

# A Coarse-Grained Model of Water Confined in a Hydrophobic Tube

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We present a lattice model of water confined in a hydrophobic nanotube. Using analytical methods and computer simulation, we find conditions where filled and empty tubes can be degenerate in equilibrium. We further find that flow of water molecules through a filled tube with appropriate but simple stochastic rules can be interpreted as water conduction in a pulse-like fashion. These two results are consistent with an atomistic molecular dynamics study of this system [Hummer et al. *Nature* **2001**, 414, 188–190]. Finally, we analyze transitions between the filled and the empty tube, and find that density fluctuations at the entrances to the tube play the rate-determining role in this process.

## I. Introduction

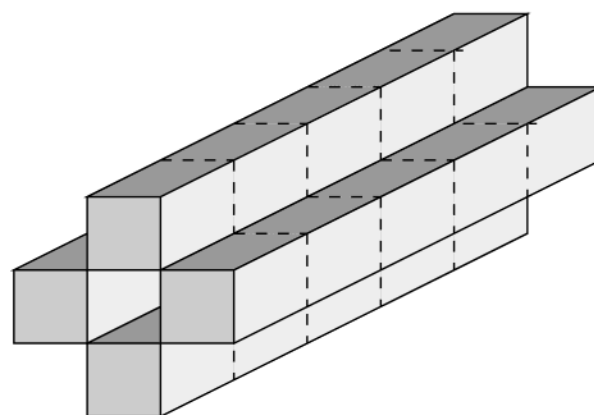
The problem of water confinement in pores on the nanometer scale is of importance to chemistry and biology<sup>1–6</sup> and has recently attracted attention in theoretical studies.<sup>7–11</sup> Of specific interest to us in this paper is the molecular dynamics study of water penetration of a nanotube immersed in water.<sup>7</sup> This work by Hummer and co-workers reported that with reasonable choices of intermolecular potential parameters, the free energy of a full hydrophobic nanotube can be very close to that of the empty tube. As such, one can view the filling and emptying as collective phenomena, perhaps akin to a phase transition. Hummer and co-workers also reported that water conduction through a filled solvated hydrophobic nanotube occurs in bursts persisting for about 1 ns each. One may wonder if these behaviors are generic liquid-state phenomena or specific to liquid water. To address this question, we have studied a lattice gas model. We demonstrate numerically and analytically that the behaviors reported in ref 7 can be understood from the properties of this simplest and most generic coarse grained model of a dense fluid near liquid–vapor phase equilibrium.

We use a coarse-grained lattice gas model on a cubic grid with Ising variables  $s_i = -1$  or  $1$  (or  $n_i = 0$  or  $1$ ), coinciding with cell  $i$  containing vapor or liquid, respectively.<sup>12</sup> The energy of the pure liquid in this model is

$$E(\{s_i\}) = -h \sum_i s_i - J \sum_{i,j(\text{nn})} s_i s_j \quad (1)$$

where the second summation is over nearest neighbor cells  $i$  and  $j$ , and the field  $h$  is, in effect, the chemical potential. We are interested in a liquid that is cold (i.e., well below its critical temperature), and at a low pressure (i.e., close to liquid–vapor phase equilibrium). Water at standard conditions is such a liquid. More details about water—conditions in addition to being cold and at low pressure—are ignored by this description. Being a cold liquid, the interaction parameter  $J$  can be associated with the surface tension  $\gamma$  of the liquid via  $\gamma = 2J/l^2$ , where  $l$  is the lattice spacing. Being close to phase equilibrium means that  $h$  is very small compared to the thermal energy,  $k_B T$ .

Since our goal is to study the behavior of the confined liquid, we choose a set of lattice cells that are not accessible to the



**Figure 1.** This arrangement of  $4 \times 5$  cells models the walls of a tube of length  $L = 5$ . The inside of the tube is accessible to the fluid, and the number  $N$  of liquid cells inside the tube can vary between 0 and  $L$ .

liquid, corresponding to the wall of the nanotube. The chosen confinement geometry is illustrated in Figure 1. As a result of this choice, the liquid inside the tube is a one-dimensional system. This is consistent with the atomistic simulation reported in ref 7, where the translational motion within a hydrophobic tube was also essentially one-dimensional.

The interaction energy between the tube and the liquid is

$$E_l(\{s_i\}) = \epsilon \sum_{i(\text{nn tube})} s_i \quad (2)$$

where the summation includes only lattice cells next to the tube wall, and  $\epsilon$  characterizes the strength of the interaction. The sign convention is such that the tube repels the liquid if  $\epsilon > 0$ . We are interested in the number of filled cells inside the tube, which is given by

$$N = \sum_{i(\text{inside tube})} (s_i + 1)/2 \quad (3)$$

To identify a reasonable strength of the tube–liquid interaction parameter  $\epsilon$ , we contrast the energies of two specific configurations. In the first, the tube is completely empty, but all the sites surrounding the tube are filled (i.e.,  $s_i = 1$  for all  $i$  outside the tube and  $s_i = -1$  for cells inside the tube). In the

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second, both the tube and its surroundings remain completely filled (i.e.,  $s_i = 1$  for all  $i$ ). The difference in energy between these states is

$$E^{(\text{filled})} - E^{(\text{empty})} = -4J + 8L\epsilon \quad (4)$$

where  $L$  is the number of cells (and therefore the reduced length) of the tube. The two states are degenerate when  $\epsilon = J/(2L)$ . This degeneracy, we shall see, is important to understanding the behavior of the atomistic simulation described in ref 7. Notice that the value of  $\epsilon$  needed to ensure degeneracy decreases with increasing  $L$ .

In the next section, we present results for the equilibrium statistics of the lattice model. With simulation, we find a free energy as a function of the tube occupation number like that found in the atomistic simulation. We analyze the effects of fluctuations on this free energy function, and we show that these effects are easily treated analytically. Then we turn to the dynamics in Section 3. Here we consider two phenomena separately: (1) the filling and emptying of the tube, and (2) water conduction through the filled tube. These two phenomena are characterized by fluctuations on different length scales. The first is a large length scale dynamics not yet studied by atomistic simulation. The second is a small length scale dynamics that has been studied in ref 7. To study the first, we employ a combination of single spin flip and nearest neighbor spin exchange (Kawasaki) stochastic dynamics models,<sup>13</sup> allowing for fluctuations on the length scale of the lattice spacing. To study the second case, water motion through a filled tube, we consider a random walk model based on the diffusive motion of water molecules inside the tube that maintain hydrogen bonding with their adjacent neighbors.

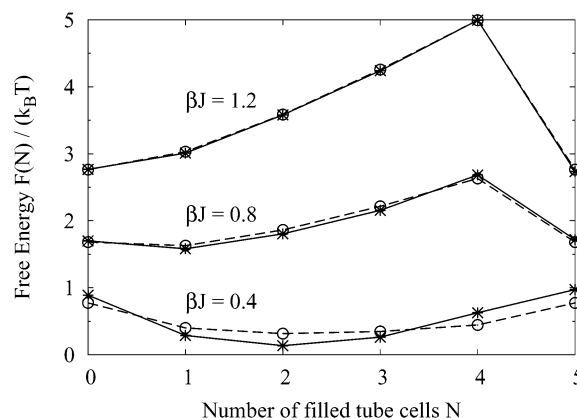
## II. Equilibrium Statistics

In their molecular dynamics simulation, Hummer and co-workers found that a nanotube immersed in a bath of water can have two stable states, corresponding to a filled and an empty tube. In this section, we study whether our coarse-grained model is able to capture this effect. We use a Monte Carlo computer simulation algorithm, where a change of a single cell's occupation number is accepted according to the Metropolis acceptance criterion.<sup>14</sup>

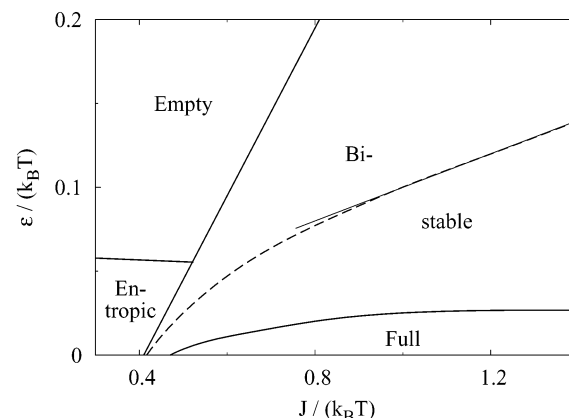
Results for a system consisting of  $10^3$  cells that contains a tube of length  $L = 5$  are given in Figure 2. Shown are the free energy curves for the water occupancy number  $N$  at different temperatures. The tube–water interaction was chosen to be  $\epsilon = J/(2L)$ , and the external field  $h$  was set to zero. As anticipated in the Introduction, this choice of  $\epsilon$  causes the filled ( $N = L$ ) and the empty ( $N = 0$ ) state to be degenerate.

When the system is cold, the free energy exhibits a maximum at  $N = 4$  of height approximately  $2.2 k_B T$ . This behavior coincides qualitatively with the bimodal water occupancy found by Hummer et al.<sup>7</sup> for an atomistic simulation. Quantitative differences could well be due to statistical uncertainties in the results of ref 7. Further, the empty and full states of the bistable atomistic model studied in ref 7 are not exactly degenerate.<sup>15</sup>

From our calculations we see that the height of this free energy extremum decreases with increasing temperature, until eventually the free energy curve assumes a convex shape with a broad minimum at an intermediate value of the occupation number  $N$ . The shape of the free energy curves (or the probability distribution functions  $P(N)$ ) can be used to classify



**Figure 2.** Free energy functions in units of  $k_B T$  (i.e.,  $-\log Z$ ) for the water occupancy inside a tube of length  $L = 5$  at different temperatures. The solid lines connect the simulation results; the dashed lines connect the results calculated using the single pair of interfaces approximation. The tube–water interaction is given by  $\epsilon = J/(2L)$  in all cases. With lattice spacing  $l = 3.7 \text{ \AA}$ ,  $\beta J = 1.2$  coincides with water at room temperature, since the liquid–vapor surface tension is  $\gamma = 72 \text{ mN/m}$ .



**Figure 3.** Behavior of the occupation number distribution function for a tube of length  $L = 5$  at coexistence ( $h = 0$ ): If the probability distribution  $P(N)$  has only one maximum at  $N_0$ , the system is called “empty” if  $N_0 \leq 1$ , “full” if  $N_0 \geq 4$ , and “entropic” otherwise. The latter corresponds to a state where entropic effects, which favor the half-filled tube, dominate the equilibrium behavior. If the distribution function has two distinct maxima, the system is classified as bistable. The dashed line shows where the two peaks in this case have equal heights. For low temperatures, this line approaches the limit  $\epsilon = J/(2L)$  (thin solid line).

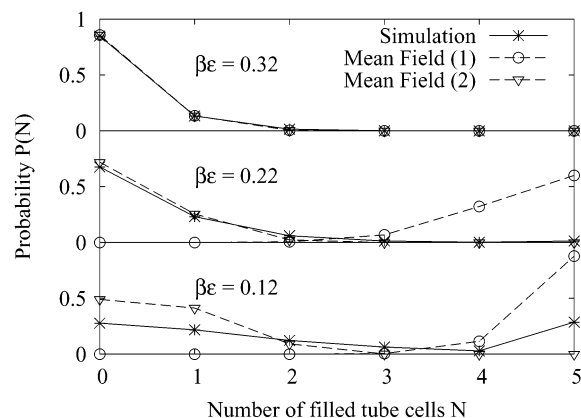
the equilibrium behavior of the system as a function of the governing parameters, as shown in Figure 3.

The maximum at intermediate  $N$  in the low-temperature free energy is indicative of two stable states—empty and full. One should not, however, confuse this maximum with the dynamical bottleneck that separates these two states. That bottleneck involves a different variable than  $N$ , as we shall show in Section III.

The low-temperature bimodal behavior is not correctly captured by the simplest of mean field treatments. Such a treatment corresponds to solving the coupled equations

$$m_i = \tanh[\beta(h - 4\epsilon + Jm_{i-1} + Jm_{i+1})] \quad (5)$$

where  $m_i = \langle s_i \rangle$  is the equilibrium average of the  $i$ th spin, under the boundary condition  $m_0 = m_{L+1} = 1$ . This equation can be solved by iteration, starting with an initial estimate for the  $m_i$ . The corresponding probability for  $N$ ,  $P(N)$ , can then be constructed from  $p_i(\pm 1) = (1 \pm m_i)/2$ , the probability that the



**Figure 4.** Probability distributions for the number of liquid cells inside the tube for three different values of the interaction parameter  $\epsilon$  as obtained from simulation and mean field treatment. The latter depends on the initial conditions under which the mean field equations (5) are solved. In case 1, the initial conditions were  $m_i = 1$ , and  $m_i = -1$  in case 2. The remaining parameters were  $h = 0$  and  $\beta J = 1.2$ .

$i$ th cell is liquid or vapor, respectively. In particular,

$$P(n) = \sum_{s_1=\pm 1} \cdots \sum_{s_L=\pm 1} \delta_{N(\{s_i\}),n} \prod_{i=1}^L p_i(s_i) \quad (6)$$

Here,  $\delta$  is the Kronecker symbol. The resulting probability distributions together with simulation results are shown in Figure 4 for three different values of the interaction parameter  $\epsilon$ . The mean field prediction coincides closely with the simulation result far away from the bimodal behavior (top panel). Approaching the bimodal behavior with  $\epsilon = J/(2L)$ , however, we see that the mean field treatment fails to properly predict the existence of two free energy minima. Rather, it predicts one of two solutions to the mean field equations, depending upon the initial value of the  $m_i$  used to solve eq 5 by iteration. In other words, mean field theory predicts coexistence of two different phases. For the one-dimensional finite system, therefore, accounting for fluctuations is important.

We can compute the effects of fluctuations in an approximate but accurate way by assuming the density field outside to be constant, i.e.,  $s_i = 1$  for all  $i$  outside the tube. The only remaining degrees of freedom are then the states of the cells inside the tube, which can assume  $2^L$  different configurations. The partition function for those degrees of freedom is

$$Z = \sum_{s_1=\pm 1} \cdots \sum_{s_L=\pm 1} \exp \left[ -\beta \left( (4\epsilon - h) \sum_{i=1}^L s_i - J \sum_{i=1}^{L-1} s_i s_{i+1} - J s_1 - J s_L \right) \right] \quad (7)$$

For any modest size  $L$ , all equilibrium quantities can therefore be calculated by simple enumeration.

More physical insight can be obtained by noting that the tube–water interaction (together with a possibly nonzero external field  $h$ ) acts like a chemical potential of magnitude  $\mu = 8\epsilon - 2h$ , which is the energetic cost for changing an empty cell inside the tube into a filled one. The second contribution to the energy comes from the formation of interfaces. The completely filled tube does not have any liquid–vapor interfaces. If an inner cell  $i$  changes its state, there will be a pair of interfaces along the tube axis, the energetic cost of which is  $4J$ . If another cell  $j$  empties out, there will be either no change in the interfacial energy if  $j$  is next to  $i$ , or an additional energy cost of  $4J$  otherwise. We can estimate the free energy by

assuming that configurations with more than one pair of interfaces do not contribute significantly to the partition function. In this approximation, only those configurations are considered where all empty cells (if any) are next to each other. This procedure leads to the expression

$$F(N) \approx \mu N + 4J(1 - \delta_{L,N}) - k_B T \ln \Omega(L, N) \quad (8)$$

where  $\delta_{L,N}$  is the Kronecker symbol, and  $\Omega(L, N)$  is the number of configurations with  $N$  filled cells in a tube of length  $L$  and no more than one interface pair:

$$\Omega(L, N) = \begin{cases} N + 1 & \text{if } N < L \\ 1 & \text{if } N = L \end{cases} \quad (9)$$

Results obtained in this approximation are compared to simulation data in Figure 2. It shows very good agreement for low and intermediate temperatures, while for high temperatures the assumptions of vanishing fluctuations outside the tube and contributions from single interface configurations only lose their validity. This interpretation explains both the location of the free energy barrier at  $N = L - 1$  and the almost linear shape for  $N < L$  at cold temperatures.<sup>16</sup> In view of this analysis, the finding in ref 7 that water can and does fill a hydrophobic tube is not surprising.

### III. Dynamics

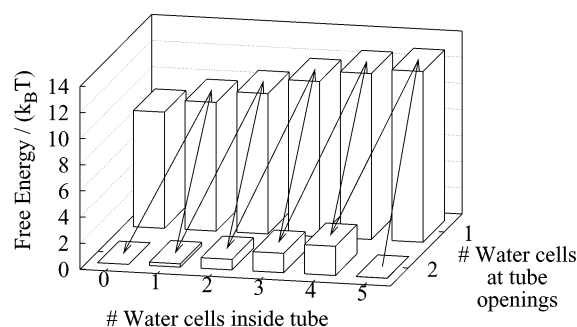
Since this simple lattice model can reproduce the bimodal behavior of the more detailed atomistic simulation, one might hope to go one step further and investigate the dynamics of this system.

**A. Filling and Emptying of the Tube.** When a completely filled tube empties (or vice versa), the density field changes over a length scale given by the tube volume. It should be therefore possible to study this process with our model, where the minimum length scale for density fluctuations is given by the lattice spacing.

We begin with the definition of appropriate dynamical rules for these fluctuations. A familiar choice for the time evolution of an Ising system is the nearest-neighbor spin exchange (Kawasaki) dynamics:<sup>13</sup> in every Monte Carlo step, a pair of neighboring cells is chosen at random. The energy change that would occur if the two spins were switched is calculated. This trial move is accepted according to the Metropolis acceptance criterion.

This kind of dynamics conserves the number of filled and empty cells in the system, and hence samples a different ensemble than considered in Section 2. We therefore partition the system into two parts: an inner part of cubic shape that contains the tube and its surroundings, and an outer shell. We are interested in the dynamics only in the former, hence we employ the conservative Kawasaki dynamics there. In the surrounding shell we use the single spin flip dynamics that was used in the previous section. This part of the system acts as a bath for liquid and vapor cells, which can diffuse across the boundary into the core region. This partition of the system allows us to investigate the movements of individual cells, while still sampling the grand canonical ensemble. During the simulation, one of the two possible trial moves is chosen with equal probability at every time step.

With these dynamical rules, the emptying of the tube is naturally related to rare density fluctuations outside the tube. Consider a completely filled tube, i.e., a configuration where  $N = L$ . Since the tube lies completely within the core region of the system where spin exchange dynamics is used, the occupa-



**Figure 5.** The free energy as a function of the number of water cells inside the tube and at the tube openings, obtained for a tube of length  $L = 5$  and  $h = 0$ ,  $\beta J = 1.2$ ,  $\beta \epsilon = 0.12$ . The arrows show the typical pathway leading from a filled to an empty tube. Before a water cell can leave the tube, a vapor cell has to appear at the tube mouth. This is a dynamically rare event, and corresponds to a high free energy barrier in the emptying process.

tion number  $N$  can change only by an exchange of a water cell at one end of the tube with a vapor cell right in front of it. Thus, a low-density fluctuation at the mouth of the tube is required for a filled cell to leave the tube. Due to the low concentration of vapor cells in the bulk liquid, this constitutes a rare event in the time evolution of the system.

The analysis is different for the reverse process, the filling of an empty tube. This asymmetry in the analysis originates from the fact that the spin field outside the tube is strongly biased toward the liquid phase. Consider an empty tube ( $N = 0$ ) immersed in a constant field of water cells. In this case, the filling of the tube, i.e., the exchange of an empty cell at one tube end with the water cell outside, could occur at any time. However, this process is energetically costly; the energy increase is  $\Delta E = 8\epsilon + 12J$ . A rare energy fluctuation is therefore required for this event.

The importance of the density field at the tube openings can be illustrated by examining the free energy as a function of two coordinates: the number of water cells inside the tube, and the number of water cells at the tube mouths. The latter can take values between 0 and 2. Such a free energy surface is shown in Figure 5. Configurations that have one vapor cell at the tube mouth have a free energy on the order of  $10k_B T$  higher than those where the immediate environment of the tube is simply the bulk liquid. Due to the nature of the dynamics of the system, these configuration form a bottleneck in the emptying and filling of the tube. The pathway that leads from a filled to an empty tube is shown in Figure 5: one of the cells in front of the tube has to become vapor before a water cell can leave the tube. This corresponds to a large increase in the free energy, and is therefore a rare event.

Our lattice model demonstrates that a low-density fluctuation in front of the tube is necessary for the tube to empty. But by limiting these fluctuations to length scales  $l$  or larger, the model will likely overestimate the free energetic cost for attaining this fluctuation. The kinetics for the atomistic model<sup>10</sup> is in qualitative accord with our demonstration. Namely, ref 10 reports that the number of molecules inside the tube,  $N$ , is by itself not sufficient to characterize the transition state between empty and full states. The additional variable employed in ref 10 to characterize the transition state ensemble in effect controls density fluctuations directly in front of the tube.

**B. Conduction of Water Molecules.** Hummer and co-workers<sup>7</sup> investigated the flow of water molecules through a nanotube, with conditions chosen such that the tube is always completely filled. A water molecule is said to have crossed the tube at time  $t_i$  if it leaves the tube at that time, provided that it

had entered the tube on the opposite end at an earlier time. As we shall see below, many of the seemingly interesting phenomena arise simply from this definition. Processing their data with a triangular filter, they find that the water flow shows sharp peaks as a function of time. These maxima are interpreted as “bursts” of water conduction, perhaps caused by collective fluctuations outside the tube. In this section, we show that a similar flow pattern can be obtained by a simple random walk model of water molecules inside the tube.

As before, we consider a tube on a discrete lattice that is  $L$  cells long. However, since the tube is always completely filled, we cannot use dynamical rules that are based on density fluctuations on the order of the lattice spacing  $l$ . Instead, we specify a configuration by the side on which each of the  $L$  water molecules had entered the tube. Since water molecules cannot pass each other inside the tube, there are only  $L + 1$  possible configurations:

0. All  $L$  water molecules entered the tube from the left side.
1. The left  $L - 1$  water molecules entered from the left side, and the rightmost water molecule entered from the right side.
2. The left  $L - 2$  water molecules entered from the left side, and the rightmost two water molecules entered from the right side.
- $\vdots$
- $L - 1$ . The leftmost water molecule entered from the left side, and the right  $L - 1$  water molecules entered from the right side.
- $L$ . All  $L$  water molecules entered the tube from the right side.

Moving from configuration  $i$  to  $i + 1$  corresponds to a shift of all water molecules inside the tube by one lattice spacing to the left, with a new water molecule entering on the right-hand side. Similarly, a move  $i \rightarrow i - 1$  is a collective translation to the right. These moves are consistent with motion of hydrogen-bonded water chains.

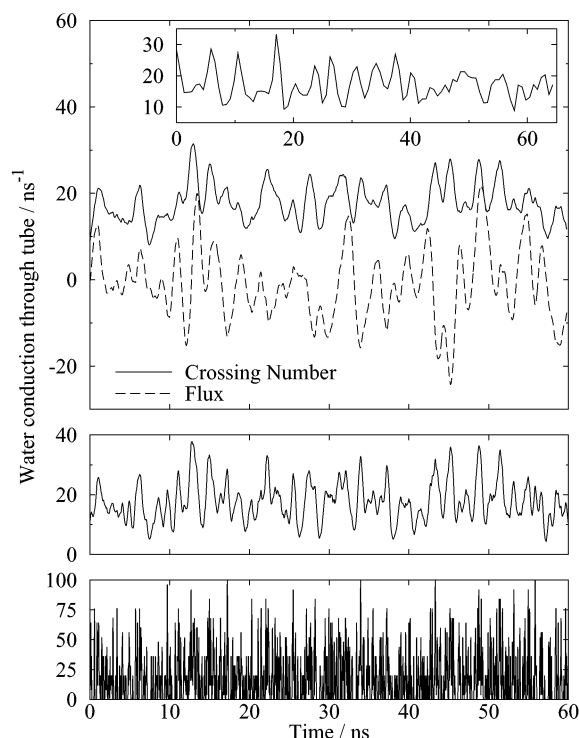
Our model of water conduction through the tube is random walk between these  $L + 1$  configurations. Starting from a configuration  $i$ , a new configuration  $i \pm 1$  is assigned with equal probability. Such a move corresponds to the one-dimensional diffusive motion of the water molecules inside the tube, and occurs on a time scale  $\tau$  which remains to be established.

The set of possible moves is different for the first and the last of the listed configurations. Possible moves from configuration 0 are  $0 \rightarrow 0$  or  $0 \rightarrow 1$ . The former corresponds to the leaving of the rightmost water molecule, which had entered from the left side, on the right-hand side of the tube, thus contributing to the water conduction through the tube. Similarly, if the system is in configuration  $L$ , the two possible moves are  $L \rightarrow L - 1$  and  $L \rightarrow L$ , and the latter corresponds to the conduction of a water molecule from the right to the left side of the tube.

We simulated the random walk model for a tube of length  $L = 5$ . The time scale  $\tau$  can be estimated by comparing the total number of conducted water molecules as observed by Hummer and co-workers<sup>7</sup> with the number of crossing events in our model. An average of 17 water molecules per nanosecond is obtained by letting  $\tau \approx 10$  ps.

Following the same procedure as in ref 7, we process the time series of crossing events by a triangular filter of width  $w$  at half-maximum. Figure 6 shows the simulation result of a 60 ns long trajectory, to which filters of various widths  $w$  were applied. The top panel corresponds to the filter used by Hummer and co-workers, and the water flow as obtained from our model indeed shows peaks of comparable width and magnitude as found in the atomistic simulation. Here, these “bursts” follow





**Figure 6.** Simulation result for water conduction through the tube. The solid lines show the number of water molecules that have crossed the tube. The data were processed by a triangular filter with a half-maximum width  $w$ : if water molecules crossed the tube at times  $t_1, t_2, \dots, t_n$ , the flow  $f$  is given by  $f(t) = \sum_{i=1}^n w^{-1}(1 - |t - t_i|/w) \Theta(w - |t - t_i|)$ , where  $\Theta$  is the Heaviside step function. In the top panel, a filter of width  $w = 1$  ns was used, as in the work by Hummer and co-workers.<sup>7</sup> Their result is shown in the inset for comparison. The dashed line shows the net flux, with different signs corresponding to the two flow directions. The middle and bottom panels show the result of processing the data with filters of width  $w = 500$  ps and  $w = 50$  ps, respectively. Note the differences in vertical scales for the different panels.

only from the diffusive random movement of the chain of water molecules inside the tube.

The middle and bottom panel of Figure 6 illustrate that the appearance of “bursts” depends strongly on the data processing. With decreasing filter width  $w$ , the curves become steeper and more rugged. Width, magnitude, and location of the peaks change as  $w$  is varied. In particular, the  $w = 1$  ns filter used in ref 7 is very wide compared to the time scale of conduction events, so that flows in opposite directions can contribute to the same peak in the crossing number. This fact is illustrated by the dashed line in the top panel of Figure 6, which shows the net flux through the tube. It vanishes whenever the flow changes its direction.

As this work was being submitted, a paper appeared<sup>11</sup> with an analysis of the apparent bursts through a nanotube that is equivalent to our analysis. Curiously, this recent publication<sup>11</sup> focuses upon the success of the interpretation rather than its implications. As the “bursts” arise from a simple random walk, we see that they are a mere consequence of the definition of a conduction event: if a water molecule was conducted from the left to the right end of the tube, the probability of another molecule being conducted in the same direction in the next time step is one-half. But a conduction event in the opposite direction cannot occur for another  $L + 1$  time steps. This accumulation of conduction events of the same directionality lead to the seemingly burst-like flow of water molecules through the tube.

## IV. Conclusion

A simple coarse-grained model of a nanotube immersed in water exhibits two principal phenomena observed in the atomistic molecular dynamics study by Hummer and co-workers.<sup>7</sup> With a properly chosen strength of the tube–water interaction, the filled and the empty tube can be energetically degenerate or nearly so, corresponding to two separate minima in the free energy distribution function. This effect is understood in terms of the energetic cost of creating a liquid–vapor interface along the tube axis, and the corresponding increase in entropy.

The appearance of a density fluctuation at the tube mouth is necessary to facilitate the emptying of a filled tube, and this facilitation is associated with a large entropic barrier. The filling of an empty tube, however, is associated with a large energetic barrier. Unlike the large length scale emptying and filling, the transport of water through a full tube does not involve largely activated events. Rather, its behavior can be understood in terms of a simple diffusive motion of the whole water column inside the tube.

These results were obtained with the simplest possible description of a cold liquid. Other than our choice of random walk steps that maintain a hydrogen-bonded chain inside a filled tube, none of our results depend on specific small length scale details of liquid water.

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- (14) Metropolis, N.; Rosenbluth, A.; Rosenbluth, N.; Teller, A.; Teller, E. *J. Chem. Phys.* **1953**, 21, 1087.
- (15) In the atomistic simulation of ref 7, the filled and the empty states seem to differ in their free energies by about  $2 k_B T$ . From eq 4 we can anticipate that  $\beta\epsilon = 0.17$  and  $\beta J = 1.2$  will yield the same result in our lattice model. Our Monte Carlo calculations on this model show that this is indeed the case. The resulting free energy curve  $F(N) - F(0)$  increases with  $N$  almost linearly to about  $3.8 k_B T$  at  $N = 4$ , and then decreases to  $2 k_B T$  for the filled state.
- (16) The bistable behavior is governed by the energetics of interface formation, and is destabilized by entropic effects. This can be seen by choosing the coarse-graining length scale  $l$  to be only one-half of its original value. The interior of the tube is then a block of  $2L \times 2 \times 2$  cells, which favors states where the tube is half-filled due to their high entropy. The coupling parameters change as  $J \rightarrow J/4$  and  $\epsilon \rightarrow \epsilon/4$ . Computer simulations show that this transformation can change an originally bistable system into one that has a single free energy minimum at intermediate occupation numbers. The bistable behavior can be recovered if the influence of entropic effects is weakened by lowering the temperature.