Single-File Diffusion of Water Inside Narrow Carbon Nanorings

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Although the theoretical predictions[1–10] of anomalous diffusion of particles in one dimension date back almost four decades, experimental verifications of these predictions are very recent.[11–17] The past few years have seen a number of experimental studies on the diffusion of particles through pores of diameter comparable to the size of the particles. This phenomenon is of central importance in many technological and biological processes.[18–21] The movement of particles in these systems is restricted to a one-dimensional (1D) channel where diffusive behavior is different from the normal mode diffusion: the particles are unable to cross each other, leading to a highly correlated motion. This dramatically reduces the translational mobility of any individual particle and is reflected in the scaling of the mean-squared displacement (MSD) with time. Transport under such conditions is non-Fickian and is termed as single-file diffusion (SFD). It has been demonstrated theoretically for an infinite system of stochastic particles, which interact by a hard core interaction,[1,6,8,9] that the MSD of a tagged particle at times long compared to the interaction time[10,12] varies as

$$\langle \Delta z^2(t) \rangle = 2Ft^{1/2} \qquad (1)$$

where F is the SFD mobility. The role of noise is extremely crucial, and the above relation is valid only in the presence of a stochastic force, which causes the particles to follow independent "Brownian" trajectories between elastic collisions. Recently, this has been generalized to the case of a system of particles interacting *via* arbitrary repulsive forces in the presence of hydrodynamic interactions.[22]

ABSTRACT We use atomistic molecular dynamics (MD) simulations to study the diffusion of water molecules confined inside narrow (6,6) carbon nanorings. The water molecules form two oppositely polarized chains. It is shown that the effective interaction between these two chains is repulsive in nature. The computed mean-squared displacement (MSD) clearly shows a scaling with time $\langle \Delta \theta^2(t) \rangle \sim t^{1/2}$, which is consistent with single-file diffusion (SFD). The time up to which the water molecules undergo SFD is shown to be the lifetime of the water molecules inside these chains. Simulations of "uncharged" water molecules inside the nanoring show the formation of several water chains and yield SFD. These observations conclusively prove that the diffusion is Fickian when there is a single chain of water and SFD is observed only when two or more chains are present.

KEYWORDS: water · carbon · nanotube · nanoring · single-file diffusion · hydrophobicity · transport · hydrogen bond

The non-Fickian diffusion in single-file systems was experimentally first realized for a system of adsorbed molecules inside artificial zeolites.[12] Here the adsorbate molecules methane and ethane with diameters of 3.8 and 4.7 Å, respectively, were confined in AlPO$_4$ zeolite channels with pore radii of 7.3 Å. The pulsed field gradient NMR method was used to measure the diffusion of the particles. However, some of the results obtained from these studies are contradictory to those from recent quasi-elastic neutron scattering studies,[13] which show that both methane and ethane exhibit normal mode diffusion in AlPO$_4$ channels.

The other recent experimental approach to study SFD has used colloidal particles inside 1D channels. Due to their mesoscopic length scales and associated slow diffusion, it is possible to study the trajectories of individual colloidal particles.[14–17] Using slightly charged silica spheres in 1D channels Lin *et al.*[14] found normal mode diffusion at short times and subdiffusion at longer times. Wei *et al.*[15] have studied the long time MSD of a system of paramagnetic colloidal spheres confined in circular trenches. They find that the MSD scales as $t^{1/2}$. Lutz *et al.*[16] have
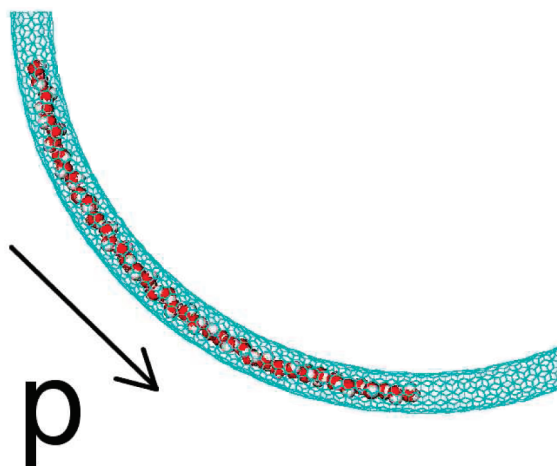
Figure 1. Polarized water chain inside the nanoring. The polarization direction p is marked.

shown that the MSD crosses over from normal mode to SFD for a system of strongly interacting charged colloids trapped by a scanning laser beam inside a circular optical trap.

Transport of water and other organic liquids in narrow carbon nanotubes can also provide an ideal testing ground for the systematic investigation of SFD. There exist a few simulation studies of transport of oxygen, methane, and ethane inside carbon nanotubes, but none of these studies[23,24] provide a clear evidence of SFD. In all of these simulations, the time over which the MSD is measured is rather short (100−500 ps) and they do not provide conclusive evidence of subdiffusive behavior of molecules inside a carbon nanotube.

Water molecules moving inside narrow carbon nanotubes seem to be a very appropriate system which should exhibit SFD. However, all existing studies that
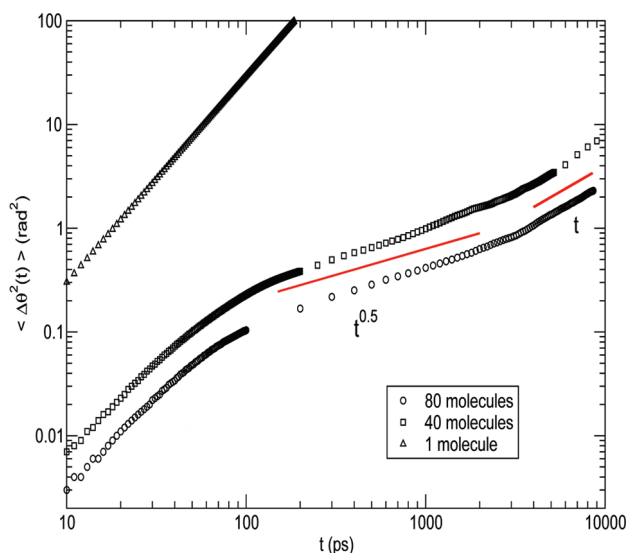

Figure 2. MSD of the confined water molecules computed in the regime where the two oppositely polarized chains are stable. Circles denote the data for the system with 81 water molecules, and squares denote the data for the system with 40 molecules. Both of these systems clearly show SFD. For comparison, the MSD of a single water inside the nanoring is also computed, which is denoted by triangles.

simulate transport of water through finite, narrow nanotubes have observed "normal" diffusion[25−33] in the sense that the MSD of the water molecules inside the nanotube is proportional to time t (instead of being proportional to $\sqrt{t}$, the behavior expected for SFD), even though the particles are prohibited from crossing each other. Hummer *et al.*[25,26] observed that the transport of water molecules occurs in bursts, although later studies of transport on lattices reveal that the pulsatory transport seems to be an universal feature of single-file systems, irrespective of the details of the interaction between particles.[34,35] As pointed out by Karger *et al.*[10] in the context of diffusion of molecules inside zeolites, the question of what conditions SFD (in the sense defined above) would be observed in finite systems is quite subtle. The answer depends crucially on factors such as interactions among the diffusing particles, effects of boundaries (closed boundaries or whether there is an exchange of particles with a bath), nature of the dynamics (deterministic or stochastic), and the time scale at which one is probing the dynamics.[36−38] In the case of water molecules inside carbon nanotubes, the strong hydrogen bonding between neighboring water molecules plays an important role in the dynamics. As shown by Hummer and co-workers,[25,26,33] the hydrogen bonding facilitates the formation of long chains of water molecules. It seems that the formation of a single large chain makes the diffusion normal, and we will see that SFD occurs only in the presence of multiple interacting chains.

In an earlier work, Striolo[30] investigated the diffusion of water molecules inside (8,8) nanotubes with periodic boundary conditions in the direction of the axis of the nanotube. The periodic boundary condition prevents the water molecules from escaping the tube. They find that the water molecules diffuse *via* ballistic mode which persists for a few hundred picoseconds and finally goes over to normal mode diffusion. A more realistic version of this calculation, incorporating the important effects of the exchange of water confined in the nanotube with a bath, has also been performed in the past few years.[25,26,31−33] The hydrogen bond between two water molecules (7 kcal/mol)[28] is much stronger than the random thermal energy at room temperature. Owing to the strong hydrogen bond and short nanotube lengths considered, the confined water molecules move in an extremely coherent fashion, and the process of filling an empty nanotube is a highly cooperative one.[25,32,33] Inside a filled nanotube, the whole group of confined water molecules can be thought of as a single large molecule that moves around, being randomly kicked by the external molecules. Hence, one observes normal mode diffusion.[26,31]

Due to the finite lifetime of the water molecules inside the nanotube, it is difficult to follow them for times longer than their "typical" lifetimes inside the nanotubes. Hence, the long time statistics are poor. To avoid
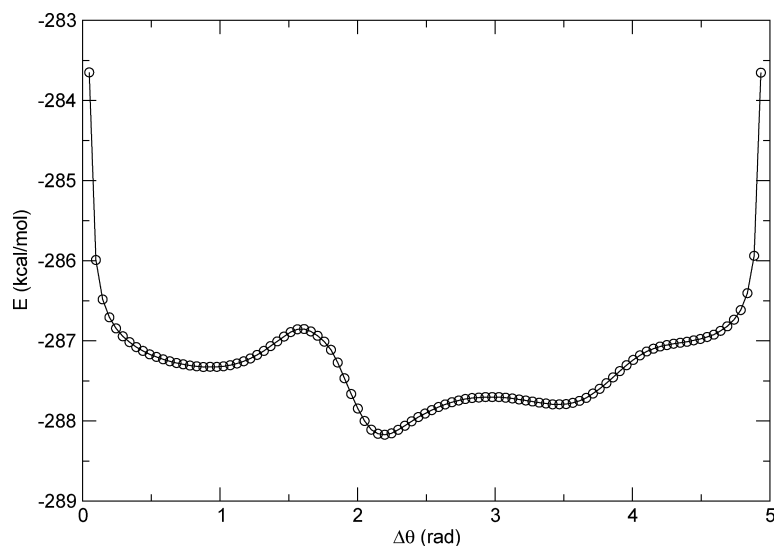
Figure 3. Electrostatic energy of the two polarized water chains is plotted as a function of the angular separation between the two chains. The bigger chain of 28 water molecules has been kept fixed, while the smaller chain of 12 molecules is translated across the ring. The curve shoots up as the angular separation tends to 0 and 5 radians because, at these configurations, the similarly charged groups come near each other, leading to strong repulsive force. This plot establishes the fact that the residual interaction between the chains is repulsive in nature and electrostatic in origin.

this problem, we confine these molecules inside closed nanorings, whereby we could follow these molecules under confinement for longer periods. Carbon nanorings have been recently fabricated[39−41] from straight single-walled nanotubes. The rings result from the folding of nanotubes onto themselves under ultrasonic irradiation. In addition to this, our study yields the effects of curvature on the structure and dynamics of the confined water. The primary difference between nanotubes and nanorings is that intermolecular forces in straight tubes are always along the axis of the tube, whereas in nanorings, intermolecular forces can be perpendicular to the length, thereby stabilizing bipolar chains. Figure 1 shows a portion of the nanoring containing the polarized chain; the oppositely polarized chain present in the other portion of the nanoring is not shown. We show that the effective interaction between these chains is repulsive and electrostatic in origin. These chains are long-lived with approximate lifetimes between 60 to 80 ns. When the MSD for the confined water molecules in this bipolar state is computed, it clearly shows scaling consistent with SFD. The time up to which the SFD is observed is equal to the lifetime of a water molecule in these chains. At times larger than this, the water molecules break away one by one from the ends of the smaller chain and join the larger one at its ends. In this process, the larger chain grows and the shorter one depletes. Eventually, the system ends up in a configuration where there is a single polarized chain. The MSD computed in the regime when there is a single polarized chain is Fickian. In order to study the behavior of the MSD when there are many chains present, we performed a simulation with "uncharged" water molecules inside the nanoring. Several chains are present in this case, and the MSD is consistent with that of SFD.

The remainder of this paper is organized as follows. Section 2 discusses various aspects of the dynamics and the energetics of the confined water molecules. In section 3, we conclude, and in section 4, we discuss the details of the simulation.

DYNAMICS

The MSD values of the confined water molecules have been calculated for the angular coordinate θ, using the formula

$$\langle \Delta\theta^2(t) \rangle = \frac{1}{N} \sum_{i=1}^{N} \langle [\theta_i(t + t') - \theta_i(t')]^2 \rangle_{t'} \qquad (2)$$

where t is the time difference, t' is a time origin, and N is the number of water molecules. The angular brackets indicate an average over time origins. In the calculation of the quantity, $[\theta_i(t + t') - \theta_i(t')]$, care was taken to keep track of how many times the particle has gone fully around the ring. Figure 2 shows the MSD of the confined water molecules. Circles denote MSD for the system with 81 molecules, squares denote the MSD for the system containing 40 water molecules, and the triangles denote the MSD for the system with a single water molecule inside the nanoring. All of these simulations were performed at 300 K. The MSD for both the 40 and 81 water systems show the same qualitative behavior, an initial ballistic regime followed by a subdiffusive regime and finally a regime with normal diffusion. This calculation has been done in the regime where the bipolar water chains are stable, which is 85 and 66 ns for the 81 and the 40 water molecule system, respectively. The onset of the normal diffusion at long times is attributed to the fact that the water molecules break off from one chain and migrate to the other. Estimation
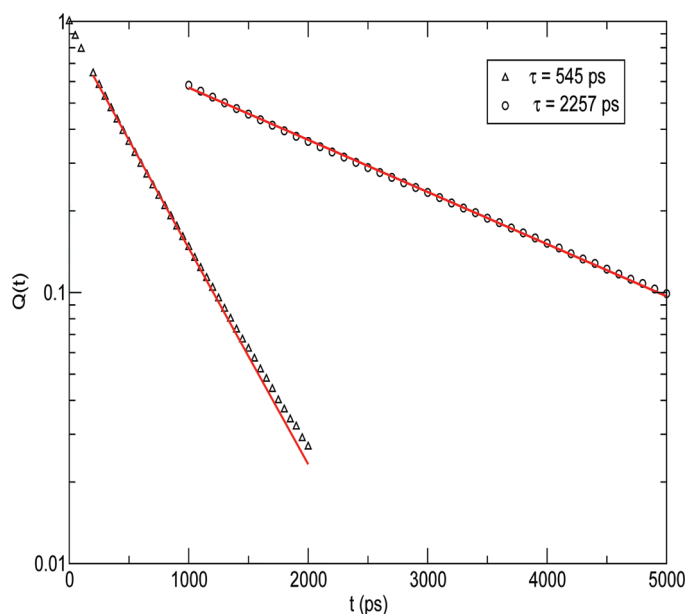
Figure 4. Survival probability of the water molecules in a chain. Triangles denote data from a simulation with 81 water molecules at 350 K. Circles denote the results of a simulation of the same system at 300 K.

of the break-off time of the water molecules will be discussed in detail below. In the absence of inter-water interactions, the system with a single molecule shows an extended ballistic regime until about 1 ns.

The MSD for the system with 81 water molecules at a temperature of 300 K fits the power law $\langle \Delta \theta^2(t) \rangle = 0.0086t^{0.56}$ between 200 ps and 2 ns, beyond which $\langle \Delta \theta^2(t) \rangle = 0.00028t^{0.99}$. The diffusion coefficient can be computed in conventional units by multiplying $\langle \Delta \theta^2(t) \rangle$ by the square of the radial coordinate of a water molecule. Typical radius is 77.7 Å; this shows that the diffusion coefficient in the final diffusive regime is 8.45×10^{-5} cm^2/s.
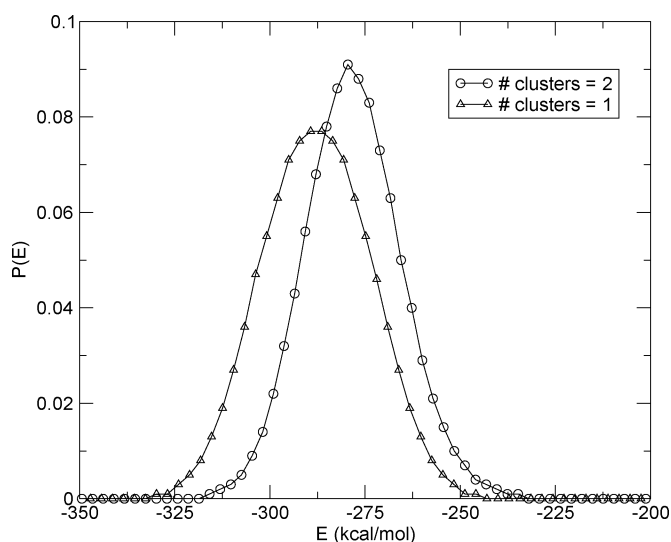

Figure 5. Histogram of the electrostatic energy of the confined water molecules. The circles denote the distribution when there are two chains, and the triangles denote the distribution when there is a single chain. The energy is lower for the single chain, and the difference is approximately equal to the energy of the hydrogen bond between two water molecules inside a (6,6) straight nanotube, which is 7 kcal/mol.

To understand the effective interaction between the oppositely polarized chains of the water molecules, we have taken a snapshot from the MD trajectory and have rigidly translated one chain, keeping the other fixed. In Figure 3, we have plotted the electrostatic energy of the generated configuration as a function of the angular displacement of the chain which is being moved. This calculation has been done for the system with 40 water molecules inside the nanoring, where one chain that had 28 water molecules and subtends an angle of 52° at the center of the ring was kept fixed, while the other chain with 12 water molecules, which subtends a 22° angle, was rigidly translated around the ring. Therefore, the total amount of angular displacement of the smaller chain is about 286°, which is about 5 radians and that is the extent of the abscissa in Figure 3. Figure 3 clearly shows that the interaction between the two chains is repulsive. The configuration that was picked from the MD simulation lies near the minimum of the landscape shown in Figure 3. The chains repel each other very strongly when the similarly charged end groups come near each other.

To calculate the mean time of a water molecule staying continuously in a chain, we proceed in the following way: Since the water molecules move in single file with no particle crossings, the sequence of particles is the same throughout the simulation. At a given time instant t, we calculate the distance between the ith water molecule and its two neighbors, the one in front and the one at the back. If both of these distances are less than a cutoff (5 Å), then the quantity $P_i(t)$ is set equal to unity and to zero otherwise. We calculate the probability that a water molecule stays in a chain continuously from the quantity

$$Q(t) = \sum_{i=1}^{N} \left\langle \prod_{t_k=t_0}^{t_0+t} P_i(t_k) \right\rangle \qquad (3)$$

where the summation is over all of the water molecules and the angular brackets denote an average over the time origin t_0. The survival probability was normalized to unity at $t = 0$ by dividing the $Q(t)$ of eq 3 by its value at $t = 0$. Configurations saved at every 1 ps interval were used in the calculation of this quantity. At long times, this probability falls as an exponential function of time. We fit these data to an exponential and find the associated time scale. The survival probability as a function of time for this system, with an exponential fit of the long time data, is shown in Figure 4. Triangles denote data from simulation with 81 water molecules at a temperature of 350 K. Circles denote simulation with 40 water molecules at a temperature of 300 K. We fit the long time portion of the survival probability to an exponential ($Q(t) \sim e^{(-t/\tau)}$) and find the associated time scales. These time scales are 545 and 2257 ps for the systems simulated at 350 and 300 K, respectively (see Figure 4). It is interesting to note

from Figure 2 that the crossover from SFD to normal diffusion occurs roughly at the time equal to the mean lifetime of the water molecules in these chains. Hence, this ascertains the fact that the diffusive mode at long times is due to the interchain transitions of the water molecules.

The survival times extracted from the survival probability within a chain yield time scales of 545 and 2257 ps for the systems simulated at 350 and 300 K, respectively. As the process of escape of a molecule from a chain involves the breaking of a hydrogen bond between two water molecules, the strength can be approximately estimated from these numbers. From the relation

$$\tau = \tau_0 e^{-(E_H/k_B T)} \tag{4}$$

where τ is the time scale extracted from the survival probability, E_H is the hydrogen bond between two water molecules inside the nanotube, one can write $\ln(\tau_2/\tau_1) = (E_H/k_B)[(1/T_1) - (1/T_2)]$, where τ_1 and τ_2 are the time scales at temperatures T_1 and T_2, respectively. Substituting the relevant times, we get $E_H = 5.72$ kcal/mol. This value is close to the energy of a single hydrogen bond (7 kcal/mol) formed between two water molecules arranged in a single file.[28]

At long times, the bipolar arrangement of the water molecules leads to the formation of a single unipolar chain. This happens beyond 85 and 66 ns for the 81 and 40 water system, respectively. This change takes place by the process of water molecules breaking away one by one from the ends of the smaller chain and joining the larger one at its extremities. Since a single water molecule is free to take any orientation inside the nanoring, it changes its "polarity" when it joins the larger chain. By this process, the longer chain grows and the shorter one depletes. Eventually, the system is in a configuration where there is only one "polarized" chain. On calculating the MSD in the single chain regime, we qualitatively recover the results of Striolo,[30] which is ballistic diffusion at small times and normal diffusion at longer times. The mean electrostatic energy decreases by about 10 kcal/mol, which is approximately equal to the energy of a single hydrogen bond (7 kcal/mol) formed between two water molecules inside a (6,6) nanotube as estimated by Zhou et al.[28] The time-averaged probability distribution of electrostatic energy of the water molecules is shown in Figure 5. The distribution when there are two stable chains is denoted by circles, whereas triangles denote the distribution when there is a single chain. The mean of the distribution shifts to a lower value when a single chain forms. This means that the single chain is energetically more favorable than the arrangement where there are two bipolar chains.

In order to have a better understanding of the diffusion behavior in a situation where there are many
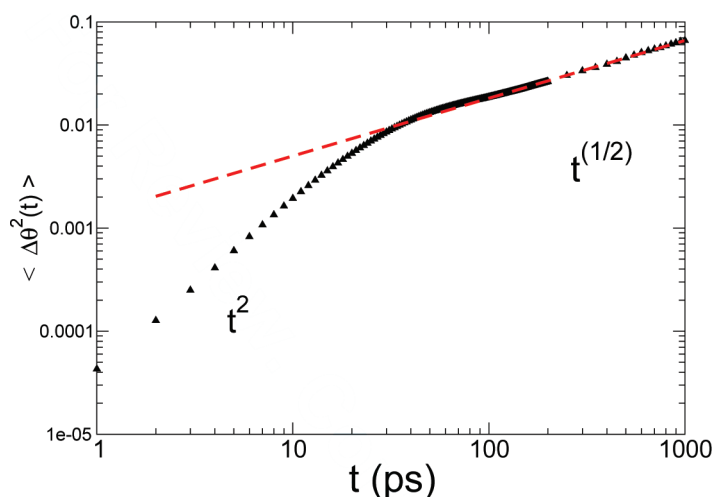

Figure 6. MSD of 40 uncharged (see text) water molecules, confined inside the nanoring.

chains in the system, we have performed a simulation on a system of 40 uncharged water molecules confined inside the nanoring. The particles form a Lennard-Jones system with only the weaker oxygen−oxygen and the carbon−oxygen interactions present. This eliminates the strong hydrogen bonds present in "real" water and prevents the water molecules from forming long chains. Typical snapshots from the MD simulation show that many small chains are present in the system, unlike the long polarized chains observed in the system simulated with the charges included. The MSD calculated for this system is presented in Figure 6. It shows a very clear initial ballistic regime, followed by a *single-file* regime, where $\langle\Delta\theta^2(t)\rangle \sim t^{1/2}$. The single-file regime starts at about 80 ps and continues up to 1000 ps. This conclusively shows that the SFD is only observed when there are two or more chains present in the system.

CONCLUSION

We show that the water molecules inside the nanoring form polarized chains. The polarization of the two chains are opposite, and when they approach each other, they do so by their similarly charged ends coming close. This leads to a strong repulsion between the two chains. The calculation of the MSD of the system of the two oppositely polarized chains shows a single-file regime with $\langle\Delta\theta^2(t)\rangle \sim t^{1/2}$. The time up to which the water molecules undergo SFD is shown to be the lifetime of the water molecules inside these chains. The interchain repulsive interactions are electrostatic and hence long-ranged, which is in contrast with shorter-ranged steric repulsion in colloidal systems, where SFD has been observed by imaging their temporal evolution. At long times, the water molecules break away from the smaller chain and join the longer one and a single unipolar chain is formed. The MSD calculated from trajectories when there is a single chain does not exhibit SFD, but shows *normal* diffusion. We have also performed a simulation on a system of 40 uncharged water molecules confined inside the nanoring.

Many chains are observed, and the MSD shows a temporal scaling consistent with SFD. These observations conclusively prove that SFD is observed when two or more chains are present in the system.

As a future project, we would like to extend the studies on the diffusion of water inside finite nanotubes in the presence of bath water outside to nanotube lengths, where it may be possible to observe SFD (MSD proportional to $\sqrt{t}$). The results described above imply that the presence of two or more chains of water molecules is necessary for SFD to be observed. Although earlier studies[25,26,31] show that the water molecules inside short nanotubes form a single chain, it is expected that the chain will break up into two or more components if the nanotube is sufficiently long—it is well-known that solid-like positional order is always short-range in one dimension. Therefore, the condition of having two or more water chains will be satisfied if the nanotube is sufficiently long. Even under these conditions, the diffusion at very long times is expected[10,36−38] to be normal (MSD proportional to t) because the diffusion behavior in a system that is in contact with a reservoir of particles would be dominated by the center of mass diffusion at long times, even if the underlying dynamics is single-file-like. However, a "mean field" estimate[10] of the crossover time beyond which normal diffusion is expected indicates that this time scale is proportional to L^2 where L is the length of the tube. Therefore, this crossover time would also be very large for large L (we estimate this time to be more than 100 ps for water inside a nanotube of length 700 Å), so that SFD can be expected to be observed over a substantial time interval. We would like to simulate systems with nanotubes of such length in order to see whether SFD is observable in a system of water inside narrow nanotubes.

METHODS

For our simulations, we took a (6,6) nanotube with 4880 carbon atoms (200 unit cells) and folded it into a nanoring and filled it up with TIP3P[42] water molecules at various filling fractions. The nanoring was held fixed with the axis along the Z axis. The simulations were performed using AMBER 7.[43] The interactions between various atoms have been described by classical force fields; the carbon and oxygen atoms are modeled as Lennard-Jones particles. The Lennard-Jones interaction parameters used are $\varepsilon_{CC} = 0.086$ kcal/mol, $\sigma_{CC} = 3.4$ Å, $\varepsilon_{CO} = 0.11$ kcal/mol, and $\sigma_{CO} = 3.28$ Å. The carbon−carbon bond length was 1.4 Å, and the corresponding spring constant was 938 kcal/(mol Å^2); the equilibrium C−C−C angle was $2\pi/3$ radians, and the corresponding spring constant was 126 kcal/(mol rad^2). Initially, the nanotube was filled up with water molecules at uniform angular separation, with their dipoles all oriented along the tangent vector to the ring at the location of the water molecule. The systems were equilibrated for 4 ns, and all of the simulations ran for 150 ns.

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