

# Strong Correlations and Fickian Water Diffusion in Narrow Carbon Nanotubes

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## Abstract

We have used atomistic molecular dynamics (MD) simulations to study the structure and dynamics of water molecules inside an open ended carbon nanotube placed in a bath of water molecules. The size of the nanotube allows only a single file of water molecules inside the nanotube. The water molecules inside the nanotube show solid-like ordering at room temperature, which we quantify by calculating the pair correlation function. It is shown that even for the longest observation times, the mode of diffusion of the water molecules inside the nanotube is Fickian and not sub-diffusive. We also propose a one-dimensional random walk model for the diffusion of the water molecules inside the nanotube. We find good agreement between the mean-square displacements calculated from the random walk model and from MD simulations, thereby confirming that the water molecules undergo normal-mode diffusion inside the nanotube. We attribute this behavior to strong positional correlations that cause all the water molecules inside the nanotube to move collectively as a single object. The average residence time of the water molecules inside the nanotube is shown to scale quadratically with the nanotube length.

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## I. INTRODUCTION

Fluids confined in nanometric scales are known to behave very differently from their bulk counterpart [1]. Structurally, they show solid-like ordering, induced by the confinement, whereas their diffusion constants are of the same order of magnitude as those of ordinary bulk liquids. Water confined in carbon nanotubes serves as an ideal example of such a system. The interest in studying such systems arises from the importance of understanding the properties of confined water and from the possibility of extrapolating the conclusions to other physical situations of similar nature, such as water adsorbed in nanopores in biological and geological systems. In recent years, Molecular Dynamics (MD) simulations have been used to study various aspects of these systems in microscopic detail [2, 3, 4, 5, 6, 7, 8]. Such studies complement experimental investigations by providing detailed microscopic understanding of some of the experimentally observed features. In some cases, simulations also make interesting predictions that can be tested in experiments.

Both structural and dynamical properties of water molecules in nanotubes have been investigated in MD simulations. Water molecules confined in nanotubes exhibit a variety of spatially ordered structures not seen in bulk water. MD studies of Koga *et al.* [5, 6] predict the occurrence of hexagonal, heptagonal, square or pentagonal ice nanotube structures inside carbon nanotubes of diameter ranging from 11 to 14Å under different conditions. Some of these structures have been inferred from x-ray diffraction [9] and neutron scattering [10] experiments. Striolo *et al.* [7] have performed Grand Canonical Monte Carlo (GCMC) simulations to study the adsorption of water in single-walled carbon nanotubes and found structures similar to those observed in neutron scattering experiments [10]. GCMC simulations on adsorption of organic mixtures of cyclohexane, methane, ethane etc. inside carbon nanotubes show ordered arrangement of the adsorbed molecules [11].

Among the dynamical properties of confined water, one that has attracted a lot of attention is the process of conduction of water molecules through nanopores. It is believed that this process is important in understanding the transport through biological ion channels [12]. Hummer *et al.* [2] studied the conduction of water molecules through narrow carbon nanotubes using MD simulations. They found that clusters of water molecules are transferred through the nanotube in the form of occasional bursts arising due to pressure fluctuations occurring outside the nanotube. Beckstein *et al.* [3, 4] have extended such simulations to

study the density fluctuations of water inside other hydrophobic pores. Transport of oxygen and organic molecules such as methane, ethane and ethylene through carbon nanotubes has also been studied [13, 14, 15, 16] through MD simulations.

Another interesting question about the dynamics of water molecules in narrow carbon nanotubes is concerned with the mode of diffusion of the water molecules. If the diameter of the nanotube is comparable to the size of a water molecule, then the water molecules can not cross one another while they are inside the nanotube and they have to move in a single file. Various earlier studies [17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27] suggest that under these conditions, the water molecules inside the nanotube should exhibit a kind of sub-diffusive behavior known as *single file diffusion* where the mean-square displacement (MSD) scales with time  $t$  as  $t^{1/2}$  at long times. A crossover from normal mode diffusion ( $\text{MSD} \propto t$ ) to single file behavior has been observed in experiments on colloidal particles suspended in water inside narrow trenches [28, 29, 30, 31] and on molecules diffusing through channels in zeolites [32].

The question whether molecules exhibit single file diffusion inside narrow carbon nanotubes has been investigated in a number of simulation studies. Lee *et al.* [13] have studied the diffusion of oxygen molecules inside open-ended carbon nanotubes of various diameters. They interpret their simulation results implying that oxygen diffuses through wide (17,0) nanotubes via normal mode diffusion, whereas inside narrow (10,0) nanotubes, the molecules exhibit sub-diffusive behavior ( $\text{MSD} \sim t^\alpha$ , where the exponent  $\alpha$  is less than unity). The simulations of Mao *et al.* [14] suggest that spherical methane molecules exhibit normal mode diffusion inside closed carbon nanotubes, whereas aspherical molecules such as ethane and ethylene diffuse by a mode which is between normal and single-file. In all these simulations, the time over which the MSD is measured is rather short (100 – 500 ps). Also, due to finite-size effects arising from the smallness of the nanotube length (these effects will be discussed in detail below), it is difficult to draw a firm conclusion about the true nature of diffusion inside the nanotube from the time-dependence of the MSD. For these reasons, we believe that the simulations mentioned above do not provide conclusive evidence for sub-diffusive behavior of molecules inside a carbon nanotube. Recently, Striolo [8] has performed MD simulations of the diffusion of water molecules inside a (8,8) nanotube using periodic boundary conditions in the direction of the axis of the nanotube. This artificial boundary condition prevents the water molecules from escaping the nanotube and hence it is possible

to obtain MSD data at long times with good statistics. These simulations show that the water molecules inside the nanotube initially undergoes ballistic diffusion ( $\text{MSD} \propto t^2$ ) which crosses over to normal mode diffusion at long times.

In this work we use MD simulations to study the structural and dynamical properties of water molecules inside (6,6) carbon nanotubes of diameter  $8\text{\AA}$  and lengths  $L$  equal to 14, 28 and  $56\text{\AA}$  in a bath of water. Since the water molecules inside the nanotube can not cross one another, a primary goal of our study is to determine whether single file diffusion occurs in this system. Here the interactions among the water molecules inside the nanotube are much stronger compared to those among the colloidal particles considered in experiments [28, 29, 30, 31] that demonstrate the occurrence of single file diffusion. This can be inferred from the packing fraction of the water molecules inside the tube. The packing fraction,  $\eta$ , is defined as  $\eta = N\sigma/L$ , where  $N$  is the number of water molecules,  $\sigma$  the diameter of each molecule and  $L$ , the length of the tube. This quantity is close to unity for the water molecules inside the (6,6) nanotube (it depends to some extent on the equilibrium density of the water molecules in the bath). This introduces strong correlations in the positions and displacements of the water molecules in the nanotube. These correlations and the effects of the open ends of the relatively short nanotubes considered in our study (in particular, the fact that the range of correlations is comparable to the length of the nanotube) have important bearings on the diffusion behavior of the water molecules.

We find that the confined water molecules are spatially ordered, much like a solid, at temperatures as high as 300 K. The MSD of the confined water molecules increases linearly with time  $t$  at relatively short times (after a very short initial regime of quadratic increase characteristic of ballistic motion), indicating normal-mode diffusion over this time scale. At long times the MSD eventually saturates. We show, by comparing the simulation results with analytic ones obtained from a simplified random walk model described below, that the observed behavior is completely consistent with normal mode diffusion of the water molecules inside the nanotube. In particular, we observe that the departure of the MSD versus  $t$  curve from the initial linear behavior is a consequence of biased sampling arising from the fact that the MSD is measured only for the molecules that stay inside the nanotube. This conclusion is consistent with existing results [33] that show that the statistics of the bursts of water molecules passing through a narrow carbon nanotube [2] are consistent with one-dimensional random walk behavior. Our work also brings out that the normal mode

diffusion found recently by Striolo [8] for water molecules in narrow carbon nanotubes with periodic boundary conditions persists in the more realistic situation of open-ended nanotubes immersed in water.

The remainder of the paper is organized as follows. Section 2 describes the details of the simulation. In Section 3 we describe the results obtained from the MD simulations for the static structure and the dynamics of the water molecules inside the nanotube. In Section 4 we propose a random walk model to explain the dynamics of the confined water molecules and compare the analytic results for the model with those obtained from our MD simulations. Section 5 contains a summary of our main results and a few concluding remarks.

## II. DETAILS OF SIMULATION

We have simulated a (6,6) carbon nanotube of  $8\text{\AA}$  diameter placed in a bath of TIP3P [34] water molecules at 300K and 1 atmosphere pressure. During the simulation the nanotube was held fixed inside the simulation box, with its long axis along the  $z$  direction. The simulations have been performed using AMBER 7 [35]. We have considered open-ended nanotubes of length  $L$  equal to  $14\text{\AA}$ ,  $28\text{\AA}$  and  $56\text{\AA}$ . A given simulation contained 1000 to 2200 water molecules depending on the size of the nanotube used. The interactions between various atoms have been described by classical force fields. The carbon and oxygen atoms were modelled as Lennard-Jones particles, the details of which are given in Table I. The carbon-carbon bond length was  $1.4\text{\AA}$  and the corresponding spring constant was  $938\text{ kcal}/(\text{mol } \text{\AA}^2)$ , the equilibrium C-C-C angle was  $2\pi/3$  radians and the corresponding spring constant was  $126\text{ kcal}/(\text{mol } \text{rad}^2)$ . The simulations were performed for periods varying between 8 ns and 20 ns (longer simulations were carried out for nanotubes with larger  $L$ ) and the coordinates were stored at an interval of 1 ps.

### III. RESULTS

To quantify the positional ordering of the water molecules inside the nanotube we have calculated the pair-correlation function for the water molecules inside the nanotube using

$$g(z) = \frac{1}{N} \sum_{i=1}^N \sum_{j=1, j \neq i}^N \langle \delta(z - z_{ij}) \rangle, \quad (1)$$

where  $z_{ij}$  is the axial separation between the  $i$  th and the  $j$  th water molecules,  $N$  is the number of water molecules inside the nanotube and the angular brackets indicate an average over time.

The calculated pair correlation functions for nanotubes of length  $14\text{\AA}$ ,  $28\text{\AA}$  and  $56\text{\AA}$  are shown in Fig. 1. The distinct peaks of  $g(z)$  suggest that there is solid-like ordering of the water molecules inside nanotube, even at a temperature of  $300K$ , for all the three tube lengths. The nearest-neighbour distance between the water molecules is  $2.6\text{\AA}$ , similar to that obtained by Hummer *et al.* [33]. The heights of the peaks of  $g(z)$  are smaller for shorter nanotubes and the peak height decreases faster with  $z$  as the length of the nanotube is reduced. However, this does not imply that the degree of positional order of the water molecules inside the nanotube decreases as the tube length is reduced. The differences between the results for  $g(z)$  for nanotubes of different length arise from a simple finite-size effect, namely that the fraction of molecules that have a smaller number of neighbors due to their proximity to the open ends of the nanotube is larger for smaller tubes. This finite-size effect on the form of  $g(z)$  is seen clearly on comparing the  $g(z)$  obtained for the  $14\text{\AA}$  tube with that calculated for the water molecules residing in the central  $14\text{\AA}$  portion of the  $28\text{\AA}$  nanotube, taking only the molecules in this central region in the sums in Eq.(1). This comparison is shown in Fig.2. The observation that the two correlation functions are identical confirms that the degree of positional correlations is the same in nanotubes of length  $14\text{\AA}$  and  $28\text{\AA}$ . That the water molecules are correlated over distances comparable to the length of the nanotube has important consequences on the diffusion behavior of the molecules, as discussed below.

We find that the trajectories of neighbouring molecules inside the nanotube are extremely correlated. In order to quantify this correlation we have calculated the quantity,  $\langle \delta z_i(\delta t) \delta z_j(\delta t) \rangle$ , where  $\delta z_i(\delta t)$  and  $\delta z_j(\delta t)$  are the displacements of the  $i$ th and  $j$ th water molecules, respectively, in a time interval of  $\delta t$ . For this calculation,  $\delta t$  was taken to be 1

ps. The angular brackets indicate averaging over time origins and pairs of water molecules inside the nanotube. This quantity was calculated as function of the separation  $z$  between the molecules  $i$  and  $j$  for nanotubes of all three lengths. Results for this correlation function are shown in Fig. 3. It decays as the separation  $z$  is increased, signifying the loss of correlation of the displacements of widely separated particles. The separation at which this correlation function decays to zero is close to the length of the tube, implying that the displacements of all the molecules inside the tube are correlated for tubes of all three lengths. This observation, consistent with the positional correlations shown in Fig. 1, implies that the water molecules inside the nanotube tend to move together as a single object.

The MSD of the water molecules inside the nanotube was calculated using

$$\langle \Delta z^2(t) \rangle = \frac{1}{N} \sum_{i=1}^N \langle [z_i(t+t') - z_i(t')]^2 \rangle_{t'}, \quad (2)$$

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. The open ends of the tube allow particle exchange with the water bath. As a result, while calculating the quantity,  $[z_i(t+t') - z_i(t')]^2$ , for the  $i$ th water molecule, one has to ensure that this molecule has stayed within the nanotube for the entire interval of time between  $t'$  and  $(t+t')$ . To ensure this, we have multiplied  $[z_i(t+t') - z_i(t')]^2$  by  $\prod_{t'}^{(t+t')} P_i(t'')$ , where the quantity  $P_i(t)$  is equal to unity if the  $i$ th molecule is inside the nanotube at time  $t$  and zero otherwise. Similarly the number of time-origins which contribute for a particular molecule  $i$  and time difference  $t$  is  $\sum_{t'} \prod_{t'}^{(t+t')} P_i(t'')$ . This way, even though the sum in Eq.(2) goes over all the water molecules present in the system, only those molecules that have entered the tube at least once contribute in the calculation of the MSD.

The finite lifetime of the water molecules inside the nanotube makes it difficult to find sufficient number of long-lived water molecules, the identification of which is crucial for good statistics of the MSD at long times. Hence, the simulation was run for 8 ns for the system with 14Å nanotube to get MSD data up to 200 ps. The run-time of the system with 28Å nanotube was 12 ns to get MSD data for a period of 1 ns. For the 56Å nanotube, even after running the simulation for about 16 ns, we were unable to get good quality data for the MSD at long times. In this method, the short time data are obtained from averages over a large number of molecules, about 300 to 400, and also a large number of time origins. The number of time-origins as well as the number of water molecules available for averaging

decrease as one goes to longer time difference  $t$ . For this reason, the long-time MSD data are more noisy. At the longest time differences for which the MSD has been reported in this work, the number of molecules contributing is approximately 50.

The time-origin averaged MSD of the water molecules inside the  $28\text{\AA}$  nanotube is shown in Figure 4 (top panel, solid line). The initial portion of the curve is linear in time, indicating normal mode diffusion. At longer times, the curve bends downward and finally it saturates to a constant value. The diffusion constant, calculated from the initial slope of the MSD versus  $t$  curve, is 2.2, 2.5 and  $2.8 (\times 10^{-5} \text{cm}^2/\text{s})$  for the water molecules inside the 14, 28 and the  $56\text{\AA}$  nanotube, respectively. Even though there is a slight length dependence, the reason for which is not clear, the value of the diffusion constant is roughly half of that of bulk TIP3P water,  $5 \times 10^{-5} \text{cm}^2/\text{s}$ . It is interesting to note at this point that the value of the diffusion constant obtained from our calculations is in agreement with that reported by Berezhkovskii *et al.* in Ref.[33]. The diffusion constant estimated from the mean inter particle separation of  $a = 2.6\text{\AA}$  (this is exactly what we get from the position of the first peak of  $g(z)$ ) and the mean hopping time  $\tau = 13$  ps, reported by Berezhkovskii *et al.*, is  $2.6 \times 10^{-5} \text{cm}^2/\text{s}$ , which is very close to the values obtained from our simulations.

A naive interpretation of the downward bending of the MSD versus  $t$  curves at longer times would be a crossover from normal mode diffusion to sub-diffusive behavior as  $t$  is increased. In particular, it is possible to find a time window in which the local slope of the MSD versus  $t$  curve in a log-log plot is approximately equal to 0.5, the value expected for single file diffusion. However, such an interpretation of the data is not correct. As discussed in detail in the next section where we present a simple model for the dynamics of the water molecules inside the nanotube and compare the simulation results for the MSD with analytic ones obtained for this model, the MSD data shown in Fig. 4 are completely consistent with normal mode diffusion of the water molecules. The fact that each molecule that contributes to the calculation of the MSD for time  $t$  is required to stay inside the nanotube of finite length for the entire observation time  $t$  leads to the downward bending and eventual saturation of the MSD at long times.

Figure 4 (bottom panel, solid line) shows the MSD calculated with a fixed time origin which is taken to be the time at which each water molecule enters the nanotube. The MSD shown in this plot is, therefore, the mean-square displacement of a water molecule inside the nanotube from its point of entry. This set of data is more noisy than the time-averaged



one due to lack of averaging over time origins. It is, however, clear that this curve saturates at long times at a value higher than the saturation value of the time-origin averaged MSD. Also, the behavior of this curve near  $t = 0$  is different from that of the time-origin averaged MSD. All these features of the results for the fixed time origin MSD can also be explained from the random walk models discussed in the next section.

Another important quantity characterizing the dynamics of the confined water molecules is the survival probability of the water molecules inside the nanotubes. This probability was calculated using the definition [36]

$$Q(t) = \sum_{i=1}^N < \prod_{t_k=t_0}^{t_0+t} P_i(t_k) >, \quad (3)$$

where the summation is over all 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.  $Q(t)$  defined above is the probability that a water molecule remains inside the nanotube for all times between  $t_0$  and  $t_0 + t$ , averaged over the initial time  $t_0$ . It is related to  $p(t)$ , the distribution of residence times of the water molecules inside the nanotube, in the following way.

$$Q(t) = \frac{\int_t^{t_m} (t' - t)p(t')dt'}{\int_0^{t_m} t'p(t')dt'}. \quad (4)$$

Here  $t_m$  is the total time of the simulation which, for all practical purposes, may be taken to be infinity. A related quantity, which is also sometimes called the survival probability, is  $S(t)$ , the probability that a water molecule that enters the nanotube at time  $t_0$  remains inside the nanotube for all times between  $t_0$  and  $t_0 + t$ . This quantity is related to the residence time distribution  $p(t)$  by

$$S(t) = \int_t^{t_m} p(t')dt', \quad (5)$$

which implies that  $p(t) = -dS(t)/dt$ . Using this result in Eq.(4), we get the following relation between the measured survival probability  $Q(t)$  and the quantity  $S(t)$ .

$$Q(t) = \frac{\int_t^{t_m} S(t')dt'}{\int_0^{t_m} S(t')dt'}. \quad (6)$$

If the residence time distribution decays exponentially with time at long times, i.e. if  $p(t) \sim \exp(-t/\tau)$ , then both  $Q(t)$  and  $S(t)$  would also decay exponentially with the same time scale  $\tau$  which would be the average residence time of the water molecules inside the nanotube.

The survival probability  $Q(t)$  obtained from MD simulations for the  $28\text{\AA}$  nanotube is shown as a function of time  $t$  in Fig.5 in a semi-log plot. It is clear from the plot that  $Q(t)$  decays exponentially with  $t$  at long times. This data is calculated from a simulation which ran for 20 ns. Results for the  $14\text{\AA}$  tube also show similar behavior. The value of the time constant  $\tau$  (the average residence time) is  $73 \pm 0.7$  ps for the  $14\text{\AA}$  tube and  $371 \pm 5$  ps for the  $28\text{\AA}$  tube. These values are roughly proportional to  $L^2$ . The exponential decay of the survival probability and the quadratic dependence of the time scale  $\tau$  on the length of the nanotube are both consistent with normal mode diffusion of the water molecules inside the nanotube. This is explained in detail in the next section.

#### IV. RANDOM WALK MODELS AND COMPARISON WITH MD RESULTS

Due to the very high degree of correlation among the positions and displacements of the confined water molecules demonstrated in the preceding section, it is reasonable to form the following approximate description of the dynamics of the water molecules inside the nanotube: the group of water molecules, each separated from its neighbors by the inter-particle spacing  $a$ , form a “solid” object of size comparable to the length  $L$  of the nanotube. This group of strongly correlated molecules moves back and forth along the tube, randomly kicked by water molecules from the bath if it happens to be near an end of the tube. If one of the molecules in this group goes out of the tube, another one enters the tube within a short time, keeping the total number of molecules inside the tube roughly constant in time. Hence the motion of this group of molecules can be described as a one-dimensional random walk of a single “effective” particle on a line segment of length  $L$ . Since we consider the dynamics of the water molecules only during the time they spend inside the nanotube (a molecule that goes out of the nanotube becomes a part of the bath and is not considered in our calculations), the one-dimensional random walk has absorbing boundaries at the two end of the tube ( $z = 0$  and  $z = L$ ). The time  $t$  is a continuous variable here. Hence we call this model a continuous time random walk (CTRW). All the results pertaining to this model can be calculated analytically. We have also considered a discrete time random walk (DTRW) model (see below) for which results were obtained from Monte Carlo (MC) simulations.

The diffusion equation for the quantity  $P(z, t|z_0, 0)$ , the probability of finding the particle

at  $z$  at time  $t$ , given that the particle was at  $z_0$  at the initial time  $t = 0$ , is given by,

$$\frac{\partial P}{\partial t} = D \frac{\partial^2 P}{\partial z^2}, \quad (7)$$

where  $D$  is the diffusion constant. The absorbing boundary conditions for the above equation are

$$P(0, t|z_0, 0) = P(L, t|z_0, 0) = 0, \quad (8)$$

whereas the initial condition is  $P(z, 0|z_0, 0) = \delta(z - z_0)$ . The solution of Eq.(7) with the initial and boundary conditions specified above is

$$P(z, t|z_0, 0) = \sum_{n=1}^{\infty} \frac{2}{L} \sin\left(\frac{n\pi z_0}{L}\right) \sin\left(\frac{n\pi z}{L}\right) e^{-D(\frac{n\pi}{L})^2 t}. \quad (9)$$

The time-origin averaged MSD can be analytically calculated from the expression

$$\langle \Delta z^2(t) \rangle = \frac{\int_0^{\infty} dt_0 \int_0^L dz_2 \int_0^L dz_1 P(z_2, (t_0 + t)|z_1, t_0) (z_2 - z_1)^2 P(z_1, t_0|z_0, 0)}{\int_0^{\infty} dt_0 \int_0^L dz_2 \int_0^L dz_1 P(z_2, (t_0 + t)|z_1, t_0) P(z_1, t_0|z_0, 0)}. \quad (10)$$

The MSD with fixed time-origin, discussed in the preceding section, is given by

$$\langle (z(t) - z_0)^2 \rangle = \frac{\int_0^L dz (z - z_0)^2 P(z, t|z_0, 0)}{\int_0^L dz P(z, t|z_0, 0)}. \quad (11)$$

The quantity  $S(t)$  defined in the preceding section, which is the probability that the particle does not go out of the tube during the time interval between 0 and  $t$ , is given by

$$\begin{aligned} S(t) &= \int_0^L P(z, t|z_0, 0) dz \\ &= \sum_{n=1}^{\infty} \left(\frac{2}{n\pi}\right) \sin\left(\frac{n\pi z_0}{L}\right) [1 - (-1)^n] e^{-D(\frac{n\pi}{L})^2 t}. \end{aligned} \quad (12)$$

The survival probability  $Q(t)$  measured in our MD simulations may be obtained by combining this with Eq.(6).

We have used these analytic expressions to calculate all the dynamical quantities measured in the MD simulations. The input parameters required for comparing the results from the random walk model with those obtained from MD simulations are the diffusion constant,  $D$  of the water molecules inside the nanotube and  $z_0$ , the position of a water molecule at time  $t = 0$ , i.e. at the moment it comes inside the nanotube. We used the value of  $D$  estimated from the slope of the MSD versus time curve near the origin. The value of  $z_0$  used in the calculation is the mean of the starting coordinate of a water molecules inside the nanotube, measured from the end through which it enters the tube. In making a comparison of the

analytic results for the CTRW model with those obtained from MD simulations, one should keep in mind the fact that the positions of the water molecules are measured at discrete intervals of 1 ps in the simulations. It is known from earlier studies of similar problems (see, for example, Ref.[37]) that this discrete sampling can make the results for dynamical quantities significantly different from those obtained from a continuous-time description. The difference in the present case arises from the fact that events in which a water molecule goes out of the tube and re-enters it between two successive measurements of its position (which are separated by 1 ps) are not detected in the discrete sampling. This makes values of the MSD and the survival probability obtained from discrete sampling higher than those calculated for the continuous time model.

To examine the effects of discrete sampling, we have used MC simulations to study the dynamics of a random walk model in which a particle, initially at  $z = z_0$ , performs a DTRW in which the length of each step is a Gaussian random variable with zero mean and variance equal to  $2D\delta t$ , where  $D$  is the diffusion constant obtained from our MD simulation and  $\delta t = 1$  ps, the time between two successive measurements of the particle position in the MD simulation. The time in the DTRW model is defined as  $n\delta t$  where  $n$  is the number of steps taken by the particle. The MC simulations were carried out with absorbing boundary conditions at  $z = 0$  and  $z = L$ , and all dynamical quantities were measured using the same methods as those in the MD simulation.

The results obtained for the CTRW and DTRW models compare well with those obtained from our MD simulations. A comparison of the results for the MSD is shown in Fig. 4 in which the top panel shows the time-origin averaged MSD, and the bottom panel shows the MSD with fixed time origin. The data obtained from the DTRW model are denoted by the dashed curve, whereas the analytic results from the CTRW model are denoted by the dash-dotted curve. While both the random walk models reproduce all the features of the MD data, the agreement is better for the DTRW results, as expected. As in MD simulations, the MSD saturates at long times and the value of the MSD at saturation depends on the length  $L$  of the tube. For the time-origin averaged MSD, the analytic CTRW model predicts that the saturation occurs when  $\sqrt{\langle \Delta z^2(t) \rangle}/L \simeq 0.31$ , whereas the MSD with a fixed time origin saturates at  $\sqrt{\langle (z(t) - z_0)^2 \rangle}/L \simeq 0.52$ . This and other differences between the MD results for the two MSDs are correctly reproduced by the random walk models. Similar agreement between MD and random walk results is also found for the 14Å nanotube.

Results for the survival probability  $Q(t)$  for the  $28\text{\AA}$  nanotube are compared in Figure 5. As expected, the DTRW results for the survival probability are slightly higher than the CTRW results. Both of these show exponential decay at long times. For the CTRW model, the time scale  $\tau = L^2/(\pi^2 D)$ , since the term corresponding to  $n = 1$  in Eq.(12) dominates at large  $t$ . This gives  $\tau = 308$  ps for the  $L = 28\text{\AA}$  tube. The numerical result for  $\tau$  obtained for the DTRW model is  $\tau = 328 \pm 10$  ps. These values are in fair agreement with the result ( $\tau = 371 \pm 5$  ps) of our MD simulation. The results for  $\tau$  for the  $L = 14\text{\AA}$  nanotube are: 84 ps (CTRW),  $94 \pm 5$  ps (DTRW) and  $73 \pm 0.7$  ps (MD). The random walk results for  $\tau$  show a slight departure from the expected  $L^2$ -dependence because the values of  $D$  used for the two values of  $L$  are slightly different. Given the extreme simplicity of the random walk models, the agreement between the random walk and MD results for the survival probability may be considered quite satisfactory. The agreement between the model and simulation results for the MSD is better than that for the survival probability. This is probably due to the fact that the details of the complicated process of water molecules entering and exiting the nanotube, which are completely neglected in the random walk model, affect the survival probability more than the MSD.

It is clear from the results discussed above that the simple one-dimensional random walk models provide a good description of all the dynamical features found in our MD simulations. From this observation, we conclude that the water molecules undergo normal mode (Fickian) diffusion inside the nanotubes under the conditions considered in our MD simulations.

## V. CONCLUSIONS

In summary, we have shown that the water molecules inside a narrow (6,6) nanotube of diameter  $8\text{\AA}$  are spatially ordered with a mean nearest-neighbor distance of  $2.6\text{\AA}$ . To mimic the motion of the spatially ordered chain of water molecules inside the nanotube, we propose a random walk model for the diffusion of a single particle in a finite 1D channel. The MSD calculated from this model agrees well with that obtained from the MD simulations. This establishes that the water molecules undergo normal mode diffusion inside these short, open-ended carbon nanotubes even for the longest observation times. It is argued that the reason behind the observation that the water molecules undergo normal-mode diffusion and not sub-diffusion, as the geometric constraints would have suggested, is the strong correlations due

to hydrogen bonding between neighboring water molecules. We also measure the survival probability of the water molecules inside the nanotube from MD simulations and calculate it from the random walk model. There is good agreement between the results from the model and MD simulation for the time scale (average residence time) of the exponential decay of the survival probability. This time scale is shown to depend quadratically on the length of the nanotube, which is another piece of evidence in support of the conclusion that the mode of diffusion is normal.

Our results have important implications for the possibility of observing single file diffusion in narrow channels of finite size. If the particles inside the channel interact with one another so strongly that they form a single strongly correlated cluster, then their mode of diffusion would be normal (Fickian) instead of single-file even if the particles can not cross one another. This is probably the reason for observing normal mode diffusion in a recent MD simulation [8] of water molecules in a narrow carbon nanotube with periodic boundary conditions – the simulation shows that the water molecules form a tightly bound cluster inside the nanotube. To observe single file diffusion in such a system, the parameters (interaction strength, temperature, length of the channel, etc.) must be such that the particles inside the channel form several clusters. It would be interesting to check, by simulations or experiments, whether a crossover from normal mode to single file diffusion occurs in such a system as appropriate parameters are changed to go from a situation in which the particles form a single cluster inside the channel to one with several clusters.

## VI. ACKNOWLEDGMENTS

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## VII. FIGURE CAPTIONS

Fig. 1. The pair correlation function  $g(z)$  for the water molecules inside the 14, 28 and 56Å nanotubes. The well separated peaks signifies a solid like positional ordering of the water molecules inside the nanotube even at a temperature of 300 K. The average spacing between the water molecules is about 2.6Å.

Fig. 2. In order to probe the effects of the open ends of the nanotube on the positional ordering of the water molecules we have compared the positional correlation of only the water molecules residing in the central 14Å within the 28Å nanotube, with those inside the 14Å tube. The fact that both the correlation functions are identical confirms that the degree of positional correlations is same in both the nanotubes.

Fig. 3. The quantity  $\langle \delta z_i(\delta t) \delta z_j(\delta t) \rangle$  as a function of the separation between the “i” th and the “j” th molecule, in units of  $a_0$ , the mean inter-particle spacing, whose value is 2.6Å. The correlation of displacements at two sites decays as one increases the separation between the sites.

Fig. 4. The time-origin averaged MSD (top panel) and the fixed time-origin MSD (bottom panel) for the water molecules inside the 28Å nanotube. The solid curve is data from MD, dashed curve denotes data from DTRW and the dash dotted curve is data from CTRW.

Fig. 5. The survival probability,  $Q(t)$ , for the water molecules inside the 28Å nanotube. The long time data obtained from MD is denoted by circles. This data has been fitted to the function  $\exp(-t/\tau)$ , the solid line is the fit for which  $\tau = 371 \pm 5$  ps. The dashed line indicates  $Q(t)$  obtained from DTRW, whereas the dash-dotted curve is result from CTRW.

<i>Species</i>	$\epsilon(kcal/mol)$	$\sigma(\text{\AA})$
<i>Carbon(CA) – Carbon(CA)</i>	0.086	3.4
<i>Carbon(CA) – Oxygen(OW)</i>	0.11	3.27

TABLE I: The Lennard Jones interaction parameters between various atomic species.

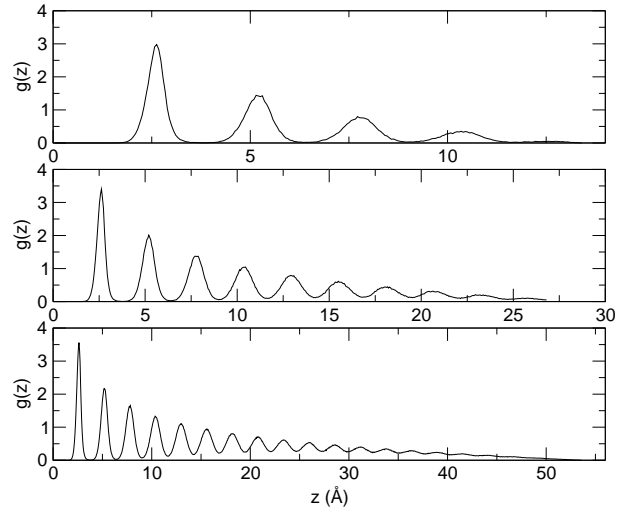


FIG. 1:

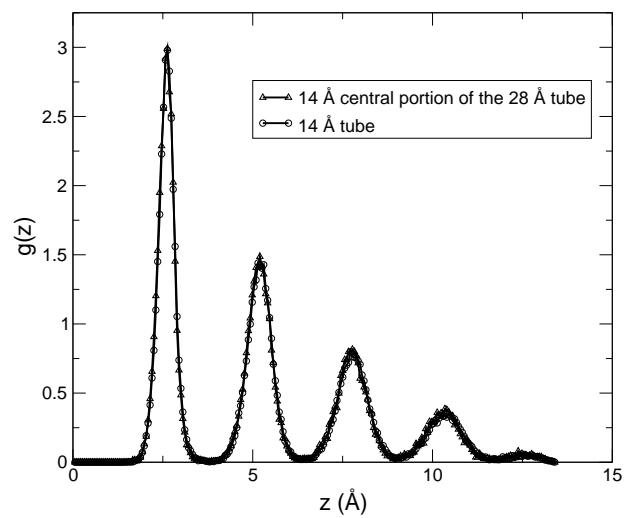


FIG. 2:

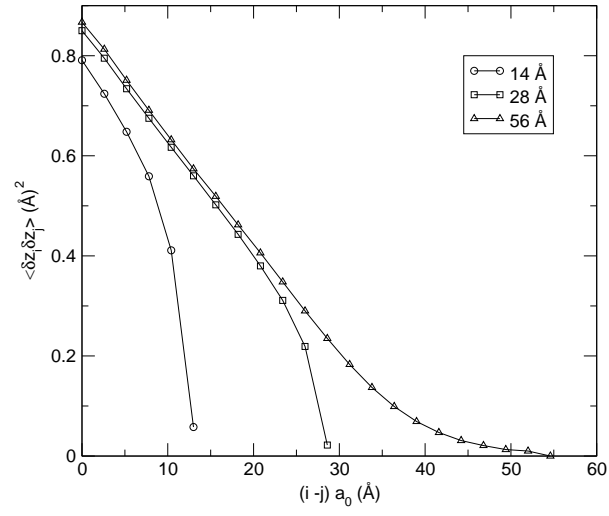


FIG. 3:

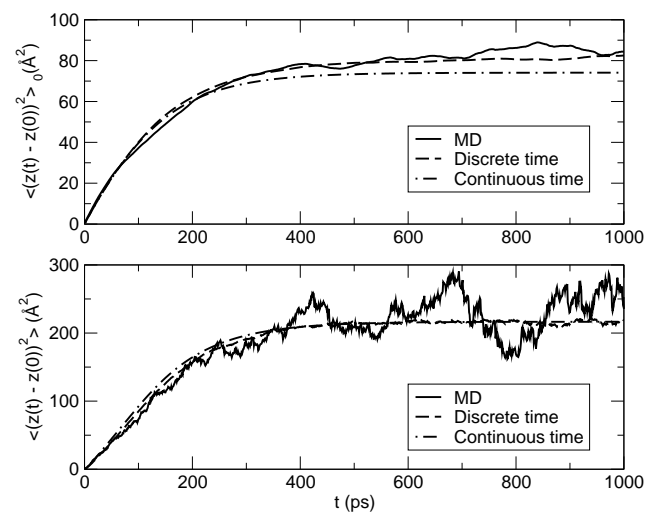


FIG. 4:

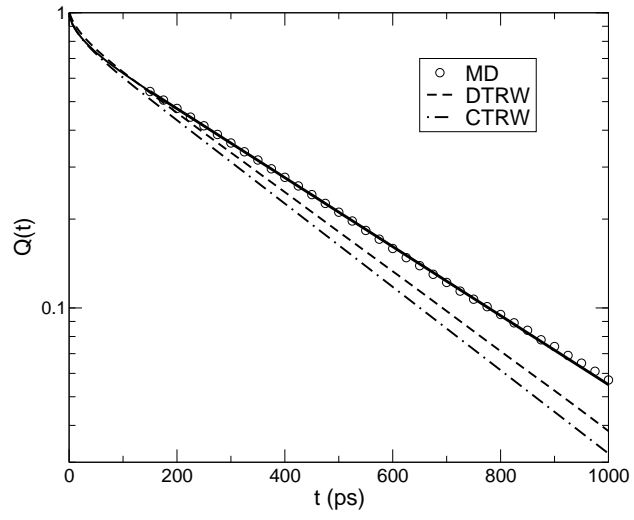


FIG. 5: