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Microscopic properties of nanopore water from its time-dependent dielectric response

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Abstract

We present a simple kinetic model for the orientational dynamics of a chain of hydrogen-bonded molecules due to the diffusion of orientational defects. We derive an event-driven algorithm which allows us to do kinetic simulations for chains from nanoscopic to macroscopic lengths, spanning huge orders of magnitude in time. Our simulations and analytical calculations show that nanopore water exhibits Debye behavior arising from the diffusive dynamics of orientational defects. For the limits of short and long chains we derive analytical expressions for the relaxation times which allow to extract the diffusion constant, the effective interaction, and the excitation energy of these defects from dielectric spectroscopy experiments. We also discuss the possibility to use such experiments to detect if the two possible kinds of orientational defects differ in excitation energy and diffusion constant.

I. INTRODUCTION

Water confined to the apolar channels of pores with a sub-nm diameter forms one-dimensional chains of hydrogen bonded molecules¹. In biological systems, such single-file water is found in the channels formed by membrane spanning proteins where the pore structure determines the transport properties of the chain. Gramicidin A, for example, allows for ion transport whereas aquaporin channels are impermeable for ions but do conduct water²⁻⁷. The geometrically simplest confinements for single-file water, however, are cylindrical pores which can be realized to a good approximation with carbon or boron nitride nanotubes^{1,8}. These tubes offer controlled conditions to investigate the physical properties of single-file water and may serve for the design of bio-mimetic devices^{9,10}. Also, the well defined pore diameter renders carbon nanotubes highly selective for ions and the smooth inner surface allows for high water fluxes^{1,11,12}. Both properties might be exploited in molecular sieves with potential application in filtration devices^{10,13-17}. Water filled carbon nanotubes might also serve as proton conductors, e.g. in fuel cells^{18,19}. Efficient proton conduction along single-file water relies on the continuity and dipolar order of the chain of hydrogen bonded molecules. Both conditions are met at room temperature and atmospheric pressure in carbon nanotubes up to a tube length of 0.1 mm²⁰. For longer tubes, orientational defects occur and destroy this macroscopic order. These order properties might be harnessed in carbon nanotube membranes with a very high dielectric constant²¹, but so far, the investigation of these remarkable order properties remains an experimental challenge.

Only recently, Cambré *et. al* were able to show in Ra-man spectroscopy experiments for the first time that carbon nanotubes fill with water down to a chiral index (5,3) corresponding to a diameter of ≈ 0.55 nm²². The observed Raman spectra provide signatures of the structural order of the water molecules and allow one to differentiate between single-file water and

water structures in wider tubes. However, it remains a theoretical challenge to link these spectra to specific structures. Alternatively, dielectric spectroscopy experiments on water-filled non-metallic nanopores may offer a way to determine not only if macroscopic order exists, but also to measure the fundamental properties of single-file water like the average diffusion constants and excitation energies of defects^{21,23}. These quantities bear clear evidence of the molecular structures and the involved relaxation processes. For example, the average excitation energy and the effective interaction of defects are determined by the dipole-dipole interaction of water molecules linked together by hydrogen-bonds to a single-file chain. Also, the average diffusion constant of defects is a result of the rotational motion of water molecules in the chain and determines the orientational relaxation of the whole chain.

In this article we expand on an earlier brief report²³ and study in detail the orientational dynamics of single-file water and the time-dependent dielectric response that results from it. To do that, we develop a kinetic generalization of a dipole lattice model we recently used to study the structure and free energetics of nanopore water^{20,24}. This kinetic model mimics the generation, motion, annihilation and recombination of orientational defects as a Markov process with rates extracted from detailed molecular dynamics simulations. An event driven version of the simulation algorithm allows us to investigate single-file water from nanoscopic to macroscopic tube lengths over timescales ranging from picoseconds to milliseconds. Performing extensive computer simulations and using a law of corresponding states, we show that single-file water at room temperature shows Debye relaxation for all tube lengths, albeit for different reasons for short and long tubes as we will discuss. We find analytical expressions for the relaxation time in the limits of short and long tubes, which together with the expressions for the static dielectric susceptibility^{21,23}, can be used to measure the fundamental properties of nanopore water in dielectric spectroscopy experiments. Moreover, these expressions might also be used to determine differences between the two kinds of hydrogen bonding defects occurring in single-file water chains. Many of our considerations are based on the analogy of our dipole model to the one-dimensional kinetic Ising model²⁵, a model system that has been used to study numerous phenomena ranging from critical phenomena²⁶ to glassy dynamics^{27,28}.

The remainder of this article is organized as follows. In the next section, we briefly introduce the dipole lattice model, discuss the kinetics of defects and its implementation in our model, and introduce the event-driven algorithm. We present simulation results for the autocorrelation function of the total dipole moment and the linear dielectric response in Sec. III and derivations for the relaxation time in the short and long chain limit in Sec. IV. The effects of two different types of orientational defects, L and D defects, on the dielectric relaxation process are discussed in Sec. V and some conclusions are provided in Sec. VI.

II. MODEL AND METHODS

The free energetics of nanopore water are well described by a recently developed dipole lattice model in which water molecules are represented by dipoles of magnitude μ located on the sites of the one-dimensional lattice with spacing a . To model the restricted possible orientations of water molecules in a single-file chain, the dipoles can assume only three different orientations: parallel or anti-parallel to the pore axis in the case of water molecules with typical hydrogen bonding, and orthogonal to the pore axis for defect molecules²⁴. Such defect molecules connect ordered segments of water molecules of opposite direction. While a water molecule within an ordered segment donates one hydrogen bond to a neighboring molecule and accepts one from a molecule on the other side, typical defect molecules either donate two hydrogen bonds without accepting any (L-defect) or accept two hydrogen bonds

without donating any (D-defect). The total energy of the dipole model is given by the sum of all dipole-dipole interactions,

$$H = - \sum_{i=1}^{N-1} \sum_{j=i+1}^N \epsilon \frac{2s_i s_j}{|j-i|^3}, \quad (1)$$

where N is the number of molecules. The spin s_i , located at site i , can either take on values ± 1 for water molecules within ordered chain segments and it is zero else. In the above Hamiltonian, $\epsilon = \mu^2/(4\pi\epsilon_0 a^3)$ sets the energy scale of the model and ϵ_0 is the vacuum permittivity. The parameters of the model were extracted from a fully atomistic molecular dynamics simulation based on the TIP3P water model yielding the lattice spacing $a = 0.265\text{nm}$, the dipole moment $\mu = 1.9975$ Debye, and the energy constant $\epsilon = 12.9118$ kJ/mol²⁰. Note that in the above formulation of the model we have assumed that all lattice sites are occupied with exactly one dipole, such that the number of hydrogen bonds in the chain is constant and does not need to be included explicitly in the Hamiltonian. Since the rotational entropy of such a chain of water molecules with an arbitrary number of defects is a conserved quantity, the rotational degrees of freedom of the molecules are effectively integrated out in our model²⁴. This model is a special case of the dipole lattice model that permits empty sites, as for instance required for the study of pore filling and emptying^{20,24}.

The Hamiltonian of the dipole model can be rewritten in terms of the interactions of effective charges located at defect sites and chain ends. In this mathematically equivalent charge picture, the Hamiltonian of the dipole lattice model is given by

$$H = \sum_{m=1}^{2n_d+1} \sum_{n=m+1}^{2n_d+2'} \epsilon q_m q_n \Phi(z_{mn}) + n_d E_d, \quad (2)$$

where n_d is the number of defects, $E_d = \epsilon 4[\zeta(2) - 1]$ is the defect excitation energy, and $\zeta(n)$ is Riemann's zeta function. The effective charges of magnitude $q_m = \pm 1$ are located at the ends of dipole ordered segments and interact Coulomb-like via

$$\Phi(z) = 2\Psi'(z) + z\Psi''(z) \approx \frac{1}{z}, \quad (3)$$

where $\Psi'(z)$ and $\Psi''(z)$ are polygamma functions and the approximation $\Phi(z) \approx 1/z$ is valid for distances z larger than one lattice spacing. The prime in the Hamiltonian of Eq. (2) indicates that we do not include the interaction of the two charges forming a defect in the sum as these contributions are included in the excitation energy. For the parameters obtained from molecular dynamics simulations, effective defect charges have a magnitude of $2\mu/a \approx 0.31 e$ and chain endpoints carry charges of half this magnitude. The defect excitation energy takes on the value $\beta E_d \approx 13.45$.

If the distances between effective charges are large, i.e., the defect density is low, the effective Coulomb interactions between defects can be neglected yielding a correspondence of the dipole model to the one-dimensional (1D) Ising model²¹. In the 1D Ising model, domains with all spins “up” and sections with all spins “down” correspond to the dipole ordered segments of water molecules in single-file water. Kinks in the Ising model then

correspond to L and D defects in a chain of water molecules and the coupling constant in the Ising model equals half the defect excitation energy, $J = E_d/2$. On the basis of this analogy between the dipole model and the 1D Ising model, exact expressions can be derived for the free energy of the system as a function of the total dipole moment as well as for the dielectric response to a static external electric field.

The dipole lattice model outlined above is the starting point for the development of a kinetic model that mimics the formation, the recombination, and the diffusive motion of orientational defects. This model will then provide the basis for the simulation of the time-dependent dielectric properties of the system.

A. Kinetic Model

The orientational dynamics of single-file water chains is determined by the generation, recombination and migration of hydrogen bonding defects, which lead to the reorientation of water molecules and hence to changes in the total dipole moment of the system. Molecular dynamics simulations show that these processes involve the cleavage and formation of hydrogen bonds and the rotation of molecules as illustrated schematically in Fig. 1. When a defect hops from one molecule to the next, the hydrogen bond between these two molecules is broken, the molecules rotate, and a new bond is formed [Fig. 1(a) and (b)]. Similarly, single defects are formed at the end of the chain, when the hydrogen bond between the end molecule and the next molecule is broken, the molecules rotate and a new bond is formed [Fig. 1(c)]. A defect is annihilated if it hops from the molecule next to the end molecule towards the end [Fig. 1(d)]. Within an ordered domain, defect pairs can be formed [Fig. 1(e)]. In this process, both hydrogen bonds of a single molecule are broken and the molecule itself and its two neighbors rotate and form new bonds. The molecules on the left and on the right of the central molecule then form the two defects. A defect pair recombines, if one of these defects hops towards the other one [Fig. 1(f)]. We point out that all of these processes alter the actual state of the chain whereas the breaking and reformation of a hydrogen bond, with the donor and acceptor molecule remaining the same, does not. The latter was analyzed in detail by Mukherjee *et al.*²⁹.

The dipole model described above can easily be modified to incorporate the basic events of defect formation and diffusion in form of dipole flips modeled as a Markov process³⁰. In this approach, time is discrete and the time unit is given by the hopping time Δt , corresponding to the average time a single defect in an infinitely long chain needs to hop to a nearest neighbor site. We only have to specify the transition rates for the displacement of a defect and for the generation of defect pairs. All other events, i.e., defect recombination and defect generation and annihilation at chain ends, can be viewed as a direct consequence of defect diffusion: If the hop of a defect to an adjacent site brings it next to another defect, then these defects recombine. If a defect hops to the molecule at the chain end, then it is annihilated. Consequently, the generation of a defect at a chain end can be modeled as a hop of a defect into the chain. The transition rates for these events follow from detailed balance to guarantee that the equilibrium distribution of states is conserved by the dynamics.

In a straightforward implementation of the kinetic dipole lattice model, we proceed in the following steps. First, we randomly choose a site and perform a trial move. Which trial move is carried out depends on the position and orientation of the chosen molecule. One of the trial moves is the displacement of a defect, which can lead to the annihilation of the defect at a chain end or to the recombination with another defect. If a molecule at a chain end is chosen, we try to generate a single defect at the molecule next to it. For a molecule within an ordered domain, we try the generation of a defect pair. Then, we accept or reject the trial move according to an acceptance criterion specified below. Note that the trial moves take into account that defects are separated from each other and from the chain ends by at

least a single molecule²⁴. This procedure of trial move generation and acceptance/rejection is repeated N times before time is advanced by Δt .

Trial moves are accepted or rejected using either the Metropolis³¹ or the Glauber²⁵ acceptance criterion, both of which obey detailed balance. In the following, we focus on Glauber dynamics and refer the reader to the Appendix for the corresponding expressions for Metropolis dynamics. In Glauber dynamics, the acceptance probability is given by

$$p_G^a = \frac{1}{1 + e^{\beta \Delta E}}, \quad (4)$$

where ΔE is the energy difference between the new and the old configuration. For the diffusion on a flat energy landscape the probability to accept a move to the left, $p = 1/4$, is equal to the probability to move to the right. Thus we have a probability of $p = 1/2$ for the defect to stay at the original position.

The connection of simulation time to real time is established via the diffusion law in one dimension,

$$\langle x(t)^2 \rangle = 2Dt, \quad (5)$$

where $x(t)$ is the displacement, t the time, and D the diffusion constant. Thus, we obtain for the hopping time, Δt , of a defect to an adjacent site,

$$\Delta t = \frac{a^2}{2D}. \quad (6)$$

At room temperature, L defects have a diffusion constant of $D_L \approx 0.03 \text{ nm}^2/\text{ps}$ and are slower than D defects, which have a diffusion constant of $D_D \approx 0.05 \text{ nm}^2/\text{ps}$ ¹⁸. For the moment, we use the average diffusion constant D given by $D = (D_L + D_D)/2$ for both kinds of defects, $D = 0.04 \text{ nm}^2/\text{ps}$. Demanding that the diffusion of a defect on a flat landscape occurs at the same speed as in molecular simulations, one sweep corresponds to a time $\Delta t_G = \Delta t/2 \approx 0.44 \text{ ps}$ using Glauber dynamics. Since Metropolis dynamics is twice as fast as Glauber dynamics, $\Delta t_M = 2\Delta t_G$, we use it for our simulations (see Appendix). As we shall see, these results agree well with predictions for Glauber dynamics, indicating that our results are not sensitive to the details of the dynamics.

B. Event-driven Algorithm

In large systems with a low density of defects, the most frequently attempted move is the generation of a defect pair, which, however, has a very small acceptance probability due to the large energy required for this process. Thus, a large amount of computing time is consumed selecting and rejecting the generation of defect pairs. To avoid these long waiting times, we introduce an event-driven algorithm which is facilitated by the introduction of a cutoff in the effective charge interaction of defect pairs²¹ for the pair generation trial move. Consequently, we can calculate the waiting time distribution for defect pair generation analytically, which allows us to bridge the long waiting times, as we shall see in the following.

Since L and D defects consist of charges of the same magnitude but opposite sign, defect pairs are charge neutral and form an effective dipole parallel to the tube axis. The dipole moment of the defect pair determines the interaction energy with other defects for large distances and decays like $1/r^2$ with distance r . This fast decay of the interaction energy with distance allows the introduction of a cutoff for the defect pair generation move. For all other moves, we calculate the interaction energy using the full Hamiltonian without a cutoff given by Eq. (2). We point out that the cutoff in the interaction energy for the generation of a defect pair introduces a small error in the total energy since no cutoff is used for all other moves. Consequently, after a defect pair is generated we calculate the energy change using the full interaction range and update our total energy. We choose a cutoff distance of 20 lattice spacings for the interaction of defect pairs with all other effective charges in the chain for the defect pair generation move. Thus, the generation of a defect pair far from all other charges, i.e., outside the cutoff region of all other defects and chain end points, happens with a known rate, which allows us to derive an event-driven algorithm akin to the Doob-Gillespie algorithm^{32,33}.

To determine the rate for defect pair generation we define two regions. Region A consists of all N_A sites that lie within the cutoff distance of any of the defects or chain ends. Region B is given by all other $N_B = N - N_A$ sites. The only trial move applicable in region B is the generation of a defect pair and since each site is further away from all other defects than the cutoff distance, the acceptance probability p_B^a is known independently from the actual configuration. For Glauber dynamics we obtain

$$p_B^a = \frac{1}{1 + e^{\beta E_p}}, \quad (7)$$

where the defect pair excitation energy is given by $E_p = 2E_d - \varepsilon[\Phi(1) + 2\Phi(2) + \Phi(3)]^{21}$.

An event in region A is defined to occur if a site in this region is chosen, i.e., a move is attempted. Thus, the probability of an event in region A, p_A , is given by the generation probability of a trial move in region A as

$$p_A = p_A^g = \frac{N_A}{N}, \quad (8)$$

because all sites are chosen with equal probability. For an event in region B, a site in this region has to be chosen and the respective move, i.e., defect pair generation, has to be successful. This is in contrast to the event definition in region A, where a trial move only has to be attempted. Note that we use this particular event definition in region A, because the acceptance probability is dependent on the configuration and therefore not known in advance. The probability of an event in B is given by the product of the generation probability $p_B^g = N_B/N$ and of the acceptance probability p_B^a , i.e.,

$$p_B = p_B^g p_B^a. \quad (9)$$

The probability that one of these events happens is given by the sum of the probabilities of an event in region A and in region B,

$$p_e = p_A + p_B. \quad (10)$$

The distribution of waiting time $p(t)$ between any of these two events, i.e., the number of time steps we have to randomly select a site until either a defect pair in region B is generated or a trial move in region A is attempted, is given by the geometric distribution,

$$p(t) = p_e (1 - p_e)^{t-1}, \quad (11)$$

where t is the discrete time. The geometric distribution is the probability distribution of the number of trials, which have a random outcome that is considered to be either a success or a failure, needed to get one success. Therefore, we can bridge the long waiting times associated with defect pair generation by drawing a time t from the geometric distribution and advancing the actual time by this time increment t . After that, we choose if we either perform an event in A or in B according to the probabilities

$$p'_A = \frac{p_A}{p_e} \quad (12)$$

and

$$p'_B = \frac{p_B}{p_e} = 1 - p'_A. \quad (13)$$

We then draw a site within the corresponding region from a uniform distribution and generate a defect pair (region B) or perform a trial move (region A). Finally, the sizes of regions A and B are updated.

The event driven algorithm presented above leads to huge time savings and allows us to do kinetic simulations for macroscopic system sizes, spanning wide time scales from picoseconds to milliseconds. Using this algorithm, we can study the length dependent orientational dynamics, and thus the dielectric response in the linear response limit, of nanopore water.

III. DIELECTRIC RESPONSE

In general, the linear response of a system in terms of the polarization, i.e., the average total dipole moment $\langle M \rangle$ per volume V , to a periodically varying electric field is described by

$$\frac{\langle M \rangle}{V} = \epsilon_0 \chi(\omega) E(\omega), \quad (14)$$

where ω is the frequency of the applied complex electric field, $E(\omega) = E e^{i\omega t}$, and $\chi(\omega)$ is the frequency dependent complex dielectric susceptibility. The latter is related to the complex dielectric constant via

$$\varepsilon(\omega) = 1 + \chi(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega), \quad (15)$$

where $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ denote the real and the imaginary part of the susceptibility, respectively. The dielectric susceptibility can be determined from the time derivative of the time auto-correlation function of the total dipole moment by Fourier transformation³⁰,

$$\chi(\omega) = -\frac{\beta}{V\varepsilon_0} \int_0^\infty e^{-i\omega t} \frac{d}{dt} \langle M(0)M(t) \rangle dt. \quad (16)$$

This expression, valid in the linear response limit, follows from the fluctuation-dissipation theorem.

Using the event-driven algorithm described in the previous section, we have performed extensive simulations of the kinetic dipole model and have determined the time auto-correlation function of the total dipole moment at a temperature $T = 387$ K, for various system sizes N as shown in Fig. 2. We have chosen to do simulations and determine the time auto-correlation function of the total dipole moment at 1.3 times room temperature, because at room temperature the time scales for orientation relaxation of long chains are too large to obtain good statistics for the auto-correlation function within a reasonable amount of computing time (see also Fig. 3). Note, however, that elevated temperatures do not necessarily correspond to the same temperature in the molecular system as we neglect the temperature dependence of the dipole moment μ of a water molecule in axis direction and the lattice spacing a .

We find that the auto-correlation functions decay exponentially for all system sizes, ranging from the two-state regime for short chains to completely disordered states for long chains. The auto-correlation functions are of the form

$$\langle M(0)M(t) \rangle = \langle M^2 \rangle e^{-t/\tau} \quad (17)$$

and are completely characterized by the average of the squared total dipole moment, $\langle M^2 \rangle$, and the relaxation time τ . Dielectric relaxation with exponential correlation functions of the form given by Eq. (17) is called Debye behavior³⁰. In contrast to the dielectric response of water chains, water clusters encapsulated in wider single-walled carbon nanotubes display Kohlrausch-William-Watts relaxation that is characterized by a stretched exponential form of the auto-correlation function³⁴.

For Debye relaxation, application of Eq. (16) yields

$$\varepsilon'(\omega) - 1 = \chi \frac{1}{(1 + \omega^2 \tau^2)}, \quad (18)$$

for the real part of the dielectric susceptibility and

$$\varepsilon''(\omega) = \chi \frac{\omega\tau}{(1 + \omega^2\tau^2)}, \quad (19)$$

for the imaginary part. Thus, the dielectric constant is completely determined by the static susceptibility χ and the relaxation time τ . The static susceptibility depends on $\langle M^2 \rangle$ and can be determined from Monte Carlo simulations²¹. Estimates of both quantities can be obtained via exponential fits to the kinetic simulation data, as shown in Fig. 2.

Figure 3 shows results for the relaxation time obtained from such fits for $T = 298$ K and $T = 387$ K²³. The relaxation time increases sub-linearly for very short tubes, linearly for short tubes, and converges to its value in the thermodynamic limit for long tubes. We analyze and quantify this behavior in the remainder of this article.

At room temperature, $T = 298$ K, we obtain an estimate of the relaxation time for $N = 10^6$ molecules from a fit to the auto-correlation function for a fraction of the relaxation time ($t \lesssim \tau/100$). At this temperature, we could not obtain an estimate of τ for a completely disordered system of size $N = 10^7$ within a reasonable amount of computing time. Thus, strictly speaking, we have not confirmed Debye behavior for these systems in our simulations. Nevertheless, we can relate the relaxation behavior at room temperature to the results obtained for the higher temperature $T = 387$ K, where we have observed Debye behavior for all tube lengths, ranging from predominately ordered to completely disordered chains. To this end, we use the law of corresponding states derived in Ref. 21 and show that the observed Debye behavior at the higher temperature is characteristic also for room temperature.

As shown previously²¹, two systems of uncorrelated, diffusing defects, whose sizes N and N' and inverse temperatures β and β' are related by

$$\frac{N}{N'} = e^{(\beta - \beta')E_d}, \quad (20)$$

display the same thermodynamic behavior. We can also establish a relation between the dynamics (and thus the relaxation times) of such corresponding systems of different sizes at different temperatures. Assuming that the smaller system is a coarse grained description of the larger one, we can rescale time using the diffusion law, i.e.,

$$t = t' \left(\frac{N}{N'} \right)^2. \quad (21)$$

Figure 3 shows relaxation times at $T = 298$ K and $T = 387$ K obtained by rescaling system size and time according to Eqs. (20) and (21), respectively. The excellent agreement for long tubes, where Coulomb-like interactions can be neglected, strengthens the assumption of uncorrelated defects for both temperatures. Consequently, the Debye behavior observed at $T = 387$ K (see Fig. 2) is a strong evidence for Debye behavior at room temperature for long tubes, for which we were only able to calculate the auto-correlation function for a small fraction of the relaxation time.

IV. LENGTH DEPENDENCE OF THE RELAXATION TIME

Our simulations indicate that the dielectric relaxation is exponential for both short and long water chains, albeit for different reasons. For short tubes, the exponential loss of correlations originates in the two-state behavior of the system with rare and uncorrelated flips between the two ordered states of all dipoles aligned either “up” or “down” the tube axis. These flips are fast compared to the persistence times of the ordered states. Thus, the kinetics of short tubes is captured by a stochastic process of a two-state system with symmetric transition rates between the two states. For long tubes, the reason for the exponential behavior can be understood by assuming that the orientational defects that destroy the order are uncorrelated. In this limit, the kinetic dipole model can be related to the kinetic Ising model which has been solved analytically²⁵. Identifying the magnetization of the Ising model with the total dipole moment, one can trace back the exponential decay of the correlation functions to the diffusive motion of uncorrelated defects. While the change in dipole moment is mainly caused by the diffusion of orientational defects, the processes of defect generation and recombination are crucial for this behavior, because these events open reaction channels to regions of the phase space that would not be accessible otherwise.

In the following we analyze the length dependence of the relaxation time in the short and long chain limits, for which we derive simple analytical expressions.

A. Short tubes

For short chains, the free energy as a function of the total dipole moment M has two minima corresponding to the ordered states in which all dipoles have the same orientation. These two deep minima are separated by a nearly flat free energy barrier with a height that corresponds to the energy required to introduce a defect at the center of the chain²⁰. On a coarse grained level, the dynamics of the system can then be viewed as consisting of long permanences in the two stable states interrupted by rapid barrier crossing events during which the orientation of the dipole chain is flipped. Since consecutive flipping events are uncorrelated, the auto-correlation function of such a two-state system decays exponentially and the relaxation time is given by

$$\tau = \frac{\tau_{\text{MFP}}}{2}, \quad (22)$$

where the mean first passage time, τ_{MFP} , is the average time it takes the two-state system to change from one state to the other.

The orientation of an entire chain of water molecules is flipped by the diffusive migration of a single defect, which is either an L defect or a D defect, from one side of the chain to the other. The free energy as a function of the defect position, which is simply related to the free energy as a function of the total dipole moment, acts as a potential of mean force on the defect, which performs uncorrelated hops along the chain. This type of defect migration can be modeled as a non-linear one-step hopping process (NOSH)³⁵, in which each value of the total dipole moment corresponds to a defect at a particular site n with free energy F_n . For hops of the defect, and hence for the total dipole moment, we define transition rates between adjacent sites. The forward transition rate, g_n , for a hop from site n to site $n + 1$ and the backward transition rate, r_n , for a hop from site n to site $n - 1$ are related to each other by imposing detailed balance,

$$\frac{g_n}{r_{n+1}} = e^{-\beta \Delta F_n}, \quad (23)$$

with $\Delta F_n = F_{n+1} - F_n$. This condition guarantees that the equilibrium distribution of states is conserved by the process. For Glauber dynamics, we obtain for the transition rates

$$g_n = \frac{1}{2\Delta t_G} \frac{1}{1 + e^{\beta \Delta F_n}} \quad (24)$$

$$r_{n+1} = \frac{1}{2\Delta t_G} \frac{1}{1 + e^{-\beta \Delta F_n}}, \quad (25)$$

where the factor $1/2$ accounts for the selection probability of the defect hopping to one side rather than the other. Here, Δt_G is the hopping time for a defect diffusing on a flat free energy profile according to Glauber dynamics. This hopping time can be related to real time through the diffusion constant as described in Sec. II A.

To calculate the mean first passage time for transitions between the two ordered states, we consider an ensemble of independent random walkers moving on a 1D lattice with N sites. A walker corresponds to a defect and its position determines the total dipole moment of the chain. The mean first passage time is given by the average time a walker needs to reach site N , the right hand side end of the chain, starting from site 1, the left hand side of the chain. If a random walker reaches site N , then it is annihilated, which corresponds to placing an absorbing boundary placed at N . We impose that all walkers starting at 1 will reach site N eventually by putting a reflecting boundary at site 1. In this case, we can write the mean first passage time as³⁵

$$\begin{aligned} \tau_{\text{MFP}} &= \sum_{\nu=1}^{N-1} \sum_{\mu=1}^{\nu} \frac{r_{\nu} r_{\nu-1} \dots r_{\mu+1}}{g_{\nu} g_{\nu-1} \dots g_{\mu+1} g_{\mu}} \\ &= \sum_{\nu=1}^{N-1} \sum_{\mu=1}^{\nu} \frac{e^{\beta(F_{\nu} - F_{\mu})}}{g_{\nu}}, \end{aligned} \quad (26)$$

where we have used the detailed balance condition, Eq. (23), to obtain the last line. According to Eq. (22), the relaxation time is then given as half the mean first passage time.

The free energy F_n experienced by a moving defect is given by the Hamiltonian in the charge picture, Eq. (2). We choose the ordered states as the reference point for the free energy, $\beta F_1 = \beta F_N = 0$, and obtain

$$\beta F_n = \beta \Delta E(n) - \ln 2 \quad (27)$$

for $1 < n < N$, where the term $\ln 2$ accounts for the two reaction channels - one for a chain flip via the diffusion of an L defect and one for the D defect. The energy difference $\Delta E(n)$ is given by the defect excitation energy plus the interaction energy of a single defect with the chain ends,

$$\Delta E(n) = \varepsilon [2\Phi(N) - \Phi(n) - \Phi(n-1) - \Phi(N-n) - \Phi(N-n+1)] + E_d. \quad (28)$$

Using this free energy, the relaxation time can be determined by numerical summation according to Eq. (26).

Simulation results for small system sizes agree very well with the relaxation times obtained from Eq. (26) for Glauber dynamics, as shown in Fig. 3. With the free energy given by Eq. (27), the relaxation time, Eq. (26), explicitly depends on the energy constant ε , which could be extracted from experimental data by a fitting procedure. Knowledge of ε could then be used to determine the dipole moment μ of water molecules in the chain. The particular form of the relaxation time as a function of chain length is related to the Coulomb-like interactions of the effective charges carried by defects and chain ends. These interactions are the origin of the $\tau(N)$ -curves in the short chain limit, in which the relaxation time is determined by rare transition between the two ordered states. The height of the free energy barrier for this process, arising from the presence of a defect at the center of the chain, is a function of the system size, because this height is essentially determined by the effective interactions of the defect with chain ends decaying as $1/r$ with distance. Since the defect at the center of the chain interacts attractively with the chain ends, making the chain longer increases the barrier height leading to the curvature of $\tau(N)$. In contrast, for a constant barrier height, increasing the chain length would lead to a linear increase of the relaxation time τ . As a consequence, experiments determining the relaxation time τ as a function of chain length N could yield information on the Coulomb-like interactions of the defects with the chain ends.

The origin of the size dependence of the relaxation time τ becomes very transparent if some simplifying assumptions are made, as explained in the following. Since the free energy barrier between ordered states is flat for sufficiently long tubes, we can approximate the free energy landscape as a rectangular barrier. The height of the barrier is given by the defect excitation energy E_d plus the Coulomb interaction of the defect located in the middle of the chain,

$$\beta F_{N/2} \approx \beta \left(E_d - \frac{6\varepsilon}{N} \right) - \ln 2. \quad (29)$$

This expression is accurate for $N \gtrsim 10$. In this case of a rectangular barrier, Eq. (26) can be simplified by counting the different terms that occur in the double sum. For Glauber dynamics, we then obtain

$$\frac{\tau_{\text{MFP}}^G}{2\Delta t_G} = (N-2)(2e^{\beta F_{N/2}} + e^{-\beta F_{N/2}} + N-2) + 2. \quad (30)$$

For system sizes N smaller than $e^{\beta F_{N/2}}$ (this is always the case in the two-state regime, in which the likelihood to have more than one defect in the system is negligible), the relaxation time is given by

$$\tau_{\text{short}}(N) \approx e^{\beta(E_d - 6\varepsilon/N)} N \frac{a^2}{4D}, \quad (31)$$

both for Glauber and Metropolis dynamics. This expressions reproduces simulation results for small chain lengths qualitatively (see Fig. 3). Note that the term $6\epsilon/N$ in the exponential of the above equation is due to the Coulombic attraction of the defect at the center of the chain with the chain ends. For increasing chain length, this attraction decreases and can be neglected for sizes $N \gtrsim 1000$ at room temperature. Then, the relaxation time becomes

$$\tau_{\text{short}}(N) \approx e^{\beta E_d} N \frac{a^2}{4D} \quad (32)$$

and increases linearly for tube lengths $1000 \lesssim N \lesssim 10^5$. Note, the defect diffusion on a rectangular free energy curve with a length dependent barrier height corresponds to a finite kinetic Ising model with open boundary conditions and a length dependent coupling constant given by $J = (E_d - 6\epsilon/N)/2^{25}$.

The basis for the above relaxation time calculations is that the system shows two-state behavior. In this case, the mean first passage time can easily be related to the relaxation time, and the dynamics of the total dipole moment are determined by the diffusion of a single defect. Systems larger than $\sim 10^5$ molecules typically display multiple defects such that the two-state assumption is violated. Relaxation time for such disordered systems will be considered in the next section.

B. Long tubes

Due to entropy, chains that are sufficiently long will typically have several defects that destroy the dipolar order. For such disordered systems we derive an analytical expression for the relaxation time under the assumption that defects are uncorrelated and behave like kinks in the 1D Ising model²¹. Glauber showed in Ref. 25 that for the kinetic Ising model with periodic boundary conditions, the time auto-correlation function of the total magnetization decays exponentially. For large excitation energies, comparison with Glauber's expression yields the correlation time

$$\tau_{\text{long}} = \alpha [1 - \tanh(\beta E_d)] \approx e^{2\beta E_d} \frac{a^2}{4D}, \quad (33)$$

where the rate α , defined via

$$\alpha = \frac{1}{\Delta t_G}, \quad (34)$$

corresponds to the hopping rates g_n and r_{n-1} given by Eqs. (24) for a defect on a flat energy surface. Note that this relaxation time, valid for large systems, does not depend on the chain length. As shown in Fig. 3, we find good agreement of this expression with simulation results using Metropolis dynamics for $T = 387\text{K}$, indicating that these results do not depend on the specific details of the chosen dynamics. For room temperature we could not obtain an estimate for τ_{long} from simulations within a reasonable amount of computation time. Equating Eqs. (32) and (33) we obtain $N = \exp(\beta E_d)$ for the crossover length, at which the system changes from a predominately ordered to a predominately disordered state.

C. Extracting microscopic properties from experiments

The length dependence of the relaxation time can be used to extract the effective diffusion constant and the defect excitation energy from dielectric spectroscopy experiments. Measurements of the frequency-dependent susceptibility of short chains yield the slope s of the linearly increasing relaxation time. Performing such experiments on long tubes provides an estimate for the relaxation time in the thermodynamic limit τ_{long} . Based on our theoretical results, the slope s is determined by Eq. (32) as

$$s = e^{\beta E_d} \frac{a^2}{4D} \quad (35)$$

and τ_{long} is given by Eq. (33). Using these equations, we can express the defect excitation energy

$$E_d = k_B T \ln \left(\frac{\tau_{\text{long}}}{s} \right) \quad (36)$$

and the diffusion constant

$$D = \frac{a^2 \tau_{\text{long}}}{4s^2} \quad (37)$$

as functions of s and τ_{long} . Note that the diffusion constant also depends on the molecule spacing $a = L/N$ given by the tube length L divided by the number of molecules N .

Up to now, we have assumed that L and D defects have the same diffusion constant and excitation energy. Molecular dynamics simulations indicate, however, that this is not the case. In the following section we therefore explore the effect of these differences between L and D defects on the time-dependent dielectric response of single-file water chains.

V. TWO KINDS OF DEFECTS

Molecular dynamics simulations demonstrate that the diffusion constant of the D defect ($D_D \approx 0.05 \text{ nm}^2 \text{ ps}^{-1}$) is almost twice as large than that of the L defect ($D_L \approx 0.03 \text{ nm}^2 \text{ ps}^{-1}$)¹⁸. The evidence for differences in the excitation energies is less conclusive. In molecular simulations of non-polar nanotubes, D defects were energetically favorable, which is consistent with the preferred orientation of water molecules entering the tube from the water bath³⁶. A different behavior is observed in polar, open pores. The curvature of nanotubes is expected to induce a static dipole moment which causes an electric field at the tube ends, pointing towards the tube center³⁷. Molecular simulations show that in such short tubes L defects are preferred over D defects^{38,39}. For long tubes, however, this effect might be neglected as the pore polarity only influences the preferred orientation of the chain segments at the ends of the tube. Different excitation energies could also arise due to different entropic contributions of the defect molecules or due to differences in the interactions of the defect molecules with molecules in ordered segments that are neglected in the dipole lattice model.

However, such differences do not necessarily influence the static dielectric response of single-file water in the limit of short and long tubes. For short tubes, the static susceptibility does not depend on the defect excitation energies and purely relies on the two-state behavior

of the total dipole moment^{21,23}. In contrast, long tubes can be described as systems of uncorrelated defects where L and D defect alternate. Therefore, half of the n_d defects are L defects and the other half are D defects. The number of possibilities to place n_d uncorrelated defects on the sites of a one-dimensional lattice is given by a binomial coefficient²¹ and the partition function given by

$$Z = 2 \sum_{n_d=0}^N \binom{N}{n_d} e^{-\beta \frac{n_d}{2} (E_L + E_D)}, \quad (38)$$

depends on the sum of the defect excitation energies only. Consequently, the static dielectric response of single-file water chains depends only on the average excitation energy $E_d = (E_L + E_D)/2$ of L and D defect²¹, and measurements of the static susceptibility as a function of chain length cannot be used to determine the excitation energies of D and L defects separately.

In the following we explore, first for short tubes then for long ones, whether time-dependent dielectric spectroscopy experiments can be used to detect differences in excitation energies and/or diffusion constants of L and D defects.

A. Short tubes

Short chains are characterized by two-state behavior, in which the relaxation time is determined by rare switches between the perfectly ordered configurations with opposite dipole orientation. During a switch, the dipoles are flipped by either a D or an L defect moving through the chain, corresponding to two separate reaction channels. Different excitation energies of D and L defects then also lead to different barrier heights and, hence, to different contributions to the overall transition rate between the two ordered states. Taking the two reaction channels into account separately, Eq. (31) turns into

$$\tau_{\text{short}}(N) = \frac{e^{\beta(E_d - 6\epsilon/N)} N a^2}{2(D_L e^{\beta \Delta E_{LD}} + D_D e^{-\beta \Delta E_{LD}})} \quad (39)$$

where we used that $E_d = (E_L + E_D)/2$ and where we introduced the difference between the defect excitation energies as $2\Delta E_{LD} = E_D - E_L$. It follows that for equal defect excitation energies E_L and E_D , the relaxation time is determined by the average diffusion constant and Eq. (39) is equal to Eq. (31). For different excitation energies, however, this is no longer true and measurements of the relaxation time in the short chain limit supplemented by measurements of the static susceptibility in both limits and as well as the relaxation time in the long chain limit allow to deduce differences between L and D defects as we discuss in Sec. V D.

B. Long tubes

To investigate the dielectric response of long chains, we again take advantage of the correspondence between single-file water and the one-dimensional kinetic Ising model^{21,25}. In the following we derive the time-dependent susceptibility defined via Eq. (14) of the 1D kinetic Ising model with different flipping rates (diffusion constants) for the two kinds of kinks (defects). To do that, we identify the time dependent average dipole moment $\langle M(t) \rangle$ with the magnetic moment of the Ising model given by

$$\langle M(t) \rangle = \mu \sum_{k=1}^N q_k(t), \quad (40)$$

where $q_k(t)$ is the expectation of spin $\sigma_k = \pm 1$ at site k ,

$$q_k(t) = \langle \sigma_k(t) \rangle = \sum_{\{\sigma\}} \sigma_k p(\sigma_1, \dots, \sigma_N, t). \quad (41)$$

Here, $p(\sigma_1, \dots, \sigma_N, t)$ is the probability that at time t the spins take the values $\sigma_1, \dots, \sigma_N$. Similarly, the spin-spin correlation function is defined as

$$r_{jk}(t) = \langle \sigma_j(t) \sigma_k(t) \rangle. \quad (42)$$

The time-dependent probability function $p(\sigma_1, \dots, \sigma_N, t)$ has to fulfill the master equation

$$\frac{d}{dt} p(\sigma_1, \dots, \sigma_N, t) = \sum_i [w_i(-\sigma_i) p(\sigma_1, \dots, -\sigma_i, \dots, \sigma_N, t) + w_i(\sigma_i) p(\sigma_1, \dots, \sigma_N, t)], \quad (43)$$

where $w_i(\sigma_i)$ is the transition rate of spin σ_i . This master equation can be written as

$$\frac{d}{dt} p(\sigma_1, \dots, \sigma_N, t) = - \sum_i \sigma_i \sum_{\sigma'_i = \pm 1} \sigma'_i w_i(\sigma'_i) p(\sigma_1, \dots, \sigma'_i, \dots, \sigma_N, t). \quad (44)$$

Multiplying the above equation with σ_k and summing over all spin configurations $\{\sigma\}$, we obtain the time derivative of $q_k(t)$ as

$$\frac{d}{dt} q_k(t) = - 2 \langle \sigma_k(t) w_k(\sigma_k(t)) \rangle. \quad (45)$$

To calculate the average spins q_k , and subsequently the total dipole moment and the susceptibility, we formulate transition rates $w_k(t)$ that obey detailed balance for vanishing field: the transition rates of L defects and D defects to the next site are given by

$$w_k(\sigma_k) = \frac{\alpha_L}{2} \quad \text{and} \quad w_k(\sigma_k) = \frac{\alpha_D}{2}, \quad (46)$$

respectively, where $\alpha_L = 2D_L/a^2$ and $\alpha_D = 2D_D/a^2$ are the corresponding hopping rates. According to Glauber's original definition, the transition rate for the generation and recombination of a defect can be written as

$$w_k(\sigma_k) = \frac{\alpha}{2}(1 \mp \gamma), \quad (47)$$

where the plus sign is chosen for the generation and the minus sign for the recombination of defects. The constant γ is defined by

$$1 \mp \gamma = 1 \mp \tanh(\beta E_d) = \frac{2}{1 + e^{\pm 2\beta E_d}} \quad (48)$$

and $\alpha/2$ is the rate of defect generation and recombination for vanishing defect excitation energy.

To write down the transition rate $w_k(\sigma_k)$ in a concise form, we have to differentiate between L defects, D defects, and defect pairs: If there is a kink between spin σ_k and one of its neighboring spin, then $\sigma_{k-1} = -\sigma_{k+1}$. If there is a kink to the left and a kink to the right of spin σ_k , then $-\sigma_k = \sigma_{k-1} = \sigma_{k+1}$. The flip of such a spin corresponds to defect recombination. If there is no kink next to spin σ_k then $\sigma_k = \sigma_{k-1} = \sigma_{k+1}$ and the flip of σ_k corresponds to defect generation. Thus, we may write the transition rate of σ_k as

$$w_k(\sigma_k) = \frac{1}{4} \left[\frac{\alpha_L - \alpha_D}{2} (\sigma_{k-1} - \sigma_{k+1}) + \frac{\alpha_L + \alpha_D}{2} (1 - \sigma_{k-1} \sigma_{k+1}) + \alpha (1 + \sigma_{k-1} \sigma_{k+1}) - \alpha \gamma \sigma_k (\sigma_{k-1} + \sigma_{k+1}) \right], \quad (49)$$

reproducing the transition rates given by Eqs. (46) and (47) for the corresponding values of σ_{k-1} , σ_k , and σ_{k+1} .

Assuming that α is given by the average flipping rate, i.e. $\alpha = \bar{\alpha} = (\alpha_L + \alpha_D)/2$, then the above equation simplifies to

$$w_k(\sigma_k) = \frac{1}{2} \left[\frac{\alpha_L - \alpha_D}{4} (\sigma_{k-1} - \sigma_{k+1}) + \bar{\alpha} - \bar{\alpha} \frac{1}{2} \gamma \sigma_k (\sigma_{k-1} + \sigma_{k+1}) \right]. \quad (50)$$

From this expression, we obtain the transition rates for a system in an external field $E(t)$ obeying detailed balance via

$$w'_k(\sigma_k) = w_k(\sigma_k)(1 - \delta \sigma_k), \quad (51)$$

where we introduced

$$\delta = \tanh[\beta E(t)]. \quad (52)$$

Thus, using Eqs. (50) and (51) we obtain for the time derivative of $q_k(t)$ defined by Eq. (45),

$$\frac{d}{dt}q_k(t) = -\frac{\Delta\alpha}{4}[r_{k,k-1} - r_{k,k+1} - \delta(q_{k-1} - q_{k+1})] + \frac{1}{2}\bar{\alpha}\gamma(q_{k-1} + q_{k+1} - \delta[r_{k,k-1} + r_{k,k+1}]) + \bar{\alpha}\delta - \bar{\alpha}q_k. \quad (53)$$

Here, $\Delta\alpha = \alpha_L - \alpha_D$. Since we are interested in the linear response of the system, we may assume that the system is in thermal equilibrium in zeroth order in E , i.e., the spin-spin correlation function takes on its equilibrium value $\eta = \tanh(\beta E_d/2)$,

$$r_{k,k-1} = r_{k,k+1} = \eta. \quad (54)$$

Thus, we obtain

$$\frac{d}{dt}q_k(t) = -\bar{\alpha}q_k + q_{k-1}\frac{1}{2}\left(\bar{\alpha}\gamma + \frac{\Delta\alpha}{2}\delta\right) + q_{k+1}\frac{1}{2}\left(\bar{\alpha}\gamma - \frac{\Delta\alpha}{2}\delta\right) + \bar{\alpha}\delta(1 - \gamma\eta). \quad (55)$$

Summing over all N equations (55), we obtain the time derivative of the total dipole moment [Eq. (40)],

$$\frac{d\langle M \rangle}{dt} = -\langle M \rangle\bar{\alpha}(1 - \gamma) + N\bar{\alpha}\delta(1 - \gamma\eta). \quad (56)$$

Note, the time evolution of the average dipole moment depends on the average flipping rate $\bar{\alpha}$ only, and not on the respective values of the flipping rates of L and D defect.

We now use the differential equation (56) for the dipole moment to derive the susceptibility. Considering weak external fields only, we approximate δ by $\delta \approx \beta E(t)$. Inserting the definition of the susceptibility, Eq. (14), into Eq. (56) and rearranging this equation we obtain

$$\chi(\omega) = \frac{\chi_{\text{long}}}{1 - i\omega\tau}, \quad (57)$$

which has the Debye form. The inverse of the relaxation time τ is then given by

$$\tau^{-1} = \bar{\alpha}(1 - \gamma) = \frac{2D}{a^2} \frac{2}{1 + e^{\beta 2E_d}} \approx \frac{4D}{a^2} e^{-\beta 2E_d} \quad (58)$$

and the static susceptibility by

$$\chi_{\text{long}} = \frac{\beta\mu^2}{\varepsilon_0 v} \frac{1 + e^{2\beta E_d}}{e^{\beta E_d} + e^{-\beta E_d}} \approx \frac{\beta\mu^2}{\varepsilon_0 v} e^{\beta E_d}. \quad (59)$$

Here, v is the volume per molecule and we used that $\exp(\beta E_d) \gg 1$ to obtain the approximate expressions. Thus, we have shown that the linear dielectric response of single-file water in

the limit of long tubes depends on the diffusion constant of L and D defects only through their average value.

To test this result, we performed simulations of the kinetic Ising model with periodic boundary conditions. The unit of time is given by a Monte-Carlo sweep during which we perform N Monte-Carlo steps: we choose a spin randomly with uniform probability, flip it, and accept or reject this trial move according to the rates given by Eqs. (46) and (47). Figure 4 shows time auto-correlation functions of the total dipole moment for a system of size $N = 100$ and twice the coupling constant given by $\beta E_d = 1$. The rate of defect generation and recombination is given by the average hopping rate of L and D defect, i.e., $x = \bar{\alpha}/\alpha = 1$, but we vary the ratio $x_{LD} = \alpha_L/\alpha_D$ of these rates. We observe Debye behavior in all cases and the relaxation times are not only independent of x_{LD} but also in perfect agreement with Eq. (58) as shown in Fig. 4.

C. Rate of defect generation and recombination

The above result is based on the physically reasonable but unproven assumption that the rate of defect recombination and generation is determined by the average of the hopping rates of L and D defect. We now address the question, if deviations from this assumption could be detected in dielectric spectroscopy experiments.

To do that, we performed kinetic simulations of the 1D Ising model and vary not only the ratio x_{LD} , but also the ratio $x = \bar{\alpha}/\alpha$ of the average hopping rate $\bar{\alpha}$ to the rate of defect pair generation/recombination α . Again, we find that the auto-correlation functions only depend on the hopping rates of L and D defect through their average value $\bar{\alpha}$ (see Fig. 4). However, the auto-correlation functions do not show single-exponential behavior for ratios $x \neq 1$. To illustrate this point we fit a single-exponential to the auto-correlation functions shown in Fig. 4 for times $t \leq 20$. For $x = 1$ the auto-correlation function is reproduced accurately by the fit, whereas for $x \neq 1$ and for $t \gtrsim 20$ the auto-correlation functions decay slower than the corresponding fits. In the latter case, the curves are well described by bi-exponential fits of the form

$$\langle M^2(t) \rangle = \langle M^2(0) \rangle \left[a e^{-\frac{t}{\tau_1}} + (1-a) e^{-\frac{t}{\tau_2}} \right], \quad (60)$$

also shown in Fig. 4, which can be attributed to the different time scales of the two relaxation processes of defect pair generation/recombination and defect diffusion. To derive an analytical expression for the bi-exponential behavior for $x \neq 1$, one has to use the general transition 6 rates given by Eq. (49) which is beyond the scope of this work.

In theory, the observation of the weak bi-exponential behavior in an experiment would bear evidence for differences between $\bar{\alpha}$ and α . However, the bi-exponential form goes over into a single-exponential form for lower temperatures, i.e., low defect densities, as shown in Fig. 5. There, we plot auto-correlation functions for systems of size $N = 10^3$ and twice the coupling constants given by $\beta E_d = 1, 2$, and 3 as a function of the time in units of the temperature dependent relaxation time $\tau(\bar{\alpha}, \beta E_d)$ given by Eq. (58). We observe that with decreasing temperature the auto-correlation functions approach $\exp(-t/\tau(\bar{\alpha}, \beta E_d))$. Also, the correlation functions approach the single-exponential form as indicated by single-exponential fits to the data for $t/\tau(\bar{\alpha}, \beta E_d) \leq 1$.

Consequently, nanopore water at room temperature and atmospheric pressure, for which $\beta E_d \approx 13.45$, shows Debye behavior and dielectric spectroscopy experiments on long tubes will yield the average diffusion constant of L and D defect. Also, since the low defect density is a

precondition for the correspondence of single-file water to the 1D Ising model²¹, it is not straightforward to relate the high temperature results for the 1D Ising model to single-file water.

D. Detecting the differences

We briefly summarize how differences in the diffusion constant and excitation energies can be determined from experiments. The static dielectric response can be used to determine the dipole moment μ and the average defect excitation energy E_d using the expressions for the static susceptibility in the long chain limit given by Eq. (59) and in the short chain limit, $\chi_{\text{short}} = N\beta\mu^2/(\epsilon_0 v)^{23}$. Using these values, the frequency dependent dielectric response of long tubes yields the average diffusion constant D via the relaxation time given by Eq. (58). Thus, we may predict the slope s given by Eq. (35) of $\tau(N)$ in the linear regime using the relaxation time in the short chain limit. Deviations of actual measurements of this slope from this prediction then indicate that there is a difference in the excitation energies and the diffusion constants of L and D defects.

With diffusion constants of L and D defect known from molecular dynamics simulations¹⁸, we can use the expression for the relaxation time in the short chain limit given by Eq. (39) to obtain an estimate for $2\Delta E_{LD}$, i.e., the difference in excitation energies of L and D defect, from the experimentally determined relaxation time.

VI. CONCLUSION

Expanding on earlier work²³, we have studied the dielectric response of nanopore water to time-dependent electric fields in direction of the pore axis. Our analysis is mainly based on a kinetic generalization of a one-dimensional dipole model, developed to study the structural properties and thermodynamics of single-file water chains in narrow pores. To simulate the model, we have developed an event-driven algorithm that is not slowed down by the long waiting times for the generation of orientational defects essentially determining the statistics and dynamics of dipole fluctuations in the water chain. Our simulations yield only a coarse grained picture in time and space as the model does not resolve the detailed atomistic mechanism for the basic defect hopping process, which involves the breaking and formation of hydrogen bonds between neighboring water molecules. As a consequence, the results are not sensitive to the details of the underlying dynamics (we have used Glauber and Metropolis dynamics), as long as the unit of time is properly chosen. Contact between the kinetic dipole model and more realistic molecular dynamics simulations is made via the diffusion constants of orientational defects calculated in earlier work¹⁸.

Kinetic models of various degrees of abstraction have been developed to study the filling of short pores^{9,40,41} and proton transport^{42–44}. The proton kinetics can be easily included in our kinetic model, because the interaction energy of a proton with other defects is captured quantitatively^{18,24}. Our kinetic model could also be extended to study how the kinetics of filling and emptying depends on the lengths of the tube. A benefit of using our model for such studies would be that the structural and energetic properties of single-file water as obtained from molecular simulations are captured quantitatively. This quantitative agreement was demonstrated for different empirical water models which, however, result in different parameter values for our model^{18,20,24}. These molecular water models most likely also yield different defect diffusion constants that can be easily incorporated into our model. The general behavior of water wires represented by our dipole model, for instance the scaling of the relaxation time with the wire length, should remain unaffected by such changes in the parameters.

Our simulations and analytical considerations demonstrate that single-file chains of hydrogen bonded water molecules inside a molecularly narrow pore show Debye relaxation behavior, i.e., a single-exponential decay of the correlations of the total dipole moment with time, for all systems sizes, implying that the time-dependent dielectric response of single-file water is completely determined by the static susceptibility and the relaxation time. Analyzing the frequency dependent dielectric constant, these quantities can be determined from experimental data. In the limit of short chains, a simple analytical expressions for the relaxation time was derived by viewing the dipole dynamics as a non-linear one-step hopping process. An analogous expression for long chains was obtained exploiting the analogy of our dipole model with the kinetic 1D Ising model solved analytically by Glauber almost fifty years ago²⁵. Moreover, we have established a correspondence to the kinetic Ising model at all tube lengths by introducing a length dependent coupling constant.

The formulas derived here permit to test earlier predictions about pore filling and macroscopic order²⁰ and to extract the fundamental properties of orientational defects (defect excitation energy, diffusion constant, dipole moment μ , and effective interactions) from dielectric spectroscopy experiments. Interestingly, the time-dependent dielectric susceptibility bears clearer information about the effective Coulomb-like interaction of defects and chain ends than the static dielectric susceptibility²¹. Both quantities might be used to determine if differences between the excitation energies and diffusion constants of L and D defect exist. The experimental determination of the microscopic properties of single-file water suggested here would provide direct evidence for orientational defects which so far have been studied theoretically for biological pores^{3,4} and for nanotubes^{9,18,20,38,45}.

To realize the suggested experiments, further progress in the fabrication of carbon and boron nitride nanotube membranes of selected chiralities is necessary^{46–49}. Membranes with a single carbon nanotube only⁵⁰ could be used to avoid pore-pore correlation effects which are bound to occur for membranes with narrowly spaced nanotubes. Porous silicon might also be used to confine water in single-file arrangement provided the pore diameters can be reduced further⁵¹.

In summary, dielectric spectroscopy experiments on nanopore water offer unique insight not only in the structure and dipolar order of single-file water, but also into the interaction energy of water molecules in quasi one-dimensional confinement and into the molecular relaxation processes. Besides, the strong length dependence of the static dielectric susceptibility and the relaxation time might be exploited for the design of purpose-built capacitors in sensor applications and other nanofluidic devices^{52,53}.

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Appendix: Metropolis dynamics

In Metropolis dynamics, the acceptance probability is given by

$$p_M^a = \min\{1, e^{-\beta\Delta E}\}, \quad (\text{A.1})$$

where ΔE is the energy difference between the new and the old state. For the diffusion of a defect on a flat energy landscape, i.e., for $\Delta E = 0$, the probability for the defect to stay at its position is $p = 0$, the probability to move to the left is $p = 1/2$ and to the right is $p = 1/2$. Since the probability of a defect to stay at its position is $p = 1/2$ in Glauber dynamics, the hopping time for Metropolis dynamics is twice that of Glauber dynamics. Consequently, Metropolis dynamics is twice as fast as Glauber dynamics in Monte-Carlo simulations.

Using Eq. (A.1), the acceptance probability for defect pair generation becomes

$$p_B^a = \exp(-\beta E_p) \text{ (compare Eq. (7)).}$$

To model the orientational dynamics of short tubes, we define the transition rates for the non-linear one-step hopping process explained in Sec. IV A as

$$g_n = \frac{1}{2\Delta t} \min\{1, e^{-\beta\Delta F_n}\}, \quad (\text{A.2})$$

$$r_{n+1} = \frac{1}{2\Delta t} \min\{1, e^{\beta\Delta F_n}\}, \quad (\text{A.3})$$

Using these rates, we obtain for the relaxation time of defect diffusion on a rectangular barrier

$$\frac{\tau_{\text{MFP}}^{\text{M}}}{\Delta t_{\text{M}}} = (N - 1) (2e^{\beta F_{N/2}} + N - 2). \quad (\text{A.4})$$

This expression differs from the relaxation time obtained for Glauber dynamics, Eq. (31). For high barriers, however, the relaxation times for Glauber and Metropolis dynamics converge to the same values.

FIG. 1.

Mechanisms determining the kinetics of water chains. Water molecules are symbolized by black, right angles and hydrogen bonds are depicted as red, dotted lines. Rotations of molecules that break (form) a hydrogen bond are indicated with red (blue) arrows at the corresponding OH bonds. (a) Hop of a D defect to the right and (b) to the left. (c) Generation and (d) annihilation of a D defect at the chain end. (e) Generation of a defect pair and (f) recombination of defects.

FIG. 2.

Simulation results for the time-dependent autocorrelation function of the total dipole moment for $T = 387\text{K}$ (symbols) and fitted single-exponentials (lines) as a function of the time divided by the corresponding size-dependent relaxation time, $\tau(N)$, as obtained from the fits for different system sizes. In the logarithmic plot at the bottom these correlation functions appear as linear functions with a slope of minus unity. Deviations from the exponential form are within the statistical accuracy of the data.

FIG. 3.

The relaxation time τ as a function of the number of molecules N (bottom axis) and the tube length (top axis) at room temperature (top) and at 1.3 times the room temperature (bottom). Estimates obtained from simulations at room temperature and at 1.3 times room temperature are shown as blue squares and red circles, respectively. Simulation data obtained at one temperature were rescaled using Eqs. (20) and (21) to the other temperature. Results from the numerical calculations of the relaxation time (NOSHP) for the two-state regime according to Eq. (26) are shown as dashed lines, and for the approximation of a rectangular free energy barrier according to Eq. (31) as thin, solid lines. The linear approximation for small sizes given by Eq. (32) is shown as thick, solid line and the thermodynamic limit given by Eq. (33) as dashed-dotted line. The relaxation time is shown in units of Monte

Carlo sweeps in a straightforward implementation of the kinetic model (left axis) and in units of milliseconds (right axis).

FIG. 4.

Simulation results for the auto-correlation functions of the total dipole moment of the 1D kinetic Ising model of size $N = 100$ at a temperature $\beta E_D = 1$ for $(\bar{\alpha}, \alpha) = (0.5, 0.5)$, $(0.5, 0.1)$, and $(0.05, 0.5)$ corresponding to ratios $x = 1, 5$, and 0.1 . Symbols indicate simulation results for different ratios $x_{LD} = \alpha_L/\alpha_D$. Dashed lines show single-exponential fits to the simulation data for times $t \leq 20$. For $x = 1$, the solid black line shows a single-exponential function with the relaxation time given by Eq. (58) and lies on top of the single-exponential fit. For $x = 5$ and $x = 0.1$, solid lines show fits of the bi-exponential function given by Eq. (60) fitted to the data for times $t \leq 60$. The bi-exponential fit parameters are $(a, \tau_1, \tau_2) \approx (0.97, 27.52, 1.53)$ for $x = 5$ and $(a, \tau_1, \tau_2) \approx (0.95, 15.81, 2.92)$ for $x = 0.1$.

FIG. 5.

Simulation results for the auto-correlation function of the total dipole moment of the 1D kinetic Ising model with size $N = 1000$ for different temperatures and for two different ratios $x = \bar{\alpha}/\alpha = 0.2$ and $x = 5$. The unit of the time is given by the corresponding temperature dependent relaxation times $\tau(\bar{\alpha}, \beta E_D)$ of Eq. (58). Symbols indicate simulation results and thin lines denote single-exponential fits to the data for $t/\tau(\bar{\alpha}, \beta E_D) \leq 1$. The thick black line indicates the function $\exp(-t)$. In this representation, all presented auto-correlation functions converge to this line from above for $x = 5$ ($\bar{\alpha} = 0.5$, $\alpha = 0.1$) or from below for $x = 0.2$ ($\bar{\alpha} = 0.2$, $\alpha = 1$) with decreasing temperature.