A charge-driven molecular flip-flop

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Abstract. Using molecular dynamics simulations, we exploit a charge-driven flip-flop that is composed of several water molecules confined in a single-walled carbon nanotube. The flip-flop has two stable states and can be used to store state information. It can toggle between the two states within 2.5–3.5 ps (286 GHz–400 GHz). We reveal that the underlying mechanism is dominated by the interaction between the water molecules and nonuniform electric field generated by point charges. Namely, each water molecule tends to maintain its lowest electric energy by moving toward the location with the highest field strength. This flip-flop may be of value for molecular computing.

1 Introduction

Traditional silicon-based computers suffer barriers to higher levels of computing performance. In an attempt to replace them, researchers are focusing on the design of computational schemes which utilize individual molecules or atoms as a means of solving computational problems. Such schemes are called molecular computing. So far, molecular computing has been most frequently associated with DNA computing because of the maximum progress \cite{1}. Nevertheless, the design of various forms of molecular computing is still in its infancy. In general, molecular computing requires a fast working speed (requirement I) and a small scale of dimension (requirement II). In electronics, a flip-flop \cite{2} is a circuit that has two stable states. The circuit is made to change states by signals applied to one or more control inputs and has one or two outputs. Accordingly, flip-flops are used as the basic storage element for storing state information. Clearly, the design of flip-flop devices is also particularly important for molecular computing.

Because water is abundant in nature, here we attempt to design a flip-flop based on individual water molecules. In brief, we confine three water molecules in a half-capped, single-walled carbon nanotube (SWCNT) beside three point charges, \( q_1 \), \( q_2 \) and \( q_3 \). The detailed design of the model flip-flop is displayed in Figure 1. Our design is inspired by the existing studies on the interaction between water molecules and carbon nanotubes \cite{3–12}. To this end, we will show that the flip-flop designed by us satisfies the above requirement I (the time for toggling between the two states is within 2.5–3.5 ps (286 GHz–400 GHz)) and requirement II (the size of the flip-flop is on the nanoscale).

2 Computational details

To proceed, we adopt the molecular dynamics simulation, which has been used for investigating the systems of water molecules and carbon nanotubes \cite{3–10,12}. Recently, molecular dynamics simulations have been adopted to design some nanoscale devices and machines, which were based on nanotubes, nanostructures and water \cite{13–15}. Our simulation framework is shown in Figure 1. Note that the SWCNT in use has an excellent electric conductivity \cite{16}. The two carbon atoms, \( C_1 \) and \( C_2 \), are respectively pulled by two external pulling forces, \( F_{y1} = 8.000 \) nN and \( F_{y2} = -8.000 \) nN, which lead to the deformation of the SWCNT with \( d_y = 1.076 \) nm and \( d_z = 0.520 \) nm, so that the three water molecules cannot escape from the SWCNT. The two external pulling forces fall within the force range of some available experimental facilities \cite{17}. For instance, in experiments, the two carbon atoms, \( C_1 \) and \( C_2 \), can connect organic groups by covalent bonds \cite{18,19}. Therefore, \( F_{y1} \) and \( F_{y2} \) can be realized by drawing the organic groups \cite{20}. By taking the midpoint between \( C_1 \) and \( C_2 \) as the origin of coordinates, \( C_1 \) and \( C_2 \) are fixed at coordinates \((-0.000 \) nm, \(-0.538 \) nm, \( 0.000 \) nm\) and \((0.000 \) nm, \( 0.538 \) nm, \( 0.000 \) nm\), respectively. We set the three point charges, \( q_1 \), \( q_2 \) and \( q_3 \), at coordinates \((-1.000 \) nm, \( 0.000 \) nm, \( 0.940 \) nm\), \((-1.000 \) nm, \( 0.000 \) nm, \(-0.940 \) nm\) and \((-1.490 \) nm, \( 0.000 \) nm, \( 0.000 \) nm\), respectively. For our simulations, \( q_1 \) and \( q_2 \) are always kept
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Fig. 1. Schematic graph for a model flip-flop. (a) The figure shows the switching component which contains three water molecules in a half-capped, armchair (6, 6) single-walled carbon nanotube (SWCNT) with length $L = 2.660$ nm and diameter $d = 0.802$ nm. (b) The figure displays the whole flip-flop, which is composed of the switching component and input/output components. In the switching component, the SWCNT can rotate around the line connecting $C_1$ and $C_2$, which is indicated by $\theta$, an angle between $z$ axis and the central line of the SWCNT. We take three point charges, $q_1$, $q_2$, and $q_3$, as the input component/two electrical circuits, A and B, as the output component, each of which consists of a resistance, a power supply and copper nanowires.

at a constant value of $+4e$ (here, $e$ is the elementary charge, $e = 1.6 \times 10^{-19}$ C) and $q_3$ is a pulse charge with a peak value of $+8e$ (see Fig. 2a). For convenience, here we simplify the input and output components in the simulations. Namely, $q_1$, $q_2$, and $q_3$ are only three assumptive charges, which are not the real charges on electrodes. Such assumptive charges are used to generate a nonuniform electric field acting upon water molecules, which can be realized by real charges on electrodes according to the superposition principle of electrical fields in electrodynamics. In addition, we assume that the ends of the copper nanowires exist in the shape of the tip of an atomic-force microscope [21, 22], and that the apex of each end is only one copper atom as shown by Cu$_1$, Cu$_2$, Cu$_3$ and Cu$_4$ in Figure 1b. We remain the four copper atoms in the simulations by fixing them at coordinates ($-0.450$ nm, $0.000$ nm, $0.840$ nm), ($0.450$ nm, $0.000$ nm, $0.840$ nm), ($0.450$ nm, $0.000$ nm, $-0.840$ nm) and ($-0.450$ nm, $0.000$ nm, $-0.840$ nm), respectively. As the SWCNT connects with Cu$_1$ and Cu$_3$, the electric circuit A is closed, thus generating an electric current in A. So, we may define the closed electric circuit A as 0 state. Similarly, as the SWCNT connects with Cu$_2$ and Cu$_4$, we are allowed to define the closed electric circuit B as 1 state. Clearly, in experiment, the 0 and 1 states can be outputted by measuring the electric current in A or B. In our simulations, without loss of generality, the 0 and 1 states are equivalently analyzed by considering the angle, $\theta$ (Fig. 2b). Namely, an obtuse angle ($\sim 111^\circ$) or acute angle ($\sim 69^\circ$) of $\theta$ stands for 0 or 1 state. For electrical neutralization, the
Fig. 2. (a) A periodic signal charge of the pulse charge, $q_3$, as a function of time, $t$. Here, $\Delta t_1 = 3.5 \text{ ps}$ and $\Delta t_2 = 40 \text{ ps}$. (b) $\theta$ versus $t$ for the charge signal as shown in (a).

opposite charges of $q_1$, $q_2$ and $q_3$ are respectively fixed at coordinates (10.000 nm, 0.000 nm, 0.940 nm), (10.000 nm, 0.000 nm, -0.940 nm) and (10.000 nm, 0.000 nm, 0.000 nm), which are far enough to have any meaningful influence on the water molecules inside the SWCNT. All the simulations are carried out in the NVT ensemble [23] at the constant temperature, $T = 280 \text{ K}$, on the basis of the molecular dynamics package Gromacs 4.0.5 [24]. Non-periodic boundary conditions are applied in our simulations. The force field parameters of the SWCNT come from Hummer et al. [3], the van der Waals (VDW) parameters of copper originate from Agrawal et al. [25], and we adopt the Tip3p water model [26] (namely, charge quantity on the oxygen atom is -0.834 e, and that on a hydrogen atom is +0.417 e). The VDW interactions and electrostatic interactions are calculated with a long cutoff, 15.0 nm, which exceeds the longest distance between two atoms in this system. The simulation for each parameter set is run for 25 ns. A time step of 2.0 fs is used, and data are collected every 40.0 fs.

3 Results and discussion

As a result of simulations for the pulse charge of $q_3$ (Fig. 2a), we find that the SWCNT shows two stable positions of $\theta = 111.1 \pm 1.7^\circ$ and $68.9 \pm 1.7^\circ$, which are just corresponding to 0 state or 1 state, respectively (Fig. 2b). It is evident that, as $q_3$ changes from “off” ($q_3 = 0$) to “on” ($q_3 = +8e$), the SWCNT can immediately shift from 0 state to 1 state, or from 1 state to 0 state on the picosecond timescale. That is, the function of the designed flip-flop is realized indeed.

To understand the phenomena reported in Figure 2b, we plot Figure 3 according to the calculations of interaction energies. From the energy summation of $E_{H_2O-Cu} + E_{C-Cu} + E_{H_2O} - (q_1, q_2)$, we find two symmetrical potential traps that exist at the two sides of the curve. This means that the SWCNT can be stably located with $\theta \approx 111^\circ$ (0 state) or $\theta \approx 69^\circ$ (1 state) with the same probability; the system shows bistability. On the other hand, from the energy summation of $E_{H_2O-Cu} + E_{C-Cu} + E_{H_2O} - (q_1, q_2)$, we observe a potential trap at the middle of the curve. This clearly indicates that the SWCNT prefers to stay with $\theta = 90^\circ$ in case of $q_3 = +8e$: the system shows monostability. So, the “off” or “on” of $q_3$ simply makes the system have either bistability or monostability, thus realizing the toggling of the SWCNT from 0 state to 1 state, or from 1 state to 0 state. Figure 3 also implies that an appropriate pulse time width ($\Delta t_1$) of $q_3$ is necessary for the successful shift of the two states as shown in Figure 2b. For the sake of clarification, Figure 4 shows the probability of the successful shifts of the SWCNT, $P$, as a function of $\Delta t_1$. Clearly $P \approx 100\%$ corresponds to 2.5 ps $< \Delta t_1 < 3.5$ ps. As $\Delta t_1 < 2.5$ ps or $\Delta t_1 > 3.5$ ps, we have $P < 100\%$ corresponding to low successful probabilities of shifts. Such results can be understood. In case of $\Delta t_1 < 2.5$ ps, water molecules cannot make the SWCNT accumulate enough shifting momentum; in case of $\Delta t_1 > 3.5$ ps, water molecules lead the shifting momentum of the SWCNT to overly dissipate near the potential trap of $\theta = 90^\circ$. It is worth mentioning that this kind of shifting momentum mainly originates from
the interaction between the water molecules and nonuniform electric field generated by point charges; see Figure 3. In detail, each water molecule tends to maintain its lowest electric energy by moving toward the location with the highest field strength.

To sum up, we have designed a flip-flop based on three water molecules confined in a SWCNT located in the vicinity of three point charges. This kind of charge-driven molecular flip-flop may be of value for molecular computing. In our simulations, the screening effect of the SWCNT has been omitted [4,6,8,10]. As a matter of fact, the charges we adopted might be regarded as effective charges, and the realistic charge quantities should be made larger by multiplying a factor related to the screening effect [4,6,8,10]. On the other hand, for experimental demonstration, the electric charges on the four copper atoms, Cu\textsubscript{1}, Cu\textsubscript{2}, Cu\textsubscript{3} and Cu\textsubscript{4}, should have a charge quantity that is much less than q\textsubscript{1}, q\textsubscript{2} or q\textsubscript{3}, so that one can neglect the electric influence of the copper atoms. Lastly, in real experiments, four copper nanowires are used instead of four copper atoms. Since a nanowire is much bigger than an atom, much stronger attractive (van der Waals) force is exerted between the nanowire and the SWCNT. Additionally, the orbital hybridization between the copper atoms in the wire and the carbon atoms in the SWCNT is also strong [27], compared with an individual single copper atom. It may give rise to a lower flip-flop speed because a stronger attractive interaction results in a larger energy barrier between the two energy levels (0 and 1 states). Nevertheless, to obtain the same simulated flip-flop speed, one might use charges with higher electric quantities by overcoming the influence of the nanowires.

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