Inducing Nematic Ordering of Cellulose Nanofibers using Osmotic Dehydration

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ABSTRACT: The formation of nematicall-ordered cellulose nanofiber (CNF) materials with an order parameter \( f_{\text{max}} \approx 0.8 \) is studied by polarized optical microscopy, small-angle x-ray scattering (SAXS), and rheological measurements as a function of CNF concentration. The wide range of CNF concentrations, from 0.5 wt% to 4.9 wt%, is obtained using osmotic dehydration with poly(ethylene glycol). The rheological measurements show a strong entangled network over all the concentration range whereas SAXS measurements indicate that at concentrations >1.05 wt% the CNF suspension crosses an isotropic-anisotropic transition that is accompanied by a dramatic increase of the optical birefringence. The resulting nanostructures are modelled as mass fractal structures that converge into co-existing nematicall-ordered regions and network-like regions where the correlation distances decrease with concentration. The use of rapid, upscalable osmotic dehydration is an effective method to increase the concentration of CNF suspensions while partly circumventing the gel formation. The facile formation of highly ordered fibers can result in materials with interesting macroscopic properties.

The will to end the dependence on fossil fuel-based chemicals and components has driven the re-exploitation of ancient materials from renewable resources, such as cellulose, silk, collagen, etc.1 Particularly, cellulose nanomaterials extracted from plants are currently very attractive due to their excellent intrinsic optical and mechanical properties and the potential novel applications that uses these characteristics.2,3 However, despite the extraordinary intrinsic properties of nanocelluloses at the nanoscopic level, the translation of the properties to the macroscopic level is not straightforward and, e.g., their mechanical properties remain more than an order of magnitude below the expected value (Young’s modulus ≈ 100 GPa).2

There are a number of cellulose nanomaterials (also referred to as nanocelluloses)3 whence cellulose nanocrystals (CNC, highly crystalline and mechanically rigid) and cellulose nanofibers (CNF, medium crystallinity and more flexible) stand out. (For a more detailed description of such cellulose nanomaterials see Ref. [2] and refs therein). In the case of CNC, it has long been known that the assembly of the crystals in a chiral nematic phase, observed in both synthetic4 and natural5 materials, results in structural colors that can be controlled to tailor the visual appearance.6 Regarding CNF, their assembly into ordered phases has remained elusive7 as its flexibility leads to more entanglements by constraining their freedom of motion which together with the influence of surface charges leads to the formation of arrested states (glasses or gels) at very low concentrations.8

Some novel routes to circumvent the agglomeration have been recently put forward to induce the nematic ordering of CNF into 1D filaments, for instance, Håkansson et al.8 and Mittal et al.9 showed that flow fields can be used to align fibers achieving a maximum order parameter \( f_{\text{max}}\approx0.4 \) and \( f_{\text{max}}\approx0.5 \), respectively, whereas Torres-Rendon et al. used wet-stretching of wet-spun \( f_{\text{max}}\approx0.6 \) and Mohammadi et al. used coagulation \( f_{\text{max}}\approx0.6 \).11 Sehaqui et al. used cold drawing of wet films to achieve \( f_{\text{max}}\approx0.7 \).12 Zhao et al. used the slow evaporation of water to form 2D films of nematically-aligned CNF13 whereas Kobayashi et al. used the slow neutralization of the surface charges in CNF to bring about a liquid crystalline order in 3D14. However, the order parameter was not determined in either case. In all the above-mentioned cases there was a dramatic improvement of the mechanical/optical properties of the obtained materials. This calls for the development of controllable methods that can bring about ordering of the fibers.

In the previous work, it has been shown that a key element in achieving the assembly of the fibers is to reduce the network formation in the gel or glass form of the arrested states by promoting the orientation of CNF while controlling the concentration. Osmotic dehydration (OD) shares some features with the flow field orientation of cellulose as there is also a unidirectional removal of water. OD has been widely used to dehydrate food at industrial level,15,16 desalination, purification and biofuel separation and it shares.17
In this work, we used OD as facile approach to prepare nematically-ordered CNF suspensions in a time efficient manner. In the following we describe how we fabricate ordered CNF suspensions with nominal concentrations (C) up to 4.9 wt% ($f_{\text{max}} \approx 0.8$) without the addition of any substance or coagulant. We show their concentration-dependent structural evolution using polarized optical microscopy, rheological measurements and small-angle X-ray scattering.

The carboxylated CNF suspensions with initial concentration 0.5 wt% (surface charge 0.6 mmol/g, mean nominal aspect ratio $a_0 = 125$, see Supporting Figure S1) were sealed in dialysis bags and immersed in a 50 wt% poly(ethylene glycol) solution during different lengths of time to obtain CNF suspensions with concentrations up to 4.9 wt% (Supporting Figure S2).

Figure 1 summarizes the macroscopic characteristic of CNF suspensions under polarized optical microscopy (POM) and their rheological properties. Figure 1A, shows the CNF suspensions in the concentration range 0.5 ≤ C ≤ 4.9 wt% between cross-polarizers. At lower concentrations, i.e., C ≤ 0.5 wt%, only small birefringent regions typical of nematic ordering are visible. As the concentration increases so does the intensity of the birefringence, displaying even iridescent colors at high concentrations (> 1.7 wt%). The images show that there are a number of domains in the suspension of up to several mm in size. Figure 1B shows the order parameter obtained from the birefringence of the suspensions from. At 0.5 wt% there is already some reduced birefringence that indicates the early nematic ordering that increases readily towards 1 wt%. A plateau on the ordering is reached above 1.7 wt% but, as the POM images show, the size of the domains increases suggesting that nematic domains start coalescing. The values for the early onset of birefringence agree reasonably well with earlier reports.

Figure 1C shows the storage modulus ($G'$) of CNF suspensions as a function of the C. We correlated the strength of the suspension with the value of the $G'$ in the linear-viscoelastic range (= 0.1 to 10 % strain, see Supporting Figure S3). The amplitude sweep reveals that in the linear-viscoelastic range the value of $G'$ of all the samples is higher than the loss modulus ($G''$) indicating a network behavior of a viscoelastic solid (see Supporting Figure S3). The networks have a large storage modulus of up to 100 Pa at relatively low concentrations. Indeed, the data in the range up to 3.4 wt% follows a power law behavior $G' \propto C^\alpha$ with an exponent $\alpha = 2.2 \pm 0.2$, consistent with an entangled network of semiflexible polymers and earlier experimental studies on cellulose fibers. The combination of surface charge and aspect ratio of suspensions (i.e., the effective aspect ratio, $a_{\text{eff}}$) studied in the present work (excluding the highest concentration) lies within the limits of the critical concentrations given by the excluded volume of the fibers and the threshold for the formation of arrested states (see Supporting Figure S4), which may also result in the formation of a strong network.

Figure 1D shows the flow point ($\tau_\text{f}$) of the CNF gel, at which the $G'$ is equal to $G''$ in the shear stress amplitude sweep. After this point $G' < G''$ and the suspensions are characterized by liquid-like character. The $\tau_\text{f}$ steeply increases from 0.5 to 0.8 wt% after which reaches a plateau, followed by a further increase at 3.4 wt% and a decrease at 4.9 wt%. Before the flow point ($G' > G''$) the CNF suspensions are characterized by interconnected network structure that is able to dissipate the shear stress by elastic deformation. The fact that the $G''$ shows a peak in the amplitude sweep (see Supporting Information S3) suggests that this structure does not collapse suddenly but gradually until the final collapse at the flow point. Passed this point the CNF samples flow with viscous liquid behavior and the CNF are entangled. The decrease of the flow point at 4.9 wt% is related to the decrease of suspension strength, probably due to (random or ordered) agglomeration phenomena between the nanofibres.

Figure 1E shows the flow transition index, FTI = $\tau_\text{f}/\tau_\text{c}$, at which the suspensions still show network behavior but irreversible deformations are present together with the reversible-elastic behavior. The FTI shows a maximum towards 1 wt%, followed by a decrease in which it approaches 1 as the solid content increases. The $\tau_\text{f}/\tau_\text{c}$ characterizes the breaking behavior of the CNF network structure. Values closer to 1 shows that the CNF suspensions become more brittle, typical of ordered (crystalline) systems.
Indeed, the POM images show an increasing fraction of the nematic phase at $C \geq 1$ wt%, and together with the rheological measurements, they both point towards the formation of arrested states in competition with the formation of the nematic phase. At 4.9 wt% the ordered fraction may be surpassing the arrested fraction, resulting in the weakening of the suspension through phase separation.

The rheological measurements show that the CNF behaves as a viscoelastic network. We carried small-angle X-ray scattering studies to study the structural characteristics of the suspensions. 2D SAXS pattern of CNF suspensions are displayed in Figure 2A. In general, all the 2D patterns appears rather isotropic below 1.05 wt% where there is a slight increase of the anisotropy at higher concentration. Such isotropic-to-anisotropic transition could be highlighted via the azimuthal plot in Figure 2B. At each azimuthal angle, $\phi$, the intensity is integrated from the radial region of $q = 0.30 \pm 0.05$ nm$^{-1}$. When the concentration is below 1.05%, the scattering intensity is uniformly distributed along the azimuthal angles, while at higher concentrations such intensities show modulation as a function of azimuthal angle $\phi$, indicating preferred orientation. The observed order parameter, $f$, gradually increases with the concentration. This observation corresponds to a small portion of the nematic domains aligned along the same direction where the majority of the nematic domains are randomly oriented. This per se is in agreement with the appearance of nematic phases observed with POM where the images show a collection of randomly oriented domains.

The information on the hierarchical structures of CNF suspension and their dependence on the concentration can be extracted from 1D SAXS profile in Figure 2C. Given the small values of anisotropy in the 2D SAXS patterns, the SAXS line profiles were obtained by integrating the 2D SAXS radially 0–360°. In all cases, $I(q)$ displays a power-law dependence on the scattering vector ($q$) at $q \leq 0.1$ nm$^{-1}$ with an exponent close to $-2$. This exponent indicates an entangled network that can be approximated with a fractal system, consistent with the rheological measurements (see Figure 1C). At higher concentrations, two additional features become increasingly pronounced in the region $q \geq 0.1$ nm$^{-1}$ that shift towards higher $q$ values as the concentration increases. Given the dominant contribution from the interference between CNFs in the network, a shape-independent model (Eq. 1) by combining power-law function and two-stage gel model$^{25,26}$ has been employed to fit the experimental data, as an analog to the traditional scattering model of polymer gels.$^{27-29}$ In Eq. (1), the power-law function with a Porod exponent $n$ mainly contributes to the intensity variation in the low $q$ region, e.g. the large structure. The two-stage network model in the high $q$ region are modeled with a Gaussian function derived from the Guinier function and attributed to entangled region with a characteristic size of $\Xi$. \(^{25,30}\)
The change of $\xi$ and $\xi$ is also illustrated in Figure 3B, where the length of $\xi$ and $\xi$ reduces as the concentration increases regardless the way of the entire network connection.

The power-law term in Eq. 1 describes the complexity of the connections of the CNF suspensions, which is typically assigned to the fractal structure in finite scale. Shown in Figure 3B, the Porod exponents are plotted as function of CNF concentrations. The Porod exponents, $n$, is assigned to a mass fractal dimension $d_m$ when $\frac{5}{3} < n = d_m < 3$; and related to surface fractal dimension, $d_s$, by $n = 6 - d_s$, when $3 < n < 4$. The values of $n$ in all our cases are between 2.0 and 2.6, indicating the existence of mass fractal CNF networks with the fractal dimension equal to the Porod exponent. For a mass fractal nanofibers structure at the given concentration, the larger fractal dimension it has, the more complex connection it may have. The fractal dimension follows an interesting trend as the concentration increases, that it first decreases from 2.5 till a minimum $\approx 2.1$ at $C \approx 1.0$ wt% and then increases till a plateau around 2.3, which is independent to the further increased concentration. The transition point around 1.0 wt% is reminiscent of the transition from isotropic to anisotropic scattering patterns in Figure 2B. Similar fractal dimension change has been reported for the structures of nanoparticles agglomerates and whey protein networks at fixed concentration, showing a decrease followed by an increasing as a function of systematically increased ionic strengths. Such phenomenon was interpreted as a consequence of the change of the self-assembly kinetics between the fast diffusion-limited cluster aggregates (DLCA) and the slow reaction-limited cluster aggregation (RLCA). When increasing the amount of salts into the initial systems, the additives first screen the intrinsic surface charges of nanoparticles and proteins until they are neutralized and then flip the sign of their surface charge by an excess of amount. As a result, the net repulsion first decreases when surface charges are neutralized and then is overcome by the attraction, suggesting a transition from a glass to a gel state.

The higher fractal dimension associated with $C = 0.5$ wt% is due to a dominant net repulsion associated with the deprotonated carboxylate groups on CNF surface, leading to high degree of random connection in the CNF network (state (i) of the schematics in Figure 3B). Whereas the low concentration limited the absolute number of connections in a unit volume, and thus lead to the low strength (low value of $G'$). As the concentration of CNF (and the counterions) increases, the decay of the Debye length leads to a net attraction increase. Then, the CNF network collapses from a structure with higher fractal dimension at low concentrations to a structure with lower fractal dimension via adjacent CNFs attracting to each other as state (ii) in Figure 3B. Such CNF attraction certainly aids the formation of nematic domains. By assuming that some of the CNF in the network are more mobile than others, they would move and stay aligned with other less mobile CNF when the concentration is increased. The fractal dimension will continue decreasing until all the mobile ones are attracted to immobile one and reaches minimum, in this case, c.a. 1.05 wt%. During this process, the density of the contact points of the network keep increasing, rendering a stronger suspension with larger $G'$. Further increasing the concentration will force the networks to condense.

Figure 3. SANS-derived correlation lengths. (A) the development of $\xi$ and $\xi$ as a function of gel concentration. The dashed lines are power-law fitting. (B) The Porod exponents or mass fractal dimension change as a function of concentration. Schematics is to illustrate the structure characteristics with green lines as CNF, red region as the entangled region whose size correspond to the length of $\xi$, and arrowed lines indicating the correlation length $\xi$. Three types of CNFs connections (i – iii) illustrates the structures in different fractal number.

The third term is in a form of Lorentzian function or so-called Ornstein-Zernicke function with a correlation distance $\xi$, which depicts that the electron density correlation $\gamma(r)$ in the system via a modulated exponent function $\gamma(r) \approx \frac{1}{\xi} e^{-r/\xi}$. For polymer gels, $\xi$ typically describes the correlation length of polymer – polymer chains interaction due to the thermal fluctuation. The detailed fitting parameters can be found in the supplementary information (Table S1).

$$I(q) = A \cdot \frac{1}{q^n} + I_0(0) \cdot \exp \left( -\frac{q^2 \xi^2}{2} \right) + I_0(0) \cdot \frac{1}{1+q^2 \xi^2} + B \quad (1)$$

The dependence of $\xi$ and $\xi$ correlation distances on the concentration can be revealed by a log-log plot in Figure 3A. As the concentration increases, both $\xi$ and $\xi$ decrease, indicating that CNF become more closely packed. This trend can be fitted via power-law decay functions with the exponents $-0.62 \ (\xi)$ and $-0.35 \ (\xi)$, respectively. For ideal semi-diluted polymer solution, the exponent of such power-law decay is predicted as $-0.75$. In this case, neither of the exponents is close to this value. Generally, when a system is compressed isotropically in 3D, the separation distance will decrease as $C^{-1/3}$. According to the fitting results, the exponent of $\xi (-0.35)$ is very close to the $-1/3$. Considering the nematic phases are randomly oriented in 3D to a large extent in our system, the decrease of $\xi$ reflects a reduction of fiber to fiber distance in the nematic phase, which is equivalent to the isotropic shrinkage of a general 3D CNF network. The size of the agglomerate, $\xi$, is scaled with $\xi$ by a power $1.77 \ (0.62/0.35)$, indicating a fractal nature. Such power-law change leads to an interpretation that the agglomerates experience approximately affine contraction. The change of $\xi$ and $\xi$ is also illustrated in Figure 3B, where the length of $\xi$ and $\xi$ reduces as the concentration increases regardless the way of the entire network connection.
into higher fractal dimensions because the CNF attraction is frustrated by the depleted number of mobile CNF. However, the rigidity of the network consisting of CNF rigid bundles will generate mechanical resistance to densification. When a mechanical balance is reached, the fractal dimension of network will remain unchanged

In summary, we characterized the concentration-dependent structural evolution of carboxylated CNF suspension by macroscopic techniques, such as polarized optical imaging and rheological measurements, as well as SAXS. The macroscopic optical and rheological properties show that the CNF suspensions consist of randomly oriented nematic domains coexisting with a random CNF network. Towards C ≥ 1 wt% the nematic ordering readily increases reaching a maximum order parameter ≈ 0.8. Using SAXS we show that, at the microscopic level, CNF appears inside (anisotropic) nematic domains and in an (isotropic) entangled network that can be approximated with a fractal system. As the concentration increases, the correlation distance shows that CNF become more closely packed, which is equivalent to a reduction of fiber to fiber distance in the nematic phase and the isotropic shrinkage of the 3D CNF network. Our work shows that the formation of nematic domains in the CNF suspension is promoted by the increase of solid content by osmotic dehydration and the dynamics involving the charge screening between nanofibers. The technique has a potential to prepare ordered materials in a facile fashion while circumventing the formation of arrested states.

MATERIALS AND EXPERIMENTAL METHODS:

Carboxylated CNFs with surface charge of 0.6 mmol/g were prepared by TEMPO-mediated oxidation, according to the protocol of Saito et al. The dimensions of the obtained CNFs are 2.4 ± 0.7 nm in height and 299 ± 168 nm in length. A Veeco Dimension 3100 AFM in tapping mode was used to acquire the pictures in which the height of 100 and the length of 300 fibrils were measured. These values were fitted with a log-normal distribution from which the statistical analysis was carried out (Figure S1).

The concentration of CNFs in aqueous media was increased from the initial 0.5 wt% to a maximum of 4.9 wt% by controlling the time of osmotic dehydration using an initial osmotic pressure p = 30 kPa. Typically, a dialysis bag (cutoff of 14 kDa) containing 30 g of the initial CNF suspension was sealed from one extremity and then immersed in a 50 wt% poly(ethylene glycol) (PEG, Mw=3500 kDa) solution under magnetic stirring. The CNF suspension was manually mixed every 20 min so as to prevent a gradient build-up (Figure S2). The concentration of the CNF suspension was determined by thermogravimetric analysis using a Perking-Elmer TGA 7 under nitrogen atmosphere with a heating rate of 1 °C/min. The average error over four measurements was about 0.01 wt%.

The birefringence of the CNF suspensions was measured using a homemade setup with cross-polars and a digital camera. The CNF samples were deposited on a clean glass slide and constrained within a 10 mm-diameter Viton o-ring and mounted vertically. The intensity of the birefringent images under cross-polars, \( I \), was extracted using the program ImageJ. The order parameter \( f_{\text{Biref}} \) from was calculated according to Håkansson as

\[
\frac{f_{\text{Biref}}}{f_{\text{ref}}} \approx \frac{I}{I_{\text{ref}}} \tag{2}
\]

where \( I \) corresponds to the intensity of the image under cross-polars and \( I_{\text{ref}} \) to the total intensity under parallel polars, which gives \( f_{\text{Biref}} \approx 1 \).

The rheological characterization of the CNF samples was carried out with and Anton Paar Physica MCR 301 rheometer in oscillatory mode by using a plate-plate geometry at 23 °C. Amplitude sweep measurements were done at a frequency of 5 rad/s with amplitude scanning from 0.01 % to 1000 % using a gap size of 1 mm.

Small-angle X-ray scattering (SAXS) measurements were carried out at P03 "MiNaXS" beamline 39 at PETRA III storage ring, Deutsches Elektronen-Synchrotron (DESY), Hamburg. The X-ray energy of the beam with a cross section of 42 × 20 μm² was set to 13.0 keV and the sample-to-detector distance was calibrated as 5386.2 ± 0.1 mm using dry rat-tail collagen. The CNF samples were loaded into borosilicate capillaries (Hilgenberg, GmbH) with a diameter of 2 mm and a wall thickness of 10 μm. Beam damage to the samples was carefully scrutinized the changes to the intensity and scattering profile on consecutive images exposed at 0.1 s. 2D SAXS patterns were collected via a Dectris Pilatus 1M detector using exposure times of 0.4 s. Data reductions and analyses were carried out using the program DPDAK. The SAXS modelling and fitting were done using the program SasView 4.1. To quantify the degree of orientation from the SAXS curves, we use the Hermans orientation factor, \( f \) (see (Eq. 3)) as previously described. The reference direction (i.e. \( \phi = 0 \)) is set at one of the symmetric peak positions \( \phi_p \) of the azimuthal curve and integrating in the region \([\phi_p - \phi_p + \pi] \).

\[
f = \frac{\int_{\phi_p - \phi_p + \pi} I(\phi) \sin \phi \, d\phi}{\int_{\phi_p}^{\phi_p + \pi} I(\phi) \sin \phi \, d\phi} \tag{3}
\]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

It contains details on morphological characterization, the osmotic dehydration setup, additional data on the rheological characterization of the suspensions and the fittings parameters of the SAXS. (file type PDF)

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The manuscript was written through contributions of all authors and all authors have given approval to the final version of the manuscript.

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Supporting Information

Inducing Nematic Ordering of Cellulose Nanofibers using Osmotic Dehydration

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1. Additional experimental details

1.1 Morphological characterization

Figure S1. (A) AFM picture of the CNF (scale bar 500 nm). (B) and (C) show the histogram of the height and length distribution of the CNF, respectively measured from 100 and 300 individual nanofibers. The corresponding log-normal distribution is shown in red solid lines.

Figure S1 shows the morphological characterization of the CNF. The CNF suspension (concentration 0.01 wt%) was deposited on freshly peeled mica substrate, which has been functionalized with 3-aminopropyl triethoxysilane (Sigma Aldrich, 99 %) to ensure electrostatic adhesion of the CNF on the mica substrate. After removing the excess of suspension by a stream of air, the sample was ready for the analysis. The height and length of the nanofibers were obtained directly from the images acquired by atomic force microscope Veeco Dimension 3100 SPM (tapping mode). A lognormal function $y = \frac{A}{\sqrt{2\pi w^2}} \exp\left(-\frac{\ln(x/x_0)^2}{2w^2}\right)$ was fitted to the data from which the mean, $\bar{x}$, and standard deviation, $\sigma$, were calculated according to $\bar{x} = e^{(x_0 + w^2/2)}$ and $\sigma = \bar{x} \cdot (e^{w^2} - 1)^{1/2}$, respectively. The CNF used in this study have a mean length $\bar{L} = 299 \pm 168$ nm and mean height $\bar{h} = 2.4 \pm 0.7$ nm, giving a mean nominal aspect ratio $\bar{a}_0 = 125 \pm 88$. 
1.2 Osmotic dehydration setup

Figure S2. The schematic shows the CNF gel inside the semipermeable membrane, immersed in the PEG solution which is stirred by a magnetic bar.

As shown in Fig. S2, a semipermeable bag containing 30 g of carboxylated CNF suspension (0.5 wt%, prepared according to a previous report) is immersed in 200 g of a 50 wt% poly(ethylene glycol) solution ($M_w \approx 3500$ kDa). The dialysis bag is sealed in the bottom by a clamp, while the top is accessible. In the insert the up-concentration and alignment of the CNF is promoted by the removal of water and the osmotic pressure applied by the PEG solution. The clamp closes the membrane in the bottom and lets it accessible from the top, which is closed by a lid. Every 20 min a sample from the suspension is taken. The inset on the left represents the CNF suspension during the up-concentration process. Thanks to osmotic pressure difference, the water is removed from the CNF gel and the nanofibers alignment is aided.
1.3 Rheological characterization

Figure S3: The storage modulus, $G'$, (red line) and loss modulus, $G''$ (black line) of the CNF suspensions plotted as a function of strain, $\gamma$. The linear viscoelastic region can be seen from $\approx 0.1$ to $10 \% \gamma$. In all the samples $G'$ is higher than $G''$, indicating that the CNF gels behave like a viscoelastic solid, with a more predominate character as the $G'$ gets higher and higher compare to $G''$.

1.4 Critical concentration as function of aspect ratio. Excluded volume and arrested states.

Figure S4. Diagram of concentration as function of aspect ratio, $a$. The experimental symbols are obtained considering the effective aspect ratio $a_{\text{eff}}$ obtained from the constant length of CNF and its variable thickness, i.e., $h_{\text{eff}} = \tilde{h} + 2 \cdot \kappa^{-1}$ where $\kappa^{-1}$ is the Debye length. The error in $a_{\text{eff}}$ is obtained using the derivative of the expression for the effective aspect ratio, i.e., $\delta a_{\text{eff}} = \frac{\delta L}{h_{\text{eff}}} + \frac{1}{2} \frac{L \cdot \delta h_{\text{eff}}}{h_{\text{eff}}^2}$ where $\delta L$ and $\delta h_{\text{eff}}$ are the standard deviations of the length and height of CNF, respectively. The dotted line corresponds to the empirical formula for volume arrested states ($C_{V,\text{AS}}^*$) obtained by Nordenström et al. for a number of CNF suspensions$^2$ whereas the continuous line corresponds to the excluded volume calculation of fibers ($C_{BV}^*$) as defined by Mason.$^3$
1.5 Small-angle X-ray scattering

Table S1. SAXS fitting parameters of Eq. 1, see main text for details.

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2. Additional references

