

Water in motion: How charged semiflexible nanofibers affect self-diffusion of water

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Even at very low concentrations, the rheology of dispersions of charged semiflexible nanofibers differs from the rheology of the pure liquid, given the fiber charge, morphology, and interactions. At the nanoscale, the thermal motion of fibers is driven by the collective motion of the solvent molecules, but to what extent does the fiber presence and motion affect the self-diffusion of the liquid molecules? By studying the self-diffusion of water in dilute nanofiber dispersions using experiments and simulations, we can show that the interplay of fiber charge and motion on water mobility is more significant than the effect of the excluded volume caused by the charged particles.

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I. INTRODUCTION

Interactions between water and semiflexible nanofibrillar components such as natural or synthetic polymers, including proteins, strongly affect various biological processes and the efficiency of fabrication processes for nanofibrous material concepts. While extensive work has characterized how such fibers respond to solvent interactions, far less is known about how the presence and motion of these fibers, especially at low concentrations, impact the dynamics of the solvent itself. Since nanofibers can have cross-section dimensions of the order of nanometers and lengths of micrometers, the interactions take place over several length scales [1,2].

At nanometer to submicrometer length scales, the interaction between the solvent and nanofibers (such as water and cellulose nanofibers) results from various forces, including van der Waals forces, hydrogen bonds, electrostatics and hydrodynamics [3,4]. An illustrative example is the cellulose nanofiber (CNF) water system, which has been extensively studied regarding biosynthesis and biological function (e.g., plant cells [5]) and materials processing (e.g., nanocellulose-based sustainable materials [6]). On the molecular scale, water affects the surface chemistry of cellulose by interacting with the abundant hydroxyl groups, strongly influencing the properties of the cellulose surfaces, as well as altering the sorption behavior. Nakamura *et al.* distinguished between different populations of water to explain the water dynamics [7]. The interactions and dynamics are essential since water

can act as the reaction medium and the reactant, e.g., in the conversion of lignocellulosic material systems [8–14]. At low concentrations in the range of a few percent, the Brownian motion of the nanofibers on the micrometer scale is ultimately controlled by the collective behavior of water molecules and fiber-fiber interactions. Concentration, aspect ratio, and stiffness of the nanofibers thereby play a significant role [15–23].

Although self-diffusion of water is affected by various parameters and has been investigated at different temperatures and pressures [24–35], the self-diffusion of water in low-concentration nanofibrous systems appears to be unexplored [36–38]. As a starting point, the assumption is that in a static network of nonmoving stiff fibers at a low concentration, the bulk self-diffusion of water would mainly be influenced by the volume occupied by the fibers, i.e., the excluded volume, and the extension of this volume through the molecular interactions close to the fiber surface. In the following, we refer to the total affected volume in this static system as the effective excluded volume.

However, if the fibers are mobile and flexible, we hypothesize that the motion of these (translation, rotation, and bending fluctuations) influences the self-diffusion beyond the effective excluded volume already at very low concentrations, i.e., the dynamic movements of the fibers result in an affected volume that is larger than the effective excluded volume. We refer to this as the dynamic excluded volume.

To study this, ¹H pulsed gradient spin-echo nuclear magnetic resonance measurements (PGSE NMR) of the diffusive behavior of water in dilute CNF dispersions were performed and results were compared with results from coarse-grained molecular dynamics (MD) simulations. The results show that at low concentrations, semiflexible nanofibers affect water's self-diffusion behavior significantly beyond the expected effect of the excluded volume.

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II. EXPERIMENTAL

A. Sample preparation

TEMPO-mediated oxidized CNFs with three different charge densities (0.37 mmol/g, 0.79 mmol/g, 1.24 mmol/g) were prepared by following the protocol of Isogai *et al.* [39].

In short, the following steps were taken to prepare the dispersions: (i) TEMPO-mediated oxidized cellulose nanofiber solutions were diluted to 0.1 wt% with deionized water; (ii) the dispersions were homogenized using an Ultra-Turrax high-shear mixer (IKA T25) at 10.000 rpm for 10 min (18 mm diameter) followed by probe sonication (Sonics VCX 750) for 10 min at 40% amplitude in a surrounding ice bath using a 13 mm diameter probe; (iii) these dispersions were centrifuged at 4696 g at 20 °C for 1.5 h (Hettich Rotina 420R) and up-concentrated in an ultrafiltration setup (Amicon Stirred Cell) at 1 bar; and (iv) deuterium oxide was added to the concentrated CNF dispersions to ensure the locking of the magnetic field in the NMR self-diffusion measurements. The resulting composition was 10% deuterium oxide and 90% water in all samples. CNF dispersions were prepared at concentrations from 0.2 to 1.0 wt%. The samples were stored in the fridge at 5 °C before being dispensed into NMR tubes with an outer diameter of 5 mm. If necessary, samples were centrifuged for 5 min at 180 g to ensure homogenous filling of the tube.

B. Pulsed gradient spin-echo nuclear magnetic resonance measurements

¹H NMR measurements were performed on a 400 MHz Bruker Avance III HD spectrometer equipped with a broadband probe. The pulsed gradient spin-echo NMR method was used to determine the self-diffusion coefficients of water in the prepared dispersions. A stimulated echo pulse sequence with longitudinal eddy-current delay (LED) and bipolar gradient pulses of trapezoidal shape was used [40,41]. The effective length of a gradient pulse was set to 1.5 ms and diffusion time to 60 ms. The gradient strength was varied linearly in the range of 1–49 G/cm. Measurements were carried out at temperatures 15 °C, 25 °C, and 35 °C regulated within 0.1 °C.

The signal in the NMR diffusion measurement decays with increasing gradient according to the Stejskal-Tanner relation [42]:

$$I \propto e^{-D(\gamma g \delta)^2 (\Delta - \frac{\delta}{3})}, \quad (1)$$

where D is the self-diffusion coefficient, Δ is the diffusion time, δ and g are the length and strength of the field-gradient pulses, respectively, and γ is the gyromagnetic ratio for protons in this particular study. The self-diffusion coefficients are obtained by fitting Eq. (1) to the signal intensities measured over the applied gradient strength range. The self-diffusion coefficients presented in this paper are the average of ten measurements of two samples with a standard deviation of $\approx 0.5\%$. To ensure comparability with literature data, diffusivity data was corrected according to Holz *et al.* [43] to account for gradient calibration and the influence of 10% D₂O as calculated from Longworth [32] for all temperatures.

C. Fourier-transform infrared spectroscopy

For complementary information on site-specific cellulose-water interactions and the structure of water, infrared spectroscopy was carried out for all samples at 25 °C and 35 °C. Absorbance spectra were recorded from 600 to 4000 cm⁻¹ with an FT-IR Spectrometer (PerkinElmer Spectrum 100) in attenuated total reflectance (ATR) utilizing a MKII Golden Gate with a diamond crystal (Graseby Specac Ltd). The samples were directly placed on the diamond via pipette, and each spectrum was averaged from 32 scans with a spectral resolution of 2 cm⁻¹.

D. Atomic force microscopy

To study the morphology of the cellulose nanofibers, atomic force microscopy (AFM) imaging (Bruker AFM Multimode 8) was carried out in soft tapping mode in air. For this, a 0.01 wt% stock solution of each differently charged CNF dispersion was prepared and subsequently diluted down to 0.0025 wt% and 0.0005 wt%. The dispersions were vortexed in between for 1 min before being further diluted, and subsequently all dispersions were homogenized with an Ultra-Turrax (IKA T25) for 3 min at 7000 rpm. Finally, the cellulose nanofibers were deposited on (3-amino-propyl)triethoxysilane coated mica substrates for characterization. Approximately 300 nanofibers were analyzed to determine the average diameter and 500 nanofibers for the length distribution of each differently charged CNF dispersion. AFM images were analyzed with NanoScope Analysis and ImageJ yielding an average diameter (d_{av}) estimate of 2.2 ± 0.5 nm for the highly charged CNFs, d_{av} of 2.5 ± 0.5 nm for the medium charged CNFs and an average diameter of 2.2 ± 0.6 nm for the CNFs with a low charge density. This indicates no significant effect of charge. Lengths varied for all differently charged CNFs from around 40 nm to 1.1 μ m with the low charged CNFs displaying comparatively longer lengths up to 1.8 μ m. This trend in length with charge density was also visible in the mode values ranging from 100 nm for the highly charged CNFs to 104 nm and 160 nm for the medium and low charge density CNFs, respectively (see Fig. S4 in the Supplemental Material [44]).

III. SIMULATION

Coarse-grained molecular dynamics simulations were conducted to model the cellulose nanofibers based on our previous works [15,53] using the ESPRESSO software package [54] for the in-depth examination of diffusion dynamics within the polymer and fluid (liquid solvent) system. To deepen the understanding of how the fluid interacts with the cellulose nanofibers in the system, 100–300 pointlike tracers were introduced in each modeled system. Their motion was analyzed and compared between different cases to understand the behavior of fluid dynamics within the nanofiber network. This comparative analysis provided a detailed view of the interplay between the tracers and the surrounding medium.

A. Tracer diffusion

The diffusion of tracers in the system can be divided into two categories based on their proximity to the fibers. Following the modeling approach presented by Motezakker *et al.* [15], tracers are classified as near fibers if their distance from the fiber axis is smaller than the maximum deflection length of the fibers, which is dictated by fiber flexibility. Conversely, tracers at distances greater than this deflection length are categorized as far from fibers. The diffusion coefficient of tracers is computed at each time step, leading to a higher number of data points and a more accurate characterization of instantaneous diffusion behavior. The tracer diffusion coefficient is obtained from the mean square displacement (MSD):

$$D_{\text{tracer}} = \frac{1}{6} \lim_{\Delta t \rightarrow 0} \frac{\langle |r(\Delta t + t) - r(t)|^2 \rangle}{\Delta t}, \quad (2)$$

where $r(t)$ represents the position of the tracer at time t , and the ensemble average is taken over multiple trajectories.

B. Fiber diffusion

The motion of fibers in the dispersion includes both center-of-mass translational motion and structural deformations. In accordance with Motezakker and Söderberg [15], fiber normal diffusion is defined as the mean square displacement in directions perpendicular to the fiber's longitudinal axis.

1. Wiggling motion of fibers

The internal motion of fibers, including bending and undulation, contributes to a diffusion mode distinct from center-of-mass diffusion. This wiggling (fluctuating) motion of fibers is analyzed by considering the full bead structure of fibers, including all monomers and not solely the center of mass. The wiggling diffusion coefficient D_{wiggle} is extracted from the displacements of individual fiber beads:

$$D_{\text{wiggle}} = \frac{1}{6} \lim_{\Delta t \rightarrow 0} \frac{\langle |r_{\text{bead}}(\Delta t + t) - r_{\text{bead}}(t)|^2 \rangle}{\Delta t} \quad (3)$$

where $r_{\text{bead}}(t)$ represents the position of an individual fiber bead at time t . The inclusion of all beads ensures that both local and global undulations are incorporated in the analysis, particularly capturing the high-magnitude fluctuations at fiber endpoints. This formulation allows for a comprehensive distinction between fluctuation-induced (wiggling-induced) diffusion and translational fiber diffusion, accounting for the role of fiber flexibility and interaction with tracers.

IV. RESULTS AND DISCUSSION

To understand how cellulose affects water mobility, we characterized how self-diffusion of water changes in dilute CNF dispersions with varying nanofiber charges from 0.37 mmol/g to 1.24 mmol/g, in the concentration range 0.2–1.0 wt%. A decrease in water mobility could already be observed at the lowest CNF concentration of 0.2 wt%, independent of surface charge density.

Within the parameter range investigated, concentration has the most substantial effect on the diffusion coefficient [see Fig. 1(a)], while the surface charge density has a comparatively weaker effect. (see Fig. S14 in the Supplemental

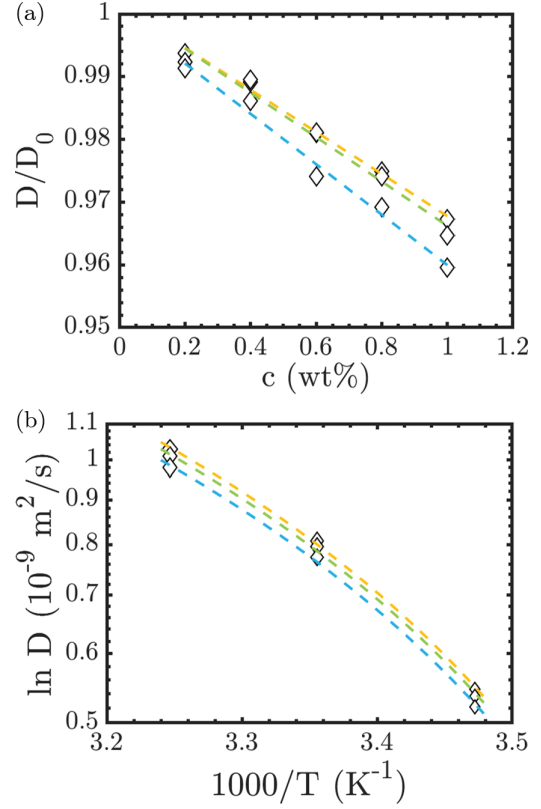


FIG. 1. Self-diffusion of water in dilute CNF dispersions as measured by PGSE NMR. (a) Concentration-dependent decrease of the normalized self-diffusion coefficient of water D/D_0 in a highly charged (blue), medium charged (green), and low charged (yellow) CNF dispersion at 25 °C. Linear regressions (dashed) are used to fit the data. (b) Temperature dependence of the self-diffusion coefficient of water D . For better visualization, only three CNF dispersions, namely, a 0.2 wt % CNF dispersion with low charge density (yellow), 0.6 wt% CNF dispersion with medium charge density (green), and 1.0 wt% CNF dispersion with high charge density (blue) are shown. The data points are fitted by a least-squares method. Error bars of the reported data points fall within the boundaries of the data markers.

Material [44]). The effect of temperature seems to follow the same trend in the investigated temperature range regardless of concentration and charge; see Fig. 1(b). Given these results, we focused on the concentration-dependent behavior and the mechanisms behind the observed effects. As seen in Fig. 1(a), measured self-diffusion coefficients follow a linear decrease with an increasing concentration regardless of the surface charge density of the CNFs, though water mobility is hindered most in the highly charged CNF dispersion.

To investigate this behavior further, we looked at the morphology of the cellulose nanofibers and the structure of water itself in combination with MD simulations focusing on the semiflexibility of the nanofibers. As the amount of CNF is increased from 0.2 wt % to 1.0 wt % and, consequently, the amount of water decreases from 99.8 wt % to 99.0 wt %, changes in the FTIR spectra can also be observed (see Figs. S1 and S2 in the Supplemental Material [44]). With an increase in concentration, absorbance bands at 1034 cm^{-1} , 1059 cm^{-1} , 1112 cm^{-1} , and 1161 cm^{-1} emerge, corresponding to the C-O stretching, C-O-C pyranose ring, the C-O stretching vibration

of ether and the C-O-C asymmetric stretching related to cellulose nanofibers, respectively [55–57], while the shoulder of the O-H stretching band at 3250 cm^{-1} decreases.

Depending on surface charge density, water's diffusivity decreases up to around 2.5–3% with increasing concentration. We hypothesize that this can be attributed to several effects leading to slower diffusion kinetics:

A. Increased surface area

Cellulose nanofibers have a high specific surface area of up to around $1200\text{ m}^2/\text{g}$, and with an increase in concentration from 0.2 wt % to 1.0 wt %, the total surface area of the nanofibers increases fivefold. With that, the number of potential interaction sites increases proportionally [3], which affects water mobility via an increased number of hydrogen bonds and the formation of more structured interfacial hydration layers [58]. CNFs consequently affect water diffusion in two ways: directly via electrostatic interactions and indirectly via structural rearrangement of the water structure in the vicinity of the nanofibers. This increase in surface area in combination with the charged nature of the CNFs thus leads to an increase in the effective excluded volume, slowing down water diffusion further. With TEMPO-mediated oxidation of cellulose nanofibers, charged groups are introduced on the nanofiber surfaces while the entire CNF network structure, similar to other nanocellulosic systems [59,60], is affected by the introduced surface charge density as well. This, in turn, influences water mobility within the CNF dispersions, with the nanofibers having the highest surface charge density exhibiting the strongest decrease in water diffusivity, as seen in Fig. 1(a).

B. Smaller interparticle distances

The higher the concentrations, the shorter the mean interparticle distance gets. Utilizing the particle density N , the mean interparticle distances L can be estimated from $L = N^{-1/3}$ to be in the submicron range for all concentrations [61]. This is considerably lower than the diffusion lengths probed in the performed NMR diffusion measurements, which are in the range of 24 to $32\text{ }\mu\text{m}$ according to the Einstein relation $L_D = \sqrt{6D\Delta}$ [62]. Consequently, the concentration-dependent self-diffusion coefficients presented here reflect the decreasing interparticle spacing in the submicron range, which contributes to the lower water mobility with increasing concentration. As the interparticle spacing decreases by a factor of 1.7, water molecules collide more with the cellulose nanofibers, hindering diffusion. Coarse-grained MD simulations showed that the internal fluctuating motions (wiggling) of the semiflexible nanofibers impeded the diffusion rate of inertialess tracer (water molecules), in agreement with the observed decrease in water diffusivity (see Fig. S9 in the Supplemental Material [44])

C. Dynamic excluded volume

The slowing down of self-diffusion of water can be understood further by considering the effects of semiflexibility [15].

The excluded volume effect on the self-diffusion of water, assuming a static system, can be estimated using a two-parameter power law [63], resulting in a roughly 0.45%

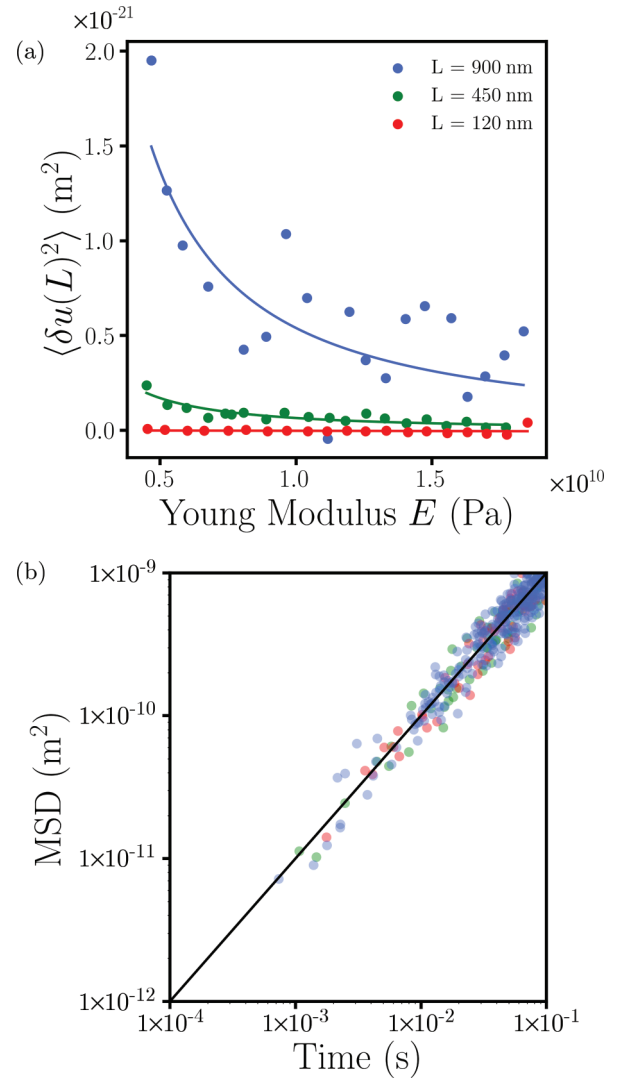


FIG. 2. Results from coarse-grained molecular dynamics simulations of nanofibers. (a) Length-dependent deviation of the endpoint of a nanofiber from its average position that is clamped on the other end showcasing the semi-flexible nature of nanofibers. (b) Mean square displacements of inertialess tracers in the fluid over time. Colors refer to systems with varying Young's modulus and nanofiber lengths from 150 nm (red) to 450 nm (green) and 900 nm (blue).

decrease of water diffusivity with the addition of 1.0 wt % CNF. This is around seven times lower than the observed decrease in water mobility, corroborating how semiflexible nanofibers hinder water diffusion beyond the effect of their excluded volume, as seen in Fig. 1. As MD simulations show in Fig. 2(a), nanofibers constantly move around their equilibrium position, depending on Young's modulus and length. By fixing one end of a nanofiber and looking at the other end of the fiber, it is clear that longer fibers and reduced Young's modulus result in a higher deviation from its average position. Consequently, more flexible nanofibers occupy an effectively larger volume that has the potential to affect the diffusive motion of the water molecules, i.e., the dynamic excluded volume is larger than the effective excluded volume.

An order-of-magnitude estimate supports the interpretation that local CNF wiggling, rather than whole-fiber

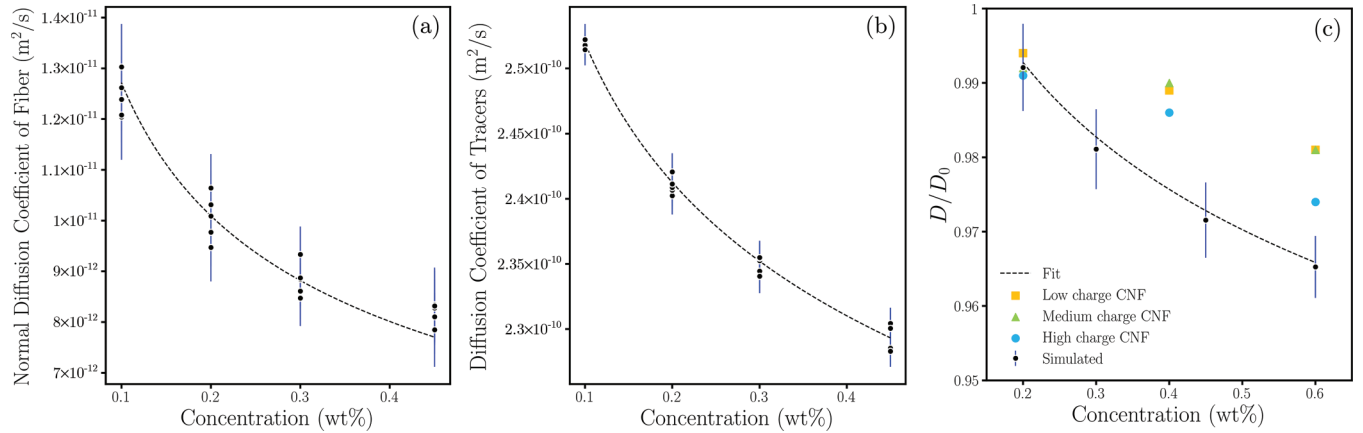


FIG. 3. Diffusion coefficients from coarse-grained molecular dynamics simulations of nanofibers and tracers. (a) Concentration dependence of the normal diffusion coefficient of nanofibers. (b) Concentration dependence of the diffusion coefficient of tracers. (c) Comparison of simulated and experimental diffusivity of tracers and water, respectively. Here, D_0 refers to tracer diffusivity determined at a very dilute concentration of 0.01 wt %.

translation, is a relevant factor in hindering water mobility (see Supplemental Material [44]). Using the measured CNF dimensions and the stiffness range employed in the simulations yield persistence lengths L_p of 1.5–6.1 μm , corresponding to an undulation envelope of 30–100 nm over the experimental length range. The local boundary motion during one wiggling event is smaller: combining the simulated wiggling diffusivity with the fluctuation times gives $\ell_f \approx 4\text{--}5\text{ nm}$, while the corresponding water diffusion length is $\ell_w \approx 10\text{--}13\text{ nm}$. By contrast, whole-fiber normal diffusion occurs on the 10^{-3} s scale and is therefore too slow to be relevant on these local length scales. These estimates do not yield a predictive law for D/D_0 , but they support the view that local CNF wiggling can contribute to dynamic hindrance on near-fiber scales.

From a condensed matter physics point of view, the dynamic excluded volume is strongly linked to the reptation model, which is used to describe the dynamics of entangled polymer chains [17]. According to the reptation model, each polymer chain's motion is confined to an imaginary tube defined by the transient network of adjacent polymer chains. From the simulations, it is clear that the diffusion coefficients of the nanofibers and the tracers decrease with increasing nanofiber concentration [see Figs. 3(a) and 3(b)], and the time required to fill the imaginary tube decreases with higher concentrations (see Fig. S7 in the Supplemental Material [44]). Thus, an increase in concentration results in decreased water mobility, both through an increased extended excluded volume, and their dynamic behavior, similar to what Nyström *et al.* [64] observed in cellulose gels. An increase in nanofiber concentration shifts the normal (transverse) diffusion of nanofibers from the millisecond range to the submillisecond range, and fiber undulations similarly slow down to the nanosecond range (see Table S5 in the Supplemental Material [44]).

When comparing our MD simulation data directly with experimental diffusivity data [see Fig. 3(c)], it is worth noting that, despite the fact that pointlike tracers were used to describe water dynamics, diffusivity values differ by about 1%, i.e., less than an order of magnitude. However, given

the nature of coarse-grained modeling, this level of agreement between simulated and experimental water diffusivity should be solely interpreted as qualitative, and does not imply near-quantitative equivalence of tracers and water molecules. The discrepancy of simulated and experimental diffusivity values can be related to (i) the nature of coarse-graining of CNFs as groups of atoms are represented by beads reducing the degrees of freedom [65]; (ii) the limitations of using an implicit fluid, e.g., not reflecting the directional nature of hydrogen bonding [66]; (iii) the negligence of CNF surface charge effects on water such as, e.g., formation of structured hydration layers [58]; and (iv) inherent limitations of MSD calculations depending on the size of the simulation box [67,68].

The experiments and simulations probe complementary aspects of the system. Experimentally, the CNF surface charge density is varied; this can affect water transport through interfacial hydration/electrostatic structuring, charge-dependent fiber-fiber interactions, and network organization, and possibly also indirectly through altered fiber dynamics. In the coarse-grained simulations, explicit electrostatics are omitted, so the simulations should be interpreted as isolating the mechanical contribution of fiber mobility and dynamic confinement. The experimental charge dependence, therefore, likely reflects coupled electrostatic, structural, and dynamical effects rather than flexibility alone.

In more flexible systems, such as, e.g., aqueous poly(ethylene oxide) solutions [58], we hypothesize that the self-diffusion is hindered in a similar fashion, while in a less flexible system containing, e.g., carbon nanotubes [69], a dynamic excluded volume plays a less significant role. To test this hypothesis, coarse-grained MD simulations of nanofiber systems with varying Young's modulus were performed. The normal diffusion of nanofibers as well as the diffusion of tracers close to the nanofiber surface decrease with increasing stiffness as shown in Fig. 4, whereas tracers further away are less affected. In contrast, nanofiber fluctuations and undulations (wiggling) increase with increasing flexibility, highlighting how semiflexibility plays a role in hindering water mobility (see Fig. 4 and Figs. S10-S11 in the Supplemental Material [44]).

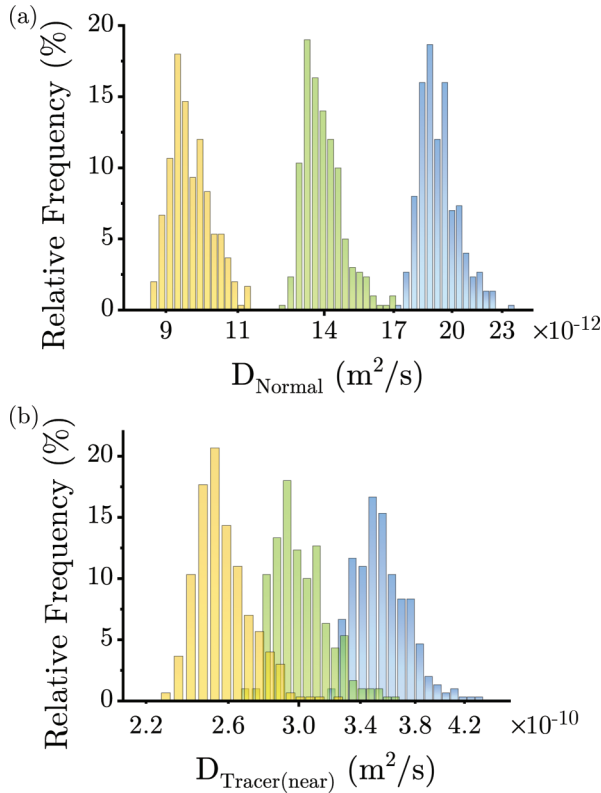


FIG. 4. Results from coarse-grained molecular dynamics simulations on nanofiber systems with varying Young's modulus. (a) Elasticity dependence of the normal diffusion of stiff (yellow), semiflexible (green), and flexible (blue) nanofibers in dispersions with 0.1 wt %. (b) Elasticity dependence of the diffusion of tracers near stiff (yellow), semiflexible (green), and flexible (blue) CNFs in dispersions with 0.1 wt %.

While several diffusion models have been established to describe diffusion in polymer solutions and gels, each model comes with constraints, limiting its applicability. To assess our hypothesis that the extended excluded volume of the cellulose nanofibers is responsible for the observed decrease in water mobility, we evaluated various diffusion models to determine which one is best suited for the description of water diffusivity in the dilute CNF dispersions studied here.

The Maxwell-Fricke model, based on obstruction effects, accounts for the extended excluded volume effects and treats diffusion as a process in a continuous, homogeneous medium (solvent) with dispersed obstructing particles [70,71]:

$$\frac{D(1-\varphi)}{D_0} = \frac{1-\varphi'}{1+\frac{\varphi'}{\chi}}, \quad (4)$$

where D and D_0 are the diffusion coefficients of the mixture and pure solvent, respectively. χ is a form factor depending on shape and orientation of the CNFs, φ is the volume fraction of the CNFs, and φ' is the CNF volume fraction incl. the immobile solvent layer bound to the CNFs. Whereas the Maxwell-Fricke model attributes the decreasing water mobility to an increased mean path length of the diffusing water molecules with increasing CNF concentration, the reduction in water diffusivity is systematically underestimated in the

dilute concentration range up to 1 wt % CNF (see Fig. S12 in the Supplemental Material [44]). This is to be expected, as diffusion models based on hindrance effects treat polymer chains as stationary with the assumption that the self-diffusion coefficient of the polymer is much smaller than the solvent's, neglecting the effects of semiflexibility [72].

To assess the impact of hydrodynamic interactions between the CNFs and water, we next evaluated the Gao Fagerness diffusion model, which describes diffusion in a noninteracting polymer network, where the steric obstruction of each individual component affects diffusion in an additive fashion [73]:

$$D = D_0 e^{-\sum K_i c_i}, \quad (5)$$

where D and D_0 are the diffusion coefficients of the mixture and pure solvent, K_i is a proportionality constant, and c_i is the concentration of the viscosity-inducing agent present in the mixture. Strictly speaking, hydrodynamic arguments were not discussed by the authors of this model, however, the exponential dependence of the diffusion coefficient in Eq. (5) is very similar in form to other diffusion models based on hydrodynamic interactions, such as, e.g., the Cukier model [74] or the diffusion model by De Gennes [75]. In these models, the exponential factor α , in this case K_i , reflects hydrodynamic screening in the dispersions and is a measure of how strongly diffusion is hindered. The Gao Fagerness model seems to fit the experimental data better than a simple obstruction model, showcasing how the self-diffusion of water is mainly dependent on the CNF concentration, as seen in Fig. 1(a) and Fig. S12 in the Supplemental Material [44]. Furthermore, Gao and Fagerness observed a similar decrease in water diffusivity across different solutions of glucose-containing molecules, demonstrating that water mobility is affected similarly in these systems independent of the nature of the viscosity inducing agent (solute).

To determine if free volume is the key factor in governing water diffusion in our dilute CNF dispersions, we employed the Yasuda model, which treats diffusion as molecular motion through a material via transient free volume (empty space) regions [76]:

$$\frac{D}{D_0} = e^{\left[\frac{B}{f_V^*} \left(1 - \frac{1}{1-\varphi_P}\right)\right]}, \quad (6)$$

where D and D_0 are the diffusion coefficients of the mixture and pure solvent, B is proportional to the diffusant size and associated with the minimum free volume needed for jump diffusion, f_V^* is the volume free of solvent, and φ_P is the polymer volume fraction. In polymer science, the term “free volume” relates to the volume not occupied by matter itself, which allows diffusing species to move through it [77]. In the Yasuda model, this free volume is assumed to come primarily from the solvent fraction, enabling the displacement of the diffusing species. Compared to the previous models, the Yasuda model deviates the most from the observed experimental data, predicting a decrease in water mobility of 0.58% at a CNF concentration of 1 wt % (see Fig. S12 in the Supplemental Material [44]). This significant discrepancy arises from the fact that no interactions between the CNFs and water are accounted for in this model next to neglected polymer diffusion as in previous models.

Each of these models has been previously used to investigate diffusion in cellulosic systems [71,73,76], yet none seem to accurately describe the self-diffusion of water in the dilute dispersions of charged, semiflexible CNFs as used here. To capture the observed hindrance beyond static obstruction, we fit the data with a modified Mackie–Meares expression [78]:

$$\frac{D}{D_0} = \left(\frac{1 - \beta\varphi}{1 + \beta\varphi} \right)^2, \quad (7)$$

where D and D_0 are the diffusion coefficients of the mixture and pure solvent, φ is the volume fraction of the polymer, and β is an empirical volume-renormalization parameter fitted separately for each charge series. It is not independently derived from measured charge density, fluctuation amplitudes, or fluctuation timescales, and the model is not intended as a predictive law outside the fitted range.

In other cellulosic systems, a mobile and less mobile water population has been observed, while only one population is observed in the dilute CNF dispersions reported here [7,79–82]. Self-diffusion coefficients measured with PGSE NMR do not vary over orders of magnitude [38]. To test the existence of different populations of water, randomly distributed tracers were placed within the fluid, and their mean-squared displacement was calculated over time, yielding similar results for the self-diffusivity independent of tracer placement, as seen in Fig. 2(b). Thus, our simulations show the existence of only one water population in nanofiber dispersions, as no significant difference in diffusivity near the fibers and further away could be seen (see Fig. S9 in the Supplemental Material [44]). These results indicate that the self-diffusivity of water probed corresponds to free or so-called bulk water. That is to be expected in dispersions with CNF concentrations up to 1.0 wt % with water diffusion likely taking place via long-range networks of percolated low-density liquid clusters of water molecules in the investigated temperature range [83].

V. CONCLUSION

In this paper, we demonstrated that even small amounts of charged nanofibers can hinder water mobility, as shown

in dilute CNF dispersions. By combining PGSE NMR and FTIR experiments with coarse-grained molecular dynamics simulations, we revealed that the joint effect of fiber charge, morphology and dynamics—particularly fiber bending fluctuations—significantly reduces water self-diffusivity.

These findings underscore how sensitive water transport is to nanofiber charge, concentration, and flexibility as the interplay of electrostatic interactions and geometric hindrance leads to a dynamic excluded volume of the nanofibers with carboxylate groups promoting interactions with the surrounding water. Beyond the specific case of cellulose affecting water mobility, our results reveal that, as we hypothesize, a general mechanism, the dynamic excluded volume, can affect molecular diffusion in any system containing mobile semiflexible structures. This has implications for understanding fluid behavior in crowded or entangled environments, from polymer solutions and nanocomposites to biological systems.

Our study thus contributes unique physical insights into fiber–solvent interactions, supporting better modeling and design of soft and hybrid materials. The coupling between solvent dynamics and the motion of nanostructures is of broad relevance across physics, materials science, and soft matter.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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