-cast (right). The  
42 micrographs are  $2\ \mu\text{m}$  wide and were flattened (by a second-order polynomial) in order to  
43 remove their mesoscale roughness: they highlight the parallel alignment of CNC particles at  
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the air/sample interface.

For graphical purposes, this work considers CNCs to have an octagonally-shaped cross-section as per Kalashnikova et al.<sup>7</sup> (Fig. 1.c). The validity of this hypothesis is discussed in SI and supported by the deconvolution of the XRD spectra and their analysis using Scherrer's equation.<sup>22-24</sup> Neglecting the extremities of the rod, a cellulose  $I_{\beta}$  nanocrystal exposes up to four different kinds of lateral surfaces, each corresponding to a lattice plane: (010), (110), ( $1\bar{1}0$ ), and (200).<sup>5</sup> While (200) surfaces primarily display C-H bonds, the three others are rich in hydroxyl groups and have roughly equivalent chemistries.<sup>6,12,25</sup> They will be referred as non-polar and polar surfaces throughout this work and be represented in yellow and blue, respectively. Hence, CNCs display a majority of polar surfaces that are combined with some non-polar ones. This is coherent with their behavior in suspensions where CNCs display a predominantly polar behavior doubled by a non-polar component.<sup>6,26</sup>

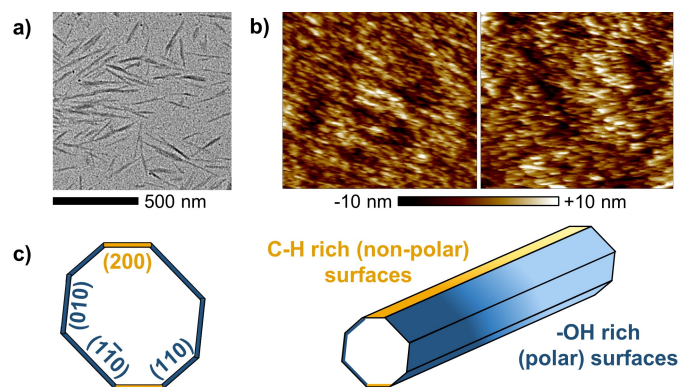


Figure 1: Morphology and representation of cellulose  $I_{\beta}$  nanocrystals. **(a)** TEM image of individual and agglomerated CNCs. **(b)** AFM height images of spin-coated (left) and oven-cast (right) CNCs. Micrographs are  $2\ \mu\text{m}$  wide and were flattened (by a second-order polynomial) in order to remove their mesoscale roughness. **(c)** On the left is the cross-section of a cellulose  $I_{\beta}$  nanocrystal: polar surfaces  $-(010)$ ,  $(110)$ , and  $(1\bar{1}0)$  lattice planes– are plotted in blue, and non-polar ones  $-(200)$  lattice planes– are in yellow. On the right is a scheme of the octagonally-shape nanocrystal: its lateral surfaces are constituted of polar and non-polar stripes.

## CNC film preparation

Spray-dried CNCs were dispersed in water at a concentration of  $30 \text{ mg}_{\text{CNC}}/\text{mL}$  using an ultrasonic probe (Cole-Parmer), which operated with a CV334 converter and a tapered microtip. The suspensions were prepared adding 15 mL of water atop 0.45 g of CNCs in a glass vial (2.1 cm of radius). As per Beuguel et al.<sup>27</sup>, an energy of 4.5 kJ ( $10 \text{ kJ}/\text{g}_{\text{CNC}}$ ) was then provided to the system at a frequency of 20 kHz and a power of  $\sim 30 \text{ W}$  using ON-OFF pulses (5s-2s) and an ice bath to avoid any overheating. Since our CNCs do not form significant structuring below  $\sim 40 \text{ mg}_{\text{CNC}}/\text{mL}$ ,<sup>27</sup> the resulting suspensions are expected to be isotropic. The suspensions were either poured in a polystyrene Petri dish (10 cm of diameter) and placed in an oven (OV-11, MBI Lab Equipment) at  $60 \text{ }^\circ\text{C}$  and near atmospheric pressure ( $\sim 0.9 \text{ bar}$ ) for 24 h, or used for spin-coating. In the latter, a few mL of suspension were placed at the center of a polished n-type Si wafer (15 cm of diameter), that was spun at 500 rpm (revolutions per minute) for 20 s in a spin-coater (Brewer Science CEE-200). Immediately after, the spun-discs were deposited on a hot plate ( $60 \text{ }^\circ\text{C}$ ) for a few minutes. Drying, evidenced by the apparition of iridescent patterns, occurred within a few seconds. The spin-coating process, from liquid deposition to iridescent patterns formation was typically shorter than 2 min.

While the oven-cast (OC) films were free-standing (thickness of  $\sim 40 \text{ }\mu\text{m}$ ) and could be analyzed as such, the spin-coated (SC) layer ( $\sim 1 \text{ }\mu\text{m}$  thick) was stuck on the support. Hence, analyses of SC thin films were carried on the layer still deposited atop the Si wafer. Those requiring a minimal thickness for the sample, such as XRD and elemental analysis, were only performed on the OC films.

## Contact angle measurements

Contact angle measurements were performed at room temperature ( $\sim 23 \text{ }^\circ\text{C}$ ) on a OCA20 tensiometer (DataPhysics Instruments GmbH) operating with a high-resolution CCD camera and a motorized syringe (0.50 mm of outer diameter). Ethylene glycol (EG) and di-



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3 iodomethane (DIM) were used as probe liquids. Through pendant drop experiments, their  
4 surface tensions were found to be within  $1 \text{ mN m}^{-1}$  ( $\sim 2\%$ ) of their theoretical values ( $48 \text{ mN m}^{-1}$   
5 for EG, and  $50.8 \text{ mN m}^{-1}$  for DIM). From casting to testing, thin films were stored with covers  
6 in a ventilated environment. Prior to analyses, their surfaces were subjected to a cleaning  
7 with compressed air in order to desorb any potential contaminant and remove humidity  
8 traces. Cleaning was achieved with a compressed air gun operating at  $\sim 2$  bar for  $\sim 1$  min.  
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11 In a typical static sessile drop experiment, a droplet of  $3 \mu\text{L}$  is grown at the tip of the  
12 syringe, far from the sample, at a rate of  $0.5 \mu\text{L s}^{-1}$ . It is then deposited on the substrate  
13 and the measurement is taken after 5 s based on the video footage.  
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16 For advancing/receding contact angle (ARCA) experiments, the tip of the needle was first  
17 cleaned with the probe liquid, dried, then placed at  $\sim 0.5$  mm from the substrate. A volume  
18 of  $4 \mu\text{L}$  (DIM as probe liquid) or  $5 \mu\text{L}$  (EG) was then injected at a rate of  $0.1 \mu\text{L s}^{-1}$ . The  
19 discrepancy between DIM and EG in terms of injected volumes arises from their differences  
20 in terms of dewetting behaviors: a lower receding CA value (as with EG) requires to grow  
21 a larger drop in order to witness any receding. Once the injection was completed, and after  
22 a delay of at least 5 s (typically  $\sim 10$  s), the liquid was withdrawn from the substrate at the  
23 same rate ( $0.1 \mu\text{L s}^{-1}$ ). The drop remained roughly axissymmetric during the whole process.  
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27 ARCA measurements were obtained based on video footages. The baseline and the shape  
28 of the drop were fitted automatically as a function of the light contrast between the drop, the  
29 substrate, and the background. The contact angle was then determined using the Young-  
30 Laplace equation. A manual fitting was performed for each test to confirm the validity of  
31 the automatically-derived measurements. Measurements were performed during the period  
32 where the base diameter of the drop,  $D^{\text{drop}}$ , was greater than 3 mm (six times the diameter of  
33 the needle) in order to minimize the influence of the needle over the shape of the droplet.<sup>28</sup>  
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# A model for the wettability of CNC films based on the orientation of their lattice plane

## Contact angles: a background

A liquid droplet sitting on a surface has a three-phase boundary between the liquid, the solid, and the air, that is characterized by its contact angle (CA).<sup>29</sup> Ideal substrates are expected to be flat, rigid, chemically homogeneous, and unperturbed by the chemical interactions they may form with the liquid.<sup>30</sup> There, the Young contact angle,  $\theta_Y$ , is the single CA that may form at rest: it is a thermodynamic equilibrium that may be met independently of the sample's or the drop's history.<sup>29</sup> According to Young's equation,  $\theta_Y$  is a function of the surface tensions of the solid,  $\gamma^s$ , of the liquid,  $\gamma^l$ , and of the interfacial tension between the liquid and the solid,  $\gamma^{s/l}$ .<sup>29</sup>

$$\gamma^s = \gamma^{s/l} + \gamma^l \cos(\theta_Y) \quad (1)$$

On real substrates, deviations from ideality create hysteresis, defined as a difference between the wetting and dewetting behaviors. Irregularities impede the progression of the liquid upon wetting, and prevent its receding upon dewetting.<sup>29</sup> In a dynamic experiment, the highest CA value is thus measured in advancing conditions: the advancing contact angle,  $\theta_a$ ; and the lowest CA in receding conditions: the receding contact angle,  $\theta_r$ . The contact angle hysteresis,  $H$ , is defined as  $H = \theta_a - \theta_r$  ( $H \geq 0^\circ$ ).  $H$  is a direct measure of a sample's deviation from ideality.<sup>29</sup>

There are two kinds of hysteresis: kinetic and thermodynamic.<sup>29-31</sup> Kinetic hysteresis arises from physical and chemical interactions occurring at the interfaces.<sup>30</sup> It includes: swelling, chemical reactions, and reorientation of the functional groups at the liquid/solid interface; evaporation at the air/liquid interface; adsorption of contaminants or vapor molecules at the air/solid interface; or the diffusion of liquid throughout the sample. Thermodynamic

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3 hysteresis is caused by surface heterogeneities in terms of roughness or chemistry.<sup>30</sup> In prac-  
4 tice, near ideal substrates have an hysteresis in the range of 1-2°, and  $H$  commonly reaches  
5  $\sim 10^\circ$  for real substrates.<sup>29-31</sup> It may be as high as 50-60° in some circumstances.<sup>32</sup>  
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9 In this work, kinetic and roughness-induced hystereses were minimized, respectively by  
10 appropriately identifying the most suited probe liquids (SI: section “Minimization of ki-  
11 netic hysteresis”) and by producing films whose surface roughness is in the range of a single  
12 nanocrystal diameter (SI: section “Thermodynamic hysteresis”). This leaves chemical het-  
13 erogeneity as the main source of hysteresis.  
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## 19 20 21 **Wettability of real chemically heterogeneous surfaces**

  
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23 Assuming an expression for the interfacial tension between the liquid and the solid,  $\gamma^{s/l}$ , it is  
24 possible to measure the theoretical Young contact angle from  $\gamma^s$  and  $\gamma^l$ , only. Several models  
25 were proposed for  $\gamma^{s/l}$ , the most employed being the Owens-Wendt-Rabel-Kaelble (OWRK)  
26 model. It splits the total surface tension,  $\gamma$ , into a dispersive,  $\gamma_D$ , and a polar component,  
27  $\gamma_P$  (Eq. 2).  $\gamma_P$  accounts both for dipole-dipole and Lewis acid/base (including H-bonding)  
28 interactions.  
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$$35 \quad \gamma = \gamma_D + \gamma_P \quad (2)$$

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38 The OWRK model expresses the total interfacial tension  $\gamma^{s/l}$  as a geometric mean that  
39 considers  $\gamma^s$  and  $\gamma^l$  components:  
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$$45 \quad \begin{aligned} \gamma^{s/l} &= \gamma_D^{s/l} + \gamma_P^{s/l} \\ &= \left( \sqrt{\gamma_D^s} - \sqrt{\gamma_D^l} \right)^2 + \left( \sqrt{\gamma_P^s} - \sqrt{\gamma_P^l} \right)^2 \\ &= \gamma^s + \gamma^l - 2 \left( \sqrt{\gamma_D^s \gamma_D^l} + \sqrt{\gamma_P^s \gamma_P^l} \right) \end{aligned} \quad (3)$$
  
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54 Note that a good compatibility between the materials results in a low interfacial tension.  
55 It is null ( $\gamma^{s/l}=0$ ) if the components of the liquid match those of the solid. Combining  
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Eqs. 1&3 yields:

$$\cos(\theta_Y) = \frac{2}{\gamma^l} \left( \sqrt{\gamma_D^s \gamma_D^l} + \sqrt{\gamma_P^s \gamma_P^l} \right) - 1 \quad (4)$$

This equation is only valid if  $\gamma^s < \gamma^l + \gamma^{s/l}$ , which, in practice, remains the case as long as the surface tension of the liquid is high enough. Otherwise, the liquid totally wets the surface, thus forming a zero-contact angle. Van Oss et al.<sup>33</sup> proposed a threshold of  $\gamma^l \gtrsim 44 \text{ mN m}^{-1}$  above which probe liquids should be suitable for the analysis of most common surfaces.

Surface roughness may shift the value of  $\theta_Y$ , and an apparent Young's ("Wenzel") contact angle,  $\theta_W$ , is measured instead.<sup>16,29</sup> In the homogeneous wetting regime, this may be accounted for by the Wenzel equation, in which  $r_{\text{surf}}$ , dimensionless, is defined as the surface area of the sample divided by its projected surface area ( $r_{\text{surf}}=1$  for a perfectly smooth surface):

$$\cos(\theta_W) = r_{\text{surf}} \cos(\theta_Y) \quad (5)$$

$r_{\text{surf}}$  stood at  $1 < r_{\text{surf}} \leq 1.02$  for all our samples due to their relative flatness (see SI). Our modeling hence assumes that  $\cos(\theta_W) \approx \cos(\theta_Y)$ .

Chemical heterogeneity may be accounted for using a generalized Cassie-Baxter equation.<sup>34</sup> CNCs are amphiphilic particles, on which the liquid is expected to form a Young's contact angle equal to  $\theta_Y^{\text{ps}}$  with polar surfaces ("ps") that have a higher surface energy, and equal to  $\theta_Y^{\text{nps}}$  with non-polar surfaces ("nps") that have a lower surface energy ( $\theta_Y^{\text{nps}} > \theta_Y^{\text{ps}}$ ). On a substrate composed by a mix of these polar and non-polar surfaces, with respective surface fractions of  $f^{\text{ps}}$  and  $f^{\text{nps}}$  (with  $f^{\text{ps}}=1-f^{\text{nps}}$ ), a composite contact angle,  $\theta_{\text{comp}}$ , is measured.<sup>34</sup>

$$\cos(\theta_{\text{comp}}) = f^{\text{nps}} \cos(\theta_Y^{\text{nps}}) + (1 - f^{\text{nps}}) \cos(\theta_Y^{\text{ps}}) \quad (6)$$

Combining Eq. 6 with Eq. 4 applied to polar and non-polar surfaces yields:

$$\cos(\theta_{\text{comp}}) = \frac{2}{\gamma^l} \left[ f^{\text{nps}} \left( \sqrt{\gamma_{\text{D}}^{\text{nps}} \gamma_{\text{D}}^l} + \sqrt{\gamma_{\text{P}}^{\text{nps}} \gamma_{\text{P}}^l} \right) + (1 - f^{\text{nps}}) \left( \sqrt{\gamma_{\text{D}}^{\text{ps}} \gamma_{\text{D}}^l} + \sqrt{\gamma_{\text{P}}^{\text{ps}} \gamma_{\text{P}}^l} \right) \right] - 1 \quad (7)$$

## CNC surface tension parameters

Eq. 7 relates the predicted contact angle formed by the liquid over the sample,  $\theta_{\text{comp}}$ , to its composition,  $f^{\text{nps}}$ . It assumes that the surface tension components of the solid ( $\gamma_{\text{D}}^{\text{nps}}$ ,  $\gamma_{\text{P}}^{\text{nps}}$ ,  $\gamma_{\text{D}}^{\text{ps}}$ , and  $\gamma_{\text{P}}^{\text{ps}}$ ) can be estimated. This was achieved by exploiting the empirical correlations between surface tension and Hansen solubility parameters (HSP). The HSP of CNCs were determined in a previous work.<sup>6</sup> HSP represent a set of three parameters:  $\delta_{\text{D}}$ ,  $\delta_{\text{P}}$ , and  $\delta_{\text{H}}$ , which account for the potential of the surface in terms of dispersive, polar (dipole-dipole), and hydrogen-bonding (and other Lewis acid/base) interactions, respectively.<sup>35</sup> They are expressed as the square-root of an energy density (in  $\text{MPa}^{1/2}$ ). The polar surfaces of CNCs had estimated HSP of  $\{\delta_{\text{D}}^{\text{ps}}; \delta_{\text{P}}^{\text{ps}}; \delta_{\text{H}}^{\text{ps}}\} = \{18.1; 20.4; 15.3\} \pm \{0.5; 0.5; 0.4\} \text{MPa}^{1/2}$ , while the non-polar surfaces were estimated at:  $\{\delta_{\text{D}}^{\text{nps}}; \delta_{\text{P}}^{\text{nps}}; \delta_{\text{H}}^{\text{nps}}\} = \{17.4; 4.8; 6.5\} \pm \{0.3; 0.5; 0.6\} \text{MPa}^{1/2}$ .<sup>6</sup> Together, they constitute the total (or ‘‘Hildebrand’’) solubility parameter,  $\delta_{\text{T}}$  (Eq. 8), that accounts for the potential of cohesion between a substrate and its environment.

$$\delta_{\text{T}} = (\delta_{\text{D}}^2 + \delta_{\text{P}}^2 + \delta_{\text{H}}^2)^{1/2} \quad (8)$$

HSP are by definition closely related to surface tension since they both relate to the amount of interactions that a material may form with its environment. Hence, it should be possible to express the surface tension as a function of HSP. While previous models also relied on molar volume,<sup>36–39</sup> Jia and Shi<sup>40</sup> recently proposed a direct correlation between  $\gamma_{\text{D}}$  and  $\delta_{\text{D}}$  that was applicable to liquids and polymers. Yu and Hou<sup>15</sup> generalized these models to the various components of surface tension. Four empirical equations were proposed,  $\gamma = f(\delta_{\text{T}})$  (Eq. 9);  $\gamma = f(\delta_{\text{D}}, \delta_{\text{P}}, \delta_{\text{H}})$  (Eq. 10);  $\gamma_{\text{D}} = f(\delta_{\text{D}})$  (Eq. 11); and  $\gamma_{\text{P}} = f(\delta_{\text{P}}, \delta_{\text{H}})$  (Eq. 12). Two further

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3 correlations explored in their work,  $\gamma_P=f(\delta_P)$  and  $\gamma_P=f(\delta_H)$ , are not considered here: these  
4 correlations have systematic deviations at high  $\gamma_P$  values (over- or underestimations). It is  
5 consistent with the fact that  $\gamma_P$  accounts for all non-dispersive interactions, i.e for polar and  
6 Lewis acid/base interactions. It should thus be predicted from both  $\delta_P$  and  $\delta_H$  as in Eq. 12.  
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$$10 \quad \gamma = 1.88\delta_T^{0.94} \quad (9)$$

$$11 \quad \gamma = 0.12 [\delta_D + 0.25 (\delta_P + \delta_H)]^{1.86} \quad (10)$$

$$12 \quad \gamma_D = 0.035\delta_D^{2.34} \quad (11)$$

$$13 \quad \gamma_P = 4.30 \times 10^{-2} (\delta_P + \delta_H)^{1.75} \quad (12)$$

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31 Eq. 9 gives estimates that are slightly smaller than those provided by Eq. 10. Consid-  
32 ered together, they provide a lower and an upper bound for CNC surface tensions with  $\gamma^{ps}$   
33 and  $\gamma^{nps}$  ranging from  $\sim 47.8$  to  $55.2 \text{ mN m}^{-1}$  and from  $\sim 30.3$  to  $32.2 \text{ mN m}^{-1}$ , respectively.  
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35 Through Eqs. 11&12, it is possible to estimate the dispersive and polar components and check  
36 that their sum fall within these ranges. Uncertainties reported here are those that arise from  
37 HSP. For the polar surfaces, the sum of  $\gamma_D^{ps}$  ( $30.7 \pm 2.0 \text{ mN m}^{-1}$ ) and  $\gamma_P^{ps}$  ( $22.4 \pm 1.0 \text{ mN m}^{-1}$ )  
38 yields a  $\gamma^{ps}$  of  $53.1 \pm 3.0 \text{ mN m}^{-1}$ . For the non-polar surfaces, it was  $\gamma_D^{nps} = 28.0 \pm 1.1 \text{ mN m}^{-1}$   
39 and  $\gamma_P^{nps} = 3.0 \pm 0.5 \text{ mN m}^{-1}$  for a sum of  $\gamma^{nps} = 31.0 \pm 1.6 \text{ mN m}^{-1}$ . These surface tension val-  
40 ues, summarized in Table 1, fall within the ranges calculated through Eqs. 11&12 and are  
41 considered in the rest of this work.  
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51 Despite being more conservative than those published previously (Table SI.4), these es-  
52 timates are in line with what can be expected from a polymeric material ( $\sim 20 \text{ mN m}^{-1}$  to  
53  $50 \text{ mN m}^{-1}$  for commodity polymers<sup>13</sup>). Historically, characterizing surface tension has been  
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challenging for cellulose rich materials.<sup>8</sup> Wood, itself, is commonly measured in a range as large as  $\sim 40$  to  $90 \text{ mN m}^{-1}$ .<sup>41</sup> Besides variations in the samples' composition, issues in contact angle measurements arise from the potential porosity, swelling behaviors, and anisotropic roughness of the material. These are all susceptible to lower the contact angle values measured at the interface between the sample and the liquid, which leads to an overestimation of the solid apparent surface tension. Since previous CA studies all relied on water as a probe liquid and that water interacts strongly with CNCs,<sup>6,17,42</sup> our interpretation is that these works<sup>8,9</sup> overestimated the surface tension of CNCs.

Table 1: Surface and interfacial tension parameters (expressed in  $\text{mN m}^{-1}$ ). Our approach distinguishes between polar and non-polar surfaces for the parameters of cellulose  $I_\beta$  nanocrystals (see Fig. 1). References for the surface tension of liquids are provided in SI. "Abbr." stands for the abbreviation through which the substrates are referred to within the text.

Substrate	Abbr.	Surface tension parameters			Interfacial tensions <sup>a,b</sup>		
		$\gamma$	$\gamma_D$	$\gamma_P$	ps	nps	w
Polar surfaces	ps	$53.1 \pm 3.0^c$	$30.7 \pm 2.0^c$	$22.4 \pm 1.0^c$	0	-	-
Non-polar surfaces	nps	$31.0 \pm 1.6^c$	$28.0 \pm 1.1^c$	$3.0 \pm 0.5^c$	$\sim 9.0$	0	-
Water	w	72.8	21.8	51.0	$\sim 6.4$	$\sim 29.6$	0
Hexadecane	h	27.0	$\sim 27.0$	$\sim 0.0$	$\sim 22.5$	$\sim 3.0$	$\sim 51.3$
Ethylene glycol	EG	48.0	22.6	25.4	$\sim 0.6$	$\sim 11.2$	-
Diiodomethane	DIM	50.8	48.5	2.3	$\sim 12.3$	$\sim 2.8$	-

<sup>a</sup> The interfacial tension with air is assumed to be equal to the surface tension  $\gamma$ .

<sup>b</sup> Estimated based on the Owens-Wendt-Rabel-Kaelble (OWRK) model (Eq. 3).

<sup>c</sup>  $\gamma = \gamma_D + \gamma_P$ , with  $\gamma_D$  and  $\gamma_P$  calculated from Eqs. 11&12, respectively. Uncertainties reflect those on the HSP values.

## Results and discussion

### Wettability results

The various phases of an ARCA experiments and the process through which they were analyzed are presented in SI (section "ARCA experiments and analyses"). The protocol was established in order for surface tension to dominate the force balance at all times.

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3 The ratio between the hydrodynamic forces and the surface tension of the liquid,  $\gamma^l$ , is  
4 defined as the capillary number,  $N_{Ca}$  (Eq. SI.4). The ratio between the gravitational forces  
5 and  $\gamma^l$  is defined as the Bond number,  $N_{Bo}$  (Eq. SI.5). In our experiments, the surface  
6 tension largely dominated the force balance by 2 to 3 orders of magnitude (see SI, section  
7 “Capillary and Bond numbers”). In terms of importance, it is followed by gravitational forces  
8 ( $N_{Bo} \approx 10^{-2}$ - $10^{-3}$ ) and then viscous forces ( $N_{Ca} \approx 10^{-5}$ - $10^{-6}$ ). ARCA results may hence be  
9 modeled based on surface tension-related considerations only. Furthermore and according  
10 to Strobel and Lyons<sup>31</sup>,  $N_{Ca} < 10^{-5}$  generally ensures that the CA measured at the moving  
11 three-phase boundary is equal to that measured just after it stops, i.e. that it corresponds  
12 to a thermodynamic state. Overall, this condition was verified during our experiments.

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15 To account for the local nature of a drop-based measurement (analysis of few mm<sup>2</sup> only),  
16 each film was analyzed on at least three locations and at least three films were produced  
17 for each condition. It represents a minimum of 9 repetitions per experimental condition  
18 (excepted  $\theta_r^{EG}$ , which is based on 3 repetitions only). Uncertainties reported in the text and  
19 error bars plotted on the graphs are standard deviations. A full breakdown of the results  
20 and their statistical analysis, including 95% confidence intervals, is provided in Table SI.5.

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23 Figs. 2.a&c plot the wettability results obtained with DIM (in purple) and EG (in green)  
24 on spin-coated and oven-cast films, respectively. ARCA measurements on OC films yielded  
25  $\theta_a$  (empty triangles up) and  $\theta_r$  (empty triangles down) values of  $41.0 \pm 4.3^\circ$  and  $15.0 \pm 1.8^\circ$   
26 with EG. It was  $46.1 \pm 1.2^\circ$  and  $16.7 \pm 1.3^\circ$  with DIM. These imply significant hysteresis,  $H$ ,  
27 of  $\sim 26^\circ$  and  $\sim 30^\circ$ , respectively.

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30 On the SC films, contact angles values dropped to  $\theta_a = 10.2 \pm 0.6^\circ$  and  $\theta_r = 0^\circ$  (no receding)  
31 with EG. The lack of any receding prevents an accurate determination of the hysteresis,  
32 which may only be said to be smaller than  $\sim 10^\circ$ . Note that no significant variations were  
33 observed by increasing the drying time of the spin-coated films from a few minutes to 24 h  
34 (same conditions as the oven-cast films). With DIM,  $\theta_a$  and  $\theta_r$  were measured at  $34.8 \pm 3.4^\circ$   
35 and  $11.6 \pm 1.8^\circ$ , corresponding to an hysteresis of  $\sim 23^\circ$ . It was a concern that the spin-coated  
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3 layer could be too thin to prevent the substrate from affecting the measurement, especially  
4 for EG, which seems to swell the film ( $\theta_r=0^\circ$ ). However, preliminary tests performed on  
5 bare Si wafers yielded EG advancing contact angles that were greater than those measured  
6 on the spin-coated films ( $14.1\pm 0.5^\circ$  instead of  $10.2\pm 0.6^\circ$ ). Furthermore, CA measurements  
7 performed on films spun at 4000 rpm (and thus thinner than those prepared at 500 rpm)  
8 yielded results that were not statistically different ( $11.2\pm 0.5^\circ$  instead of  $10.2\pm 0.6^\circ$ ). Hence,  
9 we do not believe the substrate to influence the measurements: the abrupt lowering in CA  
10 values observed with EG between oven-cast and spin-coated films may be attributed to a  
11 variation at the surface of the CNC coating rather than to an influence of the thickness or  
12 of the substrate.  
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23 Since kinetic hysteresis and surface roughness were preemptively minimized, the concor-  
24 dant variation in CA hysteresis between the samples for both EG and DIM can be attributed  
25 to the surface chemistry of the films: spin-coated films are chemically more homogeneous  
26 than oven-cast ones. The fact that this decrease in  $H$  is driven by a drop of the advancing  
27 contact angle values suggests that spin-coated films have a higher apparent surface energy.  
28 Thus, spin-coating a CNC suspension, instead of oven-casting it, leads to an impoverishment  
29 of air/sample interfaces in non-polar moieties. Furthermore, the lack of any receding with  
30 EG points to a very good interface between the SC film and the probe liquid. Since EG has  
31 interfacial tensions (Eq. 3) of  $\sim 0.6 \text{ mN m}^{-1}$  and  $\sim 11.2 \text{ mN m}^{-1}$  with the polar and non-polar  
32 surfaces of CNCs, respectively, this lack of receding is coherent with the surface being rich  
33 in polar moieties.  
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## 47 **Chemical composition of air/sample interfaces**

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49 The most likely interpretation from wettability results is that oven-cast films are richer in  
50 (200) surfaces than spin-coated substrates, which translates into a greater chemical homo-  
51 geneity for the latter. This interpretation may be confronted with the projections derived  
52 from Eq. 7 by plotting  $\theta_{\text{comp}}$  as a function of the surface fraction in non-polar surfaces,  $f^{\text{nps}}$   
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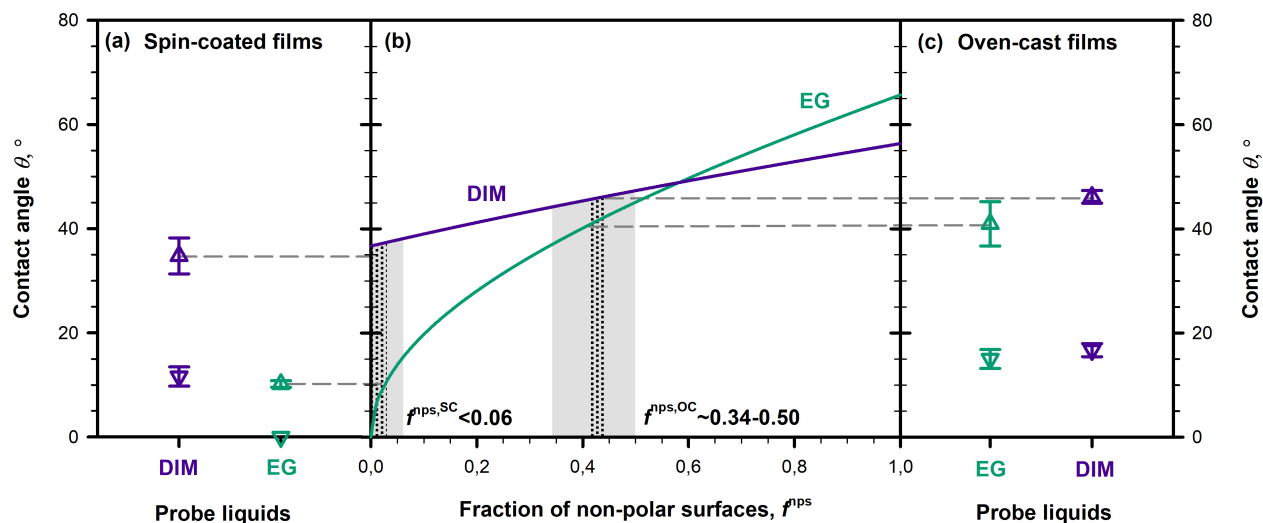


Figure 2: ARCA results for spin-coated (a) and oven-cast (c) films and their predictions in terms of non-polar fraction,  $f^{\text{np}}$ , for the air/sample interface (b). EG and DIM results are plotted in green and purple, respectively. Average  $\theta_a$  values are represented by empty triangles up and  $\theta_r$  values by empty triangles down. In (b), filled lines are the plots of  $\theta_a$  as a function of  $f^{\text{np}}$  (Eq. 7) for EG and DIM. The projection of  $\theta_a$  values (grey dashed lines) over these plots provides estimates for the samples' surface content in non polar surfaces. The consistency observed between the  $f^{\text{np}}$  predictions derived from EG and DIM (with  $\sim 0.02$ - $0.03$  between both predictions, highlighted by the dotted areas) confirms the validity of CNC surface tension parameters. Error bars in (a)&c are standard deviations. Their influence on the determination of  $f^{\text{np}}$  is highlighted by the grey areas in (b).

(Fig. 2.b). Considering the smoothness of CNC thin films and their propensity for kinetic phenomena such as swelling, the advancing contact angle is likely to be the most representative estimate of the composite contact angle  $\theta_{\text{comp}}$  in the generalized Cassie-Baxter equation (Eq. 7). Furthermore, advancing contact angles are the most representative CA to detect non-polar moieties.<sup>31,43</sup> This is because low surface tension areas tend to prevent the liquid from advancing, which reflects on  $\theta_a$  values.

Projecting the advancing contact angle values on our model (hypothesis  $\theta_a \approx \theta_{\text{comp}}$ ) returns an estimate of  $f^{\text{np}}$ . This projection is highlighted on Fig. 2 by the dashed lines that cross from Fig. 2.a to 2.b, and from 2.c to 2.b, respectively.  $f^{\text{np}}$  estimates, whether determined from EG or DIM advancing contact angle values, are consistent: they are in

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3 the range of  $\sim 0.42$ - $0.44$  and  $\sim 0$ - $0.03$  for oven-cast and spin-coated films, respectively. These  
4 ranges may be extended to  $\sim 0.34$ - $0.50$  and  $\sim 0$ - $0.06$  once the standard deviations on  $\theta_a$  values  
5 are considered. It is consistent with our previous findings: spin-coated films are poorer in  
6 non-polar surfaces and chemically more homogeneous than oven-cast substrates.  
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11 An analysis of the standard deviations highlights that reproducibility is better through  
12 spin-coating than through oven-casting. The large uncertainty observed on  $f^{\text{nps}}$  ( $0.34$  to  
13  $0.50$ ) for oven-cast films actually arises from film-to-film variations. This is highlighted in  
14 Fig 3.a, where EG advancing contact angle values measured for each film are plotted as a  
15 function of the model predictions for  $f^{\text{nps}}$ . EG was chosen for its greater sensitivity to the  
16 orientation of CNCs. Average  $\theta_a$  values for spin-coated and oven-cast films are represented by  
17 green triangles (as in Fig. 2).  $\theta_a$  values for each film are plotted in black (SC films) or brown  
18 (OC films). The figure's inset is a zoom to help the visualization of the spin-coated results.  
19 There are little deviations from sample to sample and spin-coating seems to repeatably yield  
20 thin films whose  $f^{\text{nps}}$  are in the range of  $0.02$ - $0.03$  (based on EG results). For oven-cast films,  
21 uncertainties on  $f^{\text{nps}}$  are within  $\pm 0.03$ , which suggests that surface heterogeneities are well  
22 dispersed across the sample. However, each film is statistically different from the other.  
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35 To investigate further the reproducibility of the oven-casting process, 7 new OC films  
36 were prepared and investigated through static sessile drop measurements. In our case, static  
37 sessile drop measurements fell within  $\sim 1^\circ$  of the advancing contact angle values, meaning  
38 that they constitute an effective way to quickly probe a larger amount of samples. Fig 3.b  
39 plot the distribution of 30 sessile drop CA and confirms the low repeatability of the oven-  
40 casting process: CA values spread over nearly  $40^\circ$ , from  $\sim 12^\circ$  to  $\sim 50^\circ$ . CA measurements  
41 at the bottom of the distribution (pointed by the red arrow) were measured on different  
42 locations of a same film that apparently failed to orient its non-polar fonctionnalités toward  
43 the air/sample interface. Hence, over the 10 oven-cast films we analyzed (3 through ARCA  
44 and 7 through sessile drop measurements), 9 managed to orient at different extents their non-  
45 polar functionalities to the air interface and produced EG contact angles ranging from  $\sim 30$   
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to  $\sim 50^\circ$ . The last film produced CA values ranging from  $\sim 12$  to  $\sim 16^\circ$ , which is close to what can be measured on spin-coated films ( $\theta_a = 10.2 \pm 0.6^\circ$ ). Sessile drop measurements performed on the same films with DIM (Fig 3.c) show a lesser variability from film to film, which underlines the greater sensitivity of EG to non-polar surface orientation. The red arrow in Fig 3.c points towards the results that were gathered from the film already highlighted in Fig 3.b.

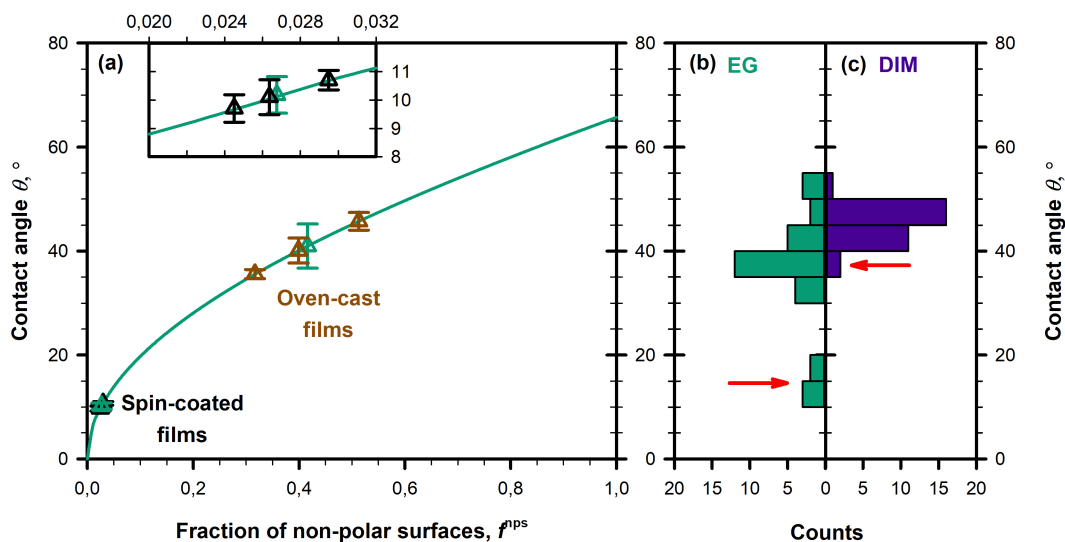


Figure 3: Repeatability of CNC orientation during the spin-coating and oven-casting processes based on EG results (a). The green line and the green triangles up are the plots for Eq. 7 and for the average advancing CA values (see Fig. 2). The black and brown triangles up represent the advancing CA values measured for each of the spin-coated and oven-cast films, respectively. The insert is a zoom of the spin-coated results for greater readability. Error bars are standard deviations. Sessile drop measurements taken on 7 additional oven-cast films with EG (b) and DIM (c). The results pointed by the red arrows are from a single data set, taken on a film that apparently failed to orient its non-polar functionalities at the air/sample interface to the same extent as the 6 other samples.

## Speculative mechanism for CNC orientation at the air/water interface

Based on Eq. 3, water has interfacial tensions of  $\gamma^{\text{ps/w}}=6.4 \text{ mN m}^{-1}$  and  $\gamma^{\text{nps/w}}=29.6 \text{ mN m}^{-1}$  with the polar and non-polar surfaces of CNCs, respectively (Table 1). To understand what may happen in suspensions, it is possible to calculate the energy variations that result from the various options available to the nanocrystal. Fig. 4 plots these various paths, which involve migration to the air/water interface and/or agglomeration, and speculates a mechanism for CNC orientation at the air/sample interface. In the case of interfacial migration, a scenario in which the nanocrystal remains fully immersed in water (with the exception of the adsorbed surfaced) was considered: the influence of CNC vertical positioning at the air/water interface over the energy variation was found to be secondary and was hence neglected. The exact normal positioning of CNCs at interfaces remains to be computed: experimentally, the nanocrystals were reported to be mostly immersed in water at air/water interfaces<sup>20,21</sup> and fully immersed in water at oil/water interfaces.<sup>19</sup> Calculations were done by amalgamating surface tensions with surface energies, which equates to neglecting the heat generated by the process.<sup>29</sup> This also neglects the energy variations caused by ionic bond dissociation (occurring on the sulfate half-ester groups of CNCs). While CNC negative charges may have an effect on the kinetics of the processes described here-below (because of electrostatic stabilization for instance), energy variations associated with these charges are small in front of interfacial phenomena and should not affect the orientation taken by CNC particles at the air/water interface (justification provided in SI). It is worth underlining that beyond energy calculations, the mechanism hypothesized in this section yet remains to be supported by experimental evidences; parts of its limitations involve the true extent to which the influence of surface charges remains secondary when compared to interfacial tension variations.

When an individual CNC (Fig. 4.a) migrates from the water bulk towards the air/water interface, it removes an air/water and a water/solid interface and creates an air/solid one.

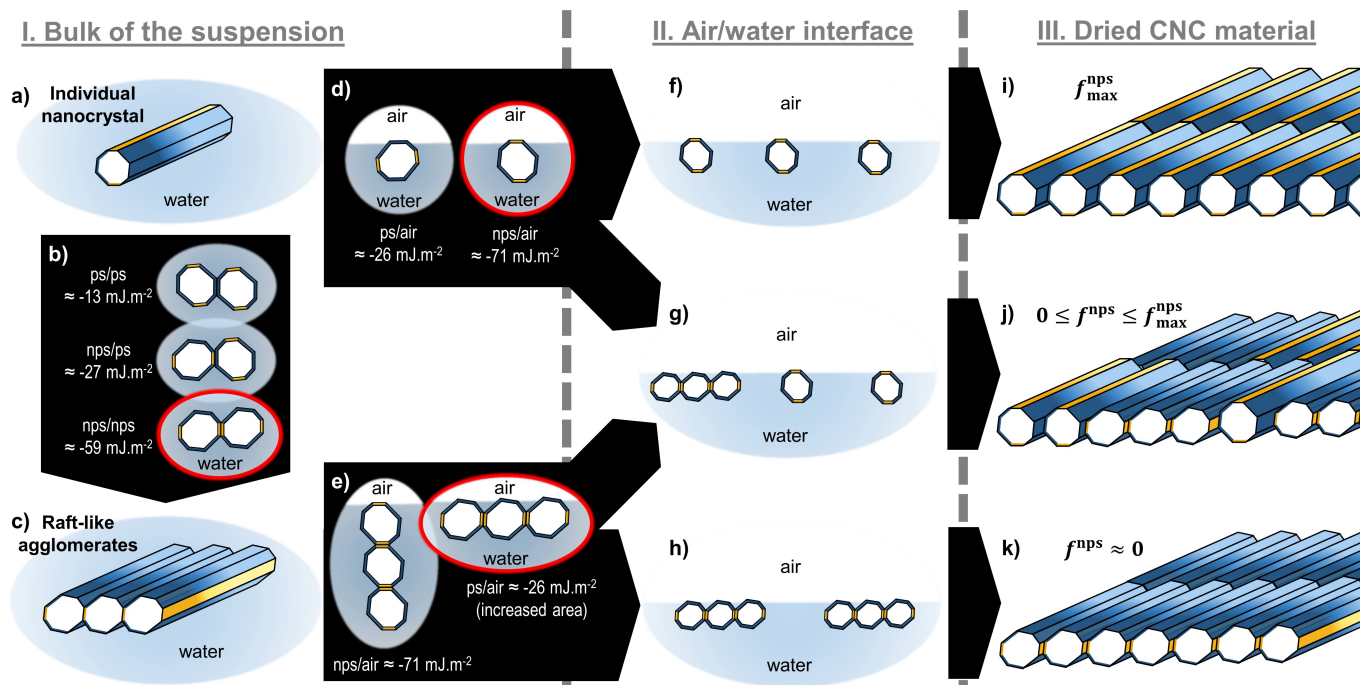


Figure 4: Speculative mechanism for CNC orientation at the air/sample interface. Assuming CNCs are initially well dispersed (a), they may either migrate to the air/water interface as individual nanocrystals or first agglomerate in the water bulk. Upon agglomeration (b), CNCs preferentially assemble their non-polar surfaces to form raft-like structures (c). Upon migration towards the air/water interface, individual CNCs orient their non-polar surfaces towards the air (d). 2-D agglomerates may, however, prefer to orient their polar surfaces if their cross-sectional aspect ratio is large enough (e). Depending on the state of CNC dispersion within the water bulk, the air/water interface may be populated by individual nanocrystals only (f), by a mix of individual and agglomerated particles (g), or by agglomerated CNCs only (h). Upon casting, these result into thin films whose surface is either amphiphilic (i)&(j) or purely polar (k). The fraction of non-polar surfaces that a film can expose should reach a maximum of  $f_{\max}^{\text{nps}}$  in (i), whose amplitude is a function of the nanocrystals' geometry, and a minimum of  $\sim 0$  in (k).

The surface energy difference may thus be calculated as  $\Delta E \approx \gamma^{\text{nps}} - \gamma^{\text{nps/w}} - \gamma^{\text{w}} \approx -71 \text{ mJ m}^{-2}$  if a non-polar surface adsorbs at the air/water interface, and as  $\Delta E \approx -26 \text{ mJ m}^{-2}$  if it is a polar surface. Therefore, the air/water interface is better stabilized by the adsorption of a non-polar surface (Fig. 4.d). This assumes that the surface areas in terms of polar and non-polar moieties are comparable, which is roughly the case for the sidewalls of an individual nanocrystal.

Instead of migrating towards the air/water interface, CNCs could agglomerate (Fig. 4.b):

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3 matching two polar surfaces together yields an energy variation of  $\sim 13 \text{ mJ m}^{-2}$ , it decreases  
4 to  $\sim 27 \text{ mJ m}^{-2}$  for a polar surface agglomerated with a non polar one, and to  $\sim 59 \text{ mJ m}^{-2}$   
5 for two non-polar surfaces together. In aqueous suspensions, CNCs hence find it more favor-  
6 able to agglomerate by matching their non-polar surfaces together. Repeating the process  
7 yields raft-like structures assembled by their (200) surfaces (Fig. 4.c). Similar 2-D aggregates  
8 were reported by Uhlig et al.<sup>44</sup> for aqueous suspensions of sulfuric acid-hydrolyzed CNCs.  
9 This trend is probably favored by the combination of solvation-induced and electrostatic  
10 stabilizations experienced by CNC polar surfaces in water.<sup>42</sup> Other works have suggested  
11 that it was hydrogen bonding networks that were responsible for the strong cohesion of CNC  
12 agglomerates.<sup>45</sup> Our calculations show that in water, at least, dispersive interactions between  
13 the (200) surfaces of CNCs particles are those that require the highest energy to be broken.  
14 This is because water molecules can form H-bonds of their own with the hydroxyl groups of  
15 CNCs, which minimizes the relative importance of these bonds from a thermodynamic point  
16 of view ( $\gamma^{\text{w/ps}} \approx 6.4 \text{ mN m}^{-1}$ ).  
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31 The formation of 2-D self-assemblies changes the aspect ratio of the nano-objects that  
32 can migrate towards the interface: if they are wide enough, it may become advantageous to  
33 orient their polar moieties towards the air/water interface (Fig. 4.e). Indeed, raft-like ag-  
34 glomeration increases the area in polar surfaces that can be exposed at the interface with air  
35 (Fig. 4.c&4.e). Hence, while polar surface adsorption still leads to surface energy variations  
36 that are smaller than for non-polar surfaces ( $\approx -26 \text{ mJ m}^{-2}$ , instead of  $\approx -71 \text{ mJ m}^{-2}$ ), a raft  
37 that is roughly 3 times larger than thicker would preferentially adsorb its polar surfaces at  
38 the air/water interface: this could correspond to agglomerates of as little as 2 to 4 nanocrys-  
39 tals depending on their exact cross-section and positioning at the interface. This threshold  
40 of aggregation is likely reached in suspension: Uhlig et al.<sup>44</sup> reported 2-D CNC agglomerates  
41 that were up to 8 times larger than thicker.  
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53 From these calculations, it is possible to propose a speculative mechanism for CNC ori-  
54 entation at the air/water interface: in circumstances where CNCs can migrate to the inter-  
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3 face prior to agglomerating, the individual nanocrystals (4.a) orient their non-polar surface  
4 towards air (4.f). The film that results from this process is amphiphilic, with stripes of non-  
5 polar and polar surfaces (4.i) and  $f^{\text{nps}}$  reaches its maximum,  $f_{\text{max}}^{\text{nps}}$ . However, in circumstances  
6 where bulk agglomeration is competitive, CNC may first form raft-like assemblies (Fig. 4.b).  
7 Upon migration to the interface, these 2-D structures orient their polar surfaces towards  
8 the air (Fig. 4.h), which leads to purely polar surfaces upon drying (Fig. 4.h,  $f^{\text{nps}} \approx 0$ ). If  
9 it only takes  $\sim 2$ -4 nanocrystals to form agglomerates that preferentially orient their polar  
10 surfaces at the air/water interface, then slight variations in the initial state of CNC aqueous  
11 dispersion (caused by the efficiency of the ultrasonication process for instance) can cause fluc-  
12 tuations to the level of amphiphilicity displayed by the films. This is illustrated in Fig. 4.g  
13 where the air/water interface is populated by a mix of individual and agglomerated CNCs,  
14 which leads to an intermediate content in terms of non-polar surfaces for the film (Fig. 4.k,  
15  $0 \leq f^{\text{nps}} \leq f_{\text{max}}^{\text{nps}}$ ). Note that the representations made in Figs. 4.i-k is coherent with the  
16 level of CNC alignment that is observed in AFM analyses (Fig. 1.b).  
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31 A process such as spin-coating, in which a significant centrifugal force is applied to  
32 the system over a short period of time, likely destabilizes the suspension and favors CNC  
33 agglomeration. Spin coating has indeed been reported to favor local concentration increases<sup>46</sup>  
34 (which may in turn favor particle/particle agglomeration). It would explain that SC films  
35 experimentally display a polar behavior ( $f^{\text{nps}} < 0.06$ ) with a small standard deviation: if  
36 the suspension is subjected to a treatment that cause CNC agglomeration, it is possible to  
37 repeatably produce a scenario where only agglomerates make it to the interface as in Fig. 4.k.  
38 It is worth noting that the shear forces generated by the process may also contribute to orient  
39 the 2-D CNC assemblies.  
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49 However, a process such as oven-casting is likely to preserve CNC dispersion long enough  
50 for individual CNCs to reach the interface, which would explain the amphiphilic behavior  
51 displayed by OC films. The impossibilities to completely prevent CNC agglomeration in  
52 suspension and to control the ratio between individual and agglomerated CNCs that reach  
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3 the interface may be responsible for the large standard deviations observed on OC films:  
4 it is harder to repeatably produce and maintain an individual dispersion of CNCs than to  
5 repeatably cause their agglomeration. In practice, while it should theoretically be possible  
6 to reach  $f_{\max}^{\text{nps}}$  (Fig. 4.i), a small fraction of the interface will be made of CNC agglomerates,  
7 which lowers  $f^{\text{nps}}$  (Fig. 4.j). The least polar film we could produce through oven-casting had  
8 a  $f^{\text{nps}}$  of  $\sim 0.55$  (Fig. 3.a), but there is no way to verify whether this really corresponds to  
9  $f_{\max}^{\text{nps}}$  or to the maximum that we could reach given our current protocol.

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11 Based on Fig. 4.i,  $f_{\max}^{\text{nps}}$  should be a function of the nanocrystal cross-sectional shape.  
12 However, CNC shape cannot be totally resolved through XRD due to the lack of peak  
13 for (010) surfaces (see SI) and  $\sim 0.55$  is currently the best estimate we can provide for  
14 our CNCs. Since the CNC dimensions and the cross-sectional shape are a function of their  
15 feedstocks,<sup>7,23,24</sup> it should be possible to tune  $f_{\max}^{\text{nps}}$  by working with other kind of nanocrystals.

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17 Calculations led here-above may confirm quantitatively whether CNCs find it favorable  
18 to orient their (200) surfaces towards the oil at the interface of oil in water Pickering emul-  
19 sions.<sup>7,18,19</sup> Note that aggregation state was also found to play a role on the interfacial  
20 stability of these emulsions.<sup>5,19</sup> Kalashnikova et al.<sup>7,18</sup> produced CNC stabilized hexadecane  
21 in water emulsions. Hexadecane has an interfacial tension of  $51.2 \text{ mN m}^{-1}$  with water,  
22  $22.5 \text{ mN m}^{-1}$  with CNC polar surfaces, and  $3.0 \text{ mN m}^{-1}$  with CNC non-polar surfaces (Ta-  
23 ble 1). Thus, hexadecane is nearly a perfect match for the (200) surfaces of CNCs: its  
24 adsorption from the water bulk to the oil/water interface leads to an energy variation of  
25  $\sim -78 \text{ mJ m}^{-2}$  ( $-35 \text{ mJ m}^{-2}$  for a polar surface). This provides a quantitative backing to the  
26 series of articles by Kalashnikova and co-workers,<sup>7,18,47</sup> which have been cornerstones in the  
27 field of CNC stabilized micro-emulsions.

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29 Another interesting result is the comparison between the theoretical energy required to  
30 disperse an agglomerate of CNCs in water and the experimental input that needs to be pro-  
31 vided to the system in order to do so. A  $\sim 7\text{-}8 \text{ nm}$  wide,  $\sim 105\text{-}120 \text{ nm}$  long nanocrystal has  
32 a specific surface area of  $\sim 350 \text{ m}^2/\text{g}_{\text{CNC}}$  (assuming a density of  $\sim 1.6 \text{ g/cm}^3$ ). Since break-

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3 ing CNC-CNC interactions in water requires from  $\sim 13$  to  $\sim 59$   $\text{mJ m}^{-2}$ , dispersing a densely  
4 packed agglomerate of CNCs will require  $\sim 5$  to  $\sim 20$   $\text{J/g}_{\text{CNC}}$  from a thermodynamic point  
5 of view. Experimentally, Beck et al.<sup>45</sup> reported satisfactory dispersion from  $950$   $\text{J/g}_{\text{CNC}}$   
6 for spray- and air-dried CNCs at concentrations of 2.8 wt% ( $\sim 1.8$  vol%). Beuguel et al.<sup>27</sup>  
7 mentioned  $10\,000$   $\text{J/g}_{\text{CNC}}$  as a safer threshold for 1 to 5 wt% ( $\sim 0.6$ - $3.1$  vol%) CNC suspen-  
8 sions. Hence, the ultrasonication process has an energy efficiency (energy provided to the  
9 system over energy required to disperse CNCs) that lies in the range of  $\sim 0.1$ - $1$  % for dilute  
10 CNC suspensions. This seems plausible since it falls within one order of magnitude of CNC  
11 volume fraction ( $\sim 0.6$ - $3.1$  vol%).  
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## 23 Conclusions

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26 This work proposes the first compelling evidence of CNC orientation at an interface. It  
27 provides experimental backing to nearly a decade of research during which this hypothesis  
28 has been used to justify the stability brought by CNCs to oil-in-water Pickering emulsions.  
29 This was achieved by investigating the influence of the casting protocol on the wettability  
30 of CNC thin films. It remained an open-ended question with contact angle variations of  
31 up to  $30^\circ$  being reported from sample to sample without convincing explanations. Here,  
32 we demonstrate that such variations could be explained by considering the amphiphilicity  
33 of the nanocrystals. Liquids are sensitive to molecular-scale heterogeneities and cellulose  
34 crystalline surfaces, whose dimensions are nano, are large enough to influence the wetting  
35 behaviors.  
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46 Based on thermodynamic calculation, a mechanism for CNC orientation at interface is  
47 proposed: while individual nanocrystals have an energy incentive to orient their non-polar  
48 surfaces to the air interface, CNC agglomerates preferentially expose their polar moieties.  
49 This is because CNCs form 2-D assemblies upon agglomeration. Previously reported by Uhlig  
50 et al.<sup>44</sup>, these raft-like structures find it more stable to orient their largest surfaces, which  
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3 happen to be polar, towards air. Hence, in a protocol such as oven-casting during which  
4 CNC dispersion is preserved over a long period of time, CNC may migrate as near-individual  
5 particles to the interface, which ultimately yields an amphiphilic film. In a spin-coating  
6 protocol, however, CNC suspensions are subject to an important centrifugal force that may  
7 favor local increases in particle concentration and thus their agglomeration: a polar film is  
8 produced. It is worth noting that this mechanism for CNC orientation at interfaces remains  
9 to be properly demonstrated: experimentally, this manuscript only demonstrates that while  
10 oven-cast films displayed an estimated 0.34-0.50 fraction of non-polar moieties, spin-coated  
11 samples stood below 0.06. Reproducibility was lower for the production of amphiphilic  
12 films from oven-casting: probably due to its high dependency to the level of initial CNC  
13 dispersion. We suggest that working with never-dried CNCs instead of spray-dried particles  
14 could improve the repeatability of the process: it would remove the variability introduced  
15 during the step of ultrasound-assisted redispersion.  
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29 Based on the OWRK model, these calculations on energies and surface composition were  
30 made possible via the estimation of CNC surface tension parameters for both the polar and  
31 the non-polar surfaces of the nanocrystals:  $\gamma^{ps}=53.1\pm 3.0 \text{ mN m}^{-1}$  ( $\gamma_D^{ps}=30.7\pm 2.0 \text{ mN m}^{-1}$ ,  
32  $\gamma_P^{ps}=22.4\pm 1.0 \text{ mN m}^{-1}$ ), and  $\gamma^{nps}=31.0\pm 1.6 \text{ mN m}^{-1}$  ( $\gamma_D^{nps}=28.0\pm 1.1 \text{ mN m}^{-1}$ ,  $\gamma_P^{nps}=3.0\pm 0.5 \text{ mN m}^{-1}$ ).  
33 They were obtained by exploiting the empirical correlations that exist between surface ten-  
34 sion and Hansen solubility parameters. These coefficients enable for quantitative predictions  
35 regarding the behavior of CNC particles at interfaces. Hence, the plausibility of CNC ad-  
36 sorption at the oil/water interface could be confirmed: their (200) surfaces are a good match  
37 for stabilizing the interface of an hexadecane in water emulsion.<sup>7,18</sup> It was also possible to  
38 estimate the energy required to disperse a densely packed agglomerate of CNCs in water:  
39 it is in the range of  $\sim 5$  to  $\sim 20 \text{ J/g}_{\text{CNCs}}$ . This provides an element of comparison and an  
40 horizon for the redispersion of CNCs:<sup>27,45</sup> the energy optimization of these protocols is cru-  
41 cial to make them industrially relevant.<sup>48</sup> Other applications involve the prediction of CNC  
42 behavior in polymer blends and the production of CNC materials with tuned wettability.  
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## Supporting Information description

Supporting Information (SI) provide: a nomenclature for the symbols and abbreviations; a morphological characterization (dimensions, sulfur content, purity, crystallinity) of the CNCs; a list of the precautions that were taken for the wettability model (Eq. 7) to apply; the description of a typical ARCA experiment and the detailed methodology with which the data was analyzed; a film by film breakdown of the ARCA results and their statistical analysis.

## References

- (1) Tang, J.; Sisler, J.; Grishkewich, N.; Tam, K. C. Functionalization of cellulose nanocrystals for advanced applications. *J. Colloid Interface Sci.* **2017**, *494*, 397–409.
- (2) Moreau, C.; Villares, A.; Capron, I.; Cathala, B. Tuning supramolecular interactions of

- 1  
2  
3 cellulose nanocrystals to design innovative functional materials. *Ind. Crop. Prod.* **2016**,  
4 *93*, 96–107.  
5  
6  
7  
8 (3) Habibi, Y.; Lucia, L. A.; Rojas, O. J. Cellulose Nanocrystals: Chemistry, Self-Assembly,  
9 and Applications. *Chem. Rev.* **2010**, *110*, 3479–3500.  
10  
11  
12 (4) Moon, R. J.; Martini, A.; Nairn, J.; Simonsen, J.; Youngblood, J. Cellulose nanoma-  
13 terials review: structure, properties and nanocomposites. *Chem. Soc. Rev.* **2011**, *40*,  
14 3941–3994.  
15  
16  
17 (5) Capron, I.; Rojas, O.; Bordes, R. Behavior of nanocelluloses at interfaces. *Curr. Opin.*  
18 *Colloid Interface Sci.* **2017**, *29*, 83–95.  
19  
20  
21 (6) Bruel, C.; Tavares, J. R.; Carreau, P. J.; Heuzey, M.-C. The structural amphiphilicity of  
22 cellulose nanocrystals characterized from their cohesion parameters. *Carbohydr. Polym.*  
23 **2019**, *205*, 184–191.  
24  
25  
26 (7) Kalashnikova, I.; Bizot, H.; Cathala, B.; Capron, I. Modulation of Cellulose Nanocrys-  
27 tals Amphiphilic Properties to Stabilize Oil/Water Interface. *Biomacromolecules* **2012**,  
28 *13*, 267–275.  
29  
30  
31 (8) Dankovich, T.; Gray, D. Contact Angle Measurements on Smooth Nanocrystalline Cel-  
32 lulose (I) Thin Films. *J. Adhes. Sci. Technol.* **2011**, *25*, 699–708.  
33  
34  
35 (9) Khoshkava, V.; Kamal, M. R. R. Effect of Surface Energy on Dispersion and Mechanical  
36 Properties of Polymer/Nanocrystalline Cellulose Nanocomposites. *Biomacromolecules*  
37 **2013**, *14*, 3155–3163.  
38  
39  
40 (10) Javanbakht, T.; Raphael, W.; Tavares, J. Physicochemical properties of cellulose  
41 nanocrystals treated by photo-initiated chemical vapour deposition (PICVD). *Can.*  
42 *J. Chem. Eng.* **2016**, *94*, 1135–1139.  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 (11) Peng, Y.; Gardner, D.; Han, Y.; Cai, Z.; Tshabalala, M. Influence of drying method on  
4 the surface energy of cellulose nanofibrils determined by inverse gas chromatography.  
5 *J. Colloid Interface Sci.* **2013**, *405*, 85–95.  
6  
7  
8  
9  
10 (12) Yamane, C.; Aoyagi, T.; Ago, M.; Sato, K.; Okajima, K.; Takahashi, T. Two different  
11 surface properties of regenerated cellulose due to structural anisotropy. *Polym. J.* **2006**,  
12 *38*, 819–826.  
13  
14  
15  
16 (13) Owens, D.; Wendt, R. Estimation of the surface free energy of polymers. *J. Appl. Polym.*  
17 *Sci.* **1969**, *13*, 1741–1747.  
18  
19  
20  
21 (14) Mazeau, K.; Rivet, A. Wetting the (110) and (100) Surfaces of I $\beta$  Cellulose Studied by  
22 Molecular Dynamics. *Biomacromolecules* **2008**, *9*, 1352–1354.  
23  
24  
25  
26 (15) Yu, W.; Hou, W. Correlations of surface free energy and solubility parameters for solid  
27 substances. *J. Colloid Interface Sci.* **2019**, *544*, 8–13.  
28  
29  
30  
31 (16) Wenzel, R. N. Resistance of Solid Surfaces to Wetting by Water. *Industrial & Engi-*  
32 *neering Chemistry Research* **1936**, *28*, 988–994.  
33  
34  
35  
36 (17) Reid, M. S.; Villalobos, M.; Cranston, E. D. Cellulose Nanocrystal Interactions Probed  
37 by Thin Film Swelling to Predict Dispersibility. *Nanoscale* **2016**, *8*, 12247–12257.  
38  
39  
40  
41 (18) Kalashnikova, I.; Bizot, H.; Bertoncini, P.; Cathala, B.; Capron, I. Cellulosic nanorods  
42 of various aspect ratios for oil in water Pickering emulsions. *Soft Matter* **2013**, *9*, 952–  
43 959.  
44  
45  
46  
47 (19) Cherhal, F.; Cousin, F.; Capron, I. Structural Description of the Interface of Pickering  
48 Emulsions Stabilized by Cellulose Nanocrystals. *Biomacromolecules* **2016**, *17*, 496–502.  
49  
50  
51  
52 (20) Bertsch, P.; Diener, M.; Adamcik, J.; Scheuble, N.; Geue, T.; Mezzenga, R.; Fischer, P.  
53 Adsorption and Interfacial Layer Structure of Unmodified Nanocrystalline Cellulose at  
54 Air/Water Interfaces. *Langmuir* **2018**, *34*, 15195–15202.  
55  
56  
57  
58  
59  
60

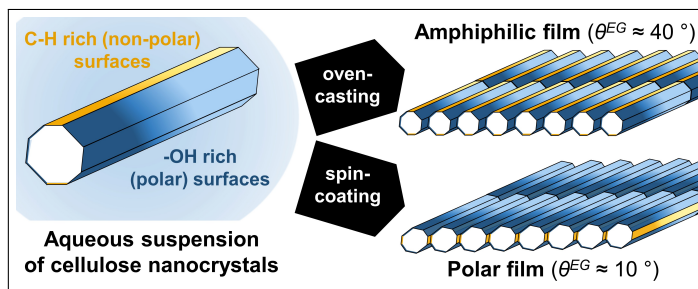
- 1  
2  
3 (21) Bertsch, P.; Diener, M.; Adamcik, J.; Scheuble, N.; Geue, T.; Mezzenga, R.; Fischer, P.  
4 Corrections to Adsorption and Interfacial Layer Structure of Unmodified Nanocrys-  
5 talline Cellulose at Air/Water Interfaces. *Langmuir* **2020**, *36*, 1848–1849.  
6  
7  
8  
9  
10 (22) Scherrer, P. Bestimmung der Größe und der inneren Struktur von Kolloidteilchen mit-  
11 tels Röntgenstrahlen. *Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen*,  
12 *Mathematisch-Physikalische Klasse* **1918**, *2*, 98.  
13  
14  
15  
16 (23) Elazzouzi-Hafraoui, S.; Nishiyama, Y.; Putaux, J.-L.; Heux, L.; Dubreuil, F.; Rochas, C.  
17 The Shape and Size Distribution of Crystalline Nanoparticles Prepared by Acid Hy-  
18 drolysis of Native Cellulose. *Biomacromolecules* **2008**, *9*, 57–65.  
19  
20  
21  
22 (24) Sèbe, G.; Ham-Pichavant, F.; Ibarboure, E.; Koffi, A. L. C.; Tingaut, P. Supramolecular  
23 Structure Characterization of Cellulose II Nanowhiskers Produced by Acid Hydrolysis  
24 of Cellulose I Substrates. *Biomacromolecules* **2012**, *13*, 570–578.  
25  
26  
27  
28 (25) Matthews, J. F.; Skopec, C. E.; Mason, P. E.; Zuccato, P.; Torget, R. W.; Sugiyama, J.;  
29 Himmel, H. E.; Brady, J. W. Computer simulation studies of microcrystalline cellulose  
30 I $\beta$ . *Carbohyd. Res.* **2006**, *341*, 138–152.  
31  
32  
33  
34 (26) Bruel, C.; Beuguel, Q.; Tavares, J. R.; Carreau, P. J.; Heuzey, M.-C. Apparent struc-  
35 tural hydrophobicity of cellulose nanocrystals. *J-FOR* **2018**, *7*, 13–23.  
36  
37  
38  
39 (27) Beuguel, Q.; Tavares, J. R.; Carreau, P. J.; Heuzey, M.-C. Ultrasonication of spray- and  
40 freeze-dried cellulose nanocrystals in water. *J. Colloid Interface Sci.* **2018**, *516*, 23–33.  
41  
42  
43  
44 (28) Woodward, R. Contact Angle Measurements Using the Drop Shape Method. 2018;  
45 <http://firsttenangstroms.com/pdffdocs/CAPaper.pdf>.  
46  
47  
48  
49 (29) Bruel, C.; Queffellou, S.; Darlow, T.; Virgilio, N.; Tavares, J. R.; Patience, G. S. Exper-  
50 imental Methods in Chemical Engineering: Contact Angles. *Can. J. Chem. Eng.* **2019**,  
51 *97*, 832–842.  
52  
53  
54  
55  
56  
57  
58  
59  
60

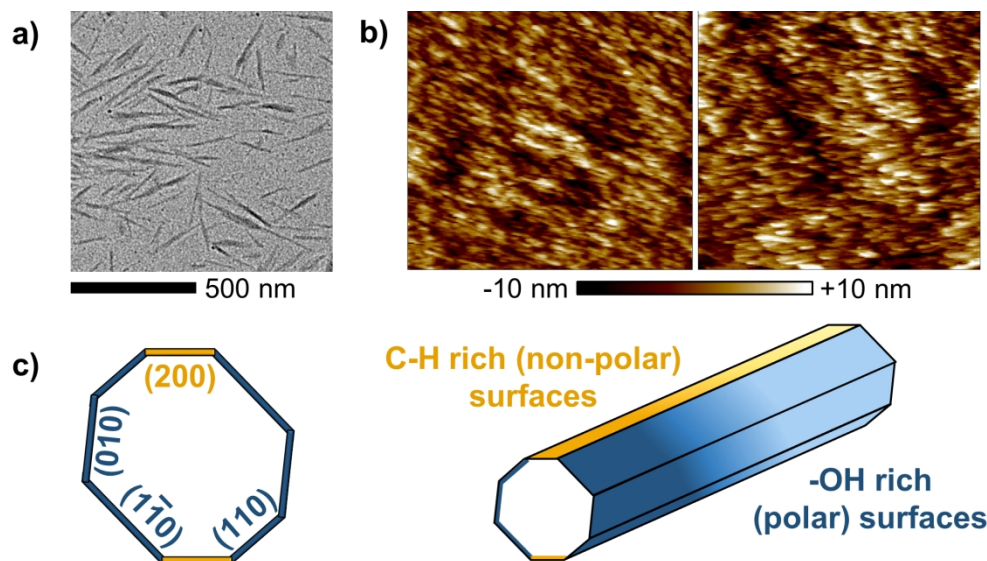
- 1  
2  
3 (30) Good, R. G. Contact angle, wetting, and adhesion: a critical review. *J. Adhes. Sci.*  
4 *Technol.* **1992**, *6*, 1269–1302.  
5  
6  
7  
8 (31) Strobel, M.; Lyons, C. S. An Essay on Contact Angle Measurements. *Plasma Process.*  
9 *Polym.* **2011**, *8*, 8–13.  
10  
11  
12 (32) Good, R. G.; Srivatsa, N. R.; Islam, M.; Huang, H. T. L.; Oss, C. J. V. Theory of the  
13 acid-base hydrogen bonding interactions, contact angles, and the hysteresis of wetting:  
14 application to coal and graphite surfaces. *J. Adhes. Sci. Technol.* **1990**, *4*, 607–617.  
15  
16  
17  
18 (33) van Oss, C. J.; Good, R. J.; Busscher, R. J. Estimation of the polar surface tension  
19 parameters of glycerol and formamide, for use in contact angle measurements on polar  
20 solids. *J. Dispers. Sci. Technol.* **1990**, *11*, 75–81.  
21  
22  
23  
24  
25 (34) Nosonovsky, M. On the Range of Applicability of the Wenzel and Cassie Equations.  
26 *Langmuir* **2007**, *23*, 9919–9920.  
27  
28  
29  
30 (35) Hansen, C. M. *Hansen Solubility Parameters A User's Handbook*; CRC Press: Boca  
31 Raton, FL, U. S. A., 2007.  
32  
33  
34  
35 (36) Beerbower, A. Surface free energy: a new relationship to bulk energies. *J. Colloid*  
36 *Interface Sci.* **1971**, *36*, 126–132.  
37  
38  
39  
40 (37) Koenhen, D. M.; Smolders, C. A. The determination of solubility parameters of solvents  
41 and polymers by means of correlations with other physical quantities. *J. Appl. Polym.*  
42 *Sci.* **1975**, *19*, 1161–1179.  
43  
44  
45  
46 (38) Vavruch, I. On the determination of the factor between cohesive energy density and  
47 surface tension. *J. Colloid Interface Sci.* **1978**, *63*, 600–601.  
48  
49  
50  
51 (39) Abbott, S. J.; Hansen, C. M.; Yamamoto, H. Hansen Solubility Parameters in Practice  
52 software, eBook, datasets. 2018; url: <http://www.hansen-solubility.com>, accessed on  
53 2020/01/16.  
54  
55  
56  
57  
58  
59  
60



- 1  
2  
3  
4 (40) Jia, L.; Shi, B. A New Equation between Surface Tensions and Solubility Parameters  
5 without Molar Volume Parameters Simultaneously Fitting Polymers and Solvents. *J.*  
6 *Macromol. Sci. B* **2011**, *50*, 1042–1046.  
7  
8  
9  
10 (41) de Meijer, M.; Haemers, S.; Cobben, W.; Militz, H. Surface Energy Determinations of  
11 Wood: Comparison of Methods and Wood Species. *Langmuir* **2000**, *16*, 9352–9359.  
12  
13  
14 (42) Bruel, C.; Davies, T. S.; Tavares, J. R.; Carreau, P. J.; Heuzey, M.-C. Self-assembly  
15 behaviors of colloidal cellulose nanocrystals: A tale of stabilization mechanisms. *J.*  
16 *Colloid Interface Sci.* **2020**, *574*, 399–409.  
17  
18  
19 (43) Mundo, R. D.; Palumbo, F. Comments Regarding An Essay on Contact Angle Mea-  
20 surements. *Plasma Processes and Polymers* **2011**, *8*, 14–18.  
21  
22  
23 (44) Uhlig, M.; Fall, A.; Wellert, S.; Lehmann, M.; Prévost, S.; Wågberg, L.; von Klitz-  
24 ing, R.; Nyström, G. Two-dimensional aggregation and semidilute ordering in cellulose  
25 nanocrystals. *Langmuir* **2016**, *32*, 442–450.  
26  
27  
28 (45) Beck, S.; Bouchard, J.; Berry, R. Dispersibility in Water of Dried Nanocrystalline  
29 Cellulose. *Biomacromolecules* **2012**, *13*, 1486–1494.  
30  
31  
32 (46) Zhao, Y.; Marshall, J. S. Spin coating of a colloidal suspension. *Phys. Fluids* **2008**, *20*,  
33 043302.  
34  
35  
36 (47) Kalashnikova, I.; Bizot, H.; Cathala, B.; Capron, I. New Pickering emulsions stabilized  
37 by bacterial cellulose nanocrystals. *Langmuir* **2011**, *27*, 7471–7479.  
38  
39  
40 (48) Nelson, K.; Turpin, D. Advancing Commercialization of Nanocellulose: Critical Chal-  
41 lenges Workshop Report. 2020; <https://doi.org/10.13140/RG.2.2.33789.59363>.  
42  
43  
44  
45  
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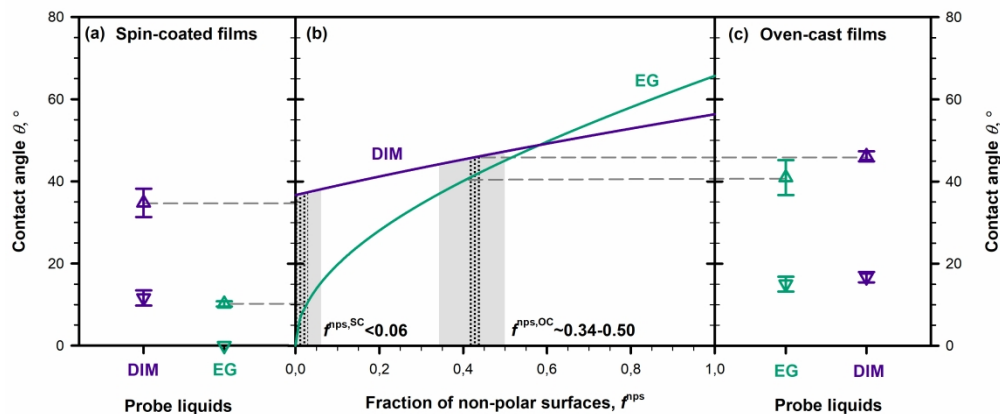
## Graphical TOC Entry





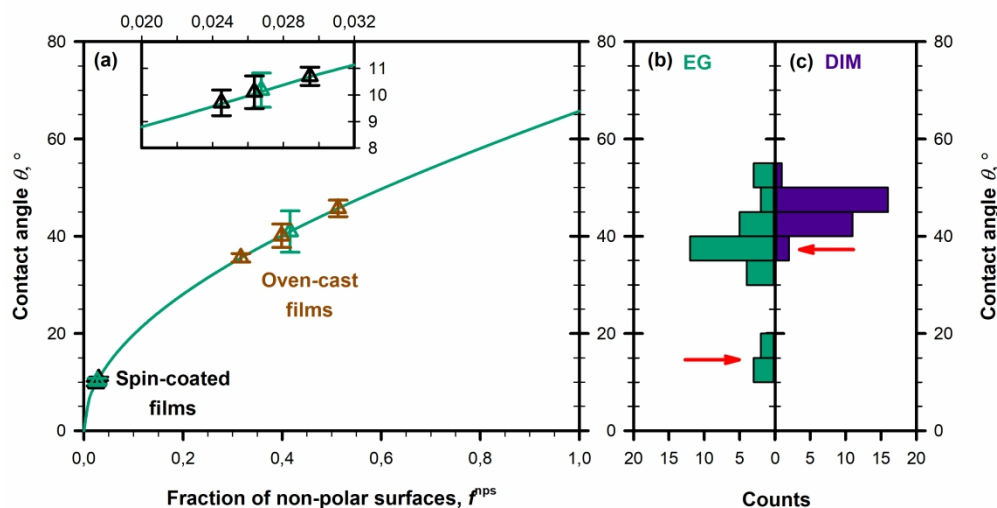
Morphology and representation of cellulose  $I_{\beta}$  nanocrystals. **(a)** TEM image of individual and agglomerated CNCs. **(b)** AFM height images of spin-coated (left) and oven-cast (right) CNCs. Micrographs are  $2 \mu\text{m}$  wide and were flattened (by a second-order polynomial) in order to remove their mesoscale roughness. **(c)** On the left is the cross-section of a cellulose  $I_{\beta}$ : polar surfaces  $-(010)$ ,  $(110)$ , and  $(1\bar{1}0)$  lattice planes– are plotted in blue, and non-polar ones  $-(200)$  lattice planes– are in yellow. On the right is a scheme of the octagonally-shape nanocrystal: its lateral surfaces are constituted of polar and non-polar stripes.

90x49mm (600 x 600 DPI)



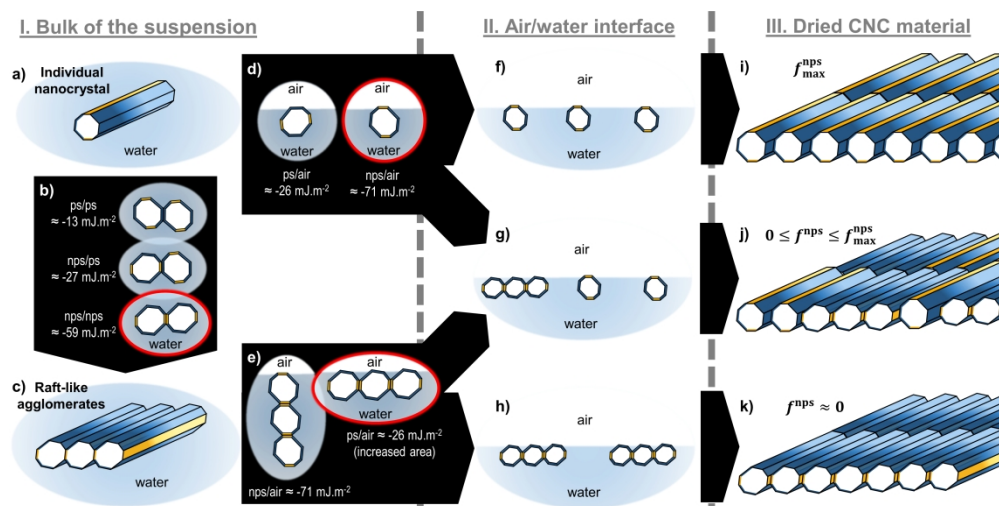
ARCA results for spin-coated (a) and oven-cast (c) films and their predictions in terms of non-polar fraction,  $f^{npS}$ , for the air/sample interface (b). EG and DIM results are plotted in green and purple, respectively. Average  $\theta_a$  values are represented by empty triangles up and  $\theta_r$  values by empty triangles down. In (b), filled lines are the plots of  $\theta_a$  as a function of  $f^{npS}$  (Eq. 7) for EG and DIM. The projection of  $\theta_a$  values (grey dashed lines) over these plots provides estimates for the samples' surface content in non polar surfaces. The consistency observed between the  $f^{npS}$  predictions derived from EG and DIM (with  $\sim 0.02-0.03$  between both predictions, highlighted by the dotted areas) confirms the validity of CNC surface tension parameters. Error bars in (a) & (c) are standard deviations. Their influence on the determination of  $f^{npS}$  is highlighted by the grey areas in (b).

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Repeatably of CNC orientation during the spin-coating and oven-casting processes based on EG results **(a)**. The green line and the green triangles up are the plots for Eq. 7 and for the average advancing CA values (see Fig. 2). The black and brown triangles up represent the advancing CA values measured for each of the spin-coated and oven-cast films, respectively. The insert is a zoom of the spin-coated results for greater readability. Error bars are standard deviations. Sessile drop measurements taken on 7 additional oven-cast films with EG **(b)** and DIM **(c)**. The results pointed by the red arrows are from a single data set, taken on a film that apparently failed to orient its non-polar functionalities at the air/sample interface to the same extent as the 6 other samples.

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Speculative mechanism for CNC orientation at the air/sample interface. Assuming CNCs are initially well dispersed **(a)**, they may either migrate to the air/water interface as individual nanocrystals or first agglomerate in the water bulk. Upon agglomeration **(b)**, CNCs preferentially assemble their non-polar surfaces to form raft-like structures **(c)**. Upon migration towards the air/water interface, individual CNCs orient their non-polar surfaces towards the air **(d)**. 2-D agglomerates may, however, prefer to orient their polar surfaces if their cross-sectional aspect ratio is large enough **(e)**. Depending on the state of CNC dispersion within the water bulk, the air/water interface may be populated by individual nanocrystals only **(f)**, by a mix of individual and agglomerated particles **(g)**, or by agglomerated CNCs only **(h)**. Upon casting, these result into thin films whose surface is either amphiphilic **(i)&(j)** or purely polar **(k)**. The fraction of non-polar surfaces that a film can expose should reach a maximum of  $f^{\text{nps}}_{\text{max}}$  in **(i)**, whose amplitude is a function of the nanocrystals' geometry, and a minimum of  $\sim 0$  in **(j)**.

180x90mm (600 x 600 DPI)