Equilibrium and Kinetics: Water Confined in Carbon Nanotube as 1D Lattice Gas

Xin Zhou, Cheng-Quan Li and Mitsumasa Iwamoto

Department of Physical Electronics, Tokyo Institute of Technology, O-okayama 2-12-1, Meguro-ku, Tokyo 152-8552, Japan

(March 22, 2022)

A simple 1D lattice gas model is presented, which very well describes the equilibrium and kinetic behaviors of water confined in a thin carbon nanotube found in an atomistic molecular dynamics (MD) simulation [ Nature 414, 188 (2001) ]. The model parameters are corresponding to various physical interactions and can be calculated or estimated in statistic mechanics. The roles of every interaction in the water filling, emptying and transporting processes are clearly understood. Our results indicate that the physical picture of the single-file kinetics is very simple.

PACS numbers: 47.60.+i, 85.35.Kt, 87.16.Uv

Transport of molecules through pores on nanometer scale is important for biology. Carbon nanotubes have been widely studied as pores filled with gases [1,2] and liquids [3,4]. Recently, using molecular dynamics (MD) simulation, Hummer and coworkers [5] studied the filling and transporting of water molecules in a very thin carbon nanotube which is a (6,6) tube with two open ends, 4 Å radius and 5.5 unit cells (about 13.5 Å in length). The interaction between carbon atoms and water molecules was expressed by Lennard-Jones (LJ) potential. They found that the LJ parameters (ε and σ) can sensitively affect the filling of water molecules. In their work, two group LJ parameters were used: (1) unmodified parameters: ε = 0.114 kcal/mol, σ = 3.2752 Å; (2) modified parameters: ε = 0.065 kcal/mol, σ = 3.4138 Å. For the former, it was found that the water molecules completely filled the nanotube (the average occupancy number n = 5, the corresponding density is about 5 times of that of bulk water, where the radius of the nanotube pore is about 0.8 Å). For the latter, water molecules fluctuated between the empty (n = 0) and filled (n = 5) states, and it was a two-state like behavior, the lifetimes of the two states follow exponential distributions. The high density filling seems be surprising in the unmodified system due to the hydrophobic property of carbon nanotube, though the sharper distribution of the water molecule binding energy inside the nanotube was found in the MD simulation [5]. The sensitive effect of LJ potential in the filling of water, the two-state like kinetics, and other remarkable MD results need to more clearly be understood in physics.

Here, based on a strict statistic mechanics treatment, we present a one-dimensional (1D) lattice gas (LG) model of water molecules confined in a thin tube with a finite length and two open ends. All parameters of this model have explicit physical sources, can be calculated from interactions. They are: (1) the local excess chemical potential Δμ of water in the tube; (2) the free energy contribution Ec from LJ potential of carbon atoms; (3) the free energy E_H from hydrogen bonds between water molecules inside the tube (the rotational free degree of the molecules can be included); and (4) the additive free energy Ec of the water molecules located at ends of the tube, which come from the interaction with the outside water molecules. In this model, LJ potential from the nanotube wall only affect the parameter Ec. The fitted parameters obtained from MD results [5] are in agreement with the directly calculated or estimated values from the corresponding interactions, that is, the obtained equilibrium properties are well consistent with the results of MD simulation for both the unmodified and modified systems. In the LG model, by analyzing transition states in which one or two water molecules partially occupied the end(s) of the tube, the whole free energy landscape, and the main reaction paths can be obtained, therefore, the two-state like kinetics of filling and emptying of water can be clearly explained.

Considering a nanotube filled with water molecules, we first partition the tube into N cells along its long axis, the length of every cell is corresponding to the length of hydrogen bond between water molecules. We form our model step by step: (1) we consider one water molecule moves into a cell from the bulk water, where the cell is only a box without any interaction except limiting the water molecule in volume V_0. In this process, the changed free energy is Δμ = −μ_w + μ_g, where μ_w is the chemical potential of bulk water, μ_g = ln(λ^3/V_0), is the chemical potential of ideal gas with density 1/V_0, t is a normalized temperature. In this paper, the energy unit is set as the room temperature 300 K, if no explicit unit is written, λ = (2πℏ^2/mk_B T)^1/2 ≈ 0.23 Å is the de Broglie thermal wavelength of water. Actually, Δμ is nothing but −μ^ex_n/l, where μ^ex_n/l is the local excess chemical potential of water inside the nanotube, about −6.87 kcal/mol ≈ −11.6 from MD simulation [5]. (2) if there is interaction V(c)(r) between the wall of the cell and water molecule, except Δμ, an additive free energy is

$$E_c = -t ln \left( \frac{1}{V_0} \int_{V_0} dr \exp [-V(c)(r)/t] \right). \quad (1)$$

For nanotubes, V(c)(r) is the Lennard-Jones (LJ) potential between the water molecule and all carbon atom of
the nanotube. Calculation shows that $V_c(r)$ is almost independent on the azimuth $\phi$ and axis position $z$ in infinite nanotubes [6]. For finite nanotubes, the result is also right, except a $z$ dependence near the ends of the nanotubes. In (6, 6) nanotube, due to its very small radius, for both the unmodified and modified LJ parameters, $V_c(r)$ can be well approximated as a box potential well, whose widths (about 0.8 Å) are in agreement with the interior radius of the tube found in MD [5], and the depths of well are about $-8 \sim -9$ and $-5 \sim -6$, respectively. It is not very difficult to numerically calculate the finite nanotubes [6], For finite nanotubes, the result is the nanotube. Calculation shows that $V \phi$ and axis position $z$.

\[ \mathcal{E}_H = -t \ln \frac{1}{V_0} \int_{V_1} dr_1 \int_{V_2} dr_2 \exp[-V_H(r_1 - r_2)/t], \quad (2) \]

due to the limit of the length of hydrogen bond and the nanotube wall, the two water molecules will occupy two cells $V_1$ and $V_2$ (both volumes are $V_0$), respectively. The freedom degree $r_2$ is limited, only some rotation can be allowed, we have,

\[ \mathcal{E}_H = E_H - t \ln \left( \frac{a \lambda^3}{V_0} \right) = E_H - \mu_g - \mu_i, \quad (3) \]

where $E_H$ is the energy of the hydrogen bond. All other contributions, including the rotation of the non-spherical water molecules, the rotation of water molecules around their hydrogen bond, and the possible angle changes of the hydrogen bonds, etc., are written as the factor $a$ ($a > 1$ indicates the existence of these freedom degrees), the corresponding free energy is noted as $\mu$. While the number ($n$) of water molecules formed a continuous hydrogen-bond chain inside the tube is not very large, we suppose that $\mu$ is independent on $n$; (4) if a water molecule locate at ends of the nanotube, besides $\mathcal{E}_c$ (while water is partially out of the nanotube, even $\mathcal{E}_c$ also increase), there is an additive free energy $\mathcal{E}_a$ from the interaction between the water molecule and the outside water. In fact, $\mathcal{E}_a$ is also from hydrogen-bonds of water molecules, but due to the lower density of bulk water, it is higher than $\mathcal{E}_H$.

Based on these considerations, the water molecules inside the nanotube can be treated as a simply 1D LG model with $N$ sites, including three parameters. Only $\mathcal{E}_c$ is dependent on LJ parameters, and the dependence can be approximately calculated. Hamiltonian of the model is,

\[ \mathcal{H} = \sum_{i=1}^N \mathcal{E}_i c_i + \mathcal{E}_H \sum_{i=1}^{N-1} c_i c_{i+1}, \quad (4) \]

where $\mathcal{E}_i = \Delta \mu + \mathcal{E}_c + \left( \delta_{i,1} + \delta_{i,N} \right) \mathcal{E}_a$, $\delta_{i,j}$ is Kronecker delta, $c_i = 1$ (occupied), or 0 (unoccupied). The model is equivalent to an Ising model, if we transform $s_i = 2c_i - 1$. For a 1D Ising model, if the external field $H = 0$, the states with $M$ and $-M$ are symmetry, and the energy barrier is very low, where $M = \sum_{i=1}^N s_i$. In the LG model, the corresponding external field $\tilde{H} = -(\mathcal{E}_c + \mathcal{E}_H)/2$. If $\mathcal{E}_c$ is very low, $\tilde{H} > 0$, water molecules can fill the nanotube, while $\mathcal{E}_c$ increases (the well depth decreases), $H$ decreases. If $H \sim 0$, there is an equilibrium between the filling and emptying states. However, some details must be considered as we try to explain the MD results of Ref. [5] by using the LG model: (1) the finite sites $N$; (2) the additive energy $\mathcal{E}_a$ at ends. Since $N$ is not very large, we can directly enumerate all $2^N$ states. For general case, Hodak and Girifalco [7] have written the partition function for the LG model with any finite sites and the additive energy.

For unmodified and modified LJ parameters, Hummer et al. have given the probability of finding exactly $N$ water molecules inside the nanotube (Figure 2 of Ref. [5]). In their MD simulation, $N = 5$. We can obtain the model parameters ($\mathcal{E}_H \approx -6.27, \mathcal{E}_a \approx -2.93$, and $\mathcal{E}_c \approx -4.96$) by fitting the MD probability data of the modified system. The regenerated free energy profile is very well in agreement with the MD probability distribution in the modified system as shown in Fig.1. Here, the fitting $\mathcal{E}_c$ is well consistent with the estimated value from LJ potential by Eq.(1). The hydrogen bond of water inside the nanotube is about 7 kcal/mol $\approx 11.8$ (Figure 3(a) of Ref. [5]), is stronger than their average value in bulk water (5 kcal/mol $\approx 8.4$). From Eq.(3), we know that the free energy contribution $\mu_i$ of all rotational freedom degrees is about 0.7. The $\mathcal{E}_a$ is only half of $\mathcal{E}_H$, the physical reason is the lower density of bulk water. Since both $\mathcal{E}_a$ and $\mathcal{E}_H$ are independent of LJ potential, their values can be used in the unmodified system. For the large statistic errors of MD data in the unmodified system, replacing to fit MD results, we directly use that estimated $\mathcal{E}_c \approx -8$. The obtained free energy profile is shown in inset of Fig.1, it is approximately in agreement with the MD probability distribution. For equilibrium states, due to the large $\mathcal{E}_H$, water is favor to the states with a single sequentially occupied sites, for example, $P(10100)$ is only about 1/500 of $P(11000)$, where $P$ is the probability of states. Similarly, water is favor to the states whose end sites are occupied. For example, $P(01100)$ is only about 1/20 of $P(11000)$ due to $\mathcal{E}_a$. For a good approximation, we can calculate the partition function only considering the states with a single sequence of hydrogen-bond chain and at least occupied an end of the tube. We call it as single-sequence end occupied approximation (SSEA). In a very current MD simulation [8], for short nanotube(13.5 Å) and long nanotube(27 Å), Hummer and coworkers carried to a longer time MD simulation, by changing LJ parameters by varying a control variable $\eta$, $\epsilon = \epsilon_1 \eta^2$, and $\sigma = \sigma_1 / \eta^{1/6}$, where $\eta = 1.0$ is corresponding to the
unmodified LJ parameters. The model can very well explain these results. For example, (1) very rare non-SSEA events are found; (2) the approximated linear free energy profile \( G(n) \) for \( 1 \leq n < N \) (Using the SSEA of the LG model, \( G(n) = n\Delta G + \text{const} \), where \( \Delta G = \Delta \mu + \mathcal{E}_c + \mathcal{E}_H \)); (3) \( \Delta G \) is proportional to \( \eta \) (Our calculations show that the LJ interaction well depth is proportional to \( \eta \), therefore \( \Delta G \) is proportional to \( \eta \)). Actually, for explaining the equilibrium property found in their MD, Hummer and coworkers have formed a free energy formula (Eq.(3) of Ref. [8]), which is equivalent to the SSEA of our model.

The equilibrium property of water filled into nanotube has been very well described in the LG model. Before investigating the kinetics, we discuss that the states with 6 water molecules inside the nanotube, its probability is not very small in MD simulation [5,8]. It may be corresponding to a state where the ends of the nanotube are partially occupied by two water molecules as shown in Fig.2. The additive free energy of a molecule partially occupied is denoted as \( \mathcal{E}'_n \), which is different from \( \mathcal{E}_n \), due to both differences of carbon-water interaction and the interaction with the outside water. Since water molecules must pass through these partially occupied states as their filling or emptying, the free energy may be comparable with the kinetic energy barrier. For the states which \( n < 6 \), the effects of the partially occupied sites can be ignored, then we have \( \mathcal{E}'_n = \mathcal{E}_n + [G(6) - G(n) - \mathcal{E}_H - \Delta \mu - \mathcal{E}_c]/2 \). We obtain that \( \mathcal{E}'_n \sim -0.8 \) and \(-1.76\) for unmodified and modified system, respectively. We write that \( \mathcal{E}'_n = (\alpha - 1)\mathcal{E}_c + \delta_w \), where \( \alpha \) is a corrected factor of the carbon-water interaction while water molecule partially move out of the nanotube, and \( \delta_w \) is the contribution from the outside water near the end of nanotube. If we suppose that both \( \alpha \) and \( \delta_w \) are independent of LJ parameters, we have \( \alpha \approx 0.67 \) and \( \delta_w \approx -3.4 \). The obtained factor \( \alpha \) is well in agreement with the calculated result of LJ potential while the water molecule is halfly out of the tube, and \( \delta_w \) is comparable to \( \mathcal{E}_c \). It maybe indicate a real physical picture.

The kinetics of filling and emptying is determined by the real reaction paths. The existence of two minimums of the free energy profile \( G(n) \) is not a sufficient condition for the two-state like behavior of filling and emptying. The understanding of the whole free energy landscape is necessary. Generally, a rate equation can be written as, \[
\frac{dP_a}{dt} = \sum_b k(b \rightarrow a)P_b - \sum_b k(a \rightarrow b)P_a, \]
where \( P_a \) is the possibility of state \( a \), \( k(b \rightarrow a) = \gamma \exp[-\beta(F_{a,b} - F_b)] \) is the rate from state \( b \) to \( a \), where \( \gamma \) is a factor, \( \beta = 1/k_BT \), \( F_{a,b} \) is the free energy barrier or saddle point (transition state) separating the state \( b \) and state \( a \) [9,10], \( F_b \) is the free energy of the initial state \( b \). Obviously, only two connected states which they have a common boundary can transit each other. For the filling, emptying or transporting of water, there are \( 2^N \) states (here we have supposed that the outside water molecules be always in equilibrium). The basic motion is that a water molecule jump a step inside nanotube or pass through an end of the tube. Since the barrier of broken hydrogen bonds is too high, the collective motion of a hydrogen-bond chain often occur [11], it means all molecules of the chains move a basic step at the same time. For any cases, the axis positions \( z \) of the all moving molecules are good reaction coordinates. In the motion of passing an end of nanotube, the free energy barrier locates nearly at the end point of the tube (molecule half occupy the end cell), so we approximately have the barrier \( \mathcal{E}_b \sim \mathcal{E}'_1 \), but for the motion of water inside of the tube, the barrier is very small (\( \approx 0 \)) due to the independence of LJ potential on \( z \). For the collective motion, the free energy barrier is the sum of the barrier of every moving molecule. Besides this, the factor \( \gamma \) is different from that of single molecule motion. Actually, \( \gamma \) is dependent on the thermal velocity \( v_T \sim \sqrt{k_BT/m} \approx 1/\sqrt{n} \), where \( n \) is the number of molecules in the collective moving chain. While the length of a cell \( l \) is very small, \( \gamma = v_T/l \) [12], so \( \gamma \approx 1.5/\sqrt{n} \ \text{ps}^{-1} \).

Consequently, based on the simple estimation, we can draw the whole free energy landscape. Obviously, any non-SSEA state can fastly transit to the connected SSEA states, but the inverse transition is very slow, and the barrier between neighbor SSEA states is lower than that between the SSEA states and non-SSEA states. For example, according to our estimation, from (10000) to (11000), the overcome barrier is about \( \Delta G + \mathcal{E}'_a - \mathcal{E}_a \approx 1.4 \), but from (10000) to a non-SSEA state (10001), the overcome energy is about \( \Delta \mu + \mathcal{E}_c + \mathcal{E}'_a \approx 4.8 \). Therefore, the reaction paths almost do not pass through the non-SSEA states in the filling, emptying and transporting processes. It indicates that SSEA describes the kinetics behavior very well. Based on their MD results that the probability of non-SSEA states is very low at equilibrium, Hummer and coworkers have formed a kinetic model only including the reaction between the neighbor SSEA states (Eq.(2) of Ref. [8]), and found that it worked very well. However, the reason of all reaction paths including non-SSEA states can be neglected is the high free energy barriers, not only the high free energy itself of the states.

Now, we can easily explain the two-state like behavior of filling and emptying: water molecules collectively moving a step into or out from the nanotube, the barriers of the middle states (\( 1 \leq n < N \)) are small (about 1.4 and 1.1, respectively), and the effect of the pre-exponent factor is not obvious, so the lifetime of these states is very short, the filling and emptying processes have a two-state like behavior. Actually, we can calculate the rate constant of every reaction and the lifetime of every middle state. For example, we have that \( k(10000 \rightarrow 00000) \approx 0.5 \), the rate constant of the inverse process is about 0.012, where unit is ps\(^{-1}\). The order of magnitude of the values is in agreement with
the estimated results of MD (about 0.3 and 0.009 [8], respectively).

As this work was being finished, we noticed a work [13], in which Maibaum and Chandler treated whole system consisting of the channel of nanotube and the outside bulk liquid as a lattice gas by a MC simulation. It was shown that there are similar behavior found in MD simulation in generic liquid states. Under some approximations, they also analytically analyzed the equilibrium property of the system. However, for quantitatively explaining the behavior of water confined in nanotube, we should consider the characters of water, for example, the average density of bulk water is only 1/5 of that of the filled state in the tube, then the interaction \( \mathcal{E}_a \) between a water molecule at an end of the tube and the outside molecules is weaker than the interaction between two adjacent inside molecules. For the equilibrium property of system, the whole outside bulk water can be thought as an aqueous reservoir and contribute an additive free energy \( \mathcal{E}_a \) to the inside molecules at ends of nanotube, but for the kinetics, we should identify these states, in which different number outside water molecules contact with an inside molecule one by one by hydrogen bonds. If we denoted the state in which \( m \) outside molecules contact with \( n \) inside molecules one by one as \( "(m)\underline{n}" [14] \), then from the state, after a filling or emptying step, the final state is \( "(m-1)\underline{n+1}" \) or \( "(m+1)\underline{n-1}" \), respectively. The complete rate chain will consist of all states with any \( m \) (from 0 to \( \infty \)). However, since the longer outside molecule chain is more instable, in our interesting time scale, the longer chain will be thought as rapidly equilibrating with the surrounding water. Depending on the considered largest \( m \), we have different order approximations of the complete rate equation. In this paper, we used the lowest order (0—order) approximation in which we supposed that one outside molecule rapidly contacted with and departed from the end inside molecule, the equilibrium can rapidly reach in our interested time scale. If we consider higher order (1—order) approximation, the details of energy barrier will be changed, but the differences between the two approximations is not very large, so we think that the principal character of the kinetics of the system has been captured by the simple 1D LG model. We wish to give more quantitative agreement on rate constants by using higher order approximation in next work.

X. Z. thanks Professor Hummer for sending him their MD data and a new paper of Ref. [8] and telling him the work of Maibaum and Chandler (Ref. [13]). X. Z. also thanks Professor Chandler for comments on an earlier draft of this paper, and Mr. Z.-C. Tu for discussions. X. Z is financially supported by the Grants-in-Aid for Scientific Research of JSPS.

(Correspondent address: zhou@pe.titech.ac.jp).

[1] M. M. Calbi, et. al., Rev. Mod. Phys. 73, 857, (2001), and references therein.
[2] A. I. Skoulidas, D. M. Ackerman, J. K. Johnson, and D. S. Sholl, Phys. Rev. Lett. 89, 185901, (2002).
[3] E. Djuardin, T. W. Ebbesen, H. Hiura, and K. Tanigaki, Science 265, 1850, (1994).
[4] K. Koga, G.T.Gao, H. Tanaka, and X. C. Zeng, Nature (London) 412, 802, (2001).
[5] G. Hummer, J. C. Rasaiah, and J. P. Noworyta, Nature (London) 414, 188, (2001).
[6] Z.-C. Tu, and Z.-C. Ou-Yang, e-print cond-mat/0211658 and a private communication.
[7] M. Hodak, and L. A. Girifalco, Phys. Rev. B 64, 035407, (2001).
[8] A. Waghe, J. C. Rasaiah, and G. Hummer, J. Chem. Phys. 117, 10789, (2002).
[9] R. Zwanzig, Proc. Natl. Acad. Sci. (USA), 94, 148, (1997).
[10] P. Hängii, P. Talkner, and M. Borkovec, Rev. Mod. Phys. 62, 251, (1990).
[11] A. Berezhkovskii, and G. Hummer, Phys. Rev. Lett. 89, 064503, (2002).
[12] T. Chou, Phys. Rev. Lett. 80, 85, (1998).
[13] L. Maibaum, and D. Chandler, J. Phys. Chem. (in press).
[14] The right contacted states are similar as the left contacted states, denoted as \( "[n]_\underline{m}\)". For filled state, it is possible to be contacted by outside molecules in two directions, denoted as \( "(m1)\underline{N}_[m2]\)".

![Figure 1](image_url)

FIG. 1. For the system with modified LJ parameters (see text), the free energy from LG model and \(-\ln p(n)\) from MD simulation are plotted, where \( p(n) \) is the possibility of finding exactly \( n \) water molecules inside the nanotube, the simulation data come from Ref. [5]. The results of the system with unmodified LJ parameters are shown at the inset.
$n = 6$ water molecules are found inside the nanotube, where two water molecules only partially occupy at two ends of the nanotube.